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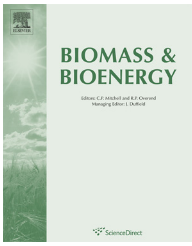

Short- and long-term flammability of biochars

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ABSTRACT

Biochar is becoming a commercial biomass-derived product that is transported, stored, and applied to land for environmental management. However, no information is available about its flammability that significantly affects how biochar can be handled. Given that biochar can have very different properties depending on how and from what it is produced, flammability may also vary significantly. The flammability of biochar and its dependency on biochar properties were quantified for a range of biochars produced at different pyrolysis temperatures and as a function of time after production. None of the studied biochars (34 samples stored for at least two years under argon gas) qualified as flammable substances, assessed using the applicable UN method. The majority of biochars (67%) had no combustion front propagation distance at all. Almost all of the studied fast pyrolysis biochars (71%) had higher combustion distances, whereas most slow pyrolysis samples (80%) did not combust. The combustion of stored biochars increased with the amount of volatiles ($r^2 = 0.27$, $p < 0.05$, $n = 11$; dominated by fast pyrolysis biochars: $r^2 = 0.62$, $p < 0.05$, $n = 5$), typical of biochars produced at lower temperatures. In contrast, the combustion of biochars within minutes of production was higher for biochars made at 723 K (450 °C) than 623 K (350 °C), but decreased to negligible levels within 1 h. Short-term flammability may be a function of the amount of free radicals and surface areas that can react with oxygen, whereas long-term flammability after storage may be a result of the potentially flammable volatile matter and some still weakly explained mechanisms for high-ash dairy feedstock.

1. Introduction

Biochars, the solid product of pyrolyzed biomass, have the potential to improve soil functions such as water infiltration and nutrient retention [1–3] while concurrently sequestering carbon [4–7]. It has been shown that some biochars reduce nutrient leaching, hence increasing nutrient availability for biomass growth [2,3,8]. In addition, biochars may alleviate the ramifications of removing crop residues [9]. Alkaline biochar can improve acidic tropical soils and thereby improve biomass yields [10,11]. Furthermore, biochars produced from animal manures can possess appreciable quantities of plant available metals, phosphorus and sulfur which are concentrated by preferential loss of organic components during pyrolysis [11–13]. These animal manure biochars have the additional benefit of being applied as a low-grade fertilizer [13–15]. These differential uses of biochars also mean that the material

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properties vary considerably, ranging from mostly carbonaceous to mostly ash materials [16,17]. A wide-spread use of biochars in agriculture requires that they be transported and stored. Since biochars are potentially flammable [18–21] and some reports suggest that they may self-ignite, this aspect of biochars requires special consideration. However, systematic studies of the extent of biochar flammability across the material spectrum to identify simple material property indicators for flammability have not yet been performed.

The United Nations Manual of Tests and Criteria specifies criteria for assessing transportation hazards of materials [22]. These are incorporated into the United States Code of Federal Regulations [23] and are the basis for testing as per Environmental Protection Agency (EPA) method 1050 [24] and shipping as per Department of Transportation [25]. The United Nations and EPA methods distinguish between self-heating and flammability. The former is a temperature-dependent, transient phenomenon arising from chemisorption of oxygen [26,27], and the latter a material property. Self-heating is managed by restricting oxygen ingress to reduce the rate of chemisorption [28] and reducing material bulk to promote heat loss [29] until the material has been saturated. Therefore, German shipping regulations for example state that lump charcoal may be shipped following a four-day aging period, while charcoal dust may be shipped after eight days [30]. Here we concentrate on flammability and its relationship to material properties of a wide range of biochars.

Both pyrolysis method and choice of feedstock determine the characteristics of the resulting biochar [16,17] and may therefore also affect its flammability. Feedstock composition affects properties such as the thermal degradation temperature of the biomass [31,32]. The heat treatment method largely controls the proportion of volatiles and surface properties [33,34]. Past studies suggest a positive correlation between flammability and the presence of volatile contents, such as alcohols and carboxylic acids [35]. Thermal action on O-functionalities and mineral impurities during pyrolysis produces free radicals [34], which accumulate at the biochar surface and consequently increase the reactivity of the sample [35,36]. Free radicals react with species from the environment, such as oxygen, solvents, halogens, and metals. The free radicals' reaction with oxygen is an established method for measuring dissociation and stabilization rates [37]. Both relatively stable carbon radicals and non-carbon radicals were found to be sensitive to oxygen [34,37] and may be related to flammability. Past findings indicate the role of gasification on the carbon structure of the resulting biochar and the sample's subsequent reactivity to oxygen [38]. However, a comparison of flammability between biochars made in very different ways from different feedstocks has not been done.

The purpose of this study was to explain and predict flammability with known properties of biochars that would facilitate the assessment of flammability for biochar application, transport, and storage. Specifically, we investigated the effects of both (1) biochar properties as affected by the type of pyrolysis (fast, slow pyrolysis, gasification), the feedstock, and the pyrolysis temperature; and (2) the time since pyrolysis on flammability.

2. Materials and methods

2.1. *Stored biochars*

Flammability tests were performed on biochars made from a variety of feedstocks using several thermal production technologies as outlined in Table 1. The precise location of feedstock origins is generally unknown, which limits reproducibility. However, this does not affect the reproducibility of the relationships between biochar properties and flammability studied here. In brief, biochars from slow pyrolysis were produced by the Best Energies Inc. facility using the Daisy Reactor (Cashton, WI, USA). Approximately 3 kg of feedstock was placed into a main chamber, thoroughly purged with N_2 while the mixer was running. Pre-dried material was isothermally charred for 80–90 min, including rising temperature to the target with a few degrees $K \cdot min^{-1}$ and holding at a final temperature for 15–20 min. After pyrolysis, the furnace was turned off and the main chamber was allowed to cool before unloading the biochar under nitrogen purge to reduce rapid oxidation and auto-ignition. Upon receipt, air-dry biochars were ground with mortar and pestle and sieved to achieve a particle size range of 149–850 μm, then transferred to glass containers for storage under argon (Ar) gas.

The flammability tests were performed according to the UN Manual of Tests and Criteria, part III N, 1 Test for readily combustible solids § 33.2.1.4.3.1 [22]. Tests were conducted in a trough modeled after Figure 33.2.1.4.1 fabricated from 3/16″ thickness, 1″ mild steel angle iron with 1-1/2″ angle iron welded to the ends (Supplementary Fig. S1). Each sample was evenly spread along the length of the trough. The oxidizing portion of a Bunsen burner flame was applied to one end either until the sample ignited or for a maximum of 2.0 min. The distance traveled by the combustion front along the length of the trough was recorded over the subsequent 2.0 min with a precision of ±0.5 mm. The criterion of having a combustion front propagation distance of 200 mm was required for the sample to be categorized as a flammable substance.

2.2. *Fresh biochars*

Flammability tests were performed on biochar freshly produced from the same bull manure with sawdust (Bull) and dairy manure with rice husk (Dairy) feedstocks as those used to produce the stored biochars. Additional biochars were produced from corn stover (Corn) and red maple woodchips (Wood). All feedstock was milled to pass 1 mm prior to pyrolysis. A mass of 300 g of feedstock, dried at 333 K, was manually placed into the pyrolysis chamber for the production of each biochar sample. The feedstock was heated at a rate of 2.5 $K \cdot min^{-1}$ and held at the target temperature for 30 min. The target temperatures for each feedstock were 623 K, 723 K, 823 K. Pre-heated Ar sweep gas was injected during the pyrolysis process at a rate of 1 L min^{-1}. After cooling to ambient temperature in the chamber, the biochar sample was immediately transferred to a 1 L glass jar and capped with a lid fitted with septa. Two needles were inserted through the septa in the middle of the lid. Ar was supplied

Table 1 – Stored biochars analyzed for flammability.

Label in tables and figures	Feedstock	Feedstock origin	Production temperature (K) (°C in brackets)	Thermal production condition
Bull	Bull manure w/sawdust	Wisconsin	623, 723, 823 (350, 450, 550)	Batch slow pyrolysis
Dairy	Dairy manure w/rice husk	Wisconsin	623, 723, 823 (350, 450, 550)	Batch slow pyrolysis
Food	Food waste	Cornell dining facilities	573, 673, 773, 873 (300, 400, 500, 600)	Batch slow pyrolysis
Hazelnut	Hazelnut shells	Unknown	623, 723, 823 (350, 450, 550)	Batch slow pyrolysis
Mixed woodchips	Chipped pallets	Cornell	773 (550)	Batch slow pyrolysis
Oak	Oak wood	Wisconsin	623, 723, 823 (350, 450, 550)	Batch slow pyrolysis
Paper	Paper mill waste	Mohawk Fine Papers Inc., Cohoes, NY	573, 673, 773, 873 (300, 400, 500, 600)	Batch slow pyrolysis
Pine	Pine wood	Wisconsin	623, 723, 823 (350, 450, 550)	Batch slow pyrolysis
Poultry	Poultry manure w/sawdust	Wisconsin	623, 723, 823 (350, 450, 550)	Batch slow pyrolysis
Carbonized pine	Pine wood	Biochar Engineering Corporation, CO	1023 (750)	Updraft pyrolysis, 250 kg h^{-1} capacity
Mixed softwood	Mixed softwood chips	Dynamotive, Canada	723 (450)	Fast pyrolysis, bubbling fluidized bed, <5 s contact time
Mixed vegetation	Unidentified vegetative material	Dynamotive, Canada	723 (450)	Fast pyrolysis, bubbling fluidized bed, <5 s contact time
Peanut	Peanut shells	Georgia	753 (480)	Ablative-updraft pyrolysis, continuous feed, 10 min contact time, 19 kg h^{-1} capacity
Rice husk	Rice husk	The Philippines	1073 (800)	Gasification, 200 kg h^{-1} capacity
Soybean	Soybean crop residue	Pennsylvania (USDA-ARS)	773 (500)	Fast pyrolysis, fluidized bed, 1 s residence time, 0.2 s contact time in bed, 5 kg h^{-1} capacity
Switchgrass	Switchgrass	Pennsylvania (USDA-ARS)	773 (500)	Fast pyrolysis, fluidized bed, 1 s residence time, 0.2 s contact time in bed, 5 kg h^{-1} capacity
Switchgrass 2	Switchgrass	Texas	773 (500)	Fast/intermediate pyrolysis, auger, 15–30 s contact time, 30 kg h^{-1} capacity
Pine 2	Pine wood chips	Texas	773 (500)	Fast/intermediate pyrolysis, auger, 15–30 s contact time, 30 kg h^{-1} capacity

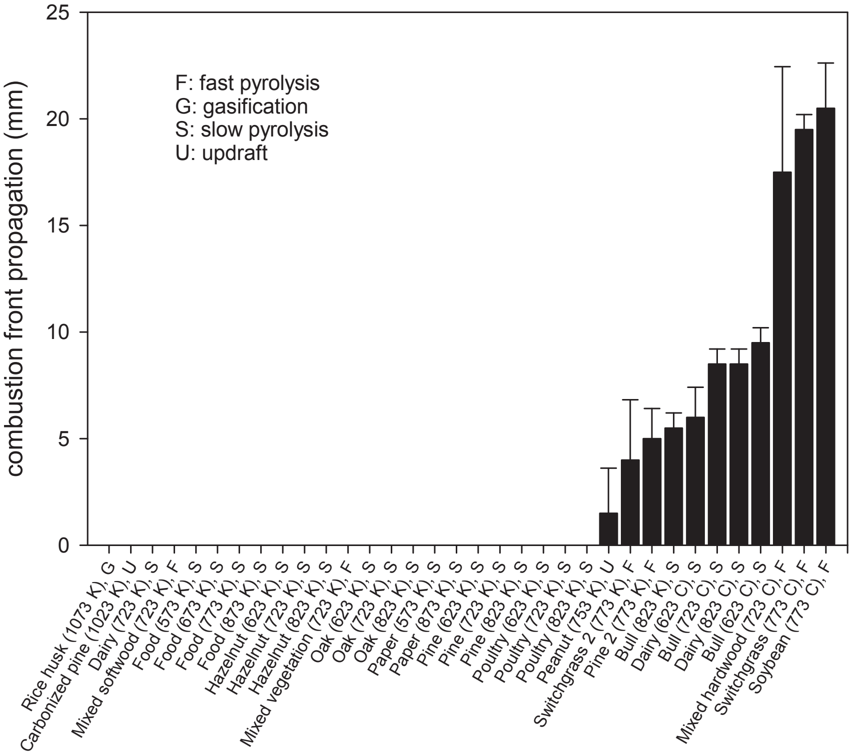

Fig. 1 – Combustion front propagation distances for stored chars.

through one needle and the sample was thoroughly flushed for 1 min while agitating. The samples were kept in the jar with Ar to minimize exposure to air.

For comparison, the flammability test was the same as that used for stored biochars. Upon opening of the jar, a subsample of biochar was immediately spread along the metal trough and ignited. The remaining biochar was then spread evenly on a tray to allow exposure to ambient air. The time at which the jar was opened was set as time zero. Flammability tests were conducted at 3-min intervals until the combustion front propagation distance reached a plateau (decrease less than 10%).

Surface area was analyzed for fresh biochars following exposure to air using a Micromeritics ASAP 2020 porosimeter (Norcross, GA). Five point BET surface area was calculated from adsorption of CO_2 at 273.15 K at partial pressures of 0.005, 0.0105, 0.0160, 0.0215, and 0.0270.

2.3. Oxygen chemisorption

The same Corn, Wood, Dairy, Bull feedstocks as used in the flammability tests of fresh biochars were used to investigate the kinetics of oxygen chemisorption. It has been established that the reactivity of biochar-type materials is correlated with the concentration of free radicals at active sites, which are most frequently measured using oxygen chemisorption [39–41]. A TA Instruments Q500 Thermogravimetric Analyzer (TGA) was used for the pyrolysis process and for adsorption measurements. A platinum pan (6.0 mm i.d. and 1.0 mm high),

Table 2 – Relationship between flammability and properties of stored biochar. (Bold denotes significant at $p < 0.05$; full data set in Supplementary Table S1; NA not available).

Biochar properties	All biochars		Only flammable biochars		Only flammable biochars (slow pyrolysis)		Only flammable biochars (fast pyrolysis)	
	r^2	n	r^2	n	r^2	n	r^2	n
Volatiles	0.022	34	0.050	11	0.056	5	0.216	6
Volatiles – ash free mass basis	−0.015	34	0.270	11	0.049	5	0.619	6
Fixed carbon	0.004	34	**−0.400**	11	−0.047	5	**−0.656**	6
Fixed carbon – ash free mass basis	0.011	34	−0.270	11	−0.049	5	−0.619	6
Ash	−0.016	34	0.225	11	−0.048	5	0.199	6
H:C (mol:mol)	0.124	20	0.048	5	0.048	5	NA	NA
H:Corg (mol:mol)	0.016	20	0.030	5	0.030	5	NA	NA
O:C (mol:mol)	−0.030	20	0.078	5	0.078	5	NA	NA
O:Corg (mol:mol)	−0.066	20	0.041	5	0.041	5	NA	NA

was filled with feedstock and heated to the target temperature in an N_2 atmosphere with a ramp rate of 5 K min^{-1}. The target temperatures were 623 K, 723 K, and 823 K. Weight losses during this thermogravimetric phase preceding the chemisorption phase of the analyses were well aligned with each other and were run to a stable weight, indicating experimental consistency (Supplementary Fig. S2). The target temperature was held for 30 min before cooling to 393 K for adsorption. According to work on various 823 K cellulosic chars, the oxygen capacity increased with higher adsorption temperatures up to about 480 K [40]. This was used as consideration for determining the adsorption temperature of our samples. After a 5 min period for the temperature to stabilize at 393 K, the gas stream was changed from N_2 to air. The weight change in the sample was continuously recorded and used as an indicator for oxygen adsorption.

2.4. *Statistical analyses*

Statistical analyses were performed with SAS (SAS 5.0, Cary, NC). JMP 9.0.2. was used to perform bivariate regressions. Differences were considered significant at $p < 0.05$ unless otherwise noted.

3. Results

3.1. *Flammability of stored biochar*

All biochar samples exhibited combustion front propagation less than 200 mm. Hence, although some of the stored biochars (33%) showed combustion front propagation, none qualify as flammable according to UN criteria. Biochars with the greatest combustion front propagation were produced by fast pyrolysis (Fig. 1). Five out of the seven stored fast pyrolysis biochars (71%) showed front propagation, compared to only five out of the twenty-four biochars from slow pyrolysis (20%). Biochar properties across all stored biochars were only weakly correlated with combustion front propagation distance (Table 2), presumably because most demonstrated no propagation distance. For biochars with combustion front distance greater than zero, the proportion of fixed carbon and volatiles correlated best with flammability, largely due to a close correlation among the biochars produced by fast pyrolysis (Supplementary Fig. S2). Biochars with low H/Corg ratios showed low combustion front propagation, while those with high ratios had both high and low front propagation (Fig. 2). Interestingly, all stored slow-pyrolysis biochars with combustion front distances greater than zero were made from dairy or bull manure.

3.2. *Flammability of fresh biochar*

The combustion front propagation distance decayed exponentially over the first 18 min after biochar was exposed to air (Fig. 3; Table 3). Corn biochar had the greatest front propagation throughout the entire experiment, whereas Wood biochar initially had high flammability but approached zero over the 18 min of experimentation. In general, biochars made at higher pyrolysis temperatures had higher flammability. These biochars also showed the greatest surface area (Table 4).

3.3. *Oxygen chemisorption*

For determining the role of free radicals in the combustion of fresh biochar, we used oxygen chemisorption at a temperature

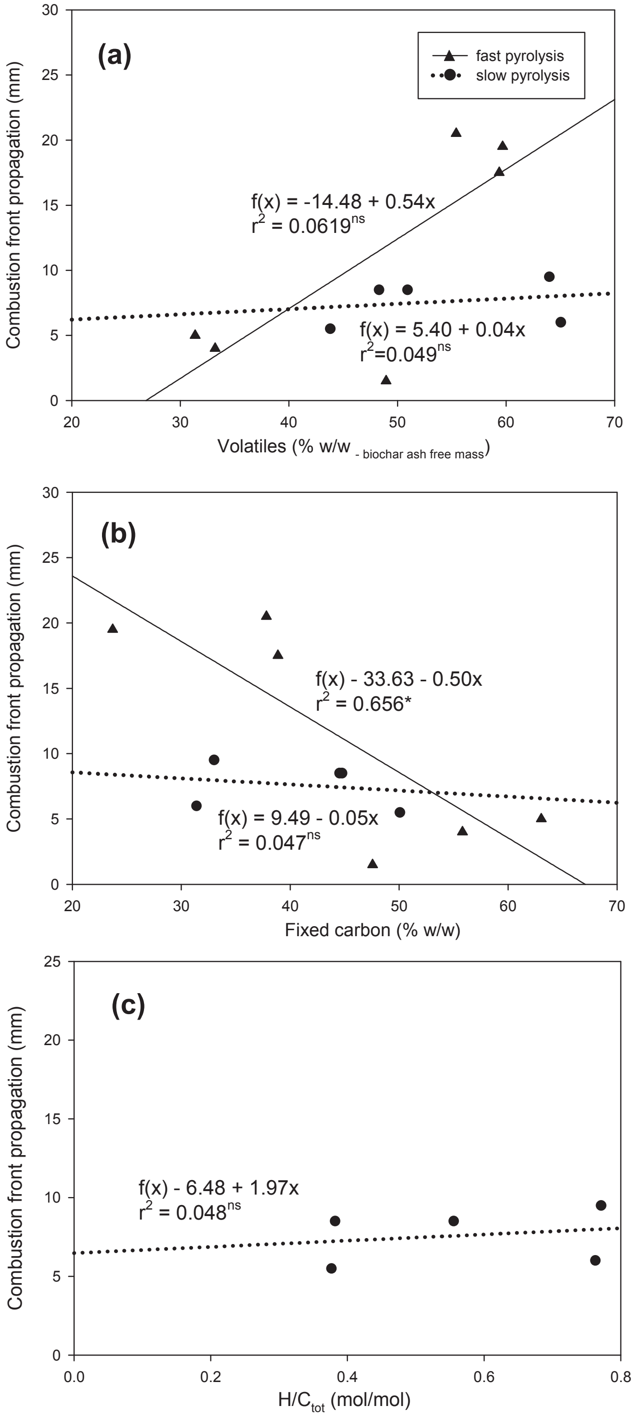

Fig. 2 – Stored biochars. Correlation between biochar combustion and (a) volatile ash-free matter, (b) total fixed carbon content, and (c) H/C ratio (slow pyrolysis only). (* and ^{ns} denote significant relationship at $p < 0.05$ and not significant, respectively).

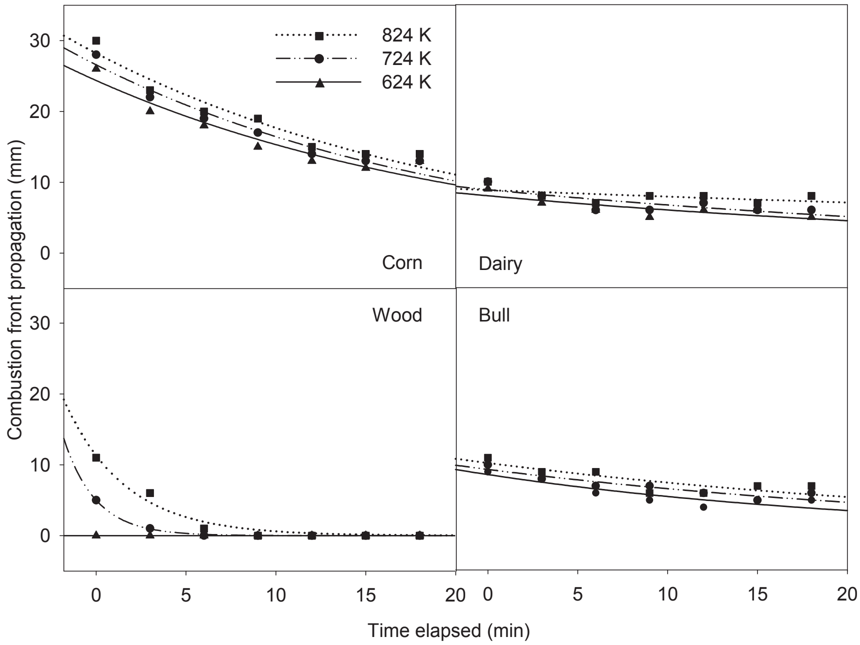

Fig. 3 – Effect of time elapsed since production on the combustion front propagation of fresh biochars.

of 393 K and an adsorption period of 120 min. Cumulative adsorption increased over the adsorption period, with greater adsorption quantities corresponding to higher pyrolysis temperatures (Fig. 4). The rate of chemisorption was calculated for the start of the adsorption period. The process follows the Elovich Kinetics, $dq/dt = a^{-bq}$, where q is the amount of oxygen chemisorbed at time t. The rate of adsorption shows an exponential rise to a maximum over the 120 min of chemisorption, consistent with the equation, and was therefore the greatest at $t = 0$. The resultant maximum adsorption rates were highest at 723 K pyrolysis temperature, except for wood biochar where it was at 623 K (Table 5). Combustion front propagation was strongly correlated with the cumulative adsorption shown by wood biochars, only weakly with that by corn stover biochar, and the weakest by the two studied manure biochars (Fig. 5).

4. Discussion

4.1. *Biochar properties and biochar flammability*

The volatile content of charcoals optimized for fuel is an important chemical property for flammability. Specifically, the initial sudden mass loss in charcoals represents the release and ignition of volatiles [42]. The relatively short combustion front propagation distances for stored slow pyrolysis biochar corresponds with lower volatile matter content as well as low H/C ratios. Low H/C ratios could also be attributed to crystallite reorientation. Laine et al. discussed the reactivity of biochar in terms of the proportion of basal plane surfaces [38]. Our findings are consistent with their considerations of chemical structure in the carbon crystallites. The increase in size and reorientation of carbon crystallites during heating yields surfaces composed of a greater proportion of basal planes [38]. Past research suggests that, during oxidation, plane intersections are sites for carbon–oxygen reactions [34,38]. Implicit in these findings is the conclusion that carbon crystallite edges are more reactive to oxygen than plane surfaces. These findings propose two factors, namely geometry and impurity concentration, to explain that crystallite edges are primary sites of reaction [38]. The geometric structure of edges increases the relative probability of carbon–oxygen bonds, compared to that of planes [34,38]. From studies on the chemisorption of oxygen in graphite, results show that the carbon–oxygen double bond occurs between a conducting π-electron and a carbon σ-electron [43]. Edge carbon atoms have unpaired σ-electrons available to form

Table 3 – Decay constants b and r^2 values for fresh biochar combustion front propagation curves in Fig. 3. (*, **, ***, ^{ns} denote significant relationship at $p < 0.05$, 0.01, 0.001, and not significant, respectively).

Pyrolysis temperature (K)	Corn		Wood		Dairy		Bull	
	b	r^2	b	r^2	b	r^2	b	r^2
623	0.046^{***}	0.941^{***}	1.000^{***}	1.000^{***}	0.029^{*}	0.664^{*}	0.045^{***}	0.798^{**}
723	0.048^{***}	0.956^{***}	0.560^{***}	0.998^{***}	0.028^{*}	0.627^{*}	0.034^{***}	0.856^{*}
823	0.047^{***}	0.903^{***}	0.294^{***}	0.969^{***}	0.011^{ns}	0.310^{ns}	0.032^{***}	0.678^{*}

Table 4 – Surface area for fresh biochar samples, means and standard errors ($n = 2$).

Biochar	Pyrolysis temperature (K)	BET surface area ($m^2 \cdot g^{-1}$)
Corn	623	31.2 ± 0.5
Corn	723	49.6 ± 1.1
Corn	823	73.7 ± 1.6
Wood	623	47.7 ± 0.6
Wood	723	224.7 ± 2.1
Wood	823	278.9 ± 2.1
Dairy	623	118.4 ± 1.9
Dairy	723	173.2 ± 2.0
Dairy	823	216.5 ± 1.8
Bull	623	125.7 ± 1.8
Bull	723	180.4 ± 1.9
Bull	823	225.4 ± 1.8

bonds with the oxygen, whereas basal plane carbon atoms are tied with adjacent atoms [34,38]. The surface homogeneity of carbon increases with prolonged heat treatment [44]. The longer heating for the slow pyrolysis biochars thus suggests a higher surface homogeneity relative to the fast pyrolysis biochars.

The findings of Radovic et al. suggest a correlation specifically between H/C ratios and the reactivity of chars produced from lignite coal [42], given the theoretical considerations of impurities in carbon crystallite structure homogeneity. Both incomplete pyrolysis (through fast pyrolysis or low temperatures) and impurities including carbonates and other minerals [45] yield smaller crystallites and dislocations, consistent with the presence of more crystallite edges [46]. This could be a factor for the striking finding that all five slow pyrolysis biochars with relatively higher combustion front propagation distances were higher-ash biochars made from animal manures.

4.2. *Effect of time on biochar flammability*

Decreasing flammability with time over the first minutes after biochar production are unlikely related to changes in volatile contents, but may be attributed to the quenching of free radicals in the formation of carbon–oxygen bonds, as the radicals are extremely sensitive to oxygen [34,37]. Oxygen chemisorption corroborates these results and is an established method for assessing free radical concentrations [39]. Flammability of biochars immediately after pyrolysis tended to increase with higher pyrolysis temperatures, which coincides with the theoretical considerations of carbon crystallite reorientations during heating [40]. These results also coincide with the findings that surface area increases with higher temperature for lignite chars, which showed a direct correlation between oxygen chemisorption at 393 K and active surface area [47]. Findings on the kinetics of cellulosic biochars also suggest that at temperatures above 573 K, trapped free radicals accumulate [48]. However, this process is accompanied by rapidly accelerating tar formation [31], chiefly composed of anhydrosugars that are less reactive than free radicals [26]. Condensation of these tars on the biochar surfaces could explain the reduction in oxygen chemisorption for cellulosic biochars at 823 K compared to 723 K, despite higher surface area.

Greater combustion front propagation of high-temperature fresh biochars with presumably lower volatile content and H/C ratios [49] contrasts with shorter propagation distances of high-temperature stored biochars, as described above. This suggests different mechanisms promoting flammability, specifically unquenched free radicals in fresh biochars, and volatile contents in stored biochars. During storage, the free radicals appear to have reacted with oxygen. Lower proportions of volatiles, as well as the greater ordering, reduced flammability when biochars were stored.

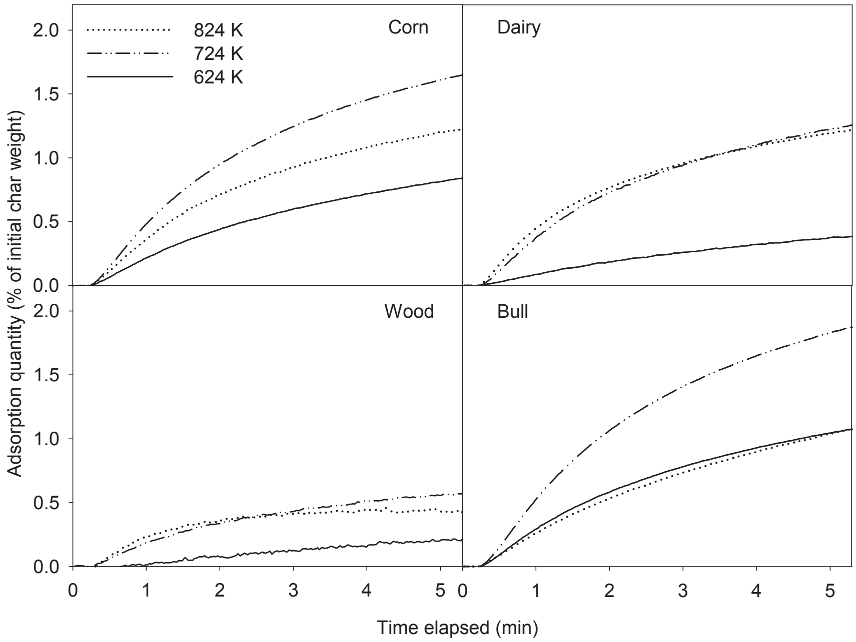

Fig. 4 – Adsorption weight gains of biochar samples during the first 5 min of oxygen chemisorption in 393 K air.

Table 5 – Maximum adsorption rate over the 120-min oxygen chemisorption period.

Biochar	Pyrolysis temperature (K)	Max adsorption rate (%·min^{-1})
Corn	623	0.33
Corn	723	0.73
Corn	823	0.70
Wood	623	0.42
Wood	723	0.31
Wood	823	0.29
Dairy	623	0.14
Dairy	723	0.77
Dairy	823	0.56
Bull	623	0.44
Bull	723	0.77
Bull	823	0.37

It has also been suggested that small amounts of impurities can catalyze the reaction of carbon with oxidizing gases [34,39]. Impurities tend to diffuse to concentrate at crystallite edges during heat treatment at higher temperatures [34,38]. This may be a contributing factor to the differences in the flammability test results between biochars made at different pyrolysis temperatures, but the specific mechanisms that determine the temperature dependence of combustion likely consist of multiple complex factors.

5. Conclusions

None of the studied biochar samples qualified as flammable substances, as defined by the UN method outlined in § 33.2.1.4. Flammability appears to be promoted in the short term by oxygen chemisorption to carbon free radicals. Given access to air, this effect decayed exponentially over 18 min as free radicals were quenched. High heating rates, short dwell times, and feedstock impurities favor the formation of carbon free radicals during pyrolysis. Impurities may also be the reason for the greater flammability of biochars made from manures but warrants further research. Post-production modifications of biochars including quenching with water were not studied but may significantly affect flammability. In addition, spontaneous combustion of bulk biochar may be related to several of the mentioned biochar properties found responsible for flammability, but was not subject of this study and should be investigated in the future. Monitoring of biochar flammability is recommended to identify feedstocks and production conditions that are safe, but our results hint at the possibility that the risks can be managed through better understanding of the processes and appropriate handling.

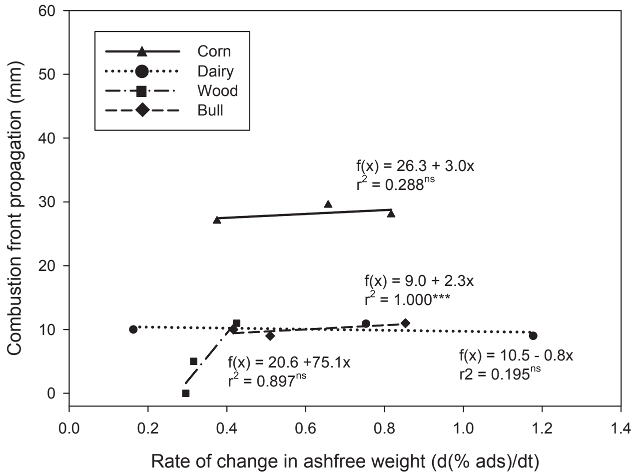

Fig. 5 – Relationship between combustion front propagation of fresh biochars and maximum adsorption rate during oxygen chemisorption, for 623, 723, and 823 K pyrolysis temperatures. (* and ^{ns} denote significant relationship at $p < 0.001$ and not significant, respectively).**

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.biombioe.2014.07.017.

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