BIOMASS AND BIOENERGY 69 (2014) 183–191

Available online at www.sciencedirect.com

ScienceDirect

http://www.elsevier.com/locate/biombioe

Short- and long-term flammability of biochars

Mary Yiyue Zhao [a], Akio Enders [a], Johannes Lehmann [a,b,*]

[a] Department of Crop and Soil Sciences, Cornell University, Ithaca, NY 14853, USA
[b] Atkinson Center for a Sustainable Future, Cornell University, Ithaca, NY 14853, USA

ARTICLE INFO

Article history:
Received 31 October 2013
Received in revised form
12 July 2014
Accepted 16 July 2014
Available online

Keywords:
Biochar
Flammability
Free radicals
Storage
Volatile matter

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

* *Corresponding author*. Department of Crop and Soil Sciences, Cornell University, Ithaca, NY 14853, USA. Tel.: +1607 254 1236; fax: +1607 255 2644.
E-mail address: CL273@cornell.edu (J. Lehmann).
http://dx.doi.org/10.1016/j.biombioe.2014.07.017
0961-9534/

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