Full Length Article

Quantifying self-heating ignition of biochar as a function of feedstock and the pyrolysis reactor temperature

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ABSTRACT

Biochar is produced from biomass through pyrolysis in a reactor under controlled conditions. Different feedstock and reactor temperatures produce materials with different physical and chemical properties. Because biomass, biochar and torrefied biomass are reactive porous media and can undergo self-heating, there is a fire hazard associated to their production, transport, and storage. This hazard needs to be tackled in biomass industries like power generation, where self-heating of biomass can cause significant problems, like the 2012 fire at Tilbury Power Plant (UK). Using basket experiments inside a thermostatically controlled laboratory oven, augmented with thermogravimetry and conductivity measurements, we experimentally study the ignition conditions of pellets and biochar made of softwood, wheat and rice husk. For softwood, we also study biochar produced at different reactor temperatures ranging from 350 to 800 °C. In total, 173 experiments were conducted with 1036 h of oven run time. By investigating the self-heating behaviour of these samples via the Frank-Kamenetskii theory, we quantify and upscale for the first time the reactivity of biochar as a function of feedstock and also of the reactor temperature. The results show that in order from higher to lower tendency to self-heating, the rank is softwood, wheat and rice husk. The reactivity of the softwood is not a monotonic function of pyrolysis reactor temperature but that biochar is most prone to self-heating when produced at 450 °C. Reactivity decreases at higher reactor temperatures, and at 600 °C the biochar is less reactive than the original feedstock. This work improves the fundamental understanding of the fire hazard posed by biomass self-heating, providing insights necessary for successful and safer biomass industries.

1. Introduction

Biomass, plant-based materials collected by humans which are not used for food or animal feed, have historically been waste material or used as a form of energy source, especially in the form of wood. So, over the past number of years, biomass has become an important part of the fuel mix for fossil fuel power plants, and its use is projected to grow significantly [1].

Torrefied biomass, a product of biomass pyrolysis, is a possible replacement for coal, as it could integrate into existing coal power plants, enabling power plants to generate clean energy without an expensive conversion process [2]. At the same time biochar, charcoal produced from the pyrolysis of biomass, is being used for soil amendment for very acidic soils. Furthermore, carbon remains sequestered in biochar for centuries, so sustainable biochar production allows for atmospheric carbon sequestration. However, there are fire safety issues associated

with both biomass and biochar. Both biochar and torrefied biomass are solid biomass pyrolysis products. They are derived from biomass through pyrolysis in a reactor under controlled conditions. Different reactor temperatures produce different pyrolyzed biomass, leading to materials with different properties and reactivities [3]. For reactor temperatures below 350 °C, this solid material is called torrefied biomass. For temperatures greater than 350 °C, this solid material is called biochar [3].

Reactive porous media such as wood, biomass, biochar, organic soils and coal have small free spaces (i.e. pores, voids) embedded in the solid together with a presence of a carbon-rich component [4]. This allows the media to be permeable to air and greatly increases its surface area per unit volume, making the organic media reactive by allowing heterogeneous oxidation reactions to take place when oxygen is present [5]. Such reactive porous media have been shown to undergo self-heating [6,7]. Self-heating is the tendency of certain porous fuels to

undergo spontaneous exothermic reactions in oxidative atmospheres at low temperatures [7]. In biomass, this process typically starts by exothermic biological reactions, which can occur at temperatures up to 70 °C [8]. The further exothermicity is then dominated by slow exothermic oxidation at low temperatures, but the reaction alone is insufficient to raise the material temperature. The temperature rise is determined by the balance between the rate of heat generation and the rate of heat losses [9]. These exothermic reactions can lead to ignition, leading to smouldering or flaming fires. The more reactive the material, the more prone it is to self-heat. Fire initiated by self-heating ignition is a well-known problem for many porous reactive media, and has been reported and studied for materials such as chemically activated carbon, sawdust, wood, coal, organic soils, biomass and shale [6,10–13]. Some work has been carried out on the self-heating ignition properties of biomass utilising themogravimetric analysis (TGA) on a variety of materials such as poplar wood and wheat straw [14–17]. TGA is very useful for determining kinetics, but is not sufficient to characterise self-heating, as the assumption for TGA measurements is that the sample can be considered 0D. In reality, self-heating requires understanding of the heat distribution in space as self-heating will occur at the centre of a sample. Therefore analysis is required to be able to analyse the bulk behaviour of biomass self-heating ignition. Some of this work is present in literature: Garcia et al. [18] carried out some of these bulk property studies on the self-heating ignition properties of biomass dust, and its propensity to ignite in storage conditions where oxygen is present and the environmental temperature is elevated enough. Jones et al. [19] studied self-heating ignition properties using TGA coupled with basket experiments for a variety of biomass feedstock including olive residue, sugars, and sunflower husks. Some work was also carried out to predict self-heating ignition of biomass by analysing emission products [20]. This work focuses on quantifying the relationship between characteristic material properties of biochar, namely pyrolysis temperature and physical properties of the char, on the tendency of the material to ignite due to self-heating.

2. Theory

2.1. Biochar reactivity

In-depth studies of biomass pyrolysis have been previously carried out in literature to determine the pyrolysis effect on the three major components of biomass: cellulose, hemicellulose and lignin [21,22]. They showed that at heating rates lower than 100 °C/min biomass decomposes first by hemicellulose decomposition, then cellulose decomposition and finally lignin which decomposes more slowly. Moisture evaporation will occur at temperatures below 110 °C. For the decomposition, hemicellulose was found to have most of its weight loss in the temperature range between 220 °C and 315 °C, cellulose in the temperature range between 315 °C and 400 °C, and lignin as a slower process with only 67% of its weight lost by 850 °C [21].

Biochar is defined as a porous carbonaceous solid produced by the thermochemical conversion of organic materials in the absence of oxygen. Because of its production temperatures above 350 °C, lignin is the main component of biochar produced from biomass. Biochar also contains aromatic-aliphatic organic compounds of complex structure which include residual volatiles, and ash. Biochar has a higher carbon density compared to the original biomass feedstock. Finally, there are voids in the biochar structure formed as pores (macro, meso and micropores), cracks and morphologies of cellular biomass origin making biochar a reactive porous structure [23]. This porous structure makes biochar prone to self-heating ignition.

2.2. Frank-Kamenetskii theory

The problem in self-heating ignition corresponds to the transient heat conduction equation. There are three main models that can be used in analysing oxidation and self-heating reactions present in this heat transfer problem [24]. The first model is the Semenov model, which describes spontaneously-heating systems by assuming uniform temperature distributions, neglecting consumption of the reactant material and assuming that the chemical reaction follows a one-step Arrhenius temperature dependence. The second model is the Frank-Kamenetskii model, which builds on the Semenov model but incorporates heat conduction through the solid material due to the chemical heat release of the material, therefore does not assume uniform temperature profiles. The third available model is known as the Thomas model and it builds upon the Frank-Kamenetskii model by additionally considering the convective heat loss effects from the surface. All three models assume a single-step global reaction, constant thermal properties of the material, no reactant consumption and no restriction of oxidizer availability [7,25]. Therefore they only apply to materials for which a global one-step kinetic model provides a reasonable approximation to the actual chemical scheme of the material. The most used model for experimental work in the literature to investigate self-ignition properties of materials is the Frank-Kamenetskii theory of ignition criticality [6,7,12,26]. The reason for this is that a basket heating experimental technique was developed based on this theory which allows the determination of critical ambient temperatures for a given sample size for ignition. The theory can be used to extrapolate data from experimental measurements to predict the expected behaviour of very large stockpile sizes of that same material. The data and the analysis serve to quantify the risks in realistic conditions if the mechanism of heat generation is unchanged when extrapolating the results to larger sizes [7,26]. These models are very effective when used to predict critical temperature and critical size for ignition, but are not as effective when used to assess the time to ignition, as the models assume steady-state conditions and therefore make the time to ignition harder to quantify. The disadvantage of using Frank-Kamenestkii theory coupled with basket experiments is that it is a very time-intensive method and requires a lot of material, as many experiments have to be carried out. However, Frank-Kamenetskii theory coupled with the oven basket methodology has been shown to give the most robust results for scaling results of laboratory-scale experiments to larger size [7,26]. Therefore despite it requiring a large time and resource investment, this method was used to obtain robust results that can be utilised to study the widest range of length scales.

To carry out the analysis of experimental results, the Frank-Kamenetskii theory of ignition assumes that the material being studied is reactive and 1D, and that the heat release is from a 1-step exothermic reaction which contains numerous chemical and biological elemental reactions as described earlier. For organic materials such as biomass there are two main sources of heat generation that make up this global 1-step reaction, a chemical process at higher temperatures and a biological process at lower temperatures [27]. The biological process can range from temperatures under 20 °C to up to 70 °C and is usually caused by growths of psychrophilic, mesophilic and thermophilic micro-organisms [28]. The biological process will have a contributing effect at lower temperatures in raising the biomass temperature. However already from 40 °C chemical oxidation will start contributing to the heat generation and as the temperature increases it becomes the dominating heat generation process [28]. This global reaction is also assumed to have a high activation energy so that a steady-state solution exists [7,26].

To solve the transient heat conduction equation, Frank-Kamenetskii theory defines a dimensionless parameter δ (Eq. (1)),

$$\delta = \frac{QEfL^2}{kRT_a^2}e^{-\frac{E}{RT_a}}$$

(1)

where E is the activation energy of the 1-step global oxidation reaction, k is the effective thermal conductivity of the sample, R the universal gas constant, T_a is the ambient temperature, L is the characteristic length of