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Effect of hydrothermal carbonization on storage process of woody pellets: Pellets' properties and aldehydes/ketones emission

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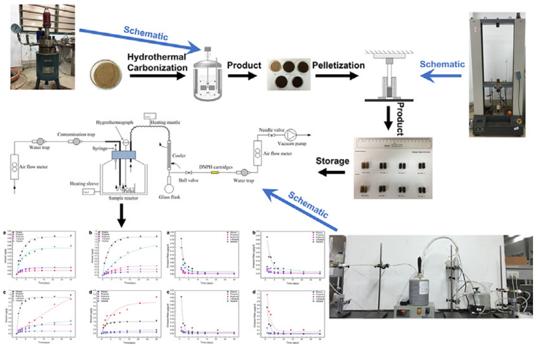
GRAPHICAL ABSTRACT



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ABSTRACT

Effect of hydrothermal carbonization (HTC) on the hydrochar pelletization and the aldehydes/ketones emission from pellets during storage was investigated. Pellets made from the hydrochar were stored in sealed apparatuses for sampling. The energy consumption during pelletization and the pellets' properties before/after storage, including dimension, density, moisture content, hardness, aldehyde/ketones emission amount/rate and unsaturated fatty acid amount, were analyzed. Compared with untreated-sawdust-pellets, the hydrochar-pellets required more energy consumption for pelletization, and achieved the improved qualities, resulting in the higher stability degree during storage. The species and amount of unsaturated fatty acids in the hydrochar-pellets were higher than those in the untreated-sawdust-pellets. The unsaturated fatty acids content in the hydrochar-pellets was decreased with increasing HTC temperature. Higher aldehydes/ketones emission amount and rates with a longer emission period were found for the hydrochar-pellets, associated with variations of structure and unsaturated fatty acid composition in pellets.

1. Introduction

Biomass pellets have drawn the increasing global attentions as their advantages over raw biomass in the reduction of transportation/storage costs and the improvement of combustion (Bai et al., 2017; Jiang et al., 2014; Xiao et al., 2015). Activities and mechanisms on pretreatment,

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pelletization, co-pelletization and pellets' characteristics have been investigated in laboratory- and industry-scales, which have significantly facilitated the development of pellets industrialization (Arteaga-Perez et al., 2017; Cao et al., 2015; Jiang et al., 2016a, 2015). More than one third of the total pellets consumption of 26 million tons in 2015 was mainly traded from the North America to Europe and Asia (Thrän et al., 2017). China had a capacity of pellets production generated from the domestic woody and agriculture wastes around 3 million tons in 2010, and is estimated to 10 million tons in 2020 (Hu et al., 2016; Jiang et al., 2016b; Li et al., 2015).

It is difficult to control the quality and safety of pellets and their feedstock, because the storage and transportation of pellets vary widely in different areas with various climate and geographical environments. In East Asia, due to the fact that the harvest of feedstock in summer and higher fuel requirement in winter, the pellets usually have to be produced in summer, and then stored in silos or warehouses until winter comes. In North America, the pellets are transported by trucks and railway from the pellet mills to the ports where they are stocked in the silos, and then transported by ship to Europe and East Asia (Boukherroub et al., 2017). The pellets are expanded as a result of friction and moisture uptake during their storage and transportation, affecting their qualities including dimension, density, hardness and moisture content (Kumar and Dubey, 2017; Wang et al., 2016). It results in the formation of fines and improvement of self-heating, and causes the explosion and self-ignition (Boukherroub et al., 2017). Meanwhile, hazardous gases, including CO, CO_2, CH_4 and VOCs, are emitted, mainly resulted from oxidation of compounds in pellets (Arshadi et al., 2009; Kuang et al., 2009). Therefore, the quality and safety controls of pellets in the storage and transportation are of great concern.

The main hazardous gases emitted from the storage and transportation of biomass involve CO, CO_2, CH_4 and VOCs (Rahman and Hopke, 2016). The previous work focuses on the emission pattern and kinetics of carbon dioxides and carbon monoxide (Kuang et al., 2009). However, VOCs as a main hazardous gas, especially aldehydes/ketones, potentially causing chronic damage to industrial workers and customers, have to be investigated at mechanism level. It was reported that autooxidation of unsaturated fatty acids is the main reason of aldehydes/ketones emission from the pellets during storage (Arshadi et al., 2009). Soto-Garcia et al. (2015a) reported that the pellets made from soft wood have the higher VOCs concentrations, while those made from hard wood have the faster emission rates. Meanwhile, the emission of aldehydes/ketones from the regular pellets is affected by both pellets' physical properties variation and unsaturated fatty acid oxidation in the surface and inner parts of pellet (Wang et al., 2016). Therefore, it may provide a potential method for removing or decomposing the unsaturated fatty acids from the sawdust, prior to pelletization, and reducing the aldehydes/ketones emission from the pellets in the processes of storage and transportation (Attard et al., 2016). However, few researches have studied effects of pretreatment on the aldehydes/ketones emission and the variation of pellet properties during storage and transportation (Attard et al., 2016; Granström, 2014). Super-critical carbon dioxide extraction ($scCO_2$) can remove 84% of lipids from the sawdust prior to pelletization, which considerably reduces the off-gases (CO, CO_2, CH_4, aldehydes and ketones) emissions from the pellets during storage with a limited impact on its production, density, durability and calorific value (Attard et al., 2016).

Moreover, reducing moisture content in biomass before torrefaction, pyrolysis, and combustion is a high energy consumption process as the hydrophilicity of biomass (Cao et al., 2015; Chen et al., 2016; Kambo and Dutta, 2014). Hydrothermal carbonization (HTC), which can deal with high moisture raw material in sub-critical solutions, can be utilized to identify the impact on the emission of aldehydes/ketones from the pellets during storage. Meanwhile, HTC may significantly change the composition and morphology of biomass, and has been widely applied in the preparation of hydrochar and liquid products (Kumar et al., 2017a; Zhuang et al., 2018).

Furthermore, HTC could be used as a pretreatment for biomass to upgrade the pellets' quality. HTC can improve the density, strength, hydrophobicity and combustion properties of pellets, which indicate that hydrochar-pellets are suitable as solid biofuels (Hoekman et al., 2014; Liu et al., 2014). The formation of furan and phenolic resins from polymerization of intermediate compounds via hemicellulose and cellulose decomposition is attributed to the improved binding ability of hydrochars (Hoekman et al., 2014). In a previous publication of authors, the emission activity of aldehydes/ketones is improved with increasing the moisture content of pellets (Wang et al., 2016). During the HTC process, hemicellulose is decomposed, which can reduce the moisture uptake of its solid product (Liu et al., 2014). Therefore, the emission of aldehydes/ketones from biomass may be reduced by the HTC process as a pretreatment. However, the influence of HTC on the aldehydes/ketones precursors (unsaturated fatty acids) variation and the oxidation pathway of the main aldehydes/ketones precursors during storage are still not fully studied.

In this study, the behavior of aldehydes/ketones emission was investigated, and pellet (untreated-sawdust-pellets and hydrochar-pellets) properties variation was studied during storage. Variations of the main aldehydes/ketones precursors in the two layers of pellet were identified. A mechanism of the coupling of HTC and pelletization processes on the formation of aldehydes/ketones during pellets' storage was illustrated. Meanwhile, an efficient way to control the formation of aldehydes/ketones during pelletsstorage and simultaneously improve the pelletization performance and the quality of pellets was found.

2. Materials and methods

2.1. Materials

Cunninghamia lanceolata (Lamb.) Hook (Cedarwood) was obtained from a local forest in Changsha (28°6′52″ N, 113°3′34″ E, Hunan province, China). Before being used in experiments, the fresh cedarwood were air-dried, grounded into fractions with particle size below 0.45 mm, and stored in sealed plastic containers at 4 °C. The hydrochar were prepared in a 500 mL autoclave reactor (GSHA-0.5, China) as reported in detail in a previous work (Li et al., 2018). After HTC, the samples were prepared by vacuum filtration method for solid–liquid separation and washing with 100 mL deionized water during the vacuum filtration process. The hydrochars were dried at 40 °C for 24 h, and then stored in sealed plastic containers at 4 °C. The color dimensions of hydrochar based on CIE (Commission Internationale de l'Eclairage) color space and other properties of the raw and hydrochar were also reported in our previous publication (Li et al., 2018).

2.2. Pelletization

The pellets were made from hydrochar using a DWD-10 universal test machine with a cylinder die and a piston installed. Detailed descriptions of the machine and the calculation of energy consumption (compaction and extrusion) were previously presented (Li et al., 2015). Prior to the pelletization, a predetermined amount of deionized water was added to the hydrochar to attain moisture content around 15%, which were then stored at 4 °C for 48 h to ensure the uniformity of their properties. The hole in the cylinder was filled with approximately 0.8 g sample to make a single pellet with approximately 7.5 mm in diameter and 17 mm in length. Prior to the pelletization, the temperature of the cylinder die was preheated to 110 °C. Meyer hardness (HM) was inversely proportional to a collapsing force and a depth of indentation as shown in Eq. (1).

$$HM = F/[\pi\,(D\mathrm{h} - \mathrm{h}^2)] \tag{1}$$

where h is the depth of indentation (mm); F is the collapsing force (N); and D is the rod diameter (mm).