Fuel 183 (2016) 314–321

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Variation in the physical properties of wood pellets and emission of aldehyde/ketone under different storage conditions

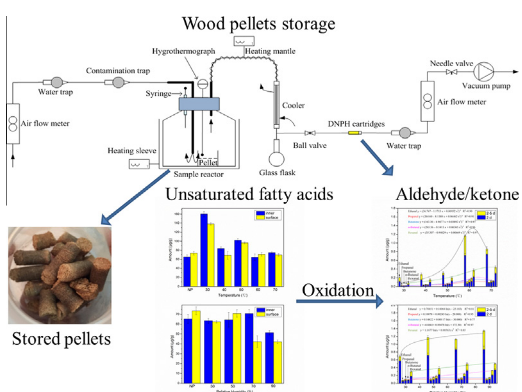
Siyuan Wang [a,b,c], Xingzhong Yuan [a,b,*], Changzhu Li [c], Zhongliang Huang [c], Lijian Leng [a,b], Guangming Zeng [a,b], Hui Li [c,*]

[a] College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China
[b] Key Laboratory of Environmental Biology and Pollution Control (Hunan University), Ministry of Education, Changsha 410082, PR China
[c] Institute of Biological and Environmental Engineering, Hunan Academy of Forestry, Changsha 410004, PR China

HIGHLIGHTS

- The pellets' physical properties and moisture content were reduced during storage.
- Ethanal and hexanal were the main compounds emitted from the pellets during storage.
- The emission of aldehyde/ketone during pellets' storage was evaluated systematically.
- A correlation between aldehyde/ketone emission and influence factors was established.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 23 March 2016
Received in revised form 13 June 2016
Accepted 20 June 2016
Available online 27 June 2016

Keywords:
Wood pellet
Aldehyde/ketone emission
Storage
Physical property
Unsaturated fatty acid

ABSTRACT

Considering self-heating and hazardous gaseous emission, the safety of wood pellets storage has become one of the important aspects for woody biomass utilization. In this study, the emissions of aldehydes/ketones were analyzed by high performance liquid chromatogram (HPLC). The properties of pellets stored in semi-closed tanks with different temperatures and relative humidity (RH) were also investigated. The emissions of aldehydes and ketones from pellets were increased with raising temperature and RH during storage, while the pellets' physical properties (dimension, density, Meyer hardness and moisture content) were reduced, except for 70% and 90% RH runs. The fatty acids compositions were extracted from both the surface and the inner part of pellets, which were analyzed by gas chromatography–mass spectrometry (GC–MS). The interaction between pellets' physical properties variation and unsaturated fatty acid oxidation was revealed by the investigation of differences of extracted unsaturated fatty acids concentration between the surface and the inner part of pellets, which affected the aldehydes and ketones emissions.

1. Introduction

Wood pellets made from raw materials such as sawdust and shavings are used as a renewable and low-carbon energy resource for industrial and municipal applications including electricity

* Corresponding authors at: College of Environmental Science and Engineering, Hunan University, Changsha 410082, PR China (X. Yuan), Institute of Biological and Environmental Engineering, Hunan Academy of Forestry, Changsha 410004, PR China (H. Li).

E-mail addresses: yxz@hnu.edu.cn (X. Yuan), lihuiluoyang@163.com (H. Li).

http://dx.doi.org/10.1016/j.fuel.2016.06.083
0016-2361/

generation and domestic heating [1–5]. When compared with the raw materials, the pellets can be more easily handled, transported and stored at a lower cost because of their uniform size and higher density [6–8]. Pellets in East Asia are usually stored in silos or warehouses with seasonal storage for the higher heating-supply price in winter. While in North America are transported in ship containers from Canada and eastern US to northern Europe by 30–45 days.

During storage and transportation, attentions should be paid to the variation in the physical properties of the wood pellets, including dimension, density, moisture content and hardness [9,10]. The insufficient stabilization of the dimension and density of pellets as well as the mutual friction among low-hardness pellets could contribute to their expansion which creates fines that may cause explosion during storage and transportation. Meanwhile, moisture uptake of pellets may be attributed to the existence of the hydrophilic functional group from the hemicellulose in biomass. Moisture absorption can promote the biological degradation of biomass, potentially leading to self-heating and spontaneous combustion of wood pellets in large-scale storage and transportation [11]. It is showed by an additive pattern that the temperature of stored pellets in large-scale silos was increased with the time and height in the silo. Moreover, temperature gradients in the silo would cause moisture migration carried by air movements [12].

Aside from the variation in the physical properties, gaseous emissions also occurred during the storage of woody biomass including wood pellets, chips, and sawdust [13–17]. Chemical degradation of wood pellets is the main reason for those emissions compared with biological degradation [18]. The dominant gaseous compounds emitted from softwood pellets are CO, CO_2, CH_4 and volatile organic compounds (VOCs) [13,14,16,19], which induce acute or chronic harms to workers dealing with the storage and transportation (ocean vessel). Some casualties and fatal accidents had occurred in ship containers during the discharging of pellets in Sweden [15]. A recent study has shown that the concentration of CO in domestic and commercial-scale pellet bins exceeded the guidance and regulatory limits for CO exposures [20]. To characterize the off-gassing rate of softwood pellets, a kinetic model of CO, CO_2 and CH_4 emissions from stored pellets was developed [21]. The amount of emitted gases will depend on the temperature, relative humidity (RH), headspace volume, available surface area of pellets, mass and the type of wood [22–24]. In consideration of the depletion of O_2 during the pellet off-gassing reaction, the emissions of CO and CO_2 have also been measured [25]. However, few literatures about VOC emissions from stored pellets were reported. Under certain conditions, it was found that high level of VOCs was emitted by stored pellets, and aldehydes were the major constituents of VOCs emitted from wood pellets [13]. Some aldehydes are known irritants to the eyes and the upper respiratory tract. For instance, hexanal exposure of 10 ppm is sufficient to cause the discomfort of eyes and noses accompanied with headaches [13]. Pentanal and hexanal are also known to cause unpleasant and irritant odors in closed space. Furthermore, methanal and ethanal are suspected carcinogens [13]. The amount and composition of VOC emitting from stored pellets were correlated with the temperature, raw material species and self-heating in the stored pellets [14,16,26]. In laboratory studies, acetone and aldehydes such as *n*-butanal, pentanal, hexanal, octanal and nonanal are also emitted from wood pellets during storage [16].

The primary mechanism for the generation of VOCs was found to be the result of unsaturated fatty acids oxidation [14,16]. Aldehydes especially hexanal are reliable indicators of lipid oxidation. A previous work on the unsaturated fatty acid oxidation products emission during wood pellets' storage found hexanal exposed in pellet warehouses and domestic pellets' storage rooms [13]. Free unsaturated fatty acid oxidation has been identified as one contributing cause of self-heating of pellets which are commonly exposed to air during storage [27]. Meanwhile, the variation of oxygen transportation via micro-pores inside wood pellets could affect the intensity of unsaturated fatty acid oxidation, resulting in the change of aldehydes production. However, few studies have been reported on the mechanism of VOCs formation from unsaturated fatty acid oxidation in combination with the variation of pellets' physical properties in different storage conditions.

In this study, the two factors temperature and RH were varied to evaluate the influences on aldehydes and ketones emissions, unsaturated fatty acids oxidation and pellets' physical properties during storage of pellets. The objectives were to investigate the changing pattern of aldehydes and ketones formation from unsaturated fatty acids oxidation in combination with the variation of pellets' physical properties in different storage conditions and to explain the related mechanism.

2. Materials and methods

2.1. Materials

Cedarwood collected from a local forest in Changsha China, were used for all experiments. After air drying, the fresh cedarwood branches with bark were grounded into fractions with particle size below 0.45 mm, and stored in sealed plastic containers at 4 °C. Before pelletization, a predetermined amount of deionized water was added to the ground samples to attain moisture content around 15%, which were then stored at 4 °C for 48 h to ensure uniformity of their properties. The properties of the raw sample are given in Table 1.

2.2. Pelletization

The pellets were prepared using a DWD-10 universal test machine with a cylinder die and a piston installed. Detailed descriptions of the machine and test procedures have been presented in our previous work [28]. 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 pelletization, the temperature of the cylinder die was raised up to 110 °C.

2.3. Experimental set-up

The storage and sampling apparatus used for the experiments are shown in Fig. 1. The sample was placed in a sample reactor (1 L volume) which was wrapped by a heating sleeve and connected with a PID system to reach the desired temperature. The temperature and RH of the reactor environment were analyzed by a hygrothermograph probe. The RH in the reactor could be

Table 1
The proximate and ultimate analysis of raw samples expressed on a dry basis.

Analysis	Raw
Proximate analysis (%)	
VM	73.23
FC	17.02
A	1.16
Elemental analysis (%)	
C	48.09
H	6.24
N	0.31
S	0.59
O[a]	44.77

[a] By difference.