Journal of Cleaner Production xxx (2016) 1–8

Contents lists available at ScienceDirect

Journal of Cleaner Production

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

Study on extracting available salt from straw/woody biomass ashes and predicting its slagging/fouling tendency

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A R T I C L E I N F O

Article history:
Received 20 January 2016
Received in revised form
21 August 2016
Accepted 21 August 2016
Available online xxx

Keywords:
Wood
Straw
Ashes
Extraction
Slagging

A B S T R A C T

Large amounts of potassium and silicon elements contained in biomass ashes can substitute for equivalent quality of raw materials to make agricultural or industrial products. In this study, a multi-step extracting method for straw/woody biomass ashes is developed to enhance their utilization efficiencies. After the same treatment processes, different products are obtained from biomass ashes at 500 °C and also characterized by X-ray diffraction (XRD) and X-ray fluorescence (XRF). In addition, the slagging/fouling tendencies of three kinds of biomass ashes were well evaluated by adapting the coupling approach, which considering two compositional ternary diagrams, some empirical indices and soluble salts content. Moreover, it was also in comparison with that of fifty three kinds of biomasses from references. The results show that potassium element in extractive products from biomass ashes mainly exists as potassium chlorides and sulfates, such as KCl, K_2SO_4, $KNaSO_4$ and $KNa_3(SO_4)_2$. More potassium salts could be recycled from ashes by decreasing the burning temperature of straw/woody biomass. The extracting ratio of potassium salts from cotton straw ashes and sawdust ashes increases sharply at first, then tends to smooth. The initial extraction ratio of 64.04% for cotton straw ashes is larger than that of wheat straw ashes and sawdust ashes. The order in the total accumulated extracting ratio of potassium from ashes is cotton straw > wheat straw > sawdust. This method could be suggested as a feasible and sustainable utilization option for biomass solid wastes. In addition, the high deposition and corrosion risk are estimated for wheat straw, and the medium one for cotton straw and sawdust with the coupling approach, if they will be used as input material for boilers.

1. Introduction

Except for coal and oil, biomass combustion has a remarkable worldwide potential in exhibiting the excellent nature of meeting this demand on reducing CO_2 emissions and replacing fossil fuels for producing heat and power. Every year large amounts of straw biomass wastes are produced in developed and specially developing countries. Unfortunately, the practice of open burning in fields is greatly prevalent, because of low cost and the easiest disposing approach considered by farmers in under developed countries. In China, the annual yield only for straw biomass is high up to around 700 million tons, which excludes other biomass resources such as the scattered wood, residues branches and leaves. Although so large amounts of straw biomass are distributed in China, its total utilization rate is only 70.6% (Xiao et al., 2010). Because the low cost disposal way of open-burning is still occurred in rural areas. It is found that this practice could result in huge amounts of fine particles emitting into the atmosphere, to affect local human health and ecological environment seriously. Therefore, how to make use of biomass or biomass ashes with greener and feasible ways will be worthy of investigation, with increasing disposal costs and biomass ash volume for developing and underdeveloped countries in future.

Biomass combustion has been widely used in many power plants in some countries worldwide. However, these power plants have always been troubled by some ash-related problems and fine particle emissions, such as slagging, fouling and corrosion. This is mainly due to substantial vaporization of alkali metal elements (K

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http://dx.doi.org/10.1016/j.jclepro.2016.08.102
0959-6526/

or Na) contained in raw materials. Several techniques have been proposed to abate these problems, such as leaching (Davidsson et al., 2002), utilization of additives (kaolin and dolomite) (Steenari and Karlfeldt Fedje, 2010; Wang et al., 2012), co-combustion (Yang et al., 2011) and fuel sulfation (Kassman et al., 2011). Moreover, the methods for processing and storing biomass ash are also a key problem at present. In China, approximately 162 biomass plants with generation capacity of 12–30 MW have been operated normally by 2013. By calculation, the annual consumption of biomass is about 150,000 tons for a 15 MW biomass plant. Huge amounts of biomass ashes were generated from biomass combustion, including 20–30% fly ash and 70–80% bottom ash. It is widely accepted that fly ashes contain more volatile salts (KCl and K_2SO_4) and bottom ashes contain less volatile salts. Additionally, biomass ashes also contain a large amount of essential nutritive elements for plants, and minor content of heavy metals. The characteristic of crystalline minerals and elemental species in biomass ashes largely determine their utilization methods. For example, high concentration of soluble K or Na element in biomass ash as fertilizers is greatly benefited for plant growth, but extremely harmful for heat transfer surfaces in furnace. Therefore, to get a detailed characterization of biomass ashes is often necessary and of vital importance for determining its utilization direction.

Several disposal ways have been proposed to study the utilization of biomass wastes in these aspects, including fertilizer and soil amendment in agriculture or forest (Huotari et al., 2015), substitute materials for mortars, concrete (Nuaklong et al., 2016), cements (Maschio et al., 2011) and bricks in construction, and removal of mercury (Bisson et al., 2013) and zinc elements (Gupta and Sharma, 2003). Biomass ash acting as forest fertilizer can increase tree production and reduce soil acidity. But the accumulation of harmful elements in plant and its effects in environment should be further investigated. Biomass ash can also be used to stabilize the liquid sewage sludge and inhibit its microbial activity (Pavšič et al., 2014). It is really a sustainable method to process biomass solid waste. But the potential harm on vaporization of potassium from additional ash is not taken into consideration if sewage sludge blending with biomass ash act as input material for furnace. In addition, the bio-briquette ash with a range from 5% to 55% as partial replacement of sand can be used for making bricks that be recommended for non-load bearing wall (Sakhare and Ralegaonkar, 2016). The concrete mixes with rice husk ash have a lower global warming potential (Gursel et al., 2016). But potassium salts (KCl and K_2SO_4) in biomass ashes can cause precipitation of gypsum and portlandite in mortars that blending with different equivalent mass of fly or bottom ash to replace cement (Maschio et al., 2011). Moreover, they also result in a significant decline in compression strength of materials. But the soluble KCl and K_2SO_4 in ashes are fairly beneficial to plant growth. So achieving multi-purpose utilization for biomass ash is quite valuable. High burning temperature can increase the vaporization of potassium salts from biomass ash and cause melting reactions between potassium salts and silica. The mineral phases in biomass ash become more complicated. But the optimal burning condition could keep more potassium salts stuck in biomass ashes with less unburned carbon. Therefore, how to realize the separation of potassium salts and silica from biomass ash would be a sustainable method to deal with solid wastes. Furthermore, the problems related to multi-purpose utilization of biomass ash in different field are still needed to be further developed and clarified in future.

This work aims to propose a multi-step leaching method to extract available salts from straw and woody biomass ashes, to achieve the higher utilization rate of biomass wastes. Meanwhile, ash characteristics of three biomass samples are analyzed in comparison with various referenced biomass ashes. Additionally, a coupling evaluation method is used to estimate slagging/fouling tendencies of straw/woody biomass, which considering several empirical indices, two compositional ternary diagrams and proportion of alkali salt extracted from ashes. The obtained information would provide a clearer understanding of potential applications of biomass ash as substitute material, as well as the pre-evaluation of ash-related problems for biomass power plants.

2. Materials and methods

2.1. Preparation of raw materials

Three types of biomass fuels, i.e., wheat straw, cotton straw and sawdust, are used to study leaching characteristic of potassium, ash-related problem and potential application of biomass ash. Wheat straw and sawdust are obtained from Shaanxi Province, and cotton straw is from Xinjiang Province, in China. Before using, these fuels were crushed and ground to a size below 300 μm to assure homogeneity. Then they were dried at 105 ± 2 °C for 24 h to get a stable mass. The proximate and ultimate analyses of these fuels are presented in Table 1.

Table 1
Ultimate and proximate analyses of three biomasses.

Item	Fuel	Wheat straw	Cotton straw	Sawdust
	Origin	Shaanxi	Xinjiang	Shaanxi
Ultimate analysis (wt%, air dried basis)	Carbon	43.92	43.99	44.75
	Hydrogen	4.47	3.40	4.98
	Oxygen	40.98	45.42	39.85
	Nitrogen	0.44	0.75	0.12
	Sulfur	0.30	0.32	0.01
	Chlorine	0.49	0.63	No data
Proximate analysis (wt%, air dried basis)	Moisture	3.88	7.22	9.87
	Ash	6.01	5.50	0.42
	Volatile	72.10	67.65	76.77
	Fixed carbon	18.01	19.63	12.94

2.2. Experimental procedure

As viewed in Fig. 1, three typical biomass ashes at 500 °C were immersed in deionized water of 90 °C with magnetic stirring for 1 h, respectively. The leachate was heated at a high temperature until the occurrence of crystalline salt. And then the obtained salt was transferred into an atmospheric dryer to dry moisture for 1 h at 105 ± 2 °C. The residual ashes were immersed again with same procedure. This process was carried out totally for six times, to get more soluble potassium salts as much as possible. Finally, available salts were obtained from wheat straw ash (WA), cotton straw ash (CA) and sawdust ash (SDA) after this process, respectively.

The accumulated extracting rate is used to evaluate the leaching properties of each ashes, which can be written as

$$M_{\text{extracting rate}} = \sum_{i=1}^{6} \frac{S_{k,\text{extracts},i} \cdot m_{\text{extracts},i}}{S_{k,\text{ash}} \cdot m_{\text{ash}}} \times 100\% \quad (1)$$

where $S_{k,ash}$ is the mass fraction of potassium element in ashes, and m_{ash} is the mass of biomass ashes, which is around 5 g for each fuel. The terms $S_{k,extracts,i}$ and $m_{extracts,i}$ are the fraction of potassium element in extracts and the mass of extracts, respectively. The subscript i represents the extracting times.

In generally, biomass fuels are burned at 550–600 °C to address the properties of biomass ashes, according to ASTM870 standard and Chinese GB/T30726-2014 standard. Because large amounts of