Fuel Processing Technology 139 (2015) 127–134

Contents lists available at ScienceDirect

Fuel Processing Technology

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

Enhancing fuel qualities of cassava crop residues by washing

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ARTICLE INFO

Article history:
Received 21 January 2015
Received in revised form 15 June 2015
Accepted 24 June 2015
Available online 4 August 2015

Keywords:
Biomass property
Biomass refining
Ash composition
Thermal conversion
Chlorine
Potassium

ABSTRACT

Cassava (*Manihot esculenta* Crantz) stems, being waste residues after harvesting starchy roots, are a potential biofuel resource. However high concentrations of ash and elements Cl, K, etc. in the stems may cause severe deposition, corrosion and particle emissions, in addition to slagging during combustion. This study tests washing by water as a pretreatment to reduce the problems. A 3-level full factorial designed experiment was conducted with washing time (<1800 s) and temperature (20–40 °C) as factors and fuel characteristics as responses. The effect of milling particle size was also examined in a supplementary experiment.

After washing, the net calorific value of the biomass tended to be higher, though not significant. Both washing time and temperature increased C but decreased H, while N and S content decreased with time only. A short washing of 50 s decreased the ash content by approximately 50% and Cl around 75%, followed by K and P that decreased to 50% after 5 min. Smaller milling size resulted in a larger amount of starch washed away, but no significant change in content of total ash and individual elements, except for Cl which was significantly higher in the smaller particles. The effect of washing on the ash composition is visualized in a ternary diagram, showing that the risk for slagging and fine particle emissions is reduced. A reduction in the risk of corrosion is also predicted as indicated by a relatively higher ratio of S/Cl and lower Cl/(K + Na). Thus, in addition to extraction of starch, the washing can also improve fuel quality of the residual biomass.

1. Introduction

In the context of sustainable development, it is important to study the possibilities of utilizing crop residues for energy purposes. Food production must be secured world-wide and the crop residues can be a large resource for fuel production [1], thus it will not only provide carbon neutral energy resources (biofuels), but may also increase the farmers' profit from existing crop fields without direct or indirect land use change [2]. There will also be a reduction of emissions produced when surplus crop residues, now widely burnt in fields, instead will be burned as refined biofuels under controlled conditions [3,4].

Cassava (*Manihot esculenta* Crantz) stems are one of the potential biofuel resources under exploration [5]. Being the fourth most important crop in the tropical and sub-tropical regions in the world, cassava provides annually about 230 million tons (wet base) of roots for food, feed and also feedstock for biofuel and other bio-based products in the world, which benefit 500–1000 million low-income people in many developing countries in Africa, Asia and Latin America [6,7]. The cassava stems whose quantity corresponds to about 50% of the root production, i.e. around 126 million tons (wet based) worldwide, are mostly leftovers today. Only 10–20% of stems are retained and used for propagation in the next season [8]. Studies on using cassava stems for energy conversion are therefore important.

Cassava stems contain high concentrations of nitrogen (N), phosphorus (P), sulfur (S), chlorine (Cl), ash and potassium (K) [5,9]. One of the severe consequences of burning the stems can be that the Cl and S form gaseous HCl and SO_2 in the flue gas [10–12] entailing a risk for acid-induced corrosion in the chimney, as well as for acidic emissions. When a high chlorine content fuel is used, the risk of the formation of polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and other chlorinated hydrocarbons may also be enhanced [13, 14]. The high concentration of K in combination with chlorine (Cl) and sulfur (S) is significantly associated with the formation and properties of fine aerosol particles [9]. In addition to the possibilities that fine fly-ash particles (size <1 μm) can be formed in biomass combustion by nucleation/condensation of gaseous mineral compounds [13], some coarse ash particles (>1 μm) may be carried away by the flue gas from the fuel bed and therefore lead to increased emission of particles, due to the high ash content of the fuel.

Our previous study [9] on the combustion of cassava stems from Guangxi, China, indicated that cassava stems caused severe depositions, resulting in high risks of corrosion, in addition to slagging, due to high content of chloride and potassium. $CaK(PO_4)$ was the major component of bottom ash and slag, and K_2SO_4 and KCl dominated in deposits and flue-gas particles [9]. A high rate of deposition and corrosion inside a

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http://dx.doi.org/10.1016/j.fuproc.2015.06.052
0378-3820/

boiler will decrease accessibility and energy efficiency and increase maintenance costs for the system [15]. This suggests that the cassava stem can be a problematic fuel when it is used in, for example, industrial heat and power production. Studies have also shown that the ash-related problems may occur in other thermal–chemical conversion processes such as gasification and pyrolysis [16–18]. Technology development must be considered, therefore, to reduce the problems mentioned above.

Many methods for pretreating biomass feedstock have been developed to facilitate the use of variable biofuels in industrial energy conversion processes. The methods vary with biomass types and industrial processes. The safe utilization of corn stover can be achieved by water washing, which was shown to remove up to 90% of alkali metals and Cl [19]. Water washing has also been studied as one of the easiest and most economical methods to improve fuel properties of other biomass species such as wheat straw, rice straw, rice husk, cotton stalk, etc. [20–22]. Where cassava stems are concerned, Pattiya et al. [23] reported an effective removal of total ash quantity by washing and size-reduction-and-screening. However, further studies are needed to clarify the changes in ash composition and consequences in ash transformation behavior during thermal conversion, which is the key issue of ash-related problems (e.g. Baxter et al. [24]). It is well-known that ash related problems may occur even if wood residues are used and total ash content is as low as <2% [25]. The problems are essentially related to the amount and concentrations of some main ash forming elements (Ca, Mg, K, Si, P, S, Cl) and may appear as slagging, bed agglomeration, fouling, corrosion and unwanted emissions [15]. The ash composition and different weight ratios between the ash forming elements can be crucial. Here, we hypothesize that washing by water may be a way of pretreatment to change ash composition and reduce the problems in connection with thermal conversion, especially combustion of cassava stems. Insofar as chlorine and potassium are bonded in the biomass as water-soluble elements, they may easily be extracted by washing. Previous studies [9,26] indicated that Cl and K in cassava stems were the most problematic elements for thermal conversion processes. Questions to be answered are: (1) Will the energy properties of the washed biomass be changed? If so, to what extent? (2) In what way will the treatment alter the fuel chemical composition, especially the ash-forming elements? (3) Which factors (time, temperature and milling size) are important in fuel quality change due to the washing? In this study we report our laboratory experiment (3-level full factorial experimental design) with the objective of answering the above-mentioned three major questions. Our hypothesis is that the water washing will enhance the fuel quality of cassava stems, so that this isolated biomass can be used as high quality feedstock for combustion, either as pellets or in powder form. Some predictions on expected changes in combustion behaviors, based on ash transformation models and empirical indexes of the remaining biomass after washing (wash-residues), will also be made.

2. Materials and methods

2.1. Material

The cassava stem material, variety SC205 – "South China 205" [27] – was obtained from a private field in Wuming County (23°7.287 N, 108°22.723 E), Guangxi Zhuang Autonomous Region in China. The cassava stems were standing in fields before they were harvested on 15 December 2008. The stems without signs of decay were manually cut at 10 cm above the ground surface. The materials were then transported in plastic bags to a laboratory where they were washed, chipped (≤15 mm in size) and dried (60 °C for 72 h). Care was taken to avoid contamination of soils during sampling and laboratory processing. The dried chips were then shipped via airway to the Department of Forest Biomaterials and Technology, SLU, where this study was conducted.

2.2. Experiment

The cassava stem chips were milled and sieved to a particle size of less than 2 mm in a knife mill (BAC-50, KAMAS Industri AB) for the main factorial experiment. Two hundred (200) gram samples of milled cassava stems were washed in approximately 5 l stirred and thermostated de-ionized water. This was done with settings of time and temperature according to a 3-level full factorial experimental design [28] (Table 1) with 3 replicates. Logarithmic time settings were used. Apart from this design, some additional experiments were made: 1) with same milling degree (particle size < 2 mm) and temperatures as above but with washing times also of 3 1/2 h and 2) with cassava stems milled and sieved to a particle size of less than 0.5 mm, washing time 300 s (5 min) and temperatures 20 °C, 30 °C and 40 °C.

The washed material was screened through a metallic wire net with approximately 125 μm aperture size (120 mesh). The material was rinsed with small amounts of de-ionized water and remaining water was pressed out. The material remaining on the net was collected and weighed after drying in 105 °C and the proportion of wash-residue was calculated. The replicate samples from the wash-residues from the 50 to 1800 second (30 min) washing time were combined and analyzed for ash content, heating value, ash fusion temperatures (SST, DT, HT, FT), C, H, N, S, Cl, starch content (including simple sugars) and major ash-forming elements (Si, Ca, Al, Fe, K, Mg, Mn, Na, P, Ti). The methods of analyses can be found in Table 1.

The filtrate was allowed to settle until a firm sediment layer, containing starch and other high density particles, was deposited. The supernatant was decanted and the sediment (containing starch) was rewashed at least two times and dried. Sediment samples from 5 minute washing (particle size < 0.5 mm, 20 °C, 30 °C and 40 °C and particle size <2 mm 20 °C and 40 °C) were analyzed for starch content. The method to extract and determine the starch can be found in Zhu et al. [8].

2.3. Ash transformation

The major purpose of the study was to evaluate the possibility to utilize wash-residues of cassava stem for thermal conversion and therefore one of the focuses was on biomass ash transformation reactions and related problems such as slagging and corrosion. Five molar ratios were used to predict/discuss the ash transformation characteristics: K/(Ca + Mg), Cl/(K + Na), S/Cl, Si/P, and (K + Na + Ca + Mg)/(Si + P). The ratio K/(Ca + Mg) has been shown to be positively correlated with slag formation during the combustion of corn stover and wheat [4,29]. According to Stromberg [30] the ratio Cl/(K + Na) may indicate the proportion of alkali that could easily be vaporized as volatile chloride. When this ratio was >0.3, there was a risk of the formation of corrosive chlorine-rich deposits. It was suggested that the ratio S/Cl be an indication of whether there is sufficient surplus sulfur to reduce the risk of corrosion in conjunction with alkali chlorides [30]. When S/Cl is between 2 and 4, the risk of chloride-induced corrosion is reduced. The ratios Si/P and (K + Na + Ca + Mg)/(Si + P) together with K/(Ca + Mg) were introduced in a previous study [9] to indicate the propensity of cassava stem ash for slagging and for formation of fine particulate emission. To be able to predict fuel quality after the washing pre-treatments, it is important to explore how these indices of ash transformation reactions change.

In addition, the ternary phase diagrams suggested by Boström et al. [15], were adopted to make general predictions of ash behavior during combustion.

2.4. Data evaluation and modeling

Data from the designed washing experiments were evaluated with multiple linear regression analysis (MLR) [31]. The modeling of the effects of time and temperature on properties of treated materials was