



Removal of introduced inorganic content from chipped forest residues via air classification



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HIGHLIGHTS

- Air classification can reduce the inorganic content of pine forest residues.
- Over 40% of the ash content was concentrated into <7% of the total biomass.
- The removed ash content was primarily introduced ash from soil.
- Air classification can be used for approximately \$2.23 per ton of biomass.

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ABSTRACT

Inorganic content in biomass decreases the efficiency of conversion processes, especially thermochemical conversions. The combined concentrations of specific ash forming elements are the primary attributes that cause pine residues to be considered a degraded energy conversion feedstock, as compared to clean pine. Air classification is a potentially effective and economical tool to isolate high inorganic content biomass fractions away from primary feedstock sources to reduce their ash content.

In this work, loblolly pine forest residues were air classified into 10 fractions whose ash content and composition were measured. Ash concentrations were highest in the lightest fractions (5.8–8.5 wt%), and in a heavy fraction of the fines (8.9–15.1 wt%). The removal of fractions with high inorganic content resulted in a substantial reduction in the ash content of the remaining biomass in forest thinnings (1.69–1.07 wt%) and logging residues (1.09–0.68 wt%). These high inorganic content fractions from both forest residue types represented less than 7.0 wt% of the total biomass, yet they contained greater than 40% of the ash content by mass. Elemental analysis of the air classified fractions revealed the lightest fractions were comprised of high concentrations of soil elements (silicon, aluminum, iron, sodium, and titanium).

However, the elements of biological origin including calcium, potassium, magnesium, sulfur, manganese, and phosphorous were evenly distributed throughout all air classified fractions, making them more difficult to isolate into fractions with high mineral concentrations. Under the conditions reported in this study, an economic analysis revealed air classification could be used for ash removal for as little as \$2.23 per ton of product biomass. This study suggests air classification is a potentially attractive technology for the removal of introduced soil minerals from pine forest residues.

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1. Introduction

Biomass feedstocks are gaining recognition as the renewable resource with the greatest potential to contribute to the energy demands of modern society [1,2]. The wide availability of biomass offers the potential to reduce the dependence of national

economies on the importation of conventional energy resources, including coal, petroleum and natural gas. As conventional resources continue to be depleted, biomass is expected to gain importance as an alternative energy source world-wide, but will be especially important for developing countries whose economies are heavily based upon agriculture and forestry [3].

Specific to the availability of forest resources, a 2006 study estimated that there were about 36.2 million dry tons (US short tons) of recoverable logging residues available in the US each year, with

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more than half of that material located in the Southeast and Southcentral regions of the US. [4]. The Billion-Ton Update released by the US Departments of Energy (DOE) and Agriculture (USDA) in August 2011 predicts that forest residues will be a significant source of biofuels [5,6]. According to projections, the logging residue supply curve plateaus with 47 million dry tons potentially available from all forest lands at \$40 per dry ton or less. The estimated quantity of forest thinnings is approximately 37 million dry tons per year at a roadside price of \$100 per dry ton or less [5,6]. Such resources may provide a significant amount of feedstock for energy conversion pathways.

The ash content of biomass is known to have significant effects on thermochemical processes, including combustion (see Table 1). The primary thermochemical conversion processes are gasification, pyrolysis and hydrothermal liquefaction [7]. The following paragraphs briefly summarize the effects of inorganic species in each of these processes, starting with pyrolysis. Pyrolysis is thermal decomposition of biomass into solid char, liquid oil or tar, and gaseous products in the absence of oxygen. Pyrolysis processes that incorporate rapid biomass heating rates to moderate temperatures in the range 480–550 °C and short vapor residence times are referred to as fast pyrolysis and are known to maximize the production of liquids. Fast pyrolysis (FP) is gaining interest as a potentially versatile, efficient, economical and environmentally favorable process for converting biomass to liquid fuels [7,8]. During pyrolysis, some ash forming elements, even at trace levels (<0.1%), can alter both the thermal degradation rate and chemical pathways [9]. The alkali metals potassium (K) and sodium (Na), and the alkaline earth metals calcium (Ca) and magnesium (Mg), are known to catalyze the thermal degradation of biomass to light gases rather than the preferred liquids [10,11]. Other studies have demonstrated negative effects of higher bulk ash content on the pyrolysis process yield [12,13]. These studies have compared the process yields of various biomass sources before and after different leaching processes and have demonstrated a negative correlation between total ash content and bio-oil yield.

In addition, studies have impregnated clean biomass or biomass constituent samples with various inorganics, including K, Mg, Ca, iron (Fe), and phosphorous (P) or salts containing those elements. In general, liquid yield was found to increase for demineralized biomass and decreased with increasing salt impregnation [14]. In another study, potassium was found to promote depolymerization/fragmentation reactions to form lower molecular weight oxygenates at the expense of levoglucosan and other anhydrosugars [15]. However, other ash forming elements had only minor effects, except for P, which resulted in a simpler product distribution dominated by levoglucosenone and furfural. Another study reported that K significantly enhanced the rate of lignin pyrolysis and char production, but with minimal change in the product distribution [16]. Fast pyrolysis of cellulose with varying concentrations of added alkali and alkaline metal chlorides and anions revealed that char formation was strongly enhanced by alkali and alkaline earth metal addition [17].

Hydrothermal liquefaction (HTL) converts biomass in the presence of a solvent at moderate temperatures (250–550 °C) and pressures (5–25 MPa) to solid, oil, aqueous, and gas fractions [18]. Although HTL has longer residence times and higher capital costs

than fast pyrolysis, HTL does not require drying of the feed materials, making it suitable for wet grasses and algal resources. In addition, bio-oils from HTL usually have lower moisture and oxygen content compared to oils from fast pyrolysis [19].

Elevated ash content has also been shown to be deleterious to the combustion of biomass for energy generation. The inorganic species silicon (Si), K, Na, sulfur (S), chlorine (Cl), P, Ca, Mg, and Fe contribute to reactions that lead to fouling and slagging [20,21]. The primary sources of problems are reactions of alkalis with silica that form alkali silicates with low melting or softening temperatures and also reactions of alkalis with sulfur to form alkali sulfate deposits that impede heat transfer on reactor surfaces. Chlorine, a minor constituent in virtually all coals and biofuels, contributes to the corrosion of boiler surfaces depending upon concentration and appears to facilitate the transport of alkalis from fuel to surfaces [22,23]. Jenkins et al. has noted that the amount of alkali vaporized during combustion often depends as strongly upon chlorine concentration as it does the alkali concentration [21,24].

Because of the published results discussed above, ash removal prior to conversion processes will become more important as forest residues and other high ash content feedstocks are used alone or in higher blend ratios in conversion processes. There are many ways to remove ash forming elements from biomass; however none of them are without associated costs. Disposal costs will rise as quantities of ash rise [25]. The key to efficient and economical biomass conversion processes will be to remove the ash forming elements from the biomass effectively, inexpensively, and in a manner that removes as little biomass from the process as possible.

Soil contamination is known to be a major contributor to the total ash content in typical forest residue samples [26], and some of this contamination can be concentrated in the smallest size fractions of the biomass [26,27]. Effective ash reduction methods in forest residue samples include improved harvest and collection systems [28], and fine particle removal after initial size reduction using sieving [25] or trommel screens [26,28,29]. The removal of fine particles from the biomass can lead to improved ash concentrations; however the high-ash biomass that is removed must either be disposed of and replaced with on-spec feedstock, or treated to remove the ash forming elements so it can be used in the conversion processes [29]. Leaching can be used to effectively remove many of the soluble ash forming elements; however, this process typically requires that the biomass be dried prior to conversion, and potentially large volumes of waste leachate will need to be treated prior to disposal. It has been shown that ash removal can be achieved through the use of different field processing systems, although at a much higher delivered cost [28,30].

Pine trees are known to have an uneven distribution of inorganic elements throughout their tissues [31,32], with needles and bark containing higher concentrations of ash than wood. The concentration of some inorganic elements is highest in the cambium, the metabolically active boundary between the sapwood and bark [33]. Cambium concentrations of K, P, Ca, and Mg were found to be an order of magnitude higher than the concentrations found in sapwood, while most inorganic elements were lowest in the heartwood [33]. In addition to chemical differences between

Table 1
Effects of ash content in thermochemical conversion processes.

Ash content/composition	Soluble ash forming elements affect fuel acidity/quality; lower oil yields; char composition and disposal; transportation costs
Potassium & sodium	Alkali metals with greatest catalytic effect for thermal degradation of lignin to increase the yield of reaction water
Calcium & magnesium	Lesser catalytic effect for thermal degradation of lignin; CaO can reduce bio-oil oxygen; ash utilization
Chlorine & sulfur	Corrosion generally; upgrading catalyst poisons
Phosphorus	Strong catalytic effect, increased char, promotes different, simplified product distribution than alkali metals

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