



Impacts of co-firing biomass on emissions of particulate matter to the atmosphere



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ABSTRACT

Gas and particle emissions from co-firing coal and two types of biomass versus coal was evaluated in a circulating fluidized bed boiler operating with a constant energy input. Compared to coal, co-firing 50% oat hulls (by weight) significantly reduced the emission of particulate matter (PM) by 90%, polycyclic aromatic hydrocarbons (PAH) by 40%, metals by 65%, and fossil carbon dioxide by 40%. In contrast, co-firing 3.8% wood chips (by weight) had a negligible impact on the emissions of PM and PAH, but caused a 6% reduction in metals. Fuel-based emission factors for PM, metals, and organic species including biomass burning markers retene and levoglucosan, were determined. Enrichment factors (EF) were computed to examine the distribution of metals across PM, fly ash, and bottom ash and demonstrated enrichment in volatile metals (e.g. Fe, Al, and Cr) in PM and fly ash. Co-firing 50% oat hulls led to a significant depletion of K in PM and its enrichment in bottom ash. Scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM–EDX) analysis revealed a wide heterogeneity in particle sizes and compositions across particles for all fuel types. Overall, this study demonstrates that co-firing a 50% oat hulls with coal provides several benefits to air quality and outlines important changes to PM composition when biomass is co-fired with coal.

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1. Introduction

Biomass is a renewable fuel that holds significant potential for electrical energy production. Biomass co-firing is the practice of adding biomass as a partial substitute for coal in high efficiency boilers. Co-firing in existing boilers is a practical approach for increasing the use of biomass as fuel, because it draws upon widely-available, existing infrastructure and presents immediate opportunity for the production of low cost renewable energy [1–5]. Prior studies have demonstrated the feasibility of co-firing coal with a range of biomasses for electricity generation including wood chips [6], straw [7], switch-grass [8], rice husk [9], sugar cane bagasse [10], and saw dust [11]. Effective use of biomass fuels requires optimizing the type and amount of biomass, fuel introduction method, equipment maintenance, and air pollution control devices. In particular, understanding how co-firing alters emissions of gases and particulate matter (PM) to the atmosphere is needed

to assess the potential environmental and health impacts of co-firing.

Among the greatest benefits to co-firing biomass is the direct reduction in the release of fossilized carbon to the atmosphere in the form of carbon dioxide (CO₂). Biomasses sequester atmospheric CO₂ during photosynthesis from the atmosphere that is re-released when burned. When regrown, biomass again serves as a CO₂ sink from the atmosphere, thus having a significantly smaller impact on atmospheric CO₂ concentrations than fossil fuels [9,12,13]. When sustainable growing practices are used, biomasses are locally-sourced, and biomass-to-coal blending ratios are high, the reductions in fossil CO₂ become more substantial.

Co-firing also has the benefit of reducing air emissions of criteria pollutants compared to traditionally coal-fired power plants [14]. Biomasses contain less sulfur, and thus emit less sulfur dioxide (SO₂), a greenhouse gas and the primary precursor for acid rain [15,16]. Combustion produces nitrogen oxides (NO_x) that are toxic and reactive gases, the levels of which depend on fuel type and combustion conditions. When co-firing coal with biomass, NO_x has been shown to decrease [15,16], but can increase when biomass is combusted alone [17]. NO_x emissions mainly depend

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on combustion temperature, which is influenced by fuel properties such as its moisture and volatile matter content [6].

Similar to NO_x , emissions of PM highly depend on the biomass to coal blending ratio. For example, co-firing 10% cedar chips increased PM emission, whereas co-firing 50% cedar chips reduced PM emission [18]. In addition, co-firing has been shown to increase the average size of PM compared to coal-only, which generally improves the particle capturing efficiency by bag houses and other particulate control systems [16,19]. Furthermore, co-firing has been shown to alter the chemical composition of the PM that is formed [18,20].

Polycyclic aromatic hydrocarbons (PAH) are semi-volatile organic compounds that have mutagenic and carcinogenic properties. PAH are emitted by burning carbonaceous fuels; the magnitude of their emissions and the distribution of species depend on the fuel type, combustion temperature, and air mixing ratio [21]. Generally, biomass contains higher volatile matter than coal which has been shown to combust more quickly and reduce PAH emissions [9,22].

Co-firing also alters emissions of trace elements, by reducing coal inputs in favor of biomass [18]. Coals naturally contain heavy metals, such as Hg, As, and Se [23]. When co-firing biomass that contains low amounts of these metals, their overall emissions are reduced. Meanwhile, the high Cl content in biomass promotes formation of volatile metal chloride species (e.g. Zn and Pb), that condense upon fine particles and exit the stack as particulate matter [24]. Further, alkali metals in biomass, such as K in the presence of Cl, S, and Si undergo undesirable reactions and can deposit on the boiler surface and increase the rate of corrosion [25,26]. Hence, emissions from co-firing cannot be represented as the sum of emissions from coal and biomass, because they do not account for the selective chemical reactions occur when biomass and coal are co-fired.

Enrichment factors (EF) provide a means of comparing the metal content of the PM, fly ash, and bottom ash generated by co-firing to the input fuel. EF correct for increases in metal content due to carbon loss by normalizing sample and fuel to a reference species in each matrix [27,28]. EF are defined as the ratio of the concentration of an element (X) to the concentration of a reference element (R) in phase *i* (either PM, fly ash, or bottom ash) relative to the input fuel (*j*) as shown in Eq. (1):

$$EF = \frac{(X/R)_i}{(X/R)_j} \quad (1)$$

EF for fly ash and PM are interpreted as follows: $EF > 1$ indicates that volatile metals have condensed or absorbed, while $EF < 1$ indicates metals are leaving particles through a selective process to the gas or ash phases. For bottom ash, $EF < 1$ indicates that the metal is lost from the matrix due to volatilization, whereas $EF > 1$ reflects that the reference species may not be conserved or indicates an additional source of that element [27]. The comparison of EF across PM, fly ash, and bottom ash reveals the distribution of an element across small and large particles. Through the comparison of EF from co-firing to coal only, the effects of co-firing biomass with coal on trace element composition may be identified.

The aim of this study is to assess how the chemical composition of PM and ash generated by firing coal is affected by the co-firing of oat hulls and wood chips in a fluidized bed boiler. This study provides emissions data on co-firing oat hulls for the first time. With an advanced combination of analytical tools, we examine the magnitude of PM emissions, its metal and organic composition, and particle heterogeneity, and their relationships to the chemical composition of fuel input. EF are used to examine the distribution of metals across PM, fly ash, and bottom ash, and how these distributions are affected by co-firing. Fuel-based emission factors for

PM, PAH, metals, and other organic species are determined, and include biomass burning markers for the first time. Through a deeper understanding of co-firing on the emission of PM to the atmosphere and its composition, a better understanding of its environmental and health impacts is gained.

2. Materials and methods

2.1. Boiler and fuel conditions

Co-firing experiments were conducted in a circulating fluidized bed boiler (#11) at the University of Iowa Power Plant in Iowa City, which has a maximum heat input rate of 223 MMBtu h^{-1} . The boiler was equipped with limestone injection system for SO_2 control and a fabric filter baghouse for PM control. The boiler was operated at consistent heat input of 208 ± 1 MMBtu h^{-1} and a steam flow of approximately 155,000 lbs h^{-1} over the three fuel conditions. Stack O_2 levels were 5%, which equates to an excess air ratio of ~ 0.3 .

The boiler was fueled with coal only on April 29, 2014, 50% oat hulls by weight (39.2% by energy input) on April 30, and 3.8% wood chips by weight (2.2% by energy input) on May 1. A pneumatic injection system was used for feeding oat hulls to the boiler to ensure accurate blending ratio, whereas wood chips were blended with coal in advance. The oat hull-to-coal ratio of 50% (by weight) represented the highest biomass fuel fraction that could be reliably maintained and represents the maximum biomass-to-coal ratio for the utilized boiler. The wood chip-to-coal ratio of 3.8% by weight (corresponding to 30% by volume) is the maximum wood chip volume that could be introduced to the boiler and also represents the maximum biomass-to-coal ratio for the boiler. Biomass fuels were locally sourced from within 25 miles of the power plant. Oat hulls, a by-product of cereal production, are obtained from the Quaker Oats facility in Cedar Rapids, Iowa; additional details are provided elsewhere [29]. The wood chips burned during the test were derived from non-native conifer trees that were harvested from Kent Park in Johnson County. The average size of the fuel input was 1.6 cm for coal and wood chips and 0.8–1.2 cm for oat hulls. Fuels underwent ultimate and mineral analyses at Standard Laboratories, Laboratories Accreditation Bureau.

2.2. Sample collection

Gases and total suspended particle (TSP) samples were collected in duplicate for each fuel condition according to United States Environmental Protection Agency (US-EPA) Method 29 for metals and PM mass [30] and Method 10 for volatile compounds [31]. Flue gas emitted from the boiler stack at the University of Iowa Power Plant was pulled through a borosilicate probe, with particles collected on a high-purity quartz filter, semi-volatiles on Amberlite® XAD-2 polystyrene resin (SUPELCO), and condensate through a series of impingers filled with acidic solution. A consistent volume of stack emission was passed isokinetically through the system during the experiment (~ 122) dry standard cubic feet (dscf). The volumetric flowrate through the stack was calculated from the average velocity of the effluent gas through the sampling set up and the cross sectional area of the duct at sampling location. In addition, fly and bottom ashes were collected in duplicate for each fuel condition into pre-cleaned containers.

2.3. Gravimetric analysis

PM mass was measured as the difference in the quartz fiber filter mass before and after sampling, according to EPA Method 29 [30] under controlled temperature (21.9 °C) and relative humidity ($25 \pm 5\%$) using a high-precision microbalance (Mettler Toledo

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