



Characterization of biomass and high carbon content coal ash for productive reuse applications



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HIGHLIGHTS

- We characterize pure coal, coal and biomass co-fired, and pure biomass ash.
- We examine physical, thermal, chemical and mineralogical characteristics.
- Up to 15% biomass co-firing with coal does not significantly change the fly ash physical and chemical characteristics.
- Co-fired ash that meets ASTM requirements for concrete can be used like coal ash.
- Biomass ash can likely be used as sorptive agents or as a fuel supplement.

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ABSTRACT

Productively reusing the waste residuals from energy production is an essential component in sustainable disposal and management of energy related waste. In the US, the world's second largest producer of coal next to China, over 118 million tons of coal combustion by-products are produced each year; only 44% of which are productively reused. In recent decades, advances in lowering CO₂, SO_x, and NO_x emissions from coal combustion have changed the characteristics of the solid coal combustion products. In particular, the residual carbon content of fly ash generated at many US coal-fired power plants has increased, and has become more heterogeneous. Additionally, utilities are exploring the use of pure biomass as a fuel source, which results in a fly ash that is generated from a purely organic source. While much research effort has been devoted to understanding the properties and potential productive reuse alternatives for coal combustion products, relatively little research has been done on the byproducts from biomass combustion or co-combustion.

In this study, high carbon content coal ash, co-fired coal/biomass ash, and pure biomass ash from several US power plants were investigated. The ashes were characterized using a number of physical and chemical analysis techniques, including: scanning electron microscopy, laser diffraction, organic carbon content, nitrogen adsorption surface area, proximate and ultimate, X-ray fluorescence, and X-ray diffraction analysis. Results showed little physical, chemical, and mineralogical differentiation between coal ash and coal co-fired with biomass ash. However, the pure biomass ashes investigated in this study, showed significantly lower specific gravity, and primary oxide content, as well as coarser particle size distribution, higher residual carbon, higher heating value, and much higher specific surface area, when compared to the coal and co-fired ashes. These results have important implications on the potential for productive reuse of these waste materials.

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1. Introduction

Slightly more than 118 million metric tons of coal combustion by-products are produced in the US every year, only 44% of which are productively reused [1]. Fly ash, the fine particulate residual material generated from coal combustion, is produced at a rate of just over 54 million tons annually in the US [1]. The majority

of this waste material is currently disposed of in impoundments on site at utilities or landfilled offsite, while 38% of fly ash is productively reused; predominantly as supplementary cementitious material (SCM) in the concrete and concrete products sector [1,56].

In 1990, an amendment to the Clean Air Act mandated a conversion to more environmentally friendly and renewable energy production in the form of low NO_x combustion processes, in addition to longstanding CO₂ and SO_x emissions restrictions. This conversion to low emissions combustion can be achieved by techniques like: flu gas recirculation, low excess air operation, coal blending,

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and staged combustion [23,24]. All of these techniques alter ambient gas concentrations and/or lower boiler temperature, producing fly ash with coarser particle size distribution, lower amorphous glass content, and most importantly, higher and more inconsistent carbon content [17,21,23,24,25,30,51]. Increased residual carbon content in fly ash reduces the marketability of this waste product as SCM in concrete. The residual carbon adsorbs air entraining agents (AEAs) added to concrete to produce stable air voids to mitigate freeze–thaw cracking [6,20,30,36,37].

Along with the low emissions strategies being implemented at modern power plants, sole combustion or co-combustion of waste biomass with coal has also become an attractive option for renewable and environmentally friendly energy production [14,33,53]. This biomass is typically in the form of chipped tree limbs, wood chips, and saw dust from urban, industrial, and agricultural sources. It is generally accepted that renewable energy generates zero net greenhouse gas emissions, while at the same time offsetting those from fossil fuel combustion [26,47,52]. In addition to the environmental benefits of biomass combustion or co-combustion for energy, mixing of biomass with coal in typical combustion processes is a simple and relatively inexpensive procedure. It is thus a particularly appealing option for power plants [2].

Understanding the physical and chemical properties of fly ash produced at power plants is necessary for improving existing productive reuse and disposal methods, as well as for developing new alternatives for both reuse and disposal of this abundant waste stream. In the US, the concrete and concrete products sector accounts for just over 21% of total coal combustion product (CCP) productive reuse, consuming 11 million tons of fly ash annually, making this the largest fly ash reuse sector [1]. The ASTM C618 standard governs the use of fly ash in concrete, allowing only fly ash from 100% coal combustion, with loss on ignition levels below 6% (by mass), to be used in such applications. There are additional chemical composition and physical requirements for the use of ash as SCM; however, the two ASTM C618 restrictions mentioned above eliminate a large portion of fly ash produced today from potential reuse in concrete applications. The use of co-fired ashes with acceptable LOI, chemical and physical characteristics is not addressed in the current ASTM C618.

As regulating bodies continue to reduce the allowable levels of SO_x, NO_x, and CO₂ emitted into the atmosphere, it is likely that there will be an increase in the number of utilities interested in transitioning from coal only combustion, to co-firing coal and biomass [55]. While a great deal of research on CCPs has been conducted over the past half century, relatively little work has been done on fly ash from this modern era that is seeking enhanced renewable energy resources. Research on the physical, chemical, and potentially beneficial characteristics of this ever evolving waste stream must continue. In this study, we aim to determine any differences between pure coal ash and biomass co-fired with coal ash, as well as pure biomass ash, through in-depth physical, chemical, and mineralogical characterization. Emphasis is placed on identifying potential productive reuse alternatives for these waste materials.

2. Experimental

2.1. Materials

Sixteen ash samples from eight different power plants located in the eastern US were investigated in this study. Table 1 shows the location and operating capacity of each plant; along with the respective pulverizing processes, boiler configurations, and types of ash received. Table 2 shows the feed coal and biomass content for each ash sample. Plant CP1 coal ash was included as a reference high quality, low loss on ignition (LOI) Class F ash (ASTM C618),

Table 1
Power plant location, operating capacity, and types of ash samples received.

Plant ID ^a	Location	Capacity (MW)	Pulverizing process	Boiler configuration ^b	Type of ash ^c
CP1	Georgia	3499	Wet ball mill	TF	LCFA
CP2	Mississippi	750	Ball and tube mill	OWF	LCFA, CBFA
CP3	Alabama	2013	Bowl mill	OWF	HCFA, CBFA
CP4	Alabama	568	Bowl mill	OWF	HCFA, CBFA
CP5	Alabama	138	Bowl mill	TF	HCFA, CBFA
BP1	Vermont	50	–	TGS	PBA
BP2	Virginia	83	–	FGS	PBA
BP3	Georgia	73	–	RB	PBA

^a CP = coal plant, BP = biomass plant.

^b OWF = opposed wall fired; TF = tangentially fired; TGS = travelling grate stoker; FGS = fixed grate stoker; RB = recovery boiler.

^c LCFA = low carbon content coal fly ash; HCFA = high carbon content coal fly ash; CBFA = coal co-fired with biomass ash; PBA = pure biomass ash.

Table 2
Initial coal and biomass content (before firing), and type for each ash sample.

Sample ID	wt% Coal	wt% Biomass	Coal/biomass type
CP1-1	100	0	Bituminous (low S, Ca)
CP2-1	100	0	Bituminous (Columbian: low S, Ca)
CP2-2	95	5	Whole-tree 1/2" Pine Chips
CP2-3	95	5	Whole-tree 1/2" Pine Chips
CP3-1	100	0	Bituminous (low S, Ca)
CP3-2	96	4	Clean 1/2" Pine Chips
CP3-3	91.8	8.2	Clean 1/2" Pine Chips
CP4-1	100	0	Bituminous (low S, Ca)
CP4-2	94.5	5.5	De-limbed 1/2" Pine Chips
CP4-3	95.1	4.9	Whole-tree 1/2" Pine Chips
CP5-1	100	0	Bituminous (low S, Ca)
CP5-2	90	10	Hardwood, green, coarse
CP5-3	85	15	Hardwood, green, coarse
BP1-1	0	100	Forrest, sawmill, urban Wood waste
BP2-1	0	100	Logging, paper mill, sawmill waste
BP3-1	0	100	Sawmill waste

Table 3
ASTM C618 chemical requirements for fly ash classes.

Class	SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃ (Minimum wt%)	SO ₃ (Maximum wt%)	Moisture (Maximum wt%)	LOI (Maximum wt%)
C	50	5	5	6
F	70	3	3	6

which is commercially marketed for use as SCM. The ASTM C618 criteria for the different fly ash class designations are summarized in Table 3.

As shown in Table 2, three samples were received from each of Plants CP2, 3, 4, and 5. The first ash sample from each plant was from the pure coal ash produced at that plant. The second and third ash samples were from biomass co-firing tests conducted at each plant. The samples from Plants BP1, 2, and 3 were pure biomass ashes from combustion of mill waste, logging, or urban wood waste without any coal. All pure coal ash samples were collected from dry storage silos after electrostatic precipitation (ESP). The co-fired fly ash samples were collected directly from hoppers at the electrostatic precipitators after the conclusion of each co-firing

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