Use of bioethanol byproduct for supplementary cementitious material production

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HIGHLIGHTS

- Unpreated corn stover ash (CSA) severely suppressed cement hydration.
- CSA pretreatments increased hydration by removing phosphorous out of the CSA.
- High lignin residue (HLR) ash is a highly reactive material for use in concrete.

ARTICLE INFO

ABSTRACT

Corn stover has the potential for use as a supplementary cementitious material (SCM) for concrete. The impact of distilled water and dilute acid pretreatments and post-treatments on the pozzolanic reactivity of corn stover ash (CSA) was studied. Additionally, the potential use of a bioethanol byproduct called high lignin residue (HLR) for SCM production was examined. Pretreated CSA and high lignin residue ash (HLRA) increased the early reactivity of cement paste when used as 20% replacement of cement in the system whereas unpretreated CSA was found to severely suppress the hydration reaction. The highest compressive strength was obtained from samples containing HLRA.

1. Introduction

Greenhouse gas emissions from fossil fuel burning have created increasing interest in the use of biomass for renewable energy production. Thermochemical and biochemical conversion techniques have been used to convert biomass, including agricultural residues, to biofuel [1,2]. Combustion, gasification, and pyrolysis are widespread thermochemical conversion techniques for converting biomass into electricity and bio-oil. Biochemical conversion of biomass involves hydrolysis of biomass into its constituent sugar followed by sugar fermentation to bioethanol [2,3]. Besides biofuel production, biomass has been used for supplementary cementitious materials (SCMs) production to reduce the carbon footprint of concrete [4–6].

Utilization of biomass for either biofuel or SCM production has posed certain challenges. The presence of alkali and alkaline earth metals (AAEMs) in the biomass can adversely affect the quality of the bio-oil and cause slagging and fouling during combustion [7,8]. It has been shown that removal of AAEMs out of the biomass prior to pyrolysis by the use of pretreatments improves the yield and the quality of the bio-oil during pyrolysis, and reduces slagging and fouling during combustion [8–12]. Biomass pretreatments are commonly performed by soaking the biomass in acidic or basic solutions [9]. It has also been shown that pretreatments, particularly dilute acid, improve the reactivity of agricultural residue ash (ARA) such as rice husk ash in cementitious systems by increasing the amorphous silica content and surface area of the ash [4,6,13].

In the biochemical conversion, the biomass undergoes three basic processes: pretreatment, enzymatic hydrolysis, and fermentation [2,3]. Pretreatments improve the biomass ethanol yield by increasing the accessibility of cellulose for enzymatic hydrolysis [14]. Enzymatic hydrolysis (saccharification) is performed on the pretreated biomass to convert the cellulose and hemicellulose to C5 and C6 sugars. After the enzymatic hydrolysis, the sugar rich liquid phase is separated from the solid residue, referred to as high lignin residue (HLR) in this paper. The liquid phase is then fermented to ethanol. Simultaneous saccharification and fermentaion (SSF) processes are also common where the solid residue is not removed until after the enzymatic hydrolysis and fermentaion [15,16]. HLR is currently burned in boilers or landfilled. Fig. 1 depicts the production process of lignocellolusic ethanol.

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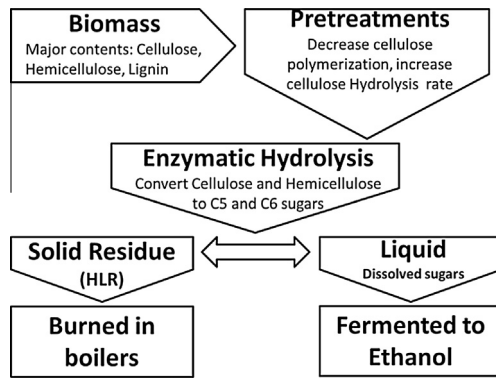 E-mail address: ataie@ksu.edu (F.F. Ataie).

Fig. 1. Bioethanol production process.

The major constituents of HLR are lignin, cellulose, and other inorganic constituents such as silica. Because HLR contains a high quantity of silica in a weakly polymerized organic structure, it could be a potential resouce for highly reactive SCMs production. If this can be shown, the cost of lignocellulosic ethanol production and the cost of SCMs produced from biomass can be substantially reduced. Additionally, if it can be shown that HLR burned at higher temperatures could result in a highly reactive ash, the HLR can be burned in biolers to produce energy and at the same time the resulting ash can be used as reactive SCM in concrete at no cost. Every year, millions of tonnes of agricultural residues are produced worldwide. In 2012, global wheat, corn, and rice production were about 697 million metric tons (MMt), 884 MMt, and 465 MMt, respectively [17]. On the basis of residue to grain ratio of 1.3 for wheat, 1 for corn, and 1.4 for rice [18], in 2012 approximately 2.4 billion metric tons of wheat straw, rice straw, and corn stover was produced. These agricultural residues are potential resources for ARA production for concrete use. Furthermore, increasing worldwide interest in the production of ethanol from agricultural residues [10], particularly corn stover, could boost the quantity of HLR available for SCM production.

This is the first study on the reactivity of high lignin residue ash (HLRA) in cementitious systems. Also, the impact of distilled water and dilute acide pretreatments on the reactivity of corn stover ash (CSA) using different burning conditions was investigated. Pretreated and unpretreated corn stover and HLR were burned at controlled temperatures of 500 °C and 650 °C for several different oven residence times. Ash characterizations, heat of hydration, and compressive strength data were used to compare the pozzolanic behavior of pretreated and unpretreated CSA with that of HLRA.

2. Materials and methods

2.1. Materials

An ASTM C150 [19] Type I/II portland cement was used for this study with the cement properties shown in Table 2. Standard graded sand [20] was used for the mortar experiments. Corn stover was purchased from a local farm in Manhattan, KS. The high lignin residue (HLR) material used was the solid residue taken after an SSF process using corn stover as the feedstock material and was supplied by the National Renewable Energy Laboratory at Golden, CO. The HLR material contained 30% cellulose and 70% lignin on dry mass. Reagent grade hydrochloric (HCl) and sulfuric acid were obtained and diluted to 0.1 N for use in the study. Phosphorus pentoxide (P_2O_5) and potassium hydroxide (KOH) used were ACS grade.

2.2. Experimental methods

2.2.1. Treatments

Hydrothermal pretreatment methods were performed on chopped corn stover (CS) using distilled water (DW), 0.1 N HCl, and 0.1 N Sulfuric acid. To pretreat the biomass, 250 g of biomass was immersed in 3100 ± 100 mL of the solution in a 4000 mL glass jar. The sample was stored undisturbed at a constant temperature

of either 23 °C or 80 °C for a given immersion period. After immersion, samples of leachate were collected for further analysis. After pretreatments, the biomass was rinsed either twice or four times, each time with 2500 mL of distilled water and dried at 80 °C in an oven.

Post-treatment for corn stover ash (CSA) was performed by soaking the 20 g of ash in 100 g of distilled water and stirring the slurry for one hour at 23 °C. After stirring, the slurry was filtered and the solid residue (post-treated ash) was dried at 80 °C in an oven. Leachate samples were collected for further analysis. Leachate Concentrations of magnesium (Mg), calcium (Ca), potassium (K), sodium (Na), and phosphorus (P) were determined using inductively coupled plasma mass spectrometry (ICP–MS).

2.2.2. Ash production

A programmable electric muffle furnace was used to heat the biomass samples to a predetermined temperature and hold time. To prepare corn stover ash (CSA), 200 g of dried corn stover was burned in each batch made. A stainless steel cage with two wire mesh shelves was used to hold the biomass during burning. A stainless steel pan was placed below the cage to catch any ash that fell through the mesh. High lignin residue ash (HLRA) was prepared by placing 100 g of HLR on the stainless steel pan and heating in the furnace. Samples were heated to 500 °C for two hours (500/2) or 650 °C for one hour (650/1). Finally, the ash was ground for one hour at 85 rpm (rpm) in a laboratory ball mill. The naming convention for ash samples is as follows: type of ash-pretreatment-washing times-burning temperature/holding time. Unpretreated samples are labeled "Cont." For example, the name of corn stover ash pretreated with 0.1 N HCl at 80 °C that was washed 4 times after pretreatments and burned at 500 °C for 2 h would be CSA-HCl80-4-500/2. CSA-650/1-Post and CSA-500/2-Post are post-treated CSA-Cont-650/1 and CSA-Cont-500/2 samples, respectively. (OPC + 650/1-leachate) and (OPC + 500/2-leachate) are paste samples in which the leachate from the post-treatment of CSA-Cont-650/1 and CSA-Cont-500/2 samples was used as mixing water, respectively.

2.2.3. Biomass ash characterizations

Particle-size distribution and surface area of the ground biomass ash (CSA and HLRA) were determined using a laser diffractometer and BET nitrogen adsorption. Also, backscattered scanning electron microscopy (SEM) images were taken to show the particle shape and size of portland cement and selected ash samples. ARA loss on ignition (LOI) was determined by measuring the mass loss after heating one gram of dry biomass ash (CSA, WSA or RSA) to 900 °C for 3 h. LOI was calculated as the percentage mass loss during firing. To determine crystalline phases of the ash samples, X-ray diffraction (XRD) analysis was performed (Cu Kα radiation with $\lambda = 1.5046$ Å). A step size of 0.02°/2s and a scan range of 5–70° 2θ was used. The chemical composition of ash samples were determined using X-ray fluorescence (XRF).

2.2.4. Biomass ash pozzolanic reactivity determination

For cement paste experiments, 20% of the cement was replaced by CSA when used. A water-cementitious materials ratio (w/cm) of 0.5 was used for all paste samples. Distilled water was added to the cementitious material and mixed using a vertical laboratory mixer at 500 rpm for 90 s, followed by a 120 s rest period, and finally mixed at 2000 rpm for 120 s [21].

For determining heat of hydration of cement pates, an eight-channel isothermal calorimeter was used in this study. Approximately 30 g of cement paste was used and the calorimeter was run at 23 °C for one week. The calcium hydroxide (CH) content of cement paste samples was obtained using thermogravimetric analysis to study the pozzolanic consumption of CH by biomass ash. Paste samples were cast in polystyrene vials. Samples were wet cured starting at 24 h after casting at 23 °C. Cement paste hydration was stopped at 7, 28, and 91 days of hydration by means of solvent exchange with isopropanol. Approximately 2 mm thick slices were cut and placed in isopropanol for 7 days. After 7 days in isopropanol, the samples were dried in a vacuum for at least 3 days. Free water content was obtained as the difference between the weight of samples before soaking in isopropanol and after drying. 25–30 mg of dried paste was heated at 20 °C/min to 900 °C in a nitrogen environment using a thermogravimetric analyzer (TGA). The CH content of paste samples was obtained using thermogravimetric analysis.

Table 1
Metal impurities concentrations measured in corn stover leachate.

Pretreatment	Leachate concentration (mg/g biomass)				
	Na	K	Ca	Mg	P
HCl23 °C	0.05	22.06	3.57	1.56	1.95
HCl80 °C	0.67	25.99	5.48	1.91	2.34
DW23 °C	0.04	19.12	1.19	0.99	1.34
DW80 °C	0.24	24.13	1.40	1.31	1.44
Sul.80 °C	0.41	26.62	5.03	1.95	2.33