



Impact of pretreatments and enzymatic hydrolysis on agricultural residue ash suitability for concrete



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HIGHLIGHTS

- Utilization of bioethanol byproduct as SCMs for concrete was investigated.
- Sodium hydroxide pretreatments negatively affected byproducts properties for SCM production.
- Sulfuric acid pretreatments improved the byproducts properties for SCM production.

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ABSTRACT

This study investigated the effects of the lignocellulosic ethanol production process on the potential use of the byproduct for supplementary cementitious material (SCM) production. Results showed that biomass pretreatment with sodium hydroxide could reduce the reactivity of byproduct ash in concrete because the sodium hydroxide dissolves much of the silica out of the biomass reducing the amount of reactive silica in the biomass ash. Sulfuric acid pretreatment was found to be an effective pretreatment method because it enhanced the byproduct properties for SCMs production. Therefore, if sulfuric acid pretreatment is used in lignocellulosic ethanol production, the byproduct could be used to produce reactive SCMs.

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1. Introduction

Awareness of global warming and anticipated depletion of fossil fuel deposits have increased interest in biofuel production, especially lignocellulosic ethanol [1–3]. As lignocellulosic materials, agricultural residues such as corn stover, rice straw, and wheat straw are potential renewable resources for biofuel production [4–9]. Lignocellulosic materials are converted to fuels using either thermochemical or biochemical pathways [2,3]. In the thermochemical route, lignocellulosic materials undergo pyrolysis or gasification to produce syngas, which is then upgraded to various types of fuels, such as ethanol and methanol [2,10]. For the biochemical approach, microorganisms convert lignocellulosic materials to fuels, such as ethanol [2,11]. During biochemical conversion, lignocellulosic materials undergo three main processes: pretreatment, enzymatic hydrolysis, and fermentation [2,3].

Pretreatment methods have been used to reduce the degree of polymerization of cellulose and remove and breakdown hemicellulose and lignin structures in lignocellulosic materials [12]. The

primary purpose of pretreatments is to increase available surface area of the cellulose to hydrolytic enzymes, thus increasing bioethanol yield [2,3,12]. Pretreatments are grouped in three main categories of physical, chemical, and biological [12]. In the physical pretreatment methods, such as size reduction, steam explosion, and liquid hot water, no chemicals or organisms are used in the process. Chemical pretreatments use acids or alkalis to remove hemicellulose and/or lignin from biomass and increase cellulose accessibility to enzymes. In biochemical pretreatments, microorganisms such as soft-rot fungi and bacteria alter lignocellulosic biomass structure and composition to enhance enzymatic digestibility of the biomass [12]. Enzymatic hydrolysis is used to breakdown cellulose and hemicellulose to glucose and other sugars, such as xylose. Sugars are fermented to ethanol after enzymatic hydrolysis.

Pretreatment is an important and also most costly step in the process of lignocellulosic ethanol production [1–3]. Pretreatments influence upstream and downstream operations during lignocellulosic ethanol production, and hence, selection of a pretreatment method depends on many factors [1]. Type of biomass feedstock, economical and technical feasibility of pretreatments, biofuel yield, and utilization of end products (byproducts) are some of the

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important factors that should be considered for pretreatments selection. Among the characteristics of efficient pretreatments are: (1) increased digestibility of cellulose in enzymatic hydrolysis, (2) limited formation of harmful compounds by reducing sugar and lignin degradation, and (3) low energy demand and cost requirements [1,2]. Numerous studies have considered these characteristics for determining effective pretreatment methods [2,3,6,7,12–15]. However, little attention has been given to the impact of pretreatments on the usage of byproducts [1,16]. Biochemical conversion leaves behind high lignin residue (HLR) materials that can be utilized in boilers to generate energy for lignocellulosic ethanol facility [1]. A better usage of byproducts could be beneficial in lowering cost of lignocellulosic ethanol production.

Burning HLR in boilers produces high lignin residue ash (HLRA) that can be rich in silica and calcium. HLRA has been shown to have the potential to be used in concrete as a reactive supplementary cementitious material (SCM) to reduce concrete cement content as well as improve concrete quality [17]. However, use of HLRA in concrete depends on its physical and chemical properties. Physical and chemical properties of HLRA depend on the burning conditions and composition of HLR. Since various pretreatments have different impacts on lignocellulosic materials [2,3,12], HLR properties and, consequently properties of HLRA, can be influenced by the type of pretreatments used during bioethanol production.

Several researchers, including the authors, have studied the impact of pretreatments such as dilute acid enhance properties on agricultural residue to increase reactivity of agricultural residue ash in concrete [17–19]. However, effects of pretreatments combined by enzymatic hydrolysis on potential use of lignocellulosic byproducts for SCMs production have not been studied yet.

This study aimed to address the influence of pretreatments on properties of lignocellulosic byproducts relevant to concrete application by investigating the impact of pretreatments and enzymatic hydrolysis on the physical properties of agricultural residue ash (ARA). Dilute sulfuric acid and sodium hydroxide, the two most commonly used chemical pretreatments, and three types of agricultural residues, namely corn stover, rice straw, and wheat straw, were used in this study. Effectiveness of pretreatments and enzymatic hydrolysis on ARA properties for concrete use was determined based on the removal of crystalline phases and inorganic compounds from the biomass by pretreatments and enzymatic hydrolysis.

2. Materials and methods

2.1. Materials

Corn stover (CS) and wheat straw (WS) were purchased from a local farm. Rice straw (RS) was obtained from Missouri Rice Research Farm, Glennonville, Missouri. The biomass (CS, WS, and RS) was ground to 5–10 mm using a hammer mill and then dried in an oven at 80 °C. An aqueous solution of cellulase from *Trichoderma reesei* (ATCC 26921) was used for enzymatic hydrolysis. ACS grade sodium hydroxide, sodium acetate, acetic acid, and sulfuric acid were used. 2% NaOH and 1% sulfuric acid were used for pretreatments. Sodium acetate and acetic acid were used to prepare a 50 mM of buffer solution for enzymatic hydrolysis.

2.2. Methods

2.2.1. Chemical pretreatment

Several studies have performed sodium hydroxide pretreatments at 1–4% concentrations and sulfuric acid pretreatments at concentrations of 0.5–1.5% for bioethanol production [6,7,13,14]. In this study, 2% sodium hydroxide and 1% sulfuric acid pretreatments were utilized. To pretreat the biomass, 40 g of biomass (CS, WS, or RS) was placed in a 1000 ml straight-sided wide-mouth glass container. 400 ml of either 2% sodium hydroxide or 1% sulfuric acid solution was then added to the container, placed in an autoclave, and heated at 121 °C for 30 min. The containers were cooled to room temperature, after which the biomass was filtered through a #100 sieve (150 µm). The filtrate was collected for elemental analysis, and the

filtered biomass was washed three times. Two liters (2 L) of tap water were used for each washing, followed by rinsing with 2 L of distilled water. Finally, the biomass was dried at 80 °C. The pretreatment process is shown in Fig. 1.

2.2.2. Enzymatic hydrolysis of pretreated biomass

Ten grams of pretreated biomass was placed in a 250 ml Erlenmeyer flask, and 150 ml of 50 mM sodium acetate buffer solution (pH = 5) was then added to the flask [4,13]. 300 µl of the cellulase enzymes solution was then added to the solution, which is equivalent to 25 filter paper unite (FPU) per gram of pretreated biomass [13]. FPU is defined as the amount of enzyme that releases 1 µmol of glucose during hydrolysis [7,20]. An incubator shaker was used to shake the flasks at 150 rpm for 48 h at 50 °C. The biomass was then filtered with a #70 sieve, and the leachate was collected for elemental analysis. Finally, the biomass was washed three times each with 2 L of tap water and once with 2 L of distilled water and dried at 80 °C.

2.3. Elemental analysis

Filtrates after pretreatments and enzymatic hydrolysis were collected for elemental analysis. Silicon (Si), calcium (Ca), magnesium (mg), potassium (K), and phosphorous (P) concentrations of the filtrate were measured using inductively coupled plasma mass spectrometry (ICP-MS).

2.4. Ashing and XRD measurements

To prepare biomass ash, 50 gr of biomass was placed on a stainless steel pan and burned in an electrical muffle furnace at 600 °C for 1 h. The biomass was burned at three different stages: before pretreatments (control ash samples), after pretreatments but before enzymatic hydrolysis (pretreated ash samples), and after enzymatic hydrolysis (hydrolyzed ash samples). Five types of ash were prepared for each type of biomass. For corn stover, the five types of ash included untreated ash (CSA-Cont), NaOH pretreated ash (CSA-NaOH), sulfuric acid pretreated ash (CSA-Sulf), ash prepared after NaOH pretreatment and enzymatic hydrolysis (CSA-NaOH-Hyd), and ash prepared after sulfuric acid pretreatment and enzymatic hydrolysis (CSA-Sulf-Hyd). A similar naming convention was used for WSA and RSA.

To determine crystalline phases of ash samples, X-ray diffraction (XRD) analysis was performed (Cu K α radiation with $\lambda = 1.5046$ Å). A step size of 0.02° 2 θ and a step time of four sec were used. A scan range of 5°–70° 2 θ was considered.

Thermal degradation of biomass at each stage of treatments was obtained by heating 8–10 mg of biomass in a thermogravimetric analyzer (TGA) in a compressed air environment. The biomass was heated to 700 °C at a heating rate of 10 °C/min. The ash percentage of biomass was calculated as weight percentage at 700 °C.

3. Result and discussion

3.1. Effect of pretreatments on the inorganic elements leaching

Inorganic elements, such as silicon, calcium, phosphorous, and magnesium, are precipitated in the form of silica, calcium carbonate, calcium oxalate, calcium phosphate, and magnesium oxalate in plant cell walls during plant growth [21–23]. Solubility of these crystalline phases is pH dependent. Solubility of silica is constant up to a pH of 9 and then dramatically increases at higher pH values [24–26]. However, solubility of calcium carbonate, calcium phosphate, calcium oxalate, and magnesium oxalate increases with an increase in solution pH [27–29].

Pretreatments removed some of these inorganic elements out of the biomass, as shown in Table 1. Removal of these inorganic elements varied by pretreatment type. The 2% sodium hydroxide pretreatment (NaOH) removed higher amounts of silicon compared to 1% sulfuric acid pretreatment (Sulf). However, the sulfuric acid pretreatment removed higher amounts of calcium, magnesium, and phosphorous. Both pretreatment types removed similar amounts of potassium from the biomass.

The pH of 2% sodium hydroxide solution used for pretreatment was 13.2, and the pH of 1% sulfuric acid pretreatment was 2.75. Therefore, the removal of low amounts of Ca, P, and Mg but high amounts of Si from the biomass by NaOH pretreatment could be attributed to high pH of the NaOH pretreatment, which increases silica solubility. Additionally, solubility of higher amounts of silicon from rice straw as compared to wheat straw and corn stover

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