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Appropriate biorefining strategies for multiple feedstocks: Critical evaluation for pretreatment methods, and hydrolysis with high solids loading

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ABSTRACT

Efficient utilization of a wide range of feedstocks requires appropriate biorefining strategies based on pretreatment methods. This study showed that alkali pretreatment was significantly more effective than acid pretreatment at similar processing conditions for grass and hardwood biomass samples; but, both methods were ineffective for softwood biomass. Separate glucose and xylose streams can be obtained for efficient fermentation from acid-pretreated biomass; nevertheless, need for more severe processing conditions to achieve effective pretreatment necessitates an additional detoxification step. High sugars concentration (10.6%, w/v) in hydrolyzates was obtained from alkali-pretreated biomass using optimum solids loading of 17.5% (w/v), which opens up an opportunity to produce high concentrations of biofuels and biochemicals in fermentation broth at reduced downstream processing costs. We propose a schematic for innovative biorefining strategies based on established pretreatment methods for different types of feedstocks. This information is very pertinent for choosing the appropriate processing methods and for setting up large-scale biorefineries utilizing multiple feedstocks.

1. Introduction

The rapid increase in global biofuel and biochemicals production in the last decade is considered as an important achievement for energy security and climate change mitigation. United State (US) bioethanol production increased from 3 billion gallons in 2003 to 13 billion gallons in 2013, which accounted for 57% of global production [1]. US bioethanol industries consumed 30% of national corn grown in 2013 to produce 13 billion gallons of ethanol, which represented approximately 4% of national transportation fuel demands. The nation has set its goal of producing 36 billion gallons of transportation fuel per year from renewable resources by 2022 [2]. Assuming the same corn production, and the same conversion efficiency from corn to ethanol, more than 80% of US corn will be consumed to meet its goal of producing 36 billion gallons of transportation fuel by 2022 if alternative feedstocks are not exploited. US government, therefore, expected to produce 58% of its target (21 billion gallons ethanol) from cellulosic feedstocks [2]. In addition, a number of platform and bulk chemicals should be produced via sustainable alternative routes, including from biomass feedstocks, to minimize dependency on petroleum-derived products. About 80% of current global power consumption is sourced from petroleum [3]. The world's finite petroleum resources have been rapidly depleting due to increased energy consumption, especially in developing countries. Still, power consumption per capita in most developing countries is much less than United Nations Human Development Index (HDI) standards: 4 kW per capita. In order to achieve this power consumption for 7 billion world population, about 28 TW total power is required, which is almost double the current global power consumption of 15 TW [3]. Exploitation of abundantly available lignocellulosic biomass for fuels and chemicals production is one of the promising alternatives to address a number of these global issues, including energy security, environmental concerns, and rural economic development [4].

Use of lignocellulosic biomass for biofuels and biochemicals production is associated with a number of opportunities as well as challenges. The beauty of the lignocellulosic biomass is its unique

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components, including carbohydrate polymers (cellulose and hemicellulose), lignin, and extractives, which can be used for a wide range of biofuels and biochemicals production [5,6]. Primarily, there are two routes for biofuels production from lignocellulosic biomass: (1) thermochemical platform – use of heat and chemical catalysts to produce fuels, and (2) sugar platform – a biochemical process to release sugars from biomass, which are subsequently converted to fuels and chemicals using microbial and/or chemical catalysts [3]. This study focused on a sugar platform route, which is comprised of four major core sections: feedstock handling and storage, pretreatment, enzymatic hydrolysis, and sugar fermentation to desired biofuels and biochemicals [7,8]. Each section in this route is associated with a number of challenges, but the greatest challenge is the need for an effective pretreatment process prior to hydrolysis of carbohydrate polymers to separate the strong outer lignin layer [9,10]; the pretreatment is the most challenging step for the thermochemical platform route as well [3]. The biomass pretreatment methods are broadly classified into biological, physical, chemical and physico-chemical process [11]. Dilute acid and alkali are the most extensively studied chemical pretreatment methods. Cellulose in lignocellulosic biomass will be accessible for cellulase enzyme after acid pretreatment due to hydrolysis of hemicellulose whereas it happens after alkali pretreatment due to removal of the lignin polymer [12]. The huge variations in composition and structure of biopolymers among different types of feedstocks [13] further complicated the optimization of pretreatment process; therefore, pretreatment processes must be separately optimized for each biomass feedstock.

Currently, crops residues, such as sorghum stalks and corn stover, are the most widely used feedstocks in lignocellulosic-based biorefineries. Dual use of land for both food and fuel is the main advantage of using crop residues as energy feedstocks. However, these feedstocks are only seasonally available. Besides, excessive removal of crop residues from farm lands and intensive fertilizer use to grow these crops degrade soil quality and increase greenhouse gas emission. In addition, the cultivation of a monoculture crop in the large area for biofuels and biochemicals production deteriorates the local biodiversity [14]. Crop rotation, and planting dedicated energy crops are sustainable approaches to maintain soil quality and supply sufficient amount of feedstocks for energy industries; some of dedicated energy crops include perennial warm-seasons grasses (such as switchgrass and miscanthus), and short-rotation woody crops (such poplar and Douglas fir) [15–17]. Therefore, modern biorefineries must be capable of utilizing a wide range of biomass resources to operate their plants at full capacity throughout the year, and separate biorefining strategies must be developed for each type of feedstock. Studies comparing biorefining strategies for different types of biomass feedstocks based on pretreatment methods is limited. In this study, three crops resides (sorghum stalks, *brm* sorghum stalks, and corn stover), one perennial grass (switchgrass), one hardwood (poplar), and one softwood (Douglas fir) were compared for acid and alkali pretreatment at similar pretreatment severity, including acid/alkali concentration, solids loading, time, and processing temperature. Pretreatment effectiveness was evaluated based on the sugars released during enzymatic hydrolysis of pretreated biomass, and inhibitory compounds produced and sugar lost during pretreatment. In addition, solids loading during enzymatic hydrolysis was optimized to get high sugars concentration in hydrolyzates for efficient fermentation and thereby reduced product recovery cost. Finally, a schematic for biorefining strategies based on acid and alkali pretreatment methods was proposed for different types of biomass feedstocks.

2. Materials and methods

2.1. Materials

Switchgrass, brown midrib (*bmr*) sorghum stalks (*bmr*12 mutant of forage sorghum, GW8528) and corn stover were obtained from the Kansas State University Agronomy Farm (Manhattan, Kansas). Regular sorghum stalks (the ground biomass) was obtained from Mesa Reduction Engineering & Processing Inc. (Auburn, New York); the sorghum was cultivated in Texas A&M University (College Station, Texas). Chopped (2–5 cm long) wild type poplar sample was provided by Edenspace, Inc. (Manhattan, Kansas). Ground Douglas fir sample was kindly provided by Dr. Michael Wolcott, Washington State University (Pullman, Washington). Novozymes, Inc. (Franklinton, North Carolina) provided Cellic CTec2 and Cellic HTec2 enzymes for biomass hydrolysis.

2.2. Sample preparation

The biomass samples were first chopped into 5–10 cm long pieces, and then ground using a Thomas-Wiley Laboratory Mill (Model 4) fitted with a 2-mm sieve. The ground biomass samples were sieved in a shaker (W.S. Tyler, Model – RX 29, Serial – 25225) fitted with two sieves with size 20 mesh (841 μm) and 80 mesh (177 μm) to get a specific particle size. The sorghum stalks and Douglas fir samples were directly sieved to get the same cut size because these samples were received in ground form. The size range of biomass was chosen based on the particle size required for biomass composition analysis without further size separation [18]. The prepared samples were packed in sealed paper bags and stored at room temperature until further processing.

2.3. Optimization of biomass pretreatment

One sample from each type of the biomass samples (grass, hardwood and softwood) was selected for the optimization of alkali pretreatment; the selected samples were sorghum stalks (grass), poplar (hardwood) and Douglas fir (softwood). Wang et al. [19] reported that 0.75% (w/v) sodium hydroxide (NaOH) solution at 121 °C is the optimum for the pretreatment of Coastal Bermuda grass, whereas Cao et al. [20] reported that 2% (w/v) NaOH solution at 121 °C is effective for the pretreatment of sweet sorghum stalks. Seven different NaOH concentrations, from 0.5% to 2.0% (w/v), were taken for the optimization of sorghum stalks pretreatment. Higher NaOH concentration is required for the pretreatment of woody biomass [21,22]; five different NaOH concentrations, from 1% to 8% (w/v), and from 2% to 10% (w/v), were taken for the pretreatment of poplar and Douglas fir, respectively. Twenty grams of ground biomass sample was mixed with 200 ml alkali solution for each concentration in a 500-ml Erlenmeyer flask and autoclaved at 121 °C for 30 min. The biomass slurry was then filtered using a 200-mesh (74 μm) sieve. Approximately 15 ml filtrate was collected to measure sugars and inhibitors produced during pretreatment, and solids residue was washed with excess distilled water until the filtrate was clear and neutral to litmus paper. The pretreated samples were then dried overnight at 45 °C and hydrolyzed as explained in section 2.5. The released sugars were measured to determine the optimum alkali concentration for pretreatment of each type of biomass.

2.4. Pretreatment of biomass

The optimum NaOH concentrations for pretreatment of