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Pretreatment of wheat straw with potassium hydroxide for increasing enzymatic and microbial degradability

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HIGHLIGHTS

- Ambient temperature KOH pretreatment over a wide loading range (2–50%) was studied.
- 20% KOH loading resulted in the maximum overall reducing sugar and methane yield.
- The maximum lignin reduction achieved through KOH pretreatment was 54.7%.
- The maximum specific hydrolysis yield achieved for pretreated wheat straw was 92.3%.
- KOH pretreatment increased the methane yield of wheat straw by 77.5%.

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ABSTRACT

The pretreatment of wheat straw with potassium hydroxide (KOH) at ambient temperature (20 °C) was investigated. The pretreatment effects on chemical composition and physical structures, and subsequent enzymatic hydrolysis and anaerobic digestion were evaluated. Wheat straw at 10% total solids (TS) was treated with KOH solution for 24 h at a wide range of KOH loadings from 2% to 50% (w/w dry basis). Higher KOH loading resulted in higher lignin reduction from the straw and chemical oxygen demand (COD) in the resulting black liquor. Maximum lignin reduction of 54.7% was observed at 50% KOH loading. In comparison to untreated straw, specific hydrolysis yields achieved 14.0–92.3% over the range of 2–50% KOH loading, and methane yields increased 16.7–77.5% for KOH loadings of 10–50%, respectively. Accounting for losses during pretreatment, 20% KOH loading resulted in maximum overall reducing sugar yield and methane yield and therefore is the recommended loading for pretreatment under these conditions.

1. Introduction

Wheat straw, as an abundant by-product from wheat production, is generated at about 529 million tons worldwide every year (Govumoni et al., 2013). As a major agriculture residue, wheat straw is an attractive potential low cost feedstock for biofuel production. However, its high lignin content limits enzymatic and microbial degradation. Considerable research efforts on pretreatment technology have been made to improve the degradability of lignocellulosic materials. Ideally, pretreatment minimizes the loss of sugars, energy consumption, quantity of unwanted by-products and fermentation inhibitors and cost while improving the biodegradability (Hu et al., 2008).

Alkaline pretreatment has been reported to efficiently improve the hydrolysis yield and methane production of many biomass materials containing primarily cellulose, hemicellulose, and lignin, which makes up about 90% of the dry basis composition of wheat straw. Lignin is an amorphous heteropolymer having three primary phenyl propane units as p-coumaryl, coniferyl and sinapyl alcohols held together with different linkages. Hemicellulose is also a diverse mixture of carbohydrate polymers often decorated with

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Abbreviations: BMP, biochemical methane potential; HPLC, high performance liquid chromatography; COD, chemical oxygen demand; KOH, potassium hydroxide; CrI, crystallinity index; S/I, substrate/inoculum ratio; DNS, dinitrosalicylic acid; TS, total solid; GC, gas chromatograph; VS, volatile solid; HMF, hydroxymethylfurfural; XRD, X-ray diffractometer.

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acetyl groups. Cellulose is a homopolymer of glucose organized in a fibrous structure with strong hydrogen bonding capacity. The first reaction of alkaline pretreatment is the solvation and saponification of intermolecular ester linkages between lignin and hemicellulose or lignin and cellulose. Alkaline pretreatment can cause cellulose swelling, increase internal surface area, decrease polymerization and crystallinity, and disrupt lignin structure (Sun et al., 1995). Therefore, the major mechanism of alkaline pretreatment is that it enhances the exposure of cellulose to enzyme attack and degradability of remaining carbohydrates (Kim and Holtzapple, 2005). Furthermore, alkaline pretreatment has shown promise as a pretreatment for anaerobic digestion by providing alkalinity and reducing the concentration of potential inhibitors during anaerobic digestion (Chandra et al., 2012) which made it the pretreatment of choice for this study.

Most previous investigations focused on pretreatments with sodium hydroxide (NaOH) solution at high temperatures (50–180 °C) (Sun et al., 1995; Han et al., 2012; Haque et al., 2012; Tutt et al., 2012). Alkaline pretreatments at high temperatures and pressures generate some products that are inhibitory to the microorganisms used in the subsequent fermentation process, such as phenolic compounds, hydroxymethylfurfural (HMF) and furfural (Zhang and Pienkos, 2009). Also, sodium use and discharge is problematic as it can lead to negative environmental impacts such as soil salinization and water pollution (Zheng et al., 2014). KOH could be a solution to this problem. The black liquor derived from KOH treatment has potential potassium nutrient and soil amendment value. The KOH treatment followed with heating treatment has also been shown to be more effective than NaOH at 5–20% concentration in modifying the lignin–carbohydrate complex structure of rice straw for enhancing enzymatic accessibility (Ong et al., 2010). The KOH has rarely been used for pretreatment in the past due to its higher chemical cost compared to NaOH, however, if potassium can be used for its nutrient value, KOH may become an economically viable alternative while preventing the environmental pollution effects. A moderate pretreatment condition was applied in this study that will not only keep the energy requirement low, but also cause less sugar loss compared to other leading pretreatments.

The effectiveness of alkaline pretreatment is dependent on the physical structure and chemical composition of the substrate as well as the treatment conditions. Crystallinity is an important indicator for cellulose microstructure because amorphous cellulose is believed to be more easily hydrolyzed (Chandra et al., 2007). Moreover, many pretreatments studies include subsequent enzymatic hydrolysis to convert the cellulose and hemicellulose to fermentable sugars that would provide fundamental data for ethanol industry (Tutt et al., 2012). Fewer studies have applied alkaline pretreatment in the context of anaerobic digestion to evaluate the biomethane production potential (Mirahmadi et al., 2010; Himmelsbach et al., 2010). Anaerobic digestion of agricultural residues is increasing in order to reduce greenhouse gas emissions and develop a sustainable energy supply. The methane produced with anaerobic digestion can be used as a renewable replacement of fossil fuels in both heat and power generation and as a vehicle fuel. The pretreatment goals of lignocellulosic materials are minimizing carbohydrate losses, preventing formation of inhibitory by-products for enzymatic hydrolysis (Keshwani and Cheng, 2009), and providing access to biodegradable portion rather than removing lignin for anaerobic digestion. It is important to consider both specific sugar or methane yields in combination with mass loss through pretreatment operations in order to account for an overall yield value.

The main objectives of this study were to compare the effects of a wide range of KOH loading conducted at low temperature on: (1) the physical structure and chemical composition of pretreated wheat straw; (2) the impact of pretreatment on enzymatic hydrolysis yields; and (3) the impact of pretreatment on anaerobic digestion performance and evaluate the experimental data with an appropriate kinetic model to allow comparison of results.

2. Methods

2.1. Preparation of wheat straw

Wheat straw was collected from a farm near Sacramento, California and air-dried for two days before hammer milling to approximately 1 cm pieces. The milled wheat straw was kept in sealed plastic bags and placed into dry storage at 25 °C until used. The overall chemical composition of wheat straw varies depending on wheat species, soil, and climate conditions, however, the chemical composition is generally similar in terms of the key parameters of interest here, cellulose, hemicellulose and lignin content, which, for this sample and as detailed subsequently, falls in the range of 33–40, 20–28, and 15–20 (% w/w), respectively, as reported by others (Talebnia et al., 2010).

2.2. Pretreatment

In this study, 25 g of dry milled wheat straw were added to 500 mL Nalgene plastic jars and mixed with 250 mL of distilled water. 0.5, 1.5, 2.5, 3.5, 5, 6.25, 7.5, 10, and 12.5 g KOH were then added to achieve 2%, 6%, 10%, 14%, 20%, 25%, 30%, 40%, and 50% (g KOH/g dry straw) loadings, respectively. KOH was weighed in glass container while wearing personal protective equipment and added to water slowly with mixing to avoid overheating due to the exothermal dissolution reaction. The samples were mixed, covered, and incubated at 20 °C for 24 h. No stirring was provided during the treatment period. As a comparison, raw wheat straw and wheat straw mixed with water were also incubated and evaluated as controls. After 24 h, the solid and liquid portions were separated with a hand held juice presser with 2 mm screen size openings. About one-third of samples were taken from the retained solids and analyzed for TS, VS and chemical composition (cellulose, hemicellulose, and lignin). Another one-third of retained solids were selected for subsequent enzymatic hydrolysis and washed with 100 mL distilled water for three times. The left retained solids were selected for anaerobic digestion with no washing. The separated liquid (black liquor) was retained for pH and COD analysis. All the samples were refrigerated at 4 °C for less than 48 h for further analysis.

2.3. Enzymatic hydrolysis

Washed, pretreated wheat straw solids (1 g dry basis, each condition, performed in triplicate) were enzymatically hydrolyzed at 2% w/v dry matter in 50 mL of 50 mM sodium citrate buffer at pH 4.8 and initial pH was confirmed to be 4.8 ± 0.1. 0.05 mL of 3% (w/v) sodium azide was also added for reduction of unwanted microbial activities. Enzyme preparations (Cellic CTec2 and Cellic HTec2) were supplied by Novozymes, North America (Franklinton, NC) and added at 0.3 mL (125 FPU/mL) and 0.05 mL (9685 XU/mL), to each sample, respectively. This amount of enzyme was used to avoid the impact of enzyme limitation on comparison of different pretreatment conditions (Pandey et al., 2012). Hydrolysis was carried out in an incubating shaker at 50 °C and 150 rpm for 72 h. 1.5 mL samples were taken at 0, 24, 48, and 72 h, respectively, and analyzed for reducing sugars as described below. Prior to analysis, samples were allowed to settle and 1 mL liquid samples obtained from the supernatant using a pipette and then boiled for 10 min in sealed tubes to denature