Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/issn/15375110

Research Paper

# Improving the bioenergy production from wheat straw with alkaline pretreatment

Xiaoying Liu [a,b], Steven M. Zicari [b], Guangqing Liu [a], Yeqing Li [c], Ruihong Zhang [a,b,*]

[a] Biomass Energy and Environmental Engineering Research Center, College of Chemical Engineering, Beijing University of Chemical Technology, Beijing 100029, China

[b] Department of Biological and Agricultural Engineering, University of California, Davis, CA 95616, United States

[c] Institute of New Energy, State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing 102249, China

ARTICLE INFO

*Article history:*
Received 8 April 2015
Received in revised form
16 September 2015
Accepted 17 September 2015
Published online 22 October 2015

*Keywords:*
Wheat straw
Potassium hydroxide pretreatment
Black liquor recycling
Enzymatic hydrolysis
Anaerobic digestion

A pretreatment process for wheat straw using potassium hydroxide (KOH) and recycled black liquor as a treatment reagent was developed and the minimum fresh chemical and water requirement were determined. Black liquor recycling in the pretreatment process resulted in a 75% reduction in fresh water use and 25% in KOH use, when compared to no recycling. It was found that after five batches of treatment, the concentrations of reducing sugar, chemical oxygen demand (COD), and $K^+$ in black liquor, reached stable levels. During the pretreatment with black liquor recycling, 32–35% lignin was reduced in wheat straw. The pretreated straw showed reducing sugar yield of 336–366 mg $g^{-1}$ [total solid (TS)] and methane yield of 290–303 mg $g^{-1}$ [volatile solid (VS)] when subjected to enzymatic hydrolysis and anaerobic digestion, respectively.



## 1. Introduction

Alternative fuels are needed in order to meet the increasing global energy demand and reduce the greenhouse gas emissions resulting from the use of fossil fuels. Biofuels produced from lignocellulosic biomass, such as wheat straw, can play an important role in producing renewable fuels. Lignocellulosic biomass is mainly composed of cellulose, hemicellulose and lignin. Due to its limited biodegradability, considerable research has been conducted on pretreatment of such biomass to increase the bioconversion rate and efficiency by breaking the cross linked chemical structure and improving accessibility of components contained in the biomass. Alkaline pretreatment is one of the most intensively studied pretreatment methods and has shown to be effective on many types of biomass (Iroba, Tabil, Dumonceaux, & Baik, 2013; Haque et al., 2013; Park et al., 2010; Wang, Keshwani, Redding, & Cheng, 2010; Zheng, Zhao, Xu, & Li, 2014; Zhu, Wan, & Li, 2010).

* *Corresponding author*. Biological and Agricultural Engineering Department, University of California, Davis, One Shields Avenue, Davis, CA 95616, United States. Tel.: +1 530 754 9530; fax: +1 530 752 2640.
E-mail address: rhzhang@ucdavis.edu (R. Zhang).

http://dx.doi.org/10.1016/j.biosystemseng.2015.09.006

**Nomenclature**

*Symbols*

| | |
|---|---|
| $B$ | cumulative methane yield (ml $g^{-1}$ [VS]) |
| $B_0$ | maximal or ultimate methane yield (ml $g^{-1}$ [VS]) |
| $E$ | natural logarithm constant equal to 2.72 |
| $\Lambda$ | lag time (d) |
| $t$ | incubation time (d) |
| $\mu_m$ | maximal methane production rate (ml $g^{-1}$ [VS] $d^{-1}$) |
| w/v | weight per volume |

*Abbreviations*

| | |
|---|---|
| COD | chemical oxygen demand |
| HRT | hydrolysis retention time |
| LAP | laboratory analysis procedure |
| OLR | organic loading rate |
| TS | total solid |
| DNS | dinitrosalicylic acid |
| KOH | potassium hydroxide |
| NaOH | sodium hydroxide |
| S/I | substrate/inoculum ratio |
| VS | volatile solid |

Sodium hydroxide (NaOH) is the most commonly used, and investigated, chemical for alkaline pretreatment. However, due to chemical treatment costs and concerns over salt discharge in the process effluent, there has been limited application on a commercial scale. More research is needed in order to develop efficient methods that use more environmentally friendly chemicals, require lower energy, reduced chemical and water inputs and therefore have lower costs.

Several studies were found in the literature that addressed the reuse or recycling of the black liquor that results from alkaline pretreatment process. Black liquor contains valuable alkali chemical and water with high pH (Ong, Chuah, & Chew, 2010; Xiao, 2005). Fox, Gray, Dunn, and Marsden (1989) showed that 35% of alkali remained after pretreatment with 0.1 g [NaOH] $g^{-1}$ [bagasse] and could be recycled and reused for another round of pretreatment. Pavlostathis and Gossett (1985) used recycled, alkali-restored filtrate after pretreatment for the solubilisation of fresh wheat straw and their results showed that solids separation and filtrate recycle appeared to be the most promising method. Xu, Zhang, and Cheng (2012) reported that pretreated corn stover with black liquor collected from 2% NaOH pretreatment of switchgrass showed comparable enzymatic hydrolysis performance with pretreatment using 1% fresh chemical. However, there is little literature on the comprehensive evaluation of pretreatment and performance with black liquor recycling and reuse. In our recently published research (Liu, Zicari, Liu, Li, & Zhang, 2015), pretreatment of wheat straw with KOH was investigated at a large range of chemical concentration (0.2–5%, w/v). The pretreatment conditions were 10% initial total solids for straw, 20 °C temperature and 24 h reaction time. The optimum concentration was 2% (w/v) KOH when fresh water and chemical was used. The KOH was applied because potassium has environmental benefits as a nutrient and for soil amendment. This study was a follow up study with a focus on the recycling and reuse of black liquor in the pretreatment process.

Considering the potential production and accumulation of chemical compounds, such as lignin derivatives, that could be inhibitory to the enzymes or microbes in the subsequent bioconversion process, ten batches of pretreatment with black liquor recycling were conducted in order to evaluate the pretreatment performance in terms of straw biodegradability and quantify any effect of accumulated toxic compounds and salts at steady-state process levels.

The novel feature of this research was the development of a sequential batch KOH pretreatment process with solids separation accompanied by black liquor recycling in order to minimise fresh water consumption, chemical consumption, and black liquor disposal. The performance of this proposed pretreatment system was evaluated in terms of reducing sugar yield through enzymatic hydrolysis and methane yield through anaerobic digestion of pretreated straw. The potential impact of potassium contained in pretreated wheat straw on a continuous anaerobic digester system was analyzed and the recommendations on the black liquor recycling and/or treatment are provided in order to prevent the inhibition of potassium to the microorganisms in the digester.

## 2. Materials and methods

### 2.1. Wheat straw preparation

Wheat straw was provided by a farm near Sacramento, California, and transferred to UC Davis after air drying. All the samples were kept in sealed plastic bags after hammer milling to approximately 10 mm pieces. The characteristics of wheat straw used, as determined by methods to be described below, are summarized in Table 1.

### 2.2. Pretreatment with black liquor recycling

Ten batch wheat straw pretreatment experiments were performed. Initial batch used KOH and fresh water, and second and subsequent batches used a combination of recycled black liquor, KOH and fresh water as reaction reagents. For the initial batch, wheat straw was pretreated with 2% (w/v) KOH and 10%

**Table 1 – Composition of wheat straw.**

| Parameter | Content (%) |
|---|---|
| Total solid (TS) | 94.1 ± 0.4[a] |
| Volatile solid (VS) | 82.8 ± 0.6[a] |
| Cellulose | 37.4 ± 1.1[b] |
| Hemicellulose | 27.9 ± 1.0[b] |
| Acid soluble lignin | 2.0 ± 0.2[b] |
| Acid insoluble lignin | 16.4 ± 0.1[b] |
| Ash | 12.0 ± 0.4[b] |
| Other | 4.3 ± 0.2[b] |

[a] Is based on wet mass.
[b] Is based on dry mass.