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Comparison of sealing and open conditions for long term storage of corn stover using low-moisture anhydrous ammonia pretreatment method

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ABSTRACT

As a promising material for bioethanol production, corn stover has been studied under various pretreatment methods prior to production of bioethanol. However, the storage of pretreated corn stover is still challenged by both weather conditions and the physical properties of its own. The main objective of this experiment is to evaluate the effect of low-moisture anhydrous ammonia (LMAA) pretreatment method on biomass quality during long periods of storage. In this study, corn stover was contacted with various ammonia loadings (0, 0.1, and 0.2 g/g DM biomass) and moisture content (20 wt.%, 40 wt.%, and 60 wt.%) from 1 day to 90 days both in sealed and open containers. As a result, the mass loss in sealed container increased with time; however, the mass loss in open container was affected by the conditions of the environment. In terms of the carbohydrate, no significant reduction was observed in either sealed or open containers.

1. Introduction

Bioethanol, a promising replacement of fossil fuel, has been studied in various ways. Generally, bioethanol can be produced from food crops, such as corn and sugarcane, known as first generation biofuel. It could also be produced by lignocellulosic biomass, which is non edible plant and energy crops (Nagarajan et al., 2013). Lignocelluloses-based renewable energy is more environmental-friendly, thus it may reduce the concerns about the global climate concerns (Jin et al., 2012). With the aim of producing 36 billion gallons of ethanol per year by 2022, 16 billion gallons was supposed to come from cellulosic biomass (Schnoor, 2011).

Corn stover, one of the most abundant lignocellulosic biomass, is mainly comprised of the stalks and leaves; and it has the great potential to serve as the biofuel feedstock. According to the estimation of Kadam and McMillan (2003), 80–100 million dry tonnes/year of corn stover could be collected, among which 80% is available for ethanol production (Kadam and McMillan, 2003). Currently, the potential of the conversion of corn stover to biofuel is targeted to be 90 gal/ton in the near future (DOE-EERE, 2009). However, the sturdy structure of lignocellulosic biomass increases the difficulty in bioethanol production.

Generally speaking, lignocellulosic biomass is composed of three parts: cellulose, hemicellulose and lignin. As is known, cellulose is a linear polymer of glucose; hemicellulose is a branched polymer containing xylose, arabinose, mannose, and some other polysaccharides. In terms of lignin, it is a highly disordered polymer which serves as the protection since cellulose is embedded in the matrix of lignin and hemicellulose (Menon and Rao, 2012). In order to open the structure and expose cellulose within lignocellulosic biomass, a pretreatment process before hydrolysis and fermentation is critical.

Pretreatment processes have been explored by numerous studies. One of the base reagents adopted by researchers is ammonia. Ammonia fiber expansion (AFEX) uses concentrated ammonia to break down the inner structure of lignocellulosic biomass for the enzymatic hydrolysis and fermentation process (Lau et al., 2010); Soaking in aqueous ammonia (SAA) for pretreatment is proved to have the ability of retaining the hemicellulose at low temperature and increasing the fermentation yield (Kim and Lee, 2005a,b); And the low-moisture anhydrous ammonia (LMAA) process is developed to minimize the water and ammonia input for bioethanol production (Yoo et al., 2011).

To successfully implement a bioconversion process, the storage process is critical since the raw materials are harvested seasonally

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and the product may not be able to trbe used immediately (Liu et al., 2013). In terms of corn stover storage, two common approaches can be applied: dry storage and wet storage (Cui et al., 2012). Dry product, which refers to 20–25% moisture content (or less) in raw corn stover, is typically harvested and packaged in round bales (Shinners et al., 2007), but the high drying cost and high dry matter losses during storage are the remaining problems (Richard, 2010). On the other hand, wet storage, also named ensilage, is a method of preserving biomass at high moisture content (>45%) (Cui et al., 2012). It could minimize the loss of nutrients and reduce the drying cost (Weinberg and Ashbell, 2003), but it still has the problem of mold growth, which may be hazardous to downstream operations (Essien et al., 2005). In order to produce bioethanol, higher effective preservation of carbohydrates during storage is required.

In this study, a low moisture anhydrous ammonia (LMAA) pretreatment process was applied before corn stover storage since ammonia could result in higher efficiency in ethanol production (Ko et al., 2009) as well as impeding mold growth. The objective of this research was to evaluate the effects of the LMAA pretreatment process on biomass quality (changes in carbohydrates, lignin, ash, and mass losses) during storage, from 1 day to 3 months. In addition, growth of fungi or other microorganisms were monitored.

2. Materials and methods

2.1. Biomass

Corn stover, freshly harvested and delivered in bales, was obtained from central Iowa, USA, 2013. It was air-dried before baling and receiving by the lab. Then, the corn stover was ground through a 2 mm screen using a grinder (Wiley Model 4), and stored at room temperature. After that, deionized water was mixed with corn stover to achieve the target moisture contents (20 wt.%, 40 wt.%, and 60 wt.%). Moisturized corn stover was placed overnight at ambient temperature to reach equilibrium.

2.2. Low-moisture anhydrous ammonia (LMAA) pretreatment process

Before contacting with anhydrous ammonia, moisture content of treated corn stover was tested using thae moisture tester (IR35M, Denver Instrumental, USA). Then the corn stover was placed into the ammoniation reactor, and contacted with various loadings of anhydrous ammonia (0 g/g DM biomass, 0.1 g/g DM biomass and 0.2 g/g DM biomass), tightly closed the valve of the reactor for 30 min after reaching the target pressure. After that, the ammoniated corn stover was transferred into several heavy-duty Ziploc plastic bags and open containers, thoroughly mixed and weighed. Sealed containers (Fig. 1) and open containers (Fig. 2) were placed at ambient temperature for 0 h, 6 h, 1d, 5d, 12d, 30d, 60d, and 90d.

2.3. Compositional analysis

Once the duration time was achieved, pretreated samples were weighed again, and surplus ammonia was evaporated in the fume hood for over 12 h. Then the compositional analysis was conducted followed by the NREL LAP procedure (Sluiter, 2011). The monosaccharides were analyzed by high performance liquid chromatography (HPLC) installed with a Bio-Rad Aminex HPX-87P column (Aminex HPX-87P, Bio-Rad Laboratories, Hercules, CA, USA) and a refractive index detector (Varian 356-LC, Varian, Inc., CA, USA). The content of acid soluble lignin (ASL) was determined by UV–vis spectrophotometer (UV-2100 Spectrophotometer, Unico, United Product & Instruments, Inc., Dayton, NY, USA). All samples were analyzed in duplicate.

Fig. 1. Sealed container.

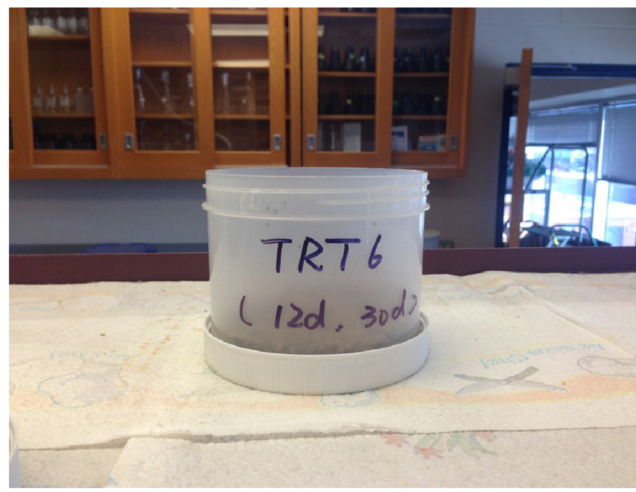

Fig. 2. Open container.

Table 1
Experimental design.

Treatment	Ammonia Loading (g/g)	Moisture Content
1	0	20%
2	0	40%
3	0	60%
4	0.1	20%
5	0.1	40%
6	0.1	60%
7	0.2	20%
8	0.2	40%
9	0.2	60%

2.4. Mold growth observation

The observation experiment was conducted both in sealed container samples and open containers. Mold growth was monitored everyday during the whole experimental period by obseving the changes in color and shape.

2.5. Experimental design

In this study, two independent variables were designed to investigate the storage effect: ammonia loading, and moisture content. Each has three levels. Moreover, full factorial design was used as shown in Table 1.