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Short communication

Process for obtaining cellulose acetate from agricultural by-products ☆

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Abstract

Agricultural residues such as corn fiber, rice hulls and wheat straw can be used as abundant low-cost feedstock for production of fuel ethanol. However, the cost of cellulase enzymes to saccharify cellulose to glucose is a major hindrance. As an alternative, a novel process to obtain industrially important cellulose acetate from these by-products after removing hemicellulosic sugars was developed. Rice-straw, wheat hull and corn fiber were treated with dilute acid at a moderate temperature to hydrolyze the hemicellulose to monomeric sugars that can be fermented to ethanol. The cellulose was then treated with acetic anhydride and catalytic amount of sulfuric acid to make cellulose acetate. The production of cellulose acetate was confirmed by NMR analysis. The pretreatment used to hydrolyze the hemicellulose was also useful for cellulose acetate production. Without the pretreatment cellulose acetate conversions from wheat straw, corn fiber, and rice hulls were 0.5, 1.8 and 13.5, respectively. After pretreatment the conversion rate increased to about 25 wt% for all three agricultural residues used.
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Keywords: Corn fiber; Rice hulls; Wheat straw; Cellulose; Cellulose acetate; Agricultural by-products; Industrial products

1. Introduction

In 2004, the production of fuel alcohol from corn starch reached about 3.41 billion gallons. Various lignocellulosic agricultural residues such as corn fiber, corn stover, wheat straw, rice-straw, and rice hull contain about 45–70% complex carbohydrates (cellulose and hemicellulose) and can serve as low-cost feedstocks for production of fuel ethanol (Saha, 2004). Four steps are generally involved in the conversion of lignocellulose to ethanol: (1) pretreatment, (2) enzymatic saccharification, (3) fermentation of mixed sugars to ethanol, and (4) product recovery. Native biomass is generally resistant to enzymatic attack (Saha & Bothast, 1999). Pretreatment of any lignocellulose is essential before enzymatic saccharification can ensue. Pretreatment with dilute acid at a moderate temperature has become a state of the art technology for any biomass substrate (Saha, 2003). This process generally hydrolyzes hemicellulose to fermentable sugars. Even though the acid helps to decrystallize cellulose depending on the substrate, it cannot degrade cellulose to glucose. Cellulase enzymes are generally used to hydrolyze cellulose to glucose. However, the rate is very slow and enzymatic saccharification by cellulases is not cost-effective (Saha & Bothast, 1999). It is estimated that the cost of cellulases needs to be lowered by at least 10-fold in order to be competitive.

As an alternative, we have attempted to convert the cellulose to value-added cellulose acetate ($1.80/pound) once the hemicellulosic sugars are removed for use as substrate for ethanol fermentation. By converting the cellulose in these residues into cellulose acetate as opposed to saccharifying cellulose to glucose the overall cost of producing ethanol from lignocellulosic biomass may be reduced. There are numerous publications and patents on the preparation and utilization of cellulose acetate (Gedon & Fengl, 1993; Heinze & Liebert, 2004; Majewicz & Padlas, 1993; Serad, 1993). However, to the best of our knowledge there are no known reports addressing the utilization of agricultural by-products/waste to prepare cellulose acetate. Wood and cotton are the major resources for all cellulose products such as paper, textiles, construction materials, and cardboard, as well as cellulose derivatives, such as cellulose esters (Serad, 1993) and ethers (Majewicz & Padlas, 1993). It is estimated that annually 1.5 billion pounds of cellulose acetates are manufactured globally. Cellulose acetate, Fig. 1, is widely used in textiles because of its low-cost, toughness, gloss, high transparency, natural feel, and other

☆ Names are necessary to report factually on available data: however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name USDA implies no approval of the product to the exclusion of others that may also be suitable.

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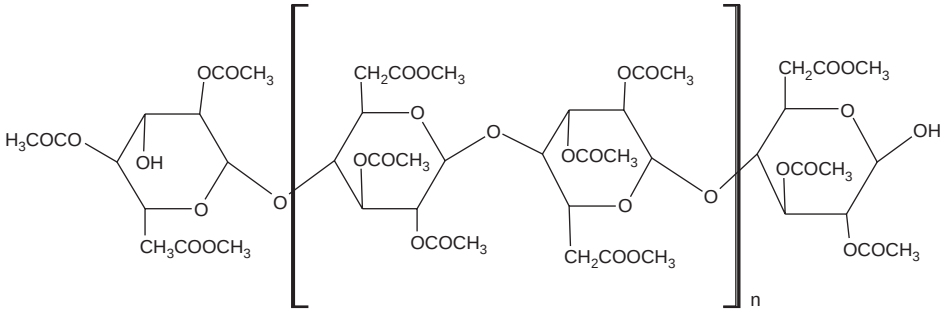

Fig. 1. Structure of cellulose triacetate, *n* is typically 400–1000.

favorable aesthetic properties. Cellulose acetate fibers in cigarette filters are designed to absorb vapors and accumulate particulate smoke components. Cellulose acetate is also used as a carrier for photographic negatives, motion picture film (celluloid), microfilm, microfiche and audio tape (Gedon & Fengl, 1993).

2. Experimental

2.1. Materials

Corn fiber, rice hulls and wheat straw were obtained from Pekin Energy Company, Pekin, IL (now Aventine Renewable Energy), Rice Hull Specialty Products Inc., Stuttgart, AR, and a local farmer, respectively. Methylene chloride and chloroform, acetic anhydride, and sulfuric acid were obtained from Aldrich. NMR spectra in $CDCl_3$ were obtained by using Bruker Instruments DRX 400 spectrometer.

2.2. Pretreatment

Corn fiber, rice hulls and wheat straw were dried in a forced-air oven at 55 °C for 24 h and milled in a hammer mill to pass through a 1.27 mm screen. The milled samples were stored at room temperature. Corn fiber was washed with hot hexane to remove the oil. Hexane washed corn fiber (15% solids, w/v) was slurried in 0.5% H_2SO_4 and pretreated in an autoclave at 121 °C for 15 min (Saha & Bothast, 1999). The pretreated corn fiber was neutralized to pH 5.0 with 10 M NaOH. Before using as a starting material, the solids were separated from the liquids, washed one time with three volumes of water and dried in an oven at 60 °C for 24 h. Milled rice hulls (15%, w/v) and wheat straw (8.6%, w/v) were slurried in 1% (v/v) H_2SO_4 separately and pretreated in an autoclave at 121 °C for 1 h (Saha, Iten, Cotta, & Wu, 2004, 2005). The pretreated substrates were neutralized to pH 5.0 with 10 M NaOH. The solids were separated from the liquids, washed one time with three volumes of water and dried in an oven at 60 °C for 24 h before using as a starting material.

2.3. Acetylation

Acetylation was performed on pretreated and untreated samples from corn fiber, rice hulls, and wheat straw. Two grams of sample along with 0.5 g of acetic acid, 5.0 g of acetic anhydride, 30 ml of methylene chloride, and 0.04 g of sulfuric acid were added to 100 ml round bottom flask. The mixture was heated to 80 °C while stirring with a magnetic stirrer. The flask was fixed with a reflux condenser and Therm-o-watch (I^2R) was used to ensure that the temperature was maintained at 80 °C. After 4 h, the reaction mixture was allowed to cool to room temperature and was sieved through a #60 Tyler screen, with the filtrate being collected in a large beaker. In order to extract the remaining cellulose acetate, the residue on the screen was collected and transferred to a beaker. Sixty milliliters of chloroform was added and the mixture was stirred for 30 min at room temperature and then sieved through a #60 Tyler screen. The filtrate was collected in a large beaker and combined with previous filtrates. The overs on the screen were discarded. The combined filtrates were further filtered into a round bottom flask using #54 Whatman filter paper. The filtrates were evaporated to dryness using a Rotavap (Buchi) to yield cellulose acetate as a film coating inside the flask. Ethyl alcohol was used to remove the acetate film from the flask. Filtration through a coarse filter paper yielded acetate as residue and ethyl alcohol as filtrate. The cellulose acetate collected on the filter paper was placed in evaporating dishes and dried at 80 °C in a vacuum oven overnight.

3. Results and discussion

Corn fiber, rice hulls, and wheat straw contain about 15, 36 and 45% cellulose, respectively (Saha & Bothast, 1999; Saha et al., 2004, 2005). Our objective was to convert cellulose into cellulose triacetate. Cellulose triacetate is soluble in methylene chloride or chloroform so it can be easily extracted from the unreacted substrate. Excess acetic anhydride was used and acetylation proceeded to the maximum extent to yield cellulose acetate having a degree of substitution of 2.8 from all the three sources. The acetylation of cellulose from corn fiber, rice hulls, and wheat straw was confirmed by proton NMR of the product cellulose acetate (Fig. 2).

The degree of substitution (DS) was determined by proton NMR, and by titration with aqueous sodium hydroxide solution. In the NMR method, we used the ratio of the seven cellulose proton absorbance in the range of 3.5–5.1 ppm to the absorbance of three methyl protons of acetyl groups in the range of 1.9–2.2 ppm. DS was calculated by 1/3 of the three methyl protons of acetyl group absorbance between 1.9 and

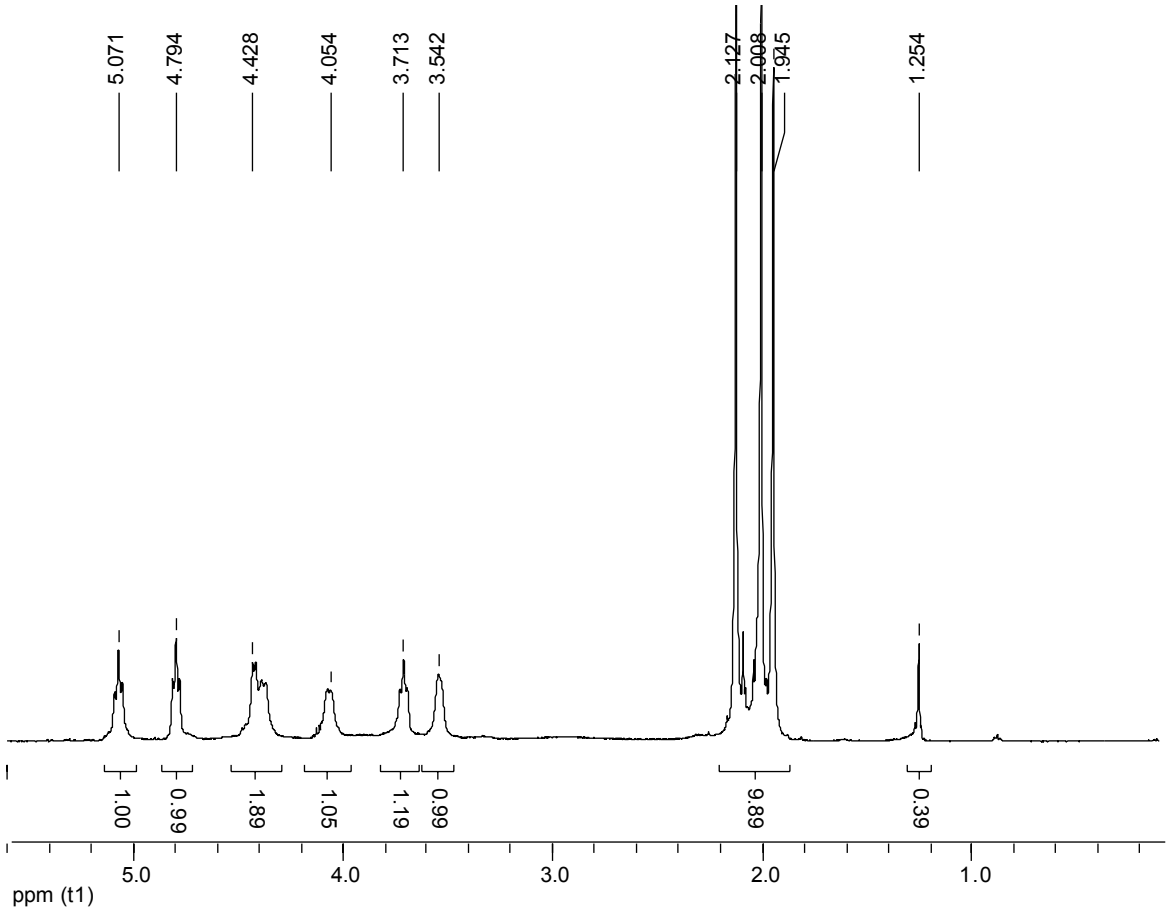

Fig. 2. Proton NMR of cellulose acetate (DS 2.8) in $CDCl_3$.

2.2 ppm divided by 1/7 of the total cellulose CH proton absorbance between 3.5 and 5.1 ppm.

Table 1 shows the yields of cellulose acetate obtained from both untreated and pretreated corn fiber, rice hulls, and wheat straw samples. When corn fiber and wheat straw were acetylated without pretreatment, the recovered yields of cellulose acetate were extremely low. When untreated corn fiber was used as the starting material only, 1.8% conversion was achieved. The amount of cellulose in corn fiber is lower (15%) than the other starting materials which may account for its low yield (Saha & Bothast, 1999). However, based on the amount of the cellulose in corn fiber, a conversion of about 12% was achieved. Untreated wheat straw gave the lowest conversion of only 0.5%. This is somewhat surprising since wheat straw contains about 30% cellulose (Saha et al., 2004). Wheat straw had the highest lignin content, however, of the substrates used. Untreated rice hulls used in the acetylation reaction gave yields of cellulose acetate, of about 13.5% conversion based on the starting weight. Rice hulls contain about 35% cellulose (Saha et al., 2005). Based on the amount of cellulose in rice hulls, the conversion of cellulose to cellulose acetate is about 35%. Since cellulose fibers are embedded with lignin, this may interfere with the acetylation reaction. Pretreatment of the lignocellulose may be essential for making cellulose acetate and the process will benefit from the pretreatment for ethanol production.

The acetylation conversion of cellulose in rice hulls, wheat straw, and corn fiber increased to about 25% for all substrates after the dilute acid pretreatment at a moderate temperature (Table 1). The increase in conversion is probably due to the pretreatment removing hemicellulose and other acid soluble materials. The result is an increase in the relative concentration of cellulose in the starting substrate. It is interesting to note that after pretreatment the acetylation conversion is about the same, regardless of the starting material. This may be due to remaining cellulose having the same reactivity. Native cellulose has an average degree of crystallinity of 70% (Daniel, 1985). It is assumed that the acetylation reaction would only work on the amorphous cellulose. This would put a theoretical conversion of cellulose to cellulose acetate at about 30%. This means that acetylation reaction of pretreated rice hulls, wheat straw, and corn fiber may be near the theoretical limit of conversion without further treatments on the cellulose to reduce its crystallinity.

Table 1
Cellulose acetate by weight from corn fiber, rice hull and wheat straw

Starting material	As is (% conversion)	Pretreated (% conversion)
Corn fiber, 2 g	0.036 g (1.8)	0.48 g (23.9)
Rice hull, 2 g	0.27 g (13.5)	0.53 g (26.6)
Wheat straw, 2 g	0.01 g (0.5)	0.51 g (25.8)

4. Conclusion

The cellulose in corn fiber, rice hulls, and wheat straw was converted into cellulose acetate. The conversion rate of untreated wheat straw and corn fiber is extremely low. However, the conversion rate is 13.5 wt% for untreated rice hulls. It is unclear why the conversion rate for untreated rice hulls is greater than for the other untreated fibers. When the substrates were preheated with dilute sulfuric acid to remove hemicellulosic sugars for alcohol production and other solubles, the yield of cellulose acetate greatly increased. We obtained cellulose acetate in about 25 wt% of the pretreated agricultural residues. We believe that the removal of the hydrolyzed water soluble materials increased the concentration of cellulose in the starting substrate available for acetylation. The acid treatment renders the cellulose more accessible to acetic anhydride and thus, more reactive towards acylation. More work is needed to improve the efficiency of the conversion. This method may improve the cost efficiency of the overall bioethanol production process by converting the cellulose in these residues into value-added cellulose acetate. Because, currently cellulase enzymes needed to saccharify cellulose to glucose for fermentation are not cost-competitive.

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