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Synthesis of cellulose acetate from cotton byproducts ☆

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ABSTRACT

Cotton burr and cottonseed hull are relatively inexpensive cotton byproducts. In an effort to derive greater value out of these natural renewable materials, we have succeeded in converting part of them into cellulose acetate without prior chemical breakdown or physical separation of cellulose, lignin, protein, and other components. The conventional approach of treating the raw materials with acetic acid, acetic anhydride, and sulfuric acid in a solvent yielded very little product. An alternative process that involved treating the materials with acetic anhydride and iodine proved to be more successful. No solvent was used in this alternative approach except during the sample workup. The process was optimized by varying the temperature and the amounts of acetic anhydride and iodine used. The best yields obtained thus far were about 15–24%, which corresponded to conversion of between 50% and 80% of the starting cellulose. Formation of the acetates and the degree of substitution were monitored via NMR spectroscopy.

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1. Introduction

Cellulose acetate is a well-known industrial product that finds many commercial applications (Edgar et al., 2001; Gedon & Fengl, 1993). A major application is in cigarette filters to remove particulates during smoking. As a fiber, cellulose acetate is used in textiles because of its relatively low cost, draping quality, softness, comfort, luster, and natural feel. The material is also used as a substrate for motion picture camera film. It also finds applications as an ingredient in sheet and molded objects and as an additive in surface coatings and inks. Its price is around $1.80 per lb.

Cellulose acetate is typically made from wood pulp through reaction with acetic acid and acetic anhydride in the presence of sulfuric acid to form cellulose triacetate (Bikales & Segal, 1971; Gedon & Fengl, 1993; Larock, 1989). The triacetate is then partially hydrolyzed to the desired degree of substitution (DS). Recently several other synthetic methods have been developed for polysaccharide esterification, including the use of ionic liquids (Wu et al., 2004), superacids (Yan, Li, Qi, & Liu, 2006), and reactions involving dialkylcarbodiimide, N,N-carbonyldiimidazole, iminium chlorides, transesterification, and ring-opening esterification (Heinze, Liebert, & Koschella, 2006). Another recent development is the use of iodine as a catalyst for the esterification of cellulose and starch in the presence of acetic anhydride (Biswas, Shogren, & Willett, 2005; Biswas et al., 2007, 2009).

In our laboratories, we are looking at agricultural byproducts and waste in an effort to provide materials with higher value. Cotton burr is a byproduct of cotton production (Thrash, 1987), and cottonseed hull is a low-value product of cottonseed oil extraction (Bailey, 1948). The hull is currently used as roughage in animal feed, as mulch, and as a substrate for mushroom production. The burr is a component of picker trash that may be used as fuel for boilers or occasionally as mulch. Both materials are readily available and inexpensive. In this paper, we would like to give the first report of the use of cottonseed hull and cotton burr for the production of cellulose acetate.

2. Experimental

Cottonseed hulls were produced from acid-delinting cottonseed to eliminate potential contamination of the hull with cellulosic linters. The seed was cracked with a Bauer mill, and the hulls and kernels were separated by air classification. Cotton burr was collected as a substantial part of the trash collected from a harvesting cotton stripper with stem pieces removed by hand. For comparative purposes, a sample of cotton fiber that had been previously scoured and bleached was included in the study. Methylene chloride, chloroform, deuterochloroform (for NMR analysis), acetic anhydride, iodine, and sulfuric acid were purchased from Aldrich (Milwaukee, WI). All reagents were used without further purification.

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

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In the first process, the burr and the hull samples were pulverized with a hammer mill until they passed through a 16-mesh screen. They were then stored in capped bottles at room temperature. In an alternative process, the burr and the hull samples were milled with a kitchen blender. Whereas all hull samples passed through a 7-mesh screen, 17% of burr samples did not. The retained burr sample appeared fibrous. Because of its appearance and its easy separation, we separately subjected this "burr fiber" to the acetate reaction.

For most hull and burr samples, a pretreatment procedure was used, similar to scouring and bleaching of cotton fiber (Bertoniere & King, 1989). In the scouring step, the sample was suspended in 6% solution of NaOH, heated in a water bath for 35 min, filtered, and washed with hot water at 95 °C to remove unwanted materials. In the bleaching step, the material was suspended in a NaOH solution at pH 12.0 with 1.5% H_2O_2 for 1 h in a hot water bath at about 95 °C. It was filtered to remove water and caustic and re-suspended in water. The pH was then adjusted to about 7 with dilute HCl. The suspension was filtered to remove the bulk of the water and salt and rinsed to remove residual salt. The resulting powder was dried at 40 °C overnight in a vacuum oven.

We first attempted the acetylation of hull and burr using conventional conditions (Bikales & Segal, 1971; Gedon & Fengl, 1993; Larock, 1989). Thus, in a 100-mL round bottom flask with stir bar, 2.0 g of sample were added to 0.5 g acetic acid, 5.0 g acetic anhydride, 30 mL methylene chloride, and 0.04 g concentrated sulfuric acid. The reaction mixture was heated under reflux (~80 °C) with stirring for 4 h, cooled to room temperature, and poured through a #60 Tyler screen to remove solid particles. The solid particles were then added to 60 mL chloroform, stirred for 30 min at room temperature and poured through a 60-mesh screen. The undissolved solid was discarded. The methylene chloride and chloroform filtrates were combined and filtered through a Buchner funnel fitted with #54 Whatman filter paper. The filtrate was placed into a round bottom flask, and the solvents were evaporated under vacuum at room temperature. Cellulose acetate formed a film on the sides of the flask. Ethanol was added to dilute the acetic acid and to remove the film. Filtration through #54 Whatman filter paper then gave the cellulose acetate product.

The preferred second approach was an adaptation of the iodine-catalyzed acetylation reaction of Biswas et al. (2009). In a typical reaction, 0.57 g of sample, 1.9 g of acetic anhydride, and 0.32 g of iodine were heated at 80–100 °C for 20–24 h. The reaction mixture was then cooled to room temperature and treated with 2 mL of a saturated solution of sodium thiosulfate while stirring. The mixture changed color from dark brown to colorless, indicating the transformation of iodine to iodide. The mixture was poured into 50 mL of ethanol and stirred for 30 min. The solid, which contained cellulose acetate, was filtered and washed with water and dried in a vacuum oven at 60 °C. The cellulose acetate was then dissolved in methylene chloride and filtered. The filtrate was evaporated under vacuum at room temperature to remove methylene chloride. Cellulose acetate formed a film on the sides of the flask. Ethanol was added to remove the film. The film was washed with ethanol and hot water at ca. 85 °C.

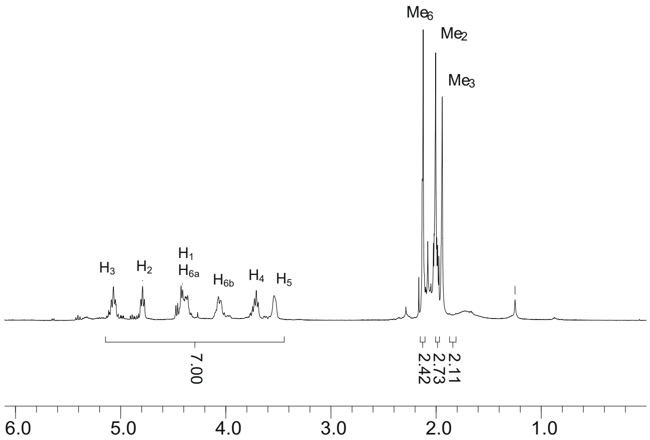

Fig. 1. ^1H NMR spectrum of a typical cellulose acetate from cotton byproduct, together with spectral assignments. Me corresponds to the methyl protons of the acetyl unit, and H to the protons on the anhydroglucose unit. Subscript refers to the position of acetyl or proton on anhydroglucose.

NMR spectra were obtained on a DRX400 spectrometer from Bruker Instruments (Carlstadt, Germany). Standard instrument conditions were used for ^1H NMR with $CDCl_3$ as the solvent. All chemical shifts were referenced to tetramethylsilane at 0 ppm. A typical ^1H NMR spectrum (e.g., cellulose acetate from hull) is shown in Fig. 1. The degree of substitution (DS) was calculated from the spectral intensities. The area between 3.6 and 5.2 ppm corresponded to the seven anhydroglucose protons, and the area between 1.9 and 2.2 ppm corresponded to the three acetyl protons. The ratio of 1/3 of the acetyl area to 1/7 of the anhydroglucose area then gave the DS. For the sample in Fig. 1, the DS was 2.42.

3. Results and discussion

Conventional acetylation of both hull and burr materials (entailing heating the burr or the hull powder in acetic acid, acetic anhydride, and sulfuric acid in methylene chloride) gave low or no yields of product (<2%). Although it might still be possible to adapt this reaction by further physical or chemical modification of the substrates, we chose instead to attempt the iodine-catalyzed reaction because it required no solvent during reaction and was relatively easy to carry out.

As it turned out, iodine-catalyzed acetylation produced much better results. We first studied the reaction on scoured and bleached cotton fiber. Because of its crystallinity and physical structure, cotton fiber was expected to be less reactive than the 20-μm cellulose powder from Aldrich (Ward, 1950). Nonetheless, cellulose acetate was synthesized without difficulty by the procedure given in the Section 2. Data are shown in Table 1. The weight

Table 1
Iodine-catalyzed acetylation reaction of cotton fiber, reacted for 20–24 h.

Sample	Weight of cotton fiber (g)	Weight of iodine (g)	Weight of Ac_2O (g)	Temp (°C)	Weight yield (%)	DS_{total}	DS_6	DS_2	DS_3
C-1	0.28	0.04	3.8	80	31	2.54	0.85	0.85	0.84
C-2	0.28	0.08	3.8	80	59	2.65	0.88	0.89	0.88
C-3[a]	0.28	0.16	7.6	80	92[b]	2.37	0.79	0.78	0.80
C-4	0.28	0.16	0.95	80	28	2.28	0.79	0.76	0.73
C-5[a]	0.28	0.16	0.95	100	20	3.73	nd[c]	nd	nd
C-6	0.28	0.16	0.95	120	13	4.69	nd[c]	nd	nd

[a] Average for duplicate runs.
[b] 57% of theoretical yield of cellulose acetate with DS 2.37.
[c] nd = Not determined.

yield depended on both the levels of iodine and acetyl anhydride (samples C-1 through C-3). DS of around 2.5 was typical for these materials. As we reduced the amount of acetic anhydride, the yield dropped (sample C-4). We attempted higher reaction temperatures (samples C-5 and C-6), but cellulose started to hydrolyze, leading to DS_{total} values larger than 3.0 and lower yields.

The same reaction was applied to the pretreated hull samples. Results are summarized in Table 2. At 80 °C, the yield again depended on iodine and acetic anhydride levels (samples H-1 through H-5). It is of interest that as the yield increased, the DS decreased. This was probably a result of crystalline structure of cellulose, which tended to resist chemical reaction. Thus, acetylation started at amorphous region, and once acetylation took place on an anhydroglucose unit, that same unit became more susceptible to further acetylation reaction, thereby leading to a large DS. It was pointed out earlier that iodine probably serves as an acetyl transfer catalyst for acetic anhydride (Biswas et al., 2009), which enhanced the acetylation reaction on cellulose; thus, with increasing iodine more cellulose units were attacked at the same time, leading to higher yield, but lower DS.

An interesting observation was found for hull at 100 °C. At this temperature we saw a notable increase in yield and relatively high DS (sample H-6). Thus, the higher temperature enabled the hull molecules to be more accessible to acetylation reaction. However, at 120 °C cellulose hydrolysis became important, leading to products with a lower yield and a DS higher than 3.0 (sample H-7). Thus, there was an optimal temperature window (at around 100 °C) for the acetylation of cottonseed hulls.

Results for the pretreated burr samples are summarized in Table 3. Here again, the yield depended strongly on iodine and acetic anhydride levels at 80 °C (samples B-1 through B-4). Compared with hull samples, burr seemed to be more susceptible to acetylation (cf. the yields of samples B-3 and B-4 versus samples H-3 and H-5). At 100 °C, burr also showed an increase in yield or DS, similar to what we observed in hull. Again, at 120 °C, cellulose hydrolysis became significant with DS exceeding 3.0 and decreasing yield. The optimal temperature for cottonseed burr acetylation was also about 100 °C.

Tables 1–3 also list the average degrees of substitution at the individual 2, 3 and 6 hydroxyl positions of the glycosyl ring (DS_2, DS_3, and DS_6). Since those numbers are approximately the same, the reactivity of the individual hydroxyl groups towards acetylation is roughly the same under the conditions employed for this work.

Finally we carried out the reactions on the "burr fiber." Results of the reaction are summarized in Table 4. In this case, the yield increased with increasing iodine and acetic anhydride levels. At 80 °C, the yield was 25% (sample F-3), albeit at a high acetic anhydride level. At 100 °C at a lower acetic anhydride level, the yield was also around 20–23% (samples F-4 and F-5). Interestingly, with

Table 2
Iodine-catalyzed acetylation reaction of cottonseed hull, reacted for 20–24 h.

Sample	Weight of hull (g)	Weight of iodine (g)	Weight of Ac_2O (g)	Temp (°C)	Weight yield (%)	DS_{total}	DS_6	DS_2	DS_3
H-1	0.57	0.04	3.8	80	1	2.03	0.67	0.69	0.68
H-2[a]	0.57	0.08	1.9	80	1	1.98	0.65	0.68	0.65
H-3	0.57	0.16	3.8	80	7	1.46	0.45	0.46	0.48
H-4	0.57	0.16	0.95	80	2	1.91	0.62	0.69	0.60
H-5	0.57	0.32	0.95	80	6	1.69	0.56	0.58	0.55
H-6[a]	0.57	0.32	1.9	100	34[b]	2.03	0.69	0.68	0.66
H-7	0.57	0.32	1.9	120	9	3.56	nd[c]	nd	nd

[a] Average for duplicate runs.
[b] 22% of theoretical yield of cellulose acetate with DS 2.03.
[c] nd = Not determined.

Table 3
Iodine-catalyzed acetylation reaction of cotton burr, reacted for 20–24 h.

Sample	Weight of burr (g)	Weight of iodine (g)	Weight of Ac_2O (g)	Temp (°C)	Weight yield (%)	DS_{total}	DS_6	DS_2	DS_3
B-1	0.57	0.04	3.8	80	0.4	1.87	0.34	0.30	0.23
B-2	0.57	0.08	3.8	80	1	1.66	0.50	0.63	0.53
B-3	0.57	0.16	3.8	80	16	1.01	0.38	0.36	0.27
B-4	0.57	0.32	0.95	80	18	1.98	0.67	0.66	0.65
B-5[a]	0.57	0.32	1.9	100	37[b]	2.09	0.70	0.70	0.69
B-6	0.57	0.32	1.9	120	7	3.84	nd[c]	nd	nd

[a] Average for duplicate runs.
[b] 24% of theoretical yield of cellulose acetate with DS 2.09.
[c] nd = Not determined.

Table 4
Iodine-catalyzed acetylation reaction of "burr fiber", reacted for 20–24 h.

Sample	Weight of burr fiber (g)	Weight of iodine (g)	Weight of Ac_2O (g)	Temp (°C)	Weight yield (%)	DS_{total}	DS_6	DS_2	DS_3
F-1	0.57	0.08	7.6	80	2	1.86	0.55	0.70	0.62
F-2	0.57	0.16	7.6	80	4	1.45	0.48	0.48	0.49
F-3	0.57	0.64	15.2	80	25	1.30	0.44	0.42	0.43
F-4[a]	0.57	0.32	0.96	100	20	1.76	0.58	0.59	0.59
F-5[a]	0.57	0.32	1.9	100	23[b]	1.93	0.65	0.64	0.64
F-6	0.57	0.32	1.9	120	28	2.00	0.66	0.68	0.66

[a] Average for duplicate runs.
[b] 15% of theoretical yield of cellulose acetate with DS 1.93.

the burr fiber at 120 °C the yield and the DS were both rather normal; thus, cellulose hydrolysis was much less noticeable here than in the case of hull or burr samples.

Regarding the mass yield values, cottonseed hull, burr, and the "burr fiber" samples all contain roughly 30% cellulose based on proximate analyses (unpublished, Cheng & Dowd). Because much of the cellulosic fraction is likely to be in the crystalline state and resistant to chemical reactions the percent of cellulose accessible to acetylation would be expected to be much less than 30%. The observation in this work of about 15–24% of the maximum theoretical yields of cellulose acetate is therefore about the level expected. The differences in yield found for hull, burr, and burr fiber at different temperatures is likely due to the different physical structure of the cellulose matrix in these materials.

4. Conclusion

This work is part of a large effort to find new uses for agricultural byproducts and waste products. In this paper, a process is described for the conversion of much of the cellulose embedded in cotton burr and cottonseed hull to cellulose acetate. It is noteworthy that we have been successful in synthesizing cellulose acetate from the whole hull and the whole burr. No prior chemical breakdown of the hull or burr material or physical separation of the lignin, protein, and other components is needed. The process involves no solvent except during sample workup. The maximum yield obtained thus far is about 15–24% of the maximum theoretical yields of cellulose acetate. The optimal temperature is slightly different with different types of samples, but they range between 80 and 120 °C.

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