Photohydrolysis of Cotton Cellulose for Producing Bioethanol

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ABSTRACT: Almost one third of the waste textiles produced from manufacturing clothing and other textile products are made of cotton. Hence, a huge amount of waste cotton is produced every year. Therefore, we aimed to develop an efficient way for conversion of cotton from waste textile into some beneficial resource in an environmentally safe manner. In this study, it was suggested a novel way to break down cotton cellulose into source of biomass glucose through a mild hypochlorite oxidation process (ca., 0.5 wt % of NaClO and 0.0125 wt % NaBr) under UV-irradiation. And, the UV light-NaBr-NaClO oxidation system was seen to induce exo-cleavage on $\beta(1 \rightarrow 4)$-glycosidic bonds in cellulose polymer. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 3782–3786, 2013

INTRODUCTION

Cotton is one of the most important textile fibers in the world, accounting for around 35% of total world fiber use. World cotton production in 2011/12 is estimated to rise 6% from a year ago to a record 123.1 million bales.[1] However, at the end of the life, most textiles made up of cotton fibers end sooner or later in waste station, and usually landfilled or incinerated.[2,3]

Cotton is typically composed of 88–96% cellulose, the remainder being protein, pectin materials and wax. Cotton must be scoured and usually bleached before use, whereby its cellulose content is enriched to about 99%.[3] Therefore, the cellulosic part of cotton-based textile waste can be used as an alternative renewable biomass for the production of value-added products via microbial process.[4] Ethanol is one of the products that can be produced from cotton-based textile waste by hydrolyzing process such as enzymatic hydrolysis followed by fermentation and chemical hydrolysis. However, bottlenecks still remain in the efficient conversion of cotton cellulose into ethanol. It is difficult to hydrolyze cellulose due to its large molecular structure, which imparts crystallinity and poor solubility.[5] Cellulose is a linear homopolymer of (1-4)-linked β-D-glucopyranose, which forms a macromolecule with a highly stable crystalline lattice structure. Thus, cellulose is strongly resistant to attack by both enzymes and chemical agents. Moreover, the crystallinity of cotton is particularly high compared to other natural cellulose resources; the crystallinity index of avicel, wood pulp, bacterial cellulose and cotton is 0.5–0.60, 0.50–0.70, 0.76–0.95, and 0.81–0.95, repectively.[6] In addition, enzymatic hydrolysis of cellulose is a slow process and is not likely to be applied in industrial practice in the immediate future;[7,8] and, chemical hydrolysis, usually acid hydrolysis in mineral acids, requires strong acid concentration and high temperature, which leads to corrosion of the reaction equipment, the degradation of production and accumulation of nonsugar by-products, and also the problem of recovery of reaction agent and resulting saccharides.[8,9]

Therefore, in this study we tried to find a new way to hydrolyze cotton cellulose quickly and environmentally friendly. Thus, we used UV light to accelerate the chemical hydrolysis of cotton cellulose in hypochlorite oxidation.

EXPERIMENTAL

Materials
Cotton fabrics (no. 400) were purchased from Testfabrics (West Pittston, PA). Sodium hypochlorite (NaClO) solution and sodium bromide (NaBr) were purchased from ACROS organics (PA). And glucose ($C_6H_{12}O_6$) and cellobiose ($C_{12}H_{22}O_{11}$) for calibration on gas chromatography-mass spectroscopy (GC-MS) were purchased from Aldrich (MO). All reagents were used as received without any further purification.

Hydrolysis of Cotton
Three gram of cotton fabrics, cut in sizes of around 2 × 2 cm^2, were each immersed in the reaction baths containing 0.0125 wt % of sodium bromide and designated concentrations of NaClO (0.2, 0.35, 0.5, and 0.75 wt %). Subsequently, the baths were gently shaken under UV light (high-intensity UV lamp; 365 nm, 7000 μW/cm^2 at 38.2 cm, Electron Microscopy Science,

Table I. Conversion of Cotton Fabric (3g) to Mono- and Disaccharide

Treatments		Breakdown product after the hydrolysis (ng/μL)	
NaClO conc. (wt %)	UV irradiation	Glucose	Cellobiose
0	Without UV for 24 h	Not found/below detection limit	Not found/below detection limit
0	With UV for 24 h	Not found/below detection limit	Not found/below detection limit
0.5	Without UV for 24 h	Not found/below detection limit	Not found/below detection limit
0.5	With UV for 24 h	142.28	3.48

Hatfield, PA) for designated times (1, 2, 5, 10, 24, and 48 h). After the hydrolysis process, the solutions were filter to separate the unhydrolyzed residue. Then, the residue was investigated by Fourier transform infrared (FTIR), thermogravimetric analysis (TGA), X-ray diffraction (XRD), and scanning electron microscope (SEM); and, the supernatant was estimated for carbohydrates by GC-MS.

Characterization

Degradation of cotton fabric was measured by the weighing method on the basis of the weight changes of cotton fabric before and after oxidation treatment. After the oxidation, the residual cotton debris were filtered and dried for 24 h. FTIR spectroscopy was performed with a Nicolet 6700 FTIR spectrometer (Thermo Fisher Scientific, Waltham, MA) with a resolution of 4 cm^{-1}. TGA was carried out with a Shimadzu TGA-50 apparatus (Shimadzu Scientific Instruments, Kyoto, Japan) at a heating rate of 10°C/min from 30 to 550°C under a nitrogen atmosphere. XRD measurements were performed at room temperature with Cu Kα X-rays ($\alpha = 1.5418$ Å) with a D8 Advance (Bruker, Germany). A theta-theta wide angle goniometer was used, and the ultimate peak resolution was $2\theta = 0.025°$. The surface morphologies of hydrogels were examined using a SEM (Philips XL30, Salem, MA). GC-MS analysis was performed using a 6890N gas chromatograph (Agilent, Palo Alto, CA) interfaced to a Pegasus III time-of-flight mass spectrometer TOF-MS) (Leco, St. Joseph, MI). Injections of 1 mL were made in split (1 : 5) mode (purge time 120 s, purge flow 40 mL/min). Helium carrier gas was used at a constant flow of 1 mL/min. The GC oven temperature program was an initial temperature of 50°C with 1 min hold time and ramping at 20°C/min to a final temperature of 330°C with 5 min hold time. Both the transfer line and the source temperatures were 250°C. The Pegasus III TOF mass spectrometer ion source was operated at 70 kV filament voltage with an ion source. After a solvent delay of 350 s, mass spectra were acquired at 20 scans per second with a mass range of 50 to 500 m/z. Data analysis was accomplished utilizing Chroma TOF software (version 3.25, Leco, St. Joseph, MI).

RESULTS AND DISCUSSION

NaClO Oxidation of Cotton Cellulose Under UV Light Irradiation

Table I shows that hypochlorite oxidation under UVA light successfully degrade cotton cellulose into glucose and cellobiose. Although the conversion rate is not that high (about 2%) com-

pared to the rate in strong acids (32.0% in 78.22% formic cid, 65°C),[10,11] the process did not involve any pretreatment of cotton for the hydrolysis and did not use any dangerous chemicals such as strong alkaline or acid, which are absolutely harmful to the environment. This degradation was found when oxygen is absorbed at certain sites on the cellulose molecule.[12,13] With this oxygen absorption, we found an increase in oxygen containing groups such as carbonyls assigned to C=O stretch at 1738 cm^{-1} and carboxylic acids attributed to O—H stretch at around 3380 cm^{-1}, as shown in Figure 1(d). As this greatly increased level of acid is released, the cellulose will be hydrolyzed, meaning the covalent bond between the rings in the cellulose chain will be broken, forming two shorter chains and releasing a hydrogen ion.[14] According to the Lewin's research,[14] the positions on the chains on which the functional groups (mostly carboxyl, aldehyde, and ketone groups) formed by oxidizing agents may be considered as vulnerable spots. In the case of hypochlorite oxidation the number of such spots per chain is in the range of 6–11. Also, oxidizing cellulose containing the electronegative aldehyde and ketone groups which are in position beta to the glucosidic linkage, are susceptible, according to the beta-alkoxyl elimination mechanism, to chain cleavage.[14–17] In particular, we observed UV light accelerates the hydrolysis of
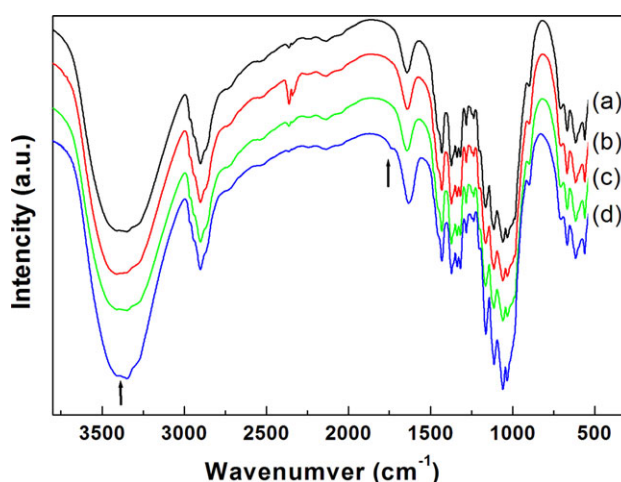
Figure 1. FTIR spectra of residual cotton after hydrolysis; (a) pristine, (b) only UV light irradiation for 24 h, (c) 0.5 wt % NaClO for 24 h in dark, (d) 0.5 wt % NaClO for 24 h under UV light irradiation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
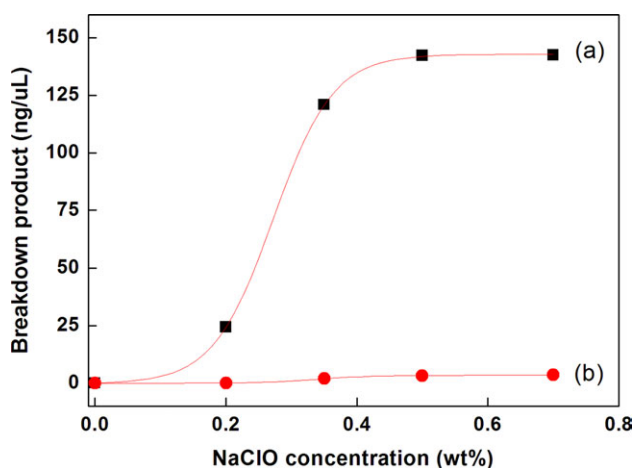
Figure 2. Breakdown product as a function of NaClO concentration; (a) glucose, (b) cellobiose (line: Boltzman fit, R^2 of (a) and (b) > 0.99). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

cotton cellulose by the hypochlorite oxidation. This seems UVA light makes the cellulose polymer vulnerable to oxidation reaction by removing electrons from the polymer chains. This is because Phillips et al.[18] studied the behavior of cotton cellulose irradiated by light in the spectral region 325–400 nm and demonstrated that most radicals were formed at wavelength 360 nm. Also, it is known that aromatic substrates are hydroxylated when irradiated by light, the first step in their photo-oxidation being a reaction between aromatic hydrocarbons and singlet oxygen.[19]

Effect of NaClO Concentration on Photohydrolysis of Cotton Cellulose

Figure 2 shows glucose and cellobiose concentration in the supernatant after cotton hydrolyzed by NaClO and UV light as a
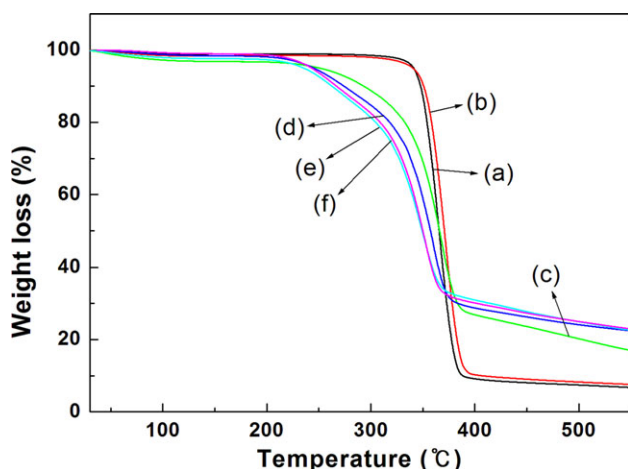

Figure 3. TGA curves of cotton fabrics after hydrolysis; (a) pristine, (b) only UV light irradiation, (c) 0.2 wt % NaClO for 24 h under UV light irradiation, (d) 0.35 wt % NaClO for 24 h under UV light irradiation, (e) 0.5 wt % NaClO for 24 h under UV light irradiation, (f) 0.7 wt % NaClO for 24 h under UV light irradiation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
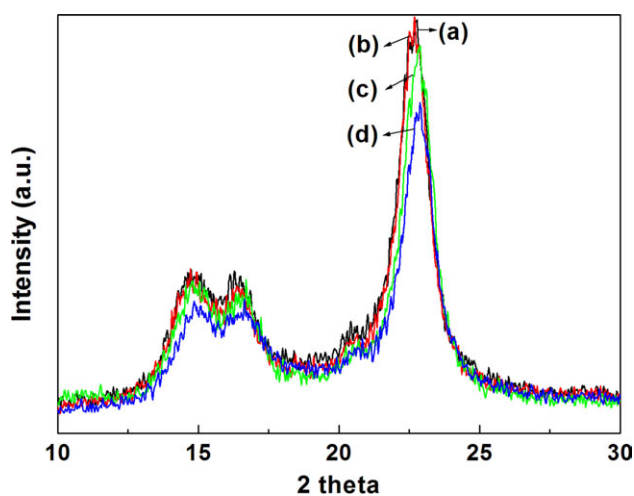
Figure 4. XRD curves of cotton fabrics after hydrolysis; (a) pristine, (b) only UV light irradiation, (c) 0.2 wt % NaClO for 24 h under UV light irradiation, (d) 0.5 wt % NaClO for 24 h under UV light irradiation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

function of NaClO concentration. The glucose concentration increased as NaClO concentration increased until 0.5 wt % concentration. After then, the glucose concentration plateau. Figure 3 shows cotton fabrics hydrolyzed by NaClO and UV light irradiation reveal lower onset temperature than pristine cotton and only UV light irradiated cotton. Also, the degradation behaviors of the hydrolyzed cotton fabrics show gentle slopes. It seems that the oxidation by NaClO and UV light combination degraded hydrogen bonds in crystalline region of cotton fabric and consequently decreased the crystallinity associated with the substitution of longer length of acyl group.[20] Conversely, degradation residue (%) of the cotton fabrics increases with increasing the NaClO concentration in Figure 3. This is plausible that during the oxidation process some cotton cellulose oligomers
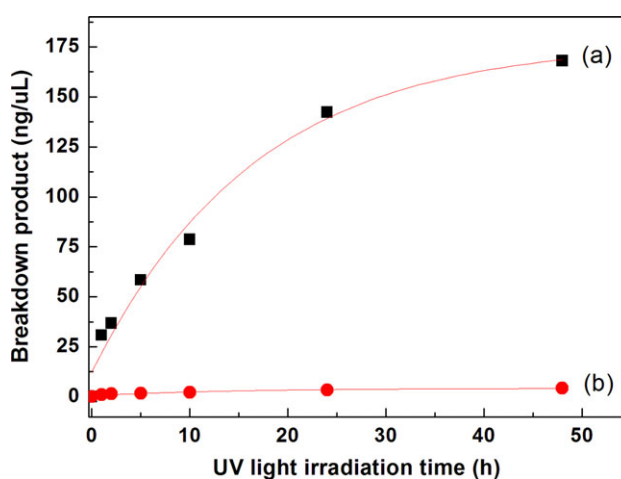
Figure 5. Breakdown product as a function of UV light irradiatin; (a) glucose, (b) cellobiose [line: Boltzman fit, R^2 of (a) > 0.97, R^2 of (b) > 0.92]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

were chlorinated by halogen element (Cl) and they became flame retardant. XRD data also indicates that significant decreases in both crystallinity and crystal width (002) at $2\theta = 22.6°$ occurred in the oxidized cotton cellulose, as shown in Figure 4; and, the three distinctive diffraction peaks at $2\theta = 14.7°$, 16.4°, and 22.6° were assigned to the cellulose I crystalline structure.[21,22]

Effect of UV Light Irradiation Time on Photohydrolysis of Cotton Cellulose

Figure 5 shows glucose and cellobiose concentration in the supernatant after cotton hydrolyzed by NaClO and UV light as a function of UV light irradiation. The glucose concentration increased as UV irradiation time increased. However, the cellobiose concentration did not change significantly with increasing UV irradiation time. From the result we knew that the NaClO and UV light combination mostly induces exo-cleavage on $\beta(1 \rightarrow 4)$-glycosidic bonds in cellulose polymer. That is to say the hydrolysis by NaClO and UV light just acts like exo-acting glucosidases. Table II shows that cotton cellulose was obviously degraded by NaClO and UV light combination and the degradation intensified with increasing UV irradiation time. And after 24 h, the reaction bath became totally slurry. This is very re-

Table II. Reduction (%) of Cotton after Hypochlorite Oxidation Process

Reaction bath	Residual cotton fabric (%)
No UV irradiation for 24 h	96.46
UV light irradiation for 2 h	91.70
UV light irradiation for 5 h	77.32
UV light irradiation for 10 h	40.72
UV light irradiation for 24 h	Totally slurry state

markable discovery for manufacturing biofuel from waste textiles. We also observed the degradation of cotton fabrics during the oxidation as shown in Figure 6.

CONCLUSION

It was found that cotton cellulose was successfully degraded in NaClO aqueous solution under UVA light irradiation. The hydrolysis seemed to mostly occur on $\beta(1 \rightarrow 4)$-glycosidic bonds in cellulose polymer and the cleavage was thought to start from ends of the polymer. From the photohydrolysis process, we obtained glucose which can be used as resource for bioethanol
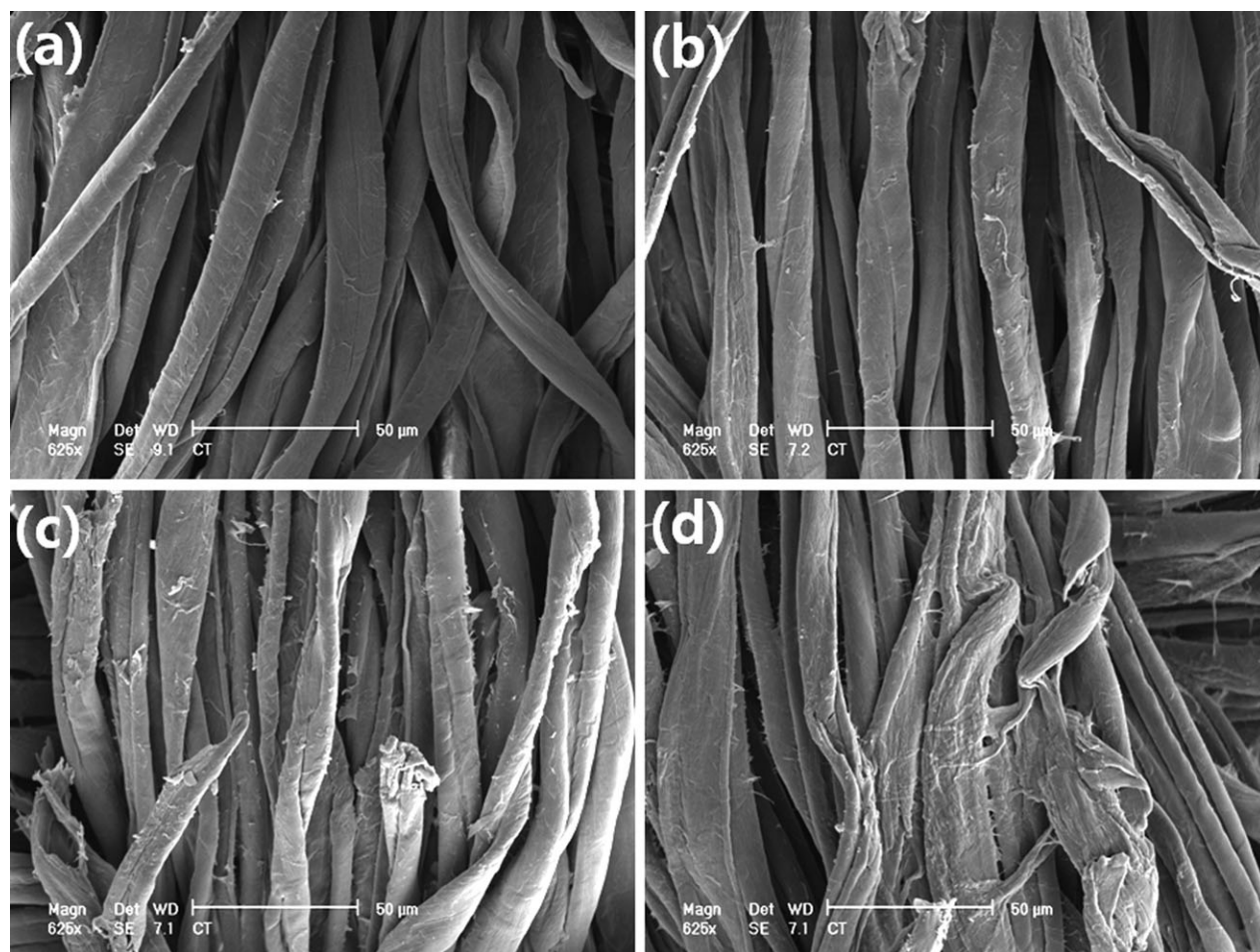
Figure 6. SEM images of residual cotton fabrics after 0.5 wt % of NaClO oxidation under UV light irradiation; (a) pristine, (b) 0.5 wt % NaClO for 2 h under UV light irradiation, (c) 0.5 wt % NaClO for 5 h under UV light irradiation, (d) 0.5 wt % NaClO for 10 h under UV light irradiation.

even though the process needs more development for industrial application. In addition, further studies would be necessary to increase the yield of glucose from the system in the future.

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