Natural resistance of raw cotton fiber to heat evidenced by the suppressed depolymerization of cellulose

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Abstract

Mechanically purified raw cotton fiber finds a growing range of applications in support of environmental sustainability, but its unique thermal stability, which is important in processes and utilization, is little known. This study shows that, at low temperatures (< 300 °C), the accelerated dehydration of cellulose was distinct in the pyrolysis of raw cotton. Compared with scoured cotton, raw cotton exhibited an intensive accumulation of dehydrocellulose in solid products, enhanced evolution of water and carbon dioxide, and increased formation of char. The amount of the crystalline region degraded together with the amorphous region was increased in raw cotton. The activation energy of thermal decomposition for raw cotton (124 kJ/mol) determined under isothermal conditions at 200-300 °C was lower than that for scoured cotton (202 kJ/mol). Such catalyzed low-temperature thermal reactions suppressed the depolymerization of cellulose at high temperatures, which produces highly volatile levoglucosan. The levoglucosan detected in raw cotton using Py-GC/MS was two orders of magnitude less abundant than that detected in scoured cotton.

Keywords: raw cotton; pyrolysis; inorganic salts; char; Py-GC/MS; TG-FTIR

1. Introduction

Scouring and bleaching of cotton fiber conducted as pretreatments to remove waxes, proteins, pectin, and natural color consume large amounts of water, energy, and chemicals, causing high chemical oxygen demand and high biological oxygen demand in the textile effluents [1]. In particular, the environmental impact of hydrogen peroxide bleaching is intensive; the consumption of chemicals including a reducing agent (i.e., sodium thiosulfate), sodium hydroxide, and a wetting agent has been estimated to be 0.118 kg/kg textile, and its energy and water consumption to be 8.34 MJ/kg textile and 50 L/kg textile, respectively [2]. In an effort to minimize such negative impacts on the environment, the use of non-scoured, non-bleached raw cotton fiber is receiving growing attention [3]. After it is harvested and ginned, cotton fiber can be purified by re-ginning and lint-cleaning without using water or chemicals [4]. This mechanical cleaning was shown to greatly reduce microbial contamination, i.e., producing a 91% drop in total aerobic microbial counts and a 99% drop in total aerobic yeast/mold counts [5]. The natural oleophilic characteristics of raw cotton fiber enable efficient processing of nonwovens for a broad range of end-use applications, such as batting for furniture and mattresses, the acoustic insulation of automobiles, and disposable protective products; it also can serve as a sorbent for oil spill cleanup [6]. Moreover, the oleophilicity of the fiber can be controlled by the hydroentangling nonwoven processing for applications, where moisture absorbency is necessary [7].

In promoting the utilization of raw cotton, understanding its thermal properties, which influence aging, deterioration, and degradation at elevated temperatures, is important. A previous study [8] has shown that raw cotton fiber in either woven or nonwoven form has better thermal resistance than scoured cotton fiber. According to thermogravimetry, differential thermogravimetry, and microscale combustion calorimetry analyses, raw cotton exhibited much slower thermal decomposition with the lowered onset decomposition temperature, leaving five times greater char and 46% smaller heat release capacity, indicating its reduced flammability. This thermal stability of raw cotton was attributed to inorganics, most of which could be removed by the scouring process. The inorganic salts in the raw cotton, which are usually reported as ash (about 1.2% of fiber dry weight), are expressed as the oxides of the elements [9]. In the ash constituent,

potassium was the most abundant metal, and appreciable amounts of magnesium and calcium and smaller quantities of sodium and iron were included (47.0% K_2O , 10.0% MgO , 7.6% SO_3 , 7.4% CaO , 4.3% P_2O_5 , 0.5% Na_2O , and 0.3% Fe_2O_3) [10]. These inorganic salts were found to catalyze the dehydration of cellulose at low temperatures to improve the formation of carbonaceous char [8].

Although the previous research has revealed the distinct thermal and combustion properties of raw cotton, the findings do not provide a comprehensive understanding of the altered thermal pathways involved. The suppression of the depolymerization route was suggested but has not yet been proved for raw cotton. Moreover, the activation energy of the thermal decomposition for raw cotton as determined from the region where the major weight loss occurred ($> 300\text{ }^{\circ}C$) did not fully elucidate the catalyzed thermal reactions at low temperatures. The objective of this study is to verify the changes in the nature of the pyrolytic reactions of cotton in the presence of naturally occurring inorganic salts. The isothermal thermogravimetric analysis at 200-320 $^{\circ}C$ was conducted to determine the kinetic parameters, including activation energy. The progress and products of low-temperature reactions greatly affected subsequent, competitive reactions at high temperatures. Such modification was demonstrated by monitoring the chemical and structural changes in the solid substrate as well as gaseous products released in the entire range of the pyrolysis temperature, using FTIR-ATR and TG-FTIR, respectively. The quantitative analysis of the composition of gas evolved by pyrolysis-gas chromatography/mass spectrometry confirmed the substantial reduction in “unzipping” depolymerization reaction in raw cotton. By combining the results of these kinetic and analytical studies, it was possible to develop a more complete picture of the pyrolytic reactions that characterize raw cotton and the resulting resistance to heat.

2. Experimental

Raw cotton plain woven fabric (greige cotton duck, 237 g/m²) was purchased from Testfabrics, Inc. Alkaline scouring was carried out using an overflow-jet dyeing apparatus (Werner Mathis Inc.). Fabric was immersed in an aqueous solution containing NaOH (1.8 g/L) and Triton X-100 (0.2 g/L) with a

liquid-to-fabric ratio of 22:1 and circulated at 100 °C for 60 min. After treatment, the fabric was washed in circulating water at 100 °C for 20 min, followed by cold-water washing for 20 min. The scoured fabric was neutralized with a solution of acetic acid (0.25 g/L) in water for 10 min and then rinsed with cold water. The fabric was then passed through a continuous hot-air dryer (Werner Mathis Inc.).

Thermogravimetric (TG) analysis was carried out using a TGA Q500 thermal gravimetric analyzer (TA Instruments, New Castle, DE) under a nitrogen atmosphere. The nitrogen flow into the furnace was maintained at a rate of 90 mL/min. About 6 mg of the sample placed in a platinum pan was heated from 30 ± 5 °C to various temperatures (200-900 °C) with a heating rate of 10 °C/min and was then immediately removed from the furnace. The images of the heated samples were taken using a digital microscope (KH-8700, Hirox) with a magnification of 10X in reflection mode. The isothermal experiments at low temperatures were conducted with 5 heating steps. The temperature was increased to 105 °C with a heating rate of 20 °C/min and held for 10 min to remove the moisture from the sample. The temperature was then increased to the specified isothermal temperature (200-320 °C) at a heating rate of 20 °C/min and maintained for 1 h. Afterward, the sample was pyrolyzed at a heating rate of 10 °C/min until 900 °C was attained. TG and DTG thermograms were analyzed using Universal Analysis 2000 software (TA Instruments). Three measurements were performed.

The evolved gas during the thermal decomposition of cotton was analyzed using TG-FTIR. A TG analyzer was equipped with a gas purge, and a TG-FTIR interface was installed inside the infrared spectrometer. Nitrogen was purged at 90 ml/min. The temperature was increased from 100 °C to 550 °C at a heating rate of 10 °C/min. A series of FTIR spectra were collected with 16 scans at a 4 cm⁻¹ resolution. Two spectra were obtained every minute.

The FTIR spectra of the samples heated at various temperatures were collected using an FTS 3000MX FTIR spectrometer (Varian Instruments, Randolph, MA) equipped with a ceramic source, KBr beam splitter, and deuterated triglycine sulfate detector. The attenuated total reflection (ATR) sampling device utilized a DuraSamplIR single-pass diamond-coated internal reflection accessory (Smiths

Detection, Danbury, CT), and consistent contact pressure was applied by a stainless steel rod and an electronic load display. Three measurements at different locations for each sample were collected over the range of 4000-600 cm^{-1} at 4 cm^{-1} resolution and 16 scans. All spectra were given in absorbance and no ATR correction was applied. Following the import to the GRAMS IQ application in Grams/AI (Version 9.1, Thermo Fisher Scientific, Waltham, MA), the spectra were smoothed with a Savitzky–Golay function (polynomial = 2 and points = 11).

Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) analysis was carried out at the Complex Carbohydrate Research Center in Athens, GA. 400-600 μg of sample was weighed and heated in the pyrolyzer at a range of temperatures. The released vapors were analyzed using GC/MS (Agilent technologies, CA). The temperature of the GC-MS interface was held at 280 $^{\circ}\text{C}$. Helium was used as a carrier gas at a constant flow rate of 1 mL/min and a 50:1 split ratio. The column temperature was increased from 50 $^{\circ}\text{C}$ to 280 $^{\circ}\text{C}$ at the heating rate of 5 $^{\circ}\text{C}/\text{min}$ and maintained at 280 $^{\circ}\text{C}$ for 5 min. Assignments of chromatographic peaks were made from mass spectral detection (NIST MS library).

3. Results and discussion

Raw and scoured cotton fabrics heated at incremental temperatures (200-400 $^{\circ}\text{C}$) under a nitrogen atmosphere were examined. Figure 1 shows that, as the temperature increased, the raw cotton was discolored faster than the scoured cotton; a brown (and black) color appeared in raw cotton at about 40 $^{\circ}\text{C}$ lower temperature. Agreeing with the color change, the raw cotton exhibited greater weight loss in the early decomposition, and this weight-loss difference increased until the temperature reached 340 $^{\circ}\text{C}$. Above 340 $^{\circ}\text{C}$, the weight-loss rates for raw and scoured cottons increased to reach the maximum weight-loss rate temperatures (T_{max}), 350.1 and 356.7 $^{\circ}\text{C}$, respectively. When the main decomposition of cellulose ended (at around 370 $^{\circ}\text{C}$ for raw cotton and 380 $^{\circ}\text{C}$ for scoured cotton), the raw cotton was consumed to a much lesser extent than the scoured cotton (75% vs. 94%). The larger amount of char produced in raw cotton was maintained until the temperature reached 900 $^{\circ}\text{C}$. Such accelerated decomposition of raw

cotton at low temperatures was further examined by the isothermal kinetics and the analyses of solid and gaseous products.

Figure 1. The optical microscopic images (10X) of raw and scoured cotton fabrics heated from 200 °C to 400 °C at increments of 20 °C in the TG analyzer under a nitrogen atmosphere.

3.1. Isothermal kinetics between 200 and 300 °C

Figures 2 (a) and (b) show the TG curves and three-dimensional profiles of conversion for raw and scoured cotton fabrics, respectively. After the first weight-loss period corresponding to the removal of moisture, raw and scoured cotton fabrics showed distinct weight-loss behaviors at various isothermal temperatures (200-320 °C). Raw cotton started to show a noticeable weight decrement ($> 5\%$) at 240 °C, whereas scoured cotton prolonged the corresponding decremental temperature to 280 °C. Until the temperature reached 300 °C, the weight loss of raw cotton was greater, but at 320 °C, the weight loss of scoured cotton abruptly increased to exceed the weight loss of raw cotton. Figure 3 (a) shows that the

isothermal process under temperatures up to 260 °C did not influence the T_{max} values for raw and scoured cottons; however, the preheating at 280 °C and 300 °C influenced the thermal decomposition of cellulose, decreasing the T_{max} . Under 320 °C, where most cellulose had degraded, T_{max} could not be observed. Figure 3 (b) shows that the isothermal treatments at low temperatures tended to increase the char yield. A similar effect was also observed in other studies [11, 12] and explained as the rearrangement of the cellulose structure through the dehydration and cross-linking reactions, which promotes the final production of char residue [13, 14].

Figure 2. Isothermal TG thermograms (left) for (a) raw and (b) scoured cotton fabrics at 200–320 °C (a–g at increments of 20 °C) and the corresponding three-dimensional profiles of conversion (right).

Figure 3. (a) temperature at the maximum weight-loss rate (T_{max}) and (b) char yield at 800 °C for raw and scoured cottons after isothermal treatment at various temperatures.

The isothermal data for raw and scoured cottons were fitted to a first-order reaction model assuming the rate-controlling role of one of the reactions in the reaction network:

$$\frac{d\alpha}{dt} = k(1 - \alpha) \quad (1)$$

where t is time (min), k is the rate constant (min^{-1}), and α is the conversion rate, i.e., the fractional sample weight loss. The α is defined by:

$$\alpha = \frac{w_0 - w_t}{w_0 - w_f} \quad (2)$$

where w_0 , w_t , and w_f are the initial sample weight, the sample weight at time t , and the final sample weight, respectively. In this study, the sample weight at 105 °C after 5 min was used for w_0 , and the weight at 800 °C was used for w_f . The integration of Eq. (1) gives:

$$\ln\left(\frac{1 - \alpha_0}{1 - \alpha}\right) = k(t - t_0) \quad (3)$$

where α_0 is the conversion of the sample from the beginning of the isothermal process at $t = t_0$. The plot of $\ln(1 - \alpha_0)$ versus $(t - t_0)$ yields a straight line with the slope equal to the rate constant k . For the determination of a rate constant, the isothermal period for the scoured cotton was additionally extended until it reached the same level of weight loss as in raw cotton. The dependence of k on temperature is assumed to obey the Arrhenius equation:

$$k = A \exp\left(\frac{-E_a}{RT}\right) \quad (4)$$

where A is the pre-exponential factor (min^{-1}), E_a is the activation energy (kJ/mol), and R is the gas constant ($8.314 \text{ J/K}\cdot\text{mol}$). From the logarithmic form of Ep. (4), the plot $\ln(k)$ versus T^{-1} yields a straight line with a slope of $-E_a/R$ and an intercept of $\ln(A)$. As shown in Table 1, all of the coefficients of determination were greater than 0.99, indicating adherence to the first-order reaction model. The rate constants (k) for raw cotton were one order of magnitude greater than those for scoured cotton. Figure 4 shows the plots of $\ln(k)$ as a function of T^{-1} , yielding straight lines. The steeper slope observed for scoured cotton indicates its higher activation energies (E_a) for the isothermal decomposition. The E_a values for raw and scoured cottons were determined to be 123.9 and 201.8 kJ/mol , respectively.

Table 1. Kinetic parameters obtained by least square fitting of the isothermal data for raw and scoured cotton fabrics based on the first-order reaction model.

Sample	Temperature ($^{\circ}\text{C}$)	n^a	k^b (min^{-1})	R^2	E_a^c (kJ/mol)	A^d (min^{-1})
Raw cotton	200	1	7.28×10^{-5}	0.9982	123.9	3.56×10^9
	220	1	3.04×10^{-4}	0.9970		
	240	1	8.22×10^{-4}	0.9944		
	260	1	2.20×10^{-3}	0.9946		
	280	1	6.25×10^{-3}	0.9984		
	300	1	2.15×10^{-2}	0.9966		
Scoured cotton	200	1	1.95×10^{-6}	0.9952	201.8	2.59×10^{16}
	220	1	8.56×10^{-6}	0.9978		
	240	1	4.78×10^{-5}	0.9962		
	260	1	3.77×10^{-4}	0.9922		

280	1	2.24×10^{-3}	0.9992
300	1	1.42×10^{-2}	0.9998

186 ^a order of reaction; ^b rate constant; ^c activation energy; ^d pre-exponential factor

187
188 **Figure 4.** Plots of $\ln(k)$ versus T^{-1} for the determination of the activation energies and pre-exponential
189 factors in the isothermal decomposition from 200 °C to 300 °C for raw and scoured cotton fabrics.

191 3.2. Analysis of solid products

192 Figures 5 (a) and (b) show the FTIR-ATR spectra of raw and scoured cotton fabrics, respectively,
193 heated from 180 °C to 880 °C. The published band assignments on the cellulose structure [15-18] are
194 given in parentheses. The cellulose characteristic bands, C-H stretching ($3000-2700\text{ cm}^{-1}$) and C-H
195 wagging (1429 cm^{-1}) bands, started to broaden at 220 °C in raw cotton, whereas these bands remained
196 stable at temperatures up to 280 °C in scoured cotton. Another noticeable difference was the development
197 of the bands at 1695 cm^{-1} and 1600 cm^{-1} , corresponding to C=O stretching of unsaturated aldehydes and
198 C=C stretching of alkenes, respectively, which indicate the dehydration of cellulose. These bands were
199 intensified at 300-380 °C for raw cotton and at 360-480 °C for scoured cotton. The facilitated dehydration
200 at lower temperatures in raw cotton was also supported by the early disappearance of C-O-C stretching

(1160 cm^{-1}) and C-O stretching (1029 cm^{-1}) bands at 360 °C (480 °C for scoured cotton). The shift of the C=C stretching band toward 1575 cm^{-1} , signifying conjugation of C=C bonds, occurred in raw cotton at 360 °C, but no such shift was observed until the temperature reached 580 °C in scoured cotton. According to Price *et al.* [19], the conversion of aliphatic char from cellulose to an aromatic form occurred at 400-800 °C in air. These results suggest that traces of inorganic salts in raw cotton allowed the aromatization of char at lower temperatures, which contributed to the increased formation of stable char. The early formation of aromatic char was also observed by flame-retardant treatments, i.e., the introduction of flame-retardant phosphoric acid into cellulose lowered the temperature for the accumulation of unsaturated carbon-carbon bonds and carbonyl groups in solid pyrolysis products [20], and inorganic phosphorus/nitrogen flame retardants led to direct formation of an aromatic char [19].

The change in the crystallinity of cellulose was examined using a previously developed three-band (800, 730, and 708 cm^{-1}) ratio algorithm [21, 22]. Figure 6 (a) shows the variations in the crystallinity index (CI) for raw and scoured cottons under conditions of increasing temperature. The scouring process slightly increased the CI. As the temperature increased, the CI values of both raw and scoured cottons noticeably increased. As shown in Figure 6 (b), the change in the intensity at 730 cm^{-1} , which is linked with the relative amount of amorphous cellulose, suggests that the observed elevations in CI were attributed to the decomposition of the amorphous region. This is supported by Basch and Lewin [23], who reported that thermal decomposition of the cellulose begins in the less-ordered regions by demonstrating a drop in the degree of polymerization and increased crystallinity for various cellulose materials during vacuum pyrolysis at 251°C. They also reported that the rate of decomposition increased as the percentage of amorphous region increased. Raw cotton exhibited a significant correlation between the percentage of the amorphous region (100 - CI) and the weight-loss rate (obtained by DTG) with a coefficient of 0.79 ($p < 0.01$), but scoured cotton exhibited no significant correlation due to the absence of appreciable weight loss until the temperature reached 320 °C. It is noted that the amorphous intensity at 730 cm^{-1} decreased faster for raw cotton than for scoured cotton. Trace quantities of inorganic salts present in raw cotton

catalyzed the thermal decomposition of the amorphous regions [24]. The CI plot for raw cotton indicates that, before its amorphous region completely degraded, the crystalline region started to degrade, yielding 80% of the maximum CI at around 240 °C. On the other hand, the decomposition of the amorphous cellulose in scoured cotton was prolonged at temperatures up to 330 °C, at which complete decomposition of the amorphous region was achieved. It should be noted that, as this algorithm was developed based on the maturity of cotton fiber, the CI values determined for heated cottons might be overestimated. The relative changes in CI, however, clearly indicate that a greater amount of the crystalline region degraded together with the amorphous region in raw cotton than in scoured cotton. It has been reported that the facilitated thermal decomposition of amorphous as well as crystalline regions, which was observed following the addition of phosphoric acid, was associated with dehydration reactions and other types of rearrangements of cellulose [25]. After reaching the maximum CI, the CI for the scoured cotton dropped steeply to 0%. The temperature for 0% CI was 360 °C for raw cotton and 480 °C for scoured cotton.

Figure 5. FTIR-ATR spectra for (a) raw cotton and (b) scoured cotton heated at incremental temperatures.

Figure 6. (a) crystallinity index calculated by the three-band ratio algorithm and (b) intensities at 740 cm⁻¹ for raw and scoured cotton fabrics heated at incremental temperatures.

3.3. Analysis of gaseous products

The real-time gaseous products that evolved during the pyrolysis process were detected by TG analysis coupled with IR spectroscopy. Figure 7 shows the 3D FTIR spectra with the coordinates of absorbance, wavenumber, and temperature for raw and scoured cottons. The evolved species consisted primarily of water (3737, 3590, 1514 cm⁻¹), methane (2977, 2918, 2819, 2725 cm⁻¹), carbon dioxide (2354, 2321, 726-617 cm⁻¹), carbon monoxide (2180, 2116 cm⁻¹), aldehydes or ketones (1745 cm⁻¹), and alcohols (1117, 1060 cm⁻¹). In accordance with the weight-loss pattern seen in the TG curve (Figure 1), two stages of evolution were observed. The first noticeable simultaneous evolution of gases was detected near 210 °C for raw cotton and 300 °C for scoured cotton; their absorbance gradually increased as the temperature increased, reaching apexes at around 325 °C and 340 °C (close to their $T_{\max}$ values), respectively. The greater evolution concentrations (i.e., higher absorbance) and wider evolution temperature intervals of water, carbon dioxide, carbon monoxide, and aldehydes for raw cotton show its progressive dehydration of the cellulose in the range of 210-280 °C, followed by the decomposition of the dehydrocellulose into gaseous products and char above 280 °C. The dehydrocellulose could be formed via

etherification between superimposed cellulose chains (C-2 and C-4) [26]. The near absence of peaks detected for carbon monoxide in scoured cotton, which is one of the decomposition products of ether groups, was consistent with its suppressed dehydration. The production of methane requiring relatively high energy in breaking methyl and methylene groups [27] was favored in the high-temperature decomposition of scoured cotton. The second evolution stage was clearly identified in raw cotton from its carbon dioxide absorbance wave, which intensified again at around 390 °C. This growing absorbance (reaching the maximum at 467 °C and stabilizing afterwards) indicates the decomposition of char formed in the previous stage. The negligible char formation in scoured cotton (Figure 1) resulted in the emission of a lower concentration of carbon dioxide. Carbon monoxide, methane, and aldehydes were rarely detected in the second stage. The absorbance band centered at 3260 cm^{-1} (O-H stretching) continuously increased throughout the pyrolysis process.

Figure 7. 3D TG-FTIR spectra for (a) raw cotton and (b) scoured cotton obtained at a heating rate of 10 °C/min.

Py-GC/MS chromatograms for raw and scoured cottons obtained at 320 °C and 530 °C are presented in Figures 8 (a) – (d). Prospective assignments of the main peaks made from mass spectral detection (NIST MS library) are presented in Tables 2 and 3. At 320 °C, raw cotton released a large variety of products, whereas scoured cotton produced levoglucosan (β -D-glucopyranose, 1,6-anhydro) as a major decomposition product. Levoglucosan is generally formed from the depolymerization of cellulose, which involves the intramolecular transglycosidation breaking the 1,4-glycosidic linkage. The resulting anhydrosugars were then converted into the more stable levoglucosan [28]; its furanose isomer (i.e., 1,6-anhydro- β -D-glucofuranose) was detected in scoured cotton. A high production rate of levoglucosan, as seen in scoured cotton, characterized the depolymerization as an “unzipping” process.

Raw cotton’s low yield of levoglucosan and production of a variety of five and six carbon compounds suggest the accelerated dehydration of the glucose units and anhydrosugars. The dehydration products detected include hydroxyacetone, furan derivatives, levoglucosenone, and pyran derivatives, which are important intermediates in char formation [29, 30]. Similarly, the rapid decrease in crystallinity of raw cotton (Figure 6) resulted in reducing its levoglucosan production [23]. It is noted that the peak area of levoglucosenone was greater than that of levoglucosan. The increased ratio of levoglucosenone to levoglucosan has been reported to be characteristic of the pyrolysis of cellulose modified with flame-retardant phosphoric acid [25, 31]. The greater abundance of levoglucosan for scoured cotton was maintained as the temperature increased to 530 °C. The maximum production of levoglucosan during the pyrolysis of cellulose was reported as occurring at around 570 °C [32]. At 530 °C, various low-molecular-weight volatiles were produced from the secondary cracking of the primary fragments. The generation of a variety of cyclopentene derivatives as well as phenol and phenol derivatives was promoted in raw cotton. The presence of 1,4:3,6-dianhydro- α -D-glucopyranose, furan derivatives, and pyran derivatives detected in scoured cotton show that the dehydration of levoglucosan occurred at 530 °C.

(a) Raw cotton at 320 °C

(b) Scoured cotton at 320 °C

(c) Raw cotton at 530 °C

(d) Scoured cotton at 530 °C

► Retention time: 24.913 - 31.099 min

Figure 8. Py-GC/MS chromatograms for (a, c) raw and (b, d) scoured cottons at 320 °C and 530 °C. (e) Mass spectrum of levoglucosan obtained at a retention time of 24.913-31.099 min and the peak area of levoglucosan as a function of temperature.

Table 2. Selected compounds identified from the Py-GC/MS analysis for raw and scoured cotton fabrics at 320 °C.

Raw cotton		Scoured cotton	
Retention time (min)	Compound	Retention time (min)	Compound
2.606	2-Propanone, 1-hydroxy	16.546	1,4:3,6-Dianhydro- α -d-glucopyranose
7.225	2(5 <i>H</i>)-Furanone	31.029	β -D-Glucopyranose, 1,6-anhydro
12.860	Levogluconone	31.759	1,6-Anhydro- β -D-glucofuranose
15.781	4 <i>H</i> -Pyran-4-one, 3,5-dihydroxy-2-methyl		
20.884	1,2,3-Benzenetriol		
21.187	5-Hydroxymethylfurfural		
23.796	3,4-Dihydro-6-hydroxy-2 <i>H</i> -1-benzopyran-2-one		
24.443	β -D-Glucopyranose, 1,6-anhydro (levoglucosan)		

Table 3. Selected compounds identified from the Py-GC/MS analysis for raw and scoured cotton fabrics at 530 °C.

Raw cotton		Scoured cotton	
Retention time (min)	Compound	Retention time (min)	Compound
1.693	Propan-2-one	4.166	Methyl 2-oxopropanoate
2.451	2-Propanone, 1-hydroxy	4.586	Furfural
4.091	Butanedial	7.150	2(5 <i>H</i>)-Furanone
4.195	Methyl 2-oxopropanoate	7.474	1,2-Cyclopentanedione
5.003	Furfural	8.380	2-Furancarboxaldehyde, 5-methyl
5.074	2-Cyclopenten-1-one	10.421	2-Cyclopenten-1-one, 2-hydroxy-3-methyl
6.940	Ethanone, 1-(2-furanyl)	13.197	2 <i>H</i> -Pyran-2-one
7.115	Butyrolactone	13.861	But-1-ene-3-yne, 1-ethoxy
7.246	2(5 <i>H</i>)-Furanone	14.048	4 <i>H</i> -Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl
7.598	2-Cyclopenten-1-one, 2-hydroxy	16.095	1,4:3,6-Dianhydro- α -d-glucopyranose
8.537	2-Cyclopenten-1-one, 3-methyl	16.903	5-Hydroxymethylfurfural
9.088	Phenol	30.198	β -D-Glucopyranose, 1,6-anhydro
10.572	2-Cyclopenten-1-one, 2-hydroxy-3-methyl	36.803	Octadecanoic acid
12.045	Furyl hydroxymethyl ketone		
13.168	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy		
15.799	1,2-Benzenediol		

16.058	1,4:3,6-Dianhydro- α -d-glucopyranose
25.184	β -D-Glucopyranose, 1,6-anhydro
33.134	n-Hexadecanoic acid
36.790	Octadecanoic acid

4. Discussion

A previous study [8] reported that the improved thermal resistance of mechanically cleaned raw cotton was linked with naturally occurring inorganic salts. Other noncellulosic organic components, such as wax (0.6%) and pectin (0.9%), present on the outer surface of the fiber [9] were assumed to have relatively small effects on the thermal decomposition of cellulose. In continuation of the work to elucidate the effects of inorganics on the thermal decomposition behavior of cellulose, isothermal treatments and analyses of solid and gaseous products yielded during the pyrolysis were conducted. The early development of carbonyl groups and carbon-carbon double bonds on the solid products and the increased release of pyrolytic water, carbon dioxide, and carbon monoxide observed by FTIR-ATR and TG-FTIR, respectively, indicate that the inorganics accelerated the dehydration of cellulose and the aromatization of char at lower temperatures. Such dehydration is one of the three main chemical pathways proposed by Kilzer and Broido [26]. Traveling this route, occurring at 200-280 °C, cellulose reacts in an endothermic process with the loss of water to yield a “dehydrocellulose.” Consistent with the chemical changes observed, the temperature, where the structural organization of cellulose (crystallinity) deteriorated, was lowered for raw cotton. The catalyzed dehydration reaction in raw cotton was further supported by the activation energies determined under isothermal conditions at 200-300 °C - 124 and 202 kJ/mol for raw and scoured cottons, respectively. As the temperature increases, the other two pathways are involved, i.e., depolymerization of the unreacted cellulose via an endothermic process to produce volatile levoglucosan and decomposition of the “dehydrocellulose” via exothermic reactions to produce light gases and char [26]. Py-GC/MS showed considerable depletion of levoglucosan in raw cotton at 320-530 °C. The depolymerization of the residual cellulose was suppressed, because a larger amount of cellulose in raw

cotton had undergone the dehydration. The combination of the kinetics and analytical studies demonstrate that inorganic salts present in raw cotton allowed dehydration reactions to proceed to the fullest possible extent to prevent a maximum yield of levoglucosan, which is a major constituent of flammable tar, as well as the early formation of aromatic char, which enhanced the yield of carbonaceous char.

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