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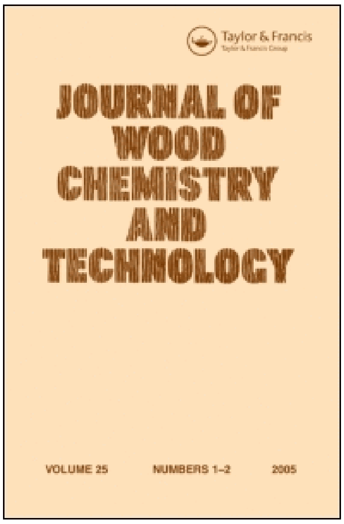

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FORMATION OF CHLORINATED ORGANIC MATTER FROM CARBOHYDRATE DURING KRAFT PULP BLEACHING

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ABSTRACT

Chlorinated organic matter is formed during chlorine bleaching of carbohydrate. After chlorine bleaching of various cellulosic materials, organochlorine is found in the cellulose substrate (e.g., about 490 μg Cl/g substrate for cotton cellulose) as well as in the spent bleaching liquor. Some organochlorine is mineralized by alkali treatment of the cellulose and some is dissolved. Some organochlorine is not removed by exhaustive extraction with organic solvents, i.e., is inextractable. The carbohydrate-originated organochlorine accounts for part of the inextractable organochlorine in fully-bleached chemical pulp (previously ascribed entirely to a lignin origin). Chlorination of unmodified simple sugars results in some organochlorine (17 to 83 μg Cl/g sugar), while chlorination of "kraft-cooked" glucose precipitate results in 6150 μg organochlorine as Cl/g substrate. Household hypochlorite bleaching of cotton fabric also results in formation of inextractable organochlorine.

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INTRODUCTION

Chlorinated organic matter is produced during wood pulp bleaching with chlorine-containing agents. Some of the organochlorine remains in the bleached pulp fibres[1] and even viscose fibres[2,3]. In fully-bleached softwood kraft pulp, the organochlorine which is inextractable by water or organic solvents is usually about 200 µg Cl/g pulp[1]. A substantial portion of this inextractable organochlorine is retained after the pulp has been dissolved and regenerated from the non-aqueous solvent systems[4].

It is generally believed that organochlorine is formed under the pulp bleaching conditions by chlorination of residual lignin and wood extractives exclusively. However, we must ask ourselves; can chlorine be covalently bound to cellulose or hemicellulose during pulp bleaching? There is extensive literature on cellulose and hemicellulose reactions with chlorine, chlorine dioxide and hypochlorite. To our knowledge, however, there has been no report of the formation of organochlorine or identification of chlorinated organic compounds from the bleaching of carbohydrates. It must be kept in mind, however, that conventional organic chemistry techniques cannot readily analyze minor or trace reaction products unless substantial effort is dedicated to the isolation of these compounds. Organochlorine resulting from carbohydrate bleaching might be demonstrated by the measurement of adsorbable organic halogen (AOX) in the aqueous phase after reaction, or by the measurement of "organochlorine" retained in the cellulose fibres. The organochlorine in the fibre is defined as the chlorine which cannot be removed by vigorous water washing.

We have hypothesized that carbohydrates contribute to organochlorine formation during pulp bleaching; and so we have

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carried out experiments on the chlorine bleaching of cellulosic materials and simple sugars.

EXPERIMENTAL

Material Preparation

Purification of Cotton

Raw cotton long fibres were kindly provided by Glendale Spinning Mill (Hamilton, Ont.). After removing all the visible dirt, the cotton sample was purified by refluxing at 3% consistency in 2% aqueous NaOH solution under N_2 for 4 hours. It was then filtered and washed with boiling water, followed by exhaustive washing with deionized water until pH 7. The fibres were then soaked in water overnight, filtered, washed with acetone and air-dried. The dry fibres were then soaked in acetone for 4 hours. The acetone was decanted and the fibres air-dried.

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Kraft Cooking of Cotton

A stock solution of white liquor was prepared by dissolving 3.5 g NaOH and 3.8 g $Na_2S{\cdot}9H_2O$ in a beaker and making up to 100 mL with distilled water. This solution has a sulphidity of 27% and effective alkali (EA) of 32 gpL as Na_2O. Two mini-cooking bombs were used for cooking, each containing 2.0 g of purified cotton with 17.8 mL white liquor (28% EA as Na_2O applied on cotton). The bombs were put into a silicone oil bath (preheated to 90 °C), and the cooking was carried out by increasing the temperature to 170 °C in 70 minutes and staying at 170 °C for 90 minutes. At the end of the cooking, the bombs were immediately cooled by cold running water. The kraft-cooked cotton was then washed thoroughly with deionized water and air-dried.

Severe Cooking of Cotton

A stock solution of white liquor was prepared with a sulphidity of 27% and effective alkali (EA) of 157.5 gpL as Na_2O (five times as much EA as in the normal kraft cooking). 10.0 g purified cotton was suspended in 90 mL white liquor in a cooking bomb. The cooking was carried out in the same way as the kraft cooking described above.

Hydrogen Peroxide Bleaching

10 g of purified cotton at 5% consistency was treated with 0.6% H_2O_2 on cotton. The system was buffered to pH 10.0-10.5 with 0.085 molar KH_2PO_4 and an appropriate amount of NaOH. The reaction was carried out at 65 °C for 3 hours. The treated cotton fibres were then filtered and washed with deionized water to pH 7 [5].

Sodium Borohydride Treatment

3.0 g of H_2O_2 treated cotton at 3% consistency was treated with 0.15 g $NaBH_4$ at room temperature for 18 hours and then washed with deionized water[5].

Periodate Oxidation of Cotton

3.0 g of purified cotton at 1% consistency was treated with 6.4 g of sodium metaperiodate in an amber-colored bottle in darkness at room temperature for 50 hours. The cotton was then washed with deionized water and air-dried[6].

Mercerization of Cotton

4.0 g of purified cotton was treated with 18% aqueous NaOH solution in a 3% consistency suspension at room temperature for 3 hours. It was then washed exhaustively with deionized water to pH 7 and air-dried.

Hydrocellulose

3.0 g purified cotton was suspended in 200 mL 0.1 M H_2SO_4 and refluxed for 1.5 hours. It was then thoroughly washed with deionized water to pH 7.

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Commercial Oxycellulose

Oxycellulose gauze (cotton cellulose oxidized with NO_2) was purchased from Sigma Chemical Company[7].

Purification of Bacterial Cellulose

Bacterial cellulose ("Cellulon" fibre) was kindly provided by Weyerhaeuser Company. 100 g of wet bacterial cellulose (18% solids content) was purified by refluxing at 2.5% consistency in a 3% aqueous NaOH solution under N_2 for 2 hours. After refluxing, the cellulose was transferred to 2 liters of 3% NaOH solution and soaked overnight. Then, it was repeatedly washed and centrifuged until pH 7.

Microcrystalline Cellulose

Microcrystalline cellulose, produced by controlled acid hydrolysis of cellulose from bleached wood pulp to the levelling-off degree of polymerization, was purchased from J.T.Baker Chemical Company.

Severe Cooking of Microcrystalline Cellulose

Stock solution of white liquor was prepared at sulphidity of 27% and EA of 157.5 gpL as Na_2O. 25 g microcrystalline cellulose was suspended in 250 mL white liquor in a cooking bomb. The cooking was carried out in the same way as the normal kraft cook. After cooking, the insoluble microcrystalline cellulose was filtered, washed with 0.5 M H_2SO_4, and washed exhaustively with deionized water to pH 7. This material was named Fraction A. It retains a light greyish color after being air-dried. On the other hand, adjusting the pH of the spent cooking liquor to pH 11 results in some precipitation. The precipitate was washed thoroughly with deionized water to pH 7 and air-dried. This dark-brown material was named as Fraction B.

Alpha Cellulose from Wood Pulp

A commercial softwood pulp, fully-bleached with the O(C+D)EDED sequence, was Soxhlet-extracted with acetone for 8 hours and then washed with deionized water. Its chlorine content after this treatment was 180 μg Cl/g pulp. It was then treated with 18% NaOH solution in a 5% consistency suspension at 4 °C for 3 hours, followed by washing and soaking in the deionized water for 2 days. After filtration, the pulp sample was air-dried. It was found to have a chlorine content of 55 μg Cl /g pulp.

Cellobiose, Sugars and Glycoside

Some carbohydrate compounds were purchased: from Sigma, cellobiose; from Aldrich, D-xylose and methyl-β-D-glucoside; from BDH, D-glucose, D-mannose, D-galactose and L-arabinose; and from J. T Baker, D-maltose and d-trehalose.

Kraft Cooking of Glucose

Stock solution of white liquor was prepared with a sulphidity of 27% and EA of 32 gpL as Na_2O. 25 g glucose was dissolved in 225 mL white liquor in a cooking bomb. The cooking was carried out under the conditions described previously. After cooking, the liquor was adjusted to pH 4 with 1 M H_2SO_4. The resulting precipitate was then filtered, washed thoroughly with deionized water and air-dried. This material was intensely colored.

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Bleaching Procedures

Chlorine Bleaching

Samples at 2% consistency were bleached with 6% chlorine on substrate for 30 minutes. The reaction was carried out in a water bath, with temperature controlled at 60 °C. After bleaching, samples were filtered, washed and air-dried. The undiluted filtrate (spent bleaching liquor) was collected. One fraction of the filtrate was used for residual chlorine titration. The rest of the filtrate was treated with sodium thiosulphate to consume the residual chlorine and stored in a refrigerator for AOX tests.

Extended bleaching of severely kraft-cooked cotton was carried out in a similar fashion except that the time of chlorination was extended to 4 hours.

Alkaline Extraction

Cellulose samples (bleached with chlorine-containing agents) were treated with aqueous NaOH solution at 3% consistency. The pH was adjusted to 11.5. The reaction was carried out at 70 °C for 1 hour. After filtration, the samples were washed thoroughly with deionized water and the spent alkaline extraction liquor was retained for AOX tests.

Chlorine Dioxide Bleaching

4.0 g purified cotton at 5% consistency was bleached with 1% ClO_2 on cotton. The reaction was carried out at 70 °C for 3 hours. The pH before and after bleaching was, respectively, 3.6 and 3.4. After bleaching, the cellulose samples were filtered and removed for further washing. One fraction of the spent bleaching liquor was titrated for residual chlorine dioxide, while the rest was treated with sodium thiosulphate and stored in a refrigerator for AOX tests.

Hypochlorite Bleaching

4.0 g purified cotton at 5% consistency was treated with hypochlorite, 1% as available chlorine on cotton, and NaOH, 0.3% on cotton, at 50 °C for 1 hour. The final pH was 10.6. the bleached cotton was then filtered and water-washed. One fraction of the spent bleaching liquor was titrated for residual chlorine, while the rest was adjusted to pH 3, treated with sodium thiosulphate and stored in a refrigerator for AOX tests.

Organic Solvent Extraction

Cellulose samples were extracted with 1:1 ethanol/toluene in a Soxhlet extractor for 8 hours.

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Organochlorine in a T-shirt

A used T-shirt, made of 100% cotton, was donated by Dr. D. A. I. Goring. It had been domestically bleached many times over many years. A sample of the shirt was cut into small pieces, washed with deionized water and Soxhlet-extracted with 1:1 ethanol/toluene for 8 hours. The chlorine content was then measured by neutron activation analysis.

Household Bleaching of Cloth Diapers

New cloth baby diapers (Brand A and Brand B) were purchased. The diapers, made of 100% white cotton, were bleached twice in a commercial washing machine, using a household bleach (containing 6% sodium hypochlorite) without addition of detergent. 250 mL of the bleach was applied in the first bleaching, and 200 mL was used in the second bleaching. The bleach was diluted by the large volume of water in the washing machine. After bleaching, sample pieces of the diapers were washed thoroughly with deionized water. The chlorine content in diapers was measured by neutron activation analysis.

Neutron Activation Analysis of Chlorine

Cellulose samples were weighed precisely in small polyethylene vials. They were then irradiated in a Slowpoke reactor for 5 minutes at 10 kW, with 2 minute delay before counting for 5 minutes. This method is used routinely in our laboratory[1].

AOX Measurement

Spent bleaching liquors were properly diluted and acidified to pH 2 with nitric acid before analysis. The adsorbable

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organic halogen (AOX) tests were made on a Mitsubishi TOX-10 analyzer, as described by Odendahl et al.[8].

RESULTS & DISCUSSION

Table 1 shows the organochlorine formed during chlorine bleaching of cellulose. The background chlorine concentration in unbleached samples is 7-17 μg Cl/g substrate. As a result of chlorine bleaching, organochlorine is formed in the cellulose substrate and is found in the spent bleaching liquor. For example, the chlorinated kraft-cooked cotton contained 440 μg Cl/g substrate (organochlorine) in the fibres and 100 μg Cl/g substrate (AOX) is found in the spent bleaching liquor. It is interesting to note that chlorination of the alkali-purified cotton produces slightly more organochlorine than chlorination of the kraft-cooked cotton. It is possible that kraft cooking removes a fraction of the cotton which is susceptible to chlorination. However, "severe" kraft cooking, with a five-fold increase of effective alkali, produced a cellulose which gives much more organochlorine on bleaching. Bleaching for an extended time (4 hours) gives even higher organochlorine content in the aqueous phase. Treatment of other cellulose, such as the alkali-purified bacterial cellulose, also results in the formation of organochlorine.

Alkaline extraction removes and mineralizes substantial organochlorine from the chlorinated cellulose as shown in Table 2. After alkaline extraction, however, some organochlorine is still present in fibre as well as in the spent alkaline extraction liquor. For example, alkaline extraction of the chlorinated kraft-cooked cotton decreases organochlorine from 440 μg Cl/g substrate to 230 μg Cl/g substrate (180 of which is retained in the fibre while the rest, 50, is found as AOX in the aqueous phase.). The severely cooked cotton retains more organochlorine after alkaline extraction.

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TABLE 1
Chlorine Bleaching of Cellulose

Cellulose Samples	Chlorine in unbleached sample (µg Cl/g substrate)	Organochlorine in fibre after chlorine bleaching (µg Cl/g substrate)		AOX in spent bleaching liquor (µg Cl/g substrate)	Total organochlorine (µg Cl/g substrate)
		Not extracted by water	Not extracted by water and EtOH/toluene		
Purified Cotton	13	490 (480)*	150	110	600
Kraft-cooked Cotton	15	440(410)*	180	100 (110)*	540 (520)*
Severely Kraft-cooked Cotton	7	710	350	110	820
Severely Kraft-cooked Cotton for Extended Chlorine Bleaching	7	690	-	500	1190
Purified Bacterial Cellulose	17	540	320	260	800

( )*, data from a duplicate experiment.
(-), not tested.

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TABLE 2
Alkaline Extraction of Chlorinated Cellulose

Chlorinated Cellulose	Chlorine before alkaline extraction (μg Cl/g substrate)	Organochlorine in fibre after alkaline extraction (μg Cl/g substrate)		AOX in spent alkaline liquor (μg Cl/g substrate)
		Not extracted by water	Not extracted by water and EtOH/toluene	
Purified Cotton	490	120	-	-
Kraft-cooked Cotton	440	180	64	50
Severely kraft-cooked Cotton	710	270	-	-

(-), not tested.

For the alkali-extracted fibres, the organochlorine which remains after further extraction with organic solvents is considered "inextractable". Therefore for the kraft-cooked cellulose, 64 µg Cl/g substrate is inextractable organochlorine. This is about one third of the inextractable organochlorine found in the fully-bleached kraft pulp.

Formation of organochlorine also resulted from chlorination of modified cellulose materials as shown in Table 3. Except for the commercial oxycellulose, organochlorine of all these chlorinated fibres lies in the range of 400-550 µg Cl/g substrate, which is very similar to the results of purified cotton, kraft cotton and bacterial cellulose (Table 1). The commercial oxycellulose is manufactured by selective oxidation of C_6 position of the cellulose anhydroglucose units through NO_2 treatment. Chlorine bleaching of this oxycellulose sample generates relatively high concentration of organochlorine, most of which (800 µg Cl/g substrate) is present in the aqueous phase and is detected as AOX.

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Modification of cellulose can occur at C_2, C_3 and C_6 positions of the anhydroglucose units as well as of the cellulose chain end groups. Periodate oxidation causes the rupture of the C_2-C_3 bond of the anhydroglucose ring[6]. Nitrogen dioxide oxidation of cellulose (i.e. commercial oxycellulose) introduces mainly carboxyl groups at the C_6 position as well as some carbonyl groups[7,9]. The cotton fibres oxidized with hydrogen peroxide in alkaline conditions are characterized by high ketone content (predominantly at the C_3 position) and very low aldehyde and carboxyl contents[10]. The ketone and aldehyde groups on cellulose can be reduced to alcohol groups by sodium borohydride. Mercerization of cotton is carried out to convert the native cellulose I into cellulose II, and also to remove any non-cellulosic polysaccharide from the cotton. As for the hydrocellulose, it is prepared by very mild acid hydrolysis which

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TABLE 3
Chlorine Bleaching of Modified Cellulose

Cellulose Samples	Chlorine in unbleached sample (μg Cl/g substrate)	Organochlorine in fibre after chlorine bleaching (μg Cl/g substrate)		AOX in spent bleaching liquor (μg Cl/g substrate)	Total organochlorine (μg Cl/g substrate)
		Not extracted by water	Not extracted by water and EtOH/toluene		
Periodate Cotton	12	420	210	160	580
Mercerized Cotton	-	400	160	120	520
H_2O_2 Treated Cotton	-	420	87	73	490
$NaBH_4$ Treated Cotton	-	550	-	88	640
H_2O_2 and $NaBH_4$ Treated Cotton	-	420	83	55	480
(NO_2-treated) Oxycellulose	14	320	160	800	1120
Hydrocellulose	-	490	-	70	560

(-), not tested.

generates new reducing ends without affecting the chemical structure of cellulose anhydroglucose units. It is interesting to notice that except for NO_2-oxidized cellulose, chlorine bleaching of all these modified cellulose materials produces organochlorine contents which are not very different from that of the chlorination of cotton or kraft-cooked cotton cellulose. The C_6 carboxyl groups in NO_2-oxidized cellulose might promote β-alkoxyl elimination or decompositions[11,12,13] which, we believe, may generate unsaturated carbon-carbon bonds and increase organochlorine found as low molecular weight compounds in the aqueous phase.

For all of these chlorinated modified cellulose materials, alkaline extraction removes a large portion of the organochlorine in the cellulose substrate as shown in Table 4. In the case of mercerized cotton, further extraction with organic solvents leaves an inextractable organochlorine content of 71 μg Cl/g cotton which is quite similar to that of the kraft-cooked cotton. The inextractable organochlorine content in hydrogen peroxide treated samples is however somewhat lower.

Chlorination of fully-bleached wood cellulose provides valuable information on the occurrence of organochlorine as is shown in Table 5. The commercial microcrystalline cellulose, which is manufactured by controlled acid hydrolysis of bleached wood pulp to its levelling-off degree of polymerization, contains 56 μg Cl/g substrate as inextractable organochlorine. Chlorination of the microcrystalline cellulose results in only a small increase in organochlorine. But new organochlorine (94 μg Cl/g substrate) is indeed formed. The low increase of organochlorine is most certainly due to the inaccessibility of the crystalline cellulose.

Cooking microcrystalline cellulose under severe conditions causes extensive changes in its chemical structure. Chlorination

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TABLE 4
Alkaline Extraction of Chlorinated Modified Cellulose

Chlorinated Cellulose	Chlorine before alkaline extraction (µg Cl/g substrate)	Organochlorine in fibre after alkaline extraction (µg Cl/g substrate)	
		Not extracted by water	Not extracted by water and EtOH/toluene
Periodate Cotton	420	180	-
Mercerized Cotton	400	130	71
H_2O_2 Treated Cotton	420	220	34
$NaBH_4$Treated Cotton	550	190	-
H_2O_2 and $NaBH_4$ Treated Cotton	420	190	35
(NO_2-treated) Oxycellulose	320	140	-
Hydrocellulose	490	250	-

(-), not tested.

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TABLE 5
Chlorine Bleaching of Wood Cellulose

Cellulose Samples	Organochlorine before chlorination (μg Cl/g substrate)	Organochlorine in chlorine bleached cellulose (μg Cl/g substrate)			AOX in spent bleaching liquor (μg Cl/g substrate)	Total organochlorine (μg Cl/g substrate)
		Not extracted by water	Not extracted by water and EtOH/toluene	Not extracted by alkali		
Microcrystalline Cellulose from Bleached Wood Pulp	56	75	69	-	76	150
Severely Kraft-cooked Microcrystalline Cellulose:						
Solid Residue	-	180	-	-	140	320
Precipitate	-	510	-	-	320	830
Extractive-free Alpha Cellulose from Bleached Wood Pulp	55	200	150	60	61	260

(-), not tested.

of the cooked microcrystalline cellulose generates a relatively high concentration of organochlorine. For instance as seen in Table 5, chlorination of the precipitate from severely cooked microcrystalline cellulose produces as much organochlorine as from the bleaching of severely cooked cotton (see Table 1).

The alpha cellulose produced from bleached wood pulp has 55 μg Cl/g substrate of inextractable organochlorine. It is prepared from a fully-bleached softwood kraft pulp (with 180 μg Cl/g substrate as inextractable organochlorine) by extraction with organic solvents and 18% NaOH solution. Chlorination of this alpha cellulose generates organochlorine in the fibres as well as in the spent bleaching liquor. This is clear evidence that organochlorine is formed by chlorination of highly purified wood cellulose. It is not yet understood, however, why the organochlorine produced is only about one half of that from the chlorination of cotton.

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Unmodified simple sugars also yield some organochlorine upon chlorination. The data in Table 6 indicate that chlorine reacts directly with simple sugars, modifies the carbohydrate structure, and generates some organochlorine. Chlorination of kraft-cooked glucose produces much more organochlorine than even from the severely cooked cellulose (see Table 6).

Bleaching of purified cotton cellulose with chlorine dioxide produces a small but measurable amount of organochlorine (Table 7). After alkaline treatment and solvent extraction, the organochlorine in cellulose is decreased to 17 ppm. Hypochlorite bleaching generates a little more organochlorine than chlorine dioxide bleaching (Table 8). Household hypochlorite bleaching of cotton fabrics such as a T-shirt (Table 9) and cloth baby diapers (Table 10) also generates organochlorine.

TABLE 6
Chlorine Bleaching of Simple Sugars

Samples	AOX in unbleached sugars (μg Cl/g substrate)	AOX in spent bleaching liquor (μg Cl/g substrate)
Cellobiose	ND	43
Maltose	ND	72
Trehalose	ND	34
Glucose	ND	17
Mannose	ND	52
Xylose	ND	41
Galactose	ND	26
Arabinose	ND	83
β-D-methyl Glucoside	ND	23
Kraft-cooked Glucose Precipitate	ND	6150

(ND), not detectable at a detection limit of 2.5 μg Cl/g substrate.

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Possible Mechanisms of Organochlorine Formation

Our conclusion that organochlorine is formed from carbohydrate during pulp bleaching is based on experimental results backed by supporting information in the literature. Pulping and bleaching cause changes in the chemical structure of cellulose and hemicelluloses. In particular, some unsaturated carbon-carbon bonds may be formed in cellulose during cooking, and these unsaturated bonds would be easily chlorinated.

Low molecular weight unsaturated compounds such as cyclic enols and phenolic compounds have been found in the

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TABLE 7
Chlorine Dioxide Bleaching of Cotton Cellulose

Sample	Organochlorine in fibre after bleaching (µg Cl/g substrate)			AOX in spent bleaching liquor (µg Cl/g substrate)	Total organochlorine (µg Cl/g substrate)
	Not extracted by water	Not extracted by alkali	Not extracted by alkali and EtOH/toluene		
Purified Cotton	68	39	17	27	95

TABLE 8
Hypochlorite Bleaching of Cotton Cellulose

Sample	Organochlorine in fibre after bleaching (µg Cl/g substrate)			AOX in spent bleaching liquor (µg Cl/g substrate)	Total organochlorine (µg Cl/g substrate)
	Not extracted by water	Not extracted by alkali	Not extracted by alkali and EtOH/toluene		
Purified Cotton	140	43	28	55	200

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TABLE 9
Chlorine Content in Household-bleached T-shirt
(μg Cl/g sample)

Sample	Cl in Original Sample	Cl in shirt after extraction with water and organic solvents
Used T-shirt	990	350

TABLE 10
Chlorine Content in Household-bleached Cloth Diapers
(μg Cl/g sample)

Samples	Cl in water-washed samples before bleaching	Cl in diapers	
		After first bleaching and water-washing	After second bleaching and water-washing
Diaper A	86	120	130
Diaper B	17	82	97

aqueous phase after alkaline treatment of cellulose and simple sugars[14,15]. It is also well established that keto-enols or even α,β conjugated carbonyl groups are formed during alkaline cooking of cellulosic materials[16]. These groups generally go through further reactions or rearrangements unless they are stabilized. For instance, if the C_2 hydroxyl is methylated, the keto-enol can actually be isolated in good yield[17]. Recently, it was proposed[18] that during kraft cooking the peeling reaction could be terminated by the presence of lignin fragments attached to the sugars (i.e. through lignin-carbohydrate complexes). The origin of kraft color has been attributed to these stabilized keto-enols[18]. In an early study, some researchers[19] suggested that during the peeling reaction of polysaccharides and cellulose many of the degradation products might give rise to color and yet not have been completely solubilized. These authors further suggested that much of the color in a kraft chlorination effluent was of carbohydrate origin. It was suggested in other studies[20] that the yellowing chromophores of alkali-treated cellulose may be keto-enol structures.

Nevertheless, little is known about the chemical changes in the cellulose macromolecule. Some oxidation is inevitable during the chemical processing of cellulosics. Carbonyl groups in oxidized cellulose may occur at the C_2, C_3 and C_6 positions of the anhydroglucose unit. These carbonyls might promote β-alkoxyl or β-hydroxyl elimination which would result in unsaturated bonds. For instance, the C_6 carboxyl groups or the C_6 aldehydic groups in oxidized cellulose can produce unsaturated carbon-carbon bonds at C_4-C_5 positions through β-elimination[12,13]. These oxidized celluloses may also go through further decomposition and form other types of carbon-carbon unsaturated compounds[12]. In our work , this is verified by the increased organochlorine formation from the chlorination of oxycellulose (Table 3).

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Thermal degradation of cellulose is a very important mechanism to be considered. Thompson and Kaustinen[21] studied cellulose and hemicellulose thermal degradation during pulping. At much higher temperatures, cellulose dehydration reactions, which result in the formation of unsaturated carbon-carbon bonds, have been reported[22]. In our experiment on the chlorination of precipitate from severe cooking of microcrystalline cellulose, the increased organochlorine formation may come from chlorine reaction with the unsaturated carbon-carbon bonds produced by dehydration (Table 5).

Caramelization of lower sugars or cellulose degradation products can occur under normal pulping conditions. However, the involatile high molecular weight fraction of the caramel is poorly understood. According to a recent review paper[23], heterocyclic and heteroaromatic carbons were reported to be present in the caramel. The aromatic character of the high molecular weight fraction was attributed to the furan derivatives. Aldol condensations were also considered to be involved in the formation of caramel. In a study of caramelization under alkaline conditions, some researchers suggested that cyclic polyenes containing carbonyl groups are formed by extensive dehydration of sugars[23]. Formation of aromatic compounds from carbohydrates, by both acidic[11,24] and alkaline[14] dehydration, has been known in wood chemistry for a long time. Recently, the polymeric substance formed during kraft-cooking of glucose has been characterized by ^{13}C NMR and aromatic structures have been confirmed[18].

Chlorine bleaching of the modified cellulose materials mentioned above will generate organochlorine through reaction with the unsaturated bonds.

For unmodified carbohydrates, chlorine reacts mainly as an oxidant. It is generally believed the reactions occur through

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radical mechanisms[25]. However, an ionic mechanism has also been proposed[26]. Fredricks et al. conclude that both mechanisms occur during chlorine oxidation of cellulose[27]. Most of the chlorine reaction products have aldonic acid type of end groups, but other types of carboxylic acids (e.g. uronic acids) are also formed[28,29]. It has been suggested that direct chlorine substitution of the C_1 hydrogen[25] or the formation of glycosyl chloride[26] occurs during cellulose or glycoside chlorination. These intermediate products, however, go through dehydrohalogenation[25,26] and so do not contribute to the formation of organochlorine. Stable deoxychloro carbohydrates[30,31,32] or chlorodeoxycellulose[12,33] have been synthesized but the mechanisms or pathways (such as nucleophilic substitution) are quite different from those feasible in the bleaching of pulp with chlorine.

Our experiment on simple sugars (Table 6) suggests that chlorine bleaching itself can modify the carbohydrate structure and introduce chlorine into carbohydrate molecules. As is seen from Table 6, however, this is not likely to occur to any significant extent in comparison with the chlorination of purified cellulosic materials. Therefore, it is proposed that, during kraft pulp chlorination, the major sources of organochlorine formation from carbohydrates are unsaturated carbon-carbon bonds generated during pulping.

SUMMARY

Treatment of cellulose samples with chlorine generates organochlorine in the cellulose substrate as well as in the spent bleaching liquor. Alkaline extraction removes substantial part of the organochlorine from the treated cellulose by hydrolysis to chloride and by dissolution. Nevertheless, some of the organochlorine can survive further extraction with water and

organic solvents and is therefore considered "inextractable". This suggests that carbohydrate-originated organochlorine may account for part of the inextractable organochlorine in the fully-bleached chemical pulp. Chlorination of "severely" cooked cellulose and NO_2-treated cellulose samples produces higher levels of organochlorine. Another interesting result with practical implications is that chlorine dioxide and hypochlorite produce very little organochlorine attached to carbohydrate under the conditions normally practiced in the pulp and paper industry. Organochlorine has also been found in cotton goods bleached with household hypochlorite bleach.

The exact mechanism of chlorine reaction with carbohydrates is not yet known. The organochlorine produced however is most likely the result of addition to the unsaturated carbon-carbon bonds generated during cooking.

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