Aldehyde Content of Dialdehyde Cellulose Determined *via* Nitrate Analysis

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Dialdehyde cellulose was synthesized *via* the heterogeneous periodate oxidation of microcrystalline cellulose in an aqueous solution. The aldehyde content of the dialdehyde cellulose was determined *via* nitrate analysis based on a two-step sequential approach. The approach first employed hydroxylamine to react with the aldehyde groups and to produce oxime groups *via* Schiff's replacement reaction. Then, the oxime groups were oxidized *via* persulfate to produce nitrate. The nitrate concentration was analyzed *via* two highly sensitive methods, *i.e.*, ion chromatography and ultraviolet light absorption. The aldehyde content was approximately one-fifth of the theoretical value. The resulting aldehyde groups were found primarily distributed over the surface layers. A solubility parameter calculation suggested that the increase of the aldehyde groups caused the detachment and dissolution of the dialdehyde cellulose chains and consequently led to the determination of a relatively low aldehyde content.

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INTRODUCTION

Cellulose is the most abundant natural polymer, consisting of anhydroglucose repeating units with one vicinal di-ol functional group per unit. The di-ol group can be selectively oxidized *via* periodate to produce two separated aldehyde groups (Atalla and Isogai 2010; Heinze *et al.* 2018; Rol *et al.* 2019; Nypelö *et al.* 2021). This product is commonly called dialdehyde cellulose. The aldehyde groups are chemically active and can be transformed into various kinds of functional groups *via* replacement, oxidation, and crossing-linking reactions (Kim *et al.* 2000; Atalla and Isogai 2010; Rol *et al.* 2019). A variety of specialized cellulose materials so far have been synthesized from dialdehyde cellulose (Zhang *et al.* 2018; Keshk *et al.* 2019; Wang *et al.* 2021). Thus, the determination of the aldehyde content is crucial and has been the subject of numerous investigations and reviews (Maekawa and Koshijima 1991; Kim and Kuga 2001; Vicini *et al.* 2004; Heinze *et al.* 2018; Lucia *et al.* 2019; Yu *et al.* 2019; Nypelö *et al.* 2021). The aim of this study was to employ a two-step sequential approach to determine the aldehyde content. The approach first used hydroxylamine hydrochloride to transform the aldehyde groups into oxime groups *via* the Schiff replacement reaction (Shriner *et al*. 1980), as shown in Eq. 1,

$$\text{Dialdehyde cellulose} + NH_2OH{\cdot}HCl \rightarrow \text{di-oxime cellulose} + HCl + H_2O \qquad (1)$$

Then, the oxime groups in di-oxime cellulose were oxidized *via* excess persulfate to become free nitrate (Imanzadeh *et al.* 2006; Yu and Wu 2015), as shown in Eq. 2,

$$\text{Di-oxime cellulose} + S_2O_8^{2-} \rightarrow \text{di-carboxylic-acid cellulose} + 2\ NO_3^- + 2\ SO_4^{2-} \quad (2)$$

The aldehyde content thus equaled the amount of free nitrate. To verify that nitrate was the nitrogen end-product, this study used acetaloxime and dimethylglyoxime as the oxime-group model compounds for persulfate oxidation. The nitrate concentration was analyzed by using two highly sensitive methods, *i.e.*, ion chromatography and ultraviolet absorption (Eaton *et al.* 2005; Skoog *et al.* 2007).

Several recent studies reported the chain detachment and dissolution phenomena of dialdehyde cellulose in an aqueous solution (Kim *et al.* 2000, 2004; Chen and van de Ven 2016; Munster *et al.* 2017; Yan *et al.* 2019; Yang and Choi 2020). If the dialdehyde cellulose chains containing a higher amount of aldehyde groups can detach from the solid surface and are dissolved in the aqueous phase, then the aldehyde content of the dialdehyde cellulose may decrease during periodate oxidation and likely have a large spread. To investigate the detachment issue, this study performed a solubility parameter calculation (Hansen and Beerbower 1971; Matsuura 1993; van Krevelen and te Nijenhuis 2009) to reveal the effect of aldehyde groups on the aqueous solubility of dialdehyde cellulose. Moreover, to reduce the spread of the aldehyde content, an air flotation treatment was used to remove the dissolved dialdehyde cellulose chains.

EXPERIMENTAL

Chemicals and Materials

Microcrystalline cellulose powder (Avocado Research Chemicals, London, United Kingdom) was used as received. All chemicals are analytical grade and were purchased from Panreac, Sigama-Aldrich, Merck, ARCOS, WS Simpson, and Wakopure Chemicals. Deionized water (Roda Ultrapur Water, Taiwan) was employed for all aqueous solution preparations.

Synthesis of Dialdehyde Cellulose

Microcrystalline cellulose powder was mixed with 75 mL of a 0.1215 M sodium metaperiodate aqueous solution. The mixture stood at room temperature in the dark for 24 or 48 h. The solid and the aqueous phases were separated *via* vacuum filtration with a Gelman glass fiber filter. The dialdehyde cellulose was washed thoroughly with de-ionized water and was separated *via* vacuum filtration several times.

Four dialdehyde cellulose samples were treated *via* the air flotation treatment (Wang *et al.* 2010) to remove the fine and dissolved dialdehyde celluloses. The air flotation treatment was carried out as follows: the dialdehyde cellulose was mixed with approximately 100 mL of de-ionized water in a vessel. Then, air was discharged into the solution for several seconds. After the air discharge, the aqueous solution became extremely turbid. This caused the fine and smaller dialdehyde cellulose particles to have a much slower settling (terminal) velocity. Upon the larger dialdehyde cellulose settling down to the bottom of the vessel, approximately 10 s after the air discharge, the upper part of the aqueous solution, including the fine and dissolved dialdehyde celluloses, was removed at a rate of 1 mL/s. The above process was repeatedly performed several times. For the purpose of comparison, the air flotation treatment was not applied to an additional four dialdehyde cellulose samples. The size of the dialdehyde cellulose was measured using four particle sieves with mesh numbers of 100 (149 μm), 200 (74 μm), 325 (44 μm), and

400 (37 μm).

Conversion to Di-oxime Cellulose

Dialdehyde cellulose was mixed with 50 mL of 0.086 M hydroxylamine hydrochloride in a di-hydrogen phosphate buffer with a pH value of 6.6 (TOA HM-30, Tokyo, Japan). The mixture stood at room temperature in the dark for 24 or 48 h. The product (di-oxime cellulose) was washed thoroughly with de-ionized water and was separated *via* vacuum filtration. The air flotation treatment then was applied to the four dialdehyde cellulose samples. Then, the di-oxime cellulose was vacuum dried at room temperature. During the vacuum drying process, the slightly moist di-oxime cellulose was ground with a pestle.

Oxidation of Acetaloxime and Dimethylglyoxime

Acetaloxime (0.38 g) or dimethylglyoxime (0.24 g) was dissolved in 250 mL of an aqueous solution containing 0.13 M of potassium persulfate and either sulfuric acid (0.25 M) or sodium hydroxide (0.5 M) in an amber glass vessel. Due to the volatility of the two compounds, the amber glass vessel was tightly sealed for the oxidation reaction. The solution then was heated to a temperature of 70 °C for 10 h for acetaloxime and 60 h for dimethylglyoxime. Then, a few mL of the solution were diluted with de-ionized water and the pH value of the diluted sample was adjusted to approximately 9. The anionic concentrations of the diluted sample were measured *via* an ion chromatography system (TOA IA300, Tokyo, Japan).

Oxidation of Di-oxime Cellulose

Di-oxime cellulose (0.60 g) was mixed with 100 mL of an acidic aqueous solution containing 2.0 g of potassium persulfate and 1.0 mL of 2.5 M sulfuric acid. The solution was heated to a temperature of approximately 65 °C for at least 6 h, and no gas bubbles were observed. The solution, including the remaining solids, was designated as solution (I). After cooling, the nitrate concentration of solution (I) was analyzed using the ion chromatography system.

Solution (I) then was adjusted to alkaline conditions by adding 2.5 g of sodium hydroxide to improve the solubility of the di-oxime cellulose in the aqueous phase. Subsequently, 2.0 g of potassium persulfate was added to the alkaline solution. The solution was heated to a temperature of approximately 65 °C for at least 50 h, and no gas bubbles were observed. The resulting alkaline solution was designated as solution (II). After cooling, the nitrate concentration of solution (II) was analyzed using the ion chromatography system and an ultraviolet-visible spectrometer (Labomate Spectro PC-8, Los Angeles, CA).

The above acidic and alkaline persulfate oxidation procedures were applied to the di-oxime cellulose samples without the air flotation treatment. The resulting alkaline solution was designated as solution (III). The nitrate concentration of solution (III) was analyzed by using the ion chromatography system and the ultraviolet-visible spectrometer.

Anionic Analysis *via* Ion Chromatography

The ion chromatography system, containing an anion-exchange column (TOA PCI-205, Tokyo, Japan), a conductivity detector, and a chemical suppressor (SPR-AN), was used to measure the anionic concentrations, including nitrate and nitrite. The chemical suppressor uses a high-exchange capacity cation-exchange membrane (fiber-type), which was regenerated with diluted sulfuric acid. The mobile phase was a carbonate and bicarbonate buffer. The flow rate was in the range from 1.0 mL/min to 1.2 mL/min. The coefficient of variation is typically 2 % for the standard anionic solution.

A few mL of the upper part of solution (I), solution (II), and solution (III) were taken and properly diluted with de-ionized water. The pH value of the diluted samples then was adjusted to approximately 9 before the ion chromatographic analysis. The dilution factor was in a range of 20 to 34.

Nitrate Analysis *via* Ultraviolet Absorption

Nitrate strongly absorbs 220 nm ultraviolet radiation (Eaton *et al.* 2005). The absorbance complies with the Beer-Lambert law (Skoog *et al.* 2007). Before performing the absorption measurement, a few mL of the upper part of solution (II) and solution (III) were properly diluted and acidified with a 0.1 M hydrochloride solution. The dilution factor was in a range of 31 to 125. The coefficient of variation for ultraviolet absorption is 1.7 % for the standard nitrate solutions.

Substantial amounts of organic acids and the suspended cellulose were produced during the persulfate oxidation of di-oxime cellulose. These organic acids and suspended cellulose might interfere with the 220 nm absorbance. The 220 nm absorbance, due to the organic acids, was estimated to be two times that of the 275 nm absorbance (Eaton *et al*. 2005). In addition, the suspended cellulose could cause light scattering. As such, this study measured the light scattering interference by using a nephelometer (Hach 2100N, Loveland, CO) (Eaton *et al*. 2005).

The flow chart of Fig. 1 illustrates the present experimental approach leading to Solutions (I), (II), and (III) as well as the aldehyde content.

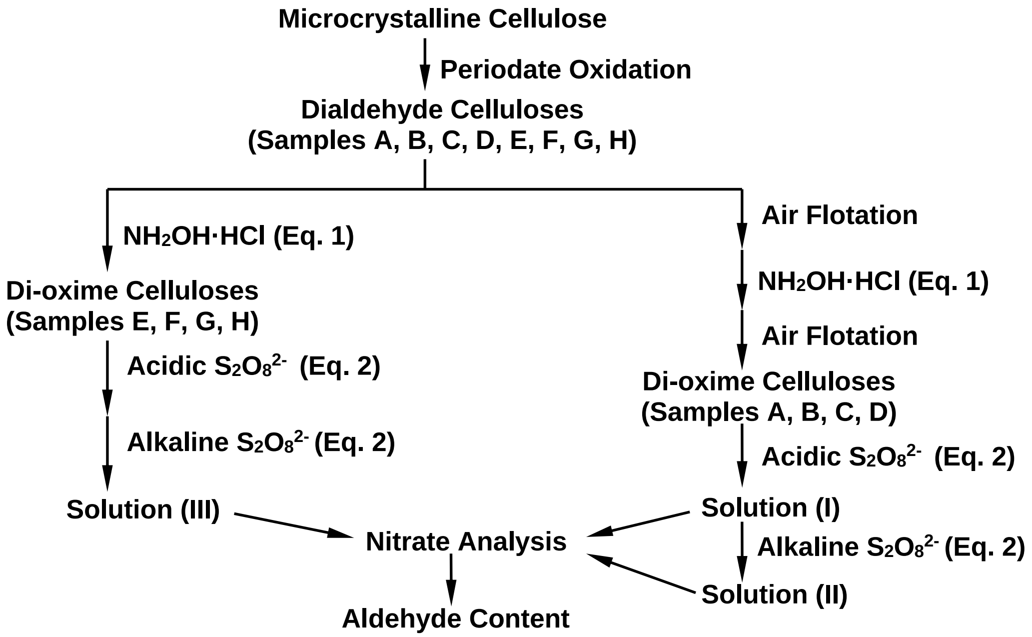

Fig. 1. Flow chart summarizing the present experimental approach

RESULTS AND DISCUSSION

Synthesis of Dialdehyde Cellulose and Di-oxime Cellulose

Table 1 lists the reaction conditions of periodate oxidation and the Schiff replacement and the resulting amount of the di-oxime celluloses. Among the eight samples, samples A, B, C, and D were treated *via* the air flotation process. The particle size of the dialdehyde cellulose retained in the samples that underwent the air flotation treatment was found to be larger than 37 μm and was mostly distributed in the range of 44 to 149 μm.

Table 1. Reaction Conditions for the Synthesis of Di-oxime Cellulose

Di-oxime Cellulose Sample	Microcrystalline Cellulose Amount (g)	Periodate Reaction Time (h)	Hydroxylamine Reaction Time (h)	Di-oxime Cellulose Amount (g)
A *	4.0	24	24	3.46
B *	4.0	24	48	3.08
C *	4.0	48	24	3.16
D *	2.0	48	48	1.41
E	4.0	48	24	3.20
F	4.0	48	48	2.30
G	4.0	48	24	2.78
H	2.0	48	24	1.38

* The air flotation treatment was applied to the sample

Oxidation of Acetaloxime and Dimethylglyoxime

Figure 2 shows the ion chromatograms of the solutions from the persulfate oxidation of acetaloxime and dimethylglyoxime. Nitrate and nitrite were identified as the only two nitrogen products. Table 2 lists the nitrogen product distribution derived from the ion chromatograms. The resulting nitrogen product distribution substantiated that nitrate was the primary end-product from the persulfate oxidation of oxime groups.

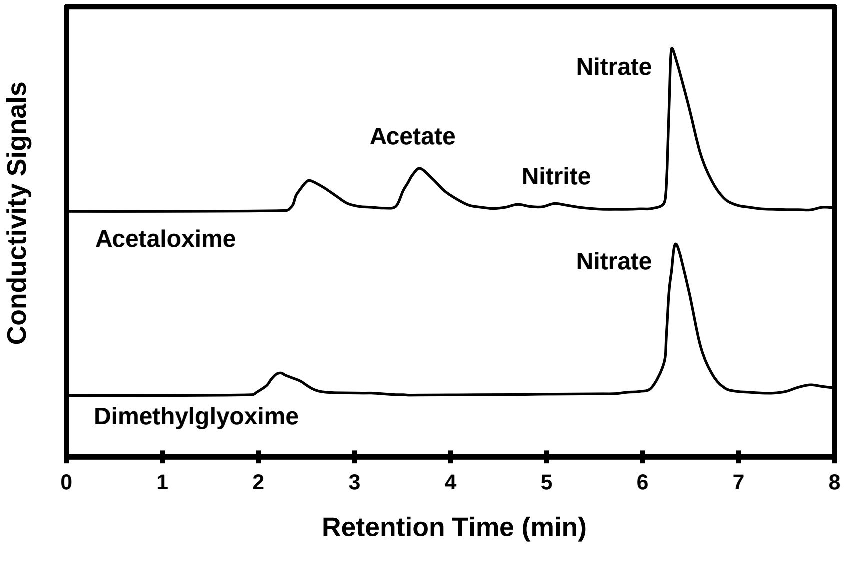

Fig. 2. Ion chromatograms of the solutions from the persulfate oxidations of acetaloxime (upper) and dimethylglyoxime (lower)

Table 2. Nitrogen Product Distribution from the Persulfate Oxidation of Acetaloxime and Dimethylglyoxime

Initial Reaction Conditions	Nitrogen Product Distribution			
	Nitrate		Nitrite	
	Amount (mmol)	Yield (%)	Amount (mmol)	Yield (%)
Acetaloxime[a]				
H_2SO_4 0.25 M	3.470	53.32	0.0955	1.47
NaOH 0.50 M	0.350	5.38	1.187	18.23
Water	0.745	11.44	0.416	0.64
Dimethylglyoxime[b]				
H_2SO_4 0.25 M	4.762	111.14	Non-detectable	-
NaOH 0.50 M	2.002	49.40	0.088	2.18
Water	3.791	94.78	Non-detectable	-
[a] Reaction condition: 70 °C, 10 h [b] Reaction condition: 70 °C, 60 h				

On the basis of Table 2 and literature (Imanzadeh *et al.* 2006; Yu and Wu 2015), the transformation of nitrogen-containing chemical species of persulfate oxidation of oxime compounds (RR'C=NOH) can be described as follows,

$$RR'C{=}NOH \rightarrow NH_2OH \rightarrow NO_2^- \rightarrow NO_3^- \tag{3}$$

where R and R' are alkyl groups or hydrogen.

Anionic Analysis of the Oxidation of Di-oxime Cellulose

Solution (I) from the acidic persulfate oxidation

The upper part of Fig. 3 is a typical ion chromatogram of solution (I). The nitrate peak was quite distinct; however, the nitrite concentration was at a non-detectable level. The blank experiment showed that the interference from the persulfate oxidation of dissolved nitrogen was negligible. Table 3 lists the aldehyde content of samples A, B, C and D derived from the nitrate amount. The resulting aldehyde contents of these four samples were similar, despite the fact that the reaction periods were different, *i.e.*, 24 h *vs.* 48 h.

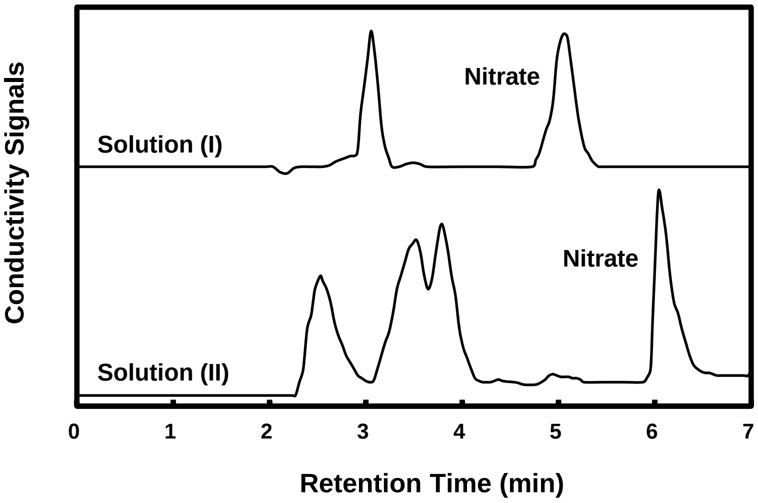

Fig. 3. Ion chromatograms of solution (I) and solution (II)

Table 3. Aldehyde Content Derived from Solution (I) and Solution (II)

Di-oxime Cellulose Sample	Amount (g)	Analytical Method *	Solution (I)		Solution (II)	
			Nitrate Amount (mmol)	Aldehyde Content (mmol/g)	Nitrate Amount (mmol)	Aldehyde Content (mmol/g)
A	0.60	IC	0.329	0.548	0.513	0.856
		UVA	-	-	0.647	1.078
B	0.60	IC	0.360	0.598	0.505	0.842
		UVA	-	-	0.595	0.992
C	0.60	IC	0.395	0.658	0.364	0.607
		UVA	-	-	0.749	1.248
D	0.60	IC	0.407	0.679	0.424	0.706
		UVA	-	-	0.506	0.844
Average	-					0.897

* IC: Ion Chromatography; and UVA: Ultraviolet Absorption

Solution (II) from the alkaline persulfate oxidation

Under the alkaline persulfate oxidation conditions, most of the remaining di-oxime cellulose solids in solution (II) were dissolved. The lower part of Fig. 3 is the ion chromatogram of solution (II). A few additional peaks appeared in comparison to the upper part of the chromatogram of solution (I). These peaks were very likely due to simple organic mono-carboxylic acids or carboxylates (such as formate and acetate) generated by alkaline degradation including the de-polymerization reaction. The resulting aldehyde content derived from the nitrate peak is listed in Table 3.

The aldehyde content determined *via* the ultraviolet absorption of solution (II) is also listed in Table 3. The turbidity measurement by the nephelometer confirmed that the light scattering interference from the suspended cellulose in terms of the ultraviolet absorption of nitrate was negligible. The interference due to the absorbance of sulfate was also found to be minute, *i.e.*, less than 10% of the total absorbance. The resulting aldehyde content determined *via* ultraviolet absorption was in good agreement with the aldehyde content of the ion chromatography. The average of the aldehyde content of the two analytical methods was 0.897 mmol/g.

Comparison of the aldehyde content derived from the three solutions

Figure 4 compares the aldehyde content derived from solution (I) and solution (II) for samples A, B, C, and D. For each sample, the aldehyde content derived from the two solutions were numerically comparable and approximately one-fifth of the theoretical value. Hence, most oxime groups had already been oxidized to become free nitrate under the acidic persulfate oxidation conditions. In contrast, the alkaline persulfate oxidation merely gained a limited amount of nitrate, although it did dissolve most of the remaining di-oxime cellulose (Isogai and Atalla 1998; Budtova and Navard 2016). Thus, the aldehyde groups were distributed over the surface layers.

The aldehyde contents of samples E, F, and GH derived from solution (III) are given in Table 4. The aldehyde content of the three samples was relatively scattered and at least twice as much as those of solution (I) and solution (II) for samples A, B, C, and D, as shown in Fig. 4. These notable differences indicated that the present air flotation treatment was capable of narrowing down the spread of the aldehyde content. Moreover, the fine and dissolved dialdehyde celluloses contained a considerable amount of aldehyde groups.

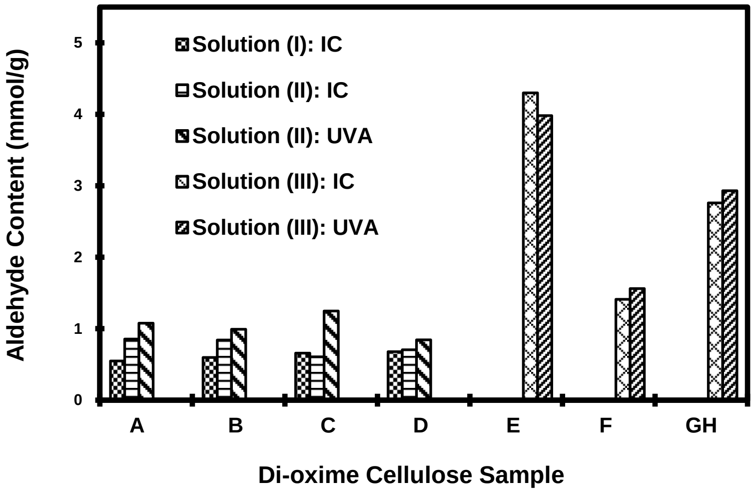

Fig. 4. Comparison of the aldehyde contents determined *via* ion chromatography (IC) and ultraviolet absorption (UVA) from solutions (I), (II), and (III)

Table 4. Aldehyde Content Derived from Solution (III)

Di-oxime Cellulose Sample	Amount (g)	Analytical Method *	Nitrate Amount (mmol)	Aldehyde Content (mmol/g)
E	0.30	IC	1.290	4.30
		UVA	1.195	3.98
F	0.30	IC	0.424	1.41
		UVA	0.469	1.56
GH *	0.25	IC	0.689	2.76
		UVA	0.731	2.93
* The sample GH was prepared by mixing equal amount of sample G and sample H				

Limit of quantitation for the aldehyde content

The lower limit of linearity of the nitrate from the present ion chromatography and ultraviolet absorption analyses was 0.05 mg/L and 0.15 mg/L, respectively. On the basis of the present analytical conditions, including the dilution factor and the sample amount, the limit of quantitation of the aldehyde content was estimated to be 3 μmol/g for ion chromatography and 8 μmol/g for ultraviolet absorption. Also, the microcrystalline cellulose raw materials must be free of lignin, in that the aromatic ring of lignin strongly absorbs ultraviolet radiation of the wavelength range from 200 to 280 nm.

Solubility Parameter calculation

Effect of the aldehyde content

It is widely believed that a low aldehyde content is primarily due to the highly ordered structure of microcrystalline cellulose *via* hindering the diffusion of periodate into the inner layers (Painter 1988). Thus, periodate oxidation can only occur on the cellulose surface during the initial period. However, as the reaction proceeds, the highly ordered structure should be gradually shattered by the formation of aldehyde groups. Afterwards, periodate can diffuse into the inner layers to generate more aldehyde groups. The aldehyde content thus should increase as the reaction proceeds. However, Table 3 showed that the aldehyde content remained consistently low for the two different reaction periods (24 h and 48 h). Therefore, besides the hindrance of the highly ordered structure, there exists an alternative mechanism causing the loss of aldehyde groups. This study performed a solubility parameter calculation, described next, suggesting that it was the chain detachment mechanism that was diminishing the measured aldehyde content.

Figure 5 depicts the influence of the aldehyde content on the solubility parameter of cellulose. The aldehyde and other functional group contributions for the solubility parameter calculations are listed in Table 5, which were adopted from literature (Hansen and Beerbower 1971; Matsuura 1993; van Krevelen and te Nijenhuis 2009). Figure 5 shows that the higher the aldehyde content, the lower the solubility parameter. The solubility parameters of both dialdehyde cellulose and water became closer; *i.e.*, dialdehyde cellulose was more hydrophilic than pure cellulose. Upon the aldehyde content reaching a critical amount, it was highly likely that the hydrophilic dialdehyde cellulose chains detached from the solid surface and were dissolved in the aqueous phase. This argument is substantiated by the good solubility of dialdehyde cellulose in water (Kim *et al.* 2000, 2004; Chen and van de Ven 2016; Munster *et al.* 2017; Yan *et al.* 2019; Yang and Choi 2020).

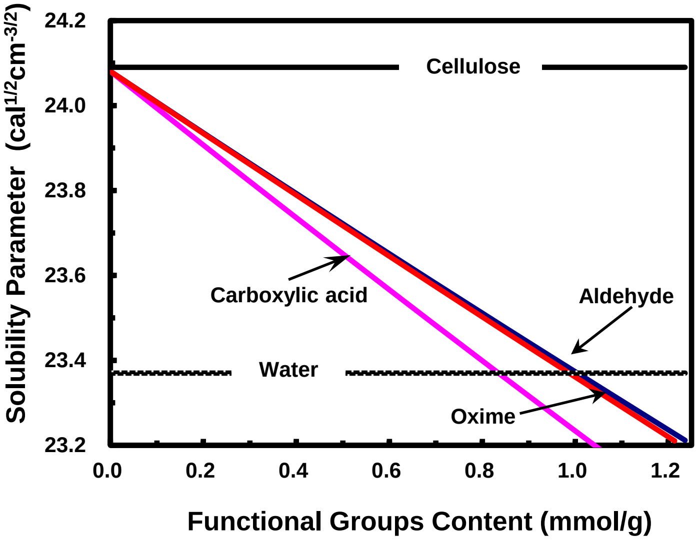

Fig. 5. The effects of the aldehyde, carboxylic acid, and oxime group contents on the solubility parameter of cellulose

Table 5. Functional Group Contributions for the Solubility Parameter calculation

<table>
<tr><td colspan="3">Structure of the Three Glucose Repeating Units:
$(CH_2)_4(CH)_{12}O_8(OH)_4(Z)_x(CH)_{8-x}(OH)_{8-x}$
Z represents the CHO, COOH, or CNOH groups
x is the number of CHO, COOH, or CNOH groups</td></tr>
<tr><td>Structural Groups</td><td>Cohesive Energy (cal/mol)</td><td>Molar Volume (cm^3/mol)</td></tr>
<tr><td>CHO</td><td>5100</td><td>22.3</td></tr>
<tr><td>COOH</td><td>6600</td><td>28.5</td></tr>
<tr><td>CNOH</td><td>6000</td><td>24.0</td></tr>
<tr><td>CH_2</td><td>1180</td><td>16.1</td></tr>
<tr><td>CH</td><td>820</td><td>-1.0</td></tr>
<tr><td>O</td><td>800</td><td>3.8</td></tr>
<tr><td>OH</td><td>7120</td><td>10.0</td></tr>
</table>

The other indication of the chain detachment is the size shrinking. Figure 6 shows the mass percentage of various sizes of dialdehyde cellulose determined by the particle sieves. As can be seen, the particle size shrank as the reaction proceeded. This observation was in agreement with the results of a recent study by Zhang *et al.* (2017) and confirmed the occurrence of the chain detachment.

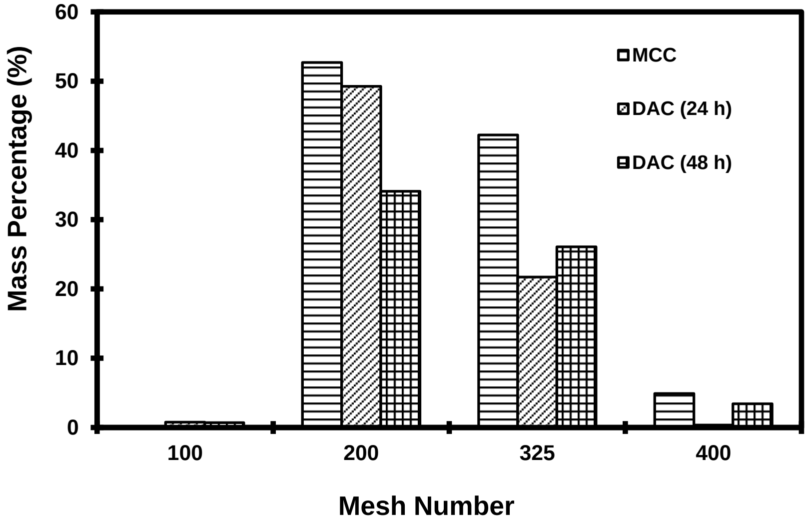

Fig. 6. The mass percentage of the size of the dialdehyde cellulose (DAC) and microcrystalline cellulose (MCC) determined by the particle sieves

After the chains detached from the solid, the inner layers became the new surface and the periodate oxidation produced aldehyde groups. Upon the aldehyde content reaching the critical amount, the chain detachment occurred again. As a result, aldehyde groups could only be distributed over the surface layers and the aldehyde content remained consistently low, as shown in Table 3. This study estimated the critical amount for the chain detachment to be 0.897 mmol/g, the average value of Table 3.

Effects of the oxime content and carboxylic acid content

Figure 5 also shows that di-carboxylic acid cellulose and di-oxime cellulose, similar to dialdehyde cellulose, are hydrophilic. For the present two-step sequential approach, using water as the solvent to perform persulfate oxidation and Schiff's replacement reaction was benefited by the hydrophilic property of di-oxime cellulose and dialdehyde cellulose.

Carboxylic acid groups can be produced *via* oxidizing aldehyde groups with iodate, dissolved oxygen, and hydroxyl radicals during periodate oxidation (Painter 1988). Although an increase in hydrophilic carboxylic acid groups can cause the chain detachment, Tables 3 and 4 show a fairly considerable amount of aldehyde groups still remaining un-oxidized. The rate of producing aldehyde groups was undoubtedly faster than the rate of producing carboxylic acid groups. Therefore, for the present periodate reaction conditions (Table 1), the occurrence of the chain detachment should be primarily due to the increase in aldehyde groups.

CONCLUSIONS

1. This study presented an analytical approach to determine the aldehyde content of dialdehyde cellulose. The approach was based on the nitrate analysis, as follows: First, the aldehyde groups were transformed into oxime groups with hydroxylamine. Then, the oxime groups were oxidized *via* persulfate to become free nitrate. The nitrate concentration was analyzed *via* ionic chromatography and ultraviolet absorption.
2. The resulting aldehyde content was only approximately one-fifth of the theoretical value, and the aldehyde groups were found primarily distributed over the surface layers. The spread of the aldehyde content can be reduced by the air flotation treatment *via* narrowing the particle size distribution.
3. Solubility parameter calculation suggested that the increase in hydrophilic aldehyde groups *via* periodate oxidation can cause the chain detachment from the surface layers. The chain detachment also decreased the particle size and caused the loss of aldehyde groups. The competition between the chain detachment and periodate oxidation resulted in the aldehyde content remaining consistently low. The critical amount for the dialdehyde cellulose chains detaching from the solid surface was estimated to be 0.897 mmol/g.

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