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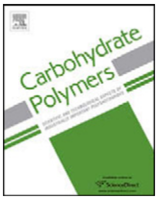

Periodate oxidation of cellulose at elevated temperatures using metal salts as cellulose activators

Juho Sirvio[a], Uula Hyvakko[a], Henrikki Liimatainen[b], Jouko Niinimaki[b], Osmo Hormi[a,*]

[a] *Department of Chemistry, P.O. Box 3000, FI-90014 University of Oulu, Oulu, Finland*
[b] *Fibre and Particle Engineering Laboratory, P.O. Box 4300, FI-90014 University of Oulu, Finland*

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ABSTRACT

The birch cellulose is effectively oxidized to the dialdehyde cellulose (DAC) at elevated temperatures by sodium periodate. Even though periodate decomposes at 55 °C and above with time, higher temperatures can be used if the oxidation time is sufficiently short and it has now been shown that temperatures up to 85 °C can be used during the oxidation. Lithium chloride can be used to further improve the oxidation efficiency. Other metal salts, such as calcium chloride can be used as well. These conditions provides possibility to use a lower amount of periodate to obtain high aldehyde contents in DAC.

1. Introduction

Cellulose is the most common organic compound on earth and an excellent source of renewable polymeric material. It is produced by plants and algae as a constituent of their primary cell walls. Wood typically consists of 40–50% of cellulose, while cotton contains even 90% of cellulose (Kamide, 2005). Some bacteria are also known to produce cellulose (Brown & Saxena, 2007).

Cellulose has long been used as the fiber source in the paper making industry. Some cellulose derivates such as a carboxymethylcellulose and a methylcellulose are also in commercial use (Pijper, 1946; Makashir, Mahajan, & Agrawal, 1994). Furthermore, there is also a growing interest to replace non-renewable polymeric materials obtained from petrochemical resources by naturally occurring polymers like cellulose (Goetz, Mathew, Oksman, Gatenholm, & Ragauskas, 2009). However, the production of cellulose derivates is often a cumbersome process because cellulose has low reactivity due to large amounts of hydrogen bonds which restrict its solubility in all common solvents (Swatloski, Spear, Holbrey, & Rogers, 2002). The derivatization of cellulose is traditionally done by heterogeneous syntheses, which may lead to uncontrollable reactions (Cao et al., 2007), the formation of unwanted byproducts (Heinze & Liebert, 2001) or in a cellulose decomposition (Possidonio, Fidale, & El Seoud, 2009). Heterogeneous reactions may also result in the formation of the desired products in poor yields (Abbott, Bell, Handa, & Stoddart, 2006).

Dialdehyde cellulose (DAC) is a cellulose derivate produced by a regioselective oxidation of cellulose using periodate as an oxidation agent. It is biodegradable and biocompatible and has a large potential to be used in many applications (Kim & Kuga, 2000; Ramirez et al., 2006). For example, aldehyde groups of DAC can be further oxidized to acids (Kim & Kuga, 2001) or reacted with an amine by the Schiff base reaction introducing an imine bond between the amine and cellulose (Wu & Kuga, 2006).

The periodate oxidation is traditionally done in water and due to the low reactivity of cellulose a great amount of periodate and long oxidation times have to be used to achieve high aldehyde contents (Calvini, Gorassini, Luciano, & Franceschi, 2006; Kim, Kuga, Wada, Okano, & Kondo, 2000). This reduces the effectiveness of the oxidation and leads to large amounts of iodine contain waste.

We have now investigated how to improve the periodate oxidation in aqueous conditions and found that the oxidation efficiency can be significantly enhanced by using elevated temperatures and metal salts as cellulose activators.

2. Experimental

2.1. Materials

The bleached birch (*Betula verrucosa*) chemical pulp and the dissolving pulp (softwood) were obtained as dry sheets and used as cellulose sources after disintegration in deionized water. The polysaccharide content was determined by using high performance

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* Corresponding author. Tel.: +358 8 553 1631; fax: +358 8 553 1593.
E-mail address: osmo.hormi@oulu.fi (O. Hormi).

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Table 1
The chemical composition of used cellulose materials.

Cellulose material	Polysaccharides			Lignin	Extractives
	Cellulose (%)	Xylan (%)	Glukomannan (%)	Total (%)	Acetone soluble (%)
Birch cellulose	74.8	23.6	1.1	0.4	0.08
Dissolving pulp	96.2	1.4	2.1	< 0.5	0.17

anion exchange chromatography (HPAEC-PAD), the lignin content by using (TAPPI-T 222 om-02) and the extractive content by using (SCAN-CM 49:03). Results are shown in Table 1. All chemicals, i.e. $NH_2OH{\cdot}HCl$, $NaIO_4$, LiCl, NaCl, $ZnCl_2$, $MgCl_2$, $CaCl_2$, glacial acetic acid and sodium acetate trihydrate used for oxidation and product analysis were obtained as p.a. grade chemicals from Sigma–Aldrich and used without further purification. An acetate buffer solution used in an oxime reaction was made by charging a 2.0 L volumetric flask with 27.4 g of sodium acetate trihydrate and adding 15 ml of a glacial acetic acid to the flask and diluting the resulting mixture to 2.0 L with deionized water. Deionized water was used throughout the work.

2.2. Preparation of the dialdehyde cellulose

2.2.1. Periodate oxidations of cellulose

12.5 g of cellulose suspension having consistency of 4% cellulose (0.5 g dry cellulose) was weighted to a 250 ml beaker or flask and 50 ml of deionized water and 0.41 g of $NaIO_4$ were added and a reaction vessel was covered with an aluminum foil to prevent the photo-induced decomposition of periodate. The reaction mixture was stirred with a magnetic stirrer in a water bath at the desired temperature. After the desired time, the product was filtered and washed several times with deionized water to remove iodine containing compounds. Products were dried in a freeze-dryer.

2.2.2. Metal chloride assisted oxidations of cellulose

Metal chloride assisted oxidations were performed in the same manner as the non-assisted periodate but adding desired amount of metal salt to the oxidation mixture.

2.3. Determination of the aldehyde content

The determination of aldehyde contents of DAC was based on oxime reaction between aldehyde group and $NH_2OH{\cdot}HCl$. The never-dried periodate oxidized cellulose (0.1 g abs.) was placed in a 250 ml beaker containing 1.39 g of $NH_2OH{\cdot}HCl$ dissolved in 100 ml of 0.1 M acetate buffer (pH = 4.5). The beaker was covered with a thin rubber foil and mixture was stirred 48 hour at room temperature with a magnetic stirrer. Product was filtrated and washed with 600 ml of deionized water after which it was dried in a freeze-dryer. Nitrogen content of the oxime derivate of DAC was determined by using a PerkinElmer CHNS/O 2400 Series II elemental analyzer. As illustrated in Scheme 1 as a reaction (2), one mol of aldehyde reacts with one mol of $NH_2OH{\cdot}HCl$ and the aldehyde content can be calculated directly from nitrogen content of the product.

3. Results and discussion

3.1. Periodate oxidation of the birch cellulose at elevated temperatures

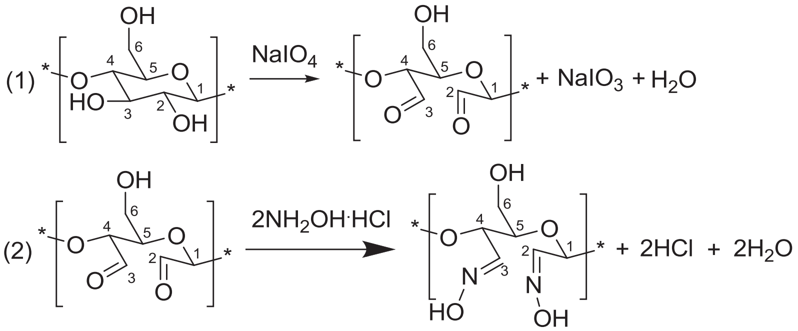
Periodate is a specific oxidant capable to oxidize the vicinal hydroxyl groups at carbon atoms 2 and 3 in an anhydroglucose unit (AGU) of cellulose to two aldehyde groups and simultaneously breaking the carbon–carbon bond between the carbon atoms 2 and 3. As illustrated in Scheme 1 as a reaction (1), one mol of iodate is liberated as waste when one AGU is oxidized to the corresponding dialdehyde derivative.

In this work we used a AGU/periodate molar ratio of 1.6. By using this molar ratio an aldehyde content of 0.086–0.432 mmol/g was achieved in 15–180 min at room temperature. Results of the room temperature oxidations are collected in Table 2. The results show clearly that the time has a crucial role in the efficiency of the oxidation as the aldehyde content is more than doubled when the oxidation time is raised from half an hour to one hour. Up to 3.5% of cellulose AGUs can be oxidized at these conditions.

Compared with related periodate oxidations reported in the literature very short oxidation times were used during our oxidation experiments. In this connection we were interested to know whether higher temperatures could be used during the oxidation in order to achieve higher aldehyde contents without a serious simultaneous periodate decomposition. The results of oxidation experiments at various temperatures are collected in Table 2.

The results presented in Table 2 show that the aldehyde content in DAC can be elevated considerably by raising the temperature. A three hours oxidation at 75 °C offers the oxidized cellulose with more than six times higher aldehyde contents compared with the corresponding oxidation at room temperature. Up to 23% of the cellulose AGUs can be oxidized to the corresponding dialdehyde units at elevated temperatures.

Furthermore, Table 2 shows also that raising the temperature from 75 °C to 85 °C does not enhance the aldehyde content further during a three hours oxidation experiment. The result indicates that the periodate decomposition may take place if the oxidation is per-



Scheme 1. (1) Periodate oxidation of cellulose, (2) reaction between DAC and $NH_2OH{\cdot}HCl$.

Table 2
Aldehyde contents of DAC produced by periodate oxidations of the birch cellulose at different temperatures (mmol/g).

Oxidation time (h)	Temperature (°C)	Aldehyde content (mmol/g)
0.25	RT	0.086
	55	0.364
	65	0.428
	75	0.658
	85	0.800
0.5	RT	0.114
	55	0.614
	65	0.708
	75	0.808
	85	1.142
1	RT	0.264
	55	0.950
	65	1.258
	75	1.450
	85	1.950
2	55	1.308
	65	1.864
	75	2.342
	85	2.672
3	RT	0.432
	55	1.678
	65	2.200
	75	2.842
	85	2.878

Table 3
Aldehyde contents of DAC produced by LiCl assisted periodate oxidations of the birch cellulose at different temperatures (mmol/g).

Oxidation time (h)	Temperature (°C)	Aldehyde content (mmol/g)
0.25	RT	0.122
	55	0.608
	65	0.736
	75	0.972
	85	1.100
0.5	RT	0.258
	55	0.814
	65	0.978
	75	1.286
	85	1.558
1	RT	0.364
	55	1.222
	65	1.664
	75	2.008
	85	2.658
2	55	1.592
	65	2.278
	75	2.808
	85	3.108
3	RT	0.804
	55	2.184
	65	2.872
	75	3.786
	85	2.564

formed at high temperatures (>85 °C) and the oxidation time is long (>2 h).

3.2. Lithium chloride assisted periodate oxidation of birch cellulose

LiCl is a water soluble alkali metal salt and $LiCl{\cdot}5H_2O$ can dissolve cellobiose and low molecular weight celluloses. By using cellobiose as model compound for cellulose, ^{7}Li NMR studies have clearly shown that Li^+ interacts with cellobiose when $LiCl{\cdot}5H_2O$ is used as a solvent (Brendler, Fischer, & Leipner, 2002).

Furthermore, LiCl can also be used to dissolve cellulose in organic solvents such as the *N*,*N*-dimethylacetamine (Röder, Morgenstern, Schelosky, & Glatter, 2001) and in 1-butyl-3-methylimidazolium acetate, which is an ionic liquid (Xu, Wang, & Wang, 2010). Results from ^{13}C NMR studies of Xu et al. suggest that Li^+ in the ionic liquid interacts with the cellulose hydroxyl oxygen atom (O(3)) at the carbon atom 3. This leads to the disruption of the intermolecular hydrogen bond between the oxygen atom O(3) in the cellulose molecule and a hydroxyl hydrogen atom (O(6)H) at the carbon atom 6 in an another cellulose molecule (Dumitrium, 2005). The diminished hydrogen bonding between cellulose molecules results then in enhanced solubility of cellulose.

In this connection we were interested to know whether LiCl in water can be used to disrupt the hydrogen bond network of cellulose and thereby improve the oxidation efficiency by making some of the hydroxyl groups more available to periodate. A molar ratio of 7 between LiCl and the AGU was used. Results from room temperature oxidations with a combination of periodate and LiCl are shown in Table 3. The results show clearly that LiCl improves the periodate oxidation efficiency of cellulose. In a three hours oxidation LiCl almost doubles the aldehyde content of the product compared with an identical oxidation without LiCl.

We also tested the effect of other LiCl/AGU ratios on the oxidation efficiency. Our results listed in Table 4 show that in 1 h oxidation experiments at 55 °C an optimal LiCl/AGU ratio is about 7. Higher and lower ratios give oxidized cellulose products with lower aldehyde contents.

Results from LiCl assisted periodate oxidations at various temperatures are listed in Table 3. Similarly to the non-assisted periodate oxidations, the results from LiCl assisted oxidations at various temperatures also show that up to 75 °C the aldehyde content increases as the temperature increases. During a three hours oxidation at 75 °C 31% of cellulose AGUs are oxidized to the corresponding dialdehyde units.

During a 3 h LiCl assisted oxidation at 85 °C an emergence of brownish color was observed in the reaction mixture which may indicate the formation of I_2 (Varma & Kulkarni, 2002). The decomposition of periodate was already observed in non-assisted oxidations at 85 °C and the observations of brownish color during the LiCl assisted oxidation indicate that metal salts may also catalyze the decomposition of periodate.

Furthermore, in the 3 h LiCl assisted oxidation at 85 °C the aldehyde content is actually significally lower than the aldehyde content in a corresponding 2 h reaction. The result indicates that side-reactions may take place when compounds that contain iodine are reduced to I_2 and a simultaneous decrease of the aldehyde content is observed.

3.3. Periodate oxidation of birch cellulose with other metal chlorides

As the results from the LiCl assisted oxidations were very promising, we were also interested to know whether other metal chlorides could be used to improve the oxidation efficiency. $ZnCl_2$ is known to interact with cellulose and $ZnCl_2{\cdot}3–4H_2O$ can readily dissolve cellulose (Fischer, Leipner, Thummler, Brendler, & Peters, 2003). Furthermore, $MgCl_2{\cdot}6H_2O$ can be used as a co-solvent to dissolve cellulose in $LiClO_4{\cdot}3H_2O$ (Leipner, Fischer, Brendler, & Voigt, 2000). Similarly to the Li^+ ion, a Ca^{2+} ion is also known to interact

Table 4
Aldehyde contents of DAC produced by LiCl assisted periodate oxidations of the birch cellulose with different LiCl concentrations in a 1h oxidation at 55 °C (mmol/g).

Amount of LiCl/0.5 g of cellulose (mmol)	Aldehyde content (mmol/g)
3.5	1.096
7	1.046
14	1.028
21	1.226
28	1.122

Table 5
Aldehyde contents of DAC produced in 1h periodate oxidations of the birch cellulose with various amounts of different metal salts at 55 °C (mmol/g).

Metal salt	Amount of salt/0.5 g of cellulose (mmol)	Aldehyde content (mmol/g)
$ZnCl_2$	3.5	1.058
	7	1.208
	14	1.164
	21	1.208
	28	1.136
$CaCl_2$	3.5	1.186
	7	1.322
	14	1.25
	21	1.386
	28	1.258
$MgCl_2$	3.5	1.022
	7	1.072
	14	1.158
	21	1.272
	28	1.272
NaCl	3.5	1.028
	7	1.158
	14	1.114
	21	1.136
	28	1.172

with cellulose and $Ca(SCN)_2{\cdot}3H_2O$ can be used to dissolve cellulose (Fischer et al., 2003). NaCl was chosen as an inexpensive common reference salt. One-hour oxidation experiments with various amounts of different metal salts were done at 55 °C and results are collected in Table 5.

In Table 5 it can be seen that all used metal salts improve the efficiency of the periodate oxidation and interestingly $CaCl_2$ affords oxidized cellulose with the highest aldehyde contents. In the $CaCl_2$ assisted oxidation three times smaller amounts of the salt can be used to achieve oxidized cellulose with a 0.1 mmol/g higher aldehyde content than the aldehyde content in the corresponding LiCl assisted oxidation.

3.4. Decomposition of cellulose during the LiCl assisted periodate oxidation

The periodate oxidation can decompose cellulose by a formation of radicals during the spontaneous decomposition of periodate in a water solution (Vicini et al., 2004). In Table 6 it is highlighted that the yield of oxidized cellulose decreases when relatively long reaction times or high temperatures are used. As seen in Table 1, the birch pulp contains about 24.5% hemicelluloses so presumably the yield decrease during the oxidation is mainly due to the dissolution of hemicelluloses. At higher temperatures cellulose starts to decompose or dissolve due to the oxidation (Kim, Wada, & Kuga, 2004).

Table 6
Yields of DAC produced by LiCl assisted periodate oxidations of the birch cellulose at various temperatures (%).

Oxidation time (h)	Temperature (°C)	Yield (%)
0.25	55	88
0.5	55	86
	65	76
1	55	86
	65	80
2	55	80
	65	74
	75	76
3	55	76
	65	76
	75	54

Table 7
Aldehyde contents of DAC produced by periodate oxidations of different cellulose materials in a 1 h oxidation at 55 °C with and without LiCl (mmol/g).

Cellulose material	Chemicals	Aldehyde content (mmol/g)
Birch cellulose	$NaIO_4$	0.956
	$NaIO_4$ + LiCl	1.164
Dissolving pulp	$NaIO_4$	0.758
	$NaIO_4$ + LiCl	1.35

To verify the effect of hemicelluloses to the yield decrease, a dissolving pulp from softwood which contains less hemicelluloses than the birch pulp was used as a reference material (see Table 1). By using LiCl assisted oxidation at 75 °C the dissolving pulp was oxidized in 0.5 h to afford DAC in 94% yield. The high yield is well in line with the hemicelluloses content of the starting material and the yield is significantly higher than in the corresponding LiCl assisted oxidation of birch cellulose.

The reactivity of different cellulose materials was investigated and results from 1 h oxidations at 55 °C with and without LiCl are collected in Table 7. Interestingly, when dissolving pulp is used as cellulose source, the aldehyde content in the non-assisted periodate oxidation is lower than in the corresponding oxidation with birch pulp as the starting material, whereas the aldehyde content in a LiCl assisted oxidation of dissolving pulp is higher than the aldehyde content in the corresponding LiCl assisted oxidation of birch cellulose.

4. Conclusion

Cellulose can be oxidized to DAC with sodium periodate at elevated temperatures to achieve higher aldehyde contents than in the corresponding oxidations at room temperature. The decomposition of periodate only affects the yield of aldehyde groups if the oxidation is performed at temperatures over 75 °C with the long reaction time (>2 h).

The efficiency of the periodate oxidation can be further improved be using LiCl and other metal chlorides as chemicals which reduce the amount of inter and intra molecular hydrogen bonds between the cellulose polymers. If especially long reaction times at high temperatures is used during the oxidation, LiCl may also catalyze an undesired decomposition of periodate. It was also found that long reaction times decrease the yield of DAC which is presumably caused by the dissolution of hemicelluloses.

By using LiCl and elevated temperatures sufficient aldehyde contents can be achieved within short oxidation times and the amount periodate can also be reduced. The results can be utilized to make the periodate oxidation more efficient and more environmentally friendly.

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