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Optimization of dicarboxylic acid cellulose synthesis: Reaction stoichiometry and role of hypochlorite scavengers

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ABSTRACT

The reaction conditions in terms of reaction time, sodium chlorite stoichiometry, and the effect of hypochlorite scavengers on the chlorite oxidation of dialdehyde cellulose (DAC) was studied. The impact of storage on the reactivity of DAC fibers was also investigated. It was found that chlorite oxidation of DAC is a rapid reaction, resulting in oxidation of 71% of the aldehyde after only 8 min when 2.5 times excess of sodium chlorite compared to aldehyde groups was used. Reactivity of DAC was observed to decrease quickly during the storage and only 68% of the aldehyde groups reacted after two weeks storage compared to the reaction performed with freshly prepared DAC. Hydrogen peroxide and sulfamic acid were observed to increase the reaction efficiency of chlorite oxidation by reducing the amount of side-reactions between chlorite and hypochlorite. A minor amount of sulfamic acid can be used to replace acetic acid as a catalyst.

1. Introduction

Development of bio-based materials to replace oil-derived products and fabricate completely new products has long been one of the driving forces in natural science and material engineering (Ragauskas et al., 2006). Bio-based materials have been considered to possess various advantages over traditional, oil-derived products, such as renewability, biodegradability, biocompatibility and low-toxicity. Cellulose, which is a biopolymer produced by various plants, bacteria, and tunicates, is most abundant organic polymer on earth and therefore one of the most promising raw materials for novel products (Klemm, Heublein, Fink, & Bohn, 2005). Cellulose has three reactive hydroxyl groups in its repeating unit (anhydroglucose unit, AGU), and it can thus be modified by typical alcohol group chemistry, such as esterification, etherification (Fox, Li, Xu, & Edgar, 2011) and oxidation (Coseri et al., 2013). The introduction of different functionalities to cellulose backbone has led to the development and commercialization of various cellulose based products.

Anionic celluloses containing carboxylic acid groups have been investigated in many applications including chromatographic (Saito, & Isogai, 2005), medical applications (Dias, Peplow, & Teixeira, 2003) and recently as a raw material in the production of nanocellulose (Abdul Khalil et al., 2014). Carboxymethylation of cellulose has long been used to obtain anionic cellulose on an industrial scale (Hollabaugh, Burt, & Walsh, 1945). Oxidation of cellulose is another potential method to fabricate anionic cellulose; however, only a few oxidation methods have been utilized on an industrial scale, including oxidation with nitrogen dioxide (Domb, Kost, & Wiseman, 1997). Nitrogen dioxide is, however, a non-selective oxidant and therefore more selective, efficient, and sustainable oxidation routes are desired.

Sequential periodate and chlorite oxidation is a selective technique to obtain anionic 2,3-dicarboxylic acid cellulose (DCC) (Kim & Kuga, 2001). In the first step, recyclable sodium periodate (Liimatainen, Sirviö, Pajari, Hormi, & Niinimäki, 2013) selectively oxidizes vicinal hydroxyls in the carbon 2 and 3 of cellulose to 2,3-dialdehyde cellulose (DAC), followed by selective oxidation of the aldehyde groups using sodium chlorite. During the chlorite oxidation of aldehyde, mole of aldehyde consumes one mole of chlorite, and an equal amount of hypochlorite is produced (Eq. (1)) (Dalcanale & Montanari, 1986).

$$RCHO + HClO_2 \rightarrow RCOOH + HClO \quad (1)$$

DCC has been used in chromatographic applications (Kim & Kuga, 2001) and in the production of nanofibrillated cellulose (Tejado, Alam, Antal, Yang, & van de Ven, 2012; Liimatainen,

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Visanko, Sirviö, Hormi, & Niinimäki, 2012) and highly charged nanocrystalline cellulose (Yang, Alma, & van de Ven, 2013). Nanofibrillated DCC has been used in fabrication of ultrafiltration membranes (Visanko et al., 2014), purification of municipal wastewaters (Suopajärvi, Liimatainen, Hormi, & Niinimäki, 2013), and nanopaper structures (Liimatainen et al., 2013). So far, large excesses of sodium chlorite and long reaction times have been employed to obtain DCC. In addition, a large amount of acetic acid is required as an acidic reaction media. In the present study, optimization of chlorite oxidation of DAC was performed by addressing the effect of the reaction time and chloritbe concentration on the production of DCC. Due to the possible side-reaction caused by the formation of hypochlorite, the effect of the hypochlorite scavengers on the reaction efficiency was studied to eliminate a detrimental side reaction. Additionally, the effect of the storage time on the reaction efficiency of DAC was clarified.

2. Experimental

2.1. Materials

Bleached birch pulp (Betula Pendula) was obtained in dry sheets and used as a cellulose material after disintegration in deionized water. The properties of cellulose are presented elsewhere (Sirviö, Liimatainen, Niinimäki & Hormi, 2011). All chemicals used in periodate and chlorite oxidations ($NaIO_4$, $NaClO_2$ (purity of 80%) CH_3COOH, NaClO (1.24 M), H_2O_2 (30%) and H_3NSO_3), and aldehyde and carboxyl content analyses ($NH_2OH{\cdot}HCl$, $CH_3COONa{\cdot}2H_2O$, NaCl, HCl and NaOH) were obtained as p.a. grades from Sigma–Aldrich (Germany) and were used without further purification. Deionized water was used throughout the experiments.

2.2. Preparation of the dialdehyde cellulose

2.2.1. Periodate oxidations of cellulose

Cellulose pulp was oxidized with periodate as previously described (Sirvio, Hyvakko, Liimatainen, Niinimaki, & Hormi, 2011). In brief, 9 g of cellulose was oxidized using 7.38 g of sodium periodate at 55 °C for 3 h in the absence of light. DAC with an aldehyde content of 1.68 mmol/g was obtained (i.e., 14% of the cellulose AGUs were oxidized). The product was stored at 4 °C in a non-dried state at a consistency of approximately 25%.

Chlorite oxidation of DAC was performed by a modified method previously reported (Liimatainen et al., 2012). At first, 2 g of DAC was dispersed in 44.4 ml deionized water by mixing for 1 min at 11,000 RPM with an Ultra-Turrax mixer (Germany). Various amounts of sodium chlorite (0.5–5 times compared to aldehyde groups) dissolved in 12% acetic acid were added, and reaction was allowed to proceed various times (15 s–18 h). With the reaction time of 3 min or less, 1 ml of propionaldehyde was carefully added and reaction was allowed to proceed for an additional 2 min to quench the reaction (Note: reaction between sodium chlorite and propionaldehyde is highly vigorous. Even though we did not encounter any problem with the current amount of sodium chlorite and propionaldehyde, if a higher amount of reagent is used, combustion of propionaldehyde may occur.) The reaction mixture was filtrated and washed with 2 l of water, redispersed in 2 l of water, filtrated, and finally washed with 2 l of water. The product was stored at 4 °C in a non-dried state.

Reactions containing hypochlorite scavengers were performed in a similar manner described above, but one equivalent (related to sodium chlorite) of hydrogen peroxide or sulfamic acid was added to reaction mixture. In addition, reaction in absence of acetic acid was performed using hydrogen peroxide or sulfamic acid as an additive or without any additional reagent. Volume of the reaction mixture was kept at 88.8 ml.

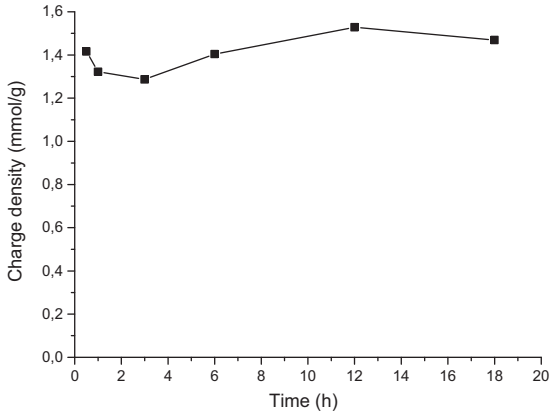


Fig. 1. Carboxylic acid content of DCC using different reaction times with five times excess of sodium chlorite compared to aldehyde content (1.68 mmol/g).

The aldehyde content of the periodate oxidized cellulose and residual aldehyde content of chlorite oxidized DAC was determined using an oxime reaction as reported previously (Sirvio et al., 2011). In brief, 0.1 g DAC was allowed to react with 1.39 g of hydroxylammonium hydrochloride at 100 ml 0.1 M acetic acid buffer (pH 4.5) for 48 h. The reaction product was washed with 1 l of water. Reaction for partially chlorite oxidized DAC was performed in a similar manner, but the reaction product was washed with 100 ml 0.1 M HCl solution followed by washing with 1 l of water. The carboxyl content was analyzed by conductometric titration using a procedure described in the literature (Katz, Beatson, & Scallan, 1984; Rattaz, Mishra, Chabot, & Daneault, 2011).

3. Results and discussion

3.1. Effect of reaction time on the chlorite oxidation of dialdehyde cellulose

In our previous study, DCC with a carboxylic acid content of 1.75 mmol/g was obtained after 48 h oxidation in 1 M acetic acid solution using five times excess of sodium chlorite compared to the aldehyde groups. Fig. 1 shows that after 0.5 h using the same reaction conditions previously reported, the carboxylic acid content of DCC was 1.41 mmol/g. When the reaction time was increased to 20 h, no significant increase in the carboxylic acid content was observed. These results indicate that the chlorite oxidation of DAC is a very rapid reaction and only a slight increase of the carboxylic acid content can be obtained after prolonged reaction times. However, as the original aldehyde group content of the DAC was 1.68 mmol/g, long reaction times are still needed to oxidize all of the aldehyde groups. Slow oxidation of the remaining aldehyde groups may be due to the formation of the less reactive hemiacetal and hydrated aldehyde groups (Mester, 1995).

3.2. Effect of reaction stoichiometry on chlorite oxidation of dialdehyde cellulose

In the view of environmental and industrial feasibility, high excess of a halogen-containing oxidant is not favored. Therefore, the role of chlorite amount in DCC synthesis was investigated. Chlorite doses ranging from five times excess to half of the stoichiometric amount compared to aldehyde group content were used. Carboxylic acid content quickly increased when the amount of sodium chlorite was increased from half of the stoichiometric amount to 2.5 times excess in a 1 h reaction (Fig. 2a). However,

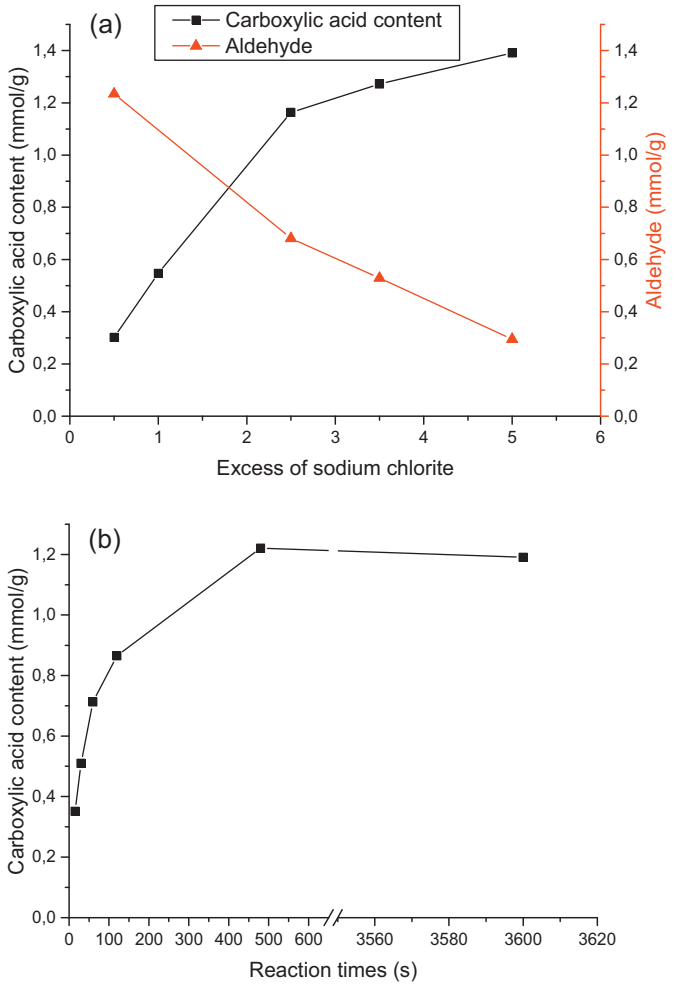


Fig. 2. (a) Carboxylic acid content of DCC using different sodium chlorite excess compared to aldehyde groups (1.68 mmol/g) at 1 h reaction time, (b) carboxylic acid content of DCC using different reaction times with 2.5 times excess of sodium chlorite compared to aldehyde groups (1.68 mmol/g).

only a small increased in the carboxylic acid content was obtained when five times excess of sodium chlorite was used instead of 2.5. The residual aldehyde contents, determined using an oxime reaction, are presented in Fig. 2a. They are in line with the carboxylic acid content, as the aldehyde content decreases simultaneously as the carboxylic acid content increases.

Fig. 2b shows how the chlorite oxidation of DAC is a rapid reaction even with 2.5 times excess of sodium chlorite. After 8 min, the carboxylic acid content was observed to be 1.2 mmol/g, and no improvement was observed when reaction time was increased to 1 h.

3.3. Effect of the storage time on the reactivity of dialdehyde cellulose toward to chlorite oxidation

As stated in Section 3.1, aldehyde groups in DAC are known to exist also in various structures other than free aldehydes, which may have an effect on the reactivity of DAC (Mester, 1995; Spedding, 1960). Aldehyde groups can react with hydroxyl groups of cellulose to form inter- and intra-molecular hemiacetal bonds and with water to form hemialdol or hydrated aldehydes (Fig. 3). As these structures may be formed slowly, we studied whether the storage time had on effect on the reactivity of DAC. DAC was stored as about 25% at dry-content at 4 °C.

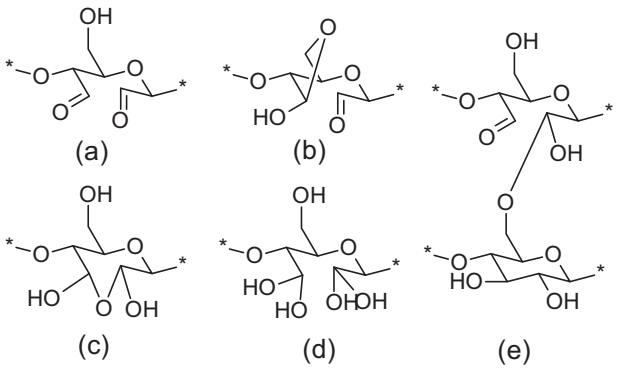


Fig. 3. Possible structures of DAC: (a) free aldehyde, (b) intramolecular hemiacetal, (c) hemialdol, (d) hydrated aldehydes, and (e) intermolecular hemiacetal.

Reactivity of DAC was observed to decrease quite dramatically during storage. When DAC was stored for two weeks at 4 °C in a non-dried state, in the 1 h oxidation reaction the carboxylic group content was only 0.75 mmol/g when 2.5 excess of sodium chlorite was used. This is only 68% of that oxidized within one week from the preparation of DAC. After two weeks, reactivity no longer decreases, indicating that equilibrium is reached quickly after the preparation of DAC. These results indicate that DAC should be used soon after fabrication.

3.4. Effect of the chlorite scavenger on the chlorite oxidation of dialdehyde cellulose

Chlorite oxidation of aldehyde produces hypochlorite as a side-product. Formed hypochlorite may cause some side reactions, such as oxidation of more sensitive groups, as it is a more powerful oxidant compared to chlorite. Hypochlorite can also react with the remaining chlorite (Eq. (2)), which will decrease the reaction efficiency of chlorite oxidation (Dalcanale & Montanari, 1986).

$$HClO + 2ClO_2^- \rightarrow 2ClO_2 + Cl^- + OH^- \quad (2)$$

In addition to reducing oxidation efficiency, reaction between chlorite and hypochlorite also produces toxic and noxious chlorine dioxide. To prevent this undesirable side reaction, various hypochlorite scavengers can be used. Hydrogen peroxide is an efficient hypochlorite scavenger, as it reacts with hypochlorite to form hydrochloride acid, water, and oxygen as a product (Eq. (3)) (Dalcanale & Montanari, 1986):

$$HClO + H_2O_2 \rightarrow HCl + O_2 + H_2O \quad (3)$$

Sulfamic acid is another well-known hypochlorite scavenger, and it reacts with hypochlorite in the following equations (Lindgren & Nilsson, 1973):

$$ClO^- + H_2NSO_2H \rightarrow ClNHSO_3H + H_2O \quad (4)$$

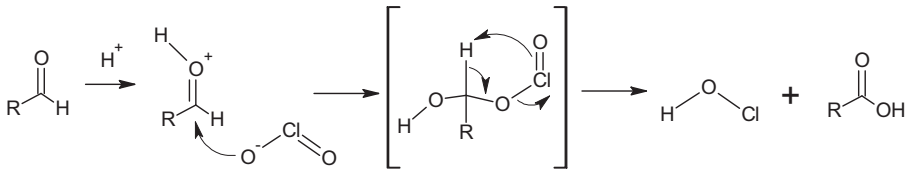
$$HClO + ClNHSO_3H \rightleftarrows Cl_2NSO_3H + H_2O \quad (5)$$

To study the effect of a hypochlorite scavenger on the chlorite oxidation of DAC, we performed 1 h chlorite oxidation in a 1 M acetic acid solution using 2.5 times excess of sodium chlorite with respect to the aldehyde group content together with equal amount of hydrogen peroxide or sulfamic acid. Results presented in Table 1 show that both scavengers increase the carboxylic acid content of the DCC (21–28%) compared to the reaction without scavengers. Hydrogen peroxide was found to be a more efficient reagent to improve chlorite oxidation efficiency (Table 1, entry 2).

As the sulfamic acid is moderately strong acid (pK_a 1.0 (Kurz & Farrar, 1969)), we performed chlorite oxidation with sulfamic acid in absence of acetic acid. In this case, even higher carboxylic

Table 1
Carboxylic acid content and the starting pH of the reaction mixture with different additives using 1 h reaction time and 2.5 times excess of sodium chlorite compared to the aldehyde groups (1.68 mmol/g).

Entry	Acetic acid (mmol/g of DAC)	Hydrogen peroxide (mmol/g of DAC)	Sulfamic acid (mmol/g of DAC)	pH	Carboxylic acid content (mmol/g)
1	44.45	–	–	2.94	1.16
2	44.45	4.45	–	3.02	1.48
3	44.45	–	4.45	1.75	1.40
4	–	4.45	–	9.91	0.31
5	–	–	4.45	1.66	1.34
6	–	–	–	10.81	0.02



Scheme 1. Mechanism of chlorite oxidation of aldehyde.

acid content was obtained compared to oxidation in presence of acetic acid (Table 1, entries 3 and 1). On the other hand, only a small amount of the aldehyde groups were oxidized without any additives (Table 1, entry 6) or in the presence hydrogen peroxide without acetic acid (Table 1, entry 4).

The chlorite oxidation is an acid catalyzed reaction as the reaction starts by the protonation of the aldehyde group, followed by the attack of chlorite (Scheme 1) (Lindgren & Nilsson, 1973). As can be seen in Table 1, the pH of the reaction mixture containing only sulfamic acid (entry 4) is lower compared to the solution containing only acetic acid (entry 5). On the other hand, the pH of the reaction mixtures without any acid or only hydrogen peroxide as an additive were basic (Table 1, entries 4 and 6), therefore, only a small amount of the aldehydes where oxidized. Sulfamic acid was found to act as both an acid catalyst and a hypochlorite scavenger. This provides good alternative for acetic acid, as about ten times less sulfamic acid is needed compared to acetic acid to obtain good reaction efficiency.

As hypochlorite, formed in chlorite oxidation, is a strong oxidant, we also studied whether it affected the oxidation reaction of DAC by using hypochlorite as a sole oxidant. After a 1 h reaction time using 2.5 excess of sodium hypochlorite compared to the aldehyde groups, the acid group content of 0.12 mmol/g was observed, indicating that at current conditions, sodium hypochlorite is a slow oxidant in the oxidation of DAC to DCC.

4. Conclusion

Reaction efficiency of the chlorite oxidation of DAC was studied, and it was found that oxidation is a rapid reaction, when the amount of sodium chlorite was decreased from five times excess to 2.5 times excess compared to aldehyde content. However, it was found that the reaction efficiency of DAC decreases quickly during storage in a non-dried state and therefore chlorite oxidation should be completed within a week of the preparation of DAC. In addition, hydrogen peroxide and sulfamic acid could be used to improve reaction efficiency of chlorite oxidation as both can act as a hypochlorite scavenger. Sulfamic acid is advantageous as it can replace acetic acid as an acid catalyst during chlorite oxidation.

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