APPLIED STUDY OF BIRCH PULP BLEACHING USING DIMETHYLDIOXIRANE TO OBTAIN ACETATE-GRADE PULP

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As a pulp bleaching agent, dimethyldioxirane (DMD) is effective and selective. In this study, it was employed as a delignifying agent or as an activating agent for hydrogen peroxide treatment in bleaching acetate-grade pulp. Brightness, kappa number, degree of polymerization (DP), and alpha-cellulose content were evaluated to determine the optimal charges of DMD: 2.5% AO, and 4% HSO_5^-, respectively. Results from the totally chlorine-free (TCF) sequences MEQMPA, MEpQMPA, and OQMPA suggested that DMD is both effective and selective as a delignifying agent but not as a brightening agent as compared to oxygen. And in a long sequence for the bleaching of dissolving pulp, acid treatment can be used in two approaches: to remove the metal ions without washing before the chelation stage, and to reduce hemicellulose and ash in the final stage.

Keywords: Birch kraft pulp; Pulp of acetate grade; Dissolving pulp; DMD; Delignification; Pretreatment; TCF sequence; Totally chlorine free bleaching

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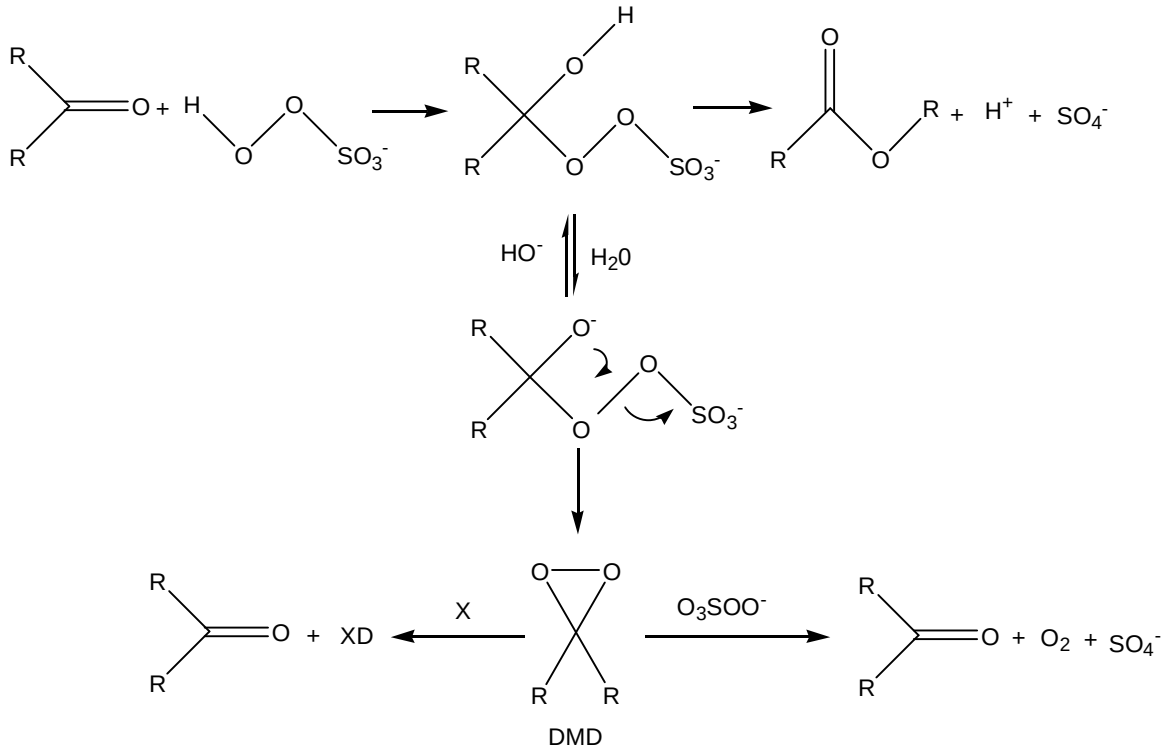
INTRODUCTION

Nowadays most pulp of acetate grade is made from cotton linters and high-grade wood dissolving pulp with high alpha-cellulose content, and the required production of this grade will be increased by 20% by 2010 (FAO 1997). To be able to meet this demand, it is critical to work over the preparation of dissolving pulp from wood.

China has been short of forest resources and wood because of excessive deforestation. There are about 100 species of birch in the world, whose scientific names include *Betula platyphylla* and other *Betula* species. A majority of them are distributed in the north temperate zone, and a minority grow in the Arctic Circle. 29 kinds of them are distributed throughout the whole of China (Wang and Pei 2000). The cellulose content of birch is similar to that of other hardwoods, and the lignin content is less than that of softwood (Liang 1996). As birch has been widely used in paper manufacture, there have been a few documentations of the use of birch in the production of dissolving pulp (Wang 2003; Köpeke et al. 2008; Janzon et al. 2006). But the levels of hemicellulose, ash, and extractives, which affect the properties of high-grade dissolving pulp and result in industrial problems such as poor filterability, turbidity, and false viscosity, are greater more than that of other hardwood species (Funaki et al. 1993; Neal 1965; He et al. 2009). So it is essential to reduce these chemical constituents in the process of dissolving pulp preparation.

Most dissolving pulps are produced from wood using the prehydrolysis kraft or acid sulfite processes (Biermann 1993; Hinck et al. 1985). Dissolving pulp usually employs chlorine dioxide as a reagents in multistage bleaching. But the liquid effluent has been deemed to be unfriendly to the environment. Totally chlorine-free bleaching has been studied in many countries. Oxygen delignification has been employed for many years, and ozone as well as hydrogen proxide were successfully used in investigations (Liu et al. 1998). But molecular oxygen has a triplet ground state, whose direct interaction with single-state organic molecules is a spin-forbidden transition, a circumstance that limits its oxidative selectivity (Suchy and Argyropoulos 2002).

Dimethyldioxirane (DMD), which is a source of active oxygen, can be generated from acetone and peroxymonosulfate and employed in-situ. Upon oxidation of a substrate with DMD, oxygen is transferred to the substrate and acetone is regenerated (Santiago et al. 1995). In this reaction, dimethyldioxirane can transfer a single activated oxygen atom onto aromatic and unsaturated substrates, and acetone acts as a catalyst in the reaction (Suchy and Argyropoulos 2002). The process of DMD generation and oxidation is shown in Fig. 1 (Ragauskas 1993). Dimethyldioxirane as a pulp bleaching agent has been tested for the first time by Lee et al. (1993) at Paprican and at the University of Missouri, St. Louis. The way in which the agent selectively delignified the chemical pulp was found to be similar to that of chlorine and chlorine dioxide.



X: Lignin; XD: Oxidized Lignin

Fig. 1. Process of DMD generation and oxidation

Dimethyldioxirane can be applied in two ways, as a delignifying agent or as an activating agent before oxygen or alkaline hydrogen peroxide bleaching stages. In delignification studies, Lee et al. (1993) achieved a Kappa number reduction of greater than 80%, and the viscosity was the same as that achieved by bleaching with chlorine-containing compounds. Qin et al. (1999a) studied eucalyptus kraft pulp treated with 5% DMD, followed by caustic extraction, and the resulting pulp had the same Kappa number as a corresponding batch of the same pulp treated with oxygen, while the viscosity and delignification selectivity were superior to that of oxygen delignification. As an activating agent, DMD pretreatment before alkaline hydrogen peroxide bleaching, investigated by Abou-Youset, Qin, and their coworkers, was shown to be effective (Qin et al. 1999b; Abou-Youset 2001).

Although there has been considerable study of DMD bleaching, only a few studies have considered the use of DMD treatment for dissolving pulp bleaching (Zhang et al. 2005; He et al. 2007). So research on this effective and selective reagent applied in dissolving pulp bleaching will benefit the development of both textiles and cigarette filter tips industries.

The aim of this study was to investigate the application of dimethyldioxirane in preparation of acetate-grade pulp. Brightness, kappa number, degree of polymerization (DP), and alpha-cellulose content were evaluated to find out the optimal charges for dimethyldioxirane delignification and dimethyldioxirane pretreating alkaline hydrogen peroxide bleaching. The pulp properties were measured to compare stage Op with M in totally chlorine-free (TCF) sequences.

EXPERIMENTAL

Materials

The birch was provided by a pulp mill in Shi Xian, in the northeast of China. Two kinds of pulp were prepared in the laboratory were used in the study, birch kraft pulp after alkaline pretreatment and alkaline-pretreated kraft pulp bleached by oxygen. The birch chips were pretreated with 10% charges of NaOH under the following conditions: solid:liquid ratio equal to 1:4, temperature 120°C, retention time 120 min, and 1.75% charges of sodium lauryl benzenesulfate (ABS). The cooking step was carried out for about 3.5 h with 16% NaOH (as Na_2O) of oven-dried chips, sulfidity 25%, 1.75% ABS, and 0.05% anthraquinone (AQ). The time to reach the max temperature of 168°C was 120 min, and the duration at 168°C was 90 min. The liquor to birch chips ratio was 4:1. The alkaline-pretreated kraft pulp bleached by oxygen had the same conditions with the birch kraft pulp after alkaline pretreatment, except that the time to reach the maximum temperature was 150 min and the duration was 120 min.

Methods

All bleaching processes were done in heat-proof polyethylene bags, except for the H_2O_2-reinforced oxygen delignification, which was carried out in a reactor. The pulp was kneaded every 15 minutes. After each stage, the pulp was removed, filtered, and washed with distilled water, except for the acid treatment before the chelation stage.

Dimethyldioxirane Bleaching (M)

$NaHCO_3$ solution was added to the pulp mixed with aqueous acetone to balance the pH within the range 7.0 to 7.5. After a 5-minite stirring, the bleaching reagent-oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) and the pulp were placed in heat-proof polyethylene bags at 25°C for 60 min retention. The procedure employed a 1.5:1 mol ratio of acetone to oxone. The consistency of the pulp bleaching mixture was 10%.

Caustic Extraction (E)

This stage after each DMD delignification was carried out at 70°C for 60 min, using 10% consistency, and 8% charges of NaOH.

Hydrogen Peroxide Reinforced Caustic Extraction (Ep)

The condition was same as that of caustic extraction, except for the concentration of H_2O_2, which was 0.8%.

Hydrogen Peroxide Reinforced Oxygen Delignification (Op)

The conditions of this stage were as follows: pressure, 0.3Mpa; temperature, 100°C; retention time, 60 min; consistency, 10%; concentration of NaOH, 2%; concentration of H_2O_2, 0.8%; concentration of $MgSO_4$, 0.5%; and concentration of Na_2SiO_3, 3%.

Chelation (Q)

This stage used 10% consistency, 0.5% charges of EDTA, and a pH of 5 at 70°C for 60 min to chelate metal ions.

Alkaline Hydrogen Peroxide Bleaching (P)

The conditions of this stage were 3% charges of H_2O_2, 2% charges of NaOH, 0.5 charges of $MgSO_4$, and 3% charges of Na_2SiO_3 at 10% consistency and 70°C for 90 min retention.

Acid Treatment(A)

2.5% charges of H_2SO_4 and 0.6% sodium hexametahposphate were employed in this stage. Other conditions were as follows: consistency, 10%; temperature, 25°C; and retention time, 60 min.

Pulp Properties Analysis

Brightness levels were determined with a YQ-Z-48B brightness tester, which can measure ISO Brightness, namely R457 brightness. Kappa number was determined using GB/T 1546-1989, the standard method, which is the same as the TAPPI test method T 236 cm-85. Alpha-cellulose, the pulp fraction resistant to a treatment in an aqueous solution containing 17.5% sodium hydroxide and indicates undegraded, was determined by GB/T 744-1989. The degree of polymerization (DP) of pulp were determined from the intrinsic viscosities [η], which were measured using capillary viscometer in cupri-ethylene-diamine (CED) solution at 25°C according to GB/T1548-1989, by the formula of $DP^{0.905}=0.75[\eta]$.

RESULTS AND DISCUSSION

Dimethyldioxirane Delignification

As shown in Figs. 2 and 3, brightness, delignification efficiency, and the alpha-cellulose content all changed linearly as the concentration of activated oxygen increased from 1% to 3%. At a lower charge of activated oxygen (AO), the delignification efficiency didn't reach 40%.

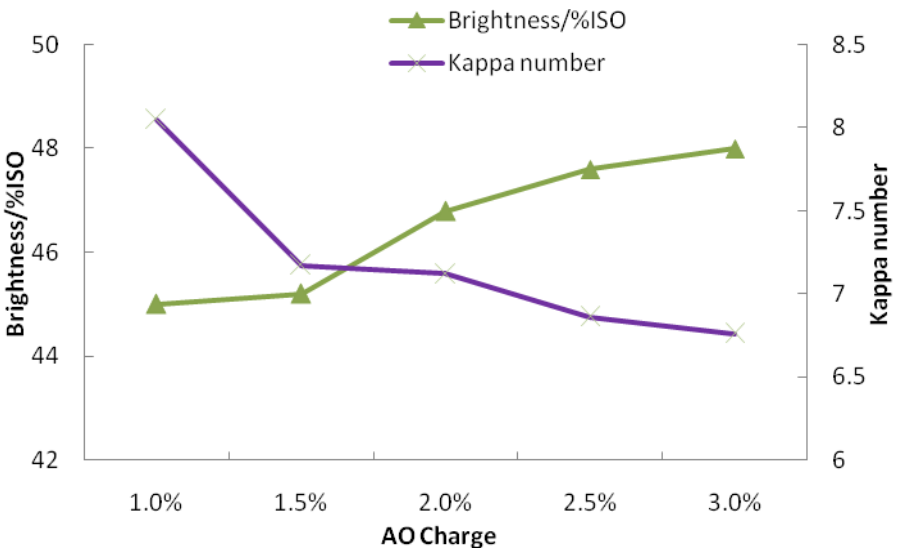


Fig. 2. Effect of the activated oxygen charge on brightness and delignification efficiency for dimethyldioxirane delignification

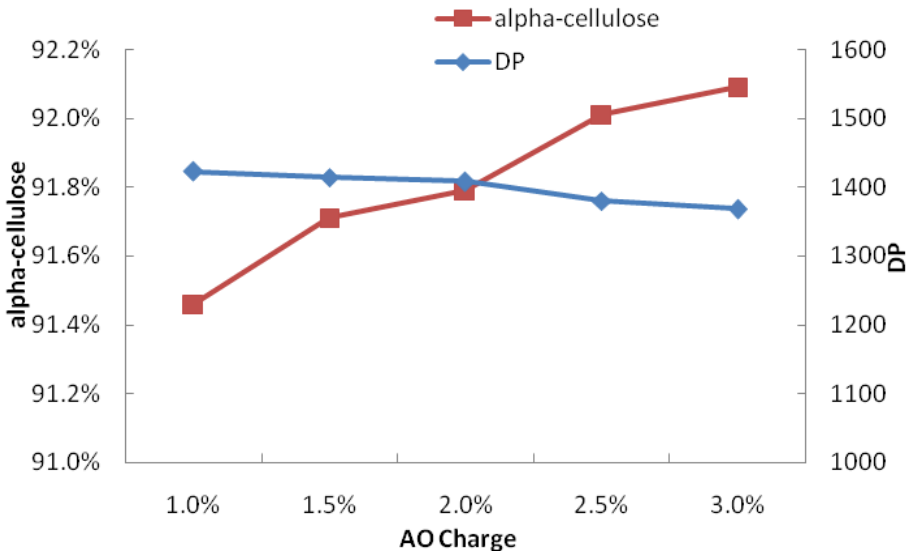


Fig. 3. Effect of the activated oxygen charge on alpha-cellulose and degree of polymerization for dimethyldioxirane delignification

When the concentration of AO was 2.5% or higher, the increasing trend of the parameters mentioned above was not obvious. And the alpha-cellulose content could reach 92%. But the highest delignification efficiency was only 50%. This may be explained as due to the fact that the original pulp was low in kappa number, and the temperature wasn't high enough for lignin removal. On the other hand, with the AO level increasing, the degree of polymerization, which declined smoothly, was still higher than 1300. This revealed that DMD was an agent that could reduce viscosity loss. Consequently, 2.5% AO was judged to be the optimum amount.

Dimethyldioxirane Pretreating Alkaline Hydrogen Peroxide

There have been two main approaches for hydrogen peroxide reaction with lignin to increase pulp brightness: attack of carboxyl on residual lignin and oxidative degradation of free phenolic hydroxyls and quinoid structures (Lachenal and Papadopoulos 1988). Argyropoulos and Sun (1996) found that DMD electrophilically oxidized the aromatic rings of both etherified and non-etherified softwood lignin model compounds. And low charges of DMD may act as activating stages prior to chlorine dioxide and/or alkaline hydrogen peroxide, since they were found to introduce free phenolic hydroxyl groups in residual lignin (Sun and Argyropoulos 1996).

H_2O_2 bleaching was pretreated by DMD at low charges, and the results are shown in Figs. 4 and 5. With the increase of HSO_5^- concentration, brightness, and alpha-cellulose were also increased. When the concentration of HSO_5^- was higher than 4%, the increasing trends of both brightness and alpha-cellulose content were not obvious. Brightness of the pulp activated by 1% charges of HSO_5^- was only 1.4% higher than the pulp without DMD pretreatment, while the alpha-cellulose content was 1% higher than the unpretreated one. However, the degree of polymerization appeared to decrease. Interestingly, all the DP values were higher than the untreated pulp. This revealed that DMD promoted the selectivity of H_2O_2 delignification, and it may be explained that there may be some condensation compounds generated by DMD pretreatment. The optimal charge of HSO_5^- was 4%.

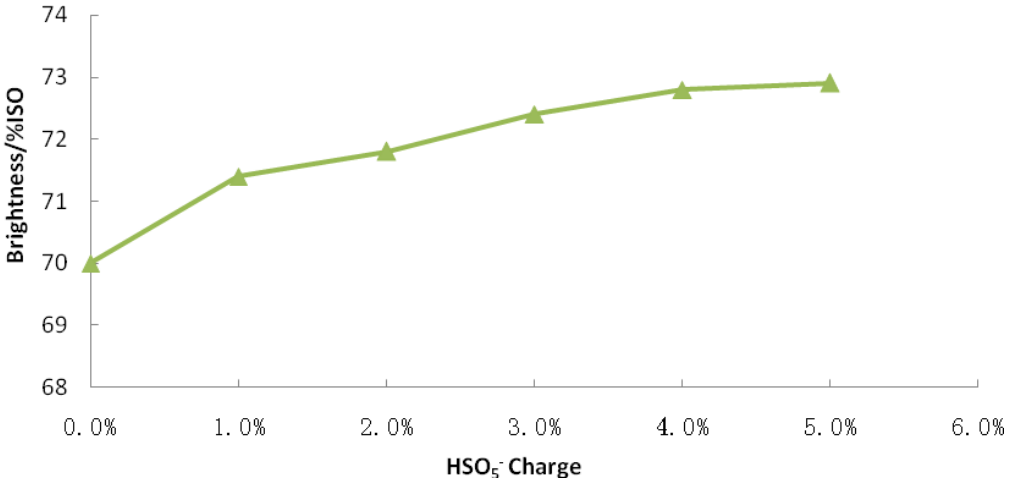


Fig. 4. Effect of the HSO_5^- charge on brightness for activated O_2 pretreating alkaline H_2O_2

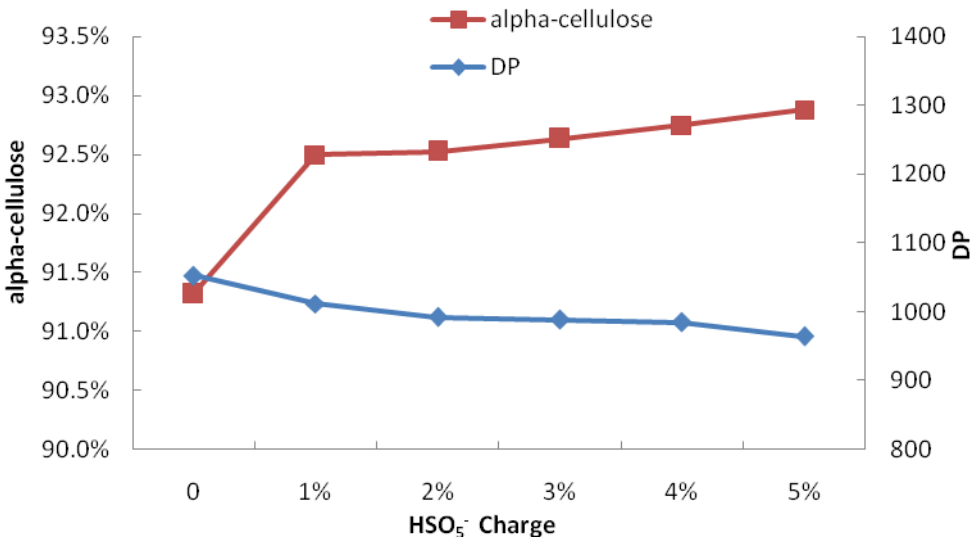


Fig. 5. Effect of the HSO_5^- charge on alpha-cellulose and degree of polymerization for activated oxygen pretreating alkaline hydrogen peroxide

Comparison between Stage Op and Stage M in the Long Sequence

Considerable study has been carried out with respect to DMD bleaching sequences by worldwide researchers. Studies directed by Lee et al. (1993) considered softwood kraft pulp produced via an OMEopQP sequence, and achieved a low kappa number (<3 units) before the final QP brightening stages. Zhang et al. (1998) used the same sequence to bleach Masson pine kraft pulp to 90%SBD brightness. In the MOQMP bleaching sequence, eucalyptus kraft pulp achieved a brightness of 85% (Qin et al. 1998). However, there has been insufficient documentation related to the viscosity or DP of bleached pulp in the long sequence, most of which were only related to brightness. He et al. (2007) obtained acetate bamboo pulp using the XEMEP sequence which had a degree of polymerization of 1021, content of alpha-cellulose 96.2%, and brightness 88.4% ISO.

Table 1. Pulp Properties for Stage M in the long Sequence

	Brightness (%ISO)	Alpha-cellulose (%)	Degree of Polymerization
Original Pulp	37.8	90.1	1449
M-E-Q-M-P-A	68.0	94.5	1460
M-Ep-Q-M-P-A	73.5	94.6	1390
Op-Q-M-P-A	82.0	93.8	804
Op-(AQ)-M-P	78.1	93.5	944
Op-(AQ)-M-P-A	80.2	93.5	928

AQ: pulp will not be washed between the stage A and the stage Q.

As shown in Table 1, the OpQMPA bleaching sequence achieved a 14% higher ISO brightness than the MEQMPA bleaching sequence, but the content of alpha-cellulose and the DP was 0.7% and 650 lower than the latter, respectively. Comparison between the two bleaching sequences mentioned above suggests that compared with oxygen, DMD is both effective and selective as a delignifying agent, but is not as a brightening agent. The difference between MEQMPA and MEpQMPA was a 5.5% brightness increase, showing an advantage of the peroxide-reinforced option.

The bleaching sequences involving acid treatment were also investigated, and the results are summarized in Table 1. The brightness and alpha-cellulose contents were 82.0%ISO and 93.8%, versus 78.0%ISO, and 93.5% for the OpQMPA and Op(AQ)MP sequences, respectively. Acid treatment after the hydrogen peroxide bleaching was helpful to the brightness and alpha-cellulose content. The may because hemicellulose and ash could be reduced in the case of acid treatment. But the degree of polymerization in the case of Op(AQ)MP was higher as compared to the sequence of OpQMPA. This could be due to the fact that metal ions were chelated sufficiently in the non-washed interstage bleaching. And the stage of AQ could reduce the viscosity loss. The Op(AQ)MPA sequence showed better properties as compared to OpQMPA and Op(AQ)MP. This implies that acid treatment can be used both in the middle of a sequence and at the end of a sequence.

The stage M in the long sequence made it possible to achieve a high DP and alpha-cellulose content pulp, but the brightness was far from 90%ISO. So more studies need to be done to get the acetate grade pulp of high alpha-cellulose content (≥96%), high brightness (≥90%ISO), and high DP (≥900).

CONCLUSIONS

Based on the reported results it is concluded that the optimum charges of activated oxygen for delignification and pretreatment were 2.5% AO and 4% HSO_5^-, respectively. Compared with oxygen bleaching, dimethyldioxirane is favorable for increasing the alpha-cellulose content and protect the viscosity, but adverse to increase the brightness. Acid could be employed as both a chelating agent and a purification agent in the process of dissolving pulp.

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