

# Degradation of Lignin and Cellulose Model Compounds by Chlorine Dioxide

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## ABSTRACT

In this paper, five lignin model compounds (vanillyl alcohol, veratryl alcohol, apocynol, veratryl methyl carbinol, biseugenol) and three cellulose model compounds ( $\alpha$ -D-glucose, methyl- $\beta$ -D-glucopyranoside, D-cellobiose) were used to study the degradation rates of lignin and cellulose with chlorine dioxide.

Biseugenol, which has unsaturated structure on the side chain of aromatic ring, was found to react with chlorine dioxide very quickly and consume large amount of chlorine dioxide. Phenolic structures, represented by veratryl alcohol and apocynol, react with chlorine dioxide much faster than nonphenolic structures represented by veratryl alcohol and veratryl methyl carbinol.

The degradations of cellulose models were generally very slight, the order of reaction rate being  $\alpha$ -D-glucose > D-cellobiose > methyl- $\alpha$ -D-glucopyranoside.

## 1. Introduction

It is well known that  $\text{ClO}_2$  is an excellent chemical in delignification and bleaching. Its oxidizing power is high and it reacts with lignin rapidly but very little with cellulose. However, during chlorine dioxide delignification and bleaching, there is still some formation of chlorinated organic compounds. This made it unfavorable to environment. Also the formation of chlorate decreases the effectiveness of delignification and bleaching. These problems can not be solved without deep studies on the delignification and bleaching chemistry.

Studies using model compounds has the great importance in understanding the reaction mechanisms of chlorine dioxide bleaching. Significant

progress has been made in this field both in the early studies<sup>1-5)</sup> and relatively recent ones<sup>6-12)</sup>. These studies, together with those focused on chlorine dioxide ionization has led to the development of various new methods such as additives-used, dual pH, low-kappa factor, higher consistency, and gas phase delignifications which were found to be either more effective or environmentally friendlier. The main lignin model compounds used in this field from the early 1950s and the near 1990s are listed in Fig. 1

Compared with the studies by lignin model compounds, less work has been done on degradation of cellulose model compounds. As early as in the 1920s, Schimidt et al. demonstrated that chlorine dioxide did not react with carbohydrate<sup>13)</sup>. Giertz et al. also established that chlorine dioxide hardly reacted with carbohydrate<sup>14-17)</sup>. It

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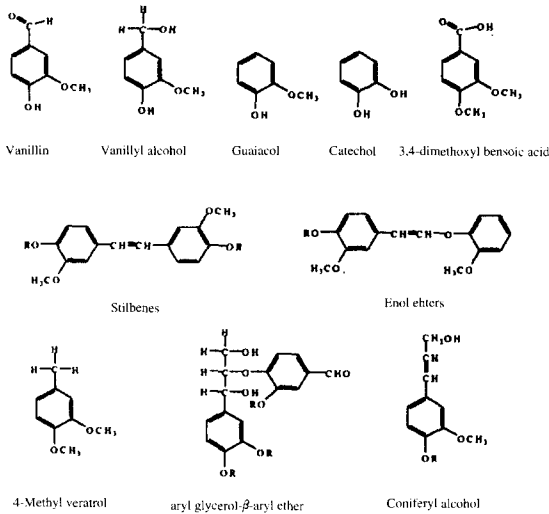


Fig. 1. Main lignin model compounds used from 1950s to 1990s.

was claimed that under acid condition, chlorine dioxide should be completely inactive towards carbohydrates<sup>18</sup>). But it was also reported that glucuronic acid units as well as minor amount of aldonic acid end groups were formed in the cellulose chain during chlorine dioxide treatment<sup>19</sup>). It is also well known that during  $\text{ClO}_2$  bleaching, a substantial decrease in pulp viscosity can be observed when conditions are unfavorable and long residence time is used in chlorine dioxide stage<sup>20</sup>). It was supposed that during chlorine dioxide bleaching, carbohydrates are degraded by acid hydrolysis as well as by the action of chlorine dioxide, especially by the action of hypochlorous acid.

Despite these, the chemical reactions between lignin and chlorine dioxide are still not fully established. The species of lignin model compounds used in mechanism studies are still not sufficient enough for representing the complicated polymeric structure of lignin. Studies by cellulose models are further needed since there is still some decrease of pulp viscosity after chlorine dioxide bleaching, although the extent is rather small compared with other bleaching agents.

In this paper, five lignin model compounds (vanillyl alcohol, veratryl alcohol, apocynol, veratryl methyl carbinol, biseugenol) and three cellulose model compounds ( $\alpha$ -D-glucose, methyl- $\beta$ -D-glucopyranoside, D-cellobiose) were used to study the degradation rates of lignin and cellulose with chlorine dioxide. The next progress will be focused on identifying the decomposed compounds, and setting up the mechanism of delignification.

## 2. Materials and Methods

### 2.1 Model compounds

The model compounds used in this study were shown in Fig. 2. Among them apocynol, veratryl methyl carbinol and biseugenol were synthesized in laboratory because they are not commercially available.

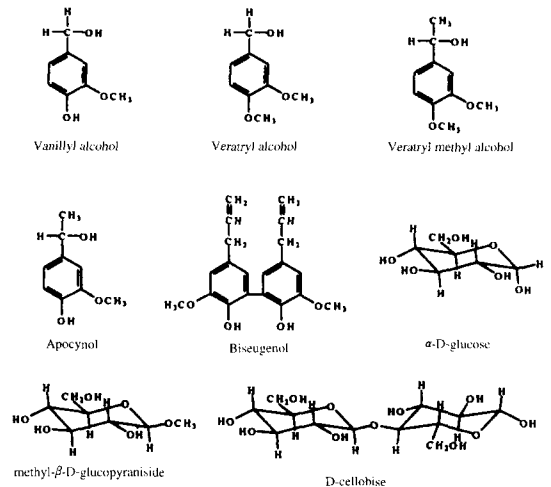


Fig. 2. Structures of Lignin & Cellulose Model Compounds Used in This Study.

#### 2.1.1 Synthesis of Apocyno<sup>[21]</sup>

3.5g acetoguaiacone was dissolved in 106ml 56% ethanol followed by addition of 1.75g sodi-

um borohydride and the reaction was carried out for 10hrs at room temperature after which another 0.5g of sodium borohydride was added and the reaction went on for another 14 hours. The reaction mixture was neutralized with 0.1N HCl solution and was extracted with several portions of ethyl ether. The ether solution was dried with anhydrous sodium sulfate and was concentrated until some crude products appeared. The crude products was dissolved in a small portion of ethanol and it was concentrated into a nujol which was immediately added to a chromatography column filled with silica gel and separated. The eluent used was a 1.0 : 3.8 mixture of benzene and ethyl acetate. The apocynol portion was crystallized into a colorless needle whose melting point is 102-103°C. The needle was checked by <sup>1</sup>H-NMR spectroscopy. The peaks and chemical shifts were δ 1.46-1.49 (d, 3H), δ 1.83 (s, 1H), δ 3.91(s, 3H), δ 4.79-4.89 (q, 1H), δ 5.62 (s, 1H), δ 6.81-6.93 (m, 3H). The yield of this method is 63%.

### 2.1.2 Synthesis of Veratryl Methyl Carbinol

3.60g 3, 4-dimethoxy-acetophone was dissolved in 100 ml 56% ethanol, 1.80g sodium borohydride was added into it and the reaction was carried out for 14 hours at room temperature. The separation and purification procedures are similar as that of apocynol except that 4 : 3 mixture of benzene and ethyl acetate was used as eluent. The product turned out to be a pale yellow nujol which was checked by <sup>1</sup>H-NMR and the peaks and chemical shifts were δ 1.43-1.47 (d, 3H), δ 2.20 (s, 1H), δ 3.84-3.86 (d, 6H), δ 4.76-4.84 (q, 1H), δ 6.78-6.91 (m, 3H). The yield of this method is 75%.

### 2.1.3 Synthesis of Biseugenol<sup>[22]</sup>

10.0g of FeCl<sub>3</sub> · 6H<sub>2</sub>O was dissolved in a flask containing 2000ml distilled water. Eugenol solution (10mL eugenol in 40ml 95% Ethanol) was added into the flask at a speed of 5ml/30min, the

mixture was mechanically stirred during addition. After 24hr, the brown sticky products was collected by filtration and dissolved again in 40ml 95% ethanol and put overnight at 4°C. The crude crystalline was filtrated and recrystallized several times in 95% ethanol in which small amount of acetic acid and active carbon was added. The melting point of pure crystalline is 106°C and it's structure was checked by <sup>1</sup>H-NMR. The peaks and chemical shifts were δ 3.35-3.38 (d, 4H), δ 3.88 (s, 6H), δ 5.05-5.15 (m, 4H), δ 5.88-6.05 (m, 2H), δ 6.03 (s, 2H), δ 6.73-6.75 (d, 4H). Especially, the free phenolic hydroxyl groups which appeared at δ 6.03 duplicated with the multiples at δ 5.88-6.05. Deuteration technique was used to tell them apart. The yield of this synthesis is below 10%.

## 2.2 Preparation of ClO<sub>2</sub> Solution and Determination of the ClO<sub>2</sub> and Cl<sub>2</sub> Concentrations.

Chlorine dioxide was prepared using 40g NaClO<sub>3</sub> and 150g oxalic acid (HCOOCOOH) which were mixed in a 500ml two-neck flask. 100ml H<sub>2</sub>SO<sub>4</sub> solution (H<sub>2</sub>SO<sub>4</sub> : H<sub>2</sub>O = 3 : 1 by volume) was added drop-wise into the flask. Nitrogen gas was streamed through the flask to bring out the produced chlorine dioxide gas which was absorbed in cooled water (under 10°C).

Chlorine was also produced due to the decomposition of chlorine dioxide. The respective contents of chlorine and chlorine dioxide were determined as follows:

15ml 1M KI and 5ml ClO<sub>2</sub> was added to 50ml NaH<sub>2</sub>PO<sub>4</sub> (1M)/Na<sub>2</sub>HPO<sub>4</sub> (1M) buffer solution (pH around 7), 0.02N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> was used to titrate it until colorless after which 5ml 20% H<sub>2</sub>SO<sub>4</sub> was added and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution was used again to titrate to the new end point. The calculation was as follows:

$$\text{g ClO}_2/\text{liter} = A \times 0.0676 \quad (1)$$

$$\text{g Cl}_2/\text{liter} = (T - 1.25A) \times 0.142 \quad (2)$$

Where T is the burette reading of total  $\text{Na}_2\text{S}_2\text{O}_3$  consumption, it is used for all the chlorine and chlorine dioxide; A is the burette reading at acidic condition, it is used for four-fifth of the chlorine dioxide.

It turned out that about 8% of the oxidation power was supplied by chlorine in the chlorine dioxide solution made above.

### 2.3 Decomposition of Lignin and Cellulose Model Compounds and HPLC Analysis

The model compounds were treated with  $\text{ClO}_2$  in homogenous solutions. The reactions were carried out respectively 1, 5, 20, 40, 60, 100, 140, and 180min at  $70^\circ\text{C}$ , after which  $\text{Na}_2\text{S}_2\text{O}_3$  solutions were added to stop the reactions and the reacted solutions were diluted into volume flasks, ultra-filtrated by membrane filter ( $0.45\mu\text{m}$ ) and analyzed by HPLC. 50% ethanol was used to dissolve vanillyl alcohol, veratryl alcohol, apocynol and veratryl alcohol, while 95% ethanol solution was used for biseugenol and water was used for the cellulose models. In lignin model analysis Waters 600S was used, the column was Nova-Pak C18 ( $60\text{\AA}$ ,  $3.9\text{mm} \times 300\text{mm}$ ), 70% acetonitrile in water was used as eluent for biseugenol and 35% acetonitrile in water was used for other lignin model compounds, other conditions were: temperature  $26^\circ\text{C}$ , flow rate 1.0 ml/min, UV280nm detector. And in cellulose model analysis, Waters 510 was used, the column was Sugar-Pak I ( $6.5\text{mm} \times 300\text{mm}$ ), water was used as eluent and other conditions were: temperature  $80^\circ\text{C}$ , flow rate 0.5ml/min, RI detector.

## 3. Results and Discussion

### 3.1 Decomposition of Vanillyl alcohol and Apocynol with $\text{ClO}_2$

It was seen from Fig. 3 that vanillyl alcohol

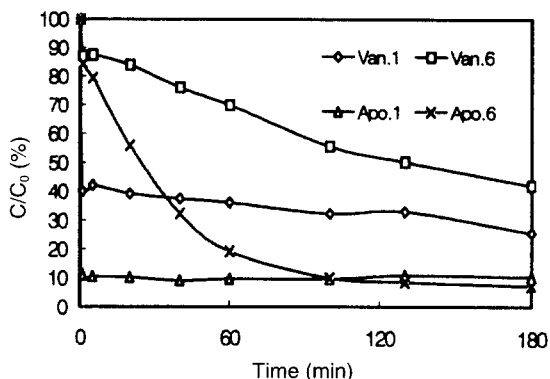


Fig. 3. Degradation of vanillyl alcohol and apocynol with chlorine dioxide at  $70^\circ\text{C}$ . (Van. 1 means the mole ratio of vanillyl alcohol to chlorine dioxide was 1 while Van. 6 means the mole ratio of vanillyl alcohol to chlorine dioxide was 6. Others are the same.)

and apocynol decomposed very quickly at the beginning of the reaction (within 5 minutes). Apocynol decomposed more quickly than vanillyl alcohol. Apocynol has a methyl group in the side chain while vanillyl alcohol does not, the presence of methyl in the side chain of apocynol contributes to increase the electron density of its  $\alpha$  carbon and also possibly to benzene ring, which may make the ring to be more easily cleaved. However, the exact reason remained to be settled in our on-going study.

But in the figure it seems strange that more apocynol was consumed in Apo. 6 (the mole ratio of apocynol to chlorine dioxide is 6) than Apo. 1 (the mole ratio of apocynol to chlorine dioxide is 1) after 90min decomposition. It may be thought apocynol, when in excess, was consumed not only by  $\text{ClO}_2$  (including  $\text{HClO}_2$  and  $\text{HClO}$  produced as intermediate) but also by some other reactions, for example, by combination or condensation with various other intermediates. Various side reactions of apocynol were known to be apt to take place when we synthesized this compound.

### 3.2 Degradation of Biseugenol with Chlorine Dioxide

From Fig. 4 it was seen that biseugenol was consumed even faster than what we observed in Fig. 3 at the beginning of reaction.  $\text{ClO}_2$  is consumed so quickly that after 30min biseugenol almost remained unchanged. Even in the case of Bis. 1/2 where the mole ratio of biseugenol to  $\text{ClO}_2$  is 1/2, there was still about 15% of biseugenol remained. This indicates that large amount of  $\text{ClO}_2$  is needed to consume all the biseugenol. Gierer and coworkers<sup>7, 8)</sup> reported that conjugated structures like stilbene and styrenes were attacked by chlorine dioxide almost exclusively on the olefinic parts, even when the aromatic moieties are phenolic groups as in the case of diguaiacyl-stilbene. Biseugenol was thought to have the same behavior since it also has unsaturated double bonds in its side chains. The result also indicates that structures with unsaturated double bonds should be eliminated as much as possible in pulping processes rather than bringing them to bleaching stages.

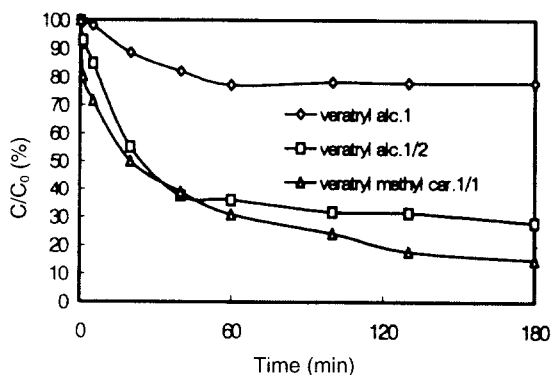


Fig. 4. Degradation of biseugenol with chlorine dioxide at 70°C.

At the very first, biseugenol was chosen in this study in order to find out whether 5-5 linkage can be destroyed in  $\text{ClO}_2$  treatment. However, further efforts, e. g., separation, purification, and instrumental identification have to be used in

order to attain this aim.

### 3.3 Degradation of Veratryl Alcohol and Veratryl Methyl Carbinol with $\text{ClO}_2$

Comparing Fig. 5 with Fig. 3, it can be seen that non-phenolic structures decompose much more slowly than phenolic structures do. In Fig. 3, both veratryl alcohol and veratryl methyl carbinol decomposed in a kind of near-exponential way.

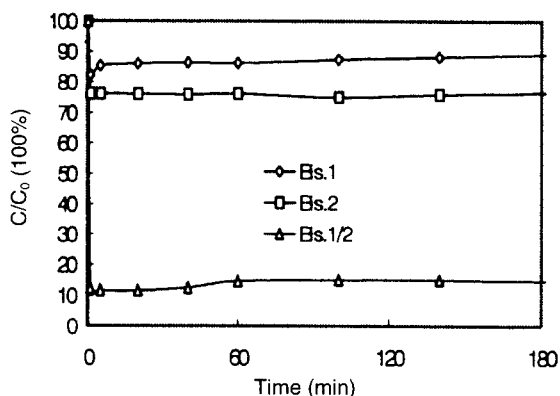


Fig. 5. Degradation of veratryl alcohol and veratryl carbinol with chlorine dioxide at 70°C.

The decomposition of veratryl methyl carbinol was quicker than that of veratryl alcohol, the reason of which is assumed to be same as that of apocynol and vanillyl alcohol.

### 3.4. Degradation of Cellulose Model Compounds with $\text{ClO}_2$

From Fig. 6 it was seen that small amount of decomposition happened during decomposition of cellulose models, the rate of which being D-glucose > D-cellobiose > methyl- $\beta$ -D-glucopyranoside. This may be interpreted as in Fig. 7, where  $\text{C}_1$  oxidation was thought to be the main reason of cellulose model decomposition. The

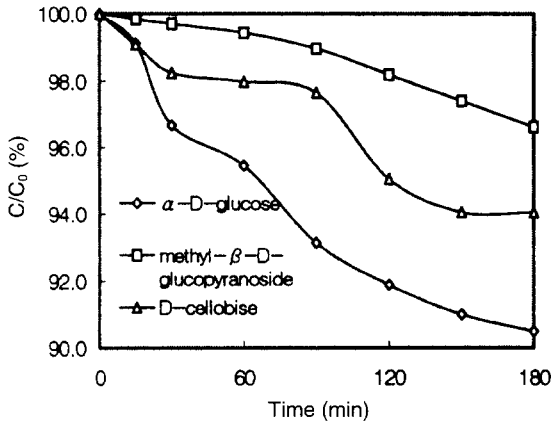


Fig. 6. Degradation of cellulose model compounds with chlorine dioxide at 70°C

hemiacetal ring in glucose or cellobiose opens to its aldehyde form that is relatively easier to be oxidized into the carboxylic form. Thus methylation or etherification should be able to improve the stability of cellulose. This is proved by the fact that methyl- $\beta$ -D-glucopyranoside turned out to be the most stable one, though the glucopyranoside form is also degradable at the attack of chlorine which is produced from the intermediate hypochlorous acid during bleaching as the below part of Fig. 7 shows.

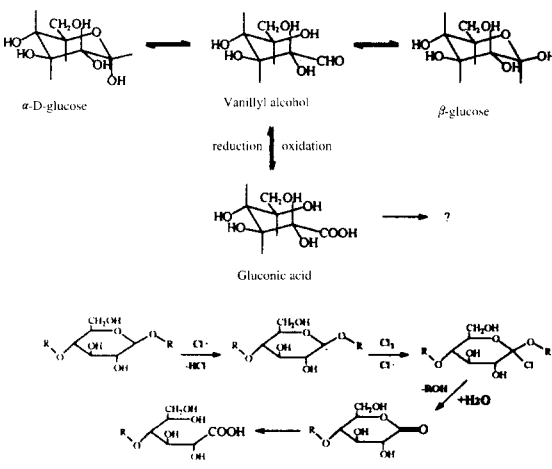


Fig. 7. Illustration of oxidation of cellulose models during chlorine dioxide bleaching.

It should be noticed that  $\text{ClO}_2$  was supplied in great excess (cellulose models and  $\text{ClO}_2$  in same mole ratio) compared with the real bleaching system. In industrial delignification or bleaching level, much less degradation of cellulose should be expected.

## 4. Conclusions

In this paper, the chemistry of chlorine dioxide delignification, especially the decomposition of lignin and cellulose model compounds by chlorine dioxide was studied to supply some basic data for developing environmentally friendly ECF bleaching methods.

Biseugenol, which has unsaturated structure on the side chain of aromatic ring, was found to react with chlorine dioxide very quickly and consume large amount of chlorine dioxide. Phenolic structures, represented by veratryl alcohol and apocynol, react with chlorine dioxide much faster than nonphenolic structures represented by veratryl alcohol and veratryl methyl carbinol.

The degradations of cellulose models were generally very slight, the order of reaction rate being D-glucose > D-cellobiose > methyl  $\beta$ -D-glucopyranoside.

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