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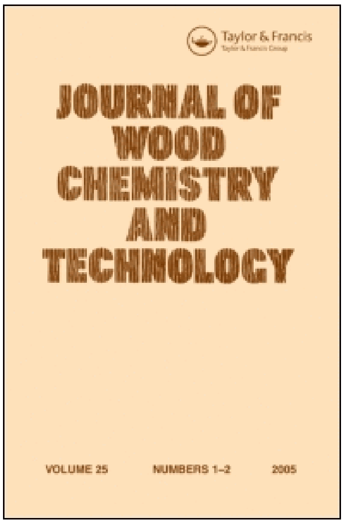

Journal of Wood Chemistry and Technology

Publication details, including instructions for authors and subscription information:
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To cite this Article Yasumoto, Mitsuo , Matsumoto, Yuji and Ishizu, Atsushi(1996) '1. Factors Influencing the Reaction Selectivity between Carbohydrate and Lignin Model Compounds', Journal of Wood Chemistry and Technology, 16: 1, 95 — 107

To link to this Article: DOI: 10.1080/02773819608545785

URL: http://dx.doi.org/10.1080/02773819608545785

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JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 16(1), 95-107 (1996)

THE ROLE OF PEROXIDE SPECIES IN THE CARBOHYDRATE DEGRADATION DURING OXYGEN BLEACHING

1. FACTORS INFLUENCING THE REACTION SELECTIVITY BETWEEN CARBOHYDRATE AND LIGNIN MODEL COMPOUNDS

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ABSTRACT

A cellulose model compound, methyl β-D-glucopyranoside (MGP), was subjected to oxygen-alkali treatment in the presence of various kinds of lignin model compounds. Only in the presence of a lignin model compound reactive with oxygen, a significant degradation of MGP was observed and the rate and the extent of its degradation were strongly dependent on the structure and the amount of a lignin model compound. Depression of MGP degradation was found to be achieved by two clearly distinguished mechanisms. One is an enhancement of the degradation of a lignin model compound without the acceleration of MGP degradation and the other is a depression of MGP degradation without significantly deteriorating the degradation of a lignin model compound. An increase in oxygen pressure and a 10% methanol addition belonged to the former case and a change in the ratio of metal ions and a 1% methanol addition belonged to the latter case. The addition of magnesium sometimes resulted in the acceleration of MGP degradation, depending on its ratio to iron.

INTRODUCTION

In past decades, the reaction of lignin with oxygen in alkali media has been extensively studied using lignin model compounds representing the structural features of both natural lignin and residual lignin in kraft pulp1). Based on this knowledge, it is possible to discuss why oxygen bleaching can not completely remove lignin from kraft pulp2,3). Recent studies on the degradation of lignin model compounds under various reaction conditions provide a new insight into active species which are responsible for lignin degradation during oxygen bleaching4,5,6).

The degradation of carbohydrates during oxygen-alkali treatment also has been studied and many results have been obtained. It is generally accepted that non-reducing end-groups and non-terminal glucose residues of cellulose are quite stable towards oxygen under the bleaching condition although reducing end groups are easily oxidized by oxygen. Therefore, in order to explain a rapid viscosity drop during oxygen bleaching, two mechanisms have been considered. One is a mechanism due to the formation of active species by reactions between oxygen and lignin. On the basis of extensive experiments using methyl β-D-glucopyranoside (MGP) and cellulose, Ericsson and his coworkers concluded that reactions between lignin and oxygen produce active oxygen species which in turn degrade carbohydrates, and the role of transition metal ions was to accelerate the formation of active oxygen species7). Minor confirmed the formation of peroxides during oxygen bleaching and found that the reduction of peroxides led to a depression of viscosity drop8). Another mechanism proposed for the degradation of non-terminal glucose residues is an auto-oxidation type mechanism9,10). In this mechanism, a reaction, probably a direct reaction between non-terminal glucose residues and oxygen, is assumed to play a role as an initiator of a chain reaction by the production of active species such as organic peroxyl radicals or peroxides.

The improvement of the reaction selectivity between lignin and carbohydrates is also an important topic. When active species are produced from reactions of lignin and oxygen, they must react not only with carbohydrates but also with lignin. For example, Gierer, Reitberger and their co-workers have already confirmed that hydroxyl radical, which can be produced from hydrogen peroxide or organic peroxides during oxygen bleaching, is responsible for the delignification reaction as well as for the carbohydrate degradation$^{11)}$. Therefore, the reaction selectivity can not be simply improved only by the depression of the formation of such active species. It is important to evaluate how an enhancement or a depression of the formation of such active species effects the degradation of both carbohydrates and lignin. In the present report, MGP was treated with oxygen-alkali under a bleaching condition in the presence of various types of lignin model compounds. First, we tried to clarify how MGP degradation depended on the structure and the amount of co-existing lignin model compounds. The ratio of transition metal ions, the oxygen pressure and the content of methanol in the reaction solvent were varied, and their effects on the reaction selectivity as well as on the degradation rate of both MGP and lignin model compound were examined. In this report, the reaction selectivity is expressed as the amount of recovered MGP at a certain consumption of lignin model compounds. Based on the results obtained here, the presence of two mechanisms which lead to a better reaction selectivity will be suggested.

EXPERIMENTAL

Dependence of MGP Degradation on Lignin Model Structure

A solution of MGP (0.2 mmol) in 50 ml of 0.5 N NaOH containing 20 ppm of ferric ions was heated at 95℃ in a glass autoclave together with 0.3 mmol of each lignin model compound under 3 kgf/cm^2 of oxygen pressure for the prescribed time. Remaining MGP was gas chromatographically determined as the acetyl derivative with inositol as an internal standard.

Factors Affecting The Reaction Selectivity

The standard condition for the oxygen degradation of MGP was, unless otherwise stated, as follows. MGP (1.2 mmol), vanillyl alcohol (VA, 1.8 mmol) and ferric chloride (6 mg as ferric ion) was mixed in 300 ml of 0.5 N NaOH and transferred into a stainless autoclave coated with Teflon. Under 3 kgf/cm^2 of oxygen pressure the reaction mixture was heated to 95℃ from room temperature in 30 min and then kept at this temperature for up to 5 hours with stirring. During the reaction, portions of the reaction mixture were collected through a pressure sealing valve at the prescribed time and subjected to the determination of remaining MGP and VA as previously described. Instead of standard condition, *10 kgf/cm^2 of oxygen pressure, or 1 and 10% aqueous methanol* as solvent were also applied. For experiments of magnesium addition, magnesium chloride was added with molar ratios of magnesium to iron 1.0, 2.0, 7.0, 11.0 and 16.0. As iron and magnesium, a standard solution for the atomic absorption (Wako Chemical Co.,) was used. Purity of NaOH used (Aldrich Chemical Co.,) was more than 99.99%. All water used in this section was deionized by an ion exchanger and purified by membrane filter.

RESULTS AND DISCUSSION

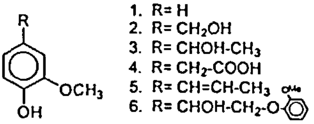
Dependence of MGP Degradation on Lignin Model Structures and on Their Amount

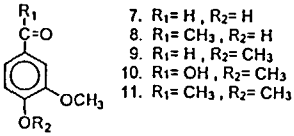
Table 1 shows the stability of MGP in the presence of lignin model compounds and iron. As will be described later, MGP is rather stable even in the presence of iron, if a lignin model compound is not present. Its degradation was significant in the presence of lignin model compounds reactive to oxygen-alkali treatment ; these included catechol and guaiacyl type compounds having a phenolic hydroxyl group except those having a carbonyl group at the α-position. Bis(p-hydroxyphenyl)methane, a model of a condensed structure produced secondarily during alkaline cooking, was very reactive and caused the degradation of MGP.

Aoyagi and his coworkers reported that a non-phenolic β-O-4 type lignin model compound carrying an α-carbonyl group is degraded by oxygen-alkali under an oxygen pulping condition (high temperature), because of the presence of a methylene group activated by the adjacent carbonyl group12). Therefore,

TABLE 1
Effect of Structures of Lignin Model Compounds on MGP Degradation

Lignin model compounds[a)]	Recovered MGP (%)
Blank	96
1. Guaiacol	53
2. Vanillyl alcohol	69
3. Apocynol	49
4. Homovanillic acid	61
5. Isoeugenol	63
6. Guaiacylglycol-β-guaiacyl ether	52
7. Vanillin	98
8. Acetoguaiacone	94
9. Veratraldehyde	96
10. Veratric acid	104
11. Acetoveratrone	98
12. Dibenzoylmethane	80
13. Bis(p-hydroxyphenyl)methane	54
14. Ethylguaiacol-α-veratrol	61
15. Catechol	50
16. Dibasic acids [b)]	99





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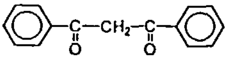

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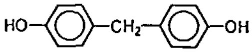

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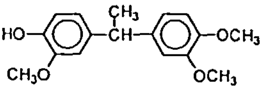

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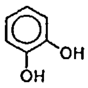

a) compound 6 and 14 were synthesized according to the methods of Hosoya[17)] and Watanabe[18)], respectively. Other compounds were commercially available.

b) an equimolar mixture of oxalic acid, t,t-muconic acid, malonic acid, malic acid, fumalic acid and maleinic acid.

compounds carrying a carbonyl group were anticipated to cause the degradation of MGP. However, as shown in Table 1, non-phenolic model compounds such as acetoveratrone and a mixture of dibasic acids containing malonic acid did not cause the degradation of MGP. Malonic acid has a methylene group substituted by two carboxyl groups and acetoveratrone has a methyl group activated by a keto group. On the other hand, dibenzoylmethane having a methylene group

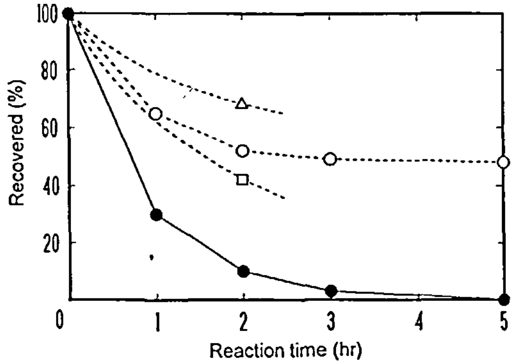

FIGURE 1 Effect of The Amount of Apocynol on MGP Degradation
------: recovered MGP under molar ratio of apocynol to MGP
△ : 0.5 ○ : 1.5 □ : 3.0
—●—: recovered apocynol under molar ratio of apocynol to MGP1.5

substituted by two benzoyl groups was not stable and caused the degradation of MGP, although the extent of MGP degradation in this case was less than those for the other easily oxidizable compounds.

Previously, Ericsson and his coworkers7) reported that a marked degradation of MGP occurred by the addition of hydroquinone, p-methoxyphenol, guaiacol, catechol or benzoquinone in the presence of iron. Our results also support such a degradation mechanism of carbohydrates in which easily oxidizable compounds are converted to peroxides, which are in turn decomposed by iron to yield active oxygen species reactive to carbohydrates. Figure 1 shows that the increase in the amount of a reactive phenolic compound enhances the degradation of MGP. After apocynol disappeared completely, MGP decomposed only to a minor extent. This suggests that active oxygen species harmful to carbohydrates are formed only during the first conversion of apocynol to some degradation products and during further degradation period no harmful species are formed.

Results obtained in this section seem to deny the direct reaction between glucose residue and oxygen as an initiation reaction of auto-oxidation type degradation of carbohydrates10) during oxygen bleaching. Active species such as hydrogen peroxide and organic peroxides are produced much easier by the

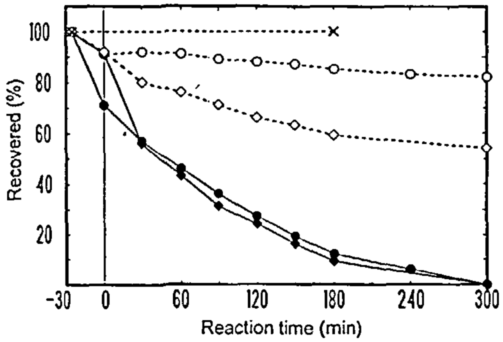

FIGURE 2 **Effect of Iron and VA on MGP Degradation**

······ : recovered MGP under
× : VA (-), Fe (-)
○ : VA (+), Fe (-)
◇ : VA (+), Fe (+) ~ standard condition
——— : recovered VA under
● : MGP (+), Fe (-)
◆ : MGP (+), Fe (+) ~ standard condition

reaction of lignin with oxygen than by the reaction of carbohydrate with oxygen. Furthermore, because lignin is thought to play a role as an anti-oxidant reagent by reacting with such active species faster than glucose residue, a prolongation of the auto-oxidation type reaction of cellulose without the participation of lignin does not seem to be real. Therefore, even though a direct reaction of cellulose non-terminal unit and oxygen is not completely prohibited, this reaction can not be a main reason for viscosity drop during oxygen bleaching.

Effect of Iron and Vanillyl Alcohol on The Degradation of MGP

MGP was treated in oxygen-alkali either with or without iron and vanillyl alcohol (VA). As is shown in Figure 2, in the presence of both iron and VA (under the standard condition) MGP was degraded and the recovery of MGP was about 55%, when VA disappeared completely. When iron was removed from the

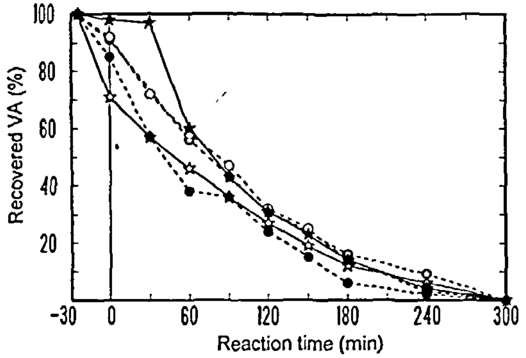

FIGURE 3 Effect of Magnesium to Iron Ratio on VA Degradation

○ : Mg/Fe = 2
o : Mg/Fe = 7
● : Mg/Fe = 16
★ : Fe(+), Mg(-)
☆ : Fe(-), Mg(-)

reaction mixture, MGP recovery was significantly improved. It should be noted that, in these two cases, no significant difference was observed for the degradation of VA, indicating that the reaction selectivity was improved by the removal of iron. On the other hand, without the presence of both iron and VA, no degradation was observed for MGP, which coincides with the results of the previous section.

Effect of The Ratio of Magnesium to Iron on The Degradation of MGP

Hydrogen peroxide bleaching is widely used in the bleaching of high-yield pulps and the addition of magnesium salts is known to be effective for retarding the viscosity drop of pulp, which is caused by hydroxyl and superoxide anion radicals produced from hydrogen peroxide in the presence of heavy metal salts. Isbell and his coworkers[13)] found that magnesium salts form a complex with iron salts in molar ratio of 6:1 and suggested that the removal of iron by the formation of this complex inhibits the formation of free-radicals from hydrogen peroxide. As to the effect of the ratio of metal ions, Abbot and his co-workers recently

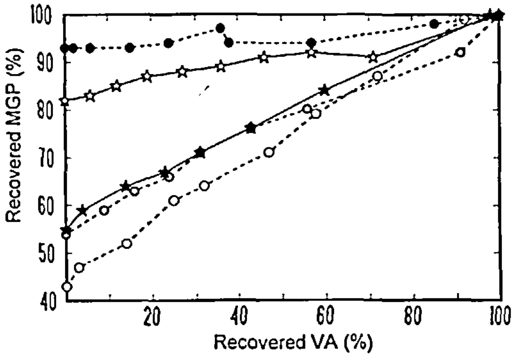

FIGURE 4 Effect of Magnesium to Iron Ratio on The Reaction Selectivity

○ : Mg/Fe = 2
o : Mg/Fe = 7
● : Mg/Fe = 16
★ : Fe(+), Mg(-)
☆ : Fe(-), Mg(-)

showed that the degradation of hydrogen peroxide is affected by the ratio between transition metal and magnesium, and implied that the protective effect of magnesium during peroxide bleaching lies here$^{14)}$.

The effect of magnesium addition on the degradation of both VA and MGP was examined under various ratios of magnesium to iron. Although magnesium to iron ratio did not affect the degradation rates of VA as significantly as the enhanced oxygen pressure or the 10% methanol addition did, a great difference was observed as to the degradation of MGP (Figures 3 and 4). When the ratio is high (16 to 1), the recovery of MGP was much higher than the case without iron. Contrary to this, the addition of magnesium with the ratio of 2:1 gave worse reaction selectivity than the standard case (with iron and without magnesium). In Figure 5 MGP recovery at 3 hr of reaction time is plotted against Mg to Fe ratio. The minimum of recovery is observed at Mg to Fe ratio of 1 ~ 2. One possible explanation for this result is that some peroxide species are degraded most rapidly at this Mg to Fe ratio and produce a maximum yield of radical species harmful to carbohydrates. Another possible explanation is that a stabilization of peroxide by magnesium does not always result in the protection of MGP. Further experiment is required to explain this interesting bi-functional effect of magnesium.

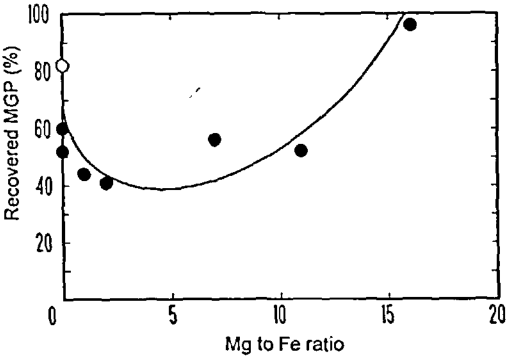

FIGURE 5 Effect of Mg to Fe Ratio on MGP Degradation
(MGP was determined after 3 hr of reaction)
○ : no addition of Fe

Effects of Enhanced Oxygen Pressure and Methanol Addition to Solvent on MGP Degradation

Abrahamson and Samuelson[15)] showed that a higher oxygen pressure during oxygen pulping gives a pulp with higher viscosity and, later, Lindgren implied the reason for this to be radical scavenging effect of oxygen[16)]. An addition of an organic solvent to the reaction mixture could lead to the same effect as enhanced oxygen pressure because of the increased solubility of oxygen. In addition to this, methanol itself could play a role as a radical scavenger through formation of methylol radical, and thus could improve the reaction selectivity.

Therefore, both the increase in oxygen pressure and the addition of methanol were expected to improve the reaction selectivity between MGP and VA. As is shown in Figure 6, both the increase in oxygen pressure and the methanol addition resulted in a better reaction selectivity than the standard run. It was quite interesting that the improvement of the reaction selectivity resulted apparently from two different mechanisms. When oxygen pressure was increased to 10 kgf/cm^2 or 10% methanol was added, the degradation of VA was greatly enhanced while MGP degradation was affected only slightly (Figure 7). Therefore, the improvement of the reaction selectivity was mainly attributed to

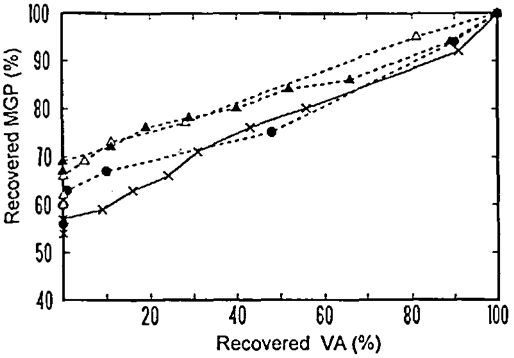

FIGURE 6 Effect of Oxygen Pressure and Methanol Addition on The Reaction Selectivity

× : standard condition
● : 10 kgf/cm^2 O$_2$ pressure
△ : 10% methanol
▲ : 1% methanol

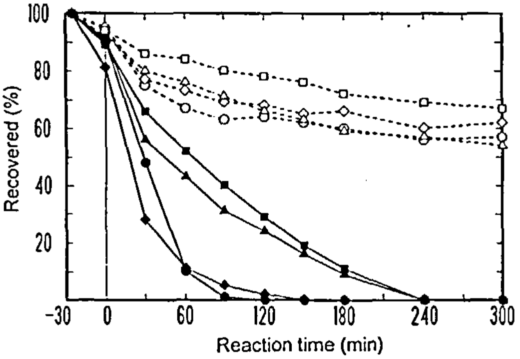

FIGURE 7 Effect of Oxygen Pressure and Methanol Addition on The Degradation of VA and MGP

------: recovered MGP under
△ : standard condition
○ : O$_2$ pressure 10 kgf/cm^2
◇ : 10% aqueous methanol
□ : 1% aqueous methanol
——: recovered VA under
▲ : standard condition
● : O$_2$ pressure 10 kgf/cm^2
◆ : 10% aqueous methanol
■ : 1% aqueous methanol

the enhancement of the degradation rate of VA. On the other hand, in the presence of 1% methanol, the degradation of VA was not significantly affected while the degradation of MGP was greatly reduced (Figure 7). Therefore, the improvement of the reaction selectivity by 1% methanol can be attributed to the reduced MGP degradation. This phenomenon is similar to the effect which was observed when the magnesium to iron ratio was increased greatly.

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