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REACTION SELECTIVITY OF ACTIVE OXYGEN SPECIES IN OXYGEN-ALKALI BLEACHING¹

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ABSTRACT

A non-phenolic lignin model compound, 3,4-dimethoxybenzyl alcohol (veratryl alcohol, VA), and a carbohydrate model compound, methyl β -D-glucopyranoside (MGP), were subjected together to the reaction with active oxygen species which were generated by an oxygen-alkali oxidation of a phenolic compound, 2,4,6-trimethylphenol (TMPH), at different temperature or different pH. The reaction selectivity of active oxygen species between VA and MGP ($\Delta VA/\Delta MGP$) under these conditions were examined. The rates of VA and MGP degradation were similar at 70°C while the degradation of MGP was much faster than that of VA at 95°C. This result indicates that active oxygen species produced at 70°C and at 95°C are different. The degradation of MGP was greater and the reaction selectivity between VA and MGP was lower (undesirable for the carbohydrate protection) when the initial reaction pH was increased. These results clearly demonstrate that the reactivity of active oxygen species produced during oxygen bleaching is significantly dependent on reaction conditions, the reaction temperature and the pH of the solution.

INTRODUCTION

Oxygen delignification processes have been widely used as a prebleaching stage, but there is a technical limitation for the process because of the carbohydrate degradation. It is confirmed that molecular oxygen is not directly involved in the degradation of carbohydrate.^{2,3,4} Active oxygen species, which are secondary reaction products of lignin and molecular oxygen, are responsible for the degradation of carbohydrate, and also for the delignification. Reducing end groups of carbohydrate are also known to generate active oxygen species by the reaction with molecular oxygen under oxygen bleaching conditions.⁵ Hence, it is important to examine the relative reactivity of active oxygen species with lignin and carbohydrate, in other words, the reaction selectivity of active oxygen species between lignin and carbohydrate. Ek and co-workers concluded that hydroxyl radical ($\text{HO}\cdot$) degrades the non-phenolic lignin model compounds five or six times faster than the carbohydrate model compounds.⁶ Their results seem to have been widely accepted as a reaction selectivity of active oxygen species between lignin and carbohydrate during actual oxygen bleaching process. However, it is not reasonable to generalize their results to actual oxygen bleaching because the reaction conditions employed in their experiments are quite different from actual oxygen bleaching, and active oxygen species produced during actual oxygen bleaching can not be restricted to hydroxyl radical. In our recent study, it was confirmed that the carbohydrate model compounds with different number and different kind of hydroxyl groups have different reactivity toward active oxygen species produced under oxygen bleaching conditions.⁷ The structural variety of the model compounds examined in their report must be insufficient to draw a general conclusion.

In the present report, we examine the relative reactivity of active oxygen species toward a non-phenolic lignin model compound, 3,4-dimethoxybenzyl alcohol (veratryl alcohol, VA), and a carbohydrate model compound, methyl β -D-glucopyranoside (MGP), during oxygen-alkali treatments at different temperatures or different pHs. The dependence of the reaction selectivity of active oxygen species between VA and MGP ($\Delta VA/\Delta MGP$) and the production of these species on the reaction conditions are presented.

The reaction of molecular oxygen with a phenolic compound, 2,4,6-trimethylphenol (TMPH), was used as a source of active oxygen species in this study. The benefits of this approach are that the effects of the reaction conditions not only on the reactivity of active oxygen species but also on the production of these species can be examined. The chemical structures of VA, MGP and TMPH are illustrated in FIGURE 1.

EXPERIMENTAL

Materials and Reaction Vessel

VA, MGP and TMPH, were purchased from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan). MGP and TMPH were recrystallized twice from ethanol and VA was vacuum distilled before use. Their purities were confirmed by NMR and gas-chromatography. As a source of iron, ultra-high purity ferric chloride purchased from Aldrich Chemical Co., Inc. (Milwaukee, WI) was used. Ultra-high purity sodium hydroxide (99.99+%) was purchased from Aldrich Chemical Co., Inc. Water was deionized and purified by the ultra-pure water generator operating by the reverse osmotic pressure (Japan Organo Co., Ltd., Tokyo).

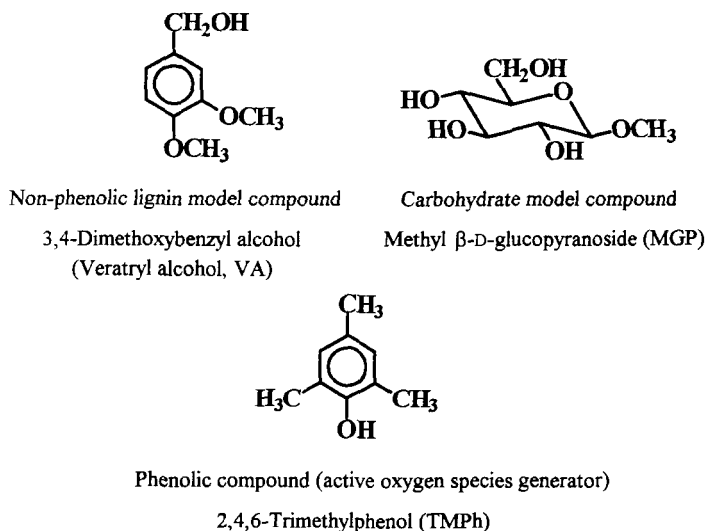


FIGURE 1 Chemical structures of VA, MGP and TMPH

The inside of the reaction vessel and the lid were covered by an approximately 0.5 mm thick Teflon lining. The reactor was equipped with a high quality stirrer (made by Teflon) which was operated at about 400 rpm during the reaction. The reaction mixture was sampled through the pressure-sealing valve without interfering with the reaction.

Oxygen-Alkali Treatment

A reaction solution contained FeCl_3 (0.36 mmol/L), VA (4 mmol/L), MGP (4 mmol/L) and TMPH (9 mmol/L). The pH of the reaction mixture at room temperature was adjusted to 11.78, 12.22, 12.38, 12.82 and 13.1 by NaOH. The

TABLE 1
Reaction Conditions Employed in This Study
(O₂ pressure 1.1 MPa)

	Temperature (°C)	Initial pH	Final pH
To examine the effect of temperature	70	13.1	13.1
	95	13.1	13.1
To examine the effect of pH	95	11.78	8.61
	95	12.22	10.38
	95	12.38	11.91
	95	12.82	12.79
	95	13.1	13.1

volume of the reaction solution was 300 mL. The reaction solution was transferred into the reaction vessel and oxygen was introduced to a pressure of 1.1 MPa. Under this pressure, the reaction solution was heated up to 70°C or 95°C from room temperature in 8 or 9 min, respectively, and then kept at these temperatures for 360 min with stirring. The reaction conditions are listed in TABLE 1. Several mL of the reaction solution was recovered periodically for the determination of residual VA, MGP and TMPH, and the pH of the solution. Residual VA and MGP were determined by gas-chromatography as their acetyl derivatives, and residual TMPH was determined by gas-chromatography without derivatization.

RESULTS AND DISCUSSION

The reaction of molecular oxygen with TMPH was used to generate active oxygen species in our reaction system, as mentioned in the introduction. One

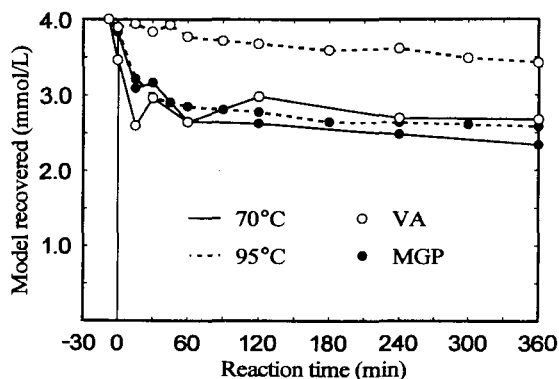


FIGURE 2 Effect of reaction temperature on the degradation of VA and MGP when these compounds are subjected to this reaction system (Initial TMPH conc. 9 mmol/L, Alkali conc. 0.5 mol/L)

benefit of this system is that the variety and the reactivity of active oxygen species produced should be almost the same to those produced in actual oxygen bleaching process. By subjecting VA and MGP to this system, the dependence of the production of active oxygen species and their relative reactivity on reaction temperature and reaction pH in actual oxygen bleaching process can be simulated.

FeCl_3 was added in all the treatments examined in this report in order to enhance the production of active oxygen species from secondarily produced peroxides.⁸

Effect of Temperature on the Reaction Selectivity

FIGURE 2 shows the degradation behaviors of VA and MGP at 70°C and at 95°C. The alkali concentration was 0.5 mol/L (pH=13.1). The extents of

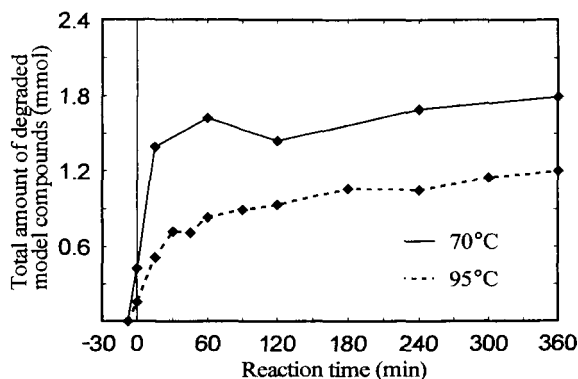


FIGURE 3 Effect of reaction temperature on the total amount of degraded VA and MGP when these compounds are subjected to this reaction system (Initial TMPH conc. 9 mmol/L, Alkali conc. 0.5 mol/L)

degradation of VA and MGP were similar during the reaction at 70°C, as can be seen from FIGURE 2. In contrast, the degradation of MGP was much faster than that of VA at 95°C. The degradation of VA was suppressed at 95°C. The total amount of degraded VA and MGP was different at 70°C and at 95°C. It was larger at 70°C than at 95°C, as can be seen from FIGURE 3. These phenomena clearly indicate that active oxygen species produced at 70°C and at 95°C are different. Active oxygen species produced at 70°C degrade VA and MGP unselectively, but those produced at 95°C degrade MGP selectively and have a lower reactivity toward VA. Therefore, as far as the reactivity of active oxygen species is concerned, the oxygen-alkali treatment at 70°C is more advantageous than that at 95°C when the alkali concentration is as high as 0.5 mol/L (pH = 13.1).

The degradation of VA and MGP are divided into two phases except the degradation of VA at 95°C. A rapid degradation of the model compounds occurs

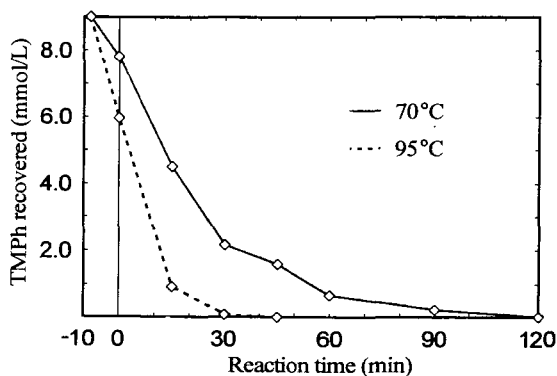


FIGURE 4 Effect of reaction temperature on the degradation of TMPH, an active oxygen species generator, in this reaction system (Initial VA and MGP conc. 4 mmol/L, Alkali conc. 0.5 mol/L)

in the first phase and a slow or only a little degradation of the model compounds occurs in the second phase. The degradation of VA at 95°C seems to have one phase in which only a slow degradation occurs. This result must demonstrate that a part of VA degradation is due to the direct reaction of active oxygen species produced at 95°C, and a main route of VA degradation at 95°C is a radical chain oxidation reaction, as the case of MGP degradation in the second phase at 95°C.

The degradation behaviors of TMPH, which was used as an active oxygen species generator in this reaction system, at 70°C and at 95°C are shown in FIGURE 4. Since the degradation of TMPH at 95°C is much faster than at 70°C, the production of active oxygen species at 95°C should be faster than at 70°C. However, the degradation of VA and MGP at 95°C was slower than that at 70°C. This may suggest that the amount of active oxygen species produced at 95°C is smaller than that at 70°C or a large amount of active oxygen species is consumed by TMPH itself at 95°C.

Effect of pH on the Reaction Selectivity

Among active oxygen species suspected to be produced during oxygen bleaching, hydroxyl radical ($\text{HO}\cdot$) is the strongest oxidant, and is believed to be a main chemical species responsible for the degradation of pulp components as a side reaction.⁹ The majority of hydroxyl radical is ionized to oxygen anion radical ($\text{O}\cdot^-$) when the pH of the solution exceeds 11.9, the pK_a value of hydroxyl radical. It is known that the reactivity of hydroxyl radical and oxygen anion radical is different, and the addition of hydroxyl radical to aromatic rings is very fast while oxygen anion radical degrades aromatic and aliphatic moieties by about the same degree.¹⁰ In addition, since peroxides (organic and/or inorganic), which are precursors of hydroxyl radical, are also ionized to the anion forms when the pH of the solution is around 11.6, the efficiency and the rate of hydroxyl radical production must be greatly influenced by the pH of the solution. Therefore, if VA and MGP are subjected together to oxygen-alkali treatments in our reaction system at different pHs, the degree of VA degradation is expected to become rather large and the reaction selectivity between these two model compounds becomes desirable when the pH of the reaction mixture is low. Hence, it is very significant to examine the reaction selectivity between VA and MGP at several different pHs.

FIGURES 5-9 show the degradation behaviors of VA and MGP at 95°C when the initial pH of the solutions were adjusted to 11.78, 12.22, 12.38, 12.82 and 13.1, respectively, and show time courses of the change in pH during the reactions. The time courses of the change in the pH are not shown in FIGURES 8 and 9 because the pH were constant during the reactions. From these figures, it can be seen that the degradation of MGP became larger than the degradation of VA with the increase in the initial pH. This seems to consistent with the known

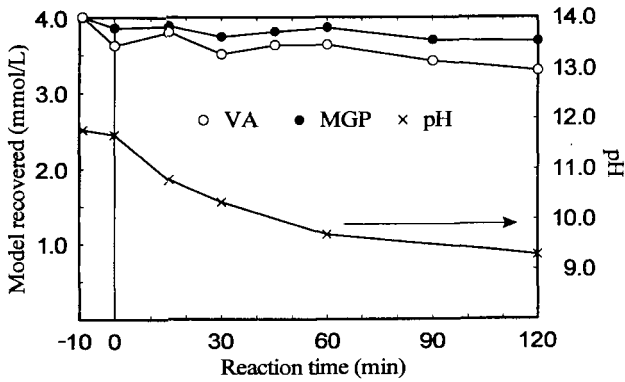


FIGURE 5 Degradation behaviors of VA and MGP at the initial reaction pH = 11.78 when these compounds are subjected to this reaction system (Initial TMPH conc. 9 mmol/L, Temperature 95°C)

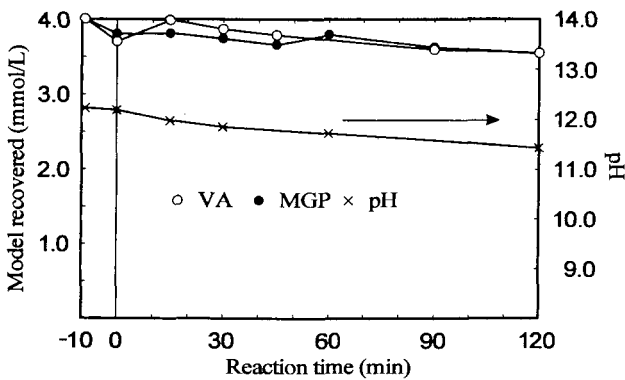


FIGURE 6 Degradation behaviors of VA and MGP at the initial reaction pH = 12.22 when these compounds are subjected to this reaction system (Initial TMPH conc. 9 mmol/L, Temperature 95°C)

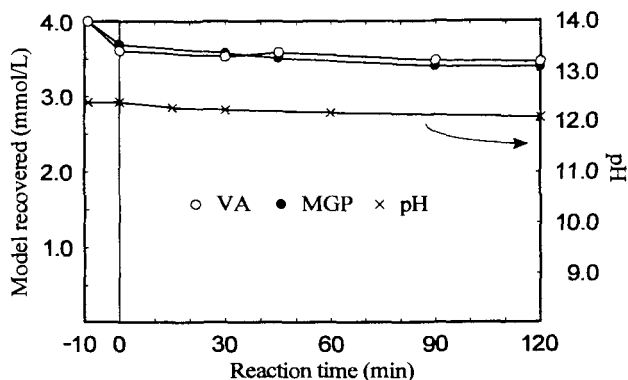


FIGURE 7 Degradation behaviors of VA and MGP at the initial reaction pH = 12.38 when these compounds are subjected to this reaction system (Initial TPh conc. 9 mmol/L, Temperature 95°C)

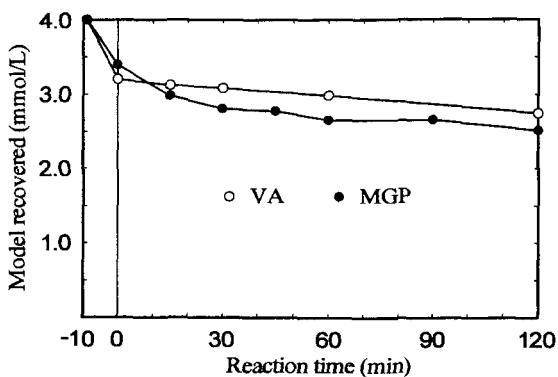


FIGURE 8 Degradation behaviors of VA and MGP at the initial reaction pH = 12.82 when these compounds are subjected to this reaction system (Initial TPh conc. 9 mmol/L, Temperature 95°C)

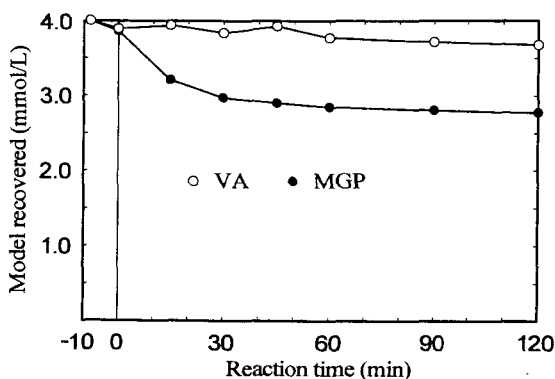


FIGURE 9 Degradation behaviors of VA and MGP at the initial reaction pH = 13.1 when these compounds are subjected to this reaction system (Initial TMPH conc. 9 mmol/L, Temperature 95°C)

reactivity of hydroxyl radical mentioned above. The fact that the degradation of MGP is much larger than the degradation of VA at pH 13.1 can be explained by the difference in the number of functional groups of VA and MGP which react easily with oxygen anion radical. MGP has three hydroxyl methylene, one hydroxyl methyl and one acetal groups while VA has only one aromatic ring and one hydroxyl methyl group. Thus, the chemical structure of model compounds chosen must influence the relative reactivity of active oxygen species examined. We already reported that hydroxyl methylene groups are much more reactive with active oxygen species in our reaction system than hydroxyl methyl groups.⁷

A significant change of the reaction selectivity between VA and MGP ($\Delta VA/\Delta MGP$) was observed when the initial pH was varied (FIGURE 10). In this figure, the ratio of VA consumption to MGP consumption ($\Delta VA/\Delta MGP$, the value of the reaction selectivity) versus the initial pH is plotted. Because the ratio becomes small with the increase in the initial pH, the reaction selectivity becomes

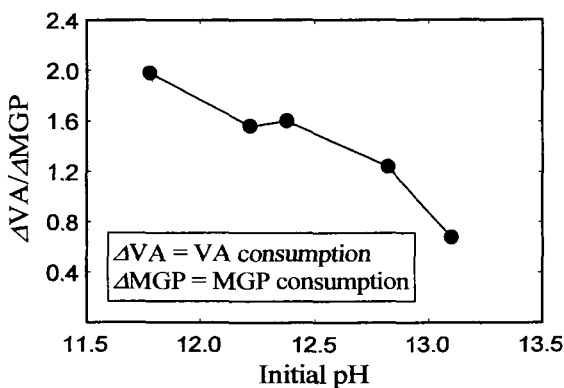


FIGURE 10 Effect of the reaction pH on the reaction selectivity ($\Delta VA/\Delta MGP$) between VA and MGP when all TPh, an active oxygen species generator in this reaction system, is degraded (Initial TPh conc. 9 mmol/L, Temperature 95°C)

undesirable for both carbohydrate protection and lignin degradation with the increase in the pH of the solution. These results clearly indicate that the reaction selectivity is significantly dependent on the pH of the reaction mixture, and a lower pH results in a better reaction selectivity.

The amount of degraded VA and MGP and the total amount of degraded these two compounds are illustrated in FIGURE 11. The amount of degraded VA does not seem to depend on the pH of the solution while the amount of degraded MGP seems to depend on the pH. The total amount of degraded these two model compounds was smaller when the pH of the solution was low than when it was high. This may suggest that the amount of active oxygen species produced is small or these species are consumed by TPh at low pH. The initial pH of the reaction mixture which gives the largest degradation of two model compounds was 12.82. The degradation rate of TPh was not influenced by the initial pH, as

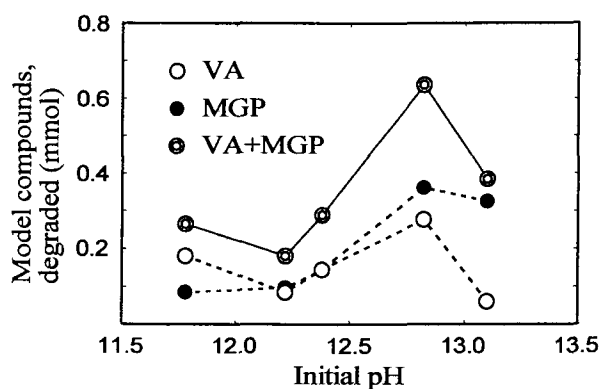


FIGURE 11 Effect of the reaction pH on the amount of degraded VA and MGP and the total amount of degraded VA and MGP when all TMPH, an active oxygen species generator in this reaction system, is degraded (Initial TMPH conc. 9 mmol/L, Temperature 95°C)

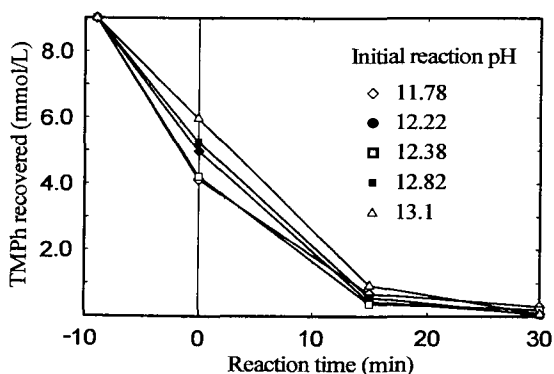


FIGURE 12 Effect of the reaction pH on the degradation of TMPH, an active oxygen species generator, in this reaction system (Initial VA and MGP conc. 4 mmol/L, Temperature 95°C)

indicated in FIGURE 12. These phenomena may indicate that active oxygen species, which are responsible for the degradation of the model compounds, are not only hydroxyl radical but also other active species in this reaction system, since the ionization of hydroxyl radical to oxygen anion radical is significant in this pH region and the reactivity of oxygen anion radical toward organic substrates, such as VA and MGP, is known to be weaker than that of hydroxyl radical.

The degradation behaviors of TMPH, an origin of active oxygen species in our reaction system, are illustrated in FIGURE 12. The difference in the reaction pH seems to have a little effect on the degradation of TMPH.

CONCLUSIONS

Active oxygen species produced by the reaction of a phenolic compound, TMPH, with molecular oxygen at 70°C and at 95°C are different. A carbohydrate model compound, MGP, is degraded more significantly than a non-phenolic lignin model compound, VA, at 95°C while these model compounds are degraded by almost the same rate at 70°C. The reaction selectivity ($\Delta VA/\Delta MGP$) is more desirable for the carbohydrate protection at 70°C than at 95°C. The reactivity and the reaction selectivity of active oxygen species produced in this reaction system are significantly influenced by the pH of the reaction mixture. The reaction selectivity becomes undesirable with the increase in the pH of the solution. When the pH of the reaction mixture is high, active oxygen species degrade a carbohydrate model compound, MGP, much more than a non-phenolic lignin model compound, VA.

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