

論文の内容の要旨

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論文題目 Study on the *erythro* or *threo* preferential degradation of β -O-4 type lignin model compounds under oxygen and hydrogen peroxide bleaching conditions
(酸素および過酸化水素漂白条件下における β -O-4 型リグニンモデル化合物のエリトロ/トレオ優先的分解に関する研究)

Introduction

The β -O-4 type is the most predominant substructure in lignin, and hence, reaction of the β -O-4 bond mainly controls the delignification behavior in various chemical reactions. The diastereomeric *erythro* (*E*) and *threo* (*T*) isomers exist in the side chain of β -O-4 substructure. It is known that reactivity of the *E* isomer is different from that of the *T* isomer in various chemical reactions. It was reported that β -O-4 substructure shows stereo-preferential degradation of the *E* isomer under alkaline pulping conditions.^[1, 2] It was also reported that *T* isomer is stereo-preferentially oxidized by several oxidation systems while the reverse tendency is observed in another laccase-mediator system using ABTS. It was indicated the Fenton's reagent does not show any stereo-preference.^[3, 4] Thus, it is significantly dependent on type of oxidizing reagent in oxidation processes which of *E* or *T* isomer is stereo-preferentially degraded. In this study, stereo-preferential degradation of the *E* or *T* isomer of a dimeric non-phenolic β -O-4-type lignin model compound was investigated under oxygen and hydrogen peroxide bleaching conditions which is nowadays commonly used as bleaching agents due to its environmental friendly.

Experimental

Oxygen treatment

In this study three different dimeric non-phenolic β -O-4 type lignin model compounds as shown in Figure 1 were synthesized according to Adler's method.^[5] A reaction solution (300 ml) was prepared to contain NaOH (0.5 mol/l), FeCl₃ (0.36 mmol/l), a dimeric lignin model compound (*1E*, *1T*, *2E*, *2T*, *3E*, or *3T* 1.0 mmol/l), and Valc (10 mmol/l), and transferred into a Teflon coated stainless steel vessel. Then, O₂ was pressurized to 1.1 MPa. Then, vessel was heated to 95°C for 10 min, which was maintained for 360 min with 200 rpm stirring rate. The reaction time was defined as 0 when the temperature reached 95°C. Each reaction was repeated 3 times to confirm the reproducibility. At several prescribed reaction times, the yield of the model compound was determined by HPLC using the internal standard compound.

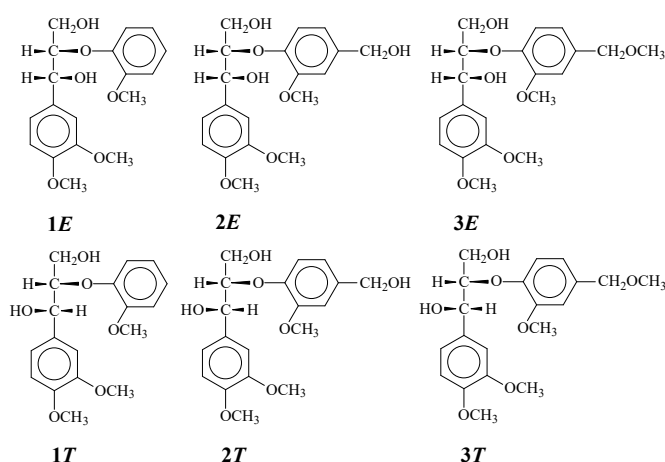


Figure 1. Chemical structure of non-phenolic β -O-4 type lignin model compounds used in this study.

Hydrogen peroxide treatment

A reaction solution (30ml) contained NaOH (various concentration), FeCl₃ (0.36 mmol/l), and a dimeric lignin model compound (**1E**, **1T**, **2E**, **2T**, **3E**, or **3T** 1.0 mmol/l) in a Teflon vessel (50 mL). The vessel was heated to 95°C in a water bath. A 30% H₂O₂ solution (20 µL) was added to the vessel to initiate the reaction. The 30% H₂O₂ solution (20µL) was added totally 10 times with an interval of 10 min. At prescribed reaction times, a portion of the reaction solution was withdrawn for quantifying residual compound **1** and degradation products using HPLC. Each kind of reaction was run 3 times to confirm the reproducibility.

Results and discussion

➤ Oxygen treatment

In the oxygen alkaline treatment, the non-phenolic type dimeric lignin model compound is not directly attacked by O₂. It is attacked and degraded by AOS generated *in situ* by the reaction between O₂ and a phenolic compound, TMPH or Valc. As to AOS generated, negatively charged oxyl anion radical (O^{•−}) is the main AOS, when Valc is employed as the phenolic compound (Valc system).^[6,7] On

the other hand, our previous studies suggested that the main AOS in the TMPH system are not only O^{•−} but also neutral peroxy radicals (ROO[•]), which are generated by the combination between O₂ and the phenoxyl radical derived from TMPH.^[6,7] These electric charges will be the key to understand the stereo-preferences observed in this study. It is also important to note that O^{•−} preferably attacks side-chain rather than the aromatic nucleus under conditions similar to those employed in this study.^[8]

All the stereo-preferences observed under O₂ treatment are summarized in Table 1. It is possible to rationally explain the observed stereo-preferences on the basis of the following 3 hypotheses.

Hypothesis 1: The α-hydroxy group of compound **1E** is relatively acidic and fairly dissociates in the systems using 0.5 mol/L NaOH to generate the negatively charged α-alkoxide at the side-chain, while this is not the case for compound **1T**. The dissociation is not very significant in the systems using 0.1 mol/L NaOH.

Hypothesis 2: The primary benzyl hydroxy group of compound **2** is more acidic than the α-hydroxy group at the side-chain. Therefore, the primary benzyl hydroxy group predominantly dissociates.

Table 1 List of stereo-preferences observed in O₂ treatment

Compound	System	O ₂ (MPa)	NaOH (mol/l)	Stereo-preference
1	TMPh	1.1	0.5	E
		0.4		T
	Valc	1.1	0.5	T
			0.1	E
2	Valc	1.1	0.5	E
			0.1	E
3	Valc	1.1	0.5	T

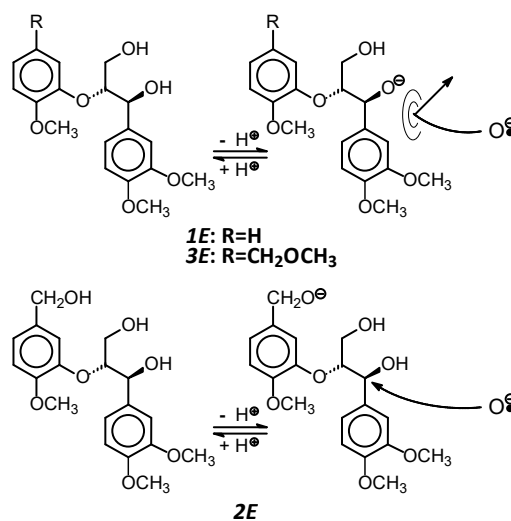


Figure 2. Schematic description of the hypothetical reaction of O^{•−} with the **E** isomers.

Hypothesis 3: The acidity of the α -hydroxy group of compound **3E** is similar to that of compound **1E**, because the more acidic benzyl hydroxymethyl group does not exist.

The stereo-preference of compound **1** was the **E** isomer in the TMPh system under 1.1 MPa. This stereo-preference is owing to the neutral nature of the peroxy radical, the stereo-preference possibly changes when oxygen pressure is not high enough to afford a neutral peroxy radical. In this case, the $O\cdot$ should be a main AOS. Because of this, the stereo-preference was reversed in the TMPh system when oxygen pressure was reduced to 0.4 MPa. The mechanism of these stereo-preferences is the presence of electrostatic repulsion shown in Figure. 2.

The stereo-preference was the **T** isomer in the Valc system using 0.5 mol/l NaOH, when compound **1** or **3** was treated. Because the main AOS is $O\cdot$ in the Valc system which preferably attacks the side-chain rather than the aromatic nuclei, the degradation of compound **1E** or **3E** is suppressed by the electrostatic repulsion results in the stereo-preferential degradation of the **T** isomer. The electrostatic repulsion is not strong enough in the Valc system when NaOH concentration was 0.1 mol/l, which results in reverse stereo-preference.

The electrostatic repulsion is not strong between the side-chain of compound **2E** and $O\cdot$ even in the Valc system using 0.5 mol/l NaOH because the preferential dissociation of the benzyl hydroxymethyl group suppresses the dissociation of the α -hydroxy group in the main carbon skeleton. This can be the reason for the slightly stereo-preferential degradation of compound **2E** over **2T**. The clear stereo-preferential degradation of compound **2E** was observed in system using 0.1 mol/l NaOH.

These hypotheses can also be confirmed by the results from H_2O_2 system where the $O\cdot$ should be the only main AOS resulting in the same stereo-preferential degradation behavior as the Valc system.

➤ Hydrogen Peroxide treatment

Several of the radical species are generated in the system including $HO\cdot$, $O\cdot$, $O_2\cdot$ as well as $HO_2\cdot$. Therefore, among those radicals, the $HO\cdot$ and/or $O\cdot$ are responsible for the delignification under the reaction employed in this study. So, the stereo-preferential degradation of **E** or **T** isomers of lignin model compounds should depending mainly on the stereo-preference of $HO\cdot$ and/or $O\cdot$.

Table 2 List of stereo-preferences observed in H_2O_2 treatment

Compound	Condition	Final pH	Stereo-preference
1	High pH	13.3	T
		12.5	E
		11.5	E
	Low pH	7.5	No preference
		6.0	No preference
		4.0	No preference
2	High pH	3.5	No preference
		13.3	No preference
		12.5	E
3	High pH	11.5	E
		13.3	T
		12.5	E
		11.5	No preference

Under high pH condition, the $O\cdot$, as the most responsible radical for lignin degradation. Under pH 13.3, the stereo-preference was **T** isomers in the degradation of compound **1** or **3**. On the other hand, the stereo-preference was not clearly observed in the reaction of compound **2**. The results can be explained on the basis of the hypotheses according to the presence of electro-static repulsion as shown in Figure 2. Under the conditions with initial pH of 12.8 and 11.9, the reverse stereo-preference was observed in any compound. In this case, the α -hydroxyl group of any compound does not dissociated resulting in the no electric-repulsion force. Therefore, the stereo-preference of $O\cdot$ is slightly toward the **E** isomer. As the results, the stereo-preferential degradation of **E** isomer in any compounds was observed.

For the low pH conditions, the results observed show that there was no clear stereo-preference was observed between the *E* and *T* isomers at any pH. Because the most responsible species for the degradation is HO•, it can be concluded that HO• has almost no stereo-preference or a very tiny preference toward the *E* isomer in the reaction with compound *I*. These observed results can be confirmed that the HO• (hydroxyl radical) shows no stereo-preference.

➤ Degradation products

The degradation products observed in the degradation of compound *I* are including veratraldehyde, veratric acid, and guaiacol. The formation of veratraldehyde indicates that the carbon-carbon bond cleaves between the α - and β -position in the side-chain of compound *I*. The formation of guaiacol shows that the β -O-4 bond of compound *I* certainly cleaves. Veratric acid was confirmed to form from veratraldehyde by a separate experiment. The total yield of veratraldehyde and veratric acid based on disappeared compound *I* was 68~78% at an initial pH of 13.3 or 12.8. These yields are fairly high result from the fact that O⁻ is the responsible species for the degradation of compound *I* at the high pH and preferably attacks the side-chain but not the aromatic part. About 20~25% of guaiacol based on disappearance was obtained at a reaction time of 120 min. This result indicates that the attack of O⁻ on the side-chain of compound *I* is fairly accompanied by the β -O-4 bond cleavage. Nothing can sufficiently be discussed at an initial pH of 11.9, because the amount of disappeared compound *I* was too small. The small amounts of veratraldehyde and guaiacol were the only degradation products detected in H₂O₂ system at an initial pH of 11.5 or lower where HO•, as the main species, attacks the aromatic nucleus of compound *I* as well as the side-chain. The 3, 4-dimethoxyphenyl nucleus of compound *I* should not have largely survived in the reaction, which resulted in the very low yield of veratraldehyde. Even if guaiacol had been once produced by the β -O-4 bond cleavage, guaiacol should have been degraded by HO•.

Conclusion

All the results indicated that the *E* and *T* isomers are degraded by AOS with different rates under both oxygen and hydrogen peroxide delignification conditions. Under oxygen delignification conditions, the reaction of AOS was affected by structural difference in lignin model compound and the change in alkaline concentration, oxygen pressure as well as the profile of AOS generated in the system. All of these observed phenomena can rationally be explained on the basis of the hypotheses on the acidity of the α -hydroxy groups.

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