

Demethylation and other modifications of industrial softwood kraft lignin by different laccase-mediator systems

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Abstract

Lignin demethylation by laccase has been investigated on an industrial kraft lignin in order to increase the latter's reactivity for phenol substitution in phenol-formaldehyde resin preparations. Different laccase-mediator combinations were compared after profound and systematic structural analysis. It was found that demethylation indeed occurs but the reaction efficiency depends on the combination. Concomitant reactions are among others polymerisation and depolymerisation.

Introduction

Phenol-formaldehyde (PF) resins are poly-condensation products from phenol and formaldehyde. Since lignin consists of polymeric phenolic structures and exists abundantly in nature, it has been suggested as a substitute for the phenol in the PF resin preparation and application [1]. However, the major challenge is the lower lignin reactivity than the phenol due to the absence of reactive *para* position and fewer reactive *ortho* positions on lignin phenolic groups, besides of the macromolecular size. Demethylation has been suggested to generate more reactive sites and thus increase the lignin reactivity. This may be achieved by an environment friendly method such as by laccase treatment as described in [2]. However, the laccase demethylation has so far commonly been investigated by solely measuring the methanol release. Few researches have been focused on comparing different laccase-mediator systems (LMS). Obviously, however, a comprehensive understanding of the effects of different laccase-mediator combinations towards lignin is needed in order to develop a compatible method for lignin utilization in resin formulations. In this study, therefore, an industrial softwood kraft lignin has been treated by different LMS followed by comprehensive structural analysis.

Experimental

The softwood kraft lignin (SKL) prepared after LignoBoost process was incubated by laccase N51002(L1) or N51003(L2) combined with ABTS, HBT or TEMPO. The products obtained were analysed by 2D-, ³¹P-, ¹³C-, and ¹H-NMR and SEC in addition to determination of methanol release by GC-FID analysis of the reaction solutions.

Results and discussion

According to the analysis results, demethylation was a common reaction for all the laccase-mediator combinations investigated; after reaction, methanol was always released into the solutions and a reduction in the methoxyl content of the lignins were generally observed in the obtained products (Table 1). Correspondingly the treatments decreased the quantities of different types of phenolic aromatic rings, G units being the most attacked structures. At the same time, decarboxylation was also detected in two of the LMS; L1-TEMPO and L2-HBT. The L1-ABTS combination has the highest demethylation rate and the most severe overall structural modification so that its modified lignin become no longer completely soluble in the mixed solvents for the ³¹P-NMR analysis and thus no functional group quantities could be determined.

Table 1. Contents of methoxyl (OMe) per aromatic ring and contents (mmol/g) of aliphatic, aromatic (guaiacyl (G), *p*-hydroxyphenyl (H), and condensed (Con) (including syringyl) phenolic), and carboxyl hydroxyl (CO) groups

	OMe	Aliphatic OH	Aromatic OH				CO-OH
			<i>G</i> -OH	<i>H</i> -OH	<i>Con</i> -OH	sum	
Starting SKL	0.94	1.91 ±0.16*	2.32 ±0.04*	0.24 ±0.07*	2.01 ±0.06*	4.57	0.46 ±0.01*
L1+ ABTS	0.55	NA**	NA**	NA**	NA**	NA**	NA**
L1+ HBT	0.79	1.96	1.96	0.27	1.85	4.08	0.45
L1+ TEMPO	0.55	1.92	1.86	0.24	1.71	3.81	0.40
L2+ ABTS	0.68	2.16	2.22	0.27	2.11	4.60	0.47
L2+HBT	0.56	1.92	2.09	0.26	1.94	4.29	0.40
L2+ TEMPO	1.05	2.02	2.01	0.26	1.94	4.21	0.44

* duplicates (values expressed as Mean±SD); ** not available, see text part.

Lignin polymerization was noticed for all treatments by increased M_p , M_n , or M_w values (Table 2). Since neither catechol nor quinone structures could be observed by ^{31}P - or ^{13}C -NMR, it may be assumed that any demethylated products with e.g. catechol structure have been oxidized into quinones and further polymerized, in accordance to what has been reported on a lignin model study [3]. The L1-ABTS combination demonstrated the highest M_p , M_n , and M_w values, the formed polymerisation products possibly being responsible for the low solubility mentioned above. At the same time, an increased polydispersity (PD) was observed for all the treatments. Once again, the highest increase in PD is found for the L1-ABTS treatment. Lignin depolymerisation also took place which is indicated by the cleavage of β -aryl bonds as observed by 2D-NMR analysis (data not shown).

Table 2. Molecular mass distributions (M_p , M_n , M_w and PD)

	M_p	M_n	M_w	PD
Starting SKL	2100	1300	3800	3.0
L1+ABTS	10000	4100	1100000	270
L1+HBT	2400	1700	10700	6.4
L1+TEMPO	2400	1900	24700	13.1
L2+ABTS	2300	1600	11000	6.9
L2+HBT	2700	1800	15600	8.9
L2+TEMPO	3900	2000	18400	9.3

In conclusion, the most efficient demethylation was achieved by N51002-ABTS. However, the subsequently highest extent of polymerization might deteriorate the reactivity of the modified lignin, which needs to be further investigated.

References

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