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The formation of LC and other aromatic end-group structures in *O*-alkyl-substituted cellulose during kraft pulping conditions

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Abstract Ultraviolet resonance Raman spectroscopy (UVRRS) was used to study the formation of aromatic and/or lignin-carbohydrate (LC) structures at the reducing end groups of *O*-alkyl-substituted cellulose under conditions simulating the initial phase of kraft pulping. The derivatives studied were methyl cellulose (MC) with degree of substitution (DS) of 1.64–1.95, carboxymethyl cellulose (CMC) with DS ~0.6, and a lignin model compound, creosol. The total alkali concentrations in the treatments were 0.1 M and 0.5 M and the sulfidities were 1%, 10%, and 30%. HS⁻ ions and creosol are both strong nucleophiles and they compete for the hot-alkali-generated unsaturated electrophilic reaction sites in the reducing end groups of the polysaccharides. The results indicated that conditions similar to those in the initial phase of conventional kraft cooking (high OH⁻ and low HS⁻ ion concentrations) increased the aromatic nature of the end groups and conditions similar to those in the initial phase of super batch cooking (low OH⁻ and high HS⁻ ion concentrations) partly inhibited the formation of aromatic and LC end groups.

Key words Cellulose ether · Creosol · Aromatic end group structure · Lignin-carbohydrate complex (LCC) · UV resonance Raman spectroscopy (UVRRS)

Introduction

During the initial delignification phase of kraft pulping of wood, below 130°C, the dissolution of lignin is slight.^{1,2} Primary peeling of the reducing end groups of wood polysaccharides is the main reaction leading to extensive loss of

carbohydrates. About 75% of the dissolved carbohydrate is glucomannan, but a major part of xylan dissolves at higher temperatures (>140°C).²⁻⁷

The peeling reaction is stopped by a competing stopping reaction involving β -hydroxy elimination. During stopping reaction of glucans (metasaccharinic acid end group formation) and during stabilization of 2-*O*-alkyl-substituted xylan, electrophilic α,β -conjugated aldehyde end groups are formed either as an intermediate product or as an end product.^{8,9} These unsaturated end groups are electrophilic and likely to react with strong nucleophiles, such as phenolic lignin, to form harmful lignin-carbohydrate (LC) linkages.¹⁰⁻¹³ The possibility for these kinds of reactions during the early stages of the kraft cooking process is increased because most of the wood polymers are still in close contact in the cell wall structure.

During impregnation and the initial delignification phase (<130°C) 70%–80% of the total alkali charge is consumed.¹⁴ The dissolution and degradation of carbohydrates depends very much on the charge and concentration of alkali and on cooking time and temperature, but proceeds fairly independently of the sulfidity. The main purpose of hydrogen sulfide ions in kraft cooking is to enhance the solubility of lignin and inhibit the condensation of degraded and dissolved lignin.¹⁵

It has been suggested that the amount of lignin-carbohydrate complex (LCC) to be formed during pulping is dependent on the process conditions.¹⁶ It is a widely known fact that modified sulfate pulps, for example, super batch pulp (high HS⁻ and low OH⁻ ion concentrations during the initial delignification phase) have better bleachability than conventional kraft pulp (high OH⁻ and low HS⁻ ion concentrations during initial delignification phase) indicating less alkali-stable linkages between residual lignin and carbohydrates. We studied the possibility of whether (during the early stages of kraft cooking) hydrogen sulfide ions, as strong nucleophiles, could restrict the condensation of lignin and carbohydrates, or, in general, restrict the formation of harmful aromatic and other unsaturated alkali-stable structures to the reducing end groups of polysaccharides.

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Experimental

Materials

Methyl cellulose

Methyl cellulose (MC) (Fluka, MC 4000 mPa.s, DS 1.64–1.95) was used as a model compound of the 1,4-linked 2-*O*-substituted polysaccharides. The degree of polymerization (DP) of the MC was decreased with a partial acid hydrolysis.¹³

Carboxymethyl cellulose

Carboxymethyl cellulose (CMC) (Noviant ZSB-16, DP 750, DS 0.32) was used as a model compound for 1,4-linked 2-*O*-substituted polysaccharides. The CMC was first carboxymethylated in order to increase its degree of substitution (DS 0.58). The solubility of the polysaccharide was thereby increased, which facilitated the control of degree of polymerization in a subsequent enzymatic hydrolysis step.¹²

Creosol

2-Methoxy-4-methyl-phenol (creosol) was obtained from Aldrich, Milwaukee, WI, USA.

Methods

Preparation of LC end groups in the presence of HS⁻ ions

The cellulose ether (~80 mg) was mixed with creosol (~10 g) in oxygen-free hot solution (0.1 and 0.5 M) of NaOH (200 ml).^{12,13} The sulfidity of the total alkali charge (NaOH + Na₂S) was 30%, 10%, and 1%. The solution was heated for 6 h at 95°C under a N₂ stream. After cooling and neutralization (CO₂), the mixture was purified from creosol and other small fragments by dialysis (Spectrum, Spectra/Por, cutoff <3.5 kDa). The freeze-dried sample was analyzed by ultraviolet resonance Raman spectroscopy (UVRRS) at 244 nm.

UVRR spectroscopy

UVRR spectra were recorded with a Renishaw 1000 Raman spectrometer coupled with a Leica DMLM microscope and an Innova 90C FreD frequency-doubled Ar⁺ laser (Coherent, Santa Clara, CA, USA) by using an excitation wavelength of 244 nm.^{12,13}

Results and discussion

The *O*-alkyl-substituted cellulose ethers were first hydrolyzed with partial acid or enzyme hydrolysis in order to

generate new reducing end groups. After hydrolysis, the mixture was filtered and fractionated by ultrafiltration (3–10 kDa).^{12,13}

Carboxymethyl cellulose

The characteristic bands of cellulose at 1440 and 1100 cm⁻¹ disappeared in the UVRR spectra when CMC was treated with hot alkali (95°C).¹² Typically, the band at 1100 cm⁻¹ disappeared first with increasing alkali concentrations. In the same time, strong resonance-enhanced bands appeared in the band area at 1600–1650 cm⁻¹ indicating the formation of conjugated carbonyl (1650 cm⁻¹) and aromatic (1600 cm⁻¹) structures. The intensity ratio of the bands 1600/1650 cm⁻¹ increased gradually as a function of NaOH concentration.¹² When CMC was treated with hot alkali and creosol, the intensity of the band at 1600 cm⁻¹ in the UVRR spectra was doubled compared with the spectra after treatments without creosol. The intensity was increased as a function of alkali concentration and time.¹³ Because free creosol was carefully dialyzed from the samples, the interpretation that new condensed aromatic structures were formed to CMC was acceptable. The condensation was suggested to occur between the reducing end groups of the cellulose ether and creosol.^{11,13} The color of the CMC after hot alkali treatments in the presence of creosol varied from yellow to brown depending on the concentration of NaOH. The increased color also indicated enhancement of the amount of UV-absorbing material.

When CMC was hot-alkali-treated in the presence of HS⁻ ions the intensity ratio of 1600/1650 cm⁻¹ decreased and overlapping of the characteristic band of cellulose at 1400 cm⁻¹ was slightly reduced (Fig. 1A). However, the difference was not very dramatic and the color of the CMC was slightly brown with or without Na₂S indicating the presence of light-absorbing material.

After treating the CMC with hot alkali (0.1 M) and creosol in the presence of HS⁻ ions, the overlapping of the characteristic bands of cellulose at ~1400 cm⁻¹ was reduced compared with the band at 1600 cm⁻¹, characteristic to aromatic structures. This indicated that the aromatic nature of the sample was decreased. The intensity ratio of aromatic structures versus conjugated carbonyl structures (1600/1650 cm⁻¹) also decreased (Fig. 1B) and the color of the CMC turned from slightly yellow to white. Cautious interpretation after these results indicates that HS⁻ ions are more likely to inhibit the LC bond formation than the aromatic end group formation to the reducing end groups of *O*-ether celluloses.

After treating CMC with hot alkali (0.5 M) and creosol with or without the presence of HS⁻ ions, the amount of aromatic structures (1600 cm⁻¹) compared with conjugated carbonyl structures (1650 cm⁻¹) was high and the overlapping of the characteristic bands of the cellulose (1100 and 1400 cm⁻¹) was not diminished. The result indicated that high OH⁻ ion concentration prohibited the formation of HS⁻ ions, and, therefore, the formation of harmful light-absorbing end groups in CMC was not prevented. Only the

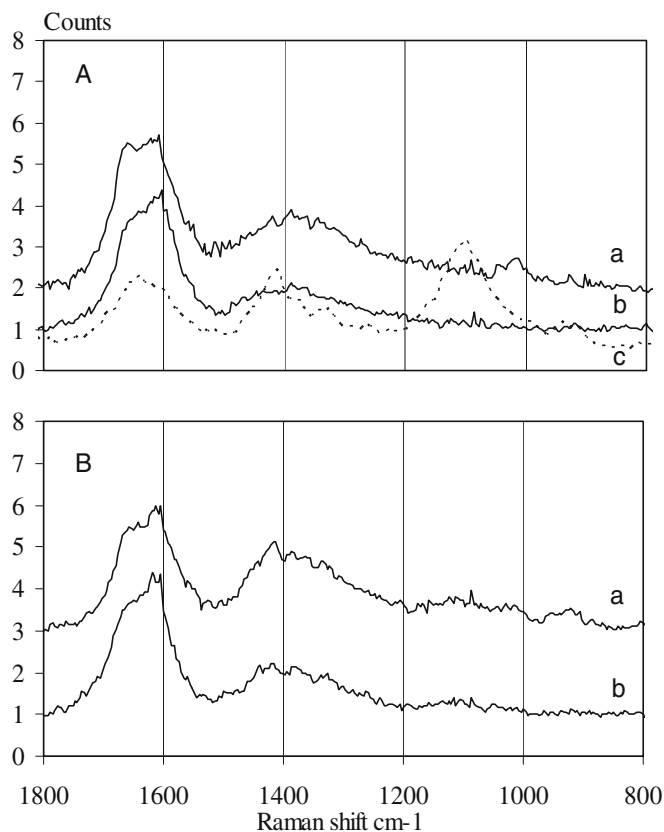


Fig. 1A, B. Ultraviolet resonance Raman (UVRR) spectra recorded for carboxymethyl cellulose (CMC) after 6 h of hot alkali treatments at 95°C with 0.1 M NaOH and **A** 30% Na₂S (a), 0% Na₂S (b), untreated CMC (c), and **B** 30% Na₂S, and 0.36 M creosol (a), and 0% Na₂S and 0.36 M creosol (b)

highest dosage of Na₂S (30%) had a slight decreasing effect on the formation of the aromatic end group structures. However, the shape of the band at the area 1600–1650 cm⁻¹ was different, indicating that some reactions appeared on the reducing end groups of the cellulose ethers when HS⁻ ions were present (Fig. 2). The color of the CMC samples after both treatments (with or without HS⁻ ions) was brown.

Methyl cellulose

When MC was treated with hot alkali, the intensity of the band at 1600 cm⁻¹ increased, indicating new UV light-absorbing aromatic end group structures. The intensity of the band at 1370 cm⁻¹ was also resonance enhanced suggesting some other structural changes in the end groups.¹³ The color of MC after hot alkali treatments changed from white to light brown. When MC was treated with hot alkali and creosol, new bands (1280 and 1590 cm⁻¹) characteristic of guaiacyl-type lignin structures appeared in the UVRR spectra simultaneously. At the same time, the band at 1370 cm⁻¹ was overlapped.¹³ The color of the MC sample treated with hot alkali and creosol was light brownish red, indicating the presence of light-absorbing material.

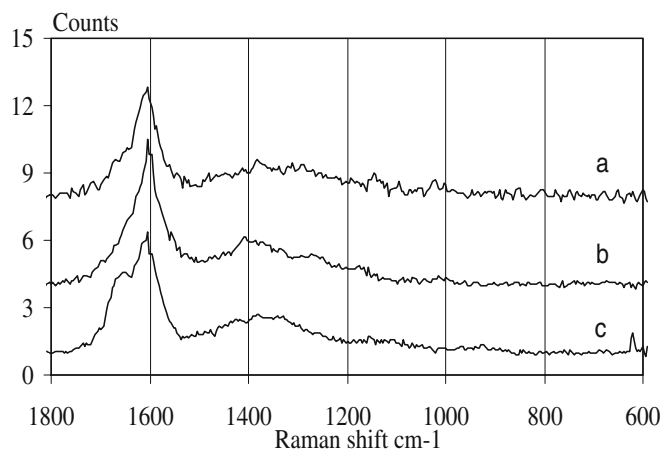


Fig. 2. UVRR spectra recorded for CMC after 6 h of hot alkali treatments (0.5 M NaOH, 95°C) with creosol (0.36 M). Sulfidity dosages (Na₂S) were 30% (a), 10% (b), and 0% (c)

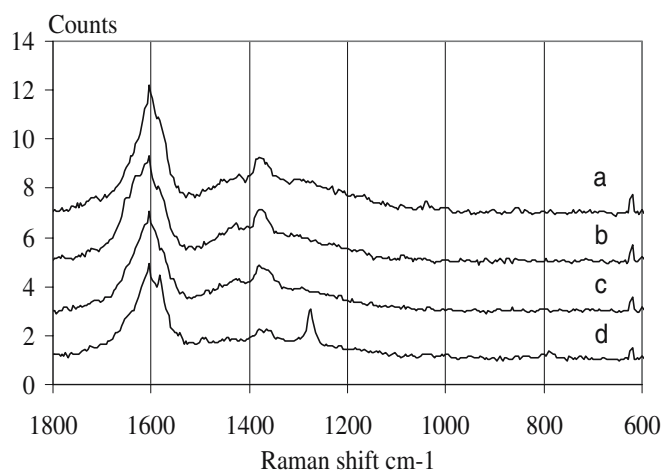
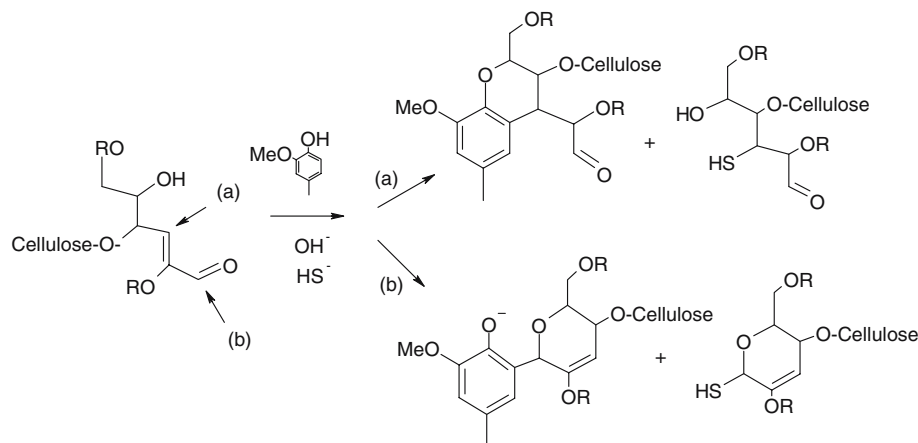


Fig. 3. UVRR spectrum recorded for MC after 6 h of treatment with 0.36 M creosol at 95°C. The alkali concentrations were 0.1 M and sulfidity 30% (a), 10% (b), 1% (c), and 0% (d)

When the MC was treated with hot alkali (0.1 M) and creosol in the presence of HS⁻ ions, the characteristic bands of guaiacyl lignin in the UVRR spectra disappeared and the band at 1370 cm⁻¹ was resonance enhanced again (Fig. 3). This was obviously due to the strong nucleophilic character of the HS⁻ ions. The repression of the condensation was clear with all Na₂S dosages. The color of the MC was slightly yellow and turned slightly red and almost white as the dosage of the Na₂S was increased from 1% to 30%.

The remaining color and high intensity of the bands at 1600 cm⁻¹ (characteristic to aromatic structures) indicated, however, that despite the added Na₂S, UV light-absorbing structures were still introduced to the reducing end groups of the MC. Not even the highest dosage of HS⁻ ions could totally inhibit the formation of aromatic structures even though the color of the sample, almost white, indicated so. This could mean that some aromatic end group structures that were formed during the hot alkali treatments (HS⁻ ions

Fig. 4. Condensation reactions of hot-alkali-treated *O*-alkyl-substituted cellulose ethers with nucleophiles (HS^- ion and creosol) modified from Létumier et al.¹¹ R = -H, $-\text{CH}_2\text{COOH}$, or -Me



present) do not absorb light. It is possible, however, that these structures are activated by light or high temperature and thereby become light absorbing later on. In any case, the results support the interpretations discussed for CMC that HS^- ions are able to inhibit to some point the formation of harmful LC bonds to the reducing end groups of the cellulose ethers, especially when the concentration of OH^- ions is low.

It is most likely that aromatic end groups are formed at the beginning of the hot alkali treatment, for example, when the pH is still high. As the pH decreases, the amount of phenolic groups ($\text{p}K_a$ of creosol is 10.27)¹⁷ in lignin increases, which makes the condensation between creosol and the reducing end groups possible. However, as the pH falls, the nucleophilic HS^- ions start to compete with creosol for the electrophilic reaction sites on the hot-alkali-treated reducing end groups.

Two kinds of coupling mechanisms are proposed between the reducing end groups of *O*-alkyl-substituted cellulose ethers and nucleophiles.¹¹ The first example is a 1,4-addition mechanism to the α,β -unsaturated end groups; the second is a nucleophilic addition to the carbonyl group of the open chain form of the end groups (Fig. 4).

Conclusions

According to UVRRS results, HS^- ion, as a strong nucleophile, could restrict to some extent the formation of harmful UV light-absorbing alkali-stable end group structures between phenolic lignin (creosol) and hot-alkali-treated reducing end groups of cellulose ethers (carboxymethyl cellulose and methyl cellulose). The effectiveness of the HS^- ions depended on the concentration of OH^- ions. When the cellulose ethers were treated with hot alkali (0.5M), the formation of UV light-absorbing end groups was not inhibited. However, when the initial concentration was 0.1M it appeared that even very low concentrations of HS^- ions (sulfidity 1%) diminished nucleophilic addition reaction (condensation) between the hot-alkali-treated end groups

of cellulose ethers and nucleophilic creosol (LC end group structures). However, HS^- ions could not inhibit the formation of aromatic end group structures at the reducing end groups of cellulose ethers during hot alkali treatments even without the presence of creosol.^{12,13}

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References

- Sjöström E (1977) The behaviour of wood polysaccharides during alkaline pulping processes. *TAPPI J* 60:151–154
- Sjöström E (1993) *Wood chemistry. Fundamentals and applications*, 2nd edn. Academic Press, San Diego
- Croon I, Enström BF (1961) The 4-*O*-methyl-D-glucuronic acid groups of birch xylan during sulphate pulping. *TAPPI J* 44:870–874
- Ahlm CE, Leopold B (1963) Chemical composition and physical properties of wood fibers, IV. Changes in chemical composition of Lobolly Pine fibers during the kraft cook. *TAPPI J* 46:102–104
- Aurell R, Hartler N (1965) Kraft pulping of pine. Part 1. *Sven Papperstidn* 68:59–68
- Hansson J-Å, Hartler N (1968) Alkaline degradation of xylans from birch and pine. *Sven Papperstidn* 9:358–365
- Simonsson R (1971) The hemicelluloses in the sulphate pulping process. *Sven Papperstidn* 74:691–700
- Rydholm SA (1965) *Chemical pulping – Kraft process*. Interscience, New York, pp 597–646
- Johansson MH, Samuelson O (1977) Alkaline destruction of birch xylan in the light of recent investigations of its structure. *Sven Papperstidn* 16:519–524
- Vikkula A, Létumier F, Tenkanen M, Sipilä J, Vuorinen T (2001) Generation of phenol-xylan complexes in kraft pulping conditions. *Proceedings of the 11th International Symposium on Wood and Pulp Chemistry (ISWPC)*, June 11–14, Nice, 1:51–54
- Létumier F, Ämmänlahti E, Sipilä J, Vuorinen T (2003) A facile route of formation of lignin-carbohydrate complexes during alkaline pulping. *J Pulp Pap Sci* 29:42–47
- Vikkula A, Valkama J, Vuorinen T (2006) Formation of aromatic and other unsaturated end groups in carboxymethyl cellulose during hot alkaline treatment. *Cellulose* 13:593–600
- Vikkula A, Vuorinen T (2006) The formation of LC and aromatic end group structures in *O*-alkyl substituted cellulose during alkaline pulping conditions. *Holzforschung* 60:378–382

14. Gullichsen J (1999) Fibre line operations. In: Gullichsen J, Fogelholm C-J (eds) Chemical pulping. Fapet Oy, Jyväskylä, Finland, pp 38–52
15. Saucedo VM, Josephson WE, Krishnagopalan A (2002) Dynamic modeling of carbohydrates degradation in kraft pulping of hardwood. *Appita J* 55:398–403
16. Karlsson O, Pettersson B, Westermark U (2001) Linkages between residual lignin and carbohydrates in bisulphate (magnefite) pulps. *J Pulp Pap Sci* 27:310–316
17. Ragnar M, Lindgren CT, Nilvebrandt NO (2000) pK_a -values of guaiacyl and syringyl phenols related to lignin. *J Wood Chem Technol* 20:277–305