Reactions of Conventional Kraft and Superbatch Pulp Residual Lignins with Peroxyformic Acid

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ABSTRACT

The residual lignins KRL and SRL, isolated from a conventional kraft pulp and a SuperBatch pulp respectively, were reacted with peroxyformic acid (PFA). The reagent consumptions were determined and the products fractionated according to their solubility. Both lignins consumed a roughly equal amount of PFA, which was nearly 50% higher than that consumed by kraft lignin. The undissolved fractions of PFA-treated residual lignins (yield > 80%) contained less aromatic units, phenolic hydroxyl and methoxyl groups, and considerably more carboxyl groups (including those of formate esters) than the untreated lignins. The extent of these modifications

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was approximately equal for KRL and SRL, which together with the similar PFA consumptions and product yields of KRL and SRL indicates that the two residual lignins showed no essential difference in reactivity toward PFA. The effect of fiber wall morphology on delignification efficiency during PFA delignification is suggested to be small because of the cleavage of lignin-carbohydrate linkages occurring under acid conditions. The part of KRL remaining insoluble after PFA-treatment had a 40% higher molar mass than KRL while in the case of SRL there was hardly any such difference in molar mass. The lignins solubilized during the PFA treatments represented the most highly degraded part of the lignins, having very low molar masses and being richer in carboxyl groups and lower in aromatic units, phenolic hydroxyl, and methoxyl groups than the undissolved lignins.

INTRODUCTION

Several modified kraft pulping methods have been developed over the past 30 years, representing a large improvement in kraft pulping technology.[1–4] These cooking processes are more selective than conventional kraft pulping and allow delignification to lower kappa numbers than conventional kraft pulping. The pulps from modified cooking can be bleached to low kappa numbers more easily than conventional kraft pulps without losses in pulp yield. The environmental impact of the manufacture of bleached kraft pulps can be further reduced by replacing chlorine (Cl_2) bleaching with Totally Chlorine Free (TCF) or elemental chlorine free (ECF) bleaching with oxygen-based chemicals (peroxyformic acid and other peracids, ozone, molecular oxygen, and hydrogen peroxide) and chlorine dioxide.

Peroxyformic acid (PFA) and other peroxycarboxylic acids are formed in the reaction between the corresponding carboxylic acid with hydrogen peroxide. Because of their high electrophilicity under acidic conditions, peroxycarboxylic acids attack the electron-rich aromatic rings, and olefinic side-chain structures of lignin. This brings about oxidative changes in lignin aromatic units such as hydroxylation, demethylation, and ring-opening to muconic acids and other carboxylic acids.[5–10] In pulp delignification, PFA is produced in situ from formic acid and hydrogen peroxide. Transition metals, present in low amounts in the pulping medium, catalyze the decomposition of hydrogen peroxide

into hydroxyl (HO·) and superoxide ($O_2^{·-}$) radicals, which cause similar changes in lignin structure as PFA.[11,12] Hydrophilic carboxylic acid groups introduced in lignin via ring-opening reactions may in part be responsible for the improved reactivity and solubility of PFA-delignified pulps during subsequent bleaching stages with e.g., alkaline hydrogen peroxide. Lignin solubilization during PFA treatment is further enhanced by depolymerization involving side-chain displacement[9] and scission of β-O-4 ether linkages by the action of PFA which also results in the formation of hydrophilic phenolic hydroxyl groups.[10,13–16]

Peroxycarboxylic acids, mainly PFA[14,15,17–19] and peracetic acid,[5,6,17,18] have been used as delignifying agents in organosolv pulping processes such as Milox (PFA/formic acid pulping) or Acetosolv (acetic acid pulping with HCl as catalyst).[16,19–21] PFA has also been used for prebleaching of kraft pulps before treatment with other oxygen-based bleaching chemicals.[22–24] In these studies PFA has been found to enhance the reactivity of residual kraft lignin toward other TCF bleaching chemicals.

In this article, the reactivities of isolated residual kraft and SuperBatch lignins toward PFA were compared. The untreated and treated lignins were subjected to chemical and spectroscopic analyses to find out what structural changes take place in the residual lignins of these pulps during PFA treatment and whether the lignins differ in their reactivity toward PFA. Also kraft lignin from the black liquor of a conventional kraft cook was reacted with PFA to gain more information about the effect of chemical structure on reactivity of lignins toward PFA.

EXPERIMENTAL

Lignin Samples

The residual lignins were isolated from a conventional pine (*Pinus sylvestris*) kraft pulp with a kappa number of 25.9 and from a Superbatch pine (*Pinus sylvestris*) pulp with a kappa number of 20 by enzymatic hydrolysis and purified with a protease.[25] The kraft lignin was isolated from the spent liquor of a conventional kraft cook of pine (*Pinus sylvestris*) to kappa number 31.

Chemical Characterization of Lignins

The methoxyl group and nitrogen contents of lignins were determined at the Analytische Laboratorien, Gummersbach, Germany. The phenolic

hydroxyl groups of lignins were quantified by a UV-ionization difference method.[25] The carboxyl group contents of lignins were determined by conductometric titration with HCl and NaOH of lignin samples (4–10 mg) dissolved in dilute NaOH under a continuous flow of nitrogen. The residual carbohydrates present in the lignins were determined according to Hausalo[26] by anion exchange chromatography coupled with pulsed amperometric detection. The molar mass distributions of lignins were determined as described by Hortling et al.[27] on a Fractogel HW-55F gel in 0.5 M NaOH using monodisperse Na-polystyrenesulfonates as calibration compounds and a UV-detector measuring at 280 nm.

Spectroscopic Characterization of Lignins

The FTIR absorbance spectra of lignins were recorded from KBr pellets on a Nicolet 740 FTIR spectrometer. The standard proton-decoupled ^{13}C NMR spectra of lignins (30–100 mg) dissolved in d_6-DMSO were recorded on a Varian Gemini-200 MHz FT spectrometer at ambient temperature operating at 50 MHz for carbon. The pulse delay was 1 s and a line broadening of 20 Hz was used for the Fourier transformation. 40,000–50,000 transients were collected. The chemical shifts (δ) were measured relative to DMSO at 39.6 ppm.

Treatment of Lignins with Peroxyformic Acid (PFA) and Fractionation of the Reaction Products

1. The treatment of kraft lignin (KL, 500 mg), residual kraft lignin (KRL, 300 mg) and residual SuperBatch lignin (SRL, 300 mg) with peroxyformic acid (PFA), formed in situ from formic acid and hydrogen peroxide, and subsequent work up of the reaction products is shown in Fig. 1. Peroxide consumption was monitored over 2 h by colorimetric titration of residual H_2O_2 with $CeSO_4$ followed by titration of PFA with sodium thiosulfate.[28] The peroxide bound in PFA was deducted from the peroxide consumption. Titrations were also performed in the absence of lignin to calculate how much of the peroxide/PFA consumed was consumed in reactions with lignin.
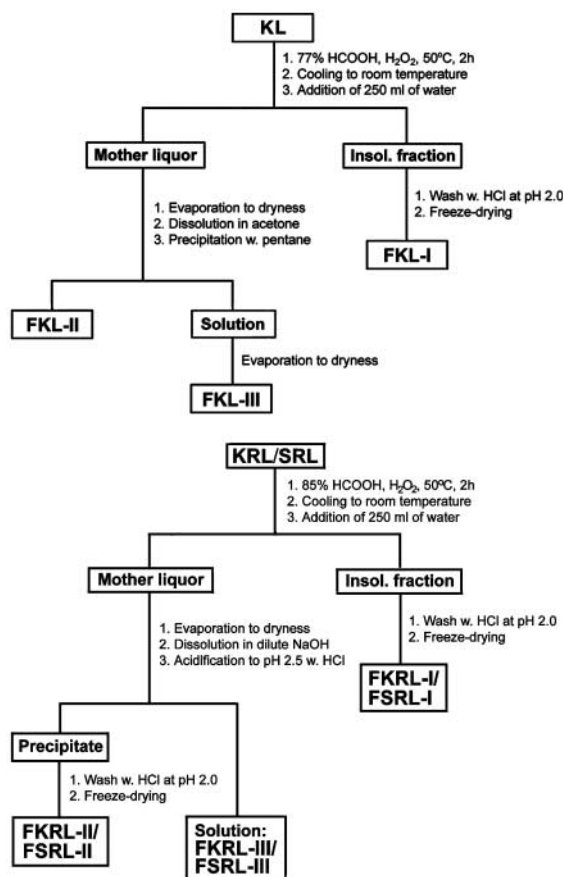
Figure 1. Treatment of kraft lignin (KL, 500 mg), residual lignin from a conventional kraft pulp (KRL, 300 mg) and residual lignin from a SuperBatch pulp (SRL, 300 mg) with PFA and fractionation of reaction products.

RESULTS AND DISCUSSION

PFA Consumption and Yield of Reacted Lignin

The formation of peroxyformic acid from formic acid and hydrogen peroxide is shown in Eq. (1).
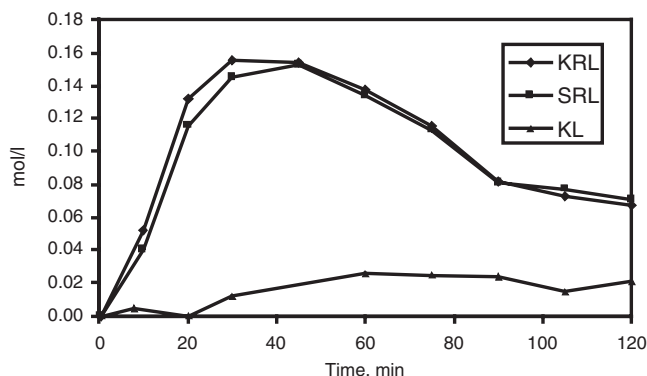
$$HCOOH + H_2O_2 \rightleftharpoons HCOOOH + H_2O \qquad (1)$$

Figure 2. Plot of the amount of PFA consumed in reactions with lignin as a function of time on PFA treatment of KRL or SRL (H_2O_2 dose 51.4% on lignin) and KL (H_2O_2 dose 43.0% on lignin). The PFA consumptions were calculated by deducting the PFA concentrations measured in the presence of lignin from those measured in the absence of lignin.

The reaction of PFA with lignin has been proposed[9] to involve the electrophilic hydroxonium ion (HO^+), formed according to Eq. (2), as the species attacking electron-rich lignin moieties, i.e., aromatic units and olefinic side-chain structures.

$$HCOOOH \rightleftharpoons HCOO^- + HO^+ \qquad (2)$$
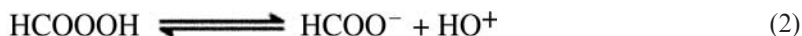
Electrophilic attack by PFA/$HO^{+[9]}$ or oxygen radicals formed as lignin decomposition products[11,12] on lignin results in aromatic ring hydroxylation and formation of muconic acid structures as ring-opening products. A comparison of the plots of PFA consumption vs. time shows that the lignins consumed part of the PFA (Fig. 2). KRL and SRL consumed approximately equal amounts of PFA at an equal peroxide charge (Table 1), assuming that all the peroxide consumed was converted to PFA.

Both KRL and SRL consumed a considerable amount of PFA. Until 30–45 min, KRL consumed slightly more PFA than SRL. This could account for the slightly lower yield (Table 2) of the I- and II-fractions from the treatment of KRL when KRL and SRL were reacted with an equal amount of PFA. The use of a higher peroxide charge resulted in an increase in PFA consumption and a decrease in the yield of the insoluble I-fraction from SRL, indicating a more extensive degradation of the lignin.

Kraft lignin exhibited lower reactivity toward PFA than the residual lignins, as also shown by the large amounts of residual peroxide and PFA (Table 1). While the I-fractions from KRL and SRL could be washed at

Table 1. Data on PFA treatment of lignins.

Lignin sample	H_2O_2 dose (wt. % on lignin)	Residual H_2O_2 (% of dose)	Final HCO_3H (% of H_2O_2 charge)	HCO_3H consumption[a] (wt. % on lignin)
KL	43.0	15.9	34.1	21.5
KRL	51.4	9	15.7	38.7
SRL-A	51.4	9	11.2	41.0
SRL-B	66.7	8	12.5	53.0

[a]Assuming that all the hydrogen peroxide consumed was converted to PFA.

Table 2. Yield of the different fractions of PFA-treated lignins.

Lignin fraction	Yield (%)	Lignin fraction	Yield (%)	Lignin fraction	Yield (%)	Lignin fraction	Yield (%)
FKL-I	48.3	FKRL-I	84.4	FSRL-AI	87.0	FSRL-BI	81.3
FKL-II	10.9	FKRL-II	0.4	FSRL-AII	2.3	FSRL-BII	2.5
FKL-III	14.4	FKRL-III	nd	FSRL-AIII	nd	FSRL-BIII	nd

pH 2.0 without any appreciable loss in yield, FKL-I was partially soluble at this pH and part of this fraction was lost when washing was attempted. The low M_w of KL (see discussion on molar masses later) reduces the number of hydrophilic groups needed to render it water-soluble. This probably accounts for the relatively low yield of FKL-I as compared to those of the I-fractions obtained from lignins having much higher M_w values.

Chemical Characterization of Lignins

As can be seen from Figs. 3 and 4, the PFA-treated lignins contain less phenolic hydroxyl and methoxyl groups than the corresponding untreated lignins. FKRL-I, FSRL-AI, and FSRL-BI all contain approximately 25% less phenolic hydroxyl and 15% less methoxyl groups than KRL and SRL, respectively. A difference of similar magnitude in phenolic hydroxyl content on PFA treatment of pine kraft pulp has been reported earlier.[29] The difference between the phenolic hydroxyl contents of KL and FKL-I is of the same magnitude as that observed
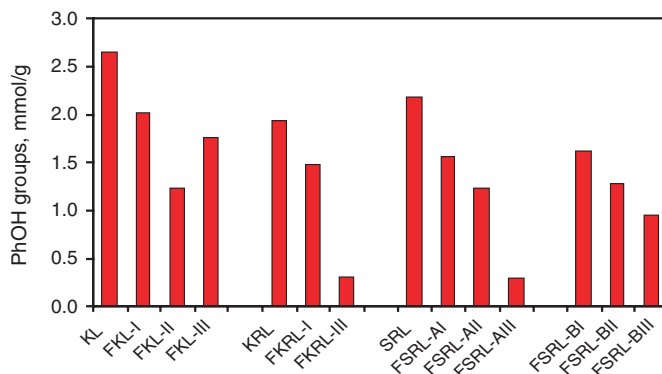
Figure 3. Phenolic hydroxyl group contents of untreated and PFA-treated lignins. Values for the untreated lignins and I-fractions are corrected for residual carbohydrates and proteins (the latter calculated by multiplication of the nitrogen contents by 6.25). See Fig. 1 and Table 1 for lignin designations.
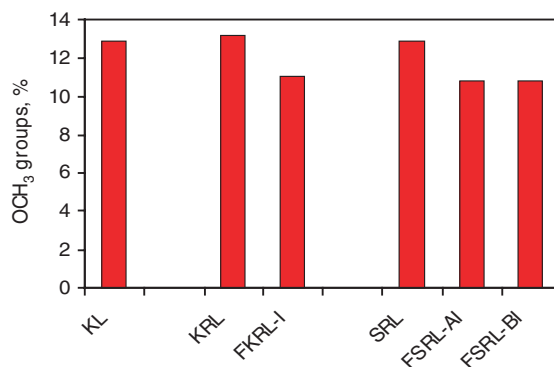
Figure 4. Methoxyl group contents of untreated and PFA-treated lignins. Values for the untreated lignins and I-fractions are corrected for residual carbohydrates and proteins (the latter calculated by multiplication of the nitrogen contents by 6.25). See Fig. 1 and Table 1 for lignin designations.

for the residual lignins. For all lignins, the dissolved fractions (II and III) are lower in phenolic hydroxyl groups than the corresponding I-fractions. These results indicate that a significant part of the lignin aromatic units were cleaved during the PFA treatments. New phenolic hydroxyl groups may have been formed by cleavage of β-*O*-4 ether linkages[9] and by hydroxylation of aromatic rings by the action of PFA[9] or hydroxyl radicals.[11] However, the results indicate that phenolic aromatic units,

Figure 5. Carboxyl group contents of untreated and PFA-treated lignins. Values for the untreated lignins and I-fractions are corrected for residual carbohydrates and proteins (the latter calculated by multiplication of the nitrogen contents by 6.25). See Fig. 1 and Table 1 for lignin designations.
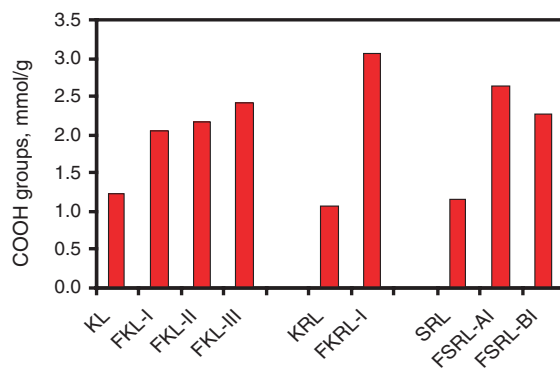
present in untreated lignins or formed during the PFA treatments, were degraded to a larger extent than new such units were formed. Also the fact that a large increase in carboxyl groups (Fig. 5) took place during the treatments suggests that aromatic rings were cleaved during the treatments, resulting in formation of muconic and other carboxylic acids. For KL, the dissolved fractions, II and III, are still higher in carboxylic groups than the I-fraction, which may in part account for their higher solubility. The higher carboxyl group content of FKRL-I as compared to that of FSRL-AI or FSRL-BI suggests that the aromatic units of KRL were more extensively degraded than those of SRL. However, it is possible that formic acid was liberated from formate esters during dissolution of lignins in alkali before the determination of carboxylic groups by conductometric titration, which could contribute significantly to the results of the carboxyl group determinations. This would make the carboxylic acid contents an unreliable measure of the extent of aromatic ring cleavage.

A smaller part of the free phenols are weakly acidic in the I-fractions than in the corresponding untreated lignins (Fig. 6). KRL and SRL have an equal proportion of weakly acidic phenols. The I-fractions of these lignins also resemble each other in this regard. The acidity of phenolic lignin units has been reported to decrease with an increase in lignin molar mass[30] rather than with the content of condensed units (C–C linkages at C5 and C6 of the aromatic ring). Therefore, it seems that either no significant formation of intermolecular condensed structures occurred
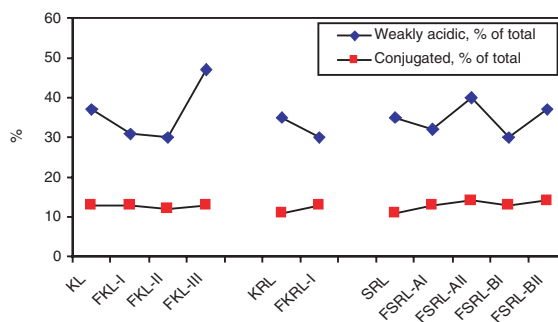
Figure 6. Percentage of weakly acidic and ring-conjugated free phenols of total free phenols in untreated and PFA-treated lignins. See Fig. 1 and Table 1 for lignin designations.

during the treatments or, if such structures were formed, their effect on the molar mass of lignin may have been counterbalanced by rupture of interunit ether (α- and β-O-4) linkages resulting in lignin depolymerization. Condensed structures such as biphenyl, biphenyl ether, and diarylmethane structures could be formed by the action of oxygen radicals formed as peroxide decomposition products[11,12] or by reactions of lignin with formic acid.[10] Also Diels-Alder reactions involving reaction products such as muconic acid derivatives and quinonoid structures, known to form in reactions between lignin and peracids,[5,6] could increase the molar mass of lignin.

All the lignin samples analyzed were found to contain an approximately equal proportion of conjugated free phenols[29] among the total phenolic units (Fig. 3). This suggests that ring-conjugated α-carbonyl groups and olefinic bonds in lignin side-chains were not significantly modified during the treatments. The survival of α-carbonyl groups agrees with the fact that the most reactive species present (PFA/HO$^+$ under acidic conditions and hydroxyl radicals) in the reaction medium are powerful electrophiles which, however, should attack electron-rich (β-carbon) sites in ring-conjugated olefinic lignin side-chains.

Molar Mass Distribution of Lignins

The molar mass distributions of lignins (Fig. 7) show that FKRL-I is more polymerized than KRL, whereas the molar masses of FSRL-AI and FSRL-BI approximately equal that of SRL. An increase in molar mass
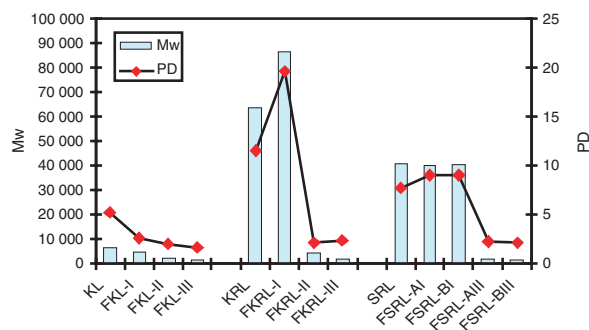
Figure 7. Weight-average molar mass (M_w) and polydispersity (PD) of untreated and PFA-treated lignins. See Fig. 1 and Table 1 for lignin designations.

during a PFA treatment may be due to occurrence of intermolecular condensation reactions and, to some extent, to esterification of lignin hydroxyl groups by formic acid.[31] In addition, an increase in ionized groups may increase the hydrodynamic volume and thus seemingly increase the molar mass. A further explanation for the high molar mass of FKRL-I is that a preferential solubilization of low molar mass fragments of KRL may have taken place during the treatment. The polydispersity of KRL is considerably higher than that of SRL, suggesting that high molar mass lignin may have enriched in FKRL-I with the lower molar mass lignin going into solution. The II-fractions have very low molar masses and those of the III-fractions are lower still, which is consistent with their high solubility.

FTIR-Spectroscopic Analyses

The assignments of FTIR spectral bands are shown in Table 3. The FTIR spectra (Fig. 8) of the I-fractions are similar but differ significantly from those of the untreated lignins. In the spectra of the I-fractions, the bands at 1708–1724 cm^{-1} from carboxylic acids and esters are more prominent relative to the bands at 1220, 1270, 1510, and 1600 cm^{-1} from aromatic units than in the spectra of the untreated lignins. This indicates that some of the aromatic units were cleaved during the PFA treatment, which is supported by the results of chemical analyses. In addition, the I-fractions also contain prominent bands from carboxyl groups centered at 1160–1170 and 1722–1724 cm^{-1}. These bands may originate largely

Table 3. Assignments of peaks in the FTIR spectra.[34]

Peak	Position (cm^{-1})	Main assignment
1	1708–1724	Formate esters (HCOOR), other esters (R_1COOR_2), carboxylic acids (RCOOH)
2	1643–1656	Carbonyl (C=O) in amides (protein contaminants), α-carbonyl groups and quinones, olefinic C=C
3	1510, 1600	Aromatic units, skeletal vibrations
4	1220, 1270	Aromatic C–O, stretching
5	1160–1170	R_1COOR_2, HCOOR
6	1030, 1080, 1150	Aliphatic C–O

from formate esters and carboxylic acid and ester groups formed as aromatic ring cleavage products. The formation of formate esters is also consistent with the lower intensity of the bands arising from aliphatic hydroxyl groups at 1150, 1080, and $1030\,cm^{-1}$ in the spectra of the I-fractions. The band at $1643–1650\,cm^{-1}$ in the spectra of the I-fractions probably arises from olefinic double bonds in aromatic ring cleavage products (e.g., muconic acids). Amide carbonyl groups of protein contaminants in the spectra of KRL and SRL show an absorption maximum at a slightly higher frequency around $1652–1656\,cm^{-1}$. In the spectra of the II- and III-fractions the bands from aromatic units are very low in comparison with those from carboxyl groups and olefinic structures. This is in line with the results of chemical analyses, indicating that the dissolved lignin fractions consist of highly degraded material.

^{13}C NMR Spectroscopic Analyses

The ^{13}C NMR spectra of the I-fractions (Fig. 9) resemble each other as expected on the basis of their FTIR spectra. The peak assignments are shown in Table 4. In particular, the spectrum of FSRL-AI (not shown) was nearly identical to that of FSRL-BI. The only notable difference between the spectra of the I-fractions is that in the spectra of FKL-I, the intensity of the prominent formate ester peak at 162 ppm is lower relative to the methoxyl peak at 56 ppm than in the spectra of FKRL-I and FSRL-BI. This is consistent with the lower carboxyl group content of FKL-I relative to those of the other I-fractions (Fig. 5). The prominence
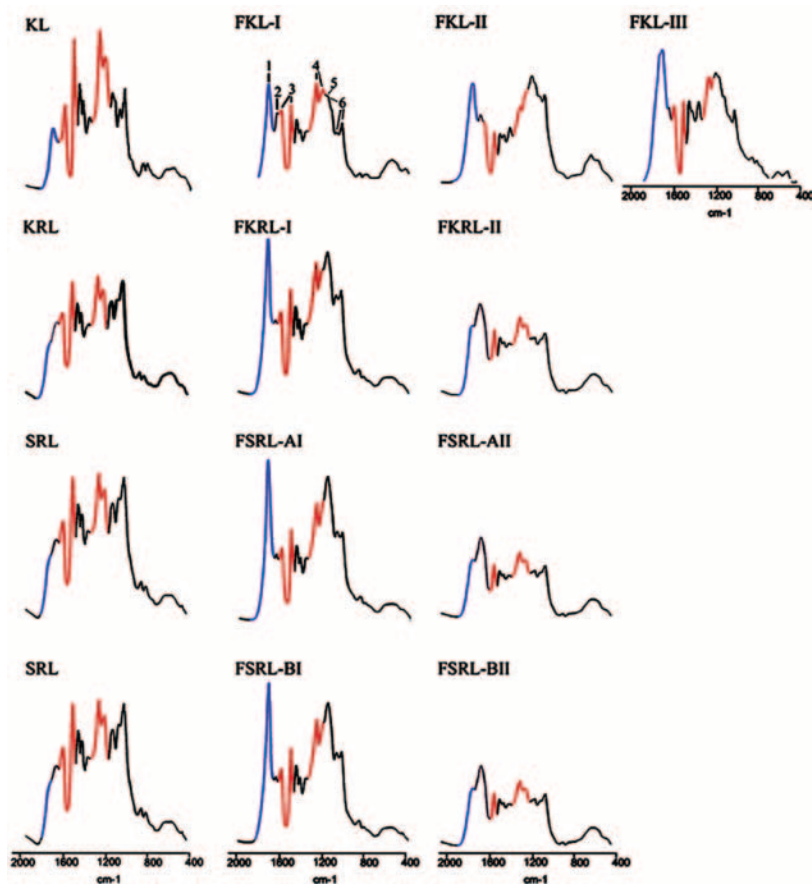
Figure 8. FTIR spectra of untreated and PFA-treated lignins. For band assignments (numbers in the spectrum of FKL-I), see Table 3. For lignin designations, see Fig. 1 and Table 1.

of the formate ester peak in the spectra of the I-fractions and the fact that the intensity of peaks from aliphatic carboxylic acids at about 170–175 ppm is not higher in the spectra of the I-fractions as compared against the spectra of the starting lignins suggest that most of the carboxylic acids detected in the I-fractions by chemical analyses may have been in fact formic acid from formate esters hydrolyzed during dissolution of lignins in NaOH before determination of carboxylic groups conductometric titration.
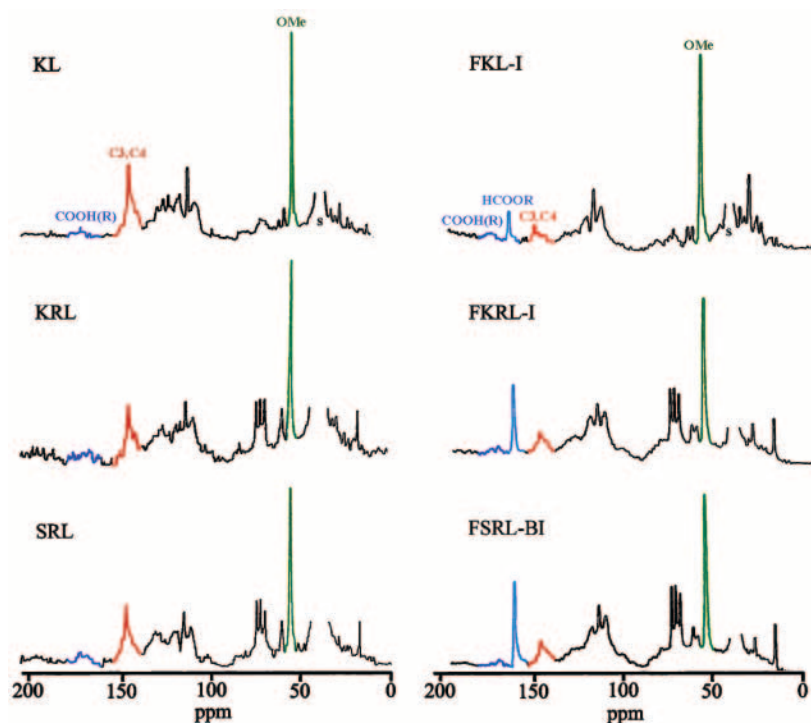
Figure 9. ^{13}C NMR spectra of untreated and PFA-treated lignins. See Table 4 for peak assignments and Fig. 1 and Table 1 for lignin designations.

Table 4. Selected spectral assignments in lignin ^{13}C NMR spectra.[31,35]

δ in ppm relative to DMSO (39.6 ppm)	Assignment
56	Aromatic OCH_3
70–80	Impurity
108–140	Aromatic C_1, C_2, C_5, and C_6, olefinic C
140–160	Aromatic C_3 and C_4
160–164	C=O in aliphatic and phenolic formate esters
170–175	Aliphatic carboxylic acids and esters
165–180	C=O in carboxylic acids, esters, and amides

All the spectra differ considerably from those of the untreated lignins in the region 100–155 ppm, containing signals from aromatic and olefinic carbons. In the spectra of the I-fractions, the signals at 123–153 ppm are lower in intensity in relation to those located in the region 108–123 ppm than in the spectra of the untreated lignins. This difference is particularly pronounced for the signals in the aromatic carbon region at 140–153 ppm from C3 and C4 of guaiacyl units relative to the region 108–140 containing peaks from other aromatic carbons and olefinic carbons. This suggests that in addition to the degradation of phenolic lignin units, shown to occur by chemical analyses, also nonphenolic lignin units were removed during the PFA treatments, e.g., by oxidative demethylation to give quinones[9] or by ring-opening reactions. The latter may be caused by PFA[9] or by superoxide radicals arising from peroxide decomposition.[12] However, the low intensity of peaks from C3 and C4 may be in part due to formylation of phenolic hydroxyl groups, changing the chemical shift of at least C4. The aliphatic formate carbonyls in a lignin model compound[31] appear at 160–161 ppm and those of phenolic formate carbonyls at 164 ppm. The formate carbonyl peaks in the spectra of the present study at 162 ppm could thus originate from both types of formate carbonyls.

CONCLUSIONS

The residual lignins KRL and SRL from conventional kraft and SuperBatch pulps, respectively, showed similar reactivities toward peroxyformic acid (PFA) in terms of PFA consumption, proportion of undissolved lignin and oxidative changes in lignin chemical structure while kraft lignin showed much lower reactivity. For SRL, an increase in peroxide charge resulted in somewhat increased lignin solubilization. Chemical and spectroscopic analyses of the starting lignins and the lignin fractions remaining undissolved (yield >80%) on PFA treatment showed that the aromatic units of KRL and SRL largely underwent ring opening. The cleavage of aromatic moieties was of the same magnitude for both KRL and SRL. The lignins solubilized during the PFA treatments consisted of highly degraded material characterized by a high content of carboxyl and formate ester groups and a low content of aromatic lignin units.

Based on the above, it can be concluded that PFA is equally effective as a prebleaching agent for both conventional kraft and SuperBatch pulps provided that reagent accessibility is not a limiting factor. The results of earlier studies suggest that PFA reactions with residual lignin

may not be dependent on the location of the residual lignin in the fiber walls due to the acid conditions under which lignin-carbohydrate bonds are split and the formylation of lignin and carbohydrates.[14] As a result, residual lignins isolated from different PFA-treated kraft pulps would have similar structures. However, in another study[32] during alkaline peroxide treatment isolated KRL and SRL showed different reactivities toward alkaline hydrogen peroxide despite the fact that residual lignins from different alkaline pulps with similar kappa numbers but different bleachabilities had been found to possess similar structures.[33] It was therefore suggested[32] that fiber wall morphology affects the bleachability of alkaline pulps with alkaline hydrogen peroxide.

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