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On the mechanistic and kinetic role of hydrogen sulfide during kraft delignification

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ABSTRACT

A mechanistic understanding of kraft delignification remains incomplete, particularly regarding the role of hydrogen sulfide in the reaction kinetics. This work examines its influence from both mechanistic and kinetic perspectives. Laboratory-scale kraft cooks on birch wood meal were conducted in a flow-through reactor, providing two main advantages: (i) continuous sampling of the immediately cooled cooking liquor, enabling snapshots of dissolved components throughout the cook, and (ii) rapid adjustments of the liquor composition, enabling kinetic evaluation without a priori assignment to simplified rate constants. The sulfide dependency was found to cease partway through the process, persisting longer than expected from the reactions typically considered to control delignification, while simultaneously indicating that said reactions are unlikely to control the rate throughout the entire process. Furthermore, significant and previously unreported differences in the molecular weight distribution between kraft and soda lignin were observed. These differences were further investigated through transient experiments and 2D NMR analysis. The results suggest that HS^- also enhances the delignification rate by the more extended demethylation occurring during kraft pulping, thereby enabling larger fractions of dissolved lignin to be removed compared with soda pulping.

KEYWORDS

Hardwood; sulfidity; soda; lignin; molecular weight

Introduction

Lignocellulosic biomass is expected to play an increasingly important role in reducing reliance on fossil carbon, with applications spanning across a wide field, e.g.: packaging, construction, pharmaceuticals, and energy. A major current use is in the paper and board industry, where global production exceeds 400 million tonnes annually and represents a market value of roughly 325 billion USD. The kraft process supplies more than 75% of this pulp,[1] meaning that even modest gains in material and/or energy efficiencies could translate into substantial economic and environmental benefits. Although ongoing research continues to target such improvements,[2] modeling and control of kraft pulping still rely predominantly on simplified empirical models rather than chemically and physically grounded models.[3] This gap underscores the need to further develop the mechanistic understanding of the kraft process.

The core operation in kraft pulping is the delignification, in which lignin is removed from the wood to liberate the fibers. The structure of lignin has since long been extensively investigated,[4] yet the full picture remains debated, and new insights continue to emerge.[5,6] It was from early on generally accepted that the key step in kraft delignification is the cleavage of the β-O-4 aryl ether linkages in lignin.[7] In the presence of HS^-, as is the case in kraft pulping, phenolic β-O-4 linkages are cleaved after a nucleophilic attack of HS^- on the quinone intermediate. In the absence of HS^- (such as during soda cooking), the quinone intermediate instead undergoes a proton or formaldehyde elimination, leaving the β–O–4 linkage intact. Under these conditions, only β–O–4 linkages in non-phenolic structures are cleaved, a process that

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also occurs independently of HS^- during the kraft process.[8] Since these reactions have been attributed as the limiting factor to the overall delignification rate, their kinetics have been the main topic of interest in many previous studies.[9–11] Based on observations of model compounds, the rate of the HS^--aided phenolic β-O-4 cleavage has been estimated to be >20 times faster than the non-phenolic counterpart[9,12] Consequently, kraft delignification has often been described as a homogeneous pseudo–first-order reaction, governed by fast and slow lignin reactions that dominate at different stages of the cook.[13]

While the presence of HS^- undoubtedly has a beneficial effect on the rate of delignification, previous reporting has been inconsistent regarding the effect of varying the concentration. The model compound studies by Ljunggren *et al.* found the phenolic β-O-4 cleavage to be independent on HS^- above a certain level (about 0.1 M),[12] which has seen support in pulping studies on chips as well.[14,15] Later studies have, however, reported a dependence on HS^- on the order of 0.1–0.4 for the majority of the cook, with only the initial and residual stage being independent on sulfide concentration.[13,16–18] In comparison, the dependence on OH^- is reported to be between slightly larger[17,18] up to twice that of HS^-.[13,16]

Despite the partly unclear role of HS^- in kraft pulping kinetics, little research has been dedicated to this topic outside cleavage of the β-O-4 bond. Traditionally, the only considered side reactions involving sulfur are the demethylation of aromatic methoxy groups, and, to some extent, its incorporation in thiolignin intermediates, neither of which has earlier been considered having an effect on the delignification kinetics.[8,19] More recently, radical-induced repolymerization reactions have also been brought up to potentially involve sulfur, although any potential effects on the delignification rate remain unclear.[20]

The purpose of this work is to revisit the role HS^- in kraft pulping kinetics. Simulated kraft cooks on birch are performed in a lab-scale flow-through reactor which allows swift variations in the process conditions. This feature enables a novel approach to study transient behaviors during kraft pulping, with the goal to discuss the role of sulfur in kraft kinetics, without necessarily limiting it to simplified reaction kinetics. The discussion is further supported by characterization of the dissolved lignin to further evaluate the relative impact from different sulfur-involving mechanisms.

Materials and methods

All experimental work was carried out on birch (*Betula pubescens*) wood meal from industrially cut chips, ground in a Wiley mill and sieved to particles passing a 1-mm mesh. The wood meal was air dried, and the dry content analyzed before each cook, typically about 92%. Pulping experiments were performed in a flow-through reactor setup as described elsewhere.[21] In short, a known mass of 4–5 g wood meal was evenly distributed within a tube reactor. The reactor was capped and connected to a pump system supplying a continuous flow of liquid, typically at 2.5 ml/min, but with an initially higher flow to counteract the alkali-consuming reaction predominantly occurring during the early stage of the cook. After impregnation at room temperature (maintaining a continuous flow of liquor), the reactor was submerged in an oil bath at 150 °C, reaching the target temperature within a few minutes. In runs with transient conditions, variations in the liquor composition were achieved by a second liquor container connected to a 3-way valve prior to the reactor inlet, with the exchange estimated to occur in below 3 min.[22] The cooks were terminated by submerging the reactor in room temperate water. The spent cooking liquor (black liquor, BL) was immediately cooled upon exiting the reactor through a heat exchanger connected to cold tap water. The pulp was then washed until neutral and dried at 105 °C overnight. Calculated pulp yields for selected experiments are reported in the supplementary material.

Cooking liquor was prepared fresh from Na2S (hydrate) flakes in de-ionized water in concentrated form and diluted to the required HS^- concentration following standard ABC titration (e.g SCAN N 2:88.) Assuming full hydrolysis of Na2S into equal parts HS^- and OH^-, the total OH^- concentration was then for all cases adjusted to 0.35 M by addition of NaOH (with the exception of comparisons made with previously published data using 0.7 M OH^-[23]). The *soda* liquor was prepared using only NaOH to 0.35 M. Five different levels of HS^- was investigated: 0 (soda), 0.008 M (Ultra-low, UL), 0.05 (Low, L), 0.15 (Medium, M), and 0.35 (High, H).

The BL was sampled at different intervals, measured from the submersion of the reactor into the heating bath: 0–5 min was sampled in a single interval, between 20 and 60 min the sampling interval was 20 min, and from 60 min onwards the sampling interval was 30 min. Each sample was denoted by the final time of the interval, e.g. liquor sampled between 60 and 90 min was denoted the "90 min" fraction. Lignin was separated from the BL by acid precipitation to pH 2.5 using H2SO4, followed by freezing and filtering, as described elsewhere.[24]

The extent of delignification was followed by determination of the remaining lignin content of the pulp

in terms of Klason (acid-insoluble) lignin, following the procedure by NREL.[25] The acid-soluble lignin (ASL) was quantified, but excluded from subsequent analysis as it is subject to several uncertainties, such as species dependent absorptivities and interference from extractives and carbohydrate degradation products.[26,27] The molecular weight of the precipitated BL lignin was estimated using gel permeation chromatography in DMSO + LiBr (10 mM) as eluent. Calibration was performed using pullulan standards ranging from 0.18-708 kDa. Accurate estimation of molecular size is challenging for lignin, particularly for hardwood kraft lignin. However, pullulan exhibits a log-linear response comparable to MALS measurements, making it suitable for relative comparison among similar samples.[28] Accordingly, any discussion of specific molecular sizes herein serves mainly to facilitate interpretation and clarify the figures. Structural characterization of the precipitated lignin was carried out using 2D NMR HSQC spectroscopy, in DMSO-*d*6, using a probe operating at 800 MHz. A full description of the analytical procedure is found in our previous work.[24]

Results and discussion

The impact of hydrogen sulfide on the delignification rate

The effect of sulfide ion concentration on the remaining lignin content in the pulp is shown in Figure 1. A clear dependence on HS^- concentration is observed, with the influence appearing more pronounced during the middle stage of the cook than at the beginning or end. The initial rate, as inferred from the slope between successive time points, continues to increase with HS^- concentration even above 0.15 M, although the impact appears to become progressively smaller. Figure 1 also presents corresponding data for variations in OH^- concentration at constant HS^-. Within the concentration ranges studied, the HS^- level exerts a relative influence on the overall delignification rate comparable to that of OH^-. These observations align more closely with reported values from wood pulping studies (e.g Nieminen and Sixta, 2012) than with earlier findings based on model compounds,[9] suggesting that the behavior of isolated model compounds may be of limited relevance for predicting kraft pulping kinetics.

Figure 2 illustrates the transient behavior of the dependence on HS^- concentration. In these experiments, the cooking liquor was switched from a regular kraft liquor (containing both HS^- and OH^-) to a soda liquor (containing only OH^-) at various times during the cook. When the replacement was performed at the beginning of the process, the average delignification rate was substantially reduced. In contrast, replacement after 60 min resulted in no significant difference compared to the pure kraft cook at the end of the process. This indicates that under the conditions studied, essentially no sulfide-dependent reactions affecting delignification occur beyond 60 min. At this point, the degree of delignification is approximately 80% (corresponding to a lignin content of 4.1% o.w.), which occurs earlier than previously reported. The Gustafsson model suggest that the transition to the sulfide-independent residual stage occurs

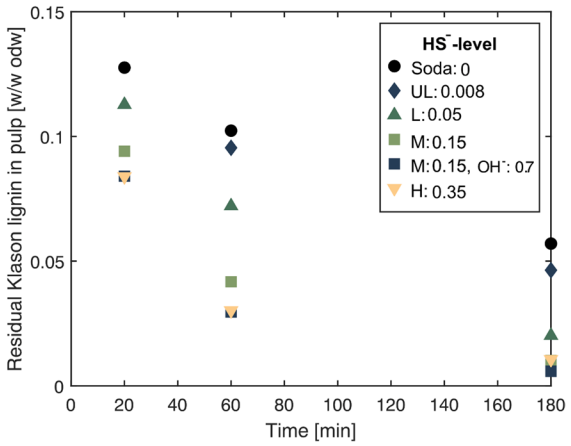

Figure 1. Variations in remaining Klason lignin content in the pulp over time during kraft pulping at Ultra-low (UL), Low (L), Medium (M), and High (H) HS^- concentrations, as well as for soda pulping. The OH^- concentration was kept constant at 0.35 M, except where otherwise indicated. Normalized to original wood weight.

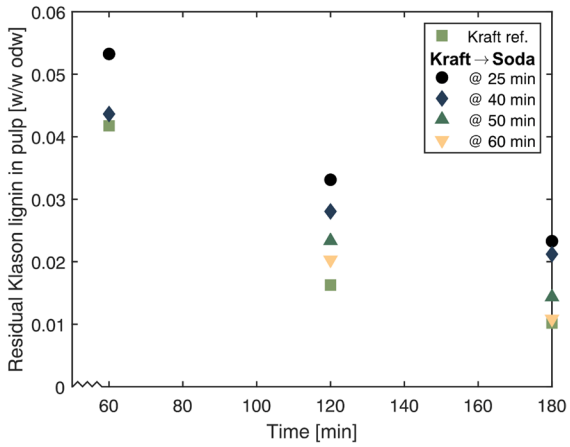

Figure 2. Variations in remaining Klason lignin content in the pulp during pulping under transient conditions. The cooking liquor was switched from Medium kraft (HS^-: 0.15 M; OH^-: 0.35 M) to soda (no HS^-; OH^-: 0.35 M) after the time points indicated in the legend. Normalized to original wood weight.

at around 2% lignin content for spruce and eucalyptus,[13,17] and even lower for birch.[29] However, models based on the Purdue approach assume that all lignin reactions are sulfide dependent,[13,30,31] although Andersson *et al.* allowed a small fraction (1.5% o.w.) of lignin to react independently of the HS^- concentration.[18] It should be emphasized, however, that these models are based on batch cooking of wood chips. Therefore, direct comparison with the present study, which employs flow-through cooking of wood meal, should be made with caution.

The impact of hydrogen sulfide on the molecular weight of the precipitated lignin

To further investigate the effect of hydrogen sulfide, lignin dissolved in the black liquor from kraft and soda cooks was precipitated and analyzed for its molecular weight distribution (MWD). The results are shown in Figure 3. Notably, the first fraction of BL contained high amounts of dissolved xylan, resulting in a precipitated "lignin" heavily contaminated (about 50%) with carbohydrates. The contamination is substantially lower for the remainder of the cook, as >75% of xylan removal occurred in the first 10 min. Correspondingly, the carbohydrate content of the 60 min fraction was 6%.

A clear distinction is observed between the MWD of soda and kraft lignin when the sulfide concentration is at least 0.05 M. Soda lignin lacks the distinct peaks at approximately 350 and 1600 Da that dominate the early-stage kraft lignin profiles. Instead, it is characterized by a single, broad peak around 3000 Da, accompanied by a smaller peak near 150 Da. Furthermore, the MWD of kraft lignin shifts progressively toward higher molecular weights over time (Figure 3c), whereas the MWD of soda lignin remains essentially constant during the first 120 min and only begins to increase at later stages (Figure 3d). At ultralow HS^- concentrations (0.008 M), the MWD closely resembles that of soda lignin, although a minor fraction of structures around 1600 Da is still present. Similar trends were noted in Figure 1, where the final degree of delignification differs clearly between the soda and ultralow-HS^- kraft cooks on one hand, and the rest of kraft cooks on the other.

Figure 4 shows the transient response of the lignin MWD when shifting from kraft to soda liquor after 60 min, together with reference kraft cooks. Notably, the distinctive peak around 1600 Da was still present

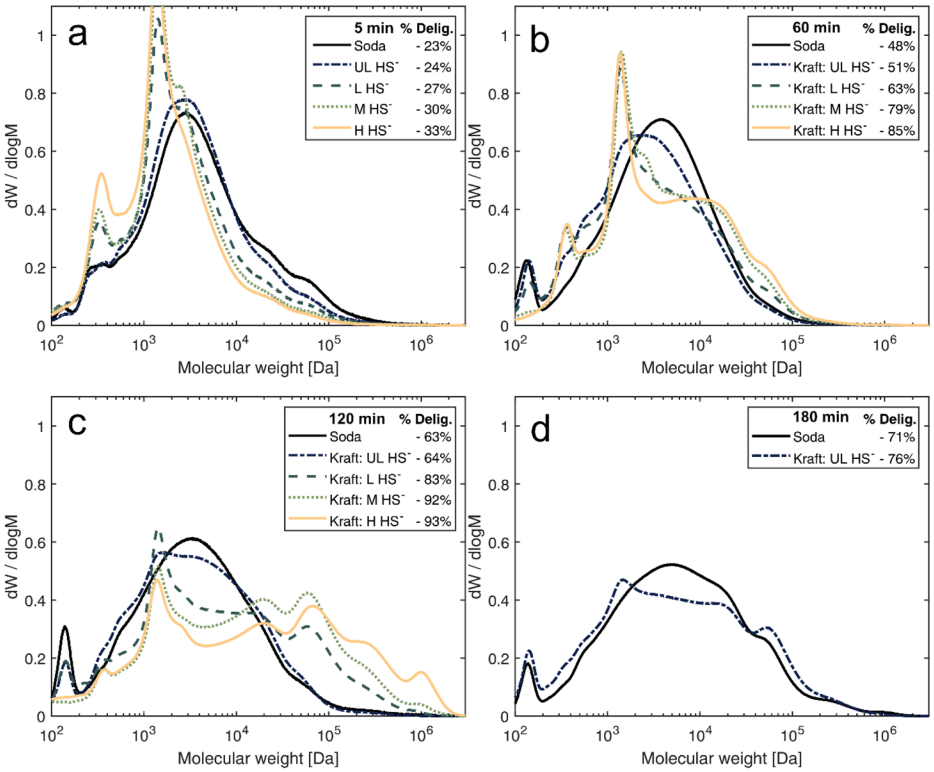

Figure 3. Molecular-weight distributions of lignin precipitated from black liquor sampled after 5 (a), 60 (b), 120 (c), and 180 (d) minutes during soda, and kraft cooks at Ultra-low (UL), Low (L), Medium (M), and High (H) HS^- concentrations. Legends include degree of delignification for each sample, which were measured (b & d) or estimated (a & c) based on the data presented in Figure 1.

in the 150-minute fraction of the kraft cook (dashed line), whereas it was completely absent in the corresponding HS-free transient data (solid line). As inferred from Figure 2, there was no significant difference in the extent of delignification of delignification between these two cases. Whatever reaction produces these peaks appears to be fast, as they emerged already at the beginning of the cook (see Figure 3a). Likewise, additional transient kraft-to-soda experiments showed that these structures are removed, either through diffusion or further degradation, within 10–20 min after switching to soda liquor (results included in the Supplementary Material).

Altogether, these results suggest that a reaction occurs continuously throughout the entire kraft cook, generating relatively low-molecular-weight structures (ca. 1600 Da) without having a significant impact on the overall delignification rate. Although the cleavage of phenolic β-O-4 linkages is known to occur predominantly under kraft conditions, this reaction is unlikely to explain the observed behavior, since it is generally considered mainly in the early stages of pulping and, in addition, to have a large influence on the delignification rate. Hence, other sulfur-involving reactions likely occur during kraft cooking, affecting both the lignin structure and, possibly, the delignification rate.

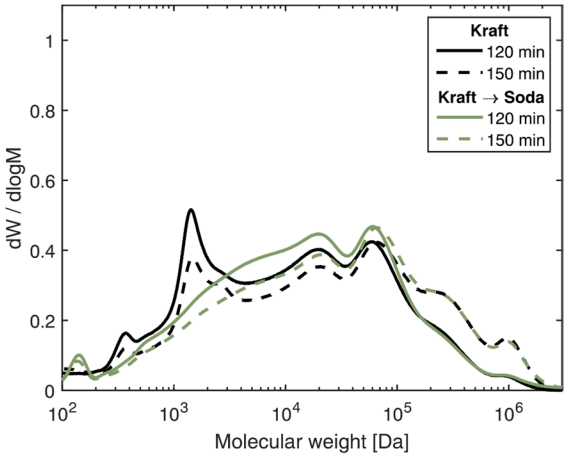

Figure 4. Molecular-weight distributions of lignin precipitated from black liquor during regular kraft (black) and transient (green) conditions. For the transient cooks, the liquor was switched from regular kraft to soda after 60 min.

Structural variations between kraft and soda lignin

Variations in the structure of the precipitated lignin was further studied using HSQC NMR spectroscopy. The resulting spectra of the aromatic regions are shown in Figure 5 for pure Kraft and Soda lignins. Spectra of the aliphatic regions, as well as of lignin from transient kraft-to-soda cooks are included in the Supplementary Material. The most notable difference in the aromatic region is the presence of several signals in the kraft lignin spectra that are absent or strongly reduced in the soda spectra. Similar trends are observed in the transient runs, where these signals are diminished when switching to soda liquor after 25 min. On the basis of the available literature, these peaks could only be partially identified.[32–35] Differences in the aliphatic region between soda and kraft lignin were relatively minor. Expectedly, the soda lignin contained more β-O-4, albeit these structures are highly dominant in the kraft samples as well. Other inter-lignin linkages (β-5, β-1, β-β' and enol ethers) were all detected in both kraft and soda lignin, though no quantitative difference could be determined due to the qualitative nature of the applied HSQC sequence.

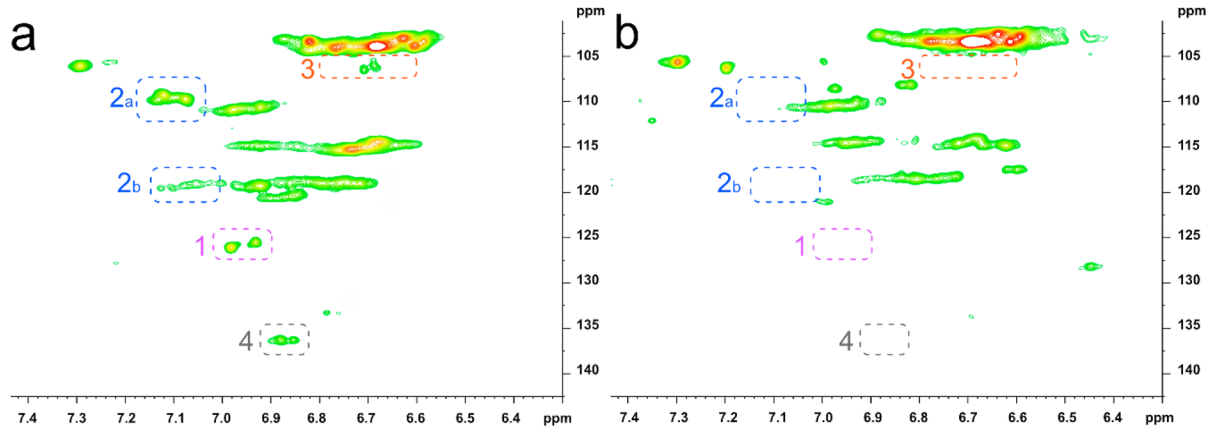

Figure 5. HSQC NMR spectra of lignin precipitated from kraft (a) and soda (b) cooks. Samples were taken after 5 min (kraft) and 20 min (soda), corresponding to delignification degrees of 30% and 34%, respectively. Highlighted areas indicate regions with substantially weaker signals in the soda spectrum. Region 4 (grey) remains unidentified.

One structure that appears only in the kraft spectra, labeled as region 1 in Figure 5, can be attributed to guaiacyl stilbenes.[36,37] Stilbene structures are known to be generated during kraft cooking by removal of formaldehyde from phenyl coumaran and β-1 structures.[5] The increased presence of stilbenes in the kraft lignin likely stems from the greater nucleophilicity of HS^- compared to OH. However, because these reactions neither cleave interunit linkages nor introduce additional charged groups, they are expected to have only a limited influence on the overall delignification rate. Conversely, these reactions remove hydroxyl groups, which may otherwise contribute positively to lignin solubility. On the other hand, it has also been suggested that stilbenes may form from condensation reactions with phenolic structures which, notably, would also result in a cleavage of β-aryl ether linkages,[38] although this view has later been criticized.[39]

Another difference between the kraft and soda spectra are the regions labeled 2, which are tentatively attributed to correspond to downfield shifted signals of the C_2 and C_6 guaiacyl peaks. Similar HSQC shifts have previously been suggested to be caused by condensed structures such as 1-1′ and 1-5′ linkages,[34,36] and the 5-5′ structure in dibenzodioxocin.[35] Similar shifts appear to occur to a greater extent also in the $C_{2,6}$ signal of the syringyl peaks in the kraft spectra, albeit the overlap with the non-shifted signals is more severe than for the guaiacyl counterpart, complicating even semi-quantitative assessment of these peaks. Further, the region labeled 3 appears only in the kraft lignin but is absent in the soda lignin. This region could possibly correspond to 4-O-5 structures,[40] although these are notoriously difficult to assign in carbon-proton HSQC as the namesake linkage itself lack C-H bonds, in addition to the overlap with the dominating $C_{2,6}$ signal of the syringyl units.

The formation of these condensed (C-C and C-O-C) linkages have been suggested to be induced by radical couplings,[39,41] which has recently gained more support.[5,34] Majtnerová and Gellerstedt proposed the involvement of sulfur as an electron acceptor in these reactions in the form of lignin disulfides, although it could not be demonstrated conclusively. Nevertheless, the results of this study lends support to this theory, as these condensed structures appears to a much greater extent in lignin from kraft liquor compared with soda liquor. However, it is uncertain whether the radical-induced condensation reactions would have any significant impact on the delignification rate, as was initially suggested by Gellerstedt et al.: Although condensation increases the molecular weight of lignin (which in general would be detrimental to the delignification rate), Crestini et al. showed that the branched structures suggested to stem from the radical-induced reactions are mostly prevalent in the easy-soluble low MW fraction.[5] Consequently, the radical reactions would then mostly result in relatively easily removed oligomeric fragments, which shouldn't hinder the overall delignification.

Such oligomeric fragments could possibly be the cause of the distinctive peaks which only appear in the MWD of the kraft lignin of Figure 3. In a similar vein, the peak appearing in the monomeric range (150 Da) predominantly occurs in the soda lignin, which could potentially stem from degradation products which haven't re-polymerized due to the absence of organic sulfur compounds. The 1600 Da peak in the MWD could also be caused by the stilbene structures which were found only in the kraft lignin, albeit our previous data showed that the stilbene signals are heavily diminished in late fractions (120 min), despite still showing a significant peak in the MWD data.[21] Consequently, at this stage, only preliminary conclusions can be drawn regarding the chemical structures responsible for the distinctive peaks in the molecular weight distribution.

The interplay of sulfide-involving mechanisms

The pulping results in this work reaffirm the well-established observation that the presence of HS- enhances the rate of delignification. However, notable discrepancies exist between previously reported experimental observations of the *apparent* HS^- dependence and the mechanistic assumptions typically proposed to account for it: Sulfides are likely only affecting the rate of β–O–4 cleavage when the linkage is of the phenolic type.[9] Yet, phenolic β–O–4 linkages constitute only approximately 17–32% of all β–O–4 structures in softwood lignin,[42–44] and as little as 6% in the S-type lignin of poplar.[43] Furthermore, as previously discussed, the reactions involving phenolic structures are believed to proceed significantly faster than those involving non-phenolic β–O–4 linkages. Therefore, if overall delignification kinetics were governed solely by these reactions, the dependence on sulfide would be expected to diminish much earlier in the process—both in terms of time and degree of delignification. This suggests that additional mechanisms must contribute to the observed overall kinetics.

A possible explanation for the extended HS^- dependence is the cleavage of non-phenolic β–O–4 linkages. Although these reactions are essentially HS^--independent, each cleavage generates a new phenolic

unit, which can subsequently participate in HS^--facilitated β–O–4 scission if it is involved in another ether linkage. This cascading transformation, sometimes described as "peeling" of aromatic units, has been proposed to contribute to overall delignification kinetics.[45] However, such a sequence can only continue while successive β–O–4 linkages are present. Given that hardwood lignin contains roughly 60 β–O–4 linkages per 100 aromatic units,[46] and assuming an approximately even distribution of linkage types,[6,47] the overall extent of this peeling mechanism is expected to be limited.

Another potential explanation for the extended HS^- dependence is that not all β–O–4 linkages are equally accessible throughout the cook. If a fraction of the lignin remains initially inaccessible—a deviation from the homogeneous-reaction assumption commonly used in kinetic models—continued reliance on HS^- could still be reconciled with the rapid cleavage of phenolic β–O–4 structures. Lignin accessibility heterogeneity has been considered primarily in the context of chip impregnation[48,49] and although some pulping models incorporate heterogeneous delignification,[31,50,51] experimental evidence remains limited.[52,53] Moreover, in the present work, pulping was performed on wood meal rather than chips, yet the prolonged HS^- dependence persists, indicating that any accessibility constraints must in this case arise at the fibre-wall scale. To our knowledge, no studies have investigated the lignin heterogeneity at the microscale during kraft cooking, as experimental verification at such scale (~μm) is inherently challenging. Regardless, cleavage of β–O–4 linkages alone cannot account for the continuously increasing molecular weight of the dissolved lignin, indicating that additional mechanisms contribute to the overall delignification rate during this time frame.

Consequently, the sulfide-dependent behavior may most probably arise from additional HS^--mediated reactions. As already addressed, the formation of stilbenes and possible radical-induced polymerization likely exert only minor influence on the overall delignification rate. However, demethylation, which mainly occurs during kraft pulping, introducing $C_{3,5}$ phenolic groups (potentially as catechols), warrants consideration. These phenolic groups enhance lignin solubility[54,55] and may in addition undergo further reactions.[5,9] Similarly, in fractionation of kraft lignin, the less soluble fractions have shown higher content of the remaining methoxy groups, further indicating that demethylation may be beneficial for lignin solubility.[5,56] A semi-quantitative evaluation of our NMR data suggests similar trends, with the kraft samples appearing more demethylated than the soda samples and the 120 min fraction more demethylated than the 60 min fraction (see Supporting Material).

Although previous research on the effect of demethylation on the delignification rate is scarce, it has been shown in enzymatic studies that these reactions enables extraction of the residual lignin in pulp.[57,58] Moreover, demethylation may be quite extensive in kraft cooking, with more than 20% of aromatic units in softwood lignin reported to be demethylated,[5,59] and likely to an even greater extent in hardwood.[60] Demethylation proceeds more slowly than β–O–4 cleavage[45] which may explain why sulfide concentration affects the kinetics for an extended period (approximately 60 min in Figure 2) without contradicting the established rapid cleavage of phenolic β–O–4 linkages.

This interpretation suggests that HS^- also contributes to delignification by enhancing lignin solubility rather than solely by cleaving phenolic β–O–4 linkages, consistent with recent views regarding the impact of lignin solubility.[45,55,61,62] If bond cleavage were the dominant effect, kraft pulping should, if anything, yield smaller dissolved fragments than soda pulping. Although this is observed early in the cook, larger fragments appear under kraft conditions after about 60 min (cf. Figure 3), pointing to the increasing role of solubility. Without HS^-—and thus with limited demethylation—lignin solubility remains insufficient to release such large fragments, even at extended times. In transient cooks (Figure 4), the high-molecular-weight fractions resemble those from continuous kraft pulping, indicating that the initial HS^--rich stage had already rendered the lignin soluble. Beyond roughly 60 min (for the given conditions), delignification is therefore governed mainly by diffusion of these large, solubilized fragments rather than by further chemical reactions.

Overall, the evidence indicates that several HS^--mediated processes may shape the delignification kinetics, extending well beyond the cleavage of β–O–4 linkages. Based on our interpretation of the data, we propose that in the early stage of the cook, rapid β–O–4-scission reactions fragment the lignin network and introduce hydrophilic groups, leading to fast, strongly HS^--dependent delignification and the formation of relatively small, uniform fragments (Figure 3a and b). Concurrently, the slower yet sustained demethylation reaction continues to generate additional phenolic groups, enhancing solubility and maintaining an HS^- influence on the overall rate. Once the bulk of the lignin has been rendered soluble, the process becomes increasingly governed by the

diffusion of the remaining large fragments, with limited further contribution from HS^-. Other HS^--dependent reactions, such as stilbene formation or radical-mediated condensation, occur concurrently but appear to have only minor impact on the overall removal rate.

Conclusions

- The effect of HS^- concentration on the kraft delignification kinetics was re-visited. The results showed a pronounced HS^- dependence which ceased partway through the delignification. This behavior cannot be explained by β–O–4-cleaving reactions alone, suggesting that HS^- affects delignification rate through additional mechanisms.
- The molecular-weight distributions of kraft and soda lignin were determined, revealing substantial and previously unreported differences. The observed trends of large, dissolved lignin fragments suggest that lignin solubility differs markedly between kraft and soda pulping in the later stage of delignification. The results are consistent with a diffusion-limited process in which sulfide-induced demethylation likely plays a significant role in promoting lignin solubility, thereby explaining the observed HS^--dependence.
- Supported by additional structural characterization the results indicated that HS^- contributed to the formation of stilbenes and low-molecular conjugated structures, neither of which appeared to significantly affect the delignification rate.

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Language improvements of the text were performed through generative AI (model GPT-5) through alterations of tone and grammar. The use did not include analysis of data, review of literature, or synthesis of original text. All revisions were manually reviewed by LK. All the authors have accepted responsibility for the entire content of this article and agreed on its submission for publication.

Authors' contributions

CRediT: **Linus Kron**: Conceptualization, Formal analysis, Investigation, Methodology, Writing – original draft, Writing – review & editing; **Hans Theliander**: Conceptualization, Formal analysis, Funding acquisition, Supervision, Writing – review & editing.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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Data availability statement

The data that support the findings of this study are available from the corresponding author, MH, upon reasonable request.

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