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Influences of 2-ethylanthraquinone on lignin degradation in alkaline cooking of *Eucalyptus pellita* wood

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Abstract

The impact of 2-ethylanthraquinone (2-EAQ) on alkaline cooking of *Eucalyptus pellita* wood was examined by analyzing pulp yield, kappa number, the structure and weight-averaged molecular weight (Mw) of dissolved lignin in black liquor and residual lignin in pulp (RL). During soda cooking under 23% of active alkaline (AA) condition, adding 0.06% 2-EAQ reduced the kappa number by 12 points compared to cooking without it. The addition of 0.06% 2-EAQ to kraft cooking increased pulp yield by about 4% at about 19 of kappa number compared to the no addition. The analysis of lignin structure by using semiquantitative heteronuclear single quantum correlation nuclear magnetic resonance (HSQC NMR) showed that the addition of 2-EAQ promoted β -ether cleavage during alkaline cooking and reduced peeling reaction of polysaccharides and prevention of the elimination of γ -OH of lignin to form enol ethers and stilbenes. Overall, the addition of 2-EAQ promoted the degradation of lignin to lower molecular weight compounds, with a more pronounced effect observed in soda cooking than in kraft cooking. Under optimal conditions, the delignification efficiency and pulp yield of soda-EAQ pulping were comparable to kraft cooking.

Keywords Anthraquinone derivatives, Alkaline cooking, *Eucalyptus pellita*, Lignin structure, HSQC NMR

Introduction

Anthraquinone (AQ) has been attracted attention as an additive for alkaline cooking since 1972 [1–3] because it improves pulp yield and reduces cooking time, chemical use, and energy consumption even if the addition is in small amounts. In the pulping reaction, AQ is thought to act as a catalyst for the reductive cleavage of β -O-4 bonds in lignin, which accompanies oxidation of anthrahydroquinone (AHQ), the reduced form of AQ, and for the prevention of polysaccharide peeling reactions by oxidation of reducing terminal aldehydes to carboxylic acids, which accompanies reduction of AQ, the oxidized form in the catalytic cycle with AHQ. However, this mechanism has

been discussed mainly by experiments using low molecular weight model compounds and has not yet been clearly elucidated.

AQ is an effective additive for pulp production; however, its mutagenic and carcinogenic potential has recently been reported [4, 5]. There are three industrial production methods for AQ: anthracene oxidation, Friedel–Crafts reaction, and Diels–Alder reaction. The purity of industrial AQ depends on the manufacturing method, and some impurities are known to be mutagenic or carcinogenic. For example, the AQ obtained by the oxidation of anthracene contains impurities such as 9-nitroanthracene, 2-nitroanthracene, and phenanthrene, the toxicity due to these impurities has been reported [6].

Recently, several research groups have reported that AQ derivatives, like AQ, also show effective performance in increasing pulp yield and reducing lignin content in pulp. 2-Methylanthraquinone (2-MAQ) was shown to be effective in increasing pulp yield in soda and kraft

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cooking of wood and non-wood lignocelluloses [7–10]. 2-MAQ had been subjected to a mutagenicity test (Ames test) using *Salmonella typhimurium*. The results showed that even high concentrations of 2-MAQ were negative for mutagenicity [8]. 2-Ethylanthraquinone (2-EAQ) is also a candidate as the additive. It is synthesized industrially as a catalyst to produce hydrogen peroxide and is more versatile than other AQ derivatives [11]. It does not contain impurities such as 9-nitroanthracene or 2-nitroanthracene and is expected to be non-toxic.

In this study, the potential of 2-EAQ as the additives for pulp production was investigated and the effect of 2-EAQ on the degradation of lignin during soda and kraft pulping processes of *Eucalyptus pellita* (*E. pellita*) was analyzed using HSQC-NMR spectroscopy and gel permeation chromatography (GPC).

Eucalyptus is one of the commonly used fast-growth wood species in the paper industry. Compared to *Eucalyptus globulus*, *Eucalyptus pellita* is more suitable for plantation in areas with high annual rainfall and can withstand intensive rainfall. Due to its high productivity and adaptability to a wide range of soil and environmental conditions, *E. pellita* is grown in plantation areas in Southeast Asia and used for pulp production [12].

The effects of 2-EAQ on the alkaline pulping of *E. pellita* have not yet been studied. The findings of this study will provide useful information to elucidate the effects of anthraquinone derivatives on the alkaline cooking of hardwoods and to promote the plantation of *E. pellita*.

Materials and methods

Materials

E. pellita was kindly provided by Marubeni Corporation (Tokyo, Japan). It was air-dried and stored at room temperature.

Preparing soluble 2-EAQ

2-EAQ was reduced to 2-ethylanthrahydroquinone (2-EAHQ) to dissolve in an alkaline solution. 2-EAQ (100 mg), glucose (200 mg), and 2 mol/L NaOH (10 mL) were added in a vial and heated at 95–100 °C for 1 h.

Soda cooking and kraft cooking

In this paper, the dosage was described based on 2-EAQ because 2-EAHQ is difficult to determine. Wood chips (50 g, oven-dried) were placed in a stainless-steel reactor and subjected to alkaline cooking with the 2-EAHQ solution (soda-EAQ cooking and kraft-EAQ cooking) with 250 mL of liquor (liquor-to-wood ratio: 5) for 3 h at 150 °C. The amount of 2-EAQ used varied between 0.03 and 0.1% based on the weight of the oven-dried wood chips. The active alkali (AA) condition used in these

experiments ranged between 21 and 25%, and 20% sulfidity was adopted in kraft cooking.

Kappa number of pulp

Pulp samples were analyzed for kappa number using TAPPI standard test methods (T236 om-13) [13] to evaluate the effectiveness of the delignification.

Preparation of dissolved lignin in black liquor

The lignin was precipitated out by adding 1 mol/L HCl into black liquor (30 mL) to adjust the pH to 2.8. The crude lignin was collected after centrifuging and washing with distilled water to remove salts and saccharides three times. The precipitate was then dried in an oven for 24 h to obtain the dissolved lignin in black liquor. The yield obtained by soda cooking without (SL) and with 2-EAQ (SL-2-EAQ) were 1.6 and 1.3 g, respectively. That obtained by cooking without (KL) and with 2-EAQ (KL-2-EAQ) were 1.3 and 1.4 g, respectively.

Isolation of residual lignin (RL)

For identifying the structure of RL, dried pulp samples were milled further using a planetary ball mill (PULVER-ISETTE 6 classic line, FRITTSCH GmbH, Idar-Oberstein, Germany) with zirconia balls (5-mm diameter, 100 g) in a zirconia jar at 600 rpm for 1.5 h (grinding for 2 min, waiting for 2 min, 15 cycles × 3 sets with 30 min intervals) to obtain a ball-milled pulp sample [14]. The ball-milled pulp samples were treated with crude cellulases (Cellulysin, Merck Millipore, USA) to prepare the RL. The ball-milled pulp (4 g) was suspended in acetate buffer (pH 4.5, 200 mL), and 50 mg of the cellulases was added. The reaction mixture was incubated and shaken on a rotary incubator shaker at 35 °C for 48 h. The insoluble residue was collected by centrifugation (9000 rpm, 30 min) using Allegra X-30 with F0630 rotor (Beckman Coulter, Indianapolis, USA). This enzyme treatment was repeated three times [15]. After washing with distilled water and freeze-dried, the RL (about 100 mg) was obtained.

Acetylation of RL

For the acetylation, RL was completely dissolved in a solvent (DMSO: *N*-methylimidazole (2: 1, v/v) followed by the addition of acetic anhydride. The reaction mixture was stirred at room temperature for 24 h. The solution was poured into cold water and then collected by filtration through a membrane filter (H050A047A, Advantec, Japan). After washing with water remove *N*-methylimidazole and acetic acid, the filtrate was freeze-dried to obtain the acetylated RL (AcRL) [16].

NMR analysis

We subjected the following samples to NMR analysis: dissolved lignins: SL, SL-2-EAQ, KL and KL-2-EAQ; residual lignins: obtained from pulp prepared by soda cooking without (RSL) and with 2-EAQ (RSL-2-EAQ), kraft cooking without 2-EAQ (RKL) and with 2-EAQ (RKL-2-EAQ). The NMR spectra were recorded in a JEOL 600 MHz NMR spectrometer (JEOL, Ltd., Tokyo, Japan) after 50 mg of each dissolved lignin, and AcRL was dissolved in 0.5 mL of DMSO-*d*₆ and transferred into NMR tubes for NMR experiments. The signals were assigned by the reported data from the literatures [17–27].

Gel permeation chromatography

The molecular weight distribution of the dissolved lignin in black liquor was determined by gel permeation chromatography (GPC) using a column filled with Sepharose CL-6B (Sigma-Aldrich, inner diameter 10 mm, length 400 mm) and a UV detector (AC5200s, ATTO Co., Tokyo, Japan) at 280 nm. 0.5 mol/L NaOH was used as an eluent at a flow rate of 1 mL/min. The black liquor from cooking experiments was diluted 5 times and then 1 mL of the solution was injected into the column. The calibration curves were created with the standards of polystyrene sulfonate (molecular weight: 210, 5400, 100000, Polysciences, Inc., Commonwealth of Pennsylvania, USA).

Results and discussion

Effect of AA and 2-EAQ dosages on kappa number of pulp

E. pellita was subjected to soda and kraft cooking at 150 °C for 3 h with three AA dosages (21%, 23%, 25%) and four 2-EAQ dosages (0%, 0.03%, 0.06%, 0.1%). Relationships between AA dosage and kappa number are shown in Fig. 1, which reveals that the kappa numbers of pulp

cooked with 2-EAQ are lower than those cooked without 2-EAQ at the same AA dosage in both soda (Fig. 1A) and kraft (Fig. 1B) cooking.

In a comparison of soda cooking and kraft cooking, the effect of 2-EAQ addition was more pronounced in soda cooking than in kraft cooking. This could be attributed to SH[−] involvement in lignin degradation as well as 2-EAQ in kraft cooking, thus reducing the effect of 2-EAQ addition.

Effect of 2-EAQ dosage on pulp yield and kappa number

At 150 °C for 3 h, the effective dosage of 2-EAQ in soda and kraft cooking was studied in 21–25% AA condition. Figure 2 illustrates the relationship between kappa number and pulp yield in soda and kraft cooking. In soda cooking (Fig. 2A), it was observed that a 0.06% dose of 2-EAQ significantly decreased kappa number by approximately 12 points (from 32 to 19) while maintaining around 50% of pulp yield. For kraft cooking (Fig. 2B), at about 19 of kappa number, the yield of the pulp increased by around 4% with the addition of 0.06% 2-EAQ. At the pulp yield of about 49% in kraft cooking, the addition of 2-EAQ reduced the kappa number in kraft cooking by about 4 points. The results indicate that 2-EAQ promotes delignification in soda and kraft cooking. Increasing the dosage of 2-EAQ to 0.1% had no significant effect on pulp yield, suggesting that a 0.06% addition of 2-EAQ was appropriate.

Considering that pulp can be damaged, it is desirable to reduce AA. Based on a comprehensive consideration of the relationship between AA and kappa number (Fig. 1) and that of pulp yield and kappa number (Fig. 2), the optimal pulping conditions for achieving a kappa number around 19 were estimated to be 23% AA for both soda and kraft pulping.

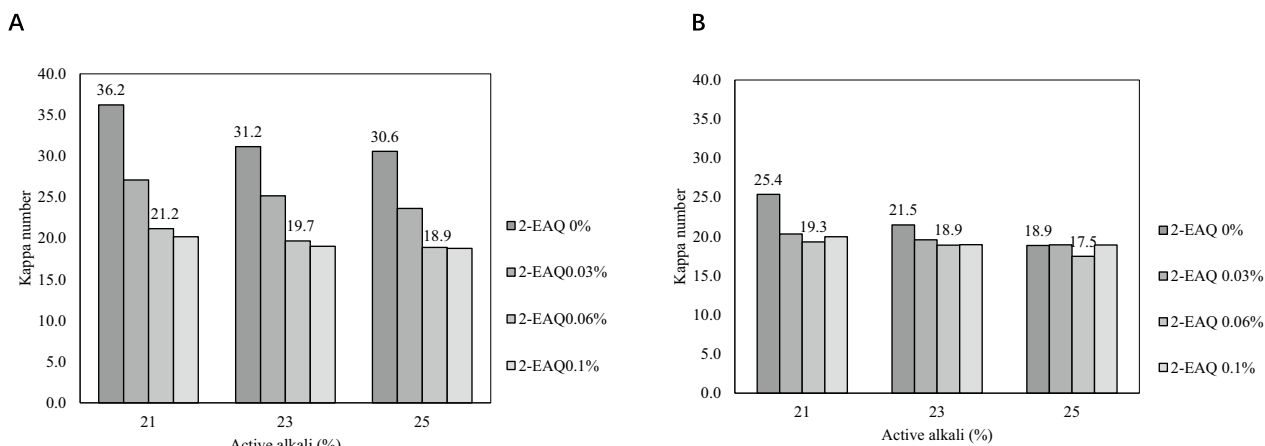


Fig. 1 Relationship between active alkali dosage and kappa number in alkaline pulping of *E. pellita*. **A** Soda cooking, **B** kraft cooking

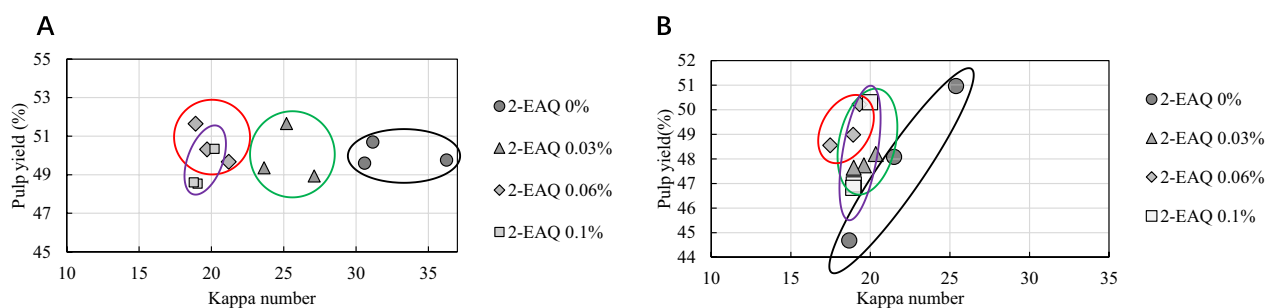


Fig. 2 Effect of 2-EAQ dosage kappa number and pulp yield in alkaline pulping of *E. pellita*. **A** Soda cooking, **B** kraft cooking

Effect of 2-EAQ addition on structures of dissolved lignin in black liquor analyzed by HSQC NMR spectroscopy

NMR is a particularly powerful tool for lignin analysis, particularly HSQC NMR experiments providing excellent sensitivity and resolution. In this study, the dissolved lignin in the black liquor was isolated by acidification. Based on the above results, the dissolved lignin obtained by cooking at 150 °C for 3 h with or without 0.06% 2-EAQ under 23% AA conditions was analyzed using HSQC NMR spectroscopy.

Figure 3A, B shows the aliphatic region of HSQC spectra of SL and SL-2-EAQ. In both spectra, β -5, β - β , aryl glycerol, and *O*-alkyl structures were detected, however, these signals of SL-2-EAQ were smaller than those of SL. The β -O-4 structures were not shown in both spectra, suggesting that β -O-4 structures were easily degraded by alkaline cooking.

Figure 3C, D shows the aromatic region of HSQC spectra of SL and SL-2-EAQ. In the spectrum of SL (Fig. 3C), the signals reveal at $\delta_C/\delta_H = 108.3/5.72$ corresponding to the α -position of enol ethers. And the signals of stilbene were also observed at $\delta_C/\delta_H = 126.2/7.02$ (α -position), $\delta_C/\delta_H = 110.3/7.08$ (2-position), $\delta_C/\delta_H = 113.7/6.60$ (5-position), and $\delta_C/\delta_H = 120.0/6.90$ (6-position). The enol ethers and the stilbenes structures were generated by the elimination of γ -OH of lignin as formaldehyde from β -O-4 and β -1 structures, respectively. On the other hand, in the spectrum of SL-2-EAQ, these signals were not detected. This result means that the addition of 2-EAQ (in its reduced form) promoted β -ether cleavage during soda cooking and prevention of the elimination of γ -OH (Fig. 4). The generation of the enol ethers and stilbenes is undesirable

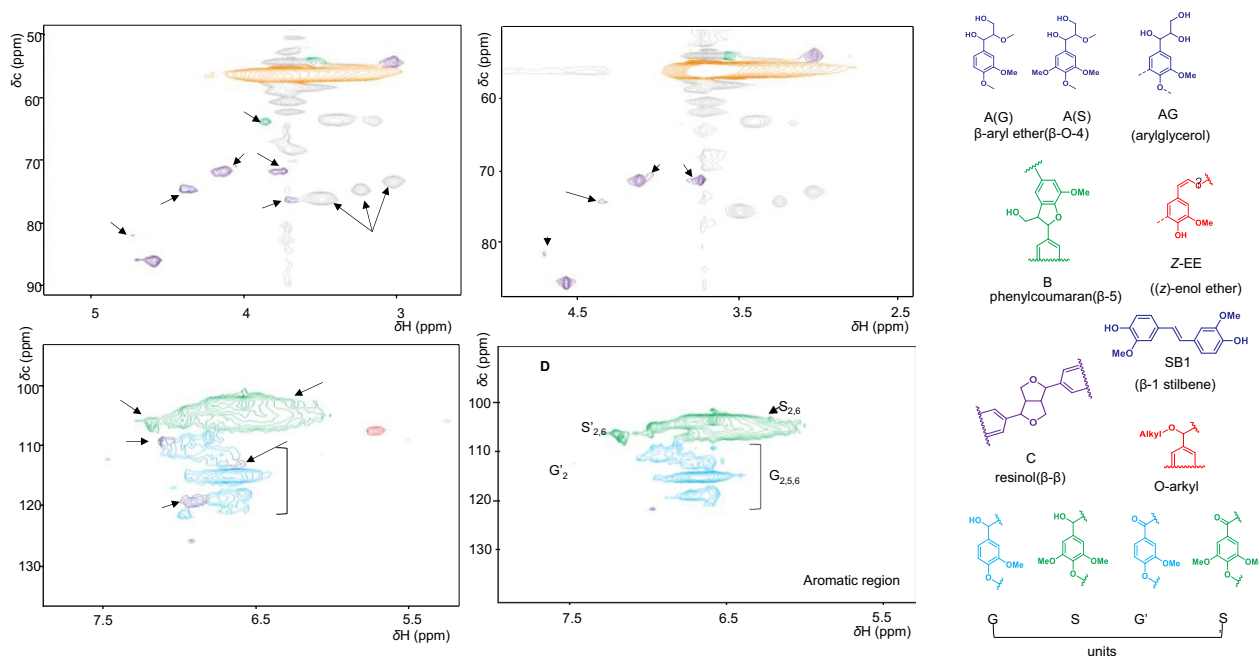


Fig. 3 Aliphatic and aromatic region of HSQC spectra of the dissolved lignin in black liquor obtained by soda pulping using *E. pellita*. **A** and **C** SL, **B** and **D** SL-2-EAQ

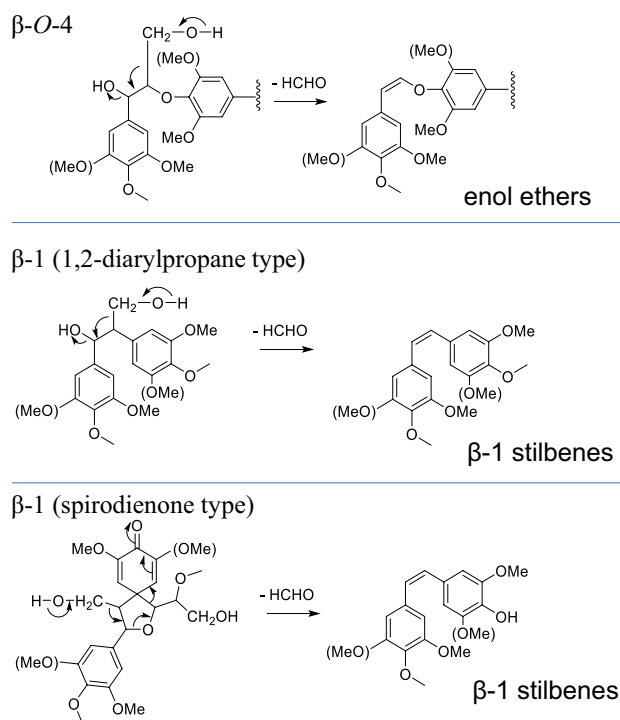


Fig. 4 Formation of enol ethers and stilbenes during alkaline pulping

in alkaline cooking because of their stability [28]. The addition of 2-EAQ allows for efficient lignin degradation without the formation of enol ethers and stilbenes.

Figure 5 illustrates the HSQC spectra of KL and KL-2-EAQ (Fig. 5A, B, respectively). The signals of the aliphatic and aromatic regions showed no significant

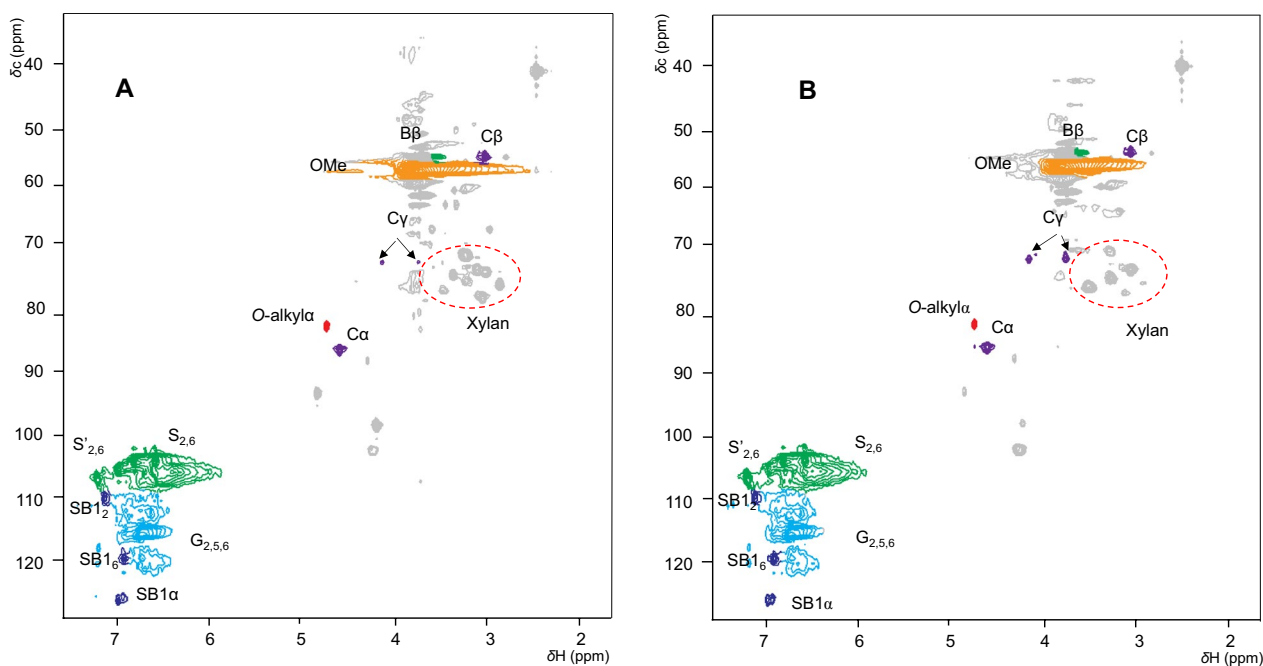


Fig. 5 HSQC spectra of the dissolved lignin in black liquor obtained kraft pulping using *E. pellita*. **A** KL, **B** KL-2-EAQ

difference between the two spectra, however, the signals of xylan in the KL spectrum were stronger than those of KL-2-EAQ. The results suggested that the addition of 2-EAQ may have suppressed the dissolution of xylan without severe degradation. The reason for this phenomenon is still unknown. This is a subject for future research.

Structural analysis of RL by HSQC NMR spectroscopy

The RL was isolated from the obtained pulp by ball milling and subsequent enzymatic treatment. Figure 6A, B shows the HSQC spectra of acetylated RL obtained by soda cooking without (RSL) and with 2-EAQ (RSL-2-EAQ). The signals of the methoxy group, as well as a small amount of syringyl (S) unit and guaiacyl (G) unit, were detected in RSL. In comparison, the signals of the methoxy group and S unit were weaker in the spectra of RSL-2-EAQ than in RSL, likely due to a more degradable S unit than G unit and a decrease in lignin content in pulp resulting from the addition of 2-EAQ.

Figure 6C, D shows the HSQC spectra of the RL obtained by kraft pulping. According to the spectra of RL from kraft pulping without 2-EAQ (RKL) and with 2-EAQ (RKL-2-EAQ), only the signals from the methoxy group and G unit were detected. From this result, the effect of 2-EAQ could not be observed.

Isolation of lignin by enzymatic hydrolysis is accompanied by minimal structural changes. However, the low content of lignin and remaining carbohydrates in the RLs cause little difference between RLs with and without 2-EAQ.

GPC of dissolved lignin in black liquor

The molecular weight distribution of dissolved lignin in black liquor was measured by GPC (Fig. 7). As a result of calculating the weight-average molecular weight (M_w), no notable effect of adding 2-EAQ was observed in kraft cooking (M_w of KL: 2904, KL-2-EAQ: 2975). On the other hand, in soda cooking, the effect of the addition of 2-EAQ had a significant effect, reducing the M_w

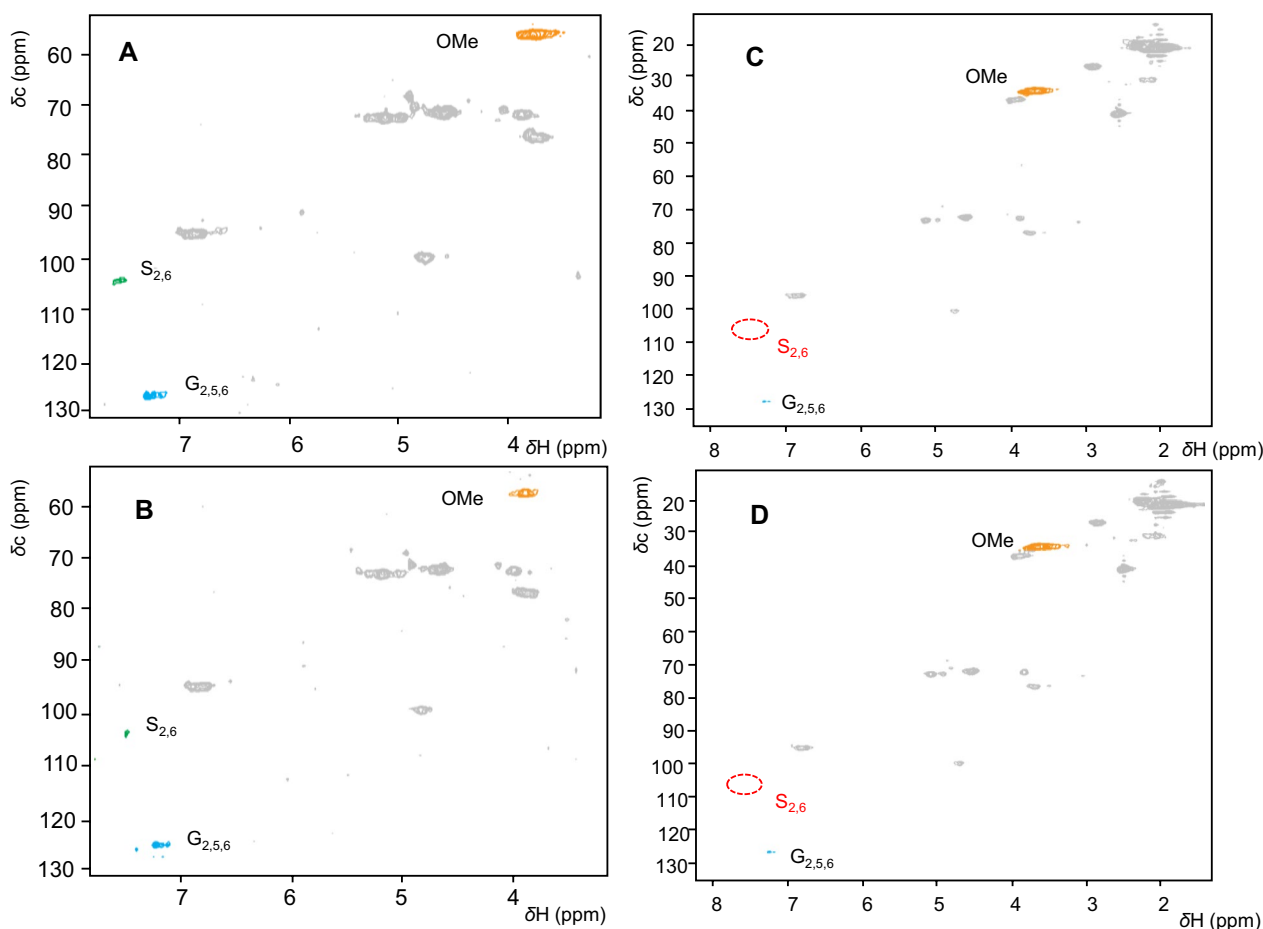


Fig. 6 HSQC spectra of RL obtained by soda/kraft pulping using *E. pellita*. **A** RSL, **B** RSL-2-EAQ, **C** RKL, **D** RKL-2-EAQ

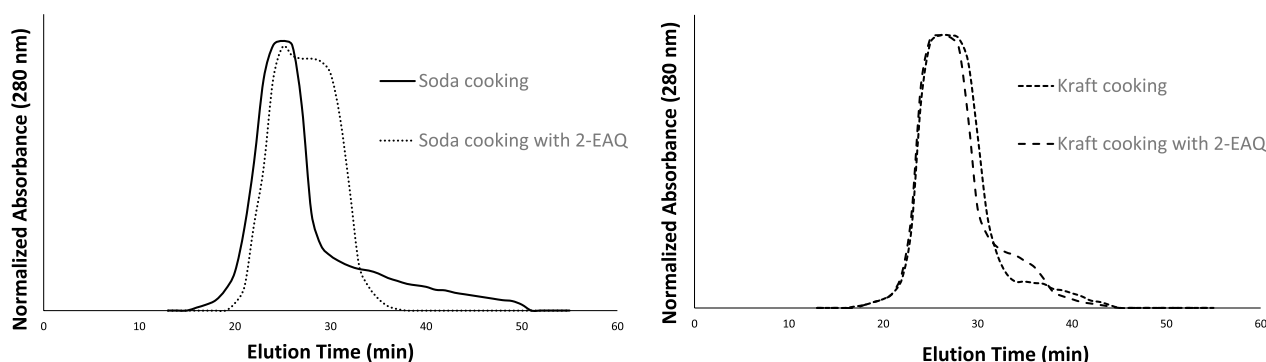


Fig. 7 Molecular weight distribution profiles of black liquor. (1) SL (*Mw*: 7404), (2) SL-2-EAQ (*Mw*: 2790), (3) KL (*Mw*: 2904), (4) KL-2-EAQ (*Mw*: 2975)

significantly from 7404 to 2790. This reduction can be attributed to the promotion of lignin degradation to lower molecular weight compounds by the addition of 2-EAQ during alkaline cooking, especially soda cooking.

Conclusions

In this study, soda cooking with 0.06% 2-EAQ decreased kappa number by about 12 points compared to that without the addition at around 50% pulp yield. The addition of 0.06% 2-EAQ to kraft cooking increased pulp yield by about 4% at around 19 of kappa number compared to the no addition.

The lignin structure of dissolved lignin in black liquor was analyzed by HSQC NMR spectroscopy, indicating that the addition of 2-EAQ inhibited the elimination of γ -OH of lignin, resulting in promoting β -ether cleavage in alkaline cooking. It also reduced the peeling reaction of polysaccharides to lead to high pulp yield.

It can be challenging to detect the impact of 2-EAQ by the analysis of the RL due to its low content. However, in this study, RL was collected by ball milling and subsequent enzymatic treatment, and then analyzed by HSQC NMR spectroscopy, indicating a slight effect of 2-EAQ addition.

The analysis of *Mw* of dissolved lignin in black liquor revealed that the addition of 2-EAQ promoted the degradation of lignin to small fragments. The degradation effect was more pronounced in soda cooking compared to kraft cooking.

In a comparison of soda cooking and kraft cooking, the effect of 2-EAQ addition was greater in soda cooking than in kraft cooking, which could be attributed to the involvement of SH^- in lignin degradation in kraft cooking, as well as 2-EAQ, thereby reducing the effect of 2-EAQ addition. Concerning the delignification efficiency and pulp yield, soda-EAQ pulping was comparable to kraft cooking under optimal conditions. Since no sulfur reagent is used in soda cooking, SL-2-EAQ contains

only sulfur-free compounds. Soda-2-EAQ cooking can be an efficient method for industrial processes because of its many advantages, such as the absence of carcinogenic and mutagenic properties, process simplicity, lack of bad odor, and the high utilization value of SL-2-EAQ.

Abbreviations

AQ	Anthraquinone
AHQ	Anthrahydroquinone
HSQC-NMR	Heteronuclear single quantum coherence nuclear magnetic resonance
GPC	Gel permeation chromatography
AA	Active alkali
NMR	Nuclear magnetic resonance

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Author contributions

KL and YM conceived the research. KL and YM conducted the soda and kraft cooking. KL and TN conducted NMR measurements. KL and YM wrote the manuscript. The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

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Availability of data and materials

The raw data can be obtained on request from the corresponding author.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare that they have no competing interests.

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