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Impact of Lignin Determination Method on Oxygen Delignification Chemistry

Soo-Jeong Shin† and Yuan-Zong Lai

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ABSTRACT

In previous report, we investigated the impact of hexeneuronic acid and some residual extractiveson lignin determination. These non-lignin components severely interfered lignin content determination which also affect on the oxygen delignification comparison between aspen and pine unbleached kraft pulps. Very different pattern was observed whether based on uncorrected conventional kappa number or based on corrected kappa number in oxygen delignification comparison. Lower kappa number aspen pulps showed poor response to oxygen delignification when kappa number was used as lignin determination method but better response with using the acid lignin method.

Phenolic hydroxyl group in kraft pulps were also compared based on uncorrected or corrected kappa numberfor lignin content. Based on uncorrected kappa number, lower kappa number oxygen-delignified pulps had lower phenolic hydroxyl group. However, lower kappa number oxygen-delignified pulps showed much higher phenolic hydroxyl group based on the corrected lignin content. For accurate comparison for residual lignin properties from different pulps, lignin determination should be corrected from non-lignin components contribution to lignin.

Key word : kraft pulp, oxygen delignification, phenolic hydroxyl group, residual lignin, extractives, hexeneuronic acid, lignin determination

1. Introduction

In oxygen delignification process, approximately half of residual lignin in unbleached pulp can be removed from unbleached pulp. Due to strict regulation for chlorine-based bleaching chemical dose, more lignin should be removed prior to bleaching sequence. Extended delignification in pulping and oxygen delignification process can reduce the incoming kappa number to bleaching tower.

Oxygen delignification is a well-developed pre-bleaching step for bleached kraft pulp

• Faculty of Paper Science and Engineering, State University of New York, College of Environmental Science and Forestry (SUNY-ESF), Syracuse, New York, USA
† Corresponding author : E-mail ; soojeongesf@hotmail.com

production (1). With a typical oxygen delignification process, 35-50% of the residual lignin inkraft pulps can be removed without serious effects on the pulp properties. One of the biggest drawbacks of an oxygen delignification system is that the selectivity of delignification drops considerably after 50% of the residual lignin is removed.

Better response in oxygen delignification in softwood than hardwood kraft pulps were reported. In a survey of kraft pulp mills using oxygen delignification, softwood kraft pulps showed a higher average degree of oxygen delignification (47.5%) than hardwood kraft pulps (40.2%) (2). Also, the reported consumption of oxygen and alkali per unit of kappa number removal was higher for hardwood kraft pulps than for softwood pulps. For each unit of kappa number decrease, softwood kraft pulps required about 0.13% sodium hydroxide (oven-dried pulp basis) and 0.14% oxygen, whereas higher sodium hydroxide (0.14%) and oxygen (0.16%) were required for hardwood pulps (1).

A similar trend was observed between softwood and hardwood kraft pulps in both high-pressure oxygen delignification (O) and low-pressure oxygenperoxide delignification (Eop) processes (3). Softwood kraft pulps yielded 3.4 % and 4.2 % more delignification than hardwood pulps for Eop and O, respectively.

We tried to investigate the cause of those differences and find out that impact of non-lignin components on kappa number determination could be one of main reason. Residual extractives and hexeneuronic acid in kraft pulps (unbleached and oxygen-delignified pulps) interfered in lignin determination and counted as lignin (4).

Ionization of phenolic hydroxyl groups to phenolate anions is the initial step for oxygen delignification. Gellerstedt et al. reported that residual lignin in oxygen-delignified pulp "has few remaining phenolic hydroxyl groups" (5). However, Moe and Ragauskas have reported that the free phenolic hydroxyl group of residual lignin decreased by only 30-40% after oxygen delignification (6). Chirate and Lachenal also found out that phenolic hydroxyl groups still remained in the residual lignin after four stages of oxygen delignification (7).

If residual extractives and hexeneuronic acid interfered in lignin determination, other data depending on lignin content should be carefully reviewed based on corrected lignin content. In this study, the phenolic hydroxyl groups were evaluated with both based on uncorrected and corrected lignin content. We also investigate the relationship between phenolic hydroxyl group content in residual lignin versus oxygen delignification.

2. Materials and Methods

2.1 Preparation of Kraft Pulps

Aspen and pine kraft pulping, oxygen delignification and extractives extraction were described in Shin and coworker (8). For white birch (*Betula papyrifere* M.) kraft pulping, we adopted same experimental condition with aspen pulping (H-factor: 650, 950 and 2300), with the exception of modification of H-factor to 1000.

2.2 Analytical Methods

Kappa numbers of unbleached and O_2-delignified kraft pulps were determined according to TAPPI Test Method T236 om-99. The phenolic hydroxyl group of the unbleached and oxygen-delignified kraft pulps were

determined in situ by a periodate oxidation methods (9). The hexeneuronic acid content of unbleached and oxygen-delignified kraft pulps was determined by a selective hydrolysis of hexeneuronic acid by mercuric chloride (10).

3. Results and Discussions

3.1 Comparison the response to oxygen delignification

Hexeneuronic acid and residual extractives in kraft pulps impact on lignin determination based on kappa number (4,8). Those impacts of non-lignin components on lignin determination can influence the comparison the response to oxygen delignification.

Since the content of residual extractives and hexeneuronic acidvaries significantly with the wood species and pulping conditions, the impact of these non-lignin components to the lignin determination should be corrected for a proper comparison of the oxygen delignification efficiency. Based on conventional kappa number (uncorrected), pine kraft pulps showed

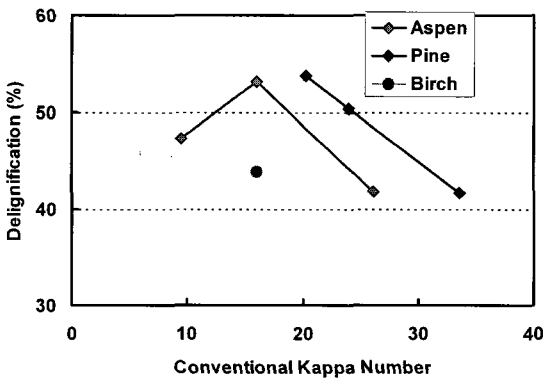

Fig. 1. A comparison of the pine and aspen kraft pulps in oxygen delignification based on the apparent reduction in kappa number as related to the kappa number of the unbleached samples.

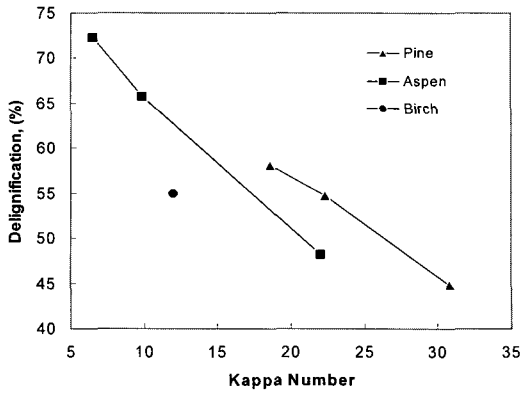

Fig. 2. A comparison of the kappa number (with the extractives and Hex A correction) the oxygen delignification of unbleached kraft pulps.

better response to oxygen delignification than those of aspen and birch kraft pulp (in Fig. 1). With correction from impact of non-lignin components on lignin determination, lower kappa number aspen pulps showed as good as response to oxygen delignification compared with pine pulps (in Fig. 2). As indicated, the difference between the pine and aspen in response to the oxygen delignification varied considerably with the lignin content of unbleached pulps, and was larger in the high-lignin content region. Comparing both pulps with lignin content above the 15 kappa number level, the aspen pulp was less response to oxygen delignification than the pine pulps. However, for pulps below that lignin content level, the aspen pulps would have a better response to oxygen delignification than the pine pulps. Thus, the relative reactivity of residual lignin in the hardwood and softwood pulps is a significant factor affecting the overall oxygen delignification process.

3.2 On Phenolic Hydroxyl Groups in Residual Lignin

In general, the oxygen delignification is

initiated with ionization of phenolic hydroxyl groups into the phenolate ions, which then react with molecular oxygen. Thus, a higher content of phenolic hydroxyl groups in unbleached kraft pulp may lead to a better response to oxygen delignification. After oxygen delignification process, more than half of the phenolic hydroxyl groups was still remained in pulps (7,11).

In this study, the phenolic hydroxyl group content was determined in situ by a periodate oxidation procedure. Fig. 3 shows the correlation between the phenolic hydroxyl group content of the pulps andtheir lignin contents. It should be noted that all the kappa number data have not been corrected for contribution form the non-lignin components. In general, the residual lignin content was calculated with a conversion factor of 0.18 to kappa number. With the exception of the oxygen-delignified pulps determined by the kappa number method (Fig. 3), all other curves showed an increased phenolic hydroxyl group with decreasing the lignin content of pulps. As indicated, the unbleached aspen kraft pulps had less phenolic hydroxyl group content than the pine pulps (Fig. 3). A similar result was also reported previously through the expepriment with kraft pulps from loblolly pine and mixed North American hardwood (12).

A different pattern was shown for the oxygen-delignified pulps determined by the kappa number method, and this, as discussed later, can be attributed to the interference with the hexeneuronic acid in the kappa number determination.

Fig. 4 illustrates the adjusted phenolic hydroxyl group content of the unbleached and oxygen-delignified pulps after correction for impact from the non-lignin components in the lignin determination. With phenolic hydroxyl group calculation based on the corrected kappa number, we noticed two main differences. First, there were no significant difference in phenolic hydroxyl group content between aspen and pine unbleached kraft pulp. We could plot the kappa

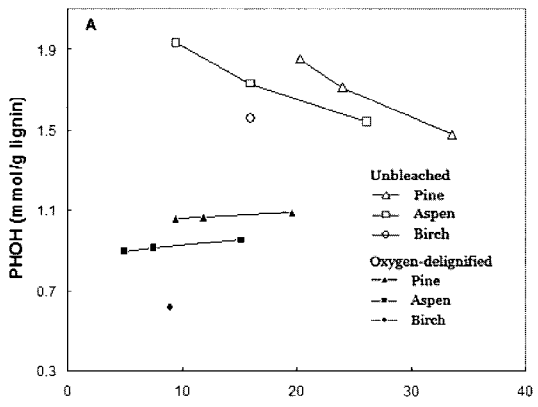

Fig. 3. The phenolic hydroxyl group (PHOH) of residual lignin based on the kappa number methods for the unbleached and oxygen-delignified kraft pulps without correction of non-lignin components.

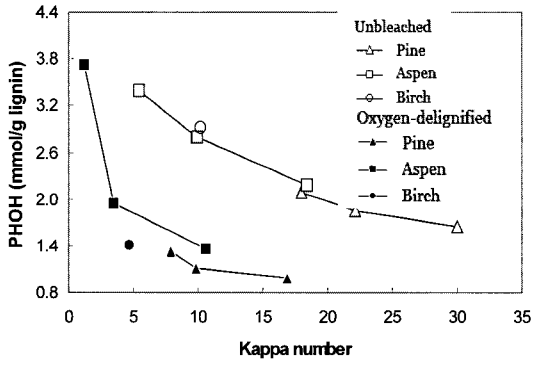

Fig. 4. The phenolic hydroxyl group(PHOH) of residual lignin based on the kappa number for the unbleached and oxygen-delignified kraft pulps with a correction of the contribution by the residual extractives and hexeneuronic acid units.

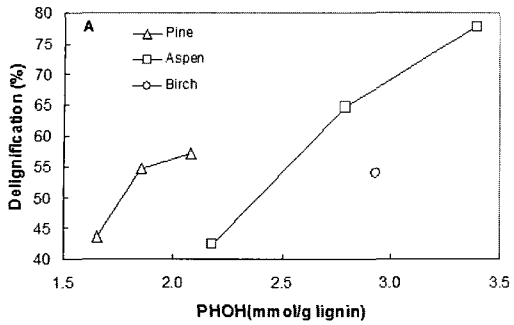

Fig. 5. The percent oxygen delignification as related to the phenolic hydroxyl group (PHOH) of residual lignin based on the kappa number.

number vs phenolic hydroxyl groupcurve almost same trend line. So, the phenolic hydroxyl group difference between aspen and pine unbleached kraft pulps may come from lignin determination error. Second, the kappa number decreasing, the phenolic hydroxyl groupin oxygen-delignified were increased. This opposite trend was observed based on uncorrected kappa number. In oxygen-delignified kraft pulps, contribution from hexeneuronic acid to kappa number is significantly higher with lower residual lignin content and made big error in phenolic hydroxyl group determination.

Based on corrected kappa number, at similar phenolic hydroxyl group level, pine kraft pulps showed higher oxygen delignification than aspen or birch kraft pulp (in Fig. 5). Higher phenolic hydroxyl group containing pulps showed higher delignification.

4. Conclusions

The study confirms the general observation that the oxygen delignification of hardwood kraft pulps was less extensive than that of softwood pulps based on the apparent kappa number reduction without considering the impact of the non-lignin components.

After correction for contributions from the residual extractives and hexeneuronic acid, the oxygen delignification of both pine and aspen kraft displayed a similar pattern showing a steady increase in delignification with decreasing the lignin content of unbleached pulps. The difference between the pine and aspen pulps in oxygen delignification increased with increasing the lignin content of unbleached pulps, and was 10-15% lower for the aspen pulp at about 22 kappa number. However, there are indications that for extensively delignified kraft pulps (15 kappa number), the aspen pulps would be comparable to or more reactive than the pine pulps.

The performance of kraft pulps in oxygen delignification is closely related to their phenolic hydroxyl group and also would vary with the condensed structures of the residual lignin. Aspen H-650 pulp showed a characteristic response in oxygen delignification both phenolic hydroxyl group consumption and delignification at a given phenolic hydroxyl grouplevel, which may come from very different residual lignin structure compared with other Aspen H-950 and Aspen H-2300 pulps.

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