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METHANOL FORMATION DURING ALKALINE WOOD PULPING

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ABSTRACT

Methanol emission in pulp mills is an environmental concern. This study validated methanol formation through alkali-catalyzed elimination of methanol from hemicellulose during wood pulping by measuring the hexenuronic acid groups in pulps and methanol in the pulping spent liquors. The study also investigated the effect of four pulping processes, i.e., soda, kraft, polysulfide kraft, and multistage kraft, and pulping conditions, i.e., different sulfidities and catalyst anthraquinone (AQ), on methanol formation. The effects of kappa number and wood species (both hardwood and softwood) on methanol formation were also studied. The results indicated that the alkali-catalyzed reactions of xylan contribute to about 40% of the total methanol formation in kraft pulping of southern pine to bleachable grade. For a given active alkali (AA) charge and kappa number, soda pulping produced more methanol than kraft and polysulfide kraft pulping processes did; furthermore, both the increase in sulfidity and the addition of catalyst AQ reduced methanol formation.

Keyword: Methanol, Pulping, Headspace Gas Chromatography, Hexenuronic Acids

INTRODUCTION

The formation of volatile organic compounds (VOCs), such as methanol, in kraft mills has been an environmental concern. Methanol has been identified as the major alcohol in pulp mill process streams [1-4].

Methanol is soluble in water and can increase the biochemical oxygen demand (BOD) [5]. Furthermore, it can also be released into the atmosphere at the process temperatures of kraft mill streams. The Cluster Rule [6] of the U.S. Environmental Protection Agency (EPA) now requires the control of the release of methanol in pulp and paper mills. Therefore, the understanding and quantification of methanol formation in pulp mills is of significant practical importance.

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Methanol is primarily produced through the pulping process in digesters. Its formation during pulping depends on the pulping time, temperature, hydroxide concentration or alkalinity, and wood species [5]. Two different mechanisms of methanol formation in pulping processes are generally accepted [7-9]: the rapid alkali-catalyzed elimination of methanol from the 4-O-methylglucuronic acid residues in hemicellulose [7] to form hexenuronic acid groups and methanol, and the demethylation of lignin [8, 9]. However, the amount of demethylated methoxyl groups in lignin in an alkaline pulping process is small according to Sarkanen et al. [9]. Therefore, it is reasonable to assume that a substantial amount of methanol is formed through the demethylation of xylan [7, 9]. Based on this argument, we conducted a methanol mass balance estimation in our previous study [10] and found that the complete (100%) elimination of methanol from xylan accounts for 70-75% of the total methanol formed (as measured from the final pulping spent liquor) in our laboratory batch pulping processes. As a result, lignin demethylation accounts for about 20% of the total methanol formed. Because most of the methoxyl groups in lignin have not been demethylated during pulping [9], they can be hydrolyzed to form methanol in the downstream processes, such as bleaching and chemical recovery, whenever a set of favorable reaction conditions exists.

In our previous study [10], the time-dependent methanol formation during alkaline pulping of southern pine and birch to bleachable grade was investigated. In this study, we conducted various laboratory batch alkaline pulping processes to study the effect of kappa number, wood species, catalyst anthraquinone (AQ), and sulfidity on methanol formation.

Rapidly and accurately analyzing methanol concentration in pulping spent liquors and hexenuronic acid groups in pulps is critical to achieve the goals of the present research. It is not a trivial task to analyze methanol in black liquors due to the dissolved solids, in particular the inorganic salts, which makes it very difficult to apply gas chromatographic (GC) analysis through direct column injection because of fouling of the GC columns. In this study, methanol concentrations in the pulping spent liquors were analyzed by the method that we developed previously [3] using headspace gas chromatography. Although several methods have been developed to measure hexenuronic acids (HUA) in chemical pulps recently, all of these methods are time-consuming and require more than several hours to obtain one measurement. UV spectrophotometry through acid hydrolysis, used by Vuorinen [11], also suffers from the spectral interference of acid-soluble lignin in the UV range. NMR spectroscopy [12] and anion exchange chromatography [13] suffer from very low hydrolysis efficiency and therefore are very time consuming. The HPLC method developed by Gellerstedt and Li [14] uses a combination of hydrolysis by mercuric acetate and peroxide oxidation coupled with thiobarbituric acid, which complicates experimental procedures for quantifying hydrolysis products. In this study, a rapid UV-spectrophometric method that we developed [15] was applied to determine the formation of HUA in chemical pulps.

EXPERIMENTAL

Pulping

The pulping experiments were conducted using eight rotating bomb digesters. The volume of each bomb digester was 500 mL. Fifty grams of oven-dry wood chips of four softwoods (Douglas-fir, white spruce, western hemlock, and loblolly pine) and six hardwoods (aspen, bass, birch, maple, oak, and sweetgum) were used in each cook. For the pulping of southern pine, the cooking liquor-to-wood chip ratio was 4.0 L/kg. Conventional kraft, soda, polysulfide kraft, and multistage kraft pulping processes to simulate RDH processes were conducted. The active alkali charge AA (as Na_2O) was maintained at 18% on wood for all the pulping processes except the multistage pulping. Three sulfidities of S=10, 20, and 30% and four AQ concentrations of 0, 0.025, 0.05, and 0.1% on wood were used in kraft pulping. A polysulfide concentration of 1.5% on wood and a sulfidity of S=18% were used in polysulfide kraft pulping. The multistage pulping processes were designed as follows: Stage 1 used black liquor with AA = 9 g/L (as Na_2O) and Na_2S = 12 g/L and lasted 20 minutes when pulping temperature was raised from 100 to 130^oC, Stage 2 used black liquor with AA = 15 g/L and Na_2S = 12 g/L and lasted 20 minutes when pulping temperature was raised from 130 to 160^oC, and Stage 3 used white liquor with AA = 18% and sulfidity S = 30% and lasted to the end of the cook and varied for different cooks. Therefore, some of the cookings may only have experienced Stage 1 or 2, depending on the total cooking time used to achieve the desired kappa number. For the pulping of the rest of the wood species, the pulping liquor-to-wood ratio was 3.7, sulfidity was 31%, and the active alkali charge was 17% for softwoods and 16% for all hardwoods. For each set of pulping conditions selected, cooking temperature was first linearly ramped from a room temperature of 23^oC to 170^oC in 70 minutes or at a rate of 2.1^oC per minute, then maintained at 170^oC to continue delignification. The pulping processes in different digesters were terminated at different pulping times to obtain the rates of formation of methanol and hexenuronic acid. By this approach, the effect of kappa number on methanol formation was obtained. The pulp kappa numbers were measured using the standard TAPPI Test Method (T236 cm-85) [16].

Methanol Analysis

The indirect headspace GC method for methanol analysis that we developed [3] uses the standard addition approach but relies on methanol material balance and liquid/vapor phase equilibrium in the sampling vial. Through the sampling of the vapor phase in the headspaces of two sampling vials (one with the standard addition of known amount of methanol), the method calculates the methanol concentration in the liquor from the ratio of the peak areas of the two headspace measurements. Therefore, calibration and direct sampling of the liquor are not required. It has been demonstrated that the method is reliable for determining methanol concentration in various kraft mill streams, including black liquors. A commercial headspace gas chromatograph (HSGC, HP-7694 and HP-6890 Hewlett-Packard, now Agilent Technologies, Palo Alto, CA) was employed. GC conditions are: HP-5 capillary column at 30°C; carrier gas helium flow: 3.8 mL/min. A flame ionization detector (FID) was employed with hydrogen and air flows of 35 and 400 mL/min, respectively. Headspace operating conditions: 25 minutes gentle shaking for equilibration of the sample, vial pressurization time: 0.2 min, and sample loop

fill time: 1.0 min., loop equilibration time: 0.05 min. The sample preparation and measurement procedures were as follows: pipette duplicate 10 mL of sample solution into two 20 mL vials, add 10 μL of pure methanol solvent by microsyringe into one of the vials, then, close the vials and place them into the headspace sample tray for measurement.

Measurement of Hexenuronic Acid Groups

The UV-spectrophometric HUA analysis method that we developed [15] uses a low absorptive mercuric chloride hydrolysis agent together with a spectral compensation technique to directly and rapidly (each measurement only takes 30 minutes) determine HUA concentration in chemical pulps. In this method, 22 mM (0.6%) mercuric chloride and 0.7% sodium acetate, of analytical grade from commercial sources, are used to make a hydrolysis solution. Then approximately 0.05 gram of air-dried pulp handsheet with a known moisture content is accurately weighed and put into a 20-mL vial with 10 mL of hydrolysis solution. The mixture is sealed in the vial by a septum. To obtain good mixing of the pulp with the hydrolysis solution, we shake the vial and then heat the mixture for 30 minutes in a water bath with a temperature range of 60-70°C. After the solution is cooled to room temperature, UV absorption measurements of the filtered solution are conducted in a 10-mm path length silica cell using a commercial spectrophotometer (UV-8453, Hewlett-Packard, now Agilent Technologies) at a wavelength range of 260 to 290 nm.

RESULTS AND DISCUSSION

Understanding Methanol Formation During Pulping

Figure 1 shows the time-dependent methanol and pulp kappa data of 3 replicate experiments of conventional kraft pulping of southern pine. The methanol data are presented as kilogram per metric ton of oven-dry pulp based on measured pulp yields and methanol concentrations in the pulping spent liquors. The time-dependent methanol data show similar characteristics to those obtained in our previous study [10] using a different batch digester (ME&K), i.e., methanol formation is slow initially due to low cooking temperature, then increases rapidly as the temperature reaches 170^{o}C, and finally levels out. A certain amount of methanol was formed instantly at the beginning of the pulping process. Although these 3 sets of experiments were conducted in a 6-month period, the results show remarkable repeatability.

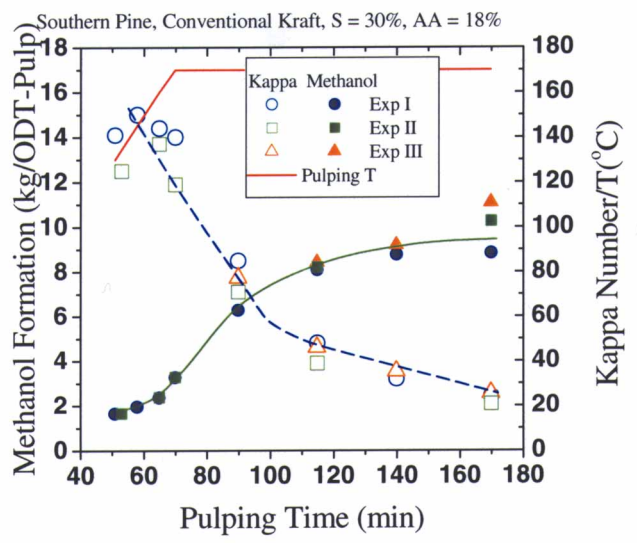

Fig. 1 Time-dependent methanol formation during conventional kraft pulping processes.

We measured the amount of HUA in the pulp samples obtained in the kraft conventional pulping processes of southern pine with sulfidity S =30% and active alkali charge AA = 18% to validate the mechanism of methanol formation through rapid alkali-catalyzed elimination of methanol from 4-O-methylglucuronic acid residues in hemicellulose [7]. According to the alkali-catalyzed methanol formation reaction of 4-O-methylglucuronic acid residues [7], the production of one mole of HUA will be accompanied by the formation of one mole of methanol. **Figure 2** shows the correlation of the measured methanol in the pulping spent liquors and the measured HUA in the corresponding pulps. Because the methanol formation is not linearly dependent on cooking time, as shown in Fig.1, the pulping temperature is not a linear function of methanol formation in Fig. 2. The data indicate that the amounts of methanol measured in the pulping spent liquors are linearly proportional to the amounts of HUA found in the pulps up to a methanol level of 53 mol/ODT-wood or 1.66 kg/ODT-wood (R^2 = 0.9938) when the pulping temperature reaches 160°C. Furthermore, the slope of the linear relationship is close to unity (0.90, to be exact, from least squares fitting of the first 3 data points, corresponding to pulping time of 65 minutes and temperature 160°C.) Therefore, the amount of HUA dissolution and the amount of methanol formation from lignin demethylation in the pulping liquor are negligible. This validates the 1:1 relationship of the amounts of methanol and HUA formed through the xylan degradation reaction. The slightly lower-than-unity (10%) slope of the linear relationship is perhaps due to the fact that some of the HUA formed associated with methanol formation is no longer with the pulp and is dissolved into the pulping spent liquors. It is noticed that the methanol-HUA linear line does not pass through the origin of the coordinate with a positive methanol intercept of 32 mol/ODT-wood (or 1.0 kg/ODT-wood) when HUA (measured) = 0. This is perhaps due to the fact that wood feedstock contains some methanol and it was released instantly at the beginning of cooking. We conducted cooking of southern pine wood chips using pure water heated up to 170°C to verify the natural presence of methanol in wood. From the measurements in the final cooking solution, about 28 mol/ODT-wood (or 0.875 kg/ODT-wood, very close to the intercept of 1.0 kg/ODT-wood shown in Fig.2) methanol was obtained.

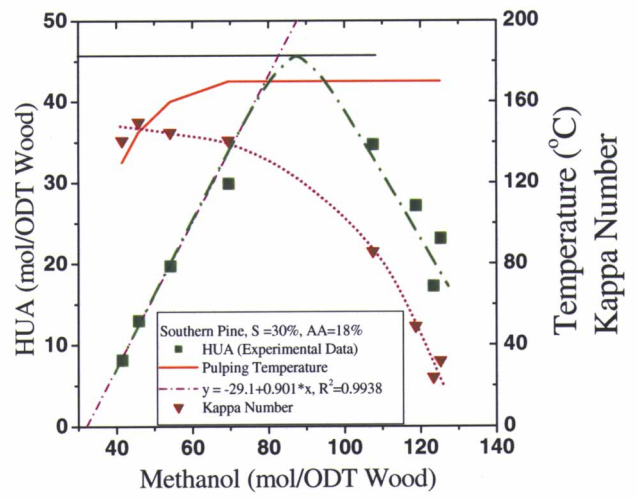

Fig. 2 The relationship of measured methanol in pulping liquors and hexenuronic acid groups in pulps in a set of conventional kraft pulping processes.

From the experimentally obtained unity slope of the methanol and HUA relationship, we can conclude that except for the methanol naturally present in wood that is released instantly at the beginning of the pulping process, the elimination of methanol from xylan is the only methanol formation mechanism during the initial pulping process and lignin demethylation does not contribute to methanol formation below pulping temperature 160°C (corresponding to a kappa number of 140). Figure 2 also shows that the methanol-HUA data deviate from the linear relationship as delignification continues after pulping temperature reaches 160°C. However, this deviation is not significant until the kappa number reaches about 120, indicating that lignin demethylation may start to contribute to methanol formation. With the completion of the methanol elimination reaction from xylan and further HUA dissolution into the solution, the HUA content measured in pulp decreases as pulping continues. One can extrapolate the maximum measurable amount of HUA content in wood (about 46 mol/ODT-wood) from the data presented in Fig. 2. Based on the extrapolation, the contribution of methanol elimination from the xylan to methanol formation can be estimated to be about 51 (=83-32, calculated from the least-square fitted equation shown in Fig. 2) mol/ODT-wood (or 1.59 kg/ODT-wood). The remaining 42 (=125-51-32, the total formation is 125) mol/ODT-wood (or 1.31 kg/ODT-wood) is the contribution from lignin demethylation. Based on this calculation, we can improve our previous estimation [10] by concluding that for bleachable grade pulping of southern pine, methanol formation from xylan is the major factor contributing to methanol formation in pulping processes, accounting for about 40% of the total methanol formed (as measured from the final cooking spent liquor). Lignin demethylation accounts for about 35%. The remaining 25% of the total methanol naturally present in wood released instantly at the beginning of the pulping process was also observed in our previous study [10], but was accounted for as originating from xylan degradation.

Effect of Sulfidity

Figure 3 shows the effect of sulfidity on methanol formation during kraft pulping of southern pine. The results plotted as methanol verses pulp kappa numbers clearly show that increasing sulfidity reduces methanol formation at a given pulp kappa number. There are two factors that might explain this phenomenon. A longer cooking time is required in a lower sulfidity pulping process to achieve the same kappa number than that required in a higher sulfidity pulping process; a longer cooking time will increase methanol formation. Secondly, a lower sulfidity means a higher effective alkali concentration in the pulping liquor because the active alkali was maintained at 18% for all the pulping processes; an increase in effective alkali (or HO^- concentration) leads to an increase in methanol formation. The HUA data obtained in our previous study [17] of alkaline pulping of southern pine (not presented in the present paper) indicate that the amount of HUA in pulp decreased with the increase of sulfidity at the same kappa number, which verifies the second argument.

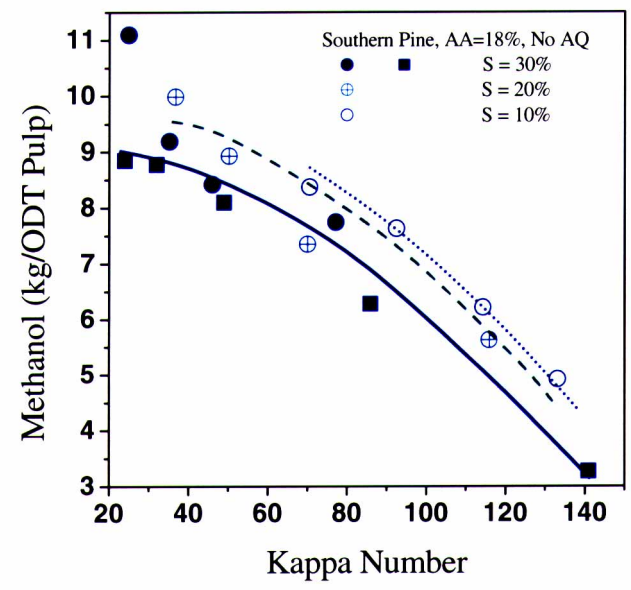

Fig. 3 The effect of sulfidity on methanol in conventional kraft pulping of southern pine.

Effect of Catalyst Anthraquinone (AQ)

Figure 4 shows the effect of AQ addition on methanol formation in conventional kraft pulping. Although the data show some scattering, the results clearly indicate that AQ can reduce methanol formation. This reduction is not very significant at a low dosage application (a single curve was drawn for the two data sets of no AQ and 0.025% AQ addition in Fig. 4). However, at a high dosage application, i.e., 0.1%, the reduction of methanol formation is very significant. This phenomenon can be explained by the accelerated delignification due to the catalyst AQ, which reduces the cooking time to achieve the same kappa number. A dosage of 0.1% AQ may

not be permitted in many mills; however, the results indicate that AQ can be used in mills not only to facilitate delignification but also to reduce methanol formation.

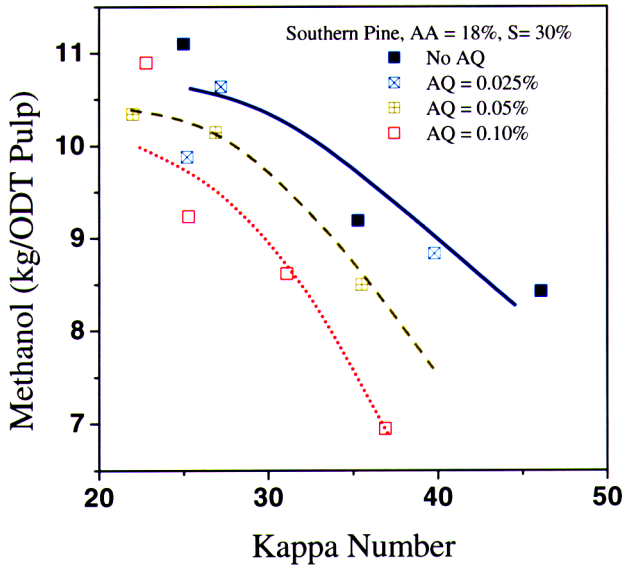

Fig. 4 The effect of catalyst AQ on methanol in conventional kraft pulping of southern pine.

Effect of Pulping Processes

Figure 5 shows the effect of pulping processes on methanol formation as a function of pulp kappa number. Data with a kappa number greater than 130 were excluded in Fig. 5. The data clearly show the difference in methanol formation among various pulping processes. Soda cooking produces much more methanol than kraft cooking at a given kappa number. There are two factors that contribute to the higher methanol formation in soda pulping. Firstly, the delignification rate is lower in soda pulping than in kraft pulping. A longer pulping time is required to achieve the same kappa number in soda pulping than that required in kraft pulping. Secondly, the effective alkali is higher in soda pulping than in kraft pulping because the active alkali was maintained at 18% for both the soda and kraft pulping processes; an increase in effective alkali (or HO^- concentration) results in more methanol formation.

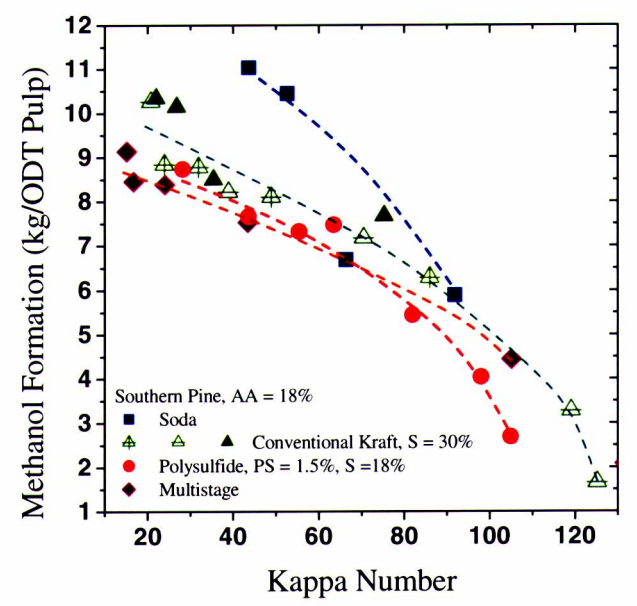

Fig. 5 The effect of pulping processes on methanol formation.

The results in Fig. 5 also show that polysulfide kraft pulping processes consistently produce less methanol than in conventional kraft pulping processes. Polysulfide can reduce the degradation of hemicellulose through the peeling-off reactions of oxidation of end groups to carbolic acid groups to reduce methanol formation. The methanol formation in RDH pulping processes is slightly less than that in kraft pulping. This may be explained by the lower effective alkali used in the first and second stages in an RDH pulping process.

Effect of Wood Species

Conventional kraft pulping experiments of various wood species were carried out to investigate the effect of wood species on methanol formation as shown in Figs. 6 and 7. The data are averaged over 2-5 replicate experiments. The specific number of replicate experiments varies with wood species. **Figure 6** shows the results obtained from the pulping of softwoods. Four softwoods of Douglas-fir, white spruce, western hemlock, and southern pine were used. Both bleachable (kappa number around 30) and linerboard (kappa number around 60) pulps were produced. Figure 6 shows that western hemlock and southern pine produce the least (7.3 kg/ODT pulp) and most (9.3 kg/ODT pulp) amounts of methanol in bleachable grade pulping of softwoods, respectively. Figure 6 also shows that Douglas-fir and southern pine produce the least (5.6 kg/ODT pulp) and most (7.3 kg/ODT pulp) amounts of methanol in linerboard grade pulping, respectively. Furthermore, the difference in methanol formation between bleachable and linerboard pulping processes is the smallest (1.3 kg/ODT Pulp) for western hemlock and largest (2.7 kg/ODT Pulp) for Douglas-fir.

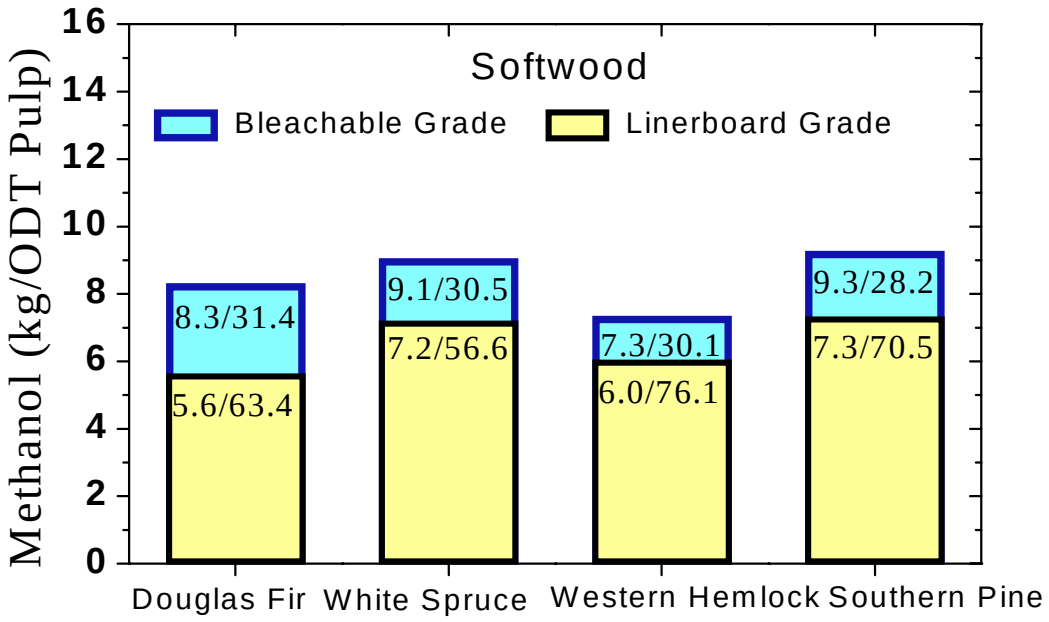

Fig. 6 The measured methanol formation data in conventional kraft pulping of four softwoods (the first number in the bar is the methanol formation, and the second number after the slash is the pulp kappa number).

Figure 7 shows the methanol formation data during pulping of six hardwoods, aspen, bass, birch, maple, oak, and sweetgum. Bleachable (kappa number around 14), liner board (kappa number around 50, a little lower than the anticipated value of 60), and an intermediate kappa (kappa number around 25) grades of pulps were produced. For bleachable grade pulp, the methanol formation is highest (15.0 kg/ODT pulp) and lowest (9.6 kg/ODT pulp) when pulping sweetgum and aspen, respectively. The variation in methanol formation in linerboard grade pulping of various hardwoods is not very significant, ranging from 4.3 to 5.4 kg/ODT pulp. However, the results show that the difference in methanol formation between bleachable and linerboard pulping is about 75-300%.

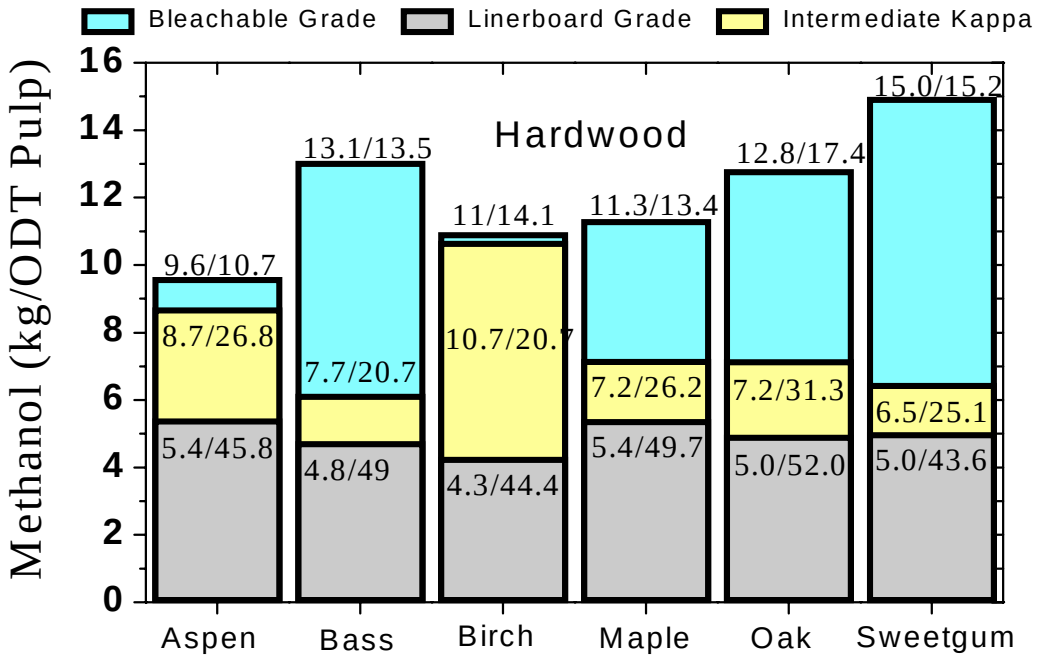

Fig. 7 The measured methanol formation data in conventional kraft pulping of six hardwoods (the first number in the bar is the methanol amount, and the second number after the slash is the pulp kappa number).

Overall, the results in Figs. 6 and 7 indicate that hardwoods produce more methanol than softwoods when producing an equivalent grade of pulp, which agrees with the results obtained in our previous study [10]. The total methanol formation varies from wood to wood mainly due to the differences in structure between softwood xylan and hardwood xylan and the variations of methoxyl group content in xylan and lignin of the woods.

CONCLUSIONS

We conducted laboratory pulping experiments using various wood species under various pulping conditions in bomb-type rotating batch digesters. We validated the methanol formation mechanism through alkali-catalyzed methanol elimination from 4-O-methylglucuronic acid groups in hemicellulose [7] of wood xylan by the direct measurements of hexenuronic acid groups in pulps. The results obtained from the pulping of bleachable grades from southern pine indicate that methanol formation from hemicellulose contributes to about 40% of the total methanol formed. About 25% of the methanol naturally present in wood is released instantly at the beginning of pulping. The remaining 35% of the methanol may be formed as a result of lignin demethylation reactions.

The results also indicate that increasing sulfidity reduces methanol formation for a given active alkali charge in kraft pulping. AQ addition in pulping can reduce methanol formation through increased delignification that results in a short reaction time. Soda pulping produces more methanol than kraft pulping at a given pulp kappa number and active alkali charge. Polysulfide kraft pulping produces less methanol than kraft pulping, possibly due to reduced hemicellulose degradation. Wood species can have a significant effect on total methanol formation. The study further confirms our previous work [10] that hardwoods produce more methanol than softwoods do.

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