Study on Odor Formation Control during Kraft Pulping

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ABSTRACT

The investigation of the formation of organic sulfur compounds (i.e., odor species), mainly methyl mercaptan and demethyl suifide, during kraft pulping has been conducted, in which both hardwood and softwood species were used. It was discovered that there is an organic sulfur compounds formation phase transition point with respect to delignification extent. The transition point occurs at a kappa number of approximately 35 and 20 for softwoods and hardwoods, respectively. The results also showed that both low sulfidity and anthraquinone (AQ) addition are helpful to control the formation of theses organic sulfur compounds during kraft pulping. Whereas Hexenuronic acid (HexA) has contribution to Kappa number, the extended delignification not only lead to low pulp yield, but also be adverse to odor control. A significant in-digester odor reduction can be achieved if the pulping is to be terminated before phase transition point and combined with AQ addition.

Keywords: Odor control, Orgainc sulfur compounds, Kraft Pulping, Phase transition point, Extended Delignification , Anthraquinone

INTRODUCTION

Kraft mill odor has long been an environmental and public relations issue for the pulp and paper industry. The kraft mill odor is caused predominantly by malodorous reduced sulfur compounds, or total reduced sulfur (TRS), namely, methyl mercaptain (MM), dimethyl sulfide (DMS), dimethyl disulfide (DMDS), and hydrogen sulfide (H_2S). MM, DMS, and DMDS are the main volatile organic sulfur compounds and are formed in the pulping process, while hydrogen sulfide is formed in the recovery furnaces. Although significant reduction of TRS emission has been achieved in the pulp and paper industry in the last decade with advanced odor abatement technologies, subjective odor nuisance at very low concentrations still causes odor problems in surrounding communities of a kraft mill.

TRS formation in kraft pulping has been studied as early as in the 1950s, 1960s, and 1970s [1-7]. Much of these research efforts have been devoted to quantification and kinetics [4-6] of the organic sulfur compound formation. The general formation mechanism of the TRS has been described elsewhere [5] and recently in Jarvensivu et al. [8]. The formation of MM and DMS is through the reaction of mercaptide ion and the methoxyl groups present in the pulping liquor [4, 6]. DMDS is not formed in the pulping process rather through the oxidation of MM when black liquor is in contact with air [4-6]. Hydrogen sulfide is not formed in the normal pulping pH conditions, rather in the downstream processes where the pH of the streams are reduced below 10 through the dissociation of sodium sulfide [3,5]. Other significant sources of H_2S formation are lime mud reburning, black liquor pyrolysis, and molten smelt dissolution processes [3-5].

There are two general approaches to abate odor currently implemented in kraft mills: Thermal oxidation and absorption using scrubbing technologies. Thermal oxidation of TRS is achieved by two steps: collecting of non-condensable gases (NCGs) in various emission vents and eliminating odorous compounds in the NCGs through combustion in lime kilns, power boilers [4], or special incinerators [7] to converting them into non-odorous compounds. Absorption is mainly implemented to destroy H_2S and MM in diluted NCGs through scrubbing using spray tower or packed column [4, 7].

Much of the work on TRS reduction has been focused on the implementation of these technologies in the later 1970s to the 1990s. Significant odor reduction has achieved. Further reduction of TRS emission using post odor formation control technologies, e.g., oxidation, scrubbing, etc., will be very difficult and costly. Kringstad et al. conducted In-digester oxidation (IDO) of kraft black liquor using oxygen and found that both MM and DMS can be reduced with the application of large amount of oxygen into the pulping liquor[1]. Tormund and Teder [2] found that significant amounts of MM and DMS formed during pulping can be converted to non-volatile compounds by reaction with polysulfide or polythionate immediately before blow (post formation in-digester reduction).

In this study, we have investigated the organic sulfur compound formations during kraft pulping at varying conditions. The intention is to achieve a reduction of

these odor species formation at its source, i.e., in-digester, through process modification and a wise control strategy.

2.1 Kraft Pulping

Conventional kraft pulping experiments were conducted in the lab. Four different softwood species of Douglas fir, white spruce, western hemlock, and loblolly pine, and six hardwood species of aspen, bass, birch, maple, oak, and sweet gum were used in the experiments. In the pulping, a pulping liquor to wood ratio of 3. 7 - 4, an 17-18% active alkali charge, three sulfidity levels of 10, 20, and 30% and four AQ concentrations of 0, 0.025, 0.05

2.2 TRS Analysis [8]

In this study, the full evaporation headspace gas chromatographic (FE-HSGC) method that we developed in a previous study [8] was employed. The FE-HSGC method is based on the principle of near complete analyte transfer from the liquid phase into the vapor phase when a very small sample is heated in a sample vial, therefore, the analyte in the liquid phase can be analyzed by direct headspace gas chromatography without any sample pretreatment requirements.

3. RESULTS AND DISCUSSIONS

3.1 Time-Dependent Organic Sulfur Compound Formation

Figure 1 shows the time-dependent formation of organic sulfur compounds, namely MM and DMS, in a set of

EXPERIMENTAL

and 0.1% were used. Cooking temperature was rampled from room temperature of 23°C to 170°C in 70 minutes or at a rate of 2.1°C per minute. Cooking times at the preset maximum temperature of 170°C were varied to study the time-dependent formation of organic sulfide compounds in pulping.

Black liquor sample collected from each digestion was analyzed for the determination of chemical strength and the organic TRS concentrations.

conventional kraft pulping processes of southern pine. The sulfidity was 30%. We did not find DMDS in the pulping spent liquor, which agree with the conclusions reported in the literature [4-6, 9]. The time-dependent data show that the formation of MM and DMS was slow at the beginning of the pulping process due to low temperature and low methoxyl group concentration, but increases exponentially as the pulping process continues. The formation rate transition point (FRTP) occurs right at the pulping temperature reaches 170℃(the 4th data point corresponding to pulping time 70 minutes). The formation of MM is much earlier than that of DMS. Figure 1 also shows that the present data agree with those obtained by Andersson [9] in 1970.

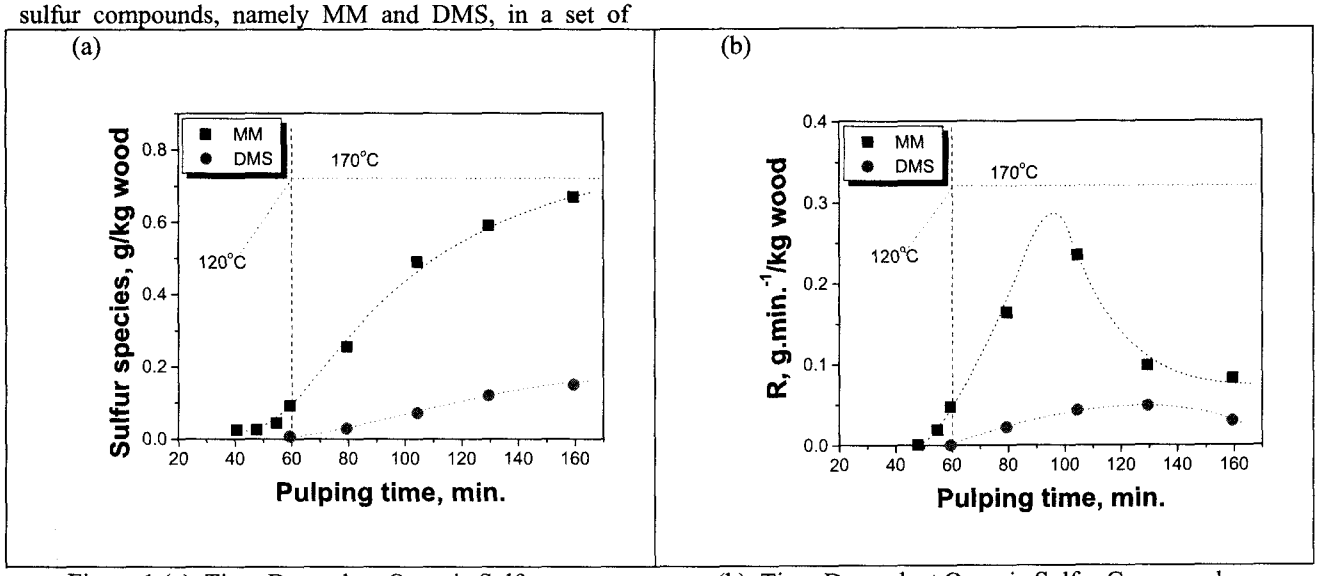

Figure 1.(a). Time-Dependent Organic Sulfur Compound Formation in kraft pulping.

(b). Time-Dependent Organic Sulfur Compound Formation Ratio.

The time-dependent volatile organic sulfur compound formation data provide detailed information about the formation kinetics and have been well documented in the literature [4-7]. The data clearly show that the formation of organic sulfur compounds experiences a slow stage at the beginning of the pulping and a rapid increase stage after the cooking temperature reaches 170℃. However, the data did not provide any information about the degree of delignification and its relation to the formation of organic sulfur compounds. Research on the correlation between the formation organic sulfur compound and delignification has not been reported in the literature. From a practical point of view, it will be very interesting and beneficial to correlate the organic sulfur compound formation to delignification. It is this approach adopted in the present study that leads to the development of the present IDOR technologies.

3.2 Effect of Sulfidity

To evaluate the effect of organic sulfur compound formation with sulfidity in kraft pulping, 3 kinds of sulfidity(i.e. 10, 20, 30%) were test in kraft pulping of southern pine. When cook to the same Kappa number, the volatile organic sulfur compound in the black liquid were compared, the results were shown in figure 2. It is obvious that, the low sulfidity pulping can reduce the organic sulfur compound formation. On the other hand, low sulfidity pulping need more cooking time than high sulfidity pulping

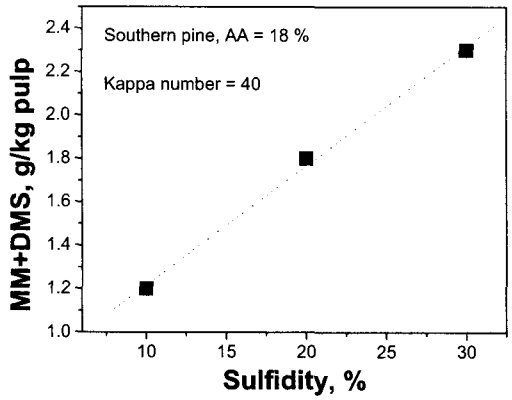

Fig. 2 Correlation of organic sulfur compound formation with sulfidity in kraft pulping of southern pine.

3.3 Phase Transition Pulping (PTP) for In-Digester Odor Reduction

To relate the formation of organic sulfur compound with delignification, we determined the kappa number of each pulp sample for data presentation in the present study. Figure 3 shows the correlation of sulfur compound formation to the kappa number for a set of kraft conventional pulping processes of southern pine (the time-dependent formation data are presented in Fig. 1). The results demonstrate that the formation of organic sulfur compounds linearly increases with the reduction of kappa number. Further reduction of kappa number as delignification continues results in a rapid increase of the formation of sulfur compounds. The transition point occurs at the about kappa number of 35 (corresponding to pulping time of 120 minutes). We call this transition point phase transition point (PTP) based on the assumption that the pulping process enters residue delignification from bulk delignification phase.

To demonstrate that PTP pulping concept is universally valid, we conducted kraft conventional pulping of 4 softwoods and 6 hardwoods. Figure 4 shows the formation of total reduced sulfur compounds, i.e., MM plus DMS, in relation to delignification pulp kappa number. The sulfidity was 30% for southern pine and maple and 31% for the rest of the wood species as stated in the experimental section. The results indicate that kraft pulping of softwoods produces much more organic sulfur compounds than that of hardwoods at a given kappa number.

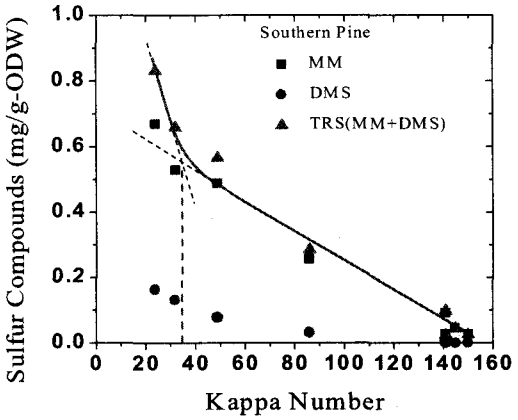

Fig. 3 Correlation of organic sulfur compound formation with delignification (pulp kappa number) in kraft pulping of southern pine.

The results also show that the total organic sulfur compounds formed from pulping of all softwoods and all hardwoods falls to a single curve, respectively, independent of the specific wood species within the general categorization of hardwood and softwood. Furthermore, the slopes of the two TRS formation curves experience an abrupt change at a critical kappa number, respectively, meaning that a PTP exists in hardwood and softwood pulping, respectively. The kappa number at the PTP is 35 and 20 for softwoods and hardwoods, respectively. When kraft cooking is terminated around the critical point for the purpose of odor reduction, we can call it as the phase transition cooking (PTC). It is our understanding that the transition point is directly related to the phase transition of kraft delignification from bulk delignification to residual delignification. Thus, when the different cooking processes, e.g. RDH or EMCC, are used, the actual kappa number of the transition may be different. In most case, it may be a lower kappa number.

The data in Fig. 4 indicate that the total organic sulfur compounds formed during the post PTP cooking stage are 70% and 50%, respectively, for bleachable grade hardwood pulping of a final kappa number of 10 and bleachable grade softwood of a final kappa number of 25. Therefore, it is feasible to significantly reduce TRS formation in kraft pulping by limiting the degree of delignification to the PTP at which the pulp kappa number is 20 and 35 for hardwoods and softwoods, respectively. The increased amount of residue lignin can

be removed through other means, such as oxygen delignification in which odor compounds will not be formed because sulfur compounds are not used.

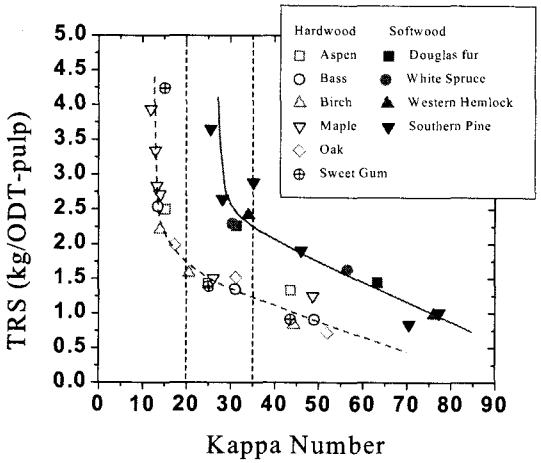

Figure 4. Correlation of total organic sulfur compound formation with delignification (pulp kappa number) in kraft pulping of various softwoods and hardwoods

3.3 AQ Addition

AQ has been well known to possess a marked capability of accelerating the delignification while at the same time stabilizing the carbohydrates toward alkaline degradation in the alkaline pulping process [10]. From the reaction kinetics [4-7], one can easily find that catalyst AQ does not affect organic sulfur compound formation, which is verified in the present study. As shown in Fig. 5, the TRS formation rate does not change with the addition of 0.05% of AQ in kraft pulping of southern pine and maple. Only when we correlate TRS formation with delignification, have we discovered that AQ can change the correlation between the formation of organic sulfur compounds and delignifictaion due to improved delignification. Therefore, we believe that TRS formation can be reduced by using a reduced pulping time with AQ to achieve an equivalent delignification (or kappa number). Considerable reduction in TRS formation with AQ addition in kraft pulping of southern pine and maple was shown in Figs. 6 and 7 over a wide range of sulfdity variations from 10 to 30%. Even in such a wide sulfidity range of 10-30%, the PTP remains the same, i.e., 20 and 35, for maple and southern pine, respectively.

To further demonstrate the effect of AQ addition on TRS formation reduction, we varied the level of AQ addition in pulping. We found that the TRS formation decreases linearly with the square root of the AQ (in percent) added in kraft pulping of southern pine as shown in Fig. 6. We found that TRS formation can be reduced by 20 and 30% with the addition of 0.05% AQ in the kraft pulping of southern pine to kappa numbers of 30 and 40, respectively. The difference in the percent of reduction of TRS formation between kappa number 30 and 40, perhaps is due to the fact that that the PTP is at kappa number of 35, indicating that the addition of AQ is perhaps more effective to the bulk delignification phase of pulping.

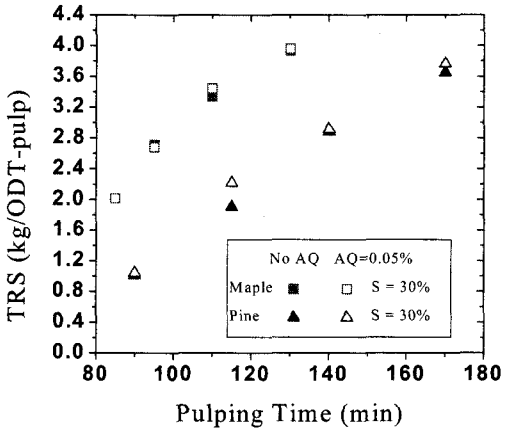

Figure 5. Effect of AQ addition on time-dependent total organic sulfur compound formation in kraft pulping.

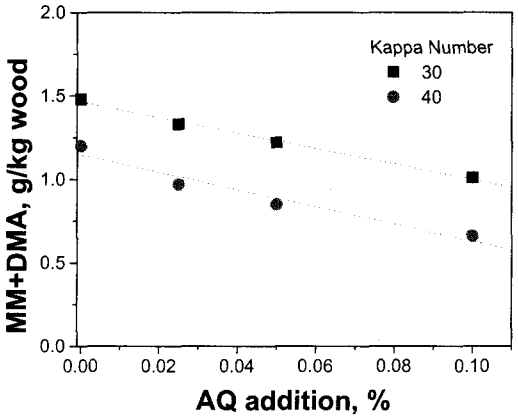

Figure 6. Correlation of total organic sulfur compound formation with AQ addition[11].

3.4 Combined effects of pre-PTP cooking and AQ-addition

From the results shown above and our previous working[14-16], it can be strongly postulated that using both pre-PTP cooking and AQ-Addition, approximately 70-90% TRS emission can be reduced from the kraft digestion as a result of their combined effect. TRS reduction effect by this in-digester odor control technology will be even higher in hardwood than softwood cooks.

3.5Consideration of Extension Deglignification

Conventionally, as much as possible of lignin is tried to be removed during the cooking process, because the high residual lignin content will result in the formation of adsorbable organochlorine compound (AOX) in the sequent bleaching process with chlorine chemicals. However, extended cooking, i.e., cooking to a low kappa

number need to be reconsidered, the main reason of which is the generation of organosulfur compound. The Kappa number dramatically decreases in the residual delignification stage, which will be misunderstood as the effective delignification. The recent researches demonstrate that HexA content in pulp is highly related to the Kappa number[14, 17]. For example, 60% of Kappa number of unbleached hardwood pulp alkaline pulps results from the HexA. HexA is stable in an alkaline solution, but it will be dissolved if the polyxylose is in degradation, which causes the decrease of the Kappa number. Our previous study has shown that HexA content relates to the pulp yield in softwood pulping process, i.e., the HexA content reduction corresponds to the pulp yield loss. Because the degradation of the HexA is obvious in the residual delignification stage and the extended delignification risks pulp yield loss, the integral strategy should be adopted to balance the pulp production and environmental protection. In recent years, the oxygen delignification process that is demonstrated to be effective in middle Kappa number deglignification process and environmental friendly is reaching mature and commonly used, which will benefit both the pulp production and environmental protection.

4. CONCLUSION

4.1 This study show that the formation of organic sulfur compounds increases as delignification proceeds.
4.2 Further removal of lignin after transition point results in a rapid increase of the formation of sulfur compounds. The transition point occurs at the about kappa number of 35 and 20 for softwoods and hardwoods, respectively.
4.3 The results also indicate that anthraquinone(AQ) as a catalytic additive can be used for the purpose of TRS reduction during kraft digestion.

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