

## RAPID COMMUNICATION

Keiichi Koda · Hiroyuki Shintani · Yuji Matsumoto  
Gyosuke Meshitsuka

## Quantitative study on the possible formation of chloroform during chlorine bleaching of kraft pulp

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Many volatile, low-molecular-weight chlorinated compounds and high-molecular-weight chloroorganics are produced during bleaching of pulp when chlorine-containing bleaching agents are used. Chloroform produced at bleaching facilities is one of the major by-products emitted into the environment through the atmosphere. Chloroform emission during the hypochlorite bleaching stage (H-stage) is particularly serious. It is also reported that chloroform precursors in the chlorination stage (C-stage) effluent, when treated with alkali, produce chloroform to a considerable degree, so chloroform production increases exponentially with the increase in the pH of the effluent.<sup>1</sup>

Appropriate methods to evaluate chloroform production during chlorination and alkali-extraction stages (C- and E-stages) are required; chloroform is a volatile compound with poor solubility in water, and it is difficult to determine chloroform levels quantitatively. The chloroform production per pulp determined in plant-scale investigations conducted by the Japan Paper Association in 1997 showed low reproducibility (50–450 g/ton o.d. pulp); so more precise methods are required.<sup>2</sup>

In this study the authors tried to eliminate chloroform leakage into the air during both reaction and sampling using a gas-tight reaction vessel in an attempt to improve the accuracy and precision of the chloroform determination.

The authors also tried to evaluate quantitatively the maximum chloroform production during C- and E-stages based on the determination of chloroform potentially produced from precursors generated in lignin during C-stage.

Well-washed unbleached softwood kraft pulp with a kappa number of 24.0 (NUKP) and oxygen-prebleached softwood kraft pulp with a kappa number of 11.3 (NOKP) served as samples (125 mg for each sample on an oven-dried weight basis). The sample was placed in a 100-ml pressure-proof, gas-tight reaction vessel (shown in Fig. 1) with a hollow screw cap to which an inner lining coated with Teflon was attached. Chlorination was performed at room temperature (26°–30°C) for 60 min at 0.5% pulp consistency (the chlorine multiple ranged from 0.10 to 0.20). The chlorine multiple – the term often referred to as the “chlorine charge factor,” the “kappa factor,” or the “chlorine ratio” in the literature<sup>3–5</sup> – is defined as the percent chlorine charge (% on pulp) divided by the kappa number of unbleached pulp. The chlorine multiple was corrected on the basis of the weight of the pulp and the concentration and volume of chlorine water used in the experiment. The reaction was finished by adding 1.0 ml of 0.2 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution to the sample with a syringe. After the reaction, 2 ml of saturated NaCl solution, a prescribed amount of NaOH solution 5 g/l, and deionized water were added sequentially with a syringe, so the total volume of the sample solution reached 30 ml. The NaOH dosage (% on pulp) was the sum of 2.5% on pulp (on an o.d. weight basis) and twice the amount of the charged chlorine (on a molar basis): NaOH charges of 5.20%, 6.56%, and 7.91% on pulp were applied to the chlorinated NUKP samples with chlorine multiples of 0.10, 0.15, 0.20, respectively, whereas NaOH charges of 3.77%, 4.41%, and 5.05% on pulp were applied to the chlorinated NOKP samples with the corresponding chlorine multiples, respectively. Warm alkali treatment was performed at 70°C for 60 min. As a separate experiment at a higher pulp consistency, NUKP (10 g) was chlorinated in a plastic bag at a pulp consistency of 5%. After filtration, parts of both the chlorinated pulp and chlorination liquor were treated with warm alkali in the reaction vessel. In this case, the alkali charge was fixed at 10% on pulp.

K. Koda (✉) · H. Shintani · Y. Matsumoto · G. Meshitsuka  
Laboratory of Wood Chemistry, Department of Biomaterial  
Sciences, Graduate School of Agricultural and Life Sciences, The  
University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113-8657,  
Japan  
Tel. +81-3-5412-5263; Fax +81-3-5802-8862  
e-mail: aa77091@mail.ecc.u-tokyo.ac.jp

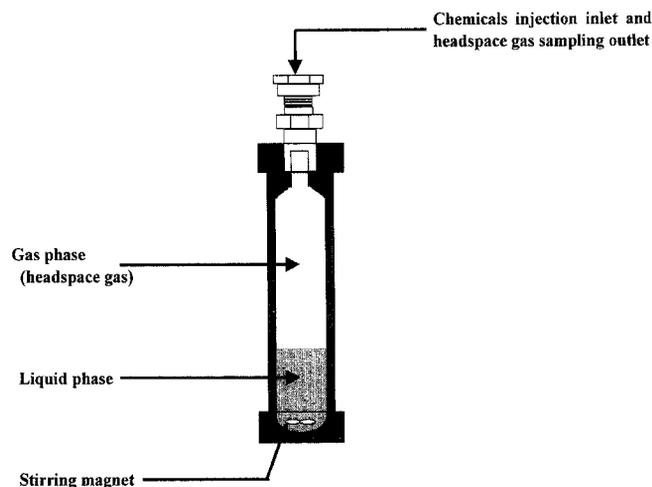


Fig. 1. Pressure-proof, gas-tight reaction vessel used in this experiment

After the alkali treatment, headspace gas chromatographic analysis of chloroform was performed with a gas chromatograph (GC-17A; Shimadzu) equipped with a mass spectrometer (QP-5000; Shimadzu) with a single-ion monitoring mode. The base ion peaks of chloroform ( $m/z$  83 and 85) were observed.

The results showed that chloroform production increases with the chlorine multiple after chlorination and alkali treatment (Fig. 2). In a separate experiment, chloroform formation during the C-stage without additional alkali treatment was estimated to be less than 10% of the values in Fig. 2 (data not shown). These results prove that substantial amounts of the alkali-labile chloroform precursors have already been generated during C-stage, the degree of which depends on the chlorine multiple. Generally, from an industrial standpoint, chlorination liquor is not subjected to alkali treatment under the conditions employed in this experiment; nevertheless, it is possible that chloroform precursors are unexpectedly modified to form chloroform during some of the chemical or biological treatment processes of the bleach effluent. This is why evaluation of chloroform precursors as a potential for chloroform formation is important. The total amount of chloroform generated from both chlorinated pulp and chlorination liquor, which were prepared from the chlorination of NUKP at a pulp consistency of 5%, is somewhat lower than that in the case of 0.5% pulp consistency. This is partly because some of the chloroform produced during chlorination was eliminated through filtration. Almost the same degree of chloroform formation after alkali treatment, however, is expected in both cases.

Softwood milled wood lignin (MWL) (4.5 mg) was chlorinated and treated with alkali in the same manner as the low consistency (0.5%) treatment of pulp using the reaction vessel. MWL was used so the weight of it corresponded to that of residual lignin in 125 mg of the NUKP used in this study. Figure 2 shows that regardless of whether MWL or residual lignin in pulp is used as a lignin sample, almost the same amount of chloroform formation can be expected from a prescribed amount of lignin, though the result with

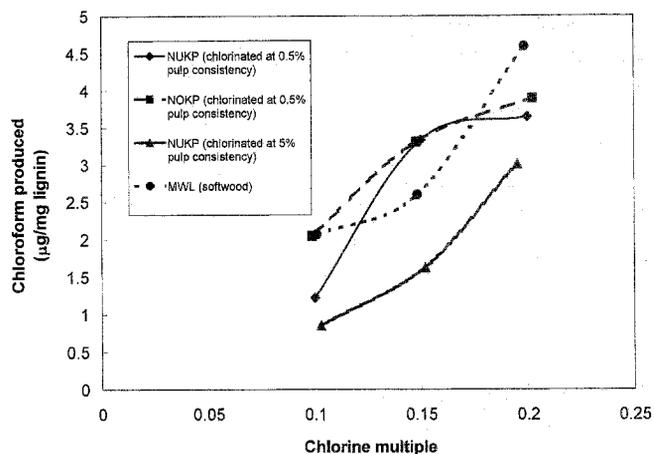


Fig. 2. Increase in chloroform production with the chlorine multiple. NUKP, unbleached softwood kraft pulp; NOKP, oxygen-prebleached softwood kraft pulp; MWL, milled wood lignin

MWL indicated a somewhat larger amount of chloroform formation. The result also illustrates that lignin is exclusively the source of chloroform formation.

Alkali treatment was performed at 70°C in this experiment, and the final pH of the samples ranged from 10.5 to 11.7. Some of the samples showed moderately increased or decreased chloroform formation when a prolonged reaction time of alkali treatment was employed (data not shown). Under the conditions employed, chloroform formation from its precursors and structural conversion of chloroform are thought to occur competitively. The reaction time of the alkali treatment employed in our experiment (1h) may be too short to hydrolyze all the chloroform precursors to produce maximum chloroform formation. In addition, chloroform in alkali solution can be modified to form formic acid, a situation that needs further investigation (unpublished data). This may affect to a greater or lesser degree the precision of each determination. However, the influence of the competitive reactions in this study at a fixed reaction time on the chloroform determination proved to be minor because our results had relatively good reproducibility (5%–12%), compared to the reproducibility reported in JIS K 0125 (10%–20%).

Headspace gas chromatography was successfully applied to the determination of chloroform. The degree of chloroform formation during the C- and E-stages by our evaluation essentially shows good correspondence with the study recently reported by Iimori et al.,<sup>6</sup> although they used oxygen-prebleached softwood kraft pulp and investigated chloroform in alkali-treated chlorination liquor by gas chromatographic analysis of the solvent extract. The results shown in Fig. 2 also illustrate that with the chlorine multiple ranging from 0.10 to 0.20, chloroform formation ranged approximately from 1 to 4 µg/mg lignin in pulp, regardless of oxygen prebleaching.

Crawford et al. reported from their plant-scale investigation that there seems to be no significant difference in chloroform generation between facilities (bleach lines) with or without the oxygen delignification process.<sup>7</sup> Their result

suggests that chloroform generation from kraft pulps with and without oxygen prebleaching depends largely on the chlorine factor but not on the kappa number (lignin content) of pulp before chlorination, which seems contradictory to the result of our laboratory-scale experiment. Our results, using well-washed pulps (NUKP and NOKP) and chlorine water containing no chlorine dioxide, shows that chloroform production depends on the kappa number and the chlorine multiple (Fig. 2).

This discrepancy can be attributed to the difference in reaction and sampling conditions. The reaction temperature of chlorination, the degree of ClO<sub>2</sub> substitution during the C-stage, pulp washing efficiency (the degree of carryover of oxidized substances to the C-stage that are produced during the oxygen prebleaching stage), and the degree of chloroform leakage into the air are assumed to be different between the two situations. These factors seem to affect chloroform production significantly during C- and E-stages, which was confirmed by the recent investigation by Iimori et al.<sup>6</sup>

By a comparison with previous studies,<sup>1,8-10</sup> it is concluded that chloroform formation during C- and E-stages can never be negligible compared to that during H-stage. The C- and E-stage effluents containing chloroform and its precursors should be treated properly before being emitted into the environment.

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