Factors affecting fatty acid oxidation and the formation of odorous aldehydes during TMP production

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ABSTRACT: This study focuses on factors that affect the formation of odorous aldehydes from pulp extractives during TMP production. The formation of odorous aldehydes was decreased by dithionite bleaching. EDTA treatment and the elimination of lime during TMP production also reduced the formation of aldehydes. Furthermore, in spite of having a significantly higher fatty acid content, pine TMP gave lesser amounts of odorous aldehydes than given by spruce TMP. The concentration of aldehydes increased during storage. However, dithionite bleaching, EDTA treatment, and a low storage temperature caused less of an increase in odorous aldehydes during storage.

Application: Food products should never be tainted by the paper used as packaging. It is important to understand the aspects of thermomechanical pulping that could affect foods wrapped in it.

Paper and board used for food packaging should not affect the packaged product in terms of its organoleptic qualities, or those qualities that affect the senses, such as the taste and smell. Paper is never completely odorless, however, and volatile compounds that originate from paper could be absorbed by the food. To prevent the paper packaging from tainting the food product, pulp and paper producers need to know how process variables affect the development of odorous aldehydes.

CHEMISTRY BACKGROUND

Wood extractives are considered one of the three main sources of pulp and paper odor, the other two being microbiological activity and process chemicals [1]. Wood extractives may produce volatile, odorous compounds such as aldehydes, alcohols, and ketones through the autoxidation of unsaturated fatty acids [2, 3]. Autoxidation occurs via a free-radical chain reaction consisting of three steps—initiation, propagation, and termination [4, 5].

Initiation:

$$X\cdot + RH \rightarrow R\cdot + XH$$

Propagation:

$$R\cdot + O_2 \rightarrow RO_2\cdot$$

$$RO_2\cdot + RH \rightarrow ROOH + R\cdot$$

Termination:

$$RO_2\cdot + RO_2\cdot \rightarrow \text{stable products}$$

Initiation starts with the abstraction of a hydrogen radical from the unsaturated fatty acid (RH), in the presence of an initiator (X·) such as a transition-metal ion or a radical obtained by the decomposition of a hydroperoxide perhaps. The alkyl radical (R·) thus formed reacts with atmospheric oxygen, giving an unstable peroxy radical (ROO·) that may abstract a hydrogen atom from another unsaturated fatty acid to form a hydroperoxide (ROOH) and a new alkyl radical. The resulting chain reaction may be terminated by the formation of products that are not radicals.

The rate of autoxidation is affected by various factors, including light, temperature, and the reactivity and concentration of reactants such as fatty acids and oxygen [6]. The concentration and composition of fatty acids in pulps is influenced by factors such as the wood species used, the pulping and bleaching process, and storage. Generally, pine contains more fatty acids than spruce contains [7].

As Ekman and Holmbom have demonstrated [8], the oxidative bleaching of spruce groundwood pulp with alkaline peroxide decreases the concentration of unsaturated fatty acids. Peroxide bleaching also increases the odor of mechanical pulp [9]. By contrast, dithionite bleaching is a reductive bleaching process [10]. When oxygen is present, dithionite is converted to bisulfite, which eliminates oxygen [11]:

$$2Na_2S_2O_4 + O_2 + 2H_2O \rightarrow 4NaHSO_3$$

This reaction is extremely rapid. Dithionite bleaching does not affect wood resins notably [12].

The rate of fatty acid oxidation increases as the degree of unsaturation increases. Furthermore, the storage temperature has been shown to have a significant effect on fatty acid oxidation and off-flavor development in soybean oil [13].

There are several reports in the relevant literature regarding the odor of individual volatile compounds [14–17]. According to these reports, volatile aldehydes ranging from C_5 to C_{10} have very low threshold values at which odor is detected. In other words, humans can smell them at very low concentrations. These common reaction products are formed by the oxidation of fatty acids.

Here we will look at the effects of dithionite bleaching, wood species (spruce vs. pine), chelating agent (EDTA), lime addition, and storage on fatty acid oxidation and the formation of odorous aldehydes in a thermomechanical pulp produced by a Norwegian mill.

MATERIALS AND METHODS

Mill process

The TMP mill that produced the pulp used in the experiments has an annual production capacity of 45,000 tons. Spruce chips are normally used as raw material. The process involves refining in two parallel, single-stage, double-rotating refiners at 115°C, bleaching with dithionite (8.3 kg/ton), dewatering, and flash drying to approximately 86% dry matter. Pulps treated with chelating agent are washed with EDTA (0.25%). Lime (2 kg/ton) is added to some pulp qualities prior to flash drying to facilitate pulp dissolution at the paper mill (not integrated).

Sample treatment

TMP samples (approximately 200 g each) were wrapped in a double layer of aluminum foil immediately after production at the mill to prevent loss or the uptake of odorous substances from the environment. The samples were sent by express mail to the Norwegian Pulp and Paper Research Institute for odor and fatty acid analyses.

For storage experiments, the samples were stored at 12°C or 20°C. The samples were contained in the original wrapping.

Analysis of volatile aldehydes

Volatile compounds were determined by dynamic headspace GC–MS analysis. In the results presented in the figures, aldehyde concentrations (O_i) are given as ng/L of headspace gas (hs).

Sample incubation and collection of volatiles

Pulp samples (50 g in small pieces < 1 cm³) were heated in a glass vessel (600 mL) for 4 h at 40°C. Afterwards, the headspace gas was collected on an adsorbent material (Tenax TA, 150 mg, 60–80 mesh) by purging with helium gas (AGA 6.0, 300 mL, 20 mL/min). If the adsorbent appeared wet, it was dried with helium gas until all condensation was removed. Nonane (100 ng) was then added as a standard.

GC–MS analysis

The volatile compounds were thermally desorbed from the adsorbent in a Perkin-Elmer Automatic Thermal Desorption unit (ATD 400) and were released to the GC (HP 6890) capillary column (Chrompak, 60 m × 0.32 mm × 1 µm film thickness). After separation by gas chromatography, the individual components were detected by a mass spectrometer (HP 5973). A spectral library was used for identification.

Calculations

The concentration of odorous aldehydes (C_{aldeh}) was calculated from the peak areas (A) in the total ion chromatogram according to the following equation:

$$C_{aldeh} = A_{aldeh} \times C_{nonane} / (A_{nonane} \times R_f)$$

where C_{nonane} is the amount of nonane standard added to the column (100 ng) and R_f is the instrument response factor for the individual aldehydes.

These response factors are given in **Table I**. Because aldehyde standards for 2-octanal and decanal were not available, the instrument response factors were set to 1 for these compounds. The analytical system could not distinguish *cis* from *trans* isomers, so the concentrations used represent all unsaturated forms of these compounds.

Analysis of fatty acids

Pulp samples were extracted (Soxhlet) with dichloromethane. A recovery standard (margaric acid, $C_{17:0}$) was added, and the extracts were dried (35°C, N_2 gas). Dry extracts were dissolved in dichloromethane, split in two parts, and dried. One part was used to determine the free fatty acids, and the other was used to determine the total fatty acids after hydrolysis (with 0.5*M* KOH in 90% ethanol, 70 °C, 4 h).

Free and total fatty acids were determined by GC-FID analysis with an HP5 column (crosslinked 5% PH ME Siloxane, 30 m × 0.32 mm × 0.25 µm film thickness).

RESULTS AND DISCUSSION

EDTA treatment and storage

EDTA treatment caused a significant decrease in the formation of odorous aldehydes from spruce TMP (**Fig. 1**). The concentration of odorous aldehydes increased during pulp storage, more so in untreated pulps than in EDTA-treated pulps. Thus, EDTA treatment not only decreased the concentration of odorous aldehydes for fresh pulps but also retarded aldehyde formation during storage.

EDTA is a chelating agent that is classified as a “preventive antioxidant” [18], which means it inactivates metal ions through the formation of stable complexes. Because metal ions are important initiators of fatty acid oxidation [6], eliminating them may retard the formation of odorous aldehydes as fatty acids break down.

The storage temperature had a significant effect on the formation of odorous aldehydes. The concentration of aldehydes was higher after 10 weeks of storage at 20ºC than after 10 weeks of storage at 12ºC. This effect held for both the untreated and the EDTA-treated pulps. The aldehyde concentration was further increased after 20 weeks of storage (data not shown).

Dithionite bleaching and lime addition

The effect of dithionite bleaching on fatty acid content and aldehyde formation was examined for two pulp, one with lime (2 kg/ton) and one without. The pH was 8.5–9.0 for TMP with lime and 5.5–6.0 for TMP without lime.

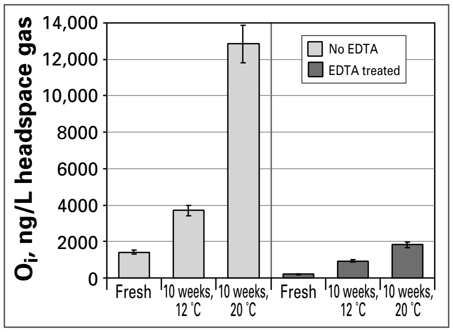
Figure 2 shows the effect of dithionite bleaching on aldehyde formation and total fatty acid content, measured after 3 and 19 weeks (storage at 12°C). The formation of odorous aldehydes was significantly lower for the dithionite-bleached pulp than for the unbleached pulp. This effect was especially pronounced in pulps that contained lime. Correspondingly, when lime was used, the total fatty acid content was significantly lower in the unbleached pulp than in the bleached pulp of the same kind. When lime was not used, however, the effects on aldehyde concentration were less pronounced, and the corresponding effects on fatty acid content were less clear. Overall, the results indicate that dithionite bleaching of TMP retards fatty acid oxidation and the formation of odorous aldehydes.

Pulp storage (at 12ºC) caused an increase in aldehyde formation and a decrease in total fatty acid content, more so in unbleached pulps than in bleached pulps. This outcome indicates that dithionite bleaching will also retard fatty acid oxidation and aldehyde formation during pulp storage. The effect of dithionite bleaching on fatty acid oxidation and aldehyde formation is probably caused by low oxygen availability, because dithionite reacts rapidly with oxygen, giving bisulfite [11]. Oxygen is needed for propagation to take place [18], which, as we have seen, is the second part of the fatty acid oxidation process.

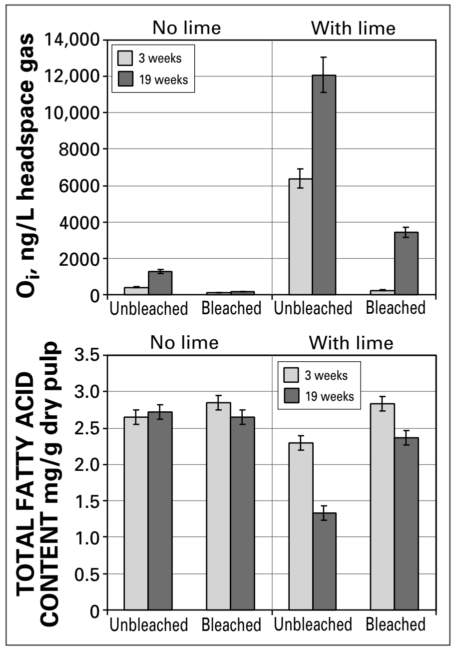
The aldehyde concentration was significantly higher in pulps that contained lime than in pulps with no lime. The corresponding fatty acid content was generally lower when lime was used, suggesting a higher rate of fatty acid oxidation at the high pH and high Ca^{2+} concentration of the lime-containing pulps. Under alkaline conditions, free fatty acids may be deposited as insoluble metal salts (Ca^{2+}-, Mg^{2+}-, Al^{3+}-) [12] and may be more easily available to oxygen [19]. A higher rate of decomposition of unstable hydroperox-

ALDEHYDE	RESPONSE FACTOR
Pentanal	0.33
Hexanal	0.45
Heptanal	0.63
Octanal	0.89
Nonane	1.00
Nonanal	1.19

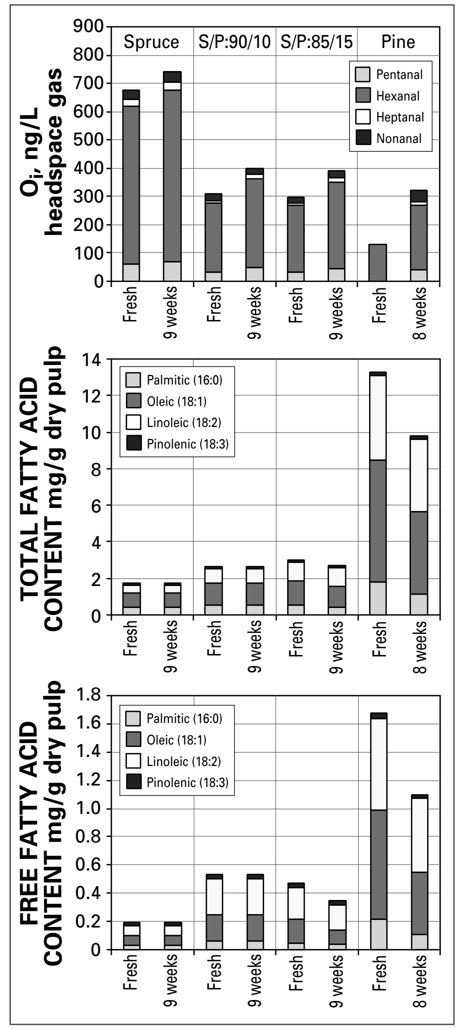
I. Instrument response factors for odorous aldehydes



1. Effect of EDTA treatment and storage on the formation of odorous aldehydes from spruce TMP. Pulps were stored at 12ºC and 20ºC.



2. Effect of dithionite bleaching, lime addition, and storage (12°C) on the formation of odorous aldehydes and total fatty acid content in spruce TMP.



3. Odorous aldehydes, total fatty acids, and free fatty acids in dithionite-bleached TMP containing spruce and/or pine. S/P gives the ratio of spruce to pine in percent. Stored pulps were kept at 12°C.

ides at high pH has also been suggested [19].

As the results suggest, dithionite may be a favorable bleaching agent for TMP intended for food contact purposes because it limits the formation of odorous aldehydes from wood extractives. However, dithionite is a less effective bleaching agent than the more commonly used peroxide. Care should also be taken with dithionite bleaching to avoid the formation of odorous sulfur compounds such as hydrogen sulfide (H_2S), which may be formed at high hydrosulfite levels and at low bleaching pH values [20].

Wood species

Figure 3 compares the aldehyde concentrations and fatty acid contents between dithionite-bleached TMP made from spruce, pine, and a mixture of the two. All pulps were bleached with dithionite to the same brightness. According to information given by the mill, the amount of dithionite added was similar in all pulps except the 100% pine pulp, in which it was slightly lower than in the other pulps. All pulps were analyzed twice. The first analysis was performed within one week after the pulp was produced, with the second performed after 8–9 weeks of storage (12ºC).

Surprisingly, as the relative amount of pine used in pulp production increased, the aldehyde concentration decreased, reaching a very low value in pulp made from 100% pine. The fatty acid concentration (total and free), however, was significantly higher in pine TMP than in spruce TMP. For all pulps, the fatty acids were mainly unsaturated. Thus, the amount of fatty acids available for oxidation to odorous aldehydes was much higher in pine TMP than in spruce TMP.

The low aldehyde concentration found at the high fatty acid concentration of pine TMP was unexpected. A possible explanation may be that components which favor fatty acid oxidation (such as heavy metals) are more available in the spruce pulp than in the pine pulp. Another possibility may be that components which limit fatty acid oxidation (such as antioxidants) are more available in pine pulp. Generally, spruce has a higher concentration of metals than pine has [21]. The metal content of wood is, however, subject to large variations depending on such factors as the place of growth, the age of the tree, and the location within the tree [21, 22].

The aldehyde concentration increased during storage in all pulps, though more so in pine TMP than in spruce TMP. This difference corresponded to a larger reduction in fatty acid concentration (free and total) in pine TMP than in spruce TMP. The largest decrease was in the concentration of polyunsaturated fatty acids (linoleic and pinolenic acid).

The dominating odorous aldehyde formed both from pine and spruce pulps was hexanal, followed by pentanal, nonanal, and heptanal. This pattern was also the case in all other pulps studied (data not shown). These aldehydes are typical oxidation products formed by the autoxidation of w-6 fatty acids such as linoleic and pinolenic acid [18]. Correspondingly, the concentration of pinolenic acid and linoleic acid decreased as the odor index increased during storage, primarily as a result of increased hexanal formation.

CONCLUSIONS

Dithionite bleaching of TMP significantly reduced the formation of odorous volatiles without any effect on pulp fatty acid content. The formation of odorous volatiles increased with storage, more slowly in dithionite-bleached TMP than in unbleached TMP. EDTA treatment significantly reduced the formation of odorous volatiles, and lime addition significantly increased the formation of odorous volatiles. Surprisingly, pine TMP gave less odorous volatiles than did spruce TMP, in spite of having a significantly higher fatty acid content (free and total).

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INSIGHTS FROM THE AUTHORS

In our lab, we have previously compared the release of odorous volatiles from various types of pulps, such as CTMP, kraft, and sulfite pulps, and from various types of paper, such as linerboard, fluting, and greaseproof grades. We have also compared bleached and unbleached grades.

In this work, the focus was on the process variables that affect the formation of odorous volatiles during TMP production. In TMP mills that produce pulp intended to come in contact with food products, the process variables identified here may affect the formation of odorous aldehydes.

The development of a reliable analytical method was critical to this work. The method currently being used has demonstrated good reproducibility. Nevertheless, it is difficult to obtain quantitative data for the individual volatile compounds. This work entailed runs with pure samples of the five dominating odorous aldehydes found in the samples, which made it possible to calculate the instrument response factors for these individual aldehydes.

It was surprising to find a low aldehyde concentration for fresh pine TMP, even though pine TMP has a higher concentration of fatty acids than does spruce TMP. Aldehydes are reaction products that are commonly formed by the oxidation of fatty acids, so we would have expected to see more aldehydes formed in pine TMP.

Our future research will focus on process variables that affect the formation of odorous aldehydes in other pulping and papermaking processes. We also hope to study other aspects of hygiene, such as the chemical and microbiological purity of pulps and paper.

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