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Formaldehyde emission from wood promoted by lignin in the presence of iron residues

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It is known that wood releases low levels of formaldehyde under natural conditions, but the mechanism for this release has not been well explored. This paper presents the lignin-mediated Fenton (LMF) reaction as a newly described mechanism for the generation of formaldehyde from wood lignin in the presence of iron. Traditional desiccator methods with Nash reagent and fluorescence spectrophotometry, and a commercial electrochemical-based formaldehyde sensor were used to examine the effects of important components in the LMF reaction i.e., iron reductant, hydrogen peroxide and lignin, on the wood formaldehyde emission in the presence of iron. The results showed that low levels of iron, especially in its reduced ferrous oxidation state, promoted the generation of formaldehyde in the presence of lignin in wood. Experiments were also conducted with additional iron reductants and hydrogen peroxide, which demonstrated additional formaldehyde generation in the presence of ferric iron and lignin, suggesting active generation of formaldehyde from wood by the LMF reaction.

Introduction

Formaldehyde emission from wood and wood-based products has been a concern because of its potential effects on human health, especially its carcinogenicity at low levels. The California Air Regulation Board (CARB) has set a long-term formaldehyde exposure limit of 2.4 ppb¹. In some cases, the amount of formaldehyde released from wood, in its natural state, has been found to exceed this CARB recommended limit. Much study has been conducted to find ways of reducing formaldehyde emissions from wood and wood-based materials by modifying parameters that are thought to contribute to anthropogenic formaldehyde generation, including manufacturing process optimization and resin replacement. However, the mechanism for the natural release of low formaldehyde levels from wood and wood products without additives remains unclear.

Generally, formaldehyde emission from wood products can be determined using analytical methods where formaldehyde is collected in chambers, flasks, or desiccators, or alternately trapped in solvents using a perforator². However, accurate measurement of low level formaldehyde release from wood has been a challenge because of the high variability of formaldehyde released from wood and the different methodologies used by different laboratories. In the past decade, sensor technology for formaldehyde detection has rapidly evolved for indoor air pollution monitoring. Compared to traditional

formaldehyde detection methodologies that require carefully controlled sampling conditions and dedicated analytical instrumentation, formaldehyde sensor technology developed in the past decade offers advantages including rapid response, straightforward operation, and compact size³. Further, current sensor technology is more sensitive and can be used for lower formaldehyde level detection than prior methods allowed. Formaldehyde sensors based on electrochemical, semiconductor, surface acoustic wave and fluorescence mechanisms are now available commercially. In our current research, we assayed formaldehyde gas using either a traditional ASTM method based on a Nash reagent fluorescence determination for formaldehyde^{4,5}, or a formaldehyde sensor module based on an electrochemical mechanism (model SKU: SEN0231, DFRobot, Inc.). Electrochemical-based sensors for formaldehyde detection work by measuring an electrochemical reaction produced by formaldehyde at the working electrode which generates an electrical signal inside the electrolytic cell⁶.

Iron is a common contaminant in wood and wood-based products, and it is naturally present in wood at low levels⁷. The effect of iron in wood materials has not been explored relative to either natural or anthropomorphic generation of formaldehyde from lignocellulose materials. The Fenton reaction ($\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{OH}^-$) is a well-known reaction that occurs in the presence of iron, and it occurs widely in nature including in the human body where it generates hydroxyl radicals ($\cdot\text{OH}$), the most powerful oxidizing agent in biological systems⁸. Fortunately, iron is typically in oxidized or oxy(hydr)oxide forms in aerated environments, and free ferrous iron typically is very limited in aerobic environments. Iron oxy(hydr)oxides are largely unreactive and thus hydroxyl radicals are not typically generated from this form of iron. However, in nature chelating compounds are secreted by most microorganisms to solubilize oxidized forms of iron and to allow those organisms to take

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up required iron⁹. Some fungi (such as brown rot fungi) that cause wood decay, have evolved a chemistry known as the “chelator-mediated Fenton” (CMF) mechanism, where environmental iron is not only solubilized, but also reduced in select micro-environments to participate in Fenton reactions generating $\cdot\text{OH}$ radicals within the wood cell wall¹⁰.

Recent research has also demonstrated that lignin-rich wood surfaces can participate in cyclic Fenton reactions, where iron is reduced multiple times by the phenolic derivatives of lignin at wood surfaces to promote CMF chemistry to function, under select environmental conditions, to depolymerize the wood cell wall¹¹. This is initiated by redox cycling of the phenolics with iron, but the “multiple iron reduction” was found to result from a cascade of reactions¹¹. When mediated by fungi, the CMF non-enzymatic mechanism allows for the generation of $\cdot\text{OH}$ within plant/wood cell walls so that the fungal hyphae are not damaged^{10, 12}. The plant cell wall is partially deconstructed by the CMF reaction as a prelude to the action of various carbohydrate-active enzymes that are also secreted by these fungi¹³. Studies on the destructive photooxidation of lignin have previously shown that hydrogen peroxide can be produced by light-mediated lignin reactions¹⁴ and this may further aid in some types of CMF chemistry at wood surfaces. The generation of hydrogen peroxide by the redox cycling of phenolics and polyphenolics in many different media at an appropriate pH is also well known¹⁵⁻¹⁹.

Studies on formaldehyde emission from the chemical composition of wood have shown that lignin releases much more formaldehyde than the carbohydrate component^{20, 21}. From a practical perspective, formaldehyde release is also not an issue of concern in products which contain pure cellulose alone. An understanding of why lignin releases formaldehyde at room temperature from lignin, or wood products containing lignin, is still lacking. Generation of formaldehyde from the methoxyl groups on lignin has not been well explored, but demethylation and demethoxylation of lignin by reactive oxygen radical species (ROS), such as $\cdot\text{OH}$, to yield methanol has previously been demonstrated^{22, 23}. The production of formaldehyde from methanol when exposed to $\cdot\text{OH}$ has also been well documented²⁴⁻²⁶. Because ROS are ubiquitous in the environment and ROS generation is promoted by the action of transition metals, which are commonly transferred into wood during the normal industrial processing, it is reasonable to speculate that ROS and metals such as iron, may be involved in natural formaldehyde release from wood. We hypothesized that this may be occurring in natural and built environments, and we explore the potential for this mechanism in the generation of formaldehyde from wood in the research presented.

Materials and Methods

For wood shaving sample production, southern yellow pine (*Pinus* spp.) sapwood boards with no knots or defects were used. The surface layer of the boards was cut away to remove contaminants, and shavings were produced using a conventional industrial planer head. Wood shavings were subjected to two 24 h sequential Soxhlet extractions with water and ethanol,

respectively. For wood flour samples, white pine (*Pinus strobus*) boards were again prepared by removing the surface material to remove surface contamination, and a titanium-coated saw blade was used with an aluminum table saw to make multiple passes through the boards to generate wood flour (sawdust) with minimal iron contamination. Chemicals used were: ferrous chloride tetrahydrate (99%+ $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ Chemsavers), ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ Home Science Tools), lignin (alkaline, Tokyo Chemical Industry America), with 2,3-dihydroxybenzoic acid (DHBA), sodium acetate (anhydrous), acetic acid and hydrogen peroxide all purchased from Sigma Aldrich. Before initiation of experiments, the wood flour and shavings were dried overnight at $103 \pm 2^\circ\text{C}$.

To enhance hydroxyl radical attack on both wood shavings and wood flour, an iron reductant (2,3 DHBA) and hydrogen peroxide were used in some sample sets. Supplemental lignin was also added to one wood flour sample set to determine how added lignin, beyond that naturally occurring in wood, affected formaldehyde generation under our experimental conditions. Deionized distilled (DD) water and stock solutions of acetate buffer (pH=4.1, 100 mM), 2,3 DHBA (5 mM and 10 mM), and hydrogen peroxide (400 mM) were prepared in advance. Ferrous or ferric chloride solutions were freshly prepared daily with DD water to bring the final iron content in wood flour to 1, 5, 10, 30, 60, or 100 ppm as detailed in the Results.

Effect of ferric iron reductant with iron in wood shavings

Wood shavings (0.2 g) were treated with 10 mL ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) in acetate buffer (pH 4, 0.1 M) and the samples were then reacted in a shaking water bath (25 °C and 125 rpm) for 2 h. Iron concentrations used to treat the wood shavings were 1, 3 and 5 mM. Iron solutions were drained from the shavings prior to the incorporation of an additional 10 mL of pH 4 acetate buffer (0.1 M), with or without DHBA (1 mM or 5 mM), and also with or without H_2O_2 (0.1 M or 0.4 M). The samples were again shaken at 25 °C for 1 h, and then drained of all solutions for analysis using the “desiccator method” described below. Wet-mixed wood shavings (0.1 g each) were transferred to a 50 ml serum bottle and kept sealed for 24 h at room temperature prior to the formaldehyde analysis. Duplicate samples were analyzed. Additional samples were used for MC determination.

Moisture content, iron reductant, peroxide, and lignin parameters with wood flour

A series of experiments were conducted to test the effect of wood moisture content (MC), iron type, iron reductant (2,3-DHBA), hydrogen peroxide and added lignin on formaldehyde emission (Table 1). Iron solutions were adjusted to produce the final iron concentrations (0 – 100 ppm, Table 1). Experiment I (Table 1, I) was conducted to test if the wood MC significantly affected detectable formaldehyde. This data was then used to standardize the effect of wood flour MC relative to formaldehyde emission when designing additional experiments (Table 1, Experiments II-V). For Experiments I and II, ferrous or ferric iron was diluted

Table 1: Experimental design for determination of formaldehyde emission from white pine wood flour with variables including moisture content, ferrous or ferric iron, iron reductant, hydrogen peroxide, and lignin. The total reactant volume for all samples was 610 μ L for 30.5% MC or 1010 μ L for 50.5% MC.

Experimental Sample Sets	Iron type and amount in wood flour sample (ppm)	MC of wood flour (%)	Final concentrations of reactants
I. Moisture content	Fe ²⁺ : 0, 1, 5, 10, 30, 60, 100	30.5	DD water
	Fe ²⁺ : 0, 1, 5, 10, 30, 60, 100	50.5	DD water
II. Iron oxidation state	Fe ³⁺ : 1, 5, 10, 30, 60, 100	30.5	DD water
III. Iron reduction agent	Fe ³⁺ : 1, 5, 10, 30, 60, 100	30.5	Acetate buffer (50 mM) 2,3-DHBA (2.5 mM)
IV. Iron reduction agent and hydrogen peroxide	Fe ³⁺ : 1, 5, 10, 30, 60, 100	30.5	Acetate buffer (50 mM)
			2,3-DHBA (1.2 mM or 2.5 mM)
			H ₂ O ₂ (100 mM)
V. Additional of 1% and 10% lignin	Fe ³⁺ : 100	30.5	Acetate buffer (50 mM)
			2,3-DHBA (1.2 mM)
			H ₂ O ₂ (100 mM)

with DD water before being stirred into 2 g wood flour to disperse the iron as uniformly as possible. For Experiment III (Table 1), ferric and acetate buffer solutions were added to 2 g of wood flour followed by 2, 3 DHBA and the mixture was stirred thoroughly. To keep the total volume of solution consistent, after mixing the ferric and acetate buffer, 2,3 DHBA and H₂O₂ were added to the wood flour in Experiment IV (final concentrations are listed in Table 1). For Experiment V, lignin was added at 1% or 10% by weight relative to the wood flour, and the lignin powder was thoroughly mixed into the wood flour before adding liquid reactants. The iron solution and other reactants was mixed and added in the same manner as in Experiments I-IV. Three replicates were performed for each iron level used in all experiments. Formaldehyde emission was detected after 24 h.

Although it is well known that water absorbs and traps formaldehyde²⁷, all wood contains some water in natural environments and therefore some formaldehyde generated by wood components will be absorbed by that water. It was necessary as part of the experimental protocol to mix some reagents with water to permit incorporation of these components into the wood cell wall.

Formaldehyde detection

For wood shavings, a “desiccator method” (ASTM D5582-14, 2014) was used with Nash reagent and fluorescence spectrophotometry (PerkinElmer LS55; excitation = 410 nm, emission = 510 nm and slit width of 10 nm)^{4,5} for formaldehyde detection. Fluorescence emission intensity was read every second over 2 min at 30 °C and averaged to calculate formaldehyde concentration by comparison to a standard curve.

Formaldehyde emission in wood flour samples was detected using a DFRobot Gravity digital/analog formaldehyde sensor (dfrobot.com) with a resolution of 0.01 ppm and a detection range up to 5 ppm. Operating temperature was 20 ± 2 °C with the sensor placed at the top of a sealable polyethylene box with dimensions of 19.4 cm × 16.5 cm × 11.4 cm. After the box lid was secured, sensor readings of formaldehyde above the wood flour were collected via a microcontroller board (DFRduino Uno V3). Formaldehyde data was collected using Arduino Integrated Development Environment (Arduino IDE) software. The maximum values over the detection period were used for data analysis.

Statistical Analysis

Means and standard deviations for formaldehyde emission were calculated and plotted for three sets of replicate samples in each experiment. A two-way analysis of variance (ANOVA) was conducted to determine how MC, iron content and their combination affected formaldehyde emission from wood flour. Independent t-tests were performed to assess statistical differences between the means of different iron types. The significance of ferric content in Experiment II, and iron reductant agent in Experiment III were tested by one-way ANOVA. Standard deviations were calculated for the studies with added iron reductant and H₂O₂ in Experiment IV, and lignin in Experiment V. All analyses were carried out using SPSS statistics at an $\alpha = 0.05$ significance level.

Results and Discussion

Effect of a ferric iron reductant with iron in wood shavings

Fig. 1 shows the total formaldehyde release from wood shavings after 24 h, a) with iron and 2,3 DHBA, and b) with iron and 2, 3

DHBA and H_2O_2 . The addition of ferric iron (Fe^{3+}) to wood shavings enhanced the generation of formaldehyde with concentrations of 5 mM and 10 mM ferric iron stimulating formaldehyde generation from the wood shavings (Fig. 1). The highest iron level used in the experiment promoted generation of more than double the amount of formaldehyde compared to that of control wood (Fig. 1a). The use of DHBA as an iron reductant was effective in enhancing formaldehyde release only when the DHBA to iron ratio was greater than 1:3. It is known that

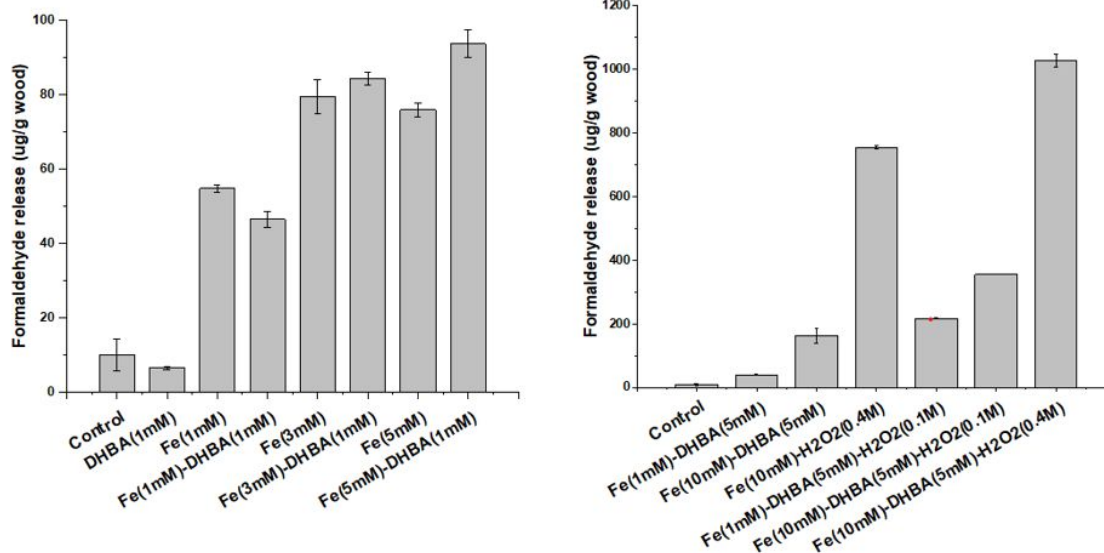


Figure 1a (left): Total formaldehyde release from wood shavings after 24 h, with iron and 2,3 DHBA added. 1b (right): Total formaldehyde release from wood shavings after 24 h, with iron and 2,3 DHBA and H_2O_2 added. Control samples were wood shavings without iron or 2,3 DHBA. All analyses were conducted in pH 4.0 acetate buffer.

catecholate chelators will promote iron reduction at low (1:1) concentrations relative to the amount of iron present, but at higher proportional concentrations of catecholates, hexadentate coordination of iron occurs which effectively prevents iron reduction²⁸⁻³⁰. Iron reduction was limited when DHBA was at relatively high concentration compared to iron, but reduction was promoted when iron levels were higher. Under the later conditions, DHBA plus free lignin moieties would also have been free to participate in redox cycling for the generation of H_2O_2 needed in Fenton reactions. When H_2O_2 was added, formaldehyde generation from wood shavings more than doubled. This suggests that when iron levels are increased in wood, greater formaldehyde generation can occur. Also, conditions that favor redox cycling of phenolic residues in wood in the presence of iron will promote additional formaldehyde release. This is because of the known relationship with redox cycling of phenolic compounds and H_2O_2 generation as reviewed in the Introduction.

Effect of moisture content

Formaldehyde was also generated in the presence of added Fe^{2+} for the wood flour samples at two different MCs (Fig. 2). For samples tested at an average 30.5% MC (Fig. 2), formaldehyde emission increased as ferrous iron (Fe^{2+}) content increased from 10 - 100 ppm. However, a comparison of wood flour at 30.5%

and 50.5% MC, treated with iron, showed that high MC greatly reduced the amount of formaldehyde that could be detected (Fig. 2) and that the MC significantly affected formaldehyde detection ($p < 0.001$, Table 2). In all samples at 50.5% MC, the amount of formaldehyde release was comparable to that of the controls. This is likely to have occurred because the excess free water in the wood flour absorbed much of the formaldehyde released as discussed in the Methods of this paper. Any water in wood flour above 30% MC would be considered to be “free water” in the

void spaces of wood cells³¹. This is water that is not hydrogen bonded to the wood cell wall and it would have the potential to react with formaldehyde²⁷, preventing it from being detected by the sensor in the head space of the collection chamber.

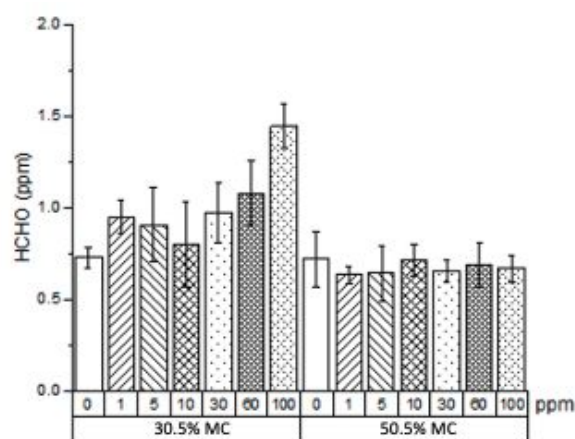


Figure 2: Formaldehyde emission from white pine flour samples with added Fe^{2+} and at two different moisture contents.

Effect of iron oxidation with and without an iron reductant

Formaldehyde release from Fe^{2+} treated wood flour samples was significantly greater than that from the Fe^{3+} treated samples (Fig.

3). When only iron was added to the wood flour, there was no significant difference in formaldehyde emission ($p = 0.713$) between the Fe^{2+} and Fe^{3+} treated wood flour samples, even with increased levels of Fe^{3+} added (Fig. 3). These results for Fe^{3+} in wood flour differ from those with the wood shavings and this is possibly due to the way the iron was added, or perhaps because of the reduced levels of iron that were used in the wood flour experiments compared to the wood shavings experiments. It was apparent, however, that an added iron reductant with ferric iron impacted these results (Fig. 4).

Table 2: Two-way Analysis of Variance (ANOVA) for formaldehyde emission from wood flour samples based on the moisture content and Fe^{2+} content.

Source of variance	Degrees of freedom	Mean Square	P value
Moisture content	1	1.193	< 0.001
Fe^{2+} content	6	0.035	0.438
Moisture content \times iron content	6	0.039	0.367

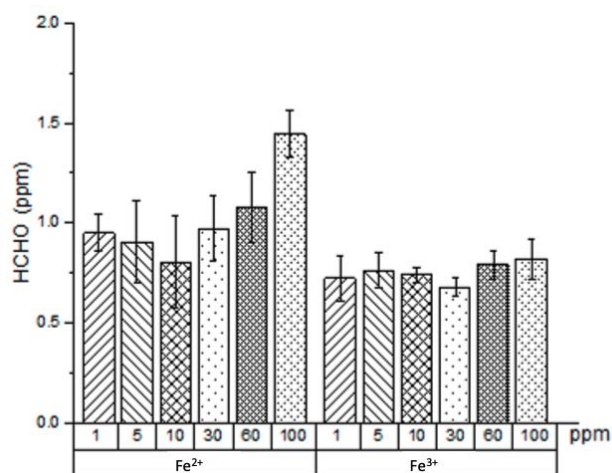


Figure 3: Formaldehyde emission in the presence of added Fe^{2+} and Fe^{3+} at 30.5% MC. A t -test showed the average formaldehyde emission from the Fe^{2+} treated samples was significantly greater than that from the Fe^{3+} treated samples when no added iron reductant, such as 2, 3 DHBA or added lignin, was present ($\alpha = 0.025$).

When an iron reductant only (2, 3 DHBA, 1.2 mM) was added to wood flour, formaldehyde emission was not significantly different compared to that of the control wood flour samples (Fig. 4). This was probably due to the order which the reagents were added to the wood flour. With the iron added first, ferric iron would have readily bound to the cellulose in wood, which may have prevented the reduction of bound iron by 2, 3 DHBA that was added later in the mixing process.

In the presence of 2, 3 DHBA and H_2O_2 , as Fe^{3+} levels increased, formaldehyde emission also generally increased (Fig. 4). This suggests that the peroxide reacted with free ferrous iron in solution (Fenton reaction) generating hydroxyl radicals, which were then able to attack lignocellulose resulting in formaldehyde generation.

Effect of lignin

It has previously been documented that lignin is the component in wood that releases most formaldehyde, with very little formaldehyde released from cellulose, starch or sugars^{20, 21}. This is further supported by practical observations indicating that pure cellulose products such as cotton and cellulose insulation do not release formaldehyde at levels of concern. Formaldehyde could potentially be released from some forms of extractives, but in the current research sapwood-only was used, and knots, defects or areas that had visible resin streaks were eliminated. Thus, we focused on lignin, and wood-containing lignin, in this research. The lignin content of softwoods varies between 25% and 35% depending on species³². Adding lignin further promoted the emission of formaldehyde in the presence of buffered Fe^{3+} , 2, 3 DHBA, and H_2O_2 (Fig. 5).

When lignin was added at a level of 10 % of the total sample mass, formaldehyde emission exceeded the maximum detection limit of the formaldehyde sensor (5 ppm). This data suggests that modification, or degradation, of lignin by hydroxyl radicals in the presence of iron promotes the generation of formaldehyde from wood.

When exogenous iron is present on wood surfaces and iron-reducing extractives or lignin fragments are also present, iron reduction will occur, leading to a type of mediated Fenton chemistry similar to that of CMF chemistry. Prior research has demonstrated that lignin fragments will function as “reducing chelators” for iron in a non-fungal CMF reaction¹³, and we now propose that this occurs in wood as a “lignin-mediated Fenton” (LMF) reaction. Prior research has demonstrated that hydroxyl radicals would be generated in this process, and that the multiple iron reduction previously observed¹⁰ would promote the generation of hydroxyl radicals and other ROS within the wood cell wall. As discussed in the Introduction, during phenomenon such as brown rot wood degradation, hydroxyl radicals are known to attack lignin, and in that process lignin is demethylated. Other processes, such as LMF chemistry, would also promote surface lignin demethylation. Formaldehyde generation from methanol after being attacked by $\cdot OH$, is also well known²⁵⁻²⁷, and we propose that the methanol stripped from lignin during LMF demethylation processes would, under appropriate conditions, generate formaldehyde from wood surfaces and interior regions where iron was present.

It is likely that the levels of formaldehyde released from wood flour, in some cases would be below the detection limits of our instrumentation when low levels of iron were present. Furthermore, any level of water in wood would trap formaldehyde to some degree, limiting its detection. In our

experiments, all samples were tested at MC levels that would exceed normal interior levels in residential/commercial structures. We therefore propose that when wood is exposed to iron during normal processing, fabrication, and use, that formaldehyde can be released via the LMF mechanism as summarized in Fig. 6. Phenolic fragments, including those derived from lignin, are known to produce hydrogen peroxide via redox cycling^{15, 17, 18, 19}, and this redox cycling would be promoted by the natural low pH of wood (approx. 5.5 pH). When conditions permit, hydroxyl radicals would be generated via LMF chemistry. These hydroxyl radicals would perpetuate the reaction by attacking additional methoxy groups on lignin, with methanol being produced in the process. Methanol would then be further attacked by hydroxyl radicals to produce formaldehyde (Fig. 6), as reviewed above.

Based on our findings we propose that low levels of iron, particularly in the reduced ferrous oxidation state, promote the generation of formaldehyde from lignin. Natural iron reductants, including lignin surfaces and potentially phenolic extractives in wood, catalyze both iron reduction and the generation of low levels of hydrogen peroxide, which participates in a mediated Fenton reaction. In our research, high moisture levels in wood affected formaldehyde detection. When the moisture content was above the fiber saturation point, formaldehyde was absorbed by free water in the wood preventing its detection. In lower moisture content wood, our results showed that formaldehyde was released from lignin when hydroxyl radicals attacked methoxyl groups to generate formaldehyde via what we have termed a "lignin mediated Fenton" (LMF) reaction.

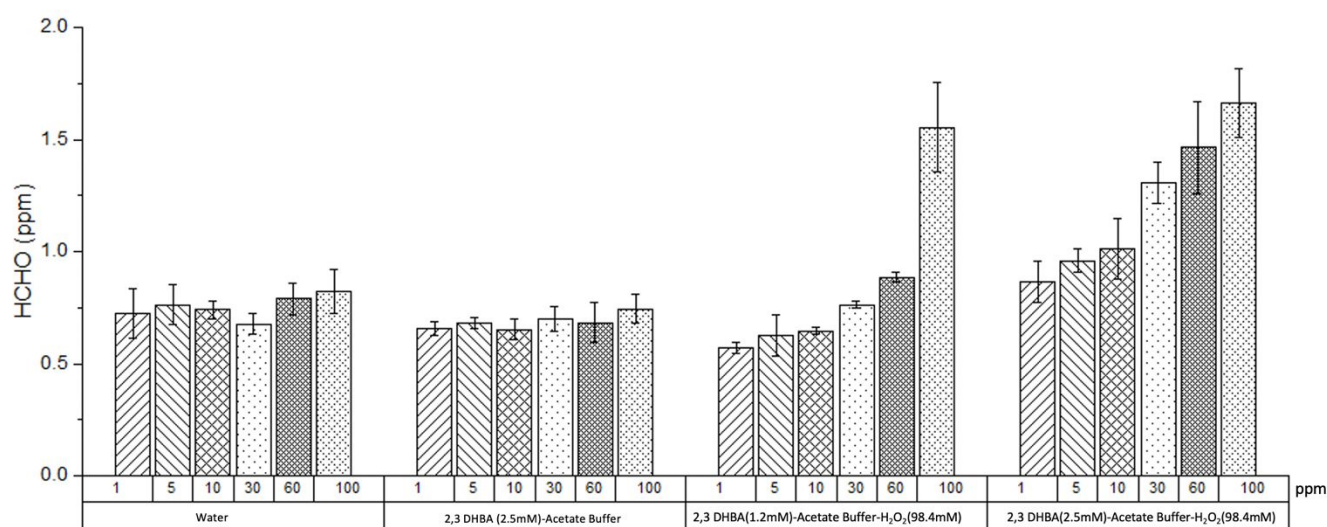


Figure 4: Formaldehyde emission in the presence of added Fe^{3+} , with and without 2, 3 DHBA and hydrogen peroxide at 30.5% MC.

Conclusions

Under the conditions used in these experiments, abundant hydroxyl radicals were generated. Considerable research using Electron Paramagnetic Resonance and other instrumentation for radical detection has previously verified that when iron and reducing catecholates are added to wood, radicals are generated within the wood via a type of chelator-mediated Fenton chemistry^{11, 33-36}. The cleavage of methoxyl groups from lignin by hydroxyl radicals is also well established in the literature^{22, 37-39}. Further, well documented literature going back 40 years demonstrates the ready conversion of methyl and methoxyl groups to formaldehyde during attack by hydroxyl radicals^{25, 26, 40}. The methoxyl group in softwood lignin is a likely source of formaldehyde as it represents approximately 17% of the molecular mass of the lignin and it is readily converted to formaldehyde by hydroxyl radical attack (Fig 6).

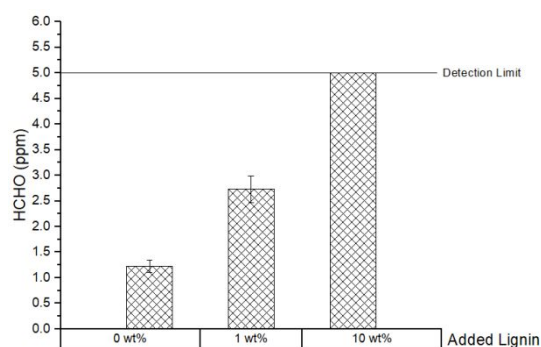


Figure 5: Formaldehyde emission in the presence of 100 ppm Fe^{3+} , 2, 3 DHBA, H_2O_2 , acetate buffer, and lignin at 30.5% MC. Increasing amounts of lignin promoted the generation of formaldehyde in the presence of iron when reaction conditions were appropriate to promote iron-reduction.

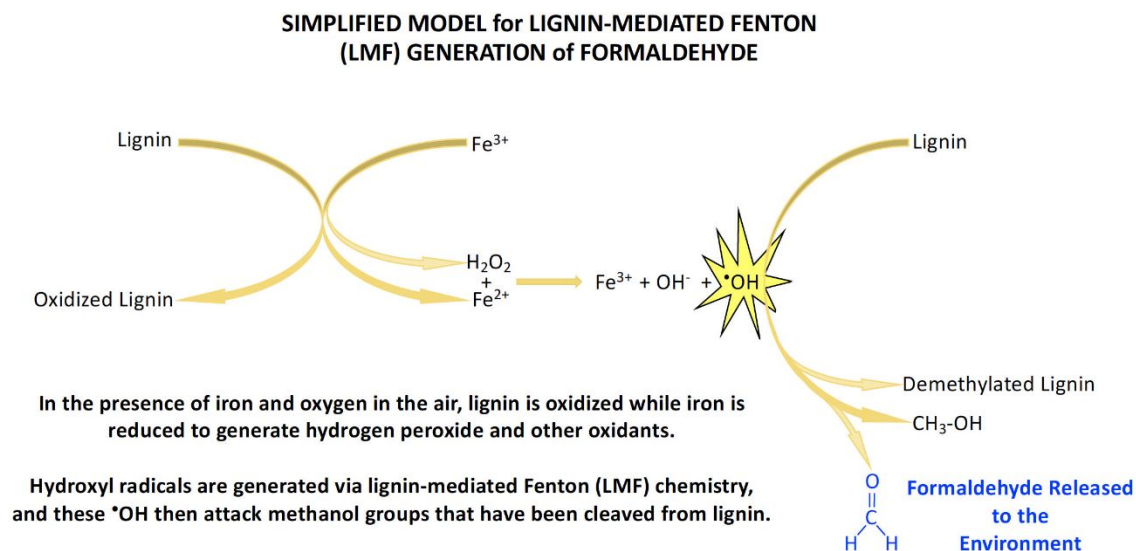


Figure 6: Proposed mechanism for the generation of formaldehyde from lignin in wood in the presence of iron and promoted by a “lignin-mediated Fenton (LMF)” reaction.

Lignin content in wood promotes the generation of formaldehyde, particularly when the conditions which promote Fenton chemistry, such as low pH, were active. Increasing iron content promoted formaldehyde emission, and the addition of an exogenous iron reductant further promoted formaldehyde release. However, iron reduction occurred only when reaction conditions and the ratio of catecholate iron reductant to ferric iron did not inhibit iron reduction. Addition of 1% and 10% mass/mass lignin to wood samples further contributed to an increase in formaldehyde emission. These results confirm that the mechanism of formaldehyde emission from wood was promoted by lignin in the presence of iron residues.

Our results suggest a newly proposed mechanism for the generation of formaldehyde from lignin in the presence of iron, which has not previously been explored. Our hypothesis based on these results is that a LMF mechanism for formaldehyde emission from wood may contribute as a primary factor in the low-level generation of formaldehyde from wood. Iron is an important factor, and iron contamination in wood product production may promote higher levels of formaldehyde emission from wood, particularly when lignin content is high, or potentially when other naturally occurring iron-reducing phenolics, such as some extractives, are at increased levels in wood.

Author Contributions

B.G. conceptualized the research. Y.F. and Y.Z. carried out the major experiments with wood flour and the sensor method and drafted the manuscript under the supervision of both S.S. and B.G. Y.Z. and Y.Z. performed the experiments with wood shavings and desiccator method. All authors provided critical feedback for the research, analysis, and manuscript writing.

Conflicts of interest

There are no conflicts to declare

References

1. C. A. R. Board, *Report to the California Legislature: Indoor Air Pollution in California*, California Environmental Protection Agency San Francisco, RPT0705.PDF, 2005.
2. M. Risholm-Sundman, A. Larsen, E. Vestin and A. Weibull, *Atmospheric Environment*, 2007, **41**, 3193-3202.
3. P.-R. Chung, C.-T. Tzeng, M.-T. Ke and C.-Y. Lee, *Sensors*, 2013, **13**, 4468-4484.
4. T. Nash, *Biochemical Journal*, 1953, **55**, 416-421.
5. R. Rapoport, I. Hanukoglu and D. Sklan, *Analytical Biochemistry*, 1994, **218**, 309-313.
6. C. M. Hussain and R. Keçili, *Modern Environmental Analysis Techniques for Pollutants*, Elsevier, 1st edn., 2019.
7. J. Jellison, J. Connolly, K. Smith and W. Shortle, *International Research Group on Wood Preservation (Sweden)*, 1993.
8. B. Halliwell and J. M. Gutteridge, *Free Radicals in Biology and Medicine. Fifth Edition*, Oxford University Press, Oxford, UK, 2015.
9. E. Ahmed and S. J. Holmström, *Microb Biotechnol*, 2014, **7**, 196-208.
10. B. Goodell, in *The Mycota: Genetics and Biotechnology II*, eds. J. P. Benz and K. Schipper, Springer International Publishing, Cham, 2020, DOI: 10.1007/978-3-030-49924-2_15, pp. 369-397.
11. Y. Tamaru, M. Yoshida, L. D. Eltis and B. Goodell, *International Journal of Biological Macromolecules*, 2019, **128**, 340-346.
12. Y. Zhu, N. Plaza, Y. Kojima, M. Yoshida, J. Zhang, J. Jellison, S. V. Pingali, H. O'Neill and B. Goodell, *Frontiers in Microbiology*, 2020, **11**, 1389.
13. D. Veličković, M. Zhou, J. S. Schilling and J. Zhang, *Journal of Fungi*, 2021, **7**, 609.

14. E. Miglbauer, M. Gryszel and E. D. Głowacki, *Green Chemistry*, 2020, **22**, 673-677.
15. M. Akagawa, T. Shigemitsu and K. Suyama, *Bioscience, Biotechnology, and Biochemistry*, 2003, **67**, 2632-2640.
16. J. C. Danilewicz, *Journal of Agricultural and Food Chemistry*, 2014, **62**, 5149-5155.
17. J. C. Danilewicz, *American Journal of Enology and Viticulture*, 2016, **67**, 13-17.
18. L. H. Long, A. Hoi and B. Halliwell, *Archives of Biochemistry and Biophysics*, 2010, **501**, 162-169.
19. C. M. Oliveira, A. C. S. Ferreira, V. De Freitas and A. M. Silva, *Food Research International*, 2011, **44**, 1115-1126.
20. M. Schäfer and E. Roffael, *European Journal of Wood and Wood Products*, 2000, **58**, 259-264.
21. G. Wan and C. E. Frazier, *ACS Sustainable Chemistry & Engineering*, 2017, **5**, 4830-4836.
22. D. J. Yelle, D. Wei, J. Ralph and K. E. Hammel, *Environmental Microbiology*, 2011, **13**, 1091-1100.
23. T. Filley, G. Cody, B. Goodell, J. Jellison, C. Noser and A. Ostrofsky, *Organic Geochemistry*, 2002, **33**, 111-124.
24. E. J. Hart, J. K. Thomas and S. Gordon, 1964.
25. A. I. Cederbaum and A. Qureshi, *Biochemical pharmacology*, 1982, **31**, 329-335.
26. K. Mopper and X. Zhou, *Science*, 1990, **250**, 661-664.
27. J. G. M. Winkelman, H. Sijbring, A. A. C. M. Beenackers and E. T. de Vries, *Chemical Engineering Science*, 1992, **47**, 3785-3792.
28. G. Xu and B. Goodell, *Journal of Biotechnology*, 2001, **87**, 43-57.
29. Y. Qian, B. Goodell and C. C. Felix, *Chemosphere*, 2002, **48**, 21-28.
30. P. Salgado, V. Melin, Y. Durán, H. c. Mansilla and D. Contreras, *Environmental Science & Technology*, 2017, **51**, 3687-3693.
31. C. Skaar, *Wood-water relations*, Springer Science & Business Media, 2012.
32. R. M. Rowell, *Handbook of Wood Chemistry and Wood Composites*, CRC Press, Boca Raton, FL, 1st edn., 2005.
33. D. Contreras, J. Rodríguez, L. Basaez, J. Freer, R. Valenzuela, H. Mansilla and P. Vanýsek, *Water Sci Technol*, 2011, **64**, 2103-2108.
34. B. Goodell, Y. Zhu, S. Kim, K. Kafle, D. Eastwood, G. Daniel, J. Jellison, M. Yoshida, L. Groom, S. V. Pingali and H. O'Neill, *Biotechnol Biofuels*, 2017, **10**, 179.
35. J. Liu, Y. Zhu, C. Wang, B. Goodell and A. R. Esker, *Int J Biol Macromol*, 2020, **153**, 433-440.
36. Y. Qian, B. Goodell, J. Jellison and C. C. Felix, *Journal of Polymers and the Environment*, 2004, **12**, 147-155.
37. L. Hildén, G. Johansson, G. Pettersson, J. Li, P. Ljungquist and G. Henriksson, *FEBS Lett*, 2000, **477**, 79-83.
38. M. S. Kent, I. C. Avina, N. Rader, M. L. Busse, A. George, N. Sathitsuksanoh, E. Baidoo, J. Timlin, N. H. Giron, M. C. Celina, L. E. Martin, R. Polsky, V. H. Chavez, D. L. Huber, J. D. Keasling, S. Singh, B. A. Simmons and K. L. Sale, *Green Chemistry*, 2015, **17**, 4830-4845.
39. K. Wu, W. Ying, Z. Shi, H. Yang, Z. Zheng, J. Zhang and J. Yang, *ACS Sustainable Chemistry & Engineering*, 2018, **6**, 3853-3861.
40. A. Monod, A. Chebbi, R. Durand-Jolibois and P. Carlier, *Atmospheric Environment*, 2000, **34**, 5283-5294.