

FORMALDEHYDE IN WOOD: WHERE DOES IT COME FROM?

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Abstract:

The research described here attempts to better understand the origin of the formaldehyde emitted by *Pinus radiata*. Previous research suggests that wood generates formaldehyde as a by-product from some degrading chemistry. It is suggested that at least some of the formaldehyde that is released from wood has been previously adsorbed by the wood. This paper compares the formaldehyde emission from natural and acetylated *Pinus radiata*; the latter having a lower equilibrium moisture content. The results indicate that acetylated wood emits less formaldehyde than untreated wood in tests where the specimens approach the oven-dry condition by the end of the test. It is also observed that the quantity of formaldehyde emitted when a test is repeated on a specimen is lower than the initial emission. It is proposed that these observations can be explained if it is accepted that part of the formaldehyde emission from wood is derived by the prior adsorption of formaldehyde by wood. It is estimated that at least 50% of the formaldehyde observed is due to prior adsorption.

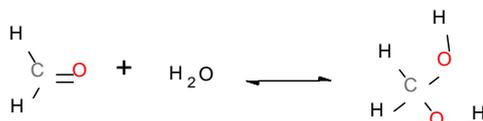
INTRODUCTION

In June of 2004, the International Agency for Research into Cancer (IARC), which is part of WHO (World Health Organization), raised the cancer rating of formaldehyde from category 2A (probably carcinogenic to humans) to Category 1B (carcinogenic to humans based on animal data). This decision was confirmed in 2009. As a consequence, the European REACH Committee reclassified formaldehyde as a category 1B carcinogen in December 2013.

Various researchers have observed that natural wood releases formaldehyde see, for example, Meyer and Boehme (1997), Schäfer and Roffael (2000) and Weigl *et al.* (2009). In all cases, the levels observed were low, but, detectable. The small amounts of formaldehyde emitted do not pose any health risk. Even so, the fact that wood is seen to emit formaldehyde may have an impact in its use for interior applications because of the increasingly stringent indoor air quality regulations across the World.

Marutzky and Roffael (1977) proposed various mechanisms by which formaldehyde might be generated by the polymers and extractives present in wood, see Fig. 1. It is argued, however, that formaldehyde, which has been previously adsorbed by the wood, makes up a part of the formaldehyde observed in tests. This seems possible because wood is hygroscopic; it will change its moisture content as a function of its surrounding temperature, humidity and pressure. Wood is also able to adsorb and desorb other polar molecules like formaldehyde. In a very simple experiment Irle *et al.* (2008) demonstrated that wood will readily adsorb formaldehyde from the atmosphere and then desorb it during a formaldehyde emission test.

Formaldehyde is omnipresent. Previous research indicates that the concentration of formaldehyde in buildings is somewhat higher than that outside. Indoor values range from $<30\mu\text{g}/\text{m}^3$ to over $300\mu\text{g}/\text{m}^3$ with a mean of $58.6\mu\text{g}/\text{m}^3$, whereas outside the concentration is typically less than $10\mu\text{g}/\text{m}^3$ (Kraus *et al.* 1991). Wood stored indoors is likely to adsorb and desorb both water and formaldehyde. Could it be possible that formaldehyde accumulates in wood? Certainly, formaldehyde is a very reactive molecule and polar. When formaldehyde is in water it forms methylene glycol (methanediol):



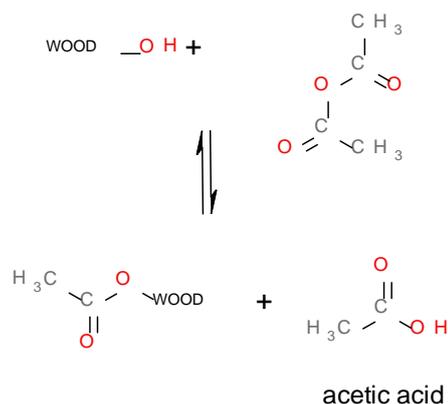
It is suggested that a proportion of formaldehyde in wood is actually in the form of methylene glycol. Some formaldehyde, on the other hand, will form hydrogen bonds with the plethora of hydroxyl groups present in wood and some may even react with the hydroxyls to form hemi-acetals.

Logically, three scenarios could explain the emission of formaldehyde by wood:

1. Wood generates the majority of formaldehyde as a by-product from some degrading chemistry.
2. The majority of the formaldehyde that is released from wood has been previously adsorbed by the wood.
3. Both mechanisms play a role.

Current thinking suggests that scenario 1 is the main mechanism. If true, then this could eventually lead to regulations that limit the quantity of wood in the indoor environment in terms of $x \text{ m}^2/\text{m}^3$ of room. If, on the other hand, most of the formaldehyde comes from an adsorption/desorption mechanism, then wood can be used with impunity. The research described here attempts to better understand the origin of the formaldehyde emitted by wood.

The approach described in this paper is to compare the formaldehyde emission of untreated and acetylated *Pinus radiata*. The acetylated wood will have a lower equilibrium moisture content, i.e. it is less hygroscopic, and so if scenario 2 has any effect, then one would expect the formaldehyde emission from acetylated wood to be lower than the untreated. Acetylation reduces the hygroscopicity of wood via chemical modification of the hydroxyl groups in wood (Rowell 2013):



It is proposed that after acetylation wood will be less able to adsorb formaldehyde and, therefore, emit less during a formaldehyde emission test. Of course, the acetylation process may also change the ability of wood to generate formaldehyde. This paper describes an experiment that compares the emission of formaldehyde from natural and acetylated *Pinus radiata*.

MATERIALS & METHODS

Pinus radiata was supplied by Accsys Group from their manufacturing plant in Arnhem, Holland. All pieces were selected from the same batch in order to minimise any differences between acetylated and untreated wood. All wood was stored in a laboratory without control of atmospheric conditions.

The pieces were numbered by Accsys so that treated and untreated pieces could be matched. The original dimensions were 25x190x800mm (thickness x width x length). Two of pieces of acetylated wood were selected together with their untreated pair. These were crosscut in half and then sawn into 40mm wide pieces thus giving specimens with nominal dimensions of 25x40x395mm.

Formaldehyde emission was measured using EN ISO 12460-3 "Wood-based panels — Determination of formaldehyde release — Part 3: Gas analysis method". The test procedure involves heating the specimens with dry air at 60°C and so, of course, the specimens lose weight during the test. Unlike the standard, the results are expressed in μg formaldehyde /100g of specimen.

After a number of initial tests, it was decided to further reduce the thickness of the specimens by cutting them in half, length ways through the thickness, to give specimens approximately 9x40x395mm. In addition, it was decided to repeat formaldehyde emission tests on some specimens. Consequently, these specimens were crosscut in half to reduce their length so that they could be rehumidified in desiccators. Each pair of halves were tested together to approximate the previous specimen size. Rehumidification was achieved by placing 200mL of deionised water in an evaporation dish in the desiccator. The specimens were reconditioned for approximately 48 hours before retesting. The formaldehyde content of the deionised water was also measured after the conditioning period.

RESULTS

The results in Table 1 present the formaldehyde emission values in terms of $\mu\text{g}/100\text{g}$ of conditioned wood (not oven dry). No statistically significant difference was observed between emission rates of untreated and acetylated for the 24mm thick specimens. This is probably because specimens do not dry out completely during the test. The average moisture contents of acetylated wood was 3.0%, whereas untreated had an average of 10.4%. At the end of the tests their respective moisture contents were 1.8% and 7.8%. Reducing the thickness to a nominal 9mm revealed a significant difference, at a 99% confidence, in emission rates between untreated and acetylated wood. Tasooji *et al.* (2017), using a completely different test method, found similar emission levels for heated *P. radiata*.

Table 1

The formaldehyde emissions observed from P. radiata

Thickness (mm)	UNTREATED			ACETYLATED		
	No.	Mean (µg/100g)	Standard deviation	No.	Mean (µg/100g)	Standard deviation
24	3	33	5.6	3	33	7.6
9	11	54	11.4	10	41	7.8

These results are probably linked to the moisture content changes during the test. The thinner have a greater surface area to volume and so they increase in temperature more rapidly and dry out more quickly. The average end moisture contents at the end of the tests were 5.1% for untreated and 0.7% for acetylated specimens.

It is well known that formaldehyde emissions are positively correlated to moisture content. For example, formaldehyde test methods like EN ISO 12460-5 contain a correction factor to normalise the observed formaldehyde concentrations to a moisture content of 6.5% and that specimens should have moisture content of between 3 and 10%

It is interesting to note that none of the chemical reactions proposed by Marutzky and Roffael (1977) nor Schäfer and Roffael (2000) include water as a reactant, rather they propose that water could be produced as part of the polymer breakdown reactions, see Fig. 1. One mechanism proposed involves the dehydration of hexoses to form oxymethylfurfurals which then degrade to furfural and formaldehyde. It would seem that the generation of formaldehyde by hemicelluloses would be favoured by drying conditions and so one would expect more formaldehyde to be generated at higher than ambient temperatures. In fact, the reverse is seen in the EN ISO 12460-3 where emission rate falls as the test progresses, i.e. as the specimens dry. Likewise none of the lignin degradation routes proposed require water as a reactant, an example is shown in Fig. 1. Therefore, purely from a chemical reaction point of view, the presence of water or not should not have an impact on the production of formaldehyde by wood. Therefore, one could conclude that the breakdown reactions should be independent of moisture content. The fact that formaldehyde emission falls, implies that the emission of formaldehyde by a chemical reaction is less important.

Given that Irle *et al.* (2008) demonstrated that wood can adsorb formaldehyde then the total formaldehyde emission from a wood object should consist of that which has been previously adsorbed and then desorbed during the test (E_{des}) and that which might be generated by breakdown of wood polymers (E_{chem}), see Eq. 1. What is not known at this stage is the relative proportions of E_{des} and E_{chem} .

$$E_{total} = E_{des} + E_{chem} \quad (\text{Eq. 1})$$

Clearly the chemical properties of acetylated wood are different to untreated wood and so one would expect E_{chem} of acetylated wood to be different to untreated. From data presented by Rowell (2014) it is known that little of the cellulose present will have reacted with the acetic anhydride. It is estimated that about 80% of OH groups in the lignin and 30% of OH in hemicelluloses would have been modified by acetic anhydride at the weight percent gain (WPG) used in commercial products. This could have an impact on wood's ability to generate formaldehyde and this may also explain the differences in emission levels observed between untreated and acetylated wood.

The EMC values of acetylated and untreated are quite different and so E_{des} are also expected to be different. The values of E_{des} and E_{chem} for both cases cannot be resolved with the information thus far collected.

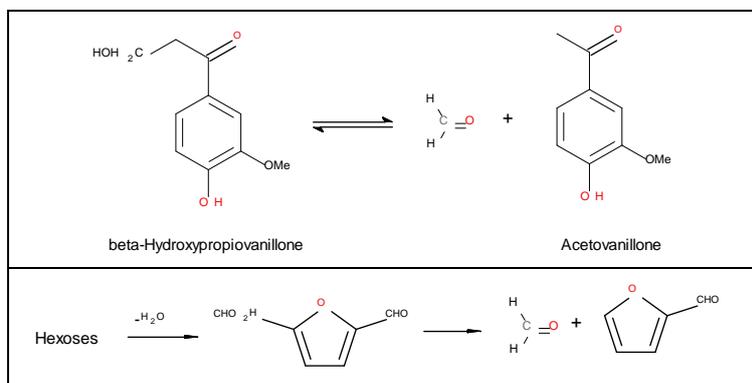


Fig. 1.

Two examples of the possible reaction mechanisms that could generate formaldehyde in wood as proposed by Marutzky and Roffael (1977) and Schäfer and Roffael (2000).

Table 2 shows the formaldehyde relative to the mass loss observed during the test. It would seem that the amount of formaldehyde emitted per gram of mass loss is higher for the acetylated wood. This is somewhat unexpected as one might expect the concentration of formaldehyde to be the same due to vapour pressure laws. The mass loss is largely due to moisture loss, but, other volatiles associated with the extractives present and certainly acetic acid in the acetylated wood also contribute to the loss.

Table 2

The formaldehyde emission relative to the mass loss of the specimens during the tests

Thickness (mm)	UNTREATED			ACETYLATED		
	No.	Mean ($\mu\text{g/g loss}$)	Standard deviation	No.	Mean ($\mu\text{g/g loss}$)	Standard deviation
24	3	11	1.4	3	23	2.5
9	11	11	2.2	10	17	3.2

An alternative approach to determine the relative importance of E_{des} and E_{chem} was tried. This involved repeat testing of particular samples. Once a specimen had completed a test it was sealed in a desiccator with deionised water as described in the methods. The idea is that the specimens would rehumidify but not have the opportunity to adsorb formaldehyde from the atmosphere. Any differences in subsequent emission tests should be more closely linked to changes in E_{des} rather than E_{chem} . The data in Table 3 show the emission levels fall with each repetition of the test. The 9R0 specimens are equivalent to the 9mm thick specimens shown in Table 1. The higher emission rates of these specimens is thought to be due to the fact that the specimens had been crosscut in half thus doubling to amount of transverse face, which is likely to aid drying and escape of volatiles like formaldehyde. To date only two repetitions have been conducted to date and so the difference may be due to chance. Each repetition of the test brings about reduced emission levels. For untreated wood the trend is linear and for the acetylated asymptotic.

Table 3

Formaldehyde emission levels observed after repeat measurements on the same samples

Thickness (mm)	UNTREATED			ACETYLATED		
	No.	Mean ($\mu\text{g}/100\text{g}$)	Standard deviation	No.	Mean ($\mu\text{g}/100\text{g}$)	Standard deviation
9R0	2	68	10.3	2	50	9.2
9R1	2	64	7.5	2	36	4.1
9R2	2	50	7.2	2	24	10.5
9R3	2	46	5.9	1	28	

Table 4 shows how the formaldehyde emission relative to the observed mass loss, changed with each repetition of test. It is clear that for both the acetylated and untreated wood that the formaldehyde emission decreases with each repetition of the test. The reconditioning step caused slightly higher moisture contents at the start of the repeat tests; this should increase the formaldehyde emission and so the reductions observed are even more remarkable. It may be coincidence, but, it seems that $\mu\text{g/g loss}$ stabilises at around $7\mu\text{g/g loss}$. The chemistry of the specimens is not thought to change a great deal between repetitions of the cycle. If so, then it the $7\mu\text{g/g loss}$ might be due to chemical reactions (E_{chem}) like that proposed by Marutsky and Roffael (1977), and therefore the values from the initial tests would indicate that E_{des} would be equal to about $6\mu\text{g/g loss}$ for the untreated wood and $13\mu\text{g/g loss}$ for the acetylated, i.e. E_{des} equates to between a little over 50% to 60% for the untreated and acetylated respectively.

Table 4

The quantity of formaldehyde emitted relative to the mass loss observed after repeat measurements on the same samples

Thickness (mm)	Final HCHO conc. in water	UNTREATED					ACETYLATED				
		No.	MC start	MC end	Mean ($\mu\text{g/g loss}$)	Standard deviation	No.	MC start	MC end	Mean ($\mu\text{g/g loss}$)	Standard deviation
9R0		2	10.1%	4.9%	13	1.9	2	3.0%	0.4%	20	3.6
9R1	59	2	12.8%	4.4%	10	1.3	2	4.0%	0.5%	11	1.5
9R2	52	2	13.3%	4.5%	7	1.5	2	4.2%	0.5%	7	3.2
9R3	45	2	12.7%	4.3%	7	0.9	2	4.2%	0.5%	8	

The quantity of formaldehyde found in the deionised water at the end of each conditioning period also fell with each repeat test, see first column of Table 4. Given the mass of wood present, it is suggested that this fall is not due to significant changes in the chemistry of the wood. Rather the reduction derives from a sort of "washing" out of free formaldehyde from the wood. It is thought that formaldehyde does not readily

diffuse out of wood once it is dry. Therefore, formaldehyde remaining at the end of an emission test is likely to remain in the wood and, hence, the low emissions observed in the final hours of the test. As the moisture content of the specimens increases the formaldehyde is more able to diffuse. Following concentration laws, some of the formaldehyde will diffuse out of the wood and into the deionised water. If wood does not generate formaldehyde so that all the formaldehyde observed has been previously adsorbed, then given enough cycles, the formaldehyde emission rate should fall to zero. What is needed, therefore, are more repetitions in two senses: one terms of the number of specimens tested and the other in terms of number of cycles a specimen is tested.

CONCLUSIONS

The results clearly show that acetylated wood emits less formaldehyde than untreated wood in tests where the specimens approach the oven-dry condition by the end of the test. It is also observed that the quantity of formaldehyde emitted when a test is repeated on a specimen is lower than the initial emission. It is proposed that these observations can be explained if it is accepted that part of the formaldehyde emission from wood is derived by the prior adsorption of formaldehyde by wood. It is estimated that at least 50% of the formaldehyde observed is due to prior adsorption. Additional tests are required to confirm this observation. Ongoing work will increase the number of repetitive tests and also observe formaldehyde emissions after specimens have been reconditioned in the laboratory for some months.

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