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On the formaldehyde release of wood

M. Schäfer, E. Roffael

The paper addresses the role of the main components of wood cellulose, hemicellulose, and lignin as well as of wood extractives as a potential source of formaldehyde. Lignin seems to have a higher emission potential than cellulose and hemicellulose. Moreover, the results reveal that on the one hand extractives release formaldehyde and on the other hand that certain wood extractives react with formaldehyde and hence act as a formaldehyde scavenger. Formaldehyde emanates from wood at temperatures as low as 40 °C. Higher temperatures increase the formaldehyde emission tremendously. Therefore, thermo-mechanical pulping enhances formaldehyde release exorbitantely. Differences in the formaldehyde emission between wood species are discussed and related to differences in their chemical composition.

Formaldehydfreisetzung aus Holz

Die Hauptbestandteile von Holz, Cellulose, Hemicellulose und Lignin, sowie Extraktstoffe des Holzes wurden hinsichtlich ihres möglichen Beitrags zur Formaldehydabgabe untersucht. Lignin scheint ein höheres Formaldehydabgabepotential aufzuweisen als Cellulose oder Hemicellulose. Die Ergebnisse zeigen, dass bestimmte Holzextraktstoffe zum einen zur Formaldehydbildung beitragen können und zum anderen als Formaldehydfänger fungieren. Aus den untersuchten Hölzern wurde Formaldehyd bereits bei Temperaturen von 40 °C freigesetzt. Höhere Temperaturen lassen die Formaldehydbildung stark ansteigen. Dementsprechend erhöht der thermo-mechanische Holzaufschluß die Formaldehydabgabe der hergestellten Fasern in großem Ausmaß. Unterschiede in der Formaldehydabgabe verschiedener Holzarten werden aufgezeigt und in Beziehung zu der chemischen Zusammensetzung gebracht.

1 Introduction

In Europe, more than 90% of particle- and fibreboards are bonded with urea formaldehyde resins (UF-resins). In the last three decades, the issue of formaldehyde release from wood-based panels bonded with amino plastic resins was a subject of intensive research work. The research work carried out focused on three main subjects: How to measure the formaldehyde release, what are the factors affecting the formaldehyde release and how to reduce the formaldehyde release. The question, to what extent the formaldehyde release of wood-based panels can be lowered, triggered research work on the formaldehyde emission from wood itself and its change during technological processes like drying and pressing (Marutzky and Roffael 1977). However, no systematic research work has been published addressing the contribution of different wood components like cellulose, hemicellulose, lignin, and extractives to the formaldehyde emission of wood. Therefore, the objective of this research work was to study formaldehyde release from main cell wall components as well as from wood extractives. Moreover, the influence of hydrothermal treatments on the emission of formaldehyde from different wood components is assessed using model compounds and different wood species.

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2 Methods

The formaldehyde emission was determined using the flask method (EN 717–3). For this purpose, wood particles and fibres etc. were subjected to thermal treatment at temperatures of 40 °C, 100 °C, and 150 °C for 3 h. For measurement of formaldehyde release, the wood particles were dried under mild conditions (20–40 °C) and fractionated to the size of ≥0.5 < 1 mm. TMP fibres from spruce were produced in pilot plant scale at temperatures of 140 °C and 160 °C for 5 min. The fibres were dried at 70 °C. To study the influence of extractives, spruce and pine wood were extracted with cyclohexane/ethanol (V:V = 2:1) for 6 h.

3 Results and discussion

3.1 Formaldehyde release from wood components under thermal treatment

The main cell wall components in wood are cellulose, hemicelluloses, and lignin. The amount of cellulose is nearly the same in all woods, while the amount and chemical composition of hemicelluloses and lignin can differ in various wood species. Softwoods have a higher lignin content (about 30%) and a lower content of hemicelluloses (about 25%), in hardwoods the hemicellulose content is higher (30–35%) and the lignin content is lower (about 20%). Hard and softwoods also contain various amounts of extractives. The term extractives covers a wide range of organic and inorganic compounds like lower and higher saturated and unsaturated fatty acids, waxes, resin acids, phenolics like tannins. Inorganic substances like potassium, calcium, and magnesium salts in woods from temperate zones and silica compounds in tropical woods

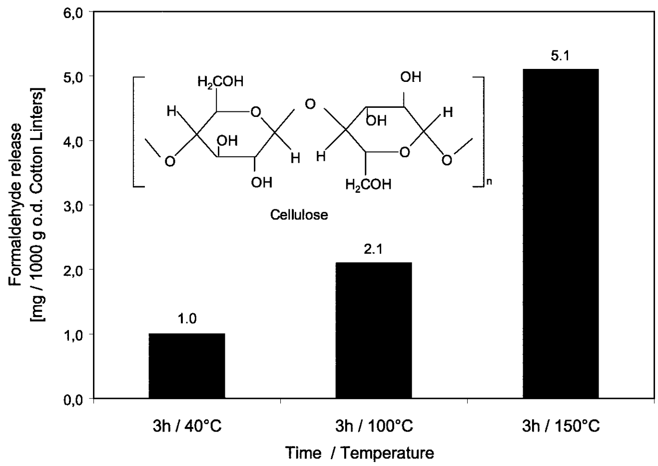

Fig. 1. Formaldehyde release from cotton linters measured by the Flask Method [mg/1000 g cotton linters]
Bild 1. Formaldehydabgabe von Baumwoll-Linters, ermittelt nach der Flaschenmethode [mg/1000 g Baumwoll-Linters]

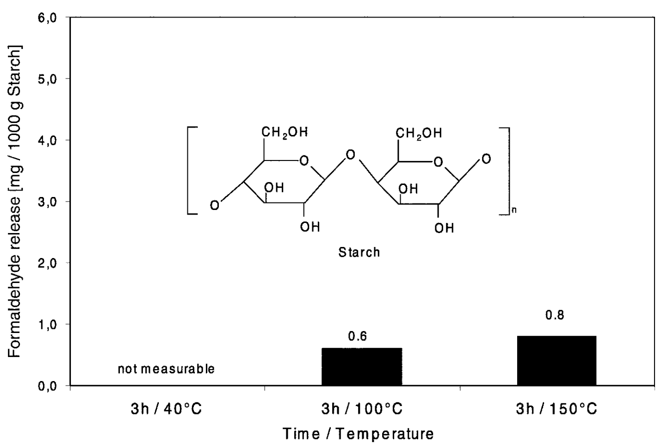

Fig. 2. Formaldehyde release from starch measured by the Flask Method [mg/1000 g starch]
Bild 2. Formaldehydabgabe von Stärke, ermittelt nach der Flaschenmethode [mg/1000 g Stärke]

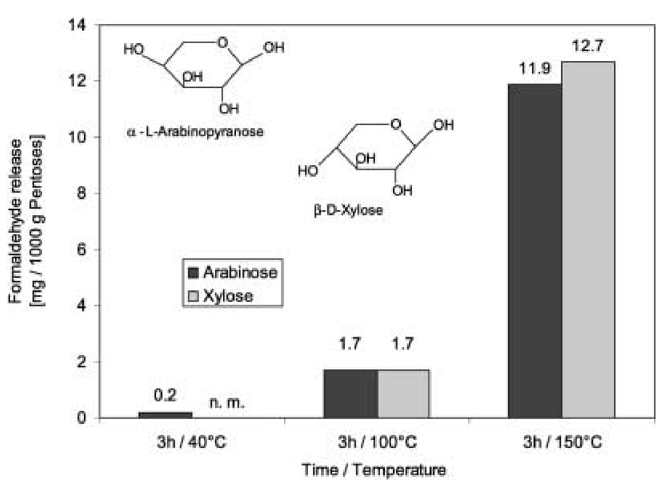

Fig. 3. Formaldehyde release from arabinose and xylose measured by the Flask Method [mg/1000 g pentoses]
Bild 3. Formaldehydabgabe von Arabinose und Xylose, ermittelt nach der Flaschenmethode [mg/1000 g Pentosen]

also belong to the extractives. However, inorganic substances do not directly contribute to formaldehyde release.

Cellulose, the major component of wood, is a linear high-molecular-weight polymer built up of glucose units linked by β-1-4-glycosidic bonds. In order to assess the formaldehyde release of cellulose cotton linters with a α-cellulose content of about 99% and a degree of polymerisation of about 5000 were subjected to thermal hydrolysis under different conditions using the flask method (EN 717–3). Under the experimental conditions cotton linters emit only a comparatively minimal amount of formaldehyde. Even raising the temperature to 100 and 150 °C seems to have no significant influence on the formaldehyde emission of cotton linters (Fig. 1).

Starch, a reserve polysaccharide present e.g. in parenchyma cells of wood tissue, also consists of glucose units. The glucose units are mainly linked by α-1-4-glucosidic

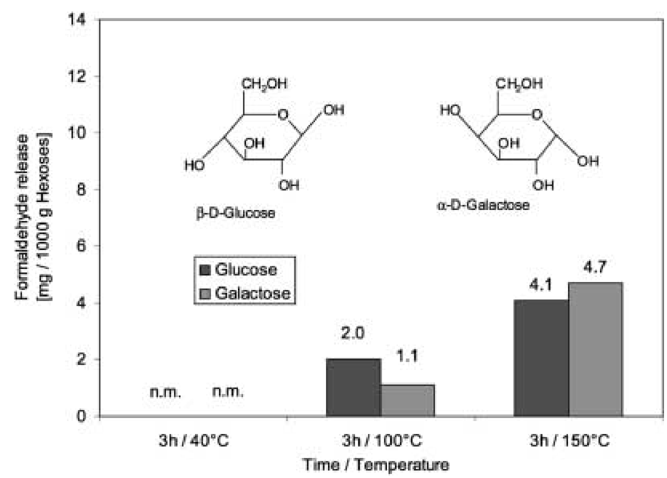

Fig. 4. Formaldehyde release from glucose and galactose measured by the Flask Method [mg/1000 g hexoses]
Bild 4. Formaldehydabgabe von Glucose und Galactose, ermittelt nach der Flaschenmethode [mg/1000 g Hexosen]

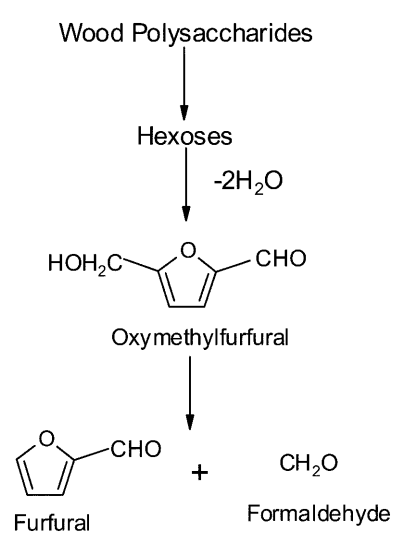

Fig. 5. Possible formation of formaldehyde from wood polysaccharides
Bild 5. Mögliche Formaldehydbildung aus Polysacchariden des Holzes

bonds to form the linear amylose; in the branched amylopectin additionally α-1-6-linkages occur. Under the above mentioned experimental conditions, the formaldehyde liberation from starch was also very low even at high reaction temperatures (Fig. 2). The formaldehyde liberation from glucose, as shown below, is more or less in the same range as that of cotton linters (Fig. 4). Insofar, the degree of polymerisation of cellulose seems to have no significant influence on the formaldehyde release.

Hemicelluloses are, compared to cellulose, branched polymers of low chain length and heterogenous chemical composition. The sugar units, which build the hemicelluloses, are pentoses such as xylose and arabinose, and hexoses like glucose, galactose, and mannose. The term hemicellulose covers also uronic acids and deoxy-hexoses as rhamnose and fucose. Softwood polyoses contain higher amounts of mannose and galactose than hardwood polyoses, whereas hardwoods are rich in pentoses carrying higher amounts of acetyl groups than softwoods (Fengel and Wegener 1984). Insofar, it was of interest to assess the formaldehyde release of different pentoses and hexoses under different thermal conditions. The results (Fig. 3) show that at high temperature Arabinose and Xylose emanate much more formaldehyde than starch and cellulose.

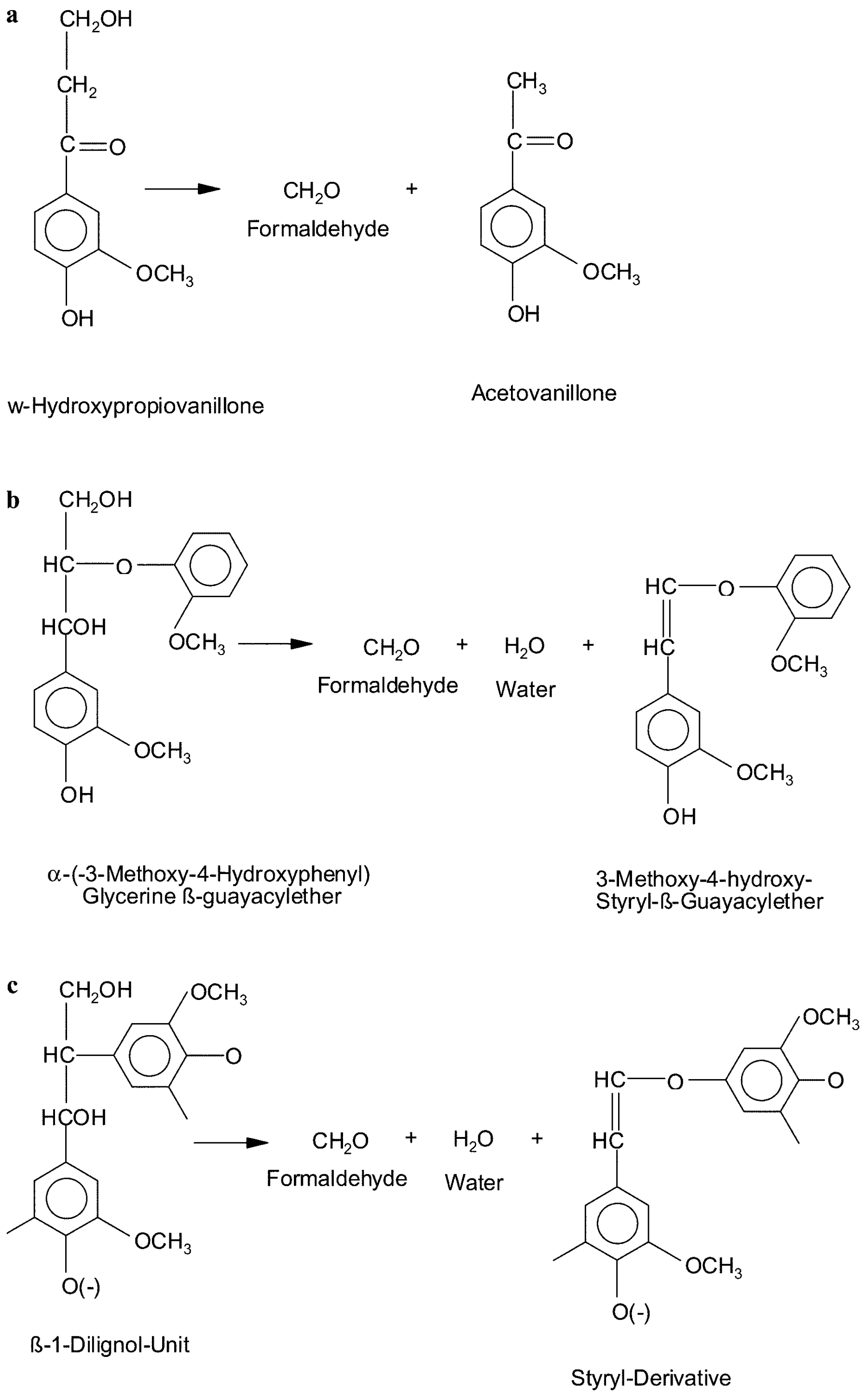

Fig. 6a–c. Three possible pathways for the formation of formaldehyde from lignin
Bild 6a–c. Drei mögliche Reaktionswege zur Bildung von Formaldehyd aus Lignin

Moreover, the formaldehyde emission of arabinose and xylose was higher than that of glucose and galactose (Fig. 4). Thermohydrolytical processing of wood can lead to formaldehyde emission from polysaccharides. Under acidic conditions hexoses degrade to oxymethyl-furfural, which decomposes to formaldehyde and furfural (Fig. 5). The degradation of polyoses can be enhanced by acetic acid liberated from the acetyl groups in the hemicellulose chain.

Besides polyoses, hardwoods and softwoods also differ both in composition and content of lignin. Softwood lignin is built mainly of guajacyl units (80%) and of less amounts of p-coumaryl (14%) and syringyl units (6%). Hardwood lignins on the other hand contain about 53% guajacyl units, 4% p-coumaryl, and 43% syringyl units (Schweers 1978). In hardwoods of the temperate zones, the lignin content lies between 20–25%, while softwoods contain up to 32% of lignin (compression wood may contain up to 41%). It is well known, that treatment of lignin with acids leads to formaldehyde liberation (e.g. Freudenberg and Harder 1927) (Fig. 6a, b, c). In the research work, instead of native lignin, sodium lignosulfonate was thermohydrolytically treated and the formaldehyde liberated during such a treatment was measured. Figure 7 reveals that particularly at high temperatures, sodium lignosulfonate emits relatively high quantities of formaldehyde. Insofar it seems that the formaldehyde release potential of lignosulfonates is much higher than that of wood.

Further work concerned the significance of wood extractives to formaldehyde release. For this purpose saturated fatty acids like palmitic (C16) and stearic acid (C18) and unsaturated acids like oleic acid as well as resin acids, such as abietic acid, were tested by the flask method. The fatty acids release only minute quantities of formaldehyde compared to resin acids (Fig. 8). Abietic acid emits much higher amounts of formaldehyde compared to saturated fatty acids (Fig. 9).

In order to find out how extractives affect the formaldehyde release, spruce (extractive content ~2%) and pine wood particles (extractive content ~4%) were extracted by ethanol/cyclohexane. Thereafter, the formaldehyde release of unextracted and extracted wood particles was determined using the flask method at temperatures of 40 °C, 100 °C, and 150 °C. Unextracted particles emanate higher amounts of formaldehyde compared to extracted particles (Fig. 10). The differences in formaldehyde liberation between extracted and unextracted particles increased as expected by raising the temperature.

Moreover, the results show that unextracted pine particles release higher amounts of formaldehyde than spruce wood particles. After extraction the formaldehyde emission from pine particles declined to a level well below that of unextracted spruce wood. Extraction of spruce wood also lowered the formaldehyde release to a great extent. As mentioned, pine wood has a higher extractive content and especially a higher amount of resin acids (e.g. Fengel and

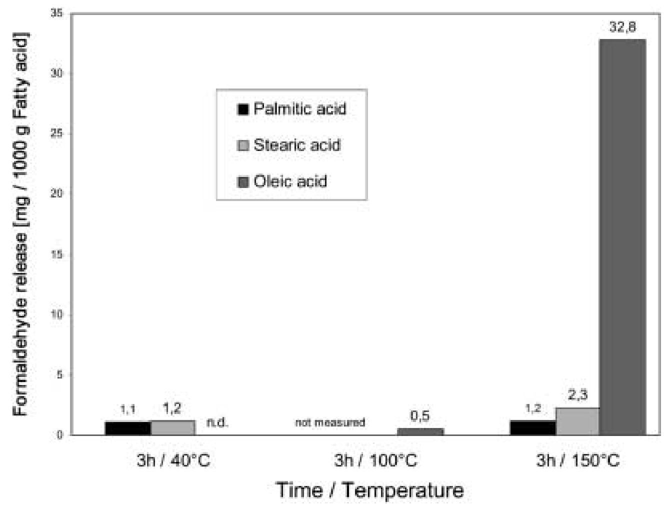

Fig. 8. Formaldehyde release from fatty acids measured by the Flask Method [mg/1000 g fatty acids]
Bild 8. Formaldehydabgabe von Fettsäuren, ermittelt nach der Flaschenmethode [mg/1000 g Fettsäuren]

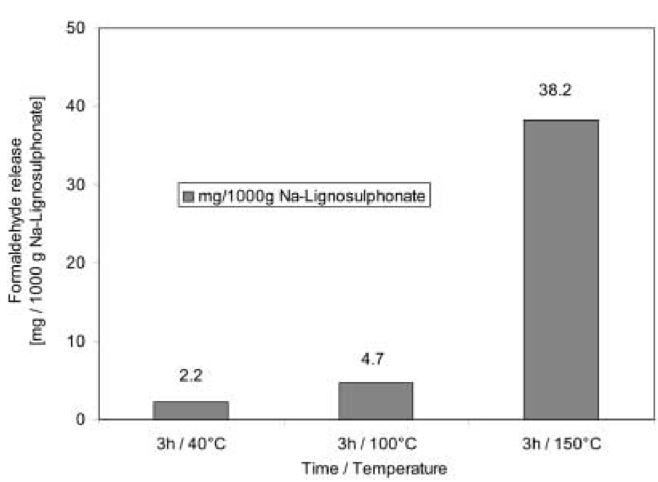

Fig. 7. Formaldehyde release from sodium-lignosulphonate measured by the Flask Method [mg/1000 g Na-lignosulphonate]
Bild 7. Formaldehydabgabe von Natrium-Lignosulfonat, ermittelt nach der Flaschenmethode [mg/1000 g Na-Lignosulphonat]

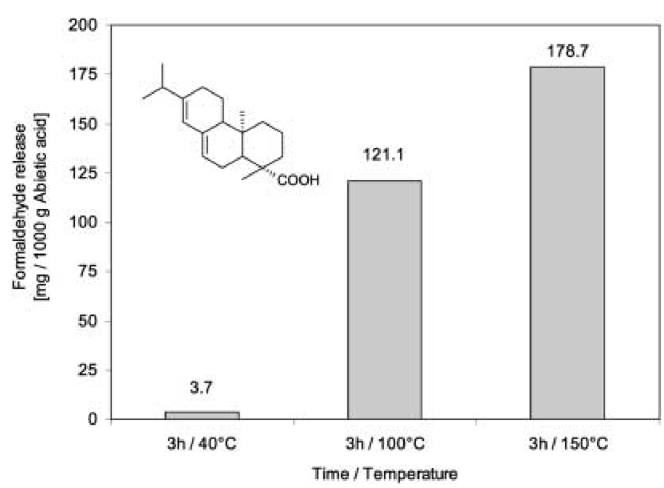

Fig. 9. Formaldehyde release from abietic acid measured by the Flask Method [mg/1000 g abietic acid]
Bild 9. Formaldehydabgabe von Abietinsäure, ermittelt nach der Flaschenmethode [mg/1000 g Abietinsäure]

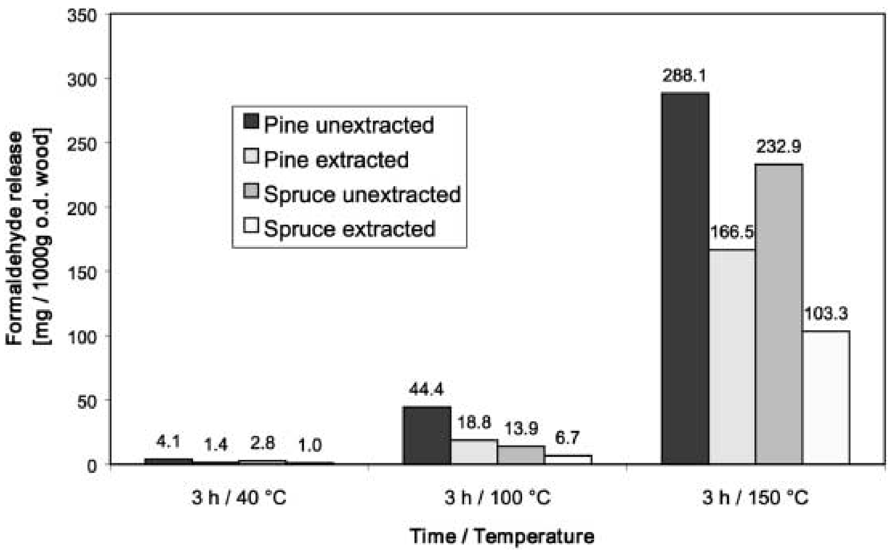

Fig. 10. Formaldehyde release from unextracted and extracted pine and spruce particles measured by the Flask Method [mg/1000 g o.d. wood]
Bild 10. Formaldehydabgabe von nicht extrahierten und extrahierten Kiefern- und Fichtenholzspänen, ermittelt nach der Flaschenmethode [mg/1000 g atro Späne]

Wegener 1984) which are relevant to the formaldehyde release. The results are in line with previous findings of Schäfer (1996) related to the influence of wood storage on the formaldehyde release of spruce and pine wood and particleboards and fibreboards prepared therefrom. Schäfer (1996) found that with increasing storage time particles of spruce and pine wood emit less formaldehyde than non – stored wood. During storage of wood the composition of extractives in wood changes and the extractive content decreases (e.g. Back and Björklund Jansson, 1987). During storage the content of free sugars, lipophilic fats, fatty and resin acids and steroles etc. decreases enormously.

Investigation on the influence of thermo-mechanical treatments on the formaldehyde release were also carried out. According to the results, the amount of formaldehyde release from wood fibres is much higher than from the original wood chips. Moreover, there is a remarkable influence of temperature during TMP process on formaldehyde release of fibres. For example fibres from spruce obtained by thermo-mechanical pulping at a temperature of 160 °C emit higher quantities of formaldehyde than fibres obtained at a temperature of 140 °C (Fig. 11). Generally, TMP fibres emit higher amounts of formaldehyde than wood from which they are generated. This is probably due to the hydrolysis of wood during its thermal treatment in the pulping process, due to which carbohydrates and lignin experience serious hydrolytic changes.

3.2 Role of wood components as formaldehyde bonding agent

Sachsse and Roffael (1993) investigated the suitability of Douglas fir (Pseudotsuga menziesii Franco), grown in Germany, for the production of rotary cut veneer. Plywood was made from heart- and sapwood of Douglas fir using acid curing urea formaldehyde resins (UF-resins) and alkaline phenolic resins (PF-resins). The results revealed that formaldehyde release of plywood from heartwood was lower than that prepared from sapwood. These results are in conformity with the work of Lelis et al. (1993). The authors found that UF-bonded particleboards of pine

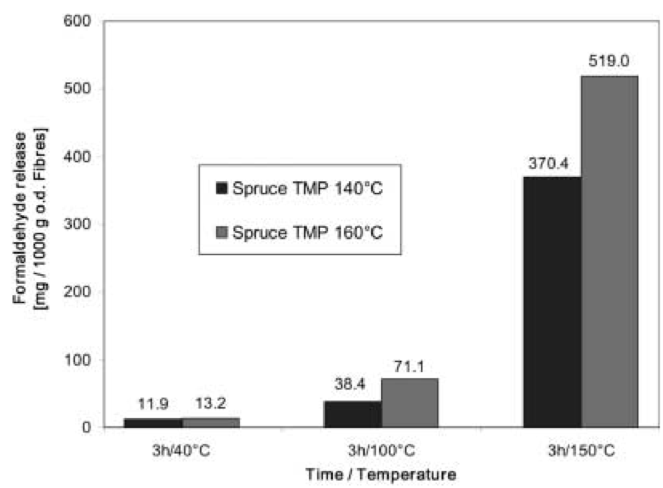

Fig. 11. Formaldehyde release from spruce thermo-mechanical pulps (TMP) measured by the Flask Method [mg/1000 g o.d. fibres]
Bild 11. Formaldehydabgabe von TMP-Fasern aus Fichtenholz, ermittelt nach der Flaschenmethode [mg/1000 g atro Fasern]

heartwood emit less formaldehyde than particleboards prepared from sapwood under the same conditions. Several authors have reported on the reaction between formaldehyde and phenolic wood compounds like pinosylvin and pinosylvinmonomethylether of pine heartwood (e.g. Kalish 1969). Accordingly, several softwood species like pine and Douglas fir wood contain noticeable amounts of wood extractives, reactive to formaldehyde.

Moreover, published work of Roffael et al. (1994) revealed that chemical interaction between heartwood extractives and formaldehyde takes place. The authors fumigated heartwood particles of Douglas fir with formaldehyde at a temperature of about 103 °C for different time periods. The results confirmed that the content of heartwood extractives soluble in hot water decreased after fumigation with formaldehyde. In similar investigations heartwood particles from black locust

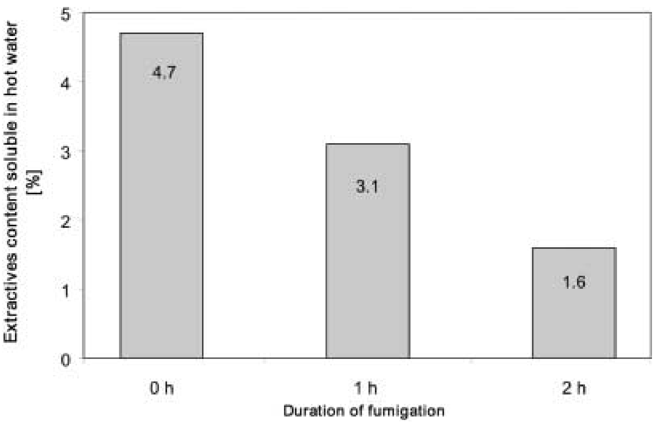

Fig. 12. Content of hot water soluble extractives from black locust heartwood (*Robinia pseudoacacia*) after fumigation with formaldehyde at 103 °C

Bild 12. Extraktstoffgehalt (Heißwasser) von Robinienkernholz (*Robinia pseudoacacia*) nach Begasung mit Formaldehyd bei 103 °C

(*Robinia pseudacacia* L.) were fumigated with formaldehyde. Also, in this case, increasing the fumigation time from 0.5 h to 2 h induced a remarkable decrease in the content of extractives soluble in hot water (Fig. 12). This shows that heartwood extractives of black locust can react with formaldehyde and therefore become insoluble in hot water. Insofar, wood extractives play a dual role, they emit formaldehyde and can act as a formaldehyde scavenger. Also lignin and lignosulphonates can react with formaldehyde under certain boundary conditions.

4 Conclusions

1. The formaldehyde emission of the main components of woods differs widely. Cellulose emanates much less formaldehyde than hemicelluloses at higher temperatures. Lignin releases much more formaldehyde than the carbohydrate components in wood. The formaldehyde emission from the extractives depends highly upon their chemical composition.
2. Thermal hydrolytic treatments of lignocellulosics as in thermo-mechanical pulping increase the formaldehyde emission tremendously. The temperature of pulping also plays a significant role.
3. Some wood extractives can act as a formaldehyde scavenger, as they could react with formaldehyde originating from the resin used as a bonding agent and decrease the over all formaldehyde release of wood – based panels.
4. As wood emits variable amounts of formaldehyde depending on different boundary conditions, the term zero release of formaldehyde in wood – based panels has to be defined.

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