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THE RELEASE OF HYDROCARBONS FROM SOFTWOOD DRYING: MEASUREMENT AND MODELING♣

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ABSTRACT

The release of volatile organic compounds (VOC) during the drying of Norway spruce and Scots pine was experimentally studied. Heartwood and sapwood were separately dried at 60 ºC. The Flame Ion Detector (FID) was used to measure the total amount of hydrocarbons (THC) released during the drying process. A large difference of the emissions course between heartwood and sapwood were found. For heartwood, a release maximum of hydrocarbons followed by a typical negative exponential course was found. When drying sapwood, the released amount of hydrocarbons was evidently more fluctuating before reducing to zero. A model describing the release of hydrocarbons during the drying with only diffusion as transport mechanism was applied. The aim was to obtain a suitable explanation of the characteristic release behavior from sapwood and develop a model describing the process.

Keywords: Wood Drying, VOC, Modeling, Picea abies, Pinus sylvestris

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INTRODUCTION

The drying of wood is an important step in the processing of competitive timber. Advantages include diminish mould damage, discolor and shrinkage of the completed wood product. Improved storage conditions, cheaper transport costs as well as improved strength of the material are other arguments for drying. When drying wood, volatile organic compounds (VOC), originating in the wood are emitted to the environment. The components released mainly consist of terpenes, however, the release of alcohols, carboxylic acids, phenols and fatty acids have also been reported (Fagernäs, 1992). In spruce and pine the most frequent occurred monoterpenes are a-pinene, b-pinene and 3-carene. VOC has for a long time been recognized as a major air-pollutant factor (Englund and Nussbaum, 2000) and (Roques, 1996). The VOCs react photochemically and take part in the formation of ozone in the lower atmosphere (Milota and Lavery, 2001), which has an adverse effect on human health, the forest ecosystem and agricultural crops (Ingram et al., 1995). The flame ionization detector (FID) has been used by different researches (Ingram et al. 2000; Shmulsky 2000a; 2000b; Banerjee et al. 1999) to measure the extent of hydrocarbon emissions from wood drying. Work treating the modeling of the hydrocarbon release is rare. However, Johansson and Rasmuson (1998) modeled the release of monoterpenes with two different models. The communicating model incorporated both advective and diffusive transport of monoterpenes and was overpredicted. The non-communicating model was based on transport by diffusion and agreed well with the monoterpene release from spruce.

This work shows that a distinction between heartwood and sapwood is necessary when studying the release behavior of hydrocarbons. The purpose of this work is to study the total release of hydrocarbons from Norway spruce and Scots pine during drying, and develop a model to describe the emissions from heartwood as well as sapwood.

MATERIALS & METHODS

Wood samples of Norway spruce (Picea abies) and Scots pine (Pinus sylvestris) was used. The samples were sawn into small pieces of either heartwood or sapwood with dimensions approximately 5x3x2 cm^3. Pieces with knots and other defects were not used. The samples were stored in -20 °C. Moisture contents (MC) in the sapwood samples were between 130 and 150 percentage. The average moisture content in the heartwood samples was between 28 and 34 percentage.

An experimental drying equipment was rebuilt and further developed to fit the emission experiment, (Figure 1). A 5-liter glass vessel was utilized as a drying chamber. A humidity and temperature sensor measured humidity from 10-95 % RH and could be used in temperatures from -40 to 120 °C. The water content in the wood samples was determined with an electronically accurate balance, which had a capacity of 100 g and a resolution up to 0.0001 g.

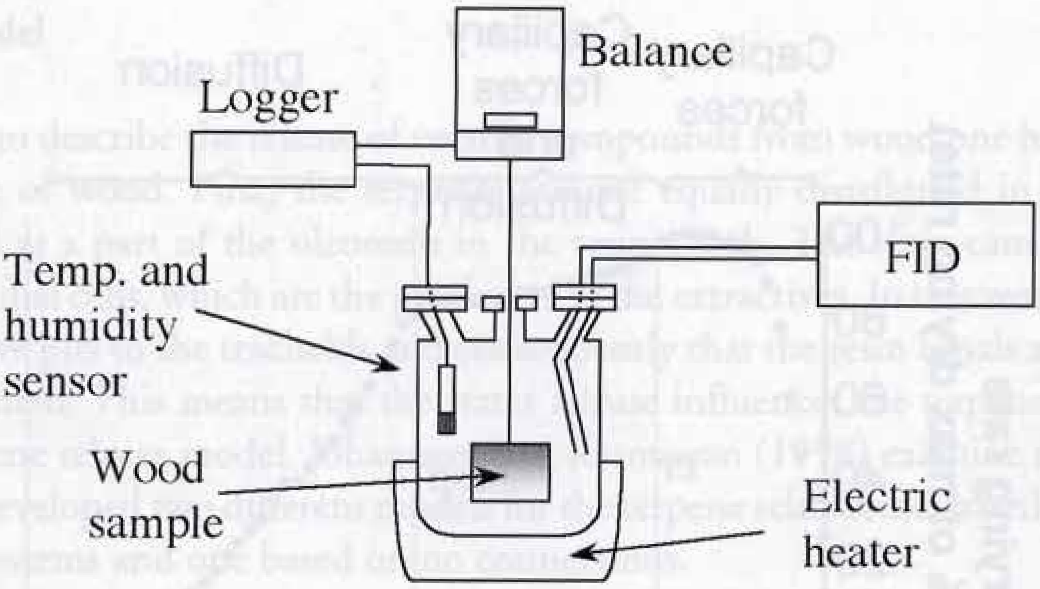

Figure 1: Outline of the experimental device.

A flame ionization detector (FID) named Thermo-FID was used to sample and measure the release of hydrocarbons continuously during the drying. The emissions were sampled continually at a flow rate of 500 ml/min. The FID uses a heated sample line (150 ºC), to transfer the hydrocarbons from the drying chamber to the analyzer. The analyzer was calibrated with spangas of propan. One drawback with the FID measurements during drying is that the humidity in the drying chamber decreases. The detector response varies with gas moisture content and has in these experiments not been taken into account.

THEORETICAL

Moisture transport in softwood

Moisture in wood can exist in different forms that must be treated separately. Free water can be found in the cell cavities, and is thus bound by capillarity to the wood. Molecular forces acting to bind water in the cell walls. Moisture in wood can also exist as vapor. During the drying process, the various forms of water are transported from the inner part of the wood outward to the surface where it evaporates and is thus released into the environment. In Figure 2, different stages of drying sapwood are illustrated (Figure 2 and 3 are experimental results that have been prepared in this work.). One can discern three major time periods, which uses different water transport potentials (Esping, 1992). When beginning the wood drying process ($MC_{sample} > MC_{cr}$), free water on the surface evaporates. As a result, capillary forces arise and transport more free water from the wood cells to the wood surface where it is then evaporated.

Consequently, the amount of free water decreases and the border between its liquid- and gas phase successively moves deeper into the wood. At this point within the wood ($MC_{sample} = MC_{cr}$), there are not only capillary driven water but also vapor and bound water that are transported by diffusion (Dinwoodie, 2000). After further drying, at the fiber saturation point, there is no free water left and consequently the last capillary forces in the center of the wood cease. Moisture transport at the end of the drying process ($MC_{sample} \leq MC_{fsp}$) occurs therefore only by diffusion in the voids.

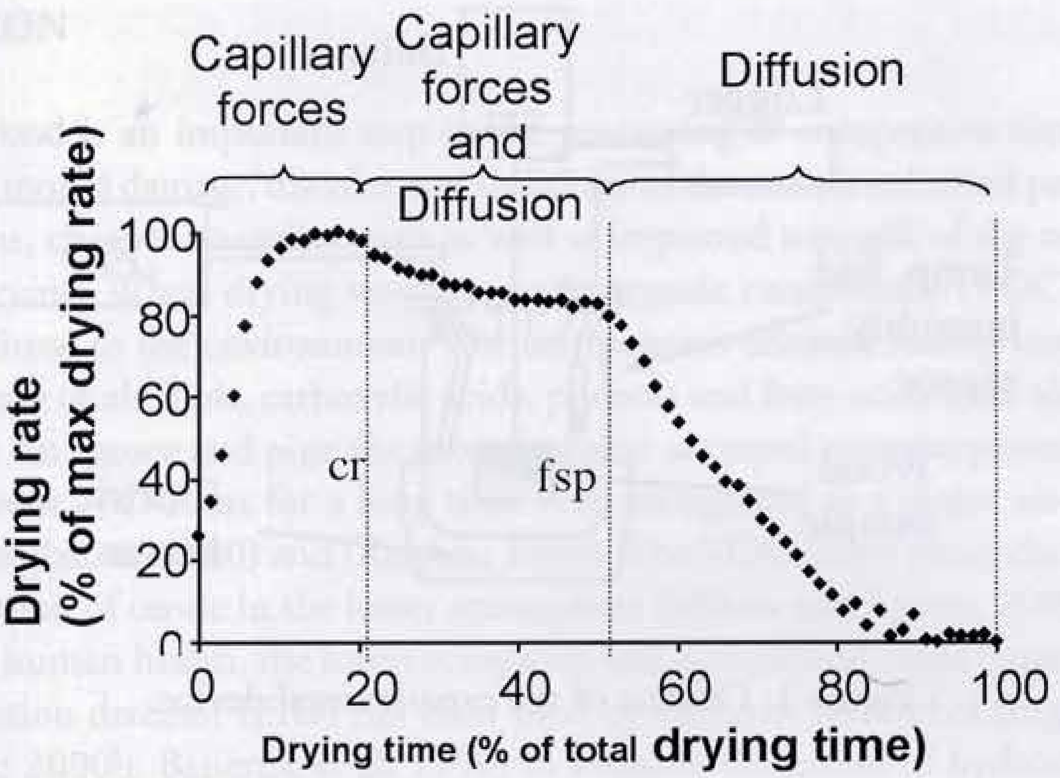

Figure 2: The sapwood drying. Three major time periods that uses different water transport potentials.

When drying heartwood, the course is different. Since heartwood contains much less water than sapwood ($MC_{sample} < MC_{fsp}$), no capillary forces arise, (Figure 3).

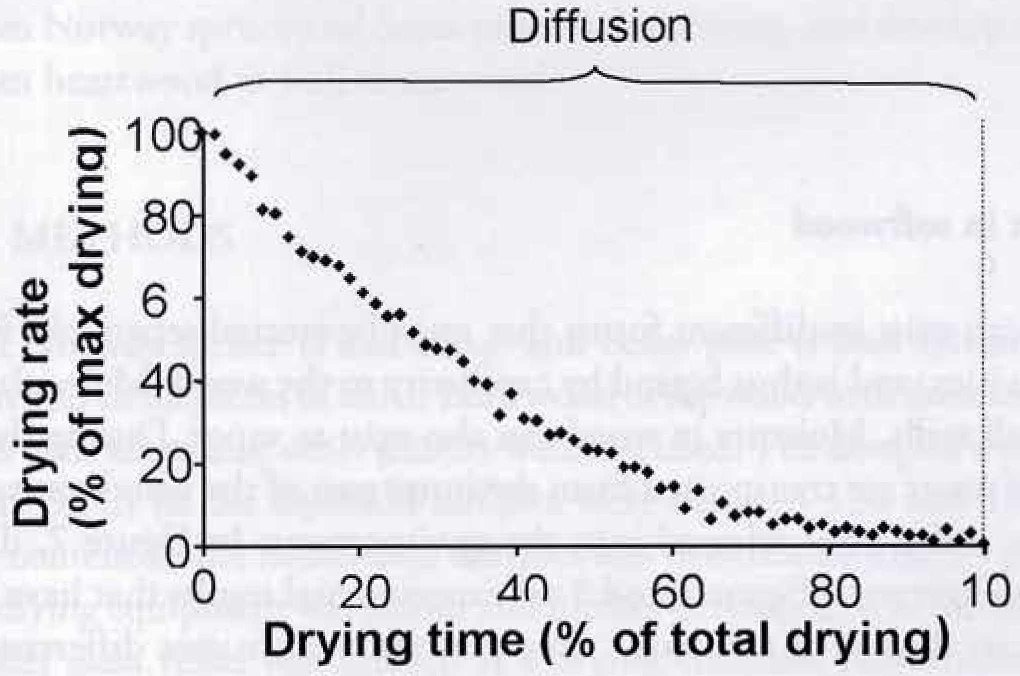

Figure 3: Heartwood drying. The low moisture content only allows diffusive forces for the water transport.

Instead there is a long stage, during the whole drying where only diffusion and possibly advection leads to transport of water. Naturally, in conventional drying, heartwood and sapwood, dries together. However, when describing not only the water release but also the release of volatile compounds this division is necessary.

The transport model

When attempting to describe the release of volatile compounds from wood one has to begin with the microstructure of wood. First, the terpenes are not equally distributed in the wood. The terpenes are found as a part of the oleoresin in the resin canals. The resin canals are internally covered with epithelial cells, which are the producers of the extractives. In this work, the epithelial cells assumes to have pits to the tracheids and consequently that the resin canals are connected to the water canal system. This means that the water release influences the terpene release. This is treated in the terpene release model. Johansson and Rasmuson (1998) examine almost the same conditions. They developed two different models for the terpene release, one based on connections between the two systems and one based on no connections.

Two phases of water in the wood are present during drying; liquid phase and gas phase. The terpenes can be transported in both of these phases. There are also two ways the terpenes can be transported; by diffusion and by advection. However, in the release model treated in this work, some simplifications have been made. First, due to the low solubility of terpenes in water, the transport of terpenes in liquid phase assumes to be neglected. Second, since low temperatures are used during the drying only small advective flow components are created. Thus, the terpenes are not assumed to be transported by advection in the gas phase, i.e. directly transported by the gas flow. In this work, only diffusion within the gas phase is considered as a transport mechanism for the terpenes.

The material balance for the terpenes treated was obtained using Fick's diffusion law:

$$\frac{\partial C}{\partial t} = \nabla \cdot (D_{gas} \nabla C) \qquad (1)$$

C is the concentration of monoterpenes in gas phase (kg monoterpenes / m^3), t is the time (s) and D_{gas} is the diffusion coefficient (m^2 / s) in gas phase. In equation 2 the diffusion coefficient in the transversal direction, D_{gas},T is given according to Perré et al. (1989):

$$D_{gas,T} = k_g \frac{D_{va}}{1125} \qquad (2)$$

D_{va} is the diffusion of vapor in air (2.6*10^{-5} m^2/s) (Siau, 1995) and k_g is the relative permeability. The relative permeability that has a direct proportional effect on the diffusion coefficient is calculated according to Perré et al. (1993) and schematically described below. According to Perré et al. (1989), the drying schedule can be divided into three different regions where the relative permeability, k_g is separately calculated (Figure 2):
In the first period of drying ($MC_{sample} > MC_{cr}$), k_g is calculated to

$$k_g = 0.05 \frac{X_{sat} - X_{free}}{X_{sat} - X_{cr}}, \qquad (3)$$

In the middle period ($MC_{cr} > MC_{sample} > MC_{fsp}$):

$$k_g = 0.95\left(1 - \frac{X_{free}}{X_{cr}}\right)^2 + 0.05. \tag{4}$$

In the end of drying ($MC_{fsp} > MC_{sample}$), k_g is presumed to be constant due to the low moisture content:

$$k_g = 1. \tag{5}$$

When drying heartwood (Figure 3), no free water is located in the wood ($MC_{fsp} > MC_{sample}$). This implies that the relative permeability, k_g is kept constant ($k_g = 1$) during the whole drying cycle.

The longitudinal diffusion coefficient, $D_{gas,L}$ (eq. 6) is calculated below according to Perré et al. (1993). The model is one-dimensional and treats only flow in the longitudinal (L) direction. The permeability in the longitudinal direction is at a magnitude of 100 to 1000 times higher than the transversal and radial one. In industrial drying this simplification could not be used due to the length of the board being at a magnitude of probably 100 times longer than the radial and transversal. The wood samples used in this work had approximately the same length in longitudinal direction, as well as radial and transversal ones. This means that

$$D_{gas,L} = 20D_{gas,T} \tag{6}$$

Fick's first law (1) is reduced to the one-dimensional diffusion equation that is referred to as Fick's second law (7):

$$\frac{\partial C}{\partial t} = D_{gas,L}\frac{\partial^2 C}{\partial L^2} \tag{7}$$

According to Englund and Nussbaum (2000) the initial amount of terpenes in fresh Norway spruce is between 0.02-0.08 % calculated on a wood dry basis. This corresponds to 0.086-0.34 kg terpenes per m^3. On average a value of 0.2 kg/m^3 could be used, but due to the fact that the wood samples were stored in a freezer several months before the experiments were performed, a terpene concentration of 0.1 kg/m^3 was used in the model.

The initial amount of terpenes assumes to be homogeneously distributed within the wood:

$$C(L,0) = C_0 \tag{8}$$

The flux of terpenes is continuous at the boundaries and is described using an external mass transfer coefficient, h_m, which is related to the external resistance to mass transfer. The rate of exchange is proportional to the difference between the concentration at the boundary $C_{boundary}$ and the low concentration $C\infty$ in the drying chamber.

$$D_{gas,L}\frac{\partial C}{\partial L}\bigg|_{boundary} = h_m\left(C\big|_{boundary} - C_\infty\right) \qquad (9)$$

This assumption can be applicable due to the fact that the drying chamber was connected to flow from the FID. In the beginning of the drying process, the diffusion coefficient is assumed to be very low due to the low initial temperature of the wood samples.

The one-dimensional diffusion problem was numerically solved using the Method of Lines (MOL). The MOL technique results in a set of semi-discrete equations (discrete in space and continuos in time). Due to symmetry, only one half of the wood sample is modeled.

RESULTS

Experimental results

The components released from wood during the drying were measured by using FID. Heartwood and sapwood from spruce and pine were dried separately.
The concentration of released hydrocarbons is depicted in Figures 4 - 7. The drying temperature in all experiments were kept constant at approximately 60 °C. Depending on the wood samples initial low temperature, the temperature in the drying chamber was reduced to approximately 55 °C during the first half-hour of drying.

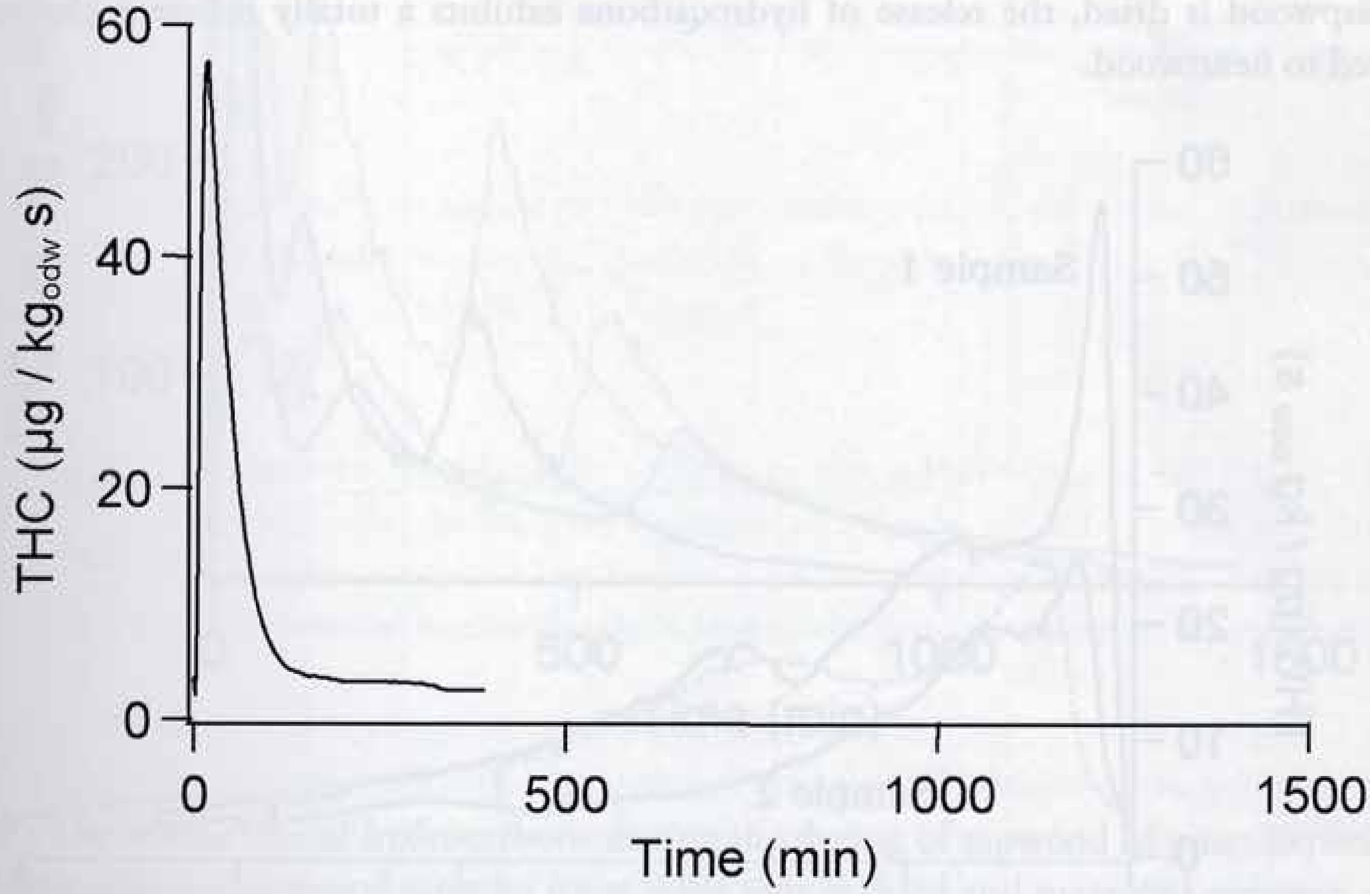

Figure 4: The release rate of hydrocarbons during the drying of heartwood of spruce: experimental results.

When heartwood of spruce and pine were dried (Figures 4 and 5), the concentration increased to a maximum, followed by a decrease as the drying proceeded. The curves behave similarly; the only difference to be found is in the amount of emitted hydrocarbons. This is in line with the fact that pine contains more extractives than spruce.

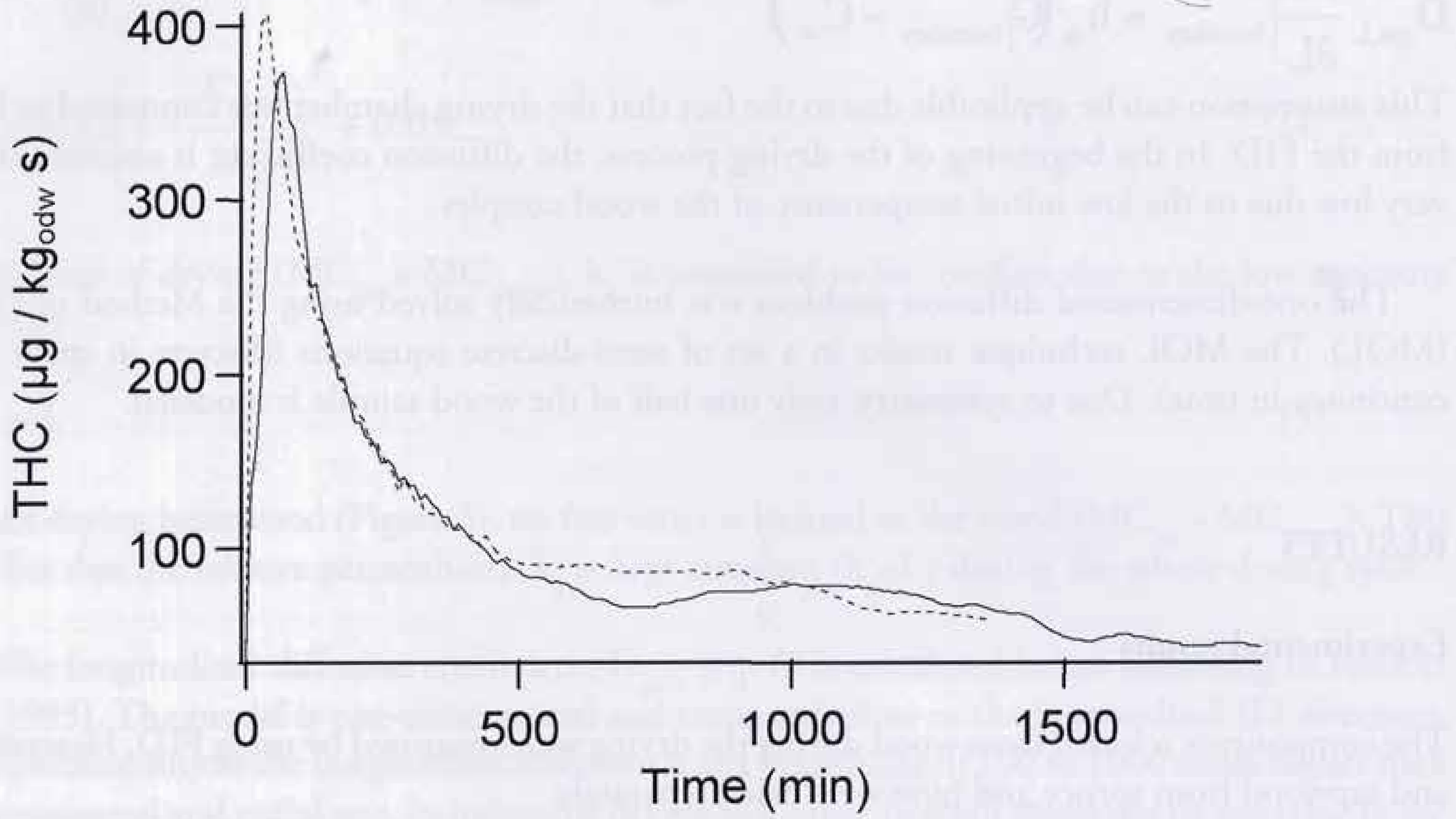

Figure 5: The release rate of hydrocarbons during the drying of two different sample of heartwood of pine: experimental results.

When sapwood is dried, the release of hydrocarbons exhibits a totally different characteristic compared to heartwood.

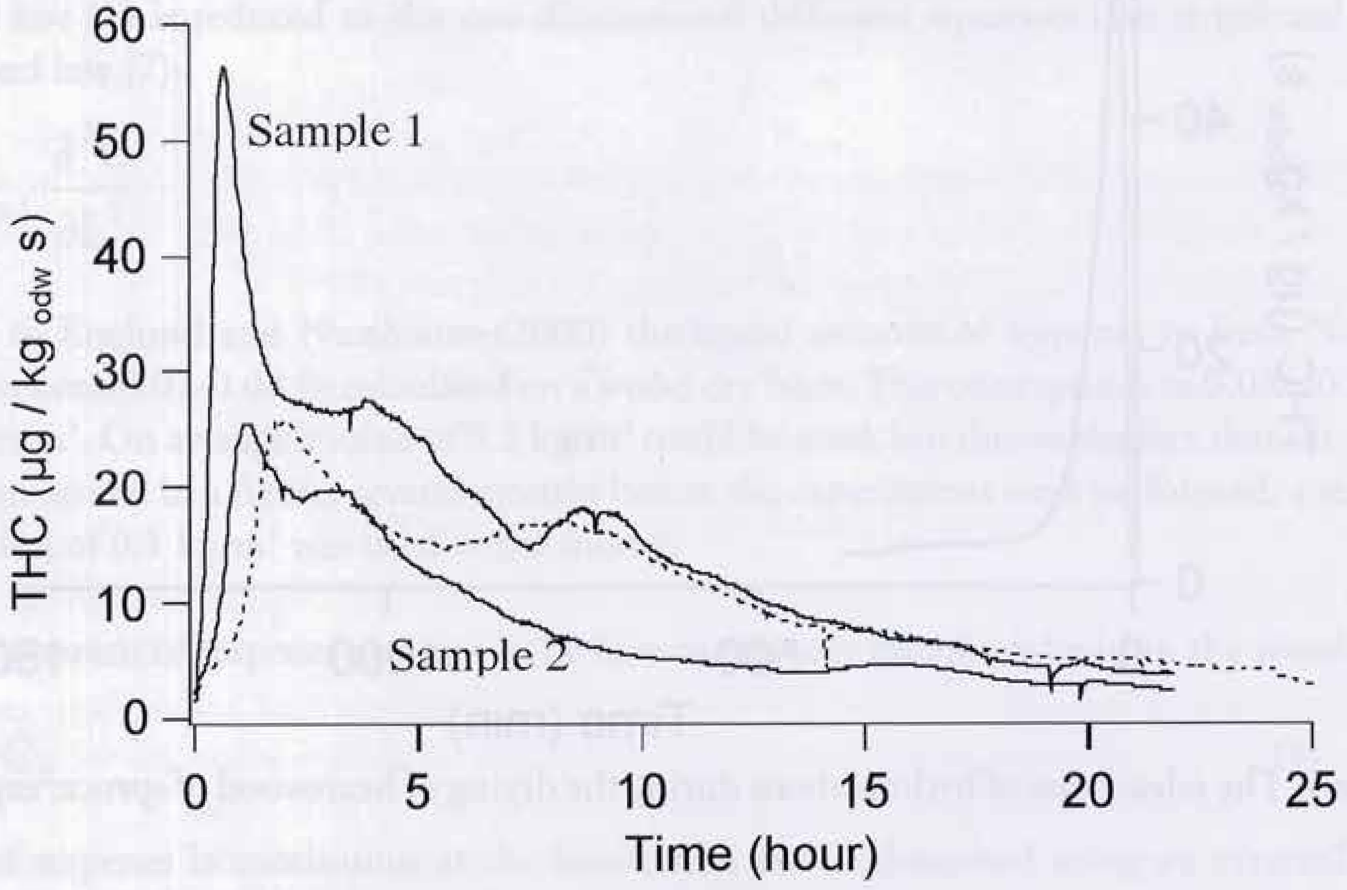

Figure 6 : The release rate of hydrocarbons during the drying of three different samples of sapwood from spruce: experimental results. The release from wood sample 1 and 2 are also further modeled.

After the first hydrocarbon concentration maximum, the release rate keeps at a nearly constant level before it successively decreases to zero.

However, the three samples of sapwood of spruce (Figure 6) do not show the same distinct behavior as sapwood of pine (Figure 7). The hydrocarbon emissions from sapwood of Scots pine (Figure 7) show three distinct peaks in hydrocarbon concentration. The measurement was repeated several times and the similar result was confirmed.

Banerjee et al. (1995, 1998) also describe a similar release behavior of VOCs from wood flake drying. The emission profiles obtained showed two maximums. Initially, the concentration of VOC emerged rapidly and then decreased. This interval corresponded to the initial drying period where the flakes were evaporative cooled, and kept a temperature below 100 ºC. The second peak appeared after the wood samples were substantially dry and reached oven temperature. The second peak, unlike the first, increased with drying temperature. The intensity of the first peak kept almost constant since the sample temperature remained constant regardless of the oven temperature. Banerjee et al. (1995, 1998) did not obtain a third increase of VOC as described in this report (Figure 7). The third peak is more complicated to understand. Measurements performed by Milota and Lavery (1999) showed that the FID detector response was intensified when the moisture in the sampled gas decreased and could be the reason to the third peak.

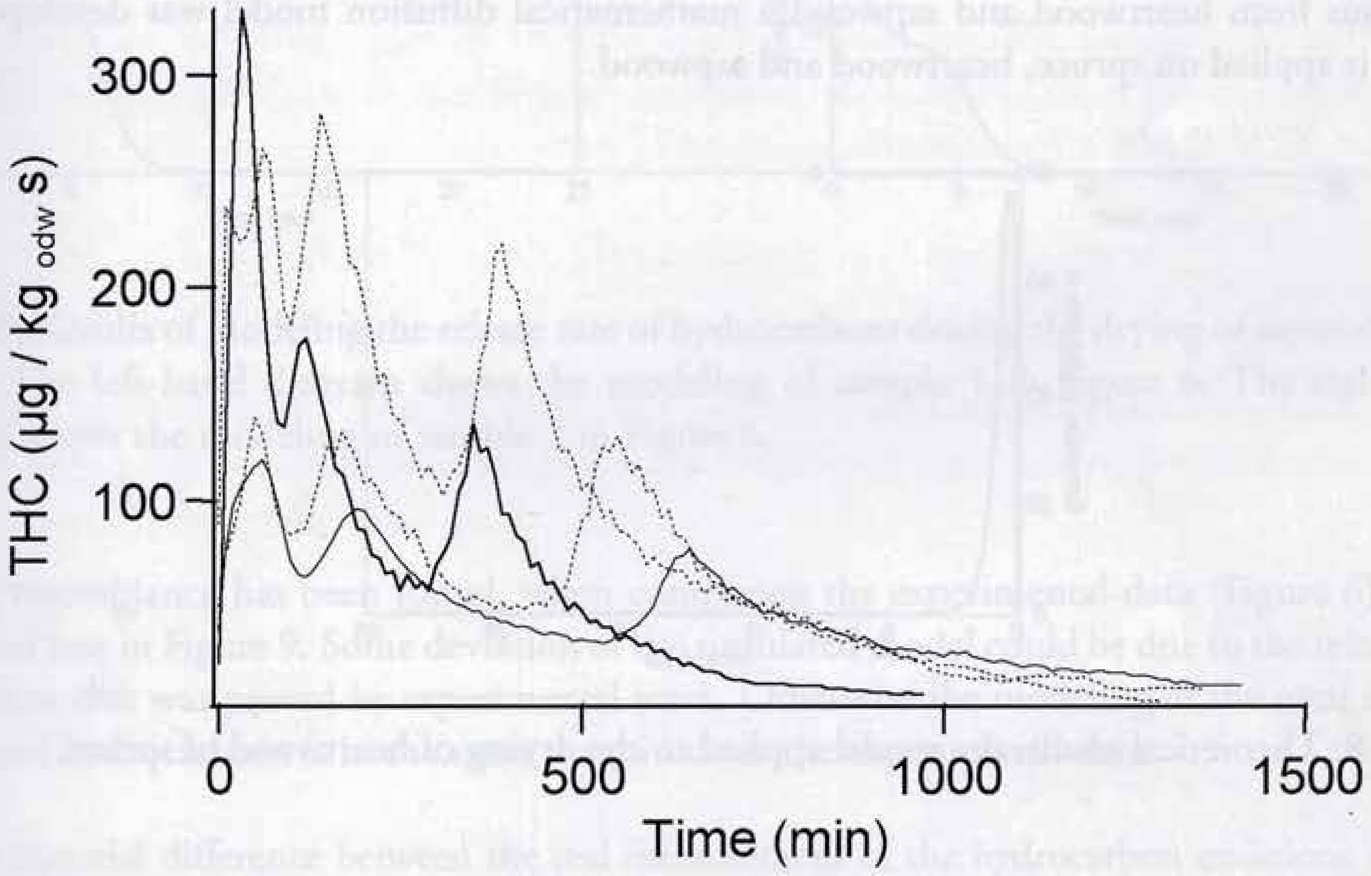

Figure 7 : The release rate of hydrocarbons during the drying of sapwood of pine: Experimental results. Four different sapwood samples from Scots pine is dried and measured separate.

Banerjee (2001) suggest three different mechanisms that contribute to the release of VOC in wood. Dissolved terpenes in the surface water moves to the wet line, where evaporation occurs and gives rise to the first characteristic peak. Banerjee (2001) suggest as a second release mechanism, a near constant transport of terpenes dissolved in water from the inner of the wood structure to the surface. Finally, when all the moisture in the wood is evaporated, the wood temperature consequently increases. This involves a more intensive evaporation of terpenes and is shown as the third peak in the emission diagram.

Banerjees explanation is not completely applicable to the measurement done to the sapwood of pine in this work. The second peak is not explained. The following statement however can explain the difference: The hydrocarbons dissolved in the surface water evaporate and give the first peak. Still there is a large amount of moisture that prevents the hydrocarbons in gas phase to be transported without obstacle. As more water releases from the wood, the cells successively open up for the transport of hydrocarbons in gas phase. This means that the relative permeability and the diffusion coefficient changes during drying. This behavior will create the second peak. The third peak is then due to the low moisture content within the wood.

In industrial drying of lumber, the drying process often end when the wood moisture contents is around 15 %. Therefor, the third peak in the drying diagram (Figure 7) will not appear. However, to obtain a physically suitable model, this conclusion should be considered.

The results of mathematical model

To describe the characteristic release behavior from sapwood and to explain the differences between emissions from heartwood and sapwood a mathematical diffusion model was developed. The model is applied on spruce, heartwood and sapwood.

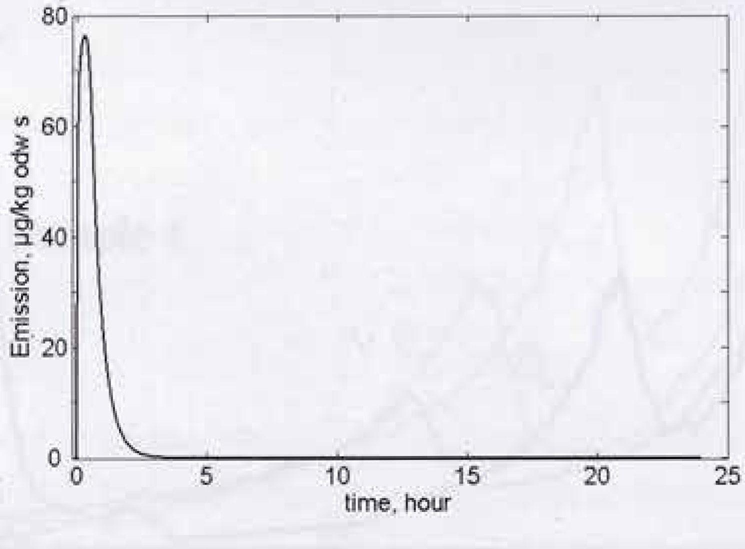

Figure 8: Theoretical result: the model applied to the drying of heartwood of spruce.

At the beginning of drying, the drying chamber contains no released hydrocarbons. Gradually, as the wood gets warm, the release starts and successively increases. When heartwood of spruce is dried, the concentration of hydrocarbons successively increases to a maximum and follows by a negative exponential decrease as the drying proceed (Figure 4). The experimental data has a satisfactory adjustment to the developed model, Figure 8.

The model includes the moisture contents dependency on the permeability. Consequently, due to the low moisture content in heartwood, the permeability and the diffusion coefficient keeps constant during the whole drying. A different diffusion coefficient is merely assumed in the beginning of drying period, due to low initial temperature of the wood samples and consequently low release rate of hydrocarbons.

Due to the low moisture content in heartwood and in accordance with Perré et al (1989,1993), the diffusion coefficient will be kept constant during the drying. This assumption holds when comparing experimental data (Figure 4) to the simulated model (Figure 8).

When applying the model to sapwood drying, a different release behavior is obtained (Figure 9). The moisture content in Sapwood is much higher than in heartwood, particularly in the beginning of drying time. The large amount of moisture prevents the movement of the hydrocarbons from the wood. In physical terms, the permeability is low when the amount of free water in the wood is high. When drying the sapwood, the moisture content decreases successively and consequently, the relative permeability and the diffusion coefficient will increase for the gas phase. This fact is valid as long as the moisture content is above fiber saturation point. At below fiber saturation point, no free water is left in the wood, which does not result in further changes in permeability. In Figure 9 one can distinguish the increasing release rate as a peek or a plateau before the diffusion coefficient becomes constant and the release rate successively decreases to zero.

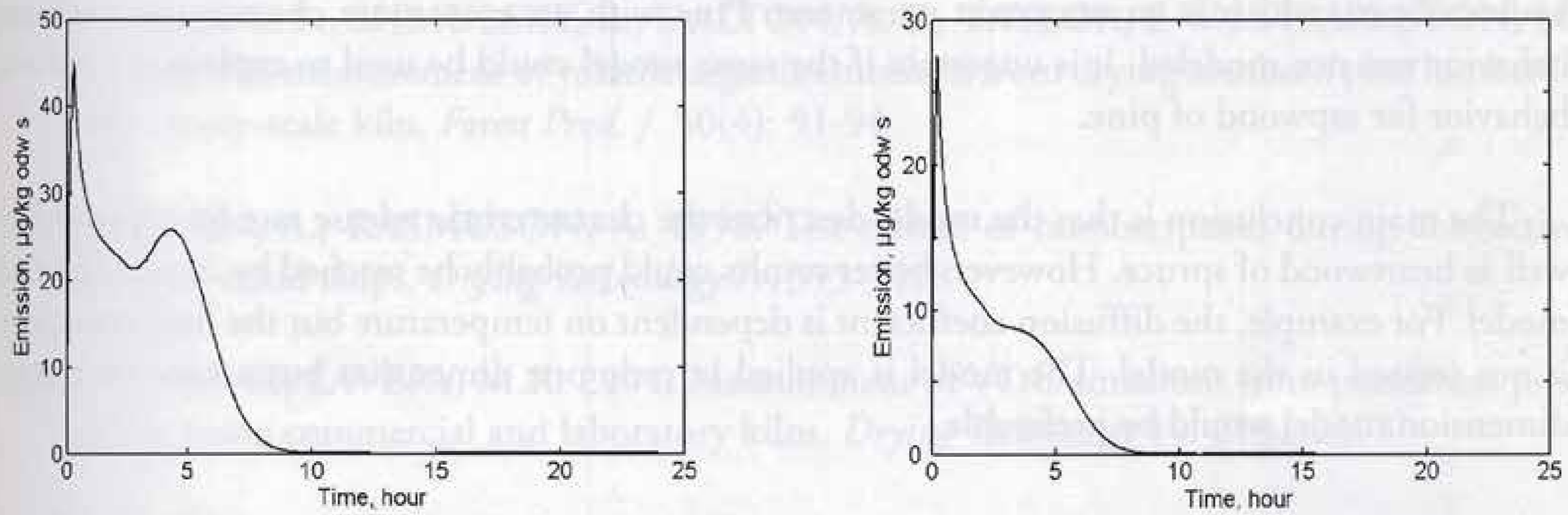

Figure 9: Results of modeling the release rate of hydrocarbons during the drying of sapwood from spruce. The left-hand diagram shows the modeling of sample 1 in Figure 6. The right-hand diagram shows the modeling of sample 2 in Figure 6.

The resemblance has been found, when comparing the experimental data (Figure 6) to the simulated rate in Figure 9. Some deviation of the simulated model could be due to the release rate fluctuation that was proved by experimental work. Otherwise the modeling of the total amount of released hydrocarbons is in the same magnitude as the experimental data.

The essential difference between the real measurement of the hydrocarbon emissions and the simulated value is that the model predicts a point of time where no further releases occur (in the simulated examples, after approximately 8 hours of drying). The experiments support that small amounts of hydrocarbons are released even after 20 hours of drying. This indicates that another release potential not has been considered in the model present. One explanation might be as described for pine sapwood that when all the moisture in the wood is evaporated, the wood temperature increases. The higher temperature implies a possibility to release more terpenes from the wood.

CONCLUSIONS

Measurements of hydrocarbons released from spruce and pine during drying was accomplished. The sapwood and heartwood were dried separately. A large difference of the emissions course between heartwood and sapwood were found. Due to low moisture content and aspirated cells in heartwood, the permeability becomes constant and the release rate of hydrocarbons is exponential decreasing during the drying. When sapwood is being dried, the conditions are quite different. Due to the high initial moisture content in sapwood, the permeability for the gas phase is low in the beginning of drying. As water leaves the wood, the canal system in the wood opens up for gas transport. This involves a more fluctuating amount of hydrocarbons being released during the drying. A diffusion model was used to describe the hydrocarbon emission from heartwood as well as from sapwood from spruce. The model explained the characteristic sapwood release well when drying spruce. The total amount of hydrocarbons being released during the drying was also in agreement with the model. However, the total amount depends on the initial concentration of hydrocarbons, which is an uncertain parameter. Pine with an even more characteristic release behavior was not modeled. It is uncertain if the same model could be used to explain the release behavior for sapwood of pine.

The main conclusion is that the model describes the characteristic release rate for sapwood as well as heartwood of spruce. However, better results could probably be reached by improving the model. For example, the diffusion coefficient is dependent on temperature but the heat transport is not treated in the model. The model is applied in only one dimension but a two- or three-dimension model would be preferable.

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LITERATURE

BANERJEE, S. 2001. Mechanisms of terpene release during sawdust and flake drying. Holzforschung 55: 413-416

BANERJEE, S.; SU, W.; YAN, H.; OTWELL, L.; HITTMEIER, M. 1999. Field-proven strategies for reducingvolatile organic carbons from hardwood drying. *Environ. Sci. Technol.* 33:1056-1059

BANERJEE, S.; SU, W.; WILD, M. P. 1998. Wet line extension reduces VOCs from softwood drying. *Environ. Sci. Technol.* 32 (9): 1303-1308

BANERJEE, S.; HUTTEN, M.; SU, W.; OTWELL, L.; NEWTON, L. 1995. Release of water and volatile organics from wood drying. *Environ. Sci. Techn.* 29, 1135-1136

ENGLUND, F.; NUSSBAUM, R. M. 2000. Monoterpenes in Scots pine and Norway spruce and their emission during kiln drying. *Holzforschung* 54: 449-456

ESPING, B. 1992. *Grunder i torkning,* trätorkning 1a. Trätek. ISBN: 91-88170-06-3

FAGERNÄS, L. 1992. Peat and bark extractives and their behavior in drying processes. Technical research center of Finland, Doctoral Thesis

INGRAM, L.L.; TAYLOR, F.W.; PUNSAVON, V.; TEMPLETON, M.C. 1995. Identification of volatile organic compounds emitted during drying of Southern pine in pilot and laboratory experiments. *Measuring and controlling VOC and particulate emissions from wood processing operations and wood based products.* Proceedings no. 7301. Forest prod. soc., Madison WI, 35-40

INGRAM, JR L. L.; SHMULSKY, R.; DALTON, A. T.; TAYLOR, F. W.; TEMPLETON, M. C. 2000. The measurement of volatile organic emissions from drying southern pine lumber in a laboratory-scale kiln. *Forest Prod. J.* 50(4): 91-94

JOHANSSON, A.; RASMUSON, A. 1998. The release of monoterpenes during convective drying of wood chips, *Drying Technology* 7:1395-1428

MILOTA, M. R.; LAVERY, M.R. 2001. Measurement of VOC emissions from ponderosa pine lumber using commercial and laboratory kilns. *Drying Technology* 19: 2151-2173

MILOTA, M. R.; LAVERY, M. R. 1999. Effect of moisture on the reading of a total hydrocarbon analyzer. *Forest Prod. J.* 49(5): 47-48

PERRÉ, P.; FOHR, J. P. ; ARNAUD, G. 1989. A model of drying applied to softwoods: the effect of gaseous pressure below the boiling point. *Drying 1989,* ed. A. S. Mujumdar and M. A. Roques, Hemisphere, New York. 91-98

PERRÉ, P.; MOSER, M. ; MARTIN, M. 1993. Advances in transport phenomena during convective drying with superheated steam and moist air. *Int. J. of Heat and Mass transfer* 36: 2725-2746

ROQUES, M. A. 1996. Environmental and safety issues in drying, *Drying 1996,* ed. C. Strumillo, Z. Pakowski and A. D. Mujumdar. 61-72

SHMULSKY, R. 2000A. Influence of lumber dimensions on VOC emissions from kiln-drying loblolly pine lumber. *Forest Prod. J.* 50(3): 63-66

SHMULSKY, R. 2000B. Influence of drying schedule on VOC emissions from kiln drying loblolly pine lumber. *Forest Prod. J.* 50(4): 45-48

SIAU, J.F. 1995. Wood : Influence of moisture on physical properties. Departement of Wood Science and Forest Products, Virginia Polytechnic Institute and State University, Virginia, USA, 227 p.

APPENDIX

To calculate the relative permeability, k_g, the moisture content X with following subscripts is used:

free free liquid

cr critical

sat saturation

X_{free} is calculated as following:

$X_{free} = X - X_{fsp}$,

where fsp is the fiber saturation point.