Colour Responses To Heat-Treatment Of Extractives And Sap From Pine And Spruce

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ABSTRACT

Scandinavian sawmills have over the last 20 years adopted ever-higher temperatures in the dry kilns. The reason for this has been improvements in drying quality and kiln capacity. However, some problems relate to this strategy, mainly discolorations and extensive resin flow from knots and heartwood in pine. In this study, underlying factors for changing wood colour were investigated for spruce and pine. From the sapwood portions of wood, sap was extruded by mechanical compression, put in glass bottles and heat-treated at different temperature levels ranging from 60 °C to 95 °C during 1 to 5 days. Then the colour of the sap was measured using a standard colorimeter. Extractives from pine heartwood were also heat-treated and analysed in the same way.

From these experiments it was concluded that much of the colour change in solid wood emanated from colour changes in constituents of the sap and extractives. Pine sap was more susceptible to colour change than sap from spruce. Also, an accelerated colour change was noticed above 70 °C for pine sap. Finally, it was observed that extracted wood that was soaked in water and then heat-treated still underwent some colour change, probably due to secondary hydrolysis of hemicelluloses.

INTRODUCTION

It is a well-known fact that wood changes colour during drying. Artificial air circulation drying of pine and spruce results in a more or less pronounced surface yellowing of sapwood. According to Terziev et al (1993) and Terziev (1995), yellowing of sapwood lumber is explained by the enrichment of sugar and nitrogenous compounds towards the timber surfaces during the initial, capillary phase of drying. Fast drying leads to an increased enrichment towards the surfaces. When this carbohydrate-enriched zone is being heated in the presence of amino acids working as catalysts, a degradation of the carbohydrates takes place at which coloured degradation products are formed. This is called Maillard reaction and is a well-known process within the food industry. Water storage of timber might also lead to a pronounced surface yellowing after drying, (Boutelje 1990, Theander et al 1993).

The development of kiln drying schedules for the industrial air-circulation drying of pine- and spruce timber has resulted in general increase of drying temperatures over the last 20 years in Scandinavia with such advantages as shorter drying time, fewer cracks and less deformation. Other consequences of higher drying temperatures are colour changes and darkening of wood but also an increase of resin flow especially around knots in pine.

Drying temperature, time, time in capillary drying phase (i.e. as long as free water is present in the timber) and water content are parameters that influence the colour change (Sundqvist 2000). According to Tarvainen et al (2001) colour change in pine heartwood increases markedly at drying temperatures exceeding 70°C, probably depending on the resin content. The same phenomenon is observed for pine- and spruce sapwood.

Wood properties that affect colour of wood during drying are extractive- and nutrition content. The concentration of soluble nutrition substances varies significantly during the year and reaches maximum levels during winter months (Terziev et al 1997, Hinterstoisser 1994, Höll 1985). According to Terziev et al (1997) the
carbohydrate content is more dependent on the time of the year than on growth conditions. Nitrogen content in pine sapwood varies less with the time of the year than does carbohydrate content. In sapwood the carbohydrate content increases towards the cambium.

In the sapwood zone where nutrition has been enriched during drying, a special type of dark discolouration called Kiln Brown Stain (KBS) often occurs at high temperatures with a typical depth of 1-3 mm beneath the surface (Kreber, Haslett 1997). Coloured substances that are formed during chemical reactions when carbohydrates degrade thermally cause KBS. When such timber is planed this dark zone is exposed which is a notable problem. The occurrence of KBS seems to vary in different species, and for Pinus radiata, a pronounced increase of KBS is reported at temperatures exceeding 60°C (Kreber et al 1997, 1998). KBS also appears when pine timber is dried (Sehlstedt-Persson 1995).

Resin flow around knots in pine timber increases markedly at higher temperatures. This appears as substantial dark brownish spots on the surface. However, this crystalline resin disappears after planing and causes no harm.

Aside from colour changes caused by yellowing, KBS and resin flow around knots and pitch pockets, a colour change in the wood substance itself may occur. When wood is heated, a thermal degradation dependent on temperature, time and moisture content takes place. Thermal degradation of wood increases markedly at temperatures over 120°C, but also occur at temperatures beneath 100°C when hemicelluloses are primarily affected. Degradation of the hemicelluloses results in a reduced hygroscopicity, since hemicelluloses foremost absorb water. Degradation substances from hemicelluloses may affect colour of wood.

Collected extracts from acetone-extracted pine and spruce samples also show variation in colour between sap- and heartwood but also between individual samples (Sehlstedt-Persson 2001).

MATERIALS AND METHODS

Timber

1.5 m sections cut from butt- and middle logs of pine and spruce timber felled in January 2002 from a stand near the seaboard of Västerbotten in northern Sweden were used in the tests.

Through careful planing of the trunk surface all remains of bark were removed before the sections were sawed into 4-5 cm thick laminae. The laminae were cut into pure sap- and heartwood sections, which were wrapped into plastic bags and kept in a refrigerator.

Sap

From the sapwood portions of each species, approximately 1.5 l sap was extruded by mechanical compression. The fresh sap was filtered in two steps: first through a roughing filter Munktell no 3 (filtration rate 700 ml/min Herzberg) followed by a second fine filtration through Munktell 00H (40 ml/min Herzberg). The filtered sap was divided into 30 ml glass bottles and stored in a refrigerator.

A TLC-test (Thin-Layer Chromatography) with petroleum ether-ethylc ether 85:15 as solvent showed no occurrence of remainders of extractives in the sap.

Extractives

Small samples cut from pine heartwood were extracted in a Soxhlet-extractor with reflux condenser for 24 hours with acetone 99.5% pro analysi (boiling point 56,2°C) as solvent. The extract was filtered through Munktell filter paper 00H to remove wood particles. The filtered extracts from each extraction were mixed in a glass container and kept in darkness.

Since extractions are time-consuming and only small amounts of solid wood samples are possible to use in each extraction, the study was limited to pine heartwood, with its higher extractive content compared to sapwood and spruce heartwood. A total of 15 extractions were done to achieve a sufficient amount of extractives.

The amount of extractives after evaporation of the solvent in a rotary evaporator was 35 gr. This amount was dissolved in 300 cl acetone and then distributed with an injection syringe into Petri dishes (diameter 80 mm, height 15 mm), 10 ml in each. The Petri dishes were kept without cover on a horizontal surface in darkness until the acetone evaporated, leaving the firm extractives evenly distributed on the bottom of the dishes. The Petri dishes were then covered with glass lids.

Heat-treatment

Heat-treatment of sap and extractives was performed in a heating chamber at 60, 70, 80, 85, 90, 95°C for 1, 2, 3, 4 and 5 days. Measurements with thermocouples and a datalogger showed that fluctuation in temperature regulation was ±0.5°C.

Colour measurements

Colour measurements were done using a Minolta CR 310 colorimeter with CIE L*C*h° colour system chosen according to the CIE standard (Hunt 1995). L*
is lightness, \( C^* \) is chroma or saturation and \( h^\circ \) is hue angle. The light source used was Standard Illuminant \( D_65 \) (average daylight including ultraviolet wavelength region).

The \( L^*C^*h^\circ \) values were transformed to \( L^*a^*b^* \) values in order to calculate the colour difference values \( \Delta E^*_{ab} \) according to the following equations:

\[
\begin{align*}
a^* &= C \cosh h^\circ \\
b^* &= C \sinh h^\circ \\
\Delta E^*_{ab} &= \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}
\end{align*}
\]

Note that \( \Delta E^*_{ab} \) states the extent of colour difference but not direction. The least colour difference \( \Delta E^*_{ab} \) possible for the human eye to distinguish corresponds to 1-3 units (Terziev, Boutelje 1998).

**Colour measurements of sap**

Using a colorimeter to measure colour in liquids is difficult, for example because of varying reflexion in the liquid surfaces. In order to avoid these difficulties, a relative method was used with colour measurements on filter papers (Munktell 00H, diameter 70 mm) soaked with heat-treated sap. Measurements were performed on both sides of each filter paper, centered on a calibration plate with colour coordinates \( L^* \ 96.65, C^* \ 3.28 \) and \( h^\circ \ 92.2 \), before they were soaked with sap. Two replicates were used for each treatment. The papers were then placed in plastic bowls (diameter 76 mm) and soaked with 10 ml of heated sap with an injection syringe. The bowls were kept in darkness while the water evaporated and then dried for 1 hour in 30°C, just before colour measurements were performed on each side of the papers.

**Colour measurements of extractives**

A relative method was used also for measuring the colour of the extractives. The measurements were made before and after heat-treatment through the bottom of the Petri dishes, which was covered with extractives. During measurement, the Petri dish (diameter 80 mm) was centered on the measuring unit of the colorimeter (diameter 53 mm) in a screen box of black cellulose plastic towards a reference panel of white MDF–board with coordinates \( L^* \ 92.6, C^* \ 3.17 \) \( h^\circ \ 94.8 \) (average values of 10 measurements with standard deviations 0.02, 0.01 and 0.7 respectively).

**Heat-treated wood samples**

Some preliminary tests with heat-treatment of extractive-free wood samples in wet and dry states were performed. 3 matched samples were cut from green pine heartwood. Two samples were extracted with acetone for 24 hours in a Soxhlet-extractor. One of the extracted samples was soaked in water in a sealed glass bottle. Heat-treatment of the samples took place during 4 days at 80°C: 1 extractive-free in the dry state, 1 extractive-free in the wet state and 1 unextracted in the dry state.

Also, two matched pairs cut from pine sap- and heartwood respectively were extracted and heat-treated at 90°C for 5 days, one from each pair in the wet state and one in the dry state.

**RESULTS AND DISCUSSION**

**Heat-Treated Sap**

Results from measurements on filter papers soaked with heat-treated sap are shown in figure 1. The results show a clear influence of temperature and time on \( L^*C^*h^\circ \) values. \( L^* \) and \( h^\circ \) decrease with time and temperature for both spruce and pine, i.e. the sap becomes darker and more reddish. The higher temperature is, the more \( L^* \) and \( h^\circ \) decrease with time. The saturation \( C^* \) increases with time and temperature.

Pine sap seems to be more susceptible to heat than spruce sap. Statistical tests of differences between average values between unpaired groups show that:

- At all temperatures spruce sap on the average was lighter than pine sap at a 1% significance level
- At all temperatures saturation \( C^* \) was higher for pine sap than for spruce sap on an average, at a 1% significance level
- Hue angle \( h^\circ \) at 60 and 70° was higher (more yellow) but at temperatures \( \geq 80^\circ \) lower (more reddish) for pine sap compared to spruce sap, at a 5% significance level.

For pine sap, the change of colour coordinates (mainly \( L^* \) and \( C^* \)) seems to accelerate at temperatures exceeding 80°. Spruce sap does not show the same behaviour.

Measurements shown in figure 1 include the coordinates of the filter paper itself. Calculation of the colour difference \( \Delta E^*_{ab} \) before and after soaking the papers with sap brings out the effect of the sap only, shown in figure 2. The value at time 0 corresponds to \( \Delta E^*_{ab} \) of fresh, unheated sap.

For both species \( \Delta E^*_{ab} \) increase with time and temperature and are in every case clearly visible for the human eye. On an average \( \Delta E^*_{ab} \) at all temperatures are higher for pine sap at a 5% significance level. An accelerated colour difference seems to occur for pine sap at temperatures >70°C.
Dry content and pH

By evaporating 50 ml of fresh, filtered sap the dry content of sap was found to be 0.32% in pine sap and 0.17% in spruce sap. The considerably higher dry content of pine sap probably explains the more pronounced colour change, since dry content indicates carbohydrate content.

Measurements of pH in fresh sap at a temperature of 15°C showed that spruce sap had a somewhat higher value of 5.46 compared to 5.10 for pine sap, which agrees well with data given by Fengel, Wegener (1984). According to this reference, the seasonal fluctuations in pH are small.

Multiple regression analysis

Multiple regression analysis of all data (a total of 144 measurements) with ΔE*ab for sap as a function of time, temperature and species gives the following linear model within the investigated intervals:

$$\Delta E_{ab}^* = 3.59 - 2.93 S + 0.048 T - 4.56 T_i + 0.078 T_i^2$$

where $T_i$ = time, number of 24-hour periods (0-5)

$T$ = temperature, degrees ° (60-95)

$S$ = species, 1 for pine and 2 for spruce

Regression models for each species are:

Pine:

$$\Delta E_{ab}^* = -1.43 + 0.066 T - 5.31 T_i + 0.09 T_i^2$$

$R^2=0.90$

Spruce:

$$\Delta E_{ab}^* = -0.19 + 0.03 T - 3.82 T_i + 0.066 T_i^2$$

$R^2=0.89$

Heat-Treated Extractives

The colour coordinates of the pine heartwood extractives, measured through the bottom of the Petri dish, show a marked influence of the heat-treatment; the colour becomes darker, the hue angle decreases (becomes more reddish) and the saturation increases with time and temperature as shown in figures 3 and 4.

The colour difference $\Delta E_{ab}^*$ before (corresponds to the state at time 0 in figure 3) and after heat-treatment is shown in figure 5.

Multiple regression analysis

Multiple regression analysis of the material (a total of 30 measurements) with $\Delta E_{ab}^*$ as a function of time and temperature gave the following linear model within the investigated intervals:

$$\Delta E_{ab}^* = -36.59 + 2.45 T_i + 0.65 T$$

$R^2=0.90$

where $T_i$ = time, number of 24-hour periods (1-5)

Heat-treatment of wood samples

The preliminary tests with heat-treatment of extractive-free wood samples heated in wet and dry states show that the moisture content in wood during heat-treatment is also of importance for the colour of the wood, figure 6. When extractive-free wood is heated in moist condition, the wood darkens and becomes reddish compared to wood heated in the dry state. The interpretation is that coloured degradation products are formed during hydrolysis of hemicelluloses.

CONCLUSIONS

- Heat-treatment of sap and extractives results in clearly visible colour changes. Lightness $L^*$ decreases, satuation $C^*$ increases and the hue $h^\circ$ moves towards red. The colour changes increase with time and temperature.

- Sap from pine shows significantly greater colour changes compared to sap from spruce at a 5% significance level. This difference is probably explained by the fact that the dry content in pine sap was higher, indicating higher carbohydrate content. Difference in pH values might have an effect as well. Only winter-felled wood was studied, which admits uncertainty since carbohydrate content fluctuates with seasons and species.

- In sap from pine an accelerated colour change is noticed at temperatures exceeding 70°C.

- Multiple linear regression models with the colour difference $\Delta E_{ab}^*$ as a function of time and temperature show $R^2$ (coefficients of determination) of approximately 90% for both sap and extractives.

- Preliminary tests with heat-treatment of extractive-free wood in dry and wet state show that heating in the wet state causes a notable change of colour. Formation of coloured degradation products deriving from hydrolysis of hemicelluloses might be the explanation.

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Figure 1 L*C*h° coordinates from colour measurements on filter papers soaked with heat-treated sap.

Upper row pine sap, lower row spruce sap 60° 70° 80° 90° +95°
Figure 2 \( \Delta E_{ab} \) for heat-treated sap at different temperatures.

\( \mathcal{S} 60^\circ \) \( \mathcal{O} 70^\circ \) \( \rho 80^\circ \) \( O85^\circ \) \( B 90^\circ \) \( +95^\circ \)

Figure 3 LCh colour coordinates for heat-treated extractives from pine heartwood

\( \mathcal{S} 60^\circ \) \( \mathcal{O} 70^\circ \) \( \rho 80^\circ \) \( O85^\circ \) \( B 90^\circ \) \( +95^\circ \)

Figure 4 Heat-treated extractives from pine heartwood.

Figure 5 \( \Delta E_{ab} \) for heat-treated extractives from pine heartwood.

Figure 6 Preliminary tests with extracted and unextracted pinewood, heat-treated in dry and wet states.