COLOUR CHANGES IN OAKWOOD DURING VACUUM DRYING BY CONTACT: STUDIES ON ANTIOXYDANT POTENCY AND INFRARED SPECTRAS IN SURFACES

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ABSTRACT

Manufacturing appearance products generally requires high-quality wood, which is expensive and not as abundant as lower-grade wood. The formation of coloured substances from phenolic compounds oxidized with air and the formation of dark materials from hydrolysis have been considered the causes of discolouration during drying. In order to reduce color changes, vacuum drying process can be used, which offers several advantages. In this work, antioxidant activities were evaluated from dust of oak-wood after vacuum drying and convective drying by using ABTS•⁺ cation (AAEAC method), DRIFT spectras are obtained, Cielab parameter were obtained with a colorimeter, and vacuum drying kinetics with conductive heating are presented for different drying conditions. The conductive heat source is maintained at different temperatures and pressure in the chamber is controlled at different intervals (60-100, 150-250, and 250-300 mbar). We found that lightness increases as temperature increases and C=O formation increases as antioxidant potency decreases.

KEY WORDS: colour, vacuum drying, oakwood, antioxidant potency

INTRODUCTION

Wood continues to be the overwhelming choice of customers, who often identify the most important attributes to be reliability, environment friendliness, pleasing appearance, and good value (Pakarinen 1999). Evidence suggests that the wood industry has an opportunity to capture the environmentally informed consumer by providing certified wood that is produced according to accepted standards of environmentally sustainable management; the customer’s perception of environmental impacts is beginning to influence the manufacturer's choice of materials (Bush et al. 1991, Meyer et al. 1992, Olah et al. 2003). The desire to create different or new appearances in furniture style led to the use of different manufacturing methods and materials, some examples are the invention of veneering and inlay, frame and panel construction, bending techniques, plywood and composite materials (Shelly 2001).

By far, the most common species used for furniture are hardwoods in solid wood form compared to softwoods, the higher density hardwoods have superior furniture manufacturing characteristics.
such as better machining and finishing, and higher strength (Wiedenbeck et al. 2003, Hansen et al. 2001). In addition, hardwoods often have more interesting application like appearance products. The term “appearance product” describes a number of finished products made from hardwood or softwood lumber. Typical products include treated wood for exterior use, sidings, decorative boards, moldings, window and door components, flooring, and furniture components (Flowers et al. 1990, Forbes et al. 1994, Bumgardner and Bowe 2002).

Proper drying of hardwoods has become quite important industrially as recent market requirements have been demanding that manufacturers provide wood that is attractive, and of a specified, uniform, and replicable colour (Hardwood Review Weekly 2002, Zanetti et al. 2003). Earlier studies by McMillen (1975) attributed chemical discoloration to the oxidation of chemical precursors present in wood. According to Charrier et al. (1992) and Koch et al. (2003), Ayadi et al. (2003) the formation of colored substances from phenolic compounds oxidized with air and the formation of dark materials from hydrolysis of hemicelluloses have been considered the causes of discoloration. When the material causing discoloration is water-soluble, these materials rise to the surface and accumulate there, discoloring the wood (Wiberg 1996).

After Yeo and Smith (2004), wood discolouration reactions are similar to the ones causing the browning of freshly cut fruit, occur in living parenchyma cells where they create amorphous globules of colored material. They found that discoloration phenomena would seem to indicate that presence of reactive oxygen with free moisture, in addition to elevated temperature, is an important component in the development of wood colour darkening during drying. Okuda et al. (1989) demonstrated that some phenolic compounds decompose quite rapidly in direct sunlight or if dried at elevated temperatures (T>40°C). In Oakwood, tannins have been related like responsible compounds of discoloration (Charrier et al. 1992, Burtin et al. 1998). A very larger number of hydrolysable tannins molecules exist in nature. The structural variation amongst these compounds is caused by oxidative coupling of neighbouring gallic acid units or by oxidation of aromatic rings (Fengel and Wegener 1989, Nonaka 1989, Okuda et al. 1990). Thompson et al. (2004) suggested than in the case of red alder wood, the thermally modified colour of wood depends on the strength of reactions that produce orange/red chromophores in the wood, thermal darkening of the wood, and destruction of orange/red chromophores. Furthermore, it is reasonable to suppose that factors such as the concentration of oxygen, moisture content and organic acid concentrations in the wood affect the colour of sapwood and heartwood differently during drying and heating (Kreber 2001, Grekin 2007).

On other hand, on the cell level, colour change may occur in cell walls due to changes in structural compounds (Kosiková et al. 1999, Alén et al. 2002) or it may caused by non-structural compounds. However, the relation of wood colour to anatomical characteristics has been studied very little. It is not known whether wood colour is dependent on cell wall and lumen size, and on other comparable cell characteristics. Luostarinen (2006) studied the discoloration of Birch wood after conventional and vacuum drying process and concluded that the characteristics related to parenchymatic cells of xylem were observed to affect colour in conventional drying and in vacuum drying wood. According to Zahri et al. (2007), a strong presence in phenolic components not protect completely against the wood discoloration and photo-degradation, and despite the antioxidant nature. Masson et al. (2000) have studied the effect of drying on the chemical composition of oak Quercus petraea Liebl. They found that part of hemicellulose (xylans and glucomannans) have been degraded during drying.

Colour and its relation to wood components

The origin of colour in natural wood has been reported to be related to chromophores among extractives (Hon and Glasser 1979, Burtin et al. 1998, McDonald et al. 2000, Koch et al. 2003, Hiltunen et al. 2006, Grekin 2007) as well as chromophoric groups in the lignin (Falkehag et al.
Wood is an excellent material to absorb and reflect light. The electron of an unsaturated bond (e.g., >C=O, >C=NH, >C=N-) can transfer easily to an excited state with a small amount of energy. In molecules containing many insaturated groupings that all are conjugated, the molecular orbitals containing the electrons in the system will extend over these groups. An atomic group having a π electron, such as an unsaturated bond, is called a chromophore. An atomic group having isolated electron pairs such as –OH, COOH, and –OR is called an auxochrome. Auxochromes assist the action of chromophores by intensifying the colouration or enabling the absorption of light having a longer wavelength (Hon and Shiraishi 1991).

Vacuum drying

A primary attraction of vacuum drying is the reduced drying times and higher end product quality that it offers in comparison with conventional drying operations (Ressel 1994). The level of vacuum generated varies with the specific systems but is generally in the range of 50 to 200 mbars. In vacuum systems water boils at lower temperature and offers the possibilities of preventing atmospheric emissions, since during wood drying a complex mixture of chemical compounds is released (Cronn et al. 1983, Risholm-Sundman et al. 1998). According to Ashida (2006), indoor air pollution by volatile organic compounds has become a serious problem for human health. HCHO emissions from wood-based materials are now legally regulated and standardized in European countries, the USA and Japan. Bucko et al. (1993) have identified the composition of vacuum kiln condensates resulting from the drying of oak; they found than condensates were highly acidic pH (3.0-3.6) and had a high chemical oxygen demand, for that, by operating at low pressures, disponibility of oxygen is reduced, and at a lower temperature, there is considerably less potential for staining wood. Moreover vacuum drying enables an important overpressure inside the material which enhanced internal moisture migration (Jomaa and Baixeras 1997, Björn 2002).

MATERIAL AND METHODS

Antioxidant potency

European oakwood samples were obtained from a freshly felled 100-year-old Quercus Pedonculae tree from a forest-land in Pessac-Toctoucau, in France. In our analysis we have put attention to avoid enzymatic reactions, so samples were stored at -30°C. For each drying experiment, 3 mm of the wood-disks was surfaced, then the particles were obtained with a wood-rasp (8g/sample), wood chips were passed in a teaspoon to homogenise the particles. Antioxidant capacity is measured for wood fine powder (0.06g per sample). The ABTS-ca scavenging was used to determine the antioxidant activity in wood samples. The amount of antioxidant capacity was calculated as ascorbic acid equivalents from the calibration curve (Packer and Cadenas 2001).

FTIR

Fourier Transform Infra Red (FTIR) spectroscopy has been found effective to analyse the chemical structure of wood (Pandey and Pitman, 2003). FTIR spectra of the ground wood samples (100 µm-sieved) were acquired with a Bruker EQUINOX 55 spectrometer (Bruker Optics Inc., Ettlingen, Germany) over the range 4000-400 cm⁻¹ and with a resolution of 4 cm⁻¹. Peak height was measured (Pandey and Pitman, 2003). Fig. 1 shows the FTIR spectra for each dust sample after vacuum and convective drying at different conditions. We measured peaks at 1741, 1595, 1505 and 1460 cm⁻¹.
Drying kinetics

Six drying kinetics are shown in Fig. 2. Naturally moisture content variation of wood always shows a variation. Temperatures in wood behaviour, during a vacuum drying experiment at 70°C, are displayed in Fig. 3. The positive impact of the internal pressure gradient within lumber is the primary motivation for drying at low pressure. In this case, a reduction of external pressure allows high temperature conditions to be attained for species that do not usually accept high temperature levels.

Fig. 2: Vacuum (VD) and convective Drying (CD) kinetics

Fig. 3: Temperature profile in wood during vacuum drying
The L*a*b* color space (also referred to as CIELAB) is presently one of the most popular color space for measuring object color and is widely used in virtually all fields. The L*C*h color space uses the same diagram, but uses cylindrical coordinates instead of rectangular coordinates. In this color space, L* indicates lightness and is the same as the L* of the L*a*b* color space, C* is chroma, and h is the hue angle. The value of chroma C* is 0 at the center and increases according to the distance from the center. Hue angle h is defined as starting at the +a* axis and is expressed in degrees; 0° would be +a* (red), 90° would be +b* (yellow), 180° would be −a* (green), and 270° would be −b* (blue). We are interested to compare the color saturation (C*) of powders for all vacuum experiments. Fig. 4 it may be noted, particularly in the case of powders sampled near the plate (heat source by contact), that saturation increase as temperature increase, so color becomes more vividness.

We investigated color changes in surfaces since, sugars, phenols, antioxidants and other extraneous substance could have been transported from the centre to the surface layer with the evaporating water (McMillen 1975, McGuinnes and Rosen 1984, Kosikova 1999, Kang 2006, Koch and Skarvelis 2007). It is well known that in several processes at the contact surfaces, these materials are exposed to high temperatures above 60°C. The heat induces thermal processes which usually lead to non-benefecial effects such as yellowing. Yellowing of wood to the formation of groups that contain oxygen, as the carbonyl groups, carboxyl, and hydrogen peroxide, the comments we have also noticed (Okuyama et al. 1990, Grekin 2007).

Fig. 4: Color saturation versus temperature

Fig. 5 shows the values of hue angle for all experiences. The overall trend imply the angle of hue is more marked for wood exposed to highest temperature, so wood shows a tendency to change from a red to a yellow hue. Yellowing can be caused by a degradation of phenolics compounds. According to Hon and Glasser (1979) the yellowing of wood is caused mainly by lignin and lignin derivatives. Lignin is held together by various chemical bonds. It is well known that during thermal treatment, the extent of alterations depends on the chemical composition of the material used. Therefore, the degradation varies within the wood species and the respective chemical composition and does not proceed to the same degree (Windeisen et al. 2007). The higher yellowness of the discoloured surface layer could be partly caused by the low-molecular-weight phenolic extractives, which mostly are pale yellow substances (Hiltunen et al. 2006). For instance, if the hardwood lumbers are kiln-dried in severe conditions (above 60°C drying temperature and 65% relative humidity), wood surface colour darkens as a result of the chemical changes in structure of lignin and hemicelluloses, we found the inverse, but
we remember the reader what in our experiments, vacuum drying was conducted without superheated vapour assistance, we applies plain vacuum drying, so wood is heated by the heat plate and drying agent not exist since to the vacuum atmosphere. Moreover, temporary accumulation of VOC’s in dryer can catalyses chemical reactions in wood surfaces (Schniewind 1984, Bucko et al. 1993), then chemical reactions are very complex to understand.

![Diagram](image1)

**Fig. 5: Hue angle versus temperature**

The lightness values are represented in Fig. 6. Brightness in the surfaces in contact with the heat source becomes more important. Therefore we could think that the increase in brightness is caused by the effect of a higher temperature. This fact can be linked with the thermal degradation of extractives, allowing a yellow tone and clarifying the surface.

![Diagram](image2)

**Fig. 6: Lightness and average temperature**

In all range of temperature, differences in tone from both sampling areas are well differentiated by color. The hue parameter in the surface samples are larger, reflecting the fact that the color of the wood tone evolves from a red to a yellow tone. Fig. 7 shows the relationship between brightness and color saturation of the wood-powder; an increase in the saturation of color is linked to an increase in the brightness of wood.
Fig. 7: Color Saturation and Lightness

Despite the application of similar drying conditions, variations in hue parameters between these two series are very likely due to variability in phenolic components concentration. We know that in the case of oakwood, ellagitannins are more chromophores that their products of oxidation (Hemingway and Hillis 1971, Nonaka 1989). The components are phenolic substances reddish tone, so color degradation is consistent with a yellow tone trend of wood color. Even when we imposed low temperature, the color of the wood can be altered from 43°C (Yeo and Smith 2004). In theory, the oxygen reactivity is higher in the presence of open water (W>W_{psf}) (Sundqvist 2002). That is why some works have tried to elucidate mechanisms of wood discoloration above from the saturation point of the fiber.

The increase in saturation and brightness can be linked to the thermal degradation of extractives (ellagitannins mainly). The coloration of the wood becomes more vividness. The brightness can be explained by a loss of phenolic compounds. In addition, the values of saturation may be linked to the degradation of hemicelluloses (Beall 1970, Hill 2006). It is well known that the extractives have antioxidant properties that may restrict the color changes during drying, these properties limiting damage caused by oxygen free radicals (Hiltunen et al. 2006). In the absence of oxygen, depolymerisation reactions can take place (Feist et al. 1973). According to Okuda et al. (1989), phenolic compounds are degraded easily at low temperatures. Complex structures of tannins are affected by water and acids. Dawson (2004) defined the discoloration as a decrease in brightness (L*) of wood, and an increase in chromaticity coordinates (a* and b*). We found the opposite results, because our values of brightness increases with temperature, these discussions are completed at the end of this paper.

In the other hand, Kang (2006), conducted various experiments drying on three species of Korean pine. He found that the parameter L* increases when the temperature increases. Okuyama et al. (1990) has also seen an increase in brightness by thermal effect at the black heartwood of Japanese cedar. Zanetti et al. (2000) studied photodiscoloration of sessile oak (Quercus petraea Liebl) using a spectrophotometer. They observed during a cycle of 500 hours-ageing two phenomena: in the first one a darkening accompanied by a yellowing of wood, and an increase of the saturation of color. The second reflect a decrease of saturation, a reddening of wood color and more important brightness of wood.

Hydrolysable compounds in the presence of free water and heat can produce gallic acid, ellagic acid and glucose. These acids may also play a role as catalysts for reactions, which complicate the understanding of discoloration phenomena. The products from hydrolysis of ellagitannins are less chromophores that the constituents of origin (Hemingway and Hillis
An increase of saturation and ellagic acid may give rise to a decarboxylation, and oxidation products. We show in Figure 8 all intensities of peak C=O powder at different temperatures. We can see the positive effect of temperature on the generation of carbonyl group (oxidation reactions products). In addition, the spectra show a slight increase in the presence of lignin most probably due to the weakening of carbohydrates by thermal effect.

**Fig. 8: Intensity C=O versus temperature**

In Fig. 9 we present the deltas of the antioxidant potential of wood sampled near from the hot plate and the loss in potential antioxidant. C=O intensity increases as delta in antioxidant potency increases. An increase in carbonyl intensity is observed for samples that have shown more important deltas (antioxidant potency losses). Then we can suggest that formation of oxidation products (increase the intensity of C=O) is linked to a loss in potential antioxidant and that these phenomena are enhanced by a rise in temperature (the side in contact with the hot plate being hotter on average 14 °C).

**Fig. 9: C=O intensity and Delta of antioxidant potency**
DISCUSSION

In order to explain colour changes in Oakwood during vacuum drying by contact, three mechanisms discoloration oak can be disputed. The first one, the volatile components emissions (VOC’s), the second one is the degradation of ellagitannins (hydrolysable tannins) and the third one the loss or alteration of carbohydrates (hemicelluloses). It is well know that VOC’s emissions occurs during drying, these compounds can catalyze the hydrolysis reactions in wood components, ellagitannins can contribute to the formation of oxidation products, and hemicelluloses are degraded by thermal effect, allowing an intensification of signal lignin in infrared spectra. In the absence of oxygen, depolymerization reactions occur. The ellagitannins are antioxidants compounds, but they are hydrolysables in the presence of free water and heat, then it is possible to produce gallic acid, ellagic acid and glucose during drying. Concerning antioxidant potency, we found that as antioxidant potency decrease as peak 1741cm⁻¹ increase. This fact is linked to the formation of oxidation products (oxidation of ellagitannins) as a consequence of antioxidant potency degradation.

About wood carbohydrates, hemicelluloses are rich in hydroxyl groups, which are responsible for the sorption moisture in the wood. The hemicelluloses are made up of polysaccharides, which can be deteriorated during drying, allowing an intensification of lignin spectra (Hill 2006). The increase of peak at 1741cm⁻¹ is related to the losses in antioxidant potency, mainly ellagitannins. The hemicelluloses are amorphous, with OH-groups available at the cell walls and presence of water and air can accelerates the formation of organic acids (acetonic acid). These acids catalyze the hydrolysis hemicelluloses (Mitchell 1940), so chemical reactions become more complex to identify, since this degradation produces methanol, acetic acid and components heterocyclic. Color, appearance and surface quality become an industrial preoccupation, since during the manufacture and processing of ligno-cellulosic materials, surfaces are necessarily in contact with heating surfaces at different temperatures, so thermal gradients, pressure, humidity, target with the quality of these materials.

CONCLUSION

According to our results, one key to control colour of wood surfaces during drying may lie meanly in the balance of temperatures during the drying process. The large thermal gradients inside wood produce significant differences in the colour of surfaces of different layers. Hence, it is important to have adequate heating systems to improve the heat transfer between layers of wood during drying. The positive impact of the internal pressure gradient within lumber is the primary motivation for drying at low pressure. In this case, a reduction of external pressure allows high temperature conditions to be attained for species that do not usually accept high temperature levels. According to experimental results vacuum drying offers a shorter time process respect to convective drying. Finally, according to results we found that increasing of color saturation is linked to the antioxidant potential loss, and to a more important presence of lignin linked to the loss of hemicelluloses. The lightness of wood surfaces increases as drying temperature increases, carboxyl groups increases as antioxidant potency decrease. Matching color in wood products is important, since color is an indication for the acceptability of a product and color is associated to the product quality and pleasant appearance.
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