Hydrothermal treatment (steaming) under atmospheric and pressure conditions

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Summary

Hydrothermal treatment (steaming) was carried out to study the effect of steaming parameters on the colour change and homogenisation of black locust heartwood. Under atmospheric conditions and maximum temperatures from 95°C (industrial steaming) to 98°C (laboratory) the minimum time to effect desired colour changes was found being four days. Under pressure conditions (semi-industrial steam vat) best results were obtained in a temperature range of 120 to 130 °C for a minimum of 2 hours of steaming time. The resulting wood surface colour can be effectively controlled by the parameters time and temperature. Surfaces of steamed wood are less susceptible to colour changes under exposure to UV-radiation than natural wood surfaces.

Introduction

Black Locust heartwood has by nature a yellowish to greenish brown colour caused by a number of chemical substances such as robinetin and dehydrorobinetin deposited in cell lumina and cell walls. Marketing of products made from Black Locust in its natural colour has met with serious problems for two reasons: a) the natural wood colour is not to the taste of most consumers, b) it is unstable under the influence of light. In order to be competitive on the market the colour appearance of products made from Black Locust, particularly those for indoor use with large exposed surfaces such as flooring or furniture fronts, needs to be technically modified and/or stabilised at some point during downstream processing.
The objective of this study was to investigate the technical feasibility as well as economic and environmental viability of industrial and laboratory scale techniques to modify and stabilise the colour of Black Locust heartwood by steam treatment under atmospheric and pressure conditions.

Part I: Steaming under atmospheric conditions

Material

Industrial steaming: 25-25 sprout and seed origin boards, respectively, with dimensions of 2500 x 250 x 60 mm³ and 75-75 sprout and seed origin boards, respectively, with dimensions 2500 x 250 x 40 mm³ were treated in an industrial steam vat at MAVFAVED company, Dombovar, Hungary.
Laboratory steaming: Specimens were prepared with dimensions of 300 x60x22mm; only material free of defects was used for the tests.

Methods

Industrial steaming: Heavy cracks which had developed in some boards due to internal stresses were first secured by clamps. Moisture content of the material destined for the steaming operation was determined before and after steaming. Steaming temperature was 95°C. Effective steaming time was 100 hours, preceded by a ten hour preheating and followed by a ten hour cooling period. After a general visual assessment, 10-10 boards were randomly selected and sampled for comparative colour measurements before and after the industrial hydrothermal treatment according to the methods described in detail in the next paragraph

Colour measurements: The wood surface colour was determined with a MINOLTA 2002 colorimeter. The reflection spectrum was measured in the 400-700 nm region. From these data the L*, a*, b* colour co-ordinates were calculated based on the D65 light source. Colour measurements were taken at 10 randomly chosen spots for each specimen and the results were used for further analyses.

Laboratory steaming experiments: Steaming was done in a steam chest at 100% relative humidity and temperatures of 90^0C, 95^0C and 98^0C. Wood specimens were placed in a large desiccator with distilled water for conditioning (maintaining maximum relative humidity). The desiccators were heated in a drying chamber to the indicated temperatures. The steaming process started with a six hour heating process. The temperature was regulated automatically around the set values $\pm$ $0,5^0$C. Specimens were removed after 1, 2, 4, 6, 9, 12, 18 and 22 days. The steaming was continued until the colour became stable, i.e., no further change could be observed by visual assessment. Generally, this situation was reached after 18 to 22 days. The steamed specimens were subsequently conditioned for one month at room temperature before making colour measurements.

Results

Industrial steaming

After termination of the hydrothermal treatment, the test boards were assessed visually. During steaming, additional end-checks had developed, especially in centrally cut boards containing pith. Initial moisture content (before steaming) varied between 24% and 30%, final moisture content (after steaming) between 31% and 42%.
For comparison of the results from industrial and laboratory steaming experiments, the L*, a* and b* co-ordinates of the boards selected for colour measurements before and after industrial steaming are depicted against those obtained from laboratory steaming in figures 3 and 4.

Laboratory steaming

The effect of chemical changes induced by steaming can be observed with the naked eye after several hours of treatment. The specimens become visibly darker and the colour changes from the unattractive greenish yellow to subjectively more acceptable reddish and brownish hues. The degree of colour change also depends on the original colour of the specimen. No significant differences in terms of colour change by steaming were observed between material originating from sprout and seed, respectively. Hence, all data were analysed together.
The visual observations described above are confirmed by objective colour measurements. The rather wide variation of the natural colour of Black Locust heartwood is shown in figure1, where the location of numerous colour spots of randomly chosen untreated (non-steamed) specimens are plotted in the a*b* co-ordinates.

Colour depth of red (a*) and yellow (b*) components

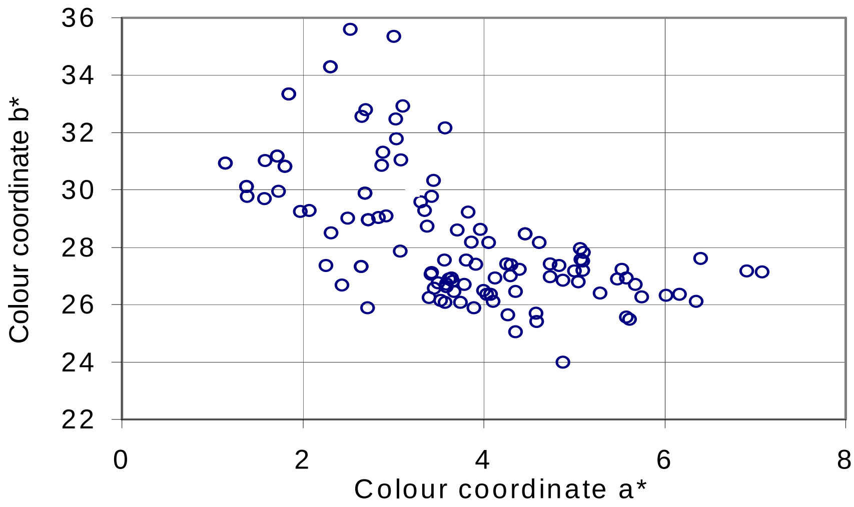

Figure 1: Natural variation of Black Locust heartwood colour depicted in the a(red) and b*(yellow) colour co-ordinates.*

This very obvious inhomogeneity in colour can be reduced by steaming. The respective results are shown in figure 2. where corresponding colour measurements taken after steaming at 98^{0}C temperature are plotted in the a*b* co-ordinates as a function of time.

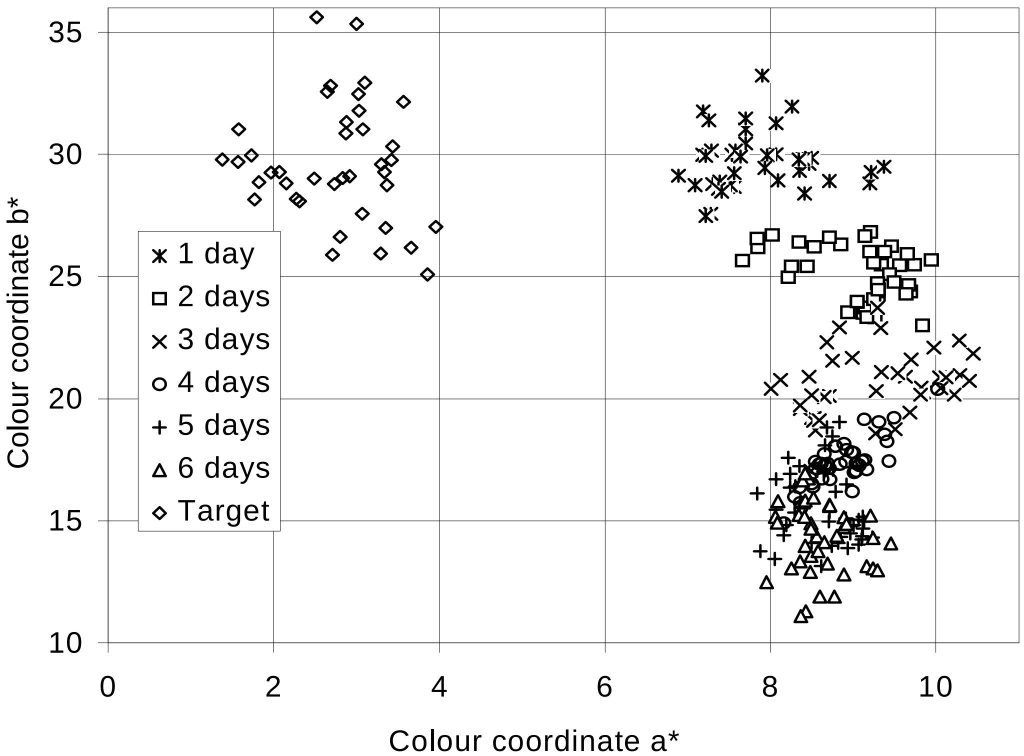

Figure 2: Colour change and homogenisation of Black Locust heartwood as a function of steaming temperature (98oC) and time as compared with untreated controls (target, upper left).

Tables 1(a-c) contain the statistical parameters of colour measurements, i.e., mean and standard deviation of brightness (L*) and colour co-ordinates (a*, b*) in the CIE L*a*b* colour system determined for the three selected steaming temperatures. Each mean value represents 100 individual measurements (10 specimens x 10 measurement spots).

Table 1a: Means and standard deviation for brightness (L), red (a*), and yellow (b*) components after steaming at 90°C as a function of time (days).*

	Steaming at 90°C					
time	L*	L*	a*	a*	b*	b*
(day)	Mean	St.dev.	Mean	St.dev.	Mean	St.dev.
0	72,28	4,23	3,78	1,03	30	1,6
1	63,62	2,65	6,18	0,35	29,2	1,5
2	60,7	0,74	7,771	0,32	25,67	0,79
4	55,5	0,75	8,91	0,23	24,31	0,4
6	51,36	1,3	10,08	0,51	19,63	0,83
9	45,86	0,45	9,26	0,2	16,48	0,31
12	45,52	0,5	9,21	0,18	16,26	0,46
15	44,02	0,7	9,67	0,26	14,05	0,63
18	45,49	1,4	9,93	0,41	15,66	0,71
22	42,85	0,4	10,24	0,11	16,81	0,21

Table 1b: Means and standard deviation for brightness (L), red (a*), and yellow (b*) components after steaming at 95°C as a function of time (days).*

	Steaming at 95°C					
time	L*	L*	a*	a*	b*	b*
(day)	Mean	St.dev.	Mean	St.dev.	Mean	St.dev.
0	73,15	4,41	3,2	0,65	31	1,8
1	68,5	2,71	6,14	0,29	30,79	0,85
2	61,29	1	8,48	0,67	27,21	1,49
4	54,04	0,26	9,09	0,48	22,09	1,38
6	46,19	1	8,32	0,31	16,2	1,19
9	44,46	1,14	8,6	0,25	15,77	1,97
12	43,18	1,65	8,54	0,46	14,21	1,25
15	42,38	1,6	7,88	0,18	12,5	1,04
18	41,25	1,7	8,18	0,33	14,7	1,1
22	41	0,6	8,58	0,28	15,62	0,72

Table 1c: Means and standard deviation for brightness (L), red (a*), and yellow (b*) components after steaming at 98°C as a function of time (days).*

	Steaming at 98°C					
time	L*	L*	a*	a*	b*	b*
(day)	Mean	St.dev.	Mean	St.dev.	Mean	St.dev.
0	70,86	4,14	2,76	0,66	29,9	2,4
1	63,48	3,13	7,87	0,61	29,5	1,2
2	57,62	1,44	9,06	0,58	25,12	1,1
4	49,95	1,58	8,87	0,38	17,37	1
6	42,62	1,2	8,65	0,35	14,32	1,46
9	39,92	0,12	8,06	0,13	11,39	0,43
12	39,26	2,2	8,13	0,79	10,9	2,2
15	38,38	0,36	8,05	0,17	10,34	0,41
18	37,32	1,01	7,76	0,24	10,41	0,65
22	36,93	0,75	7,05	0,43	10,3	0,74

The colour changes taking place during steaming can be followed more clearly in Figure 3 where the colour spot population means determined at 90^{0}C, 95^{0}C and 98^{0}C steaming temperatures are plotted simultaneously. Colour spots at the upper left represent the 0-time level (untreated wood), followed towards the lower right by those representing treated wood after 1, 2, 4, 6, 9, 12, 15, 18, 22 days of steaming.

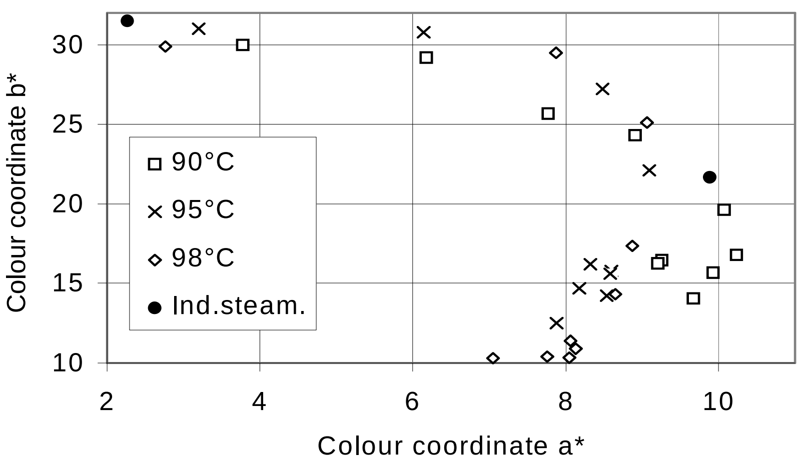

Figure 3: Colour changes in the a(red) and b*(yellow) coordinate system after steaming at various temperatures as a function of time (each spot represents the mean of 100 individual measurements).*

Brightness

Changes in brightness (L*) were also recorded as brightness forms an integrated part of the CIE L*a*b* colour system and invariably contributes to the subjective colour sensation of the human eye. The results are plotted in Figure 4. Accordingly, brightness decreases with increasing temperature as well as steaming time with the decrease being proportionally more effective in the first 6 to 7 days and more or less levelling out as of the 10^{th} day.

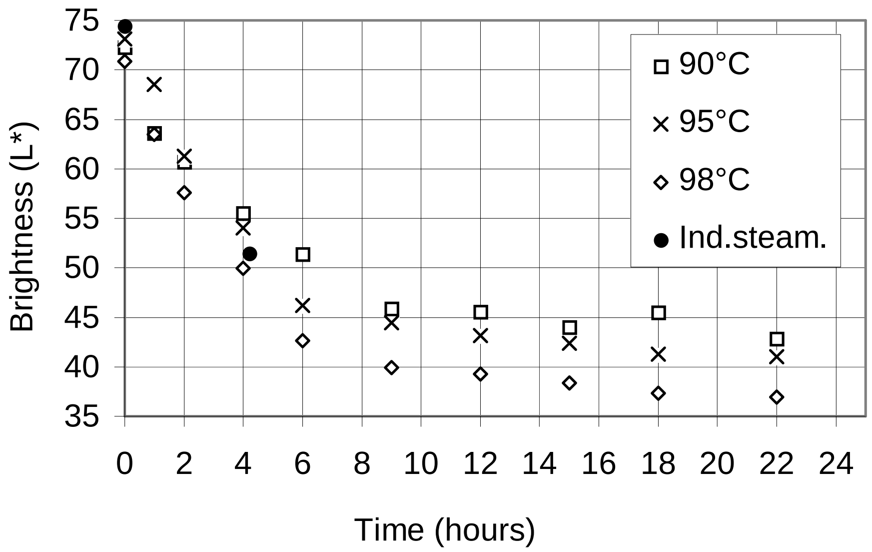

Figure 4: Changes of brightness due to steam treatment as a function of temperature and time (each spot represents the mean of 100 individual measurements).

Uniformity of colour changes

Colour changes brought about by industrial and laboratory steaming experiments were evenly distributed over the entire cross section of the specimens irrespective of the thickness. Thus uniformity of the colour modification achieved by steaming is considered a major advantage as compared to surface treatment by pigmented stains or finishes. Reprocessing of manufactured products, be it by sanding (e.g., floors) or other processes, does not bear any risk of jeopardising the preselected colour of the wood surface.

Discussion

Colour of untreated black locust wood is extremely heterogeneous as shown in figure 1, where the measured colour spots are spread over a large area within the a* and b* colour co-ordinates. Considerable differences can be observed and measured even within one specimen, more so between specimens. The natural colour spectrum is dominated by either yellow or red hues. These colour shifts cause the wide variation characteristic for the well-known colour heterogeneity of Black Locust wood in its natural state.
Steaming considerably decreases the inhomogeneity of colour and effectively shifts the underlying hues towards the red component as shown in figure 2. Colour variation decreases noticeably already after a one day steam treatment and continues until the fourth day. From this point on subsequent colour change becomes very slow.

Colour spots plotted in figure 3 display a horseshoe form. During the first day the colour is shifted towards red (increasing a* value). This change is followed by a rapid loss of yellow (decreasing b*). After nine days further colour changes become almost unnoticeable. Higher temperatures tend to speed up colour changes as shown by the increasing distance between neighbouring colour spots. The final colour depends primarily on the steaming temperature. Higher temperatures cause a quicker shift towards dark-brown hues.
As regards brightness (L*), figure 4 indicates a rather rapid decrease during the initial phase of steaming followed by hardly any alteration after nine days of steaming. In analogy to colour depth final brightness is also influenced by temperature, the darkest level reached at the highest temperature level.
The colour change of Black Locust during steaming is presumably linked to chemical changes of the heartwood extractives. The rapid colour change at the beginning indicates the sensitivity and instability of the two major compounds of Black Locust heartwood, robinetin and de-hydrorobinetin. The temperature induced degradation of this molecules produce the brown colour during steaming.
The final colour isnot restricted to any particular region (surface or interior) but is uniformly distributed over the entire cross section. There is no danger of secondary modification by further processing or subsequent exposure to UV-radiation.
The pH value of the steaming effluents containing water soluble compounds shifts towards the acidic side (decreases) with rising temperature and steaming time to values as low as pH 3, independent of the wood/water mass ratios in the steaming chamber at the beginning of the steaming process. The strong acidity of the effluents constitute a considerable process risk due to premature corrosion of the steaming equipment.
Revealing of the components of the residual water and how to neutralise them need further investigations.

Part II: Steaming under pressure

Summary

According to previous experiments conducted at HAMBURG on a laboratory scale, pressure steaming proven an effective and time saving means of controlled colour changes of Black Locust wood (Kühl 1997[1]). Subsequently a second series of experiments with pressure steaming was initiated with a specially designed, semi-industrial autoclave large enough to accommodate boards up to 200 cm in length and 25 cm in with, with a thermostat-controlled temperature range from 85°C to 180°C and a pressure range of up to 13 bar. By means of a series of preliminary experiments with temperatures up to 170 °C over periods ranging from 2 to 48 hours, an optimum temperature range of 110 to 130 °C was determined. Within this temperature range Black Locust can be steamed without any noticible additional defects (deformation, checking, etc.) to any desired colour by varying the parameter time to be set anywhere between 2 and 4 hours.

Material

Boards of up to 200 cm in length, variable width, and 30-40 mm in thickness were used for further controlled experiments with green (intitial MC around 30%) wood. Boards were then crosscut and corresponding specimens subjected to two drying-steaming cycles:

[1] Kühl, J. (1996): Farbveränderungen an Robinienholz (*Robinia pseudoacacia* L.) mit Hilfe technischer Maßnahmen. Diplomarbeit, Fachbereich Biologie, Universität Hamburg.

R1: drying (target MC 12%) followed by steaming
R2: steaming followed by drying (target MC 12%)

For comparison (reference material) 36 additional boards were kiln-dried in a vacuum-superheated steam kiln to a target MC of 12%.

Methods

Steaming parameters were set as shown in table 2. The development of temperature and pressure during the steaming operation (steam generator and autoclave) at a nominal 130°C is shown in figure 5, depicting warming, heating and cooling phases.

Table 2: Settings of time and temperature for 6 experimental steaming cycles.

Time [hours]	85°C	110°C	120°C	130°C
2				
4				
48				

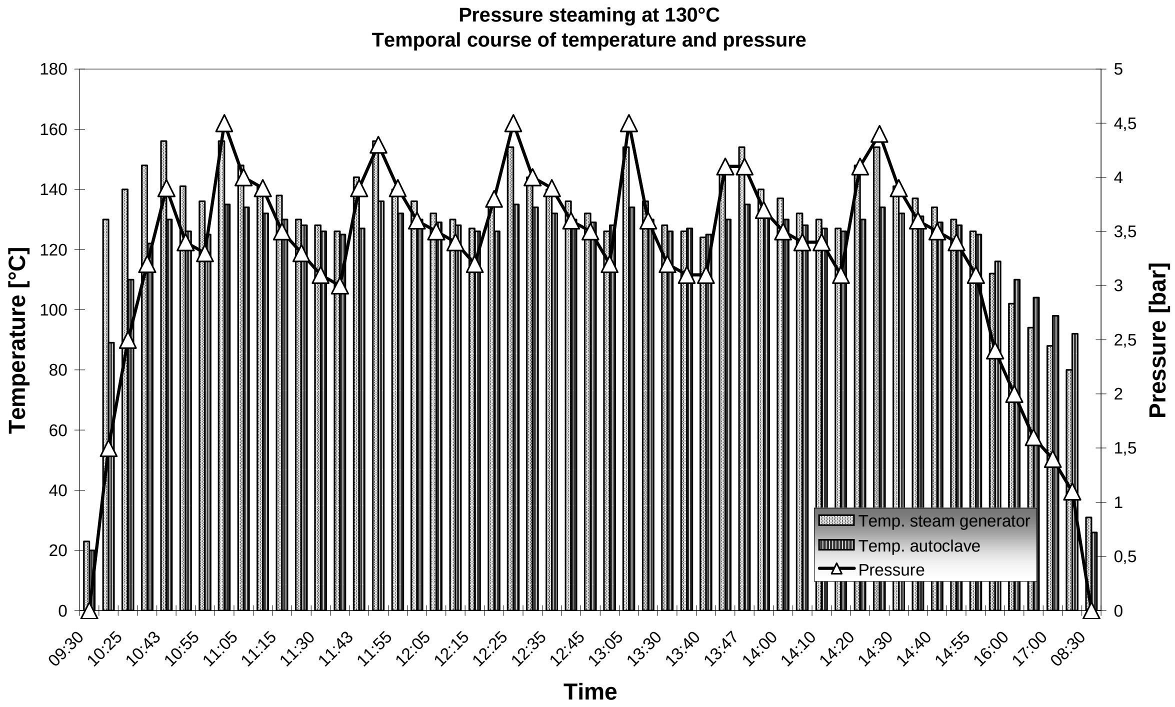

Figure 5: Course of temperature and pressure during a 130°C steaming cycle indicating the temperature during warming, heating and cooling phases for steam generator and steam vessel

Colour measurements: The wood surface colour was determined with a MINOLTA 2002 colorimeter. The reflection spectrum was measured in the 400-700 nm region. From these data the L*, a*, b* colour co-ordinates were calculated based on the D65 light source. Colour measurements were taken at 12 randomly chosen spots for each specimen and the results were used for further analyses.

Side hardness: Under the asumption that flooring will be the major enduse of Black Locust wood where colour is a decisive factor in customers' decisions for one or the other product, and based on the previously gained knowledge that steaming can reduce strength properties of wood, the influence of pressure steaming on surface hardness was also checked according to DIN C 3011 (determination of BRINELL hardness).

Sorption behaviour: Thermal treatment is known to have a more or less significant effect on the sorption behaviour of cellulosic materials prompting a permanent decrease in the hygroscopicity of wood with an accompanying reduction in swelling and shrinking. This loss of hygroscopicity is believed to be due to the decomposition of the hemicelluloses and a resinification of their breakdown products (Stamm 1964[2]). As sorption behaviour is a critical factor in dimensional stability of wood, the equilibrium moisture content of the steamed material was determined and compared with that of the unsteamed controls.

Results

The colour changes of Black Locust wood resulting from pressure steaming follow exactly the same pattern as described for steaming under atmospheric pressure. However, they occur in only small fractions of the time (figure 7, last page). The most drastic colour changes are brought about at temperatures of 120^{o}C and 130^{o}C. Considerable changes in colour can be already observed after 2 hours of steaming time. At the 120^{o}C level brightness continues to decrease significantly with a further increase in time. At the 130^{o}C level additional steaming time has no such effect, the heat-induced chemical reaction of the accessory compounds appear to have reached its termination at this point.
The variation of the red (a*) and yellow (b*) colour components decreases with increasing temperature. At the 130^{o}C level the greenish hues of the natural wood colour have disappeared after two hours of steaming. Holding the steam treatment beyond this time does not significantly alter the red (a*) and yellow (b*) values. At temperatures below 120 ^{o}C the same level of colour change can be attained only by considerably extending the steaming time.

None of the different steaming cycles has caused any significant decrease of the surface hardness. The variation observed is within the density dependent natural range of Black Locust wood.

An increase in steaming temperature improves the sorption behaviour of the wood. Equilibrium moisture content of the wood steamed at the two highest temperature levels decreased by an average of 1.5% compared to the unsteamed reference material (see figure 6). Similar results have been reported by Babiak & Németh (1998[3]). This decrease in equilibrium moisture content remains stable also under prolonged steaming cycles.

[2] Stamm, A.J. (1964): Wood and cellulose science.The Ronald Press Company, New York.
[3] Babiak, M. & R. Németh (1998): Effect of steaming on the sorption isotherms of black locust wood. In: Environment and Wood Science, Acta Facultatis Ligiensis, University of Sopron, Hungary.

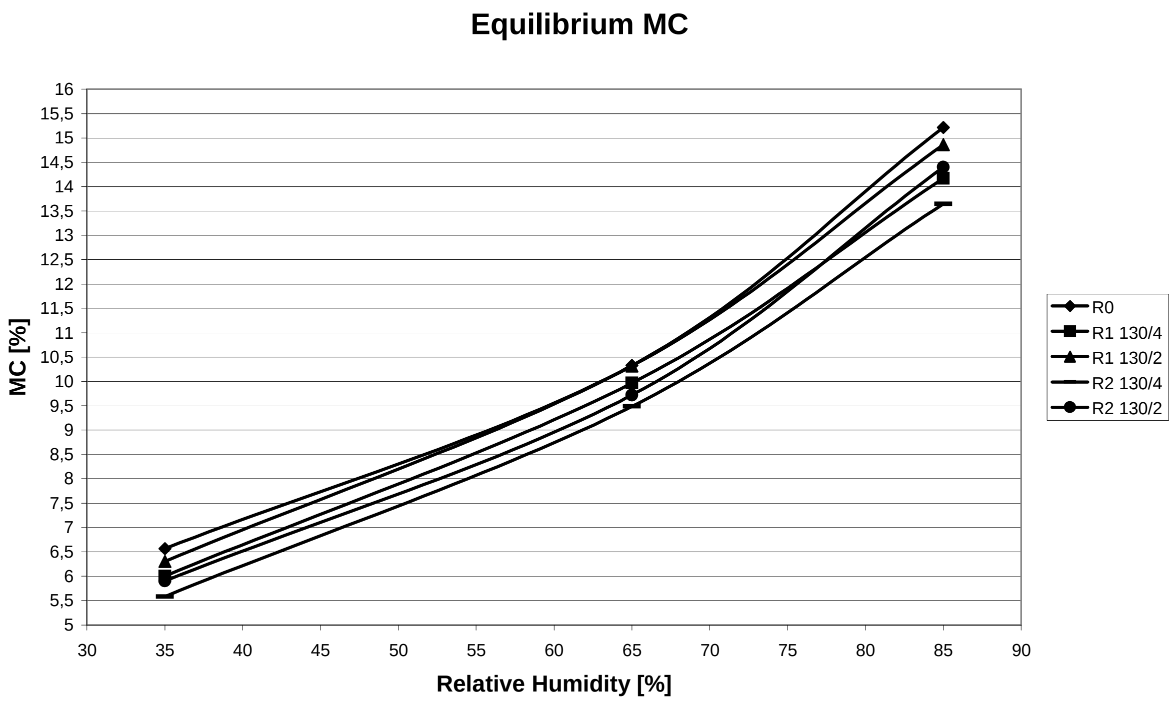

Figure 6: Equilibrium moisture content of wood steamed at 130°C (2 and 4 hours) at various relative humidities for the two samples R1 and R2.

Whether the wood is first dried and then steamed (series R1), or first steamed and then dried (series R2) does not significantly effect the results as far as colour changes is concerned. However, a preliminary study of the test material as regards residual stresses formation and relaxation strongly indicates that the wood should preferably be dried prior to steaming. Steaming under pressure apparently acts as a means of stress relaxation in a time span which is only a fraction of that required for conventional conditioning under atmospheric pressure.

Conclusions

- Steaming is an excellent means for colour modification and homogenisation of Black Locust wood. Changes in brightness and the red (a*) and yellow (b*) values follow the same course when steaming under either atmospheric or pressure conditions.
- Pressure steaming at temperatures between 120°C and 130°C is much more effective than steaming under atmospheric conditions as it can reduce steaming time to a fraction (factor 20-40) and process parameters can be controlled more precisely.
- The colour changes caused by steaming are fast at the beginning and level off after a certain time (hours in the case of pressure steaming, days in the case of steaming under atmosperic conditions).
- Steaming to predetermined colour hues can be controlled by the parameters temperature and time, independent of the steaming conditions. The little appreciated greenish and yellowish to oliv natural colour is eliminated. Attainable colour hues range from a light brown, viz. slow-grown White Oak (*Quercus spp*.), to a very dark brown resembling that of some tropical timbers such as the African Wengé (*Millettia laurentii*) or the Southamerican Sucupira (*Bowdichia spp.).*

- The final colour is not restricted to any particular region (surface or interior) but is uniformly distributed over the entire cross section. Subsequent colour changes under indoor exposure to light/oxigen are negligable.
- Pressure steaming after drying bears considerable potential for quick relaxation of the intrinsically high residual drying stresses (case hardening) in Black Locust wood.
- Pressure steaming has a positive effect on sorption behaviour of Black Locust wood.
- Pressure steaming does not reduce surface hardness significantly.
- Steaming effluents are strongly acidic (pH 3 to 4) and thus constitute a considerable risk of corrosion for the steaming equipment.

natural	85°C 48h	110°C 4h	120°C 2h	120°C 4h	130°C 2h	130°C 4h

Figure 7: Colour changes effected by steaming under pressure as a function of the controlling parameters temperature and time