

INVESTIGATION OF THE CHEMICAL CHANGES IN THE STRUCTURE OF WOOD THERMALLY MODIFIED WITHIN A NITROGEN ATMOSPHERE AUTOCLAVE

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ABSTRACT

Thermal modification beneficially alters several technological parameters of wood. The changes in the physical parameters are due to the significant/various alterations of the structure and the chemical composition of wood, which take place during the modification process. These changes are complex and some aspects/processes are still far from being completely understood. What is known, is that by increasing the temperature the nature of reactions taking place changes. Still it is unknown the exact point where the individual reactions become dominant. Various industrially important hardwood and softwood have been treated in autoclave in N₂ atmosphere. The physical (density, L-value, moisture content, bending strength, MOE) and chemical (pH, hemicellulose-, totalphenol-, soluble carbohydrate-, and volatile organic compound content) parameters have been measured and evaluated. Correlations between physical and chemical parameters have been established and discussed.

KEY WORDS: beech, acer, ash, spruce, pine, Douglas fir, thermal modification, chemical composition, physical properties

INTRODUCTION

Thermal modification beneficially changes the dimensional stability, hygroscopicity and biological durability of wood (Boonstra et al. 2007). The modification treatment is always performed between the temperatures of 180 °C and 260 °C. The use of temperatures lower than 140 °C result in only slight changes in material properties, while thermal modification above temperatures of 300 °C are of limited significance, due to severe degradation of the wood structure (Callum Hill 2006). Generally it can be established that at a few degrees

below 100 °C the weight loss of wood already begins due to thermal transformation of certain components of the wood, primarily hemicellulose (Bobleter and Binder 1980, Abatzoglou et al. 1990, Boonstra and Tjeerdsma 2006). Increasing temperatures result in the transformation of solid into volatile compounds (degradation of extractives, production and transformation of radicals originating from lignin) (Burmester 1975, Hakkou et al. 2005). Between ranges of 100 °C to 250/280 °C a mild pyrolysis generally takes place. Above 300 °C the rapid degradation of cellulose (Pfriem 2006) also contributes to the formation of the degradation products.

Various wood species with distinct chemical compositions also behave differently during the thermal modification process (Zaman et al. 2000, Militz 2002) and it is sometimes hard to interpret or interconnect physical changes with exact chemical transformations. This information is however significant in attaining the desired technological (physical and chemical) features of the product.

Chosen physical (density, L-value, moisture content, bending strength, MOE) and chemical (pH, hemicellulose-, totalphenol-, soluble carbohydrate-, and volatile organic compound content) properties have been measured in samples of industrially significant wood species that have been thermally modified in autoclave in N₂ atmosphere. Where provided/possible sapwood and heartwood samples have both been investigated. The modification process has been carried out in two steps as described by Giebler (1981) (Step 0: untreated; Step 2, Step3: increasing treatment). Through investigating linear correlations, relationships between chemical parameters (wood structure) and physical/technological features have been established and discussed.

MATERIAL AND METHODS

Material and treatment

Wood samples (beech, acer, ash, spruce, pine and Douglas fir) were treated thermally in an autoclave in N₂ gas according to the method described by Giebler (1981). Intensity of the modification increases with the number of steps. The two steps of the modification process differ in terms of pressure, residual oxygen content, temperature and duration. The reference samples were not modified (Step 0). After closing the autoclave, the vacuum is generated, which is followed by the establishment of an overpressured atmosphere using N₂ gas. The initial moisture content of the wood is between 8-10 %. The mixture of nitrogen, residual oxygen and steam, which is produced during the treatment, remains in the autoclave during the whole process. Untreated wood (Step 0) and wood samples treated in two steps (Step 2 and Step 3) have been investigated. In the case of acer there was no untreated wood sample provided. Spruce and pine were treated only until step 2. For beech we used samples from 2 different wood qualities Bu and BuP.

The physical/mechanical properties were measured approximately 6 months after production, and the chemical parameters after 12 months. Tab. 1 summarizes the samples investigated.

Tab. 1: The wood samples investigated and their nominations

hardwood			softwood		
Species	Name	Steps	Species	Name	Steps
Acer	AH	2, 3	Douglas fir sapwood	Ds	0, 2, 3
Beech I	Bu	0, 2, 3	Douglas fir heartwood	Dk	0, 2, 3
Beech II	BuP	0, 2, 3	Pine sapwood	Fs	0, 2
Ash	Es	0, 2, 3	Pine heartwood	Fk	0, 2, 3
			Spruce	Fi	0, 2

Measurement of physical properties

All the properties investigated have been measured under normal conditions, at 20°C/65% relative humidity using wood probes with the dimensions 400 x 20 x 20 mm. Density has been measured according to DIN 52182, the moisture content according to DIN 52183 and have been indicated in g/cm³ and in percentage units respectively. Bending strength and modulus of elasticity (MOE) were measured according to DIN 52186 and given in N/mm² units. The lightness parameter perpendicular to the wood fibre (L-value) was evaluated according to colour measurement using Minolta Chroma-Meter CR 200 device.

Measurement of chemical parameters

Approximately 200 g of each of the wood samples were ground and sieved. The fraction with particle sizes between 0.2-0.63 mm was used in all the measurements.

Dry mass content determination

3 g of each of the wood samples was heated at 105°C until constant weight. The dry mass content was calculated and used in the evaluation of the results.

pH

The pH of the wood samples was determined using the method of Roffael and Kossatz (1981).

Ethanol-Toluene soluble extract content

The Ethanol-Toluene soluble Extract content was measured according to the Tappi-standards T 264 cm-97 and T 204 cm-97. The extractive content relates to dry weight (dw.) and has been indicated in percent.

Total phenol determination

0.025 g of wood sample was extracted over 6 consecutive steps with 80% methanol using an ultrasonic bath with a temperature of 25°C. Extraction was carried out by applying 8 ml of extraction solvent for 30 minutes during each step. The extracts were collected into a flask and made up to a final volume of 50.0 cm³. The total phenol content was determined with spectrophotometry according to the method of Folin-Ciocalteu (Singleton and Rossi 1965) using quercetin as standard. The results have been given in mmol quercetin/100g dry wood. The measurements were carried out in triplicate.

Soluble carbohydrate content

The soluble carbohydrate content was determined from the same extract from which the total phenol content was measured. The determination was carried out according to the method of Dubois et al. (1956) using glucose as standard. The results were given in mg glucose/g dry wood. The measurements were carried out in triplicate.

Hemicellulose determination

The measurement of the hemicellulose content was carried out using the method of Polyak (1948). The hemicellulose content was related to dry wood weight and indicated in percent.

GC-MS determination of volatile components

The volatile organic components content (VOC) was analysed by HS-GC-MS. 0.5 g wood

dust (<0.1mm) was measured into a 20 ml vial. The incubation temperature and time was 140 °C and 15 min, respectively. The syringe temperature was 150 °C. A volume of 250 µl was injected into the injector (temp. 250 °C). The split ratio was 2. The components were separated on a SLB-5MS capillary column (30 m x 0.25 mm x 0.25 µm film thickness, Supelco) and analysed by gas chromatography-mass spectrometry (Shimadzu GC-MS QP 2010). The temperature program began at 35 °C (hold 3 min) and was then raised to 250 °C at 20 °C/min. All mass numbers between 25 and 500 m/z were recorded in SCAN mode. Individual components were identified by comparison of their mass spectra with Wiley and Nist library. The total area of all of the components was used for comparison of the VOC emission.

RESULTS AND DISCUSSION

Physical Properties

Tab. 2 summarizes the physical properties of the investigated hard wood samples.

Tab. 2: *Physical Properties – hardwood samples*

Sample	Density [g/cm ³]	Moisture content [%]	L-value	Bending strength [N/mm ²]	Modulus of Elasticity [N/mm ²]
AH2 ³⁵	0.561 ± 0.004	6.4	49.4 ± 0.6	95.3 ± 5.2	12009 ± 274.4
AH2 ³⁷	0.564 ± 0.009	5.7	41.5 ± 0.7	46.7 ± 7.7	10059 ± 1085.6
Bu0 ²⁷	0.738 ± 0.007	10.9	72.0 ± 0.7	132.8 ± 2.2	13140 ± 293.5
Bu2 ³⁵	0.692 ± 0.010	8.7	47.9 ± 0.8	76.7 ± 7.5	11092 ± 612.3
Bu3 ⁴²	0.656 ± 0.010	8.3	35.9 ± 0.5	53.8 ± 4.1	11776 ± 397.5
BuP0 ²⁷	0.685 ± 0.010	10.5	40.3 ± 0.6	138.1 ± 3.3	13957 ± 419.3
BuP2 ³⁵	0.629 ± 0.007	7.1	18.5 ± 0.6	101.1 ± 5.4	13596 ± 250.6
BuP3 ²⁹	0.676 ± 0.005	5.5	11.2 ± 0.4	54.5 ± 3.1	12995 ± 253.1
Es0 ³²	0.633 ± 0.010	10.6	48.0 ± 1.9	97.6 ± 3.5	9503 ± 310.0
Es2 ⁵⁵	0.659 ± 0.009	7.4	20.5 ± 0.6	96.5 ± 5.2	12002 ± 370.1
Es3 ⁴⁶	0.560 ± 0.013	5.3	10.9 ± 0.3	44.0 ± 2.8	10313 ± 362.4

In upper index behind the name of samples: Numer of samples.

Confidence interval is indicated at p=0.05.

After the treatment the equilibrium moisture content, the bending strength and the lightness parameter of the wood samples decrease. The density of the treated wood samples also decreases significantly compared to the respective untreated samples. However, the extension, as well as the influence of the treatment-intensity, does not show any uniform tendencies; e.g. in the case of BuP the density after Step 3 is higher than after Step 2. The decrease in density can also be observed in Douglas fir and in pine and there is also a dependence of this parameter on the intensity of the treatment (Tab. 3). The sapwood of Douglas fir is an exception as it shows an increase in density from Step 2 to Step 3.

The MOE parameters decrease in beech and acer, while they increase in ash and spruce. Although similar tendencies are not always observed amongst different wood species moving from Step 0 towards Step 3. In the case of Douglas fir and pine there are no similar tendencies observed in the sapwood or the heartwood samples. It can also be recognized that in the case of pine, the thermal treatment has not had any significant impact on the resulted MOE parameters. A slight increase can be observed in the value of the MOE for Douglas fir heartwood and a decrease in the case of the sapwood can be established. The bending strength decreases

drastically with intensified treatment. Although in the case of ash wood at Step 2 no significant change was observed compared to the reference sample. The BuP sample shows a slight decrease in this parameter while moving from untreated towards Step 2. In the case of beech however, this change is much higher. Bending strength decreases uniformly while modifying Douglas fir and pine wood tissues. Interestingly the reduction in the MOE (maximum reduction: 16%) is much lower than the reduction in the bending strength (maximum reduction up to 60%). Only in the case of beech, acer and ash is the decrease greater than in Douglas fir and pine.

With increasing treatment intensity the L-value is reduced, which means that the colour becomes darker. No significant relationship between the colour and the bending strength could be established. Generally it can be said that with increasing treatment intensity the bending strength lowers. While the intensification of the treatment correlates with the colour of the wood it can be generally established that the darker the wood the poorer is the bending strength (Junghans und Niemi 2005). The strength of wood however is also influenced by many other parameters.

Tab. 3: Physical Properties – softwood sample

Sample	Density [g/cm ³]	Moisture content [%]	L-value	Bending strength [N/mm ²]	Modulus of Elasticity [N/mm ²]
Fi0 ⁴⁵	0.462 ± 0.015	11.6	61.2 ± 1.6	90.6 ± 4.8	12204 ± 646.9
Fi2 ⁴⁵	0.481 ± 0.024	9.3	29.3 ± 0.7	63.7 ± 4.6	13123 ± 734.6
Fs0 ⁵⁵	0.588 ± 0.010	13.6	82.0 ± 0.6	94.3 ± 3.0	13052 ± 435.4
Fs2 ⁴⁴	0.546 ± 0.014	8.9	56.9 ± 0.5	61.9 ± 5.1	12525 ± 722.0
Fk0 ³⁹	0.552 ± 0.017	11.9	79.7 ± 0.6	87.4 ± 3.8	12138 ± 713.0
Fk2 ³⁰	0.543 ± 0.016	9.7	56.4 ± 1.0	68.0 ± 7.5	12514 ± 944.2
Fk3 ⁸¹	0.516 ± 0.009	7.2	47.2 ± 1.3	57.2 ± 5.0	12540 ± 402.4
Ds0 ⁴⁰	0.526 ± 0.011	13.8	79.1 ± 0.5	90.5 ± 3.1	13962 ± 542.0
Ds2 ²⁰	0.443 ± 0.015	9.9	56.5 ± 0.8	56.9 ± 5.2	9888 ± 826.3
Ds3 ⁴⁵	0.475 ± 0.010	6.3	47.8 ± 0.7	74.7 ± 4.0	12971 ± 428.3
Dk0 ⁵²	0.484 ± 0.013	13.4	72.9 ± 3.0	75.6 ± 3.8	11305 ± 446.3
Dk2 ²⁰	0.477 ± 0.016	7.5	57.8 ± 1.0	73.1 ± 3.8	12181 ± 548.0
Dk3 ⁹⁶	0.466 ± 0.010	6.8	47.5 ± 0.5	67.5 ± 2.3	12166 ± 390.9

In upper index behind the name of samples: Numer of samples.

s. Confidence interval is indicated at $p=0.05$.

Chemical Analyses

Differences have been noted amongst the different wood species as to the way they respond to heat treatment. The most important differences were reported between softwoods and hardwoods (Zaman et al. 2000, Militz 2002, Callum Hill 2006). Due to these facts, the wood samples investigated have been grouped and discussed as softwood and hardwood species.

The lignin fraction takes up 20-25% of hardwood and 28-30% of softwood. The composition is also different: the lignin of softwoods is mainly built-up from coniferyl- and p-coumaryl-alcohol, while in the case of hardwoods the major components are coniferyl- and sinapyl-alcohol (Németh 1997). The hemicellulose fraction of hardwoods is mainly composed of glucuronoxylans which are thermally and hydrolytically more instable than the glucomannans which are dominant in the hemicellulose of softwood. A fraction of the hydroxyl-groups in hemicellulose is acetylated (Pfriem 2006). Considering cellulose there are no significant differences mentioned between woods, regarding the structure and composition (Németh 1997).

The largest differences between the chemical compositions of different wood species are in the quality and concentration of extractives.

Non-volatile compounds

Tab. 4: The pH, the Ethanol-toluene soluble extract content, the totalphenol content, the soluble carbohydrate content and the hemicellulose fraction of the investigated hardwood samples. Confidence interval is indicated at $p=0.05$

	AH2	AH3	Bu0	Bu2	Bu3	BuP0	BuP2	BuP3	Es0	Es2	Es3
pH	3.90	3.88	4.16	3.57	3.62	4.46	3.80	3.65	4.46	4.03	4.28
Ethanol-Toluene s. extract [%]	10.3	15.5	3.6	8.5	11.9	2.4	9.6	13.7	6.5	8.4	13.5
Totalphenol [mmol/100g dw]	8.88 ± 0.34	12.72 ± 0.20	2.59 ± 0.02	6.95 ± 0.25	9.78 ± 0.64	1.85 ± 0.10	6.27 ± 0.08	10.67 ± 0.30	4.99 ± 0.19	8.37 ± 0.38	10.95 ± 0.26
Soluble Carbohydrates [mg/g dw.]	109.1 ± 14.1	81.8 ± 13.9	23.2 ± 2.2	199.2 ± 27.1	65.1 ± 7.3	16.2 ± 0.9	81.2 ± 12.4	61.2 ± 15.8	68.9 ± 5.3	103.2 ± 5.3	72.8 ± 18.2
Hemicellulose [%]	8.3	5.2	13.6	10.4	5.6	13.9	13.9	5.9	9.4	9.2	8.0

The decrease in pH can be observed when comparing samples from Step 0 and Step 2. The differences between the values of Step 2 and Step 3 of beech and ash do not indicate further acidification of the wood, but instead a slight increase of the pH. There is a remarkable change in the totalphenol content in all of the samples. The concentration of the phenolic compounds consistently increases from Step 0 to Step 3: in beech 4-5-fold, in ash 2-3-fold and in acer (between Steps 2 and 3) 1.5-2-fold. A very good correlation can be established between totalphenol concentration and the ethanol-toluene soluble extractive content ($R^2=0.955$). The correlation proves that phenolic compounds are produced during the treatment, these also have good solubility in the ethanol-toluene mixture; for this reason, these compounds are presumably simple phenols with low molecular weight. The only explanation for this could be the transformation of lignin, which stretches over wide temperature ranges.

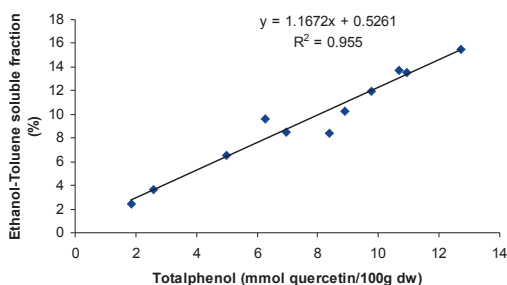


Fig. 1: Correlation for hardwood samples

A decrease in the hemicellulose concentration can be observed with progressive treatment in all the hardwood samples. On the other hand the soluble carbohydrate content increases drastically from Step 0 to Step 2, which is followed by a decrease from Step 2 toward Step 3 in all the hardwood samples. After Step 3 however, the original soluble carbohydrate content of the control sample was not reached in any of the samples apart from the ash sample. The vivid fluctuation of the soluble carbohydrate concentration clearly reflects the transformation of the structural and non-structural carbohydrates in the wood during the treatment.

Tab. 5: The pH, the ethanol-toluene soluble extract content, the totalphenol content, the soluble carbohydrate content and the hemicellulose fraction of the investigated softwood samples. Confidence interval is indicated at $p=0.05$

	Ds0	Ds2	Ds3	Dk0	Dk2	Dk3	Fs0	Fs2	Fk0	Fk2	Fk3	Fi0	Fi2
pH	4.23	3.50	3.47	3.64	3.63	3.52	4.18	3.80	4.10	3.92	3.59	4.15	3.56
Ethanol-Toluol extract [%]	0.4	6.1	5.5	2.2	8.9	8.3	2.5	7.7	6.8	7	8	2.4	4.2
Totalphenol [mmol/100g dw.]	1.22 ±0.03	2.49 ±0.01	2.69 ±0.03	4.36 ±0.07	2.47 ±0.08	3.01 ±0.03	0.708 ±0.01	2.69 ±0.03	2.25 ±0.02	2.62 ±0.11	3.72 ±0.12	2.84 ±0.05	3.25 ±0.07
Soluble Carbohydrates [mg/g dw.]	10.22 ±1.71	242.4 ±22.6	54.06 ±5.79	27.99 ±2.04	118.9 ±23.3	102.6 ±15.5	8.62 ±0.26	86.12 ±8.79	15.84 ±1.96	66.46 ±1.56	55.64 ±8.37	24.89 ±2.41	45.05 ±1.84
Hemicellulose [%]	6.3	5.6	6.2	17.2	13.3	4.9	9.5	9.5	6.8	8.7	7.3	6.9	8.0

The softwood wood samples showed a decrease in pH values with the progression of the thermal treatment. The acidification of the wood can thus be observed especially when comparing pH values obtained in Step 0 and Step 2.

The increase of the totalphenol content in softwood from Step 0 to Step 3 is not as high as in the hardwood samples (Douglas fir sapwood: 2.2-fold, spruce: 1.2-fold, pine heartwood: 1.7-fold). Totalphenol increases in the sapwood of pine 3.5-fold until Step 2. A reduction was only observed in the Douglas fir heartwood sample. Thus, a good correlation can not be established between totalphenol concentration and the ethanol-toluene soluble extractive content ($R^2=0.0755$) in softwood samples. This could mean that the extractives that are produced during the thermal modification process in the softwood, (besides phenolic compounds), also include other types of extractives in high concentrations.

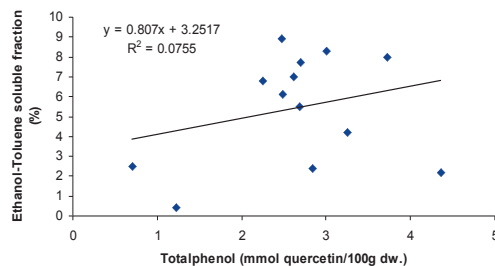


Fig. 2: Correlation for softwood samples

During the modification process the hemicellulose content also changes in softwood samples. A pregnant change can especially be observed in the heartwood of Douglas fir from Step 0 to Step 3. In other samples, especially sapwood, this decrease is not so characteristic. In spite of this fact, the soluble carbohydrate concentration increases manifold from Step 0 to Step 2 in all of the softwood samples investigated. In the sapwood of Douglas fir, a 24-fold increase can be evidenced/detected. The increase of soluble carbohydrate content from Step 0 to Step 2 indicates an unequivocal degradation of the structural carbohydrates, although no definite decrease of the hemicellulose concentration can be detected in the pine heartwood, sapwood and spruce samples. From Step 2 to Step 3 the concentration of dissoluble sugars decreases sharply again, which can be explained with the thermal degradation of simple sugars when exposed to high processing temperatures for a long time.

The results (see Tab. 5) also prove that sap- and heartwood behave differently during the technological process (Bächle and Schmutz 2006).

While comparing softwood and hardwood samples, it can also be concluded that the phenolic compounds in the hardwood samples are more readily transformed (an increase of the totalphenol level from Step 0 to Step 3) while in the softwood samples it is the soluble carbohydrate content that shows extensive changes.

Volatile compounds

The investigation of VOCs in wood materials is of great importance for several reasons (Ohlmeyer, 2007). The transformation of chemical components during the thermal treatment does not take place uniformly in each wood species. Softwood and hardwood behave differently in this regard also. Partly because the structure and composition of their hemicellulose- and lignin fraction differs, and partly because they contain extractives of different quality and quantity.

In hardwood samples (ash, beech, acer) the total amount of VOCs consistently increases with progressing treatment intensity (except the sample BuP). By Step 3, the total concentration of VOCs is higher than the respective control samples (Fig. 3).

Untreated softwood samples (Douglas fir, pine, spruce) contain large amounts of volatile extractives. These components can be transformed and be set free from the "wood('extracted')" through the treatment and heat. During the thermal degradation of hemicellulose and the transformation of lignin (such as in the hardwood samples) amounts of VOCs can be released from the wood. The sum of the degradation and transformation reactions results in different time-tendencies during the treatment of wood samples of different species.

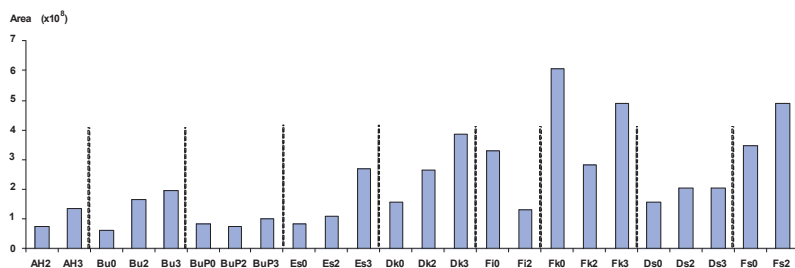


Fig. 3: The peak areas of the total volatile organic compounds (VOC) in the investigated samples

Douglas fir heartwood displays a consistent increase in VOCs. However, the heartwood of pine displays a decrease (Step 0 to Step 2) if followed by an increase (Step 2 to Step 3). In the sapwood of pine and Douglas fir a consistent increase of VOCs are detected while moving from Step 0 to Step 2.

Fig. 4 depicts the chromatogram obtained for beech samples. The most important volatile components originating from hardwoods are organic acids (formic-acid, acetic-acid, propionic-acid), furfural and its derivatives. Acetic acid is released from the cleaving of acetyl-groups from hemicellulose (Tjeerdsma et al. 1998, Boonstra and Tjeerdsma 2006, Pfriem 2006). Pentoses and hexoses are produced from the degradation of hemicellulose. These products are, in turn, further transformed into furfural and hydroxymethyl-furfural respectively (Bobleter and Binder 1980, Abatzoglou et al. 1990). Besides these compounds, aromatic hydrocarbons (i.e. Guajacol) are also detected, which could originate from the transformation of lignin (Burmester 1975, Bobleter and Binder 1980, Hakkou et al. 2005, Pfriem 2006).

In softwood, besides organic acids and furfural-derivatives, large amounts of terpenes (alpha-pinene, para-cymene, etc.) and their degradation products can also clearly be identified (Fig. 5).

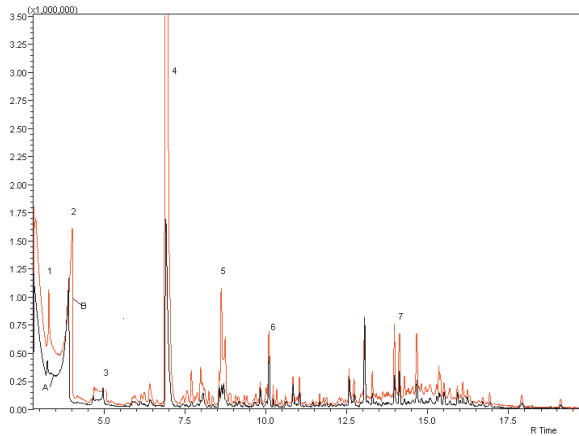


Fig. 4: The GC-MS chromatograms of the Bu0 and Bu3 samples. "A" chromatogram: Bu0; "B" chromatogram: Bu3 1: formic acid, 2: acetic acid, 3: propionic acid, 4: furfural, 5: 5-methyl-furfural, 6: guajacol

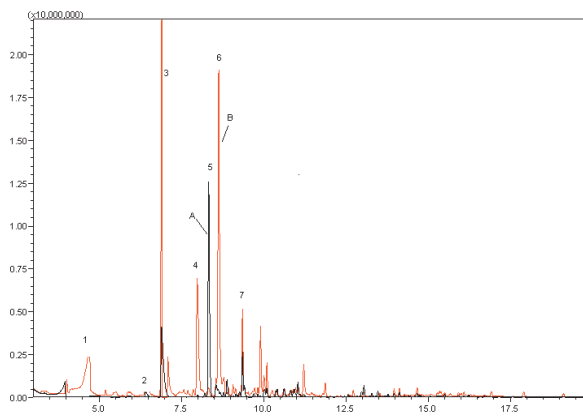


Fig. 5: The GC-MS chromatograms of the Dk0 and Dk3 samples. "A" chromatogram: Dk0; "B" chromatogram: Dk3. 1: acetic acid, 2: propionic acid, 3: furfural, 4: 1-(2-furanyl)-ethanone, 5: alpha-pinene, 6: 5-methyl-furfural, 7: para-cymene

Correlation between physical and chemical properties

The physical, technological features of the wood are altered during the treatment. The change in the physical properties of the wood is realized through the transformation of chemical components and through the alteration of the wood structure. Yet, which physical feature is influenced by which chemical parameter can only be guessed on the basis of woodchemical- and woodphysical knowledge.

Possible relationships can be quantified well by using mathematical tools (i.e. Linear correlations) and this way the influence of the treatment regarding attaining the desired technological features could be well prognosticated. The correlation coefficient (R) alters

between -1 and +1. The value of +1 indicates a positive correlation, while -1 indicates a negative correlation. A zero value means that there is neither a positive nor a negative correlation between the two parameters investigated (Inczédy 1979).

In the following tables, information can be seen regarding the most important correlations found between the measured physical and chemical parameters. Due to the previously discussed differences between softwood and hardwood, the two groups are evaluated separately.

Tab. 6: Linear Correlations between physical and chemical parameters for hardwood samples. R: correlation coefficient.

Parameter1	Parameter2	R
Ethanol-toluene extract	Totalphenol	0.9773
Totalphenol	Bending strength	-0.9297
Totalphenol	Moisture content	-0.8923
Totalphenol	Hemicellulose	-0.8776
Hemicellulose	Bending strength	0.8383
Totalphenol	Density	-0.6574
Hemicellulose	Moisture content	0.6319

The bending strength decreases ($R=-0.9297$) in hardwood samples (Tab. 6) with increasing totalphenol content. While heating up wood, the lignin is first softened (70-80 °C) then radicals are formed in the depolymerisation reactions (120-130 °C) that in turn are condensed (140-200 °C) to compounds that presumably have lower polarity. In this process the hygroscopicity of lignin decreases significantly (Pecina 1985). During the depolymerisation reactions, simple phenolic compounds can be formed that are also very soluble in ethanol-toluene mixture, as discussed above. This could be the cause for the increasing totalphenol concentrations of the wood samples. The transformation of lignin (i.e. increasing amounts on phenolic extractives in the wood) seems to be closely connected with the poor/degrading bending strength parameter in the investigated hardwood species.

The transformation of lignin and the increase in the concentration of the produced phenolic compounds also contribute to the reduced water adsorption (equilibrium moisture content) in the thermally modified hardwood samples ($R=-0.8923$). The reduced amount of equilibrium moisture-uptake, and thus the swelling and shrinking, is characteristic to thermally modified wood (Pfriem, 2006).

A reduction in the hemicellulose content is measured (-0.8776) with an increase in the totalphenol concentration. During the thermal degradation of hemicellulose the lignin-carbohydrate connections are also cleaved. The cleavage leads to the easy depolymerisation of this non-carbohydrate-bonded lignin fraction (Pfriem, 2006), which can also result in the production of simple phenolic compounds.

It seems that there is also a clear connection between a reduction in bending strength and hemicellulose content ($R=0.8383$), which proves the physical changes that take place during the degradation of hemicellulose in hardwood samples. The intense degradation of hemicelluloses, through thermal modification of wood, has already been proven by several authors (Sweet and Winandy 1999, Winandy and Lebow 2001, Pfriem und Wagenführ, 2007).

Tab. 7: Linear correlations between physical and chemical parameters for softwood samples. R: correlation coefficient.

Parameter1	Parameter2	R
Soluble carbohydrates	MOE	-0.7330
Soluble carbohydrates	Bending strength	-0.6695
Totalphenol	Bending strength	-0.5852
Totalphenol	L-value	-0.5272
Hemicellulose	Bending strength	0.0520

There are not so many good correlations between physical and chemical parameters in the softwood samples (Tab. 7) compared to hardwood samples (e.g. hemicellulose-bending strength $R=0.0520$ for softwood samples, $R=0.8383$ for hardwood samples). Softwoods have more thermally stable hemicelluloses that are mainly built up from glucomannans and besides that they also have different types and quantities of extractives than hardwoods. Sapwood and heartwood also possess different structures and compositions.

With increasing soluble sugar concentration, the MOE ($R=-0.7330$) and also the bending strength ($R=-0.6695$) decrease. Through the degradation of hemicellulose, soluble carbohydrate compounds are produced in the wood. The structure of the wood is altered which probably results in the reduced MOE and the bending strength. The correlation between totalphenol and bending strength ($R=-0.5852$) is also lower than in hardwood samples ($R=-0.9297$). Nevertheless, it will take further investigations to reveal other possible relationships between physical and chemical parameters concerning thermally modified softwood.

CONCLUSIONS

Softwood and hardwood samples behave differently during the thermal modification process carried out in a N_2 atmosphere autoclave. The different behaviour can be assigned to the distinct composition of the wood of each species. The chemical composition also influences the physical, technological features of wood.

Using correlations, the chemical reactions that take place during the thermal modification process can be better tracked and the physical properties, as well as changes of the wood material, can be better related to various stages of the process. These correlations are different for softwood and hardwood samples. Not only are different transformation reactions of the various wood types taking place during the modification treatment, but the chemical parameters investigated also contribute differently to the establishment of the physical and technological properties of the product. The results can serve as a basis for further research of the behaviour of different types of wood tissues during thermal treatment.

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