Peculiarities of the Thermal Modification of Hardwood

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ABSTRACT

The improvement of hardwood durability by way of modification is investigated to expand the application fields of the local species, especially in outdoor conditions. Studies of the structure, chemical composition and physical properties of modified birch (*Betula* spp.), grey alder (*Alnus incana*) and aspen (*Populus tremula*) wood in the water vapour medium in the temperature range 140-180 ^{o}C were carried out. The results indicate dramatic changes in wood, performing modification at 180 ^{o}C, namely, mass losses reach 15-18%, while wood density and bending strength decrease by 11-13% and 40-60%, respectively. The chemical analysis of the components indicates an essential decrease in the cellulose/lignin ratio. FTIR analysis data are indicative of an increase in the hemicelluloses degradation and relative lignin content. In turn, the TGA results indicate the growth in the thermally more stable cellulose structure. Modification at 160^{o}C does not ensure the durability of wood against brown and white rot fungi. Microscopy, wood cell wall density and water vapour sorption studies indicate that soft and medium soft hard wood reacts sensitively to the thermal action. The modification in water vapour medium at 180 ^{o}C, which is necessary to ensure wood biostability, changes undesirably the wood structure, hence the optimum temperature should be looked for in the temperature range >160 and <180 ^{o}C.

INTRODUCTION

Although also modified wood is relatively expensive, it is assumed to have good market perspectives, taking into account the restrictions of biocides' application and political solutions for the decrease in the utilisation of fossil raw materials, for sparing tropical forests and for orientation to renewable resources. Most thermo-modification processes are developed for coniferous trees, while the modification of hardwood is relatively little studied. From the whole modified wood stock, birch makes up about 7%. Thus, modification is proposed by companies in Canada, Finland, Germany (Scheiding 2008). The recently intensified studies of the thermal modification of hardwood are connected with the worsening of the quality of tropical wood, the attempts to replace softwood with fast-growing local deciduous species. The improvement of the durability and dimension stability of hardwood by way of modification is investigated with the aim to expand the application fields of the local species, especially in outdoor conditions.

EXPERIMENTAL

Wood samples of birch (*Betula* spp.), grey alder (*Alnus incana*), and aspen (*Populus tremula*) with moisture of 6-8% were modified in a laboratory multifunctional

experimental device in the water vapour medium at temperatures of 140, 160, and 180°C. Mass loss, size, wood density and cell wall density changes were determined. Changes in the wood components' composition and functional groups were analysed (chemical analysis, FTIR, TGA). The resistance against rot fungi (modified standard EN 113) was determined. Wood structure changes in the thermal modification process were assessed by the water vapour sorption method.

RESULTS AND DISCUSSION

Wood moisture after modification was within a range of 3.5-5.5% and reached 5-6% after conditioning. The initial wood average densities at a moisture content of 12% were 546 kg/m^3, 524 kg/m^3, and 719 kg/m^3 for grey alder, aspen, and birch, respectively. Table 1 shows the modification temperature dependence of wood changes.

Table 1: Modification temperature dependence of mass, volume and density changes for grey alder and birch wood

Tree species	Treatment temperature [°C]	Mass losses [%]	Decrease in volume [%]	Decrease in density [%]
Grey alder	140	1.9	-0.9	4.5
	160	6.3	1.9	8.1
	180	14.7	4.9	13.0
Aspen	140	0.8	1.5	1.4
	160	5.0	3.2	5.2
	180	14.2	5.9	11.0
Birch	140	0.6	2.2	1.2
	160	5.2	5.4	4.7
	180	18.0	9.6	11.4

Grey alder and aspen wood has similar changes under the effect of temperature. On the contrary, birch at 180°C has greater mass losses and a greater decrease in volume. The wood component composition was determined by chemical analysis methods (Table 2).

Table 2: Modification temperature dependence of grey alder and birch wood component composition

Tree species	Treatment temperature [°C]	Wood component composition [%]				
		Acetone extractable compounds	Cellulose	Lignin	Other compounds*	Cellulose/ lignin ratio
Grey alder	Non-modif.	4.0	47.3	24.7	28.0	1.9
	140	3.4	48.4	25.5	26.1	1.9
	160	9.2	48.2	28.9	22.9	1.7
	180	12.8	50.5	37.7	11.8	1.3
Aspen	Non-modif.	1.8	53.7		26.6	2.7
	140	2.7	53.5	18.2	28.3	2.9
	160	10.4	61.3	21.1	17.6	2.9
	180	12.8	61.0	30.4	8.6	2.0
Birch	Non-modif.	1.7	51.9	20.1	28.0	2.6
	140	2.0	52.8	20.2	27.0	2.6
	160	13.2	63.2	22.5	14.3	2.8
	180	14.3	61.7	34.3	4.0	1.8

** other components = 100 - (Cel + L)*

Non-modified grey alder differs from other species by a higher content of extractives and lignin, and lower cellulose content. Essential changes in the chemical composition

of wood start at the modification temperature 160 ^{o}C and are especially pronounced at 180 ^{o}C, when relative amounts of cellulose and lignin grow; the cellulose/lignin content decreases. FTIR spectrum changes in the region 1800-1500 cm^{-1} indicate that the higher is the temperature in wood treatment, the more acetyl groups are split off and the more wood is oxidised, forming oxidation products – ketones and aldehydes. The content of isolated (individual) double bonds in wood decreases (1680-1620 cm^{-1}); hence, other conjugated double systems could be formed. With growing modification temperature, the relative lignin content grows (the peak typical of lignin becomes sharper, namely, 1520-1505 cm^{-1}). At 180 ^{o}C, the shift of the carbonyl groups' absorption maximum to the long wave range at 1713 cm^{-1} testifies the formation of carbonyl groups of new type. In the region 1200-900 cm^{-1}, all peaks correspond to the functional groups typical of carbohydrates. With increasing treatment temperature, the peak's sharpness is observed, which testifies that, as a result of the degradation of the less ordered carbohydrates (hemicelluloses), the degree of crystallinity of carbohydrates (cellulose) grows. FTIR and chemical analysis data testify that, as a result of thermal treatment, mainly the degradation of hemicelluloses occurs, which is essential at the modification temperature 180^{o}C, and the relative lignin content grows at the expense of the degradation of the less thermally stable compounds. The changes of modified wood are characterised by thermogravimetry analysis (TGA), which was carried out at a constant air flow of 50ml/min (Table 3).

Table 3: Thermogravimetry analysis data for grey alder, aspen and birch wood

Tree species	Modification temperature [^{o}C]	Maximum oxidation rate temperature [T_0, ^{o}C]	Wood mass at 387^{o}C [%]	Constant mass reached at [^{o}C]
Grey alder	initial	319	15.6	468
	140	320	22.9	464
	160	318	24.9	475
	180	316	30.9	472
Aspen	initial	324	19.4	460
	140	321	21.0	460
	160	321	21.6	460
	180	316	36.5	482
Birch	initial	321	16.6	470
	140	319	15.0	475
	160	315	18.1	480
	180	313	23.6	490

With increasing modification temperature, the greatest oxidation rate temperature (T_0) decreases, which is explained by an increase in the content of volatile degradation products in wood. At the same time, the amount of thermally more stable components grows, which is testified by an increase in wood mass, for example, at a TGA temperature of 387 ^{o}C. In comparison with other species, the birch wood modified at 160 and 180 ^{o}C is characterised by a lower maximum oxidation rate temperature and deeper thermal degradation, although the formed compounds thermally degrade to completion at a higher temperature. TGA data of the components isolated from modified wood testify that minor changes are observed for cellulose only at the modification temperature 180 ^{o}C (increasing of the content of the more ordered cellulose part), while lignin has relatively high T_0 values and is much more thermally stable.The durability of modified wood against brown (*Coniophora puteana*) and white (*Coriolus versicolor*) rot fungi was evaluated (modification of the EN 113 standard)

(Table 4). The control samples are tested with *C. puteana* - pine (mass losses in the range 37-53%), and with *C. versicolor* – wood of the corresponding hard wood species (mass loss 24-37%).The resistance against rot fungi, especially white rot, is ensured by 1-h modification at 180 ^{o}C.

Table 4: Modification temperature dependence of modified wood biostability

Tree species	Treatment temperature [^{o}C]	Mass losses of modified wood [%]		
		Coniophora puteana	*Poria placenta*	*Coriolus versicolor*
Grey alder	140	45.5	-	27.0
	160	13.3	-	21.2
	180	0.2	-	1.6
Aspen	140	52.2	-	40.3
	160	7.1	-	25.3
	180	0.6	-	1.1
Birch	Non-treated	37.2	25.0	34.5
	140	36.5	19.3	35.6
	160	7.1	13.9	15.5
	180	0.2	0.1	3.7

It has been found using a helium pycnometer that the dependence of the wood cell wall density on the modification temperature goes through the maximum at a treatment temperature of 160 ^{o}C and decreases at 180 ^{o}C. These changes, which are especially pronounced for birch, are difficult to explain by the lignin structure condensation, and it is worth to pay attention to (Inari *et al*. 2007) suggested hypothesis of the formation of carbonaceous materials in the wood structure. The surface accessible for water vapours, determined by the sorption method, grows with modification temperature, but decreases in the second sorption cycle, which indicates the structure relaxation in a high moisture medium; in this, case, this process is much more pronounced for birch than for alder.

CONCLUSIONS

Carrying out thermal modification in the water vapour medium, hardwood reacts sensitively to the temperature increase, the greater changes being in the case of birch, which agrees with (Kocaefe and Poncsak 2008) conclusions. With increasing modification temperature, hemicelluloses degradation and the content of the most ordered cellulose grow, the cellulose/lignin ratio decreases and the surface accessible for water vapours decreases, while the cell wall density growth goes through the maximum at the modification temperature 160 ^{o}C. In general, the chemical and structural changes of wood result in a dramatic strength loss. The modification temperature 180 ^{o}C changes dramatically the structure of soft and medium soft hardwood, which causes a considerable decrease in bending strength.

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