ONLINE ISSN 2069-7430
ISSN-L 1841-4737
PRO LIGNO
www.proligno.ro
Vol. 13 N° 4 2017
pp. 341-350

EUROPEAN CO-OPERATION IN WOOD RESEARCH FROM NATIVE WOOD TO ENGINEERED MATERIALS.
PART 1: CHEMICAL MODIFICATION WITH NATIVE IMPREGNATION AGENTS

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Abstract:

The paper presents the results of a German – Czech – Hungarian – Slovenian wood research consortium, dealing with wood modification techniques by using renewable modification agents for the outdoor use of local, originally non-durable modified wood species like beech, poplar and pine sapwood. Higher value assortments of naturally durable and dimensional stable wood species, like oak and black locust from European forests, or others from tropical/sub-tropical forests are limited and partly criticized due to their non-sustainable production and harvesting conditions. Other reasons are the usage of non-local wood sources or the biocide treatment of non-durable species which have a higher impact on the environment because of long distance transport and the use of environmental critical chemicals. Due to simultaneously limited raw material volumes from fossil origin and their negative impact on climate and environment, the production and application of sustainable and renewable materials, like wood or further biomass assortments, become more and more important. Not only the sustainable production and use of the CO_2*-fixing material WOOD itself, but also the production and utilization of renewable liquid agents for the impregnation stage in the wood modification process-chain as well as the finishing or gluing process-steps are additionally helpful to improve the sustainability of the industrial production.*

The results show, that extracts from plant or tree residues with natural biocide or cross-linking behaviour as well as heat-treatment process residues of biomass materials, like collected liquids from thermal modification processes or hydro-thermal carbonised as well as pyrolysed or liquefied biomass or wood residues can result in a distinct improvement on the wood properties. These enhanced wood qualities enable the outdoor use of originally non-durable or non-dimensionally stable wood assortments.

Key words: *wood modification; renewable impregnation agents; outdoor wood applications; dimensional stability; durability.*

INTRODUCTION
The production and application of the sustainable and renewable material WOOD under local conditions and its higher value use under outdoor conditions have to be evaluated under following background conditions:

- Climate change, global warming, CO_2 re-emission from fossil sources
- Forest conversion, limited high value wood assortments, non-sustainable produced tropical wood assortments or biocide treatment as well as plastic, metal, or concrete materials
- Renewable, sustainable and locally produced wood, environmentally friendly chemical modification treatments (CMT) & treatment agents (impregnation, finishing, adhesive)
- Research interactions in EU-Networks (COST FP1407, DE-CZ-HU-SE-SI-NET, DANUBE-Network)

OBJECTIVE

The objective of the present research was to evaluate the possibilities of both, the utilization of non-durable local wood species as well as their property improvement for outdoor applications by wood-modification agents from native, renewable origin.

SHORT STATE-OF-THE-ART OF CMT AND EXPECTED MATERIAL PROPERTY CHANGES

During the last decades the production and utilization of renewable biomass from forest, agriculture and fast growing trees in short rotation plantations (SRPs) increased and are important for the future biomass supply with also options for different usages. Reasons for this are: 1) enhanced usage or even over use of traditionally managed forests (Mantau and Bilitewski 2005); 2) decreasing storage of fossil raw materials and energy sources (FAO 2005); 3) increasing amount of carbon dioxide in the atmosphere and global warming due to burning of fossil carbon sources (Cox et al. 2000); 4) need of higher application of more and climatically better adapted tree species under changing climate conditions (Blohm et al. 2014).

During the development of wood cell walls until maturation and functionality of the cells, wall architecture and chemical composition become distinctly changed (Zimmermann and Brown 1980; Fengel and Wegener 1989; Wagenführ 1999; Faix 2008). Secondary changes, especially in case of durable heartwood, occur at the transition from sapwood to heartwood by the incorporation of phenolic compounds in the carbohydrate-lignin complex (Hillis 1962; Klumpers et al. 1994; Faix 2004). During subsequent aging of cell walls, additional organic components (Gierlinger et al. 2003; Haupt et al. 2003; Grabner et al. 2005) or mineral elements can be bonded on or included in fibril-structure of wood cell walls (Rademacher et al. 1986; Faix 2004), leading to both increased durability and dimensional stability of wood. Also wounding (Rademacher et al. 1984; Shigo 1986; Frankenstein and Schmitt 2006), emissions (Hapla 1992) or climate stress (Schweingruber 1993) can initiate tertiary structural or chemical changes in cell walls. The knowledge about these basic mechanisms has been strengthened due to many investigations in the past (see overviews of Schwager and Lange 1998, Faix 2008, Wagenführ and Wagenführ 2008, Schmitt and Koch 2009), mainly dealing with most utilized tree species like spruce and pine or beech and oak. However, the knowledge about structure and chemistry of lesser used wood species or even the mechanism and process of technical or biotechnical changes in cell walls due to wood modification – leading to an improvement of properties – is still not fully understood (Zimmermann and Brown 1980; Ermeydan et al. 2012).

The improvement of wood properties by wood modification (Hill 2006; Militz and Mai 2008) became a more and more important goal and suitable methods have been developed for innovative and additional use of wood as a renewable raw material (Klemm et al. 2005). The transformation of our knowledge about mechanisms and processes of modification from technical (Militz et al. 1997) to small-scaled cellular (Mahnert et al. 2013) or molecular level (Grabner et al. 2005) could help to deepen our understanding and enlarge our instruments to establish new materials (Meier et al. 2001; Heiduschke and Haller 2010).

A lot of efforts have been done in the past to improve the properties of wood by chemical or mechanical treatments (Rowell 1983; Wepner and Militz 2005; Hill 2006), but the cellular or even sub-cellular mechanisms (mode of action) behind this are more or less unclear (Zimmermann and Brown 1980; Ermeydan et al. 2012). The following results deal with the exposure of basic mechanisms which lead to higher density, higher strength, higher dimensional stability and higher durability of wooden material. Collecting information on the microscopic structures as well as the chemical composition of cell walls before and after modification treatments is essential to understand the mechanisms behind changed 1) cell wall stability, 2) cell wall penetrability and 3) cell wall impregnation.

METHODS

A set of renewable agents for wood impregnation was developed for the following material-resources and processes (see also Table 1):

- Production of liquid residues from thermal treatment (TT), Hydro-Thermal Carbonisation (HTC), pyrolysis-processes (Pyrol), Liquid Wood (LW) and Robinia extracts (RobExtr); see Table 1.
- Impregnation of beech, poplar and pine sapwood samples with these liquids (using vacuum 20 kPa/1 hour) under calculation of the weight-percent-gain (WPG) and leaching tests, using 10 cycles to yield the weight-percent-remain (WPR) of the non-leached fraction.
- Concentration (1 agent : X H_2O): Pyrol 1:10; 1:2, original (1:1=100%); TT and HTC conc. 10:1; LW 1:3.
- Conditioning, drying, volume/weight, leaching, bulking measurement following standards.
- Durability tests: Bravery Test (1978); fungi: *Trametes versicolor,* time of exposure 6 weeks.
- Durability samples: 9 samples of 5 x 10 x 30 mm^3 (Bravery 1978) for each treatment.
- Swelling measurement: 10 samples of 14 x 14 x 28 mm^3 for each treatment.
- UMSP: UV-light absorption at 278 nm, using Zeiss-UMSP 80 (Koch and Grünwald 2004).
- Light and UV-microscopic investigations.

Table 1

Chemical sources and process for impregnation of wood with solutions of native origin

No.	Used Raw-Materials	Abbreviation	Synonym	Process Conditions
1	Miscanthus sp.	HTC_Misc	HTC-AG, HTC- D. Tschok,Misc.3/2013	Hydro-Thermal-Carbonisation = HTC, pressure, temp.
2	Spruce sawdust	HTC_Saw	HTC/ S. Vondran	HTC, pressure, temp.
2.2	Brewery residuest	HTC_Brew	HTC Schlamm	HTC, pressure, temp.
3	Mixed spruce, beech, oak, ash, poplar	TT_180	Thermal Treatment, Heat treatment, HT	TT, 180°C
4	Mixed spruce, beech, oak, ash, poplar	TT_200	Thermal Treatment, Heat treatment, HT	TT, 200°C
5	Canadian beech	Pyrol_Can	Bio-Oil, BO, Old Canadian	Fast pyrolysis, Canadian process (Dynamotive)
6	European beech	Pyrol_ProF1	German 1	Slow pyrolysis, D-ProFagus process
7	European beech	Pyrol_ProF2	German 2	Slow pyrolysis, D-ProFagus process
8	European beech	Pyrol_ProF3orig	Hamburg bio oil, crude Pro Fagus	Slow pyrolysis, D-ProFagus process
9	European beech	Pyrol_ProF3low	Hamburg low fraction,CHNSCCO2	Slow pyrolysis, D-ProFagus proc., supercritical CO_2-extr. low molecular weight
10	European beech	Pyrol_ProF3big	Hamburg PH 200, residue	Slow pyrolysis, D-ProFagus proc., supercritical CO_2-extr. high molecular weight
11	European beech	Pyrol_NLfre	Btg wood oil fresh, NL fresh	Fast pyrolysis, NL- BTG process, fresh production
12	European beech	Pyrol_NLold	Btg wood oil from storage, NL old	Fast pyrolysis, NL-BTG proc., stored/ old production
13	Robinia-heartwood, milled wood	Rob_Extr		Methanol-water 1:1 extract of heartwood, 3 concentrations
14	Forest poplar	LW_Pop_for1:1	LW poplar 1:1	Liquified wood
15	Forest poplar	LW_Pop_for1:3	LW poplar 1:3	Liquified wood
16	Plantation poplar	LW_Pop_plant	LW poplar, fast growing	Liquified wood
17	Forest spruce	LW_Spruce	LW spruce	Liquified wood

RESULTS AND DISCUSSION

Chemical Analysis of Robinia Extracts and thermally produced liquid Agents

Extraction process of Robinia wood with methanol-water mixture 1:1 resulted in a wide range of different concentration levels of extractives (Fig. 1). Most substances showed maximal concentration in older Robinia heartwood compared to median or young plantation wood; Robinia sapwood and especially bark have the lowest concentration of single extracts, mainly ranked from robinetinidin > dihydrorobinetin > robinetin > gallic acid > fisetin >> catechine, whereas barks shows higher catechine amount (Figure 1; Sablík and Rademacher 2013; Sablík et al. 2016).

Chemical Analysis of Process Residues after Pyrolysis Treatment of Biomass Materials

The dominating molecules in most pyrolysis process products are gallic acid, furfural, catechol and phenol, reaching or exceeding 1000µg per gram pyrolysis liquid (Fig. 2 left). Also 5-methylfurfural, syringaldehyde and eugenol reach in some processes a range of 200-400µg g^{-1}, whereas all other detected molecules show concentrations <<100µg g^{-1}. Some molecules, like gallic acid, have a widely similar range of concentrations (880-1150µg g^{-1}), while others (div. ProFagus products; Bodenfelde/ DE; e.g. ProF3) show a 2-3 times higher amount, especially compared to NL- or CAN- products.

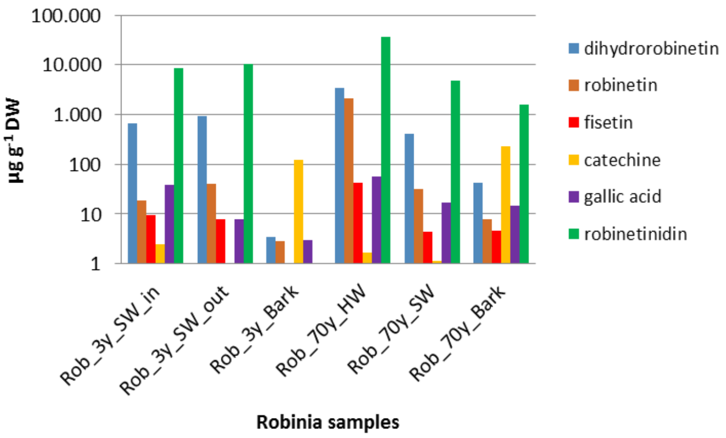

Fig. 1.
Analysis of methanol – water 1:1 extracts from Robinia (Rob): Influence of age (years; sapwood SW, heartwood HW), and stem compartment (inner and outer parts of disc, Wood or Bark) on amount of flavonoids and phenolic compounds.

Chemical Analysis of Process Residues after Thermal Treatment or Hydro-thermal-Carbonisation of Biomass Materials

In the liquid process-residues after thermal treatment of wood (TT using 180 or 200°C) or hydrothermal carbonisation of organic waste assortments (Miscanthus grass, or spruce sawdust) the robinetin-derivatives as well as fisetin, catechin and gallic acid are present in higher concentrations in the HTC-process residues (about 0.5-10µg ml^{-1}) compared to the TT process (mainly 0.1-0.8µg ml^{-1}, gallic acid also 1-5µg ml^{-1}). Furfural even appears only in the HTC-Sawdust (300µg ml^{-1}), phenol only in the TT process (30-300µg ml^{-1}). Only acetic acid in the TT process is with up to 10µg ml^{-1} about 10 times higher concentrated than in the HTC residues (Fig. 2 right).

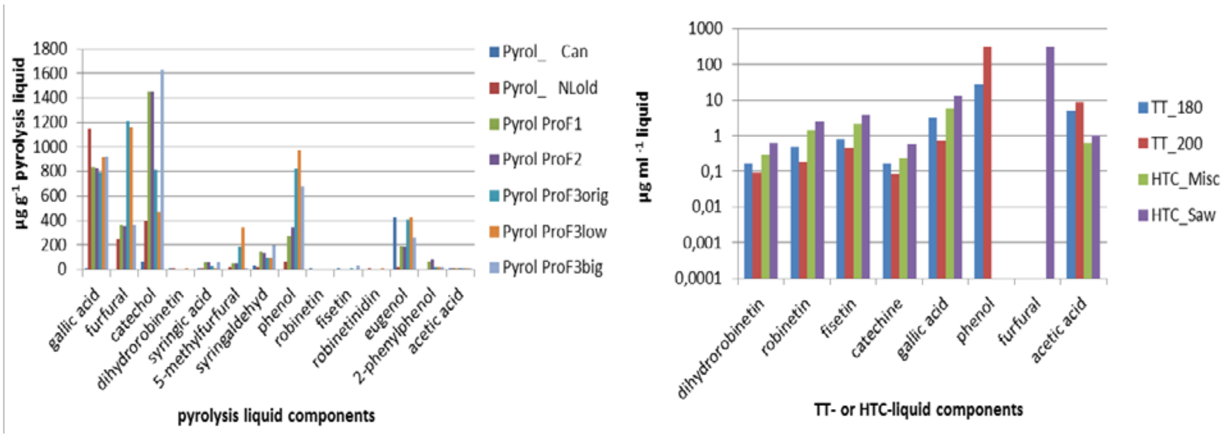

Fig. 2.
Chemical analysis of pyrolysis liquids with HPLC/ DAD in µg g^{-1} (due to high viscosity; left) and of thermal treatment residues from thermal modification with (TT: 180 and 200°C), or hydro-thermal-carbonisation (HTC: Miscanthus, spruce-sawdust) with HPLC/ MS in µg ml^{-1}.

Microscopic Observations and UV Detection of impregnated Modification Agents

Microscopy of pyrolysis-impregnated (Pyrol_Can, Fig. 3, below) beech (left) and poplar wood (right) show – compared to untreated native wood (Fig. 3, above) - a distinct deepening of the colour in the cell walls and a strong colour deepening in the cell lumina due to the more or less achieved full-impregnation of the entire micro- and macro-porous space of the wood tissue (Fig. 3). The maximal WPG, realized by full impregnation of the cell walls as well as the filling of all cell-lumina – has no further positive effect on the property improvement, because mainly the cell wall impregnation with the interaction of the impregnation agent and the cell wall hydroxyl groups results in chemical and micro-structural changes. In opposite to the cell wall impregnation the lumen filling mainly results only in an unwanted:

- Increase of the weight and colour.
- Smearing of the surface and pollution of the surrounding.
- Waste of treatment agents and increase of manufacturing costs.

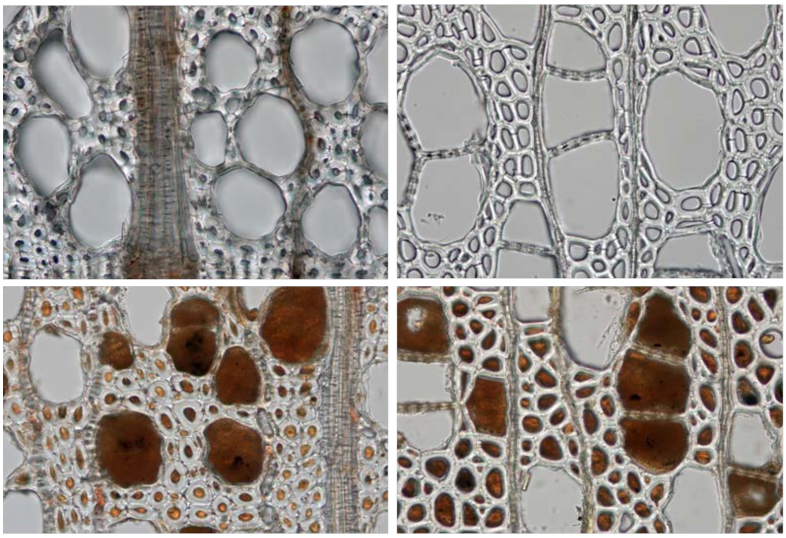

Fig. 3.
Natural (above) and pyrolysis-liquid impregnated (below) beech (left) and poplar wood (right). Photos: R. Rousek.

In order to counteract these disadvantages a post-vacuum or leaching treatment of the impregnated wood just following the impregnation process helps to minimize these problems (Fig. 4, left: after impregnation, Fig. 4, right: after leaching & post vacuum treatment) by eliminating the free liquid from the macro-pores.

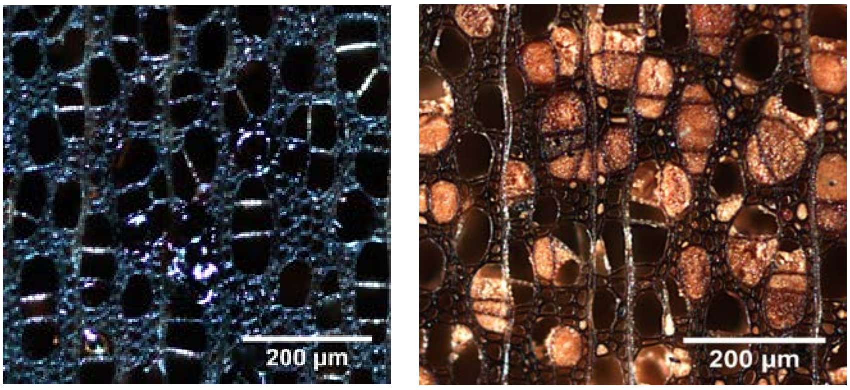

Fig. 4.
Surface images of poplar impregnated with 50% pyrolysis liquid (left; Pyrol_Can) and sample after leaching & post-vacuum (right). Photos: R. Rousek.

The microscopic view of UV-light illuminated cross sections of older Robinia heartwood as well as impregnated beech and poplar samples showed a stronger detection of phenolic compound response in kind of yellow-green fluorescence shining compared to younger Robinia or non-treated beech or poplar samples (blue colour). There was a ranking of shining, starting with native beech and poplar wood < young Robinia < leached Robinia-extract impregnated beech and poplar < Robinia-extract impregnated beech and poplar wood < old Robinia heartwood, indicating increasing phenolic compounds in the cell walls (Fig. 5).

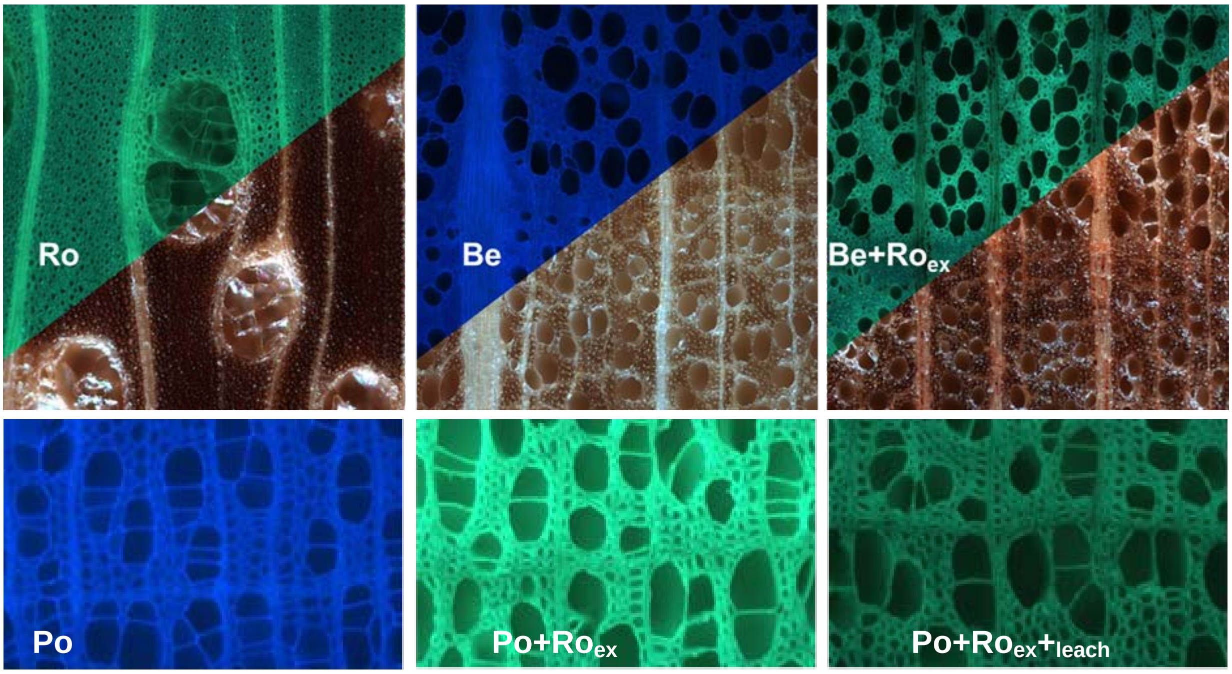

Fig. 5.
Above: Increase of UV-light induced green fluorescence shining, detecting increasing amount of phenolic compounds in cell walls of: Robinia heartwood (left; upper part of pictures: green = detection of phenolic compounds); native beech (middle; upper part of picture: blue = no phenolic compounds); Robinia - extract impregnated beech wood (right: upper part green = phenolic extract detection) compared with normal light (lower parts of upper 3 pictures: brown). Each image has a dimension of 0.9 x 0.9 mm^2.
Below: UV-light induced fluorescence shining in poplar wood: left: Reference, no impregnation (→ no green, but blue); mid: after Robinia extract impregnation (intensive green shining); right: after leaching (low green coloured). Photos: R. Rousek.

Cellular UV-Microspectrophotometry (UMSP)

UMSP images of untreated as well as pyrolysis-liquid and Robinia-extract treated poplar wood showed high differences in UV-light (278nm) absorption, indicating higher amount of aromatic, condensed components in impregnated cell walls compared to untreated wood of native poplar (Fig. 6). The presence of these components also in leached samples confirms their strong cell wall fixation.

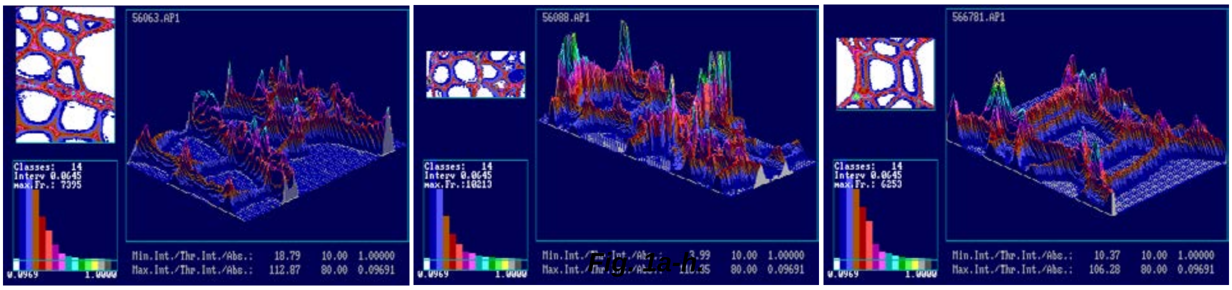

Fig. 6.
UV-absorption UMSP-field scan of reference (left) and pyrolysis-treated poplar (Pyrol_Can, mid) as well as Robinia extract impregnated poplar wood (right); wave length-setting of absorption 278 nm, absorption scale 1.0.

Weight Percentage-Gain (WPG), Weight Percentage–Remain (WPR) and Bulking Effect

The maximal WPG, possible to be reached after vacuum-pressure impregnation with thermal liquid residues is due to the lower density and higher porous system in pine sapwood about 2-times higher (up to 120% of wood dry mass) than in beech (30-70%; Fig. 7, left). In poplar wood, which has a similar or even lower density than pine, this difference as compared to beech is much lower, explained by the fact, that the facultative heartwood of poplar is classified as ‘difficult to impregnate’, whereas the sapwood is easily to treat like pine sapwood. (Kumar and Donriyal 1991; Hoffmann 2008; EN 350:2016). Due to the washout of non-fixed agent (Fig. 7, mid) after leaching test only 25-40% of the impregnated pyrolysis liquids remained in the wood, in case of low-molecular fraction after supercritical CO_2-fractionation of pyrolysis liquids and in case of liquid wood from poplar and especially from spruce the washout was even higher: only 25% of liquefied poplar wood and 15% of liquefied spruce remained in the wood, in case of low-molecular pyrolysis fraction even only 10-15% of the impregnated amount remained. The corresponding WPR was 12-45% of the wood mass in case of pyrolysis liquids, 10-30% of the liquefied wood and 5% of the low molecular fraction of pyrolysis liquid (Fig. 7, mid).

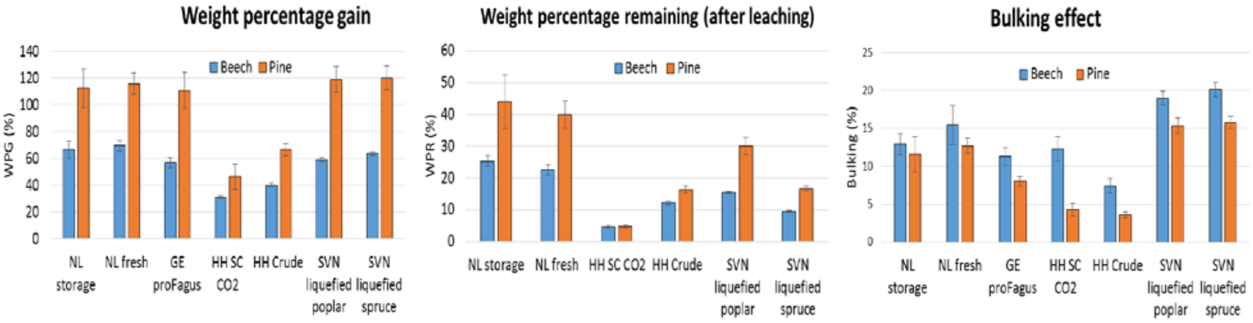

Fig. 7.
Weight-percentage-gain (left), WP-remain (right) and Bulking (permanent swelling [%; right]) without (WPG) and after leaching (WPR) of impregnated beech and pine wood using wood-processing residues (pyrolysis-liquid, liquid wood). Residues and process compare Tab. 1.

The determined bulking effect (permanent swelling of the wood due to structural modification (e.g. cross linking of hydroxyl groups in the cell wall) of the remaining agents after the leaching test was surprising (Fig. 7, right): In spite of the highest washout-rate in case of the low-molecular pyrolysis fraction and the high washout of the liquefied wood the bulking effect is still in average (low pyrolysis fraction) or even maximal (liquefied wood). This indicates that not only the amount of impregnated or remained impregnation agent is responsible for the wood-property improvement, but also the selection of reactive components with special functional groups (Ermeydan et al. 2012), especially in case of higher active slow-pyrolysed fractions after fractioning or wood liquefaction.

Moisture related Behaviour of the modified Wood

Compared to this, liquid thermal residues from thermal treatment, hydro-thermal carbonisation or Canadian fast pyrolysis process show a related behaviour between the amount of impregnated agent (WPG) and the corresponding bulking effect as well as the decreasing volume swelling response under moisture conditions (Fig. 8).

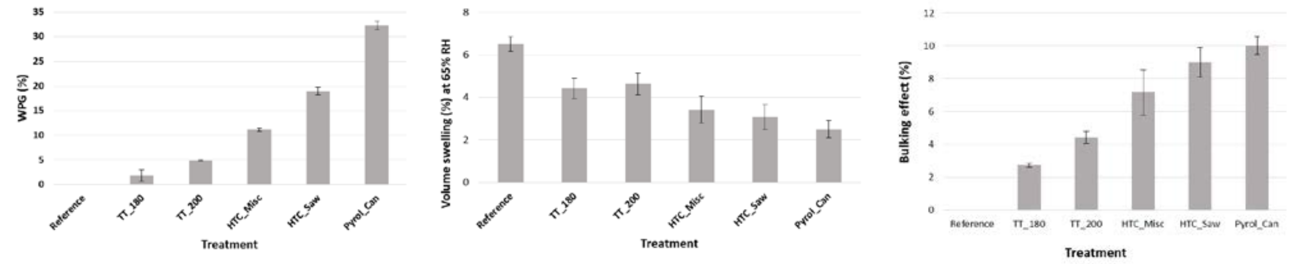

Fig. 8.
Weight percentage-gain (%; left) of impregnated poplar using wood-processing residues (thermal treatment (TT: 180 and 200°C), hydro-thermal-carbonisation (HTC: Miscanthus, spruce-sawdust) and pyrolysis-liquid from Canadian producer (Pyrol_Can), reduced volume-swelling (%; mid) and bulking effect (%; right). Residues and process compare Table 1.

The water uptake of pyrolysis and liquid wood impregnated beech wood shows (after leaching) a strong relationship (r^2 = 0.91) between the amount of impregnated agent (WPG) and the amount of included water (Fig. 9, left).

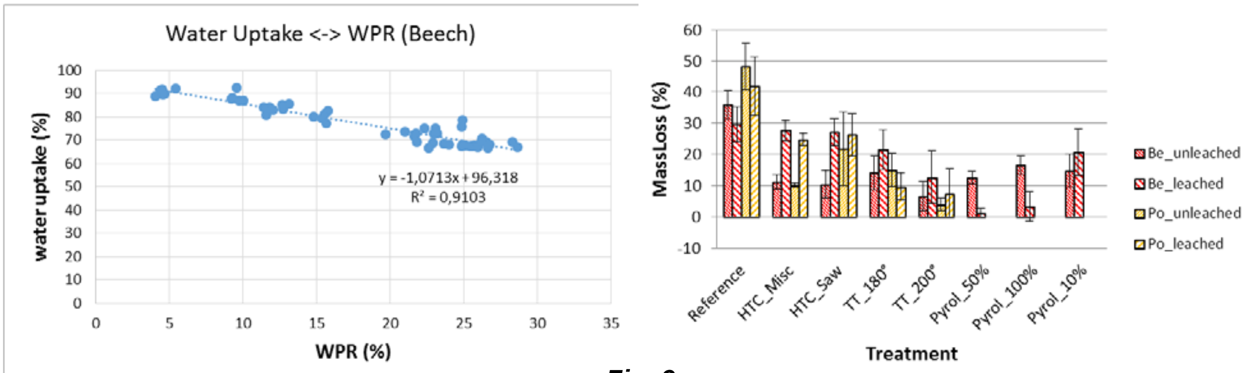

Fig. 9.
Reduced water uptake (%; left) in relation to weight-percent-remain (WPR [%]) after leaching of impregnated beech using wood-processing residues (pyrolysis-liquid, liquid wood).
Mass loss of beech and poplar wood (%, right) impregnated with native residues from technical processes. Pyrolysis-Liquids (Pyrol) of different dilution degree with water, TT = Thermal-Treatment residues, 180 rsp. 200°C, HTC solution = Hydrothermal Carbonisation of Miscanthus and Spruce sawdust residues. Residues and process compare Table 1.

Fungal Decay and Durability

The mass loss due to fungal decay (*Trametes versicolor*) of native beech (30-35%) and poplar wood (40-50%) was reduced to 2% in the case of pyrolysis treatment and to 4% in the case of TT, depending on the wood species, impregnation method, concentration and leaching process (Fig. 9, right, n = 9). HTC-treatment and also TT showed acceptable results only in the case of un-leached samples, whereas leaching resulted in 10-30% decay due to fungal activity; in contrast, the pyrolysis-treatment of beech in concentration of 100% and 50% showed good durability - less than 3% of decay - also in leached samples, resulting in durability classes 2 or even 1 against basidiomycetes, whereas concentration of 10% was too low. All un-leached pyrolysis samples showed mass losses due to leaching of exceeding amount of pyrolysis liquids out of cell lumina, which was leached under culture conditions on agar and resulted in a mass loss due to lower weight after the tests.

CONCLUSIONS

The results show that an increasing demand on additional high-quality wood assortments – following rising environmentally friendly standards – can be delivered by new bio-based processes, producing and applying renewable and sustainable produced wood impregnation agents for various wood modification processes. These innovations allow that not only the material wood, but also the entire wood modification process, can operate as a really renewable and sustainable process, excluding more and more fossil sources from the material production and application processes.

Nevertheless, the industrial implementation of natural and renewable produced wood modification or impregnation agents depend on the technical and constitutionally frame conditions. Under the viewpoint of sustainability in nature and production it has to be discussed, compared, balanced, and decided, if the application of defined and tested single modification agents from fossil origin, or the use of an undefined mixture of plant components and their process residues are more confirming with the requirements of sustainability, close to nature approach, environmental and health protection as well as renewability.

ACKNOWLEDGEMENT

Support from the COST Action FP1407 ModWoodLife project, the Swedish Research Council Formas project 942-2016-64, the European Social Fund and the state budget of the Czech Republic, project "The Establishment of an International Research Team for the Development of New Wood-based Materials" reg. no. CZ.1.07/2.3.00/20.0269, the Internal Grant Agency (IGA) of Faculty of Forestry and Wood Technology, Mendel University in Brno (IGA V 79/2013), the EFOP-3.6.1-16-2016-00018 – Improving the role of research, development & innovation in the higher education through institutional developments assisting intelligent specialization in Sopron and Szombathely, the German Federal Ministry for Education and Research (Danube Network, Grant No. 01DS17011), the Hungarian-Danube-Region- Co-financing (EU_KP_16-1-2017-0009), and the European Commission for funding the InnoRenew CoE project (GA 739574) are gratefully acknowledged.

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