Process and product quality control in (thermal) wood modification

Jakub & Anna Sandak

COST Action FP1407 Training School:
Service life of modified wood - Understanding Test Methodologies

outline

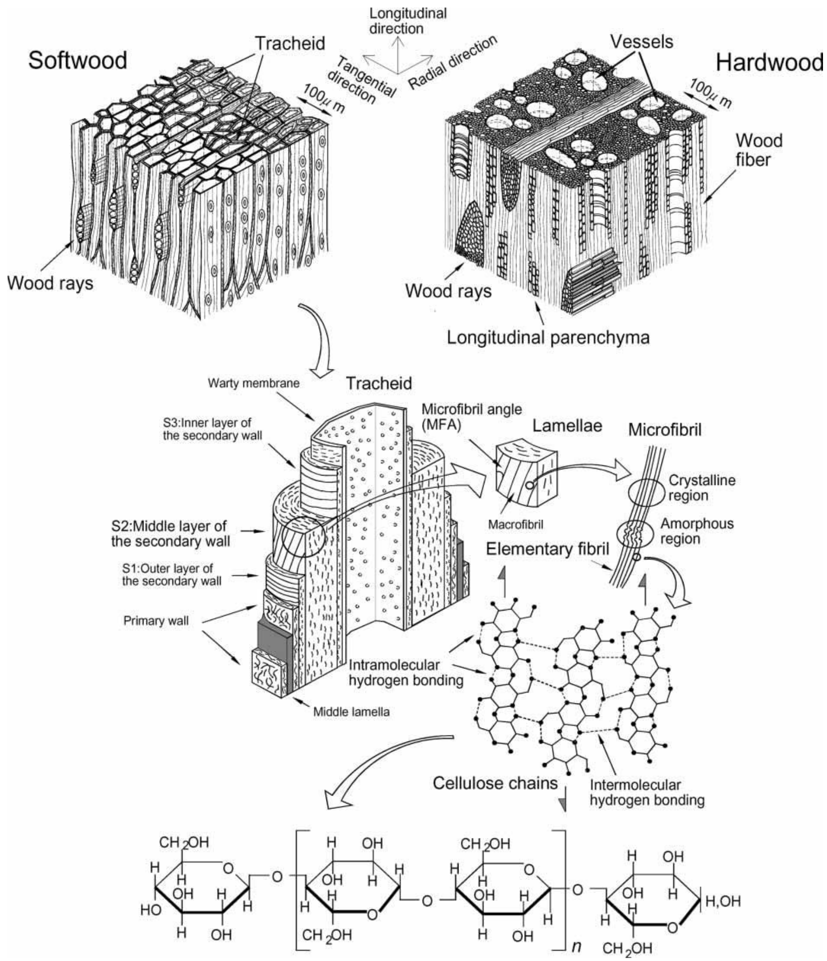
- effects of modification on wood properties/quality
    - color
    - mass
    - chemical content
    - mechanical properties
    - hygroscopicity
- literature reviews
- case study & strategy for quality control:
    - process
    - product
- concussions

Important references

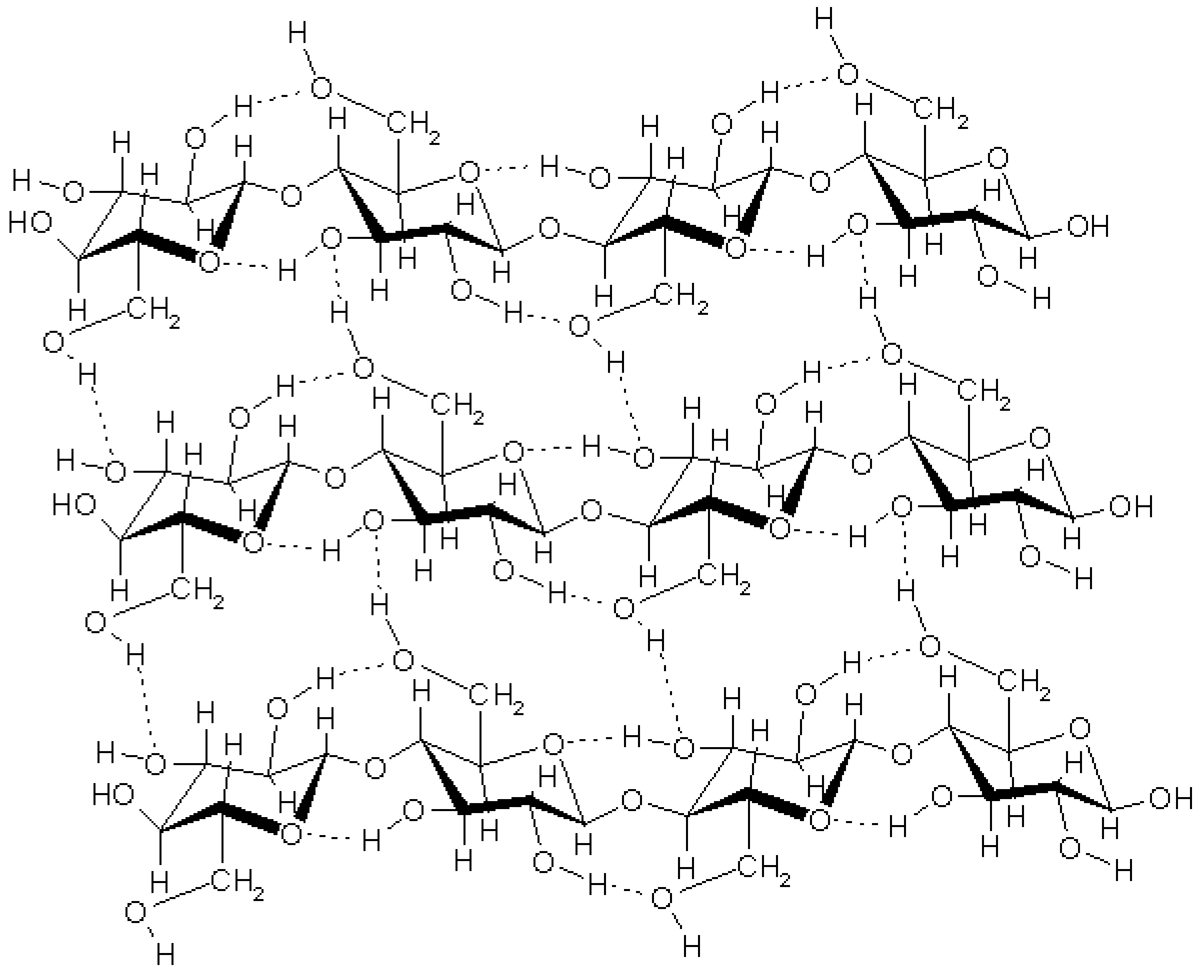
- Wim Willems, Charalampos Lykidis, Michael Altgen and Lothar Clauder **Quality control methods for thermally modified wood** Holzforshung (2015) 69(7): 875-884
- Kévin Candelier, Marie-France Thevenon, Anélie Petrissans, Stéphane Dumarcay, Philippe Gerardin, Mathieu Petrissans **Control of wood thermal treatment and its effects on decay resistance: a review** Annals of Forest Science (2016) 73:571–583

changes to wood during (thermal) modification

Wood chemical composition



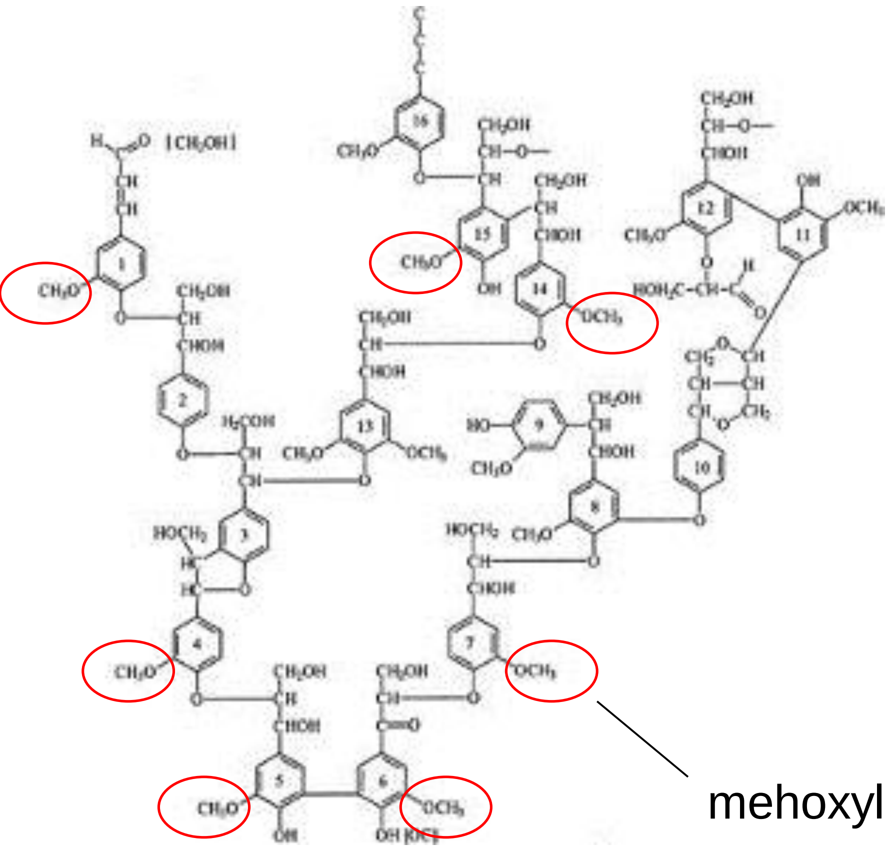
Cellulose (40-50%)

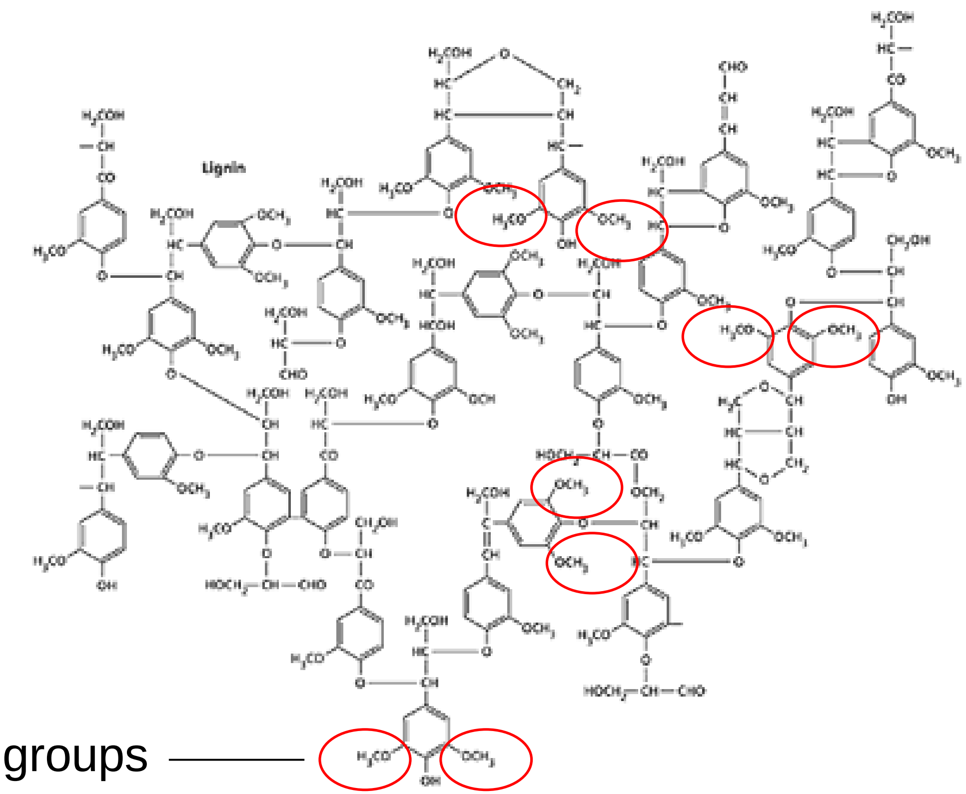


- Linear polymer
- Long chain
  (DP 5000-10000)
- B-D-Glucopyranose units
- 1,4-glycosidic bonds
- Hydroxyl groups bonds
- Different kind in wood:
  - amorphus,
  - semicrystalline,
  - crystalline

Lignin (20-30%)

Softwood (guaiacyl units) Hardwood (guaiacyl + syringyl units)

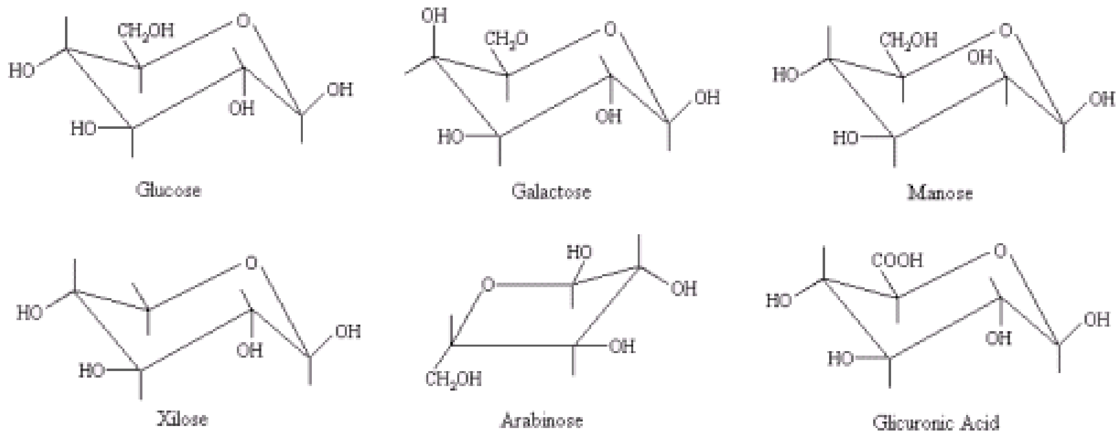




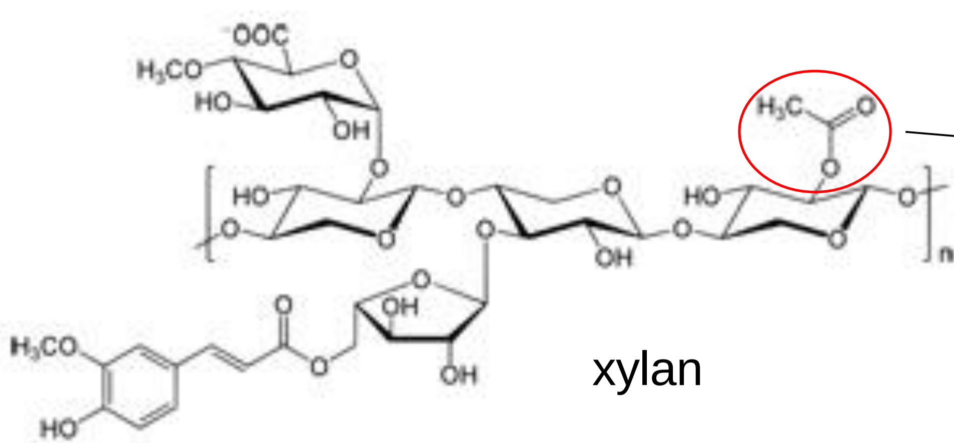
mehoxyl groups

Hardwood less stabile (syringyl units breaks easly)

Hemicellulose (25-35%)



- heteropolysacharydes
- short chain (DP 150-200)
- amorphus
- high reactivity
- ≠ composition for hardwood and softwood



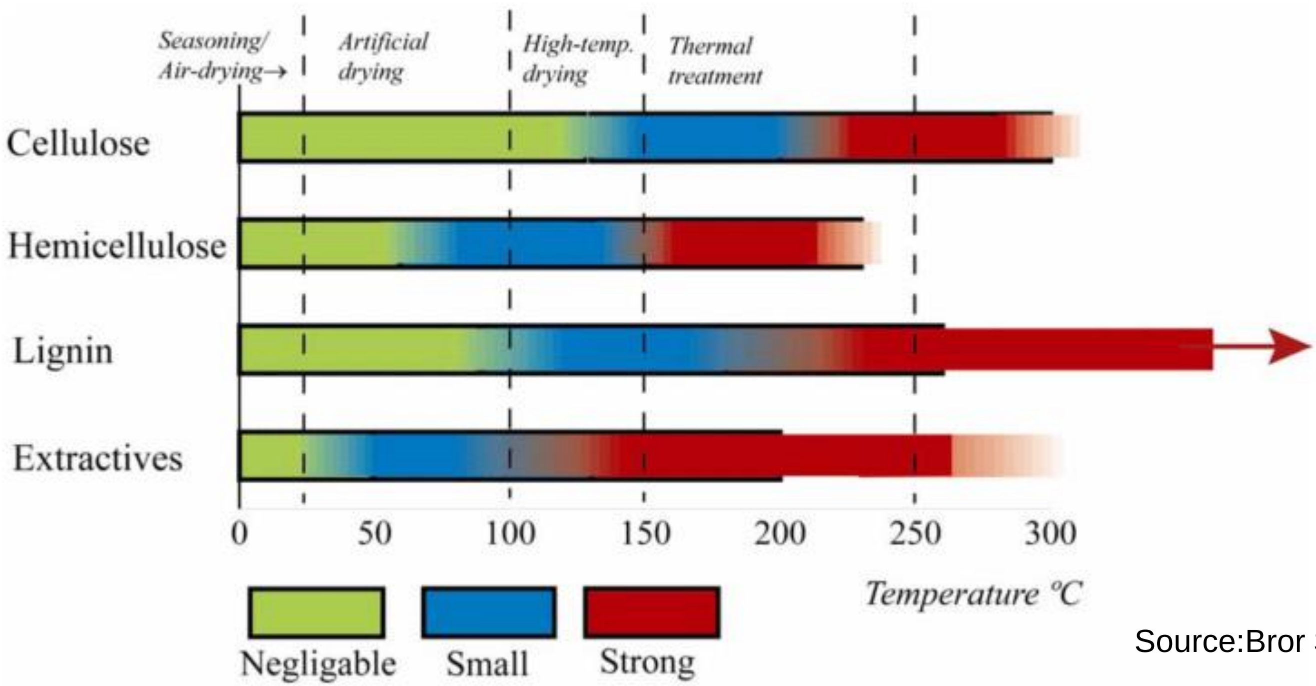
acetyl groups

xylan

Hardwood less stabile (more hemicelluloses content)

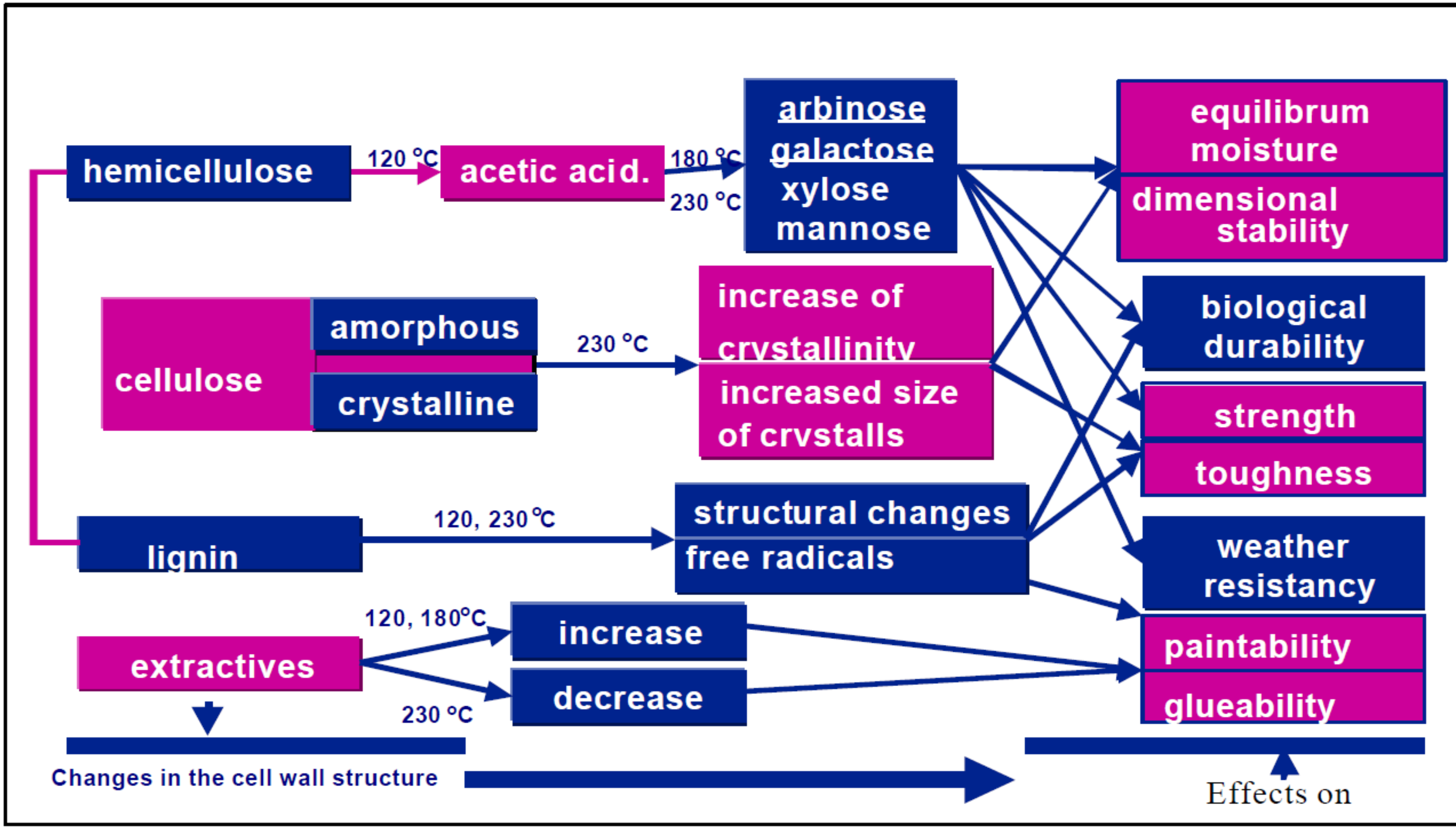
In lower temperatures

- No major changes in to principal components (lignin, cellulose, hemicellulose)
- Extractives (fatty acids, resin acids) migration to the surface: possibile covalent bonding with wood surface OH groups
- Molecular reorganization of wood polymers



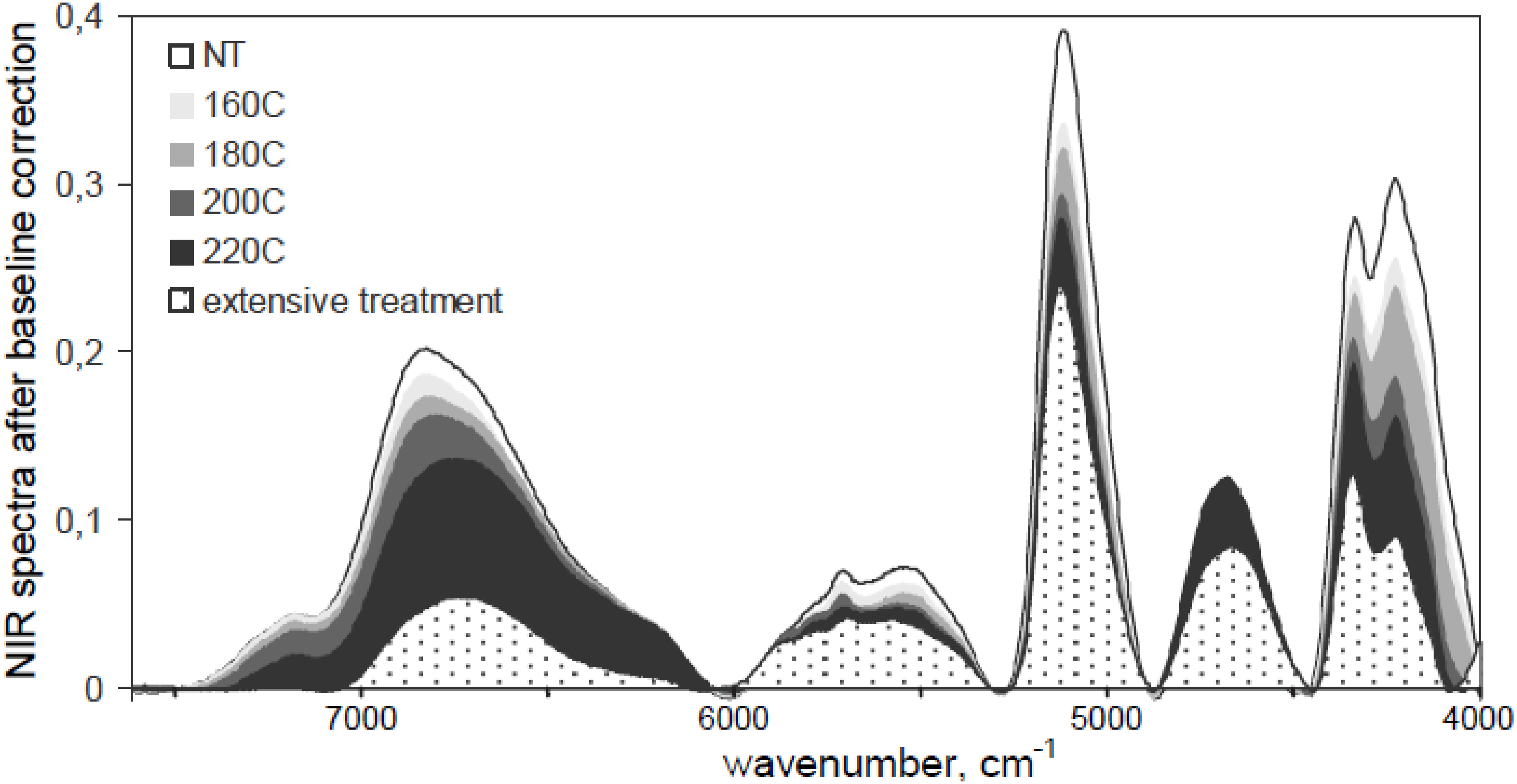
Source:Bror Sundqvist 2004

In higher temperatures

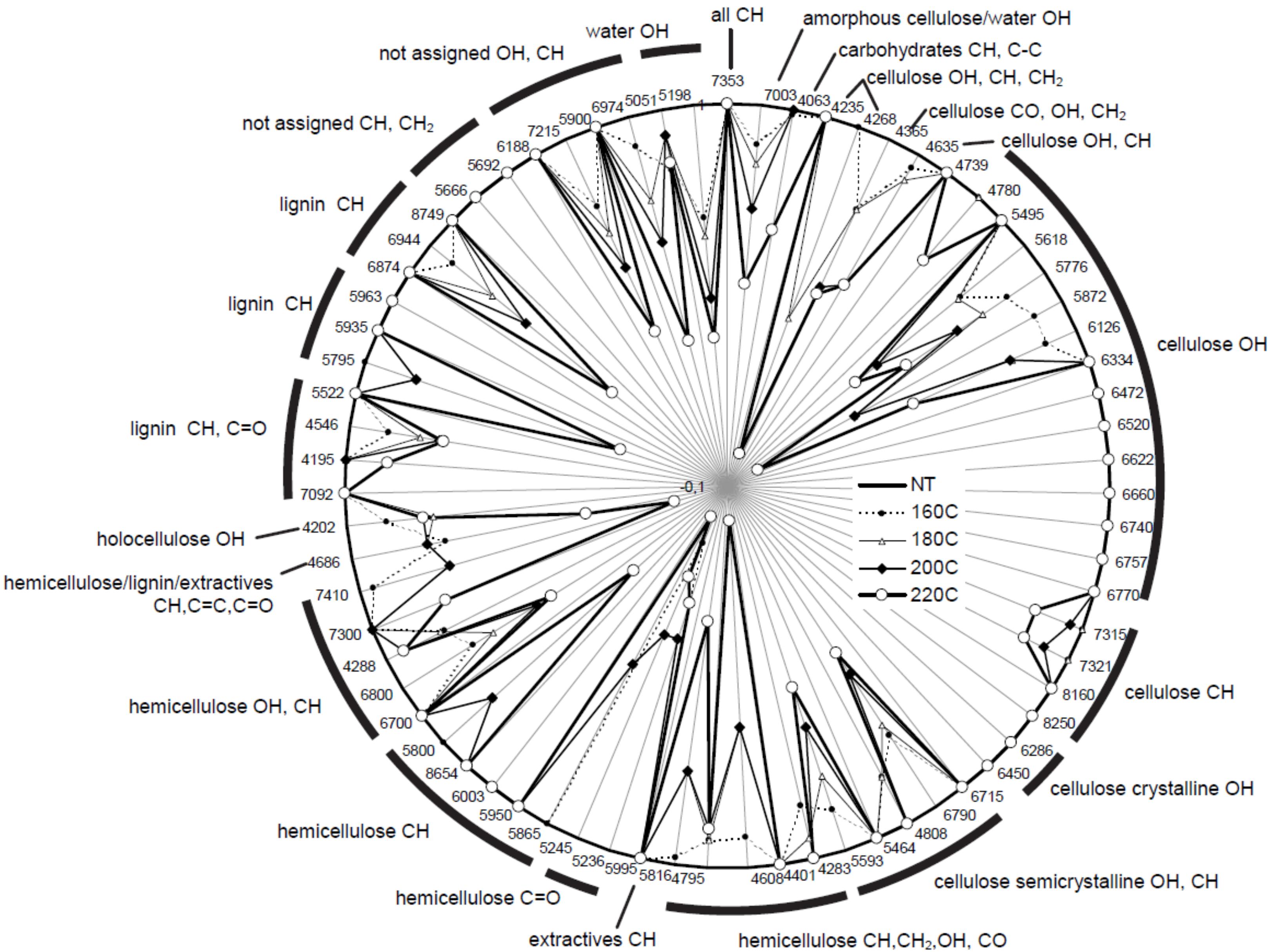


Source:VTT

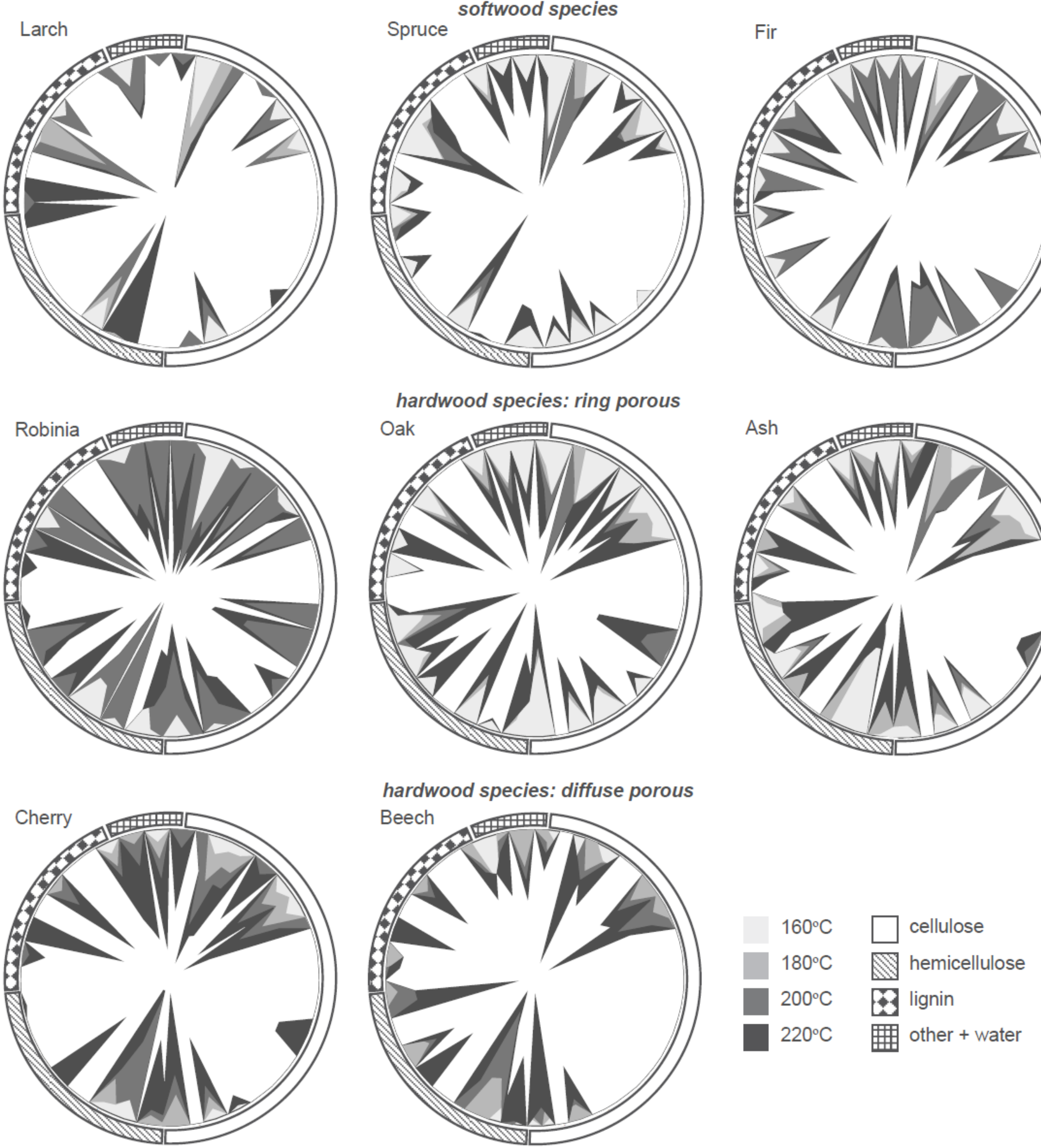
FT-NIR spectra of ash after various intensities of treatment



xylogram



all CH
water OH
amorphous cellulose/water OH
not assigned OH, CH
carbohydrates CH, C-C
cellulose OH, CH, CH2
cellulose CO, OH, CH2
not assigned CH, CH2
cellulose OH, CH
lignin CH
lignin CH
cellulose OH
lignin CH, C=O
holocellulose OH
hemicellulose/lignin/extractives CH,C=C,C=O
cellulose CH
hemicellulose OH, CH
cellulose crystalline OH
hemicellulose CH
cellulose semicrystalline OH, CH
hemicellulose C=O
extractives CH
hemicellulose CH,CH2,OH, CO
NT
160C
180C
200C
220C
1
-0,1


softwood species
Larch
Spruce
Fir
hardwood species: ring porous
Robinia
Oak
Ash
hardwood species: diffuse porous
Cherry
Beech
160°C
180°C
200°C
220°C
cellulose
hemicellulose
lignin
other + water

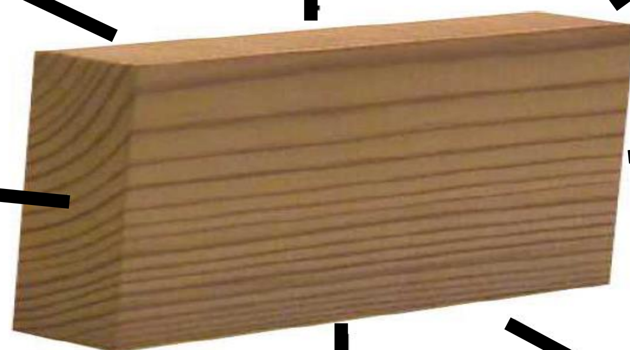
What «quality»?

Thermally treated wood

Reduced equlibrium moisture content and wettabilitty

Improved dimentional stability

Reduced thermal conductivity



Improved durability against decay and weathering

Resin removed

Loss of mechanical strenght

Constant colour through the piece

Emissions, pH etc...

Equlibrium moisture content and wettabilitty

- ↓ hydroxyl groups → ↓ water absorbed by the cell
- ↑ of cellulose crystalinity → no acesability in hydroxyl groups
- Polycondensation and crosslinking of lignin
- Fats and waxes moves along parenchyma cells

Hydrophobic surface
(effect on gluing and finishing)

Thermal conductivity

- ↓ amount of water → ↓ EMC
(thermal conductivity of water is higher then wood)
- Hemicelluloses degradation → ↓ density

Reduction of 20-25% of thermal conductivity
(advantage for sauna, doors, cladding ect.)

Resin presence

- Fats and waxes moves along parenchyma cells
- Above 180°C are not more detected

No problem of resin leakage through the knots or pitch (better esthetical properties)

Mechanical strenght

- Degradation of hemicellulose → ↓ density → ↓ bending and tensile strenght
- Polycondensation of lignin (cross linking) → positive impact in longtitudinal directions
- ↓ EMC → positive impact, but effect is supresed by chemical degradation
- ↑ cellulose crystalinity at initial stage → positive impact for Young modulus and then Ym ↓

↓

Generaly reduce mechanical properties

Dimentional stability

- Polymers formed form sugars are less higroscopic than hemicellulose
- ↓ methyl radicals in lignin units → ↑ phenolic groups → crosslinking of lignin

↓ of wood higroscopicity → ↑ dimentional stability

Durability against decay and weathering

- Some products of HT (furfural) are linked with lignin → fungi dont recognize them
- Degradation of hemicelluloses and amorphus cellulose → ↓ EMC (fiber saturation point)
- Lignin degraded compnents are less leachable then lignin

Improved durability

Colour

- Degradation of helicelluloses → darker colour
- Reaction not limited to the surface

Constant colour through the piece
(estetical properties)

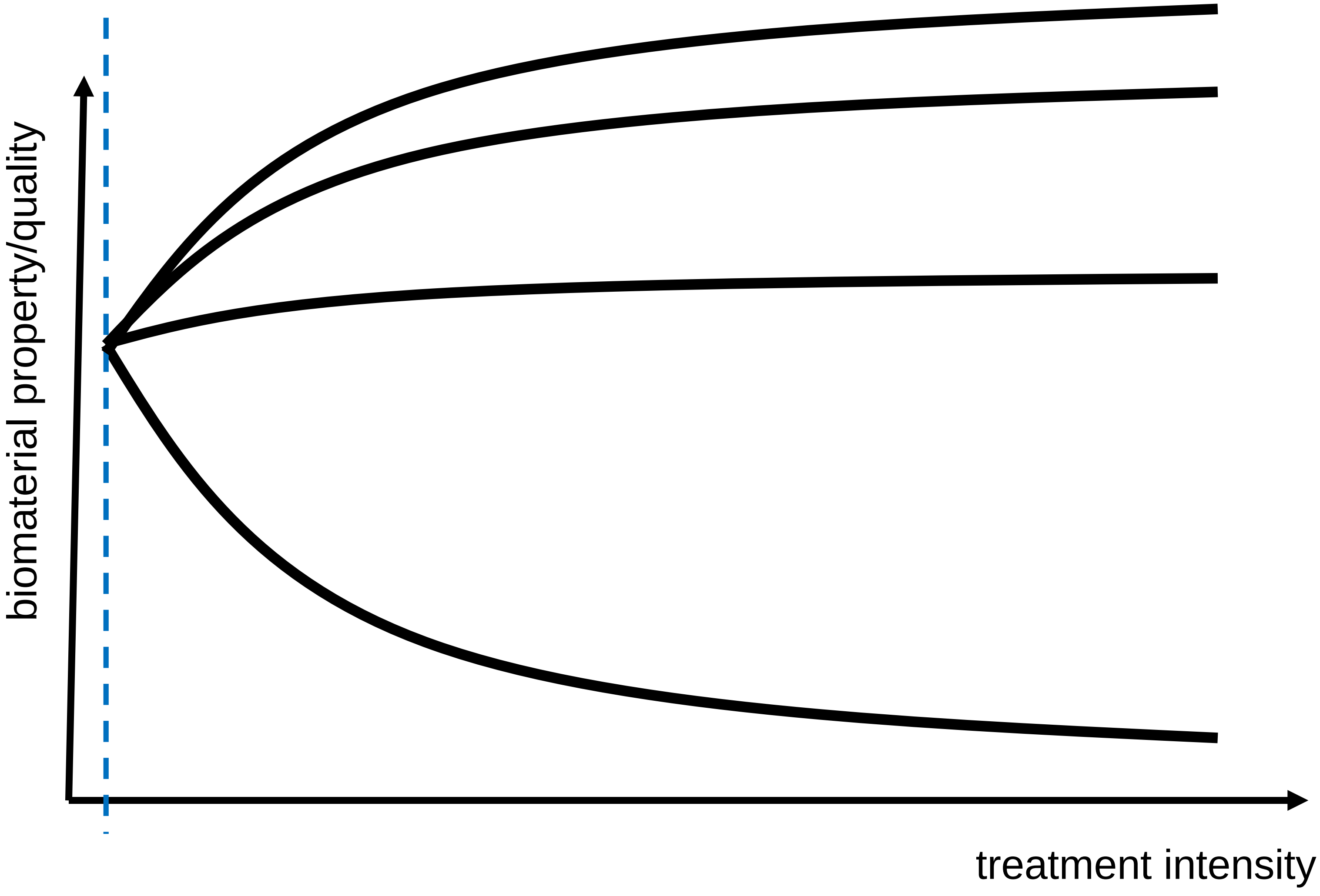
Emissions, pH etc...

- Hemicelluloses deacetylation (xylose and glucoronic chains) → acetic acid + formic acid
- Hemicelluloses degradation (dehydratation of xylose) → emission of furfural
- Lower VOC emission comparing with air dryed wood

↓

Characteristic smell, pH 4-6

What is optimal?



literature references

prediction of durability by means:

- mass loss
- spectroscopic analysis
- colour
- elemental composition (O/C) analysis
- non-destructive mechanical analysis (SW, BING, free vaibrations, US)
- process temperature kinetics

according to Candelier et. al

Characterization methods for TMW:

- mass loss
- Hygroscopicity (dimentional behaviour)
- Strength parameters
- Surface characteristics (light scatter)
- Porosity and permeability
- Electrical resistivity
- colour

according to Willems et. al

Characterization methods for TMW:

- spectroscopic analysis:
  - Electron Spin Resonance (ESR)
  - Nuclear Magnetic Resonance (NMR)
  - Mid and Near Infrared (IR/NIR)
- Thermal analysis
- Total soluble carbohydrates
- O/C elemental ratio
- Chemnical analysis of volatiles

according to Willems et. al

Summary of quality control methods for durability (from Willems et. al)

	Industrial suitability		Field suitability, i.e. independency on		
Method	Off-line	On-line	Control?[a]	Species?	Process?
Dry ML	•	x	x	x	x
EMC	•	x	•	x	•/x
DVS	x	x	•	x	•/x
CA	•	x	x	x	x
Hardness	•	x	x	x	x
HEMI	•	x	x	x	x
Surface reflectance	•	•/x	x	x	x
Electrical resistivity	•	•/x	x	x	x
Colour	•	•	•	x	x
ESR	x/•	x	•	•	x/•
FTIR	•	•	x	x	x
NIR	•	•	x	x	x
TGA	•/x	x	•	•/x	x
CHN(O)	x/•	x	•	•	•/x
Gas analysis	n.a	•	n.a.	x	x
Durability	x	x	•	•	•

[a]Is matched untreated control sample for calibration needed?

Symbols: •, yes; •/x, probably yes; x/•, probably no; x, no; n.a., not applicable.

Thermal modification of poplar veneers in vacuum conditions

Case study example

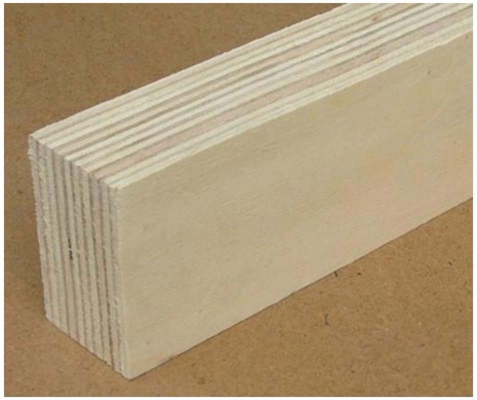
Anna Sandak, Jakub Sandak, Ignazia Cuccui, Ottaviano Allegretti, Roberto Zanuttini, Francesco Negro, Corrado Cremonini, Laura Rosso, Gaetano Castro

part presented at ECWM8 EIGHTH EUROPEAN CONFERENCE ON WOOD MODIFICATION 26th and 27th October 2015, FINLAND

Poplar resources

- fast growing species, widespread in plantations with rotation period of 5 to 20 years
- in Europe poplar plantations cover about 940.000 hectares
- 90% of their production is used for manufacturing of plywood, sawn timber, pulpwood, fuelwood and biomass for energy
- high hygroscopicity of the wood material



Thermal modifications (plywood)

Limited research about HT to wood derivatives, in particular to plywood

- 1st trials: TM of wood after panel manufacturing (Del Menezzi et al. 2009)
- 2nd trials: TM of wood before panel production (Zdravković et al. 2013, Fioravanti et al. 2013)
- 3rd trials: autoadhesion of veneers in plywood production by using heat, moisture and mechanical compression (Ruponen et al. 2014)
- mechanical performance and the bonding quality of treated samples suggested that veneers should be glued after heat treatment (Goli et al. 2014)
- production of heat treated poplar plywood is feasible but needs important improvements in order to avoid reductions in mechanical properties (Goli et al. 2015)

Experimantal samples

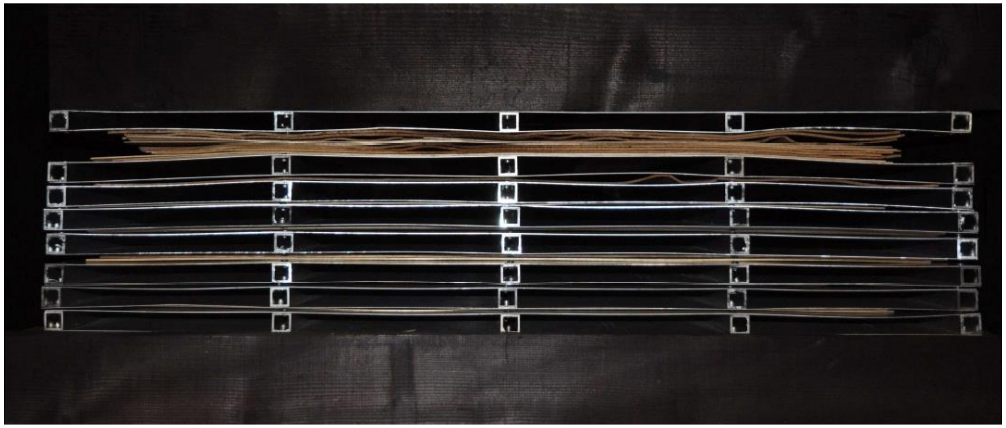
Rotary-cut veneer sheets of Poplar clone ‘I-214’ (*Populus* × *canadensis* Moench)

One sheet of plywood was prepared for each treatment

Veneers were cut to dimensions 360 mm x 150 mm x 2.5 mm

Characterized both before and after vacuum thermal treatment

Treatment set-up



Aluminium plates heated electrically which produce a heating of the conducting type were used.

Heating and cooling ramp were kept constant at 60°C/h.

The ventilation was disabled so that the test chamber only acts as a sealing system of the vacuum.

38 batch processes with various treatment conditions (temp. from 150°C to 240°C, pres. 100, 250 or 1000 mbar and time from 0.5 to 22.5 h.)

batch number	**#1**	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**	**#8**	**#9**	**#10**	**#11**	**#12**	**#13**
T max [ºC]	240	238	238	238	195	150	174	192	174	213	240	253	239
time [hours]	1.5	1.5	1.5	1.5	6.1	12.4	6.4	22.2	22.5	22.2	22.3	1.1	1
pressure [mbar]	1000	250	100	1000	1000	250	1000	250	250	250	250	250	1000
batch number	**#14**	**#15**	**#16**	**#17**	**#18**	**#19**	**#20**	**#21**	**#22**	**#23**	**#24**	**#25**	**#26**
T max [ºC]	239	239	238	241	239	239	212	203	194	182	174	165	155
time [hours]	0.5	2.12	0.24	2.22	1.07	0.5	1.08	1.1	1.07	1.07	1.07	1.07	1.07
pressure [mbar]	1000	1000	1000	250	250	250	250	250	250	250	250	250	250
batch number	**#27**	**#28**	**#29**	**#30**	**#31**	**#32**	**#33**	**#34**	**#35**	**#36**	**#37**	**#38**	
T max [ºC]	149	223	213	213	211	213	194	173	214	175	240	217	
time [hours]	1.07	1.07	2.24	4.3	0	6.42	6.1	6.4	4.7	12.9	6.6	4.8	
pressure [mbar]	250	250	250	250	250	250	250	250	100	250	250	1000	

Samples characterization

Physical properties

Mass loss (ML) was determined by weighting each sample before the treatment and immediately after it, assuring the wood was absolutely dry (0% moisture content).

The Equilibrium Moisture Content (EMC) was calculated according to the ISO 3130 standard for treated and untreated samples

Color measurement

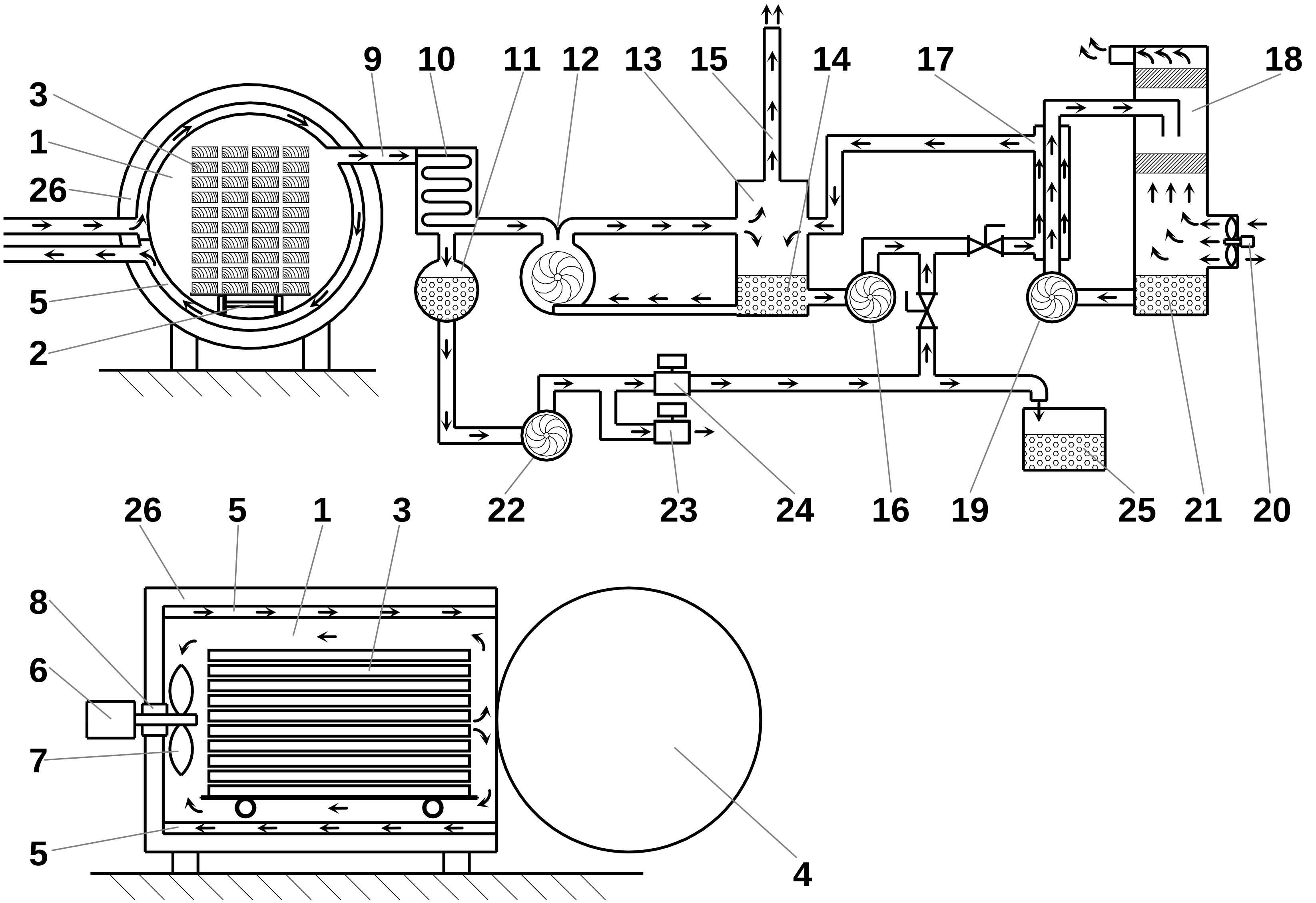
MicroFlash 200D spectrophotometer (DataColor Int), suitable for direct determination of the CIE L*a*b* colour coordinates was used for the measurement over an 18 mm diameter spot with a standard light source D65 and an observation angle of 10°. Each sample has been measured in 10 zones.

Chemical composition

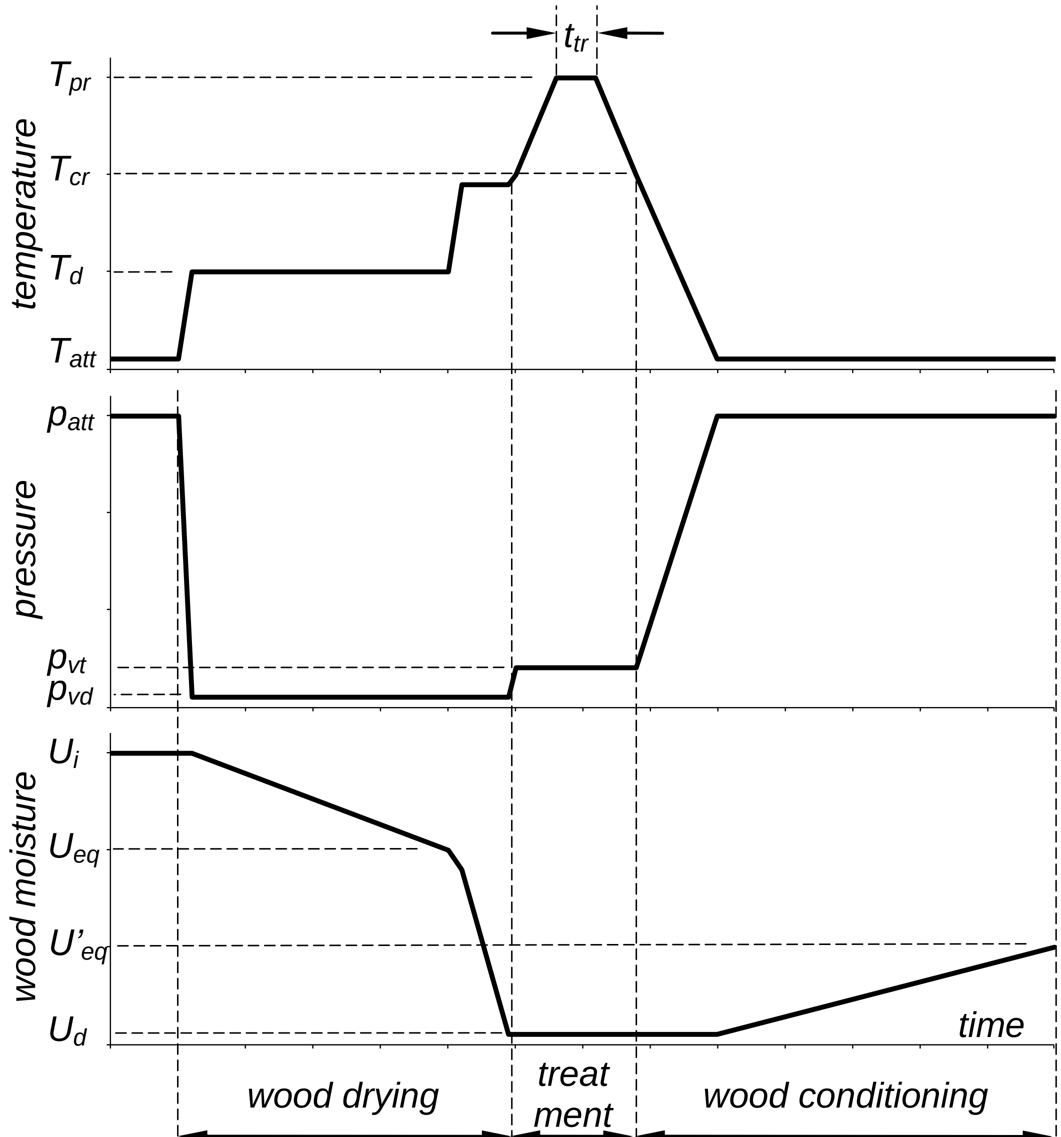
VECTOR 22-N (Bruker Optics GmbH, Ettlingen, Germany) equipped with the fibre-optic probe was used for spectra collection. The spectral range measured was between 4000cm^{-1} and 12000cm^{-1} and the spectral resolution of 8cm^{-1}. Each sample has been measured in 5 zones.

process quality control

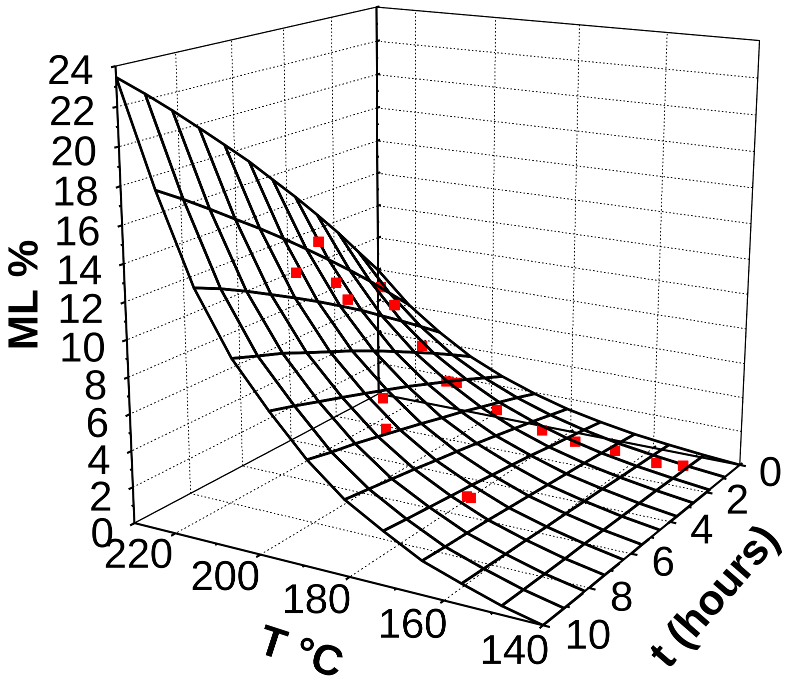
schema of TERMOVUOTO® system



Thermal treatment process conditions



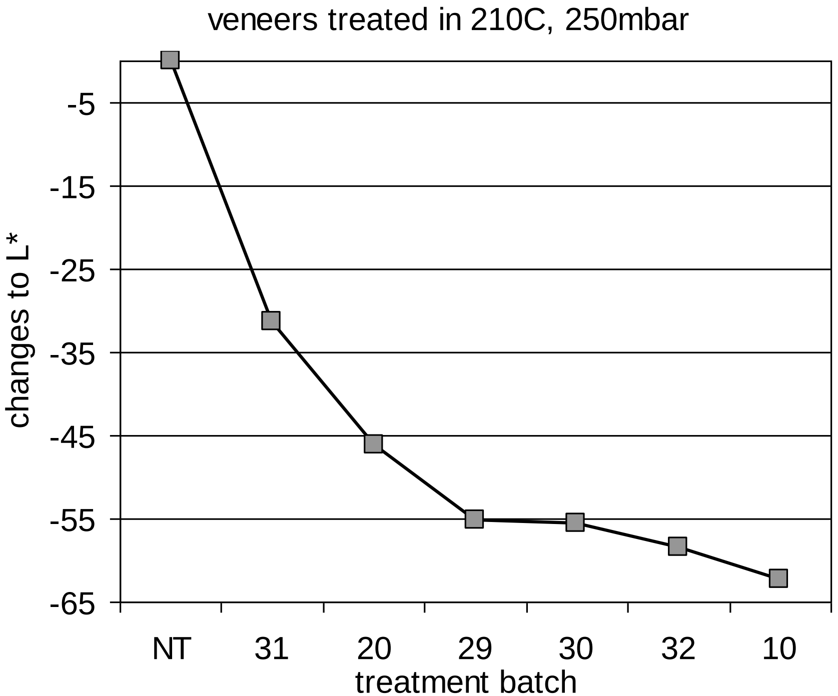
3D model regressing mass loss ML vs. treatment temperature (T) and time (t)

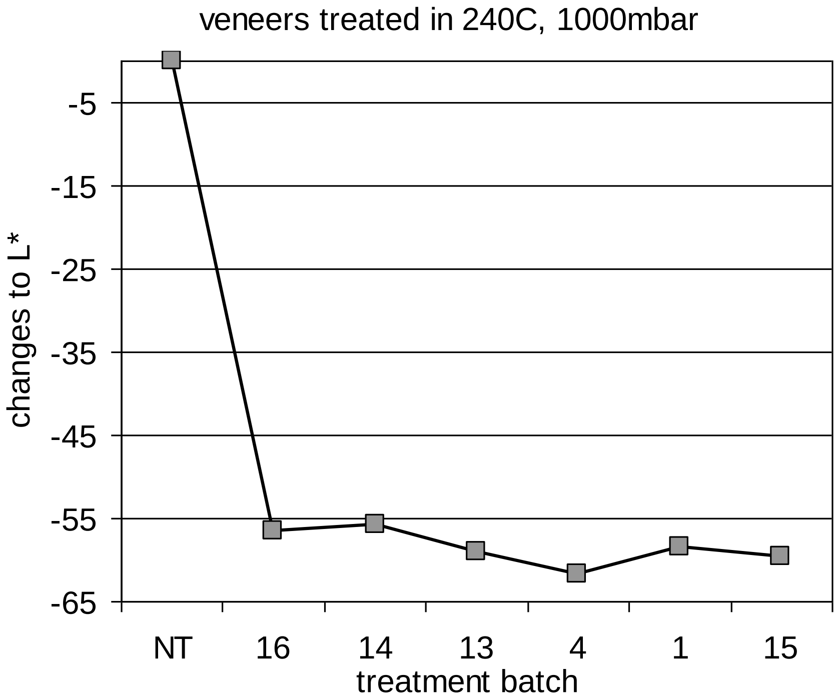


$$ML(T,t) = \left(a - b \cdot c^{t}\right) \cdot \left(\exp\frac{T - T_{cr}}{k} - 1\right)$$

a = 0.039
b = -0.033
c = 0.962
k = 33
T_{cr} = 140 °C

Color



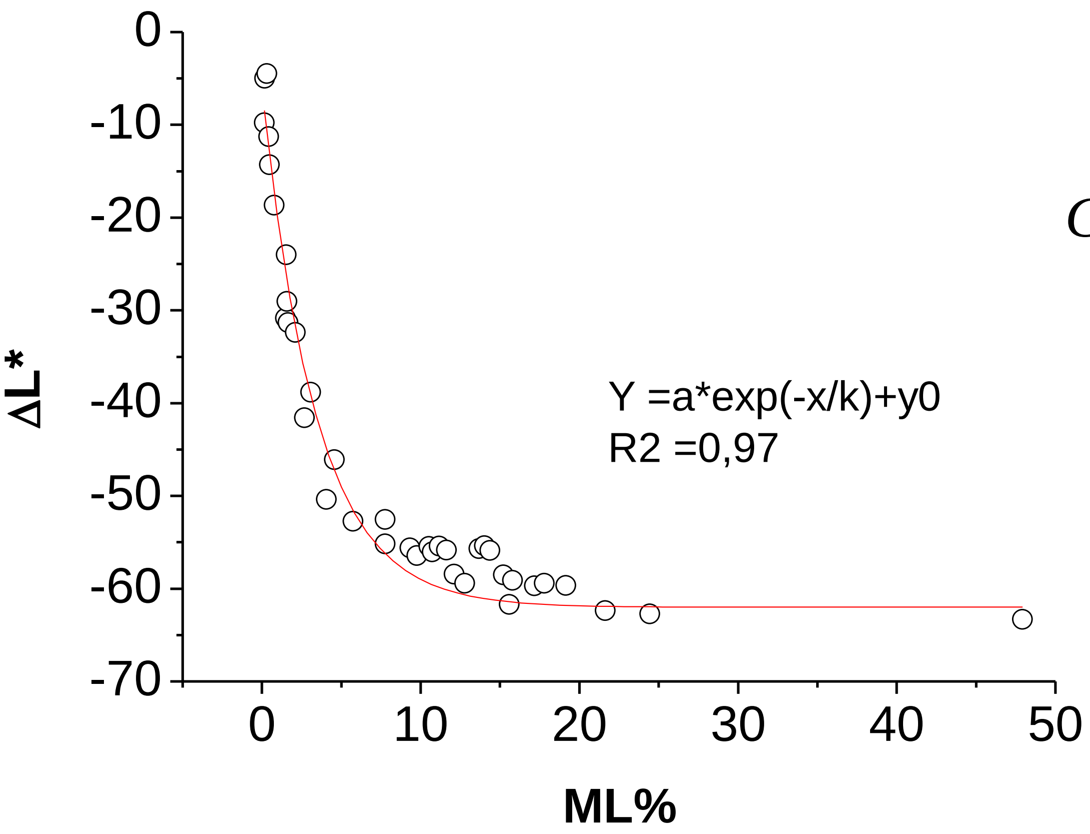


Time 0h 0h 1h 2.2h 4.3h 6.4h 22h 0h 0.2h 0.5h 1h 1.5h 1.5h 2.1h

The drop of L* is correlated with thermal treatment duration.

product quality control with mass loss

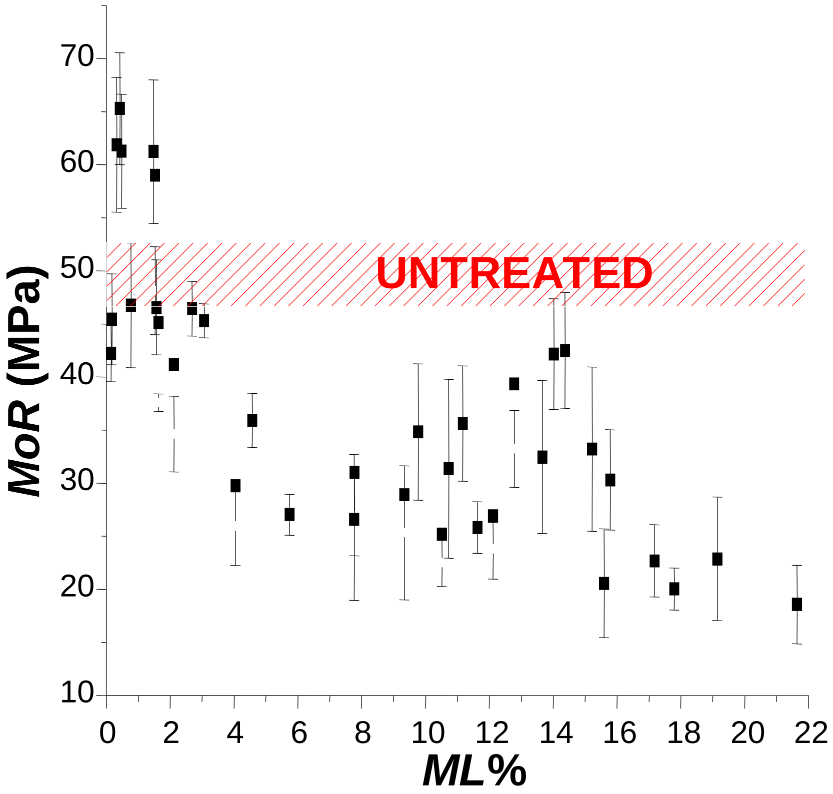
CIE ΔL* and mass loss ML

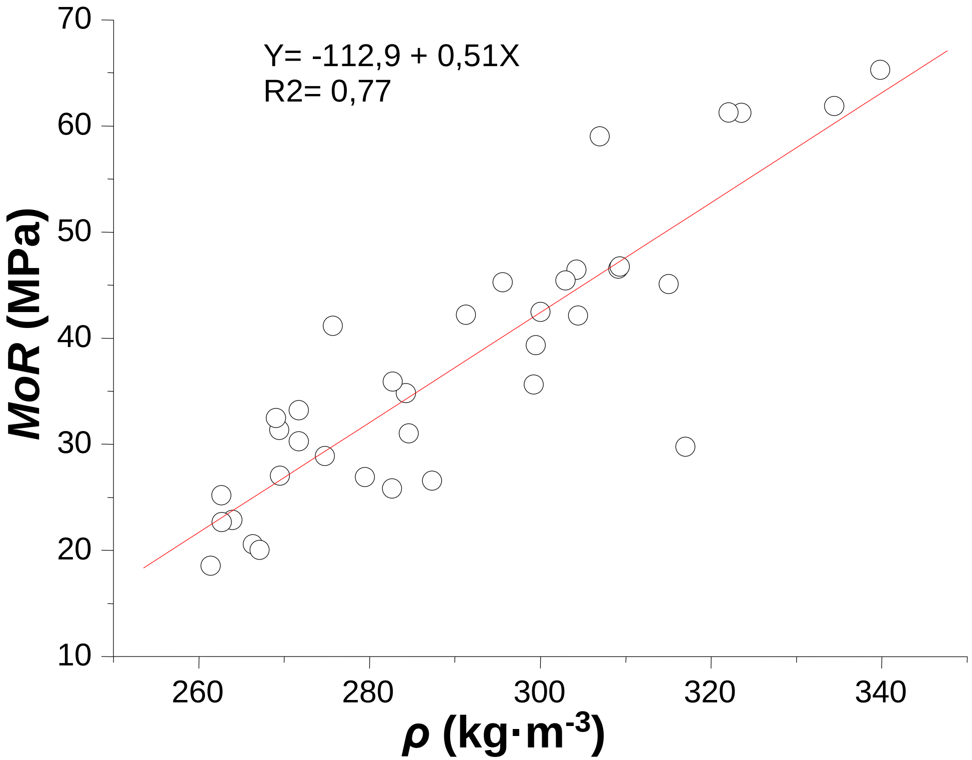


$$CIE\Delta L^{*}(ML) = a \cdot \exp\left(\frac{-ML}{k}\right) + y_0$$

a = 62
k = 0.034
y_0 = -1

mechanical strength MOR <-> mass loss ML and density ρ

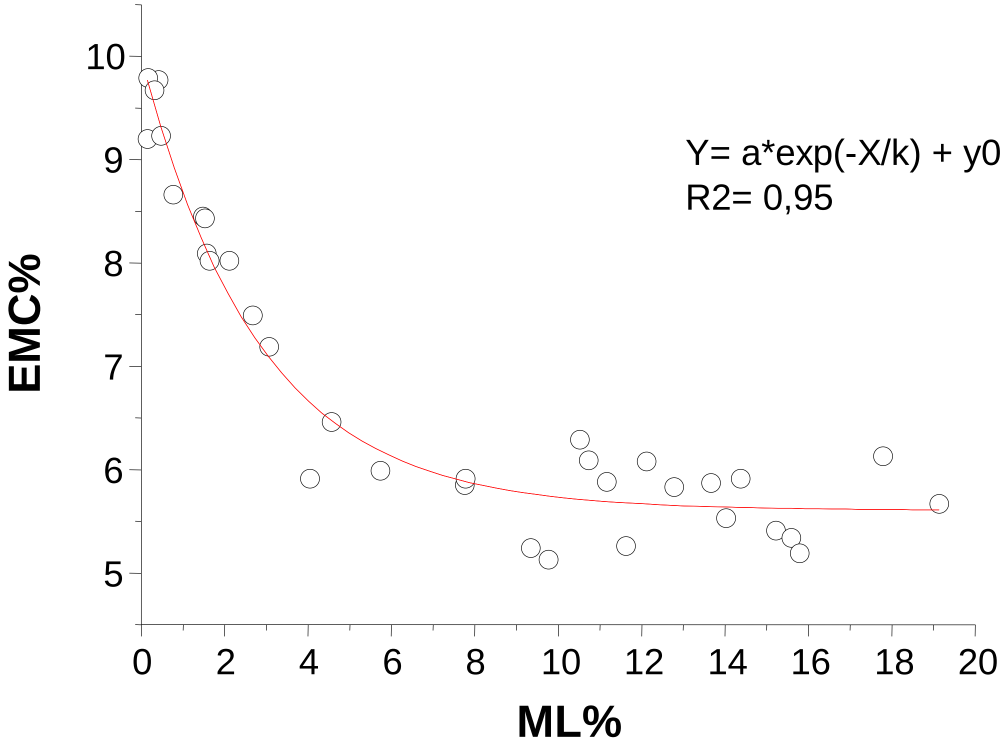




$$MOR(\rho, ML) = a + b \cdot \rho + \ln(ML)$$

a = -84.54
b = 390.9
c = -2.723

EMC and ML

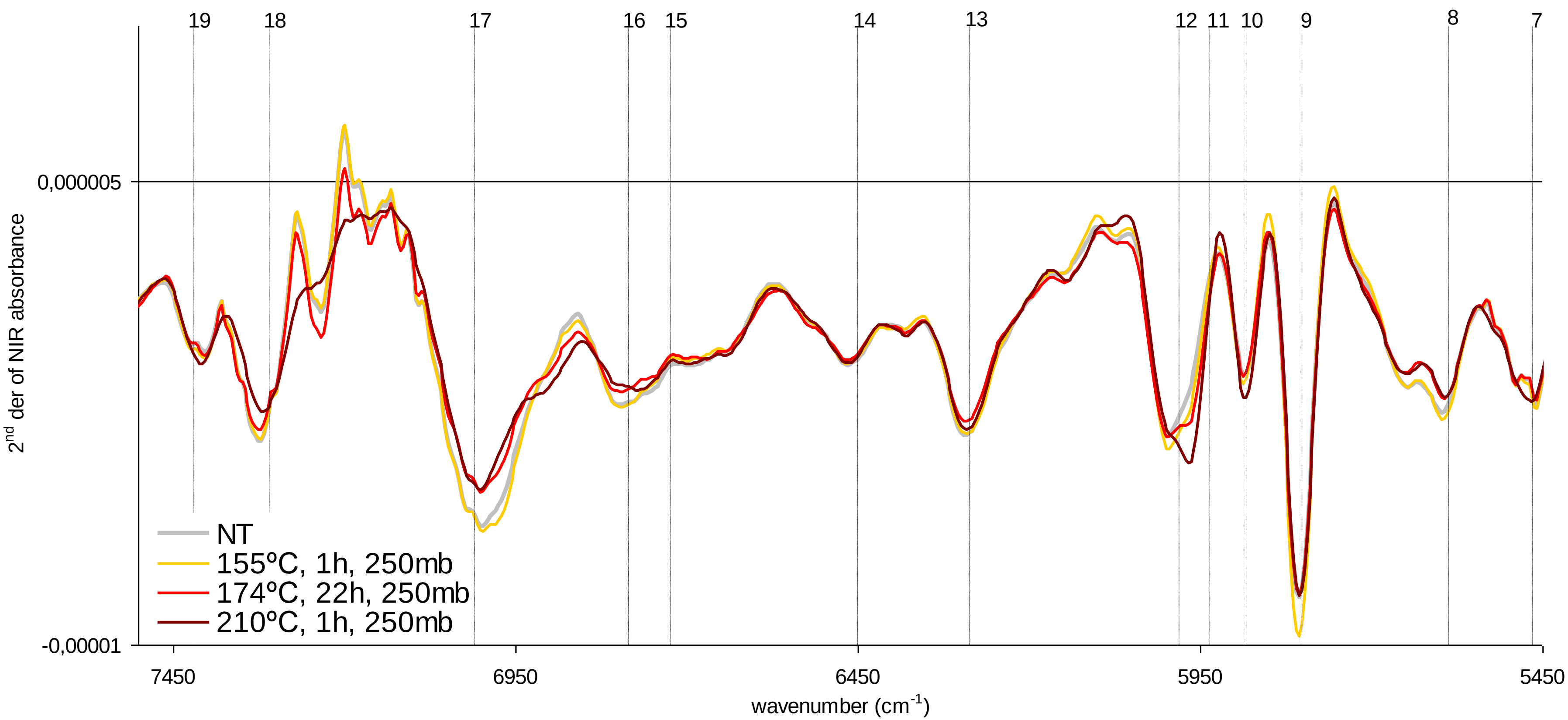


$$EMC = a \cdot \exp\left(\frac{-ML}{k}\right) + y_0$$

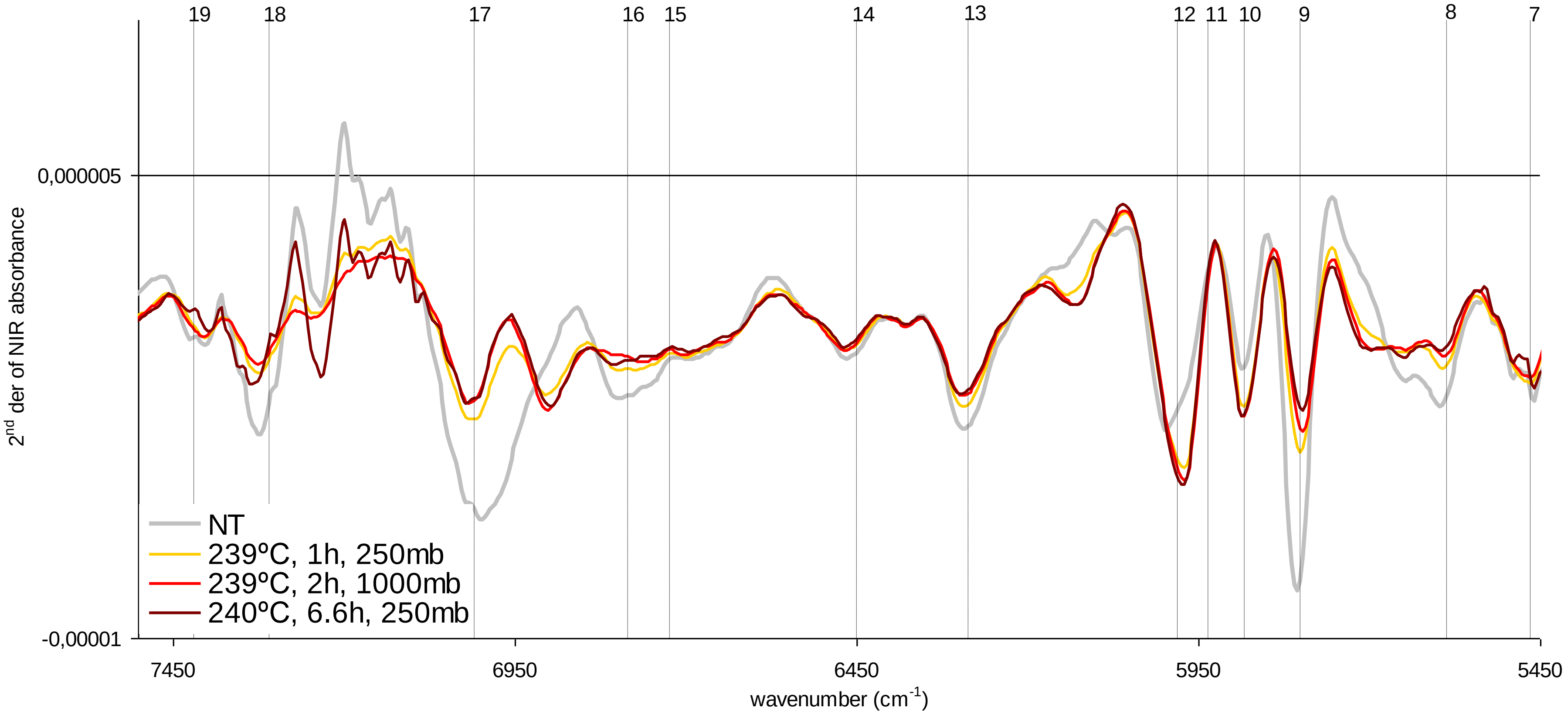
a = 0.370
k = 0.027

product quality control with NIR

Veneers in lower temperature



Veneers in higher temperature



ECWM8

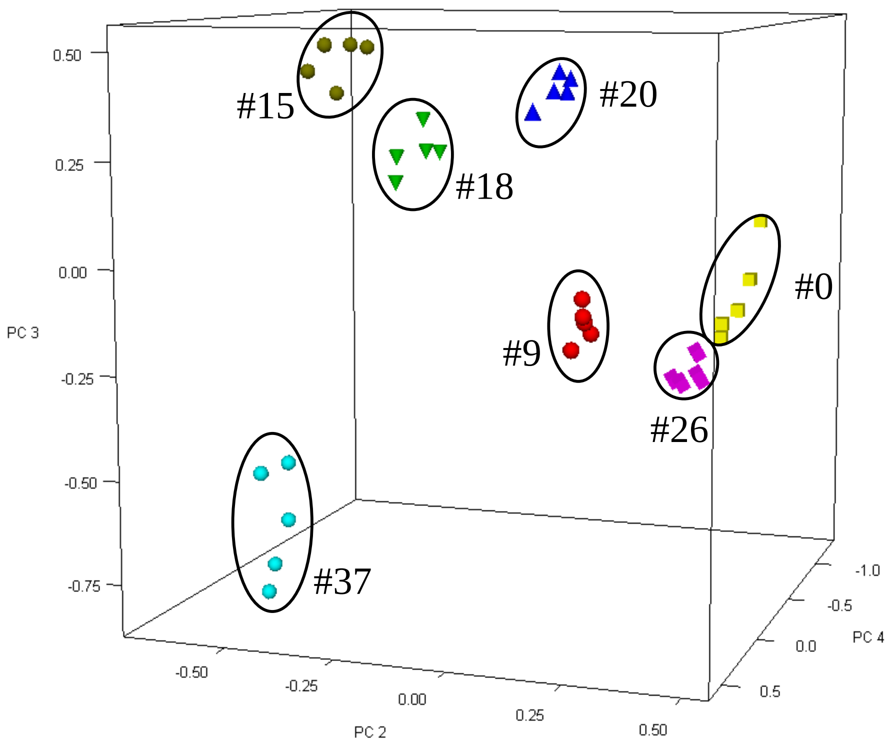
Spectra interpretation

band no.	low temperatute	high temperature	wavenumber (cm-1)	wood comonent	functional group
3	✓	✓	4204	holocellulose	OH
6	✓	✓	5219	water	OH
9	✓	✓	5800	hemicellulose (furanose/pyranose)	CH
12	✓	✓	5980	lignin	CH
13		✓	6286	cellulose crystalline	OH
16		✓	6787	cellulose semicrystalline	OH
17	✓	✓	7003	amorphus cellulose	OH
18		✓	7309	hemicellulose/cellulose	CH

Changes in EMC, ML and colour are effects of:

- migration or removal of extractives, low molecular weight sugars and aminoacids
- polymers degradation and its evaporation during the heat treatment process
- reduction of accessibility of hydroxyl groups of wood carbohydrates
- degradation of hemicelluloses and their conversion to less hygroscopic furan-based polymers
- polycondensation and crosslinking of lignin

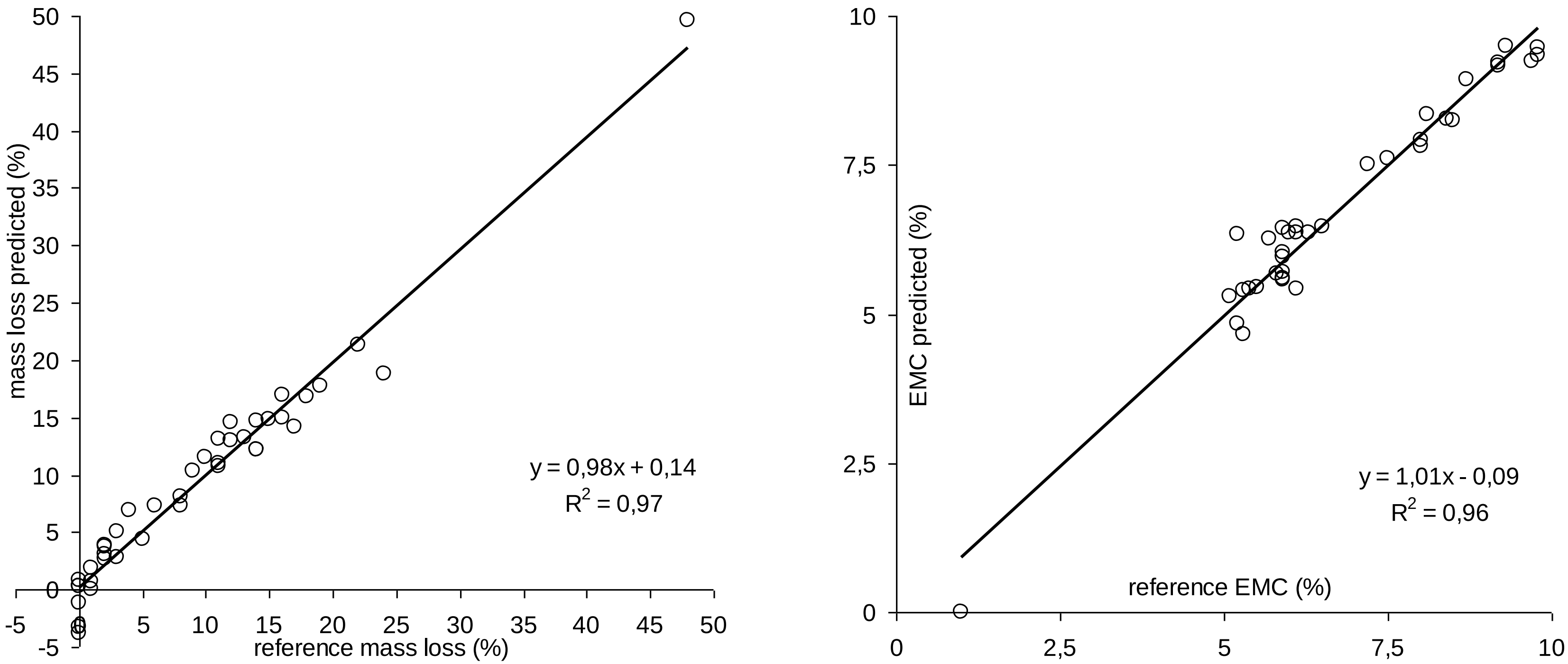
Principal Component Analysis



#0	NT
#26	155ºC, 1h, 250mb
#9	174ºC, 22h, 250mb
#20	210ºC, 1h, 250mb
#18	239ºC, 1h, 250mb
#15	239ºC, 2h, 1000mb
#37	240ºC, 6.6h, 250mb

Used for direct comparison of the effect of process parameters on the chemical composition of TMV veneers

PLS predicted versus measured values of ML and EMC



Conclussions

- MVA and chemometric modeling allowed understanding of the process mechanism and its kinetics and might be used for **selection of optimal process parameters**.
- **NIR was effectively used to predict wood physical properties**, considered as reliable indicators of the wood modification advancement.
- **Prediction errors** of validation models based on NIR spectra **were** relatively **small** (1.75% and 0.36% in case of ML and EMC respectively).
- The corresponding coefficients of determination were $R^2 > 0.97$ (ML) and $R^2 > 0.96$ (EMC).
- The **RPD** values 5.3 and 4.3 (for ML and EMC respectively) confirm **superior performance of the PLS**.

Acknowledgment

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BIO4ever

COST FP1303

Performance of bio-based building materials

Thanks!

Comments/critics/problems?

How much wood would a woodchuck chuck
if a woodchuck could chuck wood?

A woodchuck would chuck as much wood as a woodchuck could chuck if a woodchuck could chuck wood.