IMPACT OF A FORMIC/ACETIC ACID TREATMENT OF BEECH WOOD ON DELIGNIFICATION AND CHEMICAL STRUCTURE OF LIGNINS

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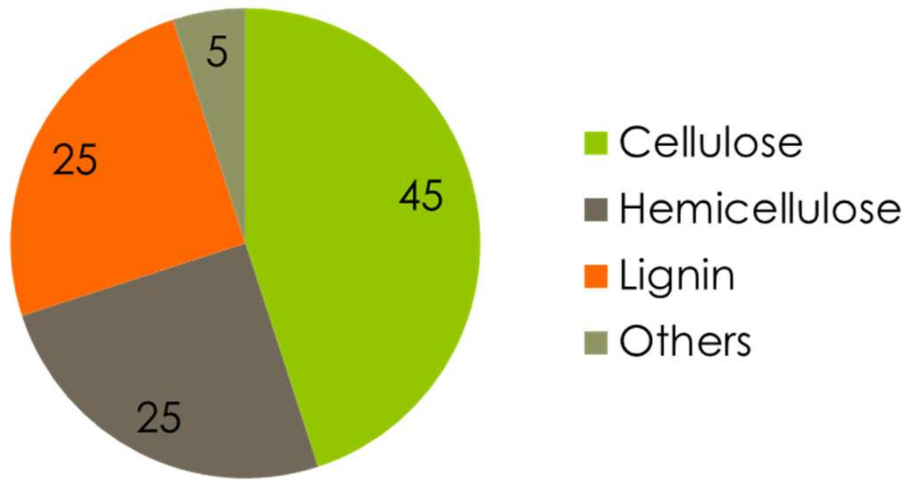
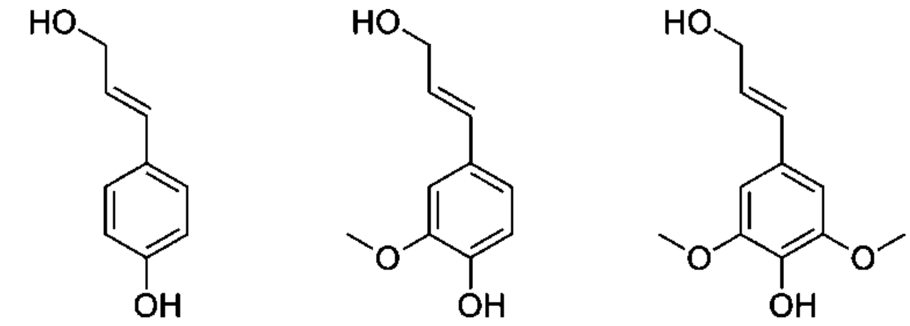
Context

The context of this study is...

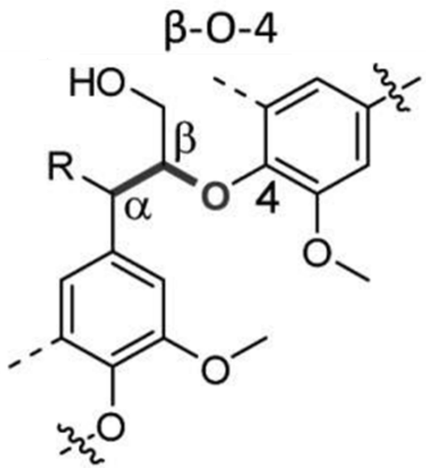
- ✓ The sustainable production of energy and biobased products from lignocellulosic substrates
- ✓ The development of integrated biorefineries
- ✓ Lignin valorization as a potential alternative to petrochemical polymers and as a promising resource for high-added value applications

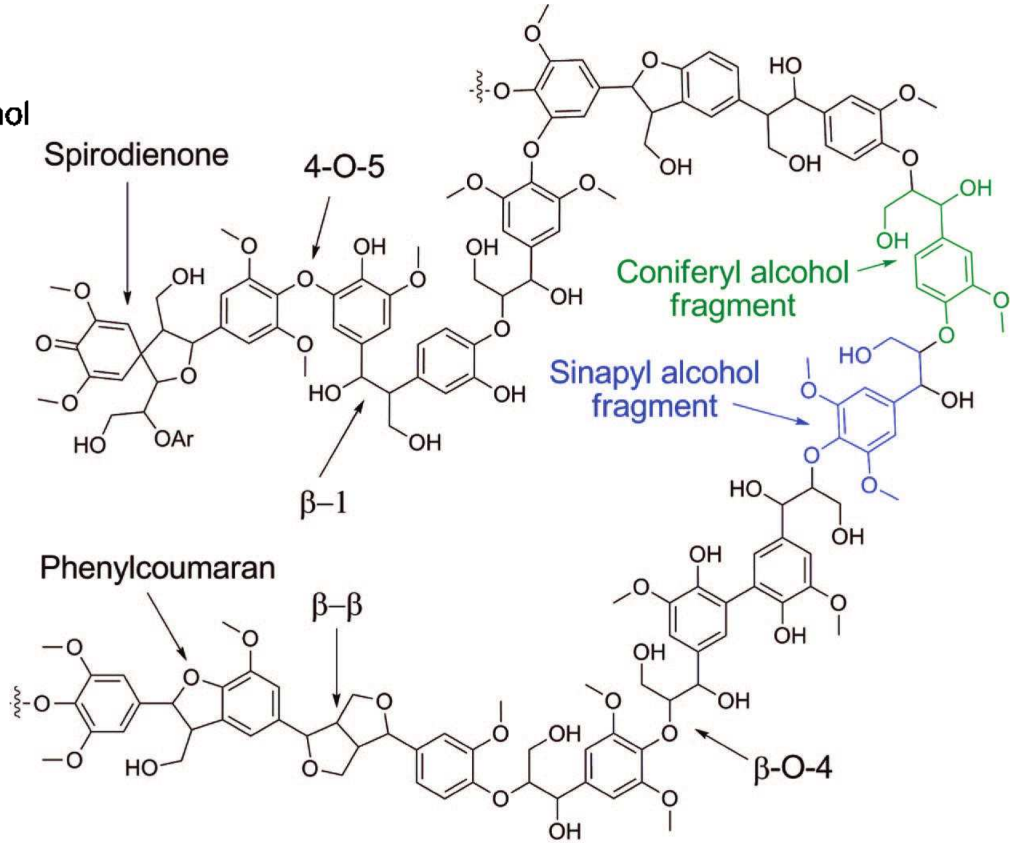


Lignin



p-coumaryl alcohol   coniferyl alcohol   sinapyl alcohol



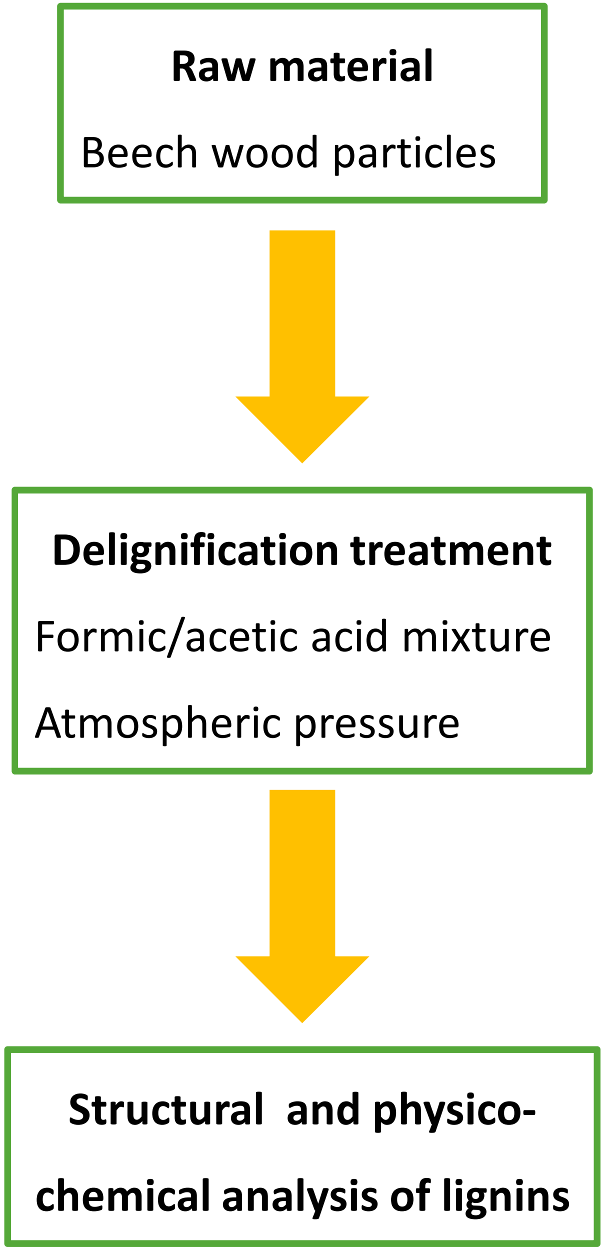


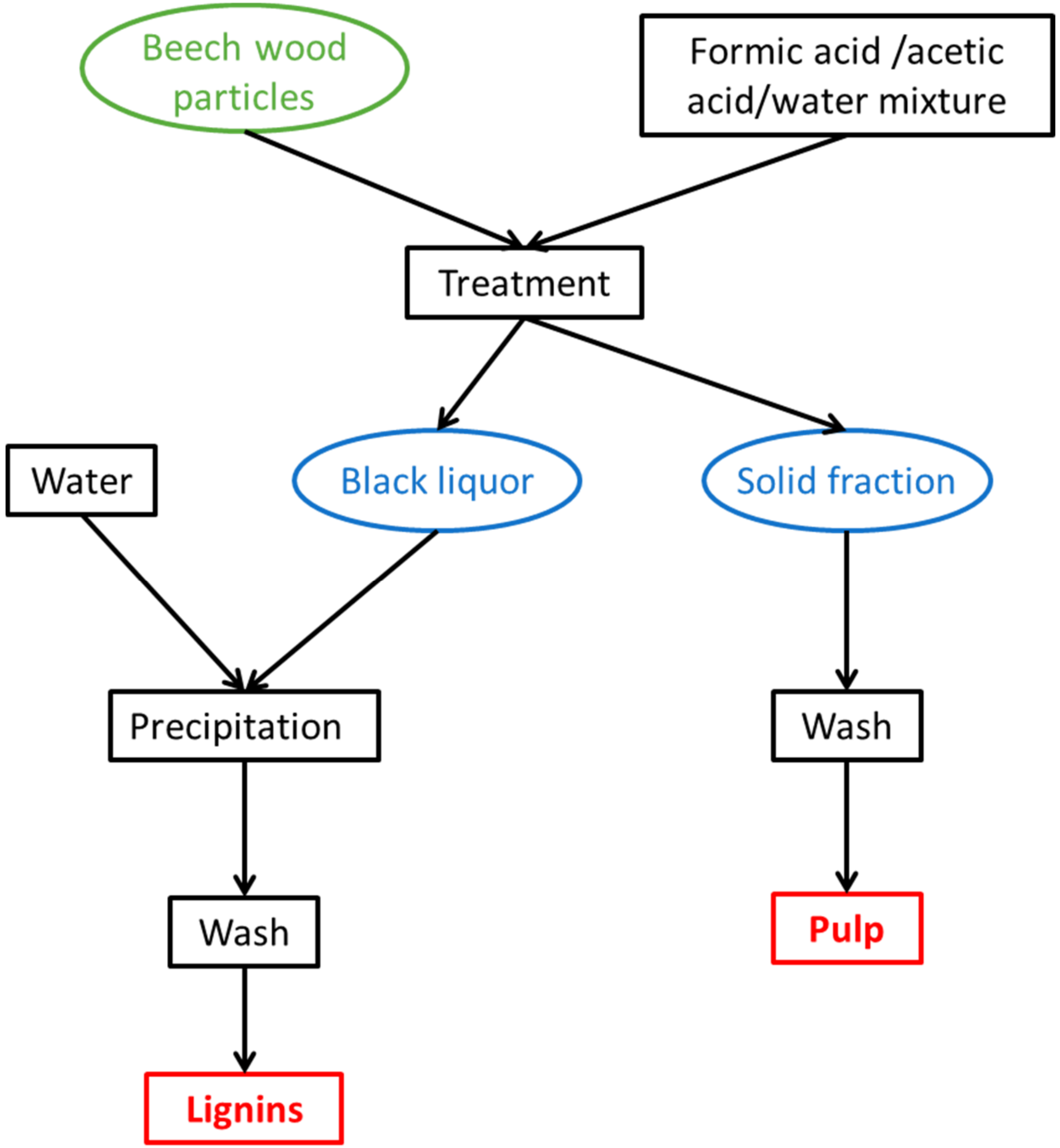
Zakzeski J. *et al.*, 2010. The catalytic valorization of lignin for the production of renewable chemicals. *Chem. Rev.*, **110**, 3552-3599.

Objectives

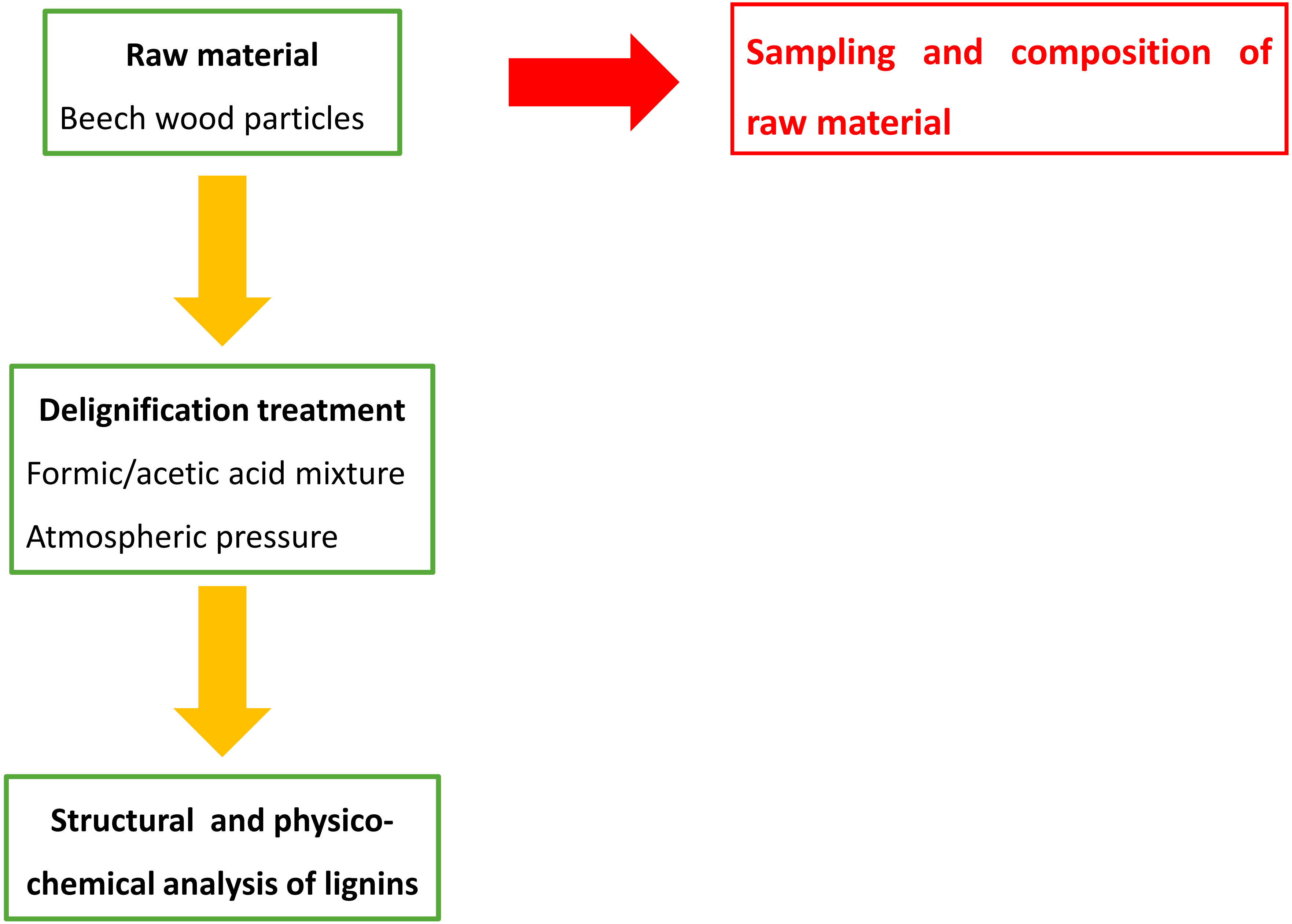
The objectives of this study are...

- ✓ The optimization of a formic/acetic acid delignification treatment of beech wood (*Fagus sylvatica* L.) particles
- ✓ The investigation of structural and physico-chemical features of extracted lignins





Vanderghem C. *et al.*, 2012. Optimization of formic/acetic acid delignification of Miscanthus x giganteus for enzymatic hydrolysis using response response methodology. *Ind. Crop. Prod.*, **35**, 280-286.


Raw material
Beech wood particles
Sampling and composition of raw material
Delignification treatment
Formic/acetic acid mixture
Atmospheric pressure
Structural and physico-chemical analysis of lignins

Sampling and composition of raw material

Sampling and production of beech wood particles

Sampling of 3 trees in the region of Gaume

↓

Manual barking

↓

First grinding

↓

Drying at 50°C for 24 hours

↓

Second grinding

↓

Particles around 4 mm

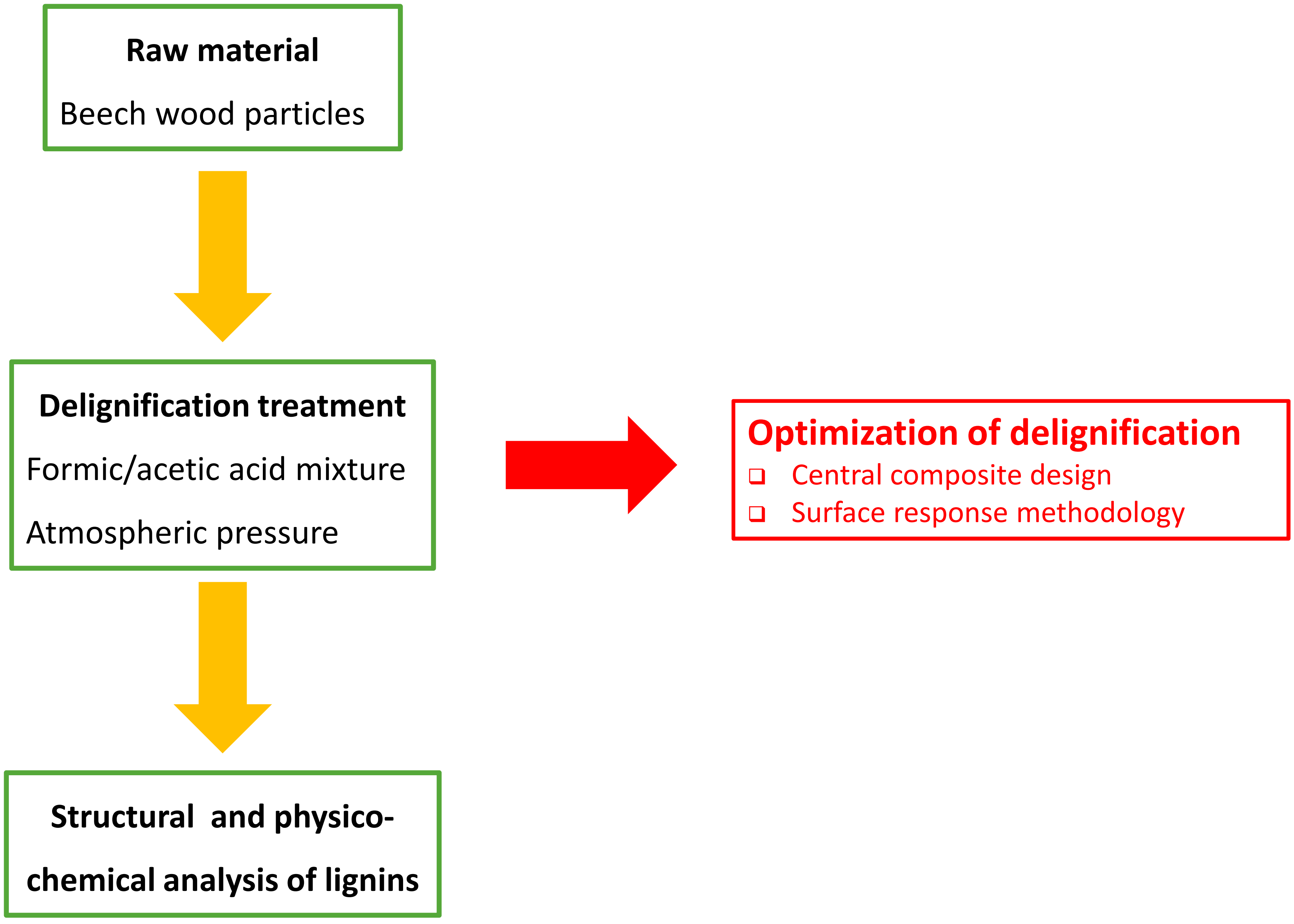
Sampling and composition of raw material

Composition of beech wood particles

Lignin content	**21,7%**
Klason lignin	19,7%
Acid soluble lignin	2,0 %

Monosaccharides composition		**60,4%**
Glucose	39,2%	
Xylose	18,1%	
Mannose	1,6%	
Galactose	0,7%	
Rhamnose	0,4%	
Arabinose	0,4%	

Other constituents: ash, extractives, uronic acids, protein...


Raw material
Beech wood particles
Delignification treatment
Formic/acetic acid mixture
Atmospheric pressure
Structural and physico-chemical analysis of lignins
Optimization of delignification
Central composite design
Surface response methodology

Optimization of delignification

Optimization of 2 independent variables

- Time (1h30, 3h, 4h30)
- Temperature (87°C, 97°C, 107°C)

Standardized to the interval -1, 1

coded units: -1, 0, 1

For four responses

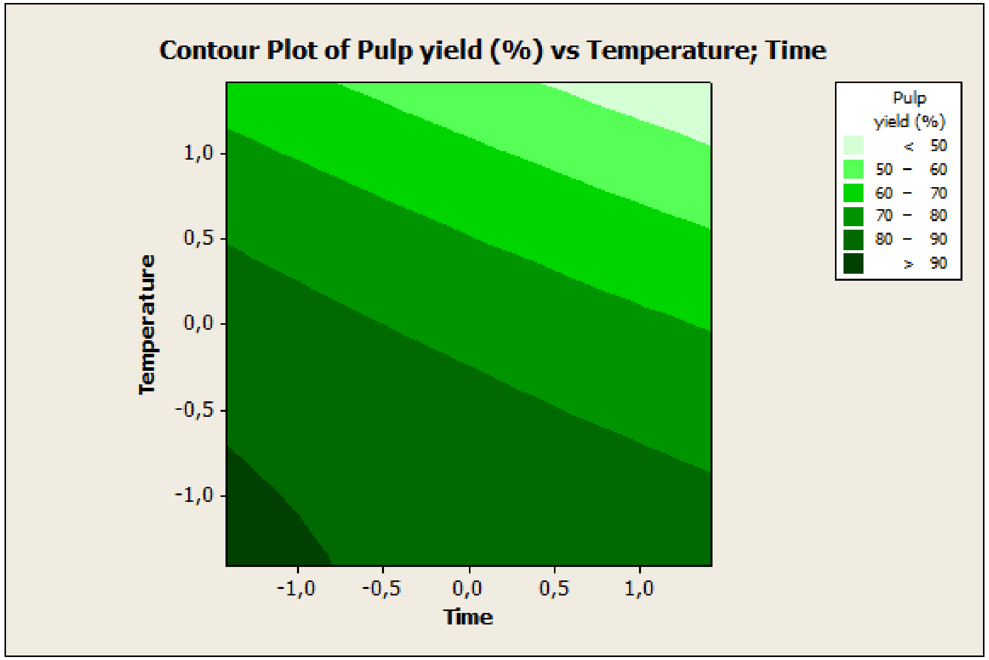
- Delignification yield
- Pulp yield
- Furfural concentration
- Hydroxymethylfurfural concentration

By the use of

- Central composite design (13 treatments)
- Response surface methodology

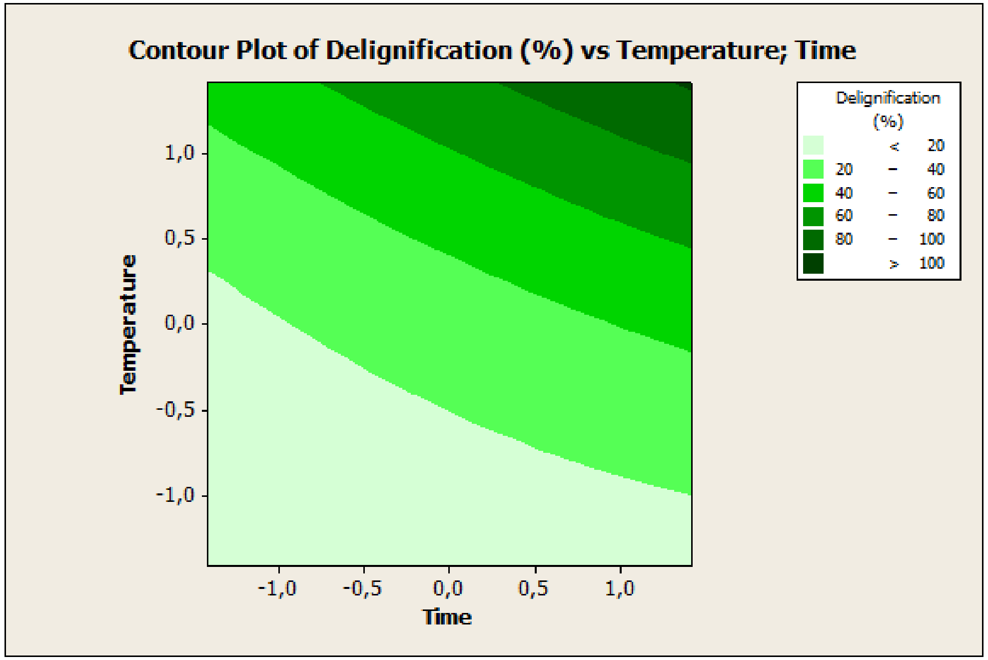
Independent variables			Dependent variables			
RunOrder	Time	Temperature	Pulp yield (%)	Delignification (%)	Furfural (ppm)	HMF (ppm)
1	1,41421	0	67,5	45,0	0,2	0,2
2	0	-1,41421	87,3	12,8	0,2	0,1
3	0	0	76,6	27,9	0,7	1,1
4	-1	-1	88,8	7,5	0,1	0,2
5	-1,41421	0	86,6	15,3	0,2	0,4
6	-1	1	68,0	41,8	2,0	1,0
7	1	-1	84,2	16,5	0,1	0,1
8	0	0	79,7	30,3	0,3	1,3
9	0	0	74,9	34,2	0,2	1,2
10	0	0	80,0	23,5	0,3	0,9
11	0	0	74,1	34,6	1,8	0,7
12	0	1,41421	*	*	*	*
13	1	1	55,3	75,4	20,0	1,6

Term	Pulp yield (%)	Delignification (%)	Furfural (ppm)	HMF (ppm)
Constant	77,12	29,82	0,67	1,03
Time	-5,55	10,57	2,25	0,04
Temperature	-12,24	22,60	5,82	0,59
Time*Time	-	-	-	-0,35
Temperature*Temperature	-3,29	6,45	4,38	-
Time*Temperature	-2,03	6,15	4,48	0,16
R^2	96,06%	97,40%	87,04%	87,55%



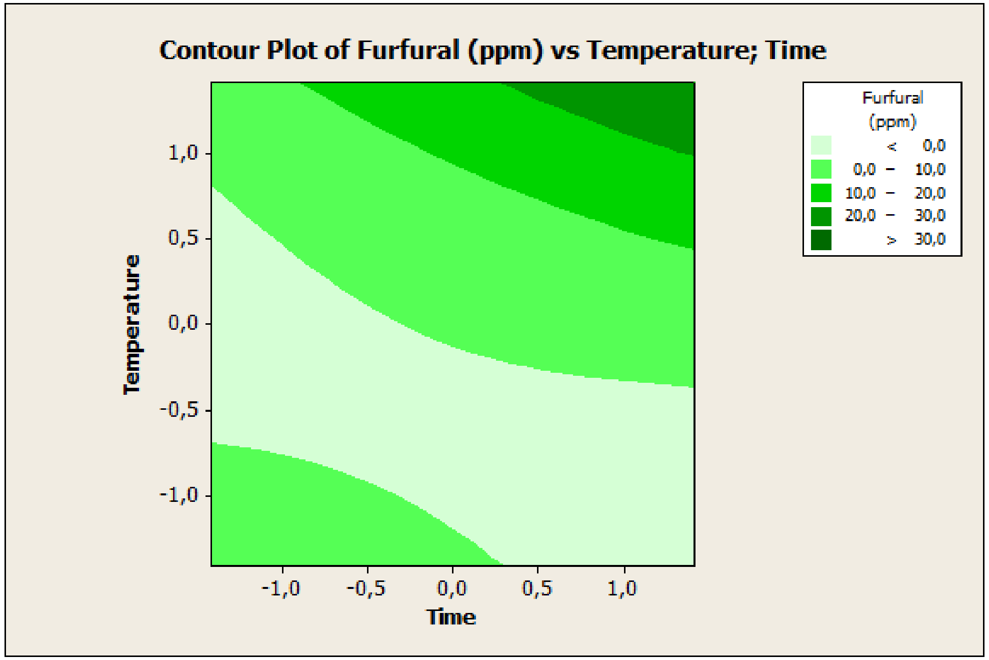
Ranged from 55,3 to 88,8%

- ✓ Dissolution of lignin
- ✓ Hydrolysis of hemicelluloses (cellulose)
- ✓ Optimal conditions: 87°C, 1h30



Ranged from 7,5 to 75,4%

- ✓ Ratio $[\text{lignin}]_{\text{pulp}}/[\text{lignin}]_{\text{raw material}}$
- ✓ Optimal conditions: 107°C, 4h30

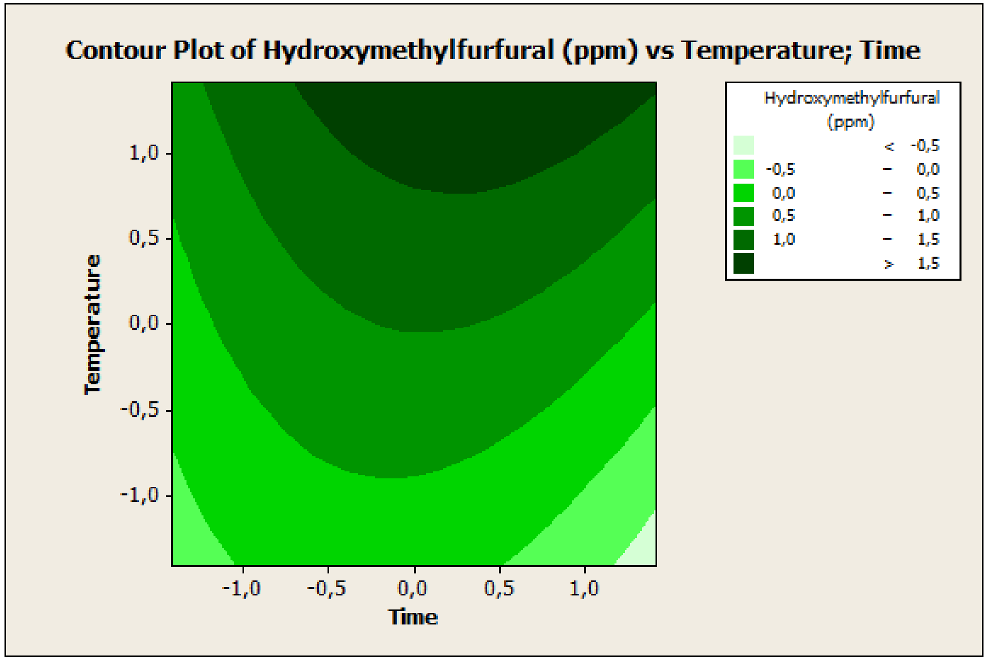


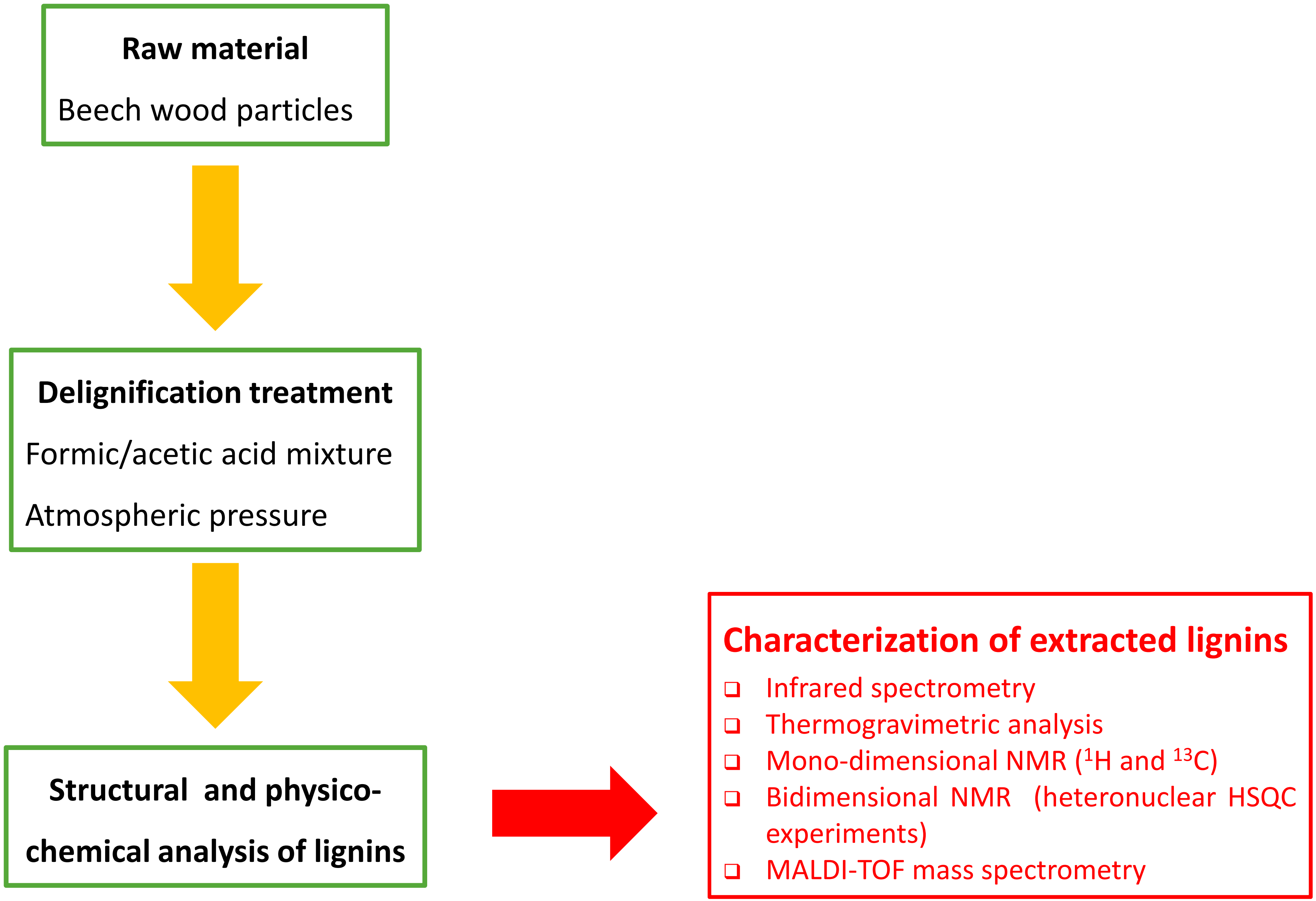
Furfural and HMF = degradation products of pentoses

✓ Below 97°C, [furfural] < 10 ppm

Degradation of HMF in furfural

✓ [HMF] <<




Raw material
Beech wood particles
Delignification treatment
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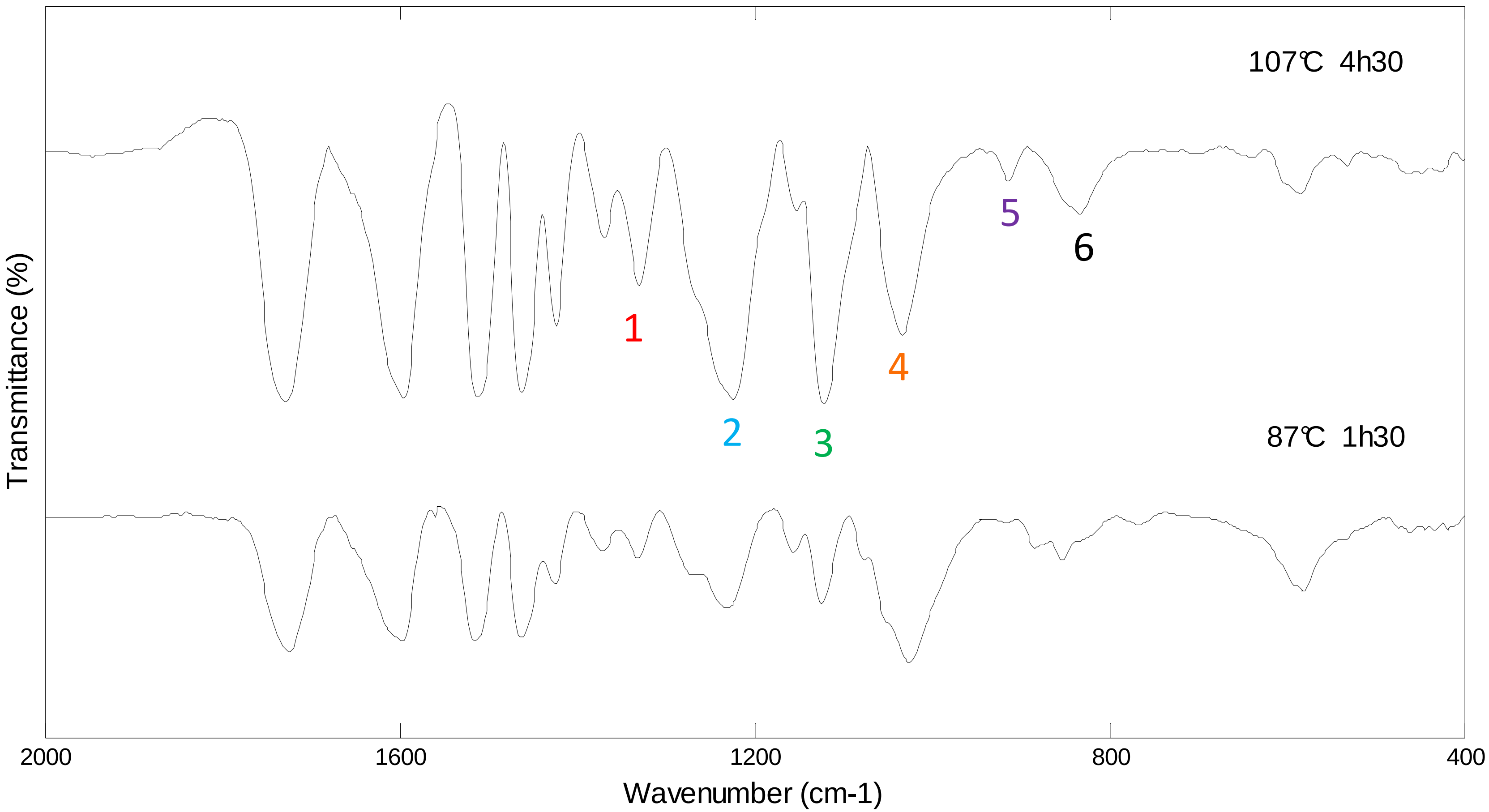
Atmospheric pressure
Structural and physico-chemical analysis of lignins
Characterization of extracted lignins
Infrared spectrometry
Thermogravimetric analysis
Mono-dimensional NMR (1H and 13C)
Bidimensional NMR (heteronuclear HSQC experiments)
MALDI-TOF mass spectrometry

Infrared spectroscopy

1) 1330 cm^{-1}: Syringyl units with C-O stretching
2) 1225 cm^{-1}: Syringyl and guaiacyl ring breathing with C-O stretching
3) 1124 cm^{-1}: Aromatic C-H in plane deformations (syringyl)
4) 1031 cm^{-1}: Aromatic C-H in plane deformations (guaiacyl)
5) 913 cm^{-1}: Aromatic C-H out of plane deformations (guaiacyl)
6) 833 cm^{-1}: Aromatic C-H out of plane deformations (syringy)

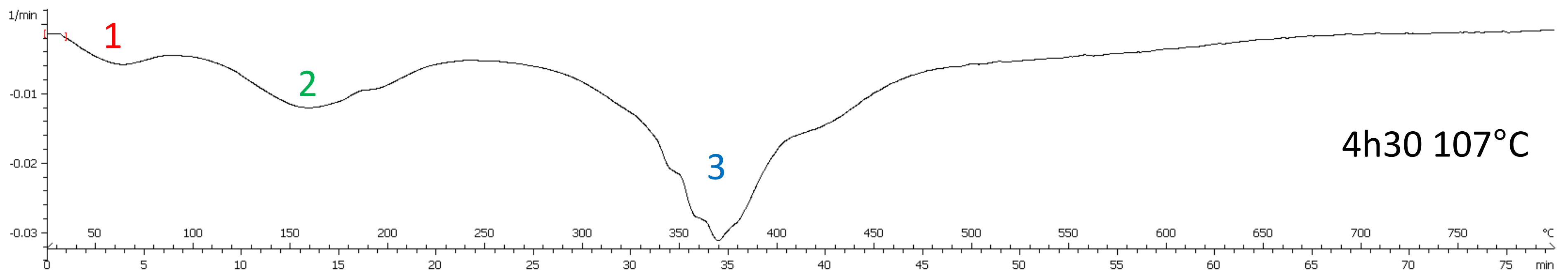


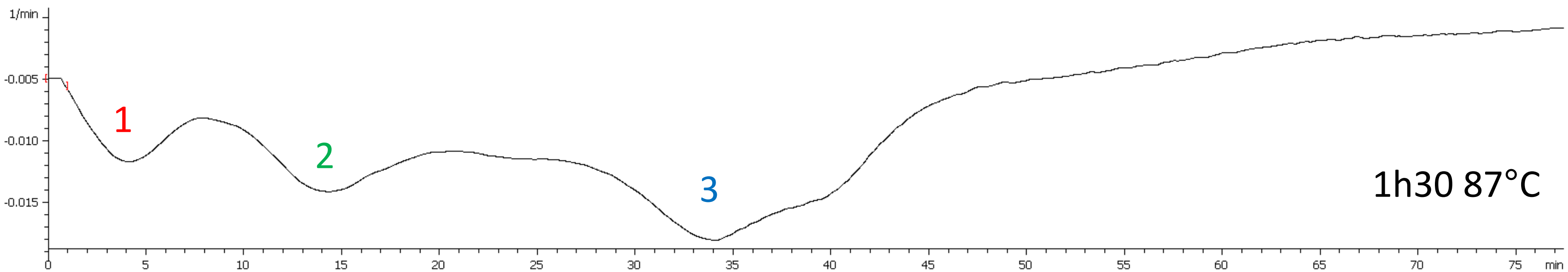
Villaverde J.J. *et al.*, 2009. Native lignin structure of Miscanthus x giganteus and its changes during acetic acid and formic acid fractionation. *J. Agric. Food Chem.*, **57**, 6262-6270.

Thermogravimetric analysis

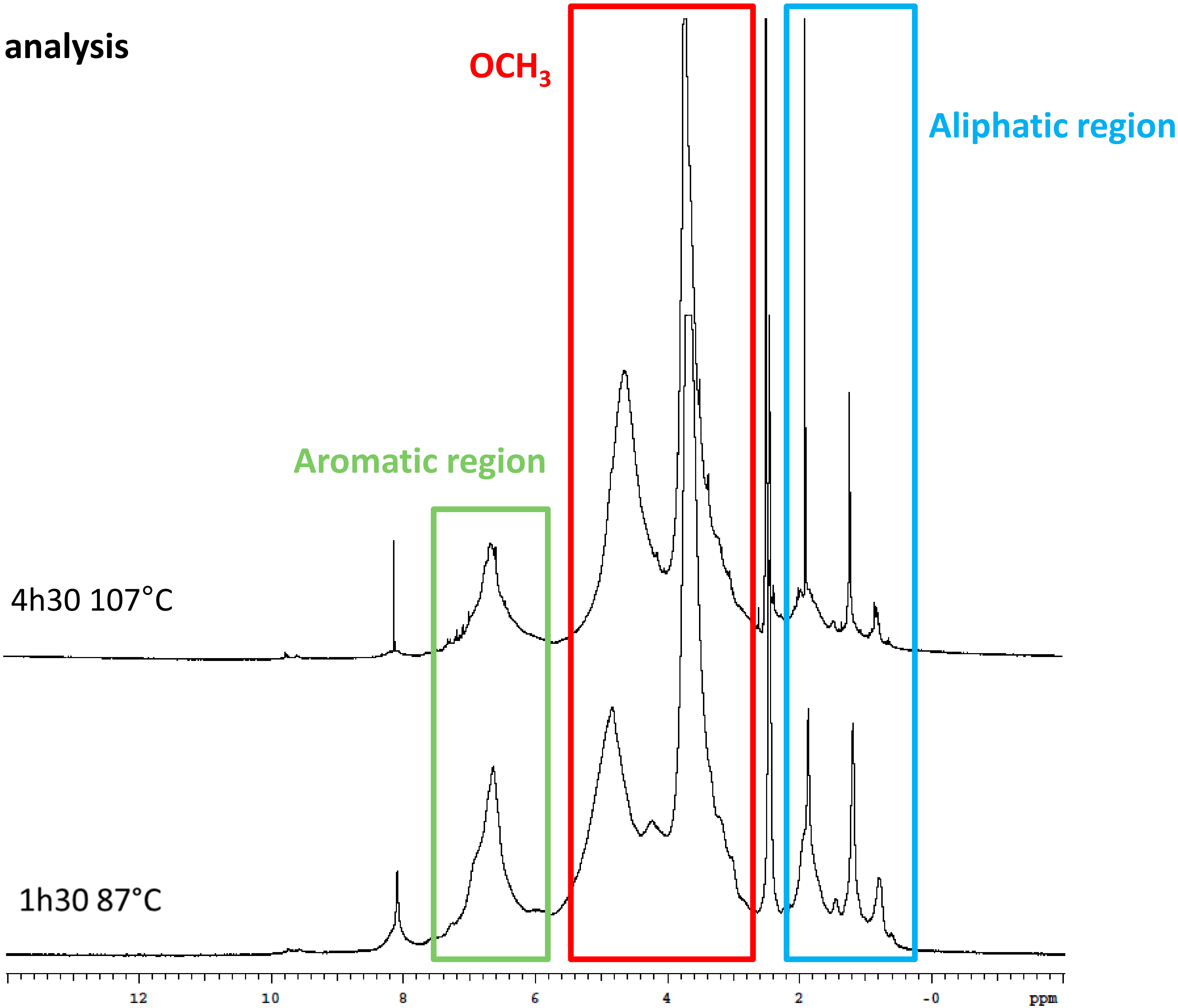
Different stages of decomposition are identified:

1) Between 50-100°C: evaporation of water
2) Between 100-200°C: evaporation of acetic acid
3) Between 250-500°C: degradation of lignins (and hemicelluloses)
   - Shouldering of the 2 degradation peaks
   - Hemicelluloses degradation begins before lignin degradation

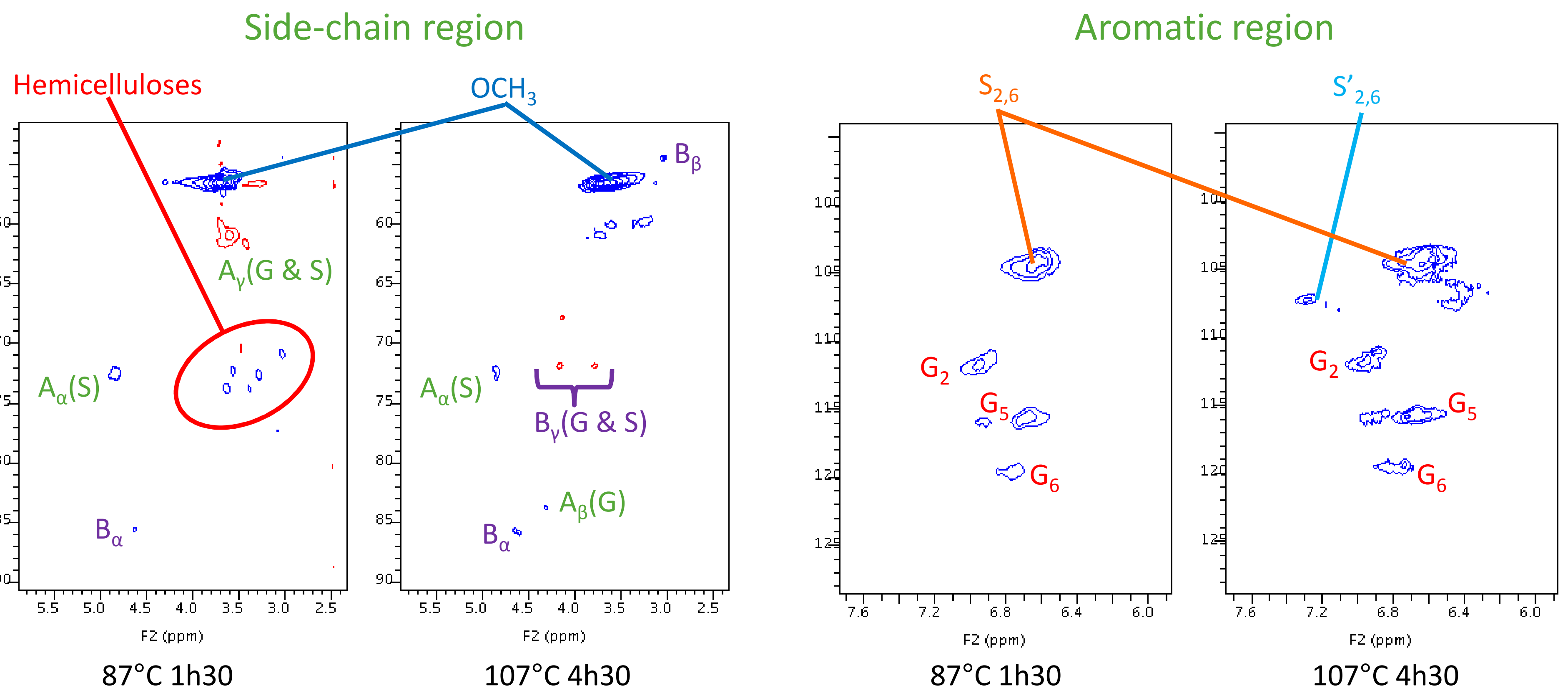


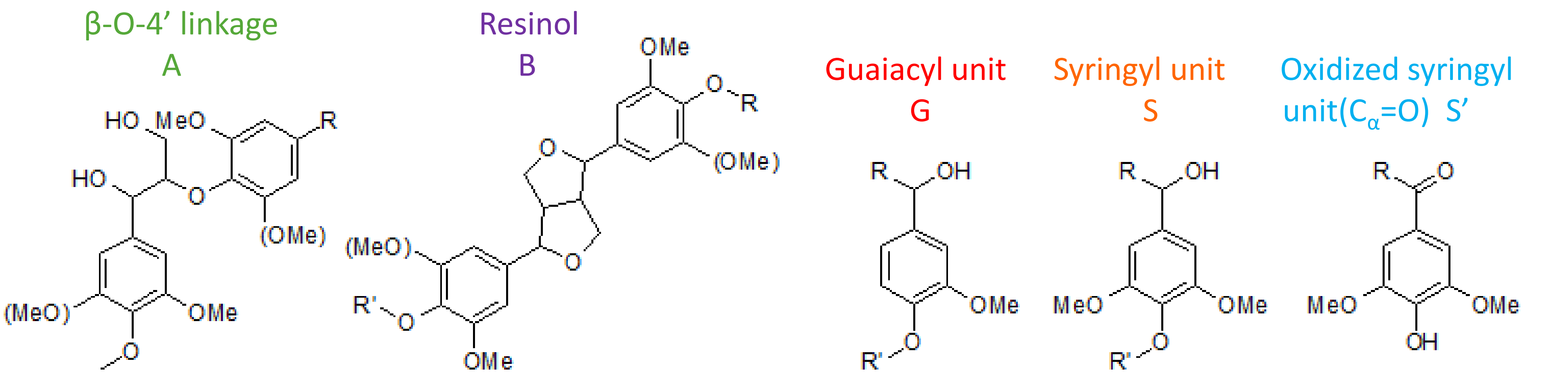


^{1}H NMR analysis



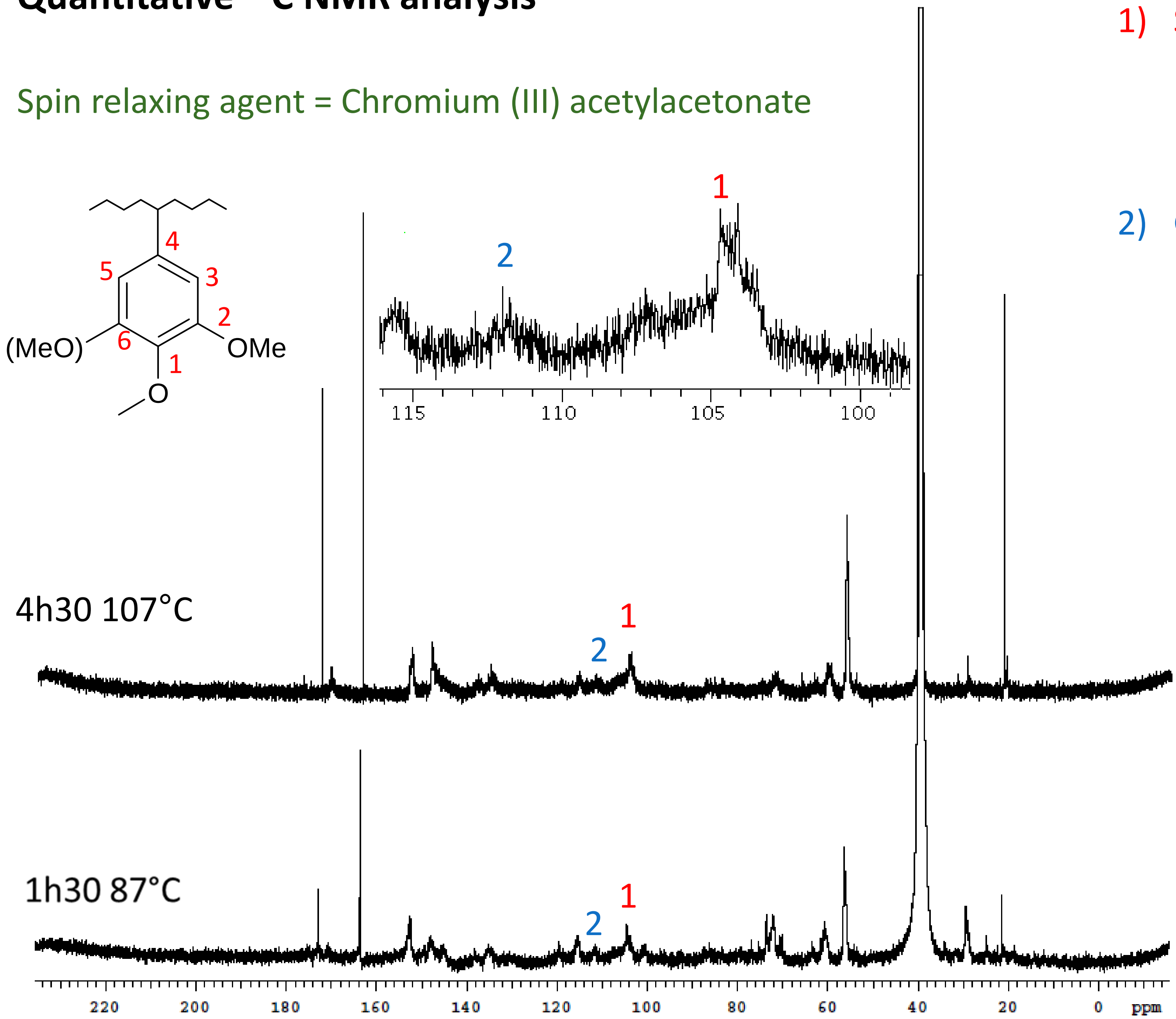
HSQC NMR analysis





Quantitative ^{13}C NMR analysis

Spin relaxing agent = Chromium (III) acetylacetonate



1) Syringyl units

   103-104 ppm

   C_2 and C_6

2) Guaiacyl units

   111-113 ppm

   C_2

Ratio G/S

1/2,05

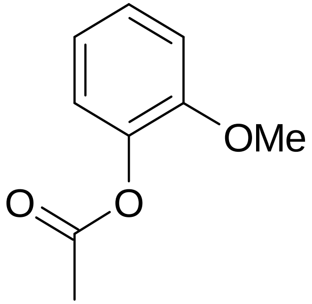
1/1,70

MALDI-TOF analysis

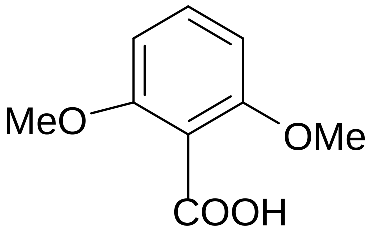
Mode d'ionisation positif

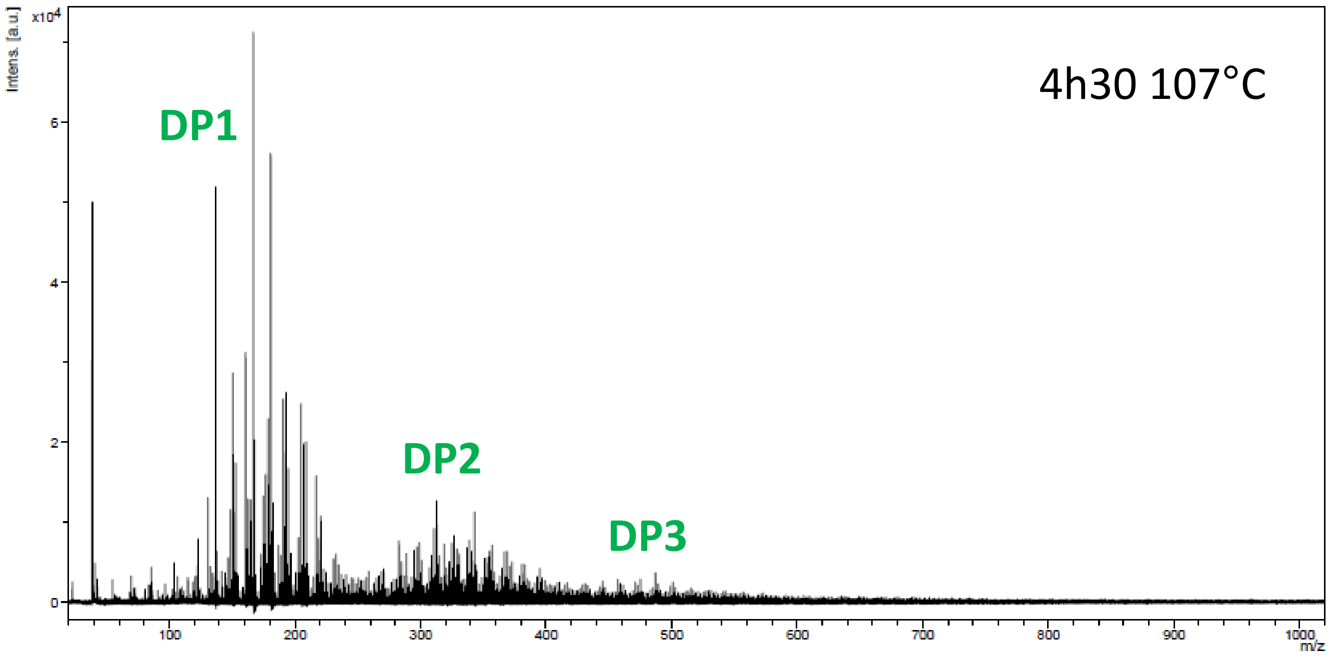
DP1

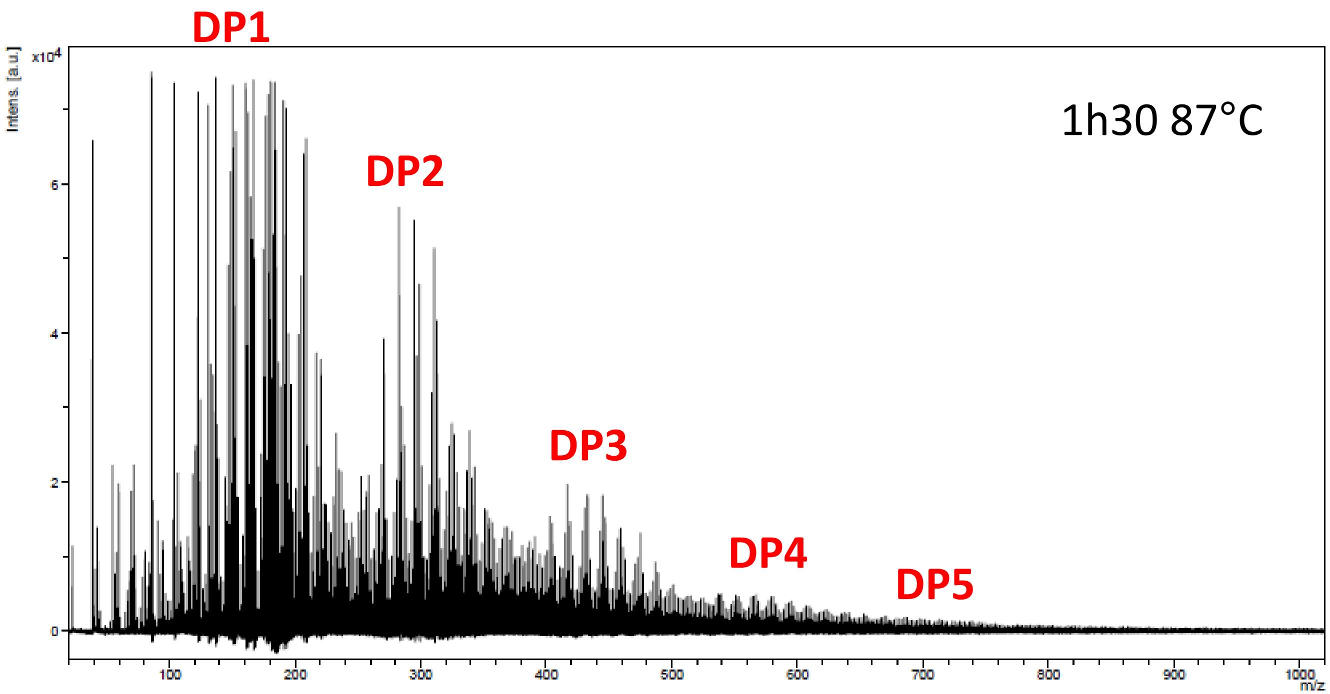
m/z 167 = $C_9H_{10}O_3 + H^+$



m/z 183 = $C_9H_{10}O_4 + H^+$





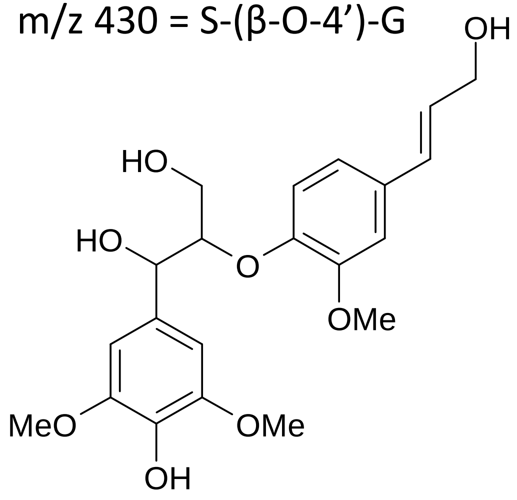


MALDI-TOF analysis

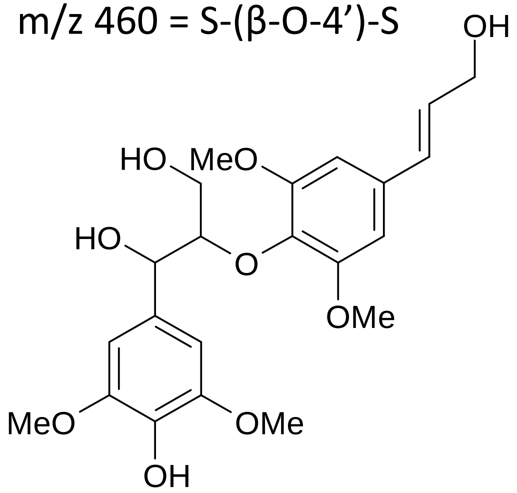
Mode d'ionisation positif

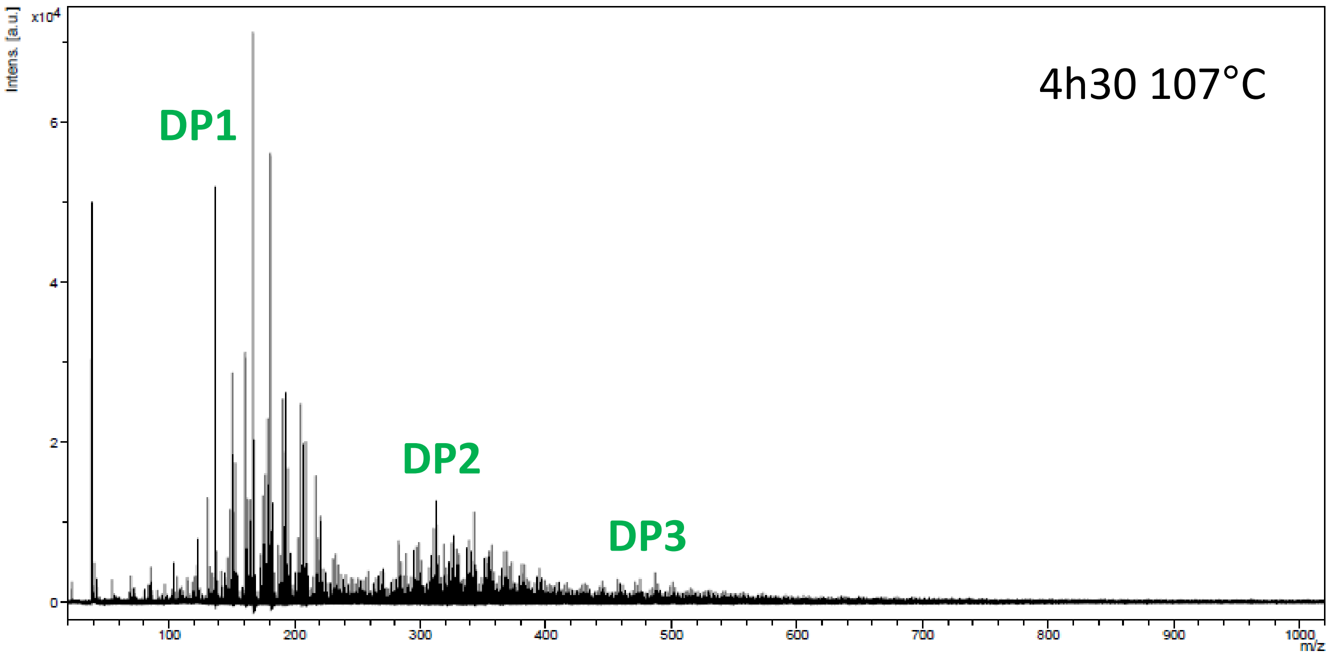
DP2

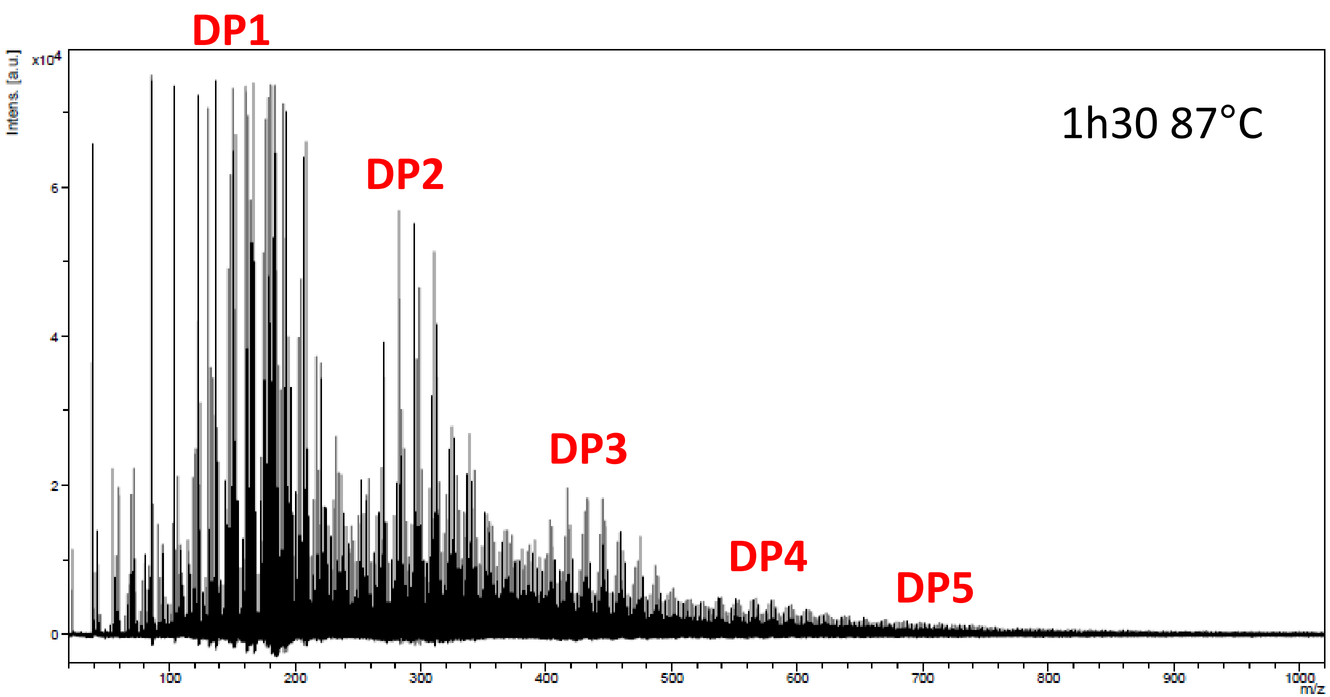
m/z 430 = S-(β-O-4')-G



m/z 460 = S-(β-O-4')-S







Conclusions

Optimization of a formic/acetic acid delignification treatment of beech wood

Central composite design and surface response methodology

Optimal conditions for delignification : 107°C, 4h30

Investigation of structural and physico-chemical features of extracted lignins

Infrared spectroscopy	Information about constitutive phenylpropanoid units
Thermogravimetric analysis	Composition of lignin samples (acetic acid, hemicelluloses, lignin)
^{1}H NMR analysis	Distinction of three characteristic regions (aromatic region, $-OCH_3$ region and aliphatic region)
HSQC NMR analysis	Information about the distribution of phenylpropanoid units and about the linkages between the units
Quantitative ^{13}C NMR	Determination of G/S ratio
MALDI-TOF analysis	Information about the degree of oligomerisation and identification of specific structural patterns

Thank you for your attention

For further information

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http://www.fsagx.ac.be/cb/