OPTIMIZATION OF A FORMIC/ACETIC ACID TREATMENT OF BEECH WOOD (*FAGUS SYLVATICA* L.) FOR DELIGNIFICATION

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CONTEXT AND OBJECTIVES

Lignin is an aromatic cross-linked heteropolymer composed of three phenylpropanoids (*p*-hydroxyphenyl, guaiacyl and syringyl units) linked together by specific ether or carbon-carbon bonds. With this phenylpropanoid structure, lignin is a rich resource of biobased products that could find high-valued applications in a lot of different areas like petrochemical polymer reinforcement and replacement, antioxidants, stabilizers, resins and vanillin production... The first challenge of the valorization of lignins is their extraction from raw materials. This extraction process needs the development of suitable biomass treatments, allowing efficient lignin recuperation without degradation.

In this study, beech wood (*Fagus sylvatica L.*) was collected in the region of Gaume (Belgium). Beech wood particles were delignified at atmospheric pressure by a formic acid/acetic acid/water mixture. A central composite design and response surface methodology were used for the optimization of treatment parameters for delignification.

MATERIAL AND METHODS

Optimization of 2 independent variables

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

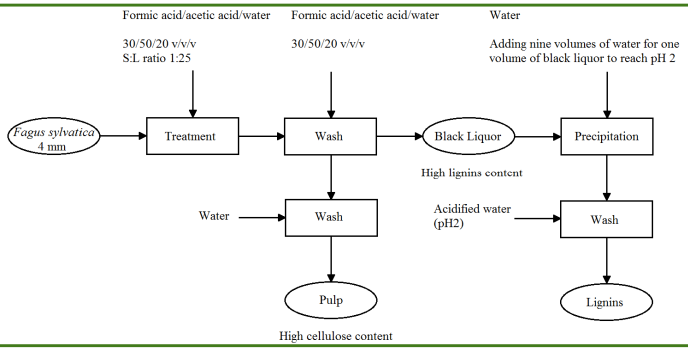
→ Standardized to the interval (-1, 1)
Coded units: -1, 0, 1

For 4 responses

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

By the use of

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



EXPERIMENTAL DESIGN AND RESPONSES

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

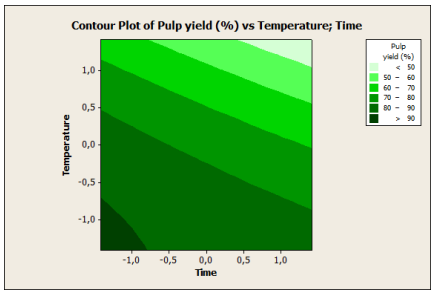
Treatment 12 was not performed because the cooking temperature could not exceed 107°C at atmospheric pressure.

REGRESSION COEFFICIENTS FOR EACH VARIABLE

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%

The response surface regression and models were expressed without taking into account the statistically insignificant terms.

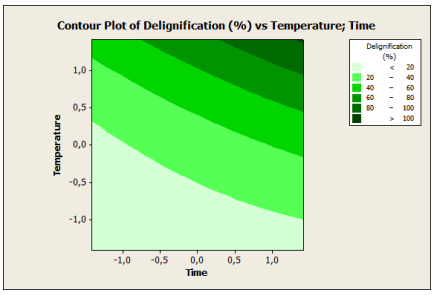
RESPONSE SURFACE OF PULP YIELD



Pulp yield was inversely proportional to the time and temperature increase and ranged from 55,3 to 88,8% (dissolution of lignin and hydrolysis of hemicelluloses and sometimes of cellulose in drastic treatments).

According to response optimization, soft conditions (in the range of 1h30, 87°C) could lead to maximum pulp yield (upper than 90%).

RESPONSE SURFACE OF DELIGNIFICATION



Delignification is expressed as the ratio (%) between the amount of lignin remaining in the pulp after treatment and the amount of lignin in the initial material.

Results of delignification ranged from 7,5 to 75,4%.

Delignification mainly depended on the cooking temperature and in minor extent on the time.

Best results for delignification (75,4%) were obtained with the treatment 13 (4h30, 107°C).

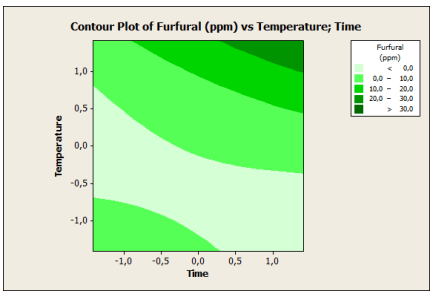
RESPONSE SURFACE OF DEGRADATION PRODUCTS

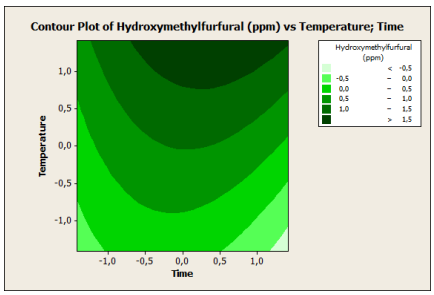
Furfural and hydroxymethylfurfural (HMF) in the black liquor were obtained from the degradation of pentoses during the treatment.

When cooking time and temperature increase, higher amounts of furfural were produced.

Below 97°C, the furfural concentration fell below 10 ppm.

Maximum furfural concentration (20,0 ppm) was obtained at high temperatures and times (107°C, 4h30).





Lower amounts of HMF were found in black liquors with regard to furfural concentrations. During the treatment, HMF was decomposed in furfural. [1]

HMF production was affected by both time and temperature but mainly by the treatment duration.

Although, the detected concentrations were too low (even at the highest time and temperatures) to occur problems.

[1] Shen D.K. & Gu S., 2009. The mechanism for thermal decomposition of cellulose and its main products. *Bioresource Technology*, **100**, 6496-6504.