Aalto University
School of Chemical
Engineering

CHEM-E1150
BIOMASS PRETREATMENT AND FRACTIONATION
Theme 1: Kraft pulping, Module 2
Prehydrolysis

Herbert Sixta, 2019

Outline Theme 1

Module 1: Raw materials and mechanical pretreatment

Module 2: Prehydrolysis

Module 3: Kraft cooking

Module 4. Screening, washing, bleaching and drying

Module 5: Pulp properties and uses

Module 2

1. Introduction
2. Chemistry
3. Kinetics
4. Technology

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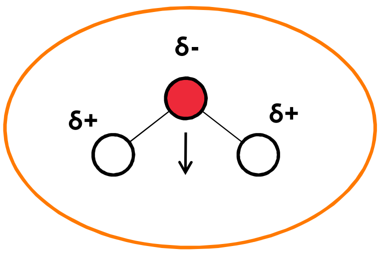
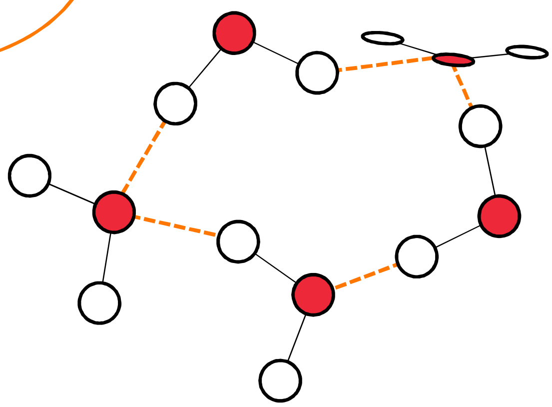
Some introductory words…History

1819	Braconnot	HCl conc	Ind.Eng.Chem. 1945,37,5-8
1923	Schöller	Percolation, 0.5 wt% SA, 170C	Ind.Eng.Chem. 1945,37,9-11
1929	Mason	Steam explosion	U.S. Patent No. 1,655,618, 1929.
1932	Babcock	Steam explosion	U.S. Patent No. 1,825,464, 1932
1937	Bergius	Batch, 40 wt% HCl at 25C	Ind.Eng.Chem. 1937, 29, 247-253
1940	Königsberg	Prehydrolysis (Soda)	Rydholm 1966
1945	Madison	Percolation, 0.5 wt% SA, 180C	report no. R1617 1946
1968	Bobleter	Hydrothermolysis	AT No. 263661, 25.7.1968
1978	Lora and Wayman	Autohydrolysis	TAPPI J. 1978, 61, 47.
1987	Overend, Chornet	Hydrothermal treatment	Phil. Trans. R. Soc. Lond.,1987, 321, 523.
1994	Antal	Aquasolv	Advances in Thermochemical Biomass Conversion; Bridgewater, A.V., Ed.; Blackie Academic and Professional: London, 1994; p. 1572.

Water

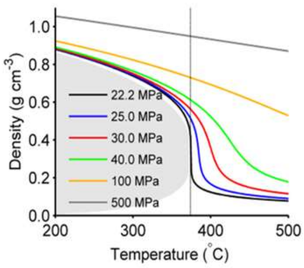


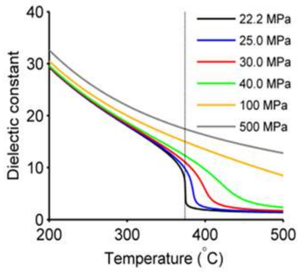
- Permanent dipole moment
- Hydrogen bonding ability
- Self-dissociation: **2 H_2O → H_3O^+ + OH^-** by proton jumping (Grotthus mechanism)



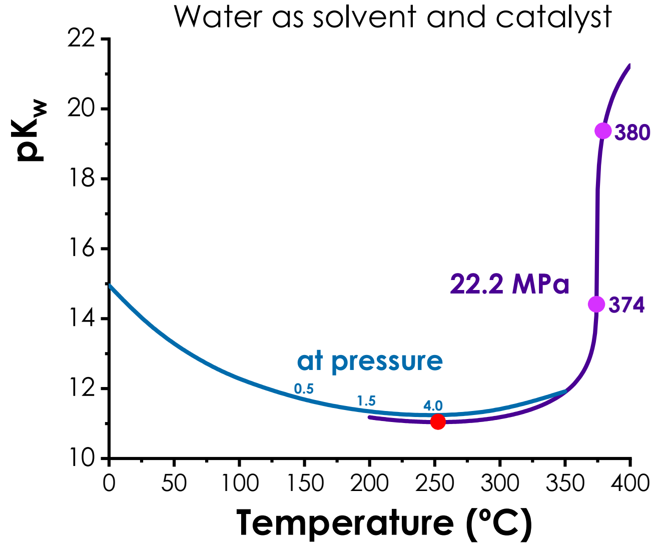
https://upload.wikimedia.org/wikipedia/commons/d/d8/Autoionizacion-agua.gif

Physical properties of water





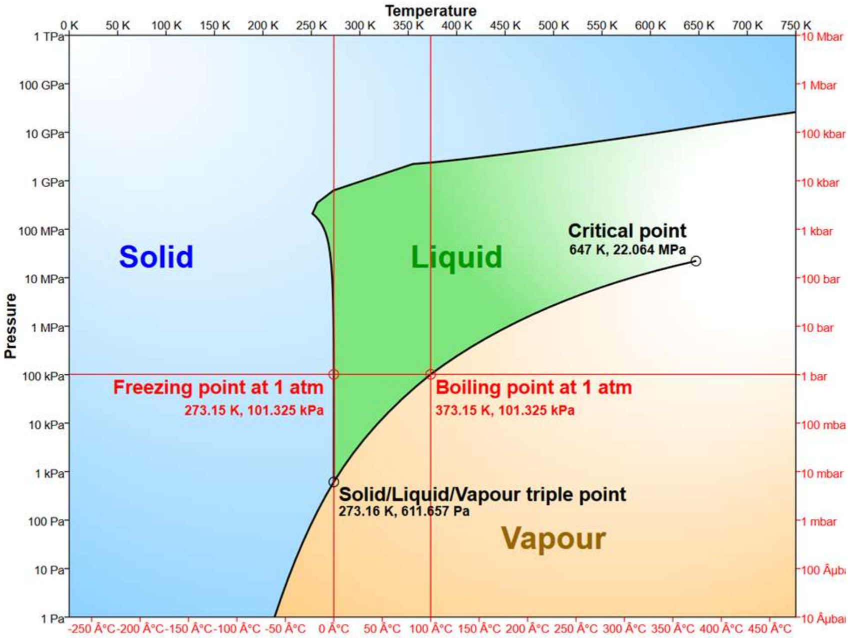
Water as solvent and catalyst



Ion product calculated according to (Marshall, Franck 1981).

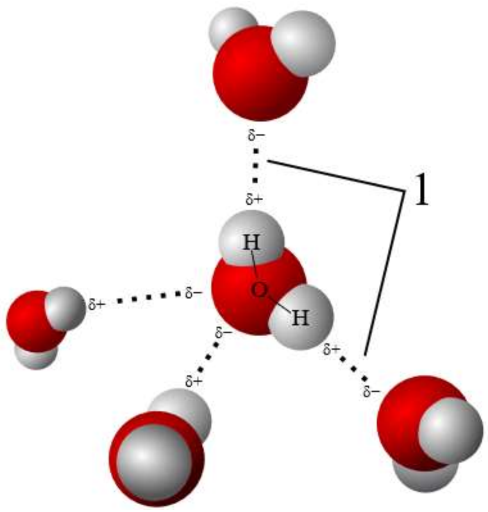
Lasse Tolonen: PhD thesis 2016

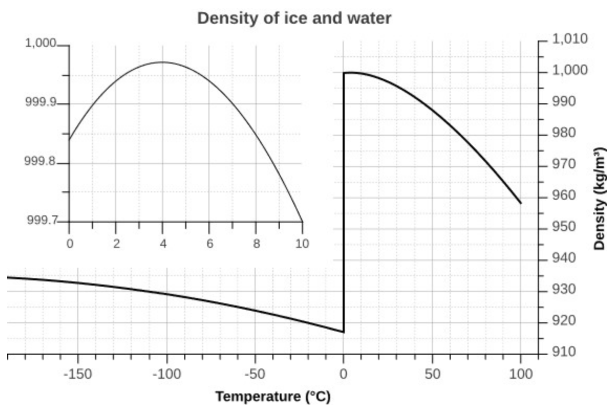
Phase diagram of water



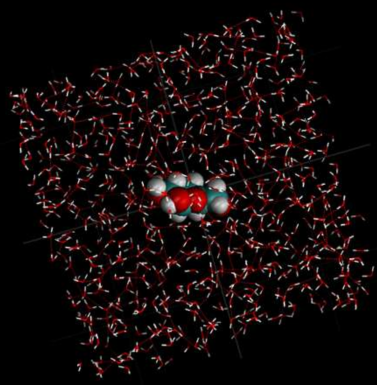
Wikipedia

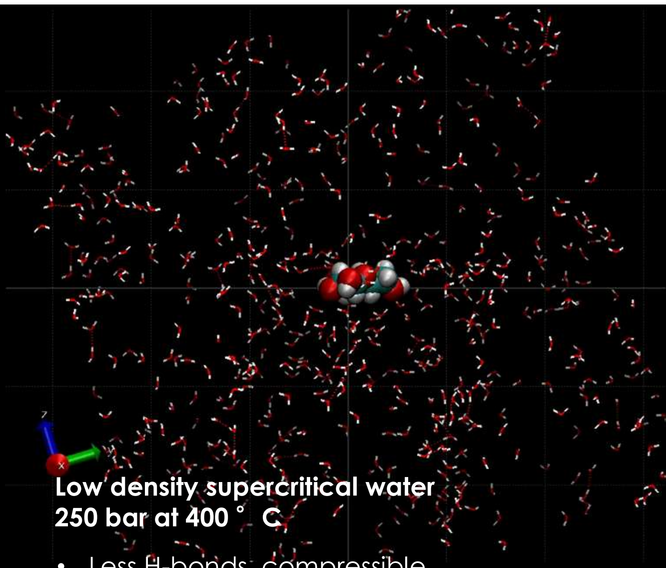
Phase diagram of water





Wikipedia





Ambient water

- Extensive H-bonding
- High dielectric constant
- Miscible with polar solvents
- Dissolves salts

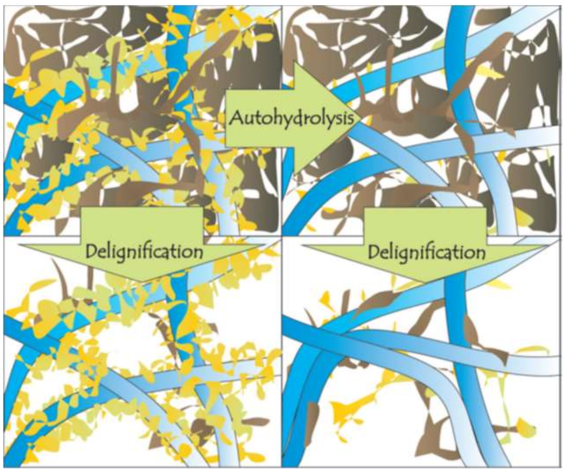
- Does not dissolve cellulose

Low density supercritical water
250 bar at 400 ° C

- Less H-bonds, compressible
- Low dielectric constant
- Miscible with non-polar solvents

- Cellulose solubility starts near the critical point; more favorable at higher pressure

Prehydrolysis



- Autohydrolysis effectively increases the cellulose surface area by hemicellulose dissolution

- The removal of lignin leads to a more accessible pore structure.

- Delignification increases the hydrophilicity of the remaining lignin, which also increases hydrolyzability

Pihlajaniemi, V. et al. *Green Chem* (2016)

Module 2

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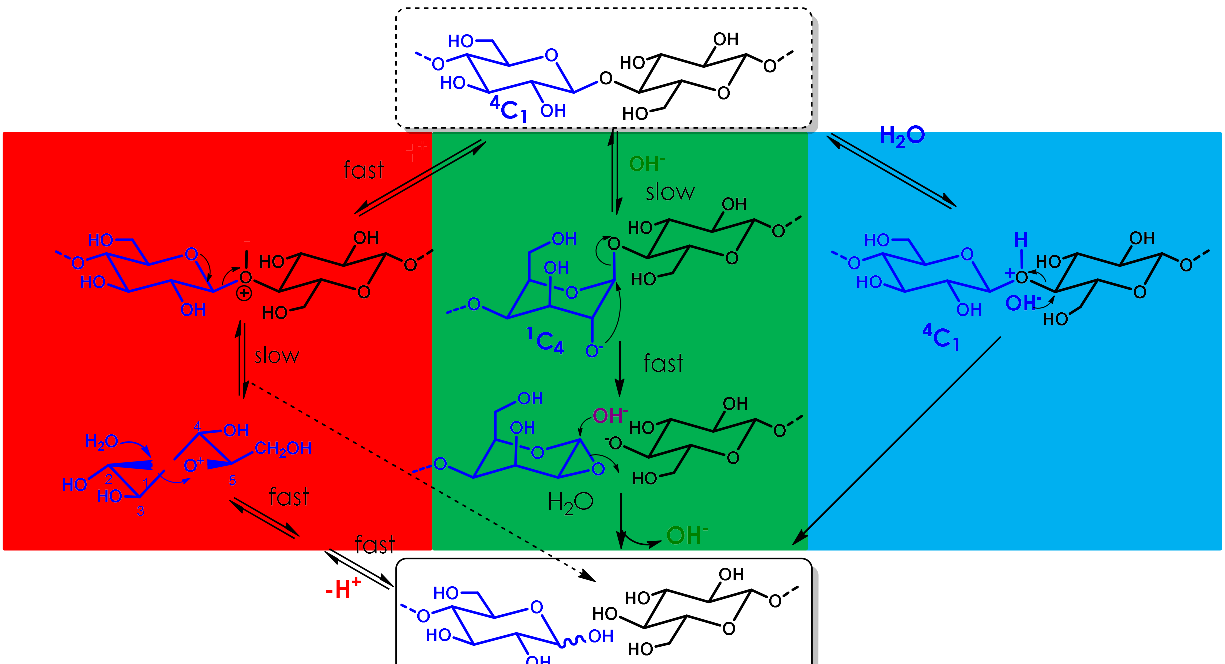
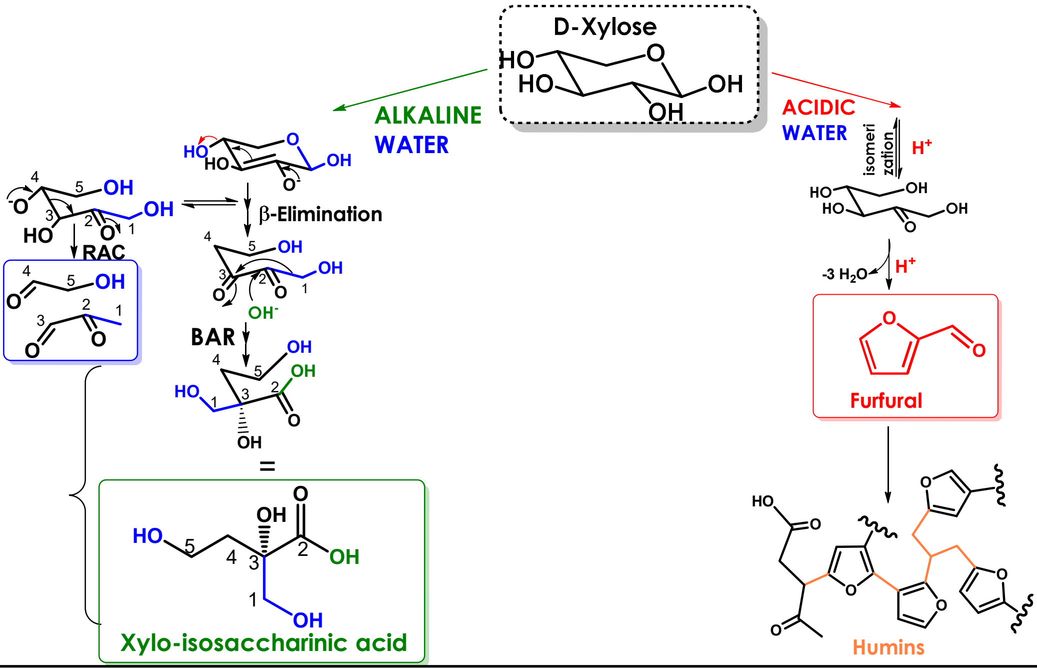
Chemistry of glycosidic bond cleavage



Edward, J.T. *Chem.Ind* (London), 1102 (1955)

Chemistry of xylose degradation in water



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Prehydrolysis of Wood

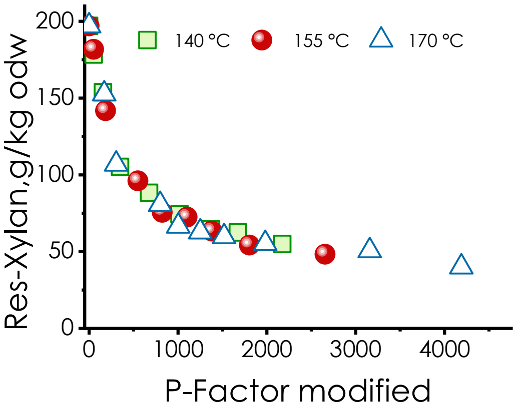
- **Comparative evaluation of birch and pine**
- Selectivity of xylan removal
- Bound and free acetic acid in the hydrolysate
- Effect of liquor-to-wood-ratio
- Effect of wood particle size
- Batch- vs. percolation reactor
- Acid-catalyzed hydrolysis

Intensity of Prehydrolysis

P-factor used in PHK[1]

$$P = \int_{t_0}^{t} \frac{k_X}{k_{100°C}} dt = \int_{t_0}^{t} Exp\left(40.48 - \frac{15106}{T}\right) dt$$

$$P_{mod} = \int_{t_0}^{t} \frac{k_X}{k_{100°C}} dt = \int_{t_0}^{t} Exp\left(58.02 - \frac{21649}{T}\right) dt$$



Severity Factor[2,3]

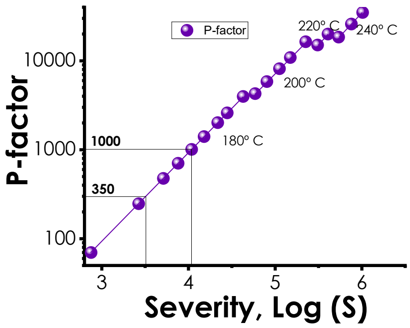
$$\boldsymbol{log(R_0) = log\left[t \cdot exp\left(\frac{T-100}{14.75}\right)\right]}$$

$$\log(R_0{}^*) = log(R_0) + |pH - 7|$$

[1] Sixta, H. (**2006**) and (**2011**)
[2]Abatzoglou, N.J. Chornet, E.; Belkacemi, K., Overend, R.P. (**1992**), Chem. Eng Sci, 47, 1109-1122.
[3]Chum, H.L., D.K. Black,S.K.; Overend, R.P. (**1990**). Appl. Biochemistry and Biotechnology, 24/25, 1-14

Birch vs Pine Prehydrolysis - Experimental

- Wood ground to particles < 1mm
- Liquor-to-wood ratio = 40:1 (m:m)
- Heating-up time converted to time at reaction temperature (t_{corr})



Leschinsky, M.; Ståhl, M.; Borrega, M.; Testova, L.; Guetsch, J. **Sixta, H.**

Wood composition

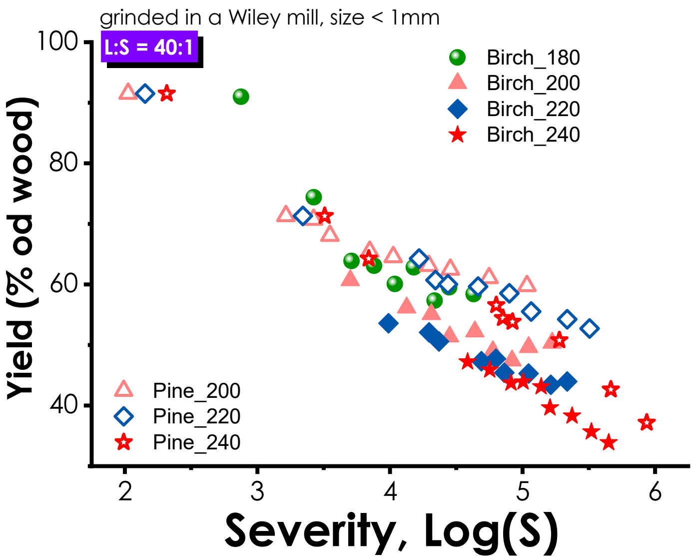
Constituent	% od birch
Acetone-Extractives	2,0
Klason Lignin	21,4
Acid soluble lignin	4,4
Total Lignin	**25,8**
Xylose	**26,1**
Arabinose	0,3
Glucose	**38,3**
Galactose	0,7
Mannose	1,8
4OMeGlcA	3,1
Acetyl	4,8
Total carbohydrates	**75,1**
Total	**102,9**

Testova, L. et al.: Holzforschung, Vol. 65, pp. 535–542, 2011

Constituent	% od pine
Acetone-Extractives	**3,0**
Klason Lignin	27,1
Acid soluble lignin	0,6
Total Lignin	**27,6**
Arabinoxylan (AX)	**9,1**
Galactoglucomannan (GGM)	**15,8**
Other carbohydrates	2,4
Uronic acids	2,1
Cellulose	**40,9**
Total carbohydrates	**70,3**
Total	**100,9**

Markus Paananen et al. : *Holzforschung 2015; 69(9): 1049–1058*
Ståhl, M. et al. *Biomass and Bioenergy 109 (2018) 100–113*

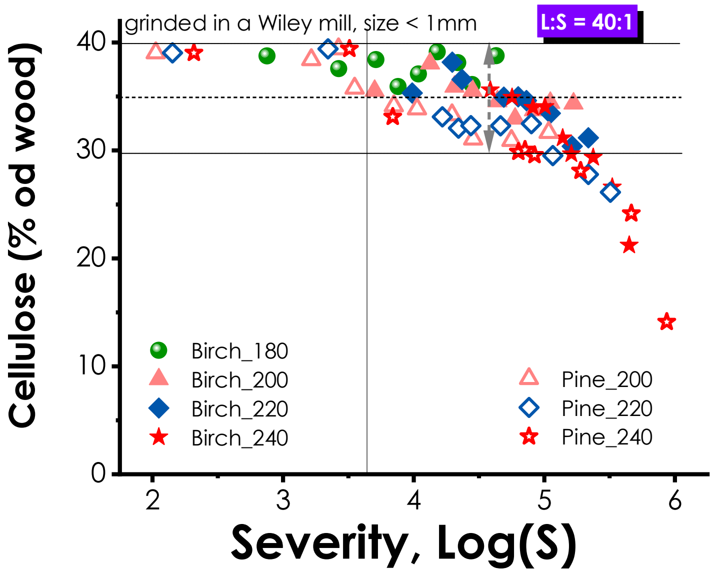
Severity vs Yield



- Log(S) ≤ 3.5: pine ~ birch
- Log(S) > 3.5: $Y_{pine} > Y_{birch}$

Leschinsky, M.; Ståhl, M.; Borrega, M.; Testova, L.; Guetsch, J. **Sixta, H.**

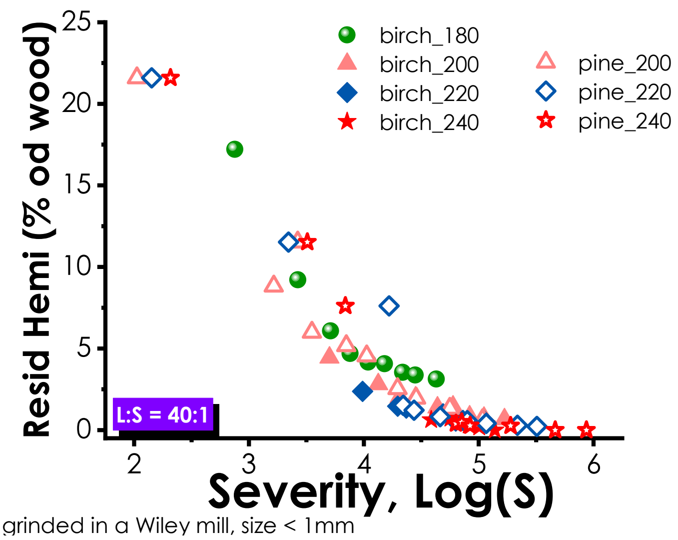
Severity vs Cellulose yield in residue



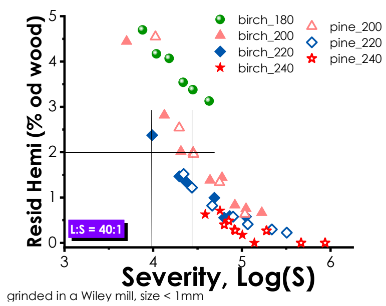
- $\text{Log(S)} \leq 3.5$: pine ~ birch
- $3.5 < \text{Log(S)} < 5.1$: $Y_{pine} < Y_{birch}$
- $5.1 \leq \text{Log(S)}$: $Y_{pine} \sim Y_{birch}$

Leschinsky, M.; Ståhl, M.; Borrega, M.; Testova, L.; Guetsch, J. **Sixta, H.**

Severity vs Hemi in residue

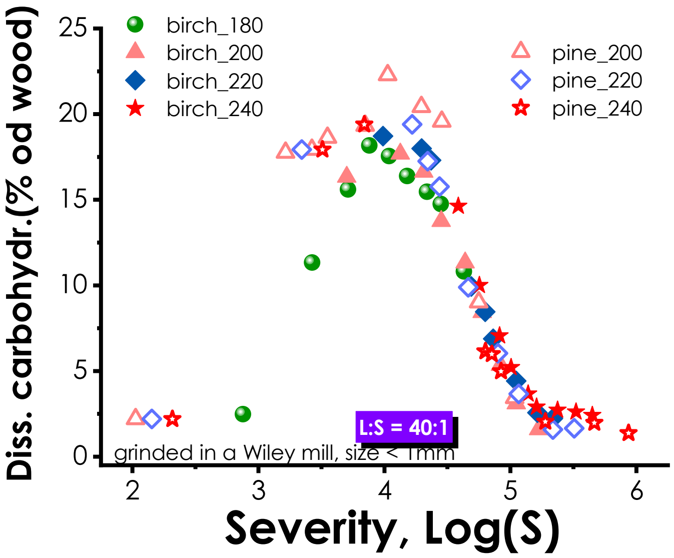


Despite the fact that pine and birch consist of different types of hemicelluloses, the removal kinetics of the sum of the hemicelluloses **seems to be quite comparable**.



Leschinsky, M.; Ståhl, M.; Borrega, M.; Testova, L.; Guetsch, J. **Sixta, H.**

Severity vs Hemi in hydrolysate



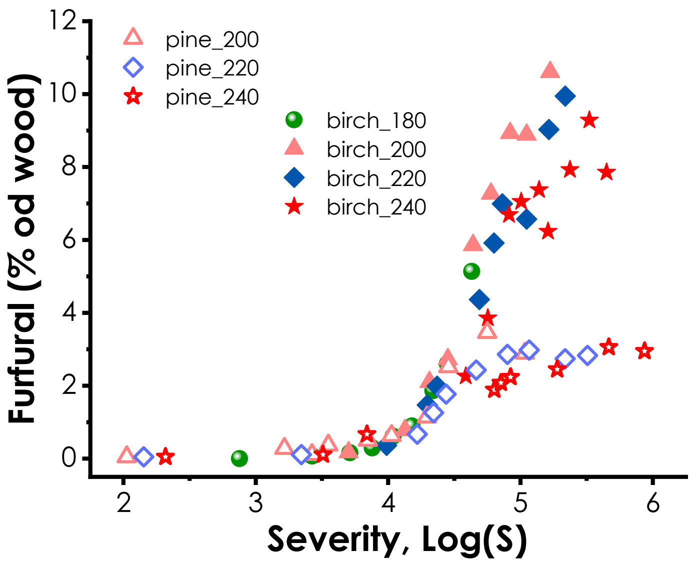
Log(S)~ 4.0:
highest amount of intact carbohydrates dissolved (pine and birch)

3.2 < Log(S) < 4.5:
More carbohydrates dissolved from pine wood

* Side chains: 4OMeGclA and Acetyl groups not included

Leschinsky, M.; Ståhl, M.; Borrega, M.; Testova, L.; Guetsch, J. **Sixta, H.**

Severity vs Furfural in hydrolysate

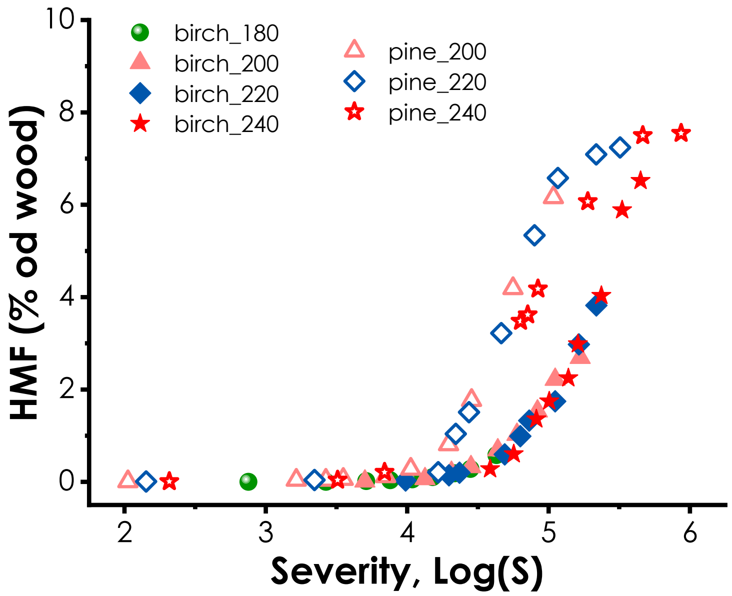


4.2 < Log(S) :
pine ~ birch

4.2 ≥ Log(S) :
birch >> pine

Leschinsky, M.; Ståhl, M.; Borrega, M.; Testova, L.; Guetsch, J. **Sixta, H.**

Severity vs HMF in hydrolysate



4.2 < Log(S) :
pine ~ birch

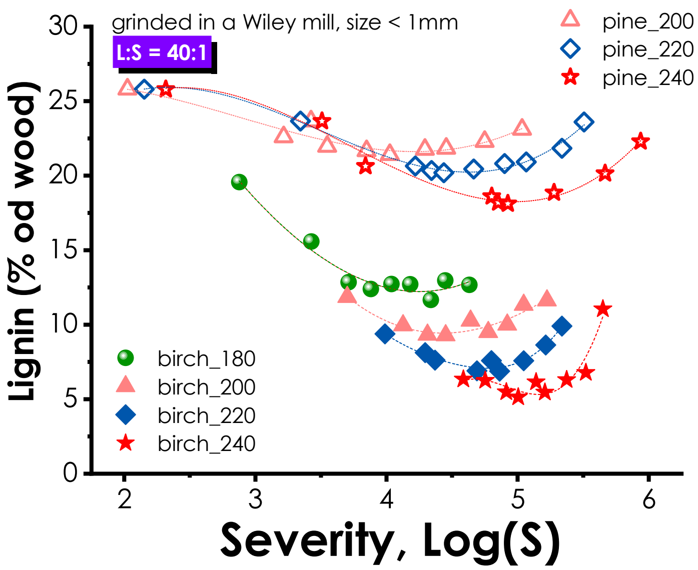
4.2 ≥ Log(S) :
pine >> birch

5.7 < Log(S):

pine ~ birch

Leschinsky, M.; Ståhl, M.; Borrega, M.; Testova, L.; Guetsch, J. **Sixta, H.**

Severity vs Lignin in residue

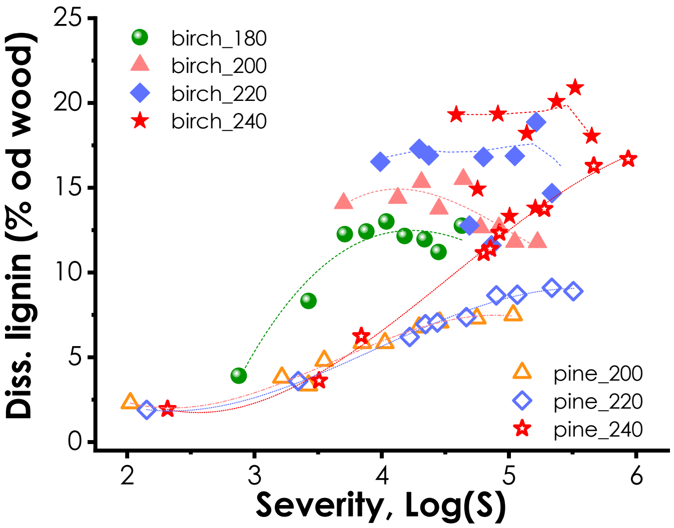


- lignin removal goes through a maximum, specific for each temperature, after which it decreased mainly triggered by progressive lignin condensation and re-precipitation

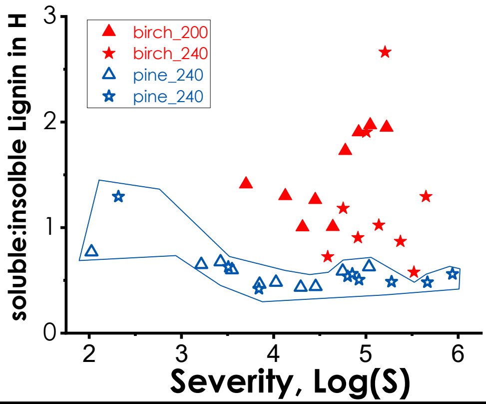
- **Lignin removal: Birch Lignin >> Pine Lignin**

Leschinsky, M.; Ståhl, M.; Borrega, M.; Testova, L.; Guetsch, J. **Sixta, H.**

Severity vs Lignin in hydrolysate



- Mirror image results in hydrolysate
- **Lignin removal: Birch Lignin >> Pine Lignin**
- **Pine: higher fraction of insoluble lignin in hydrolysate**



Leschinsky, M.; Ståhl, M.; Borrega, M.; Testova, L.; Guetsch, J. **Sixta, H.**

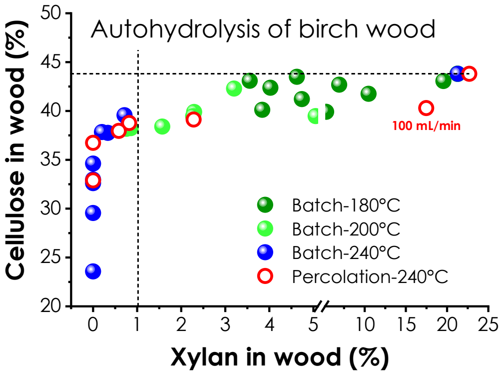
Prehydrolysis of Wood

- Comparative evaluation of birch and pine
- **Selectivity of xylan removal**
- Bound and free acetic acid in the hydrolysate
- Effect on residual lignin
- Effect of liquor-to-wood-ratio
- Effect of wood particle size
- Batch- vs. percolation reactor
- Acid-catalyzed hydrolysis

Prehydrolysis of birch wood

Selectivity of Xylan Removal

Batch-L:W=40:1. Percolation-100 mL/min



Xyl > 3% moderate cellulose loss

Xyl < 0.5% severe cellulose loss

M.Borrega, K.Nieminen, H.Sixta. *Bioresource Technology* (2011) 102 (**2011**) 10724–10732

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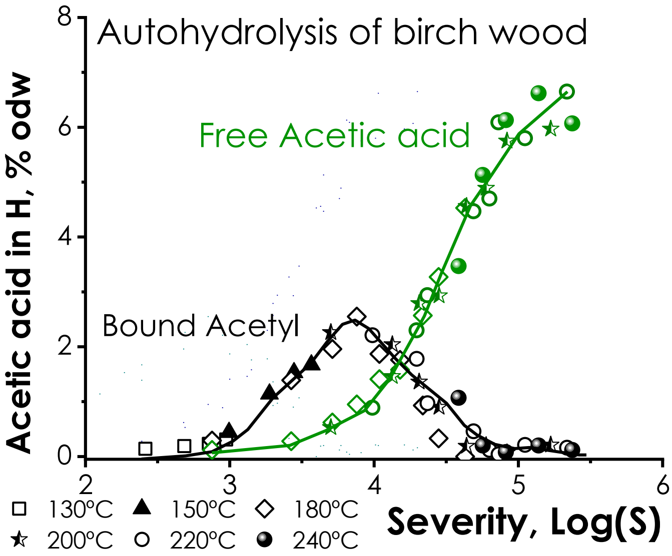
Bound and free acetic acid in Birch Hydrolysate



Testova, L. et al. Holzforschung, **2011**, 65, pp. 535–542,
M.Borrega, K.Nieminen, H.Sixta. *Bioresource Technology* (2011) 102 (**2011**) 10724–10732
Guetsch, J.G.; Nousiainen, T.; Sixta, H: Bioresource Technology 109 (**2012**) 77–85

* batch autoclave, V = 0.3 L, L:S = 40:1

Prehydrolysis of Wood

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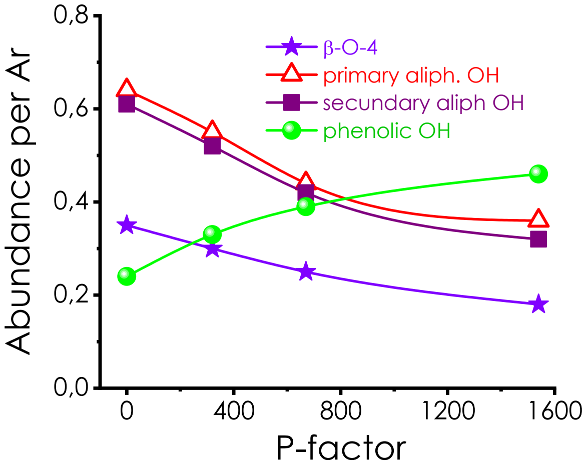
Effect on Residual Lignin of *E. globulus*

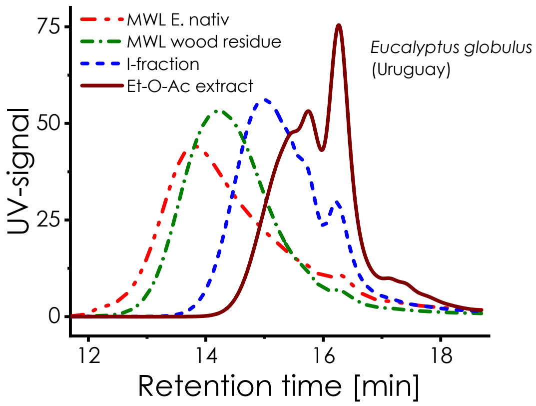


Residual Lignin (MWL)

P-factor	S/G	PhenOH	COOH
	^{13}C & Q-DEPT NMR	mol/mol	^{31}P NMR mmol/g
0	1,98	0,22	0,18
200	1,68	0,33	0,18
750	1,57	0,37	0,23

Leschinsky, M., et al., *Holzforschung*, **2008. 62**(6) 645-652
Leschinsky, M., et al., *Holzforschung*, **2008. 62**(6) 653-658

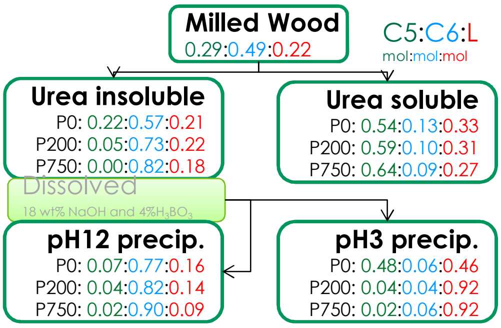
Effect on Residual Lignin of *E. globulus*



Leschinsky, Moritz: Doctoral Dissertation, Faculty of Mathematics, Informatics and Natural Sciences, University of Hamburg, **2009**

Effect on residual lignin of birch

Fractionation of
Lignin-Carbohydrate Complexes
LCCs



As the intensity of the prehydrolysis increases, the proportion of the LCC fraction in the residual lignin of the birch decreases.

Conclusions:

Prehydrolysis leads to a cleavage of the LCC bonds

Rauhala, T. et al. *NPPRJ*, **2011**, 26(4), 386-391
Guetsch, J., H. Sixta. Holzforschung, **2011**, **65**, 511-518

Prehydrolysis of Wood

- Comparative evaluation of birch and pine
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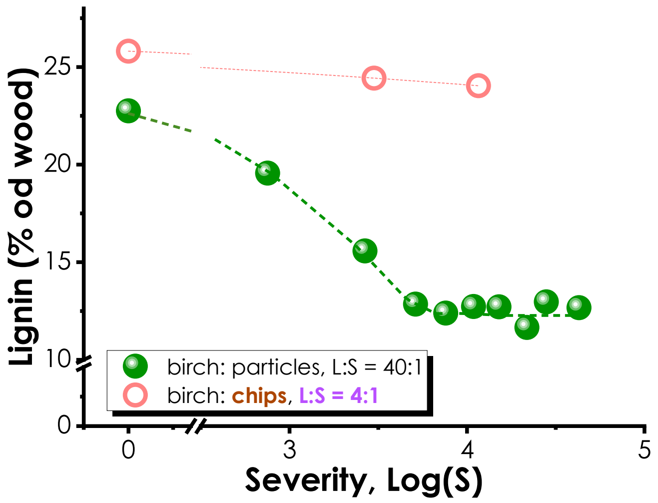
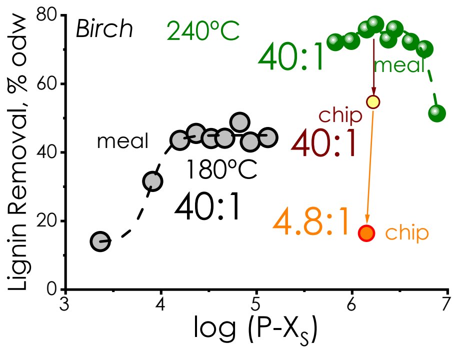
Effect of Liquor-to-wood ratio



Decrease of L:S leads to a significantly reduced delignification



Borrega, M. et al. BioResources, 6(2), (**2011**) 1890-1903
Ståhl, M. et al. Biomass and Bioenergy, 109 (**2018**), 100-113

Prehydrolysis of Wood

- Comparative evaluation of birch and pine
- Selectivity of xylan removal
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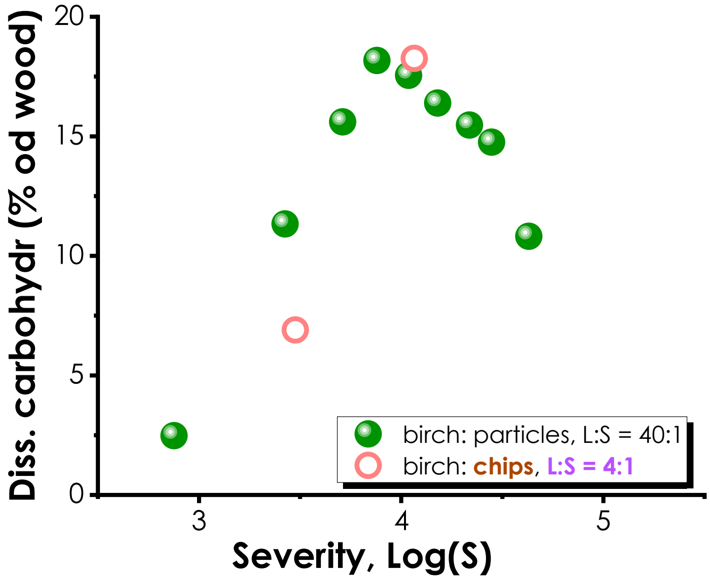
- Effect on residual lignin
- Effect of liquor-to-wood-ratio
- **Effect of wood particle size**
- Batch- vs. percolation reactor
- Acid-catalyzed hydrolysis

Particle size, L:S on carbohydrate yield



Effect of combined L:S and particle size on carbohydrate removal low

Prehydrolysis of Wood

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- Bound and free acetic acid in the hydrolysate
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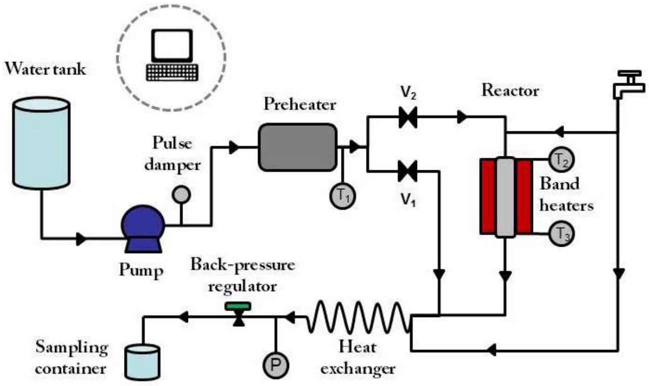
- Effect of liquor-to-wood-ratio
- Effect of wood particle size
- **Batch- vs. percolation reactor**
- Acid-catalyzed hydrolysis

Percolation-type of reactor



$V_{reactor}$ = 190 mL

Marc Borrega, PhD

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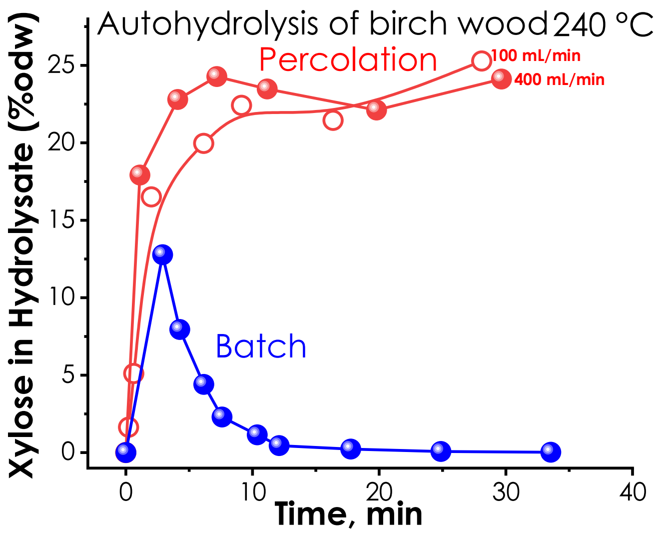
Batch vs Percolation-type of reactors



Batch: Maximum xylose yield 15 - 17% odw
Percolation: Theoretical xylose yield of 25% odw

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Prehydrolysis of Wood

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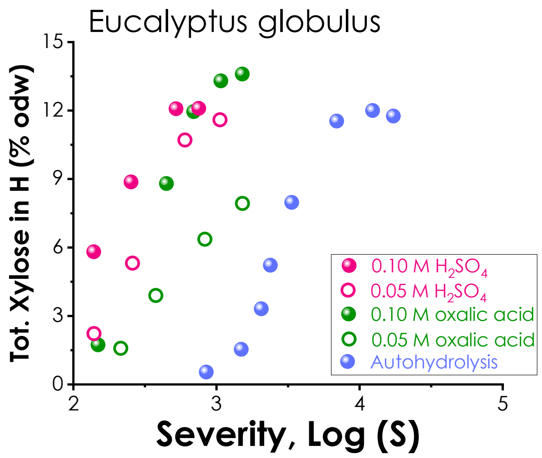
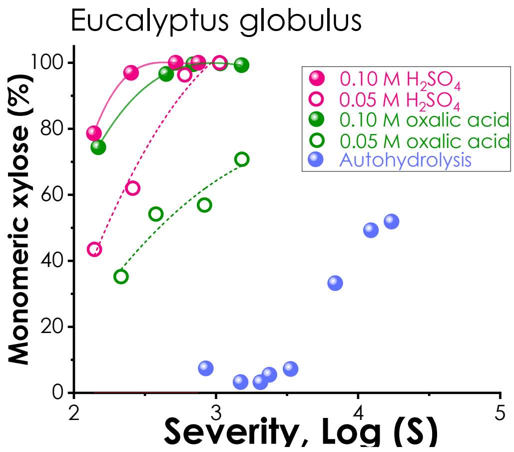
- Bound and free acetic acid in the hydrolysate
- Effect on residual lignin
- Effect of liquor-to-wood-ratio
- Effect of wood particle size
- Batch- vs. percolation reactor
- **Acid-catalyzed hydrolysis**

Acid catalyzed hydrothermal treatment

Acidity can be compensated by temperature, and vice versa!





Maximum xylose yield: 12-13 wt% odw
Realistic xylose yield: 8 – 9 wt% odw
because the xylose remaining in the void fraction of the chips, $V_V = \frac{1}{\rho_{dw}} - \frac{1}{1.53}$, cannot be recovered.

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Module 2

1. Introduction
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Kinetic Modeling of Prehydrolysis

$$-\frac{dX}{dt} = z_X \cdot k_{f,X} \cdot X_f + (1 - z_X) \cdot k_{s,X} \cdot X_s \qquad (1)$$

$$z_X = \frac{(X - X_s)}{X} = \frac{X_f}{X} \qquad (2)$$

X: fraction of original xylan remaining in the solid
X_f: fraction of the fast − reacting xylan remaining in the solid
X_s: fraction of the slowly − reacting xylan remaining in the solid
z_X: fraction of the readily reacting xylan
$k_{f,X}, k_{s,X}$: rate constants

Non-linear regression (least squares) analysis is applied to determine the best values for the coefficients in the integrated form of equ 1.

$$X = z_X \cdot Exp(-k_{f,X} \cdot t) + (1 - z_X) \cdot Exp(-k_{s,X} \cdot t) \qquad (3)$$

Sixta, H. Handbook of Pulp (2006)

Heating-up time correction

$$t_{T_0} = \int_{t_{T_t}}^{t_{T_0}} Exp\left(\frac{E_A}{R} \cdot \left[\frac{1}{T_{T_t}} - \frac{1}{T_0}\right]\right)$$

T_t: temperature during heating − up
T_0: target temperature
E_A: factivation temperature

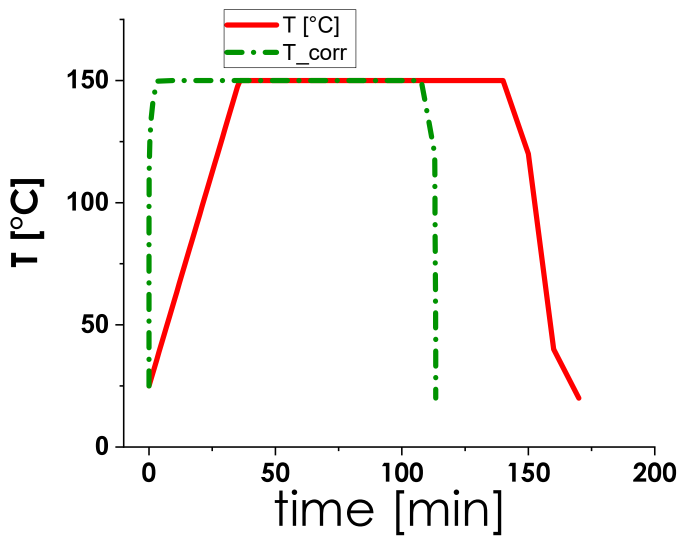
Ea, kJ/mol	120,0
E_a/R	14433
T [°C]	150
T [K]	423,15

time [min]	t_corr [min]	T [°C]	T [K]	exp(-Ea/R*(1/Te-1/Tf))	delta
0	0,0	25	298,2	0,000	0,000
1	0,0	29	301,7	0,000	0,000
4	0,0	39	312,2	0,000	0,000
7	0,0	50	322,7	0,000	0,000
10	0,0	60	333,2	0,000	0,000
13	0,0	71	343,7	0,000	0,000
16	0,0	81	354,2	0,001	0,002
19	0,0	92	364,7	0,004	0,005
22	0,0	102	375,2	0,013	0,015
25	0,1	113	385,7	0,036	0,044
28	0,3	123	396,2	0,098	0,116
31	0,8	134	406,7	0,251	0,295
34	2,0	144	417,2	0,612	0,714
37	4,6	150	423,2	1,000	1,000
38	5,6	150	423,2	1,000	1,000
39	6,6	150	423,2	1,000	1,000

$$t_{corr} = (t_t - t_{t-1}) \cdot \left(t_{t,T_0} + t_{t+1,T_0}\right)/2 + t_{corr-1}$$

Sixta, H. Handbook of Pulp (2006)

Heating-up time correction



Sixta, H. Handbook of Pulp (2006)

P-factor concept

$$P = \int_{t_0}^{t} k_{rel} \cdot dt \qquad (5)$$

$$Ln(k_{X(T)}) = Ln(A) - \frac{E_{A,X}}{R} \cdot \frac{1}{T} \qquad (6)$$

$$Ln(k_{X,100^oC}) = Ln(A) - \frac{E_{A,X}}{R} \cdot \frac{1}{373.15} \qquad (7)$$

$$Ln\left(\frac{k_{X,(T)}}{k_{X,100^oC}}\right) = \frac{E_{A,X}}{R \cdot 373.15} - \frac{E_{A,X}}{R \cdot T} \qquad (8)$$

$$k_{rel} = \frac{k_{X,(T)}}{k_{X,100^oC}} = Exp \cdot \left(40.48 - \frac{15106}{T}\right) \qquad (9)$$

$$P = \int_{t_0}^{t} \frac{k_{X,(T)}}{k_{X,100^oC}} \cdot dt = \int_{t_0}^{t} Exp \cdot \left(40.48 - \frac{15106}{T}\right) \cdot dt \qquad (10)$$

Sixta, H. Handbook of Pulp (2006)

E_a= **125,6** [kJ/mol]

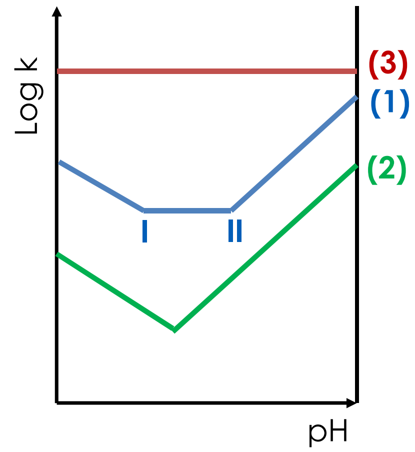
k_r=EXP((1000*E_a/373*8,31)-(1000*Ea/(8,31*(273+T)))) **[T = °C]**

Input Data Only in the yellow shaded area

Result green shaded area

Zeit min	**1143** °C	**k_r**	$(k_{ri}+k_{ri-1})/2$	**dt** min	**dt** h	**P-F1** bei t_n	**P factor**
0	80,0	0,1		0		0	**0**
4	85,0	0,2	0,1	4	0,07	0	**0**
6	90,0	0,3	0,3	2	0,03	0	**0**
8	95,0	0,6	0,5	2	0,03	0	**0**
10	100,0	1,0	0,8	2	0,03	0	**0**
18	120,0	7,9	6,3	2	0,03	0	**0**
26	140,0	50,6	41,5	2	0,03	1	**4**
28	145,0	78,4	64,5	2	0,03	2	**6**
30	150,0	120,3	99,4	2	0,03	3	**9**
34	160,0	274,5	228,5	2	0,03	8	**22**
38	170,0	603,6	506,2	2	0,03	17	**50**
40	170,0	603,6	603,6	2	0,03	20	**70**
50	170,0	603,6	603,6	2	0,03	20	**171**
60	170,0	603,6	603,6	2	0,03	20	**271**
70	170,0	603,6	603,6	2	0,03	20	**372**
72	170,0	603,6	603,6	2	0,03	20	**392**
74	170,0	603,6	603,6	2	0,03	20	**412**

General kinetics of hydrolysis reactions



$$k = k_W + k_a[H^+] + k_b[OH^-]$$

The minimum reaction rate constant
(by differentiation of k according to [H+])

$$k_0 = k_w + 2\sqrt{k_a k_b [H^+][OH^-]}$$

3 Cases

1. pH < I: $k_a[H^+] \uparrow$
   I <pH < II: $k_w \uparrow$
   pH > II: $k_b[OH^-] \uparrow$

e.g. Saponification of lactic acid ester

2. $k_w \ll 2\sqrt{k_a k_b [H^+][OH^-]}$

e.g. Hydrolysis of acid amides

3. $k_w > 2\sqrt{k_a k_b [H^+][OH^-]}$

e.g. Carbon dioxide cleavage of carboxylic acids

Skrabal, A. Ueber ein sehr allgemeines Zeitgesetz der chem. Kinetic und seine Deutung. Die Hydrolyse Geschwindigkeit der Organooxyde. ***Z. Elektrochem.* 1927, 33, 322.**

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Simplified kinetics of cellulose hydrolysis

$$[Cell] \overset{k_1}{\rightarrow} [Glu] \overset{k_2}{\rightarrow} [D\ Glu]$$

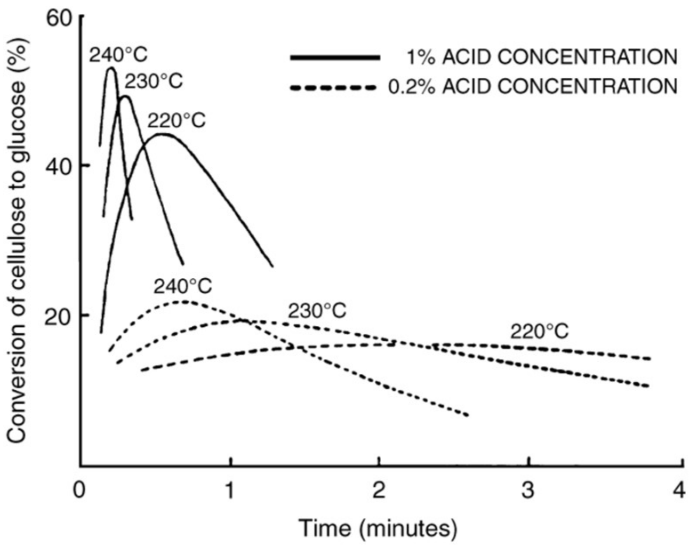
$$\frac{d[C]}{dt} = (k_W + k_a[H^+] + k_b[OH^-]) \cdot [C]$$

$$\frac{d[C]}{dt} = (k_W + k_a[H^+] + k_b[OH^-]) \cdot [C] = k_1[C]$$

$$[Glu] = [C]_0 \frac{k_1}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right)$$

High glucose formation can only be reached when $k_1 >> k_2$.

Acid hydrolysis at 1 wt% $[H^+]$ leads to 50% **Glu** at 230-240°C



Bobleter, O. Polysaccharides (2nd edition) 2005, 893-936

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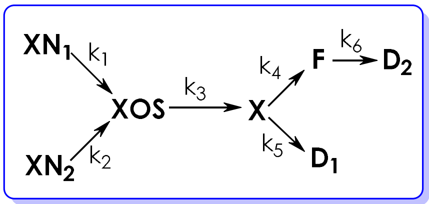
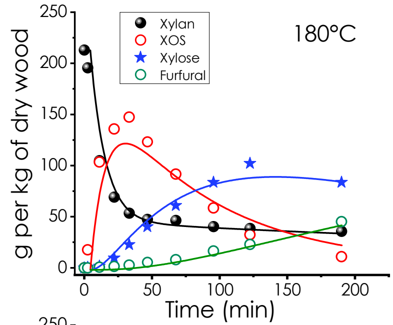
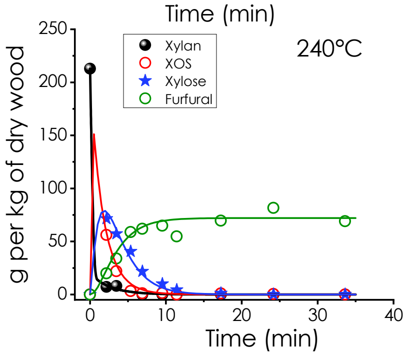
Kinetics of xylan degradation in wood

Birch Wood



$$\frac{d[XN_1]}{dt} = -k_1[XN_1]$$
$$\frac{d[XN_2]}{dt} = -k_2[XN_2]$$
$$\frac{d[XOS]}{dt} = k_1[XN_1] + k_2[XN_2] - k_3[XOS]$$
$$\frac{d[X]}{dt} = k_3[XOS] - (k_4 - k_5)[X]$$
$$\frac{d[F]}{dt} = k_4[X] - k_6[F]$$





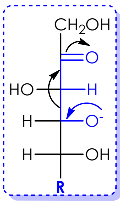
M.Borrega, K.Nieminen,H.Sixta. *Bioresource Technology* (2011) 102 (**2011**) 10724–10732

5 g extractive-free wood meal, L:S=40:1, V_{batch} =0.3 L

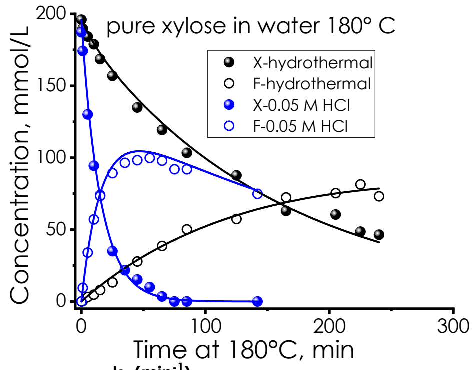
Hydrothermolysis kinetics of xylose

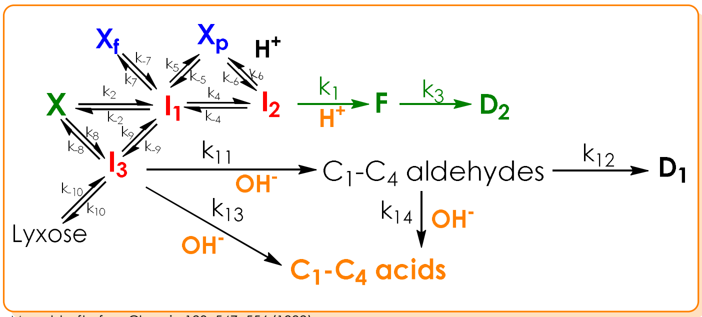
Parameter, g/kg od w	Treatments	
P-factor	**766**	**8166**
Temperature, °C	180	220
Time, min	30	25
L:W	3	3
Sugars	98	8
Furans (F+HMF)	12	59
Acetic/formic acid	19	71
C2-C4 aliphat acids2	2	9
TOTAL	**131**	**147**
YIELD LOSS	**191**	**407**

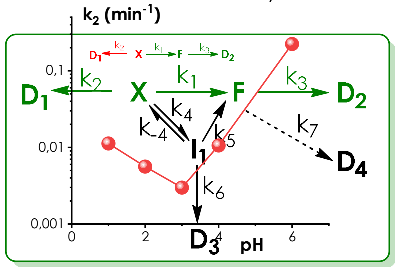
Borrega, M.; Niemela K.; Sixta, H. Holzforschung **2013**; 67(8): 871–879



Reversed aldol reaction





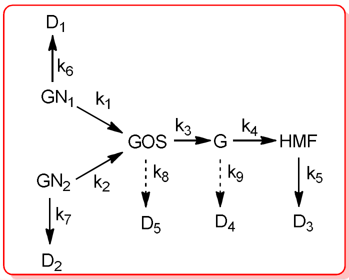


Monatshefte fuer Chemie 123, 547- 556 (1992)

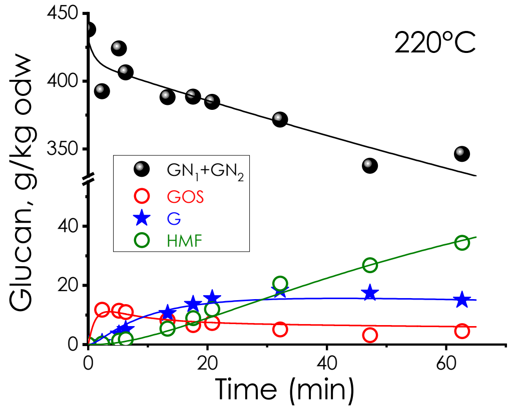
Ershova, O.; Nieminen, K.; Sixta, H. ChemCatChem 2017, 9, 3031 – 3040
Sixta, H. unpublished results (2009)

Kinetics of cellulose degradation in wood

Birch Wood



$$\frac{d[GN_1]}{dt} = -(k_1 + k_6)GN_1$$
$$\frac{d[GN_2]}{dt} = -(k_1 + k_7)GN_2$$
$$\frac{d[GOS]}{dt} = k_1GN_1 + k_2GN_2 - (k_3 + k_8)GOS$$
$$\frac{d[G]}{dt} = k_3GOS - (k_4 + k_9)G$$
$$\frac{d[HMF]}{dt} = k_4G - k_5HMF$$



M.Borrega, K.Nieminen,H.Sixta. *Bioresource Technology* (2011) 102 **(2011)** 10724–10732

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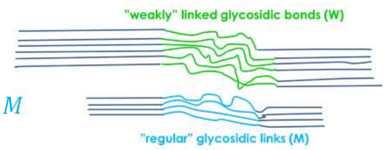
Cellulose Depolymerization Model

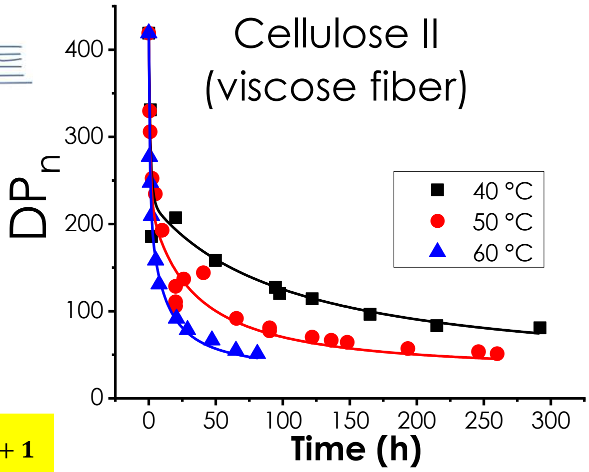


$$\begin{cases} \frac{dM}{dt} = -k_1M \\ \frac{dH_1}{dt} = k_1M \\ \frac{dW}{dt} = -k_2W \\ \frac{dH_2}{dt} = k_2W \end{cases}$$

$$\begin{cases} M = M_0e^{-k_1t} \\ H_1 = M_0(1 - e^{-k_1t}) \\ W = W_0e^{-k_2t} \\ H_2 = W_0(1 - e^{-k_2t}) \end{cases}$$

$$DP = \frac{DP_0}{H_1 + H_2 + 1}$$

$$\boldsymbol{\frac{DP_0}{DP} - 1 = CS = M_0(1 - e^{-k_1t}) + W_0(1 - e^{-k_2t}) + 1}$$



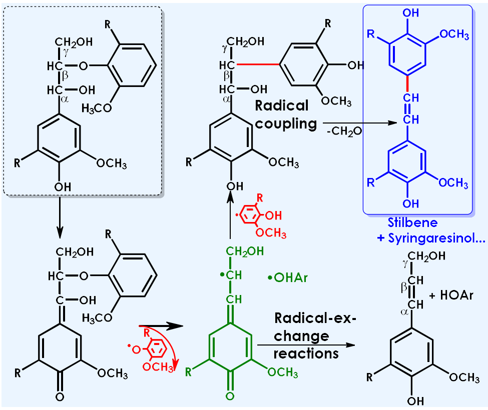
M – number of amorphous segments with normal degradation rate
W – number of amorphous segments containing weakly linked glycosidic bonds
H_1 – number of chain breaks in normal amorphous segments
H_2 – number of chain breaks in weakly linked subcategories
k_1 – normal rate constant
k_2 – fast rate constant (cleavage of weakly linked elements)

Cellulose (2016) 23:213–229
K. Nieminen, Sixta, H. (2015)

Delignification mechanisms

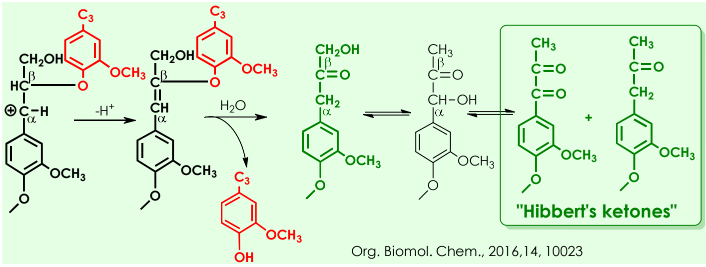
Mildly acidic conditions

Homolytic cleavage of the β-aryl ether **(C)**

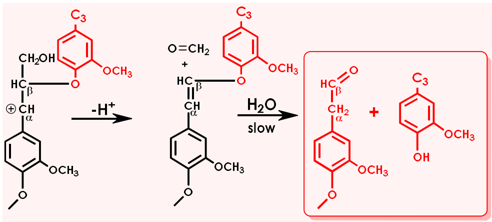


More strongly acidic conditions

β-aryl ether bond cleavage via benzylic carbo cation **(A)**



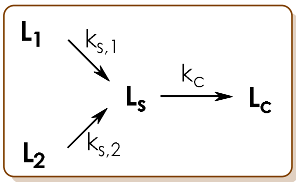
Acidolytic β-aryl ether bond cleavage **(B)**



Li, S.; Lundquist, K. NPPRJ, 2000, 15, 292

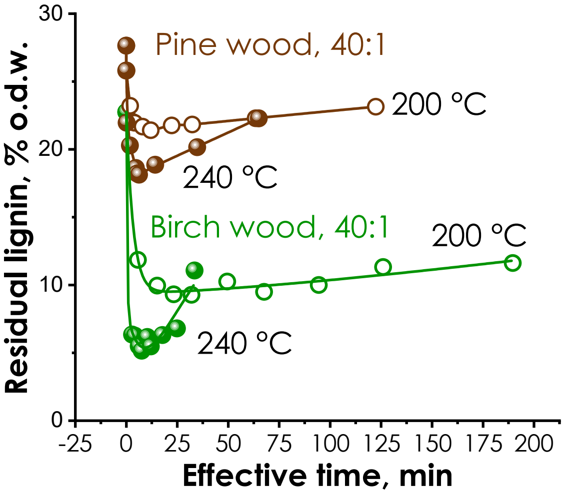
(Meshgini, M., Sarkanen, K.V. (1989))

Delignification kinetics



$$\frac{dL_1}{dt} = -k_{s,1}L_1$$
$$\frac{dL_2}{dt} = -k_{s,2}L_2$$
$$\frac{dL_s}{dt} = k_{s,1}L_1 + k_{s,2}L_2 - k_cL_s$$
$$\frac{dL_c}{dt} = k_cL_s$$

		Portions, %		Reaction rates, min^{-1}		
Species	Temp, °C	Fast	Slow	k_1	k_2	k_c
Birch	200	58	42	0,294	0,004	0,003
Pine	200	22	78	0,786		0,003
Birch	220	61	39	0,858	0,036	0,010
Pine	220	29	71	10,060	0,240	0,007
Birch	240	63	37	2,538	0,128	0,019
Pine	240	38	63	27,740	0,370	0,010



Borrega, M. et al. BioResources, 6(2), (**2011**) 1890-1903
Ståhl, M. et al. Biomass and Bioenergy, 109 (**2018**), 100-113

Module 2

1. Introduction
2. Chemistry
3. Kinetics
4. Technology→ Module 3