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Bern University of Applied Sciences
Swiss College of Agriculture SHL

Production of fuels and chemicals from wood

Dialogue platform «Novel ways in bio-refining of wood», Workshop I
Bern, December 10th 2015

Philipp Rudolf von Rohr, Thomas Pielhop
Institute of Process Engineering - LTR

Resource Wood
National Research Programme NRP 66

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Outline

- Background and state of the art
  - Resource wood
  - Chemicals from wood
  - Biochemical conversion
- Exemplary process - Steam explosion with scavenger
  - Softwood recalcitrance
  - Steam explosion
  - Chemicals addition
- Conclusions/Outlook

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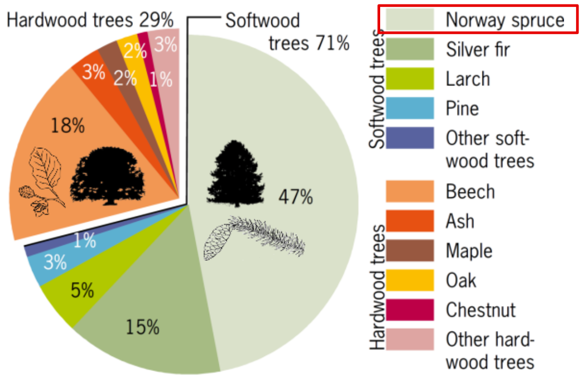
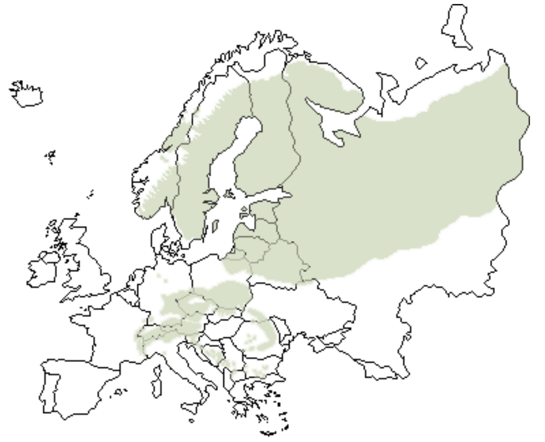
Resource wood

Distribution of wood types in Switzerland[1]





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[1] Adapted from: Swiss National Forest Inventory, 1995.
[2] linnaeus.nrm.se

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Resource wood

Wood use in biorefinery

- Flexible harvesting times → avoid long storage
- Very low ash content
- High density → cost-effective transportation
- Established pulp&paper technologies
- ➢ Attractive for biochemicals conversion if recalcitrance surmounted

Hardwood 

\+ Standard pretreatment effective

\+ Surplus available in Switzerland

\- Hemicellulose: High C5 sugar content → more difficult to ferment

Softwood 

\+ Fast and straight growing tree

\+ Hemicellulose: High C6 sugar content → easy to ferment

\- „Worst-case scenario“ due to high lignin recalcitrance

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[1] www.sekab.com

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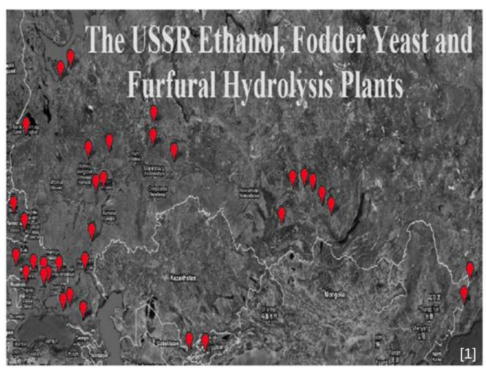
Chemicals from wood – state of the art

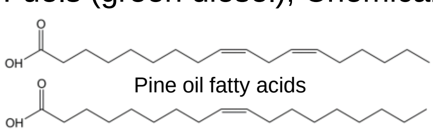
Cellulose: Fuels, Chemicals, Fibres/Pulp
Hemicellulose: Fuels, Chemicals

Example: Acid wood hydrolysis[1]

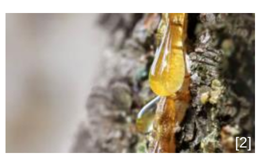
- H_2SO_4, 130-190°C
- Sugar yield: 60-70%
- Since 1933 in S.U./Russia: ethanol, fodder yeast, furfural, xylitol,…
- Currently: E85 blend, lignin pellets



Extractives: Fuels (green diesel), Chemicals



Pine oil fatty acids



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[1] M.L. Rabinovich, 2009.
[2] www.upmbiofuels.com

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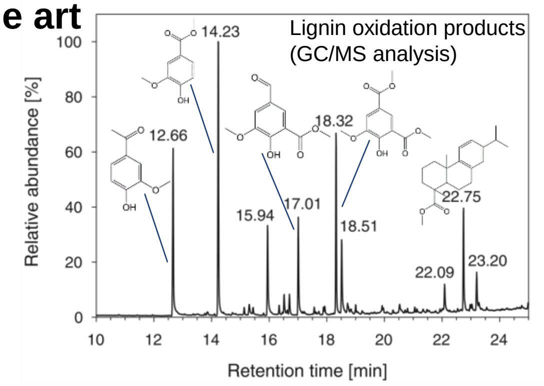
Chemicals from wood – state of the art

Lignin: Aromatic chemicals

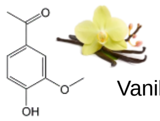
Depolymerisation

- Pyrolysis, oxidation, hydrogenolysis,…
- Vast mix of various aromatic compounds
- ➢ No high yields of a single product

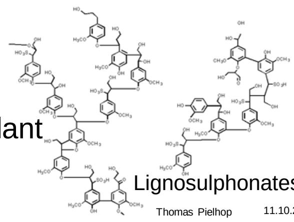


Example: Vanillin production[1]

- Alkaline oxidation of lignosulphonates
- 15% vanillin yield
- 1980's: 60% of world's vanillin supply produced in one plant



Vanillin



Lignosulphonates[2]

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[1] M.B. Hocking, 1997.
[2] Adler, 1977.

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Chemicals from wood – state of the art

Lignin: Use as polymer

Applications[1]

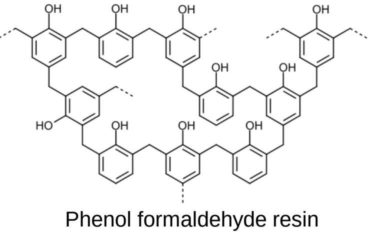
- Usually of lower value
- Used as dispersant, binder, emulsifier,…
- Polymers (e.g. phenolic resins, epoxy resins)

Dispersant

Asphalt emulsions

Lignin from biochemical conversion (steam pretreatment)[1]

- Lower molecular weight, less polydisperse, sulphur-free
- ➢ More versatile, no odor of sulphur-derived compounds



Phenol formaldehyde resin

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[1] J.H. Lora, 2002.

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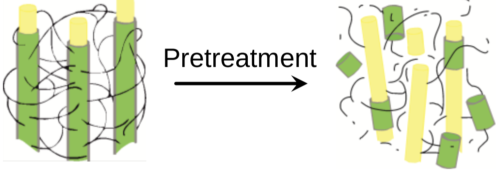
Biochemical conversion – Steam pretreatment



Key factors of a pretreatment

- Enhance cellulose digestibility (High conversion, low enzyme dose)
- Cost-effective
- Simplify downstream processing

Steam pretreatment

- No chemicals; no waste streams
- Low inhibitor formation
- „Steam explosion“ → Defibration of biomass
- ➢ Dominate at commercial scale

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Biochemical conversion – Pretreatment methods

Pretreatment	Advantages	Disadvantages	Feasibility
Milling	Effective for all biomass types	Very high energy input	−−
Liquid hot water	Hemicell. dissolved; No chemicals; Low toxic inhibitors	Average solid load; Not effective for softwood	o
Steam explosion	Hemicell. dissolved; No chemicals; Low toxic inhibitors; Defibration	Not effective for softwood	++
Dilute acid	Hemicell. dissolved; Low T and t	Average solid load; Toxic inhibitors; Acid neutralisation/recovery; Not really effective for softwood	o
Acid impreg. steam explosion	Hemicell. dissolved; Low T and t; Defibration	Toxic inhibitors; Acid neutralisation/recovery; Not really effective for softwood	+
Lime	High total sugar yield; Removes lignin; Easy lime recovery	Very low T → long t; Commercial scalability; Not effective for softwood	−
Ammonia fibre expan. (AFEX)	No toxic inhibitors; Defibration	Not suitable for softwood and hardwood	+

[1] N. Mosier et al. *Bioresource Technology*. 2005.
[2] A. Limayem and S.C. Ricke. *Prog. Energ. Combust.*. 2012.
[3] L.Shuai et al. *Bioresource Technology*. 2010.
[4] E.C. Bensah and M. Mensah. *Int. J. Chem. Eng*. 2013.

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Biochemical conversion – Pretreatment methods

Pretreatment	Advantages	Disadvantages	Feasibility
Sulphite pret. to overc. recalc. (SPORL)	Effective for hardwood and softwood; Low T and t; Defibration	Complex; Toxicity and environmental impact of SO_2; Lignosulphonates interfere with downstream processing	o
Organosolv	Effective for all biomass types	Investment and operation cost; Solvent recycling; Average solid load	−
Fungal bioconversion	Low energy and chemicals demand; Environmentally friendly	Very slow bioconversion; Average solid load	o

[1] N. Mosier et al. *Bioresource Technology*. 2005.
[2] A. Limayem and S.C. Ricke. *Prog. Energ. Combust.*. 2012.
[3] L.Shuai et al. *Bioresource Technology*. 2010.
[4] E.C. Bensah and M. Mensah. *Int. J. Chem. Eng*. 2013.

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Biochemical conversion – Commercial scale cellulosic ethanol projects

Company	Location	Opening year	Feedstock	Pretreatment	Capacity 10^6 l/year
Abengoa	USA	2014	Corn stover, wheat straw, grasses	Acid impregnation, steam explosion	95
Beta Renewables	Italy	2014	Wheat straw	Steam explosion (two-stage)	76
GranBio	Brazil	2014	Sugarcane straw	Steam explosion	84
POET-DSM	USA	2014	Corn stover and cobs	Steam explosion (two-stage)	76
Quad County Corn Processors	USA	2014	Wheat straw	Steam explosion	76
Raizen	Brazil	2014	Sugarcane bagasse	Dilute acid	38
DuPont	USA	2015	Corn stover	Dilute ammonia	95
Beta Renewables	USA	2016	Energy grass	Steam explosion (two-stage)	76
Canergy	USA	2017	Energy cane	Steam explosion	95
Energochemica	Slovakia	2017	Wheat and rapseed straw	Steam explosion	63
Mascoma	Canada	Delayed	Hard- and pulpwood	Steam explosion	76
DuPont/Ethanol Europe	Macedonia	N/A	Agricultural residues	Dilute ammonia	N/A
M&G/Anhui	China	N/A	Agricultural residues	Steam explosion	76
St1 Biofuels Oy	Finland	2016	Softwood saw dust	Steam explosion	50-100

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[1] T.R. Brown et al., 2015.
[2] S. Brethauer and M. Studer, 2015.

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Biochemical conversion – Engineering challenges

Bioprocessing vs. traditional chemical process industry[1]

- Larger reactors (100-1000L vs 10.000 – 40.000L)
- Solids handling/flow more difficult to control than gases or liquids
- Varying feedstock quality (moisture, particle size,…)
- Challenge: reliable solids feeding at high feed pressures
- ➢ Upscaling more difficult and time consuming

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[1] D. Edwards, 2015.

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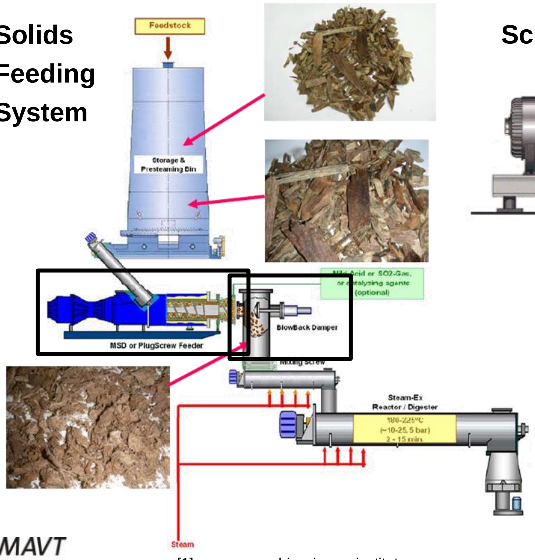
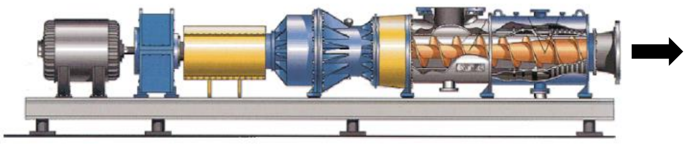
Biochemical conversion – Engineering challenges

Solids Feeding System

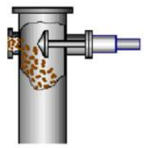


Screw feeder

Flow of material



Blow back damper



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[1] www.energybiosciencesinstitute.org

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Biomass

Steam

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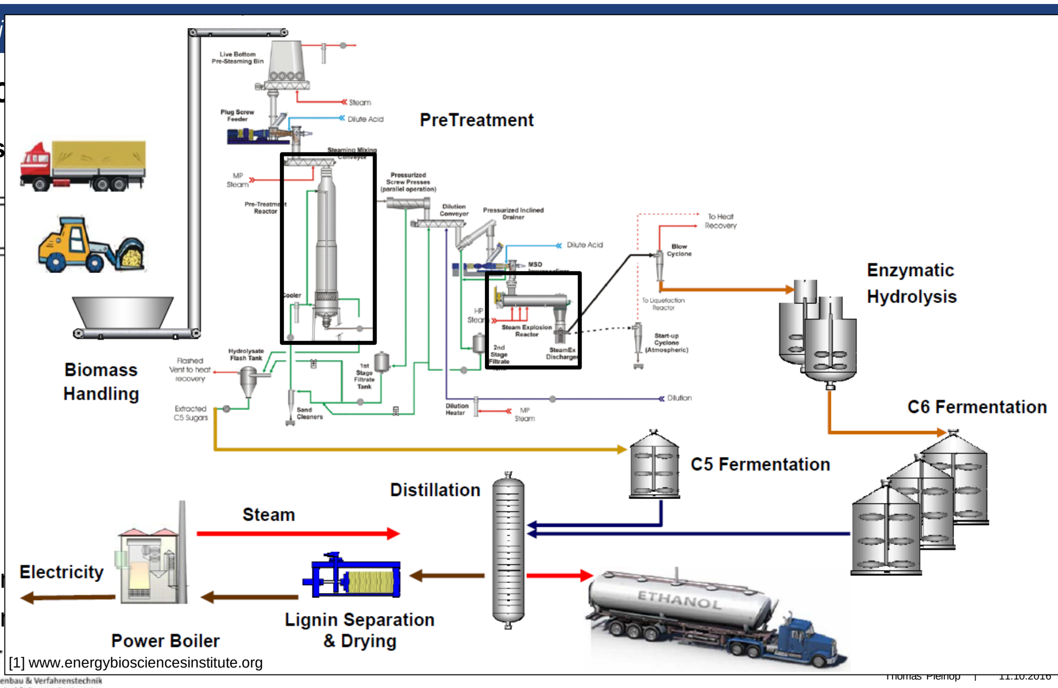

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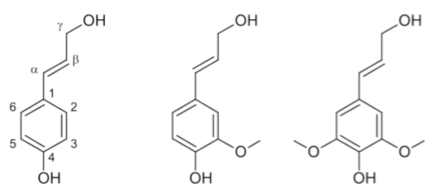
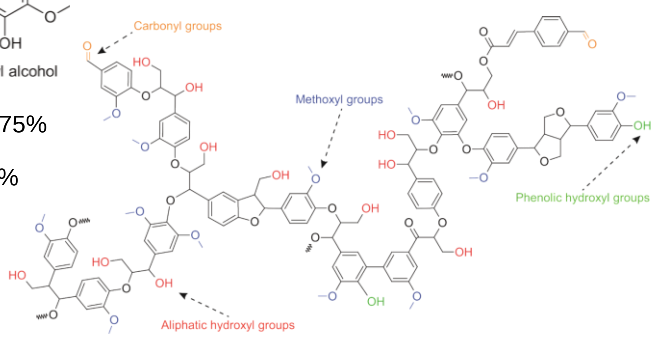
Softwood recalcitrance – Lignin structure



Monolignols	*p*-coumaryl alcohol	coniferyl alcohol	sinapyl alcohol
Hardwood	0-8 %	25-50%	45-75%
Softwood	-	> 95%	< 5%



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[1] G. Gellerstedt and G. Henriksson, 2008.

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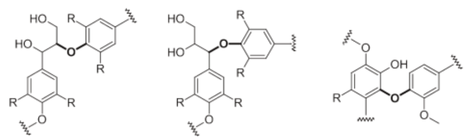
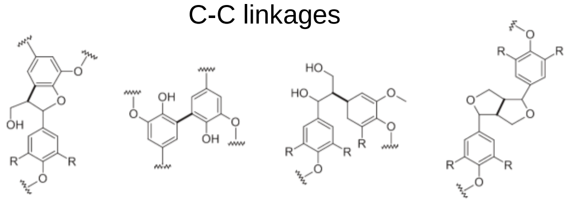
Softwood recalcitrance – Lignin interunit linkages

Ether linkages



β-O-4 α-O-4 4-O-5

C-C linkages



β-5 5-5 β-1 β-β

Linkage type	Softwood (spruce) / %	Hardwood (birch) / %
β-O-4	48	60
α-O-4	6–8	6–8
4-O-5	3.5–4	6.5
β-5	9–12	6
5-5	9.5–11	4.5
β-1	7	7
β-β	2	3
Others	13	5

Softwood lignin

- Less ether bonds/More C-C bonds
- More cross-linked
- Higher total lignin content: Softwood 31-34%, Hardwood 24-27%
- ➢ More difficult to depolymerise

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[1] E. Adler, 1977.

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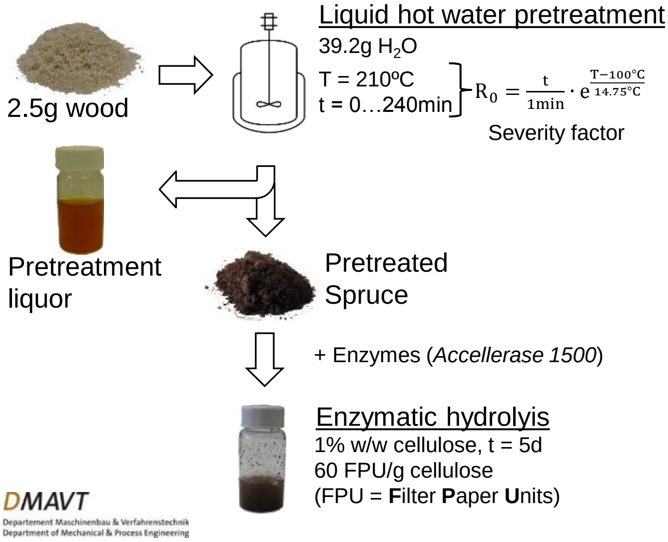
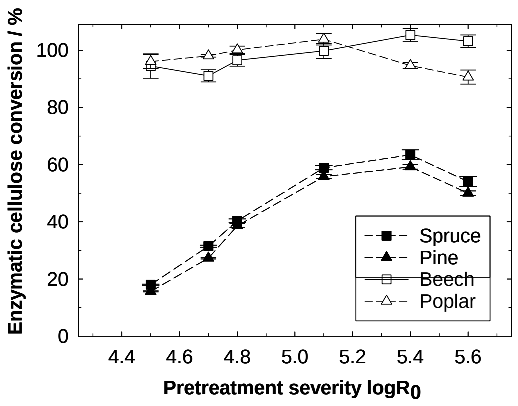
Softwood recalcitrance – Softwood vs. hardwood





- Hardwood: Lower pretreatment severity and enzyme dosage needed

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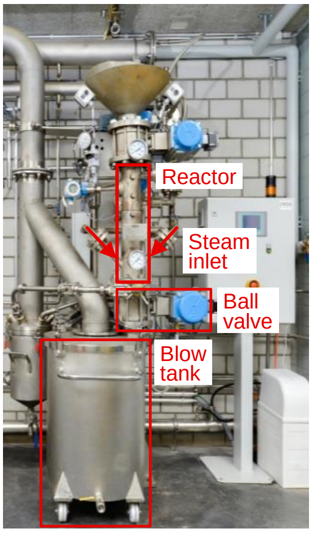
Steam explosion



Steam pretreatment

- High biomass load
- Explosion possible
- ➢ Commercial relevance[1]

Steam explosion

- Fast release of pressure
- Condensed steam in biomass re-evaporates
- ➢ „Explosion“ of biomass

Enzymatic hydrolysis

- Literature: No effect of explosion[2,3]
- Effect on scavenger pretreatment?

No explosion

Pretreatment:
$\log R_0$ = 4.4 (T = 235°C, t = 2.5min)

Explosion

[1] E. Tomás-Pejó et al. *Bioresource Technology*. 2010.
[2] H. H. Brownell et al. *Biotechnology and bioengineering*. 1986.
[3] N. Mosier et al. *Bioresource Technology*. 2005.

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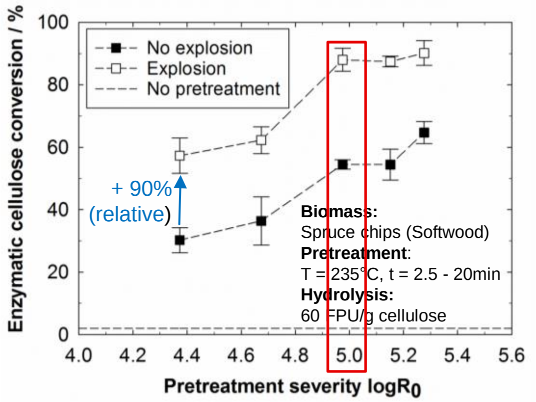
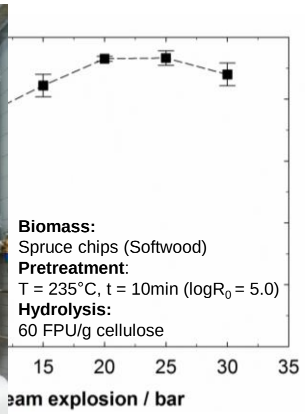
Steam explosion – enzymatic digestibility





Factors influencing explosion effect

- Explosion pressure difference
- Severity (soften up lignocellulose structure)

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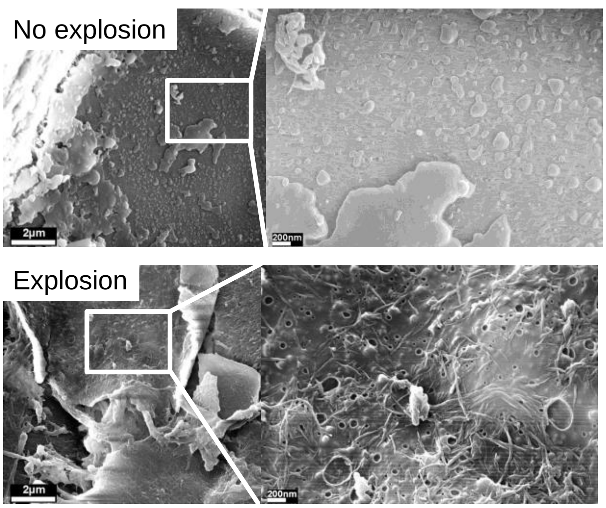
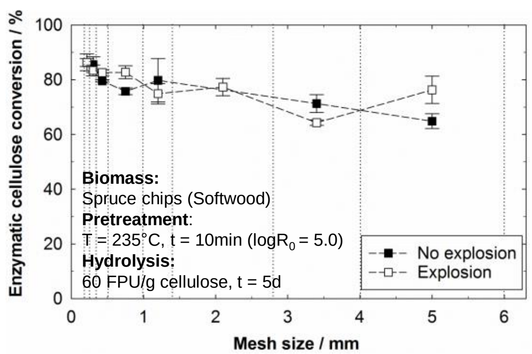
Steam explosion – effect on enzymatic digestibility



Pretreatment:
T = 235°C, t = 10min ($logR_0$ = 5.0)



Elimination of particle size influence

- Isolation of fractions with similar particle size from exploded and non-exploded biomass
- No enhanced digestibility of exploded biomass
- ➢ Explosion effect: reduction of particle size

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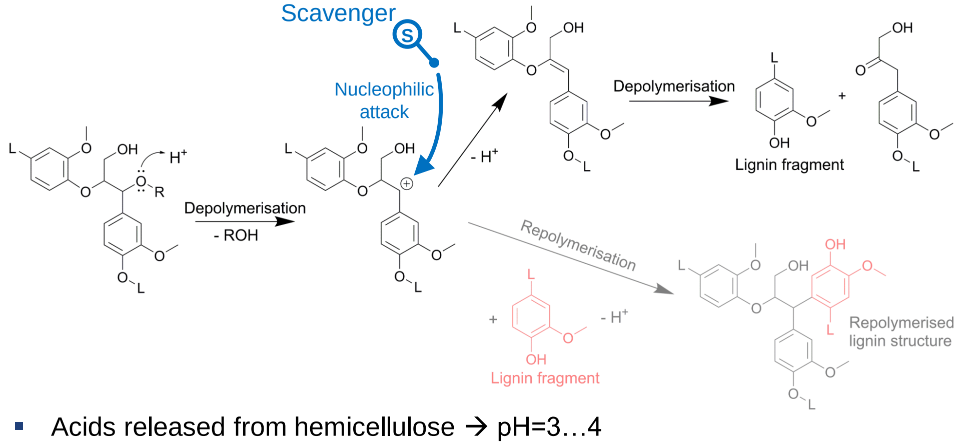
Steam pretreatment – lignin de-/repolymerisation



- Acids released from hemicellulose → pH=3…4
- Acidic conditions: formation of carbocations in lignin[1]
- Repolymerised and insoluble structures formed[2]

[1] K. L. Knut, L. Rolf. *Acta Chemica Scandinavia*. 1972.
[2] M. Wayman and J.H. Lora. *Tappi*. 1978.

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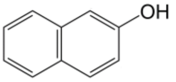
Steam explosion with 2-Naphthol

Raw spruce wood chips

1.5kg

2-Naphthol



35g (0.205mol / mol lignin C_9 unit)

2-Naphthol

- Solid under ambient conditions
- Hardly water soluble at room temperature
- Melting point: 121°C[1]

Mixing with biomass

- 2-Naphthol distribution by diffusion only
- Wood chips: mass transfer limitations?

Impregnation of biomass

- Impregnation with acetone
- 2-Naphthol has penetrated wood chips
  → mass transfer limitations reduced
- Higher „effective“ concentration inside the biomass?

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[1] *BG Chemie.* 1995.

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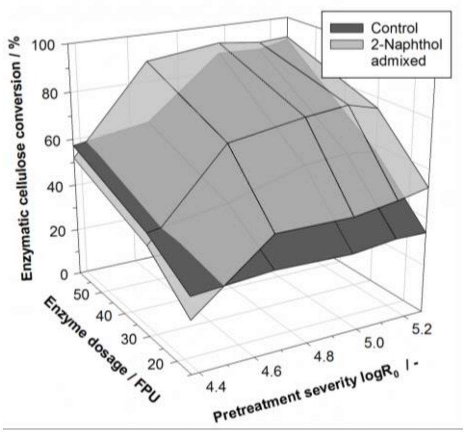
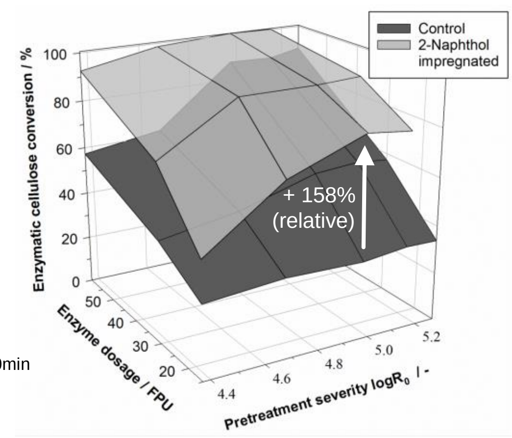
Steam explosion with 2-Naphthol – hydrolysis yields



Pretreatment:
T = 235°C, t = 2.5-20min
Hydrolysis:
t = 5d



- Glucose yield increased up to 52% (relatively)
- ➢ 2-Naphthol works in steam pretreatment

- Outstanding digestibility enhancement
- High digestibility at commercially relevant enzyme dosages (15 FPU/g cellulose[1])

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[1] B. Yang et al. *Biofuels.* 2011.

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Conclusions

- Wood: potential for bioconversion to fuels and chemicals
- High recalcitrance (in particular softwood) must be surmounted
- Overcoming recalcitrance by e.g. explosion and chemical treatments

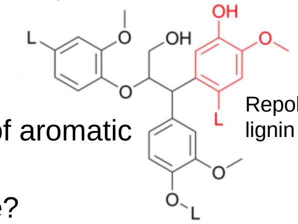
Outlook

- 1st wood-based biorefinery (sugar platform) to open next year

Lignin obtained in scavenger approach

- Less repolymerised C-C bonds; Lower molecular weight
- Higher chemical value for use in polymers or production of aromatic monomers?

➢ Improved valorisation of both cellulose and lignin possible?



Repolymerised lignin structure

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Bern University of Applied Sciences
Swiss College of Agriculture SHL

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