Advancements in the organosolv process for bioproducts

E.R. van Selow
W.J.J. Huijgen
R.J.H. Grisel
J.W. van Hal

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Edward van Selow, Wouter Huijgen,
Ruud Grisel, Jaap van Hal

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Making bio-energy work

Feedstock
- Characterization

Pre-treatment
- Torrefaction
- TORWASH
- Pyrolysis
- Biochar
- Fractionation

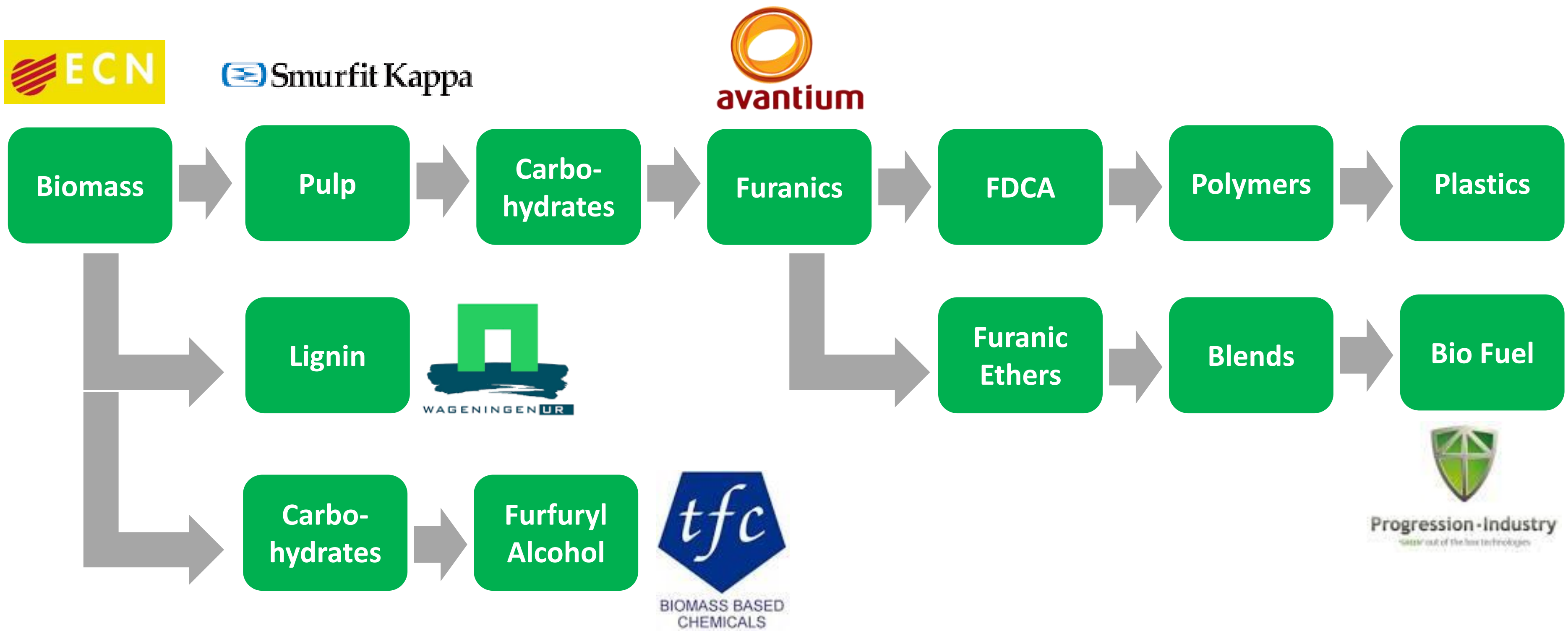
Conversion
- Combustion
- Gasification
- Biorefinery

Separation
- Tar removal
- Separation

Product Synthesis
- Synthetic nat. gas
- Bio-fuels
- Bio-plastics
- Bio-chemicals
- Electricity
- Heat & cold




The YXY Fuels project



Contents

1 Feedstock Selection

Biomass – a diverse raw material

waste wood (agricultural) residues energy crops aquatic biomass

Feedstock selected by scoring on various criteria

ECN

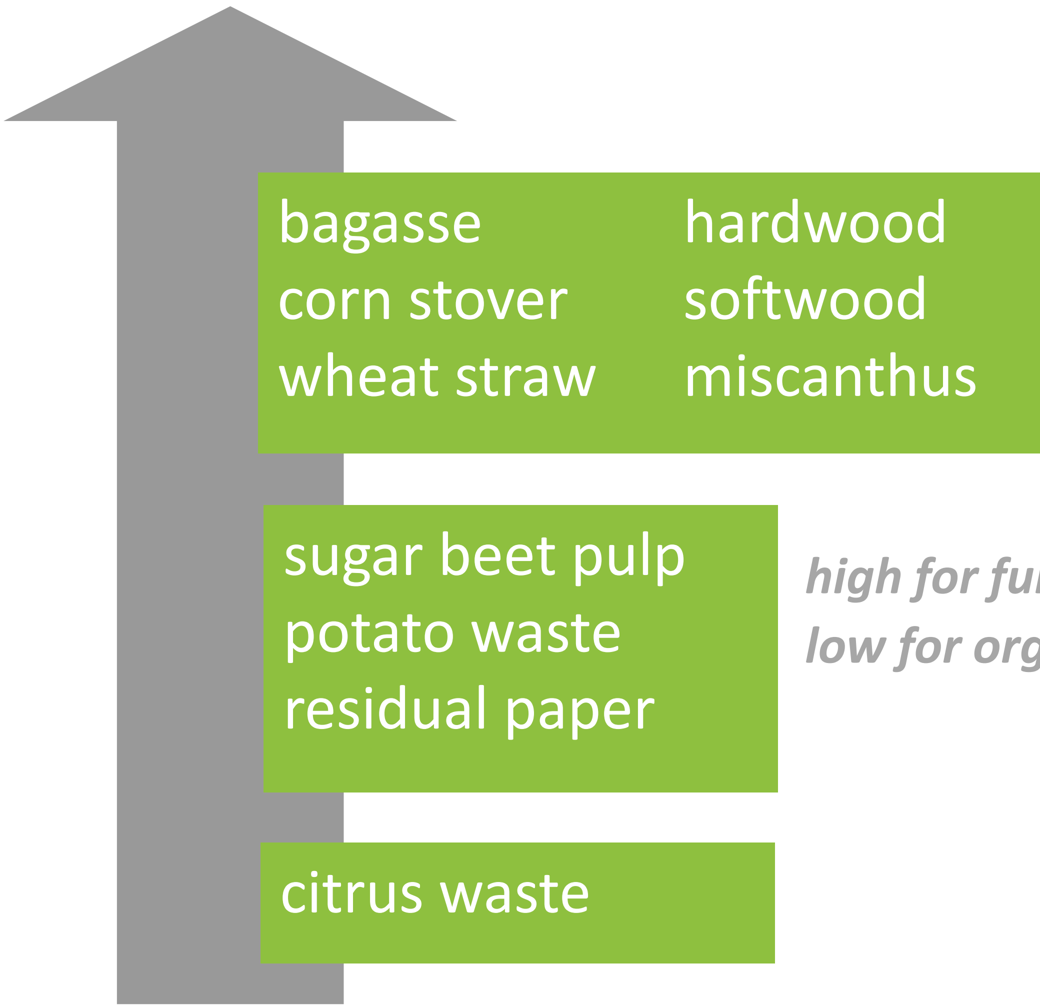
<u>10 criteria</u>, including:

Price	Available in large volumes
C6 content	Stability during storage
Lignin content	Pre-processing or feeding effort
Sustainability	…

<u>Score</u>
-2 bad
-1 poor
0 neutral/unknown
1 good
2 excellent

<u>Relevance</u>
1 small
2 moderate
3 substantial
4 high
5 essential

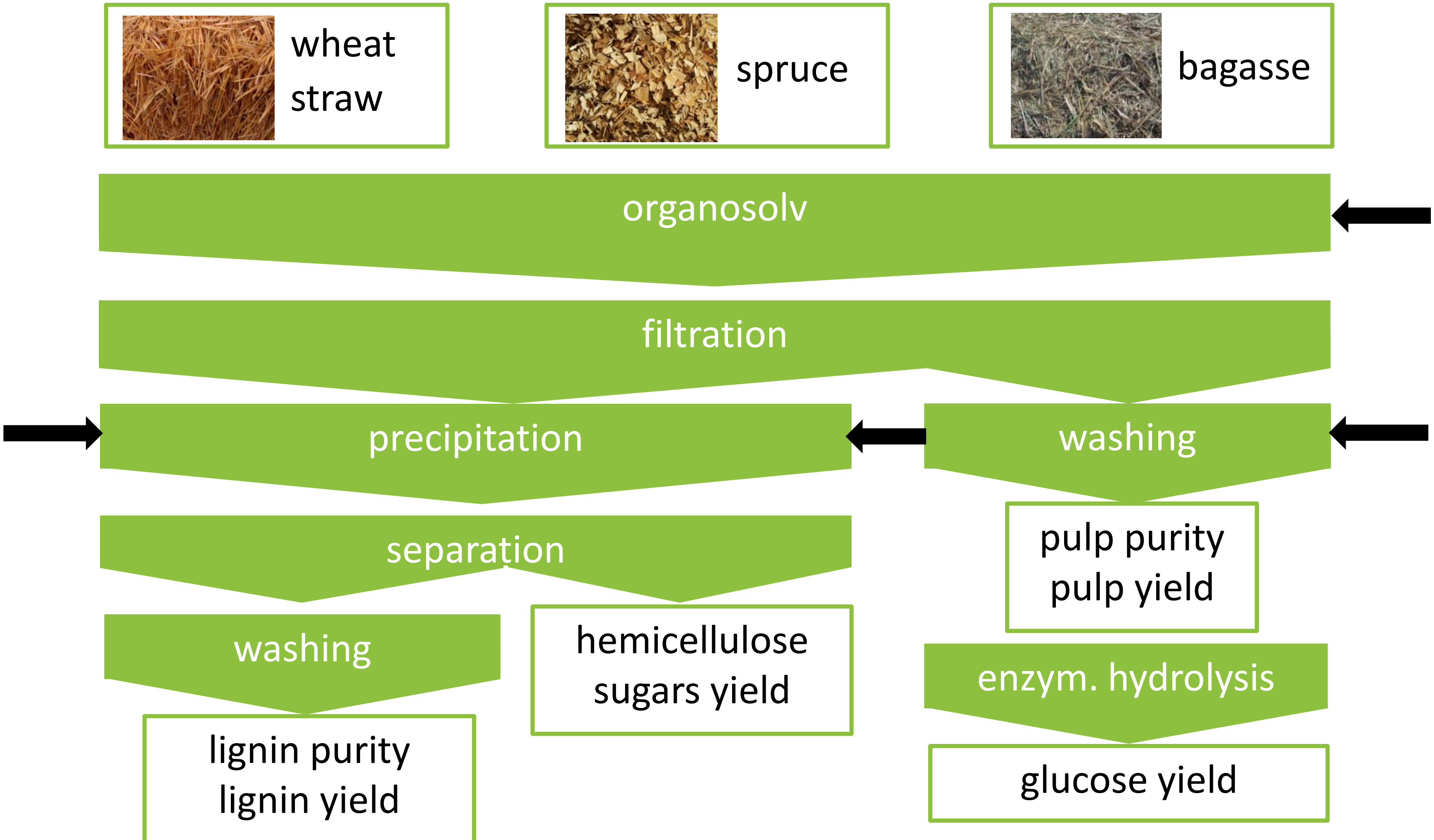
Feedstock scoring results



high for furan fuels & chemicals
low for organosolv

2 Operating Conditions

Optimising fractionation conditions



Biochemical composition

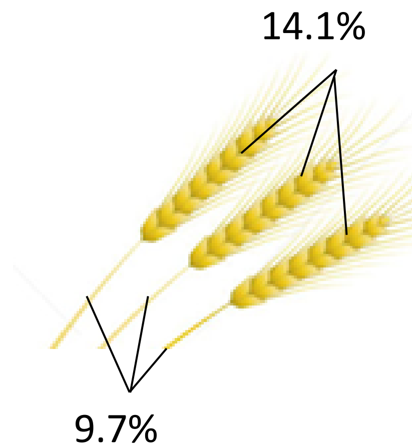
	straw	spruce	bagasse		
glucan	29.8	41.6	39.1	%	
xylan	20.6	3.6	21.8	%	
arabinan	2.0	BDL	0.9	%	
mannan	BDL	10.4	BDL	%	
galactan	0.7	1.2	0.3	%	
AIL	14.4	27.3	18.7	%	acid insoluble lignin
ASL	1.2	0.3	1.2	%	acid soluble lignin
ash	13.7	0.3	2.2	%	
extractives	7.8	7.0	12.9	%	
ANC (pH 2)	0.45	0.06	0.21	mol H^+/kg	acid neutralising capacity

Ash from straw released in fractionation

ash 13.4 ± 1.4 wt-% (*n*=6)

mostly *Si*

not removed by rinsing



organosolv

21% to liquor

79% to pulp

Parameter ranges for straw fractionation

Acid dose

60 mM

45 mM

30 mM

15 mM

increasing severity

Combined Severity

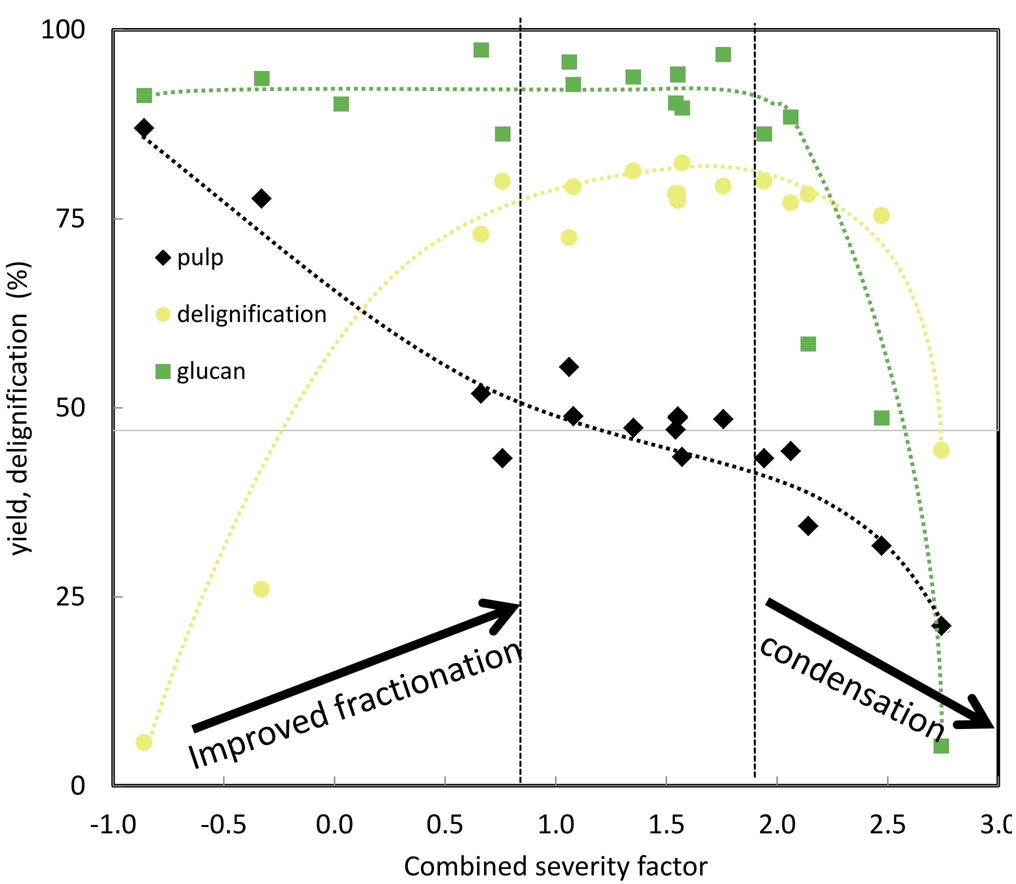
$$CS = \log\left[t \cdot exp\left(\frac{T - T_{ref}}{14.75}\right)\right] - pH$$

t = 60 min T_{ref} = 100 °C

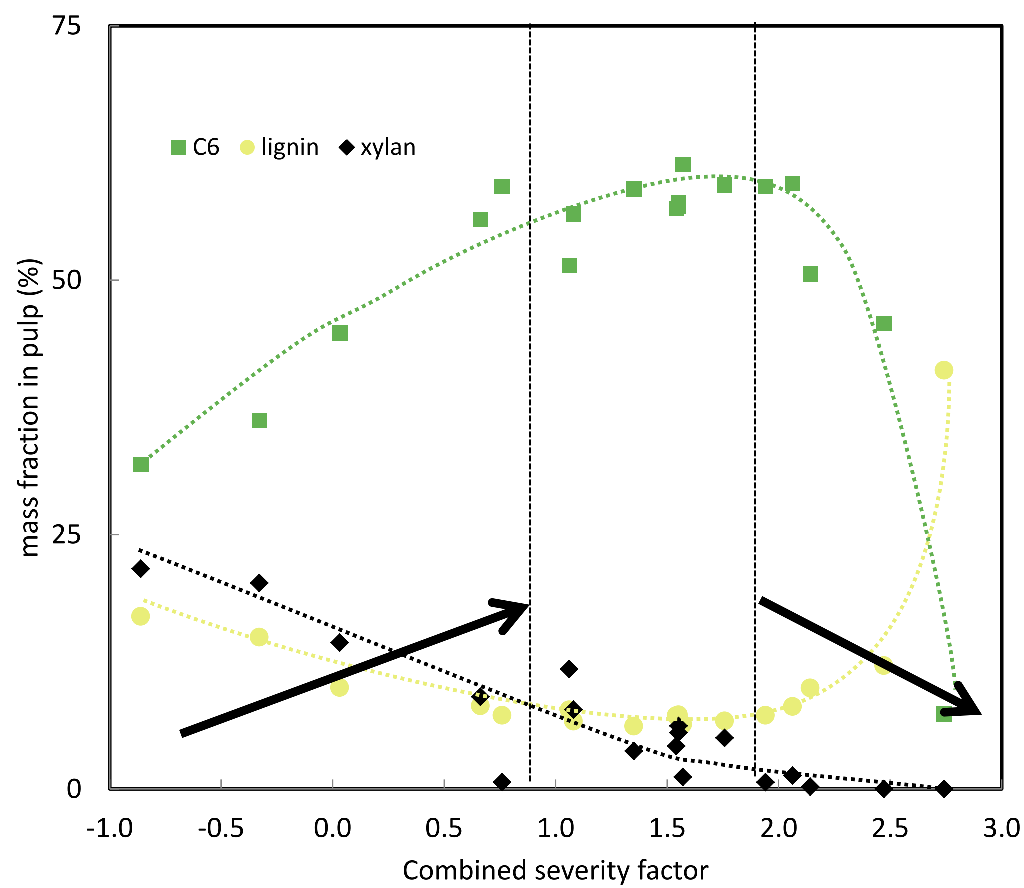
140 °C | 160 °C | 180 °C | 200 °C | T

Finding the optimum severity …

Pulp and Glucan Yield, Delignification



Pulp Composition

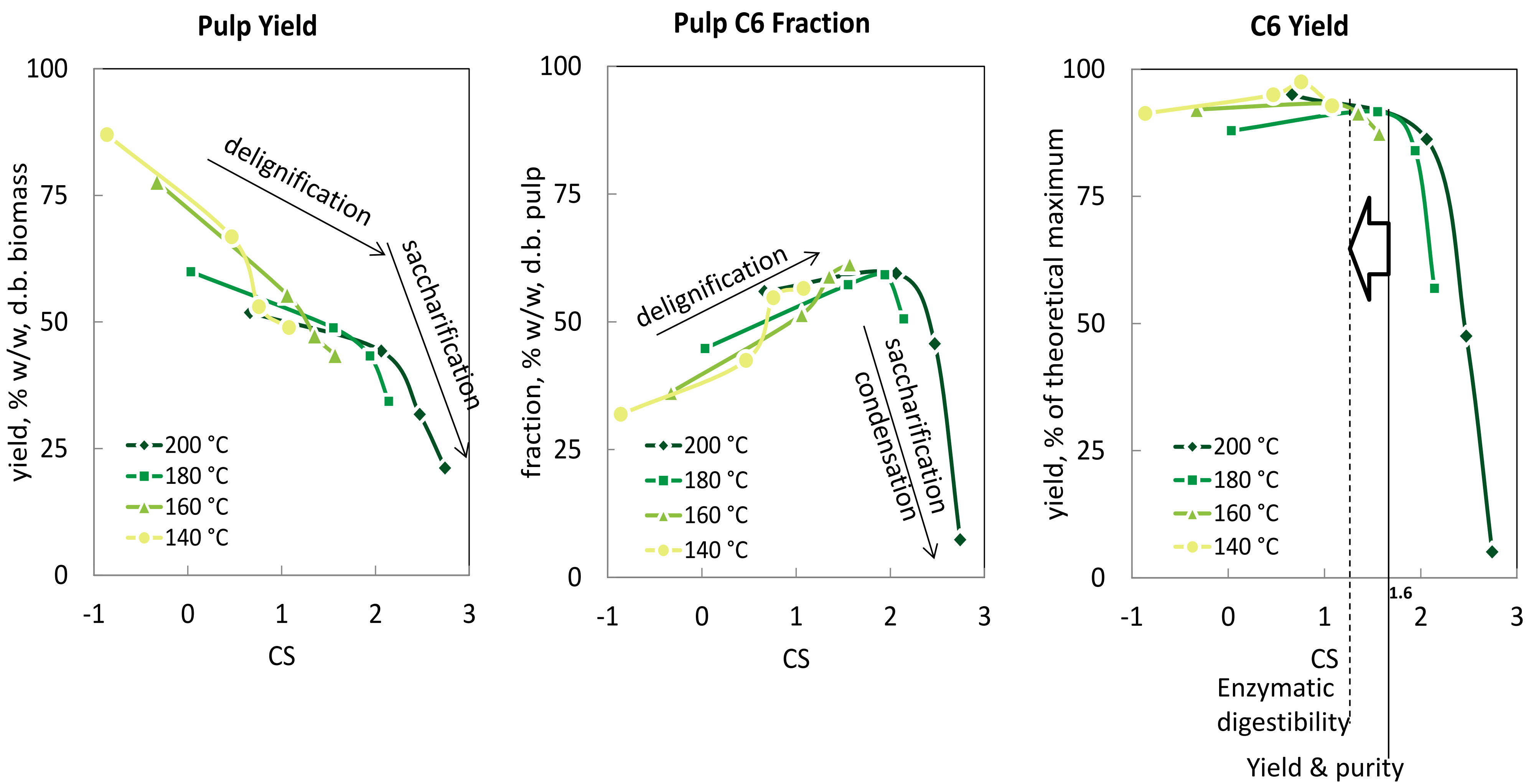


Minimising side reaction products

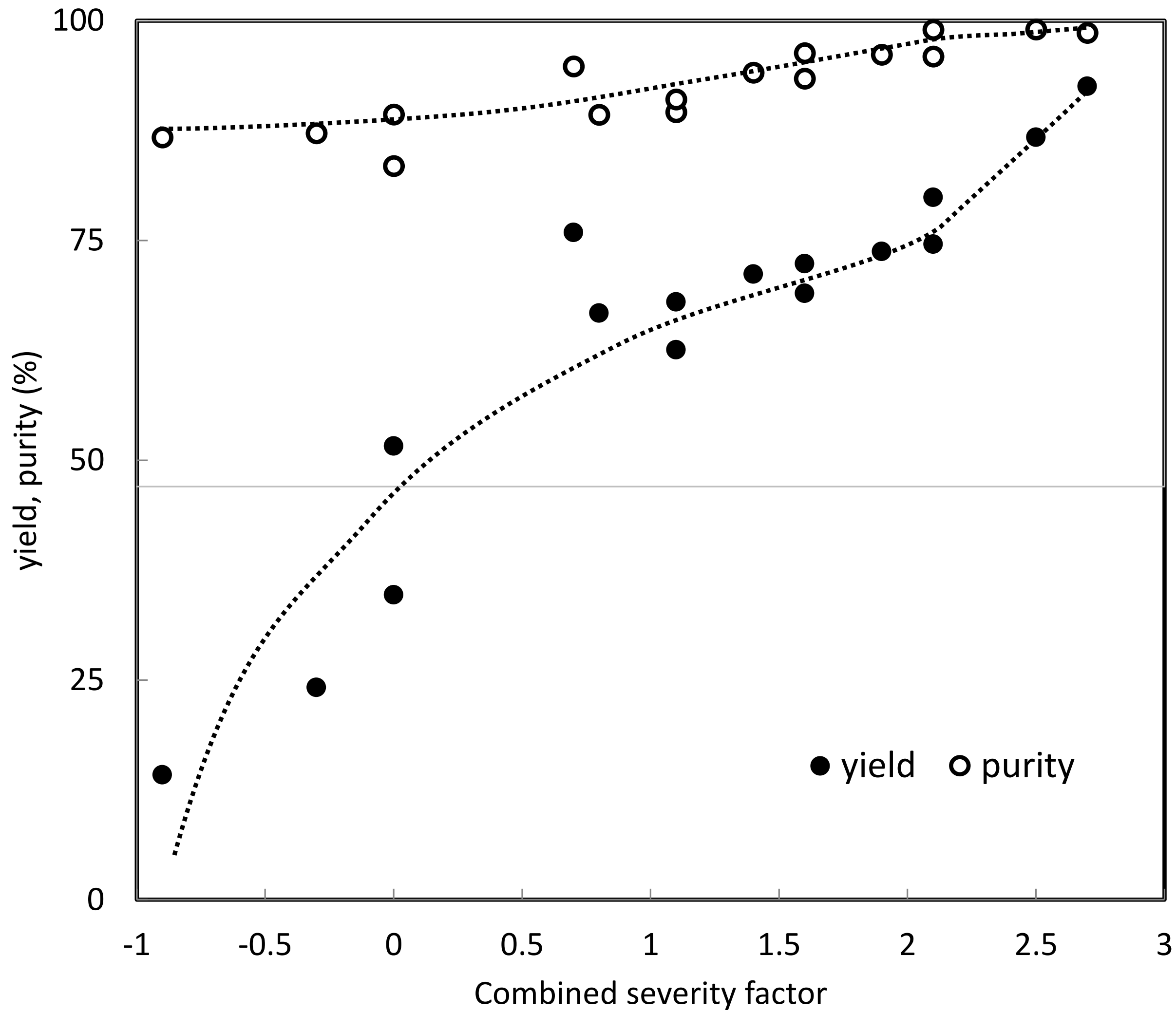
increasing severity

- ethanol → diethyl ether
- glucan → humins; pseudo-lignin; ethyl levulinate; ethyl glucosides
- xylan → furfural; ethyl xylosides; species from condensation with furfural, sugars, lignin

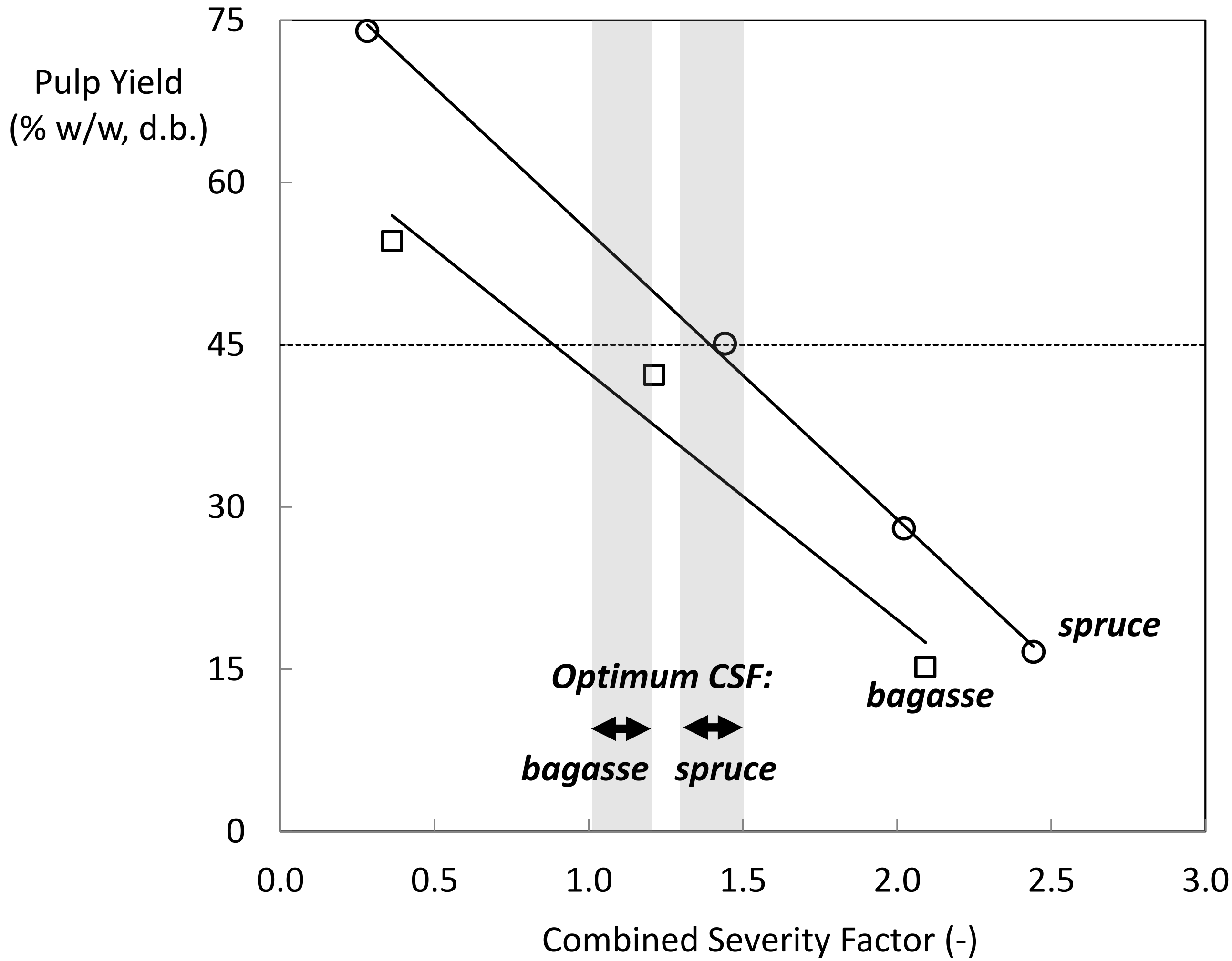
Wheat straw optimum at CS 1.4 – 1.6



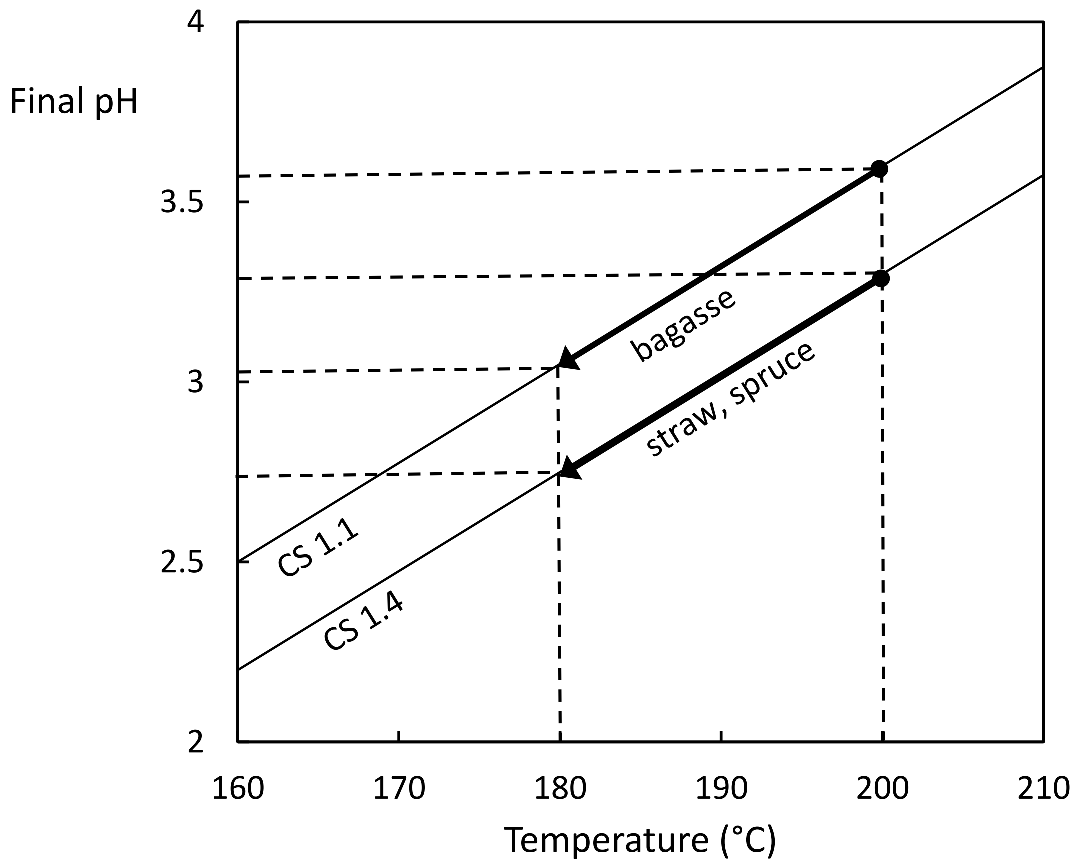
High lignin purity and yield at CS 1.4



Wheat straw, spruce and bagasse require similar severity (CS 1.1 – 1.4)



Towards lower temperature and pH



Final pH		
	200 °C	180 ° C
Straw	3.4	2.8
Spruce	3.3	2.7
Bagasse	3.6	3.0

Excess H^+ (mmol/L)	**0.25 – 0.5**	**1 – 2**

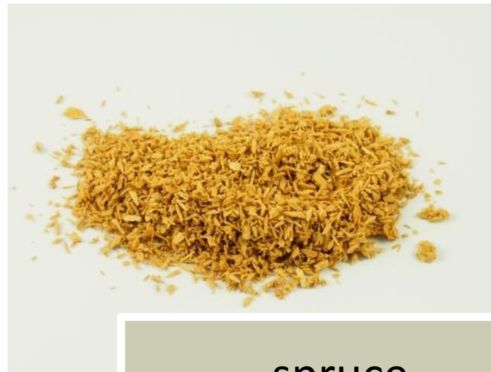
Performance by feedstock

	Wheat Straw	Spruce	Bagasse
AIL yield (%)	70	61	72
AIL purity (%)	95	97	94
Glucose yield (%)	95	80	86
Glucose yield (g/g_{feed})	0.28	0.33	0.34

3 Products

Feedstock flexible - cellulose

beech



spruce

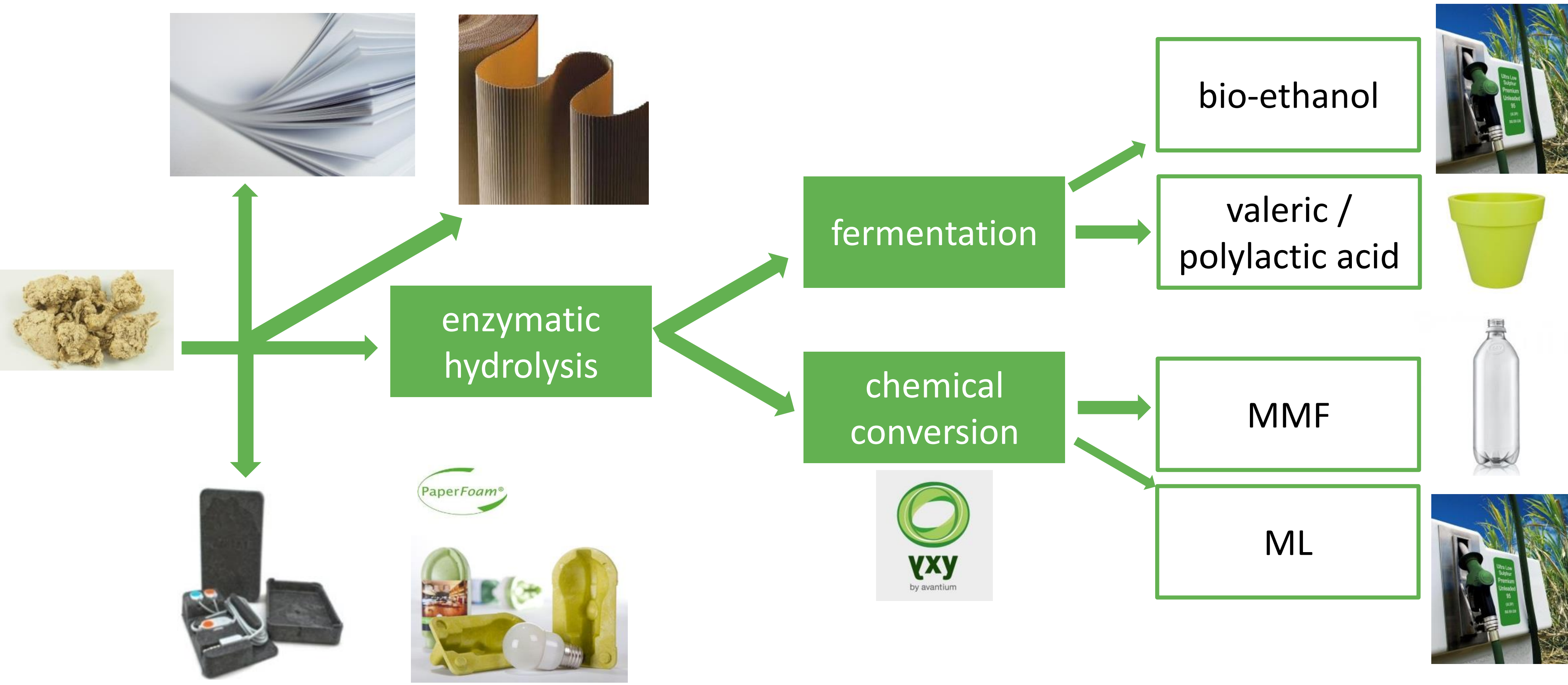
straw

poplar

pine

corn stover

Cellulose products



Feedstock flexible - lignin


beech


spruce


straw


poplar


pine


corn stover

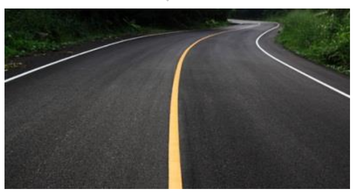
Tunable lignin

OS lignins from pine

Lignin products

biofuel
(HFO)

binder
(bitumen)



phenolic resin
(phenol-formaldehyde resin)

reinforcing filler (carbon black)

natural polyol
(polyol)

LOWER COST ⟷ **HIGHER QUALITY**

4 Techno-Economic Evaluation

Biorefinery Feeds and Products (kt/a)

straw 625

ethanol 30
methanol 22
acid 12
enzymes 17

water 3,191
air 4,844

steam & electricity

lignin 87
MMF 75
furfuryl alcohol 54
ML 11

humins 55
organic solids 158

waste water 3,374
air vented 4,913

Energy use for fractionation 20%

	Fractionation MJ/kg straw	**Downstream Processing** MJ/kg straw	**Total** MJ/kg straw
Heating	1.84	6.21	8.05
Power	0.63	0.01	0.64
Power, primary*	1.40	0.02	1.42
Total primary energy	3.24	6.23	9.47
Cooling	-1.26	-6.04	-7.30

* Efficiency 45% assumed

Primary energy use for fractionation 3.2 MJ/kg or 20% of straw input (LHV)

Basis for the economic analysis

Capacity 150 kt/a wheat straw

2010 Prices	€/t
Wheat straw	70
Cellulose	350
Furfural	625
Lignin	750

Van der Linden et al. (2012) Ethanol-based Organosolv Biorefineries… , Nordic Wood Biorefinery Conference, Helsinki (FIN).

Economy is sensitive to feed and product prices

Revenues	M€/a
Cellulose	24.0
Lignin	20.0
Furfural	3.7
Total	**47.7**

OpEx	M€/a
Raw materials	11.0
Utilities	7.7
Maintenance	6.2
Other	11.0
Total	**35.9**

CapEx per Section	M€
Mechanical pr.	6.9
Organosolv	26.1
Cellulose	12.4
Lignin	17.4
Furfural	3.4
Other	15.8
Total	**82.0**

Cash flow	M€/a
Total	**11.8**

Payback time 7 years

Towards a novel fractionation ...

Minimise ethanol losses *

- Maximise ethanol recovery
- Minimise auto-condensation of ethanol.
- Minimise reaction of ethanol with lignin.
- Minimise reaction of ethanol with hemicellulose sugars.

Improve hemicellulose sugars yield

- Either substantial losses by furfural-lignin condensation due to high temperature.
- Or formation of ethyl-xylosides. What to do with ethyl-xylosides?

Fractionation at *lower temperature* (mild)
using *non-reacting* solvent that can be *recovered more efficiently*

* Huijgen, Smit, Grisel, Van Hal. *Recent Advances in Organosolv Fractionation of Lignocellulosic Biomass.* EUBCE, Vienna, Austria, 2nd June 2015.

5 Fractionation using ketones

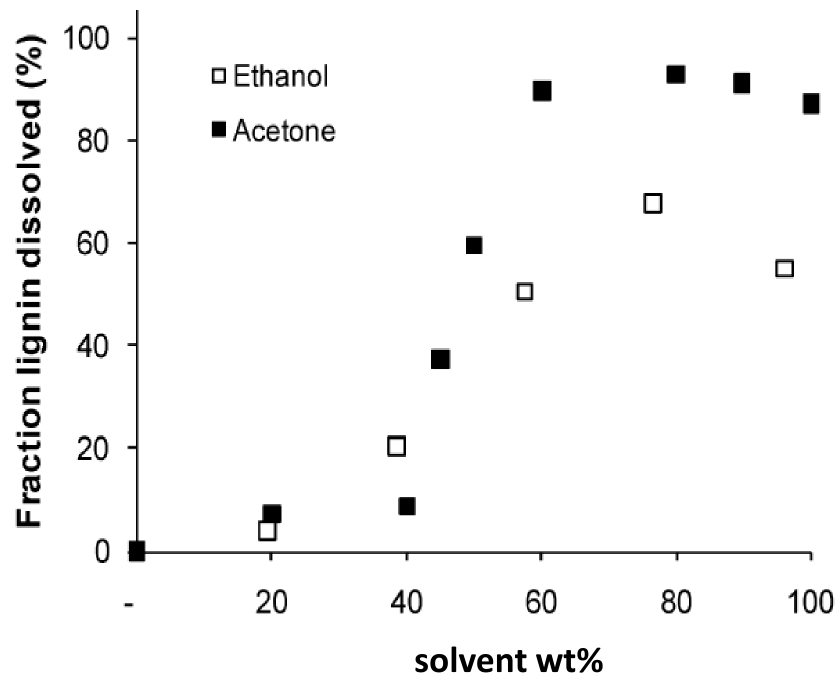
Ketones are excellent lignin solvents

'Ketosolv' fractionation

- Ethanol replaced by acetone or butanone
- Temperature decreased from 190 °C to 140 °C
- H_2SO_4 dose increased (from 20 to 60 mM for wheat straw)

Reduced solvent make-up

- Self-condensation of acetone is limited at operating conditions
- No side reactions of acetone with sugars



Huijgen, W. J. J.; Reith, J. H. & Den Uil, H. (2010) *Ind Eng Chem Res* 49(20) 10132

Effective pulping at milder conditions

Cellulose pulp

- High purity and enzymatic digestibility

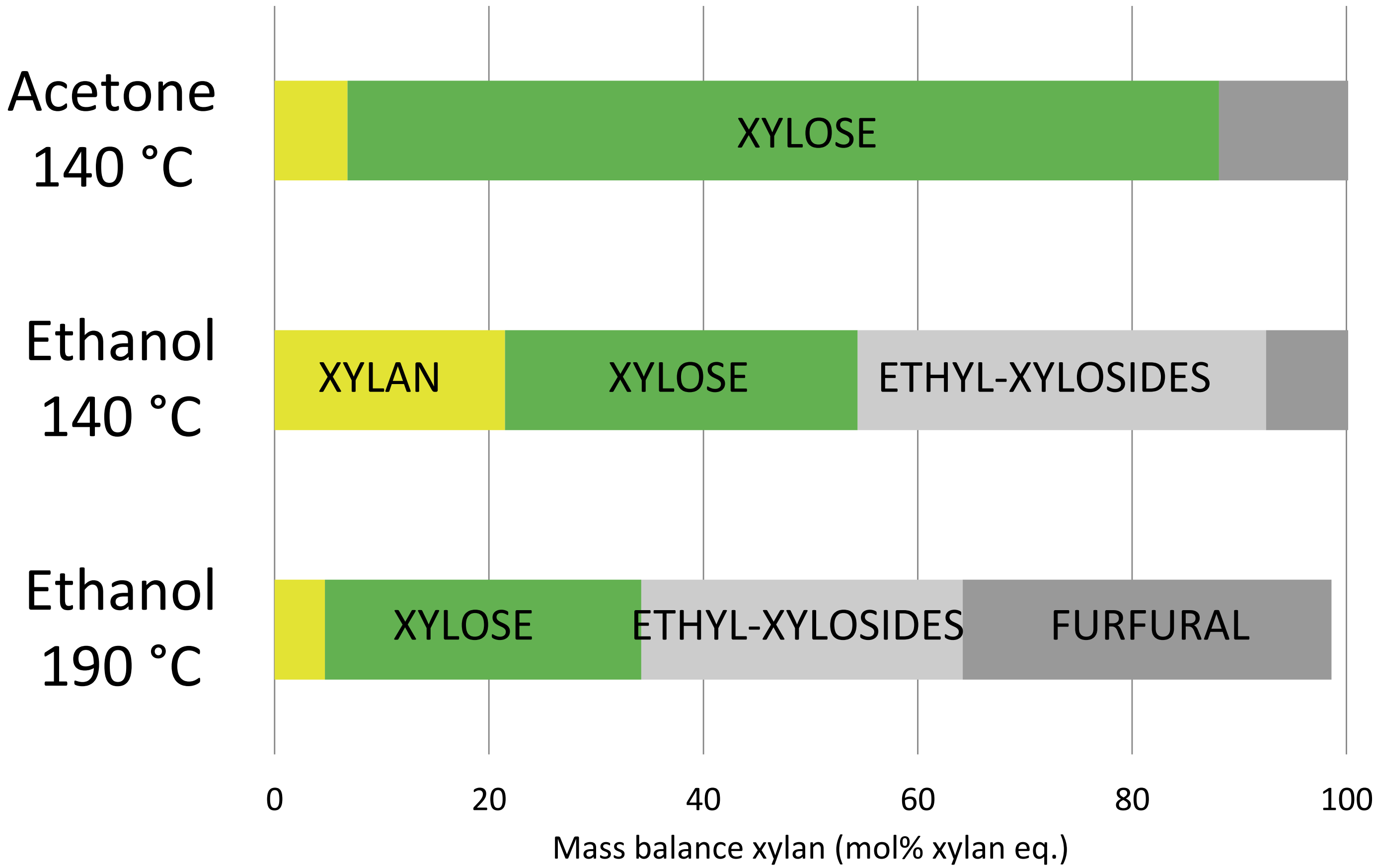
Lignin

- Good yield
- More native / less condensed

Xylose

- Higher xylose yields
- Lower formation of furfural

Highest xylose yield for ketosolv



Adapted from: Van der Linden, Huijgen, Smit, Van Hal. *RRB-11 Conference*, York, UK, 3 June 2015.

Energy use for ketosolv 12%

	Ethanol MJ/kg straw	Acetone [1] MJ/kg straw
Heating	1.84	0.72
Power	0.63	0.55
Power, primary [2]	1.40	1.22
Total primary energy	3.24 →	1.92
Cooling	-1.26	-0.35

Primary energy use for ketosolve 12% of straw input (LHV)

Cf. primary energy use for petroleum refining 6 – 10% [3]

1 Van der Linden, Huijgen, Smit, Van Hal. *RRB-11 Conference*, York, UK, 3 June 2015

2 Efficiency 45% assumed

3 Han et al. (2015) *Fuel* 157, 292

More reactive lignin for acetone OS




Lignin type	Feedstock	Number of β-O-4 ether linkages per 100 aromatic units (S+G)
Soda P1000	Herbaceous	3.4
Organosolv – ethanol	Herbaceous	4.3
Alcell	Hardwood	5.3
Indulin Kraft	Softwood	6.1
Organosolv – acetone	Herbaceous	31.1

Universiteit Utrecht

S. Constant et al (2016) *New insights into the structure and composition of technical lignins: a comparative characterisation study*. Green Chem (advance article)

Wrap up

Conclusions

Organosolv is feedstock flexible

- Herbaceous: straws, bamboo, …..
- Hardwoods: poplar, birch, beech, willow, ….
- Softwoods: pine, spruce, …
- Residues: manure, bagasse, olive trimmings, …..

Conditions can be optimised for different biomass types and product requirements, requiring a limited number of tests

Organosolv lignin is very pure

Revenues for high-value lignin are key for a business case

- lower price substitute for fossil based (e.g. resin)
- higher quality substitute for fossil based (e.g. polyurethane foam)

Pros of Acetone vs Ethanol

Operation at lower temperature

Higher value added

- higher xylose yield
- potentially improved retention of the native lignin functionality

Lower operational expenses

- lower solvent losses (avoiding formation of xylosides)
- higher energy efficiency of solvent recovery

Improved business case is expected

Outlook

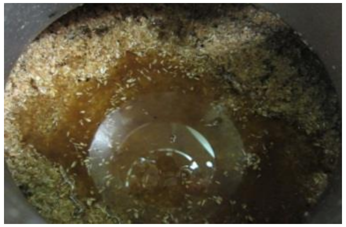
Lignin application tests with industrial customers

Construction of an integrated pilot-scale organosolv reactor

Partnering for further technology development & commercialisation:

- Biomass suppliers
- Equipment suppliers
- Customers for lignin
- Investors

Acknowledgement



ECN

Westerduinweg 3	P.O. Box 1
1755 LE Petten	1755 ZG Petten
The Netherlands	The Netherlands
T +31 224 56 49 49	vanselow@ecn.nl
	www.ecn.nl

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ECN
Westerduinweg 3
1755 LE Petten
The Netherlands

P.O. Box 1
1755 LG Petten
The Netherlands

T +31 88 515 4949
F +31 88 515 8338
info@ ecn.nl
www.ecn.nl