Organosolv fractionation: a versatile process to produce high-purity lignins

R.J.H. Grisel
A.T. Smit
W.J.J. Huijgen

August 2014
ECN-L--14-050

Organosolv fractionation: a versatile process to produce high-purity lignins

R.J.H. Grisel, A.T. Smit, W.J.J. Huijgen

Lignin 2014 – biosynthesis and utilization

Umeå, Sweden
August 27, 2014

Energy research Centre of the Netherlands (ECN)

- Mission:
  To develop expertise and technology that enables the transition to sustainable energy management with and for the market.

- Business units:
  - Biomass & energy efficiency
  - Solar energy
  - Wind energy
  - Policy studies
  - Environment & energy engineering

ECN

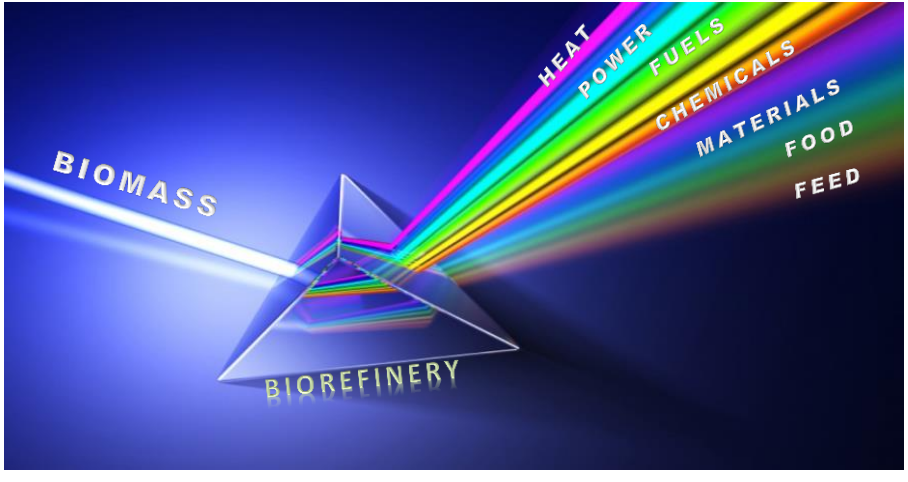
- Independent research institute
- ~600 employees
- Locations:
  - *Petten (HQ)*
  - *Amsterdam*
  - *Eindhoven*
  - *Brussels*
  - *Beijing*

Outline

- Lignocellulose biorefinery
- Organosolv fractionation at ECN
- Lignin characteristics
- Application research
- Conclusions

Biorefinery

”The sustainable processing of biomass into a spectrum of marketable products (food, feed, materials, chemicals) and energy (fuels, power, heat)”
(*definition IEA Bioenergy task 42*)



Artist impression

Various types of biorefineries depending on type of biomass

Lignocellulosic Biomass

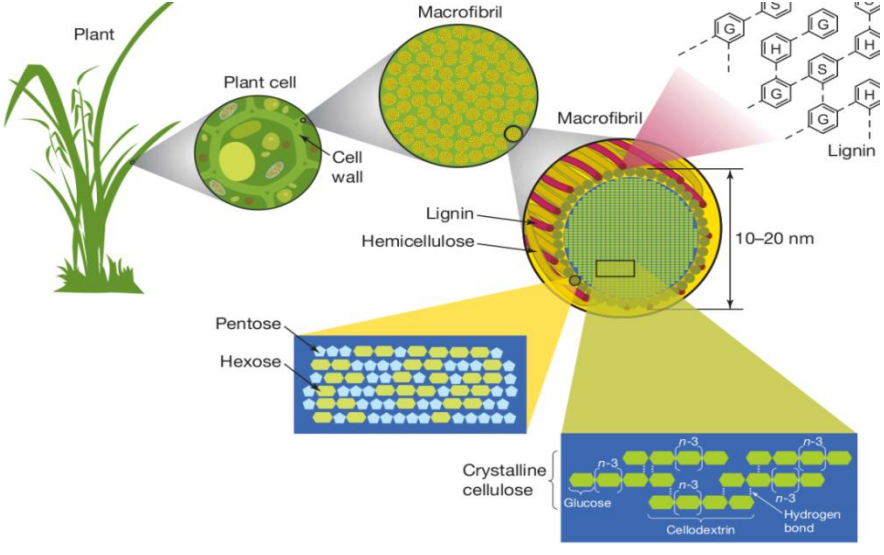
- Lignocellulosic biomass
  - Hardwood: poplar, willow, ...
  - Softwood: spruce, pine, ...
  - Herbaceous: miscanthus, wheat straw, …

- Available in form of
  - (Forestry / agricultural) residues
  - Energy crops

- Advantages compared to other types of biomass
  - Wide range of low cost feedstocks
  - No direct competition with food production
  - No inherent iLUC (especially in case of residues)
  - High CO_2 reduction of derived fuels and products

Lignocellulose Constituents

- Sugar polymers
  - Cellulose, linear polymer of glucose
  - Hemicellulose, branched copolymer of C5 and C6 sugars
- Lignin
  - Polymer of aromatic compounds
- Non-structural components
  - extractives, protein, ash, pectin
- Factors influencing composition
  - Plant species
  - Part of plant (bark, stem, …)
  - Location of cultivation, ….



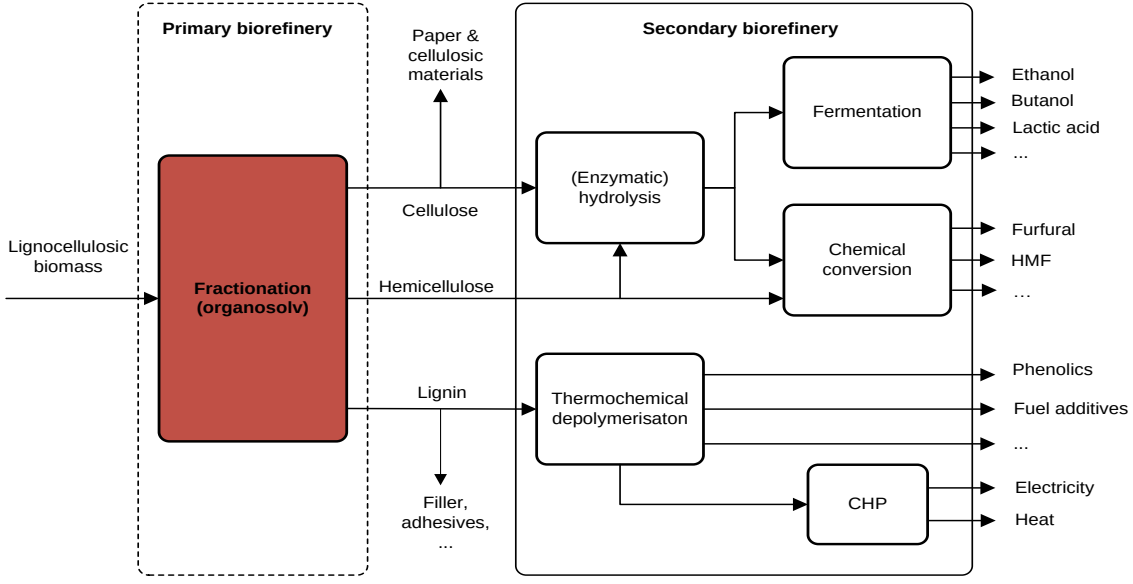
Source: University of North Dakota.

Organosolv Fractionation

Primary biorefinery

Lignocellulose Biorefinery

- Why organosolv?
  - Fractionation of all major constituents in a sufficient quality for valorisation.
  - Including extraction of high-quality lignin for production of chemicals.



Experimental Set-up Organosolv

Lignocellulose

Milling

Solvent / H_2O

Optional: catalyst

Volume: 0.5 / 2 / 20 ltr
Stirring
Temperature ↑

Filtration

Washing

Solid residue (*pulp*)

Filtrate (*liquor*)

Further purification

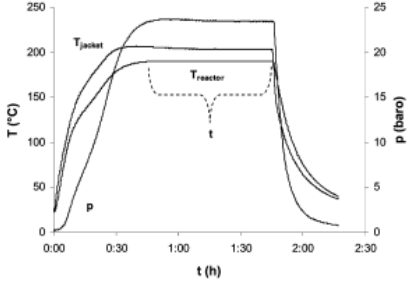
Analysis composition

Enzymatic hydrolysis

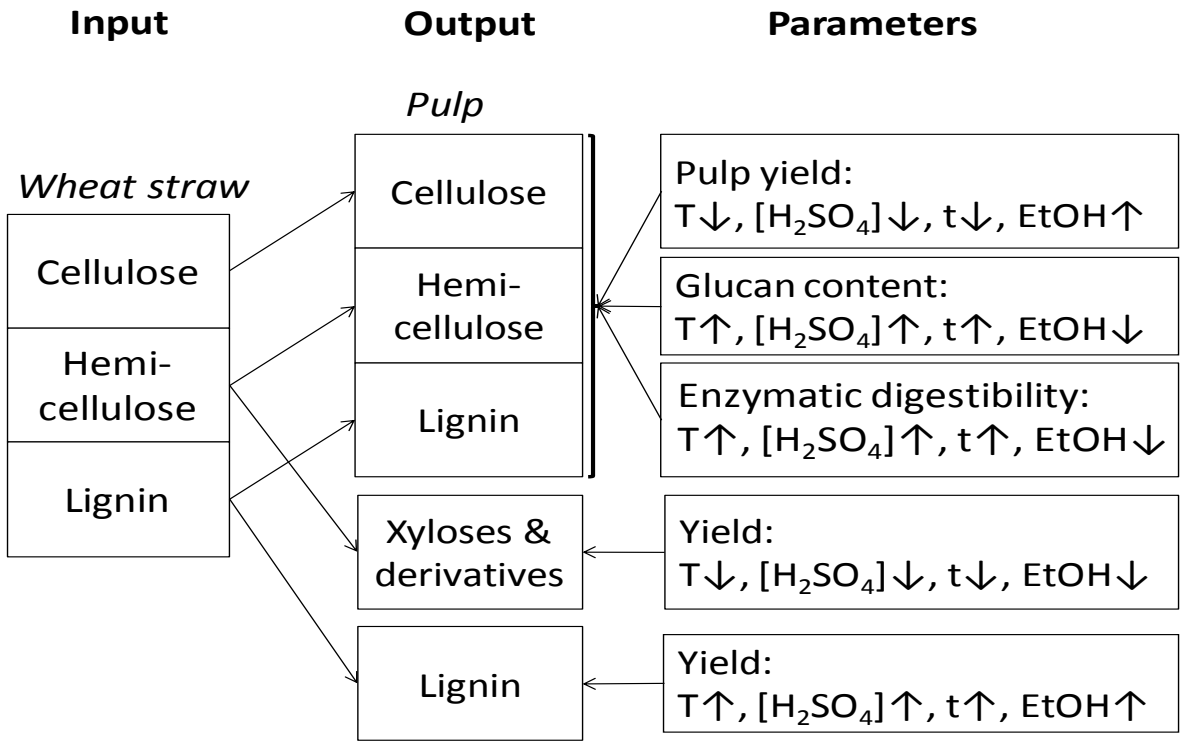
Analysis sugars (monomeric + oligomeric)

Analysis other compounds

Lignin separation & analysis



Process-Product Scheme

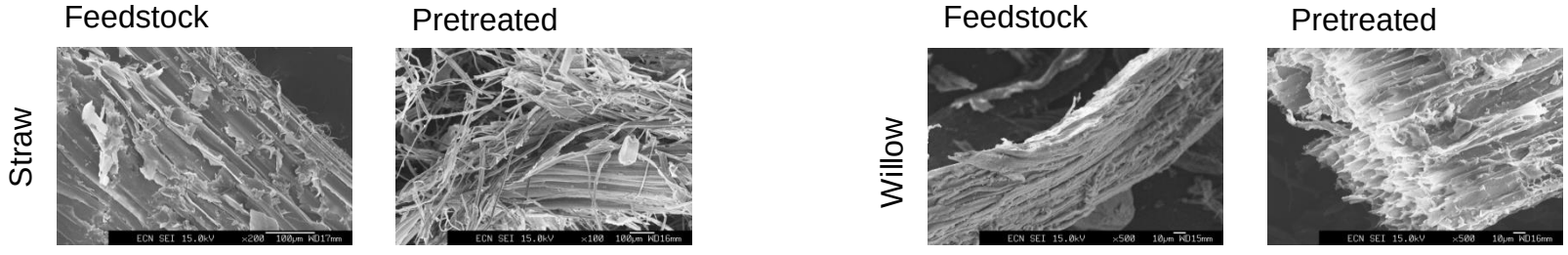


Wildschut et al. (2013) Ethanol-based organosolv fractionation of wheat straw…, Bioresource Technology 135, 58-66.

Lignocellulosic Feedstocks

- ECN primary focus on agricultural residues, like wheat straw.

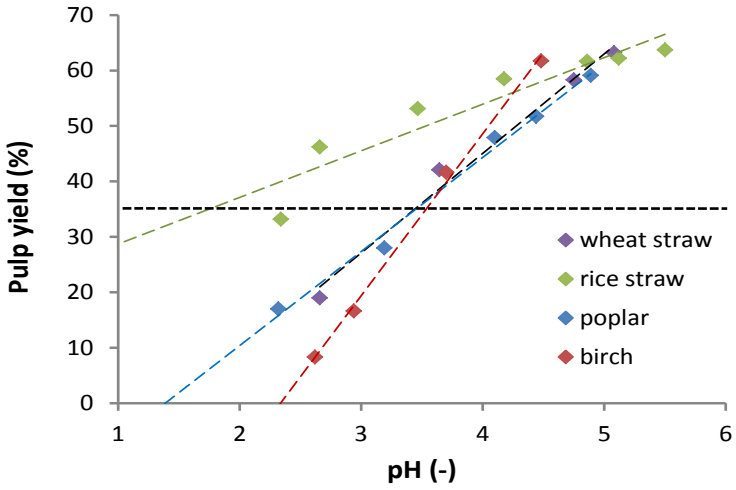
- Organosolv fractionation effective for wide range of lignocellulosic biomass
  - Large variety of feedstocks tested: straw (wheat, barley, rice, rapeseed), bagasse, corn stalks, bamboo, willow, poplar, beech, olive wood, birch, eucalyptus, spruce, pine,...
  - Response to process parameters similar, but optimum fractionation conditions feedstock dependent.



Example Comparison Feedstocks

- Ease of fractionation / pulping:
  - Birch >> wheat straw ~ poplar > rice straw
- Differences between feedstocks:
  - Acid neutralisation capacity
  - But also, structural differences
- Linear correlation pulp yield -"pH"
- Target pulp yield 40-50%
  - Cellulose recovery 90-95%
  - Delignification 80-90%
  - Hemicellulose hydrolysis 80-85%

(mol H^+/ kg dw)	pH 4
Rice straw	0.40
Poplar	0.08
Wheat straw	0.31
Birch	0.04



Huijgen et al. (2012) Progress in organosolv fractionation…, 8th Int. Conf. on Renewable Resources & Biorefineries, Toulouse, France.

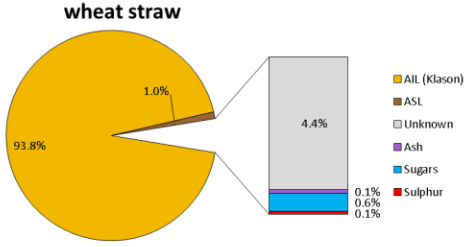
Lignin characteristics

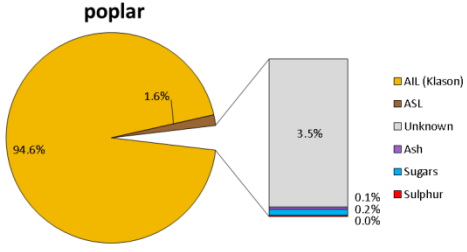
Lignin Isolation & Characterisation

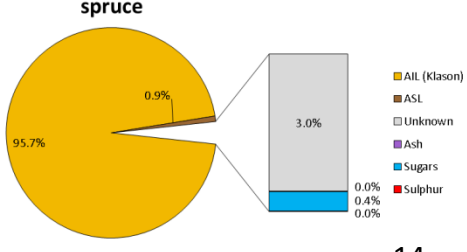
- Lignin isolation:
  - Insoluble in H_2O, soluble in ethanol & acetone.
  - Precipitation lignin from organosolv liquor.
  - Lignin isolation efficiency >90% (yield 75-85%).

- Typical lignin characteristics:
  - Light brown to black (compacted) powder
  - Klason lignin 95%, ASL 1-2% w/w, d.b.
  - Sugar residue < 1%, minerals <0.1%, sulphur < 0.2% w/w d.b.
    - Sulphur lean and virtually ash free
    - Main contaminant hemicellulose derived sugars
  - Molecular weight (relative to other types of lignins):
    - Low average (2000-3500 g/mol)
    - Narrow size distribution
  - Glass transition (110-120°C) and melting (120-160°C)

Organosolv lignin promising properties for valorisation.



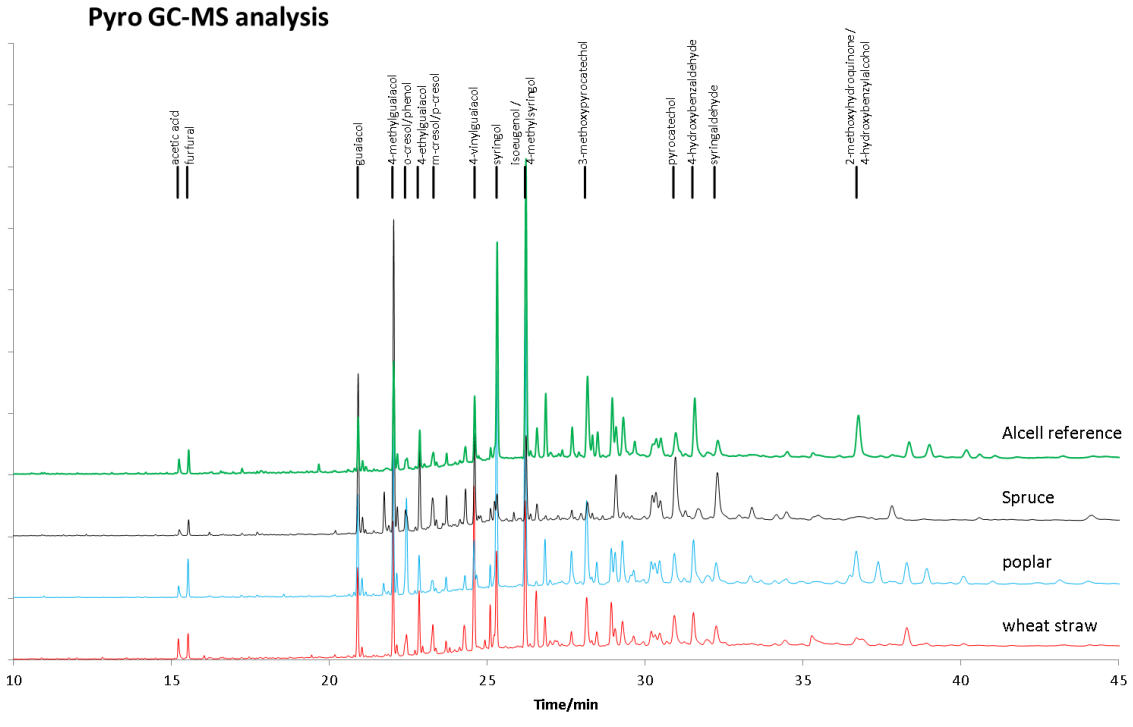




Constant et al. (2014) A structural comparison of organosolv lignins extracted from wheat straw, poplar and spruce, poster 18

Still some differences

Fingerprinting at 500C flash pyrolysis



All lignins yield mainly (alkoxy)phenols, no acids nor sugar-derivatives

Softwood

Mainly guaiacols, no syringols

Hardwood

Mainly syringols, some guaiacols

Herbaceous

Both guaiacols (relatively lot 4-vinylguaciacol) and syringols

Application tests

- Biocore FP7 framework programme
  - Replacement of phenol by lignin in phenol-formaldehyde resins (Chimar Hellas S.A.)
  - Lignin in polyurethanes (Synpo)

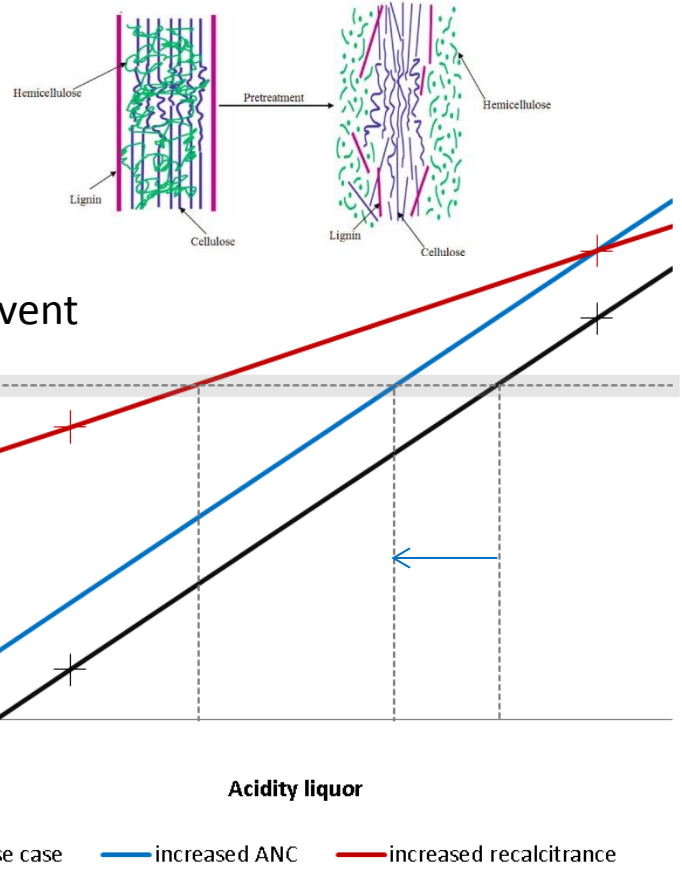
- CatchBio research programme
  - Lignin depolymerisation for further (catalytic) upgrading
    - Bio-BTX / phenols
    - Aromatic chemicals, (performance) materials
    - Fuel additives / octane boosters

- Various
  - Lignin and pyrolysis oil in bitumen / asphalt (Latexfalt BV)
  - Paint applications
  - …

Conclusions

- Organosolv fractionation establishes fractionation of various lignocellulosic feedstocks, amongst which herbaceous, deciduous and coniferous biomass
- Main process parameters influencing organosolv fractionation efficiency are temperature (T), acid dose [H^+] and solvent composition
- [H^+] or “pH” is key in steering towards optimum pulping; herein there is an linear correlation between pH and pulp yield.
- Fractionation efficiency is a function of [H+], ANC and biomass structure
- Irrespective of the biomass and process conditions, the lignins obtained via ethanol organosolv fractionation are sulphur lean, low in residual carbohydrates and virtually free of minerals
- Organosolv lignins have low molecular weight and are relatively monodispers aiding lignin miscibility & solubility and, in combination with low level of impurities, are excellent sources for catalytic valorisation

Conclusions



Thank you for your attention

More information:

grisel@ecn.nl

This work has partly been performed within the EU FP7 project BIOCORE, supported by the European Commission through the Seventh Framework Programme for Research and Technical development under contract no FP7-241566.

In addition, part of the research was funded by the Dutch CatchBio program. The authors gratefully acknowledge the support of the Smart Mix Program of the Netherlands Ministry of Economic Affairs and the Netherlands Ministry of Education, Culture and Science.

ECN
Westerduinweg 3
1755 LE Petten
The Netherlands

P.O. Box 1
1755 ZG Petten
The Netherlands

T +31 224 56 49 49
F +31 224 56 44 80

info@ecn.nl
www.ecn.nl

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