Thermolysis of lignin for value-added products

P.J. de Wild

R.R. van der Laan

R.W.A. Wilberink

Presented at
XV Meeting of the International Humic Substances Society
Tenerife, Canary Islands, Spain
27 June – 2 July 2010

ECN-L--10-071 JULY 2010

ECN

Energy research Centre of the Netherlands

Thermolysis of lignin for value-added products

Paul de Wild, Ron van der Laan, Ruud Wilberink

Outline

- Lignin valorisation, why, into what? how?
- Lignin biorefinery approach
- What is lignin?
- Experiments
- Results; characterisation of feedstock and products lignin, bio-oil, biochar
- Conclusions
- Overview LIBRA
- Acknowledgements

Lignin valorisation, why?

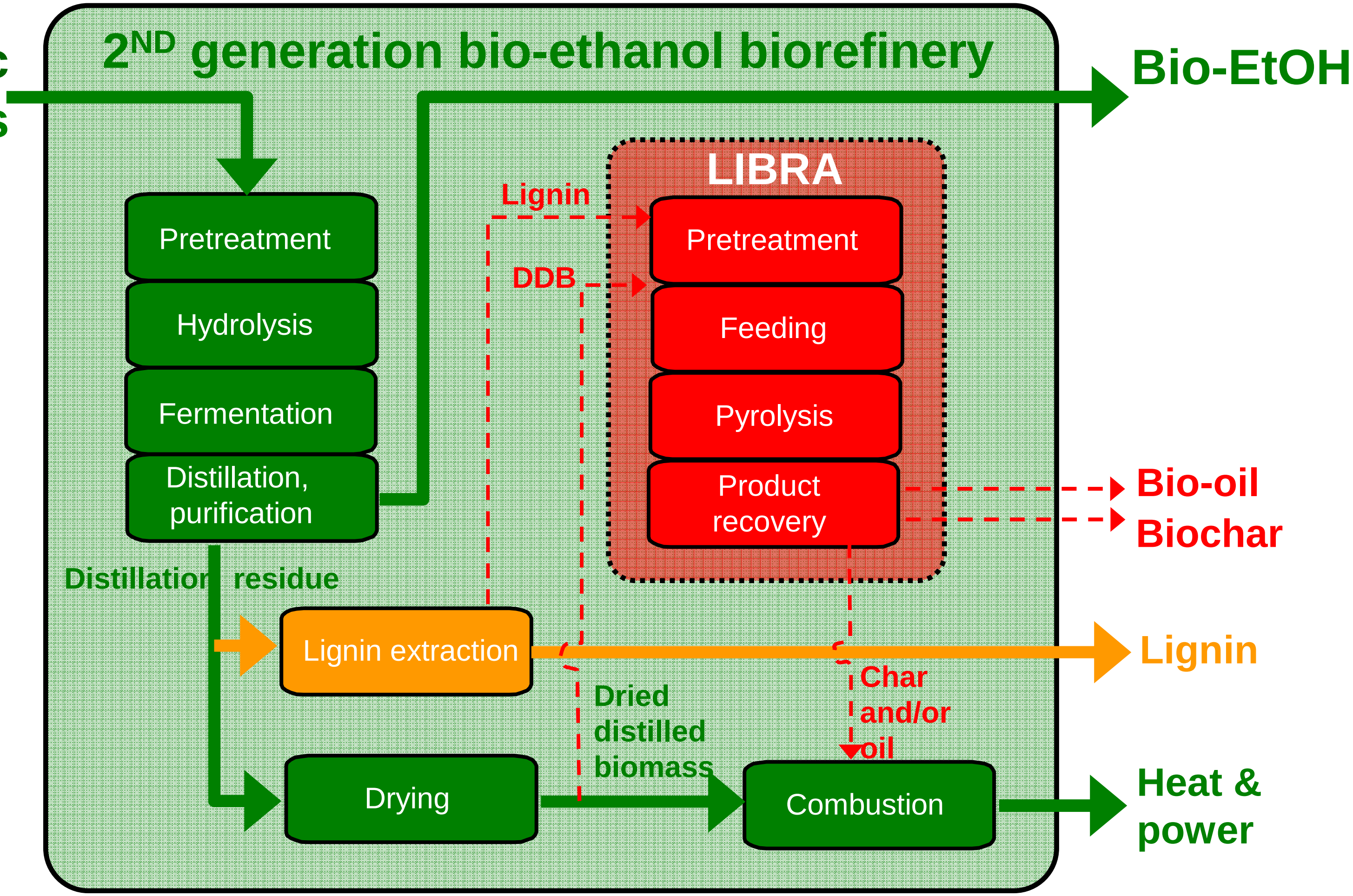
- Lignin is worlds' second most abundant natural polymer containing valuable aromatic (phenolic) structures
- Lignin is the main constituent of large residual streams in e.g. the pulp and paper sector and (future) cellulose EtOH plants, biorefineries,…
- Current lignin potential is enormous: 50 Mt/yr from the pulp and paper industry only. Only 2% (1 Mt/yr lignosulphonates, 0.1 Mt/yr Kraft lignin) is currently used for other applications than combustion (Gosselink et al., 2004)

How? and into what?

- Direct application in resins
- HDO for transportation fuels
- Combustion for CHP (main application to date)
- Gasification for syngas
- **Pyrolysis for chemicals, performance products and fuels**

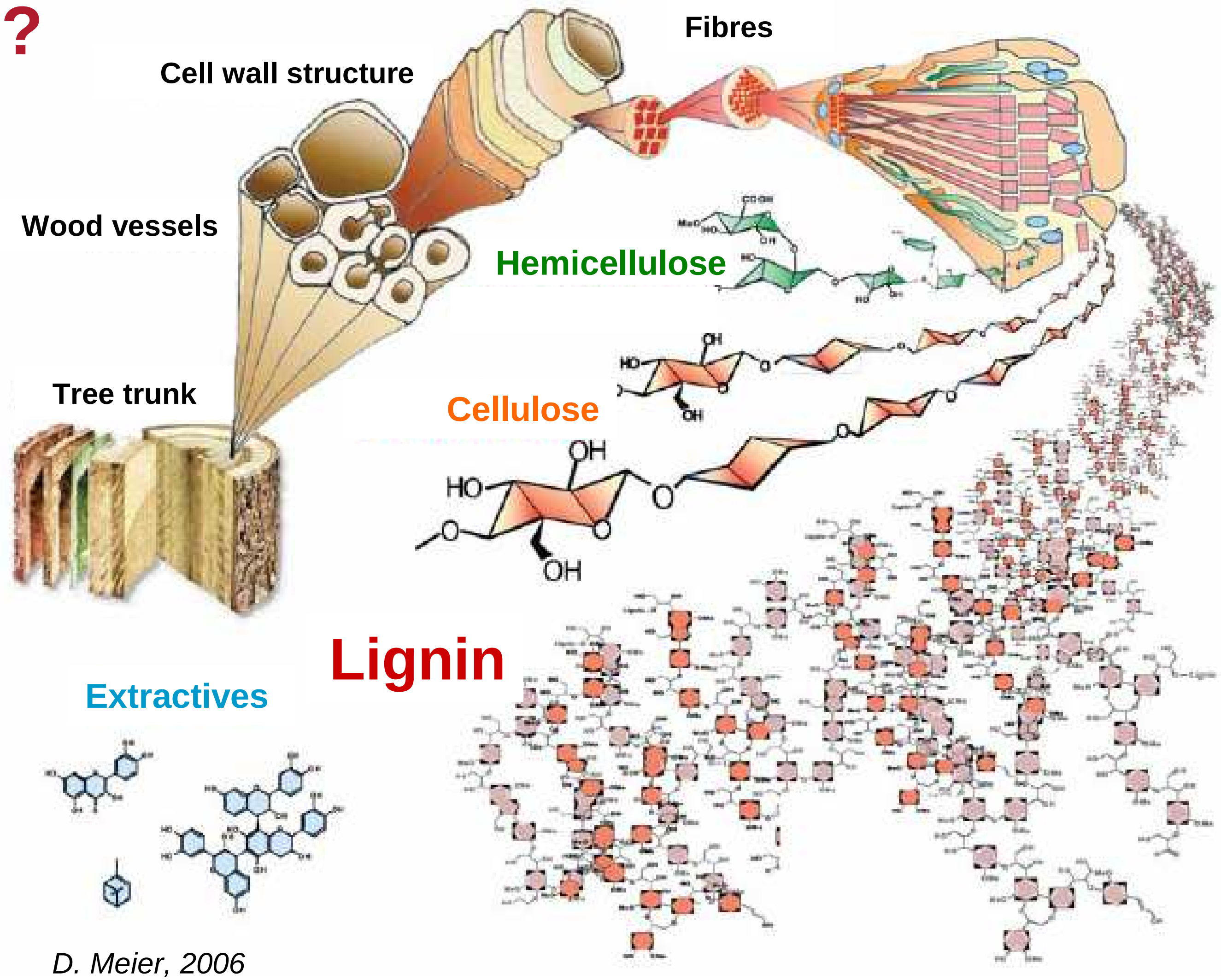
Lignin valorisation is a key-issue for an economic lignocellulosic biorefinery!

Lignin BioRefinery Approach (LIBRA)



What is lignin?

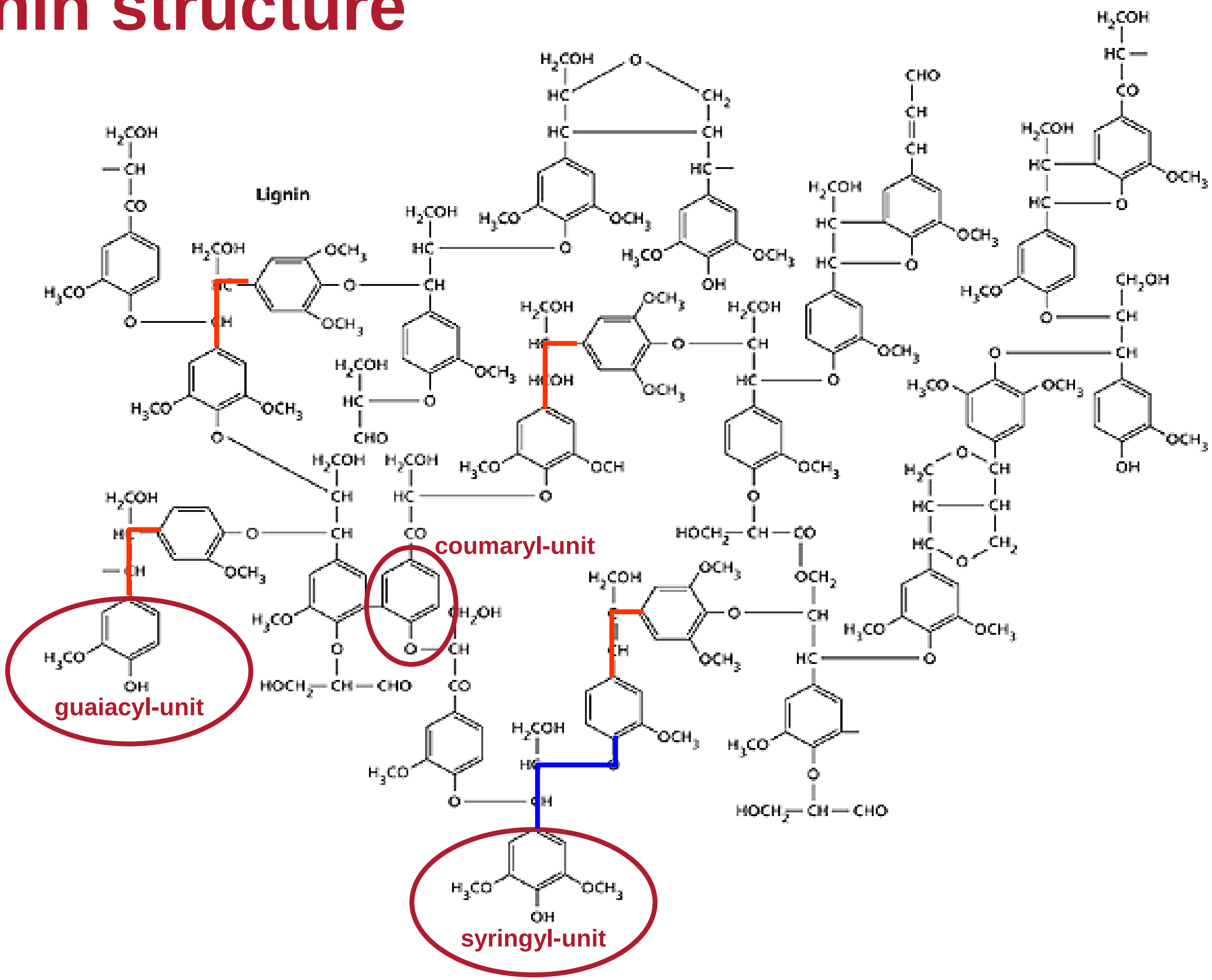
- Biopolymer, consisting of randomly linked phenylpropane units
- 'Glue' that (in combination with hemicellulose) holds the cellulosic wood-structure together
- Very complex structure that depends on plant species and growth conditions
- Highly recalcitrant



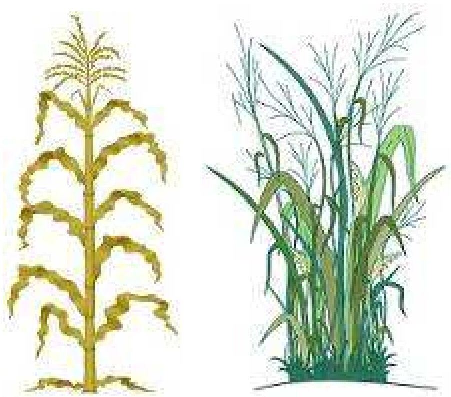
D. Meier, 2006

Simplified lignin structure

- Most bonds are of the **β-O-4** type
- Most internal bonds via the **para** position
- Great variety of other bonds
- Heterogeneous and recalcitrant structure
- Guaiacyl, syringyl and coumaryl units are the predominant structural units
- Structure is an idealised formula of a deciduous lignin



Main components lignocellulosic biomass



Deciduous woods
(e.g. beech, poplar,..)

40-50% cellulose
30-40% hemicellulose

20-25% lignin
(syringyl & guaiacyl units)

Coniferous woods
(e.g. spruce, pine,…)

40-45% cellulose
25-30% hemicellulose

25-30% lignin
(mainly guaiacyl units)

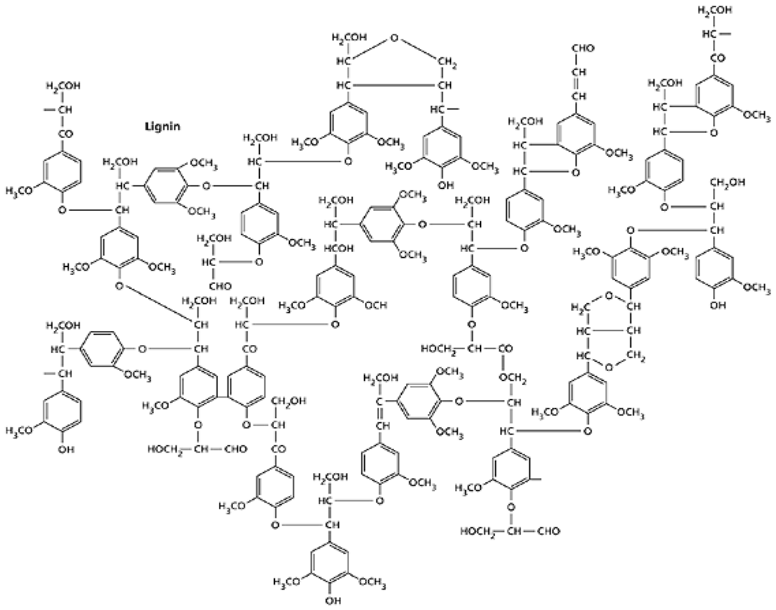
Herbaceous crops
(e.g. wheat, grass, corn,…)

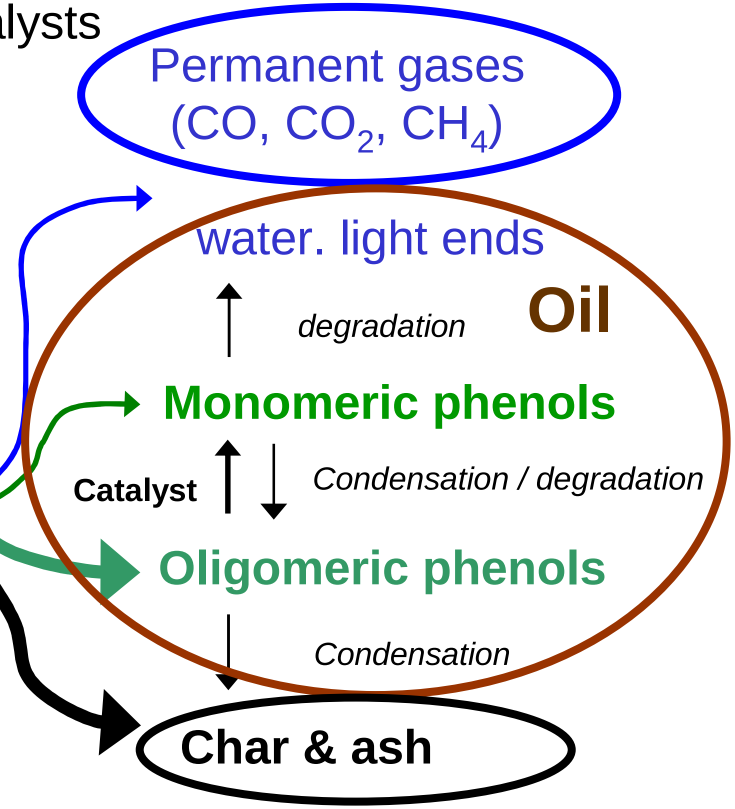
40-45% cellulose
35-45% hemicellulose

15-25% lignin
(p-hydroxyphenyl, guaiacyl & syringyl units)

Lignin thermal degradation mechanism

Goal is to optimise the thermal degradation process by application of appropriate process conditions and catalysts





Experimental

- Technical lignins (straw, grass/straw, hardwoods), biorefinery residue

Winter wheat straw,
(ECN organosolv pulping)

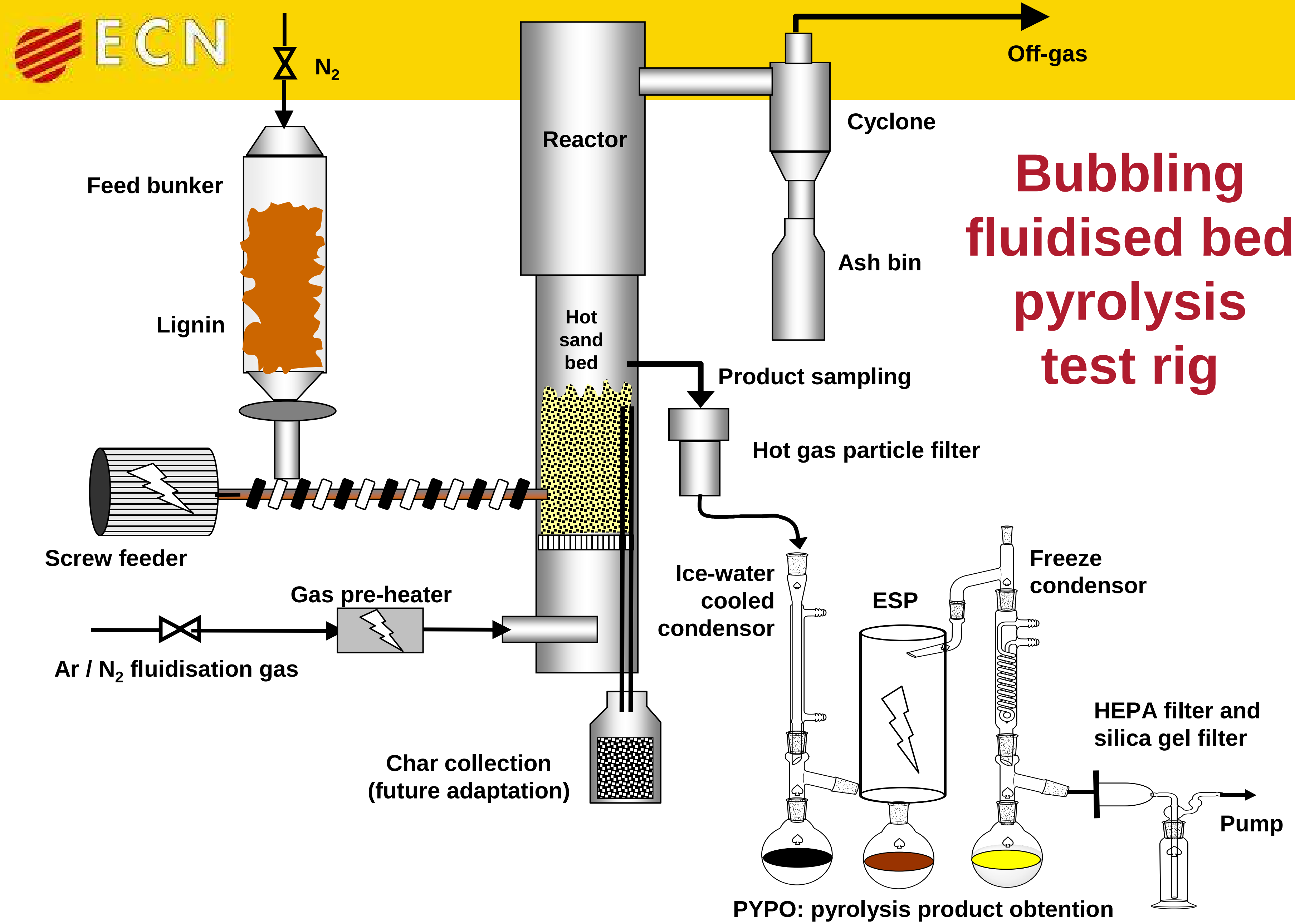
Sarkanda grass and wheat straw,
(soda pulping, Granit Protobind™)

Mix of hardwoods.
(organosolv pulping, Alcell™)

- Characterisation by TG, DSC, fusion tests, ^{13}C–SS-CP/MAS NMR (850 MHz)

- Pyrolysis experiments
  - Bubbling fluidised bed reactor (atm. pressure,1 kg/hr, 5 kW_{th})
  - Fractionated sampling of products
  - On- and off-line analysis of products by GC/MS/FID and gravimetry

Bubbling fluidised bed pyrolysis test rig

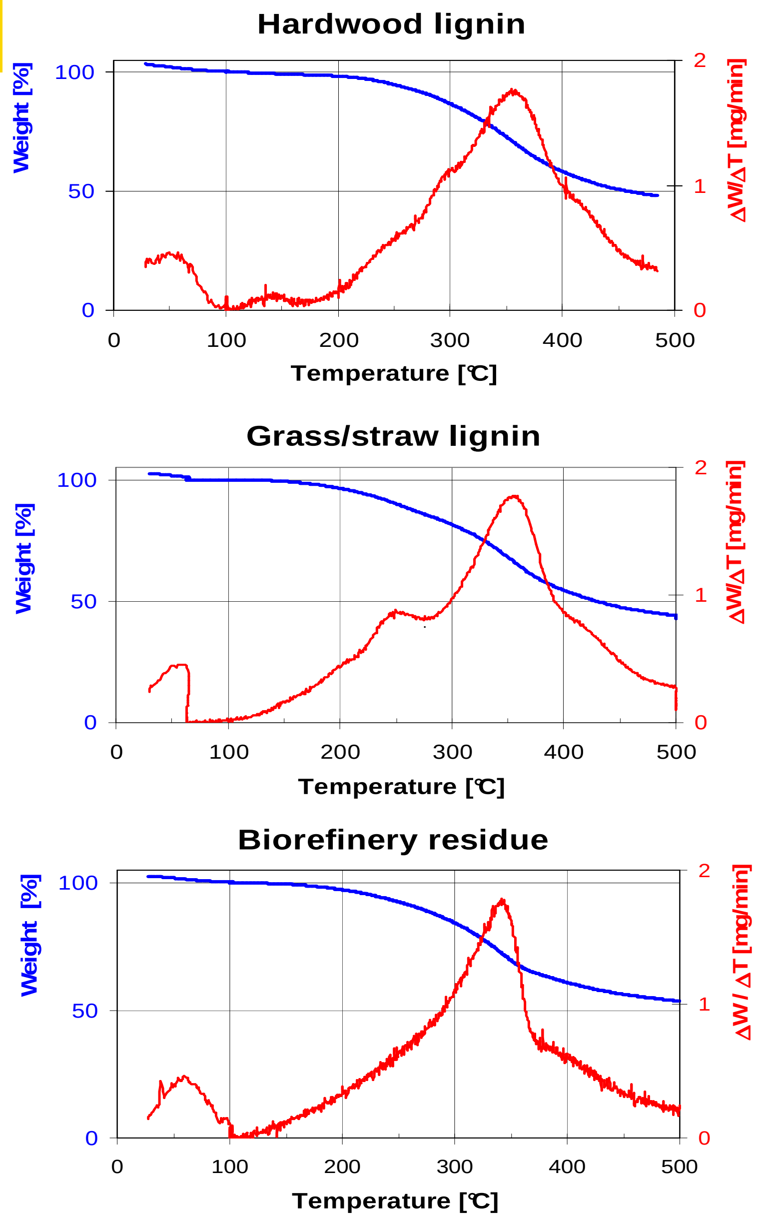


Results

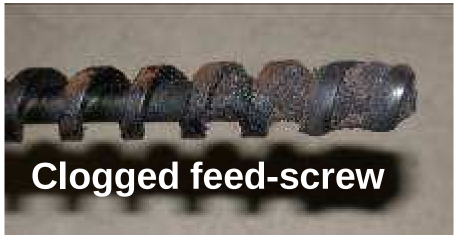
- **TGA / DTG**
  Wt loss starts at 200 ℃.
  At 500 ℃ still ~50 wt% residue (char).
  Peak around 50℃ is moisture .
  Broad range of degradation,max at 350 ℃.
  The narrow temperature range of degradation of the biorefinery residue indicates the presence of residual carbohydrates and ash minerals

  From the TGA/DTG results a temperature of 400℃ was chosen for pyrolysis.

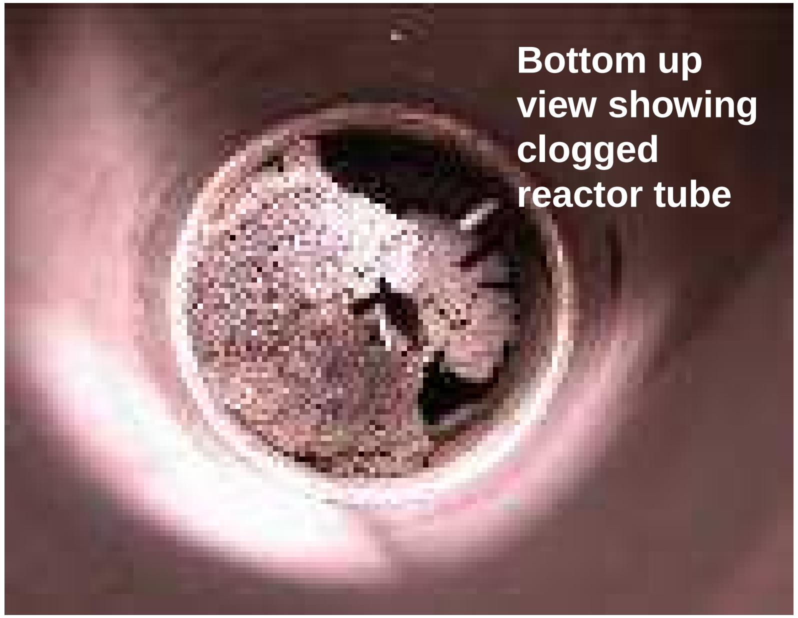
- Melting of the hardwood and grass / straw lignins occurs in between 100 – 200℃ (from DSC and fusion tests). No melting of the biorefinery residue observed.



First results for the pyrolysis of Alcell lignin: bed de-fluidisation due to agglomeration phenomena



Large lignin-sand agglomerates

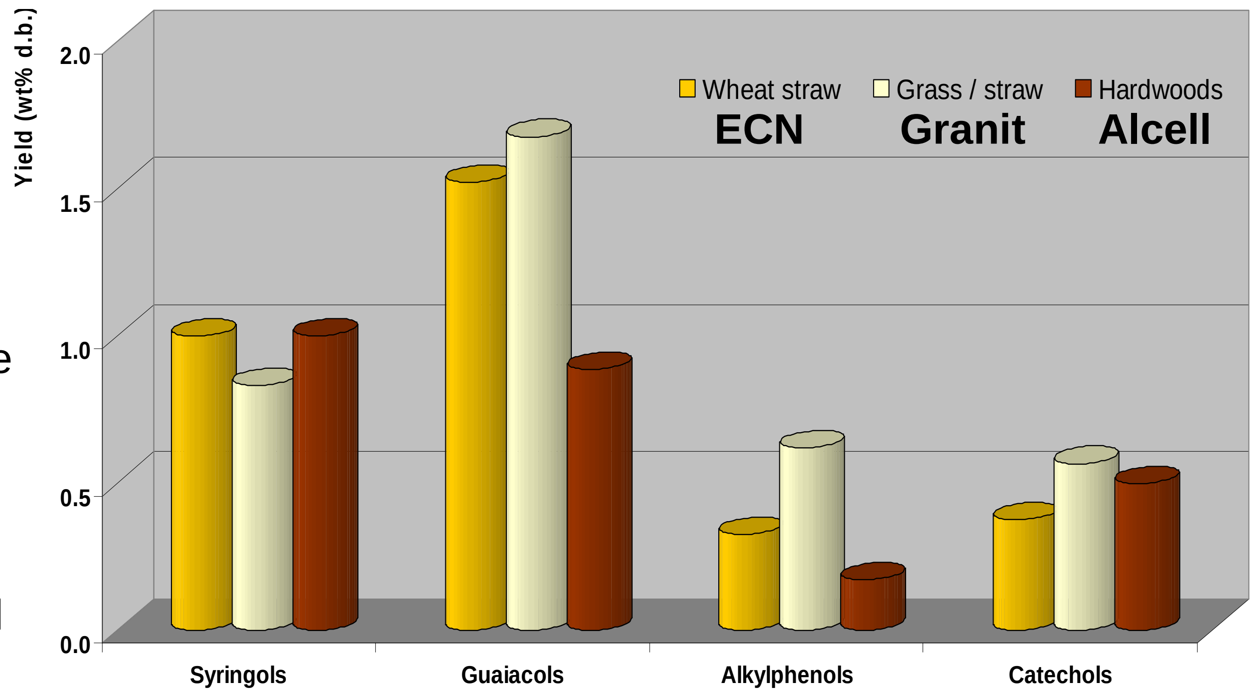


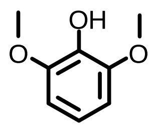
Bio-oil from the pyrolysis of pure lignins at 400 °C

- More guaiacols and alkylphenols for annual plant lignins than for hardwood lignin.
- Syringols and catechols about the same for the three lignins,
- Alkylphenols highest for the grass/straw lignin.
  This is probably due to the presence of grass-derived lignin with a relatively high content of p-hydroxyphenyl units.

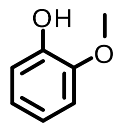
Pyrolysis results reflect compositional differences between the lignins.

Bubbling fluidized bed pyrolysis with technical (pure) lignins at 400°C
Total yield identified monomeric phenols around 3 wt% (d.b.)

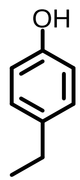




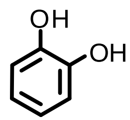
2,6-dimethoxyphenol
(syringol)



2-methoxyphenol
(guaiacol)



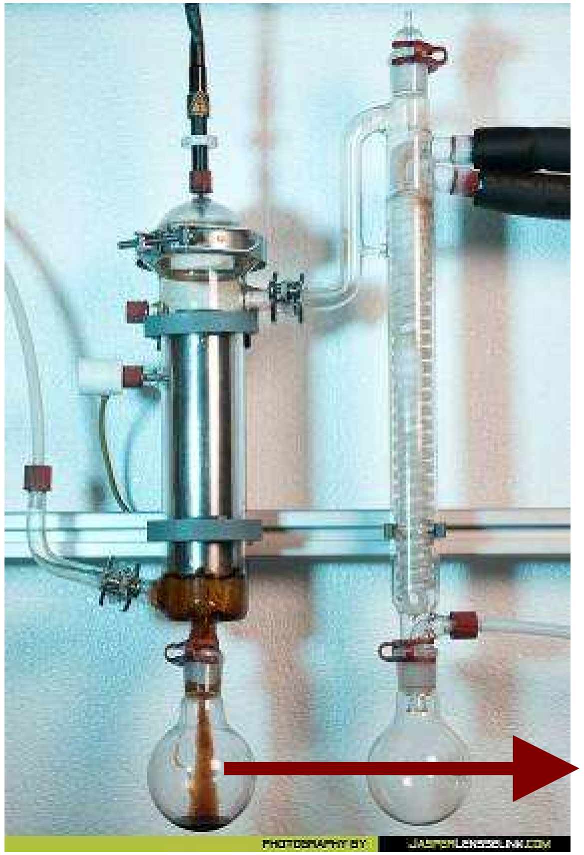
4-ethylphenol



pyrocatechol

Bio-oil from continuous catalytic pyrolysis

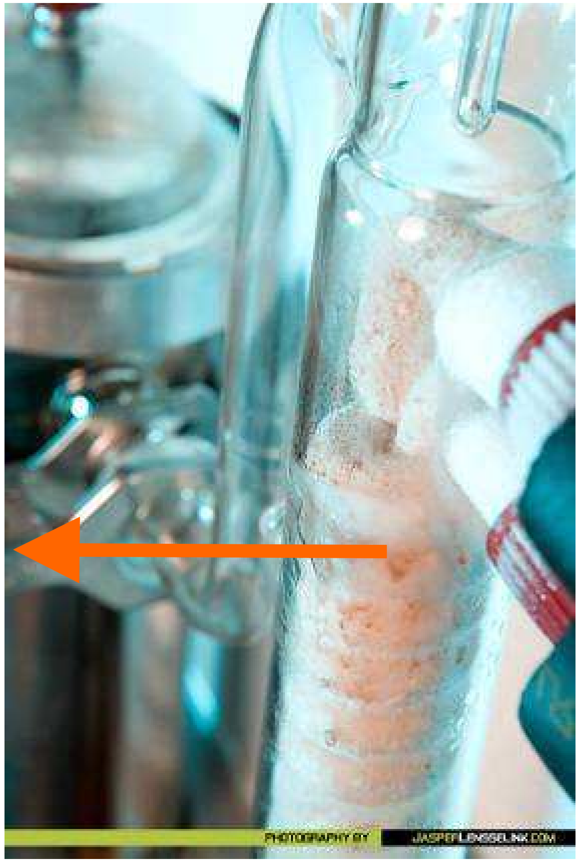
The use of specific catalysts and the development of a feeding protocol involving a cooled screw feeder enabled successful continuous lignin pyrolysis trials



Pyrolytic lignin-oil from Alcell lignin

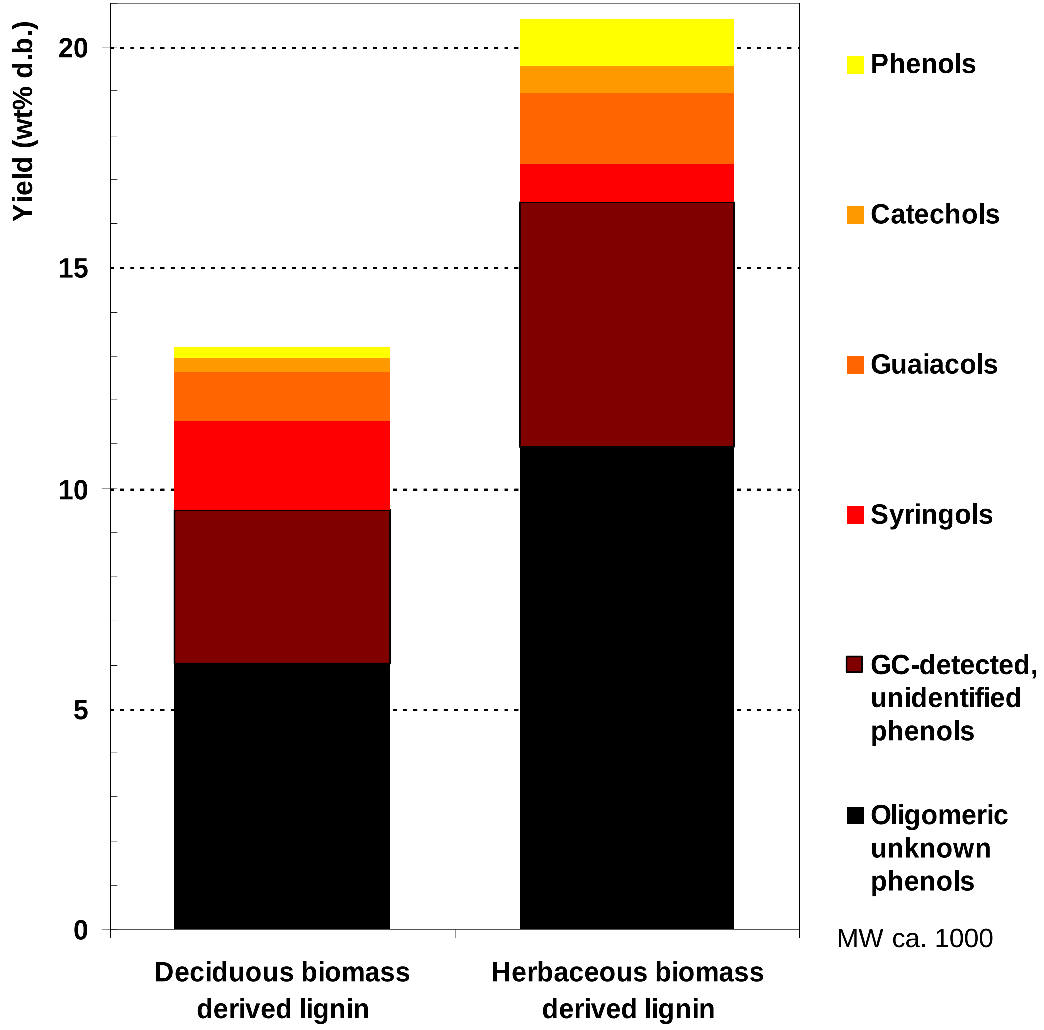
ESP fraction from captured aerosols

Freeze condenser fraction from low-boiling point components



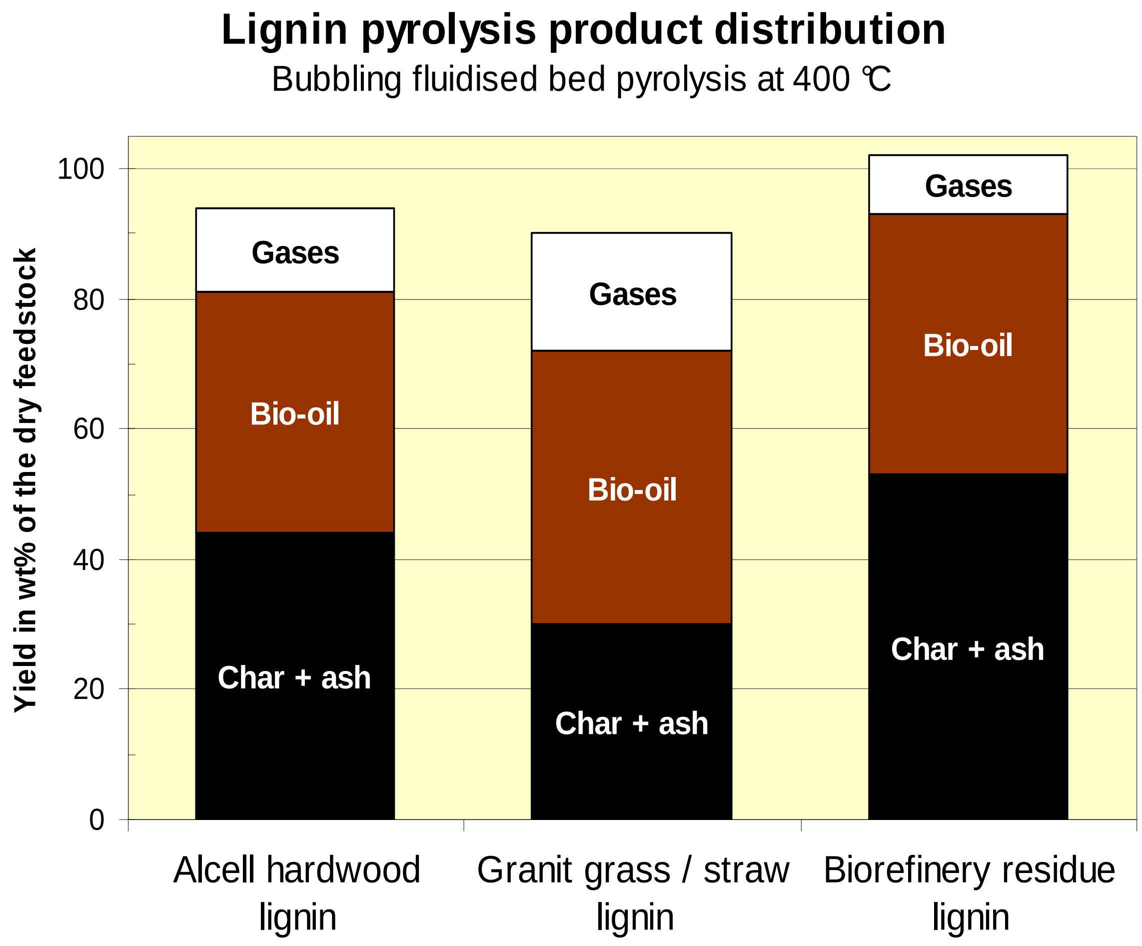
Bio-oil comparison hardwood lignin vs. grass/straw lignin

- Bubbling Fluidised Bed catalytic continuous pyrolysis at 400℃:
  - **13 wt% (d.b.) phenolics** from hardwood lignin (Alcell)
  - **20 wt% (d.b.) phenolics** from grass/straw lignin (Granit)
  - Apparently, the herbaceous lignin is easier to crack
  - Substantial phenolics yields: recent yield improvements up to 30 wt%

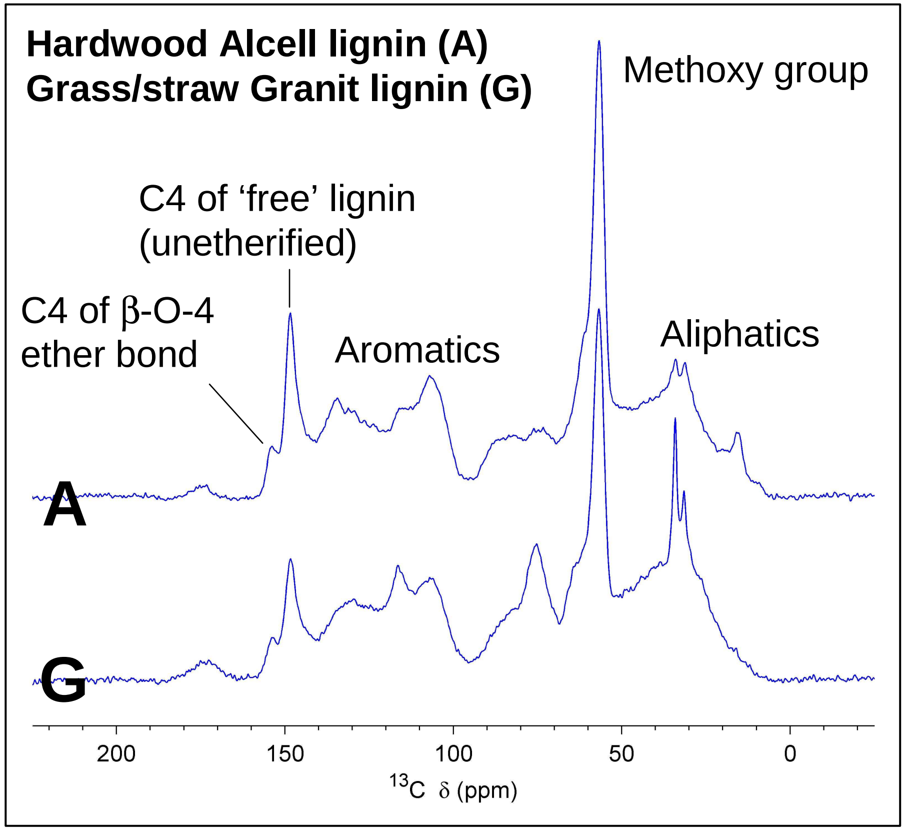


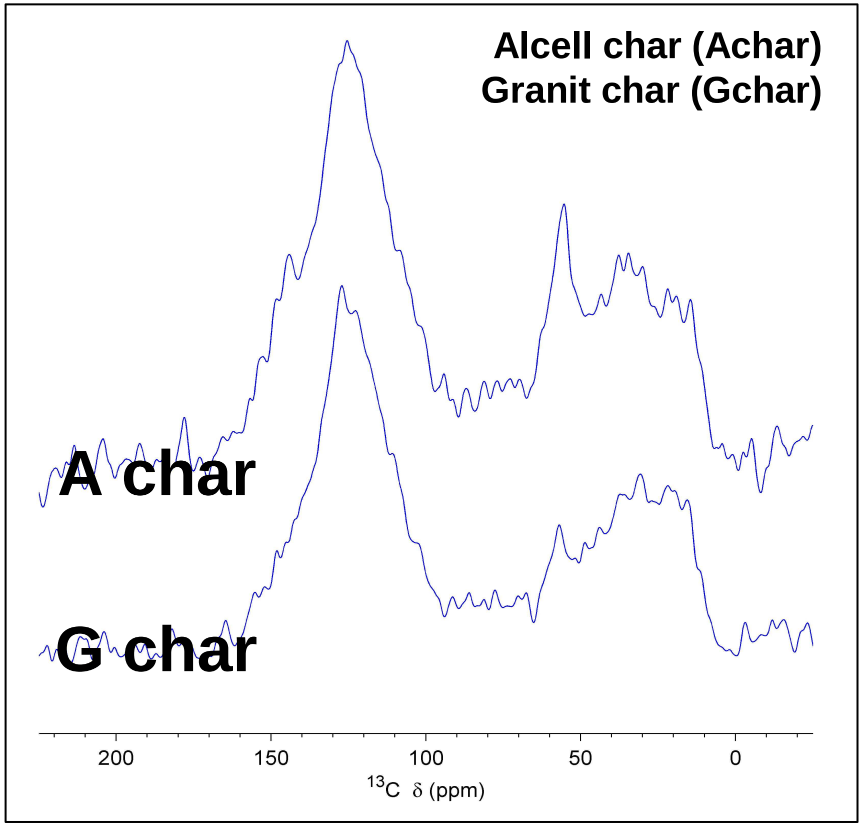
Comparison lignins

- Gases (~ 10 – 15 wt%) are predominantly CO, CO_2 and some methane
- Bio-oil (~ 40 wt%) consists of ~ 50-75% phenolics, water and light ends like methanol and acetic acid
- Little inorganics in Alcell and Granit pure lignin char, much in the char from the biorefinery impure lignin residue



^{13}C-NMR of lignin and its pyrolysis char





Courtesy of S. Habets, Radboud University Nijmegen

When compared to the native lignin in wood, the technical lignins show less β-O-4 bonds. Apparently, these are partly broken during the production process. Pyrolysis leads to extensive obliteration of the lignin structure although some methoxy groups are preserved.

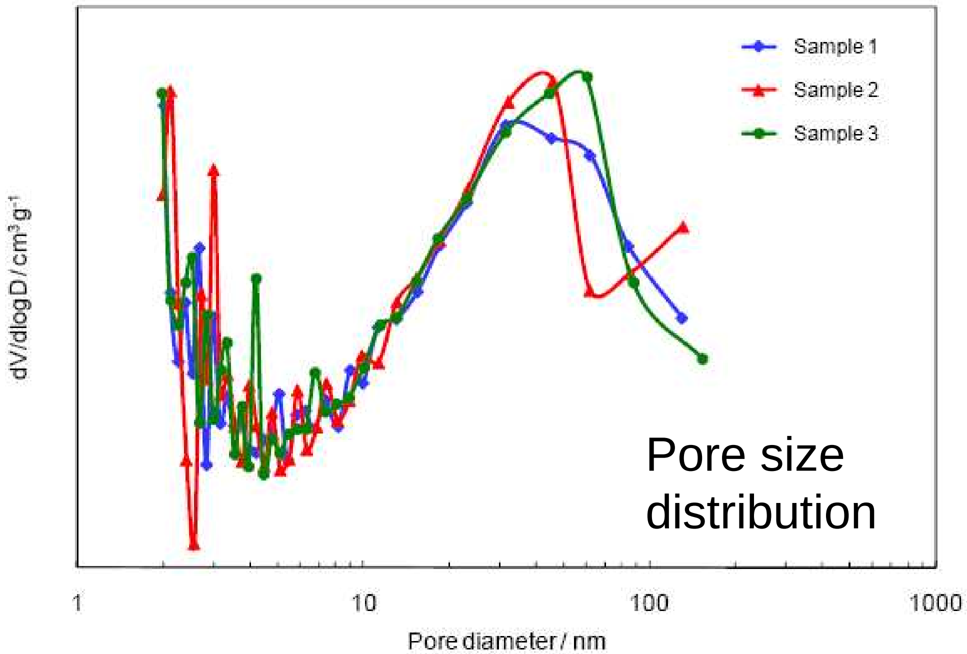
Biochar from lignin

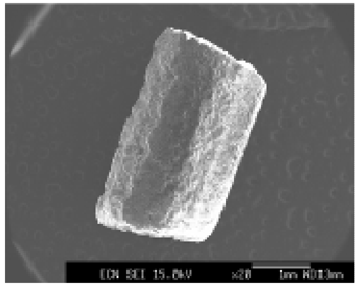
- Lignin is recalcitrant and has a high charring tendency; in a typical lignin pyrolysis process char is the major product.
- Due to its aromatic structure lignin is a good precursor for porous chars that might be suitable for soil improving, however, this is not yet scientifically proven, much remains to be investigated, especially the relation type of lignin – pyrolysis process – char soil-improving quality.
- Lignin char might be a good matrix for inorganic soil nutrients like P, K, N, and trace amounts of metals such as Mg, Fe, Al, Si, etc.



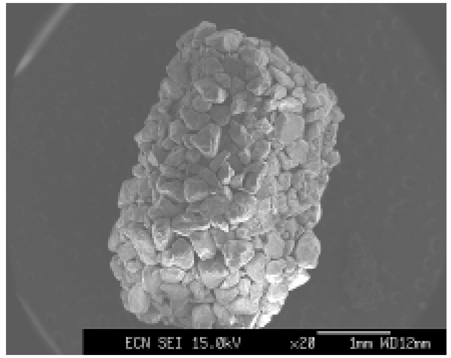
Characteristics lignin biochar

- Specific surface area 2 – 200 m^2/g; pore size distribution typical for a combined micro-mesoporous material, indications for macroporosity
- Carbon content ~ 65 wt%, oxygen content ~ 25 wt%

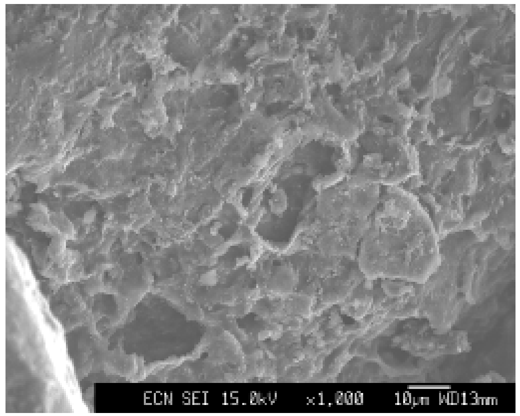




Original lignin extrudate



Silica-sand coated lignin-char particle from a pyrolysis at 400℃



Porous structure

Application of Alcell lignin char as soil improver

+ Lignin char

Control

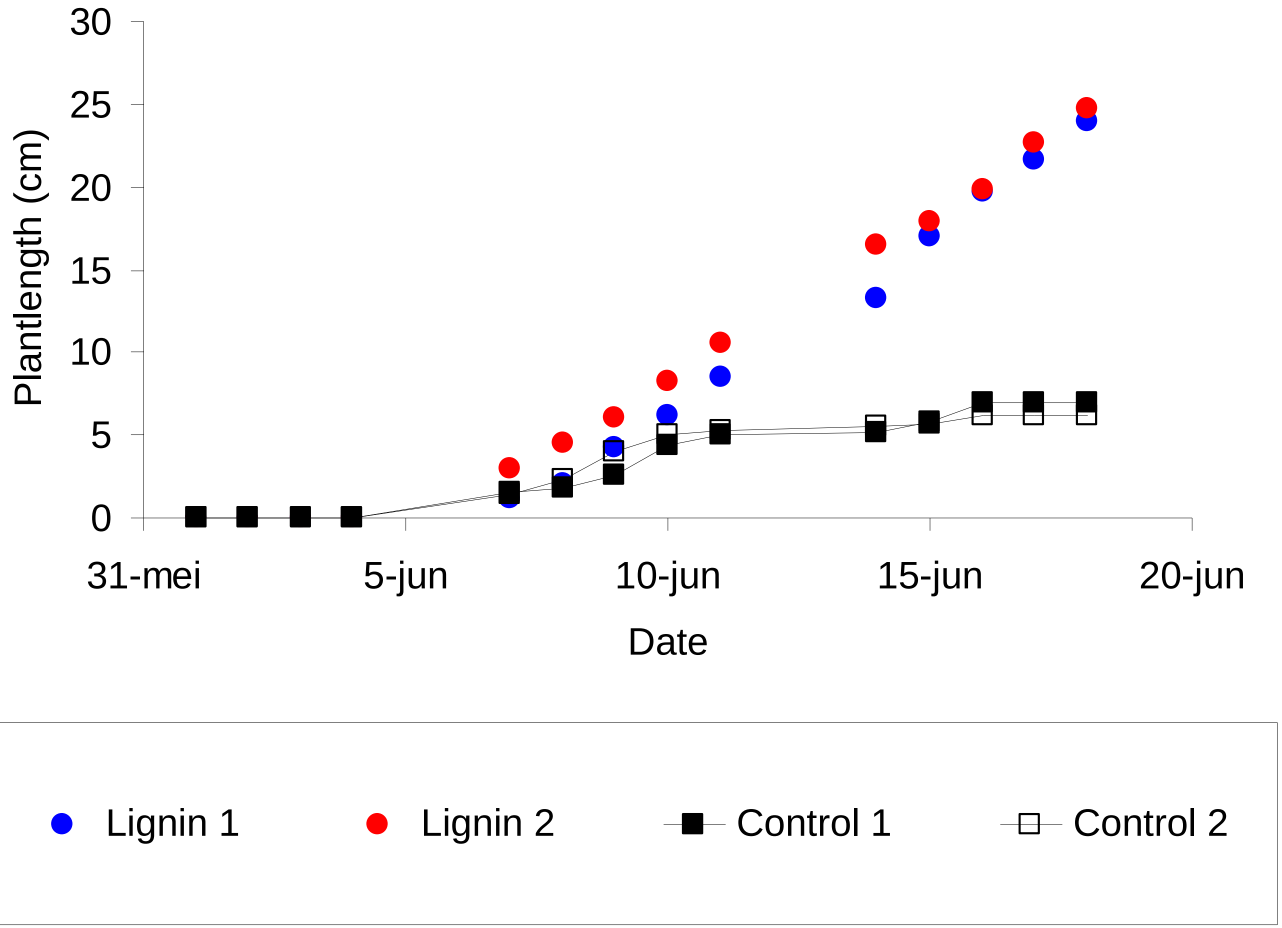
Maize plants on acidic sandy soil.

Lignin char addition = 1.75 wt% (~2 ton/ha)

Significant higher grow rate and more healthy leaves using lignin char additions

Van Zomeren et al., in preparation

Plant length as a function of time



Lignin char addition results in factor 3 higher grow rate

Possible application in agricultural industry?

Van Zomeren et al., in preparation

Conclusions

Lignin from different sources can be valorised by bubbling fluidised bed pyrolysis in a phenolic bio-oil (~ 40 wt%) and biochar (~ 50 wt%).

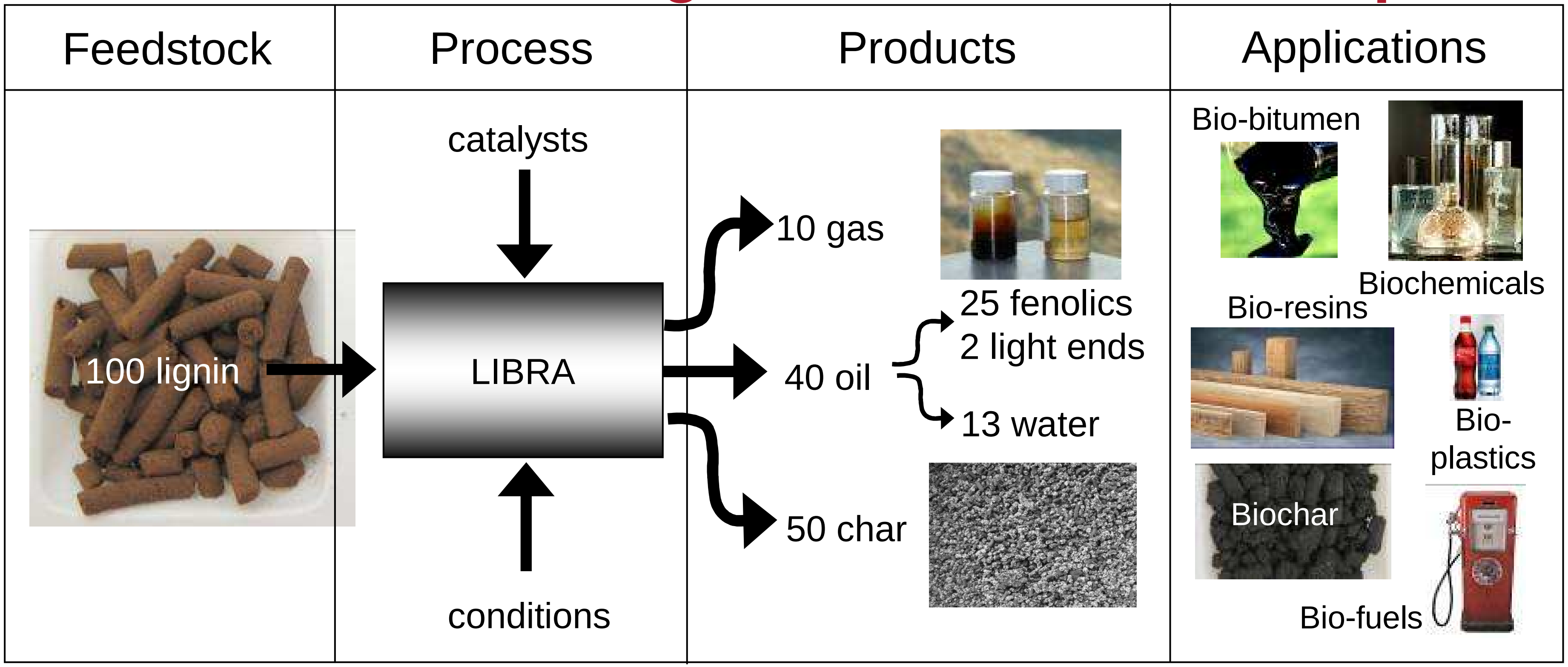
The bio-oil is a mixture of monomeric and oligomeric phenolic compounds, water and low boiling components like methanol. Up to ~ 30 wt% phenolics can be obtained by application of specific catalysts.

The phenolic compounds can be used as petrochemical substitution options for applications as wood-adhesives (resins), bio-plastics, chemicals, bio-fuels, etc.

The biochar has potential as soil improver to decrease the amount of fertiliser.

The development of a new lignin biorefinery approach (LIBRA) is based on major innovations in lignin feeding and catalytic cracking. Patent application is underway.

Lignin BioRefinery Approach (LIBRA)
Innovative ECN lignin valorisation concept



The challenges of feeding, effective thermal degradation and fractionated product collection have (at least partly) been resolved (patent application underway)

Acknowledgements

Ernst van Eck, Sander Habets (Radboud University Nijmegen, NMR)

Alex Adell, André van Zomeren, Bas Brammer, Ruud Wilberink, Ron van der Laan, Gertjan Herder, Marco Geusebroek, Cor van Egmond, Marcel Bregman, Ben van Egmond, Petra Bonouvrie, Karina Vogelpoel, Wouter Huijgen, Arjan Smit and Hans Reith (all ECN)

Part of this work was conducted in the framework of a Dutch national EOS-LT project “LignoValue” financed by the Dutch Ministery of Economic Affairs (SenterNovem).

Thank you for your attention!

For info: dewild@ecn.nl