Bubbling fluidised bed pyrolysis of lignin for value-added products

Paul de Wild

Wouter Huijgen

Ron van der Laan

Ruud Wilberink

Presented at the XIX International Conference on Chemical Reactors,

September 5 – 9, Vienna, Austria

CHEMREACTOR-19

ECN-L--10-100 October 2010

Energy research Centre of the Netherlands

Bubbling fluidised bed pyrolysis of lignin for value-added products

Paul de Wild, Wouter Huijgen, Ron van der Laan, Ruud Wilberink

XIX International Conference on Chemical Reactors, September 5 – 9, Vienna, Austria
CHEMREACTOR-19

Outline

Introduction

- Lignin valorisation, why, into what? how?
- What is lignin?
- Lignocellulose biorefineries

Experiments

- Lignin feedstocks
- Thermal and structural characterisation
- Pyrolysis tests

Results & discussion

- Feedstock characterisation
- Pyrolysis

Conclusions

Outlook / Challenges

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) Biorefinery lignin expected to increase in the coming decades > 50 Mt/yr

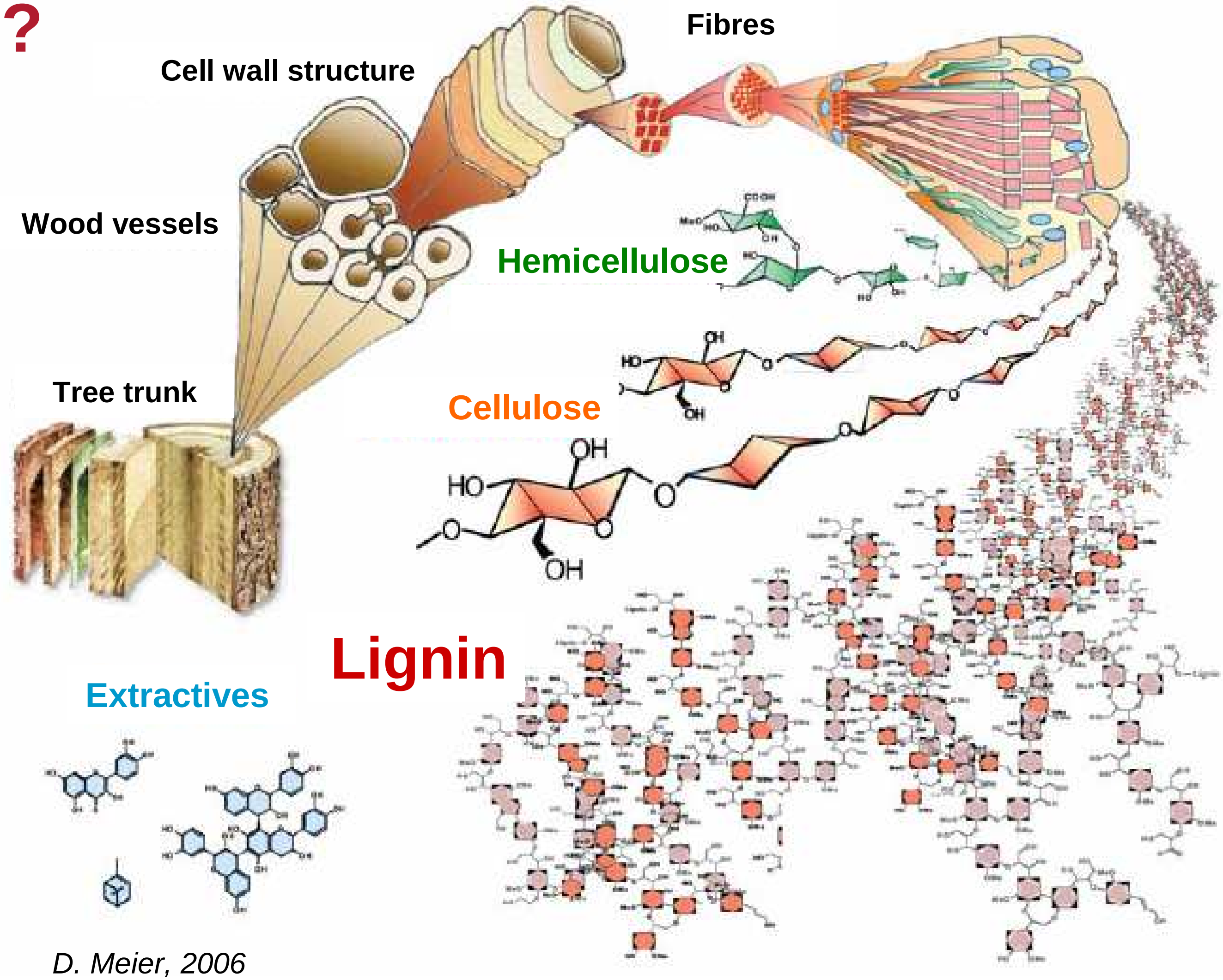
How? and into what?

- 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!

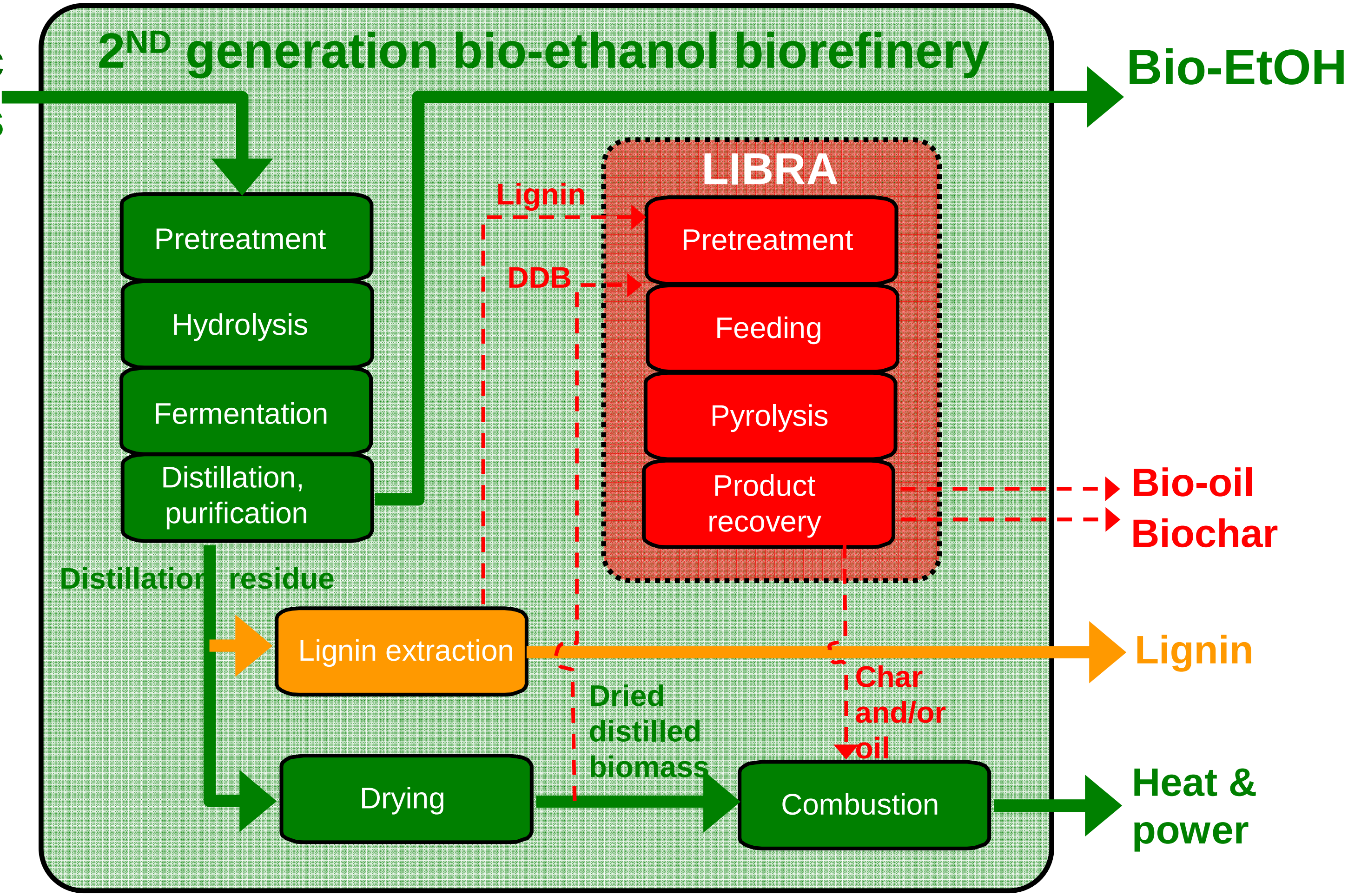
What is lignin?

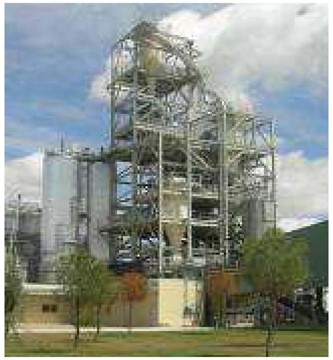
- Biopolymer, consisting of randomly linked phenylpropane units
- 'Glue' that (in combination with hemicellulose) holds the cellulosic wood-structure together
- Very complex structure that depends on plant species and growth conditions
- Highly recalcitrant



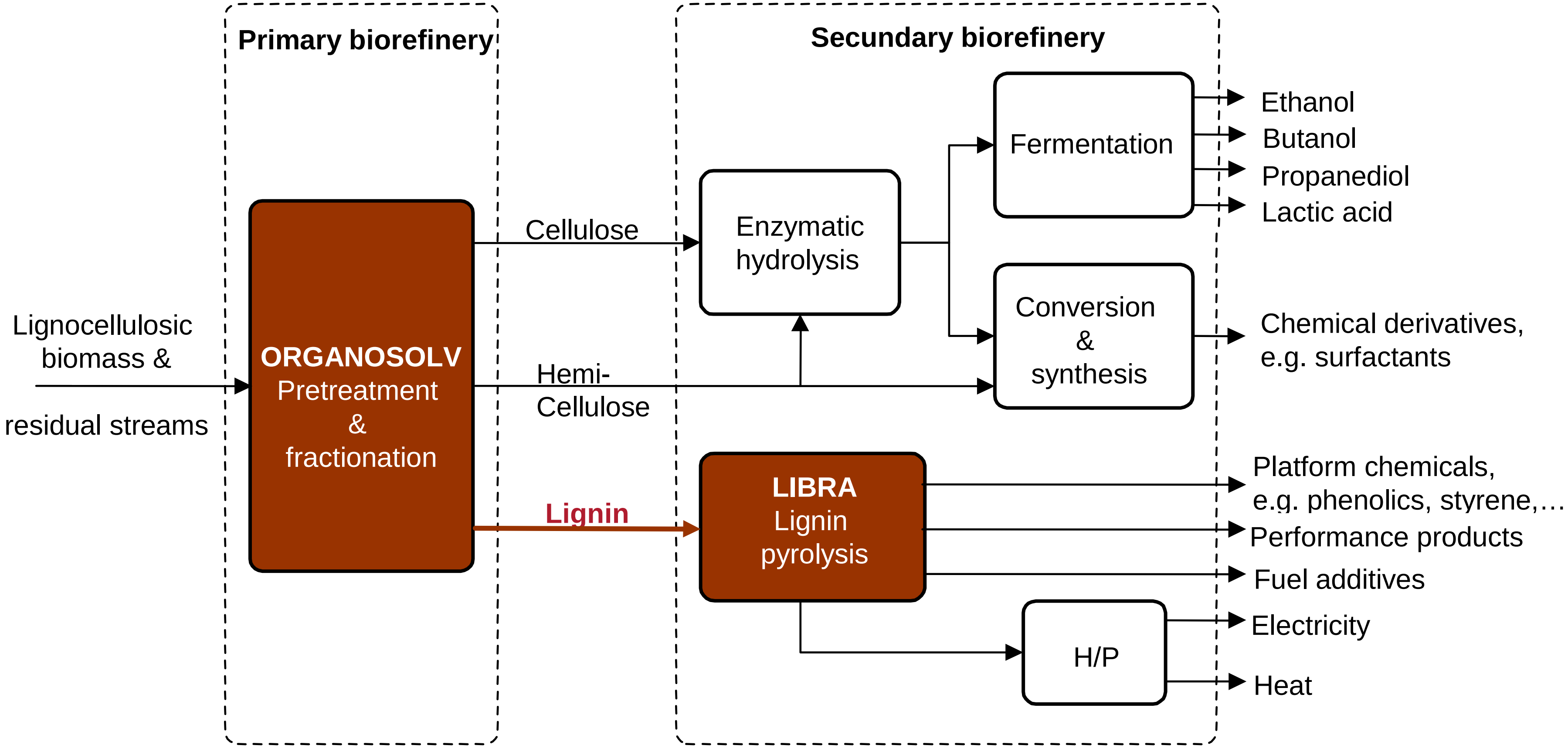
D. Meier, 2006

Lignin BioRefinery Approach (LIBRA)





Lignocellulose BioRefinery

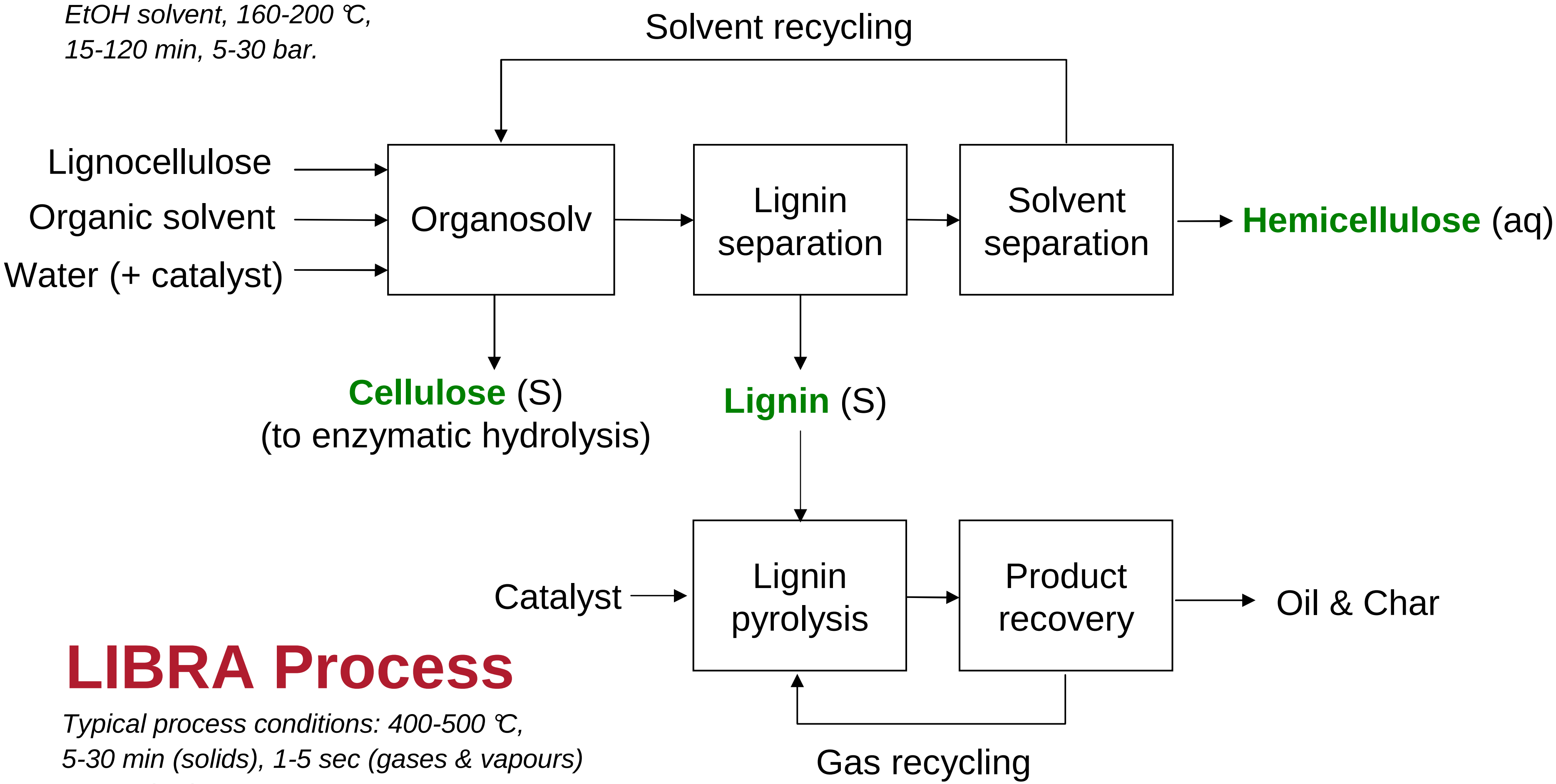


Aim ECN ORGANOSOLV + LIBRA technology:

- Fractionation of all major constituents in a sufficient quality for valorisation, including extraction of high-quality lignin for production of chemicals.
- Pyrolysis of lignin for phenolics and biochar.

ORGANOSOLV Process

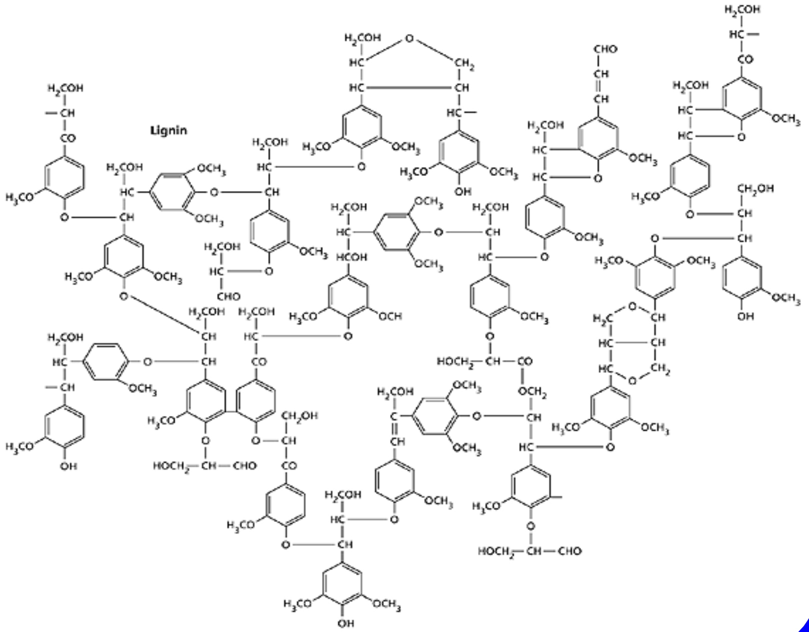
Typical process conditions:
EtOH solvent, 160-200 ℃,
15-120 min, 5-30 bar.



LIBRA Process

Typical process conditions: 400-500 ℃,
5-30 min (solids), 1-5 sec (gases & vapours)
atmospheric pressure.

Lignin thermal degradation mechanism



Goal is to optimise the thermal degradation via optimisation of process conditions and catalysts

Lignin → Melting → Pyrolysis

Permanent gases (CO, CO_2, CH_4) — **Gas**

↑ *degradation*

Light ends (MeOH, acetic acid,..)
Water

↑ *degradation*

Monomeric phenols

Catalyst ↑↓ *Condensation / degradation*

Oligomeric phenols — **Oil**

↓ *Condensation*

Char & ash — **Char**

Experiments

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

Wheat straw,
(ECN organosolv pulping)

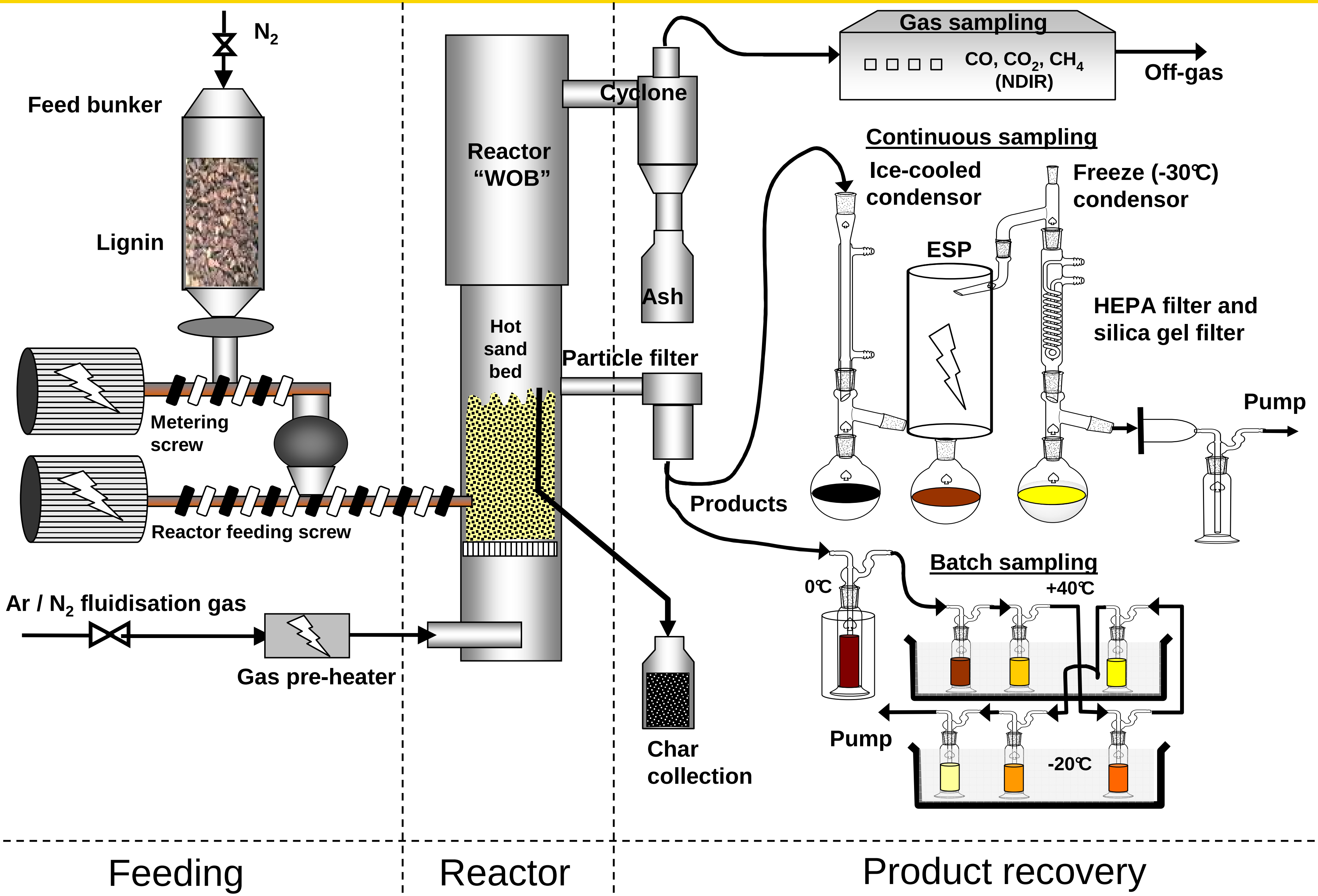
Sarkanda grass / wheat straw
(soda pulping, Granit Protobind™)

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 (atmospheric 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 reactor set-up



Bubbling fluidised-bed pyrolysis and product collection

- Sand-bed, 400-500℃, fluidised with Ar, 5 x U_{mf}
- Vapour residence times (s), solid residence time (min)
- Product collection using impingers (batch exp.) or cooled condensers and an ESP (continuous exp.)
- On-line analysis of perm. gases
- Off-line analysis of condensable products by GC/MS/FID

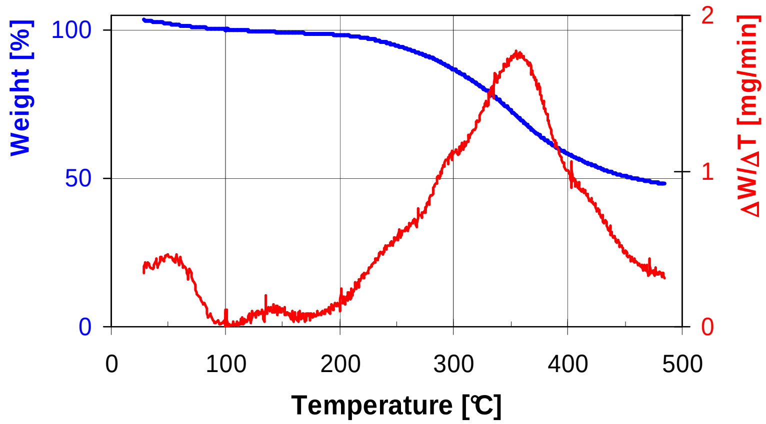
Characterisation results

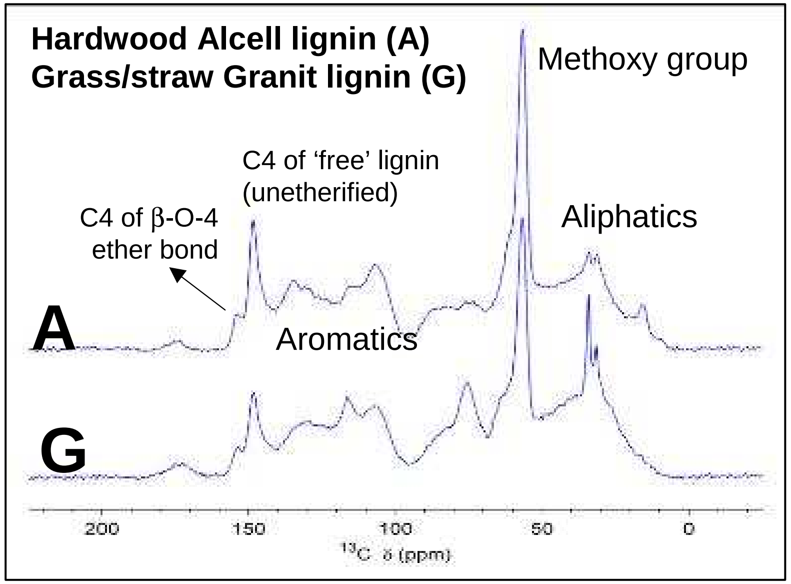
TGA / DTG / DSC (not shown)

- Wt loss starts at 200 ℃.
  At 500 ℃ ~50 wt% char
- Peak around 50℃ is moisture .
  Broad degradation range,
  max at 350 ℃.
- Melting occurs in between 100 – 200℃
  (from DSC and fusion tests)..
- **A temperature of 400℃ was chosen for BFB pyrolysis tests.**

^{13}C-CP/MAS solid state NMR

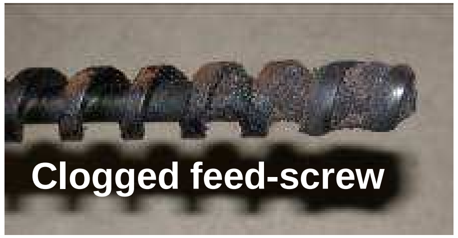
- Compared to the native lignin in wood, the technical lignins show less β-O-4 bonds. Apparently, these are partly broken during the production process.

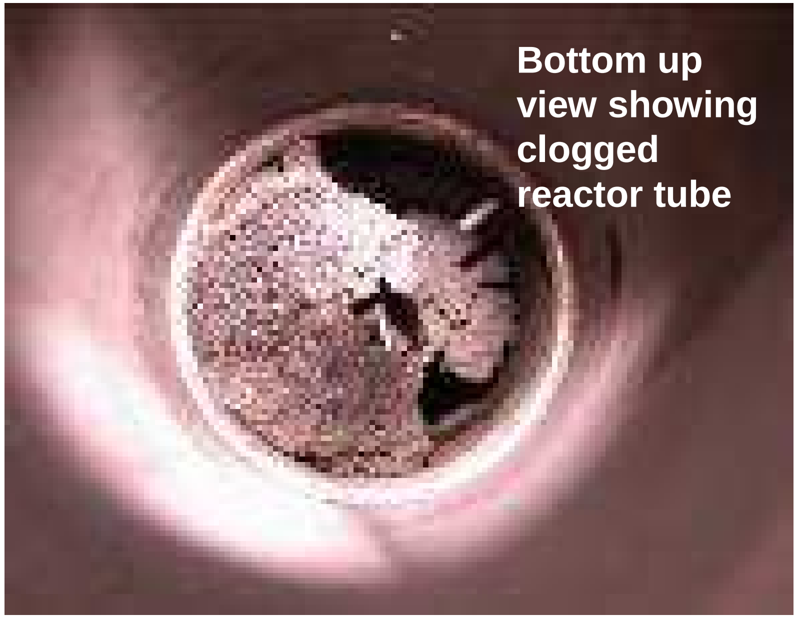




Courtesy of S. Habets, Radboud University Nijmegen

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



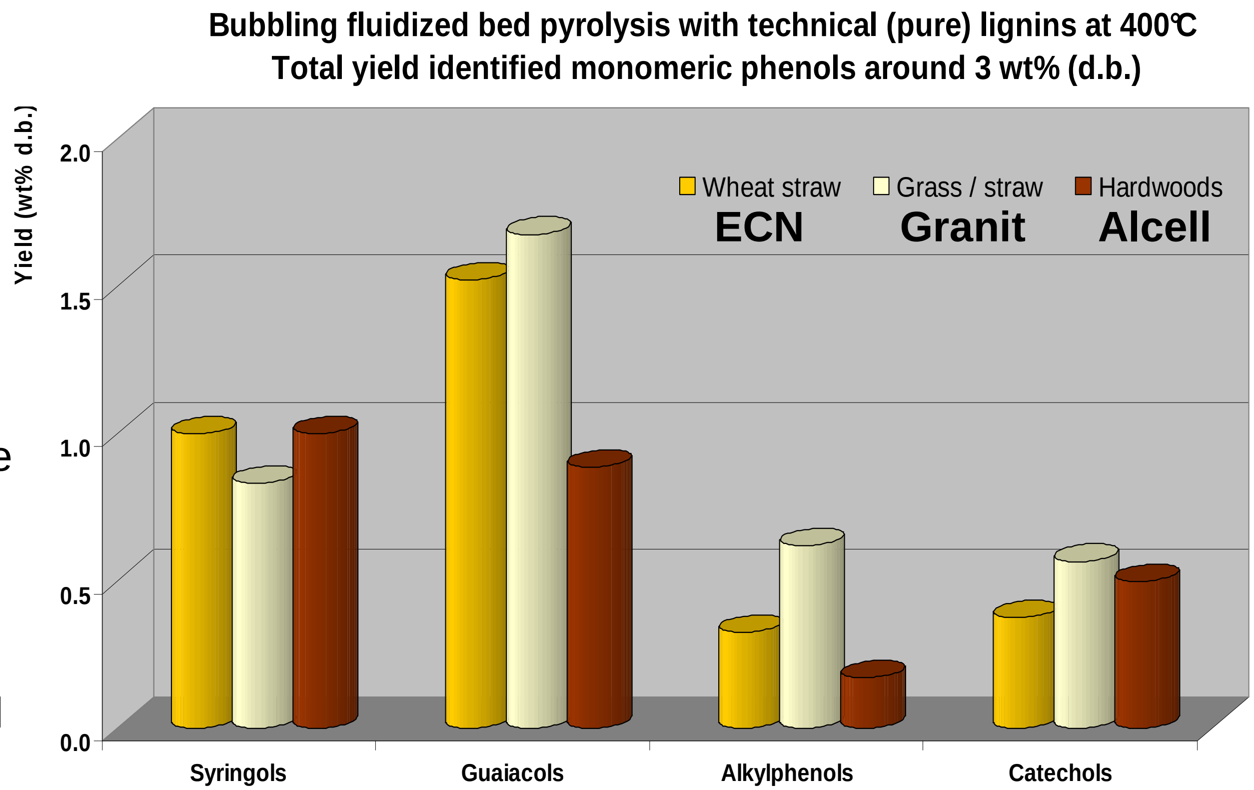


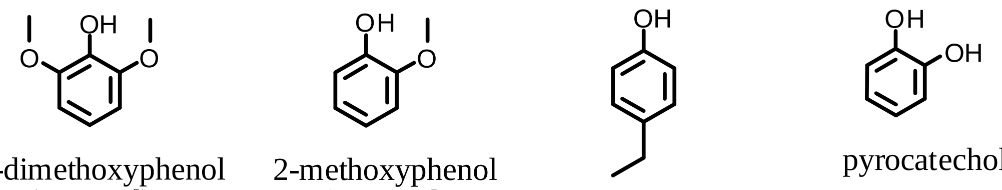
Large lignin-sand agglomerates

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.





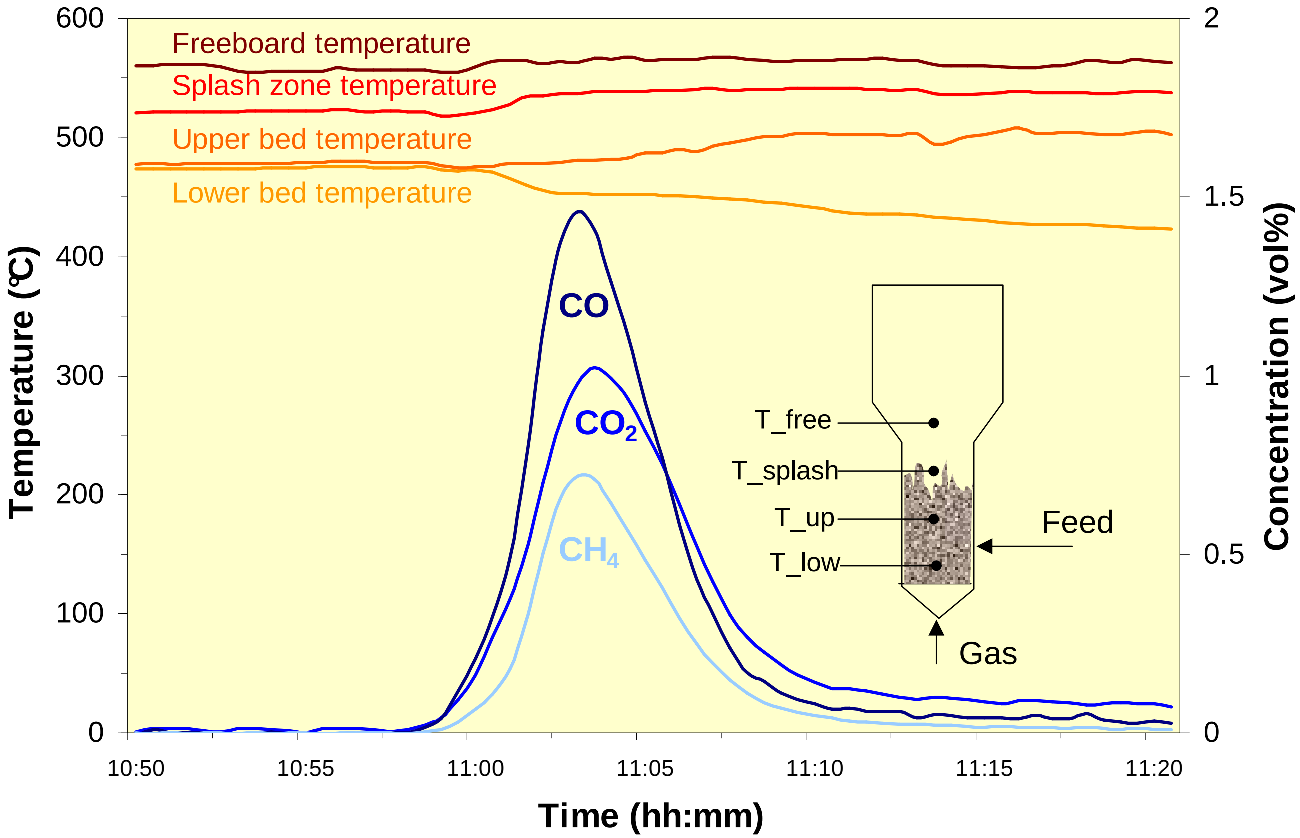
2,6-dimethoxyphenol (syringol)

2-methoxyphenol (guaiacol)

4-ethylphenol

pyrocatechol

BFB pyrolysis of ECN organosolv lignin from wheat straw at 500℃

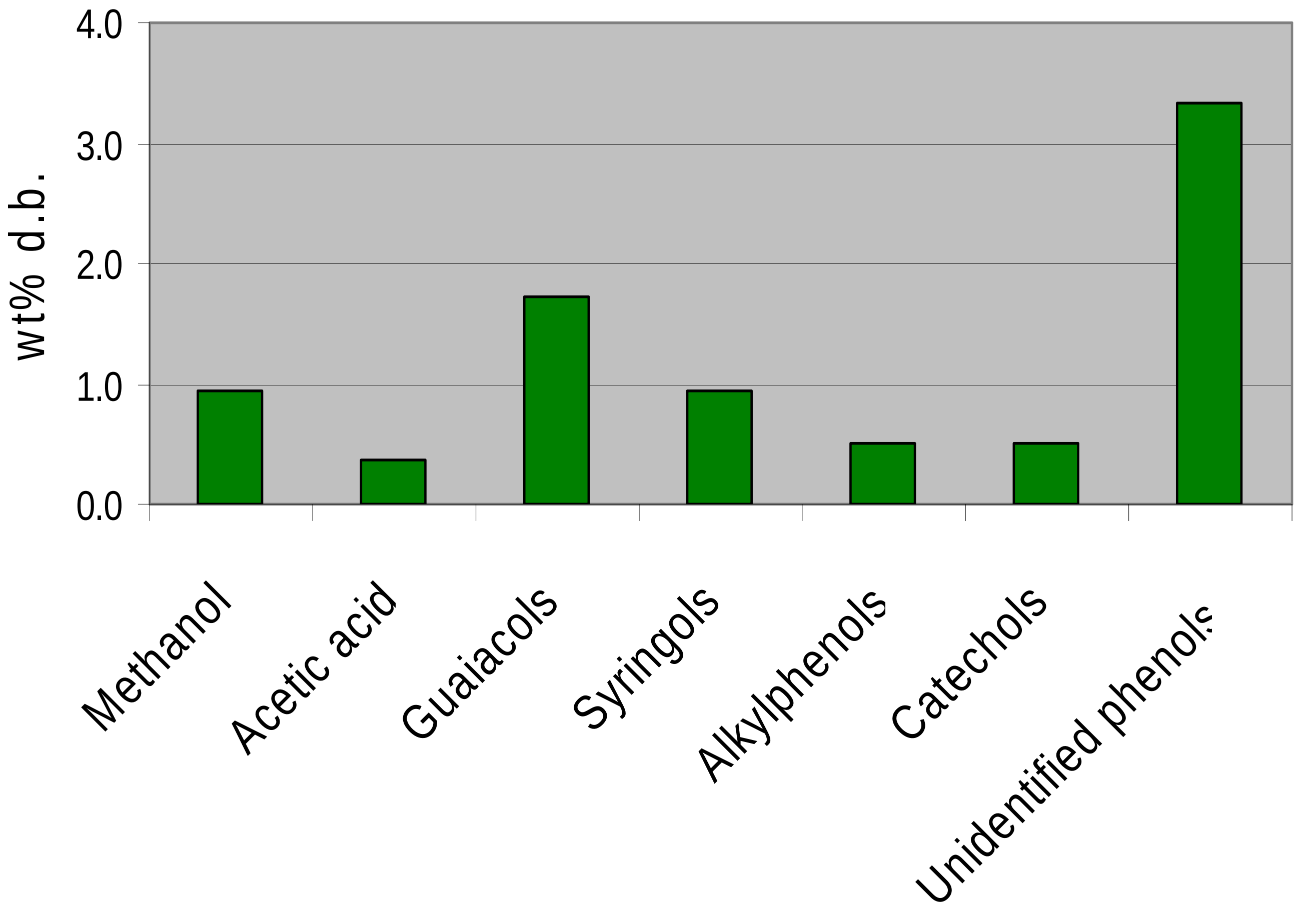


Bottom up view showing partially clogged reactor tube

Molten lignin deposits at feed-screw tip

Partial defluidisation of the reactor bed due to agglomeration caused by molten lignin at the screw tip

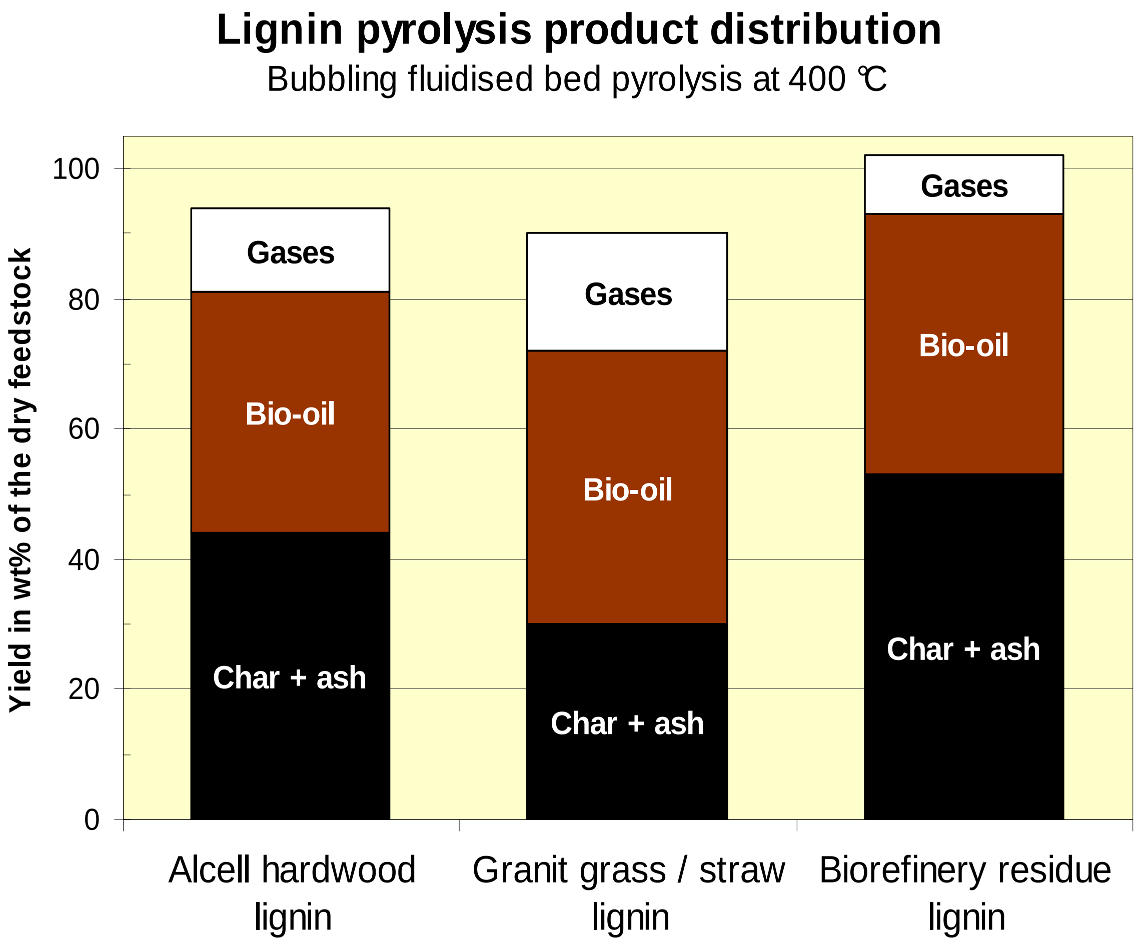
Major product yields from the BFB pyrolysis of ECN organosolv lignin from wheat straw at 500℃



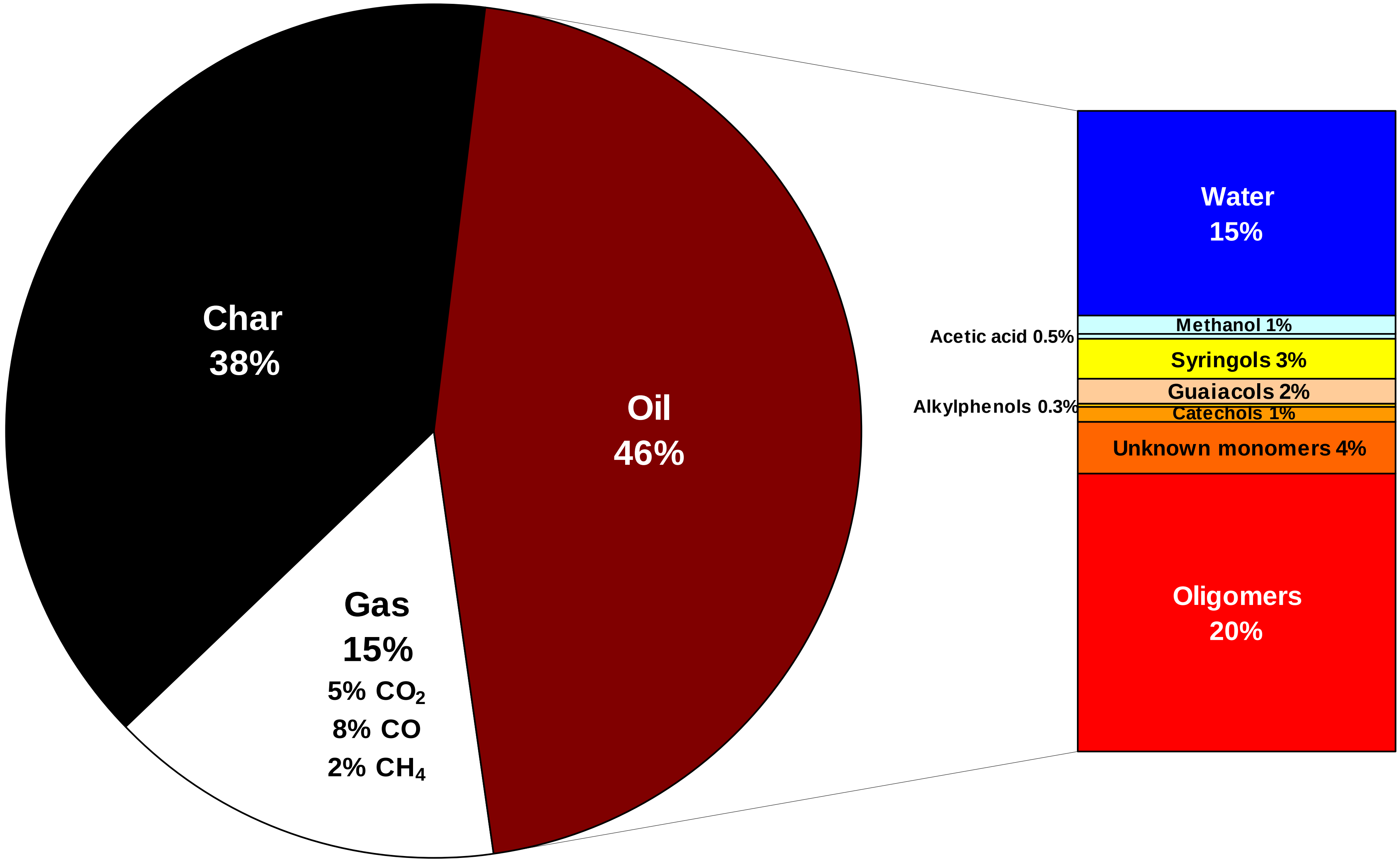
Gases	~ 10 - 20 wt%
Phenols	~ 7 wt%
Oligomers	~ 15 – 20 wt%
Lights	~ 2 wt%
Water	~ 15 – 20 wt%
Char	~ 30 – 40 wt%

Comparison lignins

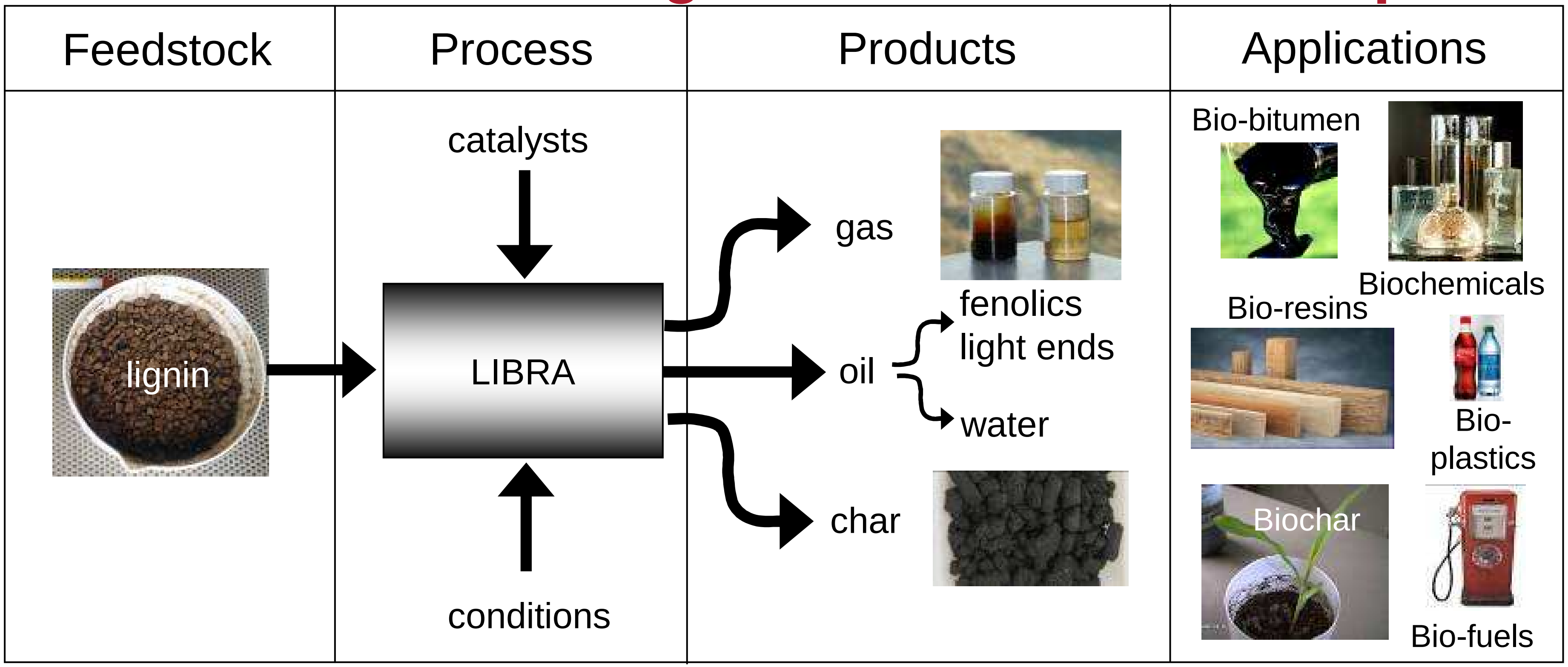
- Gases (~ 10 – 15 wt%) are predominantly CO, CO_2 and some methane
- Bio-oil (~ 40 wt%) consists of ~ 50-75% phenolics, water and light ends like methanol and acetic acid
- Little inorganics in Alcell and Granit pure lignin char, much in the char from the biorefinery impure lignin residue



Products from the pyrolysis of Alcell lignin at 500℃



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)

Conclusions

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

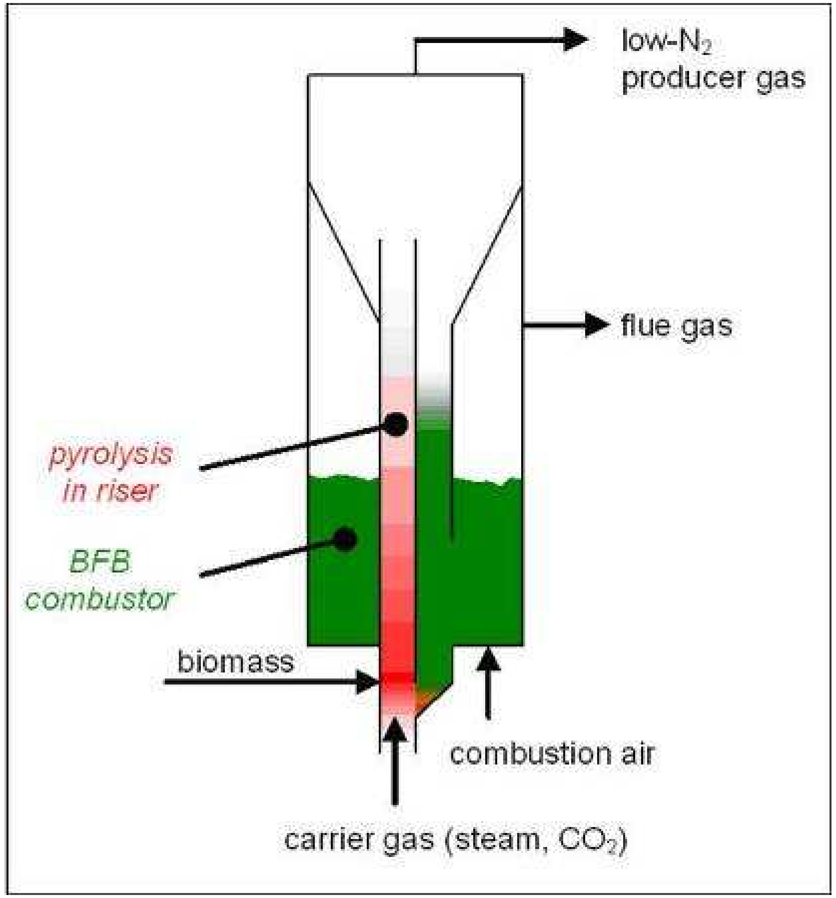
The phenolic compounds can be used as petrochemical substitution options for applications as wood-adhesives (resins), bio-plastics, chemicals, bio-fuels, etc.

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.

Outlook / challenges

- Scale-up from 0.5 kg/hr to 5 kg/hr lignin feed rate
- Construct scaled-up pyrolysis product collection rig
- Product fractionation into monomer families and oligomers
- Indentify applications, markets and added-value potential
- Conceptual design and techno-economic assessments of the LIBRA process
- Find investors / sponsors / RTD partners



Thank you for your attention!

For info: dewild@ecn.nl

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).