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Pyrolysis of lignin for value-added products by LIBRA (Lignin Biorefinery Approach)

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Outline

Introduction

– Lignin valorisation, why?, how? into what?

– Lignin Biorefinery Approach (LIBRA)

Experiments

– Feedstocks, characterisation, pyrolysis

Results

– Characterisation, pyrolysis

– System evaluation LIBRA

Conclusions

– Outlook / challenges

– Concluding remarks

– Acknowledgements

Lignin valorisation, why?, how?, into what?

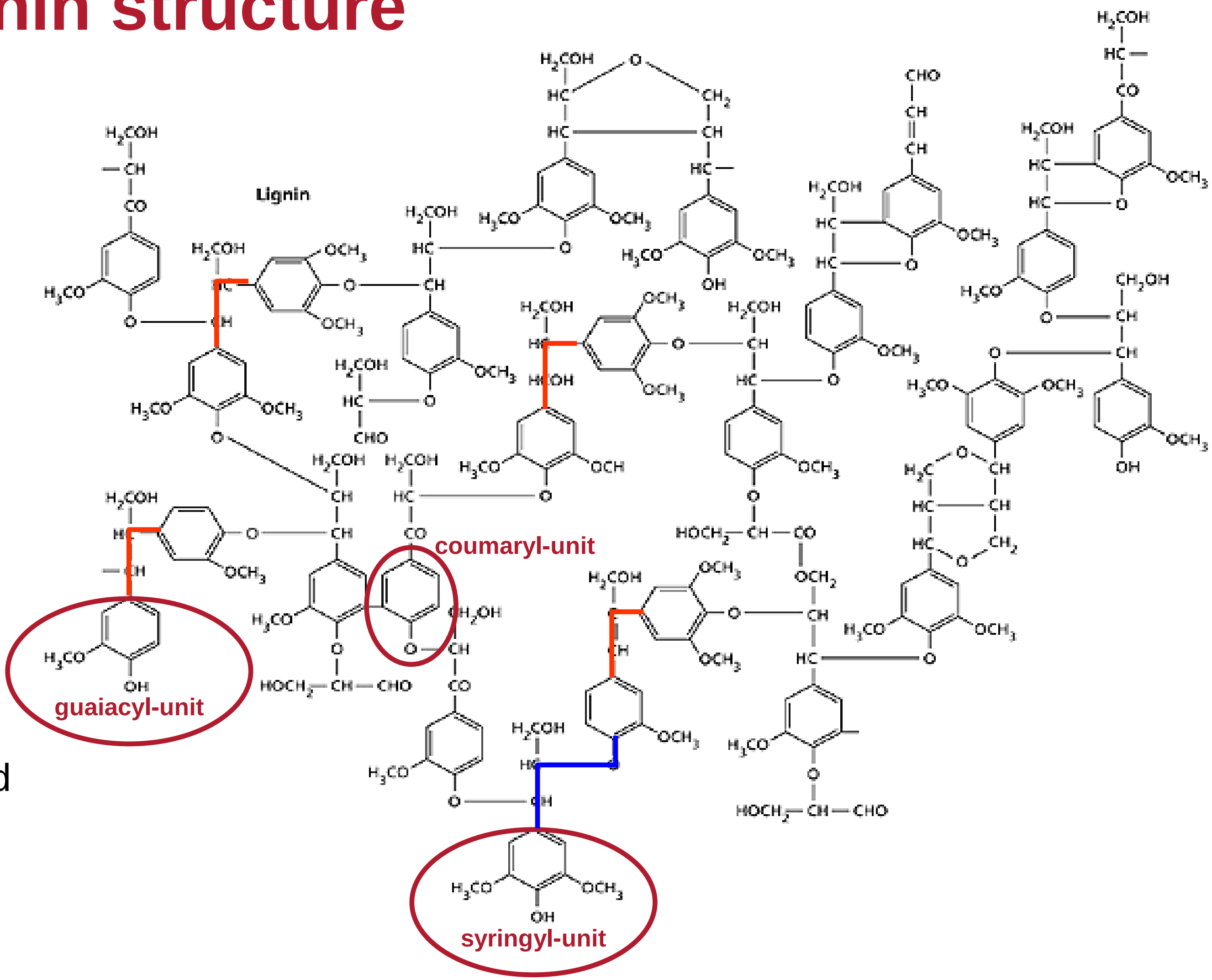
- Lignin is worlds' 2nd most abundant natural polymer. It consists of randomly linked phenylpropane units and contains valuable aromatic (phenolic) structures. In combination with hemicellulose it provides structural strength and flexibility for the lignocellulosic biomass.
- Lignin is a major residual stream in e.g. the pulp and paper sector and (future) biorefineries, current potential > 50 Mt/yr (Gosselink et al., 2004)
- 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!

J. J. Bozell, J. E. Holladay, D. Johnson, and J. F. White, 'Top Value Added Chemicals from Biomass, Volume II: Results of Screening for Potential Candidates from Biorefinery Lignin', PNNL-16983, October 2007,

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 beech wood lignin (Nimz, 1974)



Lignin in lignocellulosic biomass

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

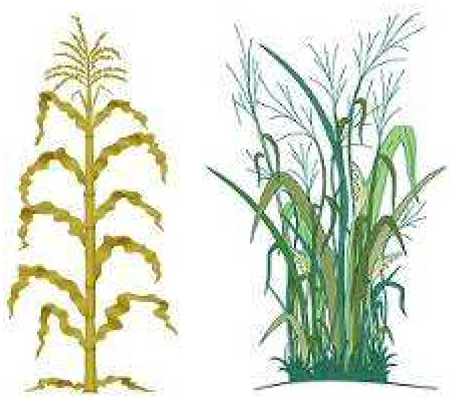
40-50% cellulose
30-40% hemicellulose

20-25% lignin
(syringyl & guaiacyl units)

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

40-45% cellulose
25-30% hemicellulose

25-30% lignin
(mainly guaiacyl units)

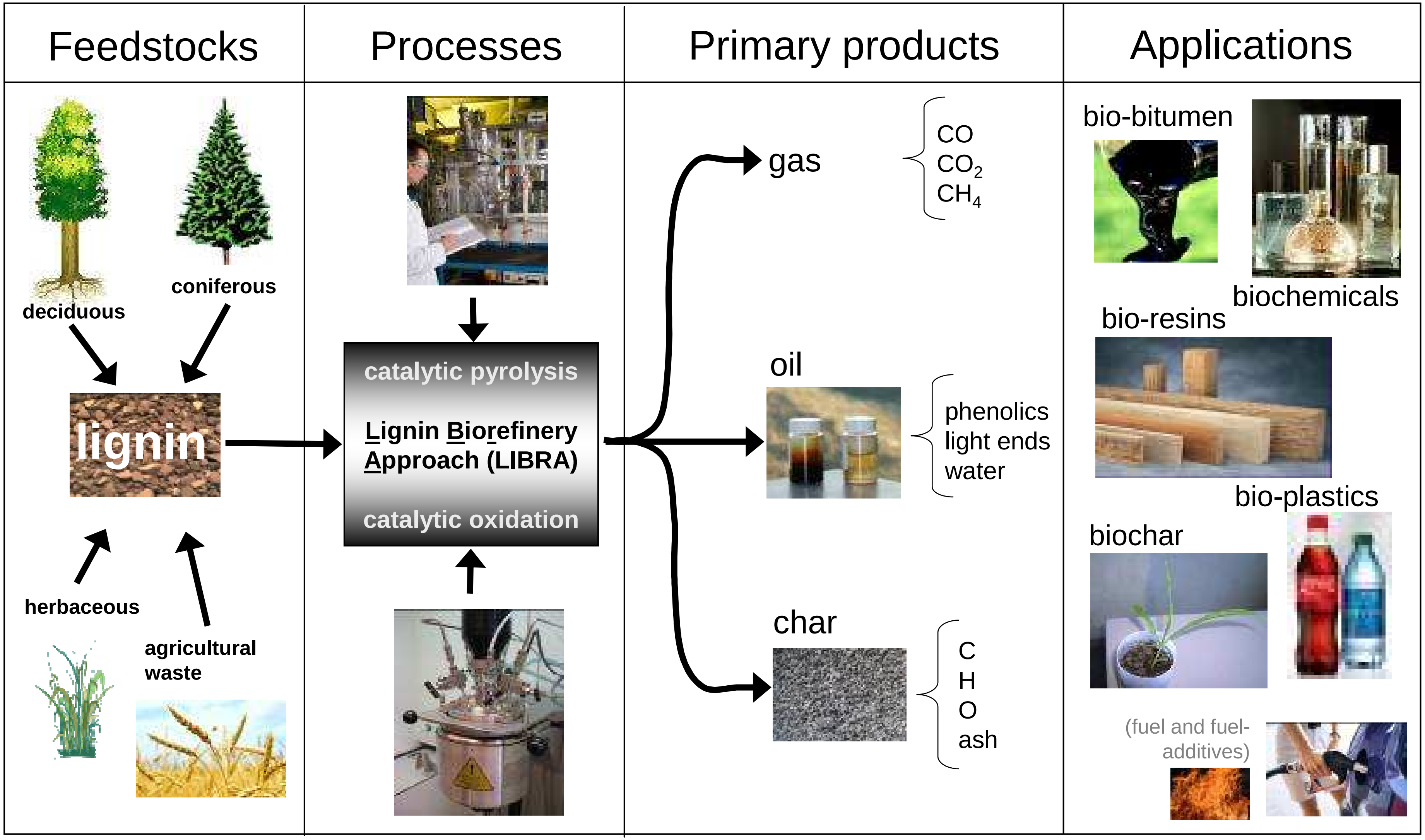


Herbaceous crops
(e.g. wheat, grass, corn,…)

40-45% cellulose
35-45% hemicellulose

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

ECN LIBRA


Feedstocks
Processes
Primary products
Applications
deciduous
coniferous
lignin
herbaceous
agricultural waste
catalytic pyrolysis
Lignin Biorefinery Approach (LIBRA)
catalytic oxidation
gas
CO
CO_2
CH_4
oil
phenolics
light ends
water
char
C
H
O
ash
bio-bitumen
biochemicals
bio-resins
bio-plastics
biochar
(fuel and fuel-additives)

Experiments

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

Wheat straw,
(ECN organosolv pulping)

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

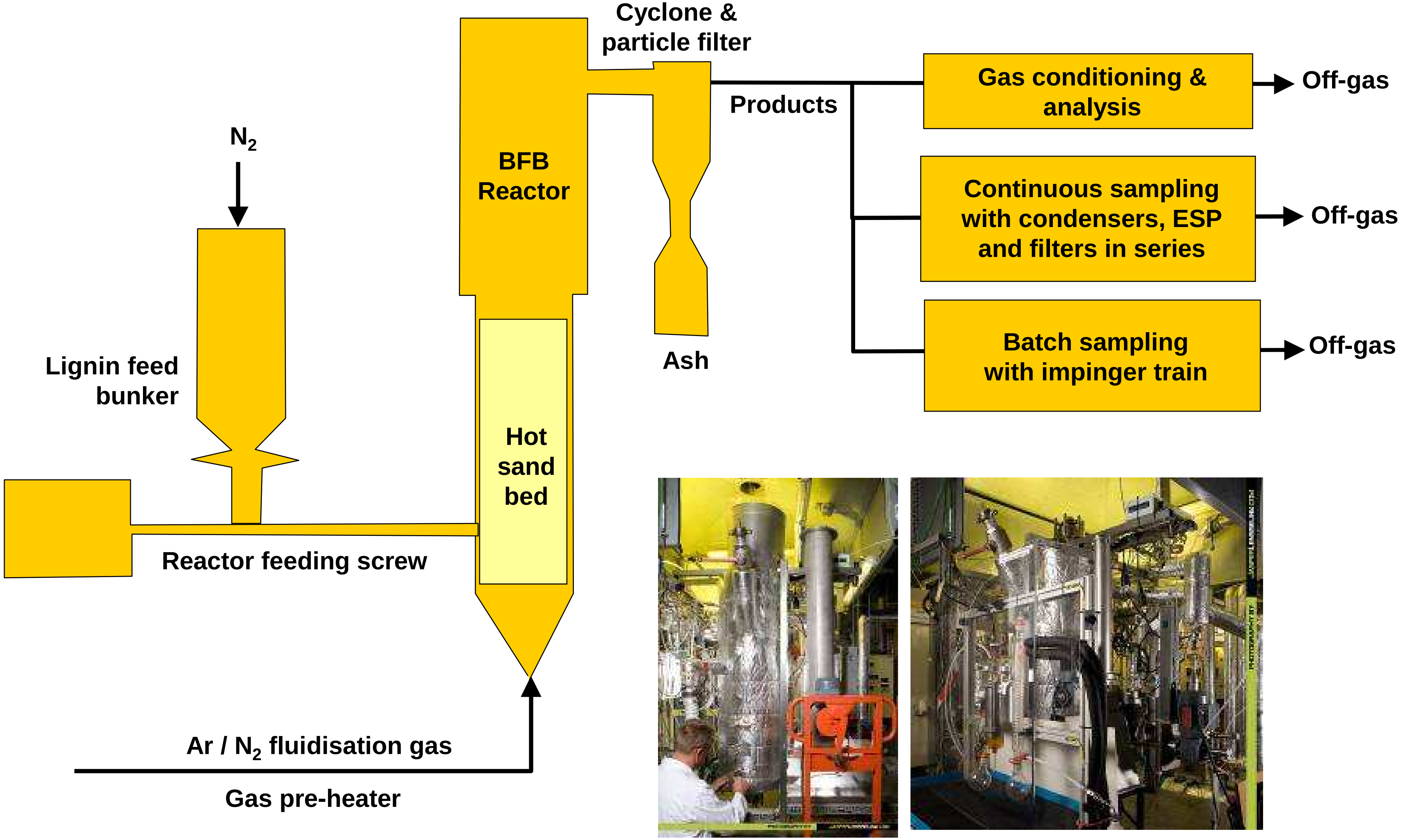
Mix of hardwoods.
(organosolv pulping, Alcell™)

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

- Pyrolysis experiments in bubbling fluidised bed reactor (1 atm.,1 kg/hr, 5 kW$_{th}$) Fractionated product sampling, on- and off-line analysis of products by GC/MS/FID and gravimetry

* Huijgen, W.J.J., Van der Laan, R.R., Reith, J.H., 'Modified Organosolv as a Fractionation Process of Lignocellulosic Biomass for Co-Production of Fuels and Chemicals', Proceedings of the 16th European Biomass Conference & Exhibition, Valencia, Spain, 2-6 June, 2008, pp 1651-55.

Bubbling fluidised bed pyrolysis reactor set-up



Bubbling fluidised-bed pyrolysis and product collection

- Sand-bed, 400-500°C, 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

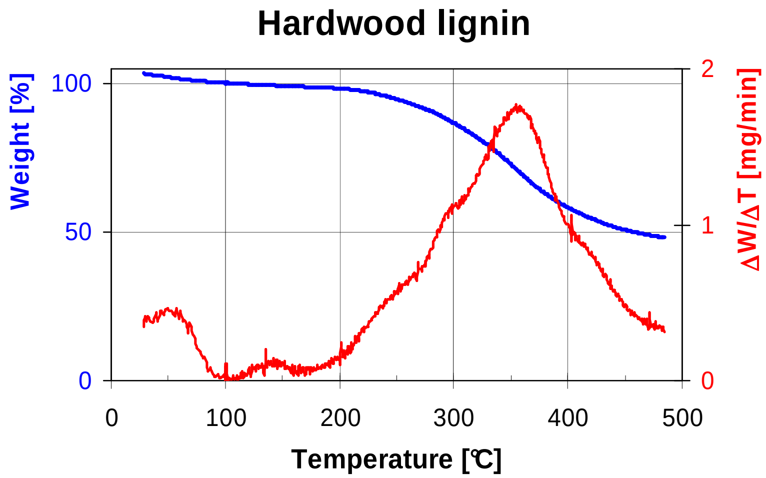
Characterisation results

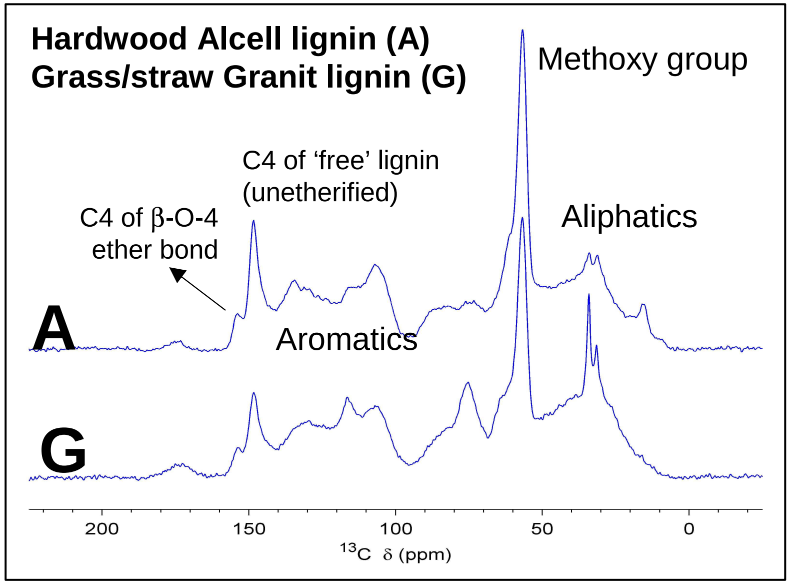
TGA / DTG / DSC (not shown)

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

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

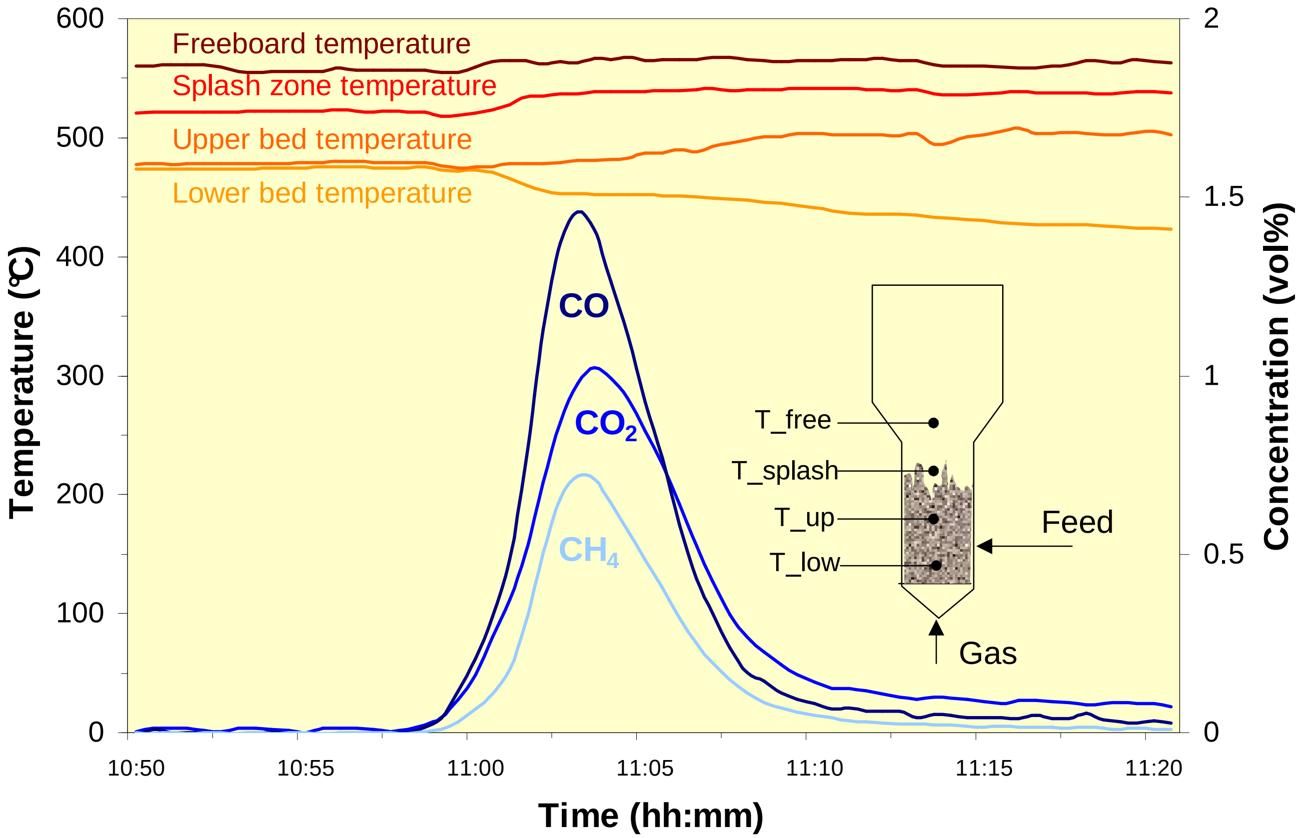
- Less β-O-4 bonds. Apparently, these are partly broken during the production process.





Courtesy of S. Habets, Radboud University Nijmegen

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

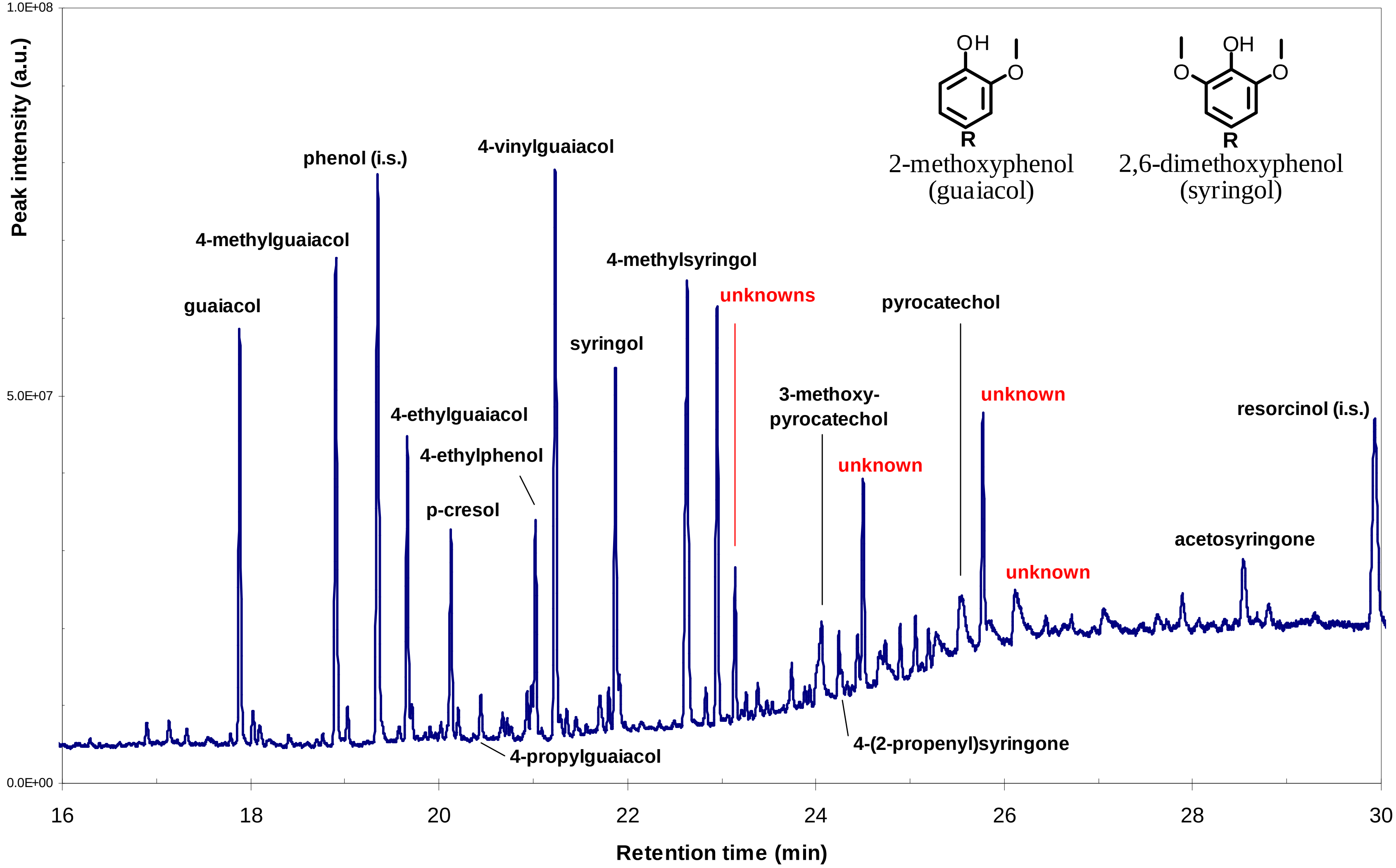


Bottom up view showing partially clogged reactor tube

Molten lignin deposits at feed-screw tip

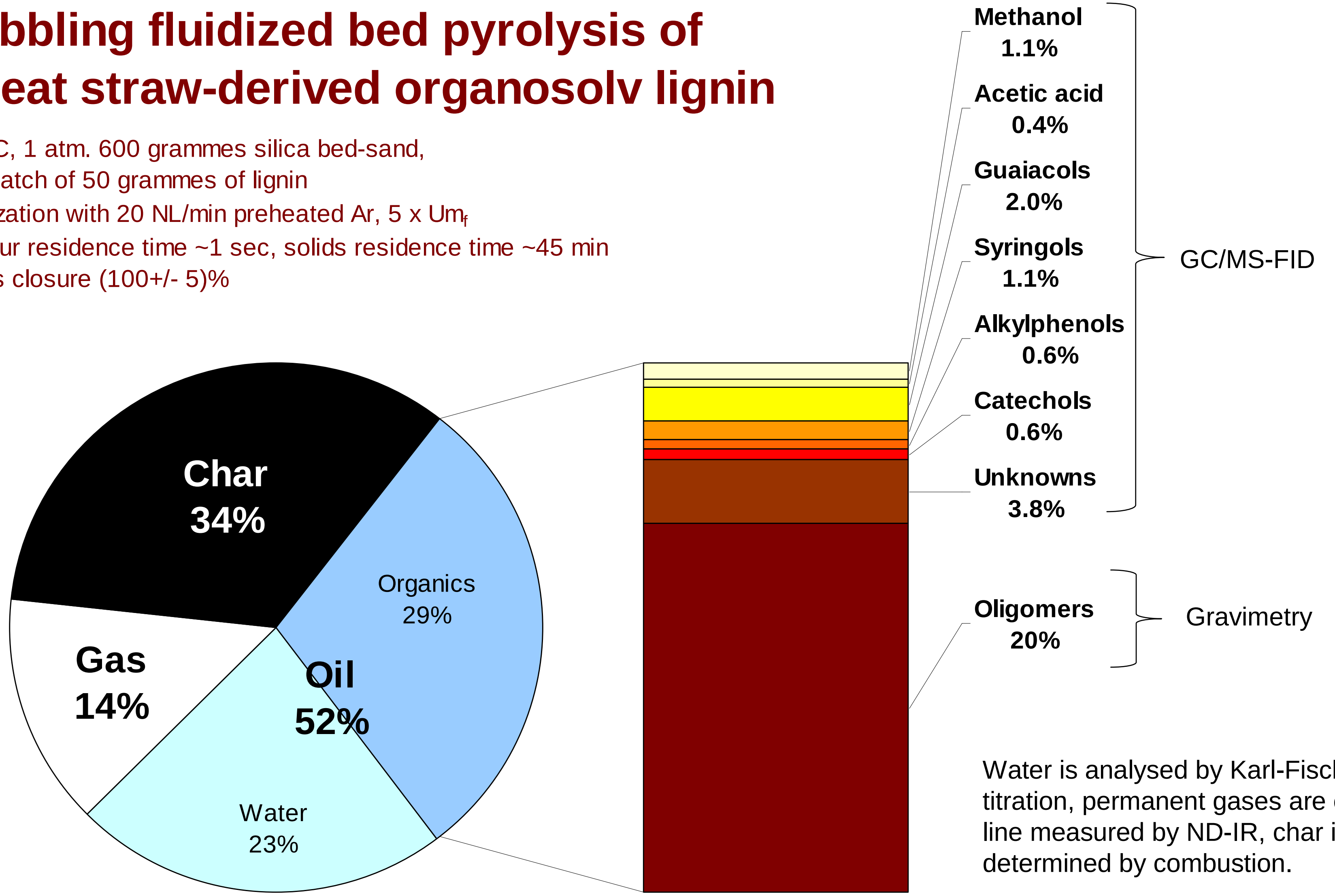
Partial defluidisation of the reactor bed due to agglomeration caused by molten lignin at the screw tip

GC data pyrolysis products wheat straw organosolv lignin



Bubbling fluidized bed pyrolysis of wheat straw-derived organosolv lignin

500℃, 1 atm. 600 grammes silica bed-sand,
fed-batch of 50 grammes of lignin
fluidization with 20 NL/min preheated Ar, 5 x Um_f
vapour residence time ~1 sec, solids residence time ~45 min
Mass closure (100+/- 5)%



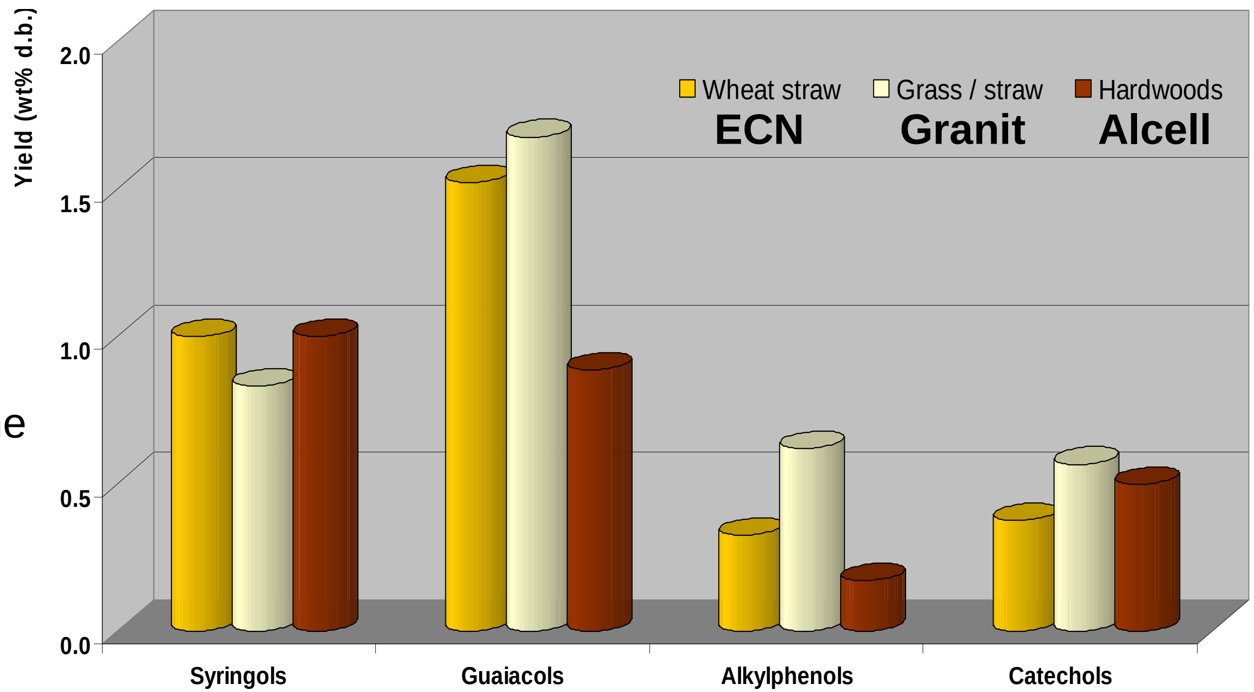
Water is analysed by Karl-Fischer titration, permanent gases are on-line measured by ND-IR, char is determined by combustion.

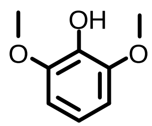
Bio-oil from the pyrolysis of pure lignins at 400 °C

- 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.

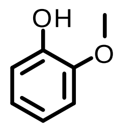
Pyrolysis results reflect compositional differences between the lignins.

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

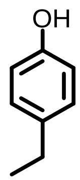




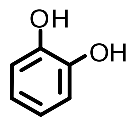
2,6-dimethoxyphenol
(syringol)



2-methoxyphenol
(guaiacol)

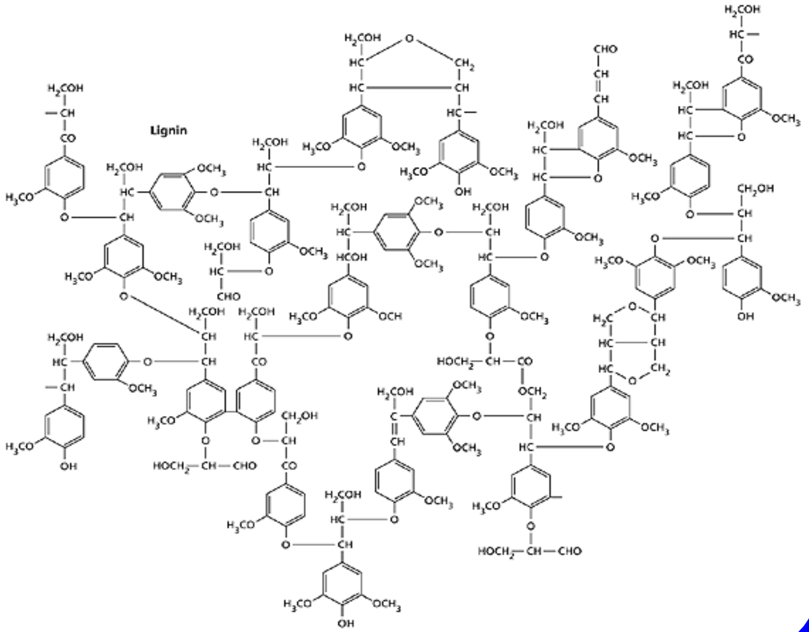


4-ethylphenol



pyrocatechol

Lignin thermal degradation mechanism



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

Lignin

Melting → Pyrolysis

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

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

↑ *degradation*

Monomeric phenols

Catalyst ↑↓ *Condensation / degradation*

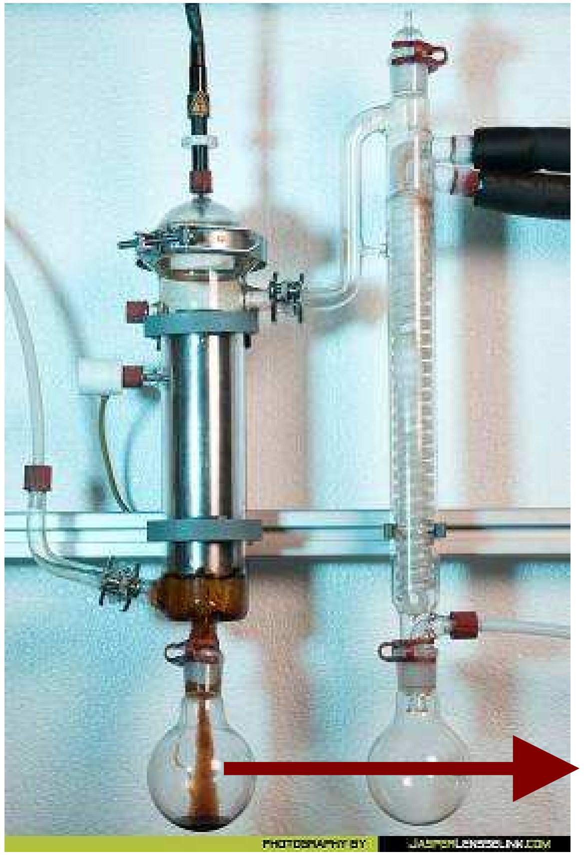
Oligomeric phenols } **Oil**

↓ *Condensation*

Char & ash } **Char**

Bio-oil from continuous catalytic pyrolysis

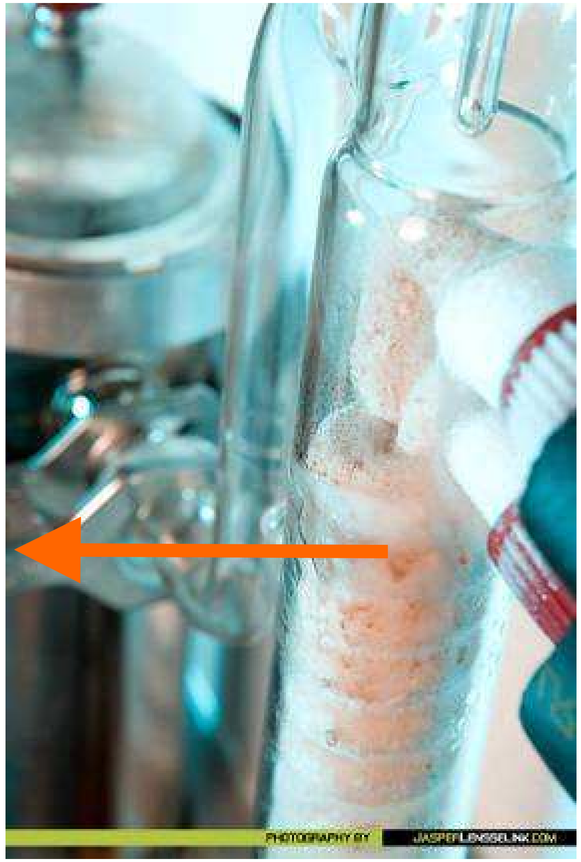
The use of specific catalysts and the development of a feeding protocol involving a cooled screw feeder enabled successful continuous lignin pyrolysis trials



ESP fraction from captured aerosols

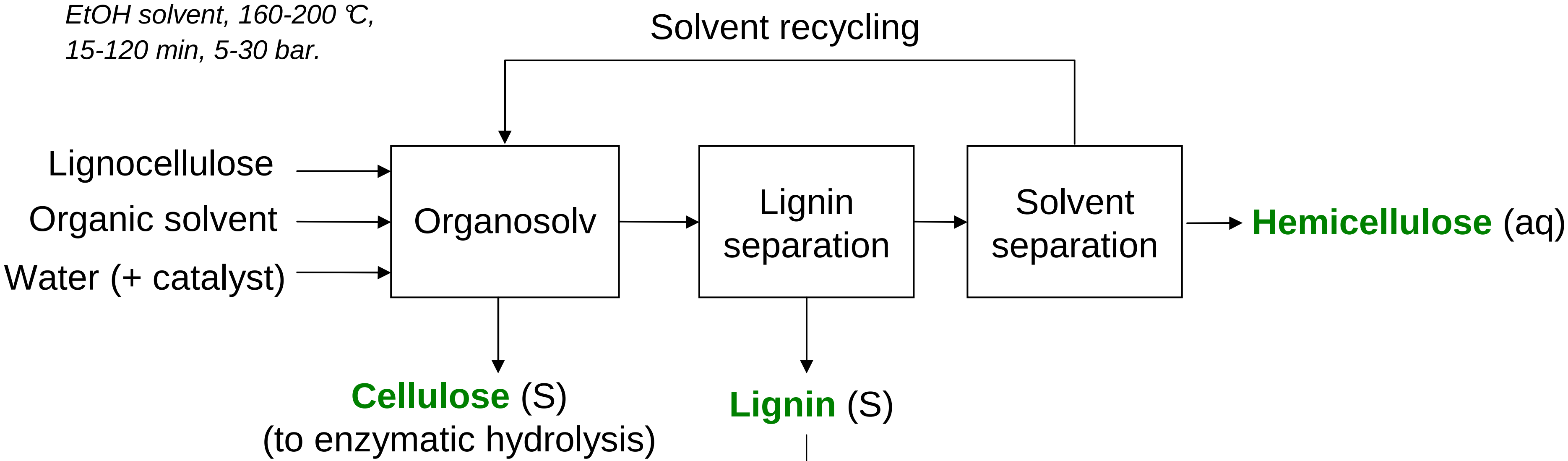
Pyrolytic lignin-oil from Alcell lignin

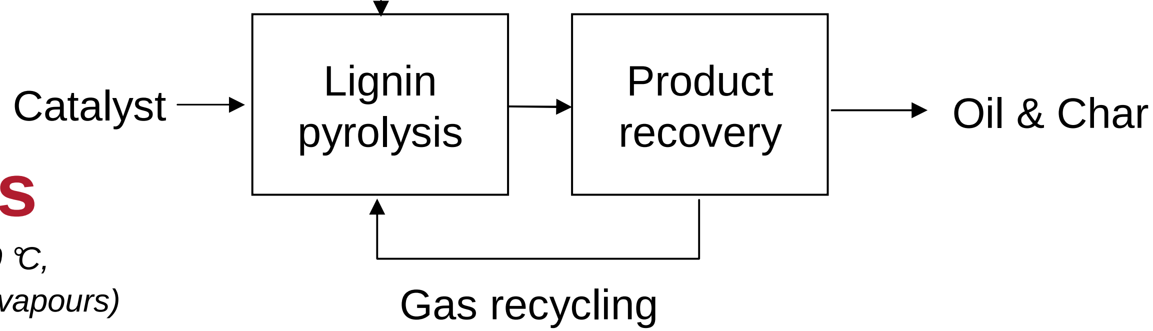
Freeze condenser fraction from low-boiling point components



ORGANOSOLV Process

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

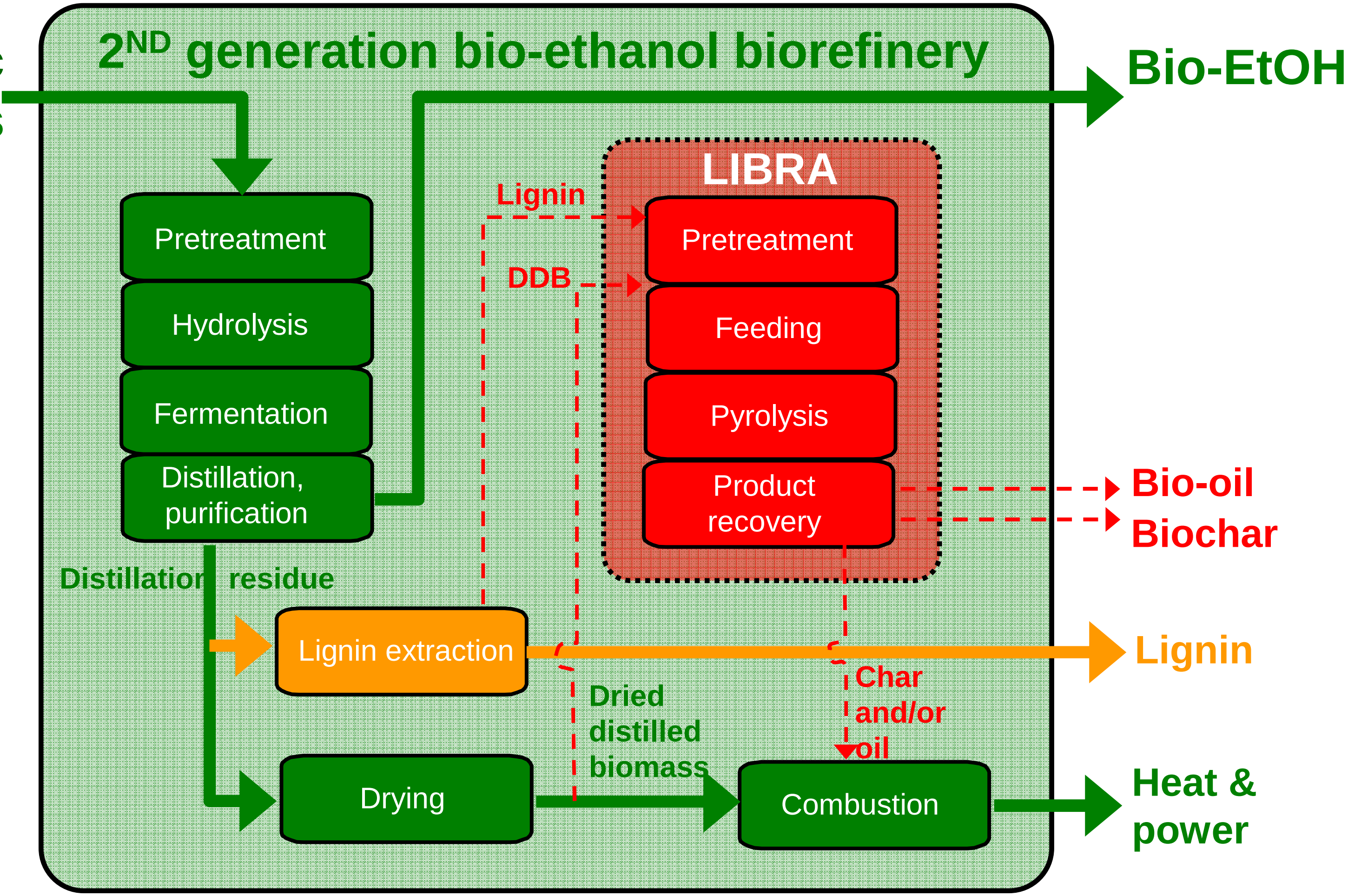




LIBRA Process

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

Lignin BioRefinery Approach (LIBRA)



Conclusions

Lignin from different sources can be valorised by bubbling fluidised bed pyrolysis in a phenolic bio-oil (up to 60 wt%) and biochar (~ 30 - 40 wt%). The bio-oil is a mixture of monomeric and oligomeric phenolic compounds, water and low boiling components like methanol.

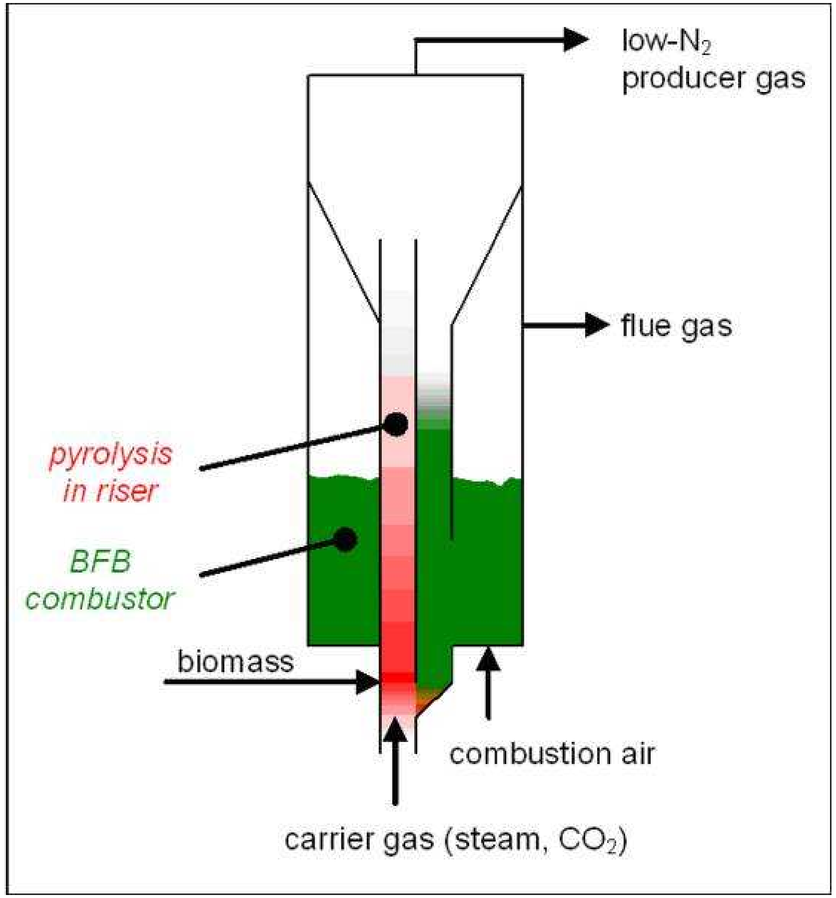
The phenolic compounds can be used as petrochemical substitution options for applications as wood-adhesives (resins), bio-plastics, chemicals, bio-fuels, etc. The biochar has potential as soil improver to decrease the amount of fertiliser.

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

De Wild, P.J., Van der Laan, R.R., Kloekhorst, A., Heeres, E., 'Lignin Valorisation for Chemicals and (Transportation) Fuels via (Catalytic) Pyrolysis and Hydrodeoxygenation', Environmental Progress and Sustainable Energy, 28 (3), 2009, 461 – 469.

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!

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