Johann Heinrich von Thünen-Institut

Institute of Wood Technology and Wood Biology (HTB), Hamburg, Germany

Processes and Products in Wood Based Biorefineries

II Latin American Congress

BIOrefineries - Materials and Energy

May 4-6, 2009, Concepción, Chile

Dietrich Meier

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- Solvolytic biorefinery approaches
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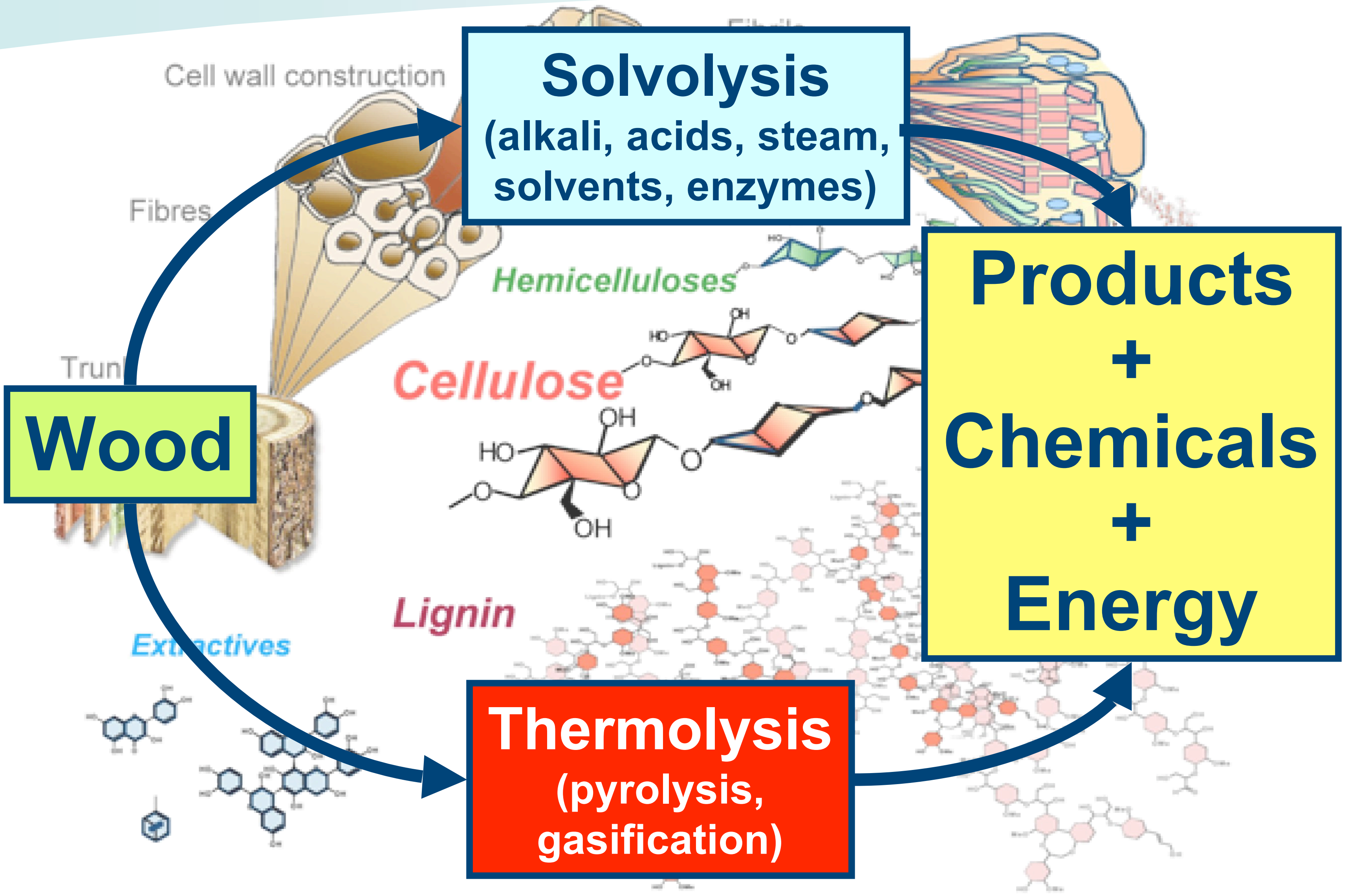
Current Biorefinery Concepts

- **Lignocellulose Feedstock (LCF)-Biorefinery**
  - Cellulose, hemicelluloses, lignin
- Cereal-Biorefinery
  - Starch -> fermentation -> ethanol
  - LC-residue -> thermochem. -> energy, chemicals
- Green Biorefinery
  - natural moisture (grass, premature cereals)
  - direct juice use -> carbohydrates, proteins, fermentation -> LA
- Two Platform Concept
  - Biochemical & thermochemical platforms

Wood Based Biorefinery Stategies

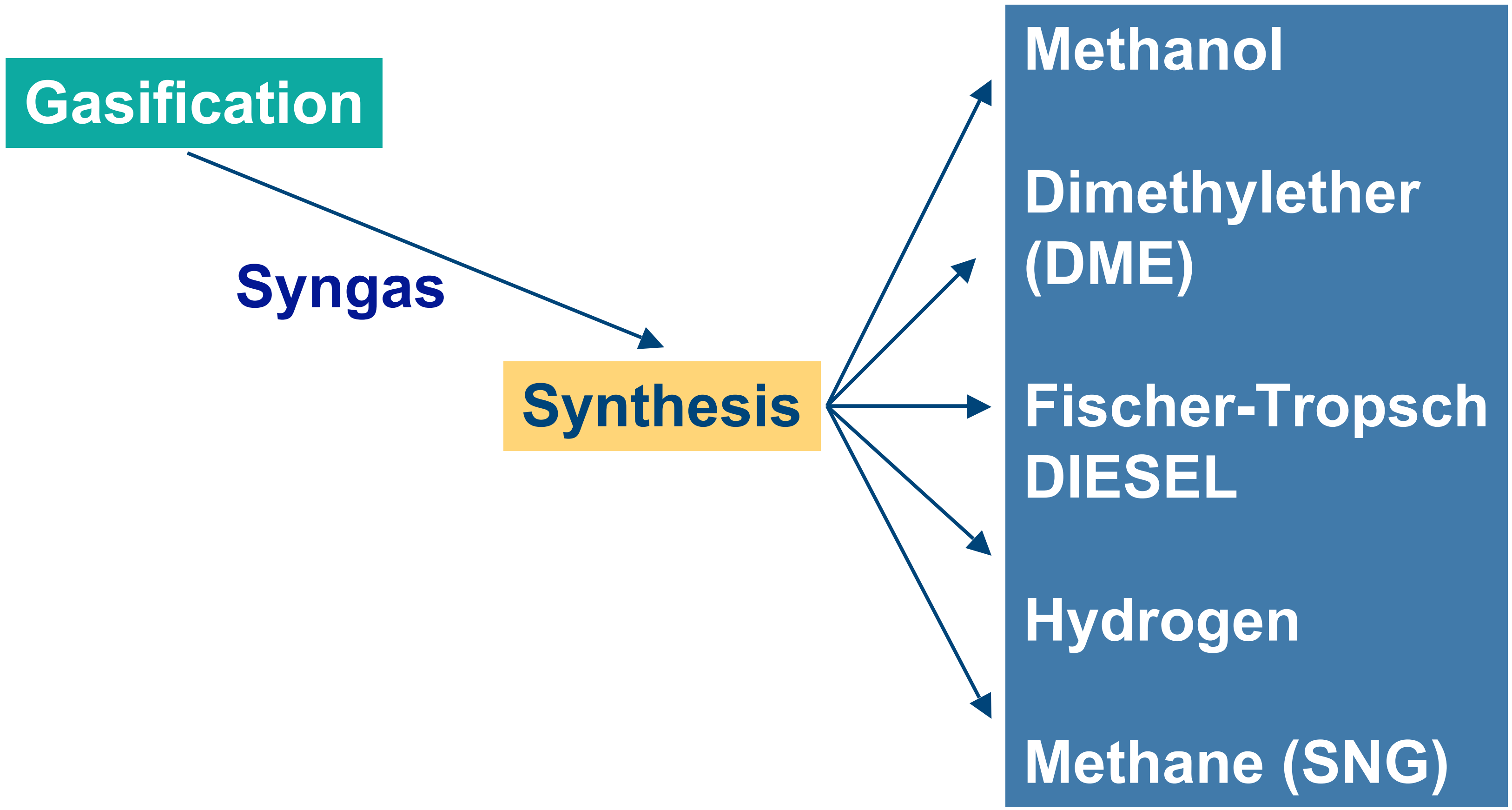


Solvolysis Approaches

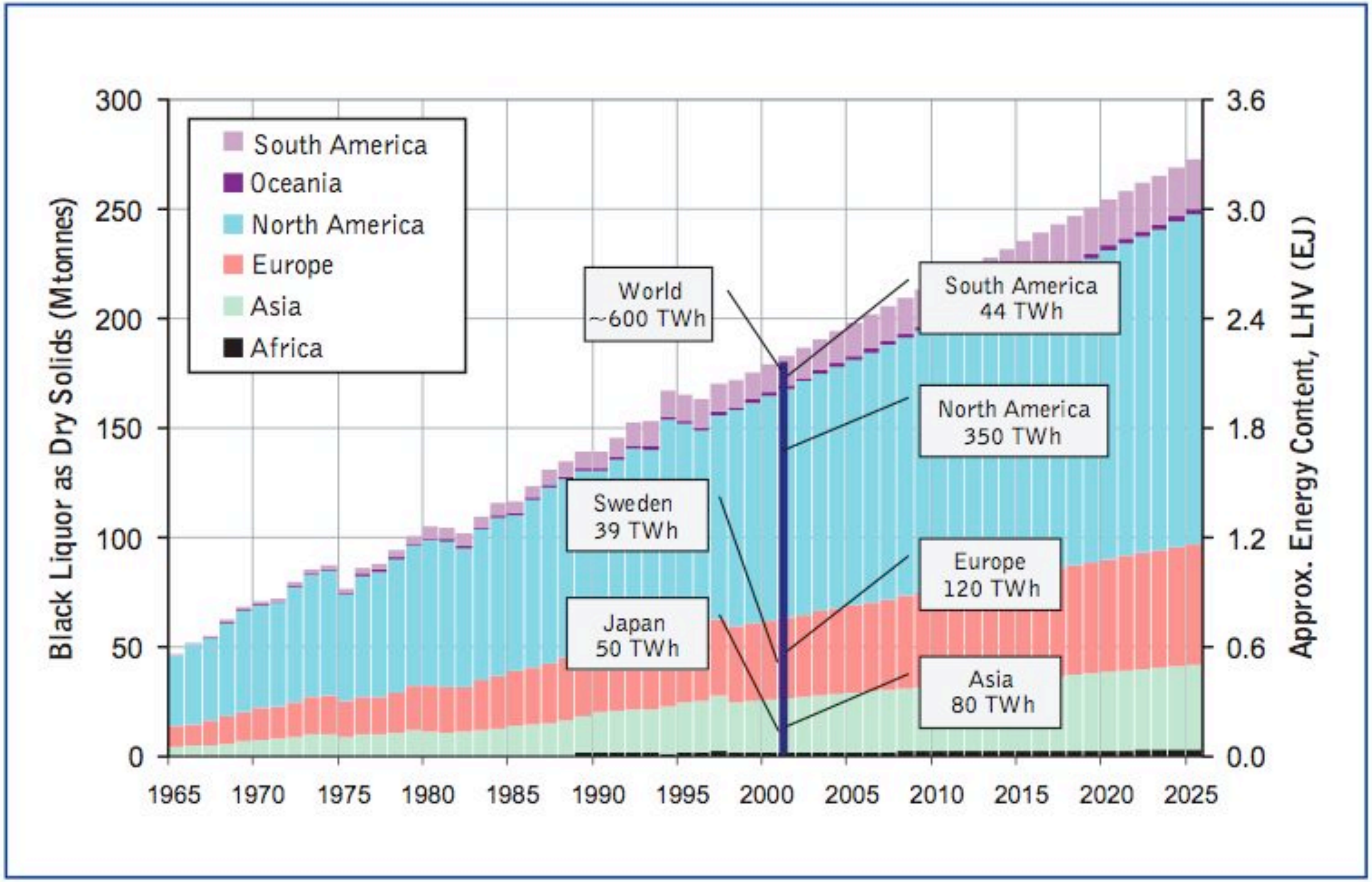
- **Kraft pulping**
  - Fibers
  - Sugars
  - **Black liquor -> gasification -> syngas -> fuels & chemicals**
  - **Lignin**
    - macromolecule -> resins, polymer fillers, carbon fibers
    - aromatic monomers -> BTX chemicals, phenol(s), aromatic polyols

- **Pretreatments**
  - Steaming, hydrothermolysis
    - opens cell wall, increase of inner surface area
    - extraction with water for hemis and alkali for lignin
    - no extractives recovery
  - **Organosolv pulping with alcohols**
    - only for hardwoods
    - Separation between cellulose, xylan and lignin is possible

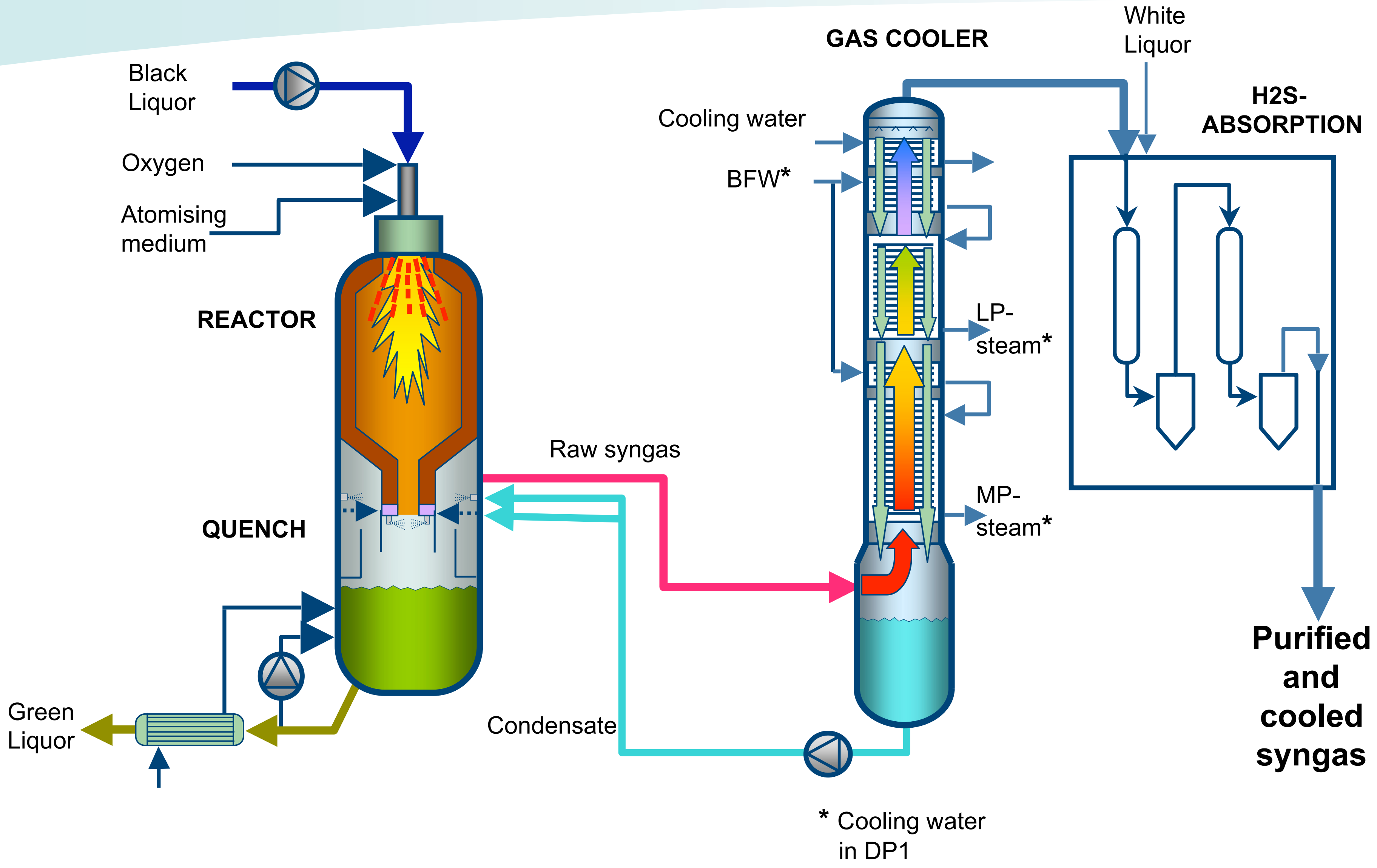
Black Liquor Gasification (BLG): Alternative Fuels Options



Estimated Black Liquor World Production
(FAOSTAT, 2001).

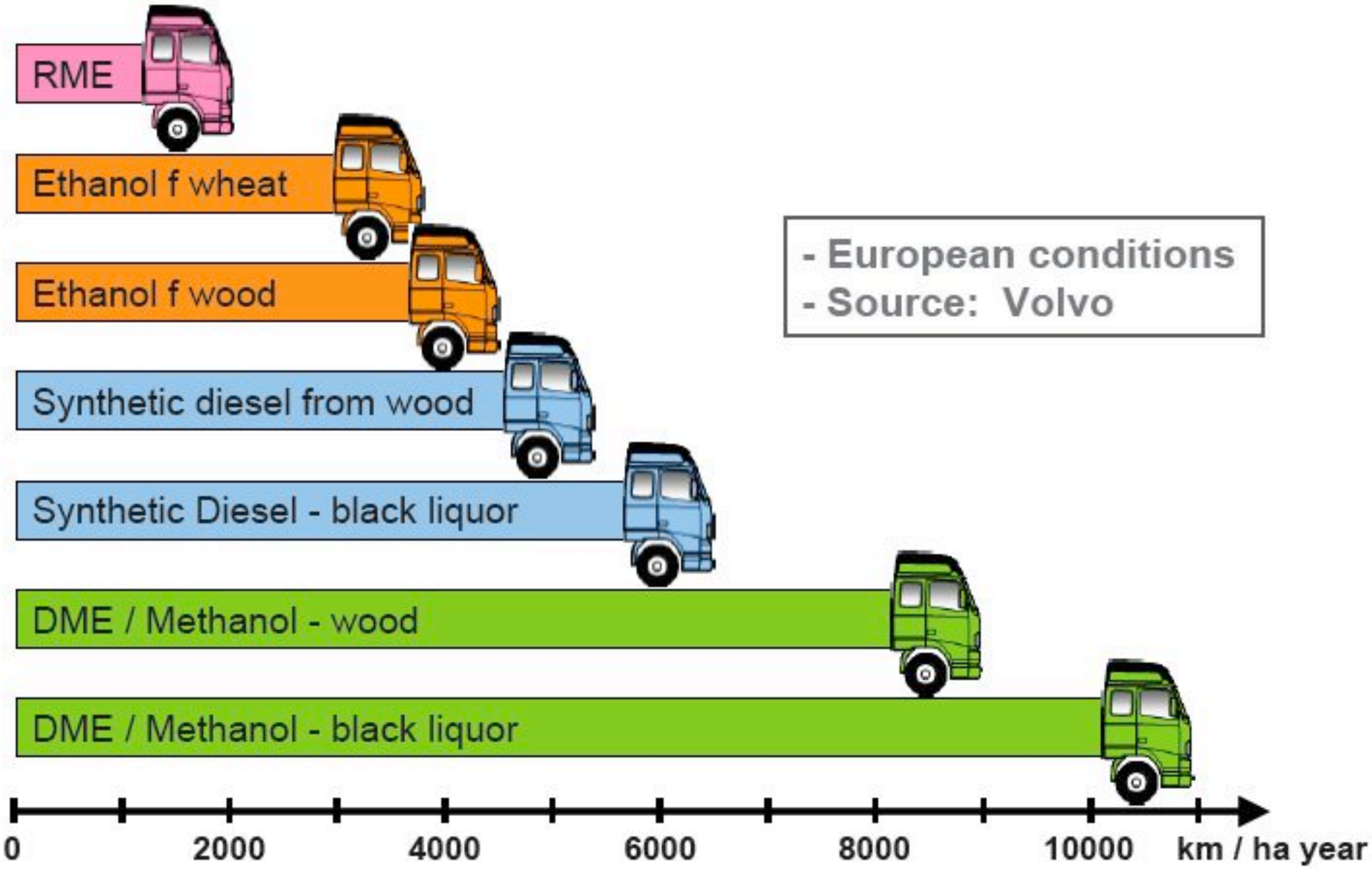


Black Liquor Gasification with Motor Fuel Production (BLGMF) using CHEMREC's Technology



BIO-DME: Land Use Efficiency

www.biodme.eu

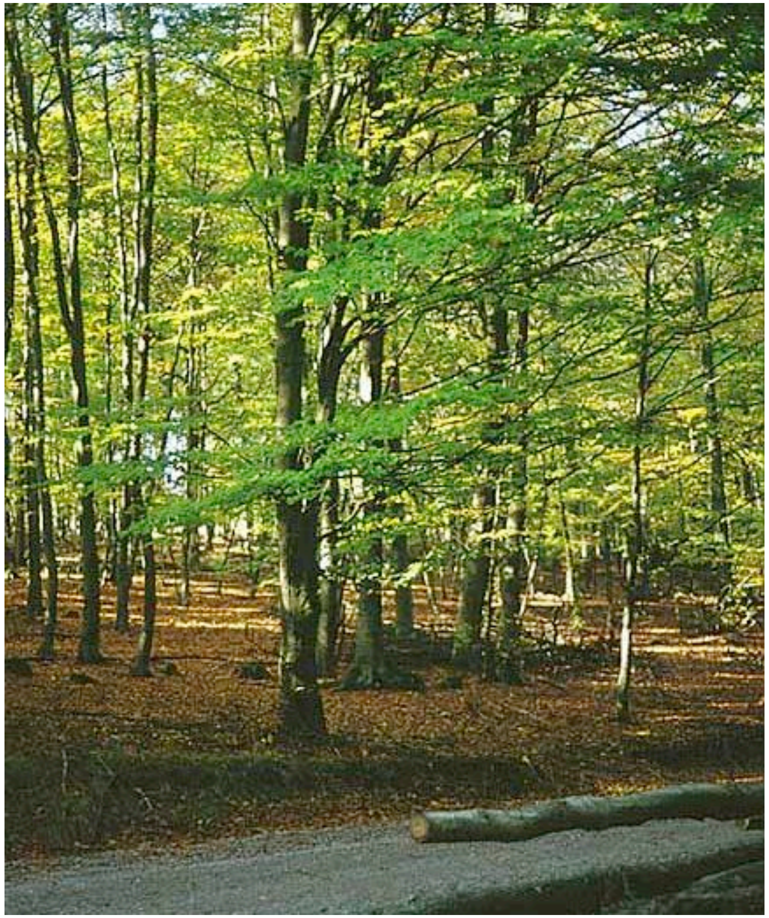


BIO-DME: DME plant in Piteå, Sweden (Chemrec/Haldor-Topsøe)

Down-stream from Chemrec's existing development plant for black liquor gasification, Chemrec and Haldor Topsøe will construct a DME plant using novel synthesis technology from Haldor Topsøe

Why Beech Wood Biorefinery?

- Moderately lignified wood (20 wt.%)
- Poor in extractives
- Only one hemicellulose (xylan) present
- Little competition with pulp and wood panel industry
- Some competition with furniture industry
- Widely available (14 % of the total forest area of 10.8 Mio ha in Germany are covered with beech)

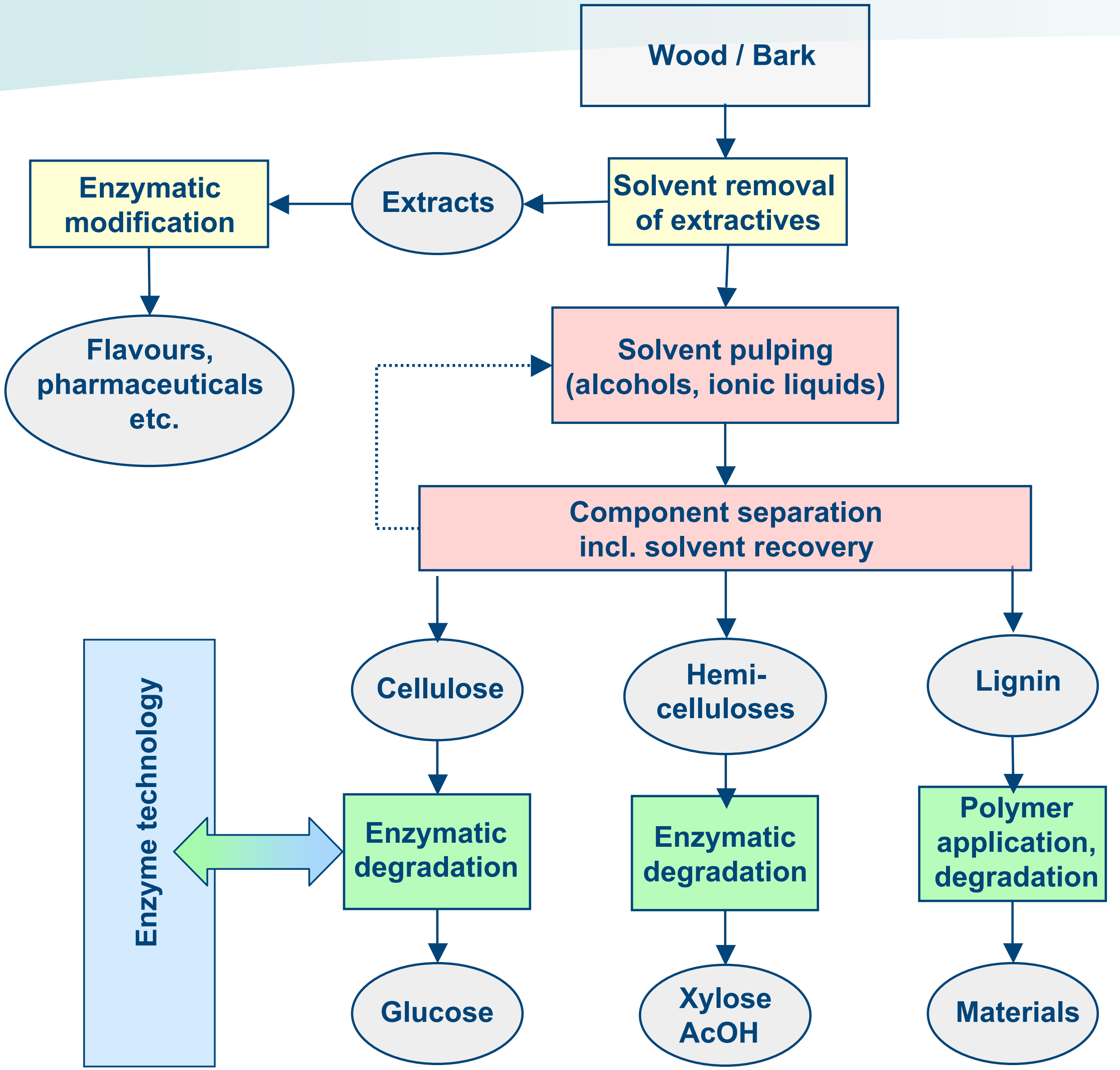


18 Partners of the German Beech Wood Biorefinery Project

Funded by German Agency for
Renewable Resources (FNR)

- Bayer Technology Services
- Biopos
- Boehringer Ingelheim
- Dechema
- Degussa Evonik Industries
- Dow Deutschland
- Dynea Erkner
- Fraunhofer Institute for Chemical Technology
- Solvent Innovation
- Tecnaro
- Universities
  - Erlangen
  - Göttingen
  - Kaiserslautern
  - Karlsruhe
  - Munich
  - Rostock
- vTI

Scheme of the Beech Wood LCF Biorefinery Concept



Materials Balance

Debarked Wood

↓

Pulping Process

Fibers (56.8 %) ← Pulping Process → Organic Solution

Fibers (56.8 %) → Enzymatic Hydrolysis

Organic Solution → Lignin Precipitation

Σ of Products:
81.3 % b.on Wood

Enzymatic Hydrolysis → Mono-saccharides (39.2 %)

Enzymatic Hydrolysis → Hydrolysis-Lignin (15.4 %)

Lignin Precipitation → Organosolv-Lignin (13.4 %)

Lignin Precipitation → Other Products:

Xylose:	5.8 %
Acetic Acid:	6.3 %
Formic Acid:	1.0 %
Furfural:	1.2 %

LCF Biorefinery: Preliminary Conclusions & Perspectives from 1st Phase

- High hydrolysis yields can be obtained by high pulping temperatures or by addition of acids at lower temperatures.
- Maximal hydrolysis yields are obtained by extension of incubation time (72 h).
- Moderate delignification allows for an effective enzymatic hydrolysis.
- No inhibition in pulping and enzymatic hydrolysis by addition of bark.
- Organosolv lignins have high purity and show promising results in resin applications.
- Application of organic acids and ionic liquids will be investigated as an alternative for H_2SO_4.
- IL‘s indicate also lignin degradation

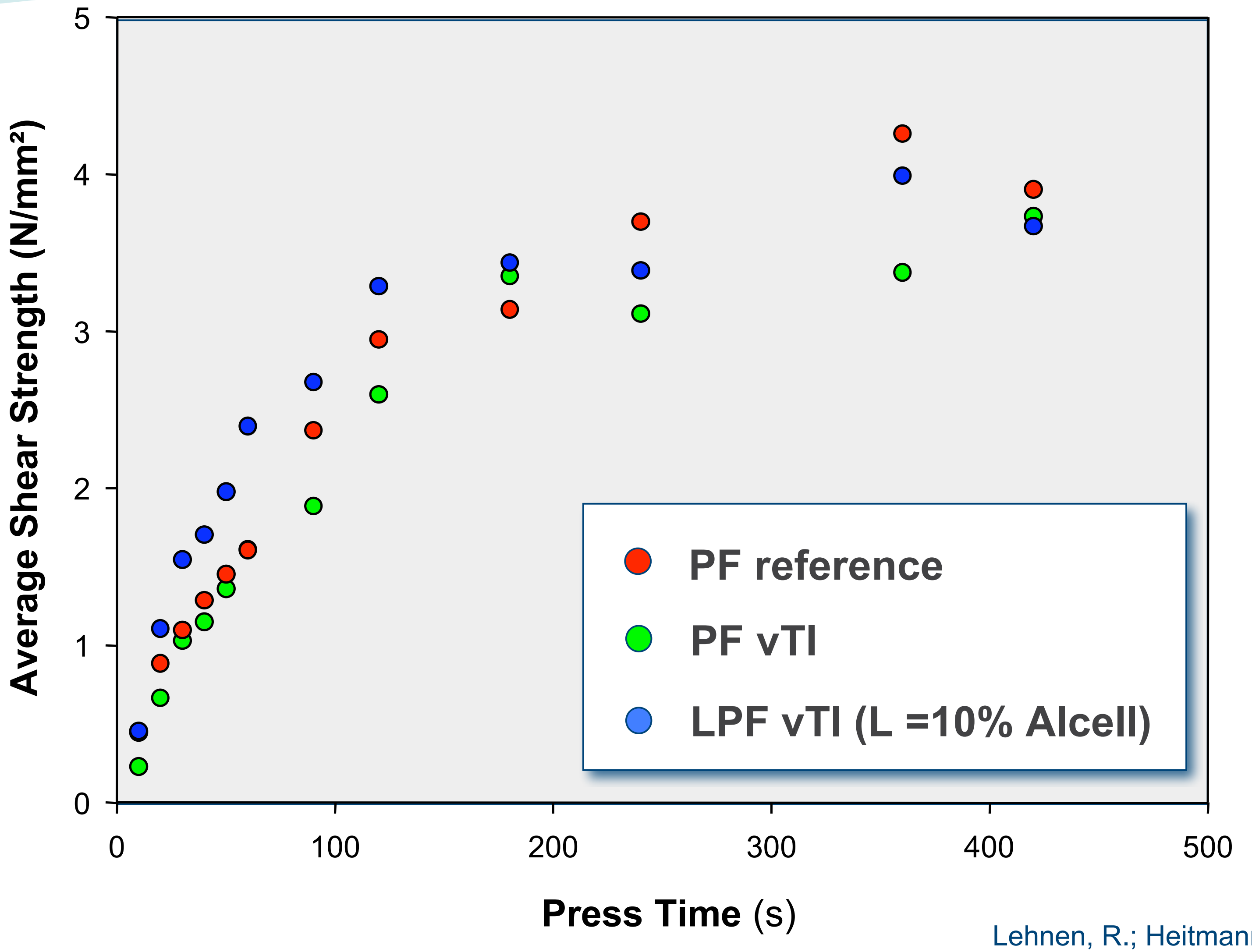
LCF Biorefinery: 2nd Phase

- Construction of pilot plant for organosolv pulping

- Sugars
  - ABE-fermentation
  - Dicarbonic acids
  - Acrylic acid
  - Polyalcohols

- Lignin
  - Phenolic resins
  - Polyurethanes
  - Compounding
  - Monomeric phenolics

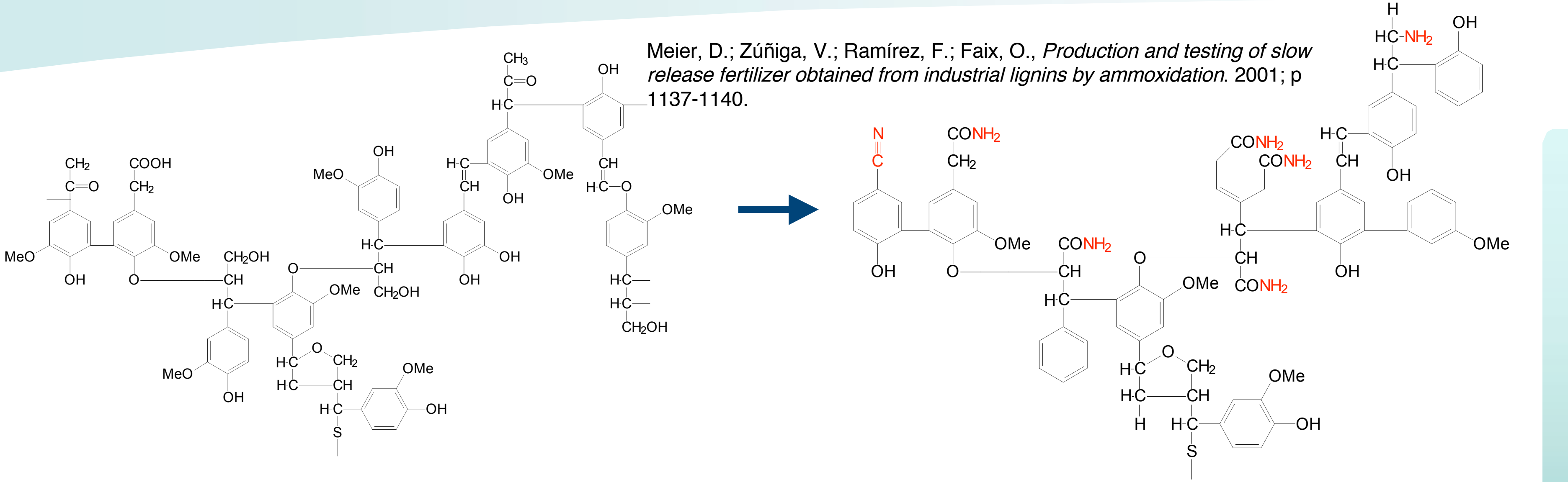
Organosolv Lignin in PF resins

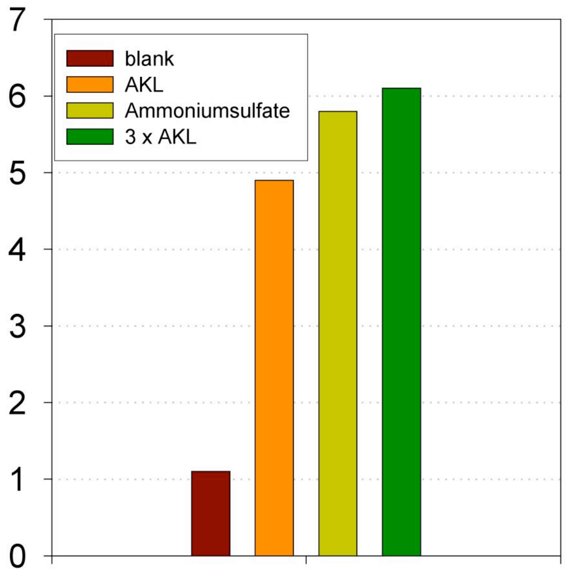


Lehnen, R.; Heitmann, M. (2009)

Lignin for Slow Release Fertilizers by Oxo-ammoniation

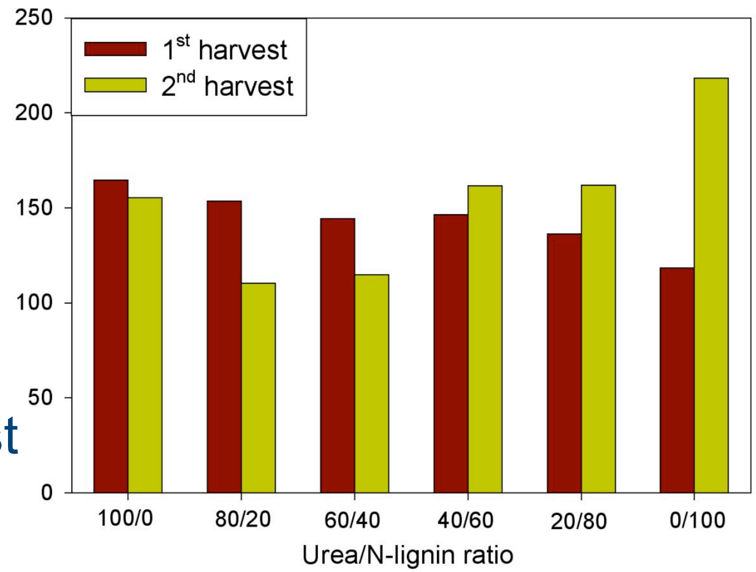
Meier, D.; Zúñiga, V.; Ramírez, F.; Faix, O., *Production and testing of slow release fertilizer obtained from industrial lignins by ammoxidation*. 2001; p 1137-1140.





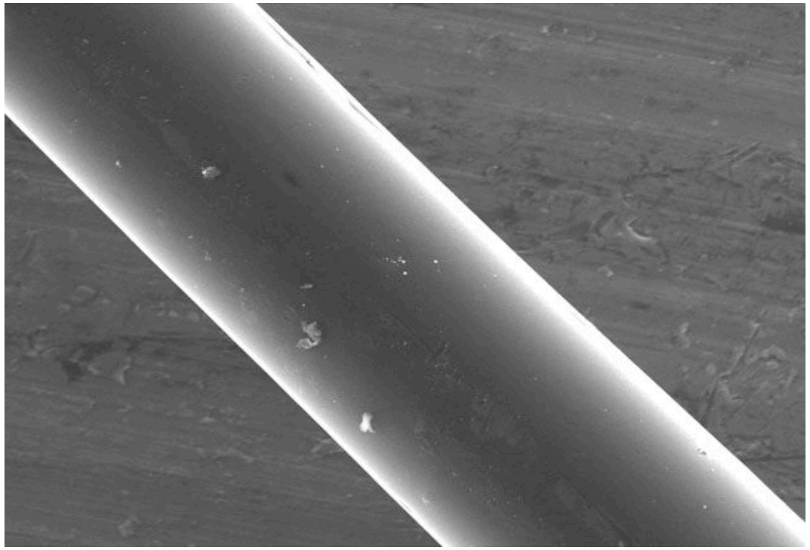
pot test

field test

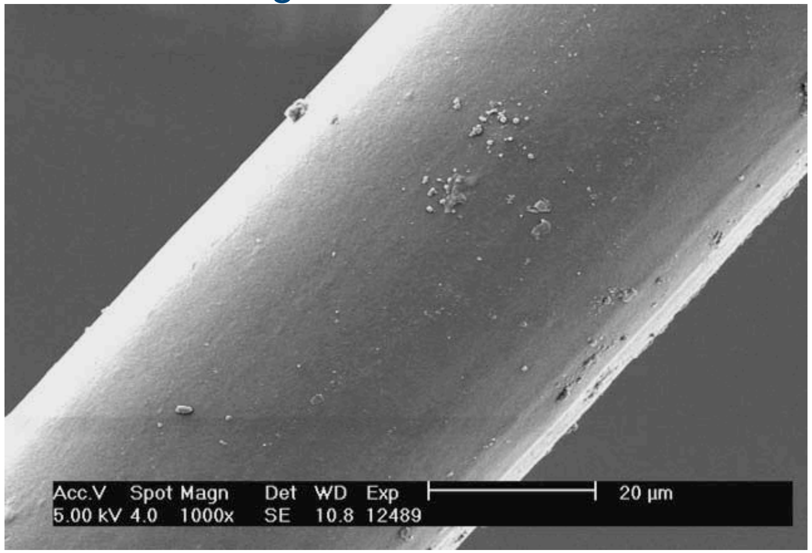


Lignin for Carbon Fibers

Scanning Electron Micrograph Showing End of As-Spun Lignin-Blend Fiber.



Scanning Electron Micrograph Showing Carbonized Lignin Blend Fiber



- New generation of vehicles
- Light weight programme

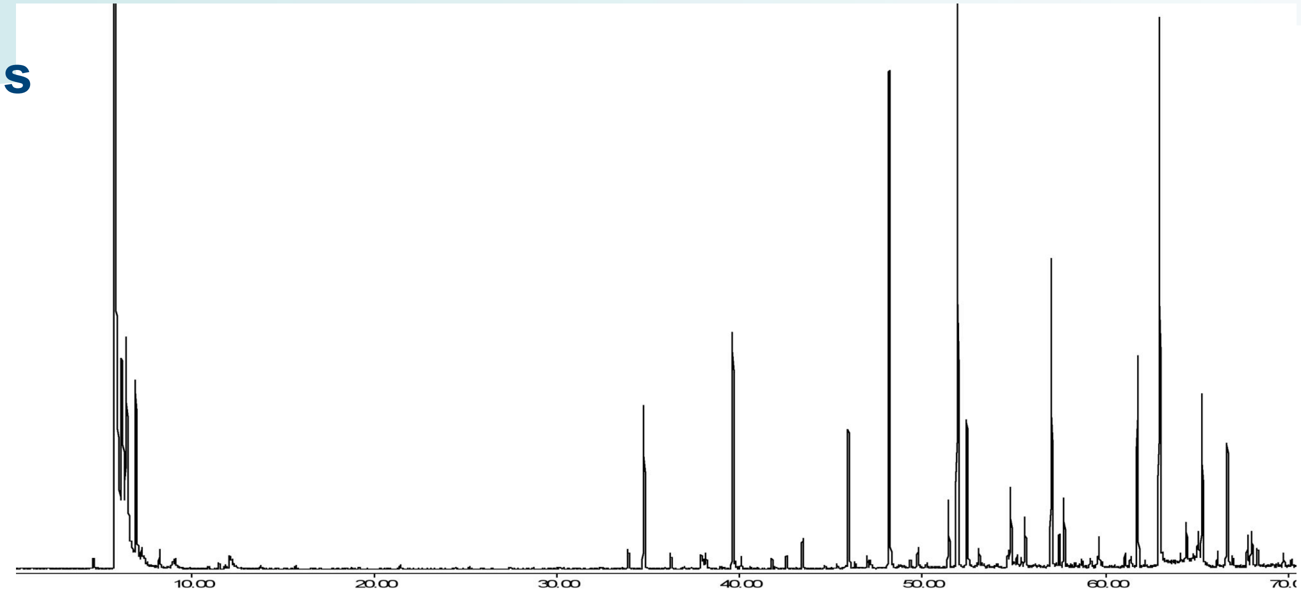
source: Oak Ridge National Laboratory, Tennessee, USA

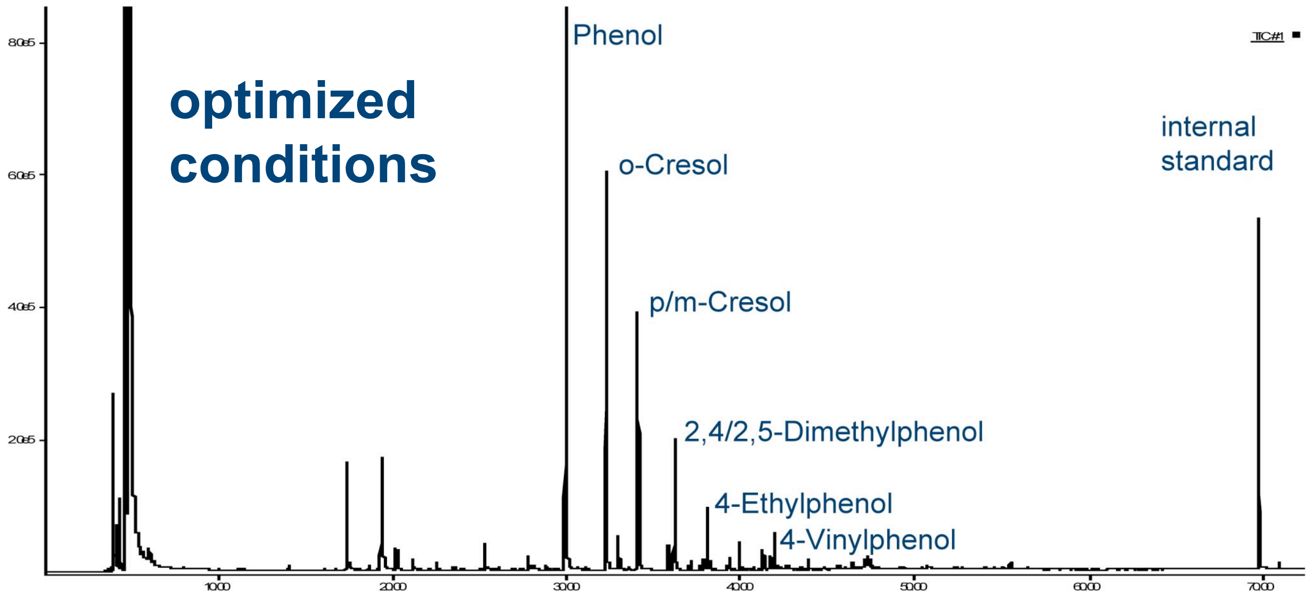
Degradation of Lignin for Chemicals

- Thermochemical degradation
  - Hydrockracking
  - Pyrolysis
  - Gasification
- Oxidation

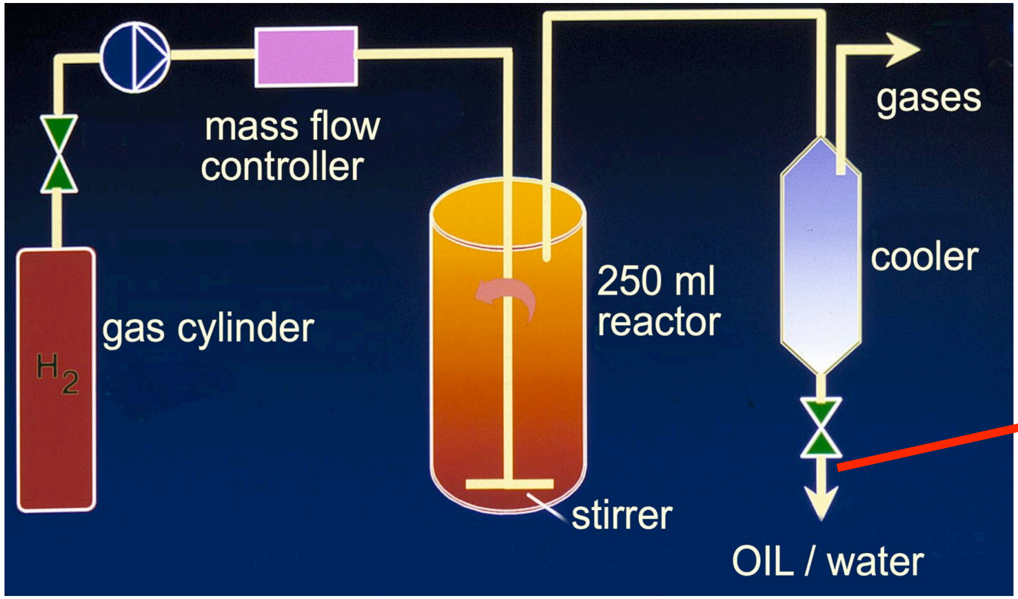
Lignin: Pyrolysis

normal conditions



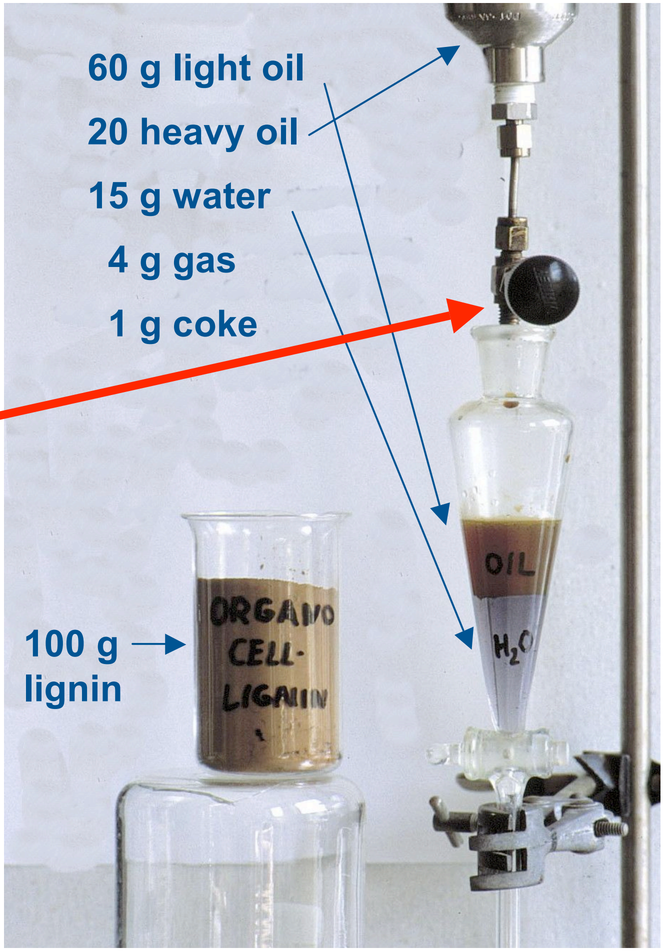


Lignin: Catalytic Hydropyrolysis



Apparatus for Hydrocracking

Mass Balance

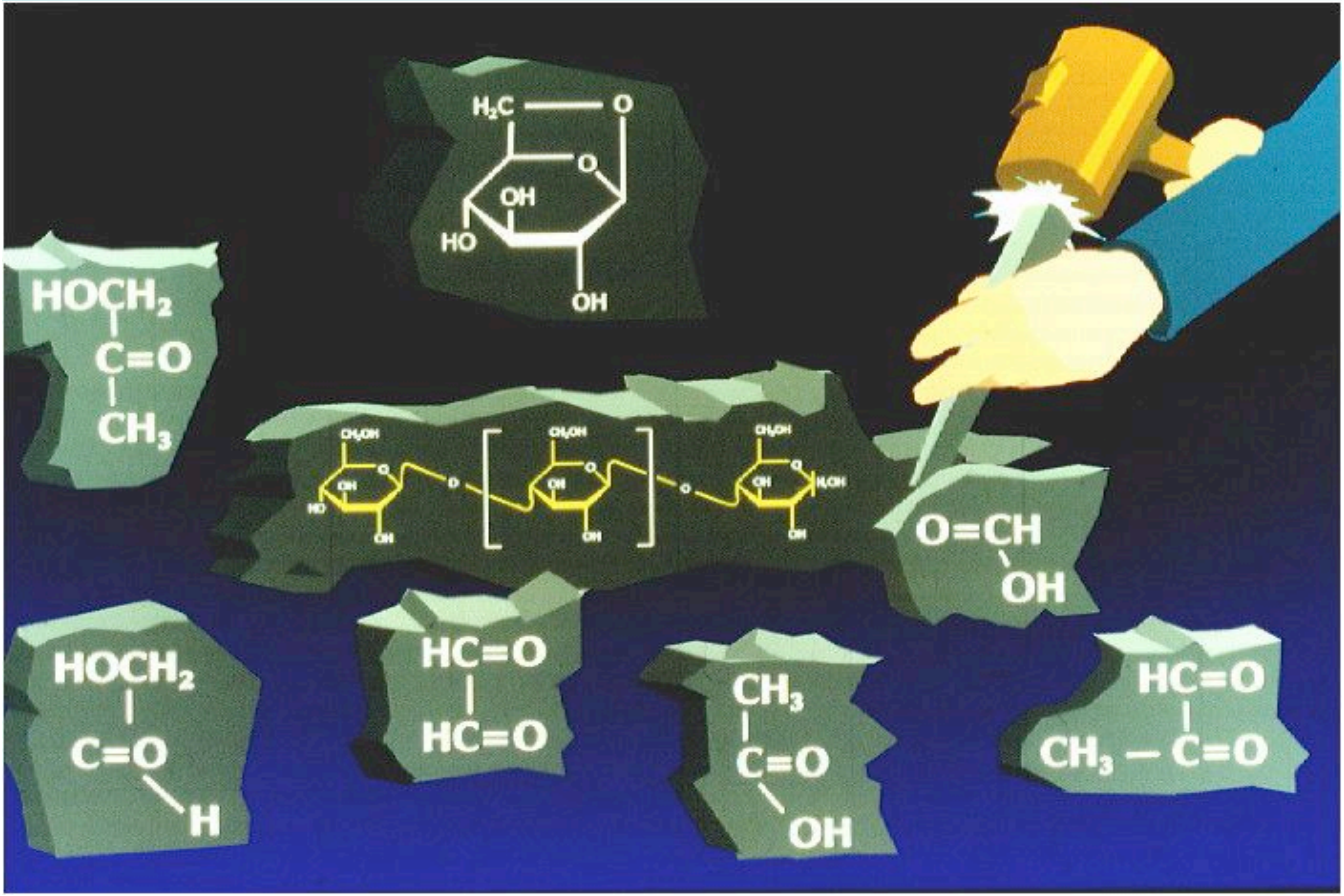


The Thermochemical Biorefinery

- Classic approach
  - **limited feedstock** selectivity (conditioning)
  - (pretreatment necessary with **pressure processes**, e.g. organosolv, steam)
  - separation & cleaning
  - Use **only after conversion** or modification (degradation to monomers, functionalisation, polymerisation)

- Thermochemical approach
  - **broad selection of raw LC** materials (e.g. straw, bark, DDGS, shells, etc.)
  - simple thermal treatment by fast-pyrolysis at **atmospheric pressure**
  - **decentral conversion - central refining** (separation & cleaning)
  - **Direct or indirect** use after modificationen

From the Idea... ... to the Concept

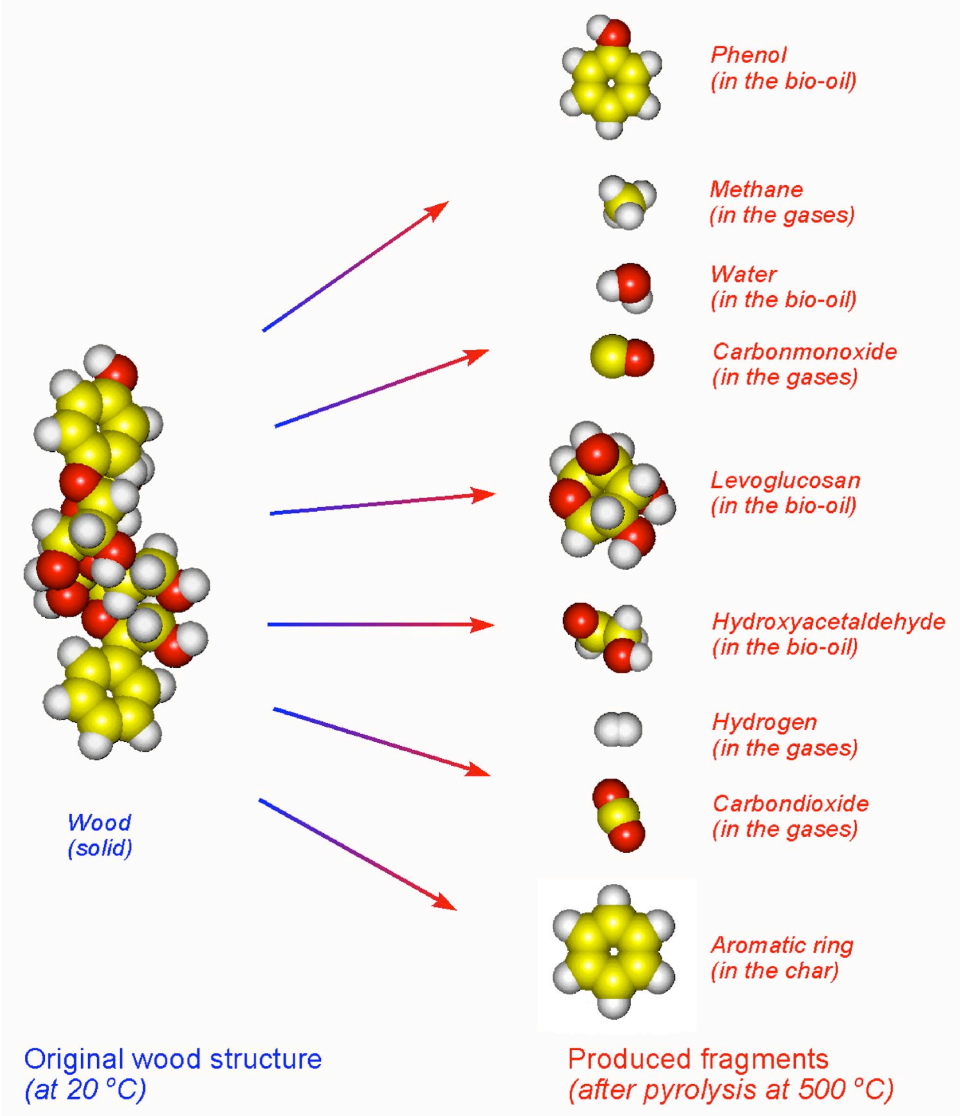


Fast Pyrolysis Principle

- Fast chemical degradation due to rapid heating in the absence of oxygen

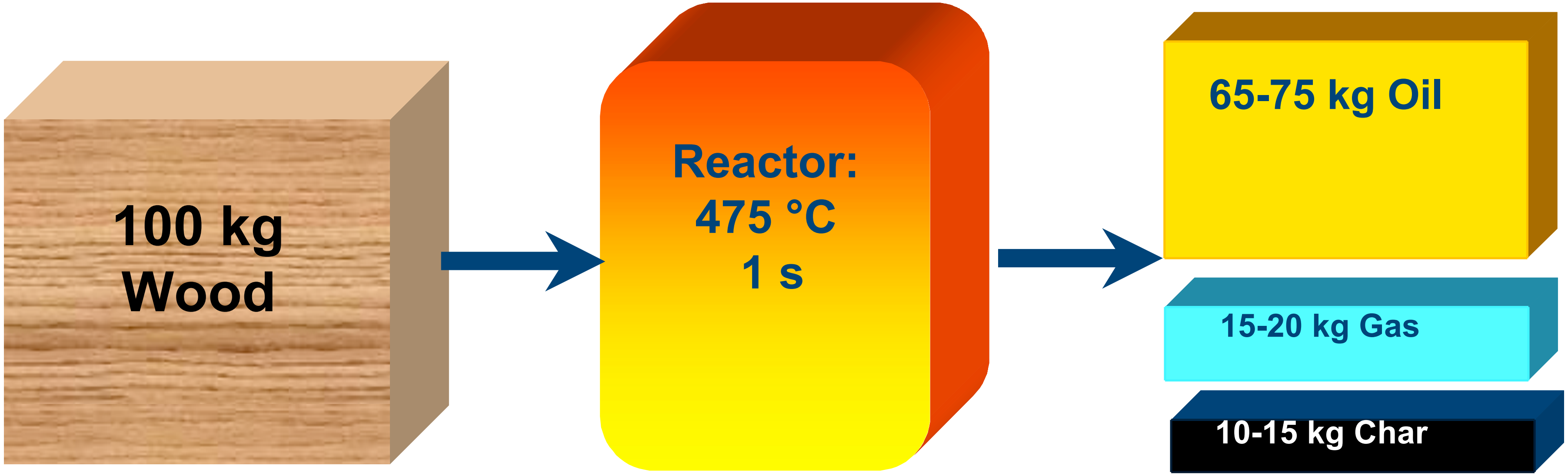
- Process characteristics:
  - Temperature 500 °C
  - Pressure 1 bar
  - Particle size < 5 mm
  - t vapours < 2 s

- The main product is a liquid: Bio-Oil or Bio Crude Oil (BCO; approx. 70 wt.%)

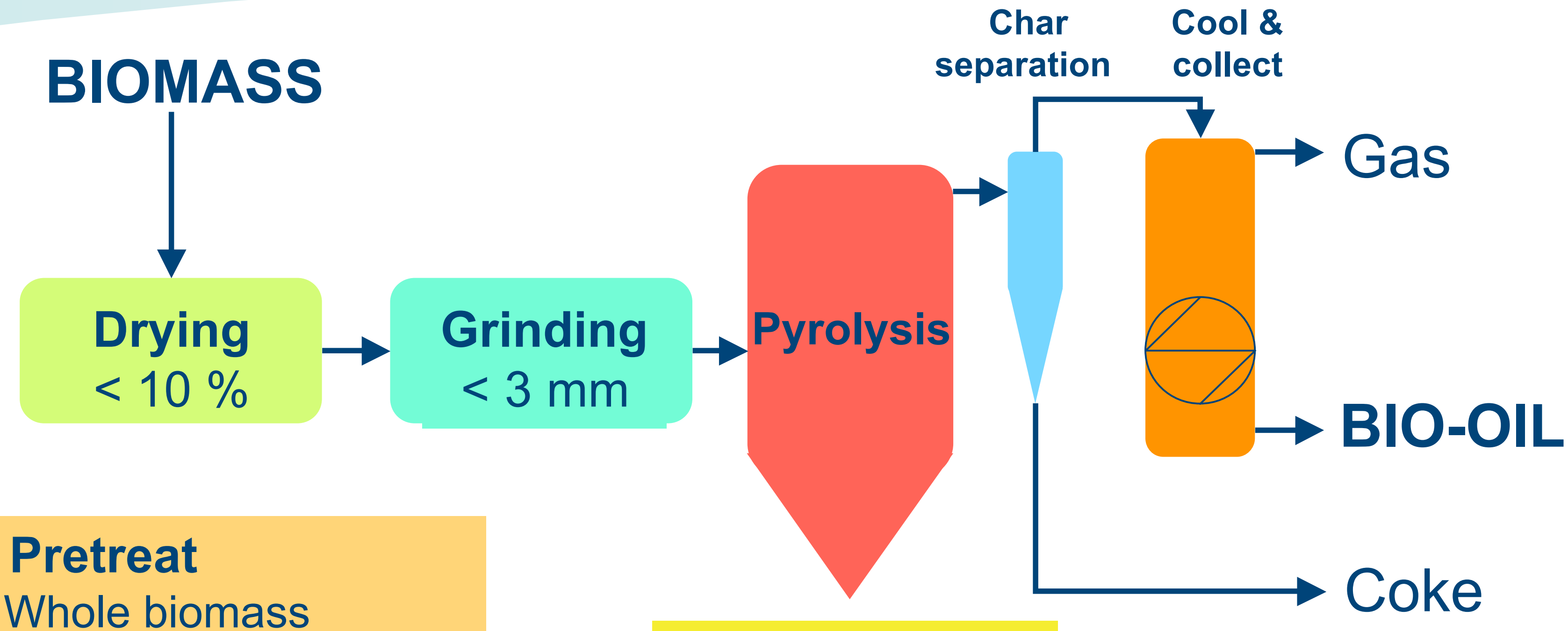


Prins, W., 2007

Typical Mass Balance of Fast Pyrolysis Processes



Pyrolysis Process Modifications



Pretreat

- Whole biomass
  - Remove ash
  - Add catalyst
- Separate bio-polymers into cellulose and lignin
  - Pulping
  - Biorefineries

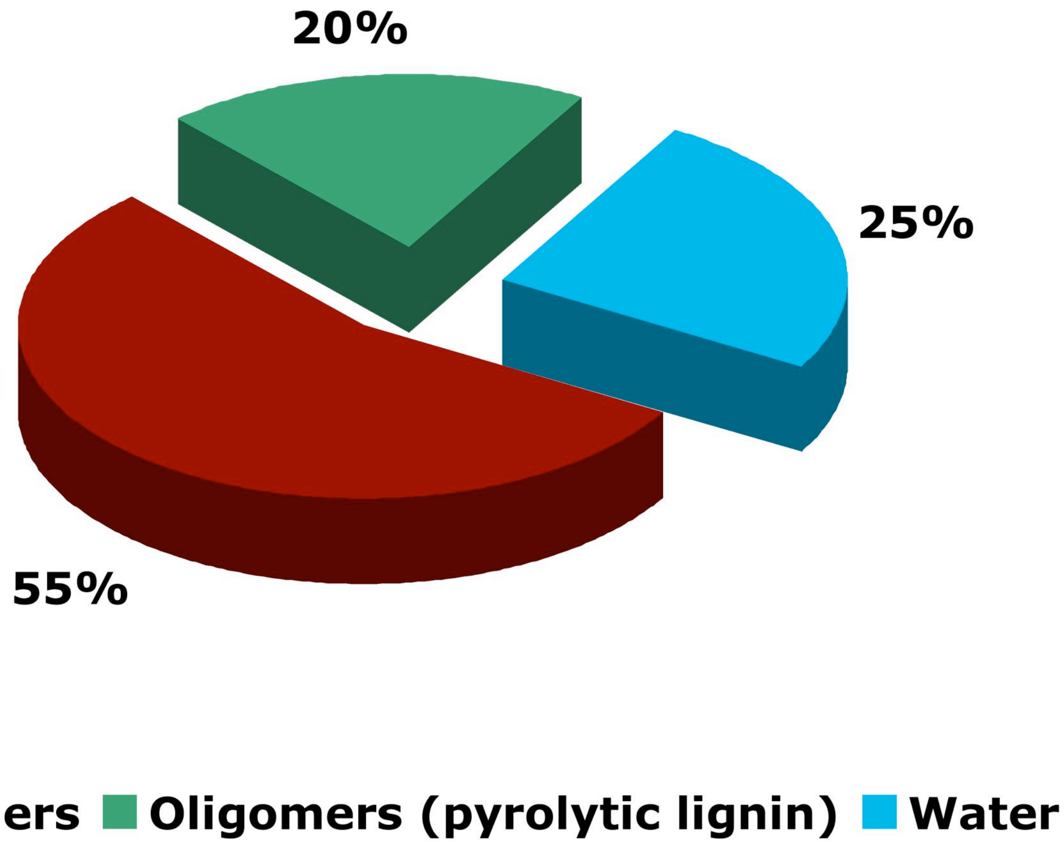
Pyrolyse

- Vary parameters
  - Temperature
  - Time
  - Pressure
  - Atmosphere
- Add catalysts

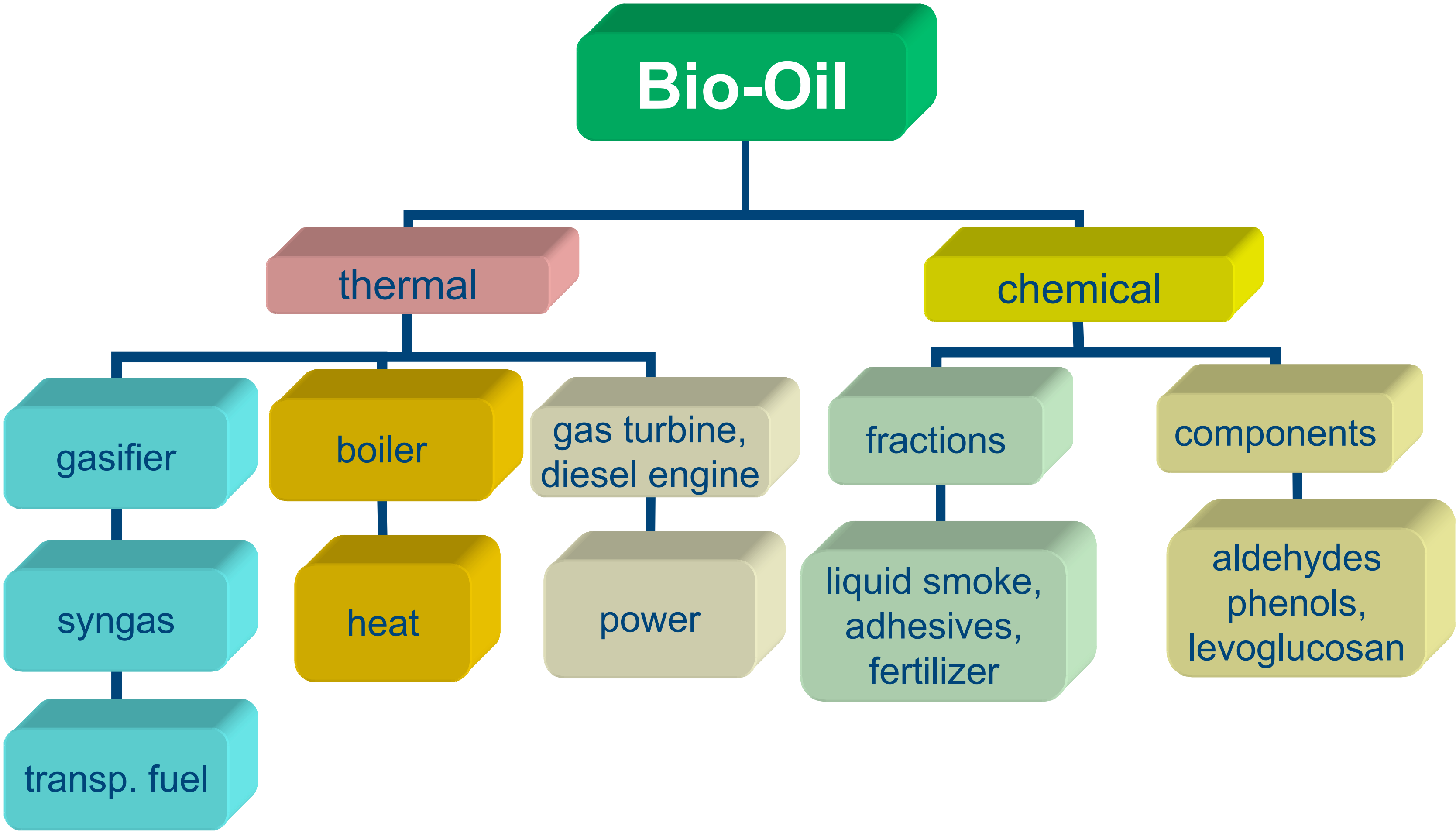
Upgrade

- Physically
  - Staged condens.
- Chemically
  - React, derivatize
  - De-oxygenate
  - Gasify to syngas

Overall Composition of Fast Pyrolysis Liquids



Utilization Pathways for Pyrolysis Liquids



FZK BioLiq-Concept
(Straw => MeOH)

regional 50 MW (th)
Fast pyrolysis plants

Conditioning
milling, drying

Fast pyrolysis
1 bar, ~500 °C, t some s

Oil/Coke-Slurry

Slurry transport by train from 20 to 40 pyrolysis plants

to a central gasification plant

Entrained flow gasifier
~1300 °C, >60 bar, t 2-3 s

teerfreies Rohsyngas

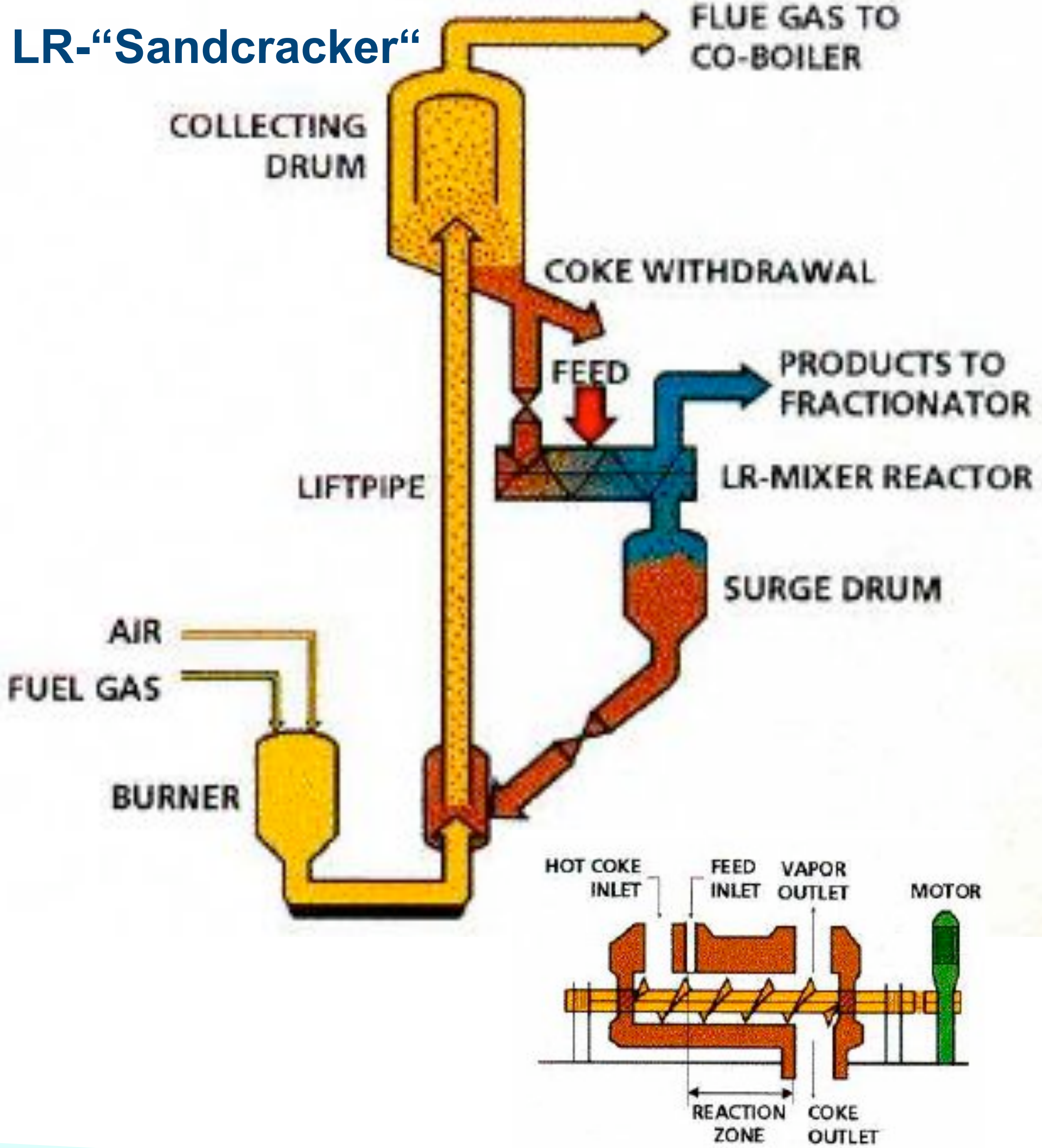
Gas cleaning
Gas conditioning

Synthesis gas

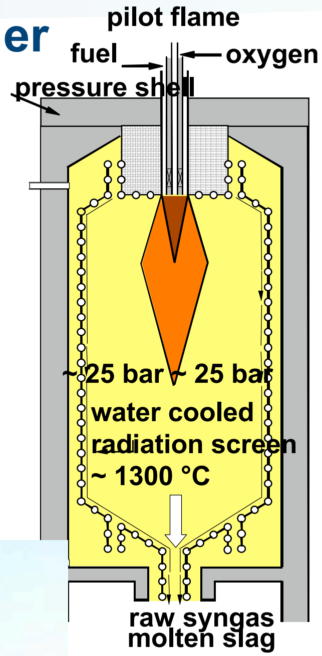
bioliq
Biomass to Liquid Karlsruhe

Features of the Bioliq-Process

LR-“Sandcracker“



Gasifier



FZK pilot plant

RTP™ Technology of ENSYN, Canada

- 6 commercial plants in operation
- 2000 t Bio-oil per month, mainly for liquid smoke aroma
- largest plant: 80 tpd

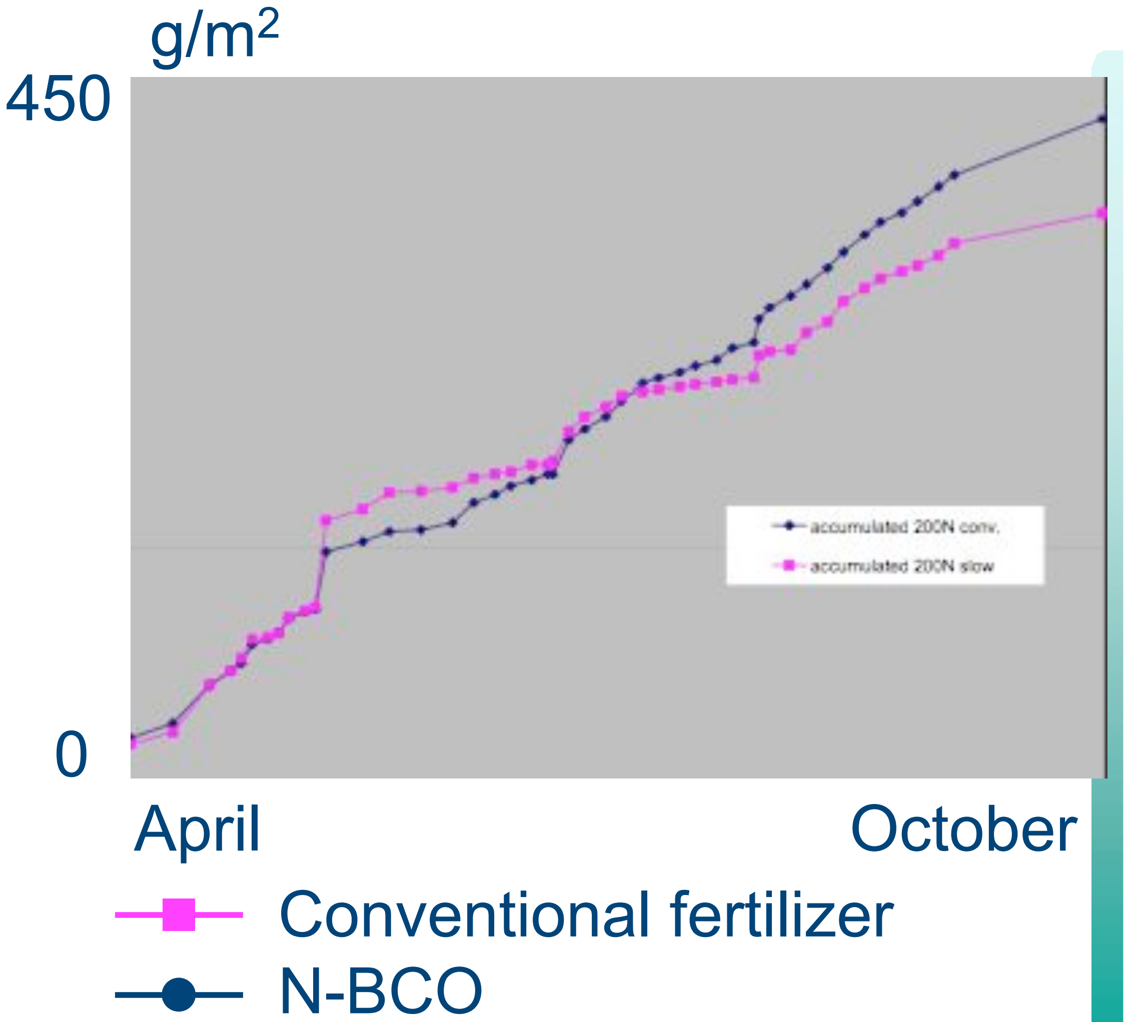
50 tpd RTP™ plant

40 tpd Rhinelander, two plants

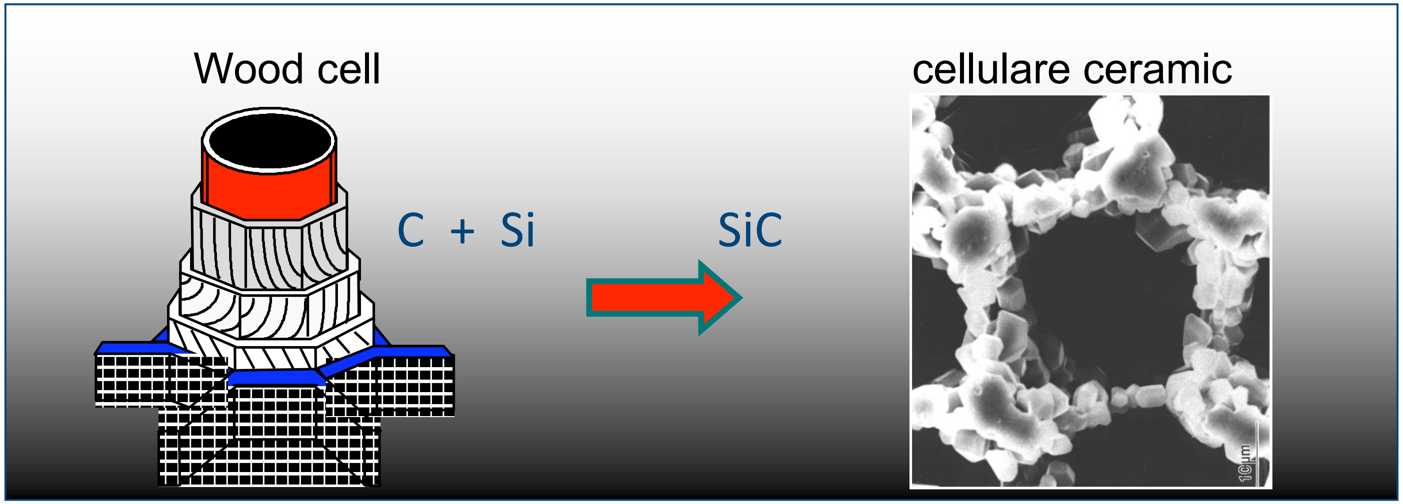
Chemicals from bio-oil

N-modified BCO

N-modified BCO



SiC Ceramics from Bio-Char



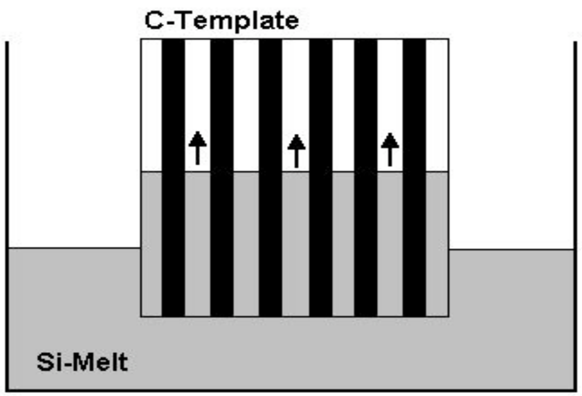
Wood before pyrolysis

Bio-Char

Ceramization

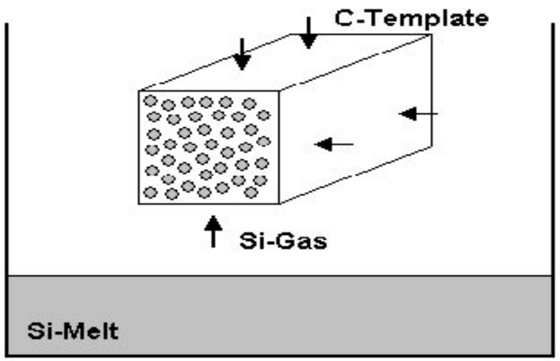
Bio-Char

Si Liquid-infiltration



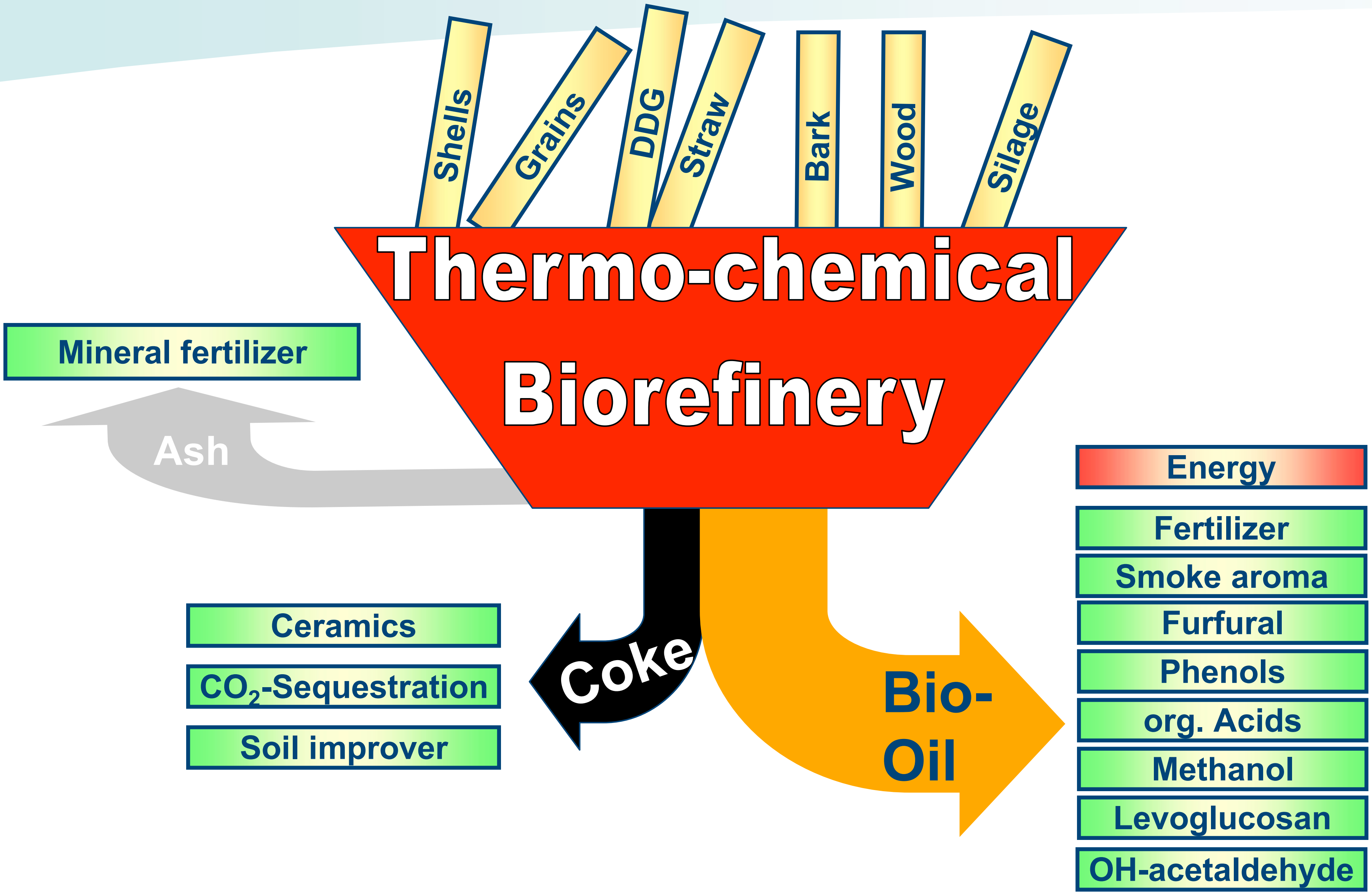
$Si_{(l)} + C_{(s)} \rightarrow SiSiC_{(s)}$

Si Gas-infiltration



$Si_{(g)} + C_{(s)} \rightarrow SiC_{(s)}$

„Zero-waste“ Concept



Conclusions

- Wood based biorefineries require certain pretreatment steps (solvolytic or thermolytic).
- Based on existing technologies from pulping by extending the utilization of by-products (BLG).
- Based on stand-alone technologies for separation of wood constituents (organosolv) and their individual processsing.
- Pyrolysis offers the opportunity for making materials and chemicals from bio-oil and bio-char.


¡Muchas gracias por su atención!
y
saludos desde Hamburgo