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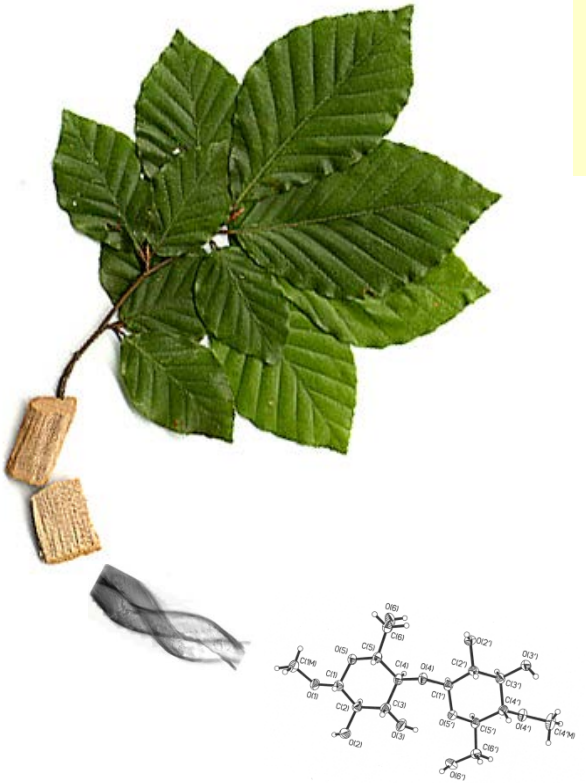
Wood as the prime starting material in biorefineries

Wood as starting material in biorefineries



Wood and its constituents - in nature

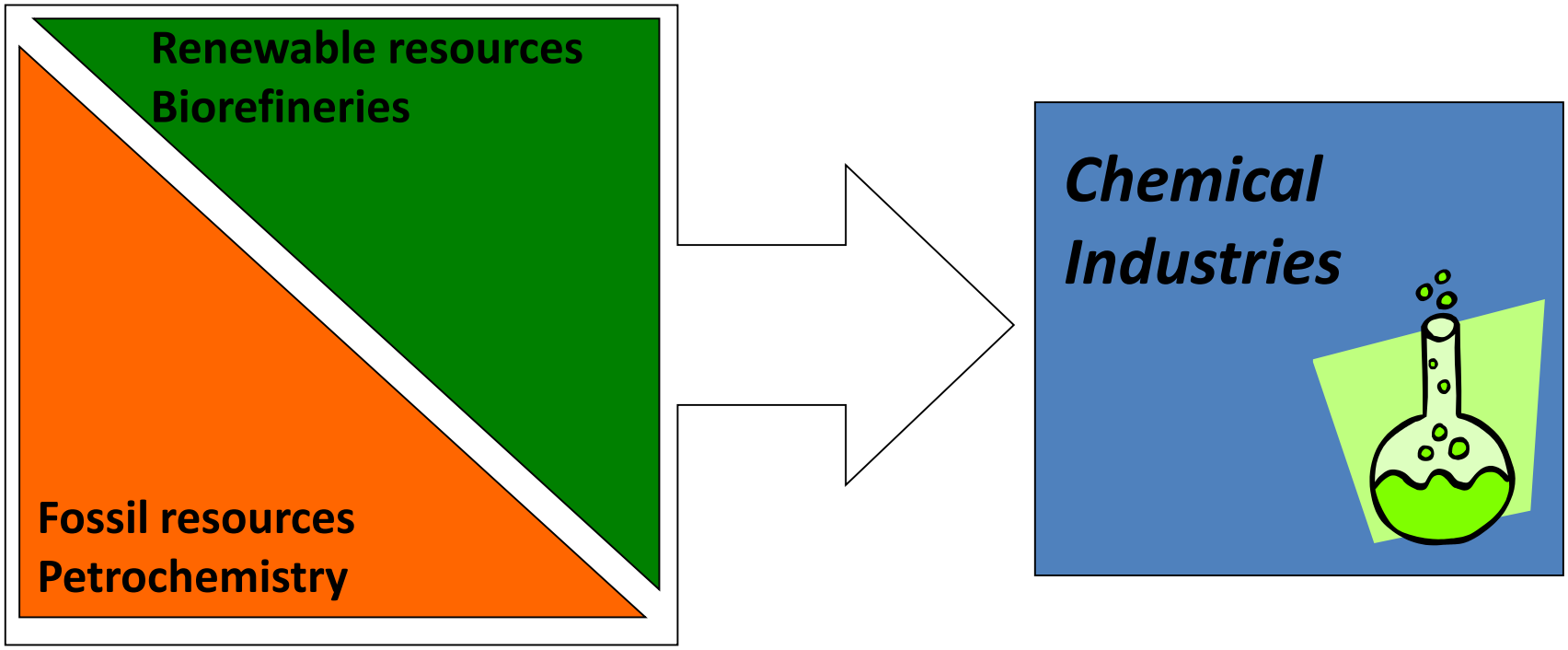
Wood and its constituents - in biorefineries

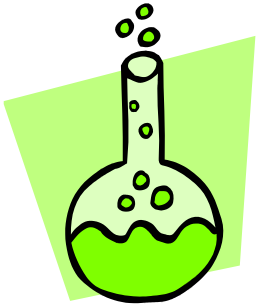
Six problems of today´s biorefineries and green chemistry

Brief conclusion

Looking into the (far) future

The basis of the chemical industries, present and future

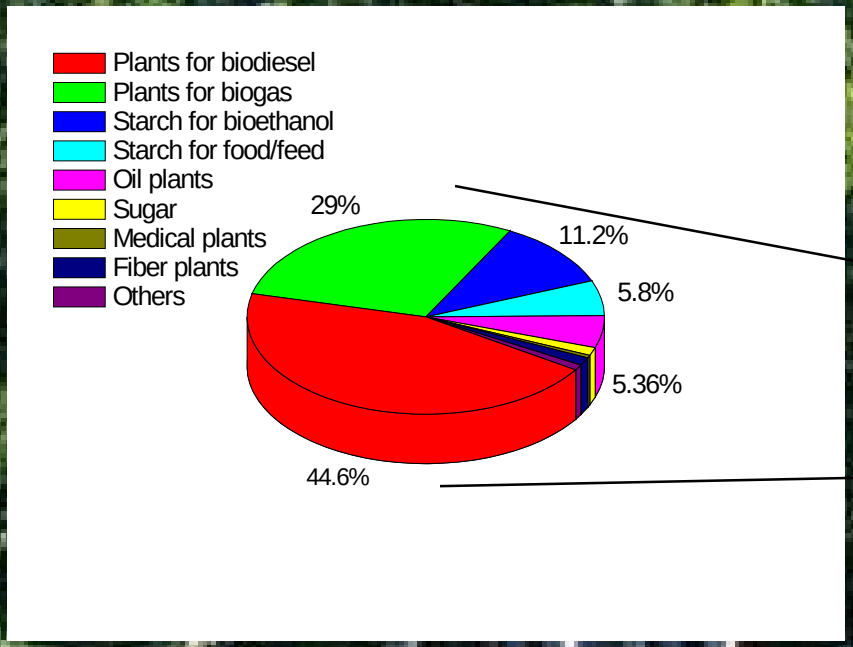


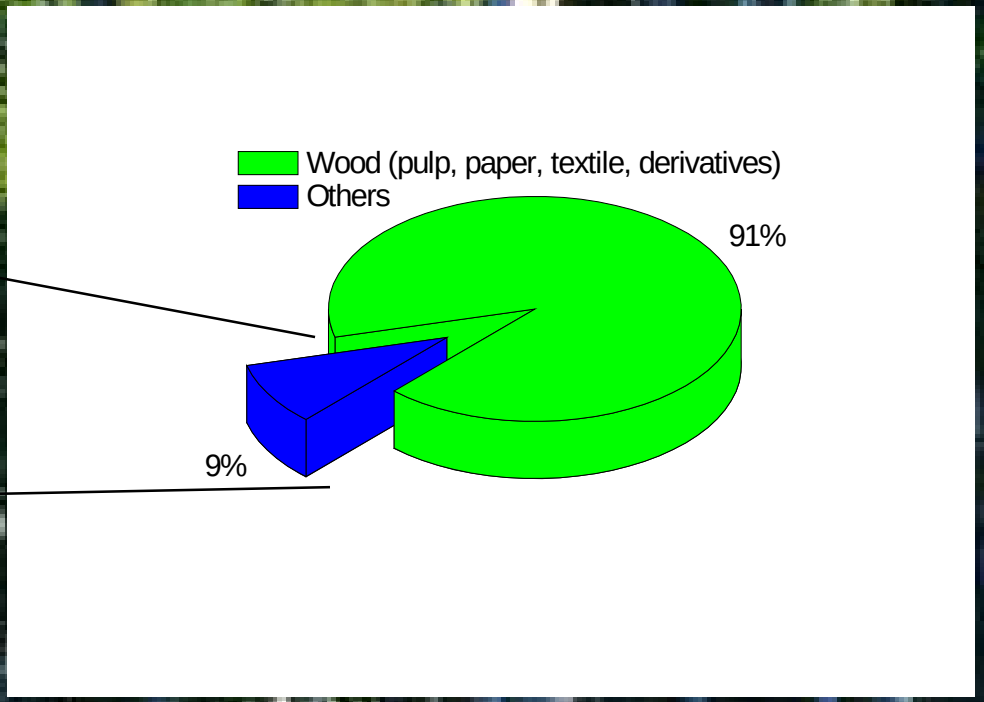


In (far) future, fossil resources WILL be used up.
If mankind is not to fall back into a rudimental, pre-industrial state, the whole production and all flows of the chemical industries will have to be changed from a ***petrochemical basis*** to a ***renewable basis***.
This requires long-term efforts and fundamental research.

„Green“ starting materials for biorefineries today

Mass balance - current situation



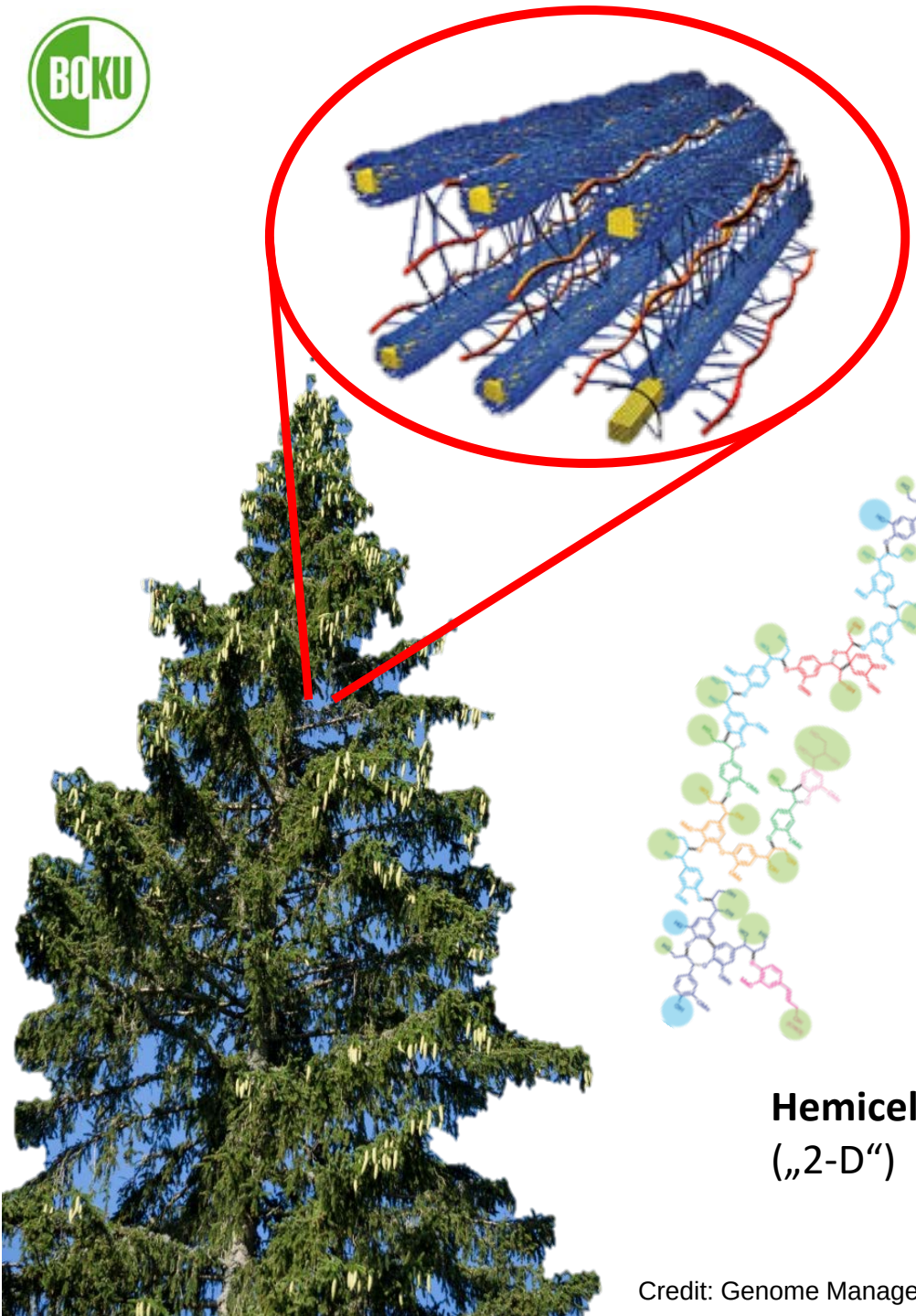


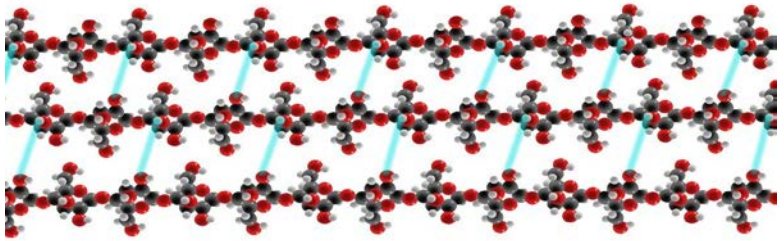
Wood is - and will remain - the most important renewable starting material for future chemical industries („biorefineries“).

Anaximenes (ca. 550 v. Chr.):
… and everything is composed of four elements [fire – water – earth – air], pure things out of one, most out of two or three, but wood requires all four of them...

ὑλη – Holz, Materie

➡ Met**hyl**, Et**hyl**, Prop**yl**





Cellulose („1-D“)

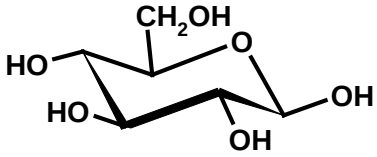
Lignin(„3-D“)

The three main wood components

Hemicelluloses
(„2-D“)

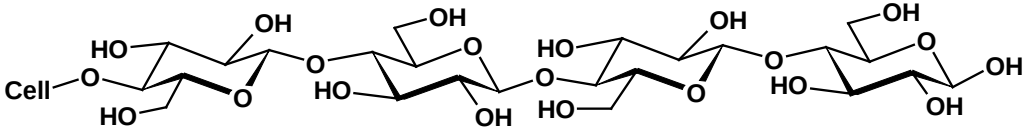
Credit: Genome Management Information System/ORNL

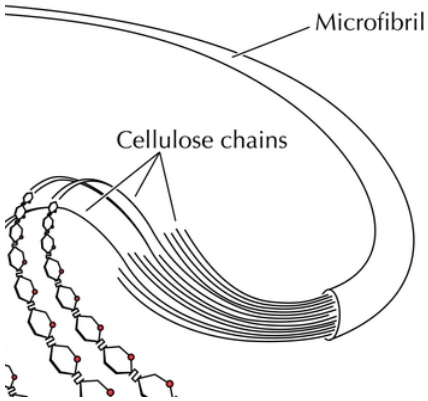
Cellulose – a short journey through its structure



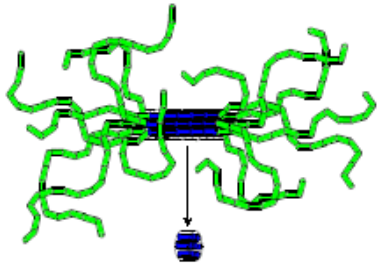
- Homopolymer of D-glucopyranose with β-1-4-glycosidic linkages

- Lineare cellulose molecules are stiffened by intramolecular H-bonds



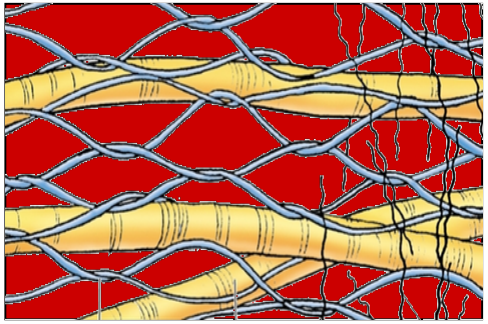


- Intermolecular H-bonds between the chains:
  Formation of microfibrils

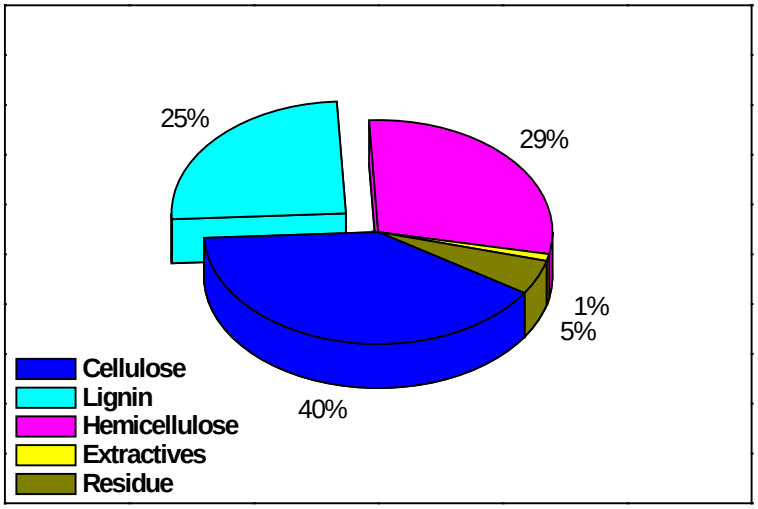


- According to the degree of order:
  crystalline and amorphous regions

- Macrofibrils in the layers of the cell wall in different orientation, lignin and hemicelluloses connect and „glue“ the network of fibrils into a high-performance natural composite material: wood



Lignin



• Lignin accounts for approx. 30% of organic carbon in the biosphere. It is the second most abundant natural polymer next to cellulose.

• Lignin was essential in the evolutionary adaption of plants from aquatic environments to land.

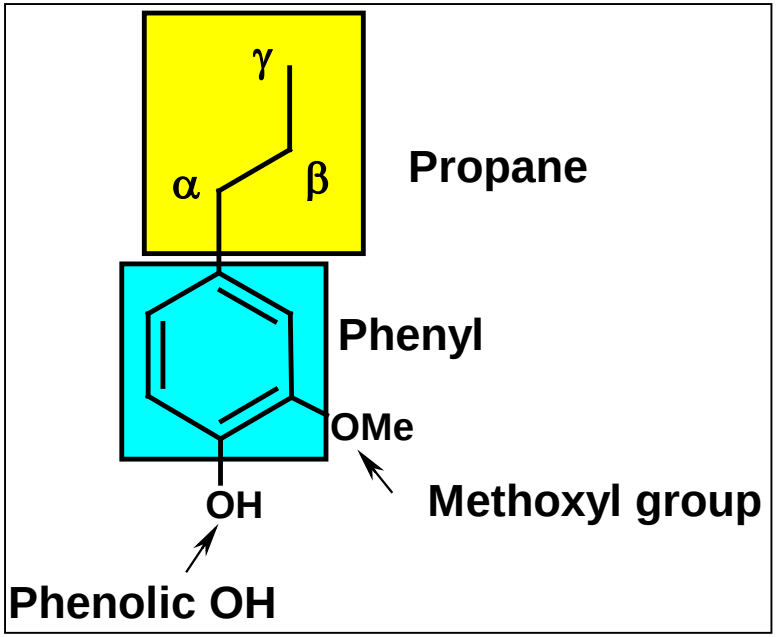
• Lignin waterproofs the cell wall, enabling transport of water and solutes through the vascular system.

• Lignin plays a crucial role protecting plants against pathogens.

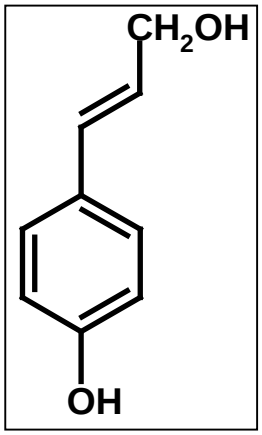
• Lignin is responsible for the mechanical strength and stiffness of plants and - most importantly - of trees.

Lignin

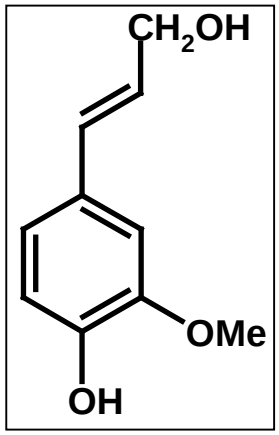
Phenylpropane units



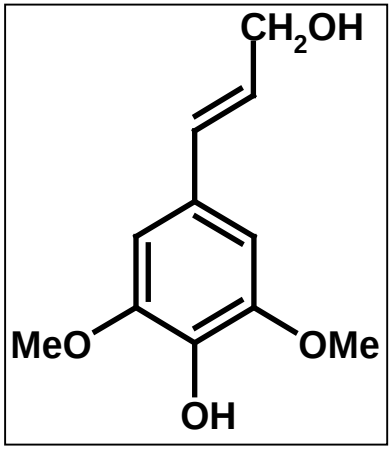
• Lignin consists of three phenylpropane units, connected by many different linkages formed in a random radical polymerization process.



***p*-Cumaryl alcohol**

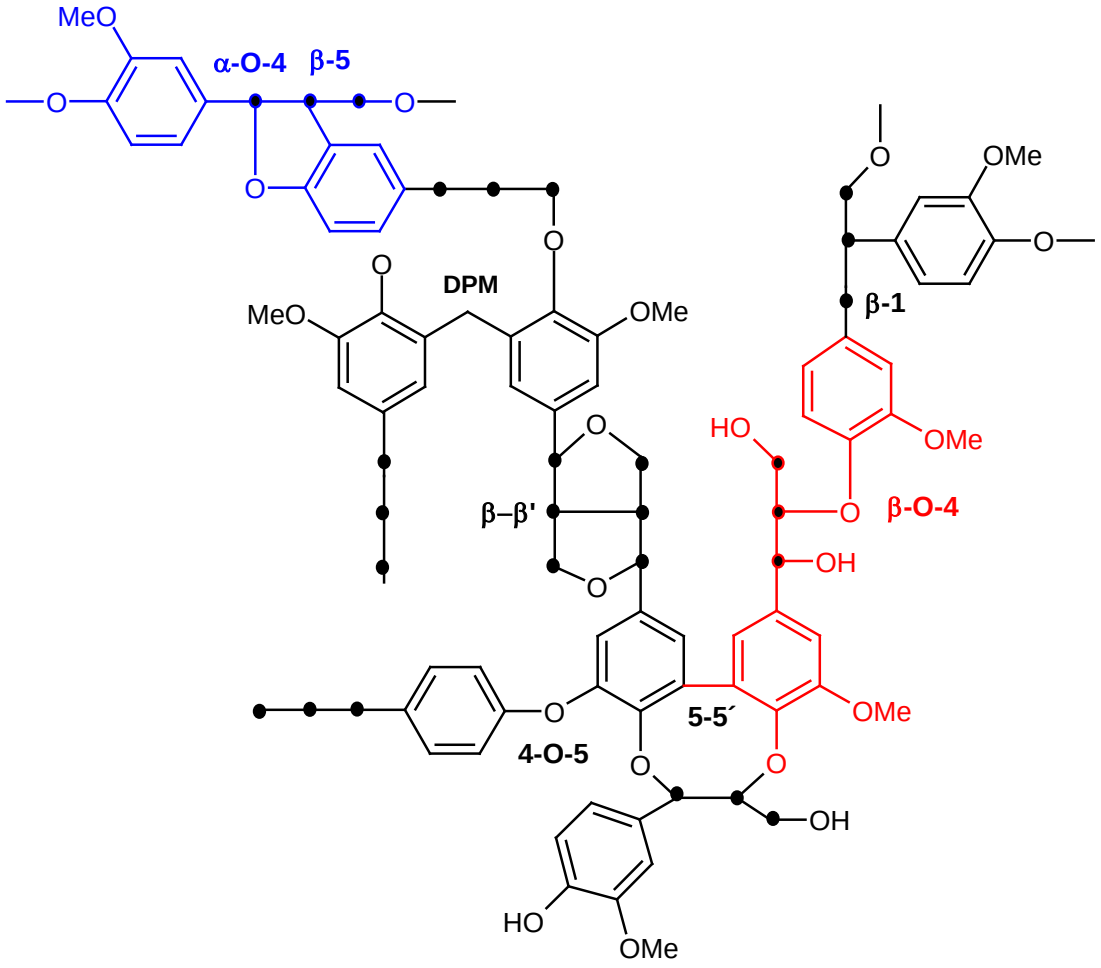


Coniferyl alcohol



Sinapyl alcohol

Lignin

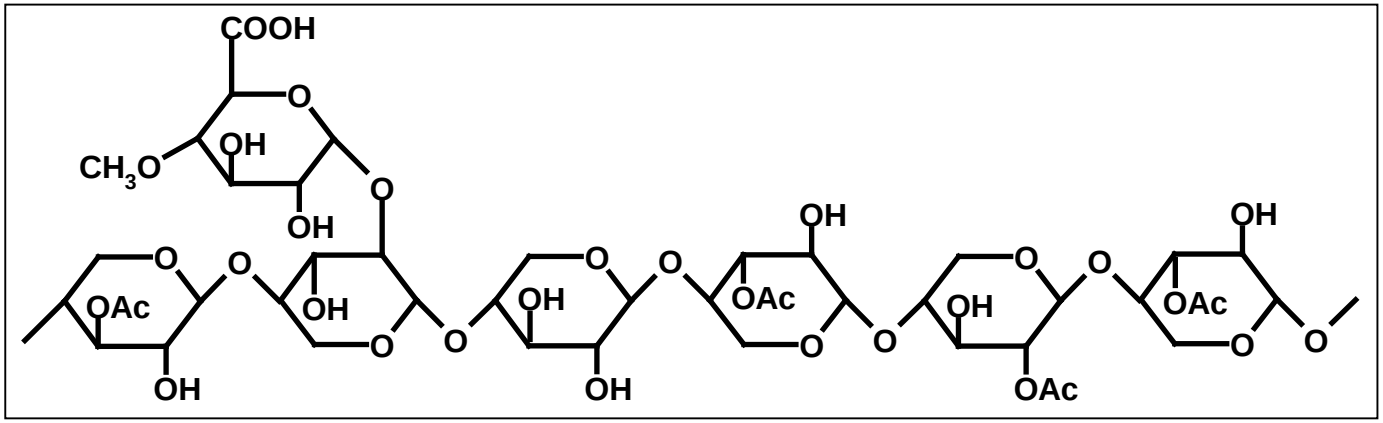


- Lignin consists of differently linked phenylpropane units.
- Lignin is an irregular polymer and a polyphenol.
- Lignins are complex, racemic, aromatic, yellow-to-brown, hydrophobic heteropolymers.

Hemicelluloses

- contain different sugar “monomers” by contrast to cellulose (hexoses, pentoses, glucuronic acid, deoxy-hexoses) → heteropolymers
- much shorter chain than cellulose, lower molecular weight
- branching, short side chains, partly acetylated
- act as “compatibilizer” between hydrophilic cellulose and hydrophobic lignin

- Hardwood hemicelluloses contain predominantly *xylose units* (xylans),
- Softwood hemicelluloses contain predominantly *mannose units* (mannans).



Structural detail from hardwood xylan: *O*-acetyl-(4-*O*-methylglucurono)xylan

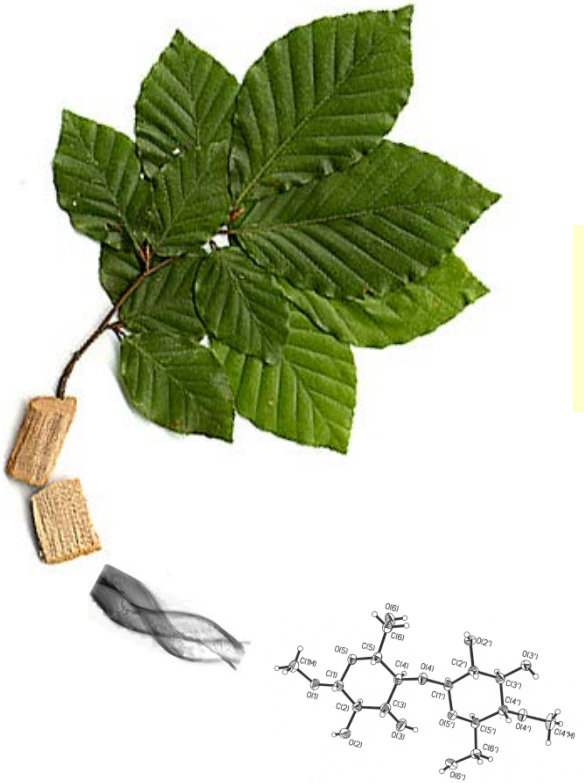
Comparison

- carbohydrate (“1D”)
- one monomer
- one linkage
- highly regular, linear
- H-bond network
- species-independent
- white
- hydrophilic
- utilization long established
- so far the main target of pulp&paper industries

- aromatic / aliphatic
- three monomers
- many different linkages
- highly irregular (“3D”)
- species-dependent
- yellow-brownish
- hydrophobic
- utilization long neglected
- becomes the main target of biorefineries (C-source)

- carbohydrate (“2D”)
- several monomers
- few different linkages
- largely regular, branched
- species-dependent
- white
- hydrophilic / amphiphilic
- utilization long neglected (remained “hidden” in paper or lignin)

Wood as starting material in biorefineries



Wood and its constituents - in nature

Wood and its constituents - in biorefineries

Six problems of today´s biorefineries and green chemistry

Brief conclusion

Chemical composition and usage of wood

wood

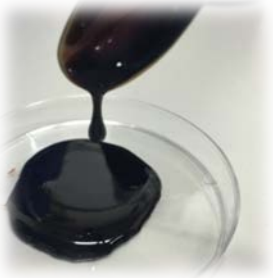
processing

pulp

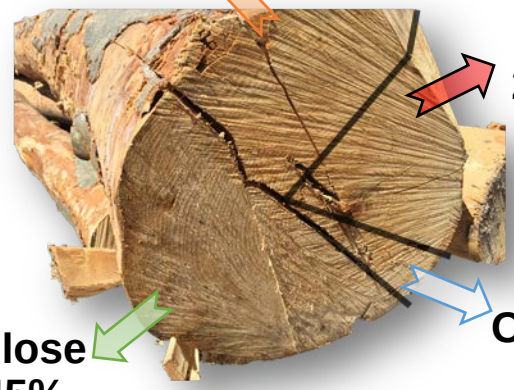
fibers

paper

spent liquor



→ 97% used for energy



Annual production of pulp: ~ 400 Mtons

We know quite well what to do with cellulose…

Tire cord

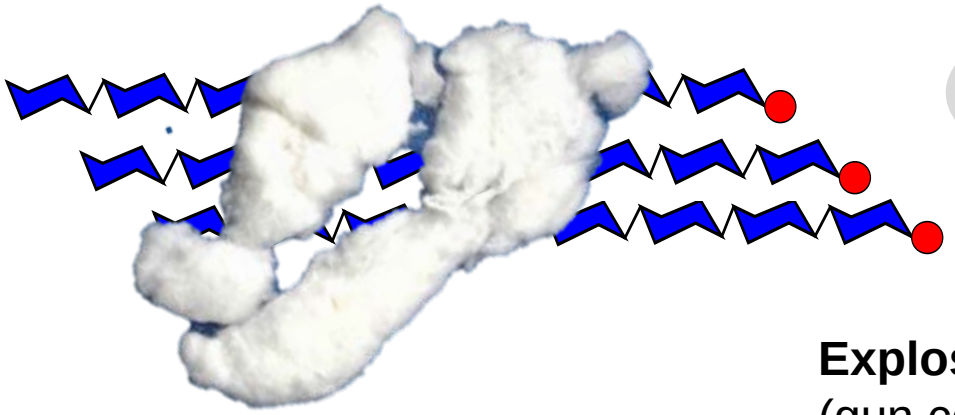
Paints

Textile fibers

Toilet paper

Cigarettes
(Filter and paper)

Tea bags



Paper

Tissue
(napkins,
kitchen roll)

Films

Packaging
(sacks, boxes)

Explosives
(gun cotton)

Diapers

Derivatives
(ice cream,
toothpaste)

Sausage skins

Wound dressings

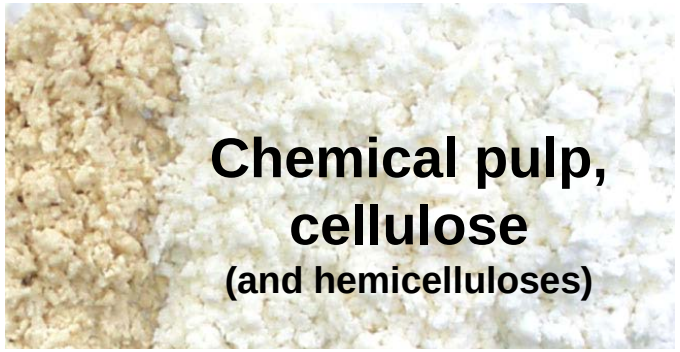
Membranes
(speakers, dialysis)

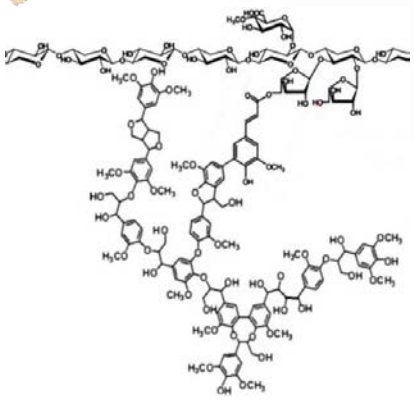
Newsprint

Wood / → Lignocellulose → Cellulose (pulp) + “black liquor”

Annual Plants

Pulping process

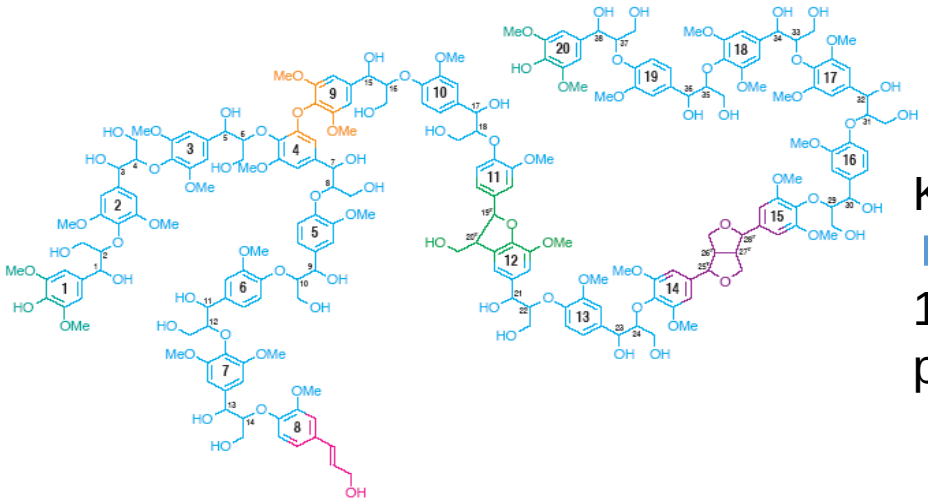




LIGNIN
20-30% in woody biomass

Black Liquor
with dissolved
lignin and hemicelluloses
(mixture of organics and inorganics)

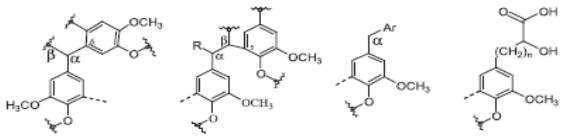
The fates of cellulose and lignin...



Native Lignin

Kraft pulping

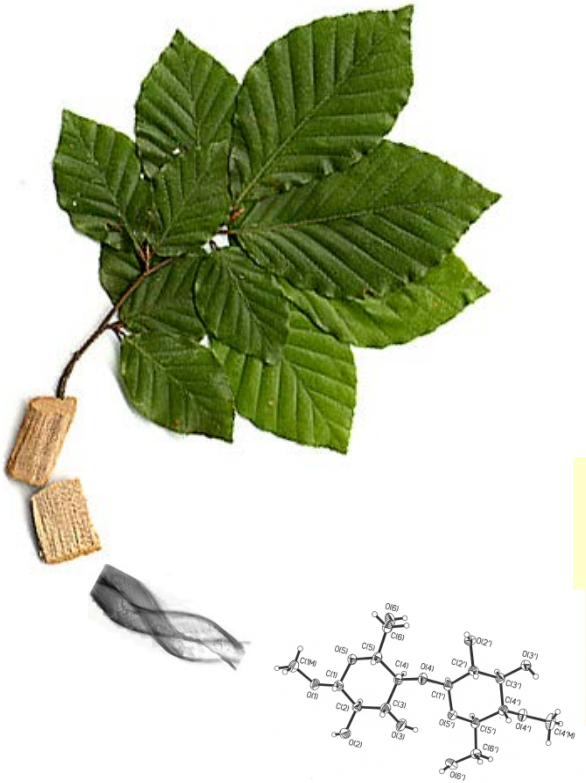
170°C, 4h
pH 14



Technical lignin

Technical lignins have structures largely different from those of native lignins.

Wood as starting material in biorefineries



Wood and its constituents - in nature

Wood and its constituents - in biorefineries

Six problems of today´s biorefineries and green chemistry („Sixpack problems“)

Brief conclusion

The sixpack of biorefinery problems in bioeconomies

1. The “time” problem

→ Time to grow: refinery 130+ years, biorefinery 25+ years only

2. The “energy *vs.* matter” problem

→ We need “CARBON” to produce materials and chemicals, but not necessarily for energy production!

3. The “lignin” problem

→ Cellulose (and hemicellulose) can be nicely used today, lignin not yet.

4. The „separation / analysis“ problem

→ Demand for new biorefinery-specific separation / purification / analysis techniques !!!

5. The “alpha – beta” problem

→ “Glucose from starch” is easy, “glucose from cellulose” is a lot more difficult.

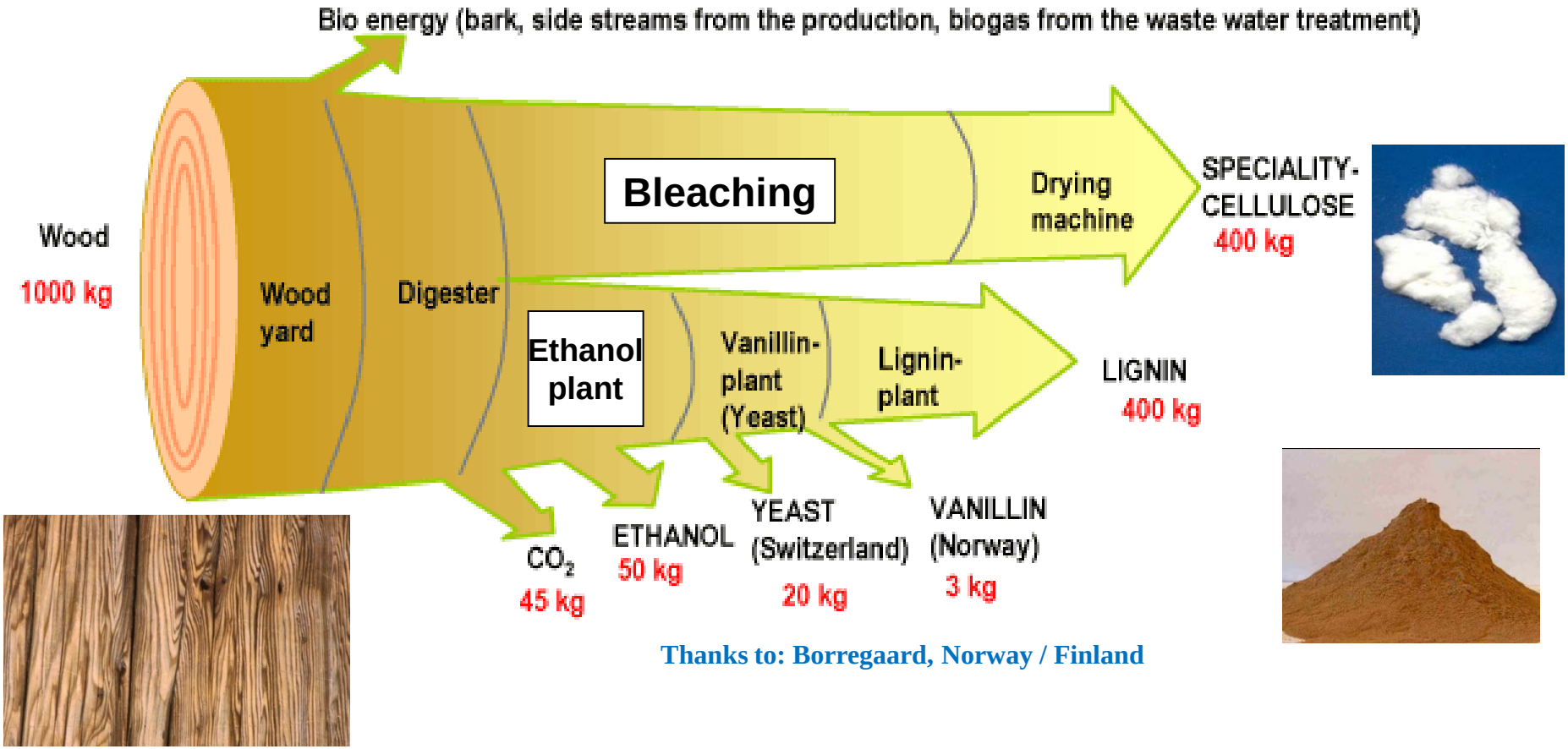
6. The “breakdown” problem

→ Is it wise to largely disregard the synthesis and optimization effort of nature?

BOKU

3. The "lignin problem"

Example: utilization of spruce wood



Thanks to: Borregaard, Norway / Finland

→ **Cellulose (and hemicellulose) can be nicely used today, lignin not yet.**

→ **<u>Meaningful</u> uses of lignin as a general *C*-source for the chemical industries are needed !!!**

4. The „separation / analysis problem“

Natural products

Extremely complex mixtures

Natural variability

Hard to process (consistency)

Unknown components

Mostly aqueous mixtures

Often low concentration (fermentation)

Unstable upon storage

→ **Demand for new biorefinery-specific separation / purification / analysis techniques !!!**

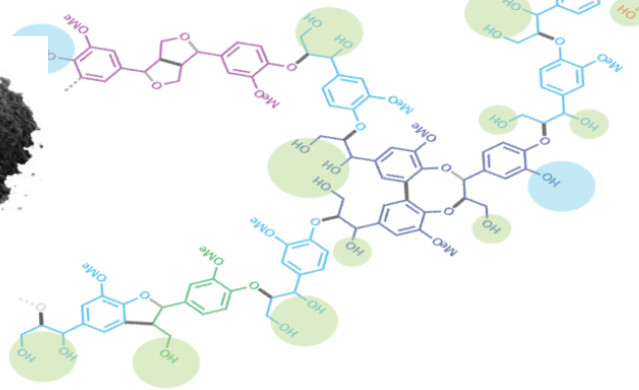
Lignin analysis (and most utilization modes) start with lignin isolation from black liquor !!

Technical lignin ≠ technical lignin.

Kraft lignin

Lignosulfonate

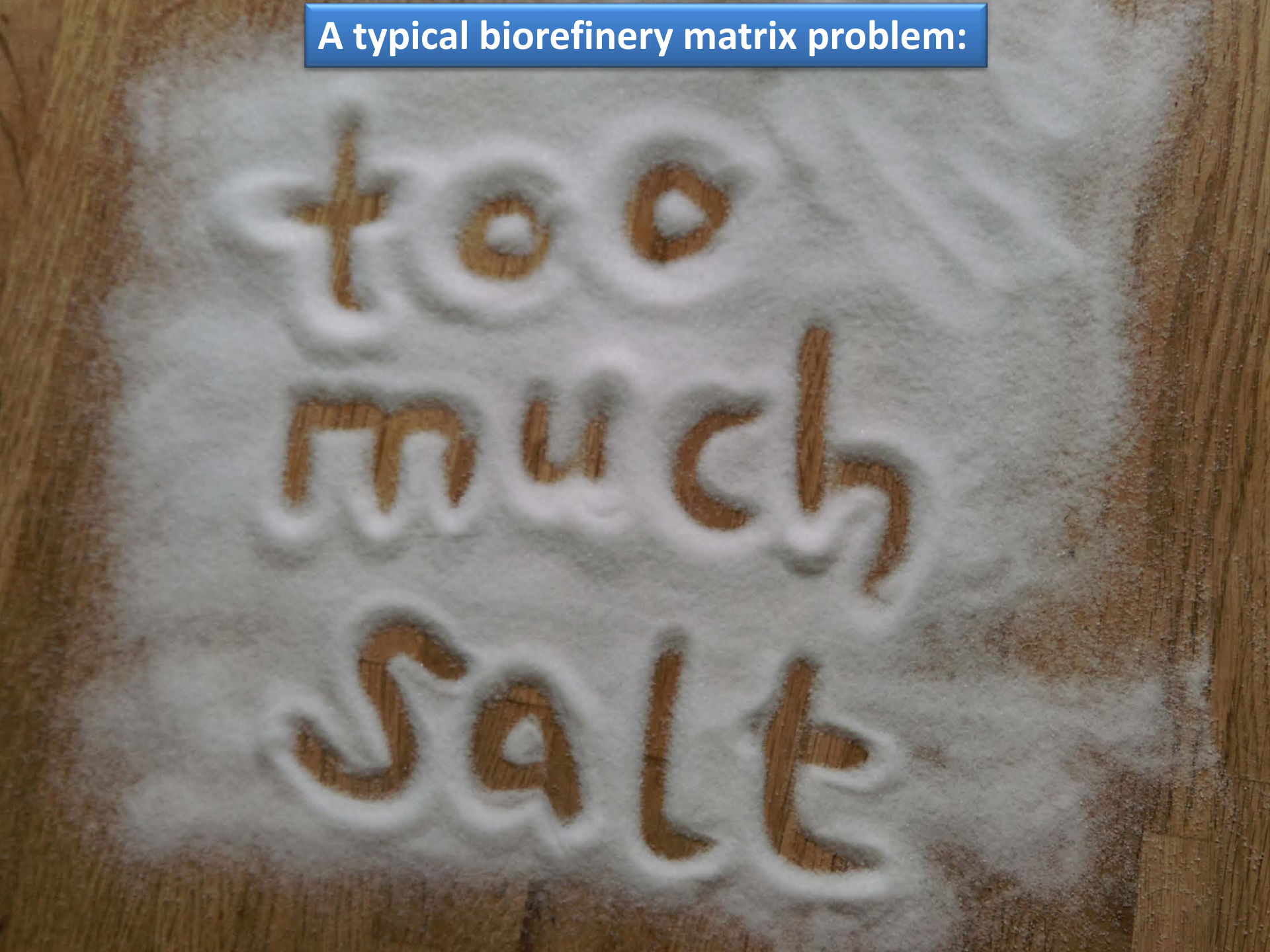
Organosolv



Flippr

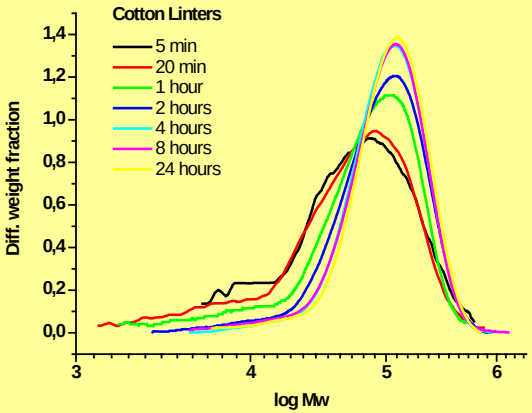
lignin platform

A typical biorefinery matrix problem:

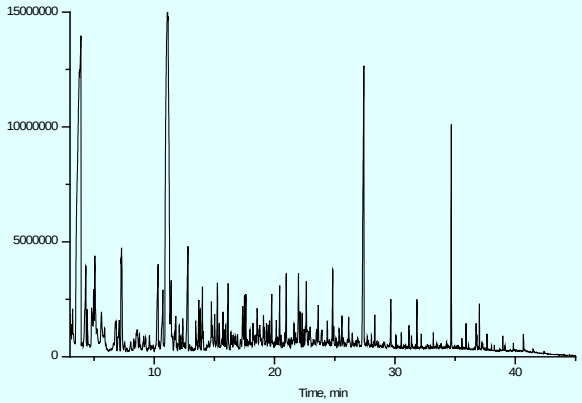


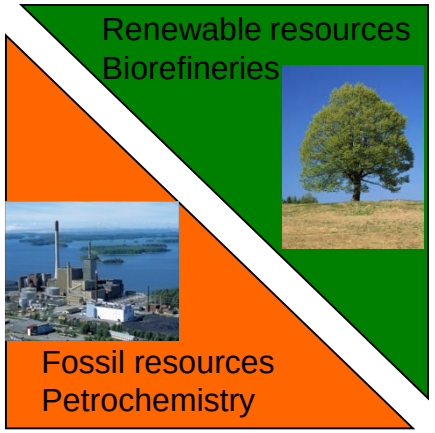
We need powerful „Biorefinery analytics“

Carbohydrate (cellulose) analysis

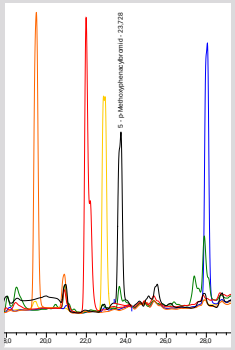


Lignin analysis





Analysis of byproducts



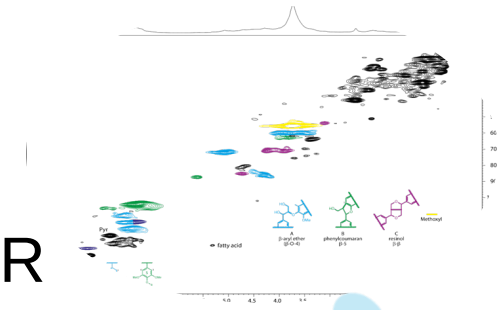
- GC-MS
- CE-MS
- NMR
- LC-MS
- DESI-MS
- GPC

Development of new products and technologies based on renewables must go hand in hand with the development of robust and reliable analytical methodology.

Comprehensive analysis of technical lignins

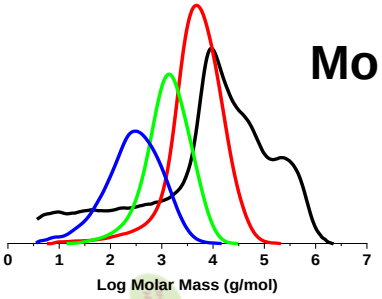
NMR

(QQ) 2D, ^{31}P, ^{1}H, ^{13}C



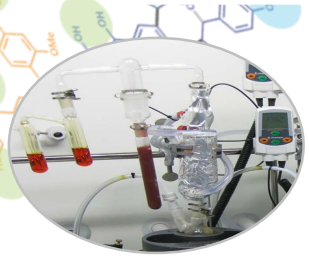
Technical lignins

Molar mass



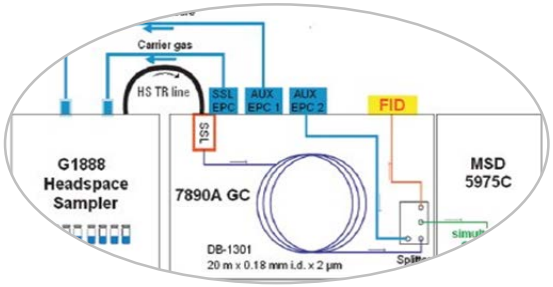
DFRC
Thioacidolysis

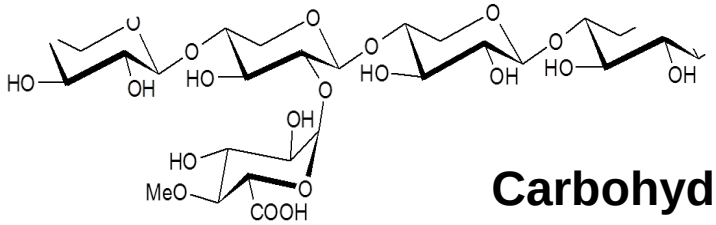
Nitrobenzene oxidation
$KMnO_4$ oxidation



-OMe/OEt

Hydroxyls, COOH,
$-SO_3H$, …





Carbohydrates

Wood as starting material in biorefineries

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Brief conclusion

ABCT (Austrian Biorefinery Center Tulln) – ABCM (Doctoral School "Advanced Biorefineries – Chemistry & Materials)

Universität für Bodenkultur Wien

All PhD candidates working in the Austrian Biorefinery Center Tulln (ABCT) are members of the ABC&M doctoral school.

The combination of research and PhD education, realized by the linkage of ABCT to the doctoral school ABC&M, ensures the availability of future biorefinery experts and long-term continuity in research.

ABC&M

DOCTORAL SCHOOL
ADVANCED BIOREFINERIES: CHEMISTRY & MATERIALS

Coordination:
Institute of Chemistry of Renewable Resources, BOKU

BOKU

Financial $upport

Alma mater viridis

Thanks to the people who are actually doing the work…


Thank you for your kind attention !

Thomas Rosenau

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