

Thomas Rosenau

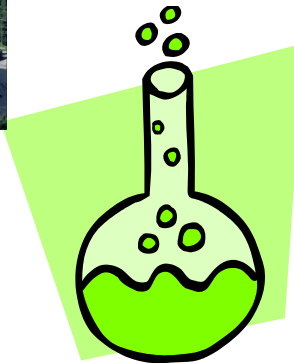
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Biorefineries

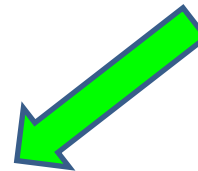
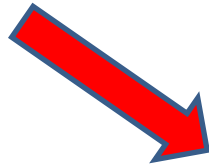
What do we know? Where are the problems?

Bioeconomy – a contradiction per se?



„CHEMISTRY“

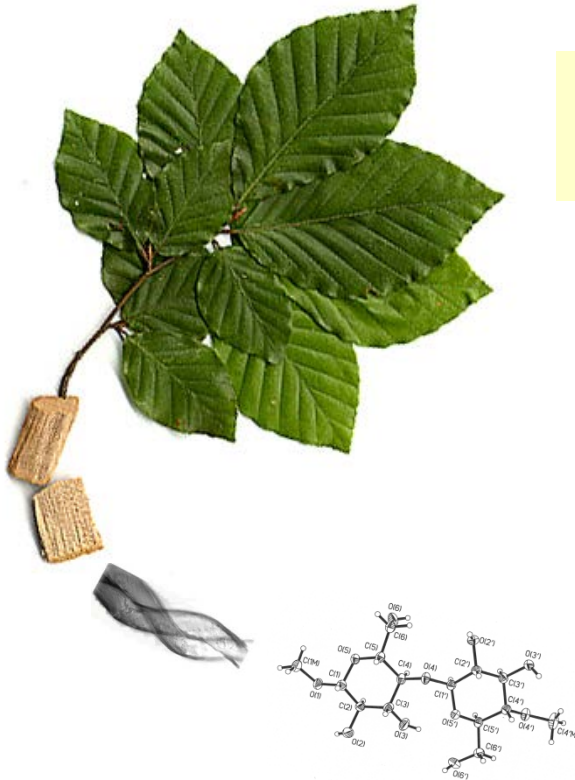
„NATURE“



BIOECONOMY & GREEN CHEMISTRY ?



Biorefineries



Biorefineries – some background

The problems of today's biorefineries (the „sixpack“)

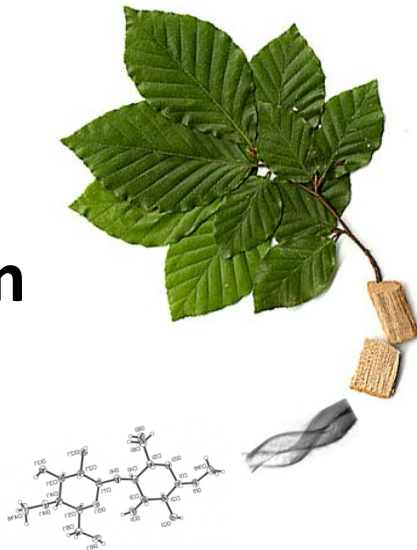


Three examples
(for a more optimistic ending)

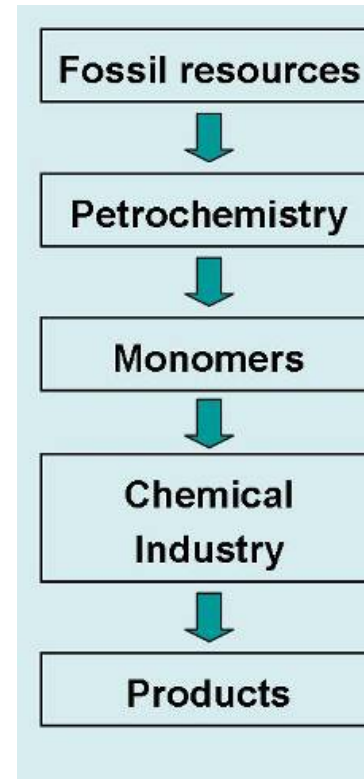


Products from bio-refineries

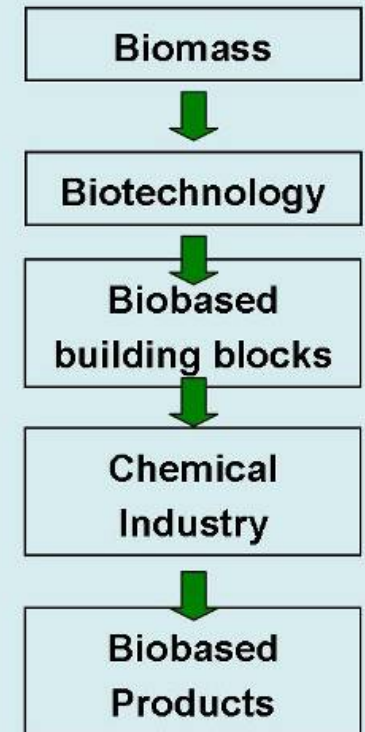
- 1) Bio-polymers
(Bio-materials)
- 2) Bio-chemicals
- 3) Bio-fuel
- 4) Bio-energy



Chemistry - Refinery



Green Chemistry - Biorefinery



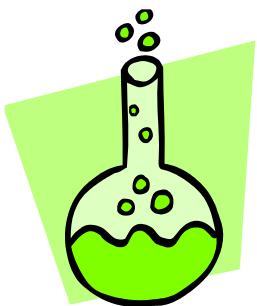
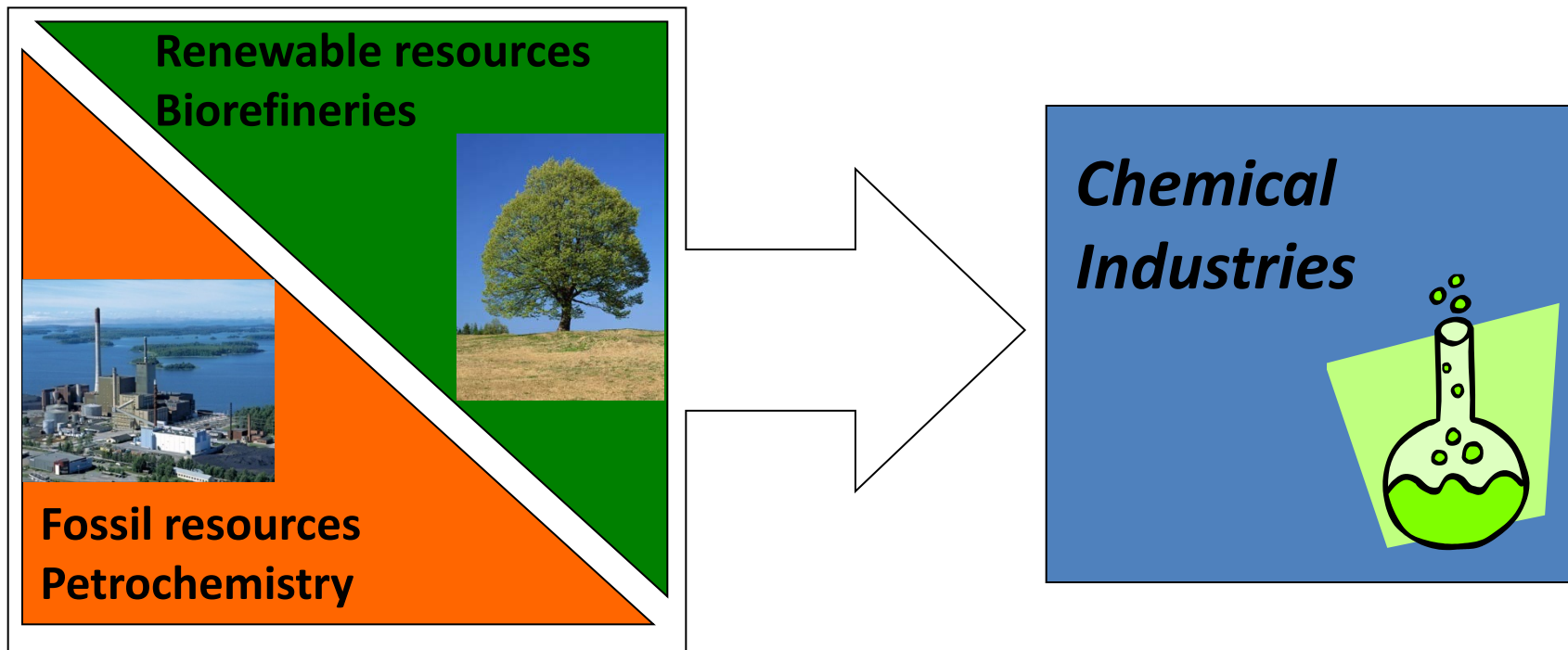
Definition: refinery / biorefinery

Fractionation (separation and purification) of fossil resources / biomass into its main components that are used further to produce an optimum of balanced products



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.

Either...

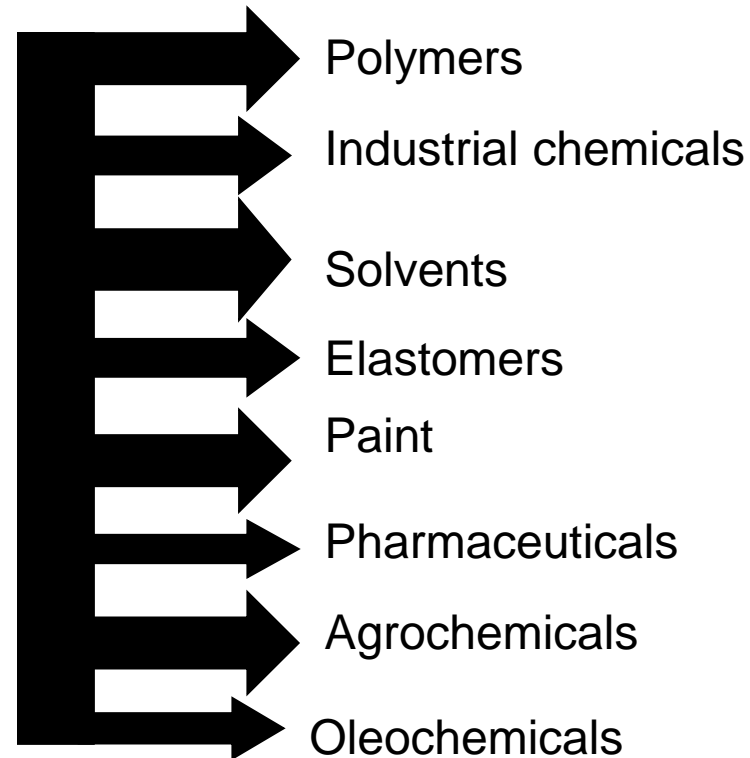


Or...

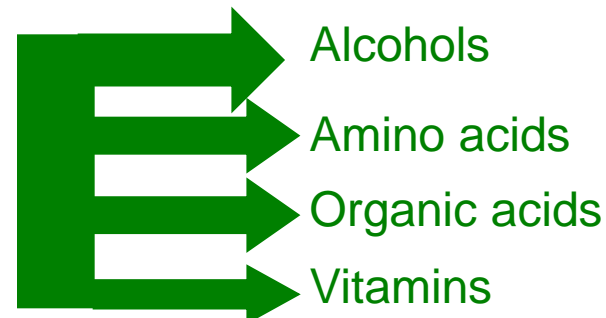


Product classes of today's „classical“ chemical industry

- Products from petrochemistry



- Products from industrial biorefineries

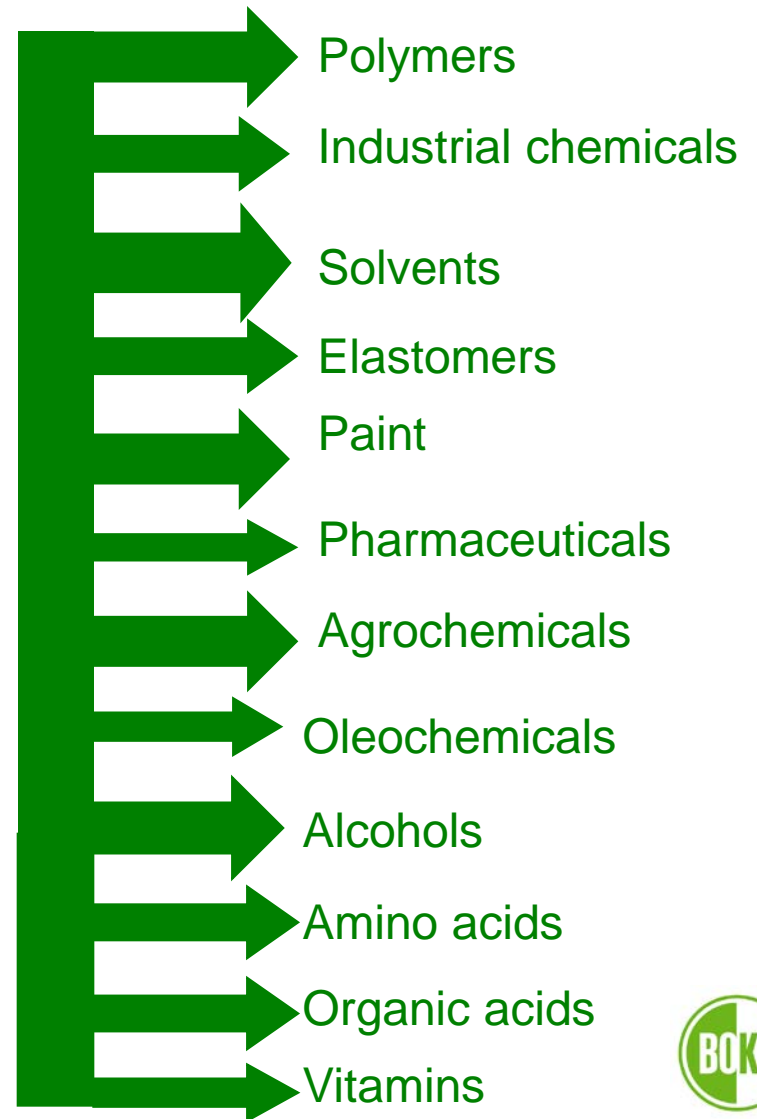


Product classes of the chemical industry in the far future

(Bio)chemical technologies producing all materials from renewables, which are nowadays mainly based on fossil resources

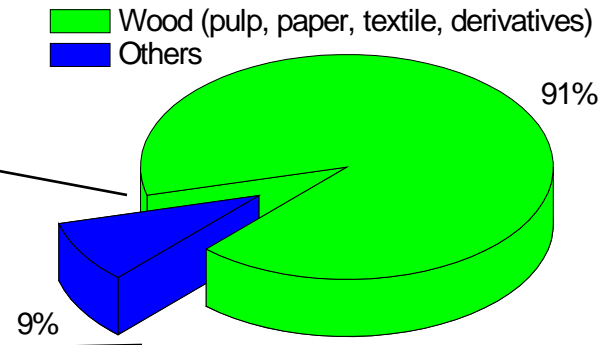
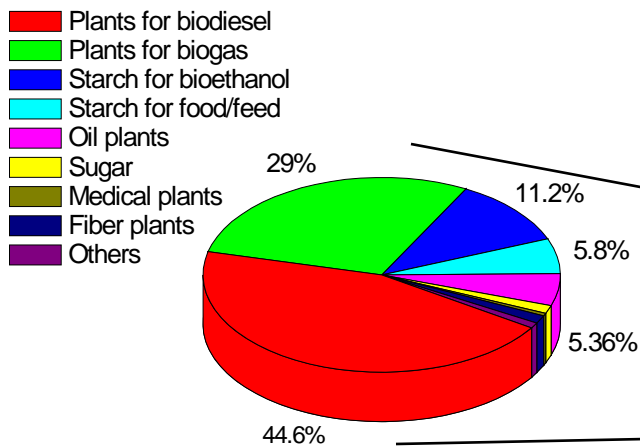
Change of the basis of chemical industries and all related production lines

Fossil → Renewables

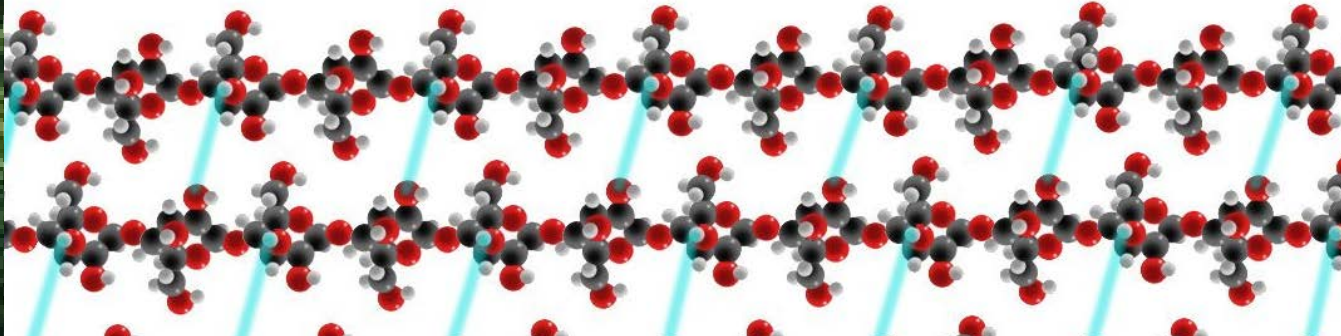
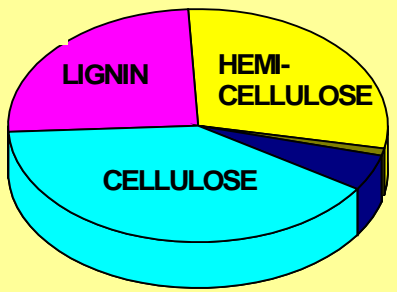


„Green“ starting materials for biorefineries today

Mass balance - current situation



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

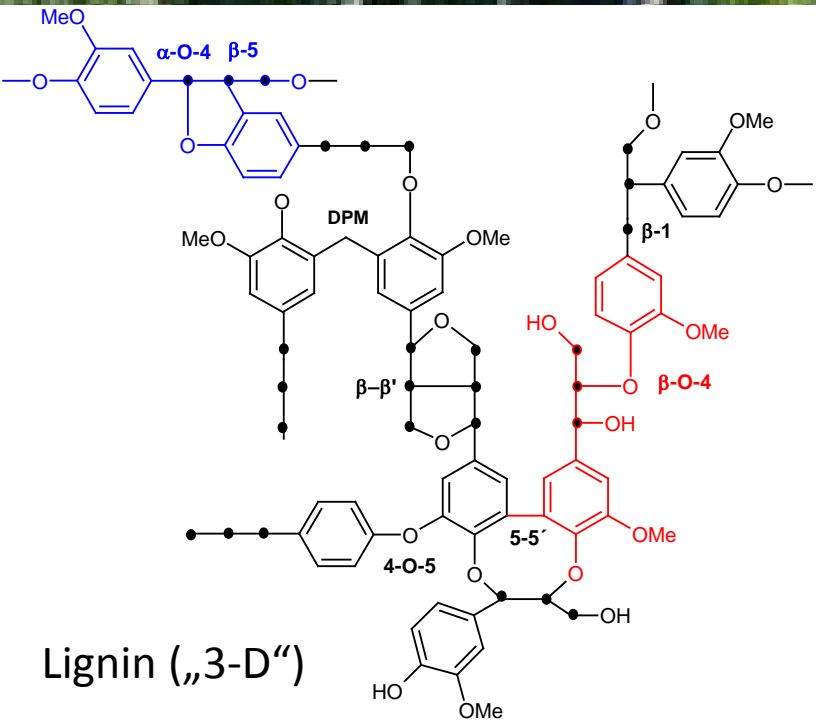


Anaximenes (ca. 550 v. Chr.):

... sind viele Dinge aus einem reinen Element [Feuer – Wasser – Erde – Luft] geformt, andere aus zweien oder dreien, **nur das Holz jedoch bedarf aller vier.**

ῥυλη – Holz, Materie

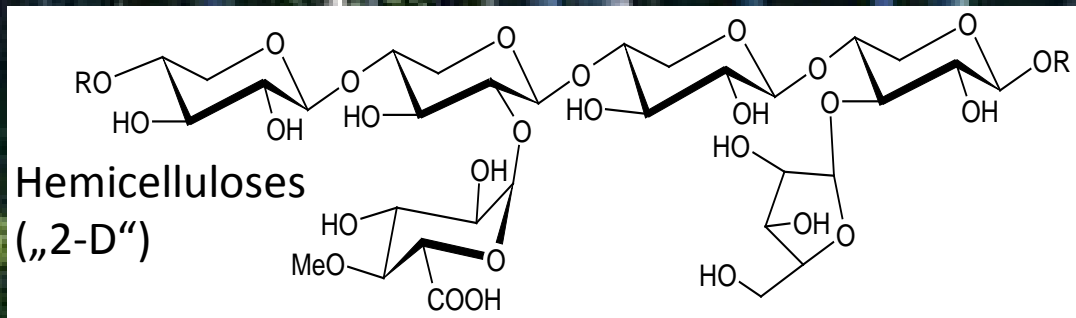
→ Methyl, Ethyl, Propyl



Lignin („3-D“)

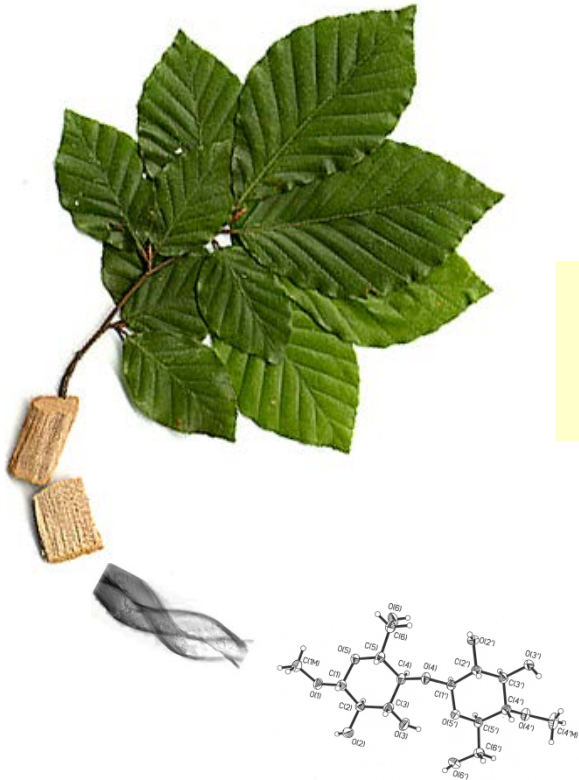
Other natural starting materials:

- Extractives (fats, oils, isoprenoids)
- Proteins
- Starch
- Other carbohydrates



Hemicelluloses („2-D“)

Biorefineries



Biorefineries – some background

The problems of today's biorefineries (the „sixpack“)



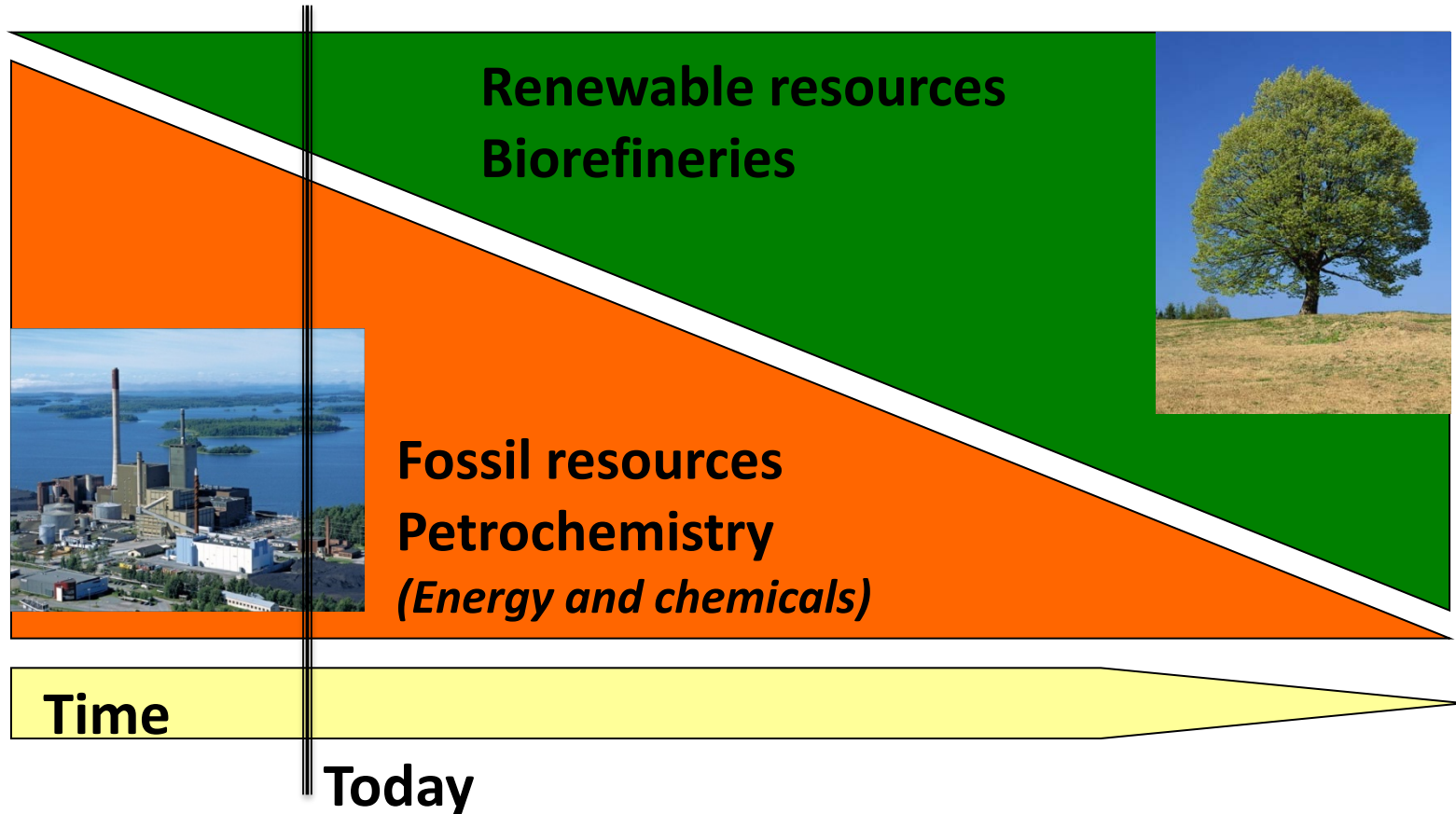
Three examples
(for a more optimistic ending)





The “time problem”

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

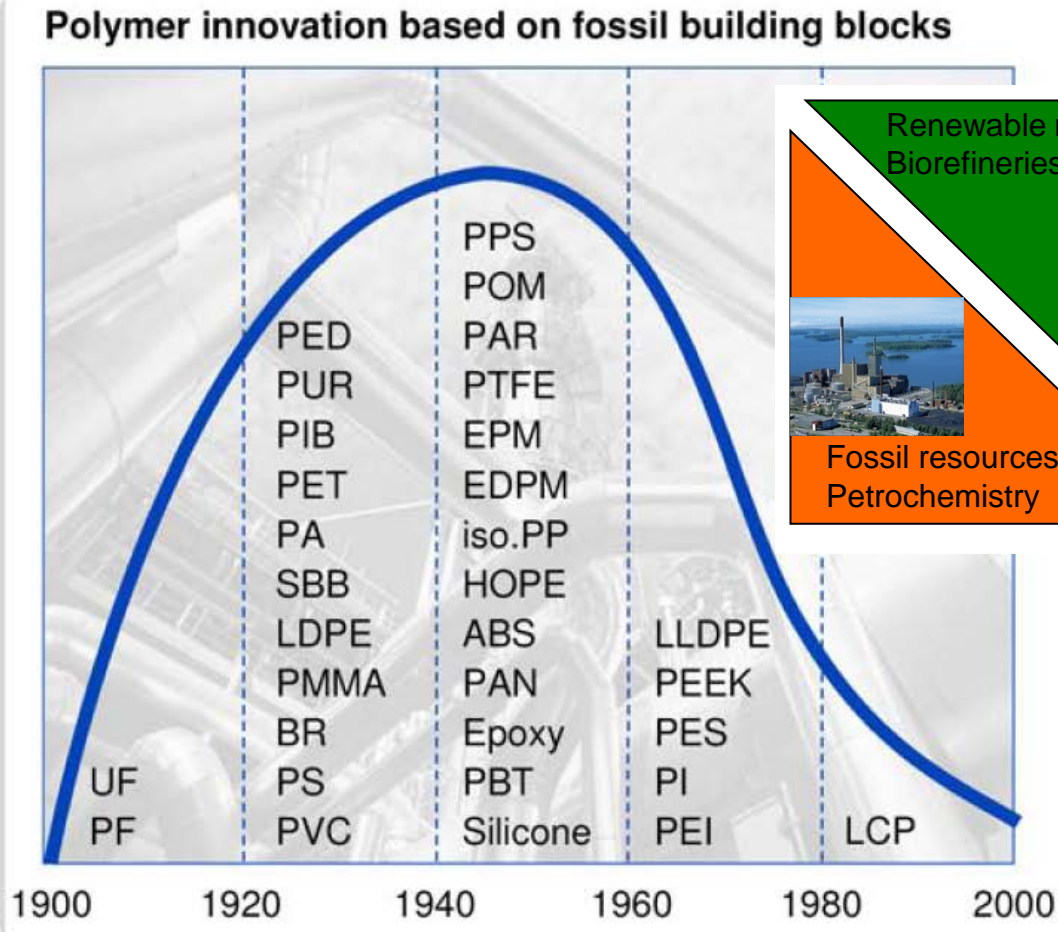


- Biorefinery is not an old science...
- There are minimum time requirements for technological and socioeconomic developments.



Development time

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



Development of polymers based on building blocks (McKinsey & Comp: Industrial Biotechnology, 2014)

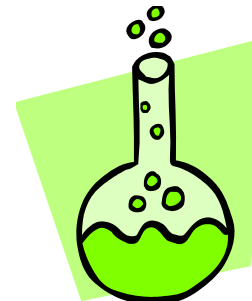
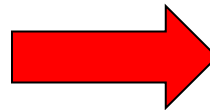
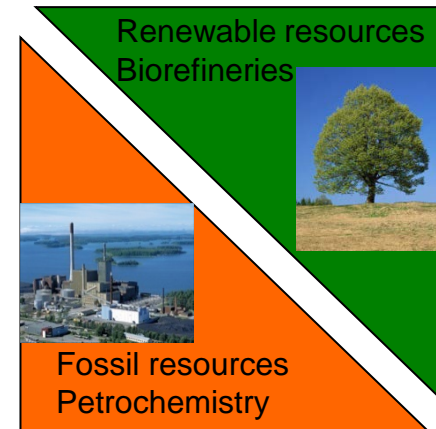
The “energy vs. matter” problem

“Use as matter”: chemicals, materials, food, feed



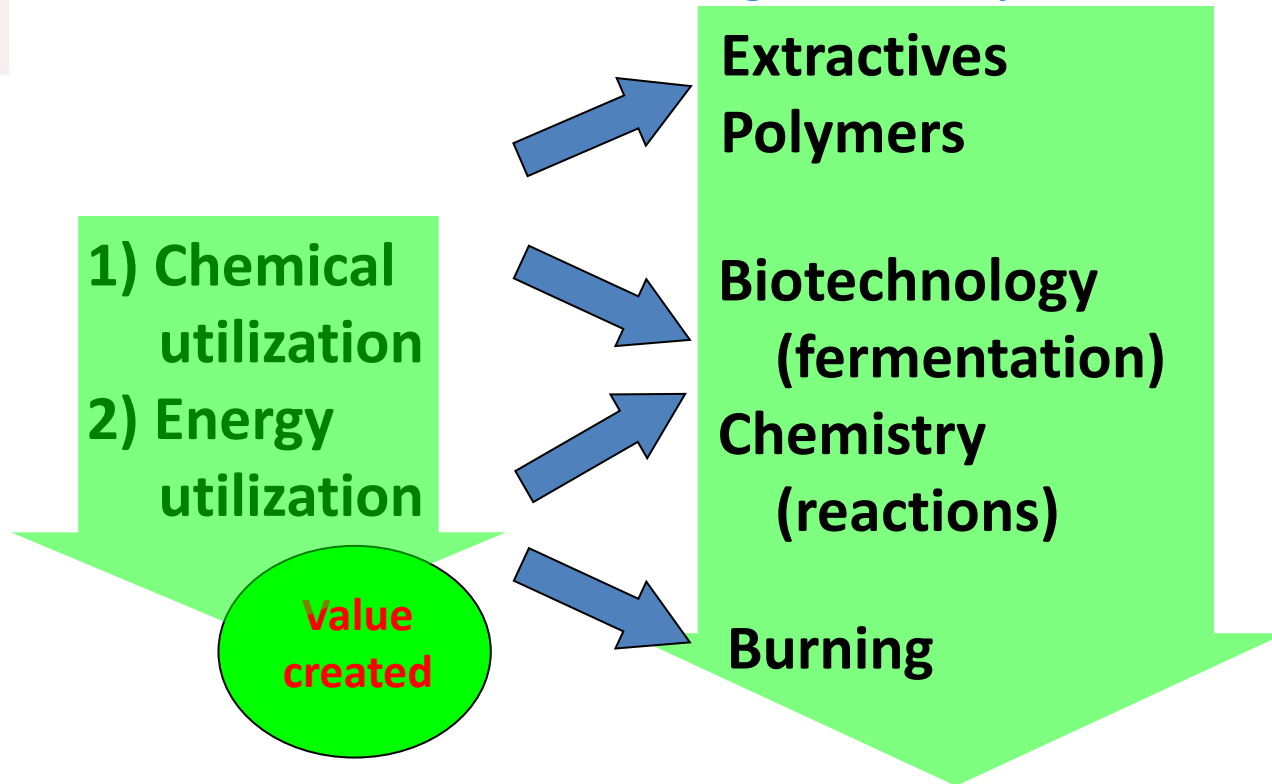
We need “**CARBON**” to produce materials and chemicals.

We don’t necessarily need “**CARBON**” for energy production (there are other and better alternatives) !



The “energy vs. matter” problem

“Cascade utilization” as the logical consequence



→ “Do something with it first! If nothing works – you can still burn it!”
(George A. Olah, Nobel Prize Chemistry 1994)

→ Energy usage modes (biogas, pyrolysis oils, direct burning) should be operated only after value-added chemical utilization.

→ A major hindrance in cascade utilization is the insufficient advancement of separation technology and analytical capability today.



The „separation / analysis problem“

Natural products

Extremely complex mixtures

Natural variability

Hard to process (consistency)

Unknown components

Mostly aqueous mixtures

Often low concentration
(fermentation)

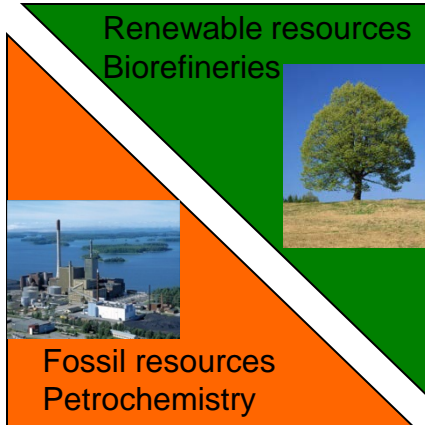
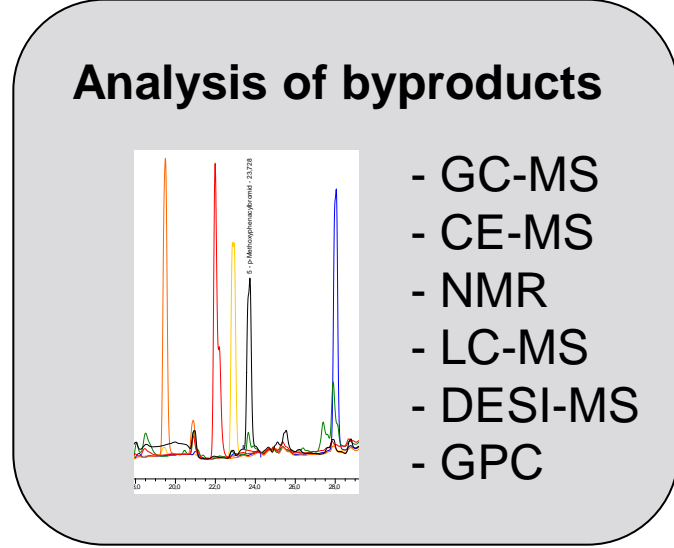
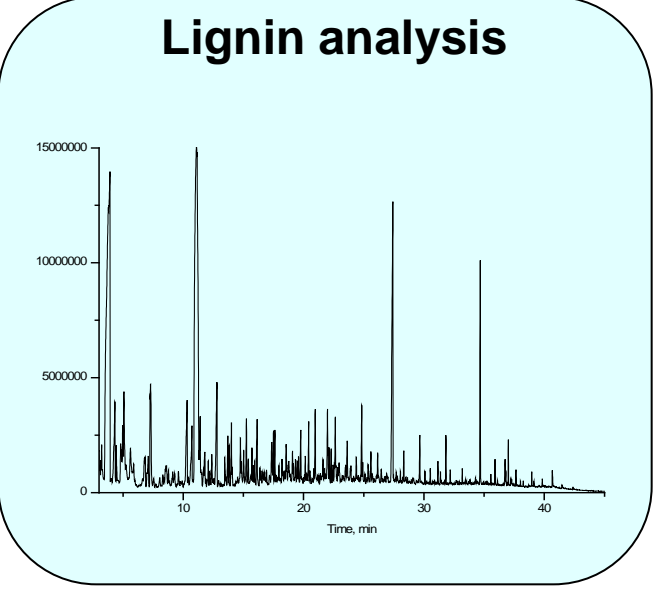
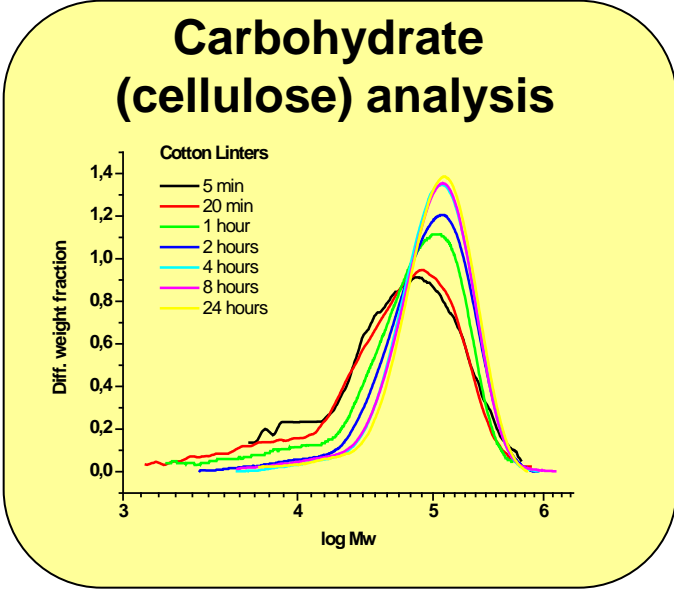
Unstable upon storage

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





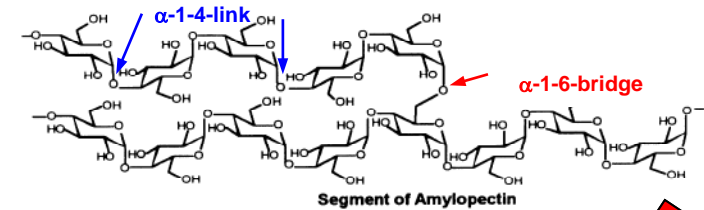
We need powerful „biorefinery analytics“



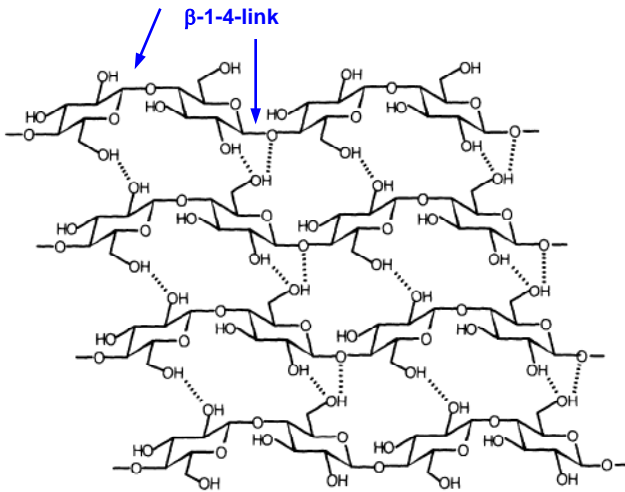
Development of new products and technologies based on renewables must go hand in hand with the development of robust and reliable analytical methodology.



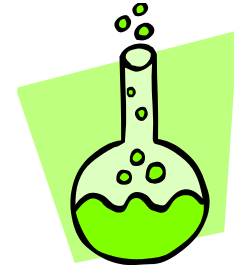
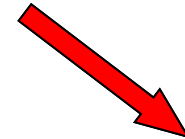
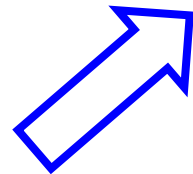
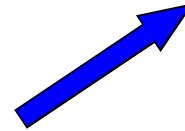
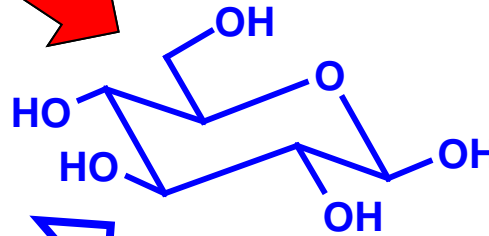
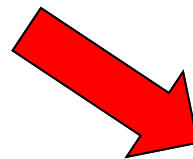
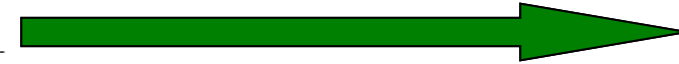
The “alpha – beta” problem



STARCH



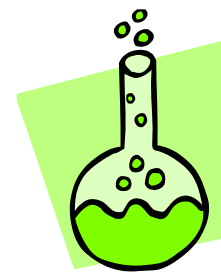
(Hemi)CELLULOSES



- “Glucose from starch” is easy, “glucose from cellulose” is not.
- On the long run, energy and chemicals / materials will be derived from natural resources that have no competitive utilization in the food / feed market.
- This requires long-term research efforts (and might require some improved ethical thinking).

The “breakdown problem”

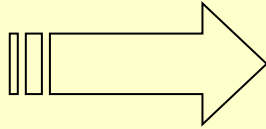
“Drop-in strategy” vs. “use-as-is strategy”



(Bio) Refinery

Chemical industries

Gas
Oil
Coal



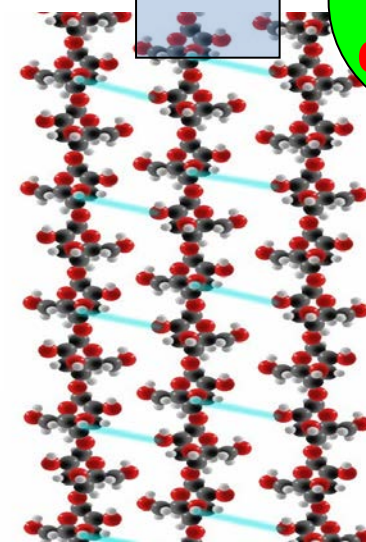
Platform
chemicals
(commodities)

Fine
chemicals
(specialties)

Synth. polymers,
fibers, paints,
pharmaceuticals

Future renewable chemistry („biorefineries“):

Providing necessary chemicals (what the fossil fuels do today)
PLUS
Biogas by cascade utilization
PLUS
Providing special and novel materials by better use of the intrinsic properties



Value created

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

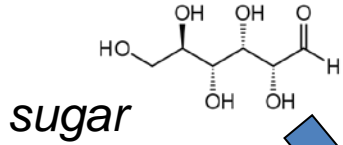
→ **Acknowledge the uniqueness of the raw materials – not just destroying them !**

Example: poly(lactic acid) (PLA)

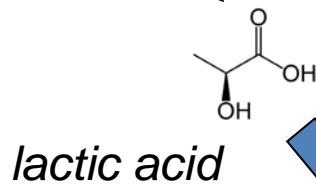
- Made from renewable resources
- Biologically degradable
- „Detour“: polymer → monomer → polymer



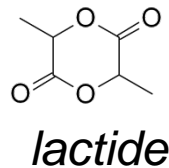
biorefinery



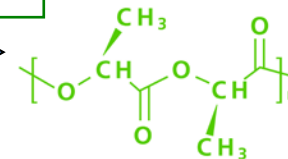
fermentation



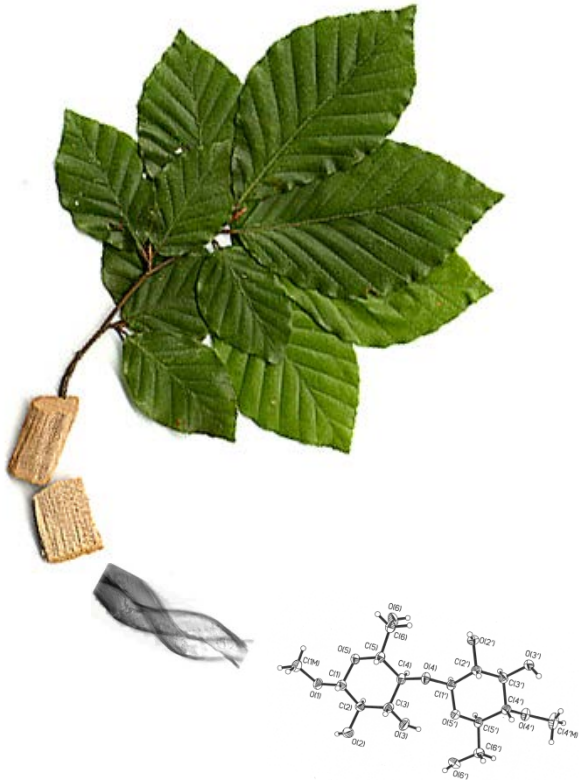
distillation



polymerisation



Biorefineries



Biorefineries – some background

The problems of today's biorefineries (the „sixpack“)



Three examples
(for a more optimistic ending)





Ammonoxidation of ligneous matter: *N*-lignins

Complex of dead organic matter

Lignin containing raw / waste materials

Topsoil
1-3 years: natural humification

Required chemicals
 O_2 , NH_3 , H_2O (T, p)

Reactor
0.5-2 h: artificial humification

- Demethoxylation
- Demethylation
- Formation of quinones

- Oxidation of aliphatic side chains
- Cleavage of aromatic ring systems
- **Nitrogen enrichment**

Natural humus

Artificial humus,
„*N*-lignins“



***N*-Lignins as multifunctional, artificial humic matter and soil improver**



Chemistry largely identical to natural humic matter
C- and N-source, analogous to natural humic matter
Short-term, mid-term and long-term fertilizing effect
Matrix effect (water and nutrient reservoir)



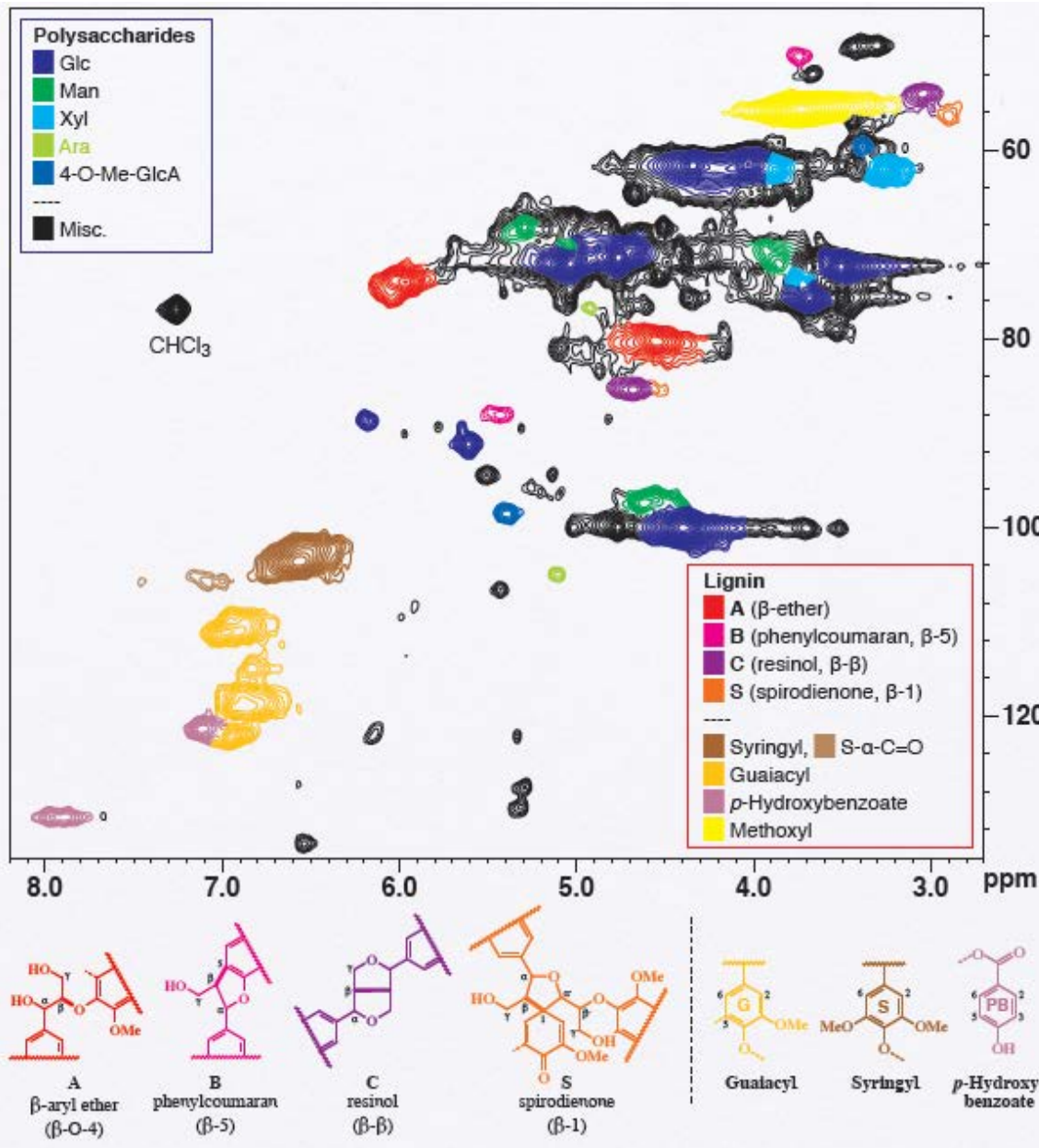
Able to utilize bulk lignin amounts

Return of lignin into natural cycles (C, N) rather than burning it to CO₂

Additional CO₂ sequestration / mineralization (carbamate / urea)



Whole plant cell wall NMR



**BOKU –
Universitäts- und
Forschungs-
zentrum Tulln
(UFT)**

Analysis of:

- Celluloses
- Pulps
- Lignin
- Biopolymers
- Biomaterials
- Paper
- Historic celluloses

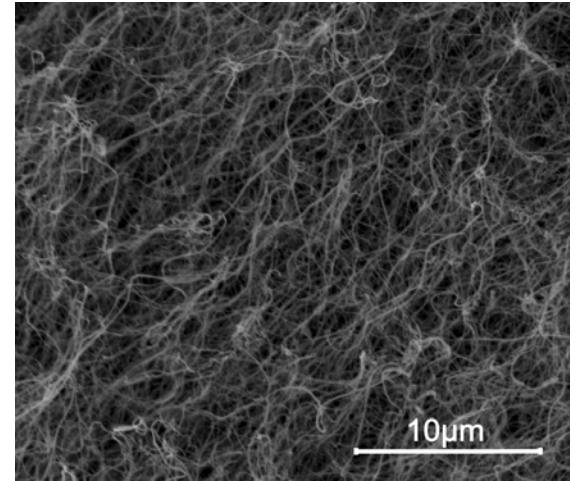
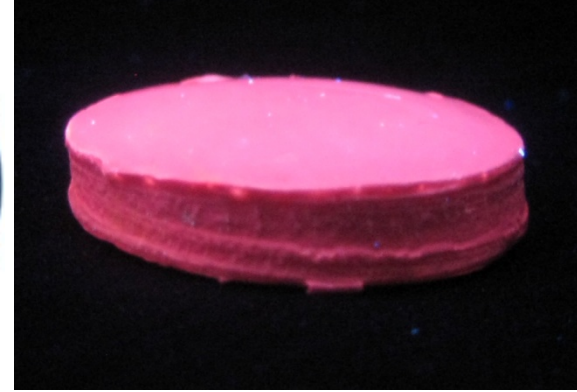


Novel analysis methods specific for green applications





Cellulose aerogels: Functional materials with fascinating properties



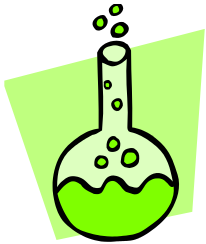
Selected properties

	cellulose aerogel	silica aerogel
● density [mg cm^{-3}]	> 0.001	> 0.005
● specific surface [$\text{m}^2 \text{g}^{-1}$]	250-800	500-1000
● α (lin) [$1/\text{K } 10^{-6}$] at RT	0.029	0.030
● sound propagation [km s^{-1}]	0.04	0.07-1.3



Ultra-lightweight cellulosic bodies for heat, sound and impact insulation and for medicine (cell scaffolds, bone replacement).

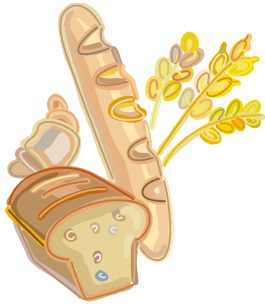
Summary: General trends in future biorefineries



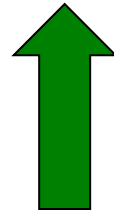
Material / chemical utilization



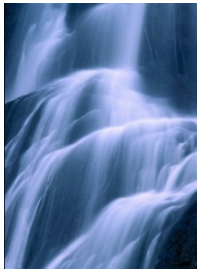
Energetic utilization



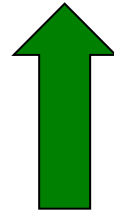
Food / feed: starch
Cellulose & lignin: chemistry



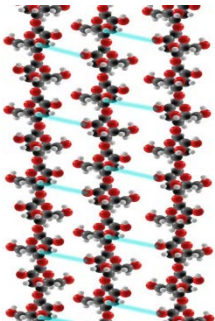
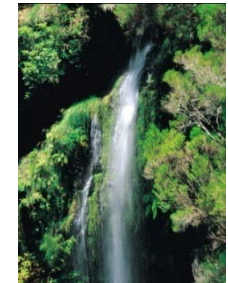
Energy / chemicals from food-/feedstock



Cascade utilization



Direct (one-step) „utilization“ by burning



Better use of nature's ingenuity in synthesis and material production



Extensive breakdown of renewables „green-to-oil“

CO , H_2 , CH_4 , C_2H_5OH

Financial \$upport



Alma mater viridis



European Polysaccharide
Network Of Excellence



FWF



FFG



National Institutes of Health

The Nation's Medical Research Agency



kemira

sappi



fzmb



ISOVER



heinzelpulp

ZELLSTOFF PÖLS AG

**Thanks to the people who
are actually doing the work...**





Thomas Rosenau

**University of Natural Resources and
Life Sciences Vienna
Department of Chemistry**

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Biorefineries

What do we know? Where are the problems?