BIOBASED AROMATICS – CHALLENGES, HURDLES AND OPPORTUNITIES

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5th Latin American Congress on Biorefineries, Concepcion, 7-9 January, 2019

Universiteit Antwerpen

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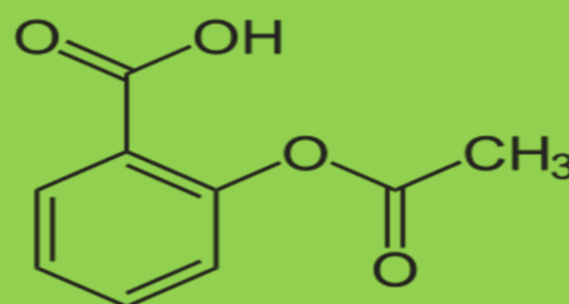
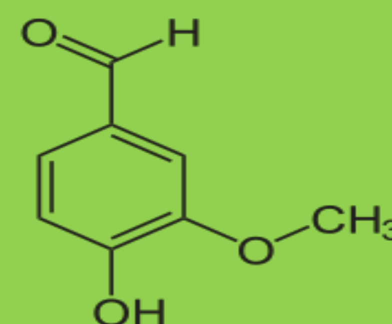
SOME LINKS TO FORMER PRESENTATIONS

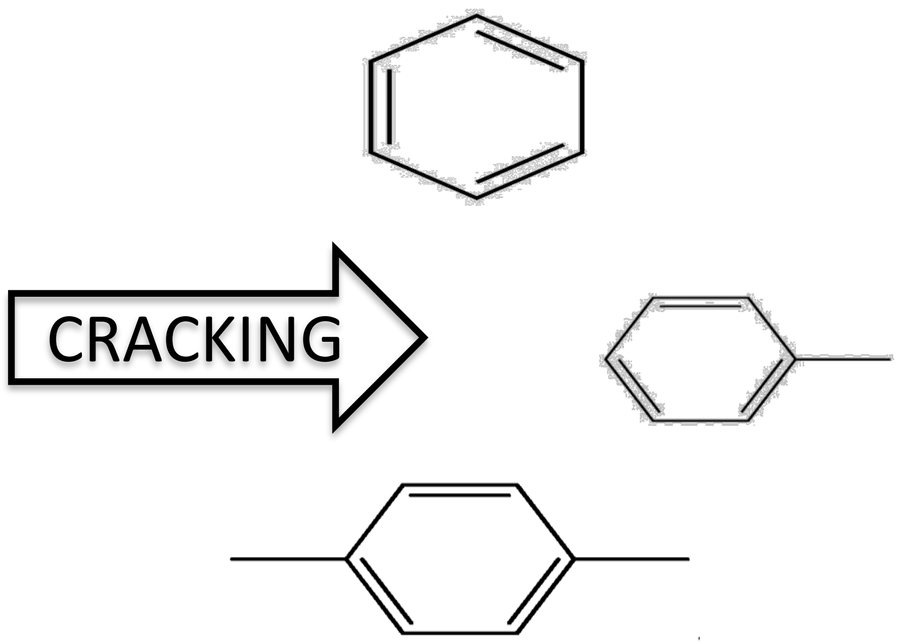
- Eduardo Falabella: co-processing of vegetable oils and bio oils is impacted by phenolics
- Marisol Berti: need for fertilizer reduction, land use change!
- Andy Perez: infections on *Pinus radiata* by *Sirex noctillo* and *Eucalyptus globulus* by *Gonripteres scutellata* ➔ new fenolic compounds
- Maria Martinez: valorization of all fractions including lignin
- Residential waste session: lignocellulose available
- Tim Schulzke: Ablative Fast Pyrolysis ➔ 10% phenolics for resin production
- Bruno Gorrini: resins from tannins because very reactive
- Henrikki Liimatainen: DES as new way of fractionation of lignocellulose
- Danny Marero: Maleic anhydride in Glycerol – SA polycondensation
- Alex Berg: Thermowood, oxygen removal in pyrolysis,…

Chapter 1 Why Aromatics?

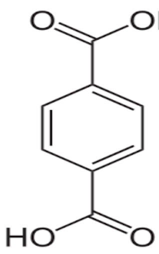


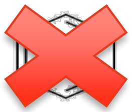


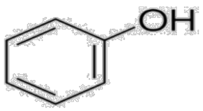
BTX as result of oil cracking



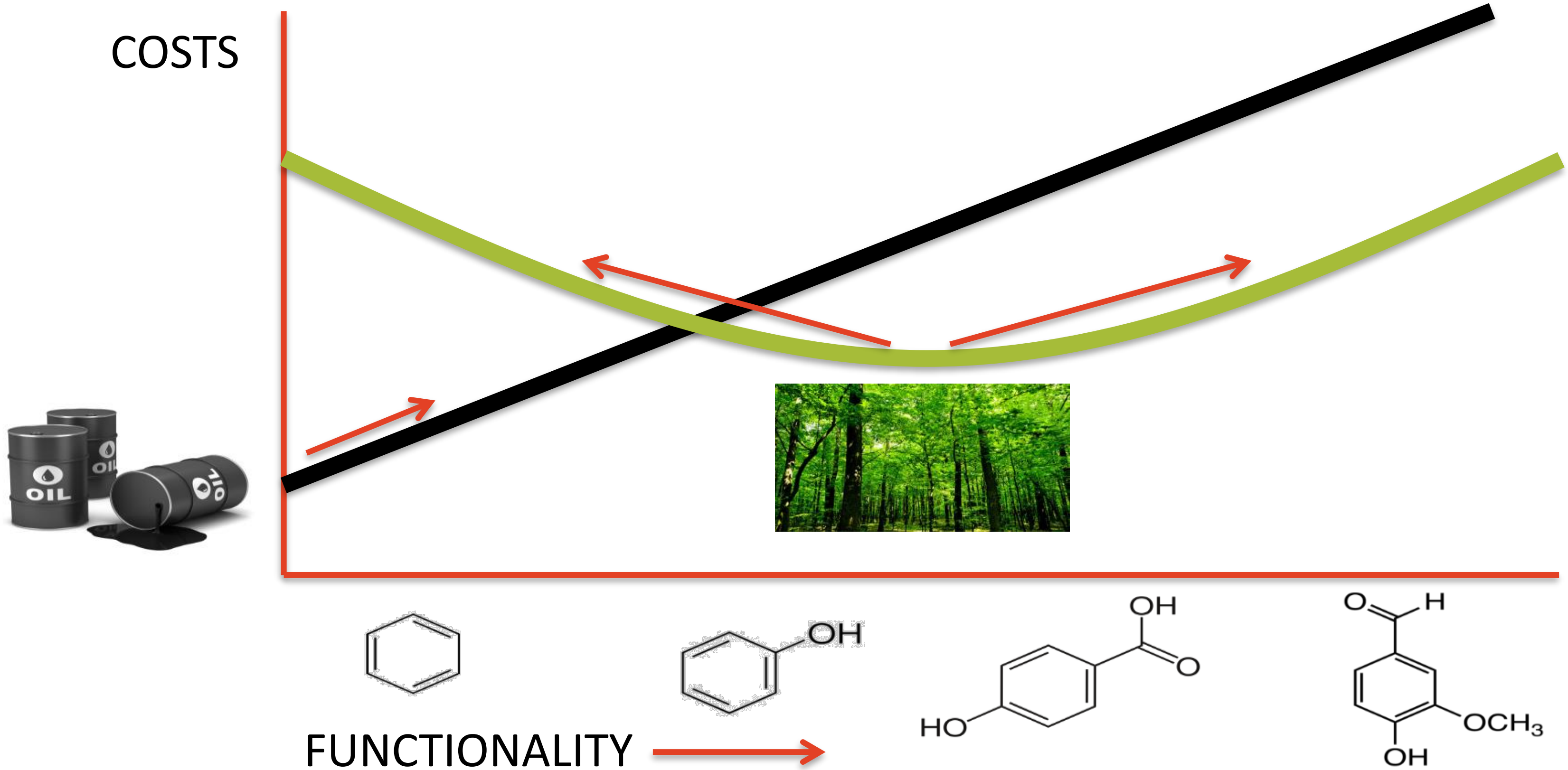
We use functionalized aromatics



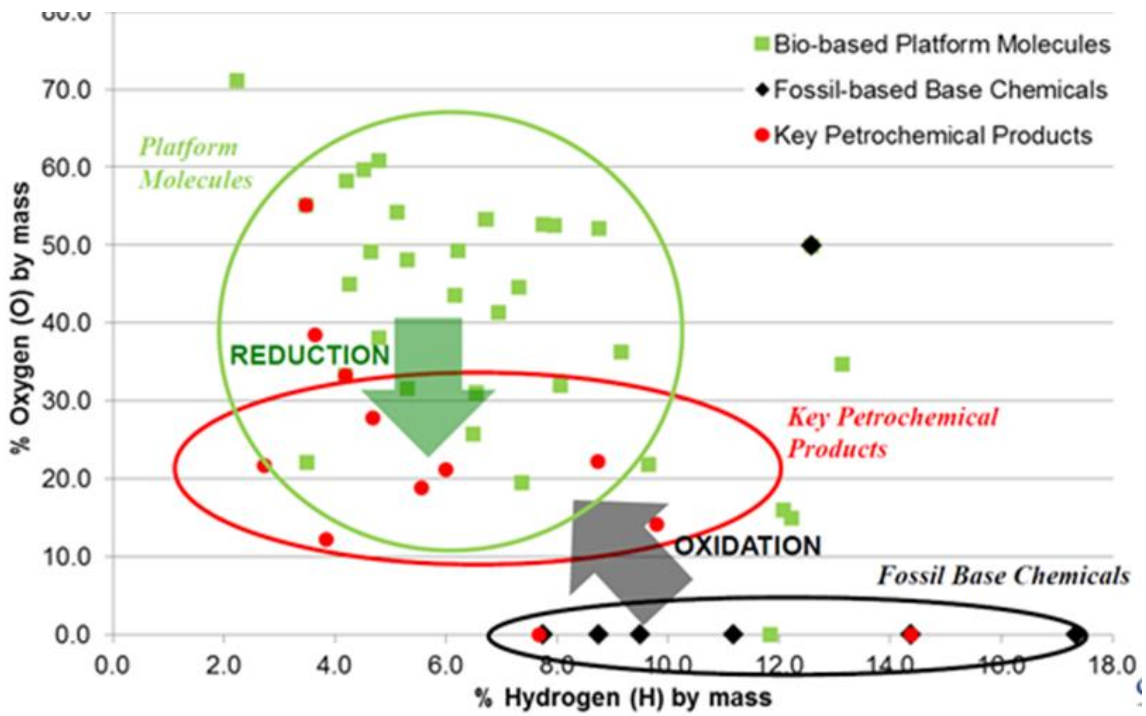




Why functionalized aromatics?



Study by Thomas Farmer, Univ. York



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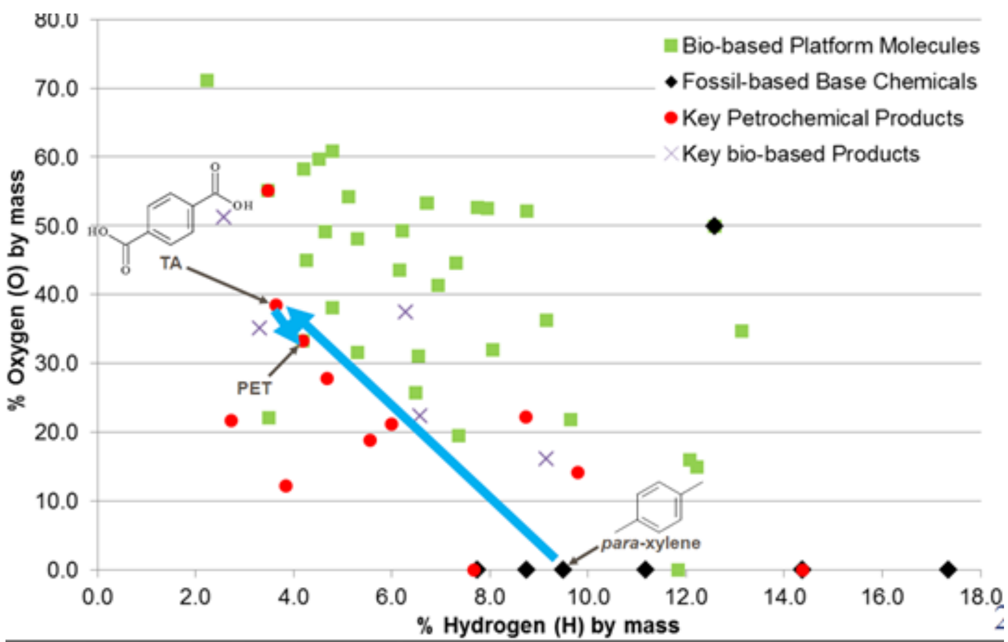
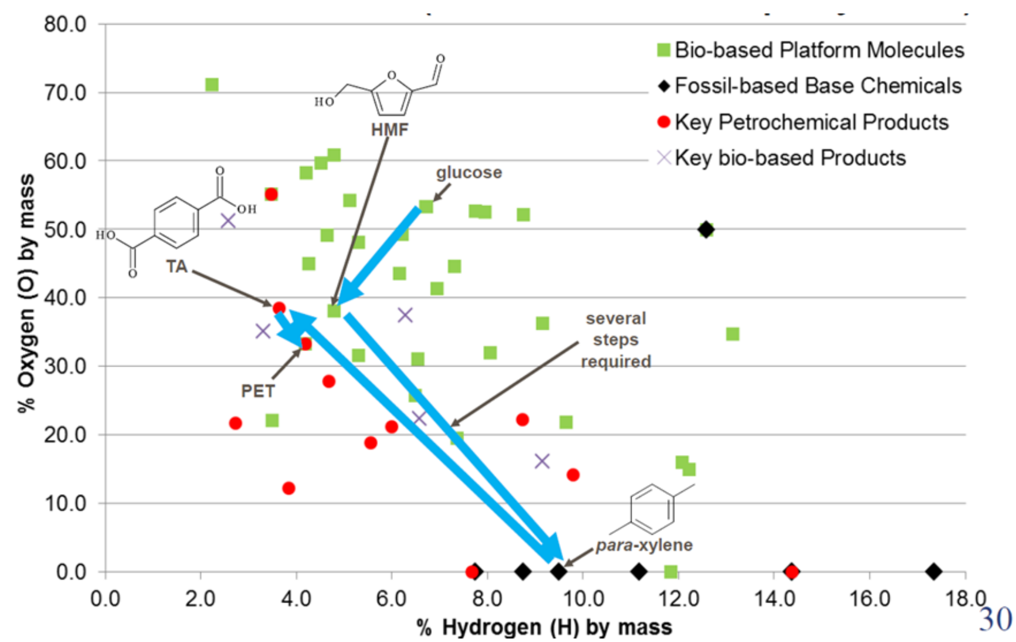
FROM XYLENE TO PET

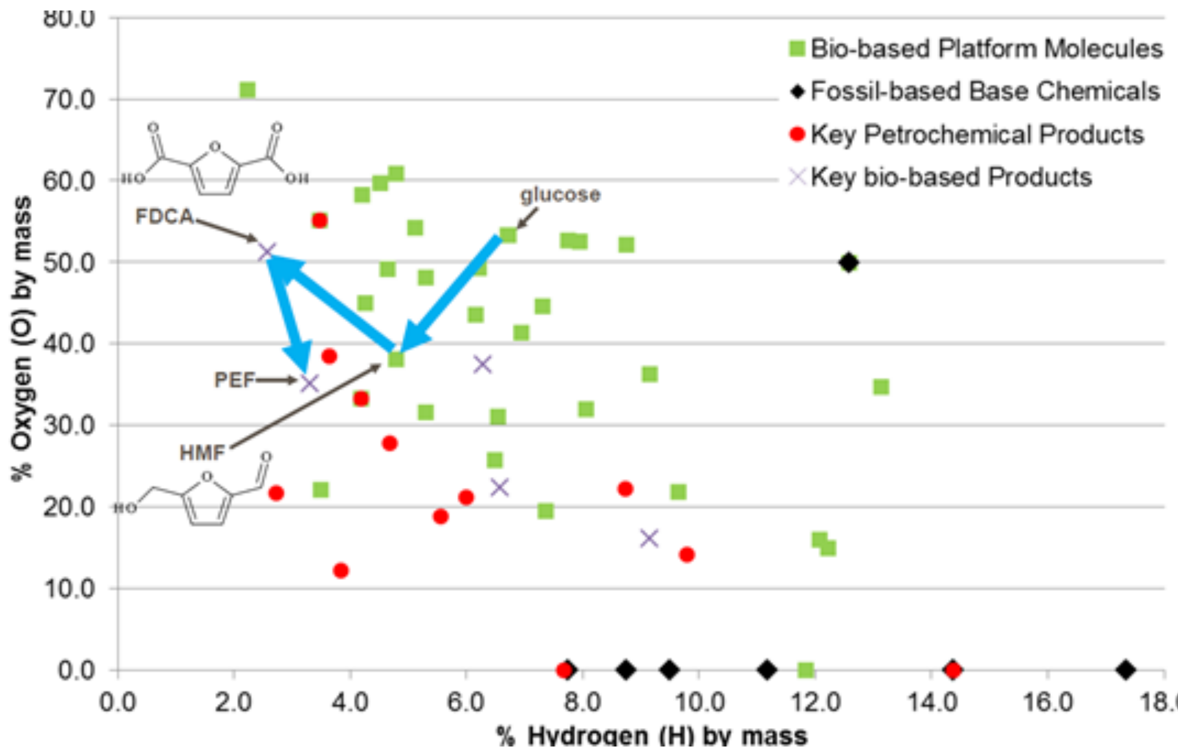
Petro-based *versus* *Bio-based*





 Thomas Farmer (Univ. York)

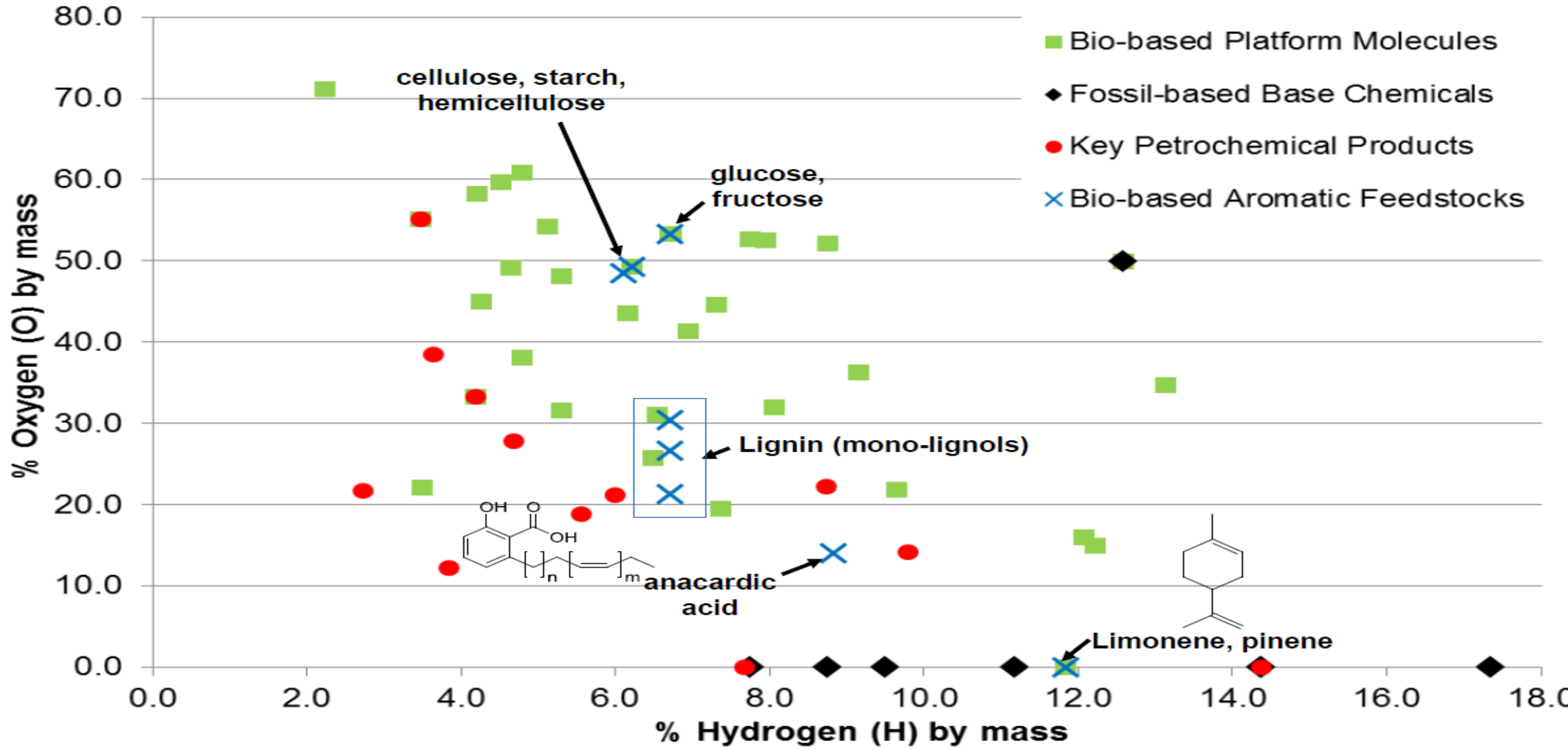
USE THE OXYGEN FUNCTIONALISATION IN A SMART WAY WITH NEW CATALYTIC MEANS



Thomas Farmer (Univ. York)

OXIDATION VERSUS REDUCTION

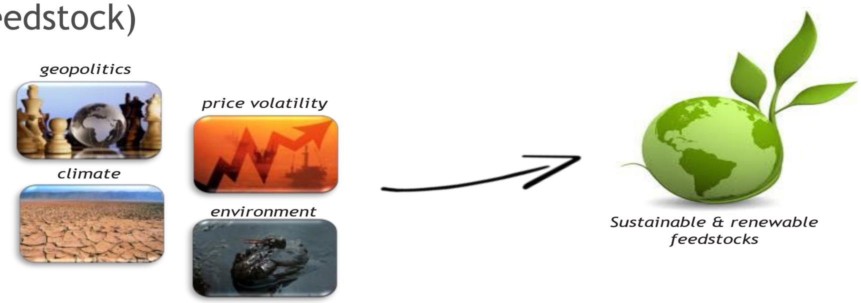
Study by Thomas Farmer, Univ. York



DRIVERS AND OPPORTUNITIES FOR DEVELOPMENT OF 'LIGNOCELLULOSIC FEEDSTCOK TO AROMATICS'

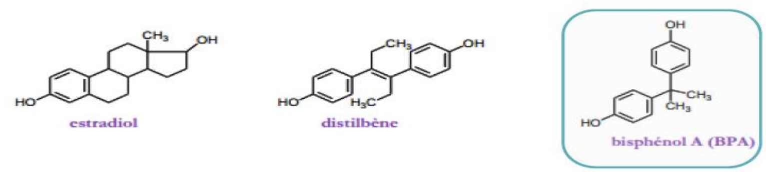
- Societal driver for transition to bio-economy (i.e. renewable feedstock)

- Reducing footprint of industrial processes
  - Use of biomass
  - Use of functionality (less steps)



- Innovation in chemicals & materials
  - Safer, performance-based products
  - Through disruptive enabling process technologies

- Economic drivers
  - 40% of chemicals are aromatic (>23 mln tons BTX-fenol)
  - Inability to valorize lignin is a lost opportunity in biorefining
  - Recovery boiler (P&P) is limited in solids content, removal of lignin solves this problem
  - Shale gas does not deliver higher than C3
  - 25% of world production in Europe (large amount of jobs)



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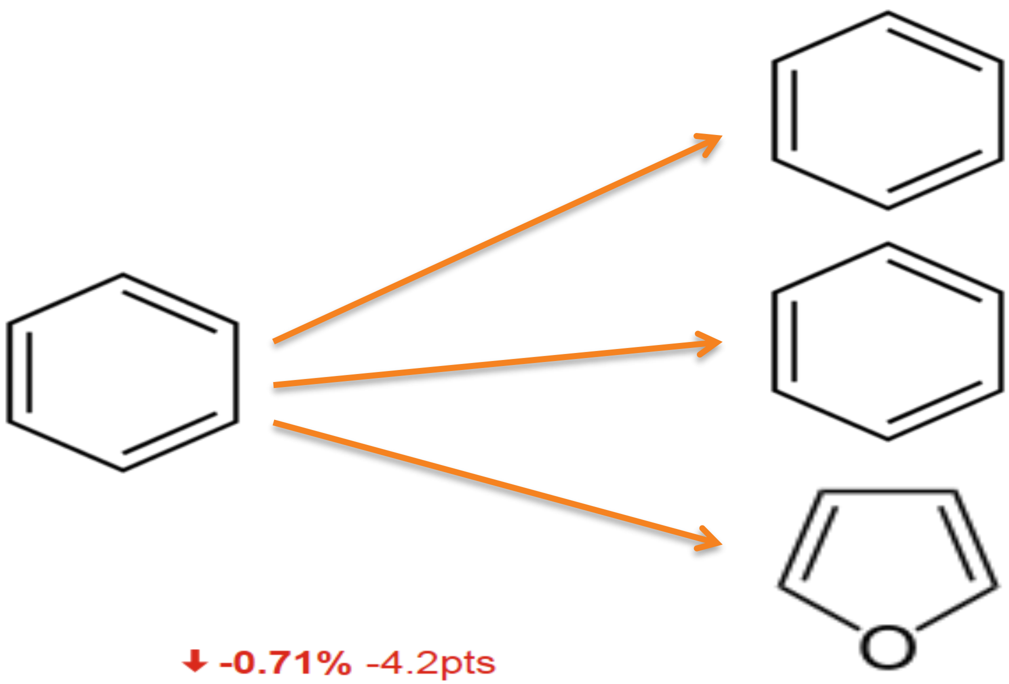
HOW CAN BIOMASS REPLACE AROMATIC CHARACTERISTICS?

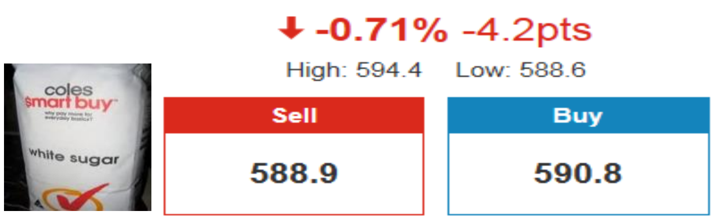
Based on the lignocellulose biorefinery



Replace by lignin-based aromatics

Replace by sugar-based aromatics via fermentation

Replace by sugar-based furan chemistry or via Diels-Alder chemistry



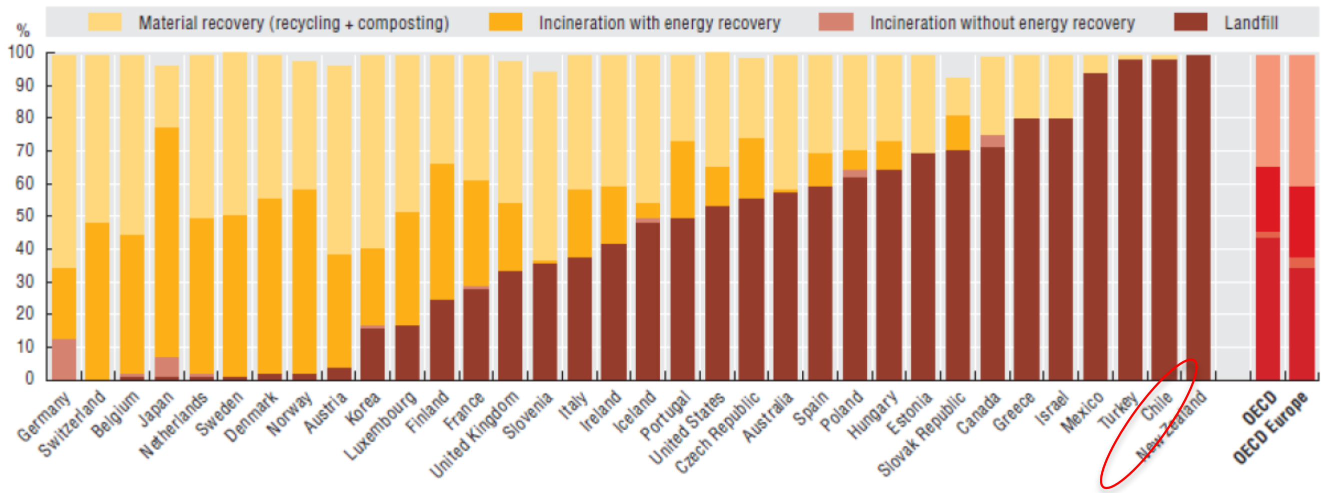
Chapter 2 Bio-economy as part of the circular economy

Food/feed use and its waste -based bioeconomy

BIO-ECONOMY AS PART OF THE CIRCULAR ECONOMY

Food & feed processing and domestic use leads to large amounts of waste

- MSW at 520 kg/p/y of which 50% is biodegradable
- Still huge amounts end up in landfills
- Global food loss and waste generate 4.4 Gtons CO2eq, i.e. 8 % if anthropogenic GHG emissions
- Only 5% of sewage sludge is converted into CH4

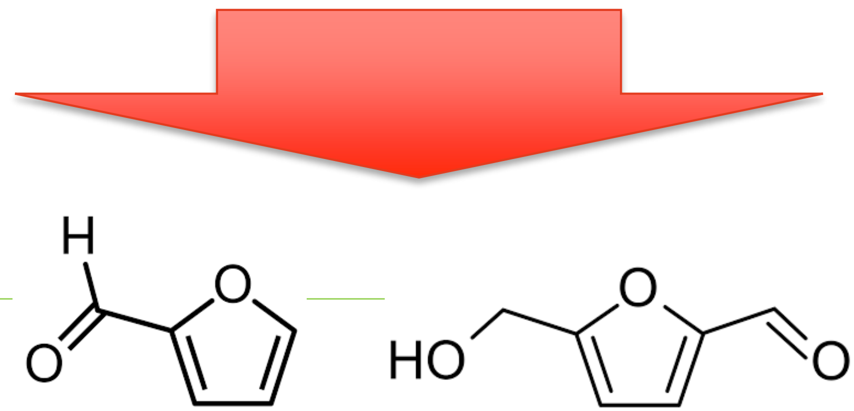


OECD, Realising the circular bioeconomy, Nov 2018, No. 60

WASTE-SUGARS TO FURANICS

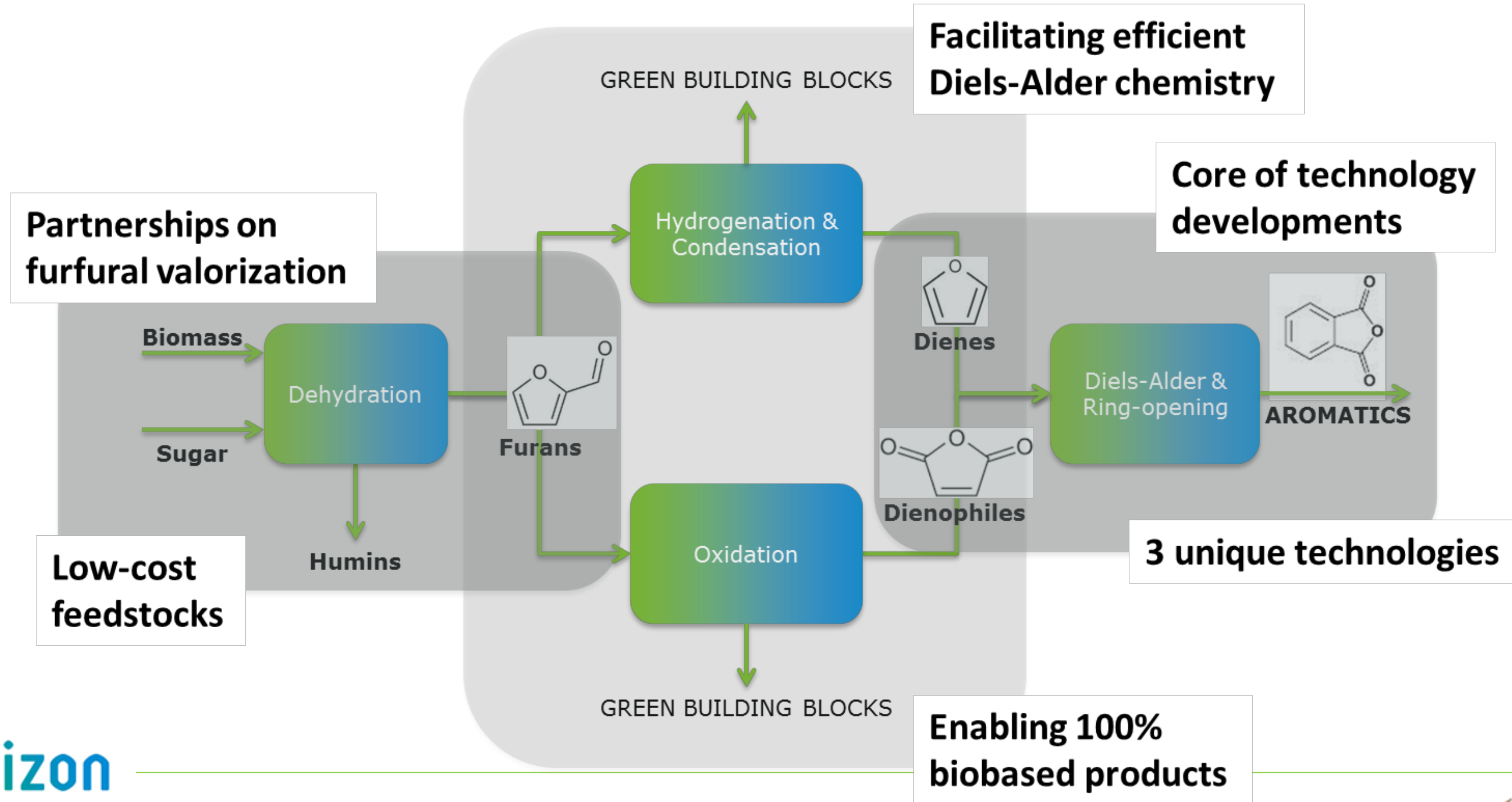
TNO

Biphasic reactor for conversion of waste into furans (kg/hr)



Biorizon
The way to aromatics

FURANS TO AROMATICS



Biorizon
The way to aromatics

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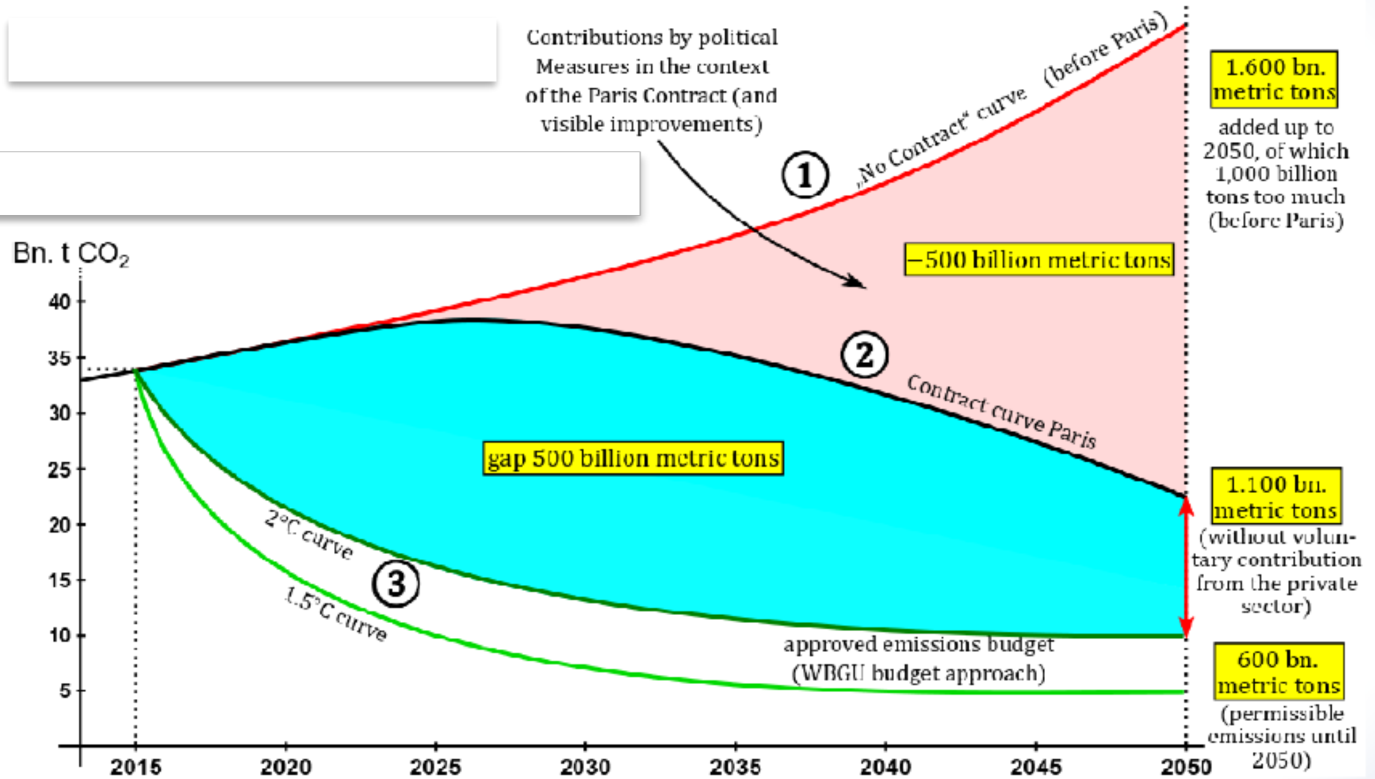
Chapter 2 Bio-economy as part of negative carbon emissions

Forests in climate change mitigation
Forest-based economy

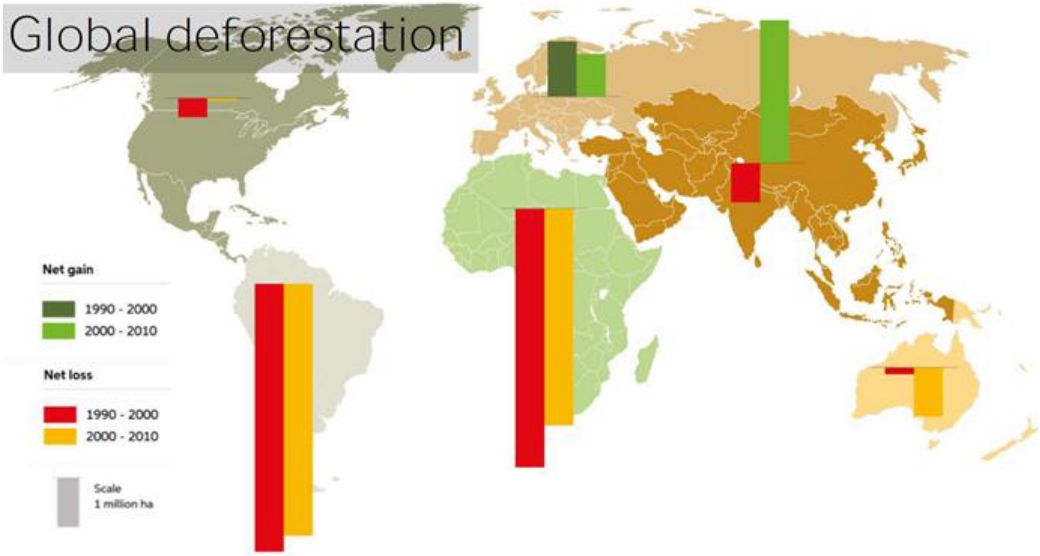
NEGATIVE EMISSIONS AND THE PARIS-GAP

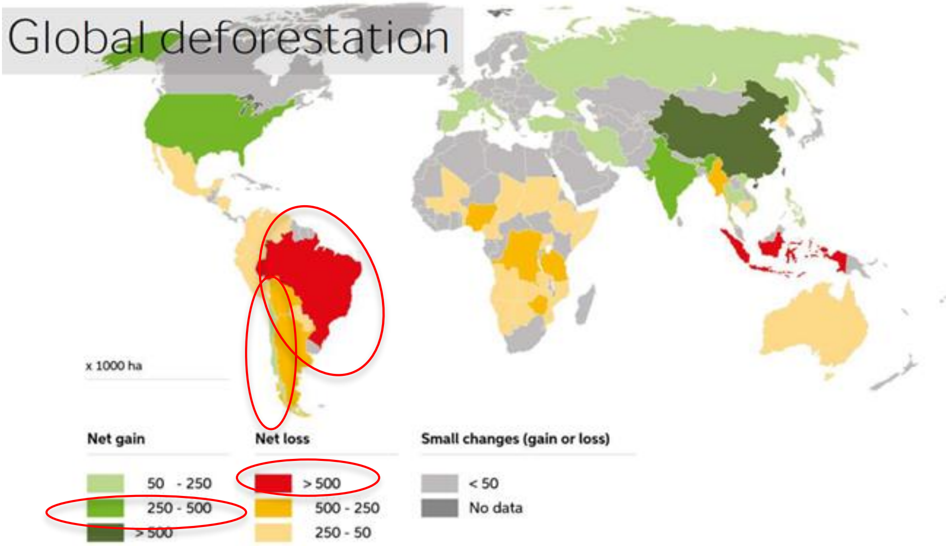
Prof. Radermacher
Uni. Neu-Ulm



GLOBAL DEFORESTATION VS CARBON STOCK AND TREE DENSITY!!!!

- *Most data about surface*
- *No data about carbon stock, carbon capture, tree density, tree renewal,…*
- *13 Mln ha forest cut down annually ➔ 20% GHG emissions*

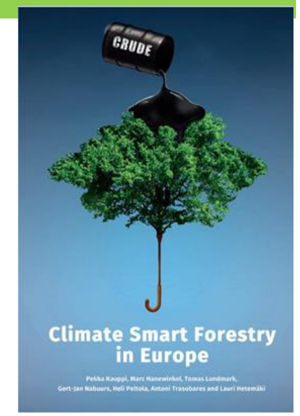




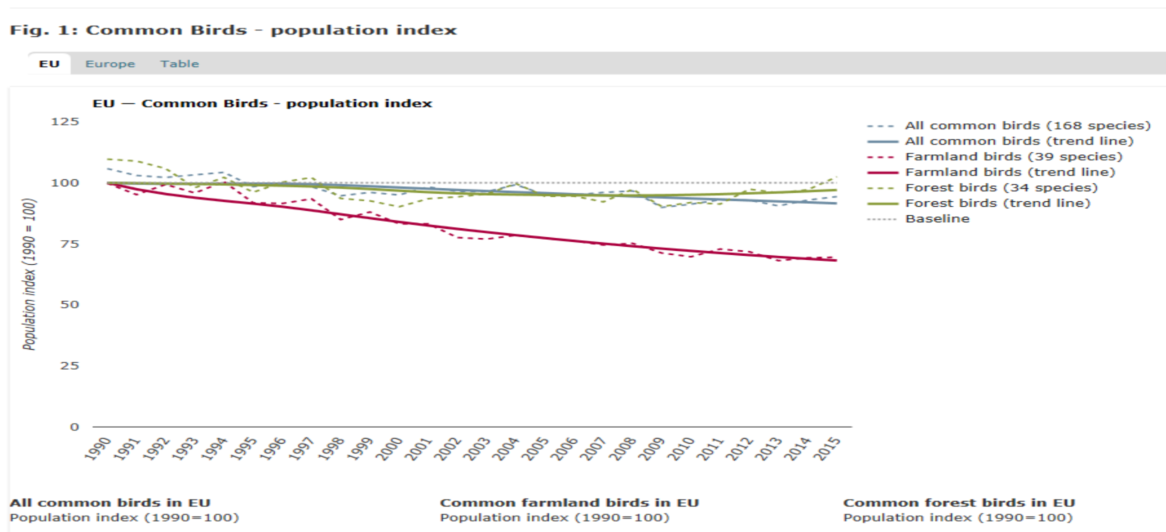
NEGATIVE EMISSIONS

From three trillions of trees to four trillions of trees! (Tom Crowther, Yale Univ., ETH-Zurich)
One trillion of trees can be added without changing biotopes
Action by UNEP and ¨Plant for the Planet"

ROLE OF FORESTS IN CLIMATE CHANGE MITIGATION



- Forests as carbon sink
- Wood products as carbon storage
- Wood/lignocellulose-based materials substituting greenhouse gas intensive materials (1,2 kgC/kgC)
- Forests for water management
- Forests as preservation in biodiversity



FORESTS UNDER THREAT BY CLIMATE CHANGE

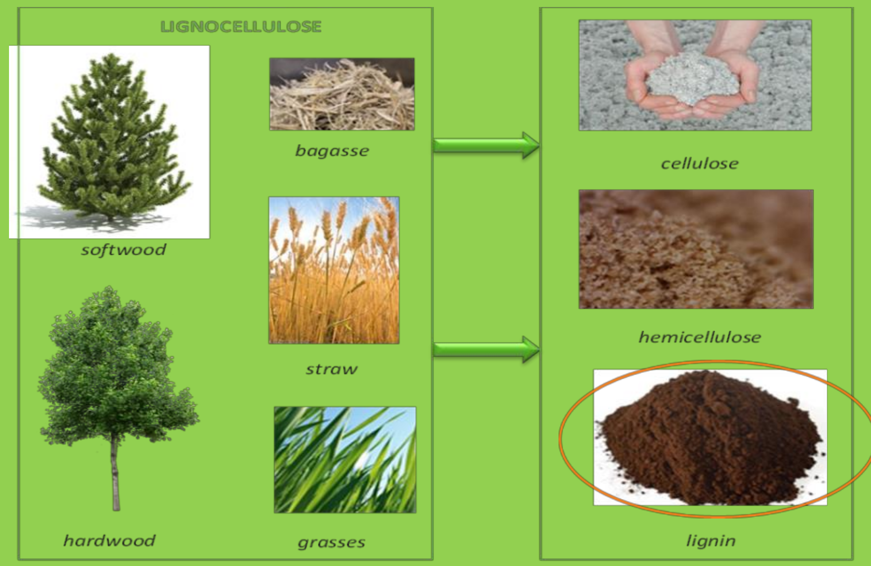
- Forests under threat by climate change ➔ increase in forest fires
- Forest density as a risk for forest fires ➔ need for fellings
- Forests under threat by climate change ➔ pine beetle infection
- Forests under threat by infection ➔ old trees are more vulnerable

➔ Need for new forest management (harvesting & planting)

INDUSTRIAL WOOD USE

- In sustainably managed forests, the forest-based economy can develop
- The lignin biorefinery is (finally) emerging in order to valorize all streams, reduce energy consumption, increase cellulose efficiency, …
- Pulp & Paper companies act as a catalyst of that movement with a focus on product positioning and creation of unique competitive advantages

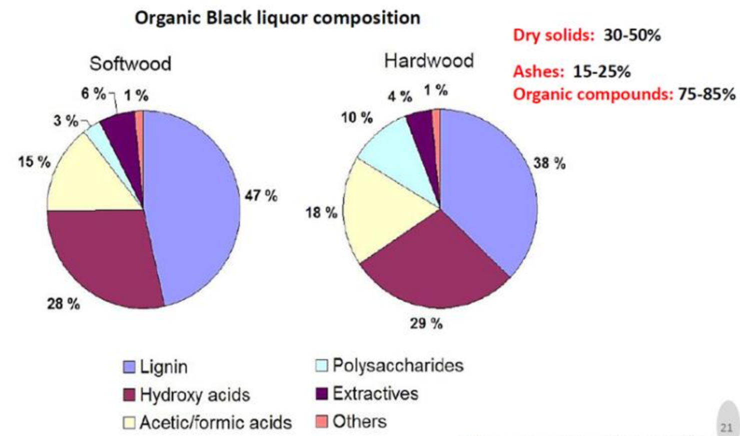
Chapter 4 How to proceed from lignin to aromatics?



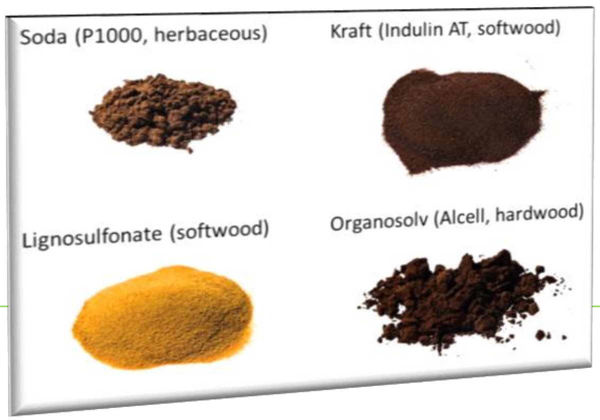
ORIGIN OF LIGNIN

Pulp & paper industry (+ upgraded lignins) or from Cellulose ethanol

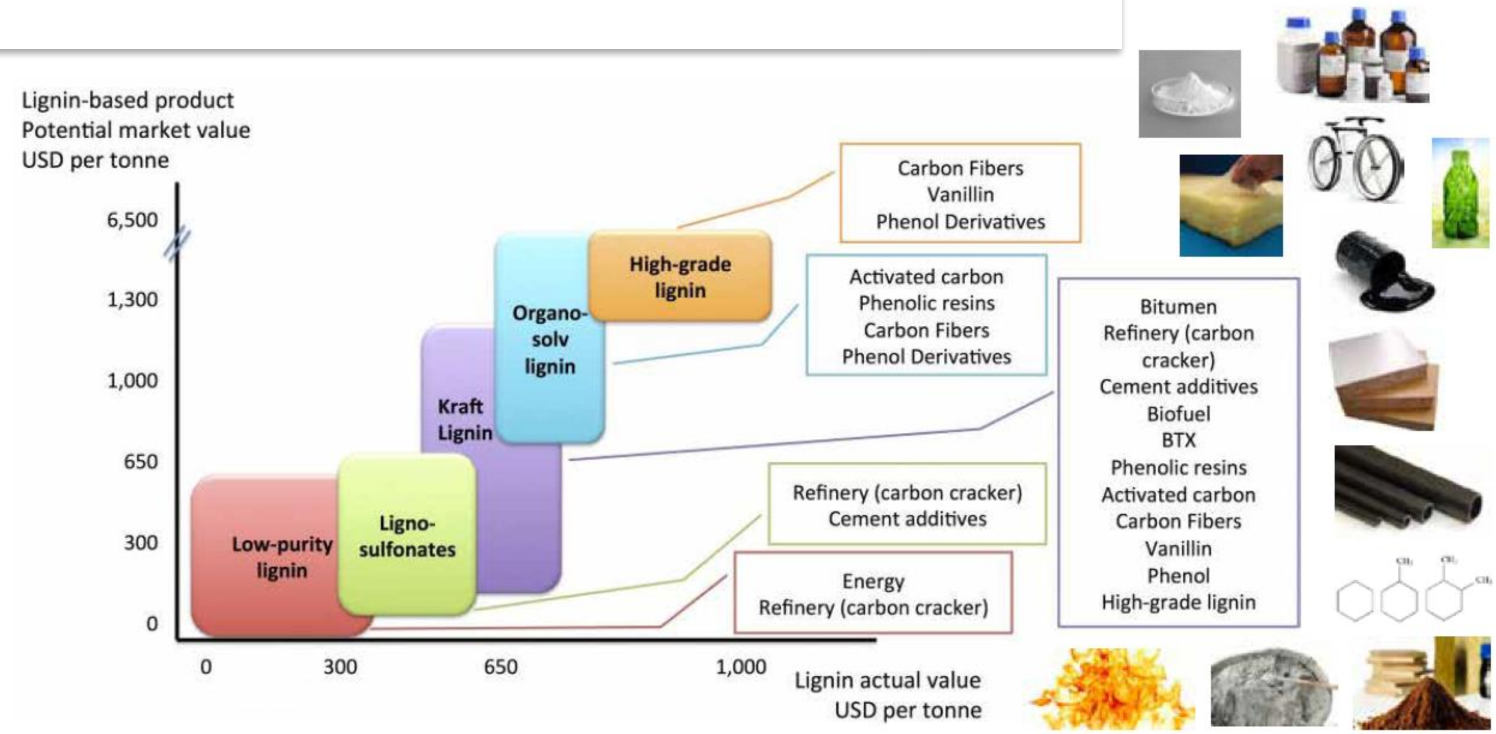
- Lignin from pulp & paper industry
  - Lignosulfonate lignin (wood)
  - Kraft lignin (wood)
  - Soda lignin (non-wood)
- Lignin modifications
  - Lignoboost (CO_2-precipitation)
  - Lignoforce (oxidation + CO_2-precipitation)
  - Ligniox (alkaline oxidation step)
  - Ecolig
  - ….
- H-lignin from cellulose ethanol production
  - Steam/ammonia explosion + enzymes
  - …
- New lignins
  - $scCO_2$, scAlcohols
  - Alkali or acid (LXP, Zambezi, Chempolis)
  - Autohydrolysis (hot water)
  - Organic solvents: Lignol, FhG, CIMV
  - Ionic Liquids/DES/ NADES
  - …



Data source: Niemalä et al. 2010



LIGNIN VALUE VERSUS LIGNIN-BASED PRODUCT VALUE

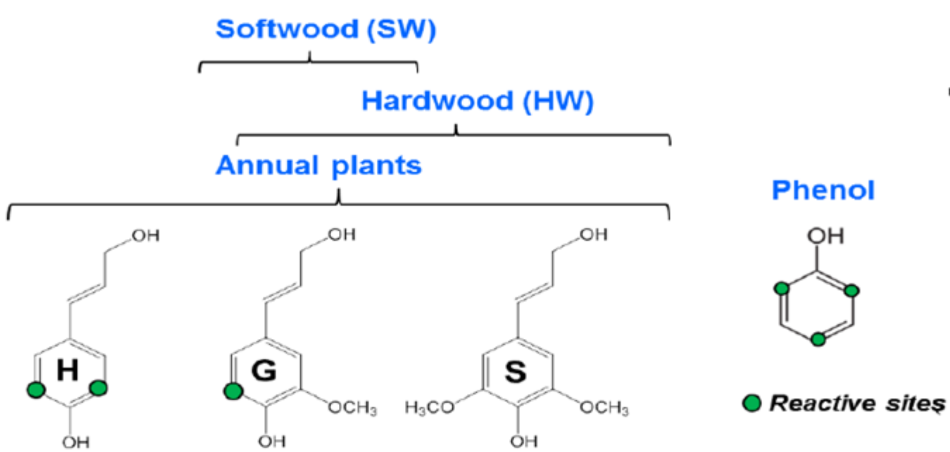


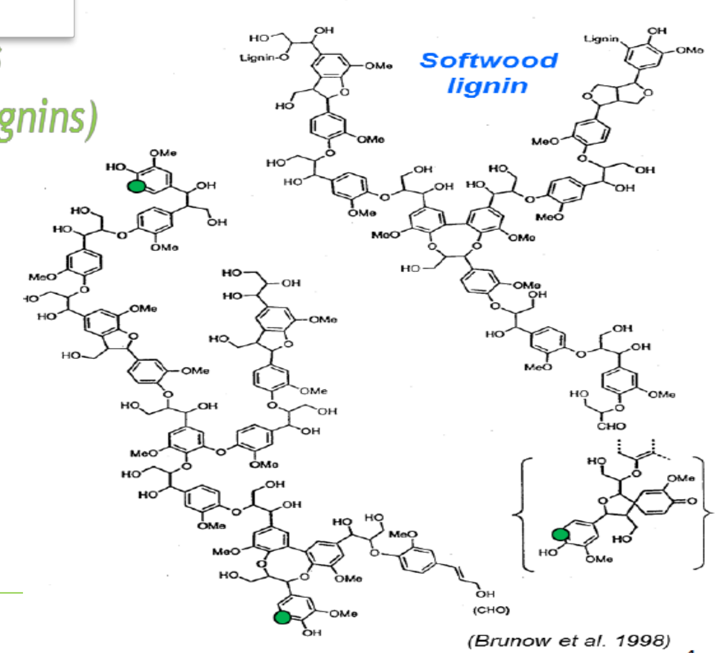
Source: Lee Enterprises Consulting, 2016-12-04.

PHYSICOCHEMICAL FACTORS PROMISE A BRIGHT FUTURE FOR LIGNIN-BASED PRODUCTS

- presence of **aromatic rings reactive functional groups**
- good **rheological and visco-elastic** properties and good **film-forming** ability
- compatibility with a wide range of industrial chemicals
- h**ydrophilic** or **hydrophobic character** depending on origin

- *Only 20-40 % phenol can be replaced with lignin in PF-resins*
- *Methoxyl groups limit the reactivity (especially hardwood lignins)*
- *Not really a technical feasible activation process*

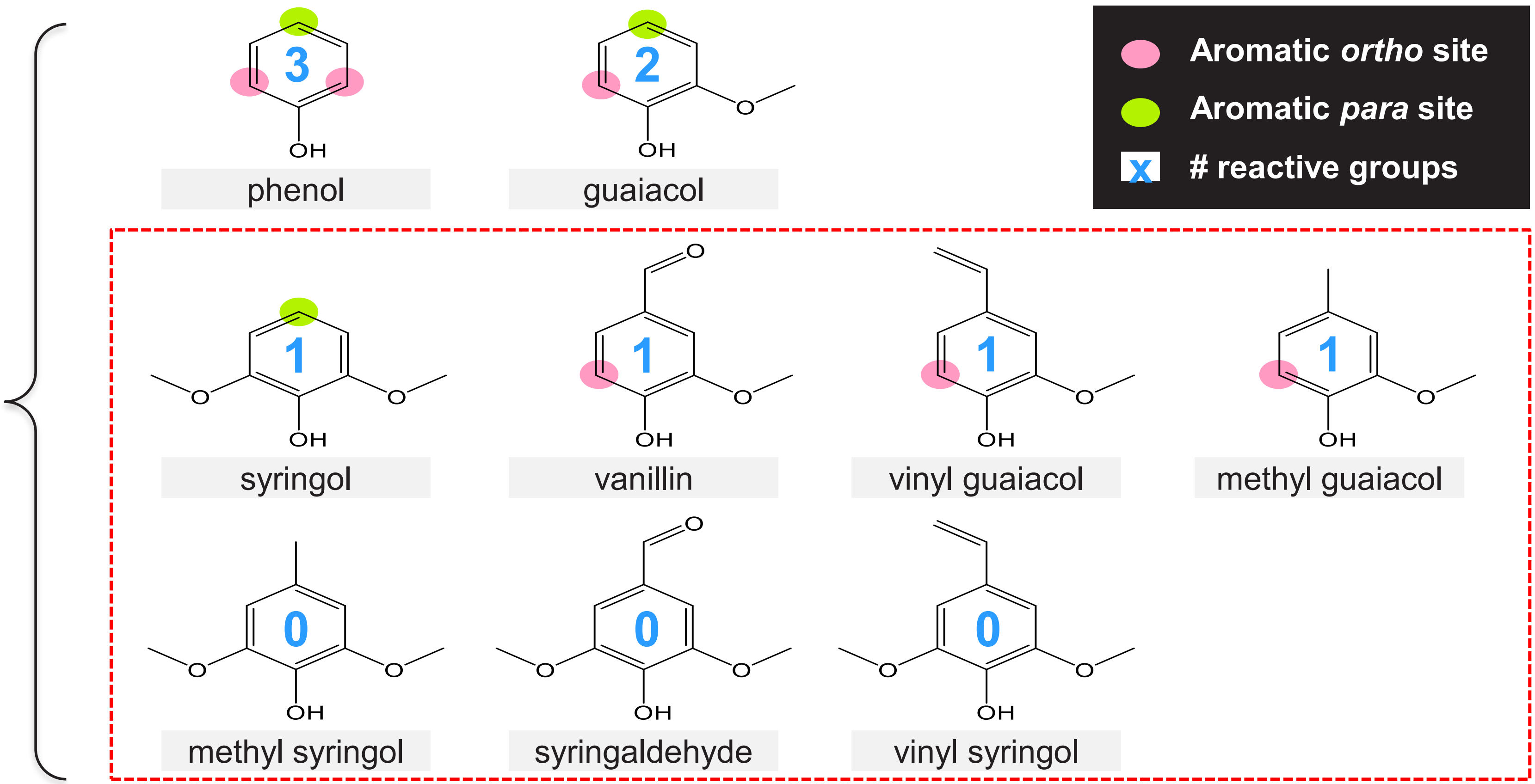




(Marie Anheden RISE)

MONOMER MODIFICATION AND REACTIVE SITES!

Major monomeric products obtained during lignin fractionation



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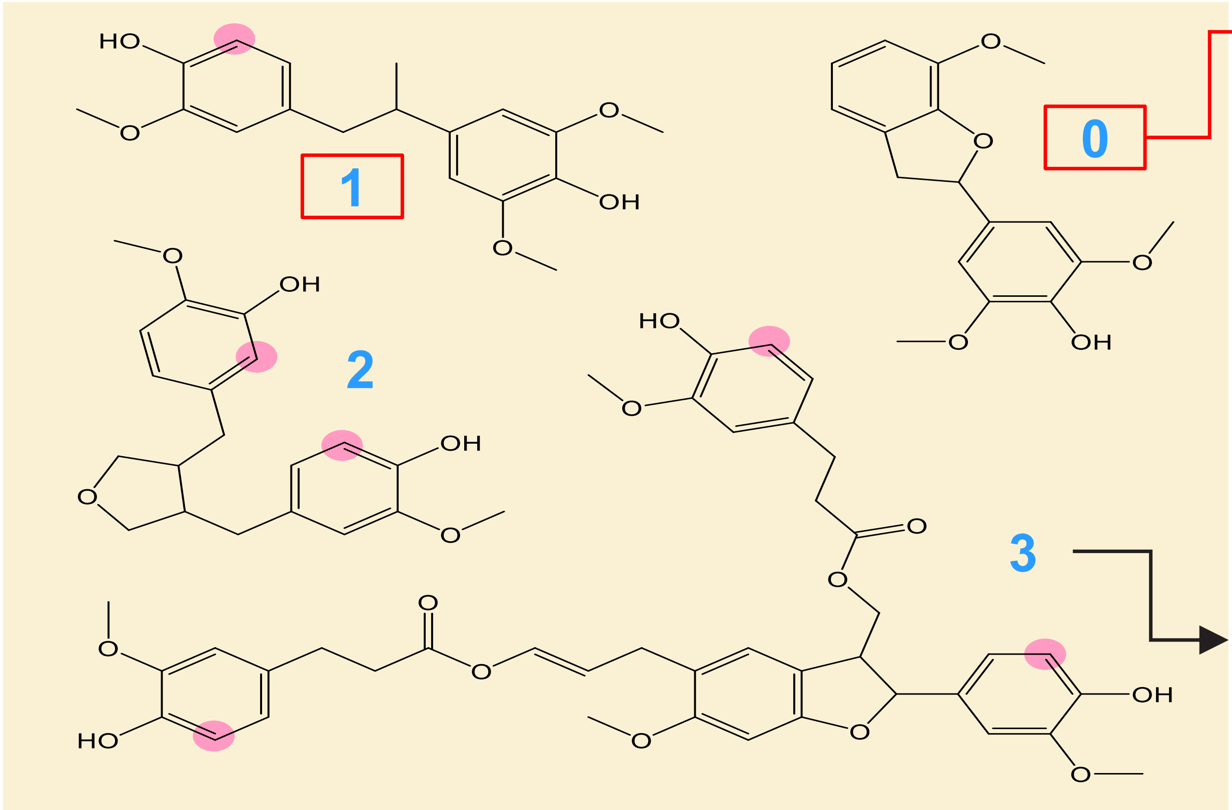
OLIGOMERS AND REACTIVE SITES!

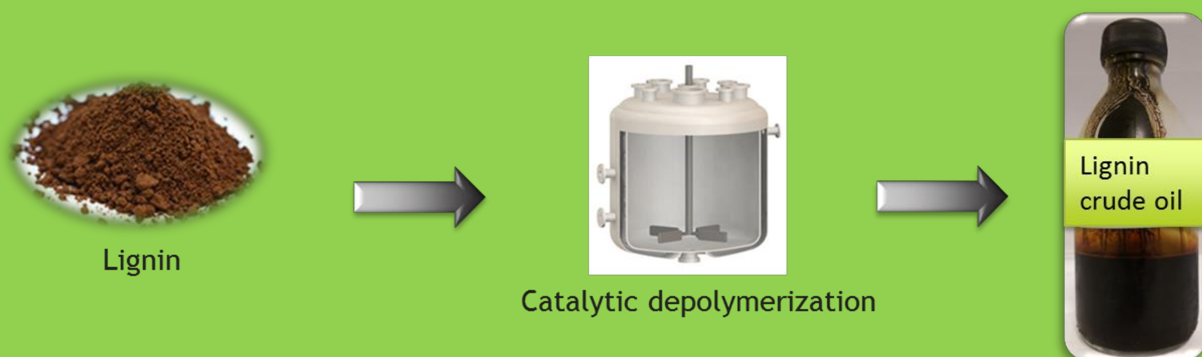
Typical structures (dimers & oligomers) obtained from the BCD process



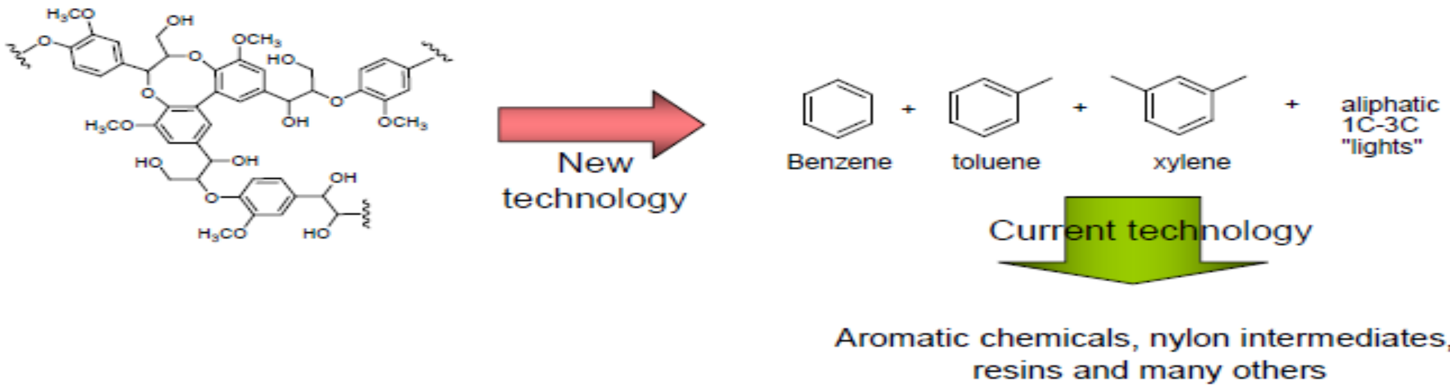
Reactivity of the dimers is better compared to monomers, but it is not always sufficient

Oligomeric structures are intrinsically more suitable than monomers for resin development (higher # of reactive groups).

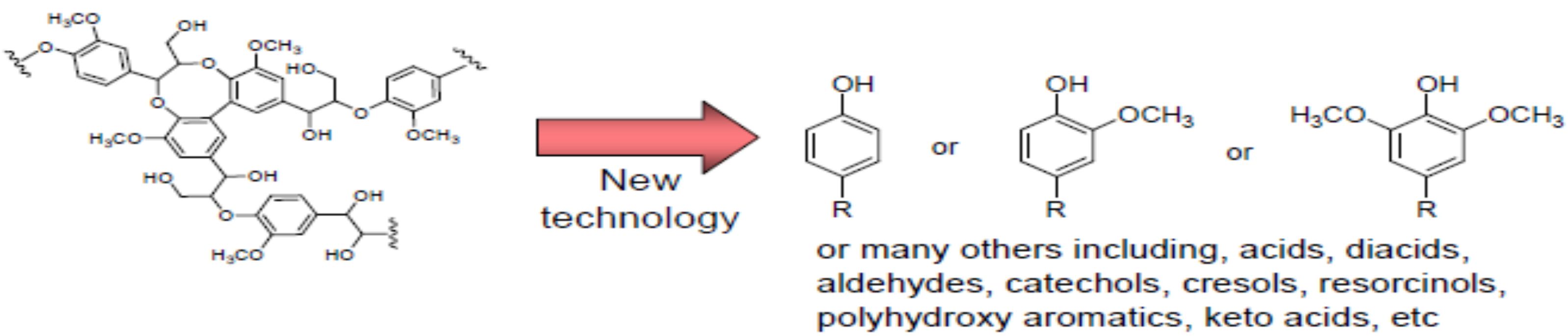
Chapter 5 Lignin depolymerization & fractionation



DEPOLYMERIZATION & FOCUS ON FUNCTIONALITY



Conversion of Lignin to BTX chemicals



Products that Preserve Lignin Monomer Structure

LIGNIN DEPOLYMERIZATION

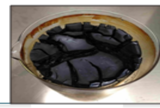
- Reductive
- Oxidative
- Solvolytic
- Thermal
- *Enzymatic*

Base Catalysed Depolymerization (BCD)

Fraunhofer

Geen IP

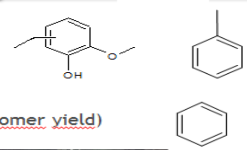
- Feedstock: Kraft lignin - Organosolv
- Solvent: water
- Catalyst: 1-5 wt% NaOH
- 250 bar H_2, 300 °C, 600 s
- 20 kg/h lignin solution (eq. 2 kg/h lignin)
- Yield: ~ca.73 %
  - ✓ BCD oil: 14.5 wt%
  - ✓ BCD oligomers: 58.8 wt%
- Cost price: €5850 for ~2 kg lignin derivatives



Catalytic supercritical ethanol process

TU/e

- Feedstock: different types of lignin
- Solvent: supercritical ethanol
- Catalyst: $CuAlMgO_x$
- 4 L reactor; 20-50 g of lignin
- 75-175 bar, 240-340 °C, 4 h
- 40-80 mL lignin oil (labscale: up to 60 % monomer yield)
- Further scale-up in BIO-HArT

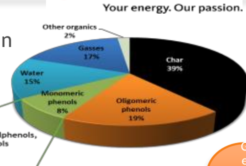


Geen IP

LIBRA process (pyrolysis)

ECN
Your energy. Our passion.

- Feedstock: different types of lignin
- Pyrolysis at 400 °C
- Proof-of-concept at 1 kg lignin/h
- Yield: ~ca.80 %
  - ✓ Pyrolytic liquids
  - ✓ Gases
  - ✓ Char formation



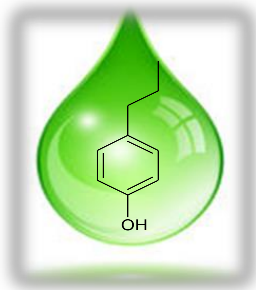
Geen IP

MOGHI

biochemtex

- Feedstock: 2G lignin from Proesa™ technology
- Catalytic deoxygenation and depolymerization
- Conversion into bio-naphta and lignin derivatives
  - ✓ Napthene: 10-15 %
  - ✓ Paraffins: < 5 %
  - ✓ Phenolics: 75-85 %
- TRL 6

IP



Applications: Specifications – Requirements

- Functionality
- Viscosity
- Impurities
- Mw
- …

What do companies want?

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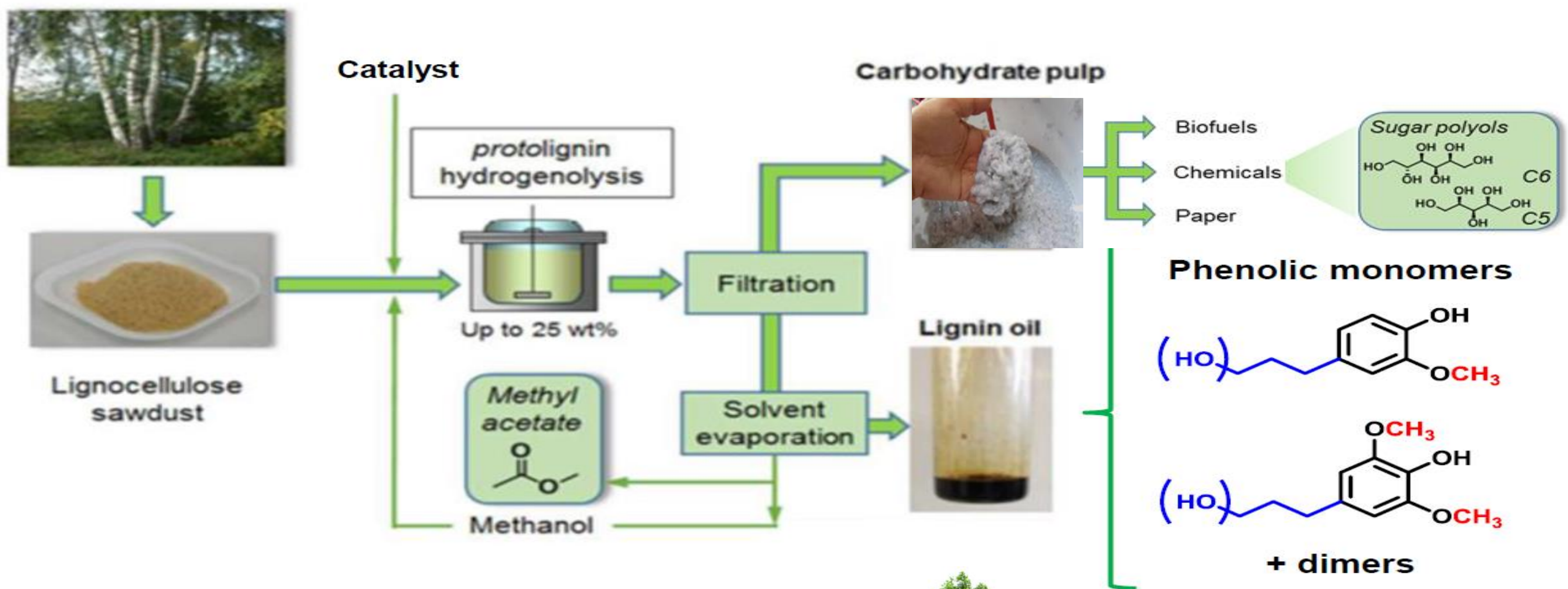

Sels, B. F. et al. *Chem. Commun. (Cambridge, U. K.)* **2015**, *51*, 13158.
Sels, B. F. et al. *Energy Environ. Sci.* **2015**, *8*, 1748.

45-100 €/ton wet wood
Up to 250 €/ton dry wood

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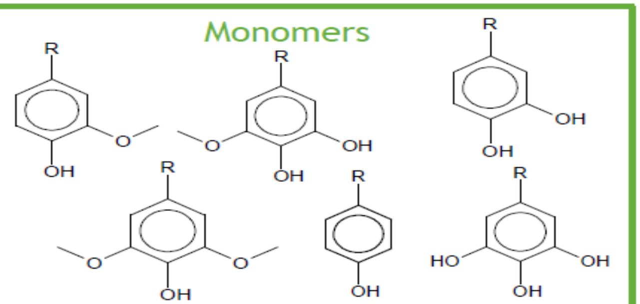
MOLECULES THAT ARE OBTAINED

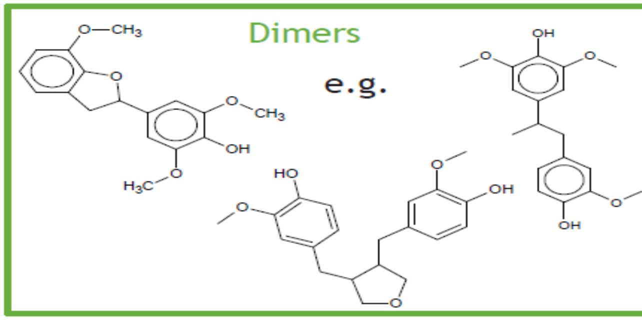
Fraunhofer

ROUTE 1: BASE CATALYZED DEPOLYMERIZATION

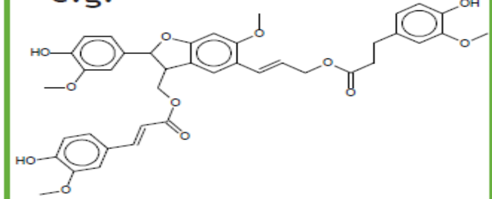
Monomers



Dimers



Oligomers



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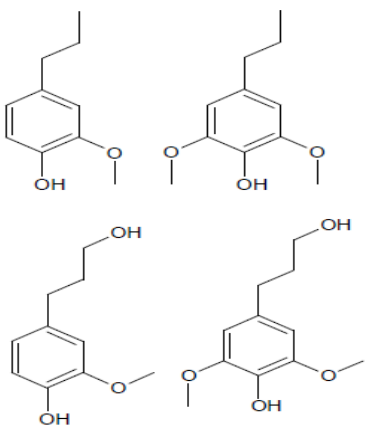
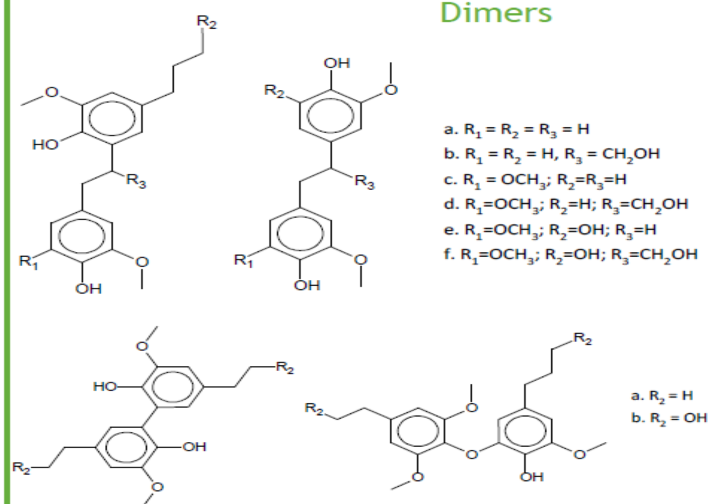
ROUTE 2: LIGNIN-FIRST

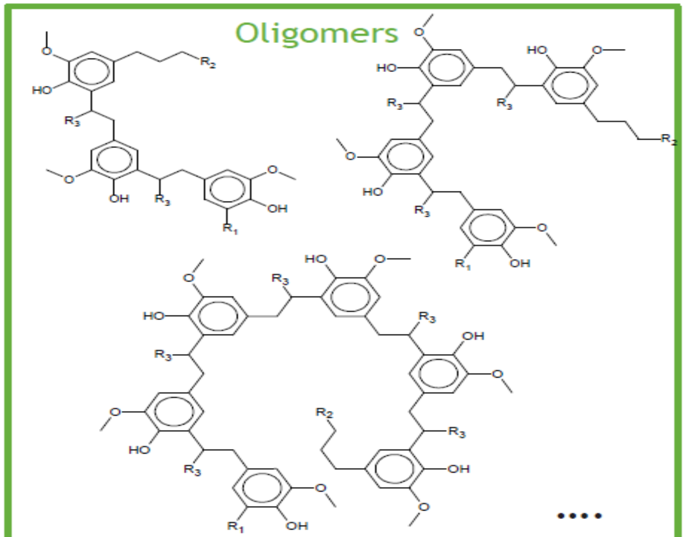
Monomers

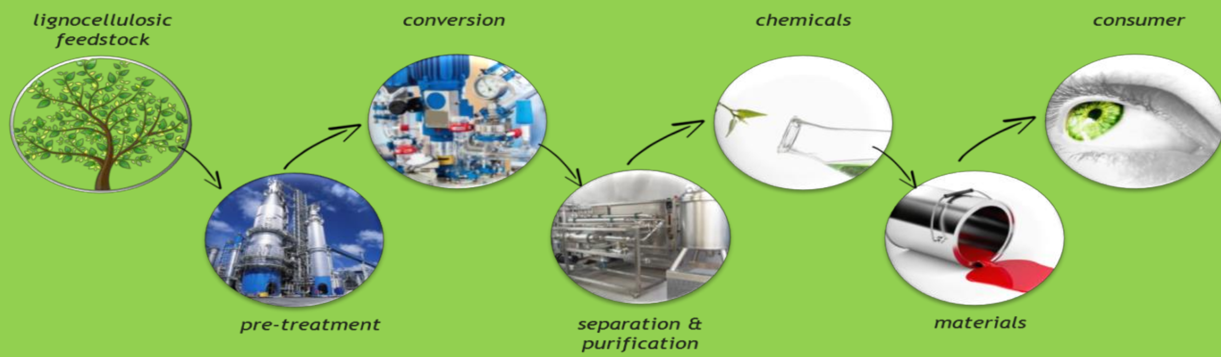


Dimers



Oligomers

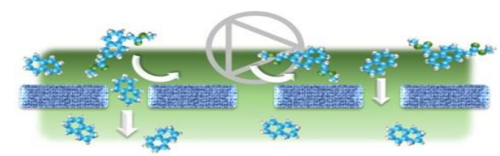


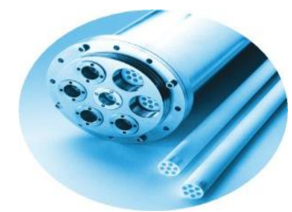


Chapter 4 Downstream separation of lignin streams using membranes: A few case studies

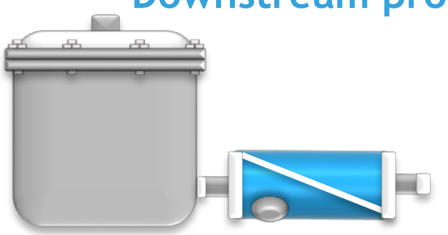
WHY MEMBRANES ?

- Non-thermal, therefore energy-efficient and mild
- No additives required
- Proven, robust technology
- Easy, flexible and scalable
- Separation based on size, charge, volatility and/or affinity
- Wide choice of membranes, modules and operational modes
- Aqueous as well as organic solvent based mixtures
- Commercial as well as newly developed membranes



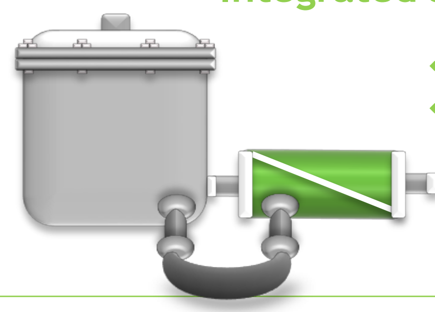


Downstream processing



- Recovery
- Concentration
- Purification
- Fractionation

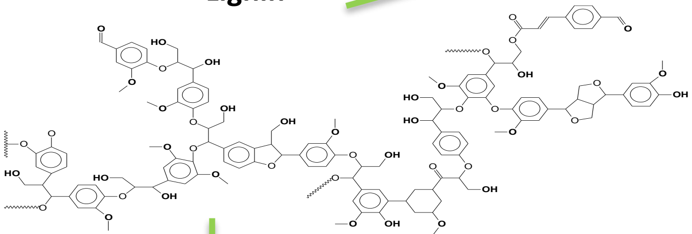
Integrated separation



- In situ product recovery
- Continuous processes

Fractionation needs dictated by application

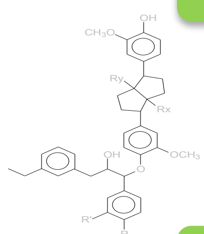
Lignin



1.

Depolymerization

Fractionation

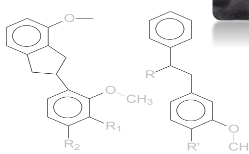


Oligomer based mix

2.

Monomer based mix

Chemicals Mix

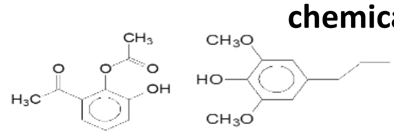


Polymeric lignin as such

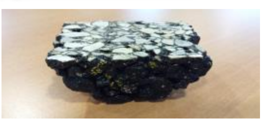
Specific fractionation / affinity-based separation

3.

Pure, single molecules/ chemicals



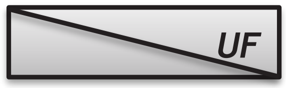
(Modified) filler

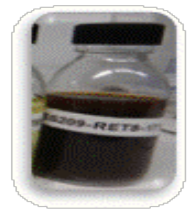


1A PURIFICATION/FRACTIONATION OF TECHNICAL LIGNINS

Water-soluble lignosulphonates

Sulphite spent liquor

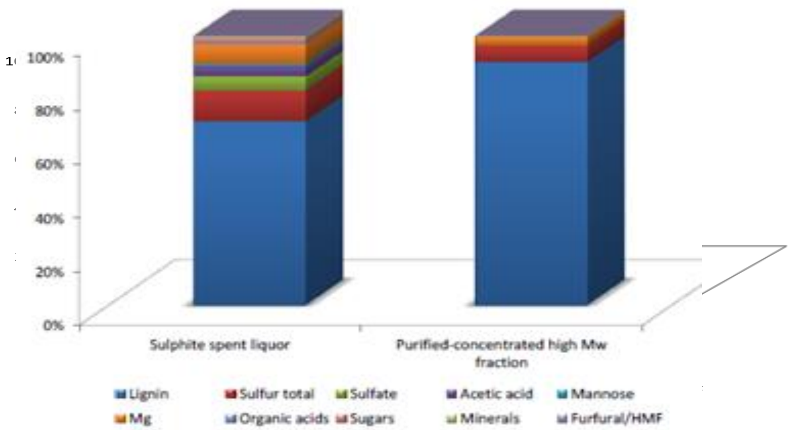




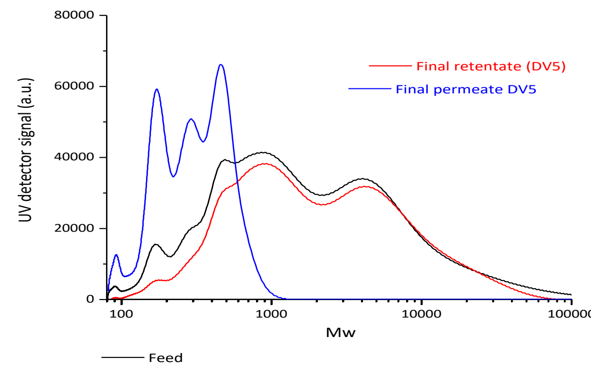
Purified high Mw lignosulphonate fraction

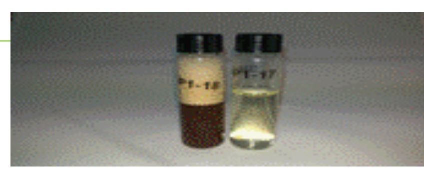
100 % removal of organic acids and residual sugars
87 % removal of minerals

- Lignin: 90 g/L
- Total S: 12.5 g/L
- Sulfate: 6.9 g/L
- Acetic acid: 4.2 g/L
- Mannose: 1.8 g/L
- Mg: 6.2 g/L
- Organic acids: 0.2 g/L
- Sugars: 3.2 g/L
- Minerals: 0.6 g/L
- Furfural/HMF: 0.3 g/L



- Lignin: 123 g/
- Total S: 10.6 g/L
- Sulfate: 2.1 g/L
- Acetic acid: 0.3 g/L
- Mannose: 0.2 g/L
- Mg: 4.2 g/L
- Organic acids: < RL
- Sugars: 0.2 g/L
- Minerals: 0.3 g/L
- Furfural/HMF: < RL





ES209, 15 bar

1b. Purification of chemically modified lignin

Pretreatment by alkaline oxidation

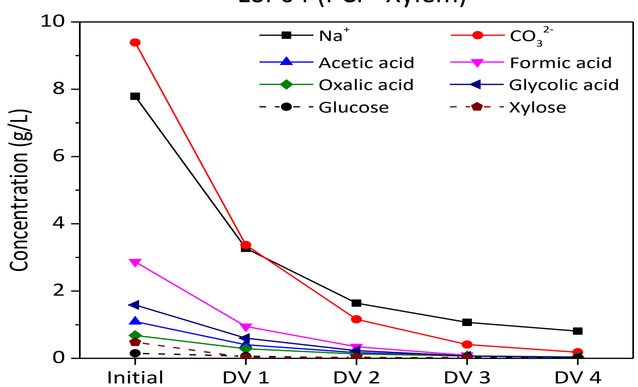
Input → **Process** → **Output**

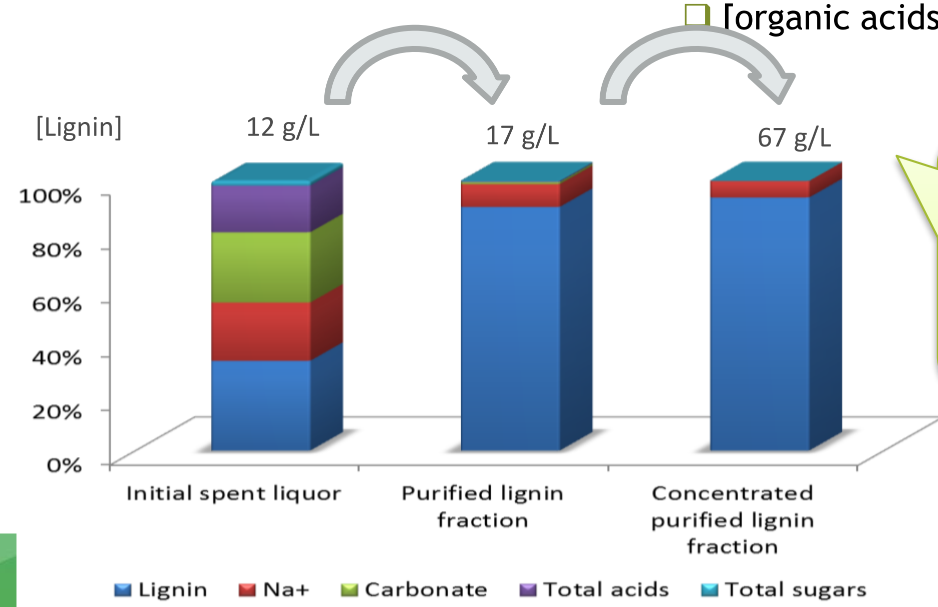
Input
- ❑ [Na^+] : 8.1 g/L
- ❑ [CO_3^{2-}] : 11.5 g/L
- ❑ [Lignin] : 12 ± 2 g/L
- ❑ MW : 200 - 4500 g/mol
- ❑ [organic acids] : 7.75 g/L

Process
- ❑ UF/NF
- ❑ Diafiltration
- ❑ Concentration

Output
- ❑ [Na+] : 0.8 g/L
- ❑ [CO_3^{2-}] : 0.2 g/L
- ❑ [Lignin] : 67 g/L
- ❑ [organic acids] < 0.7 g/L

ESP04 (PCI - Xylem)





Quasi-complete removal of CO_3^{2-}, organic acids and residual sugars 44 % removal of Na^+

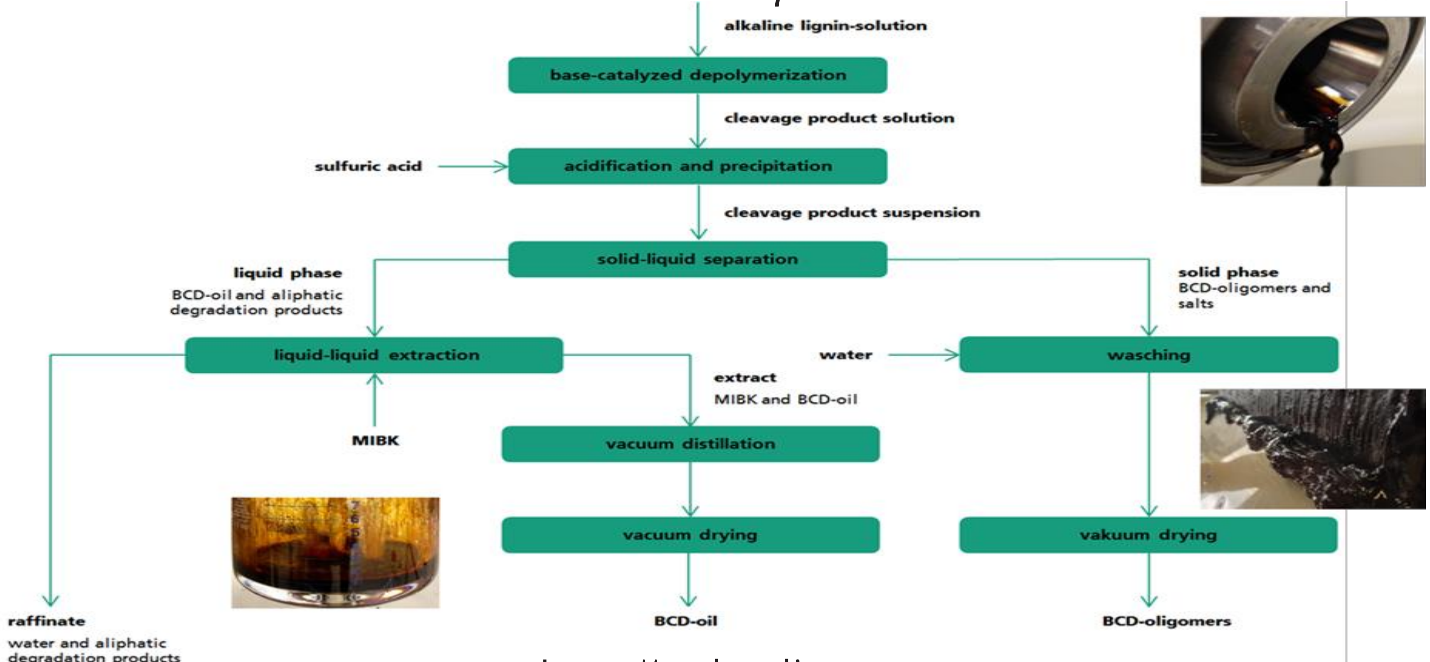
2 SEPARATION OF LIGNIN DEGRADATION PRODUCTS

Fraunhofer

SmartLi
Biorefinery concepts and processes

Base catalysed degradation (BCD)

Current DSP process



Lower Mw phenolics

Higher Mw phenolics

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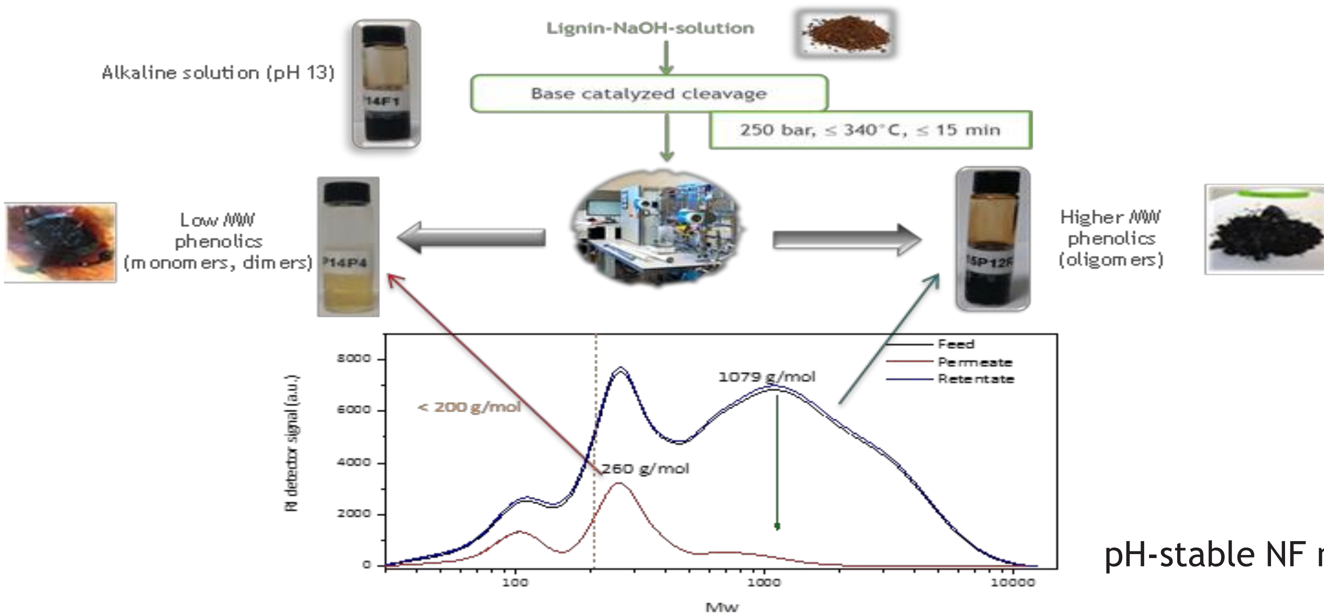
2 SEPARATION OF LIGNIN DEGRADATION PRODUCTS

Base catalysed degradation of lignin

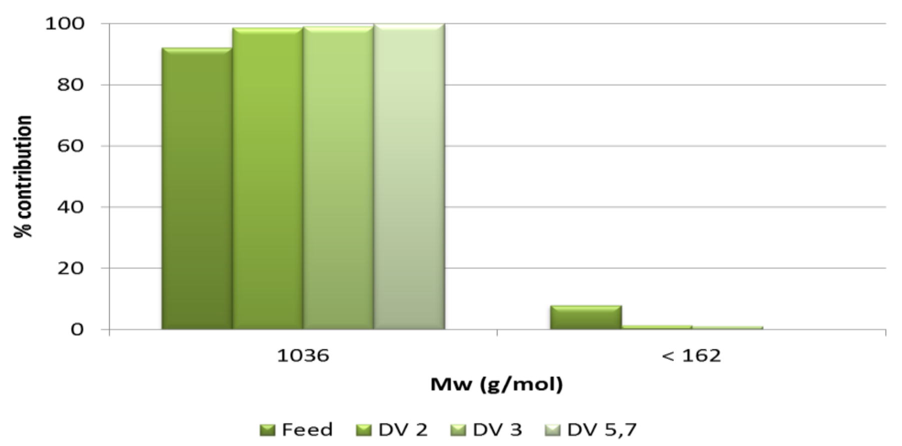
Alternative membrane process



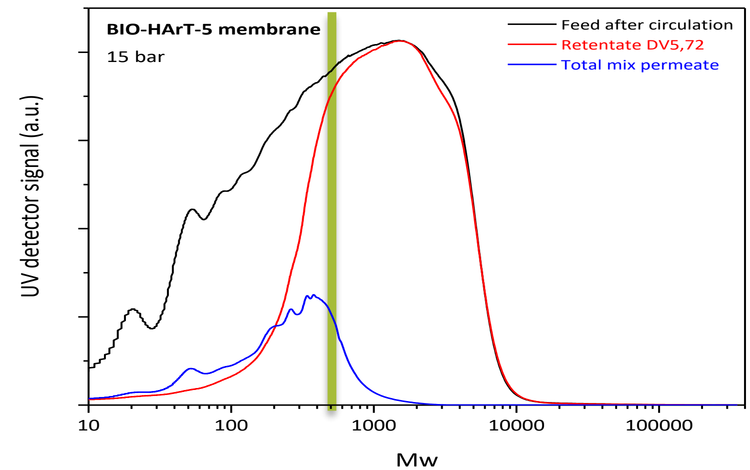
pH-stable NF membrane

2. Fractionation of LFP lignin oils

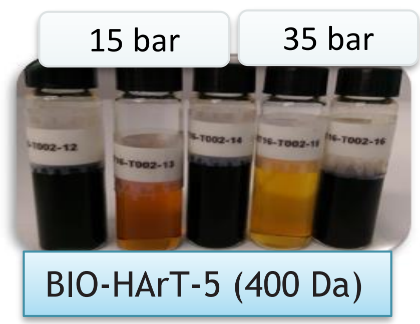
Biorizon
The way to aromatics
BIO-HArT



Evolution of Mw profile in feed-retentate during diafiltration



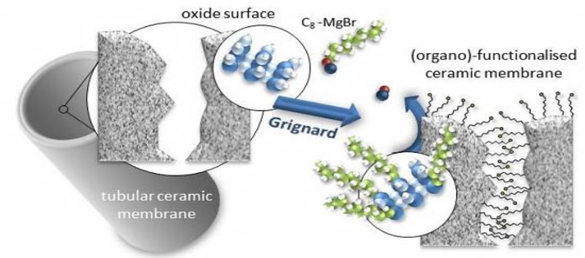
Mw profile of final fractions



- Decreased contribution of low MW compounds in Feed/Retentate
- Fractionation of lignin crude oil by MW
- Outlook: further fractionation of low MW fraction

3. Towards fine-separation of lignin derivatives

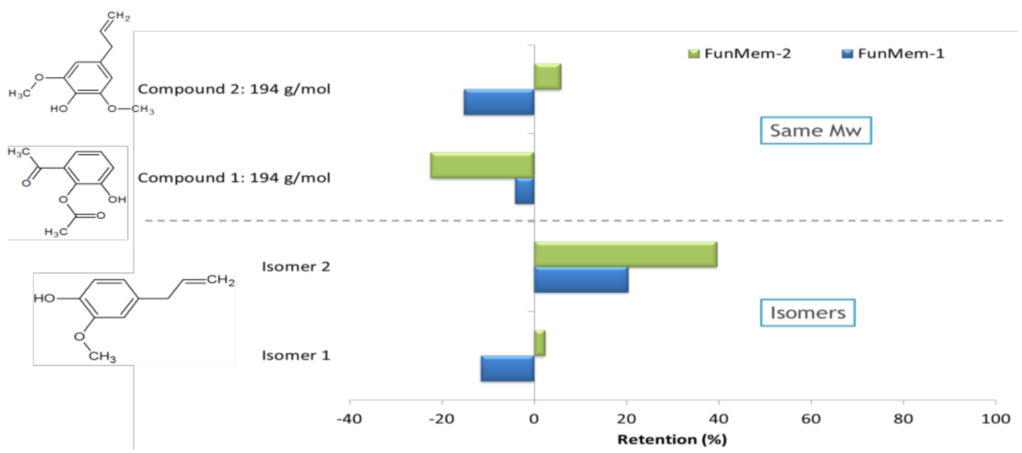
Grafted ceramic membranes: unique separation capabilities thanks to surface tailoring

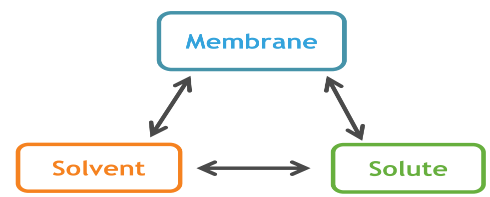


- Unique, direct M-R bond
- Stable, non-hydrolysable
- Commercial membranes
- Broad variety of functional groups
- Tailored membrane surfaces

FunMem4Affinity – Exploration of Functional Ceramic Membranes in Organic Solvent Nanofiltration (2012-14)

New flexible functionalization platform: **FunMem®**



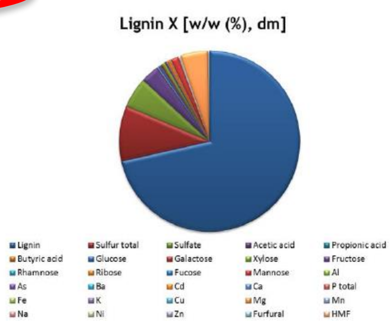


New possibilities for affinity-based separations:

- Tuning of interactions
- Beyond size-exclusion
- Selectivity by design

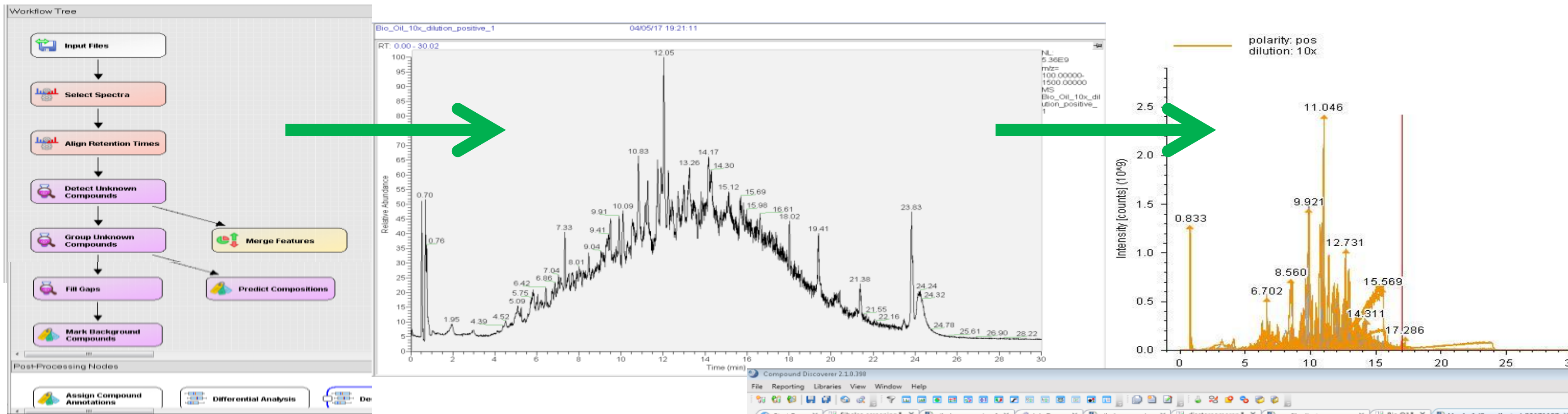
Chapter 5 Analytics and conversion of lignins

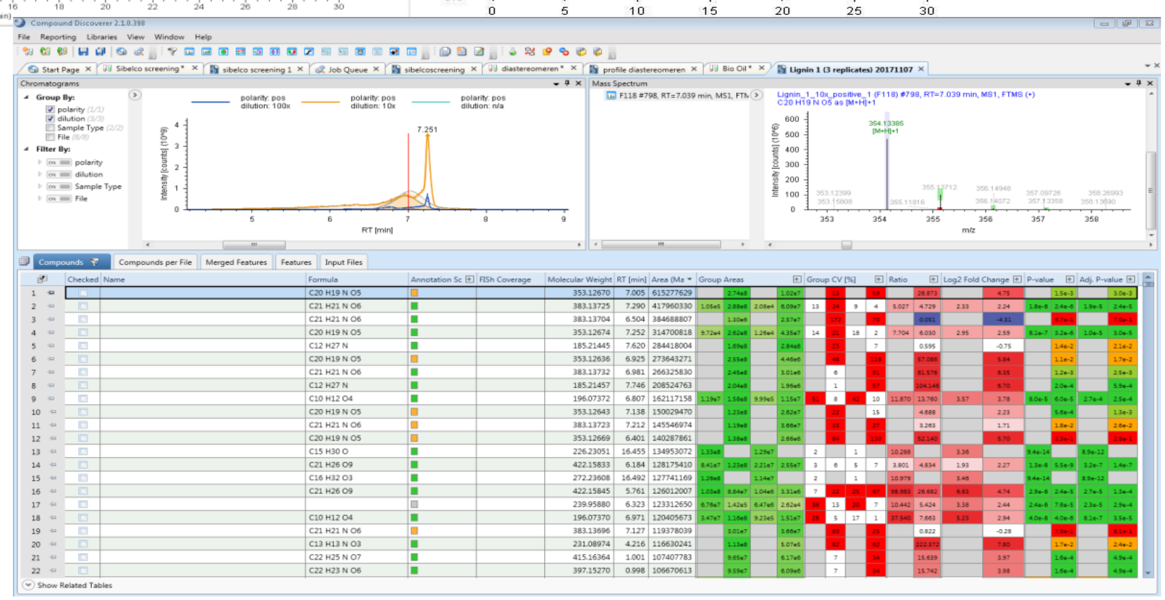
- **Lignin properties**
  - Elemental composition – C/H/N/O content
  - Mw and Mw distribution
  - Presence of functional groups – content of OH and COOH groups
  - Carbon – Oxygen identity card
- **Presence of impurities**
  - Residual sugars
  - Organic acids
  - Salts (minerals – anions)



Example of the composition of a lignin sample

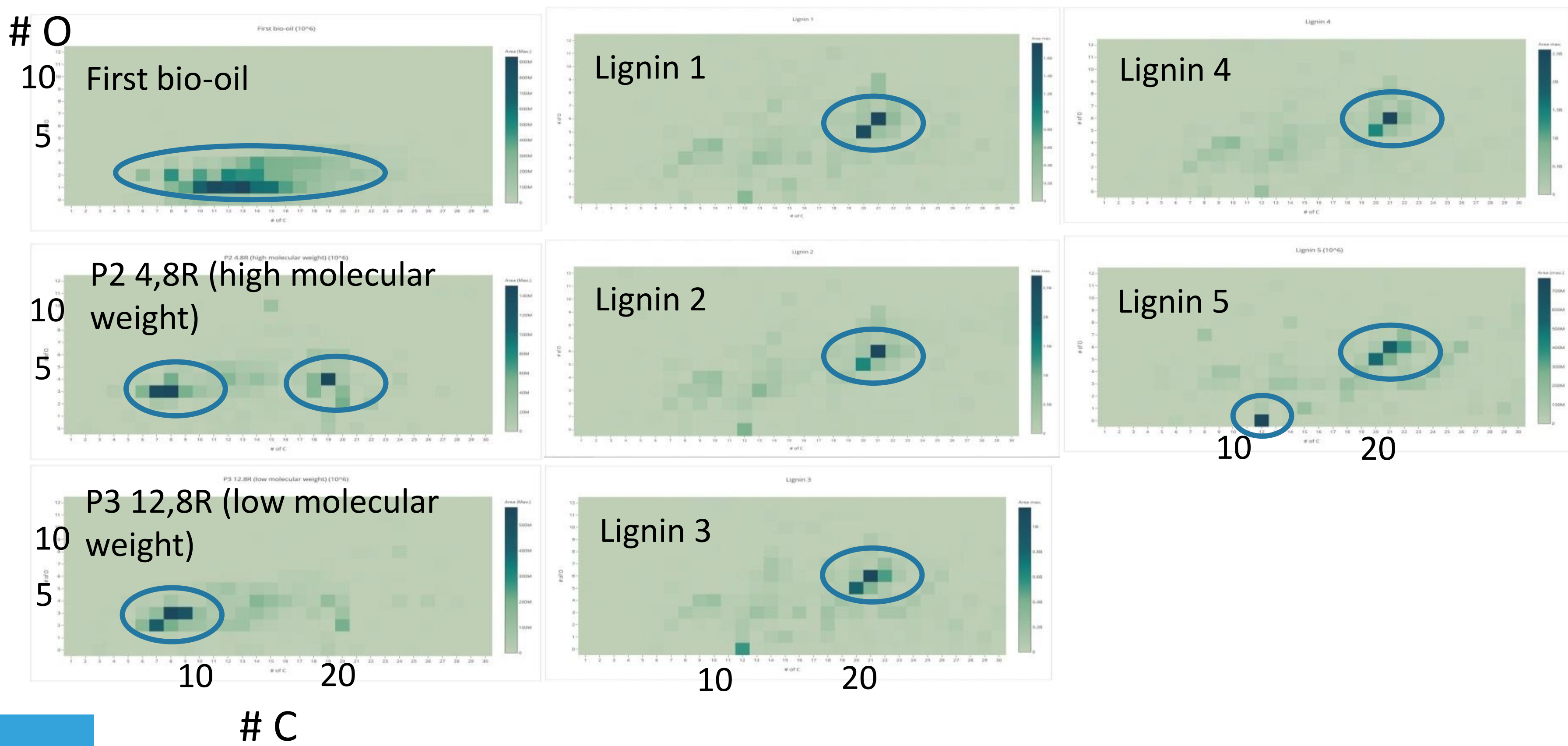
BIO-AROM-ID





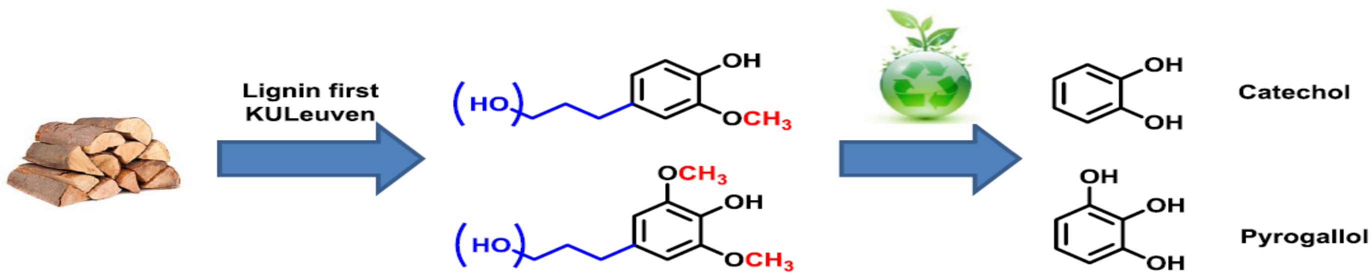
- Chemical analysis
- Mass spectra
- Statistical data treatment
- Consolidation

C OVER O ANALYSIS



DE AND REFUNCTIONALISATION

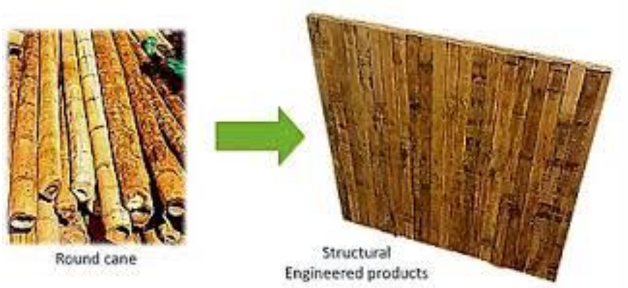
- Removal of propyl-, methyl-groups
- Removal of methoxy groups
- From alkylfenol mixture to application mixture
- Other modifications
- Developed on monomers



Chapter 6 Bio-economy as part of carbon storage

CAN THE BIO-ECONOMY BE PART OF CARBON STORAGE

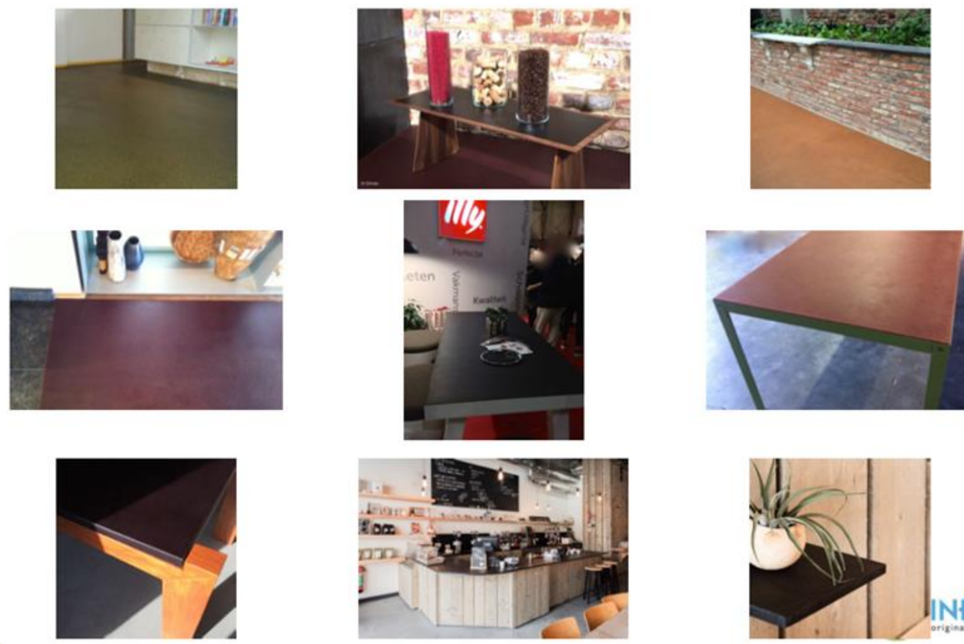
Biological carbon storage is different from a circular economy
Storage in engineered bio-based construction materials
Not only by using wood or bamboo in a direct way



Rüdiger Lainer + Partner

TRANSFORM BIO-WASTE INTO FURNITURE

But you need a hardener and a resin!!!!



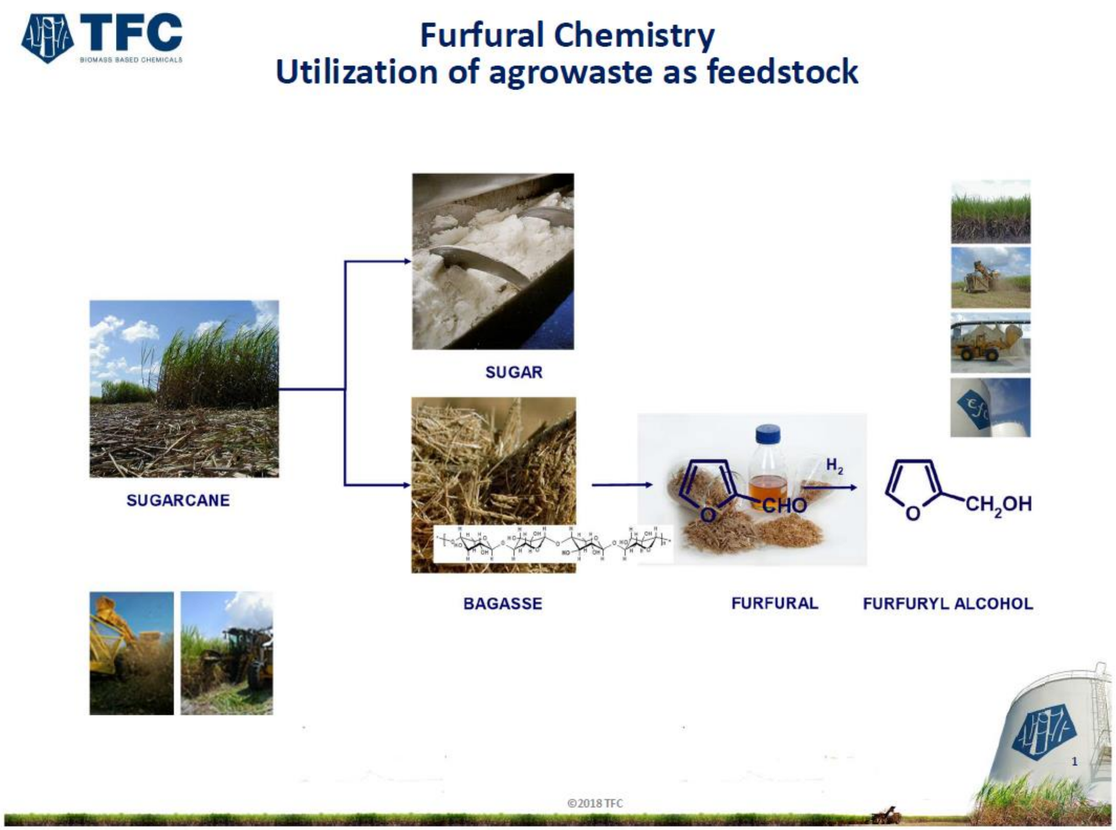
CROSS LAMINATED WOOD & ENGINEERED BAMBOO

Need for glues, resins, coatings, …?

- Replacement of phenol in PF-resins for plywood, OSB
- Replacement of PF resin in plywood, OSB
- Replacement of polyols in PU
- Replacement of bisphenol A or F in epoxyresins
- Development of coatings based on phtalic anhydrides
- Use of plasticizers and dispersants

- What is missing?

FURFURAL FROM BAGASSE



NEED FOR CHEMICALS TO IMPROVE THE USE OF BIOMASS AND BIOWASTE

- The Norvegian company Kebony converts pine wood into wood of tropical hardness by a furfural alcohol treatment (polymerization)

- Furan resins used to make natural fibre coatings

  - Use of furan resin as an agricultural waste product from the sugar industry

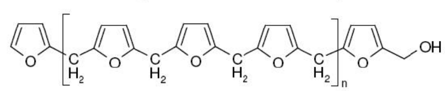
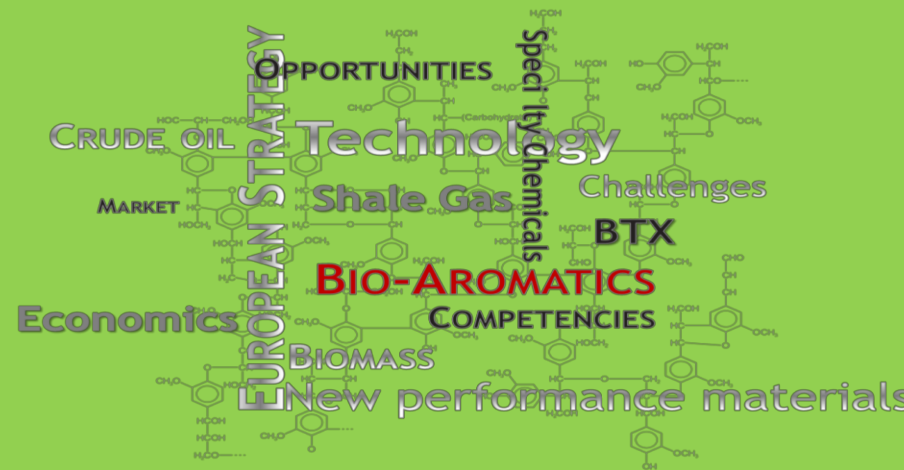


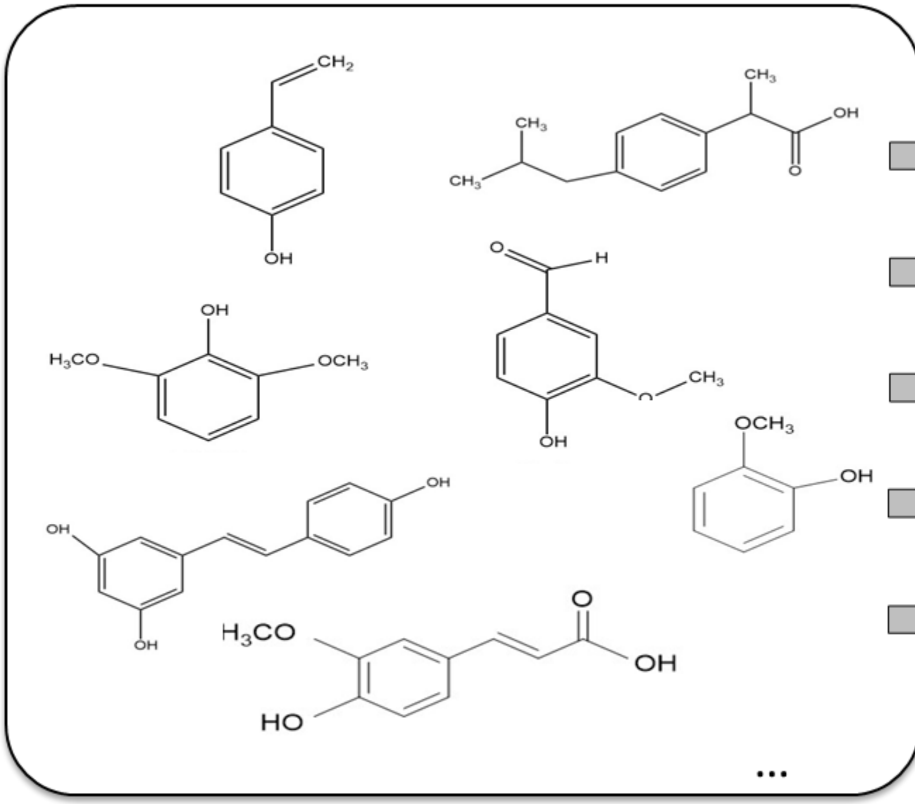
Fig. 2: Natural fibre composites in a Mercedes E-Class.



Chapter 6 Valorization of aromatics Conclusions

BIOAROMATICS VALUE CHAIN

Upgrading reactions
- **Chemical**
- **Enzymatic**
- **Whole-cell**
- **Chemo/biotech**



Coatings

Adhesives

Material applications

Additives

Antioxidants

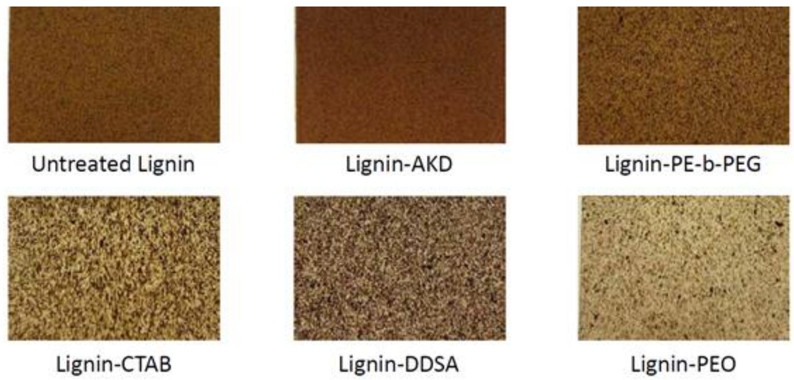
03.02.2018

vito

OR LIGNIN FROM LIGNOCELLULOSE

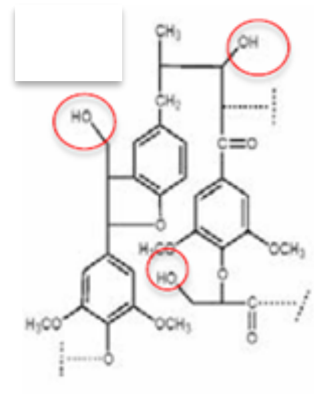
- PU: lignin (after demethylation & oxypropylation) as polyol + di-isocyanate and mixing with other polyol. In IL gives less unreacted isocyanate

- Lignin in PP with different surface activators



J. Appl. Polym. Sci. **2017**, *134*, 45103

[Lignin] = 10 wt.%



- Aerogels from lignin

LIGNIN DEVELOPMENTS

- Dispersant: Lignin oxidation + sulfomethylation ➔ OSL
- Flocculant: Lignin polymerisation in aqueous acidic environment
- Coating: LeafCOAT™ made from lignin from the Glycell™ process
- Wood preservation: Wood Honey™ supernatant of carbonated black liquor (Lignoforce, Lignoboost) + additional membrane filtration to remove salts
- Carbon fibers
- Concrete plasticizer
- Bitumen/roofing

RI.SE

WAGENINGEN UR

No plasticizer

Superplasticizer, 0.2%

Lignosulfonate, 0.4%

LigniOx lignin, 0.4%

VTT

LIGNOVALUE PILOT PLANT

€4.3 Mio budget

Design and construction of a pilot plant for the depolymerization of lignin/wood into innovative biobased aromatics

- Starting date: 30/05/2018
- Design of LignoValue Pilot plant
  - Continuous
  - Mobile
  - As flexible as possible
  - Treatment of lignin and wood
- Operational mid 2021

Technology choice

Metal-catalyzed conversion of lignin/wood in **solvent medium**

Feedstock

Solvents (Methanol, ethanol,...)

Inert atmosphere (N_2) or H_2

100 - ≥ 300 °C (medium to high)

CONCLUSIONS

Development of innovative applications via monomers as new building blocks & oligomers towards new chemistry (bio and chemical catalysis) for more sustainable materials

- Aromatics from biomass are on the move (lignin-, tannin- or sugar-based)
- Organic waste management and forestry: abate climate change ➔ feedstock provider
- Depolymerization allow to make lignin more manageable and more reactive
- Membrane separation allowed an economic viable purification of reactive fractions for further processing
- Via dealkylation and refunctionalisation
- To make additives, new polymers, resins, …
- REACH (regulation in general) is point of attention
- Analytics standardisation are needed
- Matrix: feedstock origin, pretreatment, depolymerisation process, separation, application
- Potential for combinations in biocomposites, 3-D printing, …
- We can provide molecules or materials to companies for testing by partners via Biorizon and BIG-Cluster and large amount production via Lignovalue plant

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ludo.diels@vito.be

Biorizon

The way to aromatics

www.biorizon.eu

Want to find out more?

Join our community on Biorizon.eu

E-mail: karolien.vanbroekhoven@vito.be

E-mail: kelly.servaes@vito.be

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OP-Zuid
Europees Economisch Stimuleringsprogramma

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Interreg
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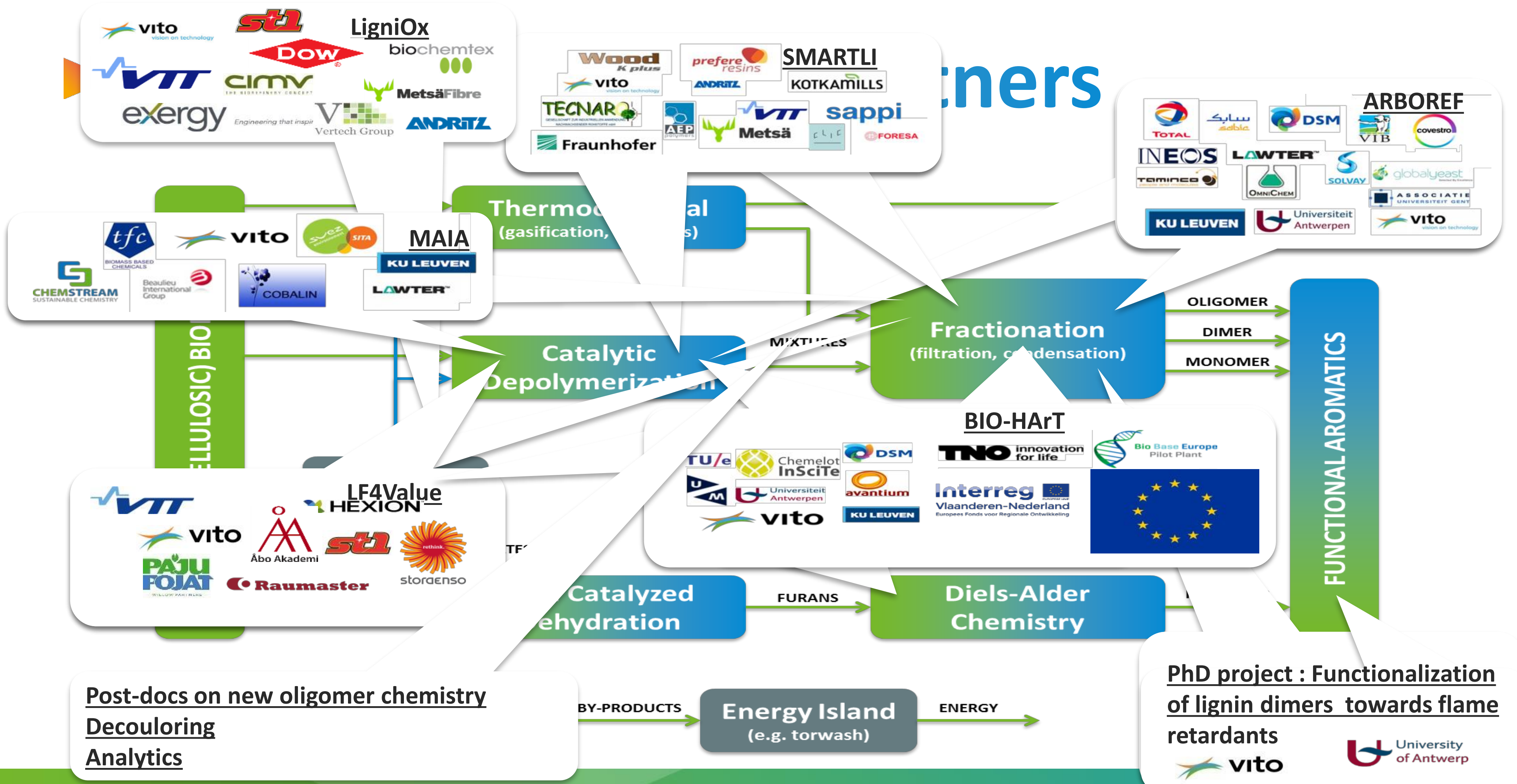
Powered by: TNO, VITO & Green Chemistry Campus

Biorizon-background.png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LigniOx
SMARTLI
ARBOREF
MAIA
BIO-HArT
LF4Value
Thermo al
(gasification, s)
Catalytic
Depolymerization
Fractionation
(filtration, condensation)
OLIGOMER
DIMER
MONOMER
FUNCTIONAL AROMATICS
Catalyzed
ehydration
FURANS
Diels-Alder
Chemistry
BY-PRODUCTS
Energy Island
(e.g. torwash)
ENERGY
Post-docs on new oligomer chemistry
Decoupling
Analytics
PhD project : Functionalization of lignin dimers towards flame retardants