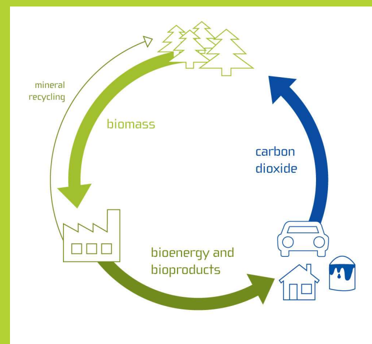
Development of Lignocellulose biorefinery for co-production of transportation fuels, chemicals, electricity and heat – Overview & results of the IP BIOSYNERGY (FP6)



J.H. Reith, R. van Ree, R. Capote Campos, R. R. Bakker, P.J. de Wild, F. Monot, B. Estrine, A.V. Bridgwater, A. Agostini

International Biomass Valorisation Conference 13 september 2010, Amsterdam

BIOSYNERGY

Contents

- Background Lignocellulose Biorefinery
- The EC Integrated Project BIOSYNERGY (FP6)
- Lignocellulose Biorefinery processes illustrated by ongoing work/results of the IP BIOSYNERGY
  - Physical/chemical pretreatment & fractionation
  - Enzymatic hydrolysis
  - Innovative thermo-chemical conversion
  - Production of biobased chemicals via (bio)chemical conversion
  - Integral biomass-to-products chain design
- Summary and conclusions

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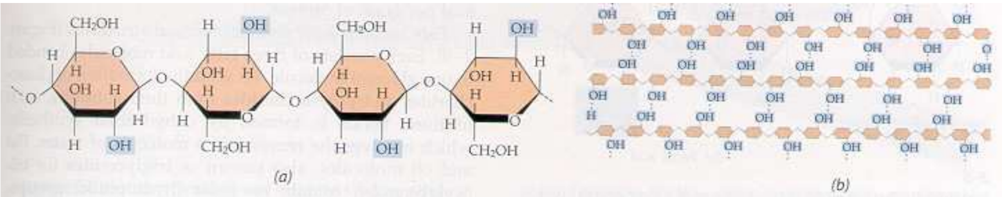
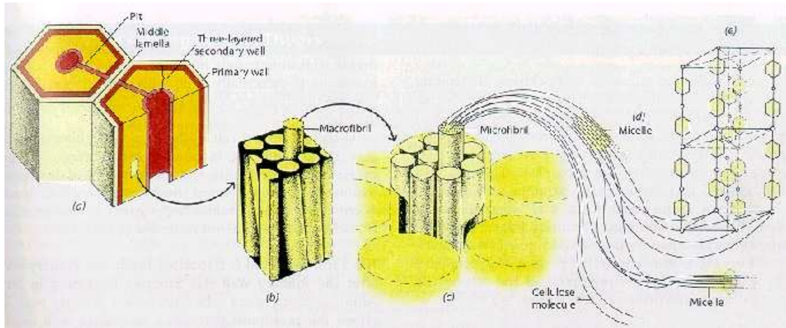
Lignocellulosic biomass

Complex raw material due to complex structure of the plant cell wall: intermeshed carbohydrate and lignin polymers.

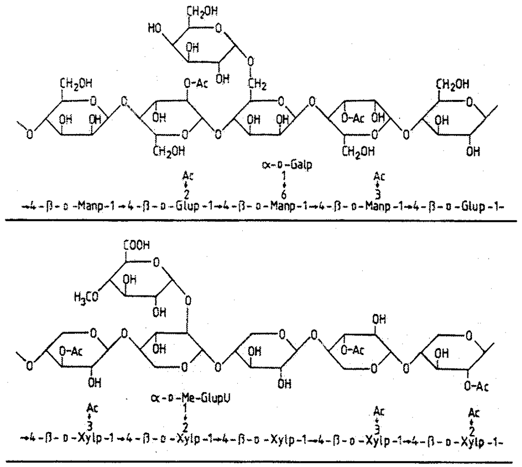


Cellulose= linear, highly crystalline glucose polymer

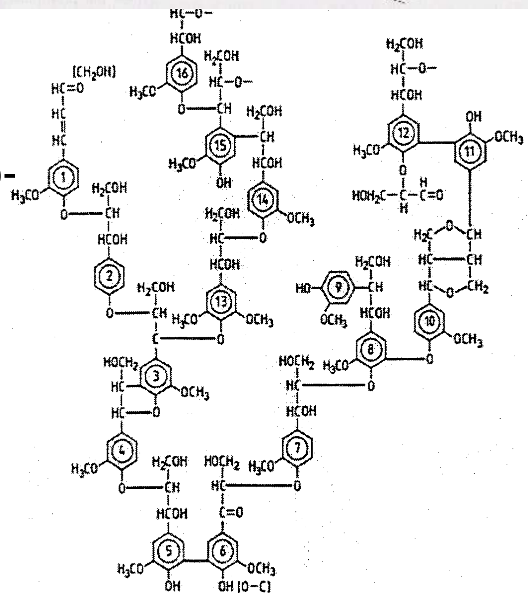


Hemicellulose: branched co-polymer of C5 (Xyl, Ara) and

C6 sugars (Glc, Man, Gal)



Lignin: random co-polymer of fenyl propane units: matrix or ‘glue



Large variety in composition and structure esp. hemicellulose and lignin fractions

Polymers have differential reactivity to thermal, chemical and bioprocessing

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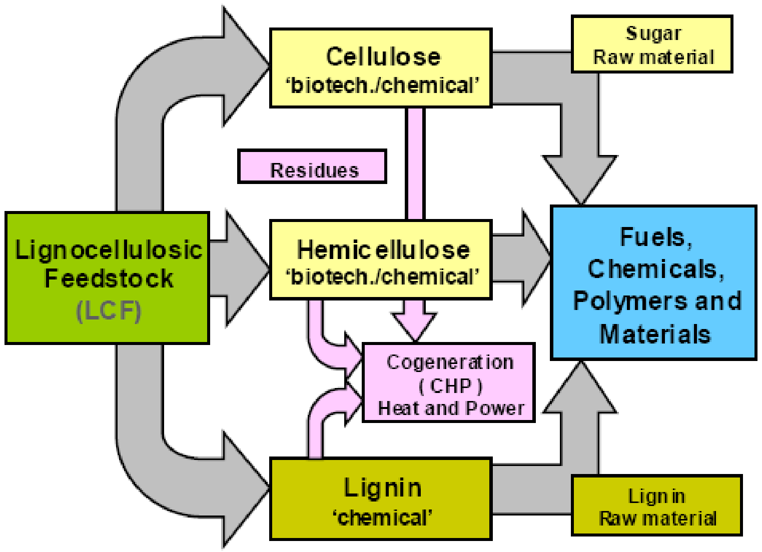
Lignocellulosic Feedstock Biorefinery



Source: Kamm et al., Wiley-VCH, 2006

- Abundant low-cost feedstock: wood, straw, corn stover, residues
- Limited interference with food/feed
- Multiple products : transportation fuels, chemicals, electricity and heat

- **Aim: full feedstock valorization and to optimize revenues + ecological footprint**

- Physical-chemical pre-treatment & fractionation of lignocellulose
- Enzymatic hydrolysis of (hemi)cellulose
- Fermentation / chemical conversion of intermediates
- System integration
  - CHP from process residues
  - Heat integration, water recycle

Features Integrated Project BIOSYNERGY

BIOmass for the market competitive and environmentally friendly **SYN**thesis of bio-products – chemicals and/or materials – together with the production of secondary en**ERGY** carriers – transportation fuels, power and/or CHP – through the biorefinery approach.

- Overall aim: Development **multiproduct cellulose-ethanol based biorefinery** technology
- **Focus on valorisation of residues from cellulose ethanol production** to make the production of this biofuel more cost competitive
- Bioprocessing and thermochemical pathways combined
- Process development from lab-scale to demonstration at pilot-scale.

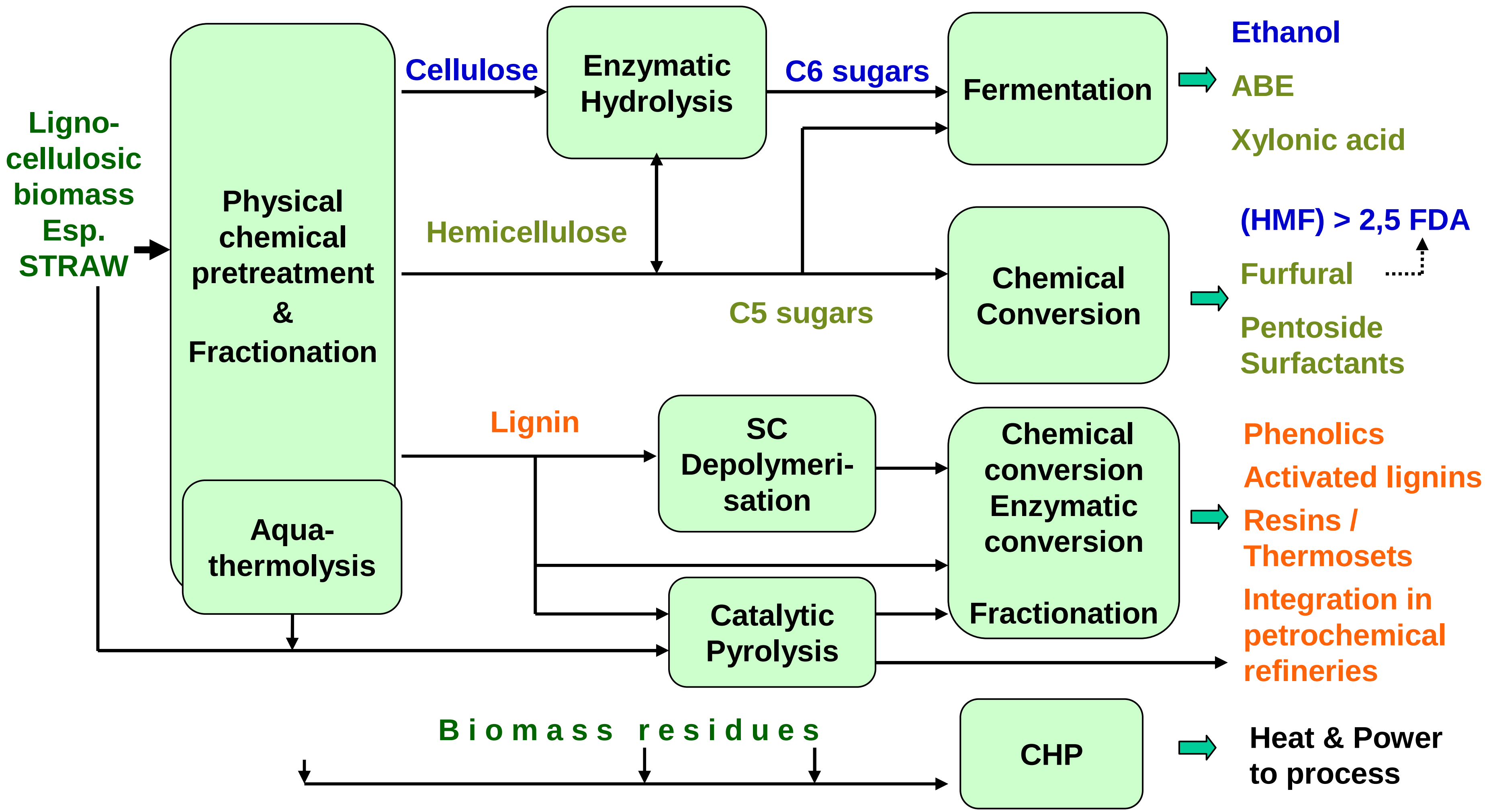
EU FP6 Program: Contract No. 038994 – SES 6. EC Officer: Silvia Ferratini.

Duration: 1-1-2007 – 31-12-2010 (48 months). Budget: 13.4 M€, EC grant 7M€

BIOSYNERGY

Product lines in the IP BIOSYNERGY

Multi-product biorefinery, Focus on residues cellulose ethanol: **C5 and lignin valorisation**



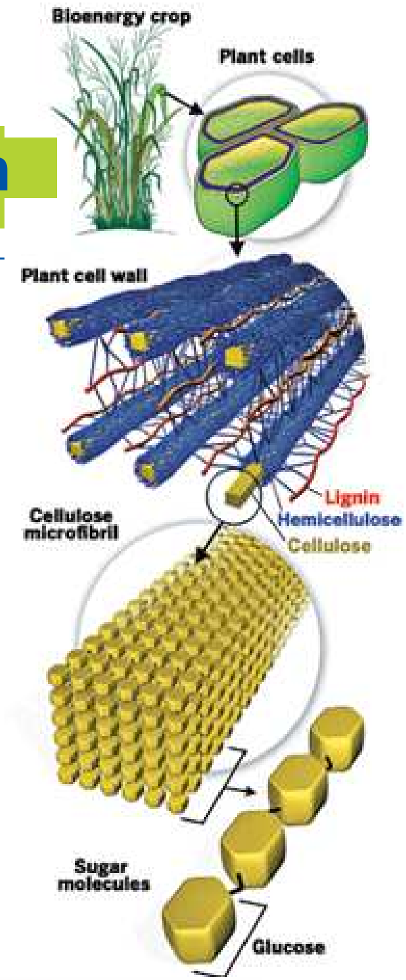
BIOSYNERGY

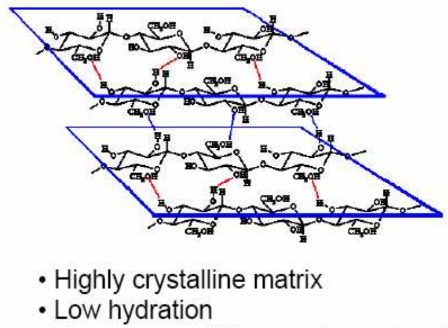
Physical-chemical pretreatment & fractionation

- Pretreatment/Fractionation of Lignocellulose is:
  - major cost factor in biorefining
  - vital for quality of intermediates, processing options, end products and for techno-economic feasibility

- Aims:
  - Controlled fractionation of lignocellulose into fractions with optimum quality for production of (bio)chemicals: cellulose, hemicellulose, lignin
  - Enhance access of cellulose for enzymatic hydrolysis to sugars in high yield /low enzyme use
  - Minimize by-product formation and the use of chemicals, water and energy (>Reduce costs)

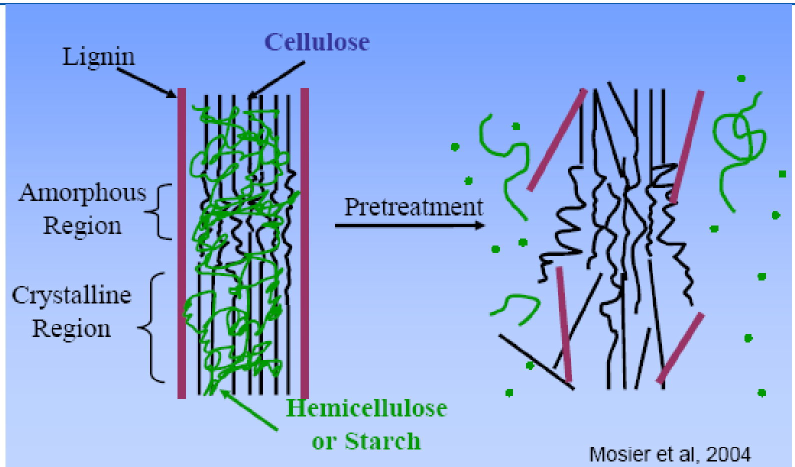
- Challenge: Biomass recalcitrance caused by
  - Complex structure of the plant cell wall
  - high crystallinity of cellulose





Physical-chemical pretreatment & fractionation (2)

- Routes under development:
  - Mild-acid/thermal pre-treatment
  - Steam pre-treatment / explosion
  - Ammonia Fibre Explosion (AFEX)
  - Mild alkaline pretreatment
  - Organosolv



Mosier N, Wyman C, Dale B, Elander R, Lee YY, Holtzapple M, Ladisch MR, 2004.

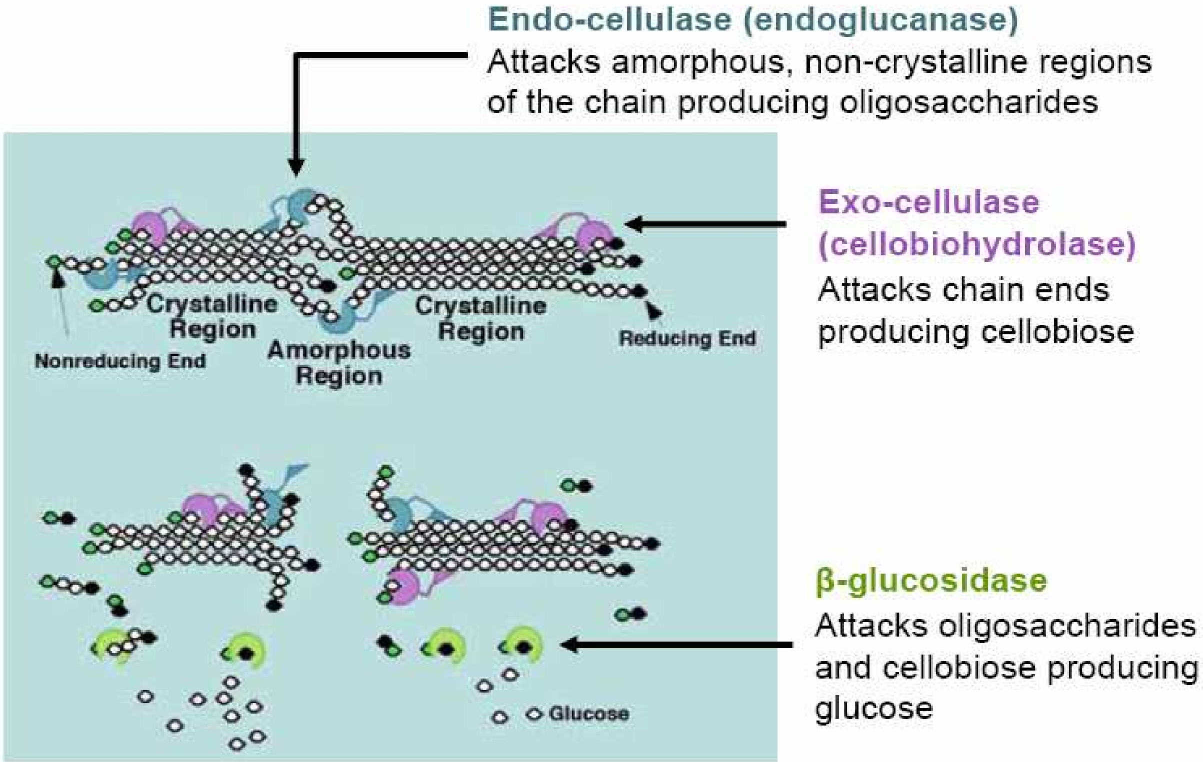
- No cost-effective full scale industrial technology for biorefining available today

- Most processes suffer drawbacks: formation of inhibitors, high use energy or chemicals, waste production, high cost etc.

- Most routes produce relatively low quality lignin residue mostly suitable for CHP

Enzymatic cellulose hydrolysis

3 types of enzyme activity required



Source: Kevin A. Gray Ph. D. , 2007. Conversion of lignocellulosic biomass into liquid transportation fuels Diversa Corporation/Celunol, San Diego, CA , USA. http://www.epobio.net/workshop0705/presentations/KevinGray.pdf

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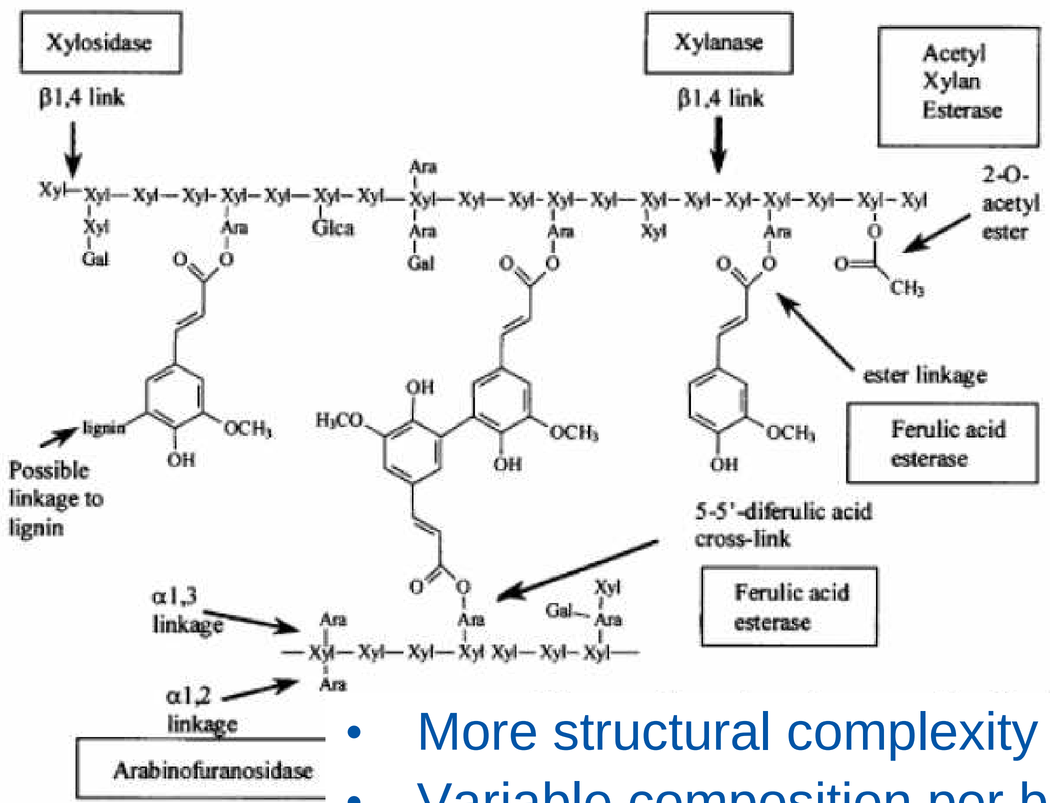
Enzymatic hemicellulose hydrolysis



Source: Kevin A. Gray Ph. D. , 2007. Conversion of lignocellulosic biomass into liquid transportation fuels Diversa Corporation/Celunol, San Diego, CA , USA. http://www.epobio.net/workshop0705/presentations/KevinGray.pdf

- More structural complexity than cellulose
- Variable composition per biomass source
- Tailor made combination of enzyme activities required

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Status enzymatic (hemi)cellulose hydrolysis

- **Specific enzyme cocktails/activities** required per feedstock type
- Field of active development; **Recent cost reduction cellulases** claimed by manufacturers Novozymes, Genencor, Dyadic, for on-site enzyme production.
- Enzyme cost no longer the major cost driver cellulose ethanol: from approx. 45% to << 10% of production cost. Actual cost unclear.
- **High solids processing required for economic reasons** >> Enzymatic pre-hydrolysis required to reduce feedstock viscosity

Photo: Enzymatic hydrolysis of pre-treated wheat straw (12 wt%) WUR-AFSG, EET project K01116

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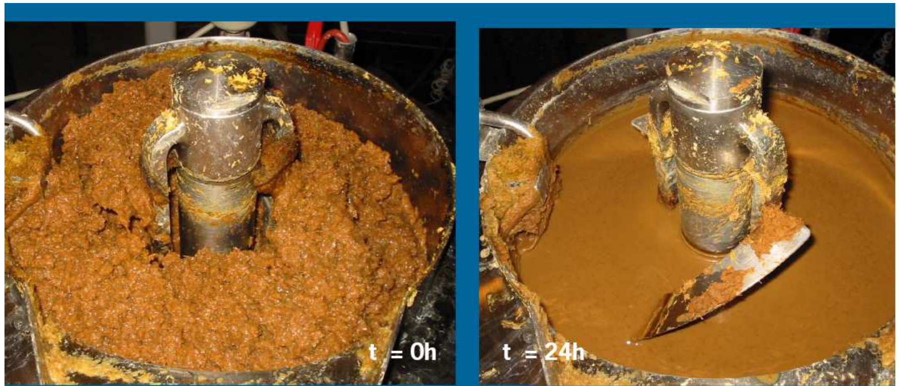


Reactor during enzymatic hydrolysis at t = 0 and t=24 h after adding enzymes

- Enzyme development must be tailored to feedstock AND pretreatment as well as to fermentation. Further cost reduction required.

Advanced physical/chemical fractionation (WP1)

- Major cost factor in biorefinery
- Model feedstocks: **wheat straw**, woods

Processes studied

- Mechanical/Alkaline Fractionation (MAF; A&F)
- Ethanol/water Organosolv (ECN)
- Organic acid organosolv (Avidel process; ARD)
- Acid hydrolysis (Biorefinery.de)
- Reference technology: steam explosion (ABNT)

Ethanol/H2O Organosolv,ECN

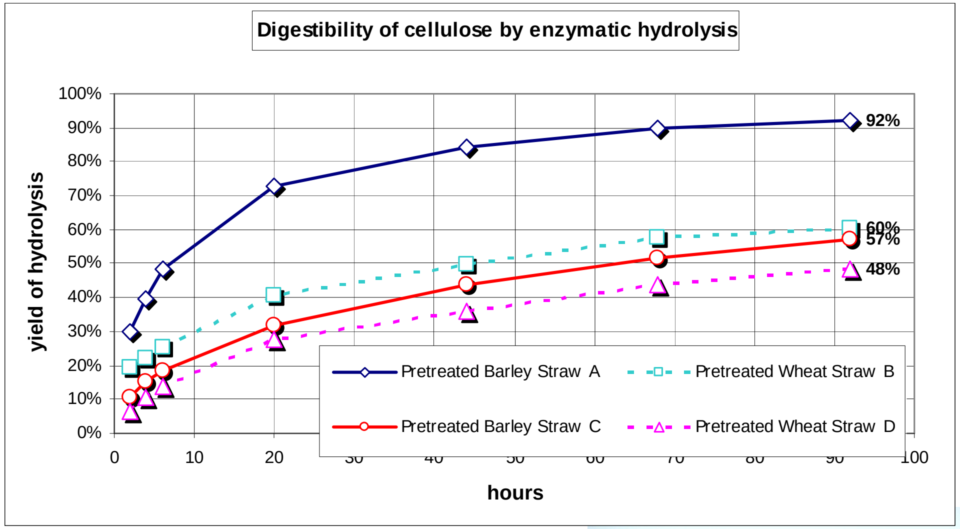
Mech/alk pretreatment A&F

Acid organosolv Pilot plant ARD

Partners: A&F, ABNT, ARD, Bioref, ECN, TUD

Conclusions pretreatment/fractionation

- No clear "winner": All studied routes lead to significant fractionation of C5, C6 sugars and lignin from lignocellulose
- Differences in cellulose hydrolysis yields



- Processes need to be optimised toward a particular goal, for example:
  - Hemicellulose hydrolysis for further processing of C5
  - High enzymatic degradability of the cellulose fraction
  - Recovery of a high quality lignin stream (: organosolv , MAF)

Lignin products from Modified Organosolv Fractionation (ECN)

BIOSYNERGY

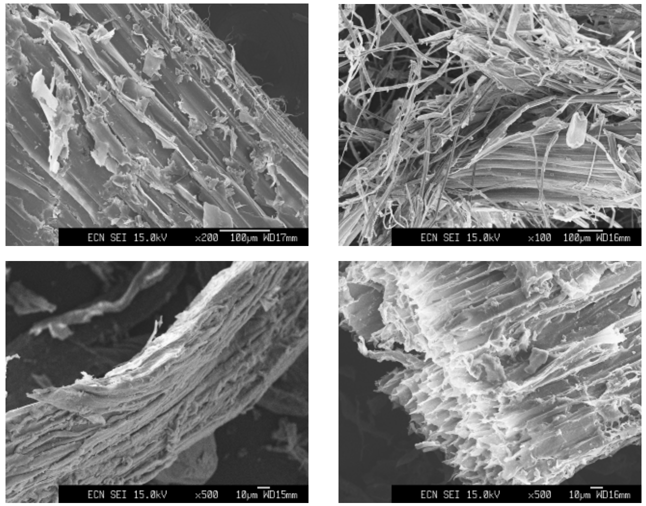
Ethanol/water organosolv: efficiency of pretreatment and lignin quality

- Good pre-treatment hardwoods and straw
- Effective extraction of hemicellulose and lignin
- Cellulose fibrous structure remains intact
- Good access for enzymes: Hydrolysis yield > 90%
- Purity and MW distribution of lignins indicate suitability for chemicals production
- Solvent recycle crucial for energy use and costs

Fresh | Pre-treated

Wheat straw

Willow



200℃, 60 min, EtOH-H_2O 60:40 (w/w)

Biomass	Pulp yield (dw%)	Xylan hydrolysis (%)	Delignification (%)	Enzymatic degradability (% cellulose feedstock)
Barley straw	51	80	57	92
Wheat straw	62	45	55	60
Willow	66	50	64	71
Poplar	71	28	ND	39
Spruce	73	NA	33	ND

Feedstock / sample	Mw	PD
Poplar	2419	3.5
Barley straw	3006	4.1
Willow	3452	4.1
Alcell®	2985	3.6

Innovative thermo-chemical conversion (WP2)

Focus on thermochemical processing of **biomass and lignin.**

Development of:

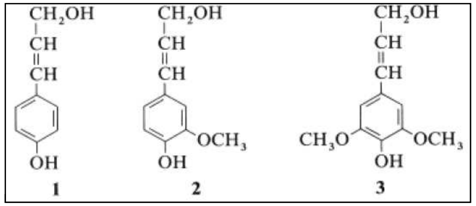
- Hybrid, staged processing concept: aquathermolysis followed by fast pyrolysis
- Catalytic fast pyrolysis
- Separation and upgrading technology

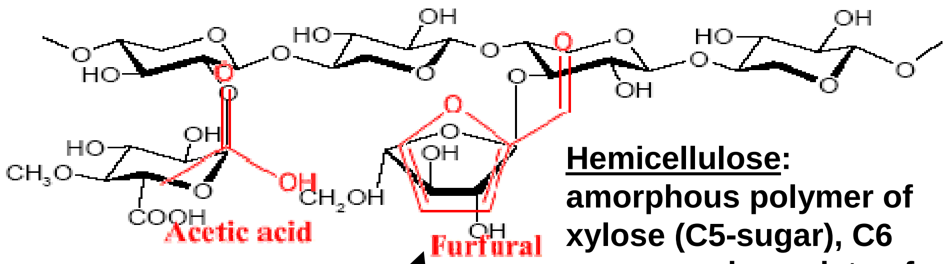
BFB reactor ECN

Partners: ECN, Aston, BTG

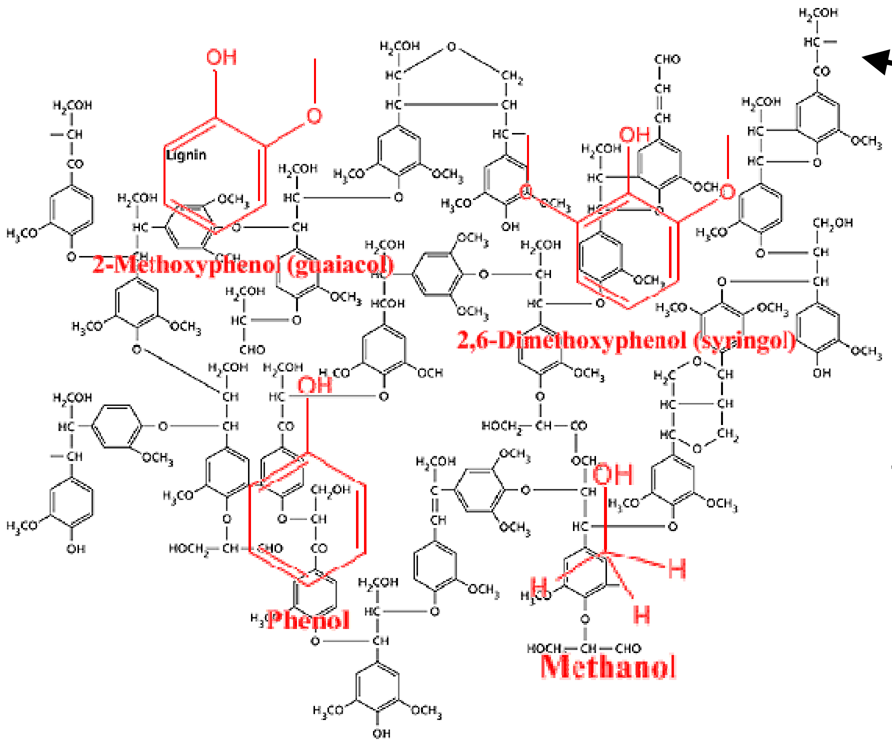
Thermochemical production of chemicals from wood

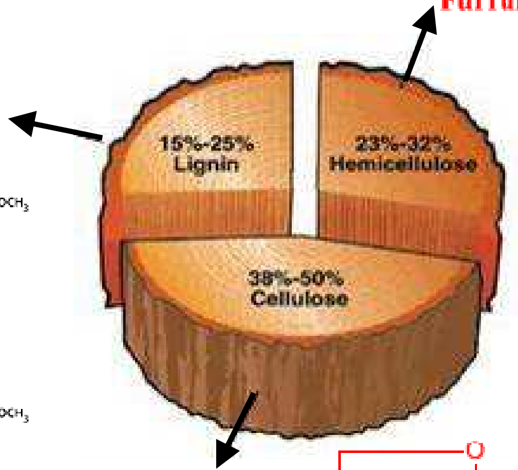
<u>Lignin</u>: amorphous copolymer of phenyl-propene units; formed via a random radical copolymerisation of: (1) coumaryl alcohol, (2) coniferyl alcohol, (3) sinapyl alcohol



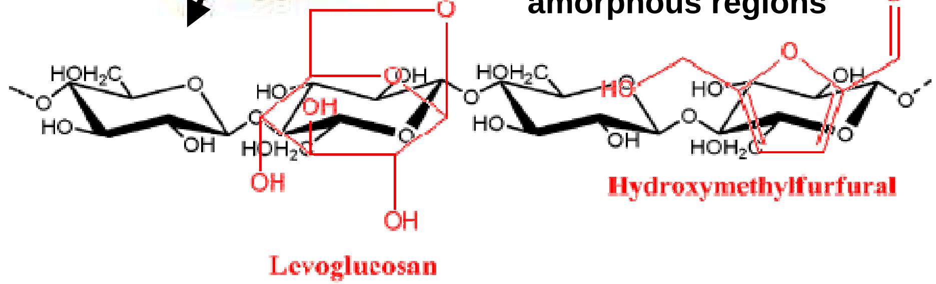


<u>Hemicellulose</u>: amorphous polymer of xylose (C5-sugar), C6 sugars and a variety of side-chains





<u>Cellulose</u>: polymer of glucose (C6-sugar) with both crystalline and amorphous regions



BIOSYNERGY

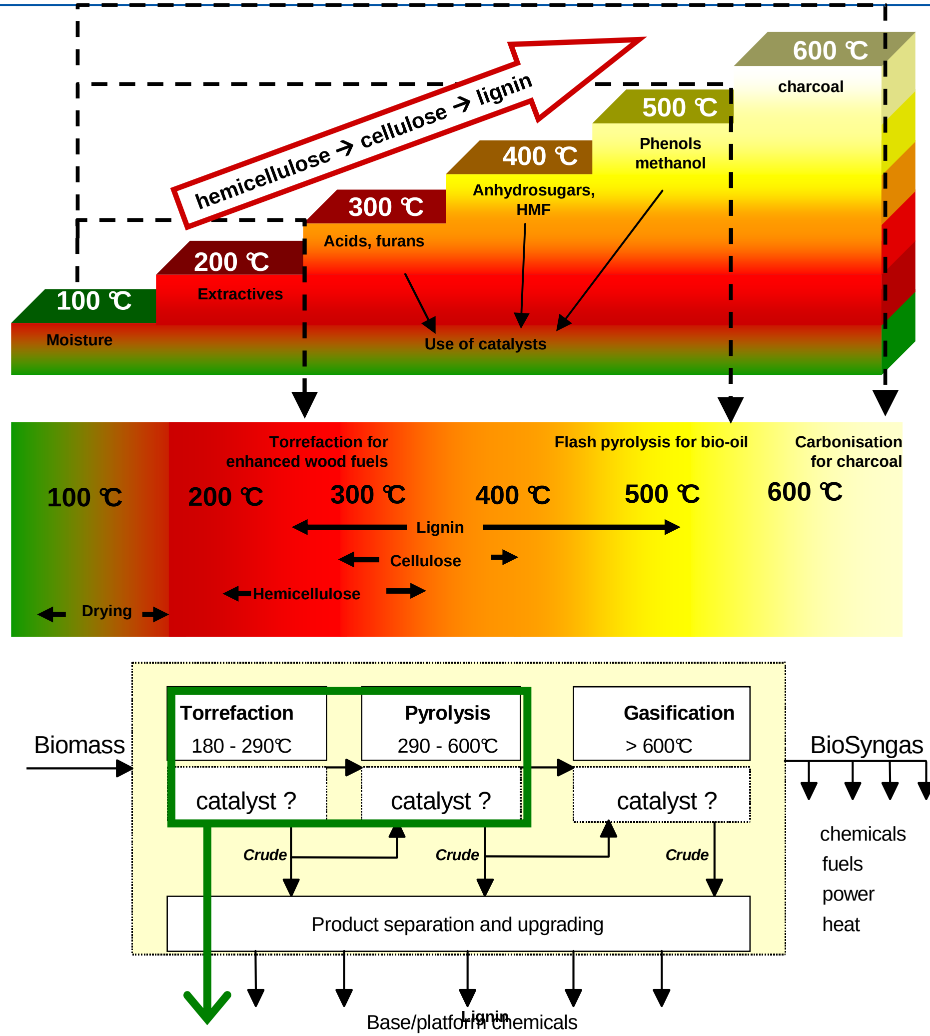
Staged thermochemical processing

Opportunities

- Sequential thermal decomposition hemicellulose > cellulose > lignin
- Condensable products: C2-C4, acids, furans, anhydrosugars, phenolics (+ char and syngas)

Challenges

- Optimisation of individual product or product group yields via catalysis, process conditions: temperature, heating rate, vapour and solid residence times
- Product separation and upgrading **from complex mixtures**

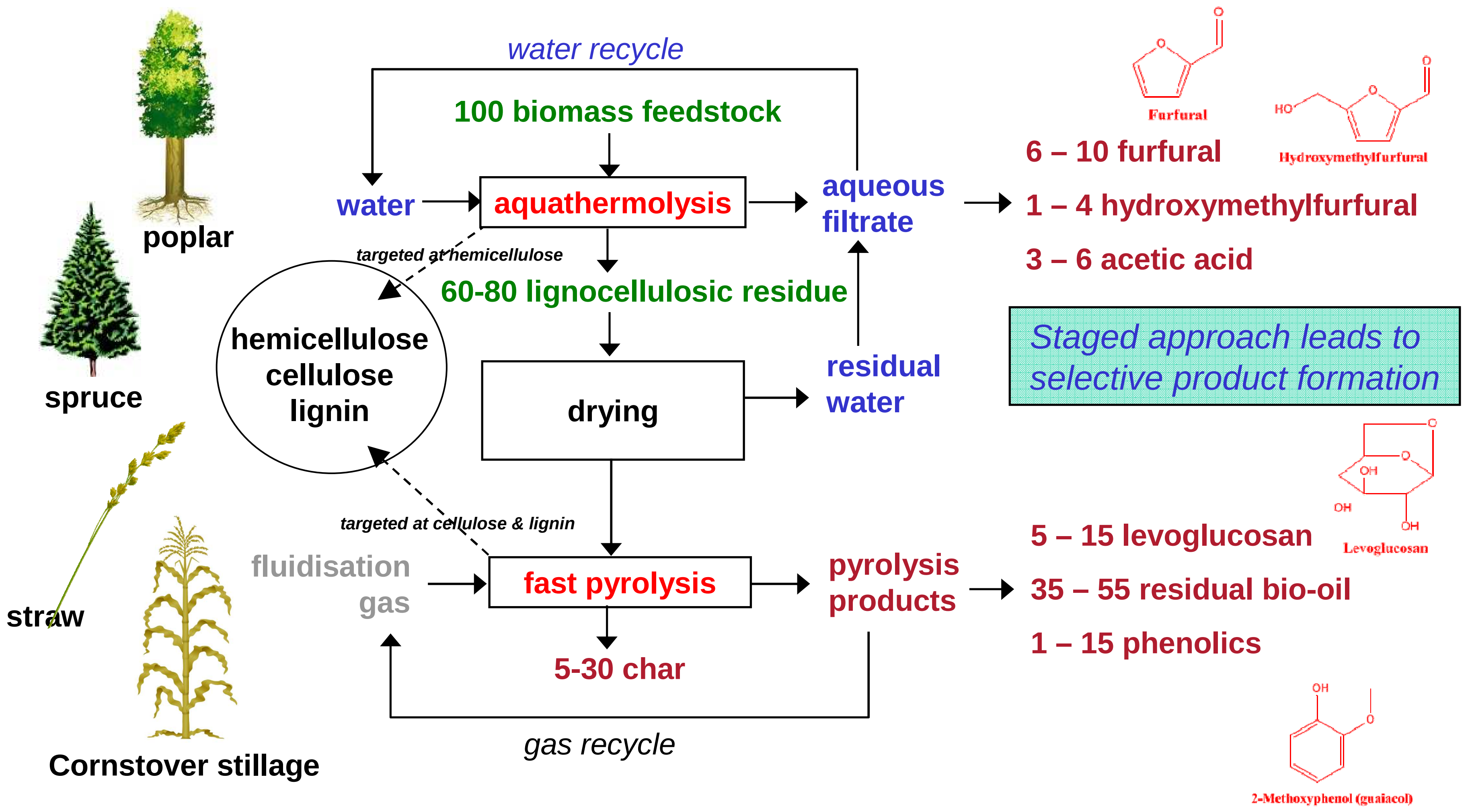


Bio-cascade for drying, torrefaction and pyrolysis

BIOSYNERGY

Hybrid staged process for biomass conversion

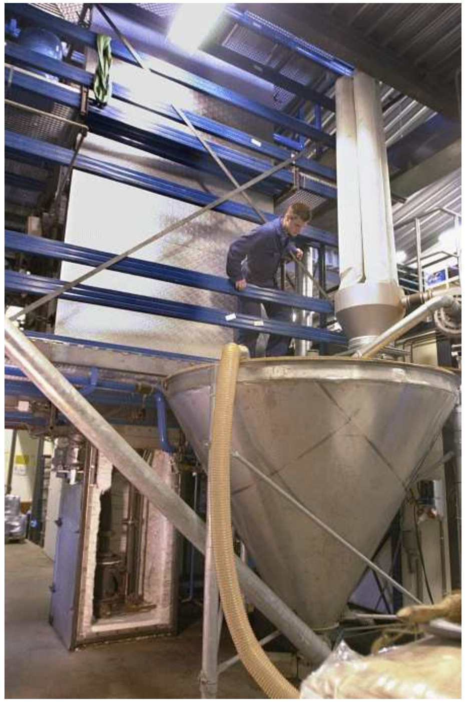
- **aquathermolysis:** pressurised hot water (pre)treatment (200 °C, 30 min.)
- **followed by BFB fast pyrolysis** (350-400°C, vapour residence time 1-2 sec.)



Upgrading of bio-oils

Successful development of:

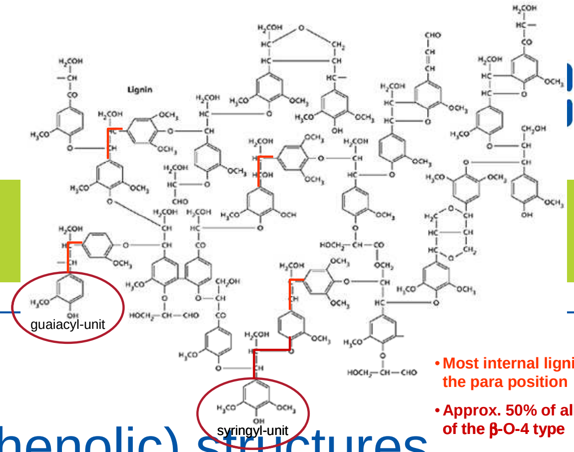
- Procedures to improve quality of fast pyrolysis oil (filtration, dewatering)
- Fractionation of bio-oil into enriched fractions suitable for resins and wood preservatives



80-250 kg/hr rotating cone fast pyrolysis pilot plant at BTG

BIOSYNERGY

Lignin valorization



- Most internal lignin bonds via the para position
- Approx. 50% of all bonds are of the β-O-4 type

- Lignin contains numerous valuable aromatic (phenolic) structures
- Valorisation to products (even partial) improves carbon footprint and revenue of the biorefinery

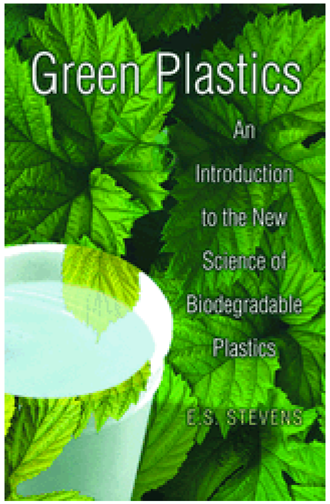
<u>Technologies</u>

- Combustion for heat and/or power (main application to date)
- Gasification for syngas
- Hydroliquefaction for transportation fuels (reformulated gasoline)
- Direct application 'organosolv' lignins in resins*
- Enzymatic processing (laccases) to improve reactivity*
- Pyrolysis for chemicals, performance products and fuels*

BIOSYNERGY

Potential applications of lignin-derived phenolics

Biobased plastics



- **epoxies**
- **polyolefins**

Wood-adhesives and resins

- **Fuel additives** (aromatic ethers, cyclohexanone)
- **BTX**
- **Binders**
- **Bio-bitumen**

- **Carbon Fiber (for CF composites)**

Specialty phenolics for high-value applications such as fragrances and pharmaceuticals

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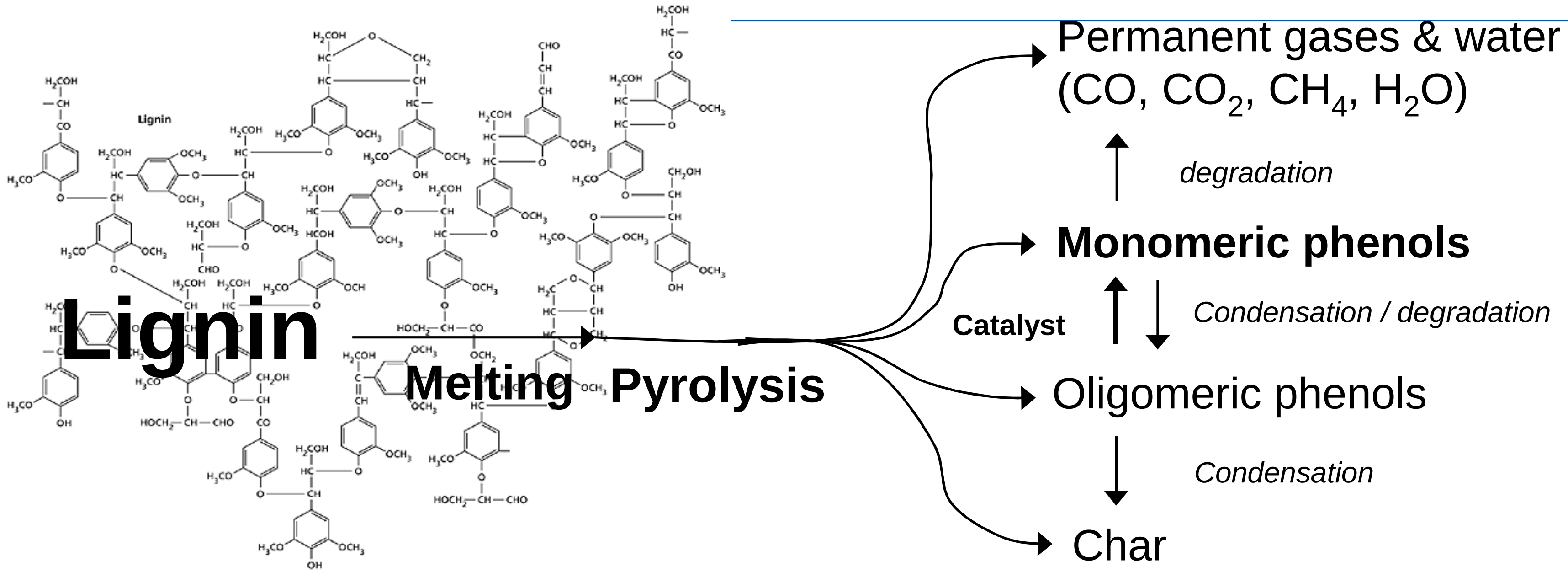
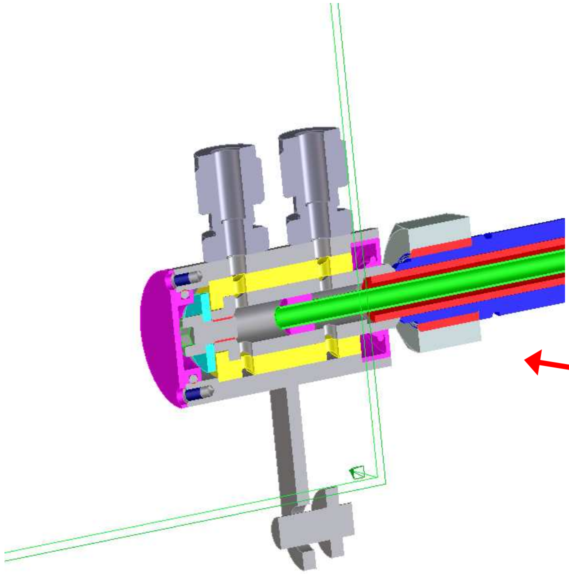
Lignin thermal conversion via pyrolysis is complex



- First of all a proper feeding procedure is required to overcome lignin's thermoplastic behaviour that causes severe operational problems such as screw feeder clogging by molten lignin, agglomeration and subsequent defluidisation of the reactor bed.
- For a maximal conversion of lignin into (monomeric) phenols there is a narrow window of pyrolysis conditions such as temperature, heating rate, vapour and solid residence time.
- Use of catalyst to improve product selectivity and yield

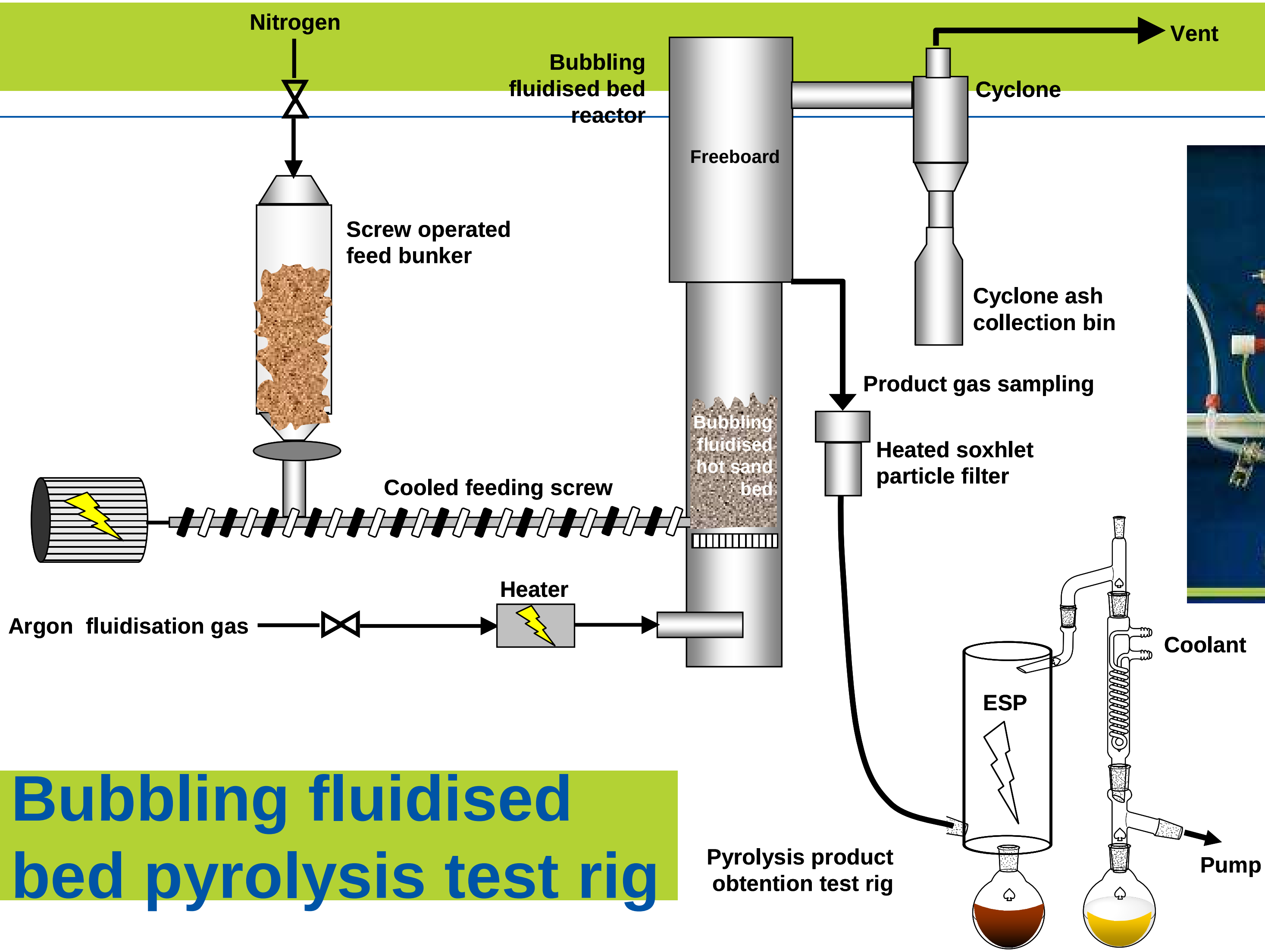
Improving feeding behaviour: construction of a water-cooled screw feeder



- Hollow screw design

Recent work Paul de Wild c.s.ECN

Bubbling fluidised bed pyrolysis test rig

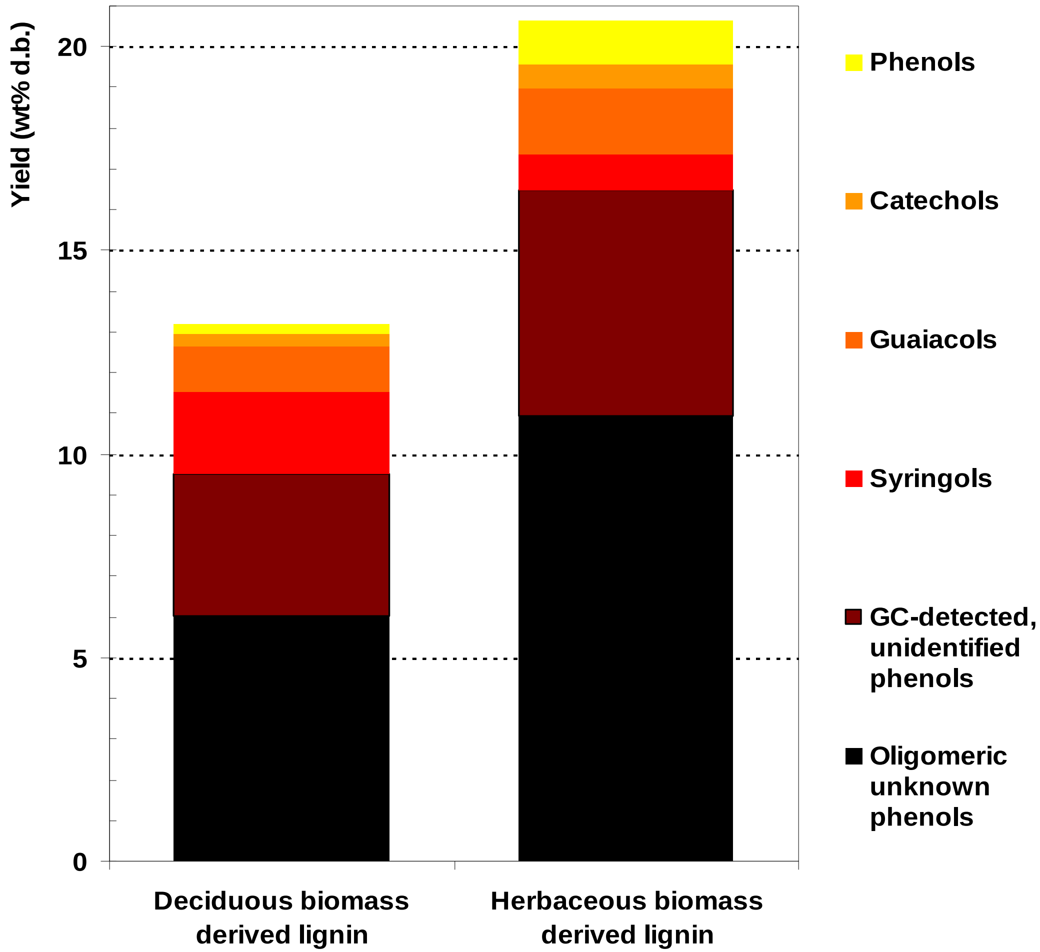


Continuous catalytic pyrolysis of organosolv lignin (WP2)

100 lignin pyrolyse to:
- 15 - 20 gas (CO, CO_2, CH_4)
- 20 - 25 water
- **15 - 25 organic condensables**
- 30 - 35 solid (char)

continuous cat. pyrolysis at 400℃ gives **high yields of phenolics:**

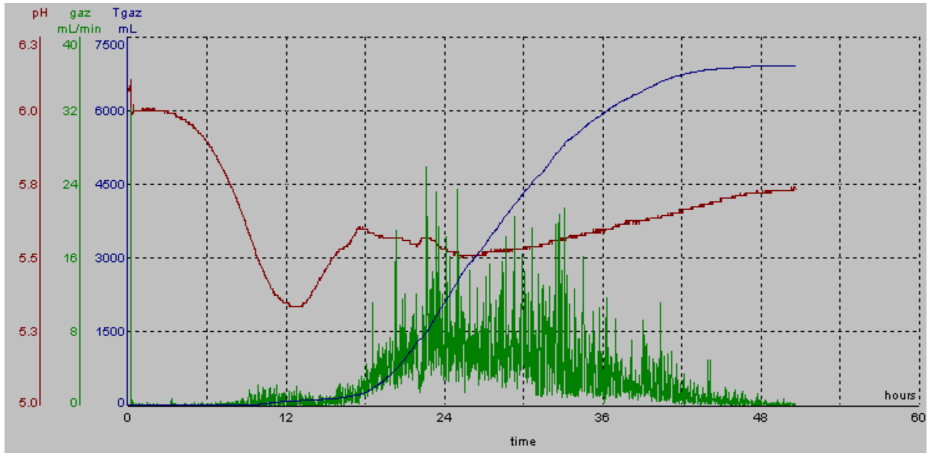
- **13 wt% (d.b.) phenolics** from hard wood derived Alcell organosolv lignin
- **20 wt% (d.b.) phenolics** from herbaceous derived lignin from soda pulping of grass/straw mixture

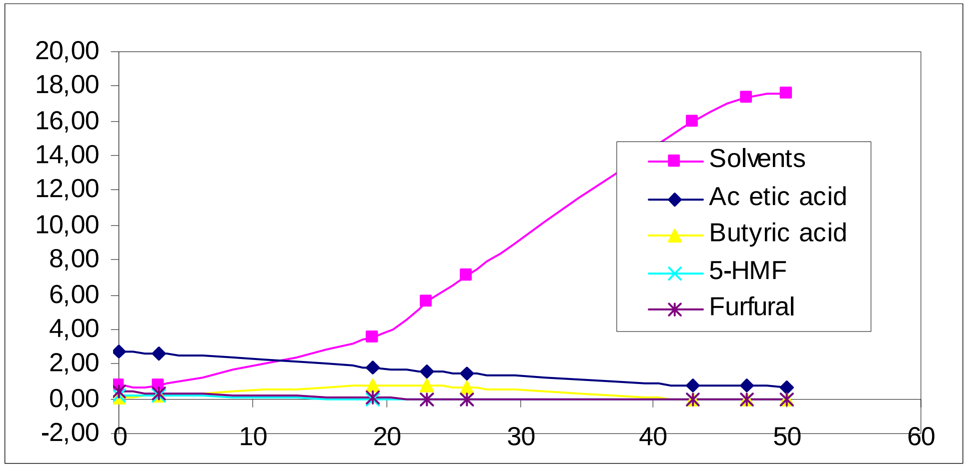


BIOSYNERGY **Advanced biochemical conversion (WP3)**

ABE Fermentation wheat straw hemicellulose hydrolyzate IFP/A&F

- Successful screening and selection of strains on pure substrates
- **ABE Production on wheat straw hemicellulose hydrolyzates prepared by steam explosion** in mild acidic conditions
- 50% Hydrolysate in synthetic medium (60 g/L total sugars (Glu 9; Xyl 51 g/L)
- Strain *Clostridium beijerinckii* NCIB 8052 / pH controlled at 5.3
- **Good lab scale results : Final solvents (ABE) : 17,6 g/L**
- **Continuous fermentation still a challenge**
- **ABE separation from fermentation broth rotating disc separator demonstrated**





BIOSYNERGY **Advanced biochemical conversion (WP3)**

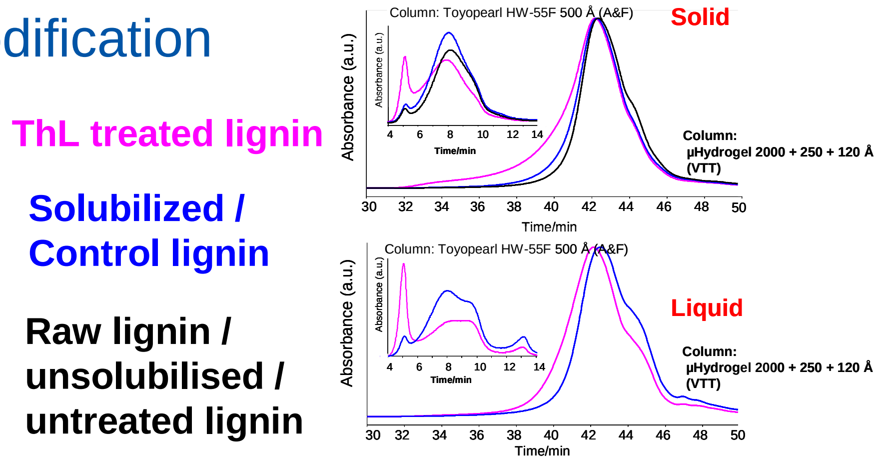
Xylonic acid fermentation and lignin activation (VTT)

Xylonic acid production from xylose

- Successful fermentation results in batch and continuous cultures
- acid hydrolyzed DDGS and wheat straw pentose hydrolysates

Functional lignin derivatives: lignin ‘activation’

- *Aim:* improvement of reactivity (cross linking behaviour) to enhance product options
- Successful enzymatic lignin modification by *Trametes hirsuta* laccases



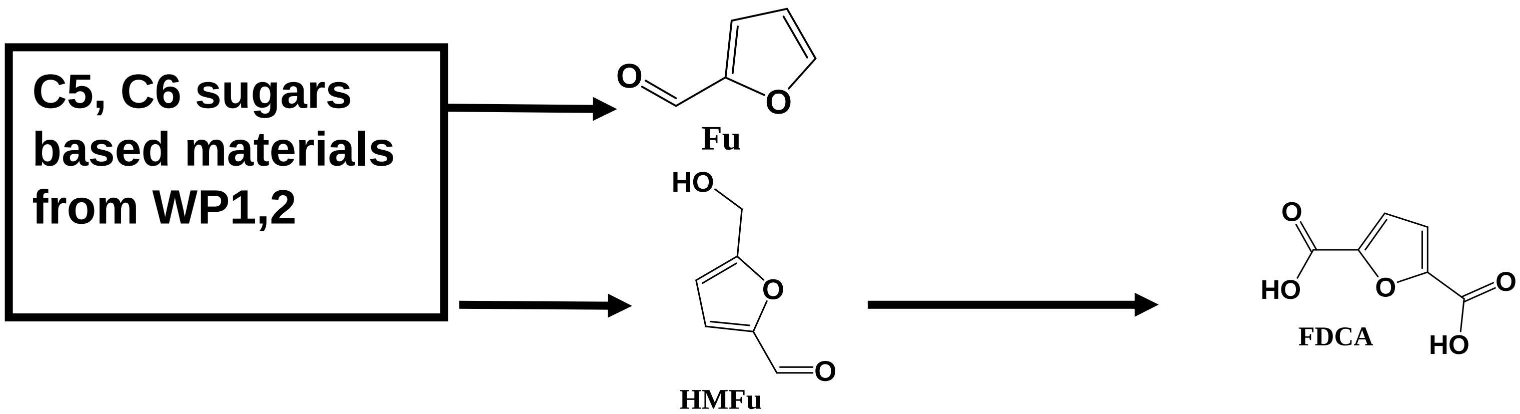
Characterization of modified lignin polymers by chemical and spectroscopic methods.

Mattinen et al. (2008). "Polymerization of different lignins by laccase," *BioResources* 3(2), 549-565.
Mattinen et al, (2009) "Modifications of lignans by Trametes hirsuta laccase" *BioResources* 4(2), 482-496.

Production & characterisation platform chemicals (WP4)

Partners: DOW, A&F, ARD, Bioref, GIG, Chimar, TUD

- Lignin depolymerisation in supercritical CO_2 (A&F) **Improved yield >10%**
- Analysis kinetics furfural (Fu) synthesis from xylose and modelling to improve furfural production process: TUDelft. **Yield improvement > 85%**



- Hydroxymethylfurfural production from glucose dehydration>> **substantial yield improvement by use of ionic liquids (Bioref)**
- **Synthesis 2,5-Furandicarboxylic acid (2,5-FDCA)** from HMF with **high yield > 90%** (Bioref/ A&F). FDCA potential replacement for TFA in PET.

BIOSYNERGY

Application testing and market validation

- Application testing 2,5 FDCA-derived polymers: **promising initial results, further work in progress**

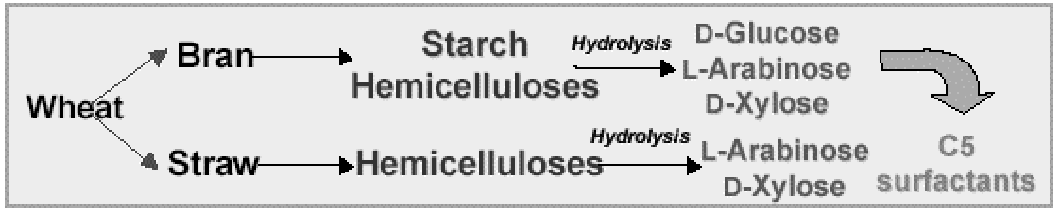
- **Phenol substitution up to 25 wt%** by (organosolv) lignin in thermosetting phenol-formaldehyde resins for particle board application (test results Chimar)

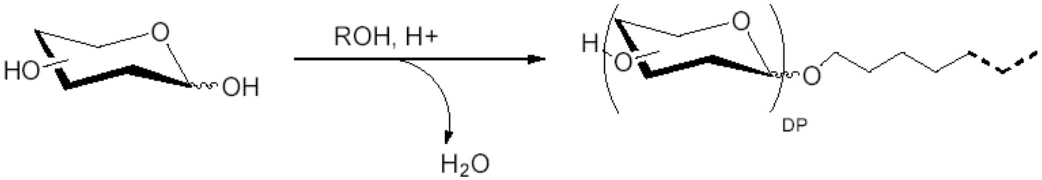
- **Performance pentose based surfactants for paper impregnation** comparable to petrochemical products

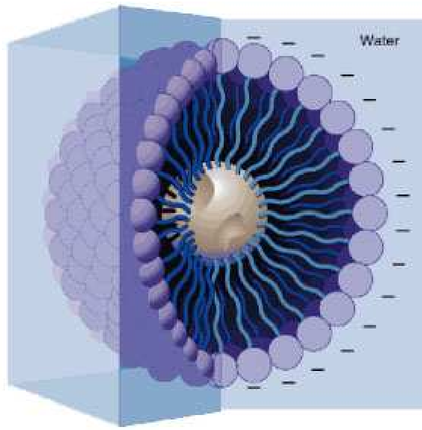
BIOSYNERGY

Pentose valorisation as raw material for surfactants; ARD

New approach developed by A.R.D. for new agro-surfactants





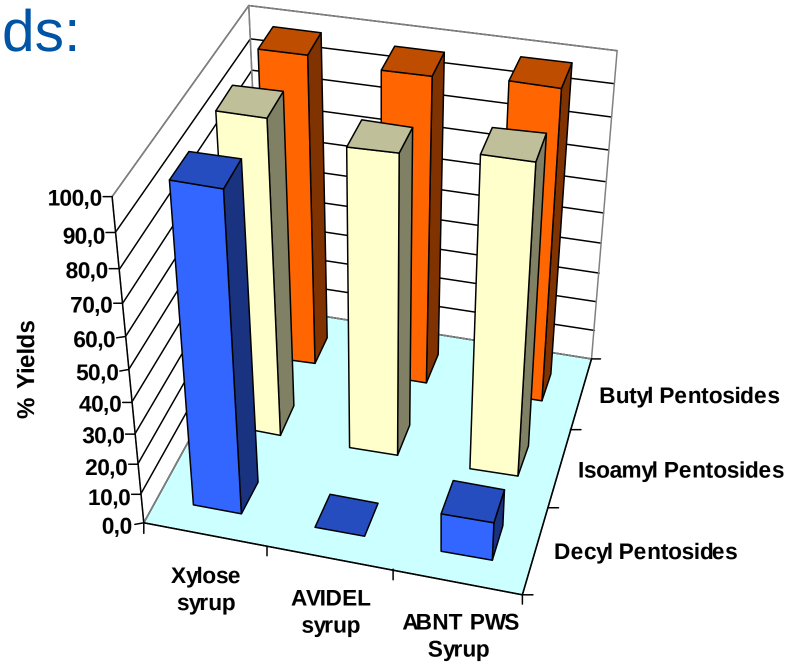


- Reaction of: Pentoses + Fatty alcohols (ROH) C:4 - C:18

- **Aim**: Production of pentoside surfactants by a green technology in order to access the price level of fossil based competitors (~1500 €/ton)

Pentose valorisation as raw material for surfactants; ARD

Direct conversion of pentose containing hydrolyzates to surfactants in high yields: **good progress obtained**



Yields of Alkyl pentosides obtained for three pentose syrups and for 3 types of alcohols.

Short tail Pentoside surfactants prepared **in quantitative yields from straw derived <u>unpurified</u> pentose syrups**

Integration of results in Conceptual design biorefinery plant (WP5)

Basic design for integral lignocellulose biorefinery plant at an existing cellulose ethanol site: AB BCyL demonstration plant, Salamanca.

- Targeted outputs:
  - bio-ethanol,
  - chemicals, materials, CHP
- 5 EtOH based biorefinery types
- maximum revenue and minimum environmental impact

Partners: ABNT, Aston, ECN

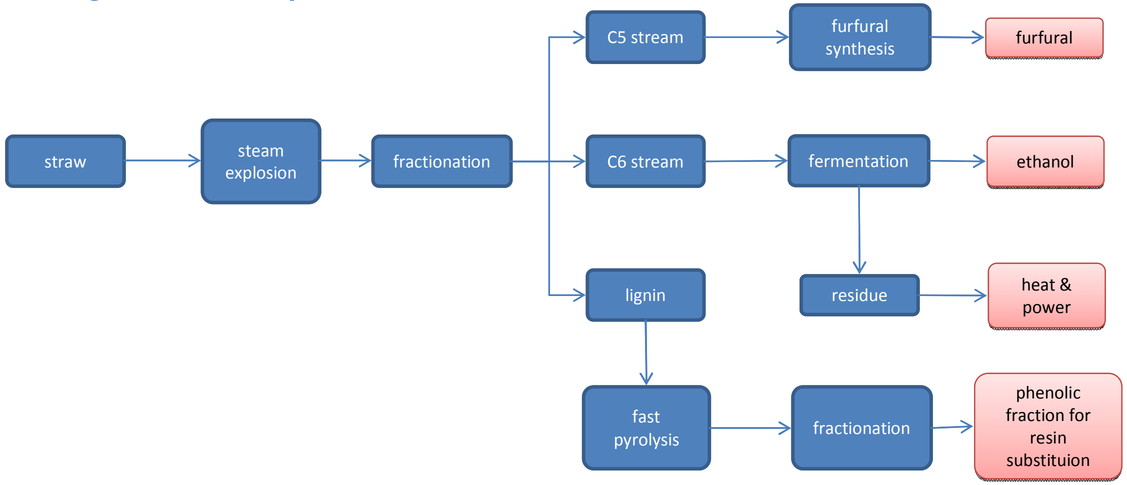
BCyL cellulose ethanol demo plant AB, Salamanca, 5 Million L EtOH/yr from 25,000 ton straw. ***Operational since Oct. 2009****.*

BIOSYNERGY

Biomass-to-products chain design (WP6, Aston)

Aim: Identification of the most promising biorefinery chains for the EU

- **Modelling tool with modular structure** developed
- **Process synthesis and simulation**: ongoing, in final stage
- **Process comparison** using **MCDA** (**incl. economics, LCA, socio-economics**)



Focus on ethanol based biorefineries: Biorefinery co-producing **ethanol, furfural, phenolic resins and CHP**

*Preliminary results economic evaluation indicate that **biorefinery processes** (ethanol + chemicals) have **better economic perspective** than cellulose ethanol only plus lignin combustion for steam generation.*

Partners: **Aston,** ECN, IFP, CRES, JR, JRC, Cepsa, ABNT.

Summary and conclusions

- **Lignocellulose** is a low cost, but complex feedstock with **numerous product options incl. major chemical building blocks.**

- **Development LC Biorefinery** -combining bioprocesses and chemical processes- offers **good perspectives** to exploit lignocellulose. Biosynergy R&D provides a solid basis to **valorize C5 sugars and lignin.**

- **Pretreatment and enzymatic hydrolysis are a major cost factor** and are **critical** for the quality of intermediates and end products and for **techno-economic feasibility**
  - Pretreatment technologies need to be **optimized toward a particular goal** / end products. Organosolv and MAF are good candidates to valorize all fractions AND produce a high quality lignin.
  - For further improvement an **integrated approach** of the trajectory feedstock<>pretreatment<>hydrolysis<>fermentation is required

Summary and Conclusions (2)

- **Lignin valorization** (at least in part) to chemicals is an **important tool for economic profitability** and for (further) reduction of the carbon footprint. **Promising results** for lignin valorization attained for:
  - direct application of (organosolv) lignin in resins
  - catalytic thermochemical processing (pyrolysis) of lignin to phenolics
  - enzymatic lignin conversion to improve reactivity

- **Separation technology** development **vital** for both biochemical and thermochemical processing technologies

- **Biorefinery of lignocellulose to ethanol + chemicals + CHP shows better economic perspectives than production of only cellulose ethanol + CHP.**

Acknowledgements

Contributions by Paul de Wild (dewild@ecn.nl) and Wouter Huijgen (huijgen@ecn.nl)

The BIOSYNERGY project is supported by the European Communities through the Sixth Framework Programme for Research and Technological Development (2002–2006) with a grant up to 7.0 million € under contract number 038994 – (SES6). It started on the 1st of January 2007 and has a duration of 48 months.

SenterNovem EOS-LT

The project is financially supported through a grant from the Programme Economy, Ecology and Technology (E.E.T.) by the Netherlands' Department of Economic Affairs, the Department of Public Housing, Spatial planning and Environmental Protection, and the Department of Education, Cultural Affairs and Sciences.

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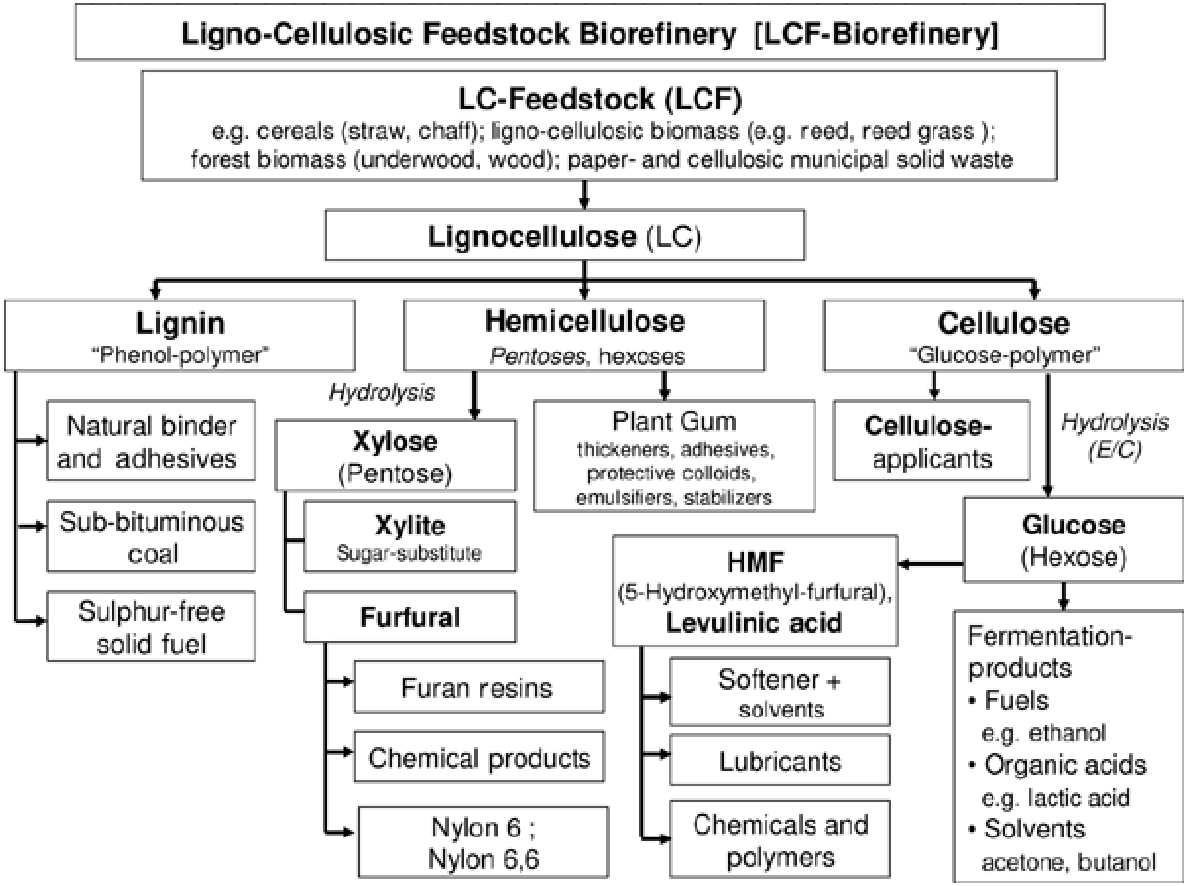
Potential products Lignocellulose Biorefinery

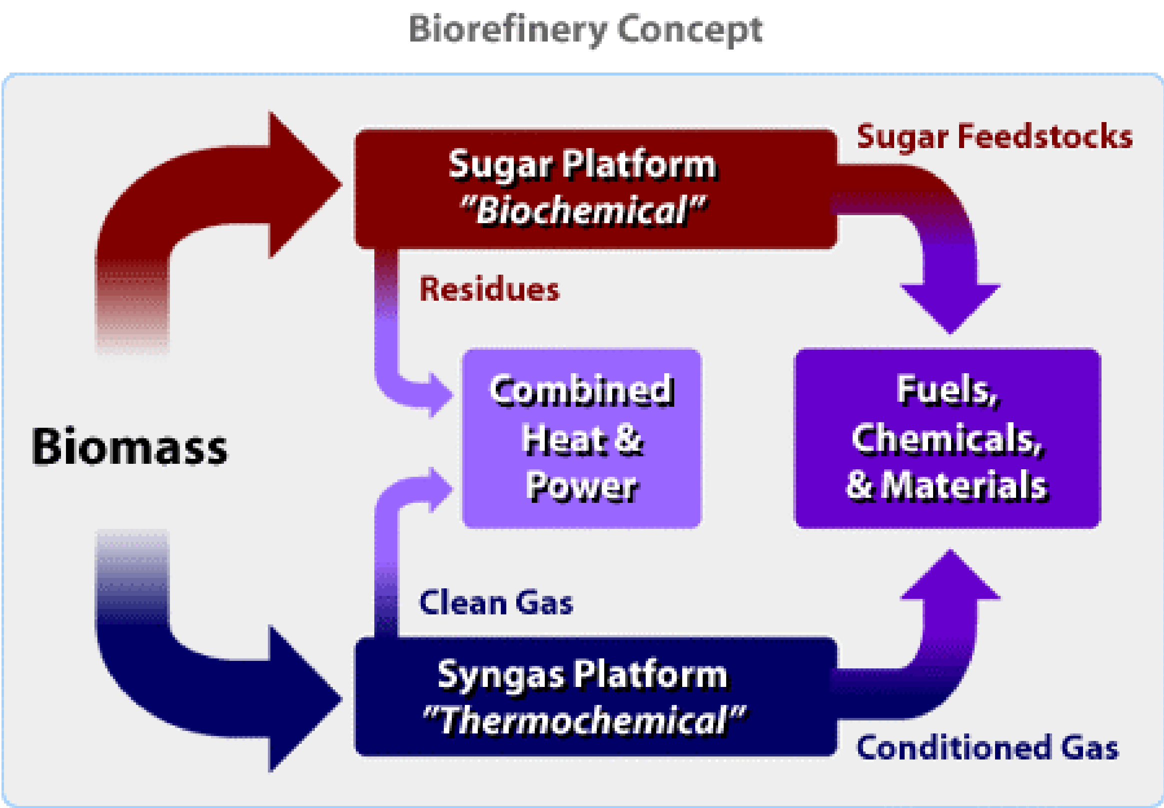


Products generated via

- (Thermo)chemical conversion
- Bioprocessing
- Natural monomer structure largely preserved
- Products have a good position in the current (petrochemical) market and future biobased market (building blocks):
  - Furfural
  - HMF
  - Fermentation products

Kamm, B.; Gruber, P.R.; Kamm, M.; Biorefineries, Industrial Processes and Products, Wiley-VCH, 2006

Thermochemical biorefinery: syngas platform



National Renewable Energy Laboratory (NREL)

BIOSYNERGY

Integrated Thermal Biorefinery 500 MW_{th}

Compound	composition [vol%]	yield [kg/tonne]	annual yield [ktonne]
CO	34.2	364	309
H_2	20.9	16	13
CO_2	26.1	438	372
CH_4	11.6	71	60
N_2	0.52	5.6	4.7
ethylene (C_2H_4)	3.87	41	35
acetylene (C_2H_2)	0.39	3.8	3.2
ethane (C_2H_6)	0.26	3.0	2.5
benzene	0.97	29	24
toluene	0.14	4.8	4.1
xylenes	0.09	3.6	3.0
NH_3	0.47	3.0	2.5
tars (sum)	0.35	17	14
- heavy tars	~	*6.4*	*5.4*
- light tars	~	*10*	*8.9*
- phenol	~	*1.8*	*1.54*
- indene	~	*1.5*	*1.24*
- naphthalene	~	*2.7*	*2.27*
- antracene	~	*0.5*	*0.46*
TOTAL	100	1000	850

Major products/chemicals:

- Syngas (H_2/CO)
- Methane
- Ethylene
- BTX
- Tar compounds (*e.g.* naphthalene)

The biorefinery scale and the amount of chemicals produced match with typical chemical manufacturing processes.

- O2 blown CFB gasifier
- ca. 900 kton wood / year
- Yields per tonne dry ash-free wood
- With preceding Torrefaction plant