

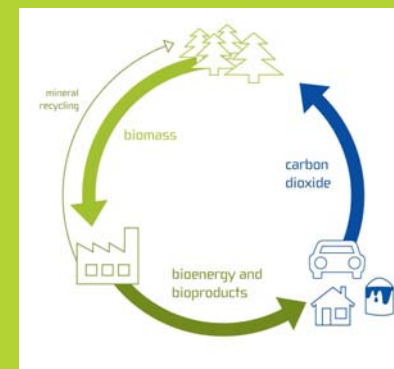


BIOSYnergy



Lignocellulosic feedstock biorefinery for co-production of chemicals, transportation fuels, electricity and heat – Overview 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 Workshop on Biorefinery, 22 June 2009, Madrid



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- Background Lignocellulose Biorefinery
- The EC Integrated Project BIOSYNERGY (FP6)
- Lignocellulose Biorefinery development 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 & optimisation
- Preliminary conclusions & perspectives

Lignocellulose as feedstock

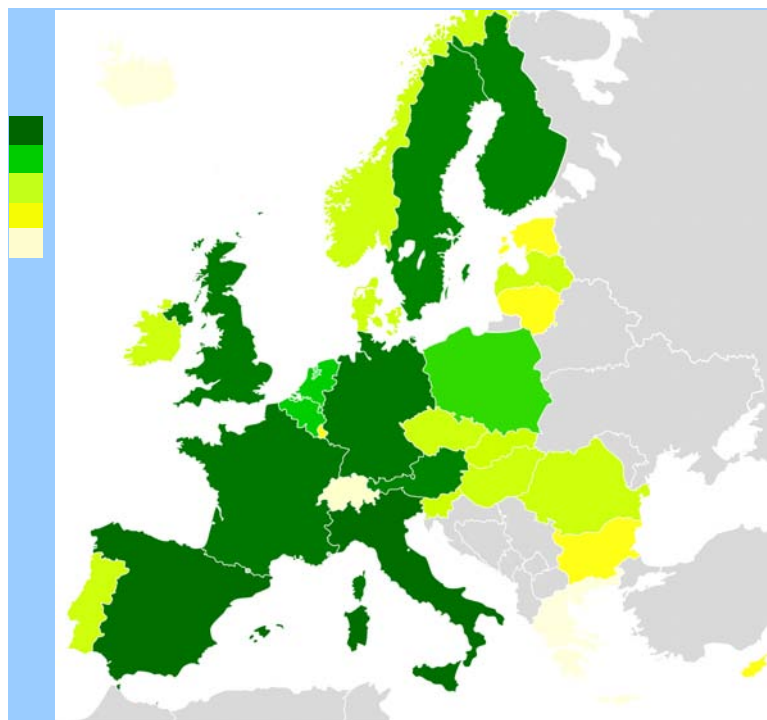
- Low-cost feedstock (~50-60 € / ton d.w.; 3-4 € /GJ) e.g straw, wood residues, energy crops,...
- Alternative source of sugars (to replace starch and sugar agrofeedstock)
- High availability / Limited competition with food production
- High CO₂ reduction when used for 2-G biofuels and biobased products



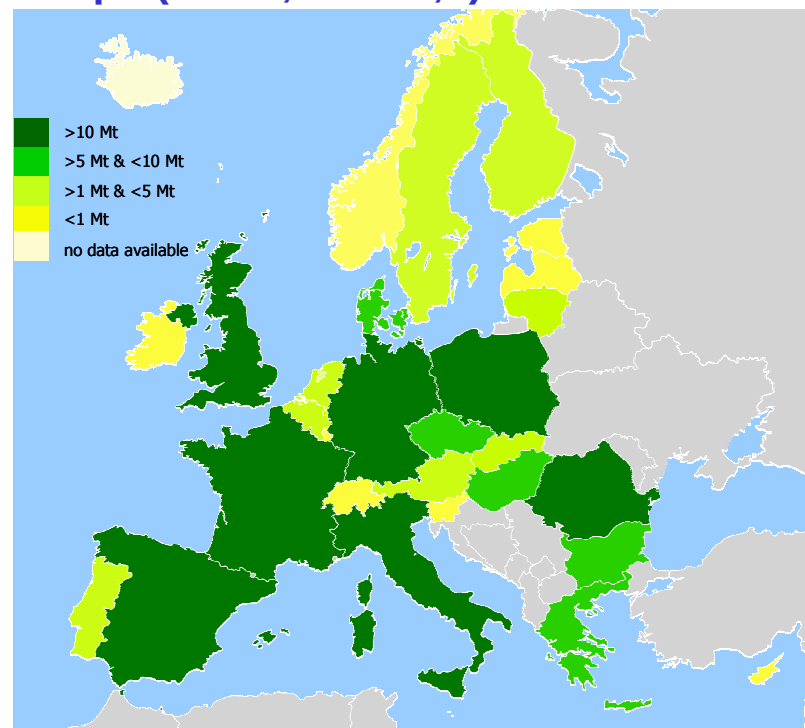


Availability of lignocellulose in the EU-27

- 1) Residues from wood & wood products, pulp and paper production
- 2) Agricultural residues of food and feed crops (straw, stover,..)



Production of wood and wood products, pulp, paper and paper products in EU27; Data 2004, Eurostat

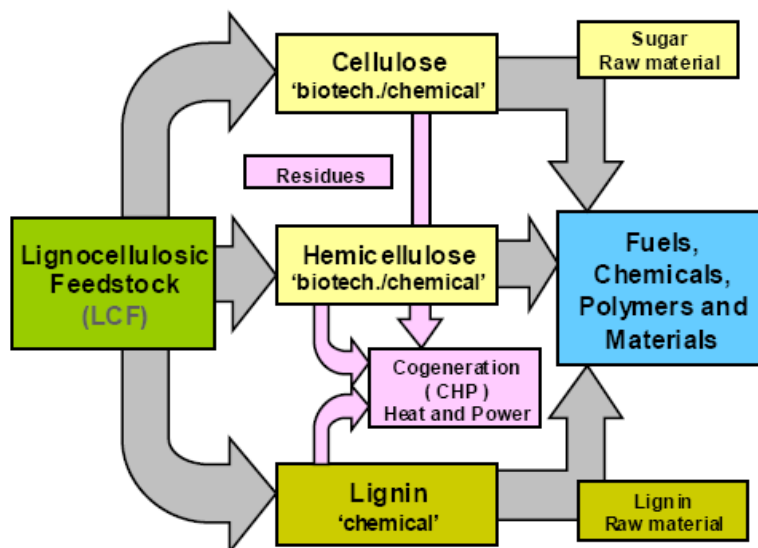


Agricultural residues of food and feed crops (data for 2000) in EU27+, Source: Refuel,2007

Environmentally compatible bio-energy potential EU-25: 7,950 PJ / 530 Mton d.b.(2010) to 12,350 PJ / 820 Mton d.b. (2030). Source: EEA, 2007.



Lignocellulosic Feedstock Biorefinery



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

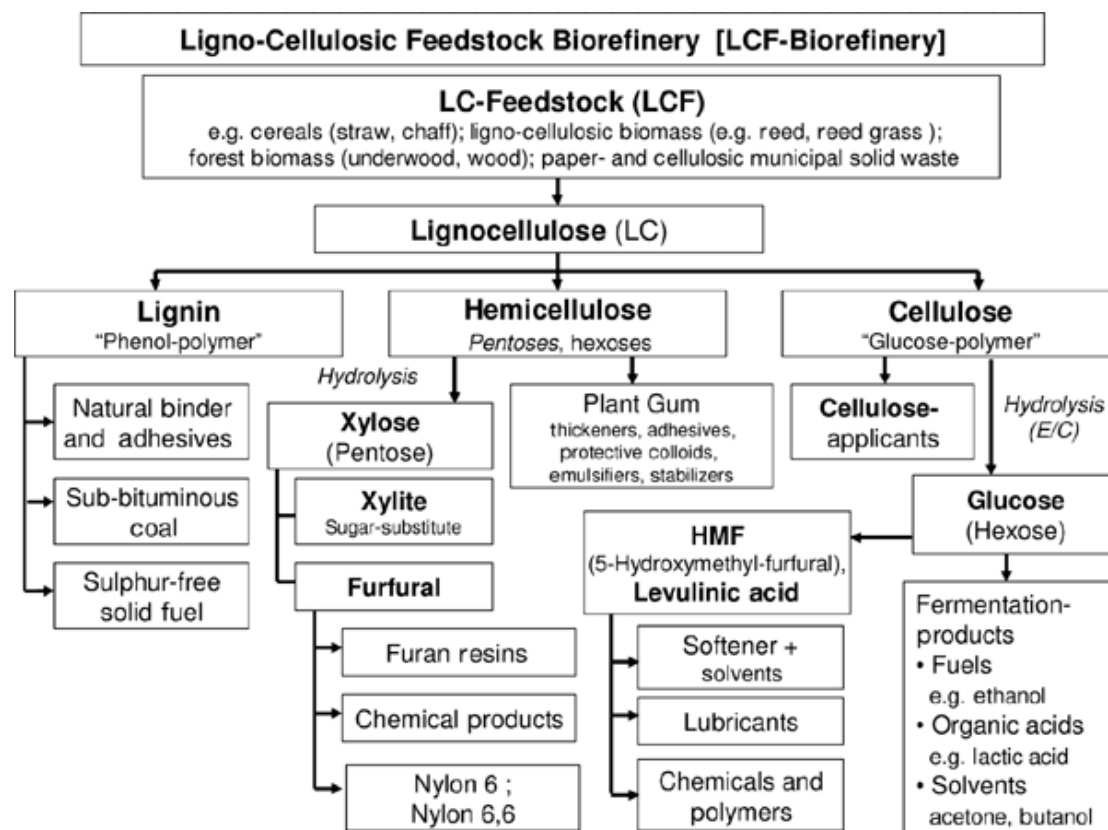
- Abundant low-cost feedstock: wood, straw, corn stover, cellulose containing residues and waste
- Multiple products : transportation fuels, chemicals, polymers, materials electricity and heat
- Aim is to optimize revenues and minimize environmental impact

- 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



Potential products Lignocellulose Biorefinery

Biorefinery is the sustainable processing of biomass into a spectrum of marketable products and energy (IEA Definition)



Products generated via

- **Fractionation**
- (Thermo)chemical conversion and bioprocessing

Natural monomer structure largely preserved

Products have a good position in the market as “building blocks” e.g.:

- Furfural
- HMF/Levulinic acid
- Fermentation products



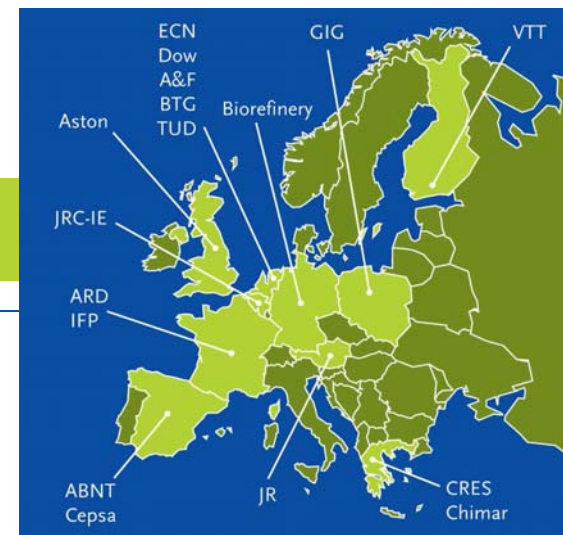
Integrated Project BIOSYNERGY

BIOmass for the market competitive and environmentally friendly
SYNthesis 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.

- Development of integral cellulose-ethanol based LC Biorefinery
- 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.

17 partners from industry, R&D institutes and Universities from 10 EU countries
 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€

17 partners from industry, R&D institutes
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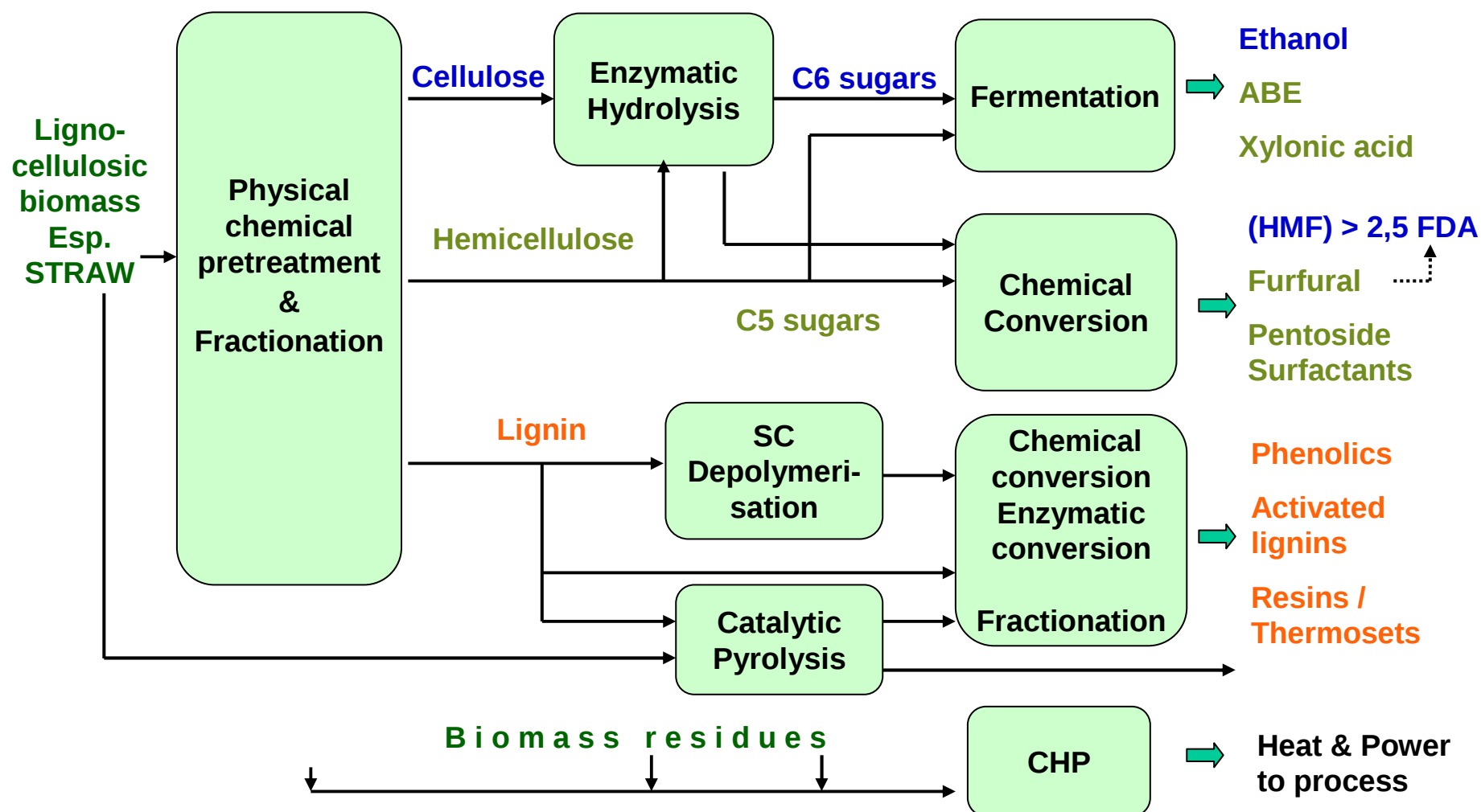


1	Energy research Centre of the Netherlands (ECN)	The Netherlands	NL
2	Abengoa Bioenergía Nuevas Tecnologías S.A. (ABNT)	Spain	ES
3	Compania Espanola de Petroles S.A. (Cepsa)	Spain	ES
4	DOW Benelux B.V. (Dow)	The Netherlands	NL
5	VTT Technical Research Centre of Finland (VTT)	Finland	FI
6	Aston University (Aston)	United Kingdom	UK
7	WUR Agrotechnology and Food Innovations B.V. (A&F)	The Netherlands	NL
8	Agro Industrie Recherches et Développements (ARD)	France	FR
9	Institut Francais du Pétrole (IFP)	France	FR
10	Centre for Renewable Energy Sources (CRES)	Greece	EL
11	Biomass Technology Group (BTG)	The Netherlands	NL
12	Joanneum Research Forschungsgesellschaft m.b.H. (JR)	Austria	AT
13	Biorefinery.de (Biorefinery)	Germany	DE
14	Główny Instytut Górnictwa (GIG)	Poland	PL
15	Joint Research Centre – Institute for Energy (JRC-IE)	The Netherlands	NL
16	Chimar Hellas S.A. (Chimar)	Greece	EL
17	Delft University of Technology (TUD)	The Netherlands	NL



Product lines in the IP BIOSYNERGY

Multi-product biorefinery, Focus on residues cellulose ethanol i.e. C5 and lignin valorisation

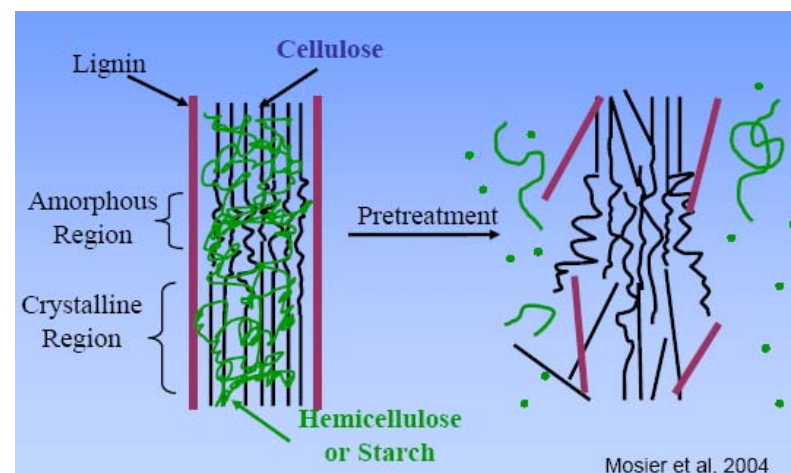




Physical-chemical pretreatment & fractionation

Goals:

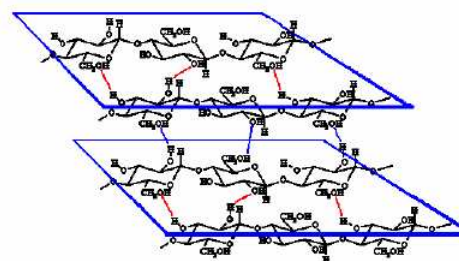
- Controlled fractionation of lignocellulose into fractions with sufficient quality for production of (bio)chemicals: cellulose, hemicellulose, lignin
- Enhance access cellulose for enzymatic hydrolysis to sugars in high yield /low enzyme use
- Minimize by-product formation and the use of chemicals, water and energy
- Preferably lignin as high purity byproduct available
- Reduce costs: Fractionation is a major cost driver.
- Vital for DSP and quality of end -products



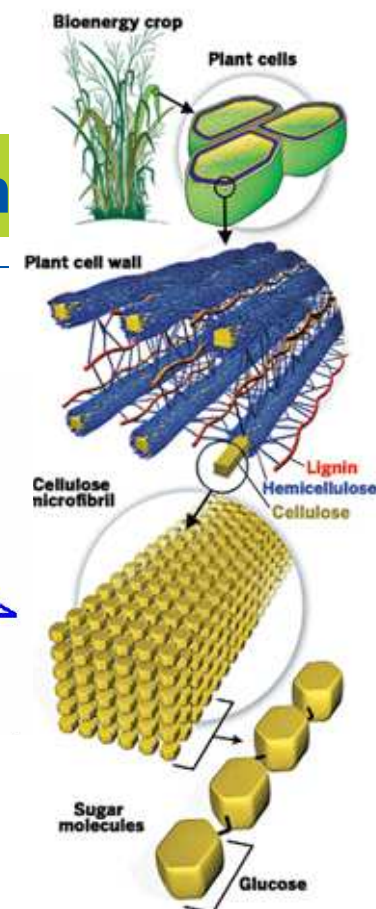
Mosier N, Wyman C, Dale B, Elander R, Lee YY, Holtzapple M, Ladisch MR, 2004. Features of promising technologies for pretreatment of lignocellulosic biomass. Bioresource Technology, Volume 96, Issue 6, April 2005, Pages 673-686

Physical-chemical pretreatment & fractionation

- Challenge: Biomass recalcitrance caused by
 - Complex structure of the plant cell wall
 - high crystallinity of cellulose
- Several routes under development:
 - Steam pre-treatment
 - Mild-acid/thermal pre-treatment
 - Mild alkaline pretreatment
 - Organosolv
 - Ammonia Fiber Explosion (AFEX)
 -
- Most processes suffer from drawbacks: formation of inhibitors, high use energy or chemicals, waste production, high cost etc.
- Most routes produce relatively low quality lignin residue



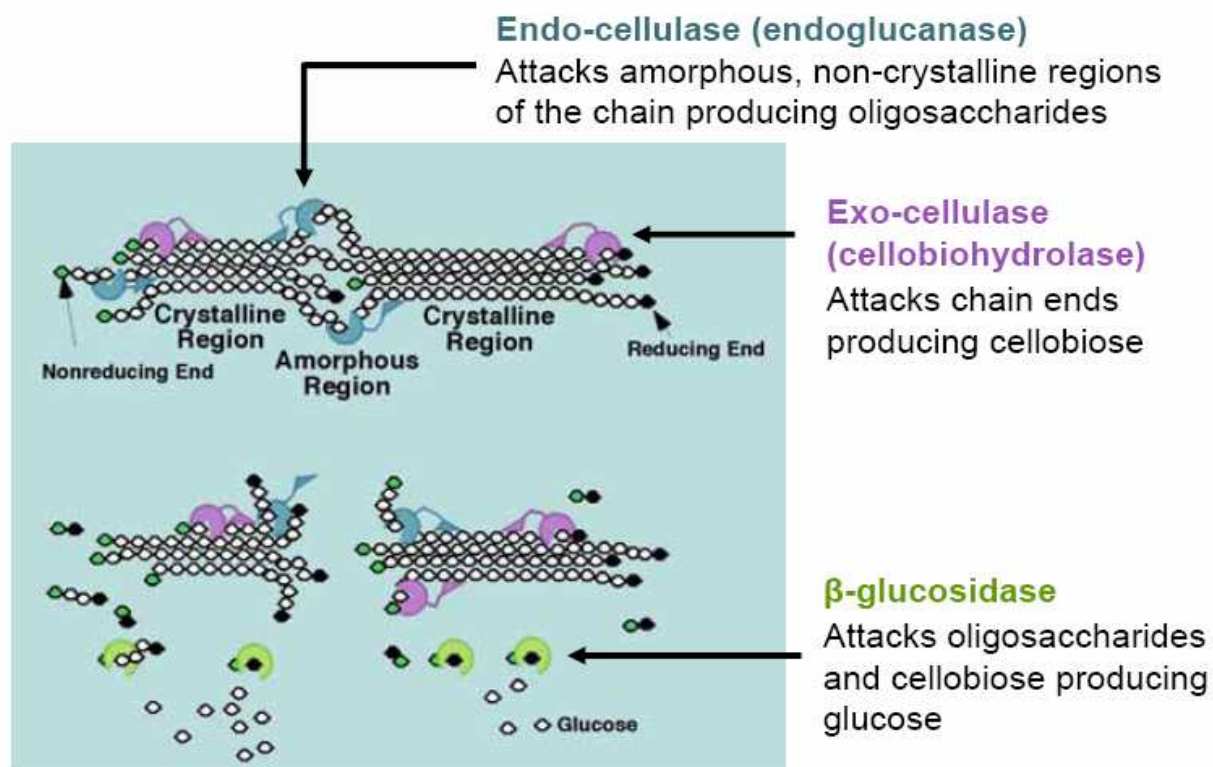
- Highly crystalline matrix
- Low hydration





Enzymatic cellulose hydrolysis

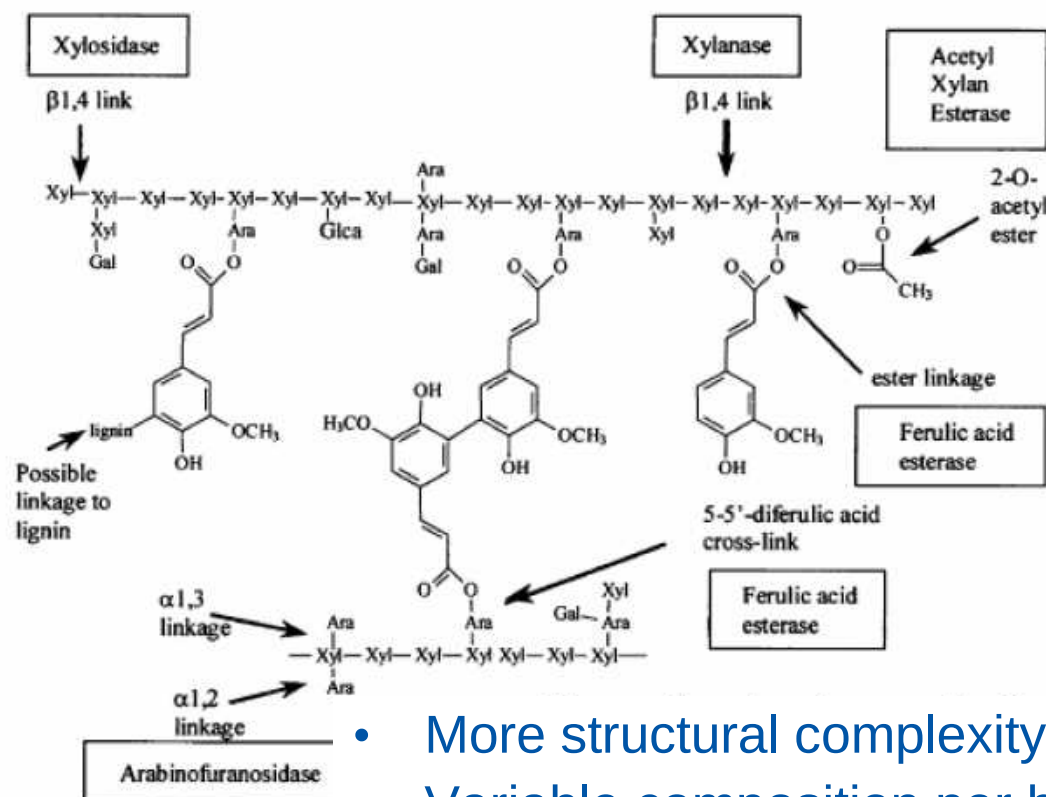
3 types of enzyme activity required for cellulose hydrolysis to glucose



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>



Enzymatic hemicellulose hydrolysis



- More structural complexity than cellulose
- Variable composition per biomass source
- Specific, tailor made combination of enzyme activities required per feedstock

Source: Kevin A. Gray Ph. D. , 2007. Conversion of lignocellulosic biomass into liquid transportation fuels Diversa Corporation/Celunol, San Diego, CA , USA.

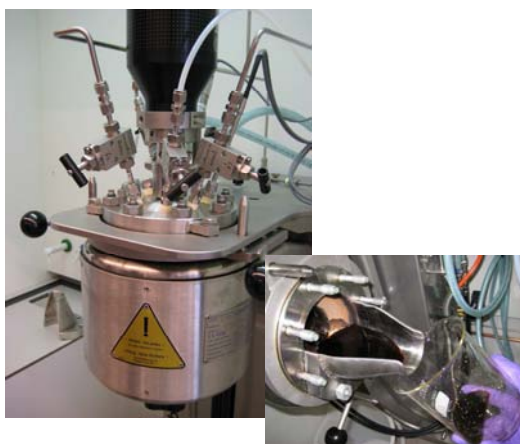
<http://www.epobio.net/workshop0705/presentations/KevinGray.pdf>

Advanced physical/chemical fractionation (WP1)

- Model feedstocks: straw, woods

Processes studied

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



Ethanol/H₂O Organosolv, ECN



Mech./alk pretreatment A&



Acid organosolv Pilot plant ARD

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



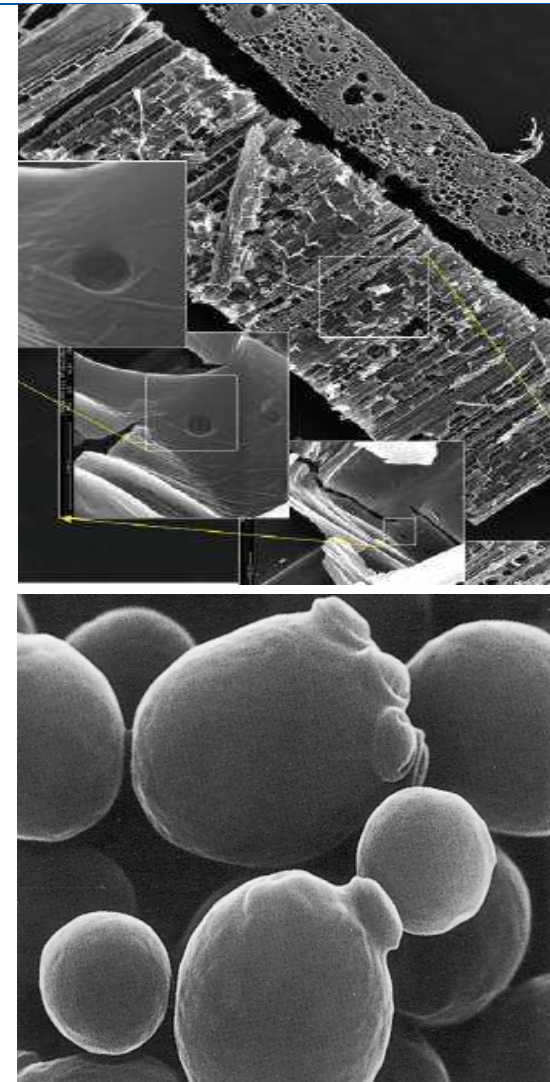
Enzymatic Hydrolysis (WP1)

- Tests with commercially available enzymes on BIOSYNERGY cellulose fractions by A&F, Bioref, ARD
- Target ABNT: Developing tailor-made enzyme mixture able to hydrolyse substrates at costs < 0,02 €/l ethanol
 - High productivity strains (>100 g protein per liter broth)
 - Increased effective activity (dosages < 5mg protein/g glucan entering hydrolysis)
 - Developing a host able to produce the required enzyme mixture for the ethanol production process at industrial scale
 - Developing the enzyme mixture processing and manufacturing technology using the selected host

Enzymatic Hydrolysis (WP1)

Progress ABNT to date

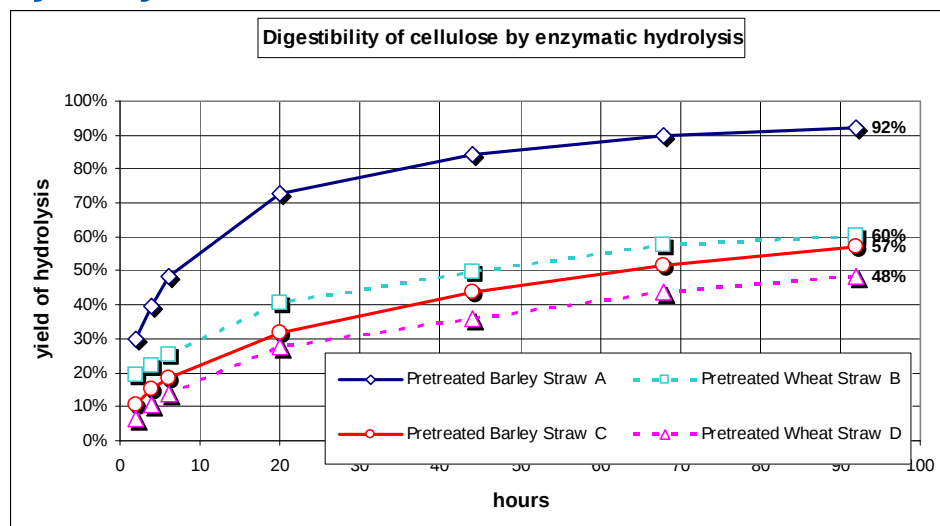
- Selection of base enzyme cocktail for setting up process conditions.
- Expression and purification of selected enzymes from the cocktail.
- Enzyme supplementation studies.
- Cost reduction fermentation media.
- Conceptual design on-site enzyme production plant.





Preliminary 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
- Benchmarking/Economic evaluation in progress

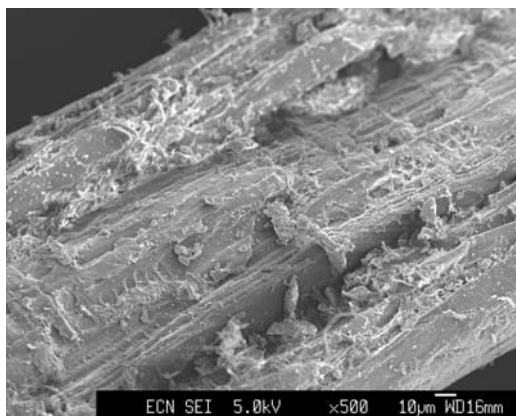


Lignin products from Modified Organosolv Fractionation (ECN)

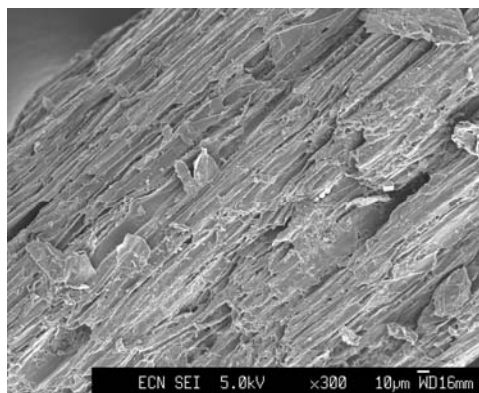


Ethanol/water organosolv offers efficient pretreatment and good lignin quality

Fresh willow



Pre-treated willow (190°C, 60 min, 60wt% EtOH)



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

- Cellulose fibrous structure remains intact
- Effective extraction of hemicellulose and lignin (up to 60%)
- Good access to enzymes. Cellulose hydrolysis yield up to 90%
- Purity and MW distribution of lignin indicate suitability for chemicals production > tests underway
- Acid organosolv (Avidell) also produces good quality lignin
- Solvent recycle crucial for organosolv methods

Innovative thermo-chemical conversion (WP2)

Topics

- Staged (catalytic) thermochemical processing of biomass and lignin
- Catalytic fast pyrolysis
- Integrated development of separation/upgrading technology

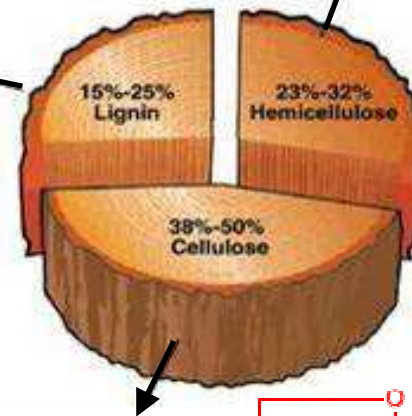
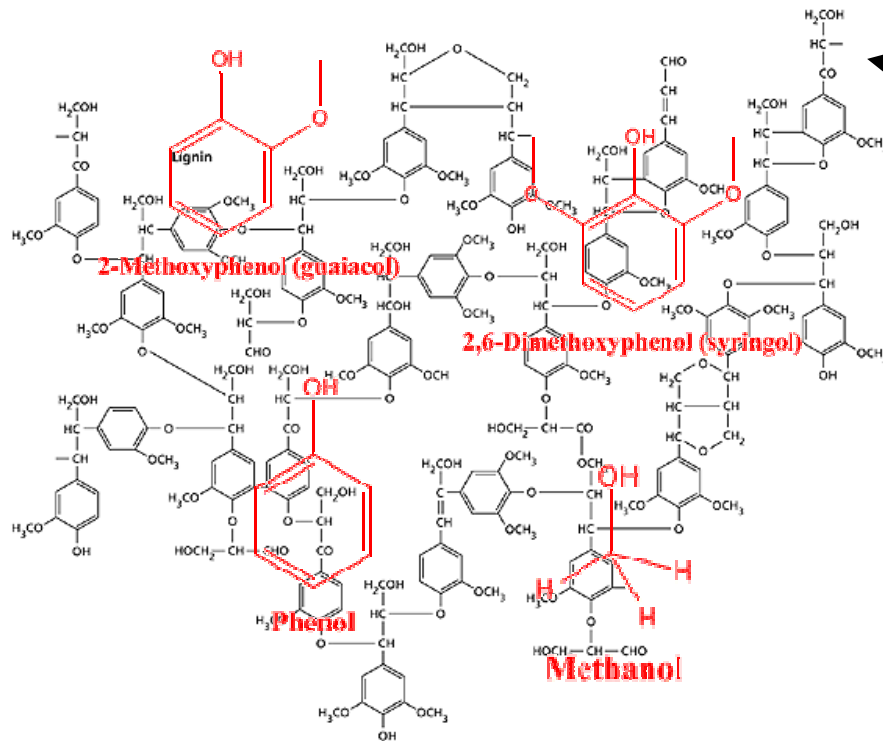
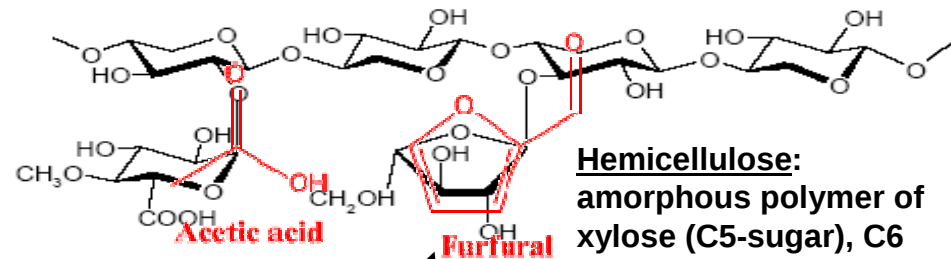
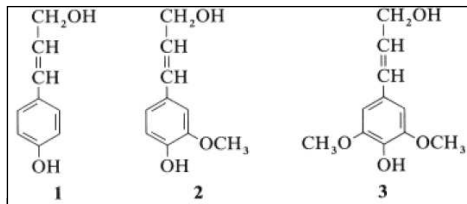
Partners: ECN, Aston, BTG



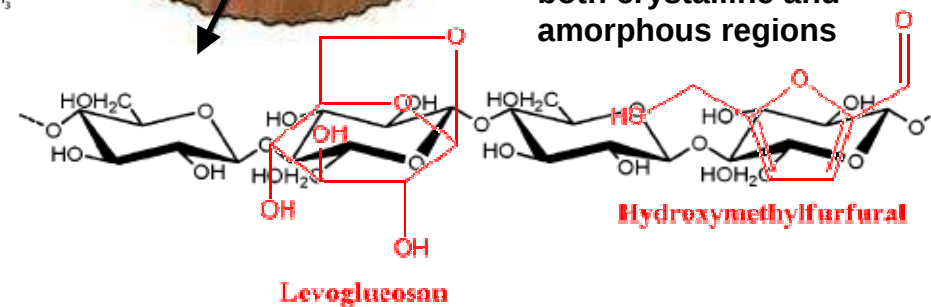
BFB reactor ECN

Thermochemical production of chemicals from wood

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



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



Products arise in mixtures



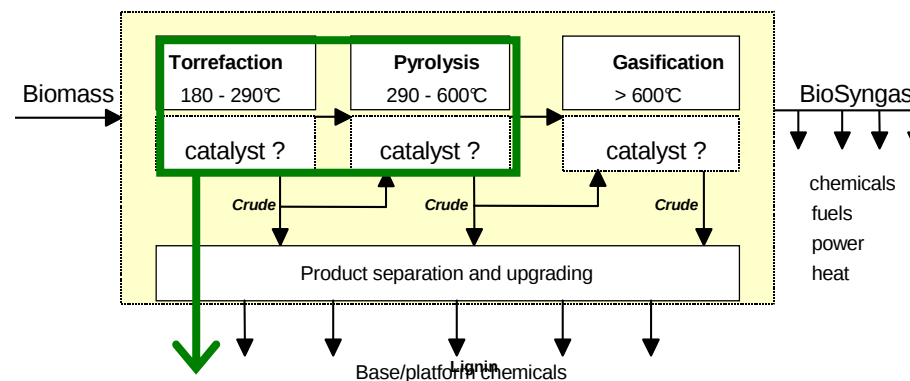
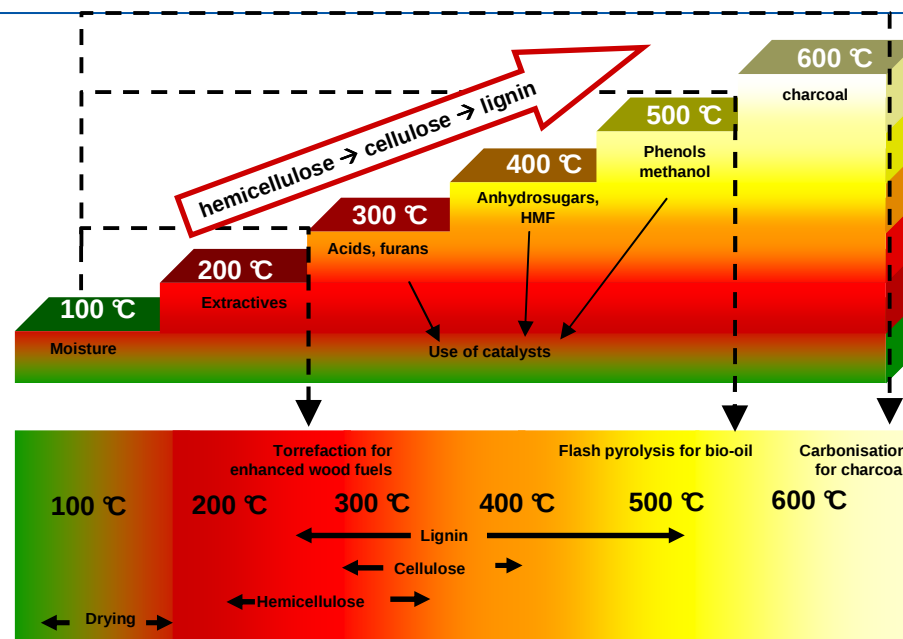
Staged thermochemical processing

Opportunities

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

Challenges

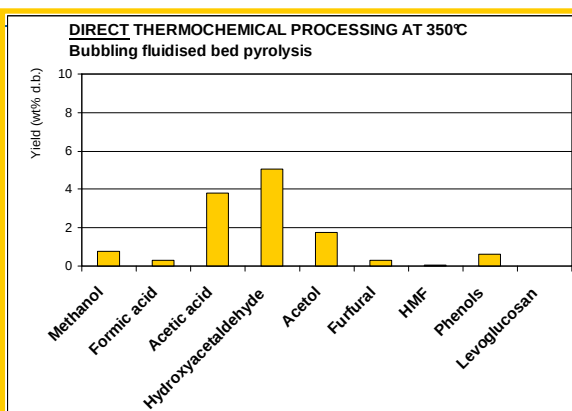
- Optimisation of individual product or product group yields via catalysis, process conditions: temperature, heating rate, vapour and solid residence times
- Product separation and upgrading



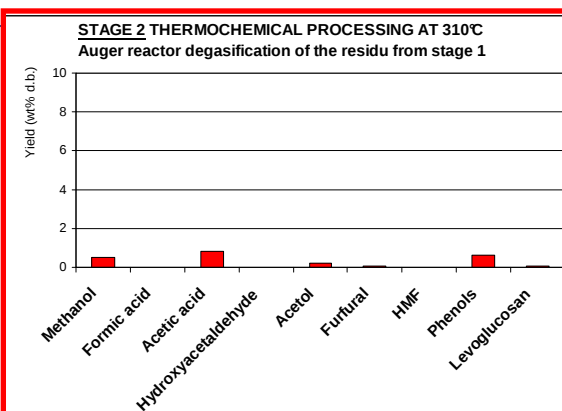
Bio-cascade for drying, torrefaction and pyrolysis



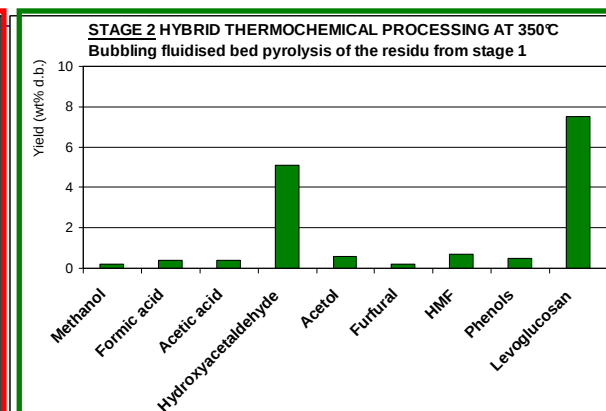
Comparison thermochemical processing straw



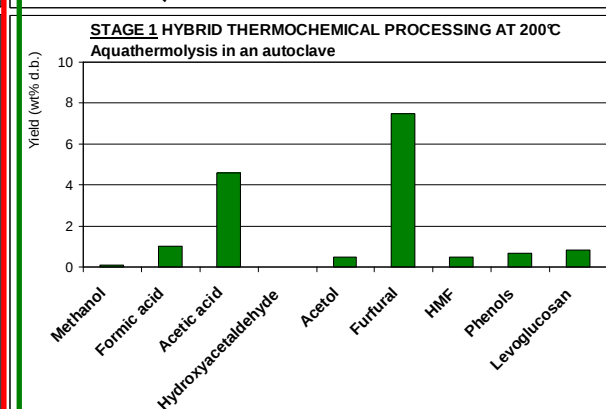
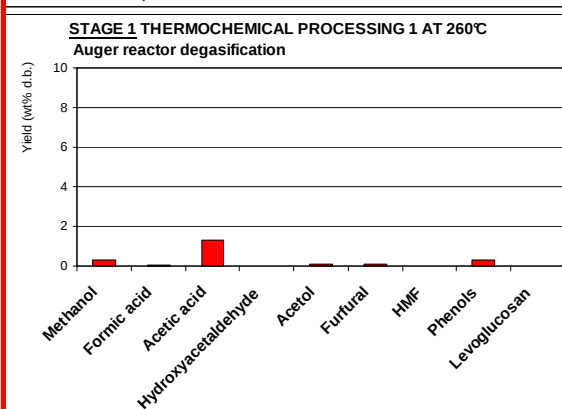
One-step BFB pyrolysis



Staged (de)gasification



Hybrid thermochemical processing



Selected chemicals from wheat straw via 1-step BFB pyrolysis, via staged degasification in an auger reactor and via hybrid thermochemical processing involving aquathermolysis and BFB pyrolysis showing the superior performance of the hybrid concept

P.J. de Wild et al, "Biomass valorisation by a hybrid thermochemical fractionation approach"; submitted to International Journal of Chemical reactor Engineering, 2009



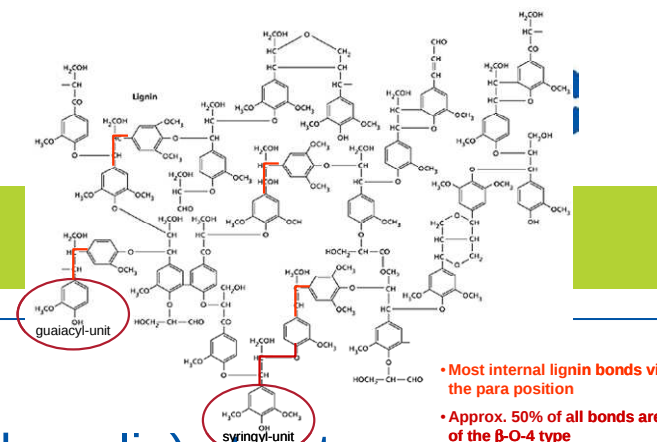
Upgrading thermochemical product mixtures & bio-oils

- Staged condensation for separation of (groups of) chemicals from pyrolysis vapours
- Procedures to improve quality of pyrolysis oil (filtration, dewatering)



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

Lignin valorization



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

Technologies

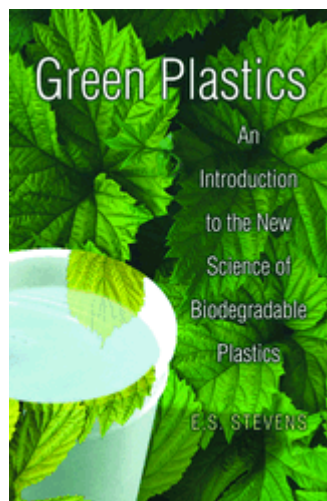
- Combustion for heat and/or power
- Gasification for syngas
- Hydroliquefaction for transportation fuels (reformulated gasoline)
- Direct application 'organosolv' lignins
- Pyrolysis for production of chemicals (monomeric phenols) and/or performance products

Successful valorisation of lignin is a key-issue for an economically viable lignocellulosic biorefinery.



Potential applications of lignin-derived phenolics

'Green' plastics



- epoxies
- Poly-Urethanes
- polyolefins

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

Wood-adhesives and resins



- Fuel additives (aromatic ethers)

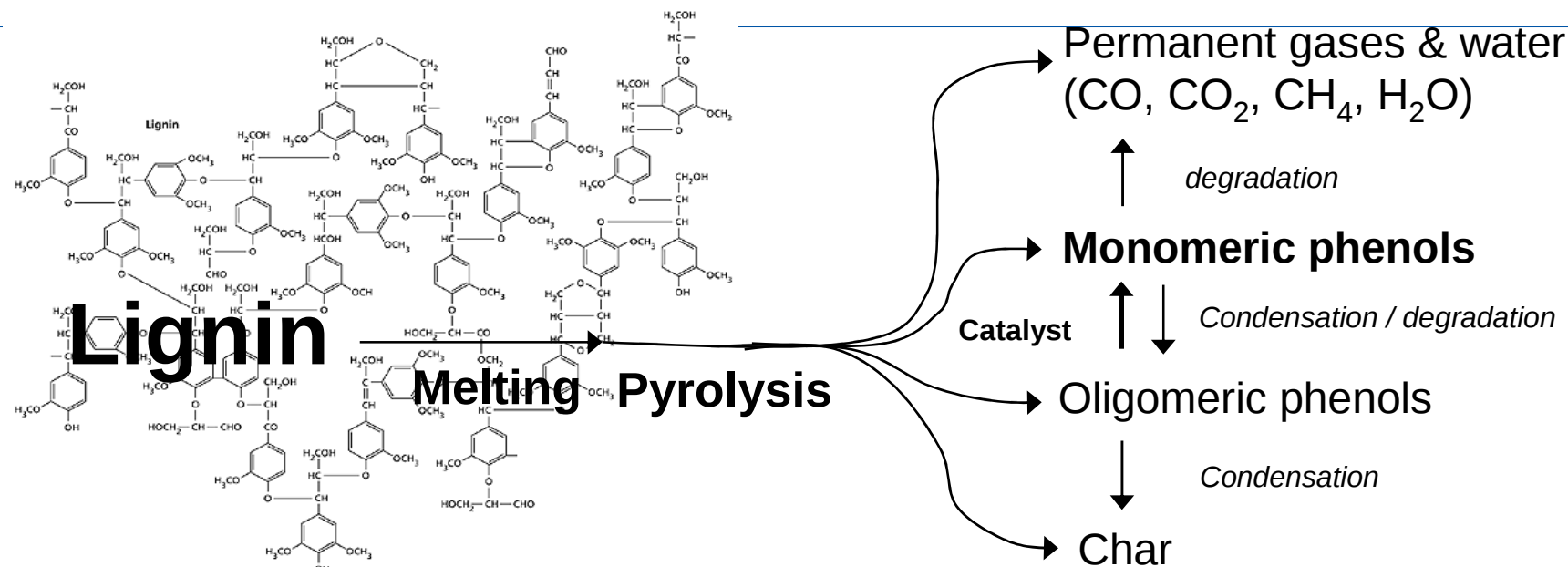
- BTX
- Binders

- Carbon Fiber (for CF composites)



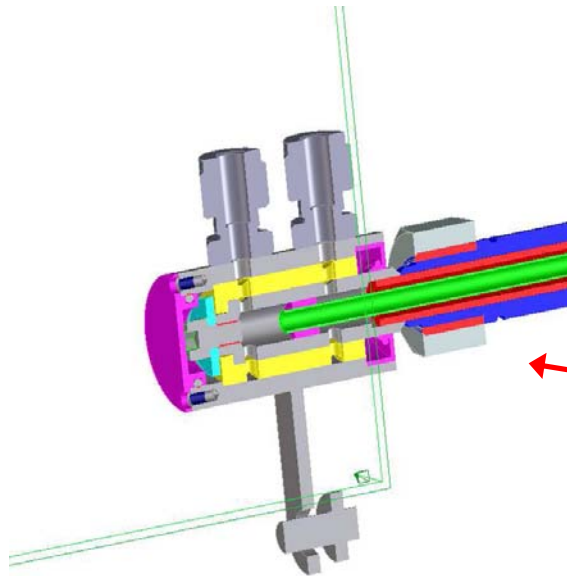


Lignin thermal conversion via pyrolysis: challenges



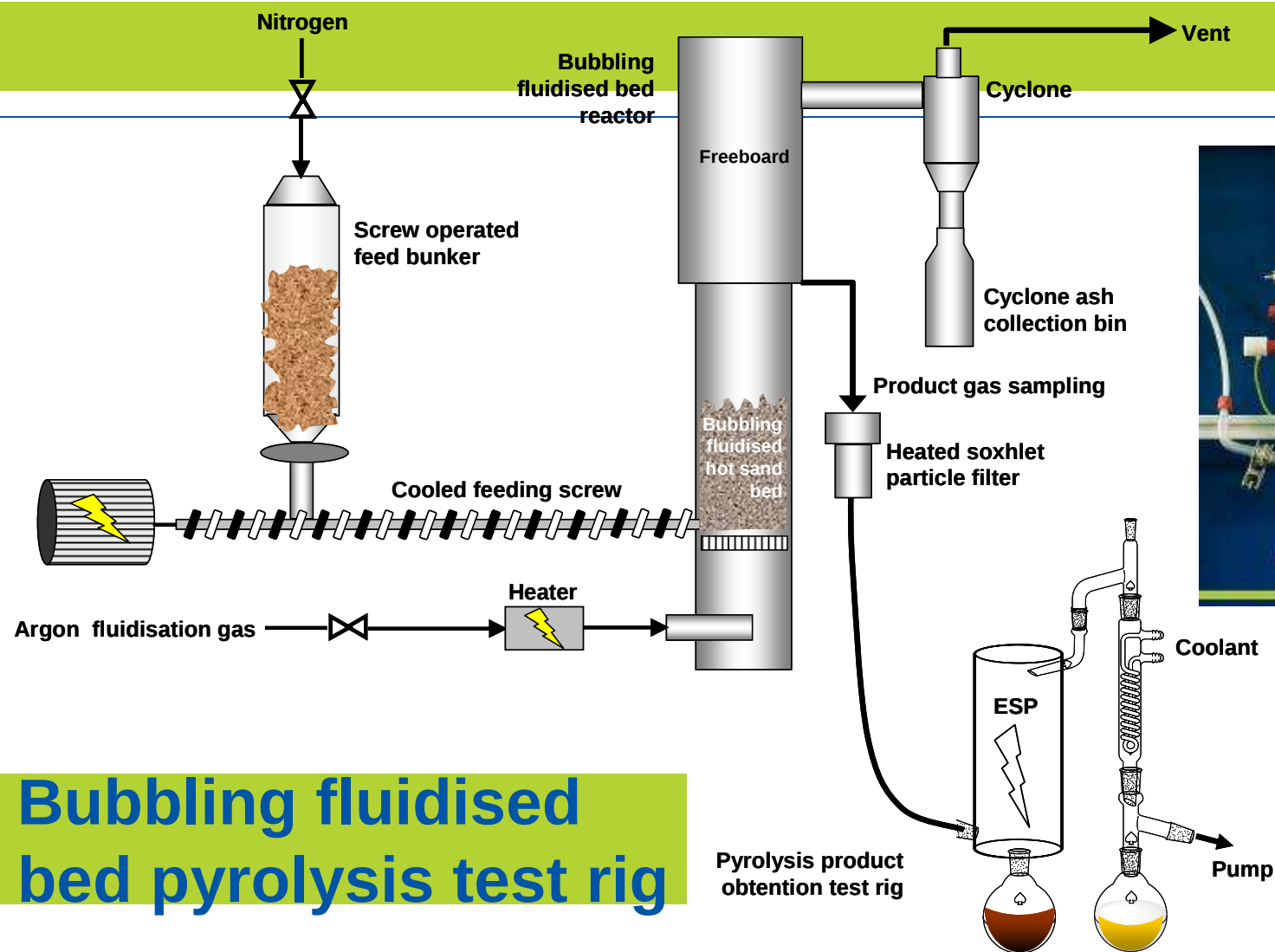
- First of all a proper feeding procedure is required to overcome lignin's thermoplastic behaviour that causes severe operational problems such as screw feeder clogging by molten lignin, agglomeration and subsequent defluidisation of the reactor bed.
- For a maximal conversion of lignin into (monomeric) 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



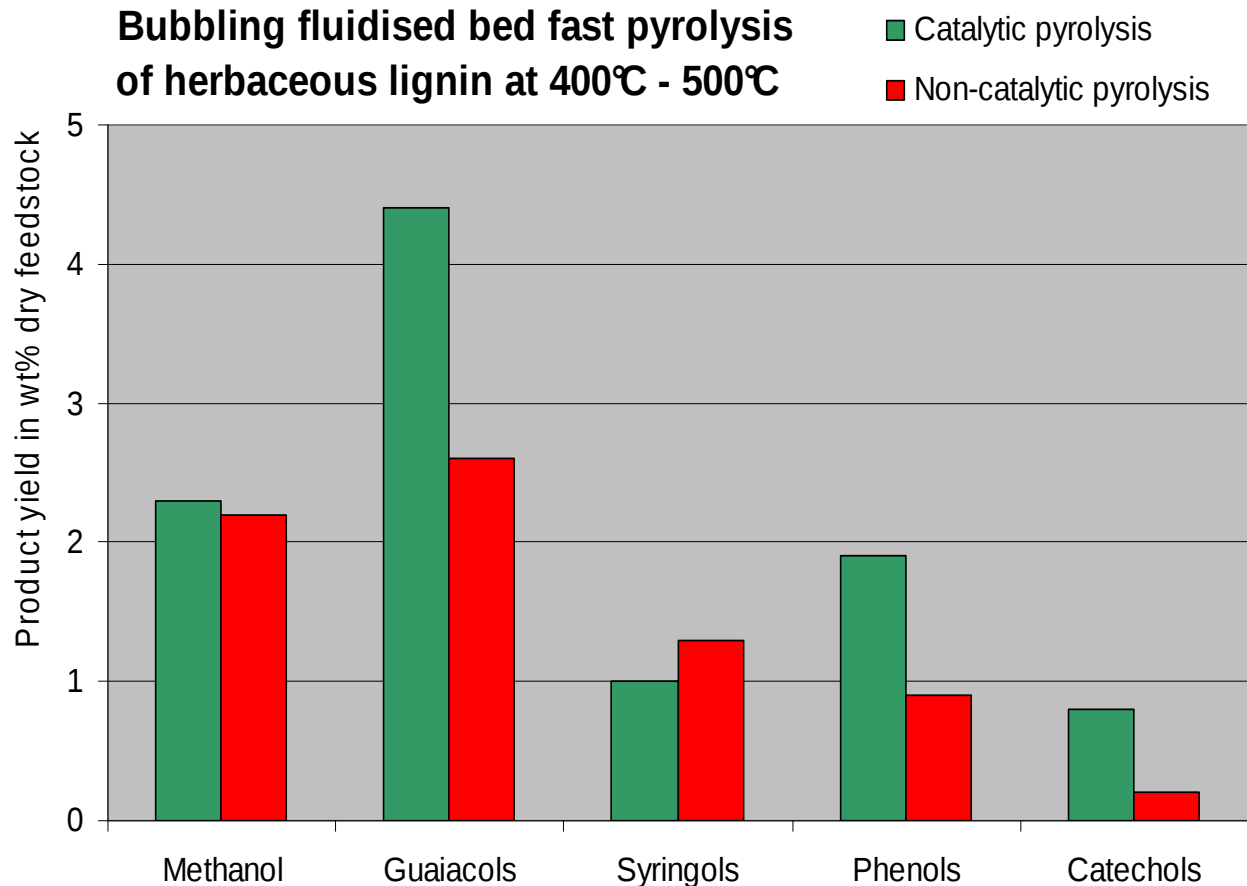
- Hollow screw design





Improving thermal processing by application of a catalyst

**Bubbling fluidised bed fast pyrolysis
of herbaceous lignin at 400°C - 500°C**



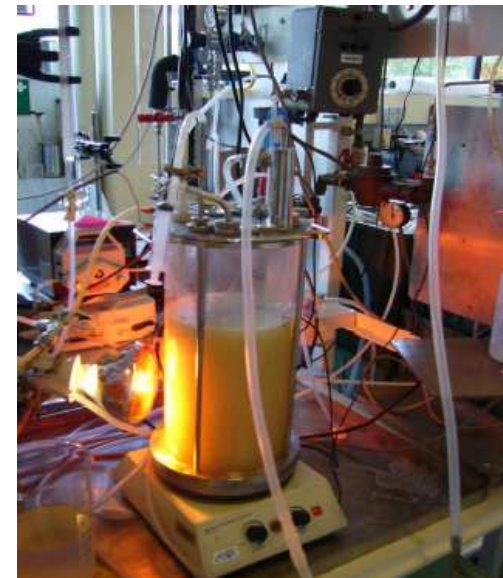
Up to 10 wt% monomeric phenols (20 wt% incl. oligomers) from
straw lignin produced

Advanced biochemical conversion (WP3)

Objectives

Development of advanced biochemical processes for conversion of sugars and lignin into value-added products

- Acetone-butanol-ethanol (ABE) fermentation: IFP-A&F
- Xylose conversion to xylonic acid VTT
- Production and analysis of functional lignin derivatives: VTT
- Separation of product mixtures by Multiphase Rotating disk Contactors: GIG

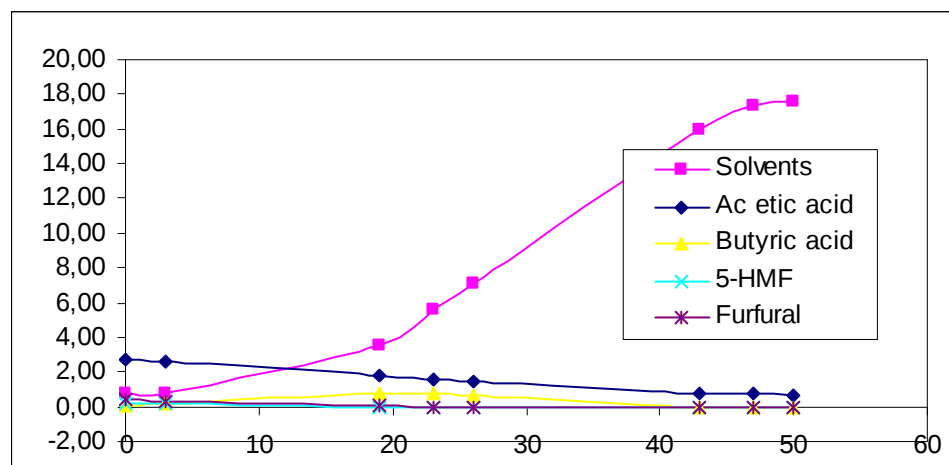
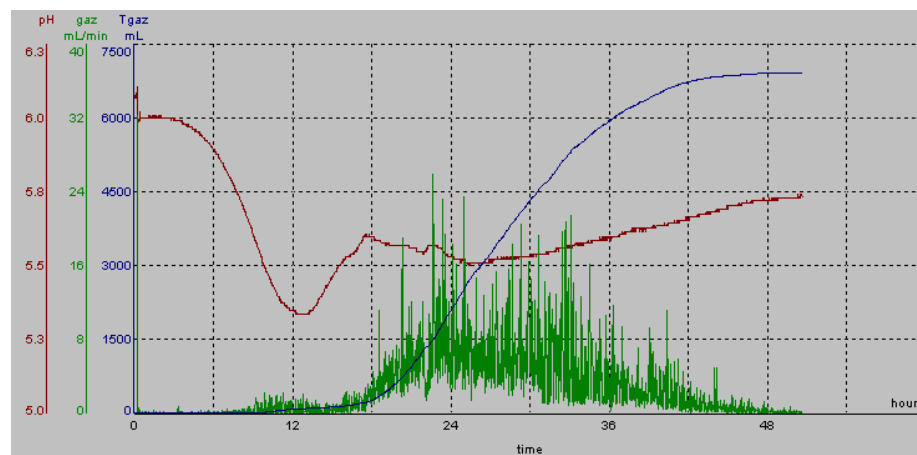


ABE fermentation at IFP



ABE – Production on wheat straw hemicellulose hydrolyzate

- 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
- Results :
 - Gas release : 8.9 L / L
 - Final solvents (ABE) : 17,6 g/L

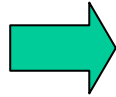




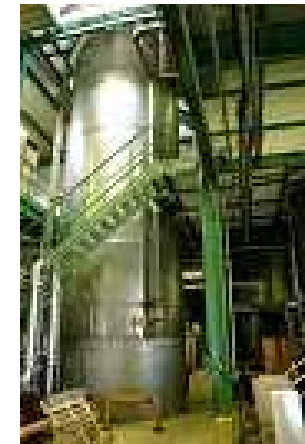
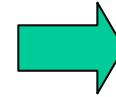
Planned scale-up ABE fermentation (ARD/IFP/A&F)



Lab-scale (150L)



Intermediate scale (10 m³)



Fermentor 80 m³



Membranes purification



Functional lignin derivatives: lignin 'activation'

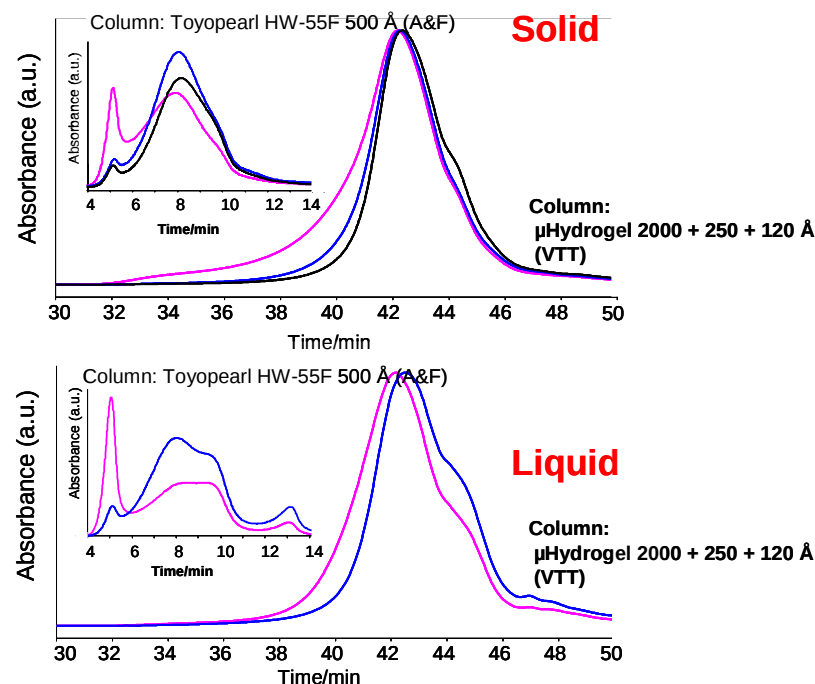
- Enzymatic lignin modification by *Trametes hirsuta* laccases
 - Aim: improvement of reactivity (cross linking behaviour)
- Characterization of modified lignin polymers by chemical and spectroscopic methods.

SEC of a model lignin

ThL treated lignin

Solubilized /
Control lignin

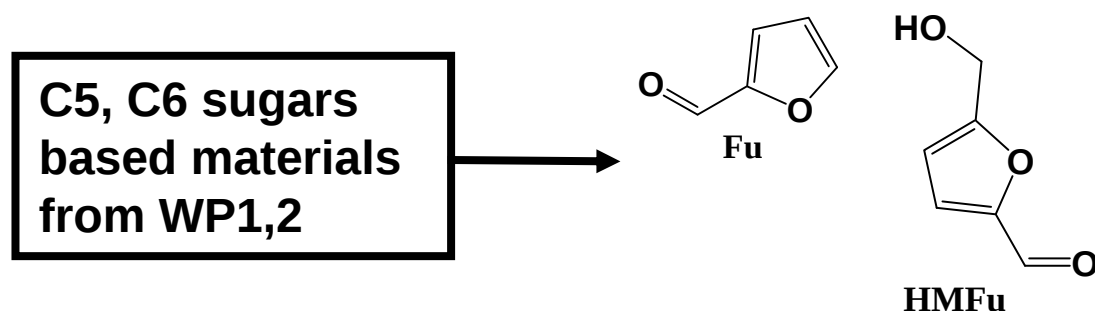
Raw lignin /
unsolubilised /
untreated lignin



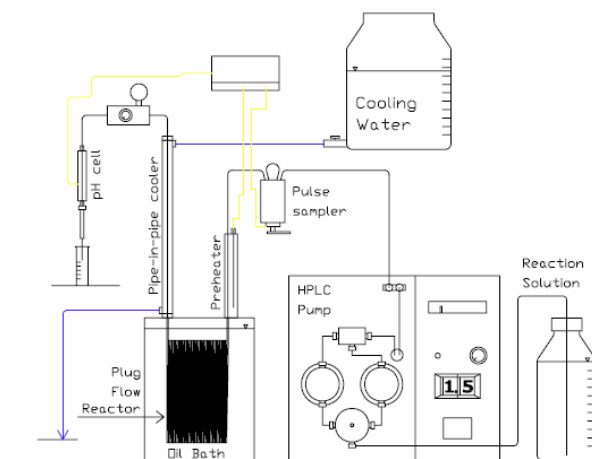
Production & characterisation platform chemicals (WP4)

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

- Products from Lignin, Cellulose and Hemicellulose fractions
- Lignin depolymerisation in supercritical CO₂: A&F
- Hydroxymethylfurfural production from glucose dehydration>> high conversion rates and selectivity Biorefinery.de
- Analysis kinetics furfural synthesis from xylose and modelling furfural production process: TUDelft



Marcotullio G., Heidweiller H.J., De Jong W. Reaction kinetic assessment for selective production of furfural from C-5 sugars contained in biomass. Paper presented at the 16th European biomass conference and Exhibition in Valencia, Spain, 2-6 June 2007

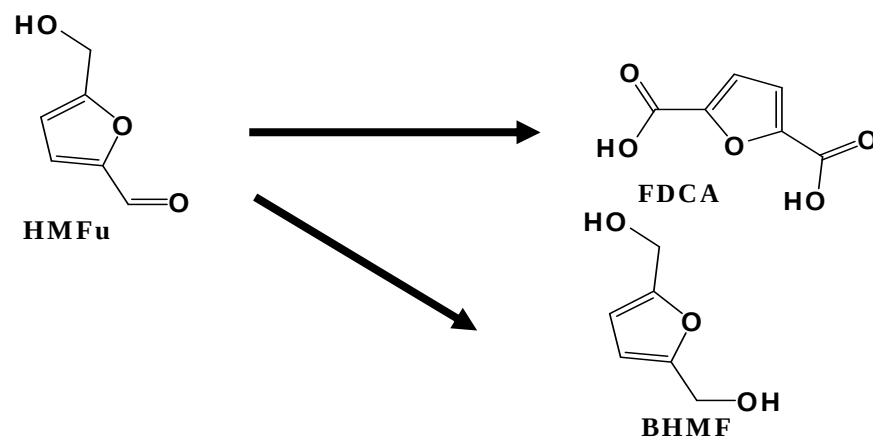


•Scheme of lab scale reactor TUDelft



Value added chemicals from platform chemicals

- Synthesis of 2,5-furandicarboxylic acid from HMF: Biorefinery.de / A&F
- Development of technologies for production of Diol-Components



- Polymerisation trials and application testing in progress

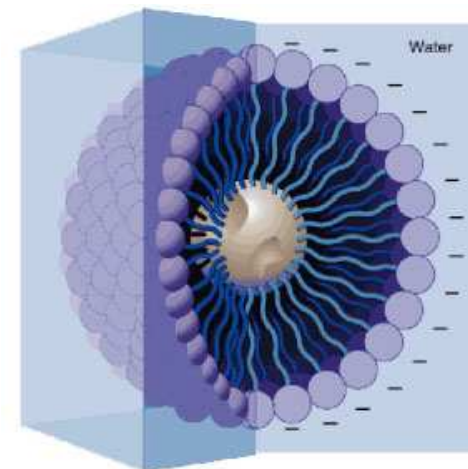
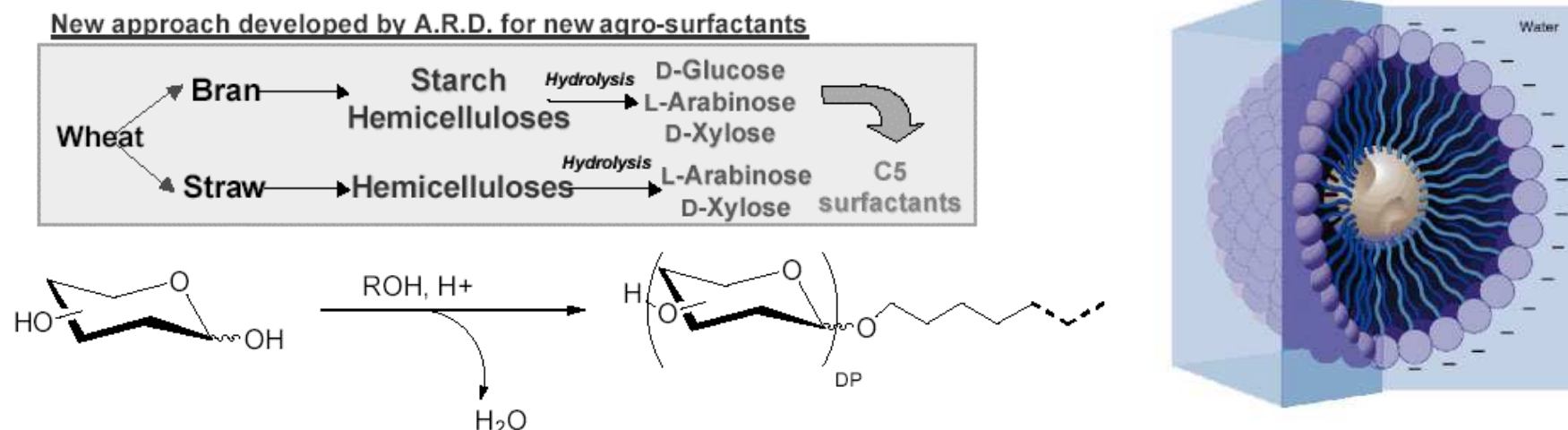


Application testing and market validation

- Successful tests performed by Chimar thermosetting phenol-formaldehyde resin with phenol substitution up to 50 wt% by (organosolv) lignin for particle board application (lab scale)
- Use of pentoses based surfactants for paper impregnation in the wood-based industry



Pentose valorisation as raw material for surfactants; ARD



- Reaction of: Pentoses + Fatty alcohols (ROH) C:4 - C:18
- Production of pentoside surfactants by a green technology in order to access the price level of fossil based competitors (1.5 €/kg)
- Development of technology to directly convert pentose containing hydrolyzates to surfactants in high yields: good progress obtained

Some market applications of pentose based surfactants



Planned scale up pentoses valorisation in surfactants ARD



- Production pentoside surfactants from C5 hydrolyzates at 100-1000 kg scale (ARD)



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
- maximized revenue and minimized environmental impact

Partners: ABNT, Aston, ECN

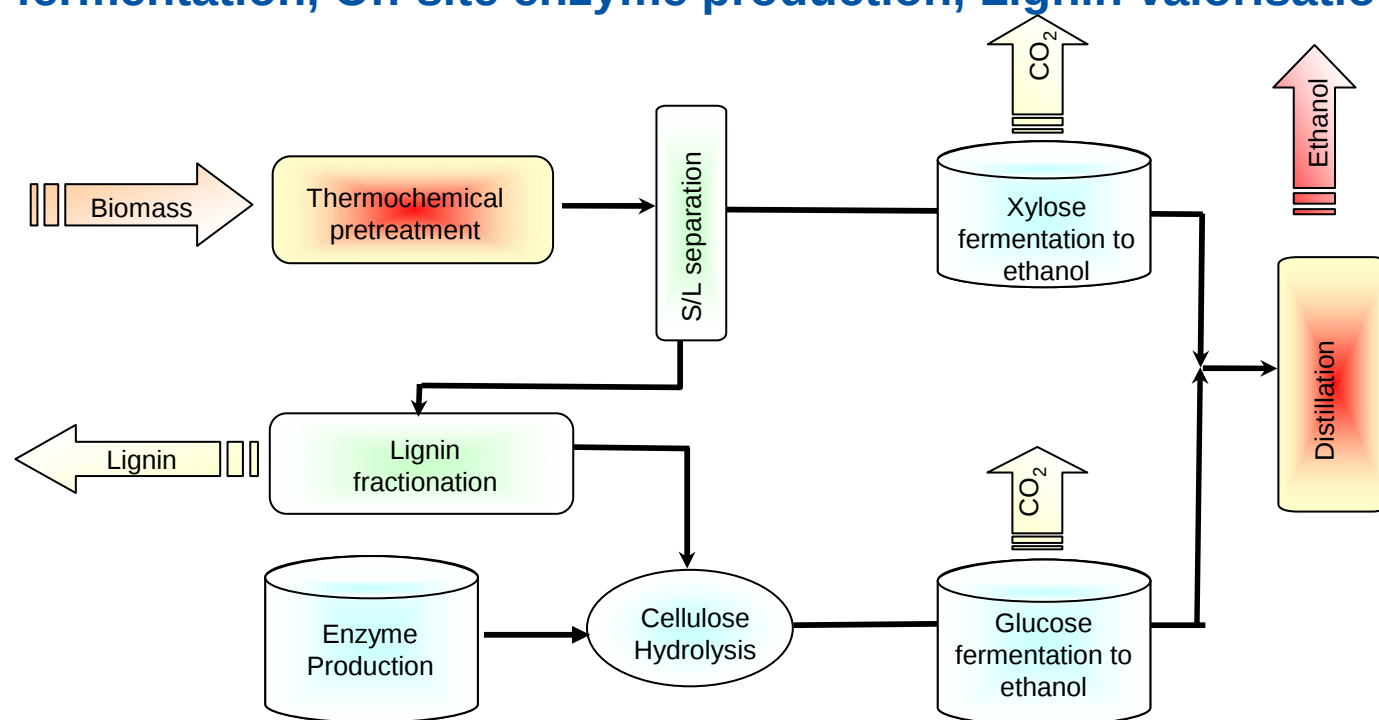


BCyL cellulose ethanol pilot plant AB, Salamanca, 5 Million L EtOH / year



Conceptual design biorefinery plant (WP5)

- Integral model for the BCyL lignocellulose to bio-ethanol process scaled-up to 400 ton/day of wheat straw incl. biomass fractionation, C5 fermentation, On-site enzyme production, Lignin valorisation



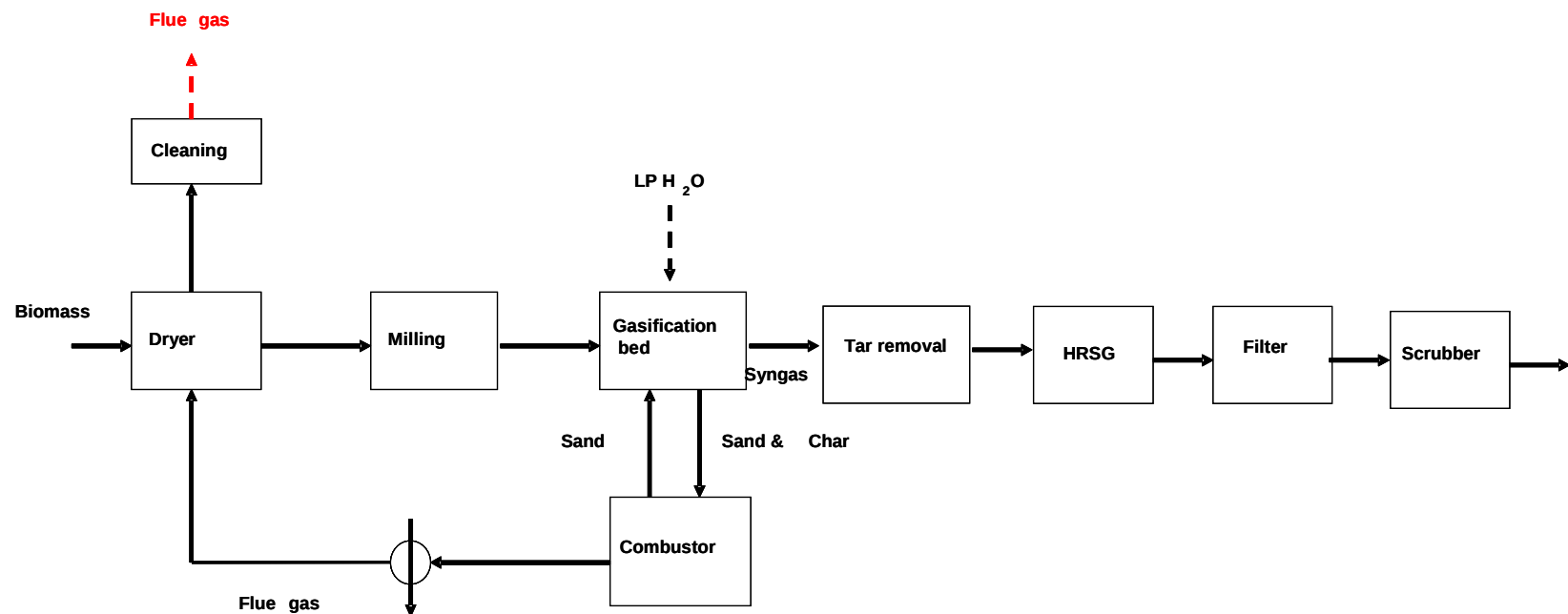
- Economic model to evaluate design concepts and scenarios
- First economic results when integrated it in the developed concept



Conceptual design biorefinery plant (WP5)

- Additional concept: BCyL biomass to bioethanol up-graded model + biomass gasification + synthesis of ethanol = **100% Ethanol Biorefinery**

- Gasification and catalysis model

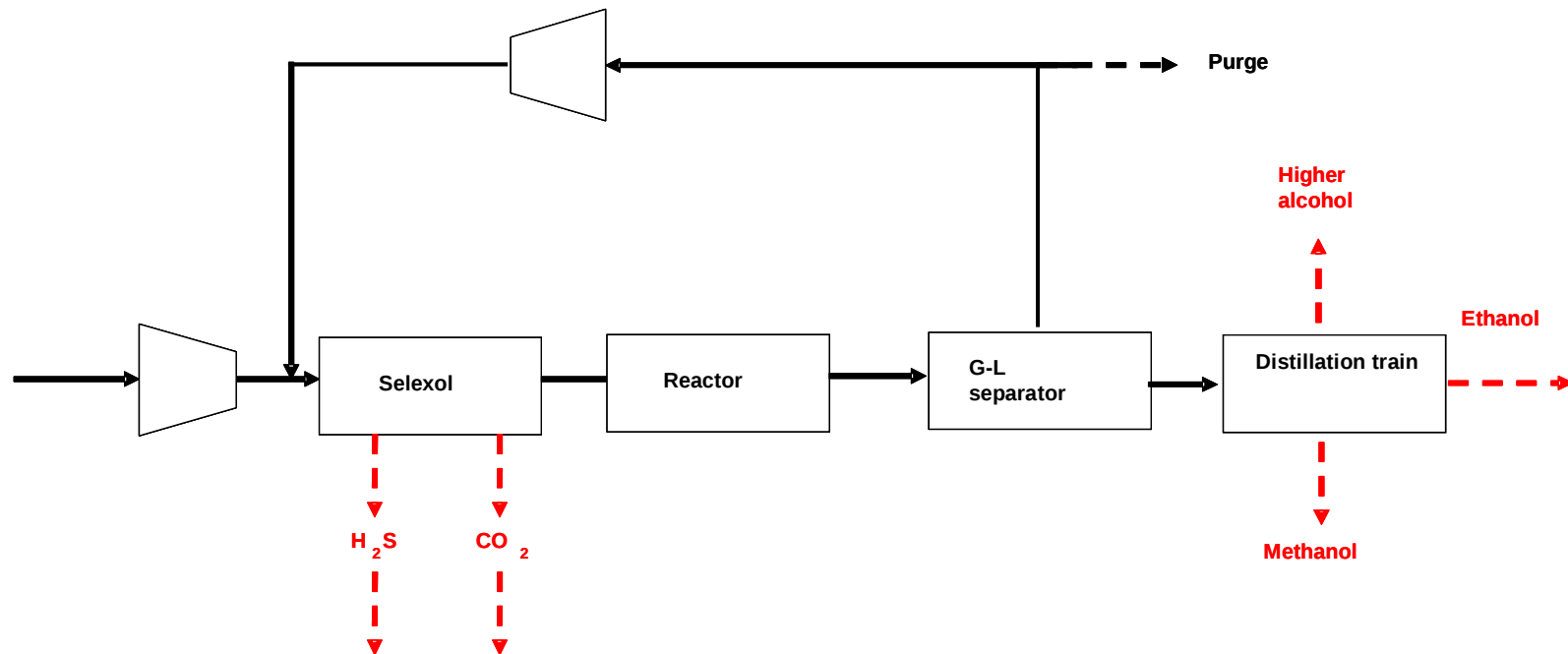


- Gasification and gas cleaning section



Conceptual design biorefinery plant (WP5)

- BCyL biomass to bioethanol up-graded model + biomass gasification + synthesis of ethanol = **100% Ethanol Biorefinery**
 - Gasification and catalysis model



- Synthesis section



Biomass-to-products chain design (WP6)

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

Objectives

Identification of the most promising biorefinery chains for the European Union, in terms of:

- Performance as yield and efficiency,
- Energy efficiency,
- Environmental performance as LCA,
- Cost as capital, operating and product costs
- Socio-economic aspects

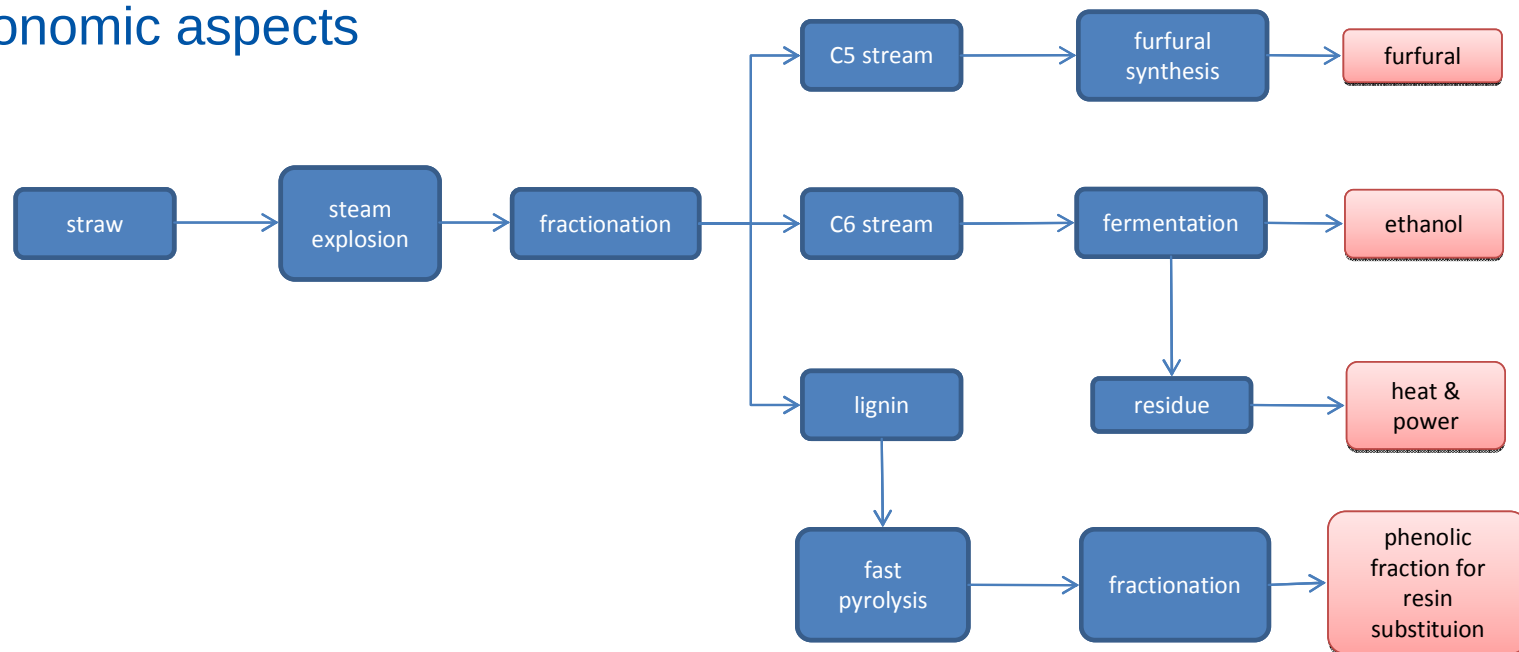
Focus on ethanol based biorefineries



Biomass-to-products chain design (WP6)

Development modelling tool with modular structure

- Process synthesis
- Process simulation
- Process comparison using MCDA incl. LCA, economics, socio-economic aspects



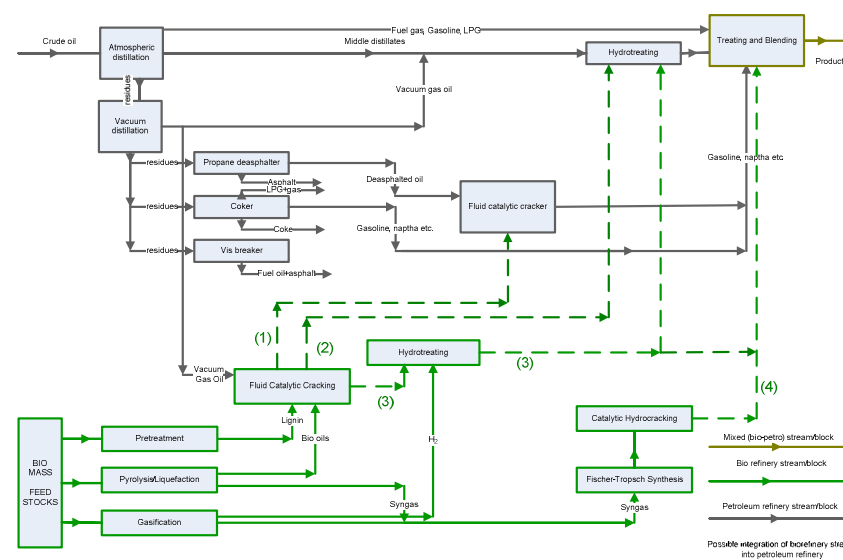
Biorefinery co-producing ethanol, furfural, phenolic resins and CHP



Integration in conventional petrochemical refinery

Substitution of fossil fuels by biomass or biomass-derived intermediates in an existing petrochemical refinery

Partners: Aston, Cepsa, IFP, ECN, JRC



Petrochemical complex of Cepsa is taken as base-case to:

1. identify potential substitution places for bio-based intermediates
2. select matching upstream technologies
3. to perform integral techno-economic and environmental chain assessments
4. to calculate overall costs and environmental data



Integration in conventional petrochemical refinery

Approach

- Desk study and modelling
- Conversion tests fast pyrolysis bio-oil by Cepsa underway





Preliminary conclusions & perspectives

- Development LC Biorefinery –combining bioprocesses, chemical processes + CHP – offers good perspectives to fully exploit the potential of lignocellulose.
- Biosynergy RTD shows good progress and provides a basis for large-scale valorization of C5 sugars and lignin. Scale-up is planned for several conversion routes.
- Pretreatment and enzymatic hydrolysis are critical for fractionation and therefore for the quality of the end products and techno-economic feasibility:
 - Pretreatment technologies need to be optimised toward a particular goal.
 - Enzymes are a major processing tool in the LC Biorefinery. Further development and cost reduction are needed.
 - Integrated development of the trajectory Feedstock-pretreatment-hydrolysis-fermentation is required.



Preliminary conclusions & perspectives

- Lignin valorization (at least in part) to chemicals is an important tool for economic profitability and for reduction of the carbon footprint.
- Direct application of (organosolv) lignin, catalytic thermochemical processing (pyrolysis) and enzymatic lignin conversion show promising results for lignin valorization
- Separation technology development is vital for both biochemical and thermochemical processing technologies
- Development of integrated processes / chain optimisation is a major success factor and is also one of the major challenges. This includes process integration but also the integration of environmental and socio-economic aspects.



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SenterNovem EOS-LT

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BIOSYNERGY Team during
Technical Excursion at ECN in April
2008. Photo: Jasper Lensselink.

