



Energy research Centre of the Netherlands

Advances in lignocellulose biorefinery technology focusing on valorisation of residues from cellulose ethanol production

**Final results of the IP BIOSYNERGY (FP6)
(2007-2010)**

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*Presented at the 19th European Biomass Conference and Exhibition (EU BC&E),
ICC Berlin, Germany (Conference 6-10 June 2011 - Exhibition 6-9 June 2011)*



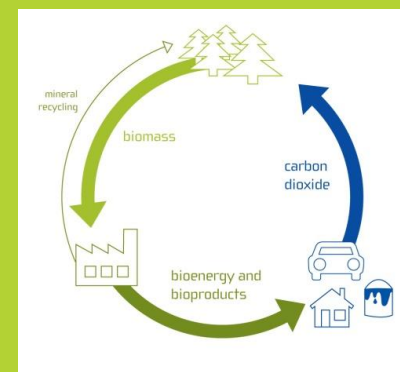
BIOSYnergy



Advances in lignocellulose biorefinery technology focusing on valorisation of residues from cellulose ethanol production

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19th European Biomass Conference and Exhibition, 6-10 June 2011, Berlin



Features 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.

- Overall aim: Development multiproduct cellulose-ethanol based biorefinery technology
- Focus on valorisation of residues from cellulose ethanol production
- Bioprocessing and thermochemical pathways combined
- Process development from lab-scale to pilot-scale

EU FP6 Program: Contract No. 038994 – SES 6. EC Officer: Silvia Ferratini, Philippe Schild. Duration: 01-01-2007 – 31-12-2010 (48 months). Budget: 13.4 M€, EC grant 7M€



BIOenergy



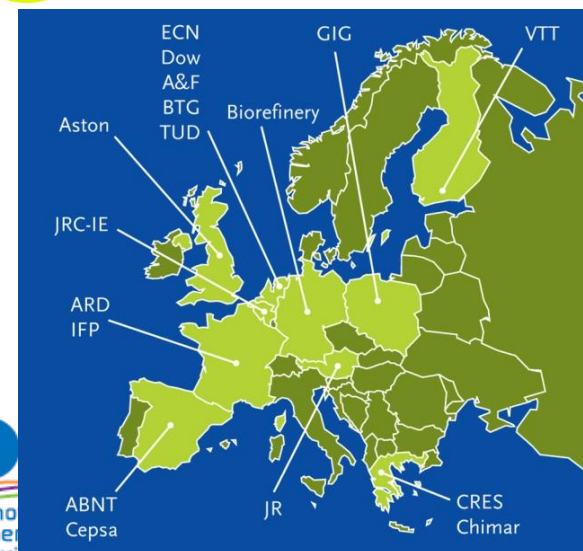
ABENGOA BIOENERGIA
NUEVAS TECNOLOGIAS



Chimar Hellas S.A.



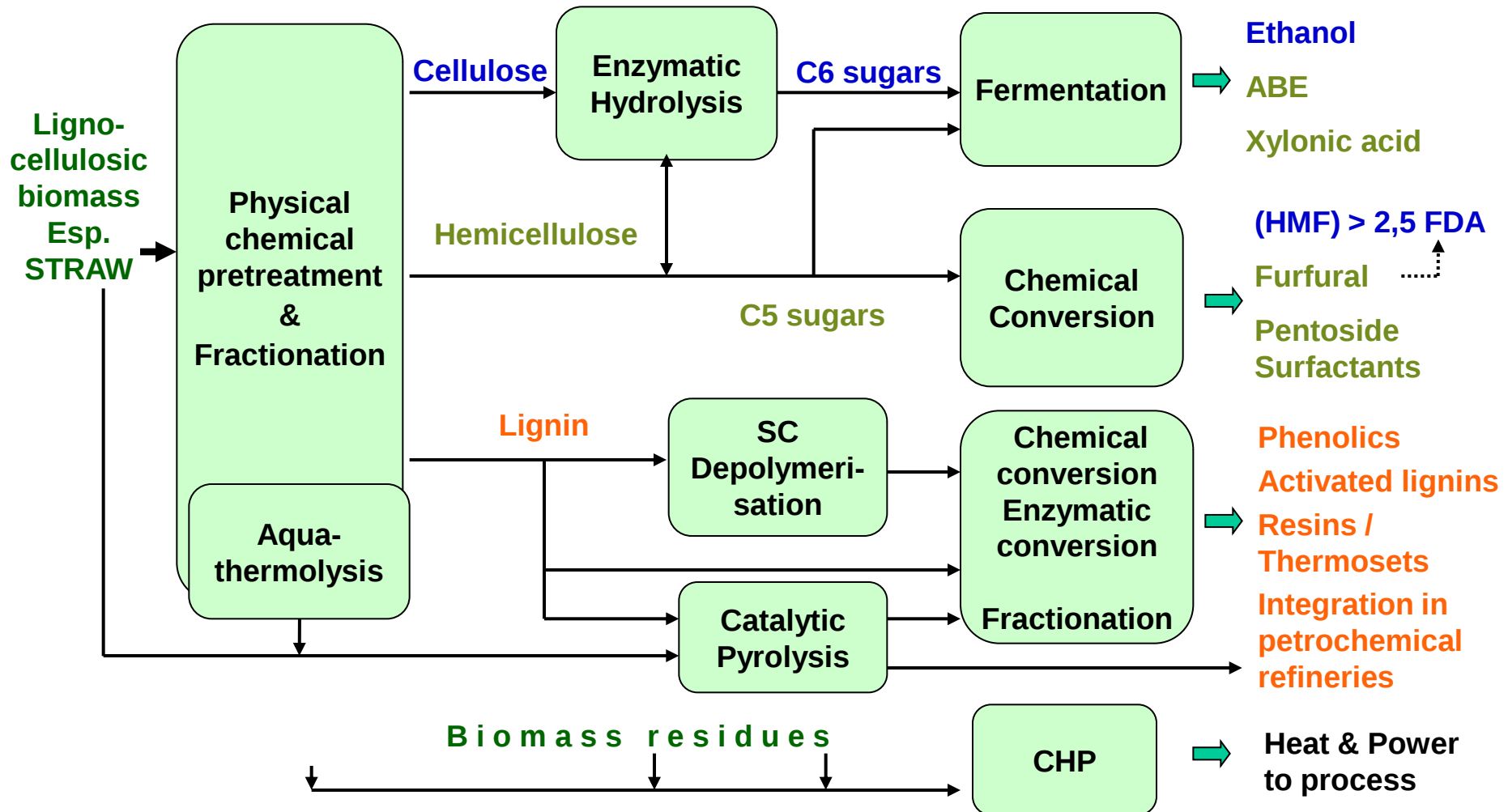
7 Industries, 8 R&D Institutes and 2 Universities
from 10 EU countries





Product lines in the IP BIOSYNERGY

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

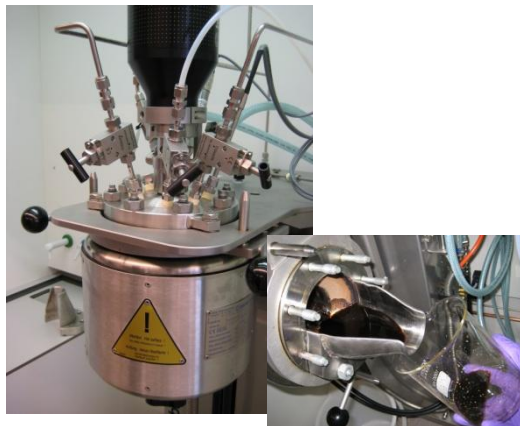


Physical/chemical pretreatment/fractionation

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

Processes studied

- Mechanical/Alkaline Fractionation (MAF; WUR-FBR)
- 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 FBR

Acid organosolv Pilot plant ARD



Conclusions pretreatment / fractionation

- All studied routes lead to significant fractionation of lignocellulose to C5, C6 sugars and lignin.
- No single optimum technology due to trade-off desired effects
 - In general: high enzymatic digestibility of the cellulose fraction reached
 - Differences in hemicellulose hydrolysis, lignin yield and purity

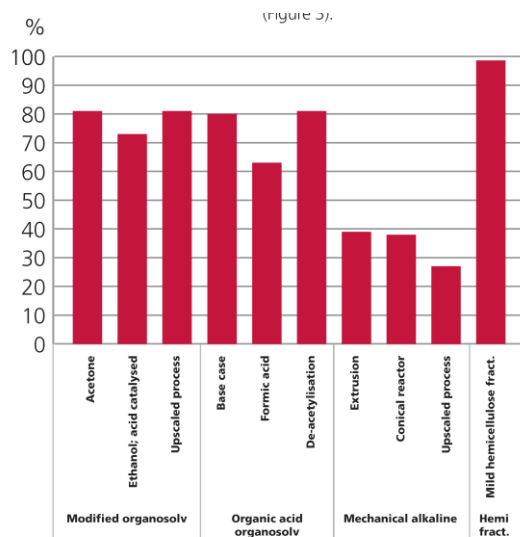


Figure 3: Hemicellulose hydrolysis (% of total hemicellulose)

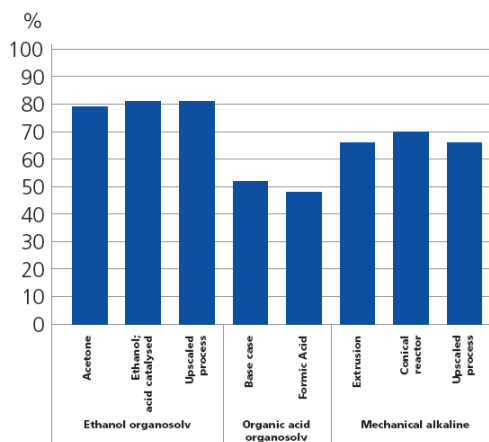


Figure 2: Delignification of wheat straw (% of lignin removed)

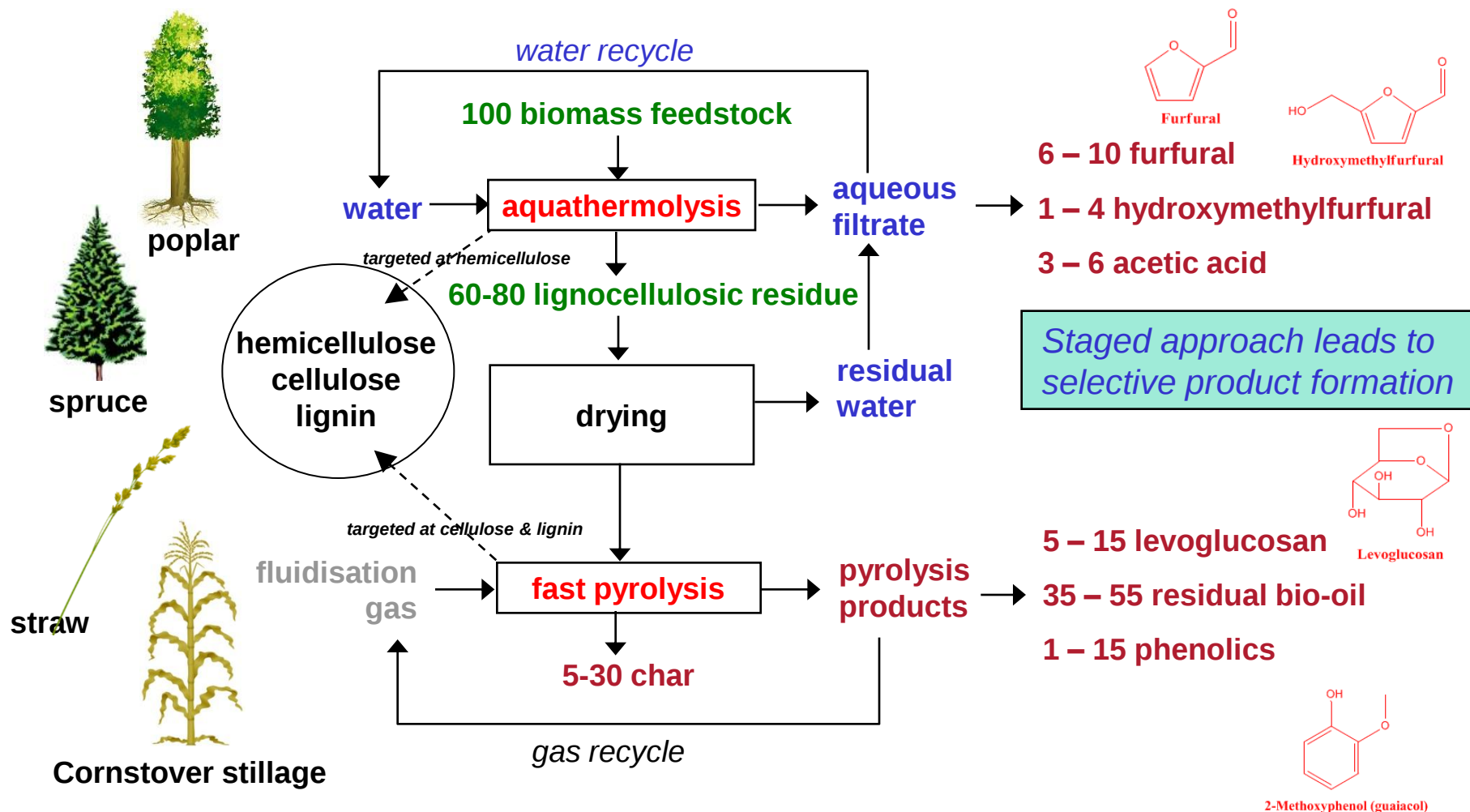
- Processes should be optimized for specific feedstock & products
- Review and results benchmark to be published



Hybrid, staged process for biomass conversion

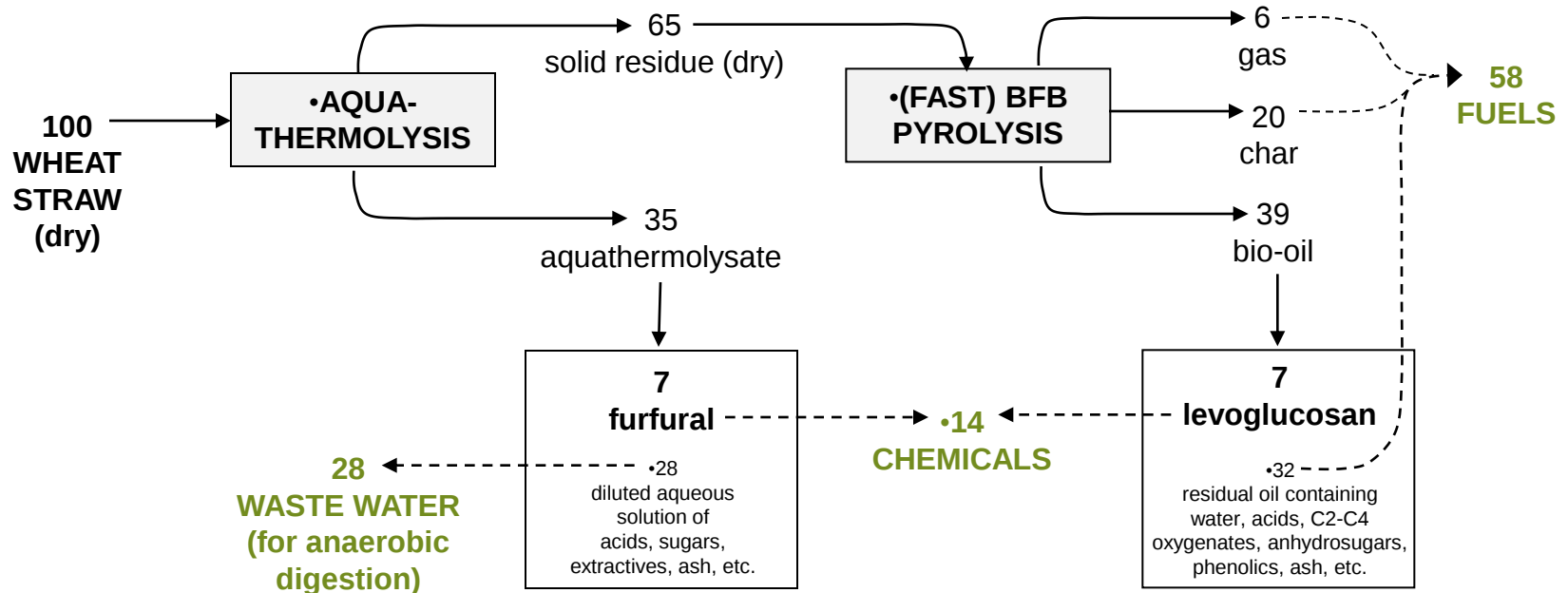
aquathermolysis: pressurised hot water (pre)treatment (200 °C, 30 min.)

followed by BFB fast pyrolysis (350-400 °C, vapour residence time 1-2 sec.)





Hybrid staged conversion: chemicals and fuels



Results (ECN, BTG)

- **Proof of concept** staged conversion delivered
- **Feasibility anaerobic digestion** aquathermolysate shown on lab scale (Univ. Southampton)



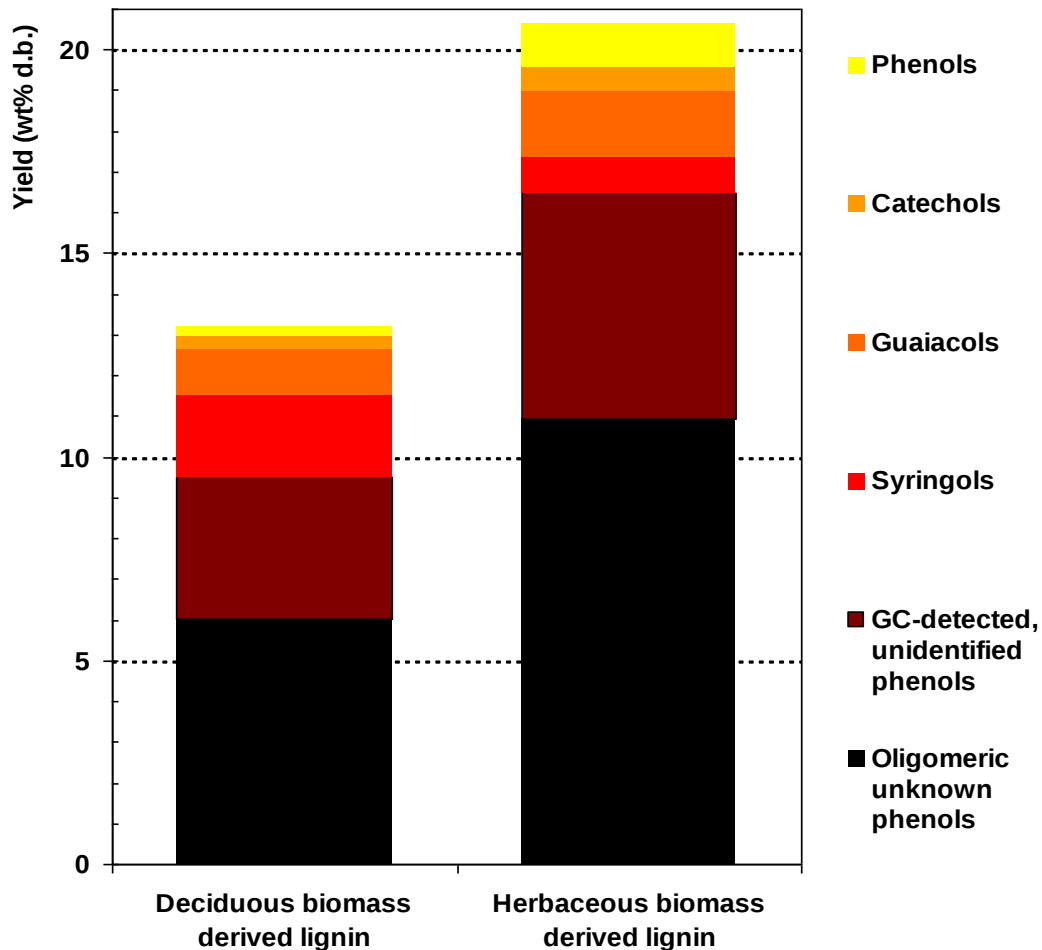
Continuous catalytic pyrolysis of organosolv lignin

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

Results (ECN, Aston)

Continuous cat. pyrolysis at 400°C
 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



Upgrading of fast pyrolysis oils (BTG)

- **Improvement of bio-oil quality** (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



Fermentation routes: ABE (Acetone-Butanol-Ethanol)

- **Aim: ABE Production on wheat straw hemicellulose hydrolyzates**
 - Hydrolysate 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 (IFP, WUR-FBR)

- **Final conc. solvents (ABE):17.6 g/L**
- **Continuous fermentation is still a challenge**
- **ABE separation from fermentation broth by rotating disc separator demonstrated**

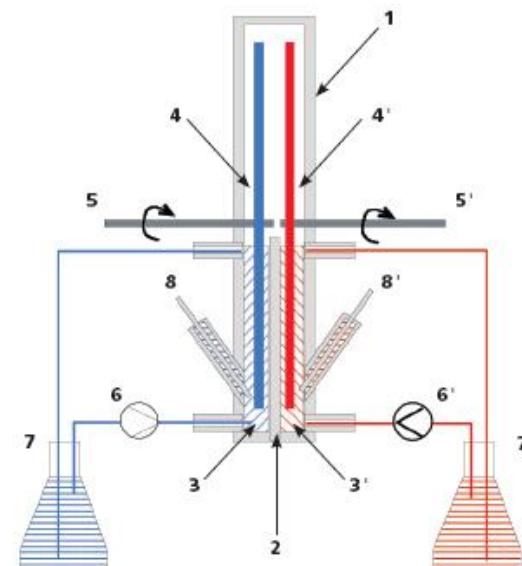
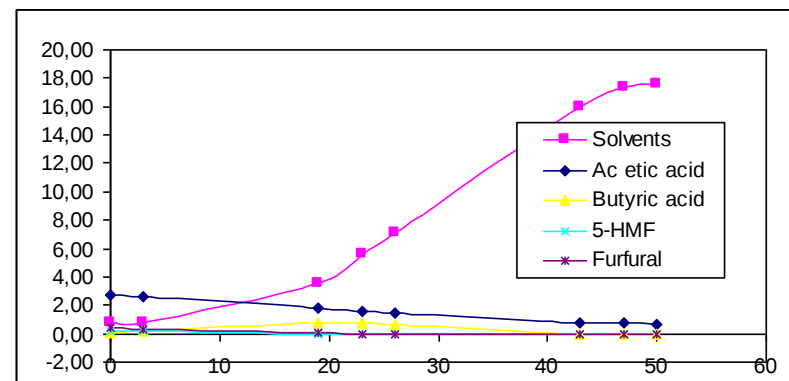


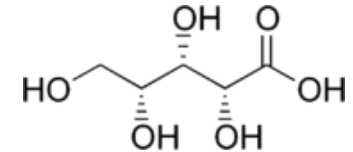
Figure 3: Twin rotating disc contactors containing an emission disc (blue) and a capture disc (red) separated by a gas phase



Fermentation routes: Xylonic acid

Xylonic acid

Applications: Dispersant, esters, lactones (cyclic esters)



Aim

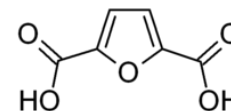
- Xylonic acid production from fermentation of xylose (C5-sugar)
- Sources
 - Acid-hydrolyzed DDGS (dried distillers grains with solubles)
 - Wheat straw C5-sugar hydrolysates

Results

- **Successful fermentation** results in batch and continuous cultures (VTT)

Chemical conversion: glucose $\rightarrow$ HMF $\rightarrow$ **2,5 FDCA**

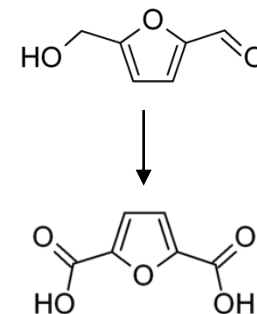
2,5 FDCA (2,5 Furan Dicarboxylic Acid)



Applications: Building block for bulk polyesters (replace TFA in PET) and polyamides

Aim

- HMF production from glucose (C6) dehydration
- Oxidation of HMF to **2,5-FDCA**



Results

- **Substantial yield improvement of HMF** by using ionic liquids (Bioref)
- **High yield (> 90%) conversion of HMF to 2,5-FDCA** (Bioref/ WUR)
- **Application testing 2,5 FDCA-derived polymers promising results** (DOW)



Chemical conversion routes: furfural

Furfural

Applications

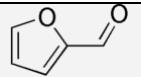
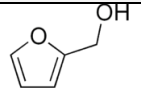
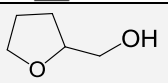
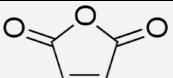
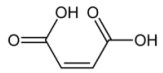
- Chemical building blocks
- Resins, adhesives
- Fuels

Aim

- Experimental analysis kinetics furfural synthesis from xylose
- Modelling to improve furfural production process

Results (TU Delft)

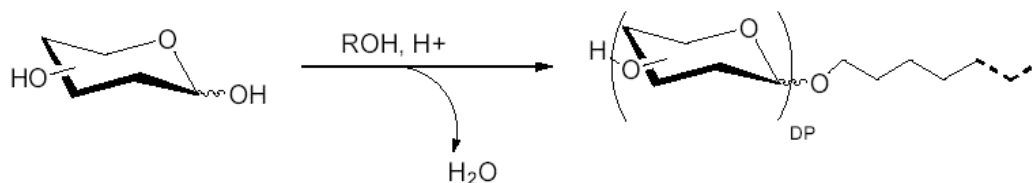
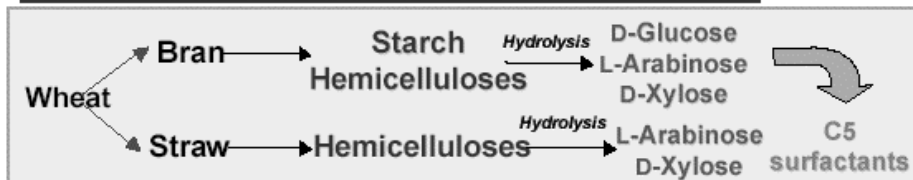
- **Yield improvement to >90%**
- New patented process design with **85-95% reduction of energy use**

Chemical building block		Route from furfural	World production (t/a)	Biobased world production (t/a)
Furfural		-	See biobased production	200.000-300.000
Furfuryl alcohol		Hydrogenation of furfural	120.000-180.000	-
Tetrahydrofurfuryl alcohol		Hydrogenation of furfuryl alcohol		-
Tetrahydrofuran (THF)		Hydrogenation of furfural ¹	200.000 ²	-
Maleic anhydride		Ring cleavage of furfural		-
Maleic acid		Hydrolysis of maleic anhydride		-

Chemical conversion routes: surfactants (ARD)(1)

C5-sugar based surfactants

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



Route: C5-sugars + fatty alcohols (ROH) C:4 - C:18

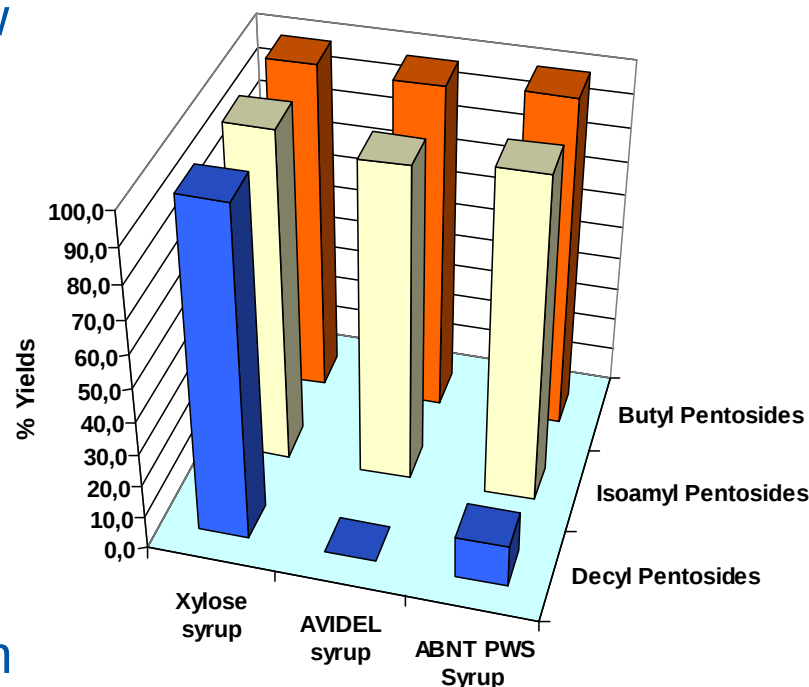
Aim

- Production of "green" surfactants at competitive price level (~1500 €/ton)

Chemical conversion routes: surfactants (ARD) (2)

Results

- Short tail surfactants prepared from straw derived **unpurified pentose syrups**
- **Successful scale-up** (63 L reactor) with high isolated yields (>90%):
 - cost target confirmed
 - successful standard application tests
- **Direct surfactants production from straw**
- **New application for amyl pentosides** in the preparation of **wetting agents for paper impregnation** in the wood-based industry: comparable performance vs. petrochemical counterparts



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

Lignin conversion

Supercritical depolymerisation (WUR-FBR)

Aim: Lignin depolymerisation in supercritical CO₂

Result: **Improved yields** (>10%)

Functional lignin derivatives: lignin 'activation' (VTT)

Aim: Improvement of reactivity (cross linking behaviour) to enhance product options

Result: **Successful enzymatic lignin modification** by *Trametes hirsuta* laccases

Phenol substitution (Chimar)

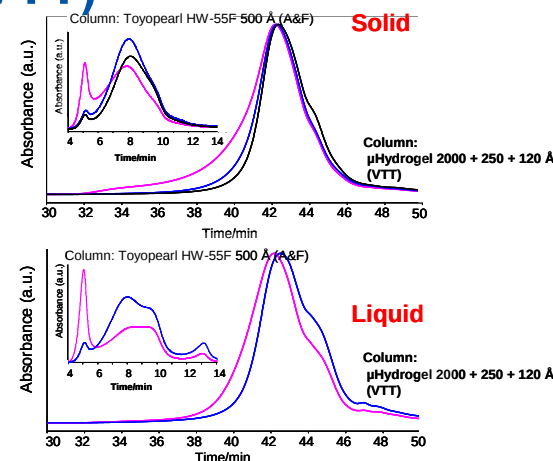
Aim: Phenol substitution in PF resins for particle board applications

Result: **25% phenol substitution** by (organosolv) lignin

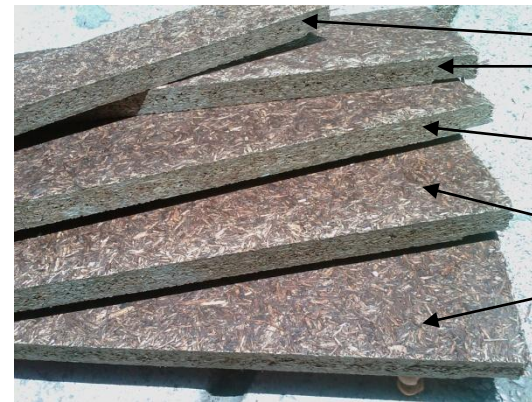
ThL treated lignin

Control lignin

Raw lignin



Pilot scale production of wood-based panels



PF std

PFL-15% Ph sub.

PFL-25% Ph sub.

PFL-35% Ph sub.

PFL-45% Ph sub

Particleboards produced with PF resins where phenol was replaced by ARD lignin at various levels



Step of plywood panels production.



Plywood panels



Testing of plywood at CHIMAR premises

Integration of results in Conceptual design biorefinery plant

Basic design for integral lignocellulose biorefinery based on cellulose ethanol demonstration plant AB BCyL plant, Salamanca.

- Targeted outputs:
 - bio-ethanol,
 - chemicals, materials, CHP
- **5 EtOH based biorefinery types designed and evaluated**



*BCyL cellulose ethanol demo plant AB, Salamanca, capacity 5 Million L EtOH/yr; 70 ton straw per day. **Operational since Oct. 2009.***



Integration of results in Conceptual design biorefinery plant

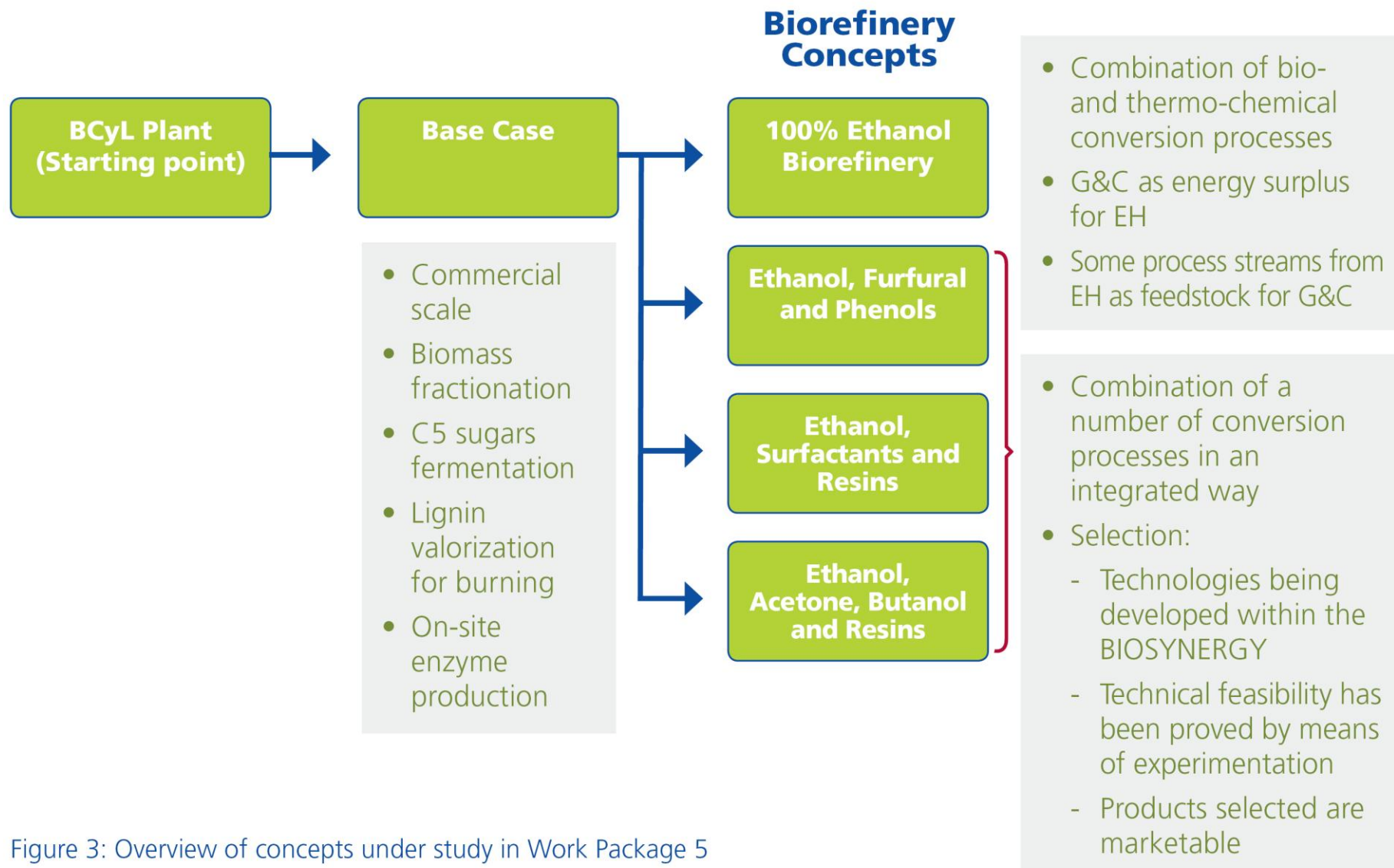


Figure 3: Overview of concepts under study in Work Package 5



Integration of results in Conceptual design biorefinery plant

Main conclusions

- **Integrated biorefinery scenarios** (ethanol + chemicals) show improved economic performance vs. base case cellulose-ethanol plant (= ethanol + lignin combustion for steam generation only)
- **Considerable uncertainty** due to
 - o early stage technology development
 - o future price of biobased products unknown

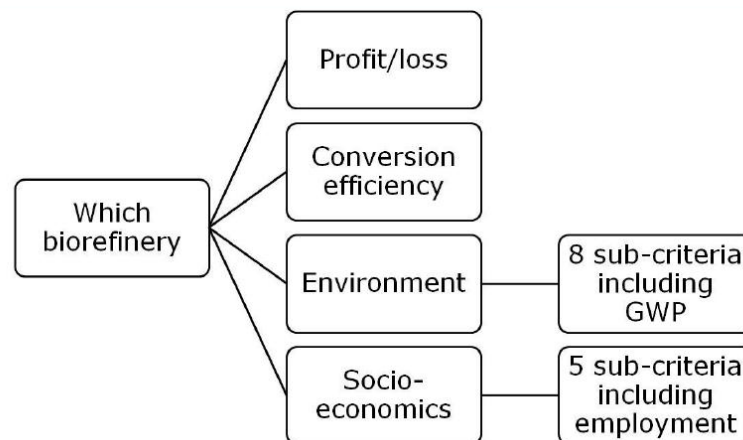
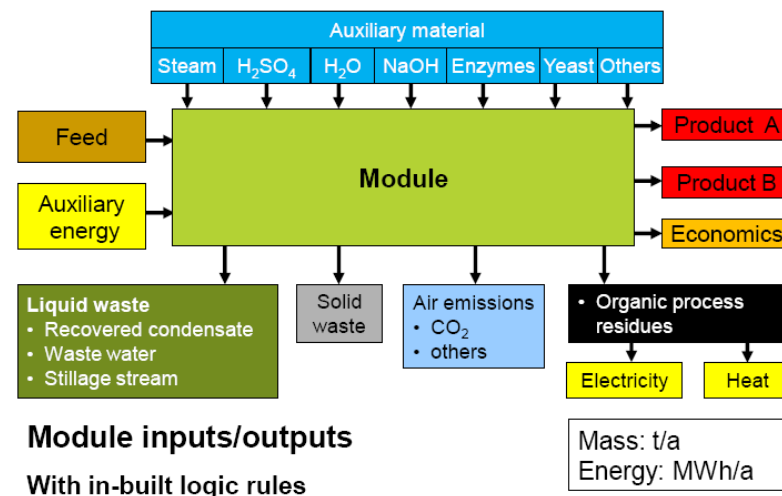
Biomass-to-products chain design (Aston)

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

Results:

- **Robust modelling tool with modular structure** developed. Allows process synthesis and simulation of 1000's biorefinery combinations.
- **Evaluation 27 biorefinery concepts (500 kt/a)** by performance, economics, socio-economic impacts and LCA. **Focus on cellulose-ethanol based biorefineries.**
- **Process comparison using MCDA**

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





Conclusions chain comparison

- **Most promising biorefineries:**
 - Produce specialty chemicals in addition to ethanol
 - Simple processing routes
 - Utilise all biomass fractions producing only value added products

Table 1: Most promising biorefinery concepts identified

Feed	Pre-treatment	C5	C6	Lignin
Straw	Fluidised bed fast pyrolysis	Bio-oil		
Straw	Steam explosion	Xylonic acid	Ethanol	Dry lignin product
Straw	Conc. HCL pre-treatment	Furfural	Ethanol	Dry lignin product

- **Least promising biorefineries:**
 - Poor conversion efficiency combined with -€ loss
 - High heat and power demand >>Heat/power provision becomes expensive and biomass requirement too high.



Overall conclusions & perspectives (1)

- **Biosynergy results provide a solid basis for valorization of C5 sugars and lignin**
 - o Substantial advances reached on lab/bench scale. Several processes demonstrated on pilot scale.
 - o Valuable information obtained on most promising technologies and co-products for cellulose-ethanol based biorefineries incl. integration of processes
- **Lignin valorization to chemicals is an important tool for economic profitability of the biorefinery**
 - o direct application of (organosolv) lignin in resins: 25 wt% phenol substitution reached
 - o catalytic pyrolysis of lignin to phenolics
 - o enzymatic lignin conversion (laccases) to improve reactivity



Overall conclusions & perspectives (2)

- **Biorefinery of lignocellulose to ethanol + chemicals + CHP shows better economic perspectives than production of only cellulose ethanol + CHP.**
- **Exploitation of project results**
 - o 4 new patents + 2 under investigation (+ existing IP Portfolios)
 - o 26 areas of exploitable knowledge for follow-up RD&D by consortium partners and other interested parties in pilot and demonstration facilities and commercialisation



Contributors IP BIOSYNERGY



Thank you for your attention!

More information:

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www.biosynergy.eu

- Publications (30+ peer reviewed publications)
- Report + presentations Final Workshop Nov.17th 2010, Reims
- **Brochure with major project achievements and highlights**
- Public Plan for using and dissemination of knowledge (forthcoming)

