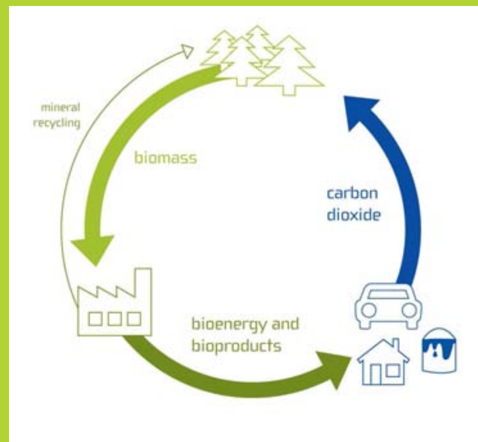
Development of integrated lignocellulose biorefinery for co-production of chemicals, transportation fuels, electricity and heat

Overview and preliminary results of the EU FP6 Integrated Project BIOSYNERGY



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

Biorefinica 2009, 27 & 28 January 2009, Osnabrück, Germany

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Objectives

1. To develop the best thermochemical/(bio-)chemical fractionation and conversion technologies for major side-streams of an ethanol fermentation plant, but also applicable for other wet and dry feedstocks.
2. To define the potential of identified platform chemicals for chemical and petrochemical industries.
3. To come from lab-scale to pilot-scale processes using techno-economic assessments and clear exploitation guidelines.
4. Making the production of biofuels more cost competitive by utilisation of all biomass components at maximum added value

- (Bio)chemical and thermochemical pathways combined
- Focus on valorisation of residues from bio-ethanol production

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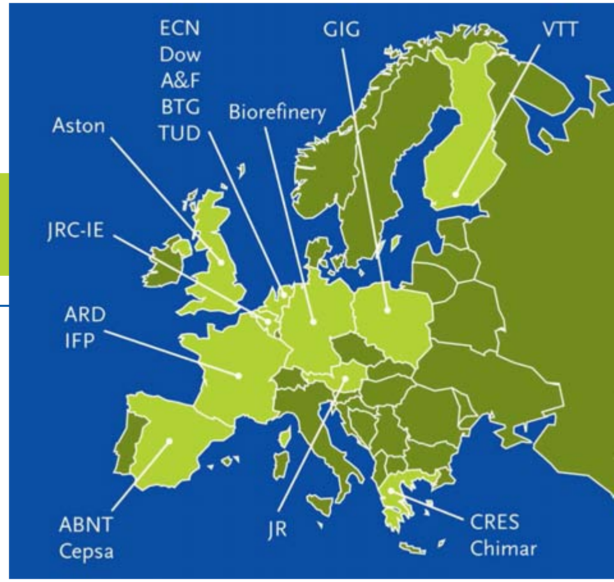
Consortium



17 partners from industry, R&D institutes and Universities from10 EU countries

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	Glowny Instytut Gornictwa (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

Work Packages

Man	WP 0 – Management activities
RTD	WP 1 – Advanced physical/chemical fractionation
	WP 2 – Innovative thermo-chemical conversion
	WP 3 – Advanced biochemical conversion
	WP 4 – Innovative chemical conversion and synthesis
	WP 5 – Conceptual design Biorefinery pilot-plant BCyL of ABNT in Salamanca
	WP 6 – Integral biomass-to- products chain design, analysis and optimisation
Demo	WP 7 – Demonstration at pilot-scale
T/Diss	WP 8 – Training and knowledge dissemination

WP1: Advanced physical/chemical fractionation

Objective: Coordinated development of physical/chemical fractionation technologies for raw biomass

Processes studied:

- Mechanical/Alkaline fractionation (A&F)
- Modified Organosolv (ECN)
- Fractionation with organic acids (Avidell process; ARD)
- Acid hydrolysis (Biorefinery.de)
- Hemicellulose acid hydrolysis (TuD)

- Reference case: steam explosion (ABNT)

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

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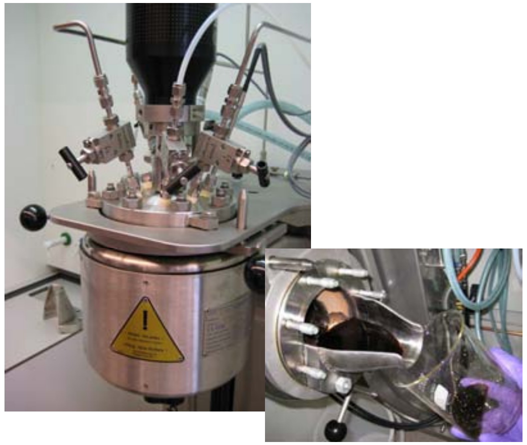
WP1: Advanced physical/chemical fractionation

Model feedstocks:
straw, woods, DDGS



Organosolv R&D at ECN

Mech./alk pretreatment A&F

Pilot plant ARD

Main applications for fractions produced

- C6 sugars to ethanol
- C5 sugars to Acetone Buthanol Ethanol (ABE) fermentation
- C5 and C6 sugars to furans, surfactants, diols, di-acids,…….
- Lignin for higher value applications
  - Component in resins
  - Functional lignin derivatives: Nanoparticles, enzymatically modified lignin polymers
  - Depolymerisation of lignin for chemicals production

Lignin products from Modified Organosolv Fractionation (ECN)

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Fractionation: Results to date

- Experimental R&D 5 fractionation routes
- Enzymatic hydrolysis tested and compared
- Modelling of fractionation routes + benchmark
  - investigate costs of fractionation routes on similar basis
  - Compare results to the reference case

Wheat straw	
Amount	1000
%DM	93,0%
DM Amount	930,0
%Cellulose/DM	37,3%
Cell. Amount	346,9
%Xylan/DM	24,7%
Xylan Amount	229,7
%Lignin/DM	16,4%
Lignin Amount	152,5

Water	
Amount	12333

Blend	
Amount	13333
%DM	7,0%
DM Amount	930,0

Sum of side streams	
Amount	2329
%DM	0,09%
DM Amount	2,1

Cellulose stream		
Amount	3561	
%DM	14,8%	
DM Amount	527,0	
%Cellulose/DM	65,0%	
Cell. Amount	342,6	**99%**
%Xylan/DM	15,0%	
Xylan Amount	79,1	**34%**
%Lignin/DM	9,0%	
Lignin Amount	47,4	**31%**

Xylan stream		
Amount	7074	
%DM	4,0%	
DM Amount	283,0	
%Cellulose/DM	0,0%	
Cell. Amount	0,0	**0%**
%Xylan/DM	50,0%	
Xylan Amount	141,5	**62%**
%Lignin/DM	4,0%	
Lignin Amount	11,3	**7%**

Lignin stream		
Amount	369	
%DM	32,0%	
DM Amount	117,9	
%Cellulose/DM	0,0%	
Cell. Amount	0,0	**0%**
%Xylan/DM	0,0%	
Xylan Amount	0,0	**0%**
%Lignin/DM	80,0%	
Lignin Amount	94,3	**62%**

Example of modeling Fractionation (ARD)

Preliminary Conclusions

- All studied routes lead to significant fractionation of C5, C6 sugars and lignin from lignocellulose
- Processes need to be optimised toward a particular goal, for example:
  - Hemicellulose hydrolysis for further processing of C5
  - Recovery of a high quality lignin stream
  - High enzymatic degradability of the cellulose fraction
- Economic evaluation of the studied fractionation routes is on-going

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WP2: Innovative thermo-chemical conversion

<u>Topics</u>

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

BFB reactor ECN

Partners: <u>ECN</u>, Aston, BTG

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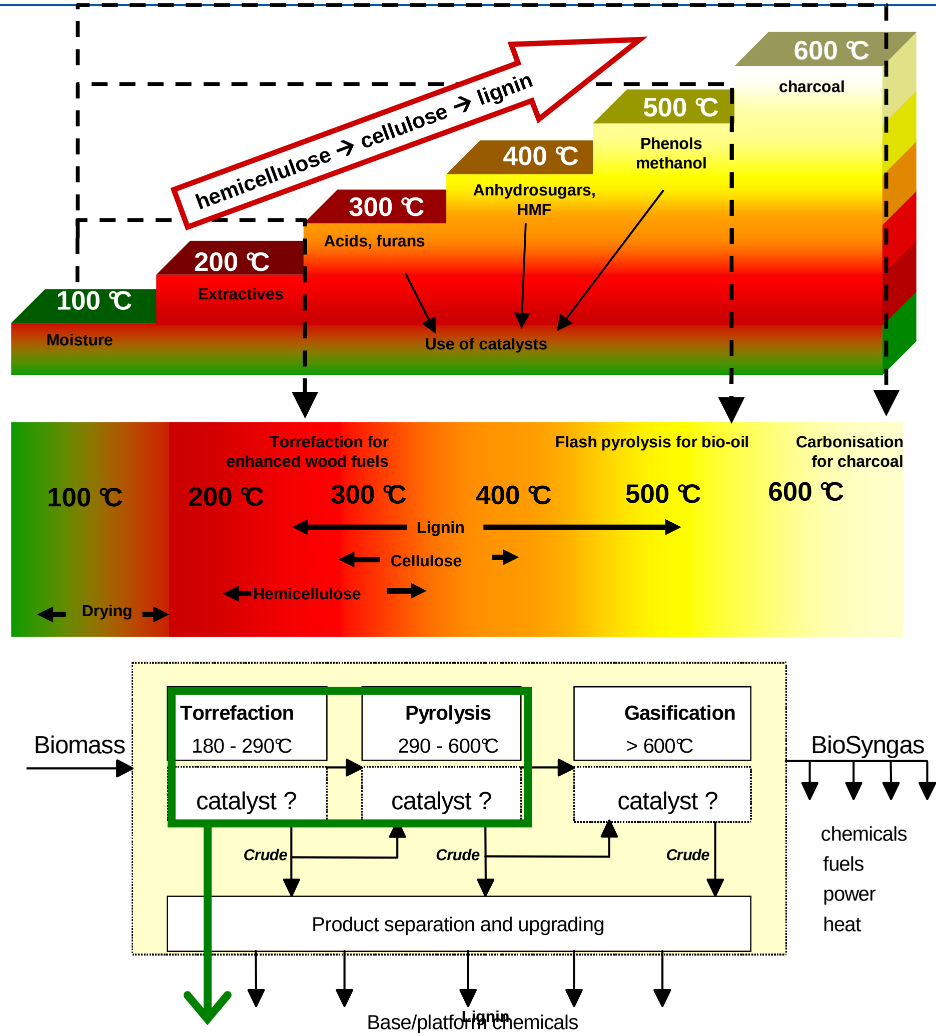
Staged thermochemical processing

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

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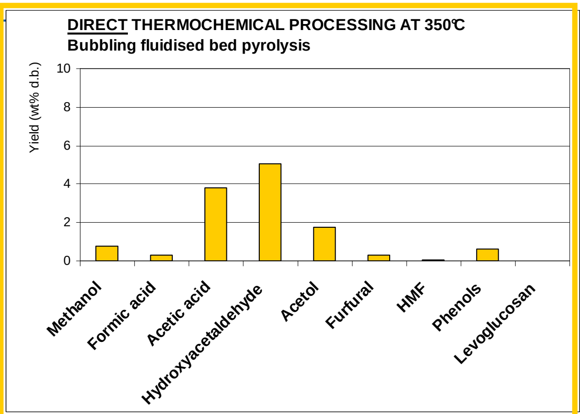
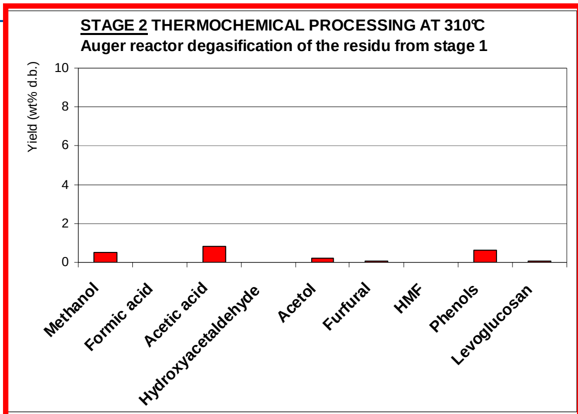
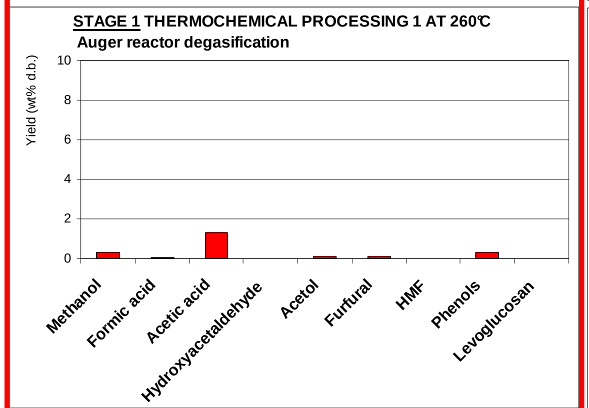
Comparison thermochemical processing straw

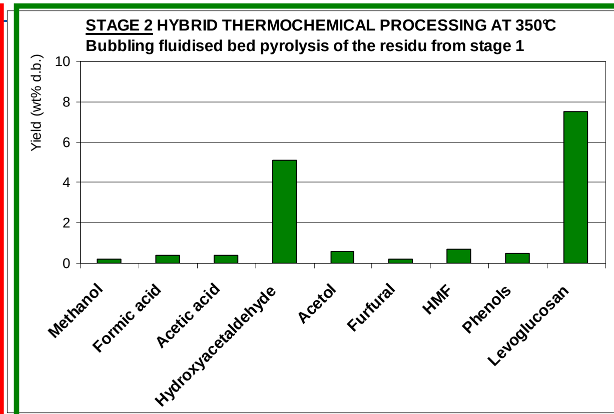


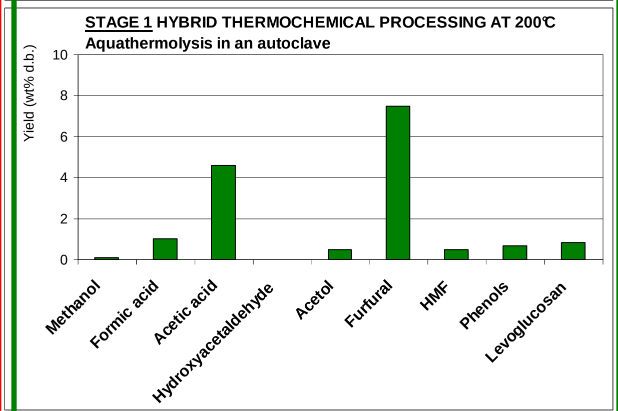
One-step BFB pyrolysis





Staged (de)gasification





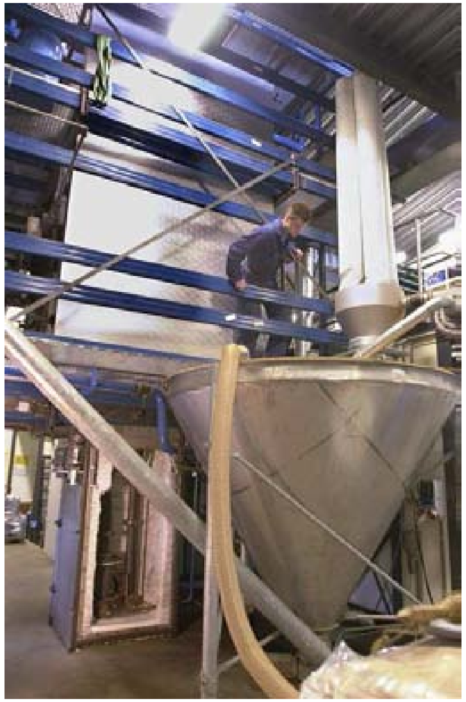
Hybrid thermochemical processing

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 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

Separation/upgrading

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



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

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WP3: Advanced biochemical conversion

Objectives

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

- Acetone-butanol-ethanol (ABE) fermentation: IFP-A&F
- Sugar conversion to platform chemicals VTT
- Production and analysis of functional lignin derivates: VTT
- Separation of product mixtures by Multiphase Rotating disk Contactors: GIG

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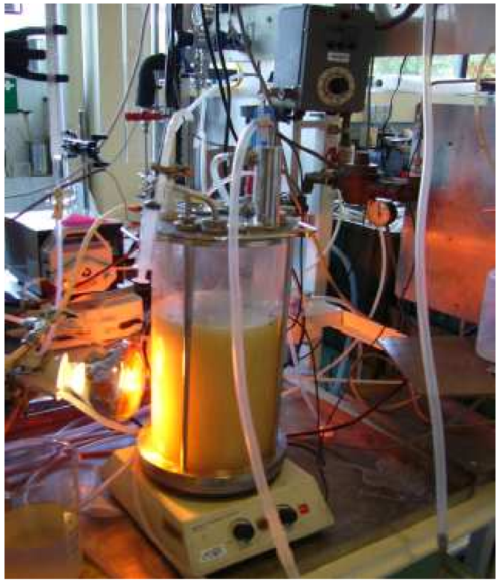
ABE fermentation: Preliminary results

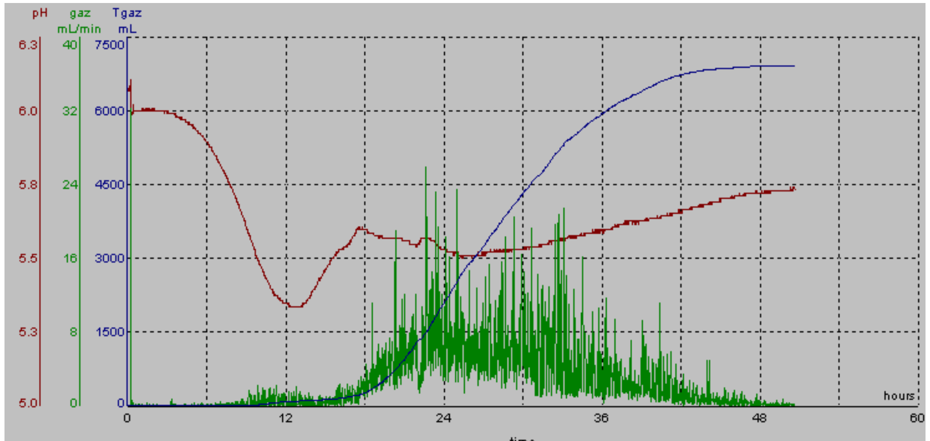
- Screening of strains on pure substrates
  - tests in flasks
  - tests in lab-scale reactors
- Production on wheat straw hemicellulose hydrolyzates prepared by steam explosion in mild acidic conditions



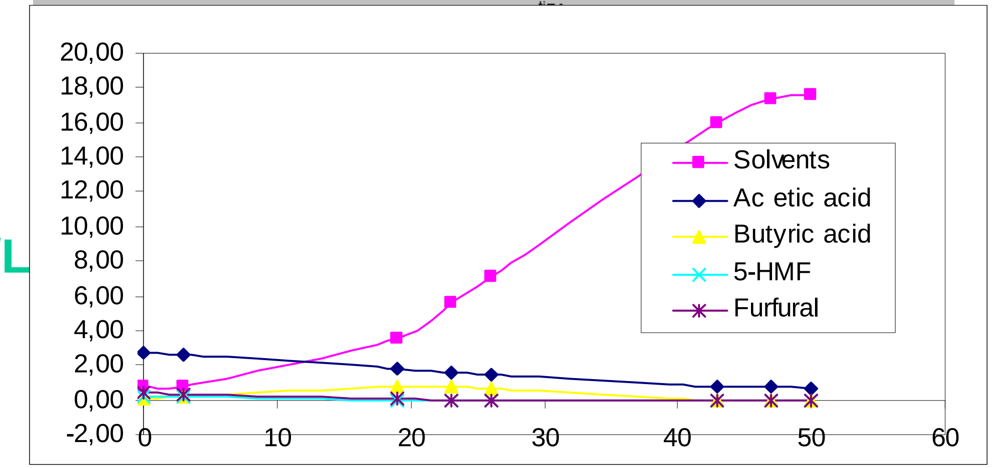
ABE fermentation at IFP

ABE – Production on wheat straw hemicellulose hydrolyzate

- **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**



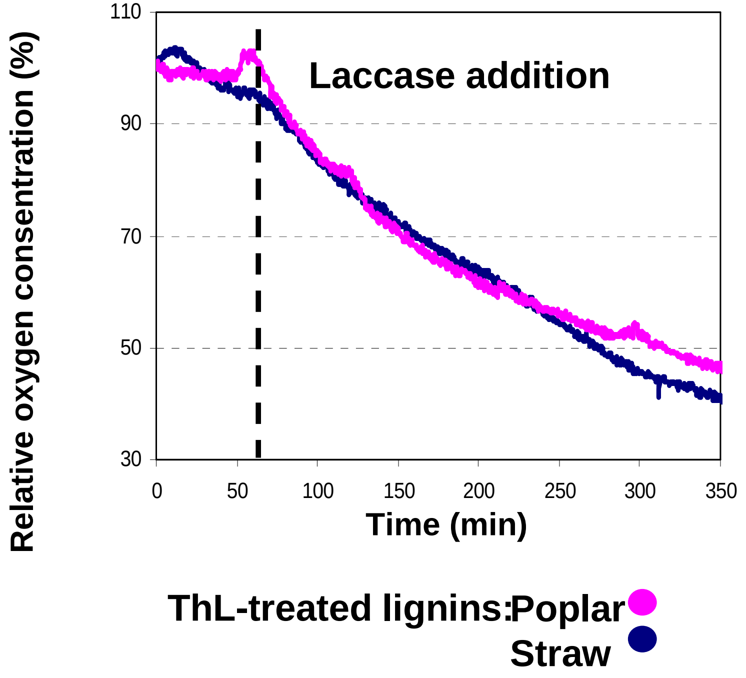
- **Results :**
  - **Gas release : 8.9 L / L**
  - **Final solvents (ABE) : 17,6 g/L**



Functional lignin derivatives

- procedure for lignin nanoparticles
- enzymatic lignin modification by laccases

Reactivity of Biosynergy lignins with *Trametes hirsuta* laccase



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Functional lignin derivatives

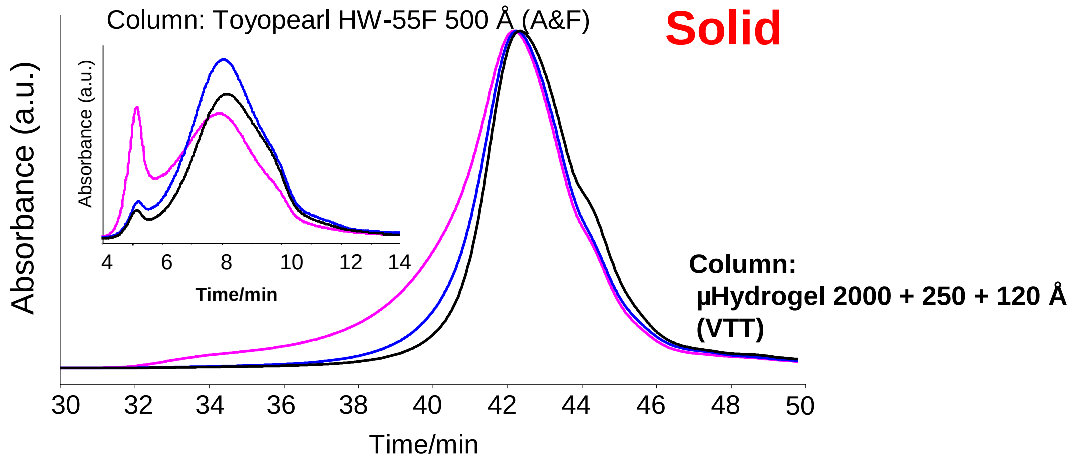
Modified lignin polymers have been prepared on lab scale by *Trametes hirsuta* laccase treatment and they have been characterised by chemical and spectroscopic methods.

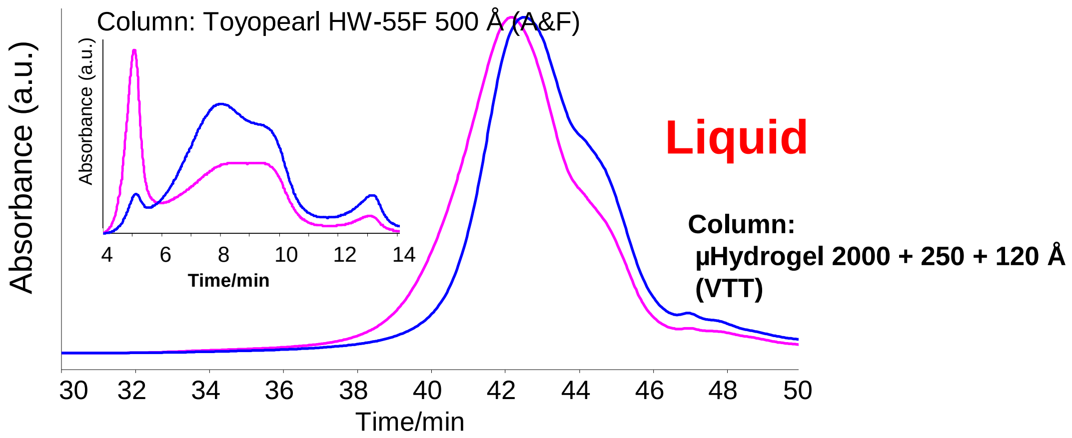
SEC of a model lignin

ThL treated lignin

Solubilized / Control lignin

Raw lignin / unsolubilised / untreated lignin





Mattinen et al. (2008). "Polymerization of different lignins by laccase," *BioRes.* 3(2), 549-565.

WP4: Innovative chemical conversion and synthesis

Objectives

- Definition and technical development of reaction chemistries and process designs for a well-defined portfolio of value added products

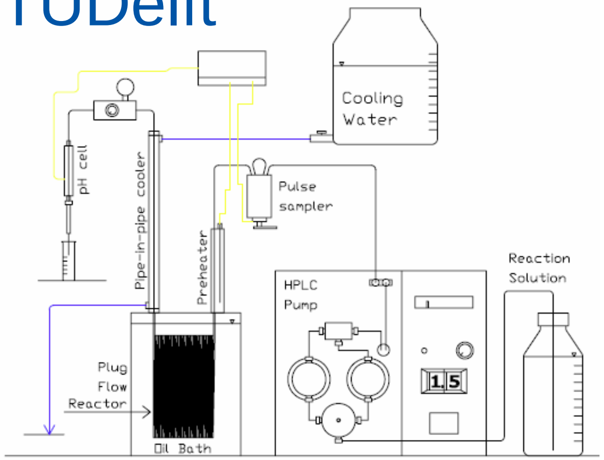
- Validation of commercial opportunities for the products portfolio in existing and also new industrial and consumer markets and applications

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

Production & characterisation platform chemicals

- Products from Lignin, Cellulose and Hemicellulose fractions
- Lignin depolymerisation in supercritical CO_2: A&F
- Hydroxymethylfurfural production from glucose dehydration>> high conversion rates and selectivity
  Biorefinery.de
- Analysis kinetics furfural synthesis from xylose and modelling furfuralproduction process: TUDelft

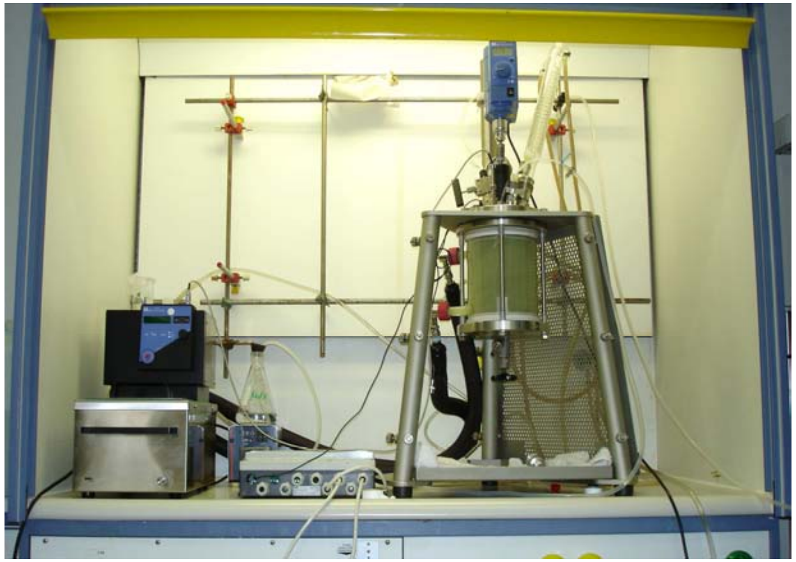
Marcotullio G., Heidweiller H.J., De Jong W. Reaction kinetic assessment for selective production of furfural from C-5 sugars contained in biomass. Paper presented at the 16th European biomass conference and Exhibition in Valencia, Spain, 2-6 June 2007



•Scheme of lab scale reactor TUDelft

Added value chemicals from platform chemicals

- Synthesis of 2,5-furandicarboxylic acid (2,5-FDA) starting from methyl furoate (to be obtained from furfural): A&F
- Synthesis of 2,5-FDA from HMF: Biorefinery.de



- Development of technologies for production of Diol-Components
- Evaluate use of resulting chemicals in polymer synthesis

Pentoses valorisation as raw materials for surfactants ARD

- Production of pentoside surfactants by a green technology in order to access the price level of petrol based competitors (1.5 €/kg)

- Development of new technology to directly convert pentoses containing raw material in surfactants in high yields: good progress obtained

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Applications testing and market validations

- Succesfull tests thermosetting phenol-formaldehyde resin for wood-based panel with phenol substitution up to 50% by lignin for lab scale particle board application.

- Use of pentoses based surfactants for paper impregnation in the wood-based industry

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WP5: Conceptual design biorefinery plant

Objectives

Basic design for innovative lignocellulose biorefinery plant at an existing cellulose ethanol site: ABNT BCyL plant, Salamanca

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

- targeted outputs: bio-products (chemicals, materials), bio-ethanol, power and/or heat.
- maximized profit and minimized environmental impact

Partners: ABNT, Aston, ECN

WP5: Conceptual design biorefinery plant

Progress to date:

- Integrated 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.
- Draft flowsheeting model for integrated biorefinery

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WP6: Biomass-to-products chain design, analysis and optimisation

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

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

WP6: Biomass-to-products chain design, analysis and optimisation

Progress to date:

- Creation and validation of process synthesis methodology and modelling tool to identify the optimum process chain design and literature review;
- Definition of the main structure of the LCA model and Collection of data
- Choice of 10 initial concepts for modelling and LCA

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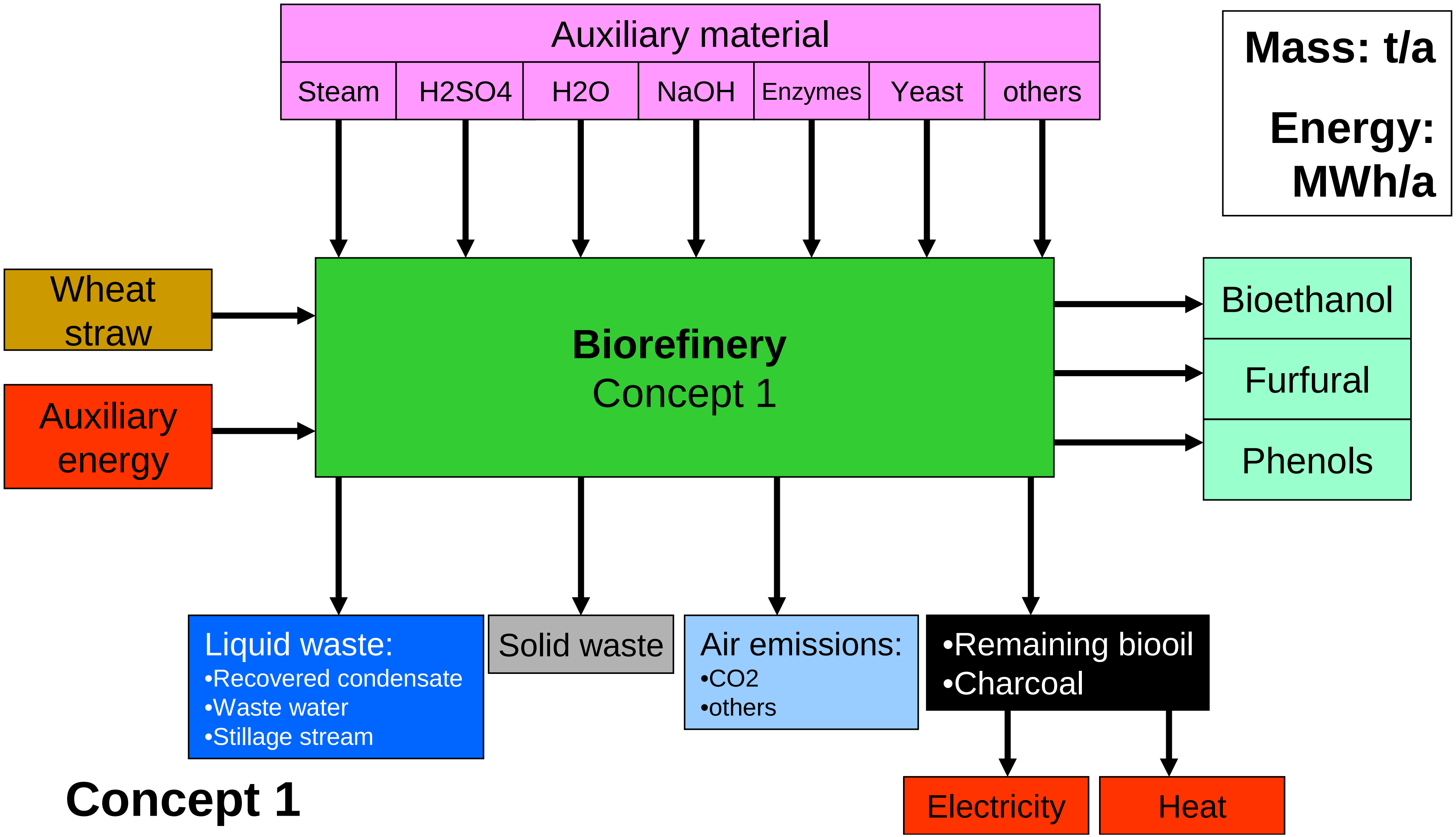
Example: LCA data requirement



Concept 1

WP7: Demonstration at pilot scale

Objectives

To use pilot-scale facilities to

- produce samples of bio-based intermediates for lab and bench-scale technology developments (WP1-4)
- Examine scale-up potential developed technologies

Partners: A&F, ABNT, Aston, ECN, ARD, BTG, Bioref

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WP7: Demonstration at pilot scale

Progress to date:

- Steam pre-treated straw delivered by ABNT
- Pilot-scale pyrolysis 280 kg bio-oil rotating cone reactor BTG

ABNT York Pilot plant

1 MW Flash pyrolysis pilot plant BTG

- Scale up developed technologies 2009 & onward

Hybrid Thermochemical processing

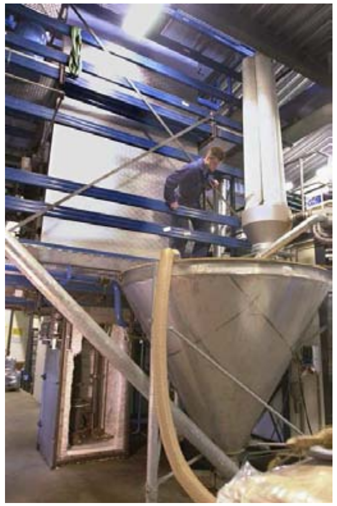
Poplar chips → **Aquathermolysis steam treatment** → Aquathermolysed poplar chips → **(Catalytic) intermediate / fast pyrolysis** → Residu (ash, charcoal)

Furfural

Levoglucosan
Bio-oil

93 m³ industrial batch thermolyser reactor

1 kg/hr BFB test rig at ECN



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

Pilot scale ABE fermentation at ARD

Lab-scale (150L)

Intermediate scale (10 m^3)

Fermentor 80 m^3

Membranes purification

Pentoses Valorization as surfactants

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



- Application testing (Chimar)

Perspectives

- R&D shows good progress
- Development of integrated processes / chain approach is one of the major challenges
- Lignin valorization is an important tool for economic profitability

BIOSYNERGY

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