Lignocellulosic feedstock biorefinery for co-production of chemicals, transportation fuels, electricity and heat – IP BIOSYNERGY and beyond


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
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, sugar agro feedstocks)
- High availability / Limited competition with food production
- High CO2 reduction for 2-G biofuels and biobased products

1) wood & wood based residues
2) agricultural residues of food and feed crops (straw, stover,...)

Production of pulp for paper in EU27+ (2006)
Source: FAO Statistics


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

---

**Lignocellulosic Feedstock Biorefinery**

- Abundant low-cost feedstock: wood, straw, corn stover, cellulose containing residues and waste
- Multiple products: transportation fuels, chemicals, polymers, materials, electricity and heat

- 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

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

#### 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 enERGY carriers – transportation fuels, power and/or CHP – through the biorefinery approach.**

- Development of integral LC cellulose-ethanol based 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
Duration: 1-1-2007 – 31-12-2010 (48 months)
Budget: 13.4 M€, EC grant 7M€
Product lines in the IP BIOSYNERGY

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

Goals:
- Controlled fractionation of lignocellulose into fractions with sufficient quality for production of (bio)chemicals
- Enhance access cellulose for enzymatic hydrolysis to sugar monomers in high yield /low enzyme use
- Minimize by-product formation and the use of chemicals, water, energy and costs
- Preferably lignin as high purity byproduct available

**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)

- No cost-effective industrial pre-treatment technology available yet
- Most processes suffer from major drawbacks: formation of inhibitors, high use energy or chemicals, waste production, high cost etc.
- Most routes produce low quality lignin residue

**Enzymatic cellulose hydrolysis**

3 types of enzyme activity required

- **Endo-cellulase (endoglucanase)**: Attacks amorphous, non-crystalline regions of the chain producing oligosaccharides
- **Exo-cellulase (cellulobiohydrolase)**: Attacks chain ends producing cellobiose
- **β-glucosidase**: Attacks oligosaccharides and cellobiose producing glucose

Enzymatic hemicellulose hydrolysis

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

Status enzymatic (hemi)cellulose hydrolysis

- Specific enzyme cocktails/activities required per feedstock type
- 20-30 fold cost reduction cellulases claimed by enzyme manufacturers Novozymes, Genencor. 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 required for economic reasons >> Enzymes required to reduce in-process feedstock viscosity

- Enzyme development must be tailored to feedstock AND pretreatment as well as to fermentation. Further cost reduction required.
WP1: Advanced physical/chemical fractionation

- 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)
- Enzymatic cellulose hydrolysis

Ethanol/H2O Organosolv, ECN
Mech./alk pretreatment A&F
Acid organosolv Pilot plant ARD

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

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)
**WP2: Innovative thermo-chemical conversion**

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

Partners: ECN, Aston, BTG

---

**Thermochemical production of chemicals from wood**

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

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

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

Comparison thermochemical processing straw

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

Separation/upgrading thermochemical produced bio-oils

- Staged condensation for separation of (groups) of chemicals
- Procedures to improve quality of pyrolysis oil (filtration, dewatering)
- Separation technology is a vital issue

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 revenue 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

<table>
<thead>
<tr>
<th>'Green' plastics</th>
<th>Wood-adhesives and resins</th>
<th>Fuel additives (aromatic ethers)</th>
</tr>
</thead>
<tbody>
<tr>
<td>• epoxies</td>
<td></td>
<td>• BTX</td>
</tr>
<tr>
<td>• polyolefins</td>
<td></td>
<td>• Binders</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Carbon Fiber (for CF composites)</td>
</tr>
</tbody>
</table>

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

### Lignin thermal conversion via pyrolysis: complex

- Lignin → Melting → Pyrolysis → Monomeric phenols → Oligomeric phenols → Char
- Permanent gases & water (CO, CO₂, CH₄, H₂O) → degradation
- Condensation / degradation

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.

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.

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

<table>
<thead>
<tr>
<th>Product yield in wt% dry feedstock</th>
<th>Methanol</th>
<th>Guaiacols</th>
<th>Syringols</th>
<th>Phenols</th>
<th>Catechols</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalytic pyrolysis</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-catalytic pyrolysis</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Continuous catalytic pyrolysis results

- 100 lignin pyrolyse to:
  - 17 - 20 gas (CO, CO$_2$, CH$_4$)
  - 20 - 25 water
  - 13 - 20 organic condensables
- 30 - 35 solid (char)
- The liquid product has been collected in two fractions, a thick, homogeneous oily liquid with an aromatic smell and an aqueous fraction with a pungent smell
**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 derivates: VTT
- Separation of product mixtures by Multiphase Rotating disk Contactors: GIG

![ABE fermentation at IFP](image.png)

**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)

- Lab-scale (150L)
- Intermediate scale (10 m$^3$)
- Fermentor 80 m$^3$
- Membranes purification

Functional lignin derivatives: lignin ‘activation’

- Enzymatic lignin modification by *Trametes hirsuta* laccases
- Aim: improvement of reactivity
  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

WP4: Production & characterisation platform chemicals

Partners: DOW, A&F, ARD, Biorel, 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


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 2,5-FDCA and application testing in progress
Applications testing and market validation

- Successful tests thermosetting phenol-formaldehyde resin with phenol substitution up to 50% by (organolsolv) 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

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

- Development of technology to directly convert pentose containing hydrolyzates to surfactants in high yields; good progress obtained
Planned scale up pentoses valorisation in surfactants ARD

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

WP5: Conceptual design biorefinery plant

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

- Targeted outputs: bio-ethanol, bio-products (chemicals, materials), power and/or heat.
- Maximized revenue and minimized environmental impact
- Process integration:
  - CHP to provide heat and electricity to the plant
  - Heat-integration
  - Water recycle

Partners: ABNT, Aston, ECN

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

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
Summary/Conclusions

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

- Further development LC Biorefinery -combining bioprocesses and chemical processes- offers good perspectives to fully exploit the potential of lignocellulose.

- Pretreatment and enzymatic hydrolysis are critical items for techno-economic feasibility. Pretreatment technologies need to be optimised toward a particular goal. Organosolv is a good candidate when the aim is to valorize all fractions AND produce a high quality lignin.

- Enzymes are a major processing tool in the LC Biorefinery. Further development and cost reduction are needed.

---

Summary/Conclusions

- Integrated development Feedstock-pretreatment-hydrolysis-fermentation is required.

- Lignin valorization (at least in part) to chemicals is an important tool for economic profitability and for reduction of the carbon footprint.

- Catalytic thermochemical processing (pyrolysis) and enzymatic lignin conversion show promising results for lignin valorization.

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

- Development of integrated processes / chain approach 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.
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.

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.

Participants IP BIOSYNERGY

<table>
<thead>
<tr>
<th>Alessandro Agostini</th>
<th>Richard Gosselink</th>
<th>Gianluca Marcotullio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bert Annevelink</td>
<td>Gareth Griffths</td>
<td>Frederic Martel</td>
</tr>
<tr>
<td>Ricardo Arjona Antolin</td>
<td>Pablo Gutierrez</td>
<td>Maija-Liisa Mattinen</td>
</tr>
<tr>
<td>Eleftheria Athanasiadou</td>
<td>Elina Gytopoulos</td>
<td>Frederic Monot</td>
</tr>
<tr>
<td>Philippe Aubry</td>
<td>Henk Hagen</td>
<td>Eleftheria Papadopoulou</td>
</tr>
<tr>
<td>Cantinte Ajmard</td>
<td>Paulien Harsman</td>
<td>Miguel Pfezer Pascual</td>
</tr>
<tr>
<td>Rob Bakker</td>
<td>Jacco van Haveren</td>
<td>Merja Pentila</td>
</tr>
<tr>
<td>Cecile Barrene-Titeca</td>
<td>Regina Heddes</td>
<td>Wolter Prins</td>
</tr>
<tr>
<td>David Baxter</td>
<td>Elke Heijnen</td>
<td>Jacinta van der Putten</td>
</tr>
<tr>
<td>Bert van de Beld</td>
<td>Yvon le Henaff</td>
<td>René van Ree</td>
</tr>
<tr>
<td>Rolf Blauw</td>
<td>Bwre Houwelings-Tan</td>
<td>Hans Reith</td>
</tr>
<tr>
<td>Carmen Boeriu</td>
<td>Wouter Huijgen</td>
<td>Anna Rogut</td>
</tr>
<tr>
<td>Anthony Bosin</td>
<td>Wimboom de Jong</td>
<td>Jan Rogui</td>
</tr>
<tr>
<td>Tony Bridgewater</td>
<td>Gerfried Jungmeier</td>
<td>Petra Schöncke</td>
</tr>
<tr>
<td>Reyes Capote Campos</td>
<td>Sjaak Kaandorp</td>
<td>Philippe Schild</td>
</tr>
<tr>
<td>José Caraballo</td>
<td>Birgit Kamm</td>
<td>Agnes Maria Stepan</td>
</tr>
<tr>
<td>Mariaa Charisoi</td>
<td>Richard op den Kamp</td>
<td>Jan Stoutjedijk</td>
</tr>
<tr>
<td>Katie Chong</td>
<td>Boyan Kavakov</td>
<td>Muzaffar Syed</td>
</tr>
<tr>
<td>Myrsvin Christou</td>
<td>Kees van Keeken</td>
<td>Tarja Tamminen</td>
</tr>
<tr>
<td>Ioannis Efthieradis</td>
<td>Evert Leijenhoff</td>
<td>Wouter Teunissen</td>
</tr>
<tr>
<td>Maria Fe Elia Miguel</td>
<td>Marcel van der Linden</td>
<td>Arnoo Togitena</td>
</tr>
<tr>
<td>Dana van Es</td>
<td>Raimo van der Linden</td>
<td>Herman den Uil</td>
</tr>
<tr>
<td>Boris Estirne</td>
<td>Angelika Lingitz</td>
<td>MarJan Wiatowski</td>
</tr>
<tr>
<td>Silvia Fasulini</td>
<td>Ana Maria Lopez Contreas</td>
<td>Marilyn Wiebe</td>
</tr>
<tr>
<td>Antrela Foyga</td>
<td>Michael Lukas</td>
<td>Paul de Wild</td>
</tr>
<tr>
<td>Maria Georgiadou</td>
<td>Michael Mandl</td>
<td>Emma Wylde</td>
</tr>
</tbody>
</table>
Thank you for your attention!

More information:

Hans Reith, coordinator IP BIOSYNERGY  
+31-(0)224-564371  
reith@ecn.nl  
www.ecn.nl

www.biosynergy.eu

www.biobased.nl/lignovalue  
www.biorefinery.nl  
www.biorefinery-euroview.eu  
www.biorefinery.nl/biopol

Thermochemical biorefinery: syngas platform

National Renewable Energy Laboratory (NREL)
Integrated Thermal Biorefinery 500 MWth

<table>
<thead>
<tr>
<th>Compound</th>
<th>Composition [vol%]</th>
<th>Yield [kg/tonne]</th>
<th>Annual yield [ktonne]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>34.2</td>
<td>364</td>
<td>3.0</td>
</tr>
<tr>
<td>H₂</td>
<td>20.9</td>
<td>16</td>
<td>1.3</td>
</tr>
<tr>
<td>CO₂</td>
<td>26.1</td>
<td>438</td>
<td>3.72</td>
</tr>
<tr>
<td>CH₄</td>
<td>11.6</td>
<td>71</td>
<td>0.6</td>
</tr>
<tr>
<td>N₂</td>
<td>0.52</td>
<td>5.6</td>
<td>0.47</td>
</tr>
<tr>
<td>ethylene (C₂H₄)</td>
<td>3.87</td>
<td>41</td>
<td>0.35</td>
</tr>
<tr>
<td>acetylene (C₂H₂)</td>
<td>0.39</td>
<td>3.8</td>
<td>0.32</td>
</tr>
<tr>
<td>methanol</td>
<td>0.26</td>
<td>3.0</td>
<td>0.25</td>
</tr>
<tr>
<td>benzene</td>
<td>0.97</td>
<td>29</td>
<td>0.24</td>
</tr>
<tr>
<td>toluene</td>
<td>0.14</td>
<td>4.8</td>
<td>0.41</td>
</tr>
<tr>
<td>xylenes</td>
<td>0.19</td>
<td>3.6</td>
<td>0.30</td>
</tr>
<tr>
<td>N₂O</td>
<td>0.47</td>
<td>3.0</td>
<td>0.25</td>
</tr>
<tr>
<td>heavy tars</td>
<td>0.36</td>
<td>17</td>
<td>0.14</td>
</tr>
<tr>
<td>light tars</td>
<td>-</td>
<td>6.4</td>
<td>0.54</td>
</tr>
<tr>
<td>phenol</td>
<td>-</td>
<td>1.0</td>
<td>0.09</td>
</tr>
<tr>
<td>furfural</td>
<td>-</td>
<td>1.8</td>
<td>0.14</td>
</tr>
<tr>
<td>-lignin</td>
<td>-</td>
<td>1.5</td>
<td>0.12</td>
</tr>
<tr>
<td>-naphthalene</td>
<td>-</td>
<td>2.7</td>
<td>0.22</td>
</tr>
<tr>
<td>-anthranilic</td>
<td>-</td>
<td>0.5</td>
<td>0.046</td>
</tr>
<tr>
<td>TOTAL</td>
<td>100</td>
<td>1000</td>
<td>850</td>
</tr>
</tbody>
</table>

Major products/chemicals:
- Syngas (H₂/CO)
- Methane
- Ethylene
- BTX
- Tar compounds (e.g. naphthalene)

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

- Yield per tonne dry ash-free wood
- 8000 operational hours
- With preceding Torrefaction plant

References

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


http://www.epobio.net/workshop0705/presentations/RalphOverend.pdf

www.forestplatform.de/download.php?id=155


http://www.ecs.umass.edu/biofuels/Images/Roadmap2-08.pdf