CONVERSION OF LIGNOCELLULOSICS TO BIOFUELS

Bioenergy - I:
From Concept to Commercial Processes
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OUTLINE

Policy

The lignin factor in bioconversion of lignocellulosics

Portuguese pulp and paper industry

Scenarios for Fischer Tropsch diesel conversion

Overall considerations
EXTERNAL DEPENDENCE ON PRIMARY ENERGY SOURCE

Source: Ministry of Economy and Innovation, Nov 2005
In the resolution of the Council of Ministers nº 63/2003, the Portuguese Government lists its objectives for Portuguese energy policy. Its implementation follows three strategic axes:

1 - Maintain security of national energy supply
2 - Promote sustainable development
3 - Promote national competitiveness
**NATIONAL STRATEGY FOR THE ENERGY SECTOR**

### Promotion of Technologies for the Development of Renewables
- New objectives for energy from renewable sources
- Flexible administrative processes
- Introduction of biofuels (Directive EU/2003/30/EC)
- Valorization of forest biomass
- Program for solar-heated water

### Implementation of a Plan for increasing Energy efficiency
- Creation of a carbon tax
- Legislation on efficient energy use in buildings
- Application of the Directive on cogeneration
- Introduction of alternative fuels

### Technologies for the Development of Renewables
- Wind energy (2 - 3 000 MW)
- Solar-heated water
- Biofuels
- Biomass

### Increase in Energy efficiency

**Source:** Ministry of Economy and Innovation, Nov 2005
# RESIDUES FROM MAIN INDUSTRIAL ACTIVITIES

<table>
<thead>
<tr>
<th>ACTIVITY</th>
<th>Non-toxic residues</th>
<th>Toxic residues</th>
<th>nd</th>
<th>Total (ton)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production of textiles</td>
<td>1 471 782</td>
<td>15 008</td>
<td>10</td>
<td>1 486 801</td>
</tr>
<tr>
<td>Clothing industry, dyeing</td>
<td>374 598</td>
<td>116</td>
<td>70</td>
<td>374 784</td>
</tr>
<tr>
<td>Leather tanning and finishing</td>
<td>1 377 012</td>
<td>279</td>
<td>47</td>
<td>1 377 338</td>
</tr>
<tr>
<td>Cork and wood industry</td>
<td>2 205 155</td>
<td>12 404</td>
<td>605</td>
<td>2 218 164</td>
</tr>
<tr>
<td>Pulp and paper industry</td>
<td>582 272</td>
<td>2 078</td>
<td>0</td>
<td>584 350</td>
</tr>
</tbody>
</table>

Source: INR – Instituto Nacional de Resíduos 2004
RESIDUES FROM WOOD PROCESSING INDUSTRIES

10^3 ton

ALGARVE | ALENTEJO | Tejo LVT | CENTRO | NORTE
---|---|---|---|---
22 | 10 | 570 | 1290 | 690

Portugal Map:
- ALGARVE
- ALENTEJO
- Tejo LVT
- CENTRO
- NORTE
### TYPICAL % COMPOSITION OF DIFFERENT LIGNOCELLULOSICS

<table>
<thead>
<tr>
<th>Material</th>
<th>Lignin</th>
<th>Ash</th>
<th>Cellulose</th>
<th>Hemicellulose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Softwood</td>
<td>27 - 30</td>
<td>2</td>
<td>35 - 40</td>
<td>25 - 30</td>
</tr>
<tr>
<td>Hardwood</td>
<td>20 - 25</td>
<td>2</td>
<td>45 - 50</td>
<td>20 - 25</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>15</td>
<td>8</td>
<td>33</td>
<td>25</td>
</tr>
<tr>
<td>Waste newspaper</td>
<td>16</td>
<td>trace</td>
<td>61</td>
<td>20</td>
</tr>
</tbody>
</table>
From enzymes ....
LIGNIN AND CELLULOSE STRUCTURE

Lignin "monomer"

R = C\_R'__R'__R'__C

R' = \{-H, -OH, or =O\}

Sample Lignin Polymer Structure

Cellulose molecule

- Glucose
- Cellobiose

Crystalline cellulose
In vivo labelled pine by growth on \([^{14}\text{-C]}\)-ferulic acid (different positions)

Synthetic lignins (DHPs) coniferyl alcohol labelled

\(^{14}\text{C}-\text{kraft pulp (CLKP)}\)

Mineralization can be followed by the release of \(^{14}\text{CO}_2\)
**Phanerochaete chrysosporium**

1983 - LiP  
1984 - MnP
POSSIBLE COUPLING OF LIGNIN AND CELLULOSE BIOTRANSFORMATION

Phanerochaete chrysosporium

CDH = cellobiose dehydrogenase
CBQ = cellobiose:quinone oxidoreductase
LOW MOLECULAR WEIGHT REDOX MEDIATORS

Wood cell wall
Buffered, higher pH environment of the wood cell wall
1-3 nm wood cell pore size

Wood cell lumen
Low pH environment

Fungal hyphae
30-70 nm enzymes

H₂O₂ → OH⁻ + Fe III

Fe II-chelate
Fe III

30-70 nm enzymes
**Pleurotus sp.**

Versatile peroxidase/laccase

a. ether linkage
b. C4 ether breakdown
c. aromatic ring cleavage
d. Cα-Cβ breakdown
e. demethoxylation
f. re-oxidation
h. repolymerization

AAD = aryl alcohol dehydrogenase
AAO = aryl alcohol oxidase
Given our incomplete understanding of how lignin is biotransformed, need to invest more in R & D.

Many potential benefits/applications in developing a simple & cost-effective biosystem
eg. for pretreatment of biomass for bioenergy

.....or for application in
the pulp and paper industry
EU PULP PRODUCERS

Source: CELPA 2004 STATISTICS BULLETIN
SOURCE OF SOLID RESIDUES WITHIN PULP AND PAPER PROCESSING INDUSTRY

Source: CELPA 2004 STATISTICS BULLETIN
FATE OF RESIDUES FROM PULP AND PAPER PROCESSING INDUSTRY

Source: CELPA 2004 STATISTICS BULLETIN
FROM LIGNOCELLULOSICS TO FT-DIESEL

SCENARIO I
Biomass is used for generating energy
Hydrogen via the homogeneous water gas reaction
Oxygen and nitrogen via air separation
Biomass to diesel conversion ratio (w/w) 9.3 : 1 (35% water)

SCENARIO II (future)
Energy, hydrogen and oxygen produced from renewables
Biomass to diesel conversion ratio 3.4 : 1 (35% water)

ASSUMPTIONS
Equivalent conversion for different residues
Transportation of biomass about 100 Km
RESIDUE DIESEL EQUIVALENT
SCENARIO I

10^3 ton

- shavings+bark
- sludge
- recycled paper
- ash+dust
- other

Year:
- 1999
- 2000
- 2001
- 2002
- 2003
- 2004

Tons:
- 0
- 5
- 10
- 15
- 20
- 25
- 30
- 35
- 40

Legend:
- 1999
- 2000
- 2001
- 2002
- 2003
- 2004

103 ton
TOTAL RESIDUE DIESEL EQUIVALENT

10^3 ton diesel

<table>
<thead>
<tr>
<th>Year</th>
<th>Scenario I</th>
<th>Scenario II</th>
</tr>
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<tbody>
<tr>
<td>1999</td>
<td>103 ton</td>
<td></td>
</tr>
<tr>
<td>2000</td>
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</tr>
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<td>2001</td>
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<td>2003</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2004</td>
<td></td>
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</tbody>
</table>
OVERALL CONSIDERATIONS I

Technological Challenges

Biomass
- Process is versatile; feedstock; wet feedstocks do not need to be dried
- Feedstock cost is important (at 4 €/GJ accounts of about half of overall cost)
- Biomass supply chain needs to be established
- Transportation costs need to be considered (vs pyrolysis oil option)
- Biomass pre-treatment variable?

Gasification
- Gas clean-up

Economy of scale
- FT diesel can be “designed” to meet developments in engine design
PORTUGAL

- FT diesel production is in tune with the activity of major Portuguese energy suppliers
  - Greater market penetration in Europe
- Sustainable development of deserted rural areas (e.g., Alentejo) by energy crops
- Forest fires
  - Since 1980 30% of Portugal burnt out by fires
  - (2001-2004) 450,000 ha of plantations plus 335,000 ha of forest (wild)
    - 17.7% of pine
    - 13.2% of Eucalyptus

- Net energy needs of the pulp and paper industry can be met
Thank You !