Biomass conversion into low-cost and sustainable chemicals*

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Biomass
Mixture of highly functionalised chemicals: Structural categories

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starch</td>
<td>1%</td>
</tr>
<tr>
<td>Sucrose</td>
<td>0.1%</td>
</tr>
<tr>
<td>Plant oils</td>
<td>0.1%</td>
</tr>
<tr>
<td>Hemicellulose (Xylanes)</td>
<td>24%</td>
</tr>
<tr>
<td>Lignin</td>
<td>5%</td>
</tr>
<tr>
<td>Others (Proteins, terpenes, ....)</td>
<td>20%</td>
</tr>
<tr>
<td>Cellulose</td>
<td>50%</td>
</tr>
</tbody>
</table>

Total: 180 bn t/a
Key technologies

Biomass:
- a mixture of highly functionalised chemicals
- low transport density
- low energy density

Issues:
- solid handling
- fractionation
- dilute solutions
- defunctionalisation

⇒ Key technologies:
- refinement
- catalysis (chemical & biotechnological)

O/C ratio
mol. weight

chemicals
naphtha

Biorefinery technology

“A biorefinery is an overall concept of a processing plant, where lignocellulosic biomass feedstocks are converted and extracted into a spectrum of valuable products.”

~25% hemicellulose
~50% cellulose
~25% lignin

biofuels
energy
chemicals

sources: US department of energy, IEA, Faix & Lehnen
Efficient refinery technologies are essential

Value added chains (1)
Example: grain – based

Grain
- Corn
- Wheat

65%
Sugar: C₆ glucose

35%
Protein Oil

Value added:
- Animal and human nutrition

Catalysis
- Ethylamines
- PTT
- PLA
- THF
- Levulinic acid
- Ester

C₂: Ethanol, MEG
C₃: Lactic acid, MPG, 1,3 PDO
C₄: Succinic acid, BuOH
C₅: Levulinic acid
C₆: Lysine, sorbitol
C₆: PHA¹

¹ PHA: Polyhydroxyalkanoates
² PLA: Polylactic acid
³ PTT: Polytrimethylene terephthalate

Catalysis is the key technology
Process idea and overview
Basic flow scheme of bioethanol production

![Flow scheme of bioethanol production](image)

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Process idea and overview
Adaption for fine chemical fermentation processes

![Flow scheme for fine chemical fermentation](image)

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Optimized process
- Corn
  - Milling
  - Liquefaction
    - α-Amylase
  - Saccharification
    - β-Glucosamylase
  - Fermentation
  - Solid-Liquid-Separ.
  - Downstreaming
    - Fine chemicals
      - e.g., amino acids, vitamins, enzymes, ...
    - Concentration
    - Drying

Biomass & solids
- Thin stillage
- Syrup
- DDGS-equivalent co-product
### Process idea and overview
Pilot-scale development

![Overall view pilot plant](image)

### Fermentation sugar sources
Comparison of existing technologies & BASF process

<table>
<thead>
<tr>
<th>Process</th>
<th>Sugar mill</th>
<th>Wet-milling</th>
<th>Dry-milling (BioEtOH)</th>
<th>BASF process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw material</td>
<td>Sugar cane</td>
<td>Corn</td>
<td>Corn</td>
<td>Corn</td>
</tr>
<tr>
<td>Fermentation sugar purity</td>
<td>&gt; 98%</td>
<td>&gt; 99% (food-grade)</td>
<td>~ 70%</td>
<td>&gt; 90%</td>
</tr>
<tr>
<td>Autonomy of sugar production</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>Raw material costs</td>
<td>World market</td>
<td>World market</td>
<td>World market</td>
<td>World market</td>
</tr>
<tr>
<td>Investment costs</td>
<td>Low</td>
<td>High(^1)</td>
<td>Low</td>
<td>Medium</td>
</tr>
<tr>
<td>Production costs</td>
<td>Low</td>
<td>Low(^2)</td>
<td>Low</td>
<td>Low</td>
</tr>
</tbody>
</table>

\(^1\) World-scale plants (>1.5 Mio tons/a crushing capacity)

\(^2\) World-scale plants (>1.5 Mio tons/a crushing capacity)
### Value added chains (2)

**Example: lignocellulose**

<table>
<thead>
<tr>
<th>Refinement</th>
<th>Catalysis</th>
<th>Catalysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignocellulose</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;: Ethanol, MEG</td>
<td>Ethylamines</td>
</tr>
<tr>
<td>Wood</td>
<td>C&lt;sub&gt;3&lt;/sub&gt;: Lactic acid, MPG, 1,3 PDO</td>
<td>PTT&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td>Straw</td>
<td>C&lt;sub&gt;4&lt;/sub&gt;: Succinic acid, BuOH</td>
<td>PLA&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>...</td>
<td>C&lt;sub&gt;5&lt;/sub&gt;: Furfural, levulinic acid</td>
<td>THF</td>
</tr>
<tr>
<td></td>
<td>C&lt;sub&gt;6&lt;/sub&gt;: Lysine, sorbitol</td>
<td>Levulinic acid</td>
</tr>
<tr>
<td></td>
<td>...</td>
<td>ester</td>
</tr>
<tr>
<td></td>
<td>C&lt;sup&gt;n&lt;/sup&gt;: PHA&lt;sup&gt;1&lt;/sup&gt;</td>
<td>....</td>
</tr>
</tbody>
</table>

**Refinement and catalysis are the key technologies**

1<sup) PHA: Polyhydroxyalkanoates
2<sup) PLA: Polylactic acid
3<sup) PTT: Polytrimethylene terephthalate

### 2nd generation biorefinery concept

**biofuel / chemicals production via fractionation**

- **why fractionation?**
  - tailor-made conversion conditions for each stream
    - space time yield
    - capital investment
    - flexibility

**Source cartoon:** Faix & Lehnen
Example: biomass pretreatment
ionic liquids

- liquid below 100 °C
- non flammable
- immiscible with many organic solvents
- BASF know-how & production
- various emerging applications
- dissolution of (ligno-)cellulose
- exclusive license from the University of Alabama (patents of Prof. Rogers)

Example: biomass pretreatment
biorefinery with ionic liquids

- screening of >50 ILs
- screening of parameters:
  - temperature
  - precipitating agent
  - water content of the IL
  - precipitation protocol
- series of experiments in closed process cycles
- two patents filed:
  WO 2008090155
  WO 2008090156
Example: biomass pretreatment
digestion of switchgrass by cellulases

- disintegration of the lignocellulose structure (hydrolysis rate x7)
- challenges:
  - >99% IL-recycling
  - high investment costs
  - energy costs

Example: biomass pretreatment
digestion of switchgrass by cellulases

- favorable price ratio of renewable versus fossil feedstocks
- integration into existing value added chains (BASF „Verbund“)
- feedstock change without product change
- competitiveness (economy of scale)
- sustainability (BASF eco efficiency analysis)
**Chemicals via Fermentation**
Succinate as Intermediate and Monomer

**Glucose + CO₂**

- **Bacterium**
- **Succinate**
- **Succinate**
- **Product**

**Chances:**
- Succinate as monomer and intermediate
- Potential for 100% yield
- CO₂ fixation

**Challenges:**
- Identify suitable production organism
- Improve microbial strain & fermentation
- Develop “in broth chemistry”

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**Chemicals via Fermentation**
Succinate as Intermediate and Monomer

**Renewable raw material**
- Sucrose
- Glucose
- Glycerol
- Succinate
- Polyester

**Fossil raw material**
- Butadiene
- N-Butane
- MA
- Acetylen
- Butynediol
- Butanediol
- THF
- Poly-THF
- GBL
- Pyrrolidon
- VP
- PVP
Chemicals via Fermentation
Diaminopentane – New Monomer by Synthetic Metabolic Pathways

Example: glycerol conversion
Example: propylene glycol
alternative process based on glycerol

- hydrogenation of glycerol

\[
\text{H}_2 \text{O}_2 + \text{H}_2 \xrightarrow{\text{catalyst}} \text{H}_2 \text{O} + \text{H}_2 \text{O}
\]

- challenges
  - volatile & rising glycerol price
  - reliable sourcing of >100,000 t/a difficult

- state of the art: epoxidation & hydrolysis of propylene

Example: aromatics from lignin

- biomass: 20-30% lignin
- max. yield of phenol/benzene = 45% from lignin
Summary

Chemicals from renewable raw materials

- Renewable raw materials are well-established in the chemical industry
- Sufficient renewable raw materials must be available at competitive prices:
  - A rising price ratio of ‘fossil to renewable raw materials’ elevates the importance of renewable raw materials
  - An increasing raw material competition between chemical products based on renewable raw materials, biofuels and nutrition may be expected
- Cost effectiveness and technical feasibility of base chemicals from renewable raw materials have to be explored
- Sustainability has to be analyzed carefully for every alternative process or product (life cycle analysis, e.g. via BASF eco-efficiency analysis)
- Chemical products from renewable raw materials require:
  - Verbund structure and value added chains based on renewable raw materials
  - A broad technology portfolio:
    - chemical catalysis: higher selectivity and stability
    - biotechnological catalysis: higher stability and space time yield
    - chemical engineering: solid handling and downstream