Upgrading of by-products from biodiesel and sugar industry by bioconversion and chemical catalysis

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ExCo59, Golden, USA
25 April 2007
Some Important Steps in Biorefineries

The whole process combines physical, chemical and biotechnological steps

➔ Pretreatment, Conservation, Separation
  ➢ Physical, mechanical (destructure, milling, sieving)
  ➢ (Thermo)chemical (heat, acid, base, …)
  ➢ Biological (enzymes, microorganisms)
  ➢ Combination of all

➔ Conversion
  ➢ Biotechnological (bacteria, fungi, enzymes)
  ➢ Chemical-catalytic (e.g. noble-metal-catalysis)
  ➢ (Thermo)chemical (pressure, heat, …)
  ➢ Combination of all

Biorefineries in Germany

Existing

Sugar
Ethanol, Products

Starch
Ethanol, Products

Oil
Biodiesel, Glycerol

Ligno-cellulose

Biogas
Just starting with biogas (energy maize)

Residues
waste streams
Biorefinery in Germany
The main problem: costs

Cost reduction in Biorefinery

⇒ Transportation efficiency
  ➢ Energy-density of feedstock and products
  ➢ Infrastructure, distances

⇒ More efficient processes
  ➢ Biocatalysts, chemical catalysts
  ➢ Productivity
  ➢ Product concentration

⇒ Cheaper and more efficient feedstocks
  ➢ Agricultural/industrial residues
  ➢ Lignocellulose
  ➢ Additional use of waste water/-air

Processes
Starch, Sugar

Sugar-Refinery (for example: Südzucker, crop energies)

<table>
<thead>
<tr>
<th>Starch-/Sugar Plants</th>
<th>Sucrose</th>
<th>Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residues</td>
<td>Glucose</td>
<td>Products</td>
</tr>
<tr>
<td>Biogas</td>
<td>Glucose/Fructose</td>
<td>Products</td>
</tr>
<tr>
<td>Electricity, Heat</td>
<td>Fructose</td>
<td>Products</td>
</tr>
<tr>
<td></td>
<td>Palatinit</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fertiliser, Animal feed</td>
<td></td>
</tr>
</tbody>
</table>
Top 12 Platform Chemicals From Biomass

- 1,4-Succinic, fumaric and malic acids
- 2,5-Furan dicarboxylic acid
- 3-Hydroxypropionic acid
- Aspartic acid
- Glucaric acid
- Glutamic acid
- Itaconic acid
- Levulinic acid
- 3-Hydroxybutyrolactone
- Glycerol (1,3-propanediol)
- Sorbitol
- Xylitol/arabinitol

Source: Top Value Added Chemicals From Biomass, PNNL & NREL, 2004

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Immobilisation in Biotechnology
Example: ethanol-production with immobilised yeasts

- Sugarbeet starch, sucrose
- Wheat

Immobilised yeasts or bacteria (biokatalyst)

Hydroxyethyl starch

Biofuel, chemical feedstock

Ethanol
Bead Production with JetCutter
Scheme and operation

- $u_{\text{fluid}}$ = fluid velocity
- $u_{\text{wire}}$ = wire velocity
- $m$ = motor
- $n$ = rotations
- $D$ = diameter of the nozzle

Animation of the Cutting Process
JetCutter
optimisation of settings for low spray losses

unsuited adjustments
→ high losses

suited adjustments
→ almost no losses

Bioethanol Production
Advantage of immobilisation

<table>
<thead>
<tr>
<th>microorganism</th>
<th>free cells</th>
<th>immobilised cells</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>activity</td>
<td>activity</td>
</tr>
<tr>
<td></td>
<td>[kg EtOH/(kg BDM·h)]</td>
<td>[kg EtOH/(m³ cat·h)]</td>
</tr>
<tr>
<td>yeast</td>
<td>0.5 – 1.4</td>
<td>25 - 70</td>
</tr>
<tr>
<td><em>Saccharomyces cerevisiae</em></td>
<td></td>
<td></td>
</tr>
<tr>
<td>bacterium</td>
<td>4 - 5</td>
<td>190 - 230</td>
</tr>
<tr>
<td><em>Zymomonas mobilis</em></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Ethanol Fermentation: Production Plant
Conventional or with immobilised cells

Conventional fermentation

- Nutrients
- Molasses
- 6 x 200 m³
- Separator
- Biomass recycling
- Ethanol
- Buffer

Process design with immobilised cells

- Nutrients
- Molasses
- 3 x 60 m³
- Separator (smaller)
- Ethanol
- Buffer

BMA Braunschweig, capacity: 60,000 litres EtOH / 24 h

Ethanol-Fermentation: Pilot Plant
Immobilised yeast, continuously, 3-step

© BMA-Braunschweig
Palatinose-Production
Example for immobilisation on an industrial scale

immobilised cells of Protaminobacter rubrum

saccharose \rightarrow \text{palatinose}

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Palatinose-Production
Bioconversion

Sucrose\rightarrow\text{Enzyme reactor}\rightarrow\text{Enzyme reactor Invertase}\rightarrow\text{Ion exchange}\rightarrow\text{Palatinose}
Industrial Production of Palatinose with Immobilised Microorganisms

80,000 tons per year

Itaconic Acid Production
The process

Sugar

or

glycerol 10%
(byproduct of biodiesel production)

Fungi, aerobic
Yeast, aerobic

Itaconic acid
chemical feedstock
Itaconic Acid Production
Fermentation from glucose

- **Glucose** [g/L]
- **Itaconic acid** [g/L]

**Conditions**
- Batch (without pH-control)
- Mineral-salt medium, P-limitation
  - pH 1.7
  - 33°C

**Result**
- Final concentration: > 80 g/L IA
- Max. productivity: > 1 g/(L·h)
- Yield: 0.6 g/g = 83% of Theory

**Other substrates?**

- **Glucose** [g/L]
- **Saccharose**
- **Glycerol**
- **Lactose**

**Conditions**
- Batch (without pH-control)
- Mineral-salt medium, P-limitation
  - pH 1.7
  - 33°C

**Result (for Glucose)**
- Final concentration: > 80 g/L IA
- Max. productivity: > 1 g/(L·h)
- Yield: 0.6 g/g = 83% of Theory
Innovative Technologies
Chemical catalysis with gold catalysts

Sugar acids
Complexing agents
Ingredients for cosmetics, food, pharmaceuticals
Functional Food

Sugar
Glucose
Gluconsäure

Gold catalyst supported

T = 40-60°C
pH = 7-9

Oxygen

Sugar acids
Complexing agents
Ingredients for cosmetics, food, pharmaceuticals
Functional Food

Sugar acids
Complexing agents
Ingredients for cosmetics, food, pharmaceuticals
Functional Food

Oxidation of Monosaccharides
Selectivity of the gold catalyst (HPLC-data)
Processes
Oil mill, biodiesel plant

Rapeseed → Residues → Biogas → Electricity, Heat

Rapeseed meal → Fatty acids, Fats

MeOH → RME (REE), Biodiesel → Glycerol

1,3-Propanediol → Acroleine

1,2-PD + 1,3-PD → Biotensides

MeOH → RME-production

Seed oil (40...45 %) → Oil mill

90 % biodiesel

10 % glycerol

rapeseed cake (6...12 % oil)

rapeseed meal (1...2 % oil)

about 40 % protein
Biodiesel
Production capacity in Germany

Tons per year

Data: UFOP, *estimated

Price of Raw Glycerol

glycerine 80% crude

2007: < 100 €/t
1,3-Propandiol from Glycerol

- glycerol 10% (byproduct of biodiesel production)
- bacteria, anaerobic
- chemical feedstock (polymers)

1,3-Propanediol Fermentation
Strain NRRL1024 (from culture collection)

- conditions
  - fed-batch (pH-controlled)
  - mineral-salt medium + YE
  - pH 7.0
  - 35°C

- results
  - final concentration: > 72 g/L 1,3-PD
  - productivity: > 1.7 g/(L·h)
1,3-Propanediol Fermentation
Strain IK123 (from screening)

- **Conditions**
  - Fed-batch (pH-controlled)
  - Mineral-salt medium + YE
  - pH 7.2
  - 32°C

- **Result**
  - Final concentration: > 100 g/L 1.3-PD
  - Productivity: > 2 g PD/(L·h)

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1,3-Propanediol-Fermentation: Cost Reduction
Influence of glycerol and nutrients price
Processes in Future
Lignocellulose

Pretreatment

Lignocellulose → Glucose → Products

Xylose → Products

Lignin → Products

? → Biogas

Biogas → Residues, Wastewater

Electricity, Heat

Energy from Renewable Resources
Biogas

feedstock

crops

manure

residues

by-products

food- and agro-industry, e.g. fats

biogas plant

sulfur removal

reforming

reforming compression

liquid storage

gas boiler

heat

motor-CHP

electricity, heat

fuel cell

electricity, heat

fuel
Biogas Plants in Germany

Number of biogas plants in Germany from 1990 to 2006. The chart shows an increasing trend in the number of plants, with a significant jump in the last few years. The number of plants in 2006 is estimated at 3400.

Electricity from Biogas

A fuel-cell pilot plant located at the FAL is highlighted, which generates 55 PJ of gas power, equivalent to 0.85 GWh of electric power, heat, auxiliary power, and losses.

Source: German Biogas Association and own data.
Biorefineries
Manifold interactions

Biorefinery
Products
Heat, power
Fuels
Materials
Feed & Food?

Market
Consumer, Products
Heat & Power

Policy
Directions, Rules
Subsidies, Tax Benefits

Economy
Energy Situation
Prices,
Globalisation
Foreign Trade
Feedstocks

Man
Needs
Population development
Social aspects

Biomass
Yield, Quality, Price
Seasonal Availability

Auxiliaries
Energy, Seed, Fertilizer
Pest Management

Technology
Methods
Processes
Transport

Locality
Climate, Soil, Water
Infrastructure, Logistic
Industry

Thank you for your attention!