Biorefinery, the bridge between agriculture and chemistry

Greening Agriculture and Nitrogen

Copenhagen, 24 April 2013
Johan Sanders, professor Biobased Commodity Chemicals
The new challenges in a biobased Economy:

Biomass sources
- Agro-food production
- By products & waste

Logistics & storage
- NL production
- Imports

Existing conversion

Existing production

New production
- Performance materials
- Base & platform chemicals
- Performance chemicals
- Biobased energy

Biobased Products
- Biobased materials
- Bio-based chemicals
- Bio-fuels
- Bio-energy

Existing non-food:
- Paper
- Construction wood
- Additives
- Fibres/clothes
- Wood for cooking

Food
- Healthy, tasty, sufficient

Biomass production

1st

Agro logistics

Food pretreatment

Food conversion

Food production

Logistics & storage

NL production

Imports
Biomass use today and in 2050

- Food incl. feed*: 4 – 5000 Mton
- Wood, paper, cotton: 2000 Mton
- Wood for cooking: 4000 Mton
- 30% of 1000EJ in 2050 = 20 000 Mton
- All bulk chemicals in 2050: 600 (= 2000 input!)

* Excluding grass and seafood
Design rules for a sustainable Bio-economy

- Increase field yield but *keep components on the field that are required for soil fertility*
- Use all biomass components and *choose the right raw material*
- Use each component at its highest value: *(molecular) structure is much better than caloric*
- Reduce capital cost to speed up innovation and *to benefit from small scale without the disadvantages*
How do these design rules work out for N?

- Annually 140 M tonnes of NH₃ is produced worldwide
- Appr 120 Mtonnes is used as fertilizer, 10 Mtonnes as chemical feedstock
- Agriculture produces about 600M tonnes of protein (including natural protein production this is appr 3000M tonnes)
- Human population requires about 70-100M tonnes of protein
- Dependent on feeding regimes cattle get appr 4-5 times more protein than ends up in milk and meat, for pigs this is appr. 3 times. And actually is misused
- A lot of the surplus 500 M tonnes of protein is ‘misused’ as fertilizer (eg beet leaf), as feedstock for biogas(eg corn), for power generation (wheat grids), used at a too low value (most residues in animal feed), 30% of food is not consumed!
- Cattle and pigs and poultry can get much more tailored protein/ amino acids without increasing the costs

*Higher efficiency leads to lower NH₃, N₂O, NO₃ emissions*
## F - ladder

### How to get the best value from biomass?

<table>
<thead>
<tr>
<th></th>
<th>€/ton</th>
</tr>
</thead>
<tbody>
<tr>
<td>Farma</td>
<td>High</td>
</tr>
<tr>
<td>Fun</td>
<td>High</td>
</tr>
<tr>
<td>Food ingredients</td>
<td>5 - 20000</td>
</tr>
<tr>
<td>Food nutritional</td>
<td>100-500</td>
</tr>
<tr>
<td>Feed young</td>
<td>100-500</td>
</tr>
<tr>
<td>Feed pigs</td>
<td>100-300</td>
</tr>
<tr>
<td>Feed cattle</td>
<td>50-250</td>
</tr>
<tr>
<td>Functional chemical</td>
<td>500-800</td>
</tr>
<tr>
<td>Fibre</td>
<td>500</td>
</tr>
<tr>
<td>Fermentation</td>
<td>150-400</td>
</tr>
<tr>
<td>Fermentation bulk</td>
<td>100-300</td>
</tr>
<tr>
<td>Fuel</td>
<td>100-300</td>
</tr>
<tr>
<td>Fertilizer</td>
<td>+/- 200-100</td>
</tr>
<tr>
<td>Fire</td>
<td>50-150</td>
</tr>
<tr>
<td>Flare</td>
<td>0</td>
</tr>
<tr>
<td>Fill</td>
<td>+/- 300</td>
</tr>
</tbody>
</table>
Use of plant molecular structures

- N-Vinylpyrrolidone
- Acrylonitrile
- N-Methylpyrrolidone
- Diaminobutane
- Glutamic acid
# The route to NMP, new vs conventional

## New route

<table>
<thead>
<tr>
<th>Step 1</th>
<th>Step 2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Biomass</strong></td>
<td><strong>Step 1</strong></td>
</tr>
<tr>
<td>Glutamic acid</td>
<td>Glutamic acid</td>
</tr>
<tr>
<td>- CO₂ enzyme, 30 °C</td>
<td>- H₂ cat, 180-240 °C</td>
</tr>
</tbody>
</table>

## Conventional route

<table>
<thead>
<tr>
<th>Step 1</th>
<th>Step 2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gas</strong></td>
<td><strong>Step 1</strong></td>
</tr>
<tr>
<td>CH₃OH</td>
<td>CH₃OH</td>
</tr>
<tr>
<td>- H₂ cat, 90-150 °C</td>
<td>- H₂ cat, 300-550 °C</td>
</tr>
<tr>
<td>NH₃</td>
<td>NH₃</td>
</tr>
<tr>
<td>+ CH₃OH cat</td>
<td>cat 400 °C</td>
</tr>
</tbody>
</table>

Amino acids contain N and O.

- Less steps (= factories) & energy for the same product!
Biobased NMP, makes an ethanol plant profitable

500 Million liters bioethanol (~ 400 kton) = 200 M€

360 kton DDGS (~130 € / ton) = 46 M€

23 kton NMP (~2500 € / ton) = 58 M€/y
Enzymatic hydrolysis and extraction of proteins

Protein recovery after 3 hours incubation without enzymes (■) and additional by the enzymes (■) (M = meal).
Integrated conversion and separation

Anode

Cathode
Lignocellulose hydrolysate, not an ideal substrate yet

- mixing problems, low oxygen transfer, low substrate concentrations, fermentation inhibitors
- Complex: implications for product recovery
Biorefining of agricultural residues

Protein content

- 0%
- 5%
- 15%
- 35%
- 50%

Examples

- Wheat straw
- Cocoahulls, Corncobs, Sugarcane leaf
- Coffee pulp, Rape straw, Beet leaf
- Rape meal
- Soy meal

Cost (€/ton)

- 50-80
- 50-110
- 100-140
- 150-180
- 300-350
Biorefinery enables power generation at 45€/ton and high quality 2\textsuperscript{nd} generation fermentation raw materials for 200€/ton.

- Wood chips
- Straw (field)
- Straw (collected)
- Straw (washed)
- Rape meal
- Multiproduct biorefinery
protein/oil/ethanol/biogas from small scale corn-biorefinery

Less investment costs/liter ethanol than American ethanol production that operate at 200 x larger scale
Byosis/Zeafuels (Lelystad, Netherlands)
The separated components of grass value 700 – 800 €/ton as compared to 50 – 70 €/ton raw materials

- Protein / Amino acids 20% (1000)
- Polysaccharides 15% (1500)
- Fibers 30% (100)
- Oligo-saccharides 3% (1500)
- Lipids 3% (2000)
- Organic acids 5% (2000)
- Mono/di-saccharides 15% (150)
- Minerals 10% (500-1000)
- Dry substance 10-20%
Mobile grass refinery unit Grassa (the Netherlands)

Grass juice concentrate → Grass juice → compound feed → HTU-Biofuel

Protein:
- Green grass protein
- White grass protein

Fibers:
- Construction material + paper
- Polymer extrusion products

Grass protein (products)

Ethanol
Coupling two chains can further optimize values

Raw materials
From abroad

Field

Manure

Now

Biorefinery

Protein

Maize

Grass

Manure

Energy

Fibres

Raw materials
From abroad

Manure

Reduction of soy import from Brazil reduces ILUC and manure problem and creates regional income
Improving N efficiency and land use

![Graph showing N efficiency and land use](image)
conclusions

• Use of all biomass components at their highest value enables even to compete with oil, coal and natural gas

• Use of molecular structures needs much less capital and energy

• Economy of scale is loosing its competitiveness

• Many economic ways to valorise excess of N are facilitated by the Bio based economy
Decentrale optimalisatie van raapschilfers

 oliemolen → raapschroot raapschilfers → verdun loog → Eiwitoplossing kalium, opgeloste stof → zuur, 90°C → K, organische stof → veld

 onopgeloste vezels → 95°C → ontsloten vezels (50% ds) → rundvee

 eiwit (50% ds) → varkens
Example: Glutamic acid and other aminoacids in byproduct streams

Amino acids in residual proteins

Maize DDGS
Wheat DDGS
Sugarbeet vinasse
Sugarcane vinasse
Rapeseed meal
Soybean meal
Jatropha meal
Palmoil meal
Chlorella microalgae

- Ala
- Pro
- Glu
- Asp
- Tyr
- Phe
- Ser
- Gly
- Arg
- His
- Val
- Leu
- Ile
- Trp
- Thr
- Cys
- Met
- Lys
Bulk chemicals from Biomass: e.g. lysine

<table>
<thead>
<tr>
<th>fermentation</th>
<th>direct plant products</th>
</tr>
</thead>
<tbody>
<tr>
<td>State of the art ADM, Degussa, Ajinomoto</td>
<td>Plant GMO</td>
</tr>
<tr>
<td>Anaerobic fermentation</td>
<td>Biorefinery from Plant residues</td>
</tr>
</tbody>
</table>

- **Fossil chemical reference**: 18 GJ
- **State of the art ADM, Degussa, Ajinomoto**:
  - Fossil raw materials (fermentation): 21 GJ/ton €/ton
  - Biomass raw materials
  - Capital (fermentation): 37 GJ/ton €/ton
  - Capital (recovery): 3 GJ/ton €/ton
- **Anaerobic fermentation**:
  - Fossil raw materials (fermentation): 300 GJ/ton €/ton
  - Biomass raw materials
  - Capital (fermentation): 500 GJ/ton €/ton
  - Capital (recovery): 6 GJ/ton €/ton
- **Plant GMO**:
  - Fossil raw materials (fermentation): 350 GJ/ton €/ton
  - Biomass raw materials
  - Capital (fermentation): 1345 GJ/ton €/ton
  - Capital (recovery): 110 GJ/ton €/ton
- **Biorefinery from Plant residues**:
  - Fossil raw materials (fermentation): 110 GJ/ton €/ton
  - Biomass raw materials
  - Capital (fermentation): 620 GJ/ton €/ton
  - Capital (recovery): 70 GJ/ton €/ton
- **Fossil raw materials (recovery)**:
  - 18 GJ/ton €/ton

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The Chemical Products of the Port of Rotterdam
How to reduce the extraction volume?

- **Fixed volume:**  
  - t: 2h; T: 95°C;  
  - Amount of NaOH: 4mmol/g  
- **Variable volume:** v/w ratio

**Critical parameter:**

Alkaline Amount! = pH \* v/w

Combination of 8ml/g with 0.4mmol/ml NaOH:

- High protein yield (>85%)
- 4 times less in heating cost
- High protein concentration (30mg/ml)
- High concentration of other constituents

--- Fixed [NaOH]  
— Fixed amount of NaOH
Small scale biorefinery reduces transport cost and seasonality.

**Fields**
- Present: 100%

**Farm**
- Present: 100%
  - Return flow: 10%

**Processing**
- Present: 100%
  - Concentration: 100%
  - Fermentation: 100%

**Concept**
- Small scale processing: 100%
  - Return flow: 70%

**Wageningen University**

**Additional Information**
- 30%
Grassa Process scheme

8 ton freshweight leaf/ hour
Mobile containers

Grassa Process scheme

8 ton freshweight leaf/ hour
Mobile containers

Grassa Process scheme

8 ton freshweight leaf/ hour
Mobile containers

Grassa Process scheme

8 ton freshweight leaf/ hour
Mobile containers
Appendix 1: Critical parameters

Tested the collective influence on protein extraction yield by fixing two parameters

- Fixed:
  - [NaOH]: 0.1N
  - v/w ratio: 40

- Variables:
  - T(25-100 °C)
  - t (0.5-24 h)

- Fixed:
  - T: 80 °C
  - v/w ratio: 40

- Variables:
  - [NaOH]: 0-0.1N
  - t: 0.5-24h

- Fixed:
  - t: 4h
  - v/w ratio: 40

- Variables:
  - T: 25-100 °C
  - [NaOH]: 0-0.1N

When extraction time is longer than 2h, Temperature and [NaOH] are critical parameters
## Economie

<table>
<thead>
<tr>
<th>Kosten</th>
<th>Inkomsten</th>
</tr>
</thead>
<tbody>
<tr>
<td>gras+ maai/haksel+ energie</td>
<td>85</td>
</tr>
<tr>
<td>arbeid</td>
<td>42</td>
</tr>
<tr>
<td>transport en droogkosten</td>
<td>35</td>
</tr>
<tr>
<td>chemicals</td>
<td>60</td>
</tr>
<tr>
<td>overig</td>
<td>15</td>
</tr>
<tr>
<td><strong>totaal</strong></td>
<td><strong>237</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Marge</th>
<th><strong>Payback time</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>3.2 jaar</strong></td>
</tr>
</tbody>
</table>

| Capaciteit                                                           | 8000 ton/jaar      |
| investering                                                         | 1000000            |

| Absolute marge                                                      | 312000 €/jaar      |
Achterhoek produceert eigen diervoeder uit gras en mais en reduceert mestpobleem

Maak eigen eiwit rijk veevoer i.p.v. soja import

Bioraffinage geeft een betere verhouding N en energie
Kleine schaal en nat veevoer mogelijk
-houdbaarheid
-vervoerskosten
Total crop yields

Wet Weight and Dry Weight Yields

- **Cassava**
- **Grass**
- **Lucerne**
- **Maize**
- **Oil palm**
- **Potato**
- **Rapeseed**
- **Sorghum**
- **Soya bean**
- **Sugar beet**
- **Sugar cane**
- **Sunflower**
- **Switchgrass**
- **Tobacco**
- **Wheat**
- **Willow tree**

**Tons per hectare (ton/ha)**
- **Wet Weight**
- **Dry Weight**

**Total Biomass Production**
**Best Practice Yields**

Above 30ton/ha/a dry weight = Fantastic
Above 20ton/ha/a dry weight = Great
Above 10ton/ha/a dry weight = Good
Our daily food needs a twenty fold higher energy input

2500 kcal/day = 55 PJ
Cyanophycin mainly in cyanobacteria as nitrogen and energy reserve material

= Asp + Arg

Granule 35% (wt/wt) and slow growth

Ethanol and Cyanophycin building blocks from yeast: two products for the price of one
N-chemicals from cyanophycin

Focus:
- cyanophycin hydrolysis
- α-decarboxylation of L-aspartic acid
- L-arginine hydrolysis
- L-ornithine decarboxylation

poly-L-aspartic acid + H₂O → L-aspartic acid
L-aspartate α-decarboxylase → β-alanine → acrylamide

poly-L-aspartic acid

L-arginine + H₂O → urea
L-ornithine + H₂O → 1,4-diaminobutane → nylon-4,6

Biomass → cyanophycin

Nylon-4,6 hydrolysis

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