Biorefinery, the bridge between agriculture and chemistry
Opportunities for the Biobased industry

Bioeconomy in Argentina: Present and Future
Buenos Aires, 22 March 2013
Johan Sanders, professor Biobased Commodity Chemicals
The New Biomass value chain by biorefinery:

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

**Logistics & storage**
- NL production
- Imports

**1st Agro logistics**
- Food pretreatment
- Food conversion
- Food production

**Food**
- Healthy, tasty, sufficient

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

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

**BIOMASS**
- Base & platform chemicals
- Performance chemicals
- Bio Energy

**Existing conversion**
- New production

**Existing production**
- Imports
### Biomass use today and in 2050

<table>
<thead>
<tr>
<th>Category</th>
<th>Mton</th>
</tr>
</thead>
<tbody>
<tr>
<td>Food incl. feed*</td>
<td>4 – 5000</td>
</tr>
<tr>
<td>Wood, paper, cotton</td>
<td>2000</td>
</tr>
<tr>
<td>Wood for cooking</td>
<td>4000</td>
</tr>
<tr>
<td>30% of 1000EJ in 2050=</td>
<td>20 000</td>
</tr>
<tr>
<td>All bulkchemicals in 2050</td>
<td>600 (= 2000 input!)</td>
</tr>
</tbody>
</table>

* Excluding grass and seafood
How to compete with fossil under sustainable conditions?

● 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
● Reduce integral costs by integrating process steps
How biomass can best compete with fossil feedstocks

Value of biomass is **10 times** higher as chemical building block than to use it for biogas or bio-electricity
## F - ladder

<table>
<thead>
<tr>
<th>Item</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>

**How to get the best value from biomass?**
Good use of biomass?

Value of glycerol: €/GJ

- Epichlorohydrin: 30 - 40
- Transportfuel: 10
- Electricity: 3

Glycerol 25.3 GJ/tonne

Per GJ product ca 0.65 GJt input can be saved
Epichlorohydrin

Solvay ‘Epicerol’ process: glycerol to epichlorohydrin

Price: € 1300 - 1500 per tonne

Volume: 0.5 mln tonnes per annum
Use of plant molecular structures

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

**New route**

- **Biomass**
  - hydrolysis, separation

  Glutamic acid

  - step 1: $\text{COOH} \xrightarrow{- \text{CO}_2 \text{ enzyme, } 30 ^\circ \text{C}} \text{NH}_2\text{COOH}$
  - step 2: $\text{NH}_2\text{COOH} \xrightarrow{+ \text{CH}_3\text{OH \ cat, } 250 ^\circ \text{C}} \text{NMP}$

**Conventional route**

- Gas $\xrightarrow{\text{cat, } 90-150 ^\circ \text{C}}$ CH$_3$OH $\xrightarrow{+ \text{H}_2 \text{ cat, } 80 ^\circ \text{C}}$ HO-C=C-OH $\xrightarrow{\text{cat, } 180-240 ^\circ \text{C}}$ HO-C=C-COOH

  - $\text{N}_2 + 3 \text{H}_2 \xrightarrow{\text{cat} \ 300-550 ^\circ \text{C} \ 150-250 \text{ bar}} \text{NH}_3$ $\xrightarrow{+ \text{CH}_3\text{OH \ cat} \ 400 ^\circ \text{C}}$ CH$_3$NH$_2$

  - CH$_3$NH$_2$ $\xrightarrow{\text{200-350 ^\circ \text{C} \ 100 \text{ bar}}}$ NC$_3$H$_7$

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) = \(200\text{ME}^\text{€}\)

360 kton DDGS (~130 €/ton) = \(46\text{ME}^\text{€}\)

23 kton NMP
(~2500 €/ton) = \(58\text{ME}^\text{€}/\text{y}\)
3D-foamed polylactic structures (Wageningen UR)

- Expandable bead technique
  - Good cell structure
  - Density <30 g/l
Total crop yields

**Wet Weight and Dry Weight Yields**

- Total Biomass Production
- Best Practice Yields

Above 30 ton/ha/a dry weight = Fantastic
Above 20 ton/ha/a dry weight = Great
Above 10 ton/ha/a dry weight = Good

Cassava, Grass, Lucerne, Maize, Oil palm, Potato, Rapeseed, Sorghum, Soya bean, Sugar beet, Sugar cane, Sunflower, Switchgrass, Tobacco, Wheat, Willow tree
Proportion of constituents

- Cassava
- Grass
- Lucerne
- Maize
- Oil Palm
- Potato
- Sorghum
- Soya Beans
- Sugar Beet
- Sugar Cane
- Sunflower
- Switchgrass
- Tobacco
- Wheat
- Willow Tree

- Fat
- Protein
- Lignin
- Complex Carbohydrates (C.C.)
- Simple Carbohydrate (S.C.)
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..

<table>
<thead>
<tr>
<th>Protein content</th>
<th>0</th>
<th>5 %</th>
<th>15 %</th>
<th>35 %</th>
<th>50 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Examples</td>
<td>Wheatsstraw</td>
<td>cocoahulls, Corncobs, Sugarcane leaf</td>
<td>Coffee pulp, Rape straw, Beet leaf</td>
<td>Rape meal</td>
<td>Soy meal</td>
</tr>
<tr>
<td>Cost (€/ton)</td>
<td>50-80</td>
<td>50-110</td>
<td>100-140</td>
<td>150-180</td>
<td>300-350</td>
</tr>
</tbody>
</table>
Biorefinery enables power generation at 45€/ton and high quality 2\textsuperscript{nd} generation fermentation raw materials for 200€/ton.
Integrated production of chemicals & power

Rape meal → Protein + K

NaOH →

Agricultural residues

Ca(OH)₂ → 95°C 1 day → Fibres

Amino acids → Lignocellulose → Ferm → Amino acids + phosphate

Cellulase

Ca(lactate)₂ → Recalc.lignocellulose → heat → Prec → Electricity

Ethanol

Recalcitrant Lignocellulose → CHP

Waste paper/CaCO₃ → heat

Heat

CaO
## Income per tonne rape meal

<table>
<thead>
<tr>
<th>Product</th>
<th>Mass</th>
<th>Income €</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protein</td>
<td>300</td>
<td>240</td>
</tr>
<tr>
<td>Amino acids</td>
<td>100</td>
<td>30</td>
</tr>
<tr>
<td>Animal feed</td>
<td>200</td>
<td>100</td>
</tr>
<tr>
<td>Ethanol</td>
<td>(200)</td>
<td>(20)</td>
</tr>
<tr>
<td>Fibres</td>
<td>100</td>
<td>20</td>
</tr>
<tr>
<td>PO₄</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>Lignocellulose</td>
<td>200</td>
<td>10</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>920</strong></td>
<td><strong>330-410</strong></td>
</tr>
</tbody>
</table>

Costs rape meal = 180 €/tonne (November 2011)
6 Mtonnes oil seed meal will enable 2.5 TWh
(3 Mtonnes of protein, 1.5 Mton fermentation raw materials and 0.75 Mton fibers)

World production of:
Rape meal 42 Mtonnes/y
Sunflower meal 22 Mtonnes/y
Palm kernel meal 130 Mtonnes/y

Dutch import of seeds and meals is 7.8 Mtonnes/y
## Small scale can be competitive

<table>
<thead>
<tr>
<th></th>
<th>Output (kton/y)</th>
<th>Investment (M€)</th>
<th>Turnover (M€/y)</th>
<th>Investment/ton (€)</th>
<th>Turnover/investment (€/€)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neste Oil</td>
<td>800</td>
<td>760</td>
<td>480</td>
<td>950</td>
<td>0.63</td>
</tr>
<tr>
<td>2nd generation ethanol</td>
<td>175</td>
<td>300</td>
<td>87</td>
<td>1700</td>
<td>0.30</td>
</tr>
<tr>
<td>2nd generation multi product</td>
<td>30</td>
<td>15</td>
<td>12</td>
<td>500</td>
<td>0.8</td>
</tr>
</tbody>
</table>
Small scale biorefinery reduces transport cost and seasonality

Fields
Present
 100%

Farm
Return flow 10%

Processing
100%
concentration
fermentation

Concept
100%
Small scale processing

Return flow 70%

30%
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.
Mobile grass refinery unit Grassa (the Netherlands)

Grass protein (products)
- White grass protein
- Green grass protein

Grass juice
- Concentrate
- Ethanol

Protein
- Compound feed

Fibers
- HTU-Biofuel
- Construction material + paper
- Polymer extrusion products
Mobile Cassava starch refinery in Africa
Bio-commodities is a necessity for the industry to start!

- Pyrolysis oil
- Torrefaction pellets
- HTU biocrude
- Non purified syngas
- (hydrous) ethanol
- lactate
- Biodiesel
- Pure plant oil
- Rape seed
- Soy beans
- Cereal grains
- Crude protein (hydrolysates)
Carbohydrates as the building blocks

Why do aerobic fermentations have low $Y_s$

- Lysine: 0.45 g/g
- Glutamic acid: 0.48 g/g

While anaerobic fermentations have high yields

- Lactate: 0.95 g/g
- Ethanol: 0.95 J/J
Anaerobic fermentations

Productivity: up to 5 times higher as compared to aerobic

Less cooling equipment
No compressor
Much less stirring

Leading to much lower capital costs per ton of product
Bulk chemicals from Biomass: e.g. lysine

<table>
<thead>
<tr>
<th></th>
<th>State of the art ADM, Degussa, Ajinomoto</th>
<th>Anaerobic fermentation</th>
<th>Plant GMO</th>
<th>Biorefinery from Plant residues</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fossil raw materials (fermentation)</td>
<td>21</td>
<td>37</td>
<td>215</td>
<td>500</td>
</tr>
<tr>
<td>Fossil raw materials (recovery)</td>
<td>7</td>
<td>37</td>
<td>300</td>
<td>500</td>
</tr>
<tr>
<td>Capital (fermentation)</td>
<td>3</td>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Capital (recovery)</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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conclusions

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

• Use of molecular structures needs much less capital and energy

• Anaerobic fermentation gives high substrate yield and low capital costs

• Economy of scale is loosing its competitiveness
Why soy?

- Important food crop – can we use it also for non-food? Biorefinery is the key: co-production of food/feed/other products
- Soy is a good binder of Nitrogen from air
- Crops available both natural and genetically modified
- Substantial crop: 91 mio ha globally, 2,2 ton/ha soy seeds
  - AND
- 6 ton soy-hay and soy rests per ha: valuable components!
- 1,7-3,4 ton soy/ha normal conditions; 4 ton/ha optimal conditions
Soy biorefinery

• Soy: food and feed
• Decentral (on spot) pressing of waste, selling the protein juices
• Sugars: more centralised production of ethanol through fermentation
• Ligno cellulose: second generation bioethanol
  ▪ Biorefinery gives access to chemical industry and higher outputs in terms of money.
Soy for example

- Soy contains:
  - celluloses 17%
  - hemi celluloses 4%
  - sugars 7%
  - proteins 41%
  - oil 18%

- Soy seeds: only 1/3 of total dry plant mass =>
- plant adds enormous quantities of valuable products
Summary

- Use of ag residues (soyleaf/stems, cane-leaf, etc) for the production of protein, animal feed and bulkchemicals
- Protein hydrolysates and the crystallization of pure aminoacids for feed, chemicals and pharma
- Yeast Coproduction of chemicals and ethanol
- Small scale biorefining of rapeseed/ Jatropha/ oil crops in rural areas for the production of biodiesel, protein and minerals
- Small scale production of ethanol and protein from starchy crops
- Low capital and operational cost anaerobic sugar fermentations to bulkchemicals
- In planta (Cane/ Soy/..) production of bulkchemicals by GMO
Ethanol and Cyanophycin building blocks from yeast: two products for the price of one

Cyanophycin mainly in cyanobacteria as nitrogen and energy reserve material

= Asp + Arg

Granule 35% (wt/wt) and slow growth
Our daily food needs a twenty fold higher energy input

**635PJ**
- Net Import 160
- Dutch Agriculture 475

**575PJ**
- Food Industry 150
- Household 165
- Transportation Food 100
- Greenhouses/Food 100
- Other Agriculture 60

2500 kcal/day = 55 PJ

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Decentrale optimalisatie van raapschilfers

1. Oliemolen
2. Raapschroothoudende raapschilfers
3. Verdund loog
4. Eiwitoplossing kalium, opgeloste stof
5. Zuur, 90°C
6. Eiwit (50% ds)
7. Organische stof
8. Veld

- 95°C
- Onopgeloste vezels
- Ontsloten vezels (50% ds)
- Rundvee
- Varkens
Example: Glutamic acid and other amino acids in byproduct streams

Amino acids in residual proteins

- Maize DDGS
- Wheat DDGS
- Sugarbeet vinasse
- Sugarcane vinasse
- Rapeseed meal
- Soybean meal
- Jatropha meal
- Palm oil meal
- Chlorella microalgae

Amino acids: Ala, Pro, Glu, Asp, Tyr, Phe, Ser, Gly, Arg, His, Val, Leu, Ile, Trp, Thr, Cys, Met, Lys
The Chemical Products of the Port of Rotterdam
Bulkchemicals from Waste 2 Resource:
Upstream integration, downstream benefits
Brazil from feed to doubled feed + biobased

<table>
<thead>
<tr>
<th></th>
<th>Soy</th>
<th>Grass</th>
<th>Cane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protein</td>
<td>24 Mton</td>
<td>24 Mton</td>
<td>36 Mton</td>
</tr>
<tr>
<td>Biodiesel</td>
<td>12 Mm³</td>
<td>36 Mm³</td>
<td>6 Mm³</td>
</tr>
<tr>
<td>Cattle feed</td>
<td>24 Mton</td>
<td>24 Mton</td>
<td>12 Mton</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Mton</th>
<th>€/ton</th>
<th>M€</th>
<th>PJ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protein</td>
<td>24</td>
<td>300</td>
<td>7200</td>
<td>420</td>
</tr>
<tr>
<td>Biodiesel</td>
<td>12</td>
<td>400</td>
<td>4800</td>
<td>420</td>
</tr>
<tr>
<td>Cattle feed</td>
<td>24</td>
<td>25</td>
<td>600</td>
<td>420</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>12.240</td>
<td>4% of GNP</td>
</tr>
<tr>
<td>€/ha = 510</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</table>

<table>
<thead>
<tr>
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<th>Grass</th>
<th>Cane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protein</td>
<td>18 Mton</td>
<td>42 Mton</td>
<td>40 Mton</td>
</tr>
<tr>
<td>Biodiesel</td>
<td>9 Mm³</td>
<td>36 Mton</td>
<td>6 Mm³</td>
</tr>
<tr>
<td>Cattle feed</td>
<td>18 Mton</td>
<td>25 Mton</td>
<td>12 Mton</td>
</tr>
<tr>
<td>Pig feed</td>
<td>24 Mton</td>
<td>100 Mton</td>
<td>500 Mton</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>12.925</td>
</tr>
<tr>
<td>€/ha = 1219</td>
<td></td>
<td></td>
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<table>
<thead>
<tr>
<th></th>
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<tr>
<td>Protein</td>
<td>12 Mton</td>
<td>40 Mton</td>
<td>36 Mton</td>
</tr>
<tr>
<td>Biodiesel</td>
<td>6 Mm³</td>
<td>6 Mton</td>
<td>4 Mton</td>
</tr>
<tr>
<td>Bioethanol</td>
<td>72 Mton</td>
<td>200 Mton</td>
<td>500 Mton</td>
</tr>
<tr>
<td>Cattle feed</td>
<td>36 Mton</td>
<td>25 Mton</td>
<td>12 Mton</td>
</tr>
<tr>
<td>Pig feed</td>
<td>24 Mton</td>
<td>100 Mton</td>
<td>4 Mton</td>
</tr>
<tr>
<td>Chemicals</td>
<td>12 Mton</td>
<td>500 Mton</td>
<td>600 Mton</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>38100</td>
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<tr>
<td>€/ha = 1588</td>
<td></td>
<td></td>
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J.W.A. Langeveld and J.P.M. Sanders in Langeveld et al, The Biobased economy, Earthscan, 2010; chapter 21
Economics food chain (sugar beet)

Biomassa-grondstof (65 ton bieten per ha a €27 ton)

1755 €/ha

Suiker (100% ds)
10 ton/ha á €410/ton

Betacal (65% ds)
4 ton/ha á €20

Perspulp (28% ds)
11 ton/ha á €20/ton

Melasse (80% ds)
2.4 ton/ha á €90/ton

Voedsel

4100 €/ha

Grondverbeteraar

80 €/ha

Laagw. veevoer

220 €/ha

Veevoer of EtOH

216 €/ha

4616 €/ha
Economics biobased chain (Sugar beet)

- Biomassa-grondstof (65 ton bieten per ha a €27 ton)
  - Blad (12% ds) 40 ton/ha 1755 €/ha
  - HW Chemicalien 1.3 ton/ha á 800 €/ton
  - Perspulp (28% ds) 11 ton/ha

- Betacal 4 ton/ha á €20

- Melasse (80% ds) 14.9 ton/ha

- 5470 kg (6924 L) EtOH

- 1016 kg (1286 L) EtOH

- 31 GJ (8.6 MWh) stroom + 70 GJ warmte (~2690 m³ gas)

- Grondverbeteraar 80 €/ha

- Chemie (58 GJ) 1040 €/ha

- Ethanol (8210 L EtOH/ha; a €0.35/L 174 GJ/ha) 2874 €/ha

- Stroom (€0.032/kWh) 275 €/ha

- Warmte (€6.71/GJ) 469 €/ha

- 4738 €/ha
Mobile Cassava starch refinery in Africa