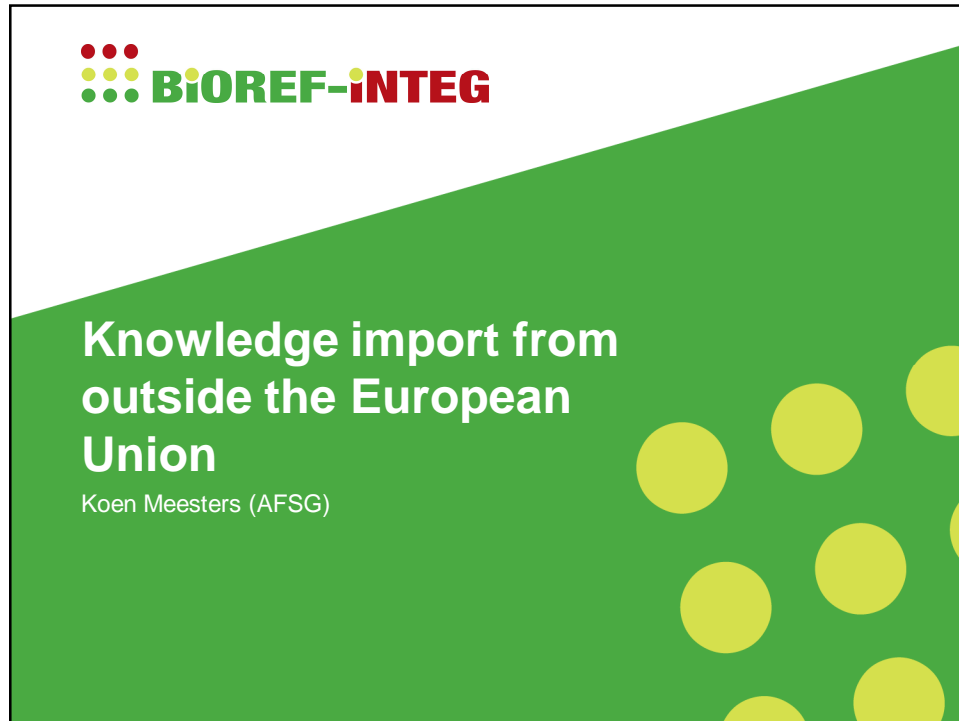


**Knowledge import from
outside the European
Union**

Koen Meesters (AFSG)



Introduction

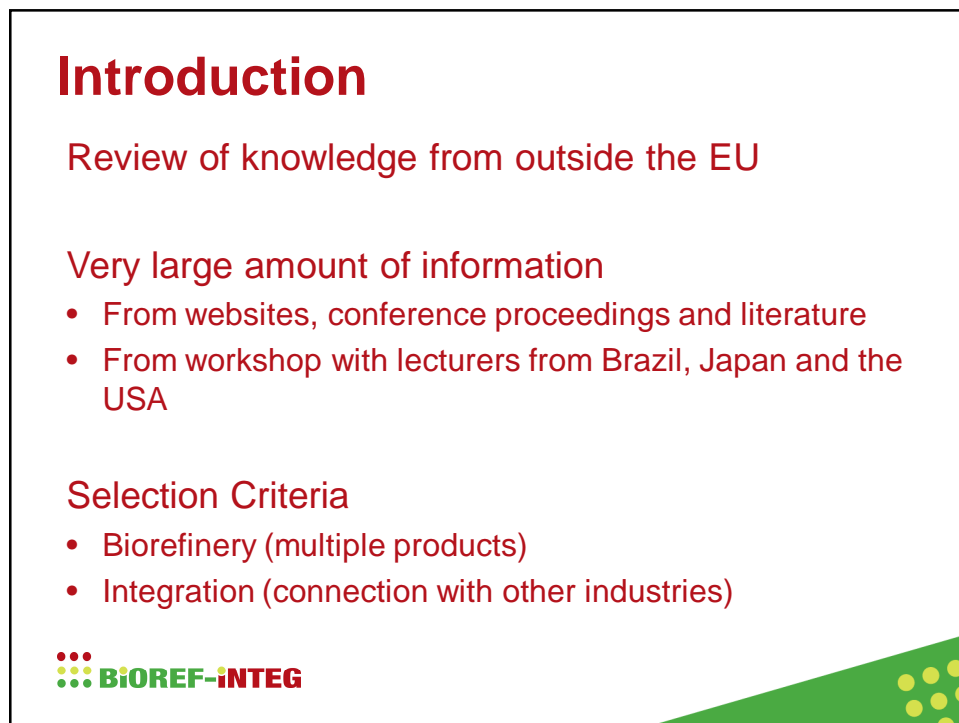

Review of knowledge from outside the EU

Very large amount of information

- From websites, conference proceedings and literature
- From workshop with lecturers from Brazil, Japan and the USA

Selection Criteria

- Biorefinery (multiple products)
- Integration (connection with other industries)



Bio Ethanol

Problems:

- Low value products (ethanol, DDGS)
- High input of capital and (fossil) energy

Focus of biorefinery and integration research often on:

- production of **more** ethanol from lignocellulosic feedstocks (corn stover)
- use of stover as a fuel to **reduce** fossil energy demand

Problems not solved / heat integration only

Other solutions will be presented



EnerGenetics

Process:

- Start with genetic crop that produces nutraceuticals
- Use wet micro-milling
 - Producing protein isolate
 - Leaving fibres in solid phase
- Ethanol is a by-product
- Use membranes instead of distillation



EnerGenetics

5 problems tackled:

- High added value products
 - Nutraceuticals
 - Protein isolate (sold @ 6 USD/kg)
 - Fibres in solid phase (no DDGS)
- Ethanol is a by-product
- Less energy demand (through membranes)
- No need for large scale processes
 - Less transport costs



Centre for Crops Utilization Research (CCUR, Iowa State University)

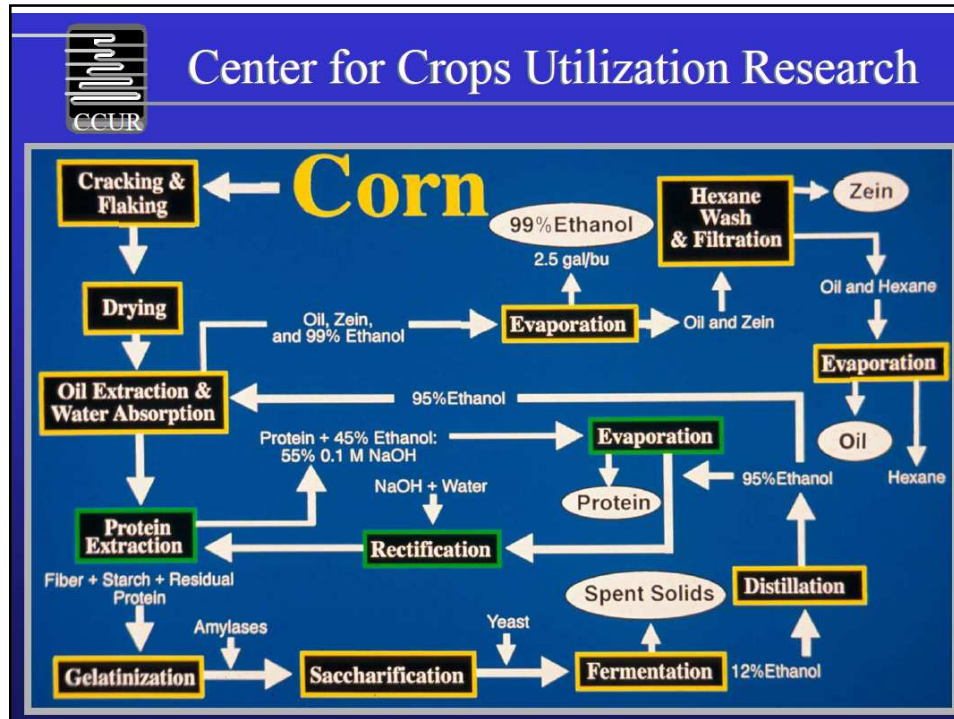
Use wet milling technology

Produce multiple products from corn:

- Zein (a high value protein)
- Oil
- Protein
- ...and ethanol

Instead of only ethanol and DDGS





Lignocellulose as a substrate

Lignocellulose consists of mainly 3 components:

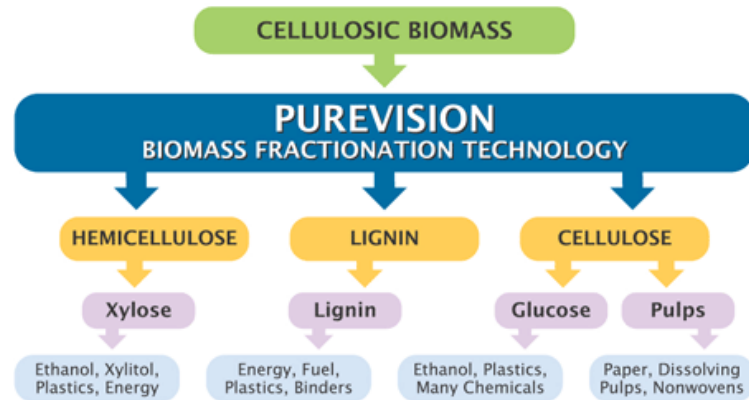
- Lignin
- Cellulose
- Hemi cellulose

Separation is difficult:

- Often rough conditions applied (side products formed)
- Low yields (high impurities)
- High demand for chemicals (large waste streams)

PureVision

Fractionation of lignocellulosic biomass:



 **BiOREF-INTEG**

PureVision:

- Fractionation via Counter Current Extraction
 - Hot water → hemicelluloses
 - High pH → lignin
 - Left → cellulose
- Patent: WO 2008/019228jhg

 **BiOREF-INTEG**

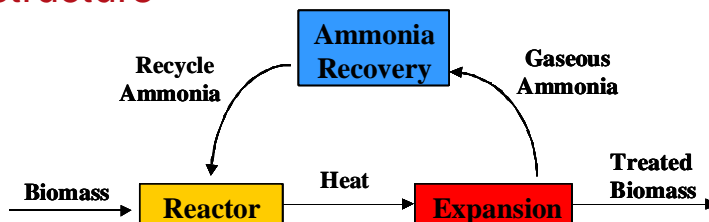
PureVision tackles 5 general problems

- Unwanted side products
→ Mild conditions
- High usage of chemicals
- Low yields
- Low concentrations
- Low purities
→ Counter current extraction



AFEX (Workshop presentation by Bruce Dale)

- Ammonia Fibre EXplosion
- High temperature treatment with ammonia followed by expansion opens up biomass structure



Process

Conditions:

- 20 - 30 bar
- 70 - 140 °C
- 5 - 10 minutes

- Dry process:
 - No extra water involved (no dilution)

- Ammonia is a gas:
 - Easy recovery of chemicals



2 general problems are tackled

Lignocellulosic biomass is:

1. not accessible to cellulolytic enzymes
2. very bulky (120 kg/m³ after baling of straw)

AFEX:

1. opens up lignocellulosic complex: 90% glucan yield from cellulose after 72 hours of enzymatic treatment
2. product is easily pelletized to 400 kg/m³ (lignin serves as glue)



Advantages of AFEX

Densified biomass allows:

- Long distance transport
- Centralized large scale biorefinery

Problems tackled without running into new problems:

- Loss of chemicals (ammonia is a gas)



Ames

Biodiesel production (transesterification):

Plant oil + methanol → biodiesel + glycerol

2 problems:

- Low added value product (fuel)
- Glycerol waste



Glycerol to 1,3-propanediol



- $\text{R}_3\text{Si-H}$ as a reductant
- $\text{F}_3\text{C-COOH}$ as a catalyst

Propanediol is interesting building block for co-polymers (also 1,2-PDO, 3-HPA)

More valuable side product makes production of biodiesel profitable



Paper pulping (American Process Inc.)

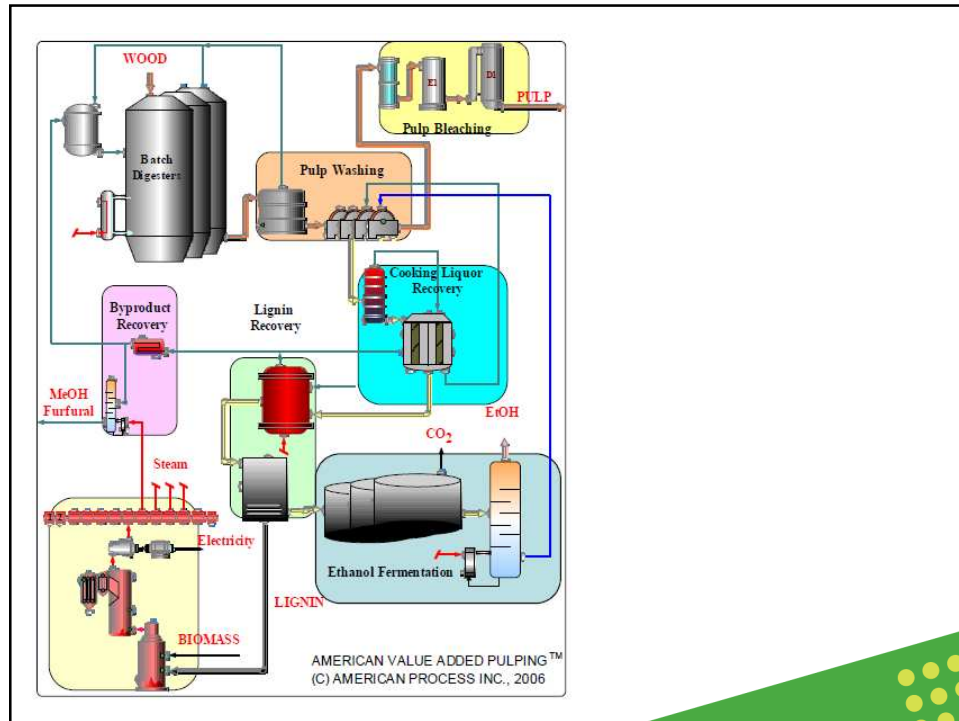
AVAP (American Added Value Pulping)

Pulping with:

- Ethanol
- Sulfur dioxide

C_5 sugars used for ethanol production





Problems solved

Not only pulp; also ethanol, methanol and furfural

Hemi cellulose is not wasted (higher yield)

Possibility for added value products from lignin

Thermal processes

Advantages:

- fast

Disadvantages:

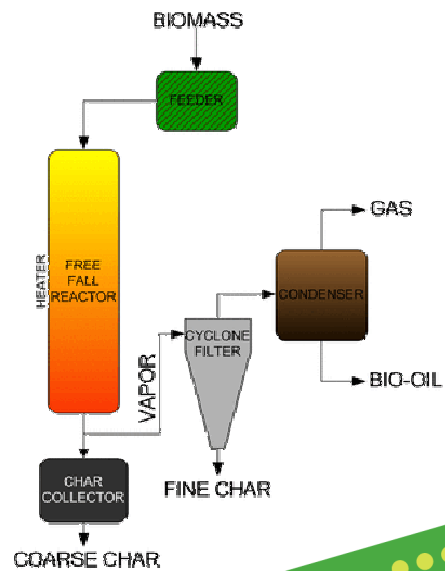
- loss of quality
- loss of mass
- high capital costs
- operational problems



Iowa State University

Problems solved:

- Clogging
- No FT needed
- Solid (densified) fuel produced
- Smaller scale = less transport



Conclusions

Biofuel production:

- High capital costs, difficult DSP, low added value

Biorefinery:

- High added value products

Integration:

- Other main products
 - Can reduce biofuel DSP costs
 - Can prevent by-products



Thanks for your attention

- Questions?



Lignocellulosic biomass

General problems:

- Low yields
- Low purities
- Low concentrations
- Rough pretreatment → unwanted side products
- High usage of energy and chemicals
- Bulky



WP leadership

- Mladjan Stojanovic has left AFSG
- Koen Meesters will take over the WP leadership



DOW

- 3.1 Analysis of conference, seminar, workshop proceedings and websites on biorefinery related information
- 3.2 Gathering information from the IEA bioenergy implementing agreement
- 3.3 Organising an internal workshop



Finished

- Workshop (WP 3.3)

Today

- Analysis of knowledge from outside EU
 - Koen Meesters
 - Work executed by Mladjan Stojanovic and Laura Bermudez
- Knowledge from EIA
 - René van Ree

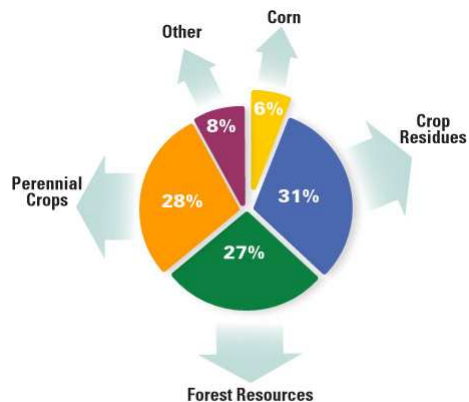


Knowledge import from outside EC

- A list of symposia, websites etc. was generated
- This list is rather boring; it will be made available to you all
- Today: A 'Pick of the day', some trends, some insights, not a complete review
- Put into European perspective



Biofuel Resources USA



Projected U.S. Biofuel Sources

Source: Biomass as Feedstock for a Bioenergy and Bioproducts Industry: Technical Feasibility of a Billion Ton Annual Supply, 2005, DOE and USDA.

- Large focus on ethanol from corn today
- This will change!
- Lignocellulosic biomass will be used



Developments on ethanol production

- Use of wood as fuel for distillation
- Use of straw or corn cobs as fuel for distillation
- Around 15% of straw is needed for distillation
- Distillation energy is high, a renewable resource for this energy leads to large improvement of GHG-efficiency



Ethanol from cellulosic materials

- More ethanol from corn cobs and corn fiber (POET)
- C₅ to ethanol
 - Zymomonas Mobilis (DuPont)
 - ABNT
 - Escherichia Coli (Mexico, Japan)
- Cellulose to ethanol 'bug'
 - Isolated from forest (Massachusetts, USA)
- Ethanol from lignocellulosic wastes (Range Fuels, Verenium)



Straw refinery/prehydrolysis

- Consecutive extraction of straw with hot water with dilute acid (@210 °C) and alkaline solution
- Hemicellulose and lignin extracted, cellulose remains
 - ABNT
 - Simulated Moving Bed extraction (PureVision)
- Concentrated sulfuric acid treatment (BlueFire), focus on reduction of sulfuric acid



Europe

- Primary goal of biofuels is GHG mitigation
- Food/feed discussion
- Concern about indirect land use change
- Therefore GHG efficiency (expressed in $\text{tonCO}_2/(\text{ha}\cdot\text{yr})$) is crucial
- Lignocellulosic materials and wastes: no land use change: far better GHG efficiency than plant cultivations

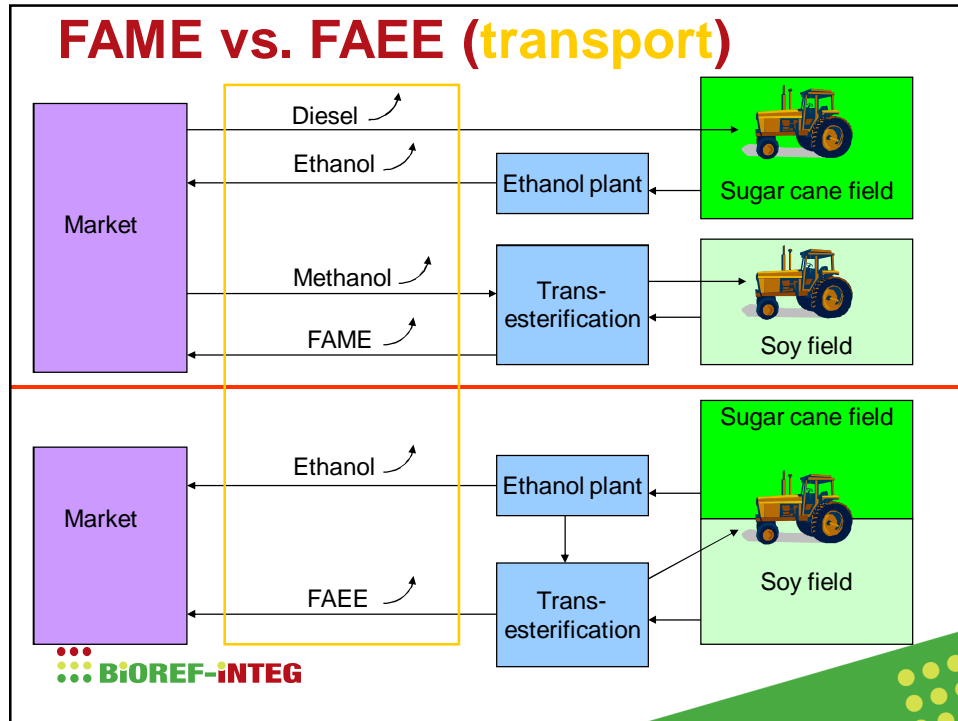


'Novel' products

- FAEE
- Alkenes
- PHA
- Adhesives, elastomers and foams

Ethanolysis

- Use of ethanol instead of methanol for transesterification
- Production of FAEE instead of FAME
- Case in Brazil



Advantages

- Less transport of diesel
- No transport of methanol
- Less transport of ethanol
- Less transport of biodiesel,
- 100% renewable biodiesel

In Europe methanol is very cheap, transport distances are shorter → not as interesting

Ethenolysis

Conversion of FAME to alkene and methylalkene-ester



- Cargill, Caproleic acid production
- Other high value products
- In Europe only attractive if renewable chemicals are rewarded



Others

- Kernel, germ, fiber and endosperm fractionation (ICM)
- Corn oil from DGS (VeraSun)
- PHA from corn starch (Metabolix/ADM)
- Adhesives, elastomers and foams (Rohm & Haas Company)



Thermal processes

- Combustion
- Pyrolysis
- Thermo-chemical liquefaction (HTU)
- GTL (Gasification, FT synthesis)

- Thermo-chemical processes might complement biological pathways (lignin)

- These processes might overtake biological pathways (especially looking at fast developments of electric car technology)



Densifying of straw

- Transport of bulky materials (straw) is expensive
- Densifying at the spot
 - Briquetting (China)
 - Torrefaction (production of char)
 - Pyrolysis (production of oil)

- Europe: also valid for thinnings, tops and branches



Lignocellulosic biomass

General problems:

- Low yields
- Low purities
- Low concentrations
- Rough pretreatment → unwanted side products
- High usage of energy and chemicals
- Bulky