Lignocellulose to bioethanol

R&D project in The Netherlands

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Contents

1. **Current production of bioethanol**
2. **Bioethanol from lignocellulose**

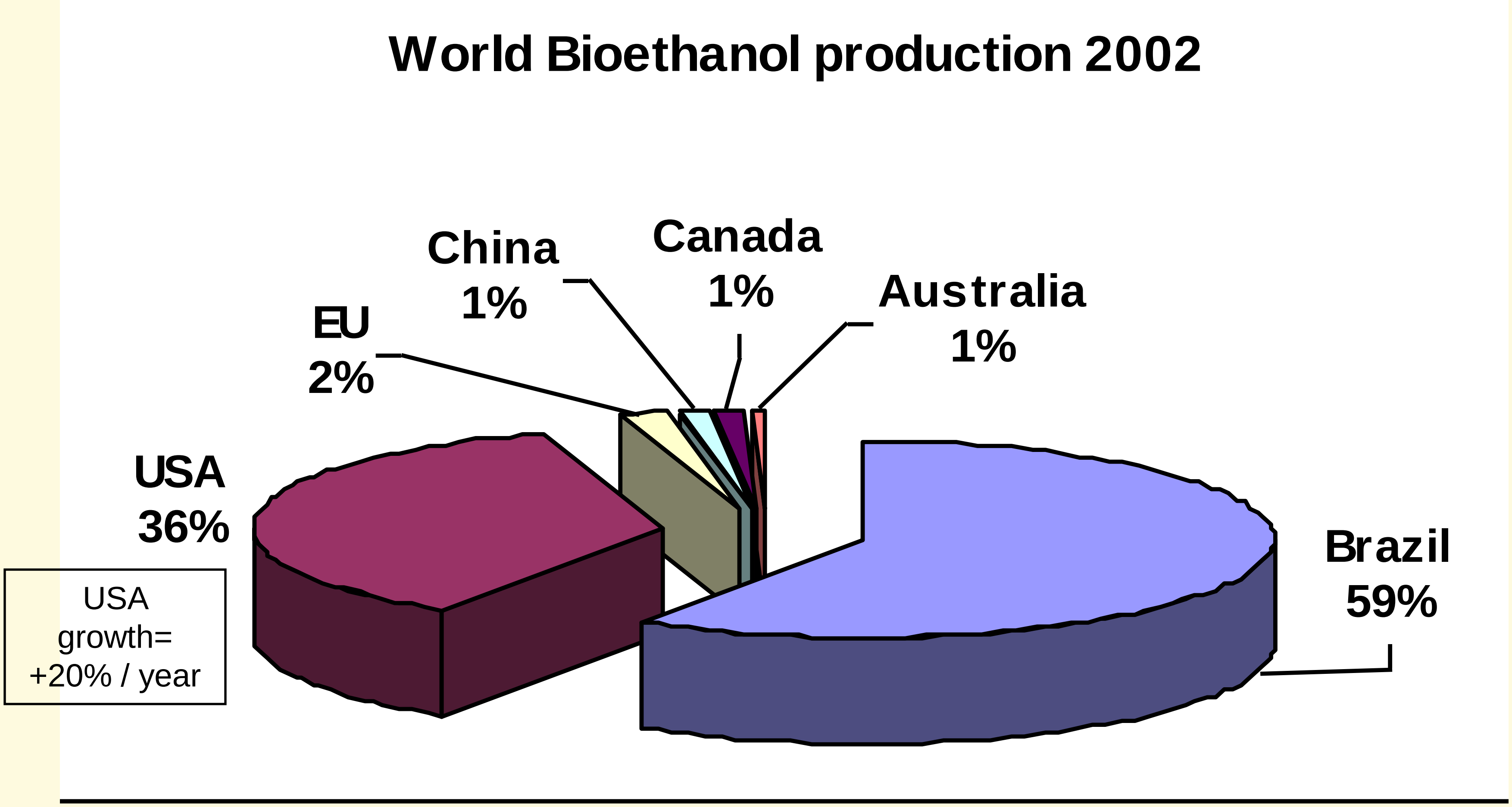
   Two projects by consortia in The Netherlands:

   - Feasibility study (2001)
   - Current R&D project (2002-2006)

   Aspects of xylose metabolism (TUDelft / Bird Engineering/ NEDALCO/ KU-Nijmegen)
3. **International developments**
4. **Conclusions**

Current bioethanol production (1)

Fermentation of sugars from sugar cane & starch crops



World production 2002 :17 Mton Ethanol (460 PJth)

Current bioethanol production (2)




- Brazil : sugar cane 7.5 € / GJ = 0.16 € /l
- USA : corn 16.2 € / GJ = 0.34 € /l
- EU (France, Spain, Sweden) limited production from sugarbeet, grains

➔ price of gasoline 7.3 € / GJ = 0.24 € /l

Application of bioethanol

- **Internal combustion engines**

- **Fuel Cells (SOFC, PEMFC) with fuel processors**

Bioethanol is an excellent transition fuel !!

EU policy for promotion of biofuels

Objectives EU "Biofuels Directive"

- reduce CO_2 emissions from transport
- reduce reliance on external energy sources (oil)

- short term: “conventional” biofuels: bioethanol from starch crops, biodiesel, etc.
- longer term “advanced” biofuels: bioethanol from lignocellulose, syngas fuels: FT-diesel

Year	EU target % substitution	50% bioethanol Mton/yr
2005	2	2.5
2010	5.75	7.5
2020	10	12.5

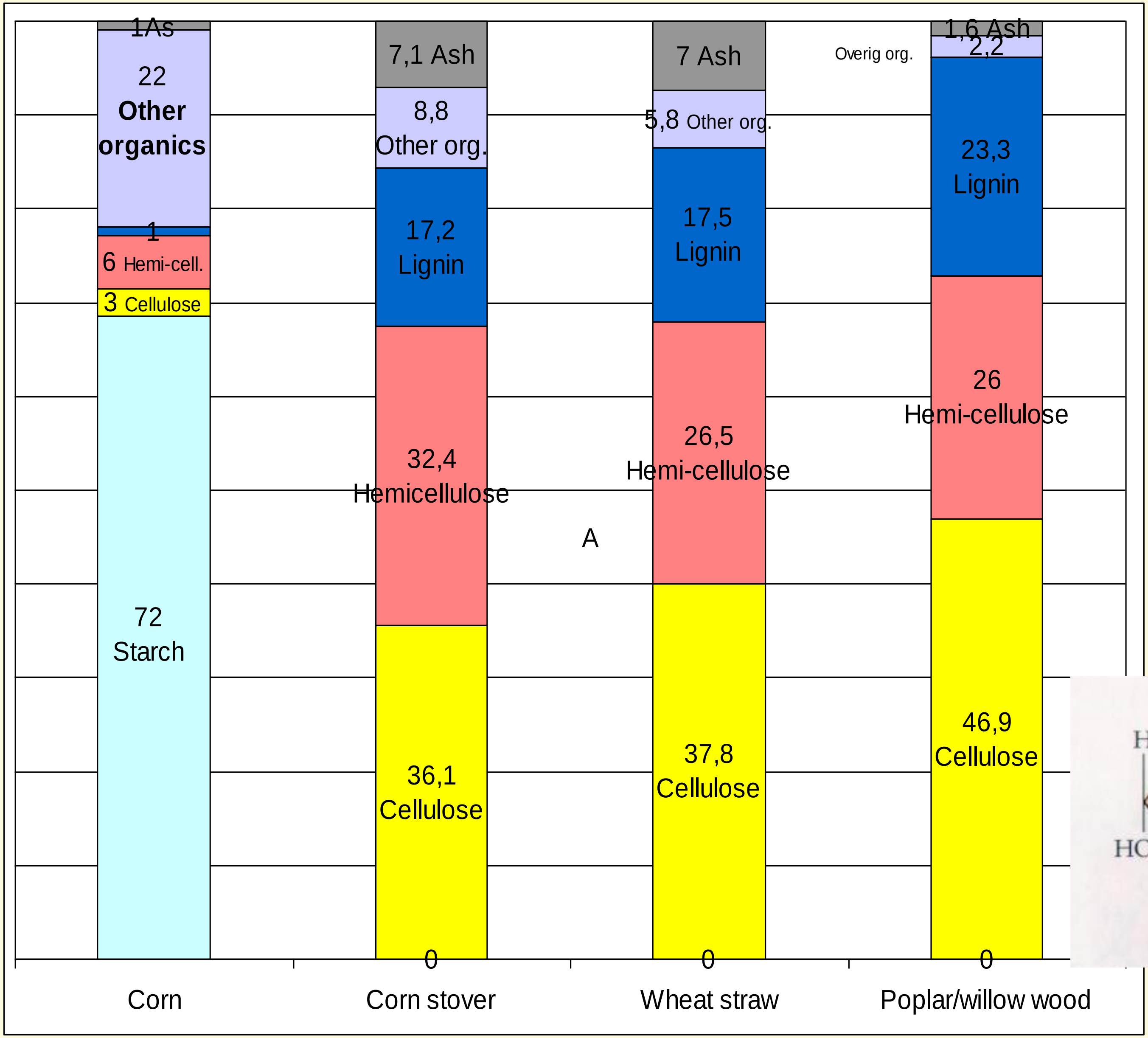
EU bioethanol production in 2000: 0.3 Mton

Lignocellulose as a source of sugars (1)



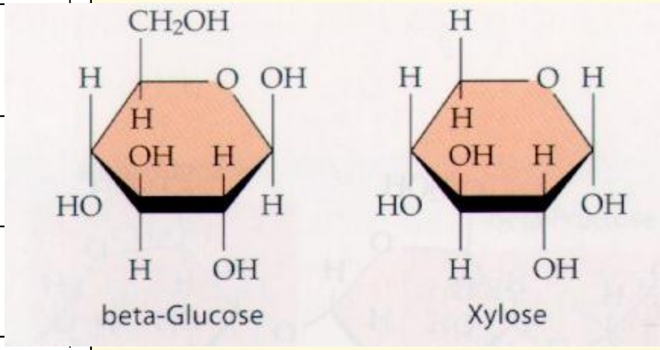
- starch/sugar crops: limited availability and high cost, while lignocellulose (residues) are abundant & cheap
- increase EtOH production volume & reduce costs
- higher CO_2 reduction in transport (80% vs. max. 50%)
- low-cost sugars for other fermentations e.g. lactic acid
- use of lignin as fuel for Combined Heat and Power (CHP) or products

Lignocellulose as a source of sugars (2)



Starch & Cellulose:
  Glucose (C6)

Hemicellulose:
  Xylose (C5)



Feasibility study(2001): Bioethanol, electricity and heat from biomass residues

- inventory available feedstocks in the Netherlands
- status (international) technology development
- techno-economic system evaluation

→ identify R&D issues and approach

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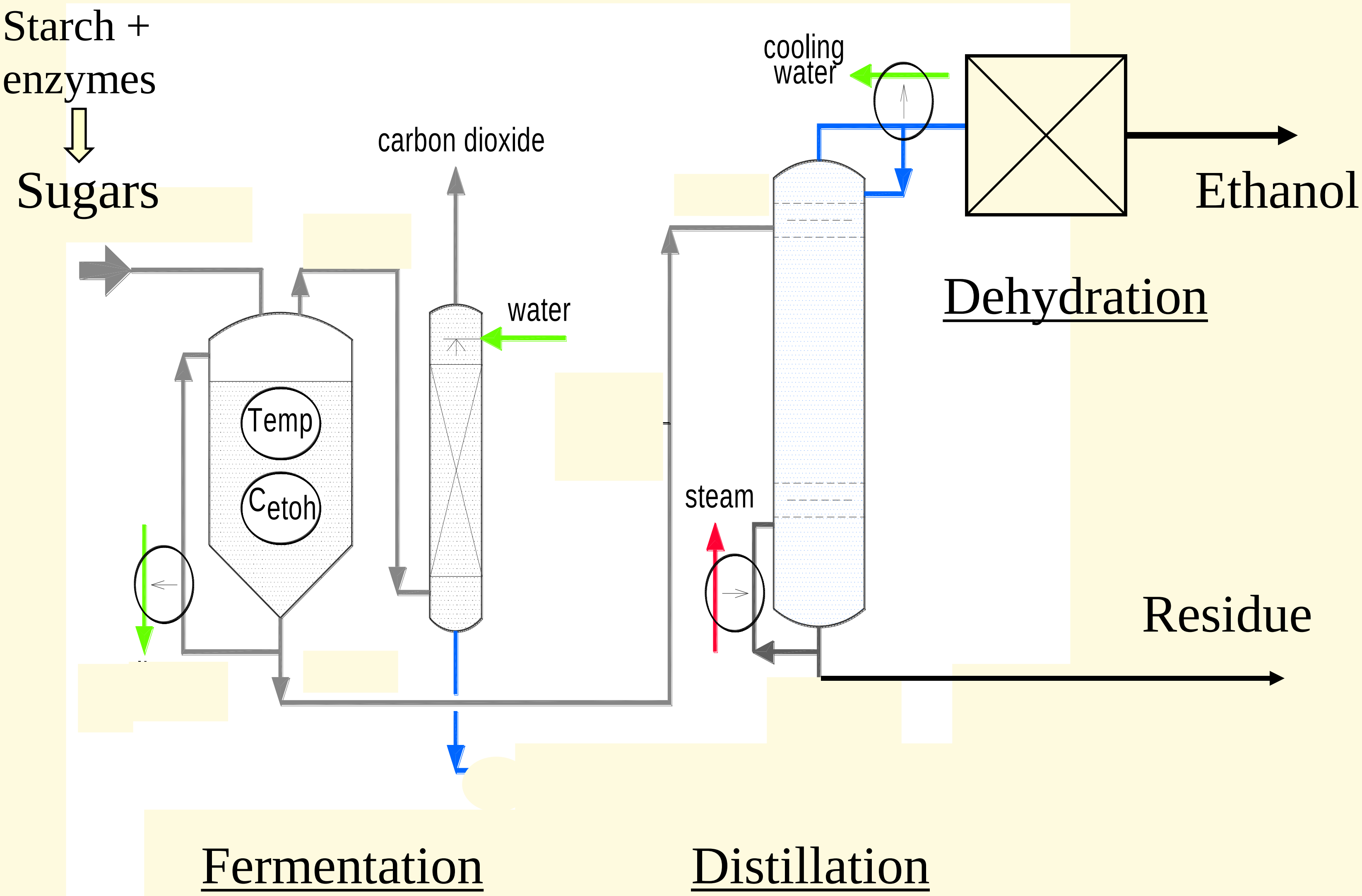
Feedstocks in the Netherlands

- variety of suitable biomass/residues available:
  total 12 Mton dry weight >>2.5 Mton ethanol (70 PJth)
- 150 kton EtOH/yr plant requires >>700 kton dw feedstock
- no uniform 'local' streams of sufficient size available
  - multifeedstock plant
  - long distance supply/import

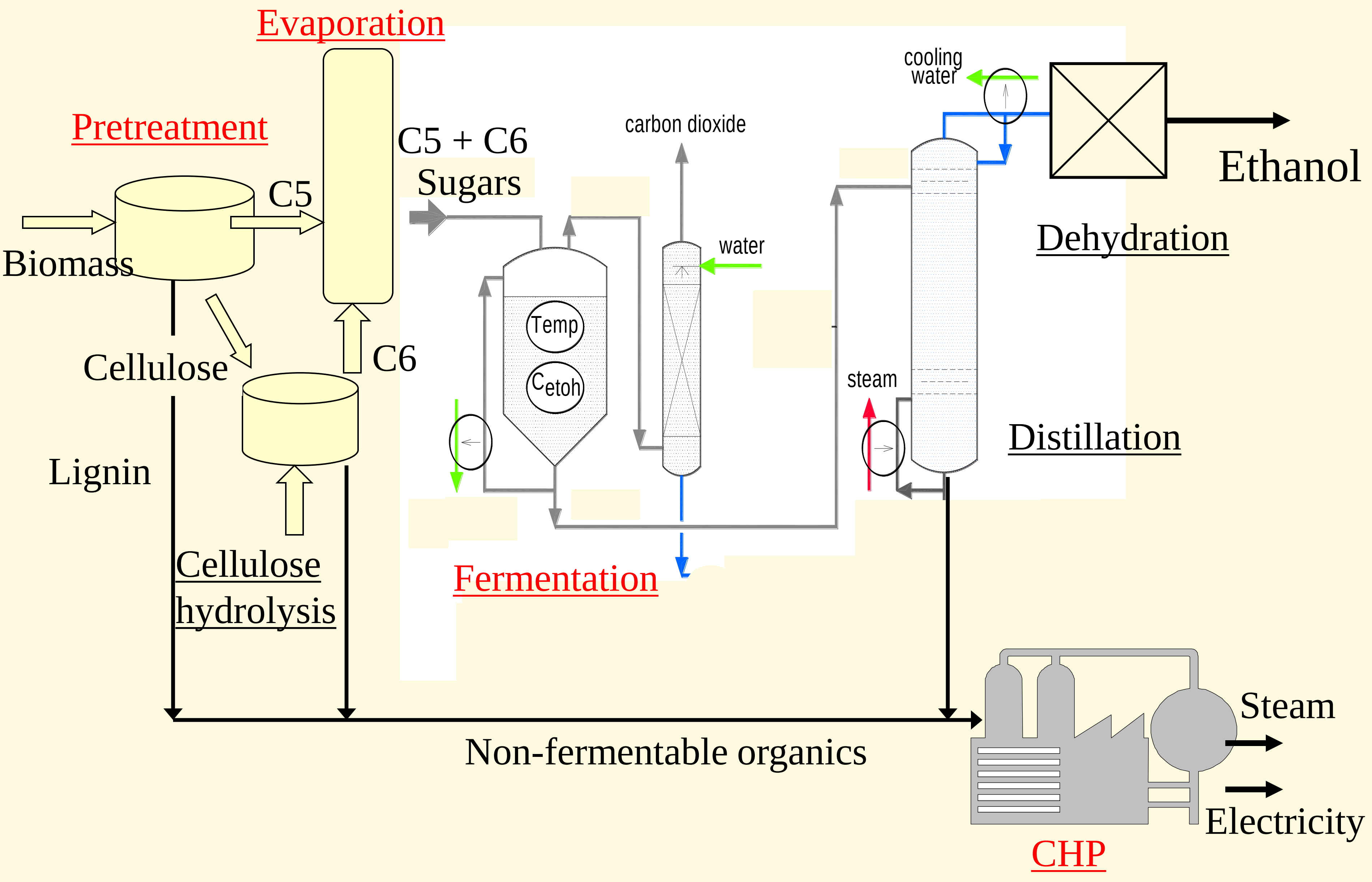
➢ Short and medium term: focus on agro-industrial residues, straw, verge grass and other wastes

➢ Longer term: imported biomass (e.g willow)

Current process



Lignocellulose-to-ethanol process



System evaluation

- **156 kton/yr ethanol plant**
- **feedstocks**
  - verge grass
  - wheat milling residue
  - willow wood
- **mild alkaline pretreatment;** $Ca(OH)_2$, 85% Ca recycle
- **enzymatic cellulose hydrolysis;** industrial cellulases
- **thermal conversion non-fermentables (mainly lignin) to electricity and heat in Gasifier CHP plant**

Mass & energy balance

		Verge-grass	Willow tops	Wheat milling residue
Mass balance				
Feedstock	(kton dw/yr)	650	550	470
Water	(l/l ethanol)	54	46	28
Energetic efficiency				
- Ethanol	(% LHV)	40	47	55
- Electricity to grid	(% LHV)	15	15	12
- Total	(% LHV)	56	62	68

- process energy demand (steam + electricity) fully covered
- surplus electricity to grid: -10% gross EtOH cost
- high water use: ~50 l/l EtOH vs. 10-15 l/l in current production

Economic analysis

Investment costs + cellulase costs are major cost drivers

Sensitivity analysis shows:

- **- 10 fold reduction of cellulase costs**
- **- 30% reduction of capital investments**

required to reach ethanol costs comparable to corn ethanol (0.34 € /l)

Bioethanol and lactic acid from lignocellulose (2002-2006)

Project website:

www.bemz.ecn.nl

Bioethanol and lactic acid from lignocellulose
2003-2006

- **Efficient production of fermentable sugars from lignocellulose**

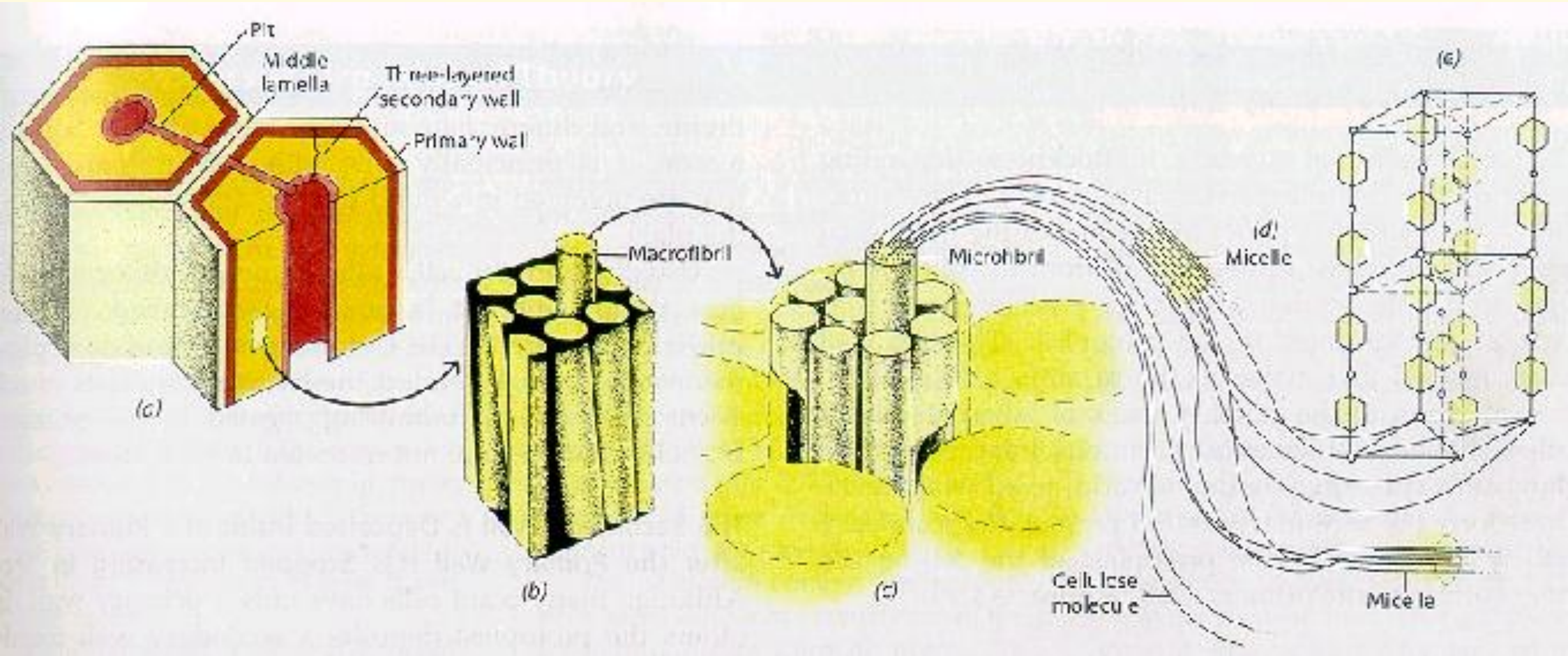
- Integrated approach feedstock-to-fermentation products

straw<>pre-treatment<>enzymatic hydrolysis<>fermentation

- - hot water/mild acid pretreatment
  - mild alkaline extraction
- test and optimise effectivity of available industrial enzymes
- ethanol and lactic acid fermentation

- **Combined Heat & Power Production non-fermentables**
- **Process design and process integration (energy, water)**
- **Formulation and logistics of bioethanol fuel blends**

Pretreatment (1)



Objectives

- Delignification
- Increase accessibility of (hemi)cellulose polymers for enzymes
- Hydrolysis of hemicellulose (dependent on method)

Pretreatment

PROCESS	Yield fermentable sugars	Inhi-bitors	Chemicals recycling	Wastes	Invest-ments
Weak acid	++	--	--	-	+/-
Strong acid	++	--	--	-	-
Steam explosion	+	--	++	+	-
Organosolv	++	++	--	+	--
Wet oxidation	+/-	+	++	+	+
Mechanical	-	++	++	++	+
Alkaline extraction	++/+	++	--	-	++
Carbonic acid	++	++	++	++	+

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Alkaline extraction	++/+	++	--	-	++
Carbonic acid	++	++	++	++	+

Pretreatment (2)

- Options: chemicals,T, P
- Criteria:
  - Yield/Effectivity (% monomers, enzyme-use)
  - Formation of unwanted side products/‘inhibitors’>> organic acids/furans/aromatics
  - Use of auxillary chemicals/ waste production
  - Costs

Pretreatment (3)

- Model feedstock: wheat straw

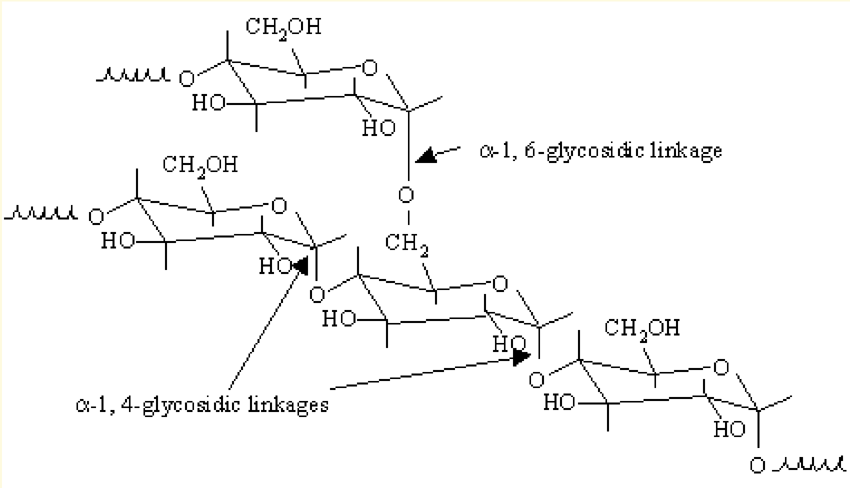
- Mild acid pretreatment (0,5-1 vol. %) in pressurized water (180-200 °C)
  - Short residence time
  - Cellulose intact, hemicellulose hydrolysis
  - some inhibitor formation
  - waste production ($CaSO_4$)

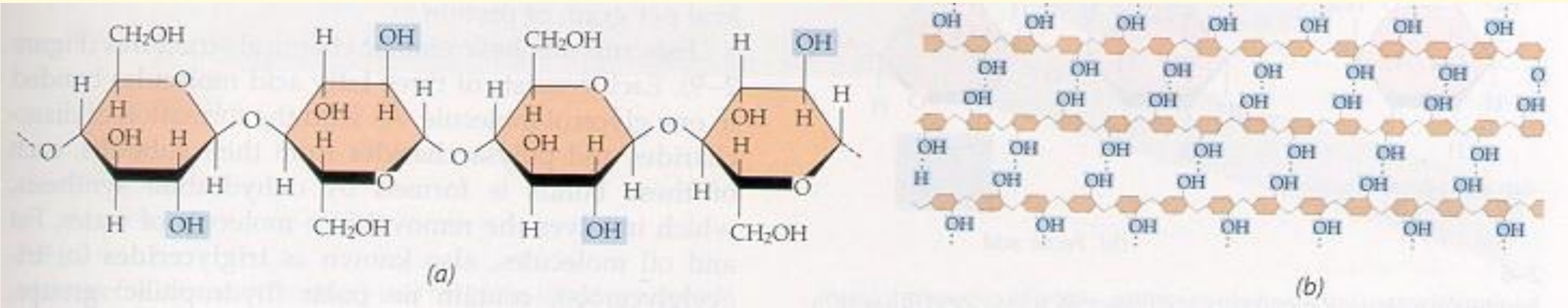
- Mild alkaline extraction ($Ca(OH)_2$, 80 °C) recycle 85%
  - Longer residence time
  - Unhydrolyzed cellulose and hemicellulose
  - No inhibitor formation
  - Wastes: $CaCO_3$ or $CaSO_4$

Enzymatic cellulose hydrolysis (1)

Starch and hemicellulose:

easy hydrolysis through amorphous, branched structure



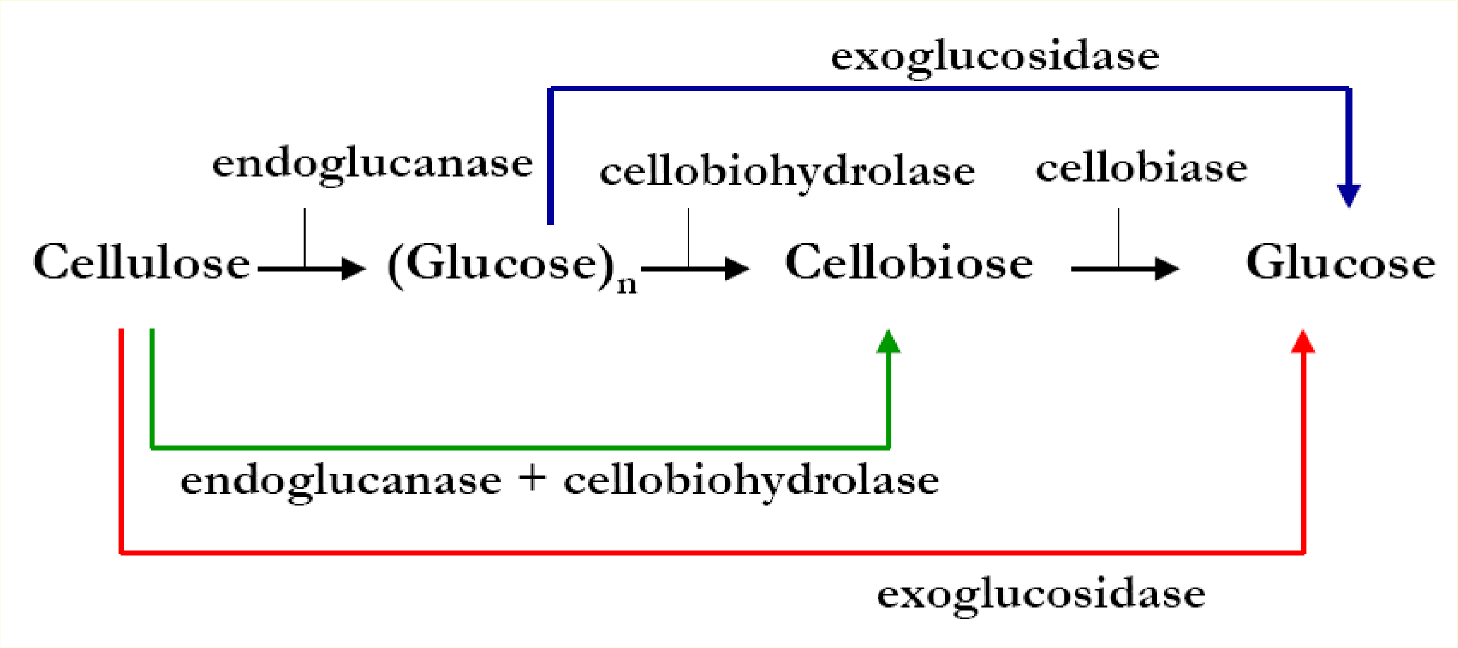


Cellulose:

linear glucose-polymers (1-4 glycosidic) bundled to "microfibrils" via H-bonding

difficult hydrolysis through linear, crystalline structure

Enzymatic cellulose hydrolysis (2)



- Cellulase = mixture of enzymes
- Expectation: strongly lower costs in the longer term
- Optimization through novel biochemical/genetic tools

Enzymatic cellulose hydrolysis (3)

Current obstacles:

- end-product (glucose) inhibition
- high costs

Modelling shows:

SSF is a good solution to glucose inhibition

Recent claims DoE sponsored R&D:

20 - 30 fold cost reduction (Novozymes, Genencor); by production on-site (no product recovery/formulation)

Longer term: increase specific acitvity and thermostability

Optimize cellulase enzyme mix

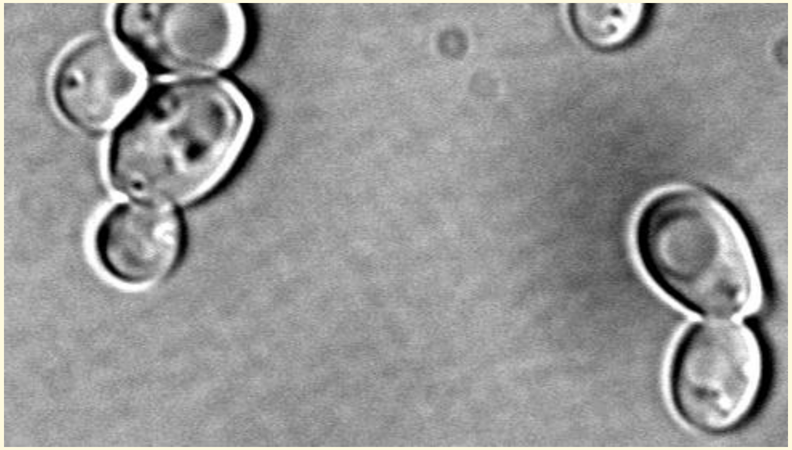
Co-fermentation C5 & C6 sugars

$3\ C_5H_{10}O_5 \rightarrow 5\ C_2H_5OH + 5\ CO_2$

Xylose

$C_6H_{12}O_6 \rightarrow 2\ C_2H_5OH + 2\ CO_2$

Glucose



S. cerevisiae wildtype cells**

Industrial yeast *Saccharomyces* only ferments C_6 sugars

Obstacles:

- xylose (C_5) uptake
- overproduction of xylitol due to redox problems

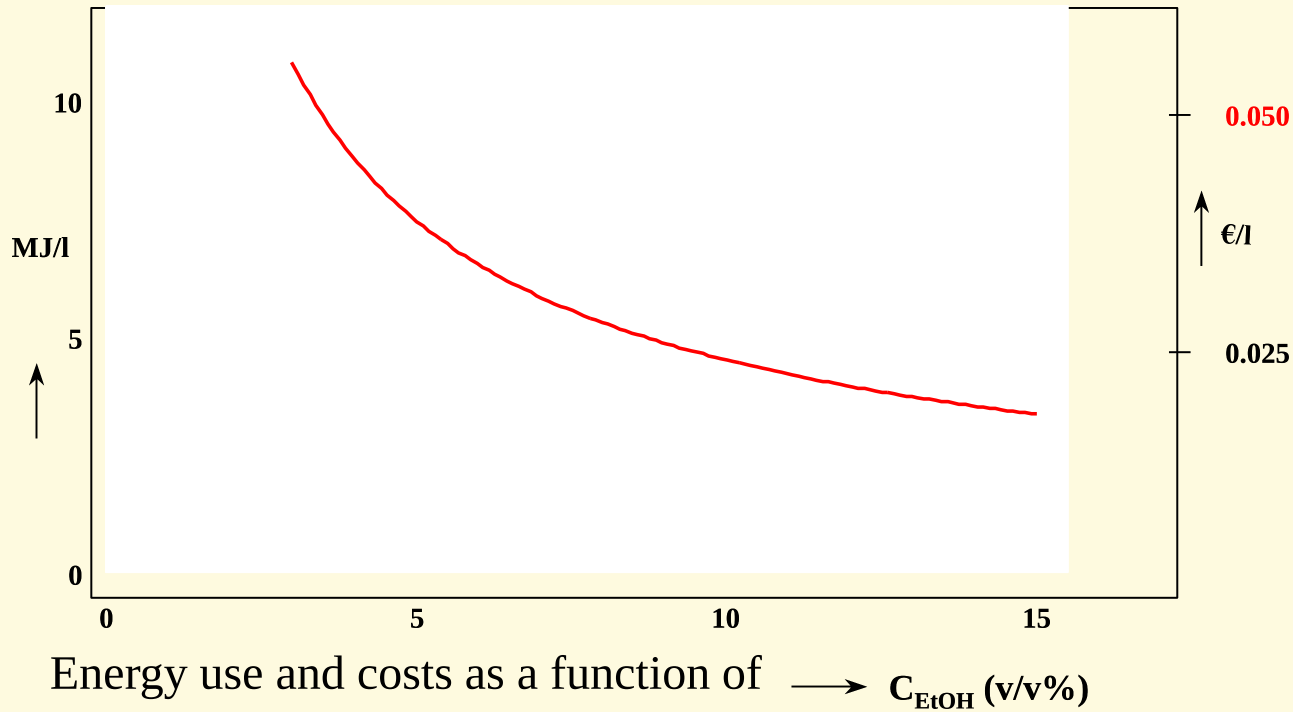
**) Source: http://genome-www.stanford.edu/Saccharomyces/yeast_images.html

Metabolic engineering of yeast for the production of ethanol from xylose

- Several initiatives world-wide
- In The Netherlands, joint activity by TU Delft, Bird Engineering, Nedalco and University of Nijmegen

Ethanol purification

Distillation(45 vol%); rectification (95 vol%) + dehydration (99.9 vol%) molecular sieves



Energy use and costs as a function of Ethanol concentration in fermentation

Ethanol concentration in fermentation broth

>> 5 % required

CHP from biomass residues

- Residu is ~1/3 of feedstock (mainly lignin)
- Base case: fluidized bed combustion
- Issues:
  - fuel conditioning
  - effects of process chemicals (Ca, S) on process and installation
  - utilization of ashes in building materials or fertilizer
  - techno-economic and environmental performance
  - energy integration with production plant

Recent international developments

- Demo plant IOGEN, Canada
  max. 40 ton grain straw /day; 3-4 million l ethanol/yr
  “modified steam explosion”

- R&D pilot plant ETEK, Zweden
  2 ton softwood/d; 140.000 l ethanol/yr
  “mild acid pretreatment”

Conclusions

Lignocellulose into ethanol or lactic acid is a complex undertaking

Several hurdles to be taken including:

- pretreatment,
- enzymatic hydrolysis,
- metabolism of xylose,
- product recovery,
- use of lignin as fuel for combined heat and power,
- system evaluation based on results for many parameters

Economics depends on various process parameters

Current project on wheat straw serves as an example, allowing to assess the options for the bioconversion of lignocellulosics in general.

economieecologietechnologie

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