Biorefinery: A new source for green chemicals?

Presentation to the National Research Programme NRP66
"Dialogue field 2: Novel ways in bio-refining of wood"

at Paul Klee Zentrum, Berne, 10 December 2015

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Questions for today

- Biorefineries – What is the technical potential?
- Biorefineries – Is large-scale possible and sensible?
- Biotechnology for bulk – How to assess and what are the lessons learnt?
- Second generation feedstocks – A value proposition?
- Value-added compounds – How to pinpoint?

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Project “PROBIP” – Market study

Universiteit Utrecht

Product overview and market projection of emerging bio-based plastics

PRO-BIP 2009

Final report

June 2009
Revised in November 2009

- Full study: http://www.uu.nl/sites/default/files/copernicus_probip2009_final_june_2009_revised_in_november_09.pdf
- Shen et al.: Present and future development in plastics from biomass. Biofuels, Bioproducts and Biorefining, Volume 4, Issue 1, January 2010, pp. 25-40

Technical substitution potential - for plastic applications

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% Substitution	PE-LD	PE-HD	PP	PVC	PS 1)	PET	PUR	PA	ABS 2)	PC	PBT	PMMA	Other Polyacrylates	Epoxy resins	Synthetic rubber	Other
Starch plastics	8	8	8		8		8					4				
PLA		10														
PHA	20	20														
Cellulose films																
Bio-based PE	72	62														
Bio-based PP																
Bio-based PVC 3)																
Bio-based PET 3)																
Bio-based PTT 3)																
Bio-based PUR 3)																
Bio-based PA																
Bio-based Polyacrylates 3)																
Bio-based Epoxy resins 3)														75		
Bio-based ABS 3)									90							
Bio-based PB 3)															80	
Sum percentages	**100**	**100**	**100**	**100**	**48**	**100**	**98**	**70**	**100**	**20**	**100**	**19**	**100**	**75**	**80**	**0**

Total polymer consumption worldwide:
~ 230 million t p.a.

Technical potential bio-based:
~205 million t p.a. (90%)

(1,000 t)	PE-LD	PE-HD	PP	PVC	PS 1)	PET	PUR	PA	ABS 2)	PC	PBT	PMMA	Other Polyacrylates	Epoxy resin	Synthetic rubber	Other	Total	% subst
Global consumption 4)	37,100	30,700	44,900	35,280	16,105	15,498	12,285	2,730	7,455	3,150	954	1,400	660	1,150	10,889	6,930	227,186	100
Technically replacable volumes	37,100	30,700	44,900	35,280	7,731	15,498	12,039	1,911	7,455	630	954	266	660	863	8,711	0	**204,698**	**90**

1) PS (all types) and EPS
2) ABS/SAN, include also other styerene copolymers.
3) Partially biobased polymer
4) For PE, PP, PVC, PS, PUR, ABS, PA, PC and PBT, consumption data are for 2007 based on the projection of Kunststoffe (10/2007); the PET data is also projected for 2007 but based on the consumption data in 2006 from PlasticsEurope (Simon, 2008) and growth projection according to Kunststoffe (10/2007); for PMMA, the consumption data is for 2006 (Kunststoffe 10/2007); For other polyacrylates, consumption data are for 2003 (PlasticsEurope, 2004); For Epoxy resin and synthetic rubber, consumption data are for 2000.

Shen, Haufe and Patel, 2009
http://en.european-bioplastics.org/wp-content/uploads/2011/03/publications/PROBIP2009_Final_June_2009.pdf

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Cellulose fibres

Existing process

– **Lenzing Viscose/Modal and Tencel**

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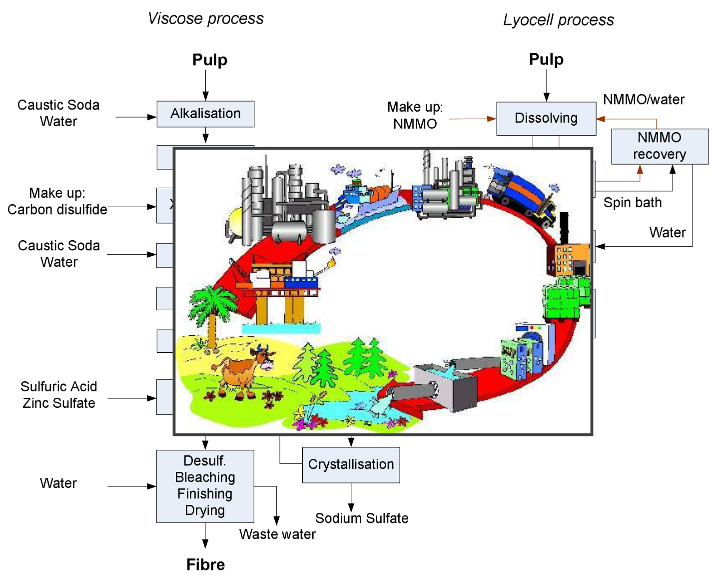
Lenzing Viscose/Modal and Tencel



Shen et al., 2012a & b (Lenzinger Berichte); Shen et al., 2012 c (RCR)

Net Greenhouse Gas Emissions (t CO_2 eq./t fibre)

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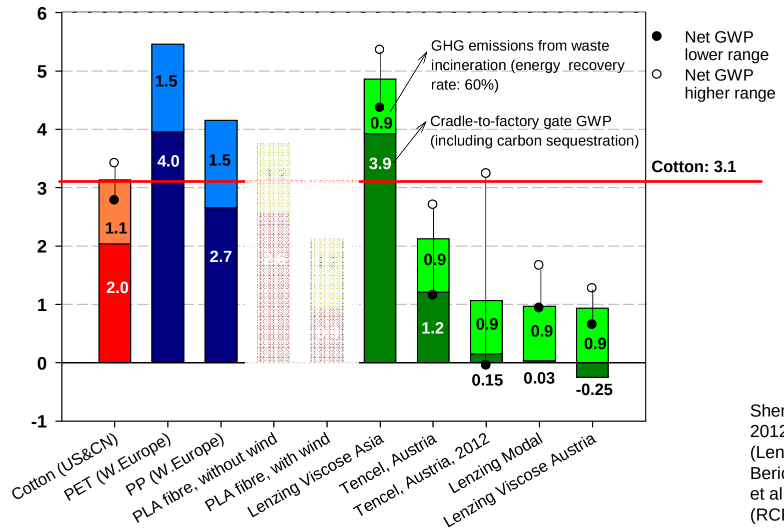
Cradle-to-factory gate plus post-consumer waste incineration with energy recovery



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The BREW Project (http://www.chem.uu.nl/brew/)

Medium and long-term opportunities and risks of the biotechnological production of bulk chemicals from renewable resources

Universiteit Utrecht

NatureWorks®

Fraunhofer ISI Institute Systems and Innovation Research

uniqema

DSM

Plant Research International

bp

CERISS

ROQUETTE

Agrotechnology & Food Innovations Wageningen UR

DuPont The miracles of science®

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degussa.

We gratefully acknowledge support from the European Commission's Directorate General for Research (GROWTH Programme Award No. G5MA-CT-2002-00014).

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White Biotechnology products studied within BREW

1. Acetic acid → **PVAc and other acetic acid esters**
2. Acetone/Butanol/Ethanol → **Acetone + Phenol → Bisphenol A → PC, Epox**
3. Acrylamide → **Polyacrylamide**
4. Acrylic acid → **Polyacrylates**
5. Adipic acid → **Adipic acid + HMDA → Nylon 6,6**
6. Caprolactam → **Nylon 6**
7. Citric acid → **-**
8. Ethanol → **Ethylene → PE, PS, PVAc, PET, EPDM etc.**
9. Lactic acid → **PLA**
10. Lysine → **Lysine polymers**
11. Mono-/Diglycerides → **Plasticizers (various fatty acid esters)**
12. Oleyl oleate → **Plasticizers (various fatty acid esters)**
13. Polyglycerol monoester → **Plasticizers (various fatty acid esters)**
14. Polyhydroxyalkanoates → **Polyhydroxyalkanoates**
15. 1,3-Propanediol → **Polytrimethyleneterephthalate (PTT)**
16. Succinic acid → **Polybutylene succinate (PBS)**

Source: BREW Study, Utrecht University 2006

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BREW Project – Approach & Findings

Flowsheeting

- Material balances and energy requirements for main unit processes (productivity, yield and concentration; DSP)

Environmental assessment

- LCA approach (cradle-to-factory gate and cradle-to-grave)
- Environmental indicators: Non-renewable energy use (NREU), renewable energy, GHG emissions and land use

Economic assessment

- Standard business economics

Benchmark

- Equivalent petrochemical product

* "*BREW study*", 2007, http://www.chem.uu.nl/brew/
* Hermann et al., *Environ. Sci. Technol.*, 2007
* Hermann et al., *Applied Biochemistry and Biotechnology*, 2007

BREW Project

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Principle assumptions of Generic Approach

TODAY

- Data from literature, companies and institutes

FUTURE

- Yield = 90 mol-% of theoretical
- Productivity = max. 10-20 g/l/h (aer.), max. 50 g/l/h (anaer.)
- Moderate/no increases in concentration
- C_5 and C_6 sugars interchangeable
- Substantial progress in downstream processing (DSP)

BOTH

- Scale WB products: 100 kt p.a. (sensitivity: larger)

Exemplary flowsheet 1,3-PDO

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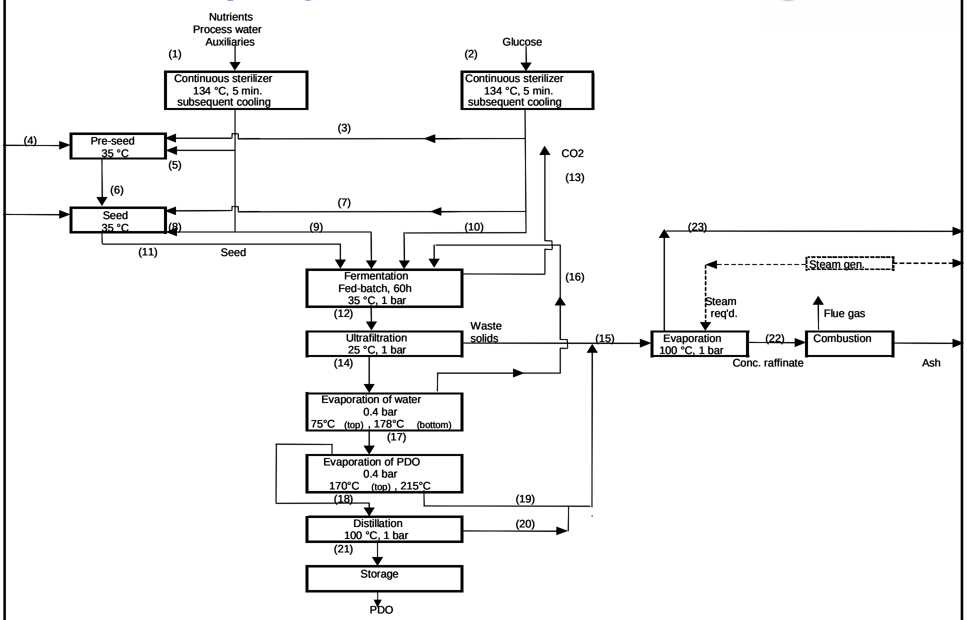

BREW Project

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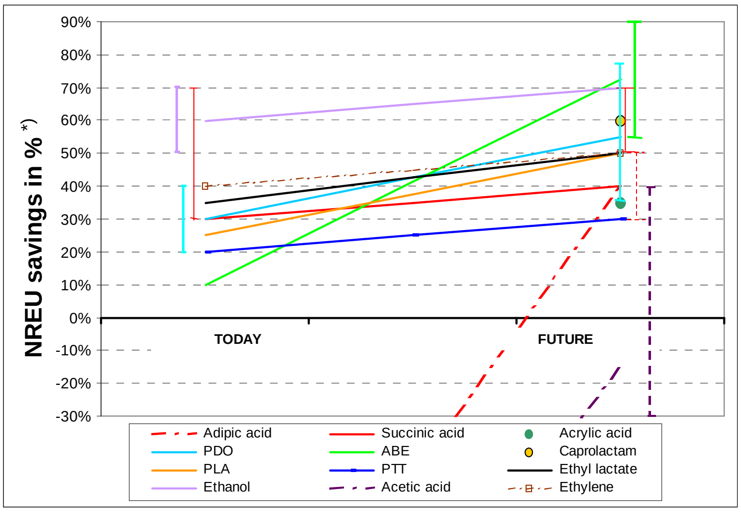
White Biotechnology - Environmental attractiveness

All products from maize starch – Non-renewable energy use (NREU, cradle-to-factory gate)



*) Savings of cradle-to-factory gate non-renewable energy compared to petrochemical

Sources:
* BREW project (2003-2006): http://www.projects.science.uu.nl/brew/
* Hermann, B.G et al., Environ. Sci. Technol. 2007, 41, pp. 7915-7921
* Hermann, B.G. et al., Appl. Biochem. & Biotech., Vol. 136 (2007), pp.361-388

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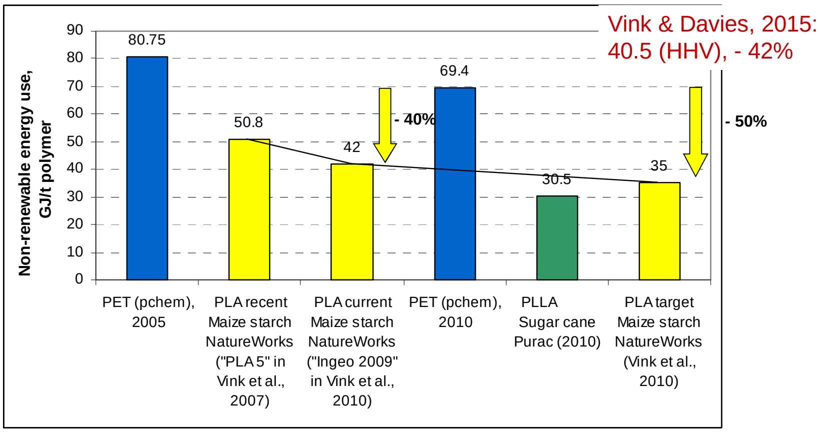
Where do we stand today? (1/3)

Polylactic acid (PLA)
Non-renewable energy use, cradle-to-factory gate



Chen, G-C. and Patel, M. K., Chemical Reviews (Chem. Rev.) 2012, 112, pp. 2082–2099

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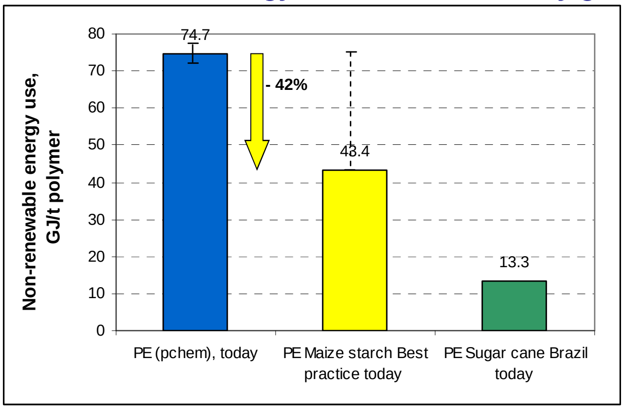
Where do we stand today? (2/3)

Bio-based polyethylene (PE)
Non-renewable energy use, cradle-to-factory gate



Chen, G-C. and Patel, M. K., Chemical Reviews (Chem. Rev.) 2012, 112, pp. 2082–2099

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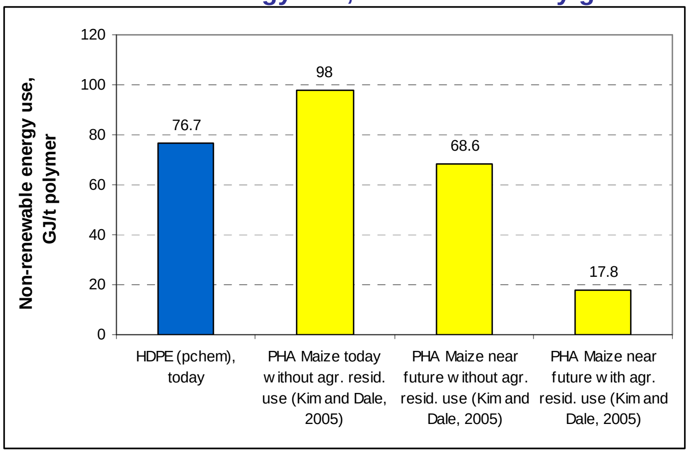
Where do we stand today? (3/3)

Polyhydroxyalkanoates (PHA)
Non-renewable energy use, cradle-to-factory gate



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Chen, G-C. and Patel, M. K., Chemical Reviews (Chem. Rev.) 2012, 112, pp. 2082–2099

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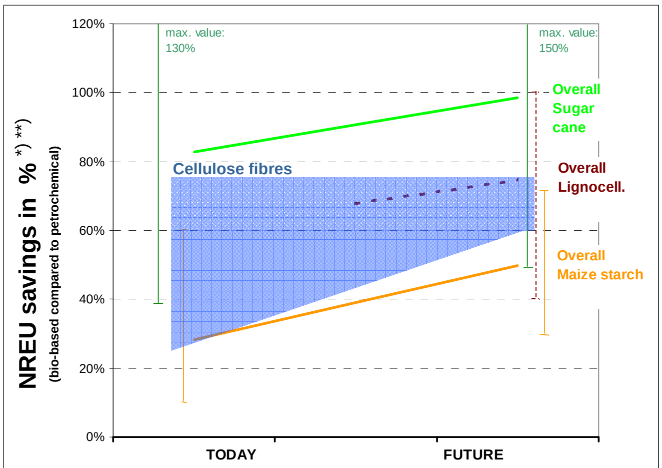
Non-renewable energy use (cradle-to-factory gate) for White Biotechnology products and other bio-based products versus petrochemical products



*) Without acetic acid and adipic acid. Ranges indicate values for individual products (not average values).
**) Savings of cradle-to-factory gate non-renewable energy compared to petrochemical

Source: Several UU studies, among them BREW

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2nd generation feedstocks

– Yields
– Energy
– Geenhouse gas emssions
– Economics

Research is ongoing.

DA Dilute Acid
LHW Liquid hot water
SE Steam explosion
SCW Supercritical water
AFEX Ammonia fiber explosion

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Green Chemistry principles

Prevent Wastes
Renewable materials
Omit derivatization steps
Degradable chemical products
Use safe synthetic methods
Catalytic reagents
Temperature, pressure ambient
In-process monitoring
Very few auxiliary substances
E-factor [and atom economy]
Low toxicity of chemical products
Yes, it is safe.

LCA

Environmental Life Cycle Assessment

- Provides quantitative environmental indicators
- Based on flowsheet and considers all stages of process chain

Apply principles as guiding rules
Qualitative assessment (+, -, 0)
Multicriteria analysis
Ex-ante LCA
Full-fledged LCA

Limited data availability — Extensive data availability

Anastas (2000) — ISO standards

Early R&D stage — Commercial plant

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CatchBio ex-ante assessment methodology (1/2)

Bio-based (CatchBio) process | **Total Score** | Conventional process

Economic constraint (0.3)	Environmental impact of raw materials (0.2)	Process costs and Environmental Impacts (0.2)	EHS Index (0.2)	External risks and benefits (0.1)
Price ratio	Cumulative Energy Demand	Energy loss index	Environment	Feedstock availability
Practical yields	GHG emissions	Product concentration	Persistency	Market size
Allocated raw material costs		Water content	Air hazard	Compatibility with current infrastructure
Market price		Boiling point Δ	Water hazard	EU/Regional feedstock potential
		Mass loss index	Solid waste	Inherent benefits of molecules/pathways
		Reaction energy	Health	
		No. of co-products	Irritation	
		Pre-treatment	Chronic toxicity	
			Safety	
			Mobility	
			Fire/Explosion	
			Reactivity	
			Acute toxicity	

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Patel, A.D. et al., Energy Environ. Sci, 2012;
partly based on Sugiyama, Ph.D. thesis, ETHZ, 2007

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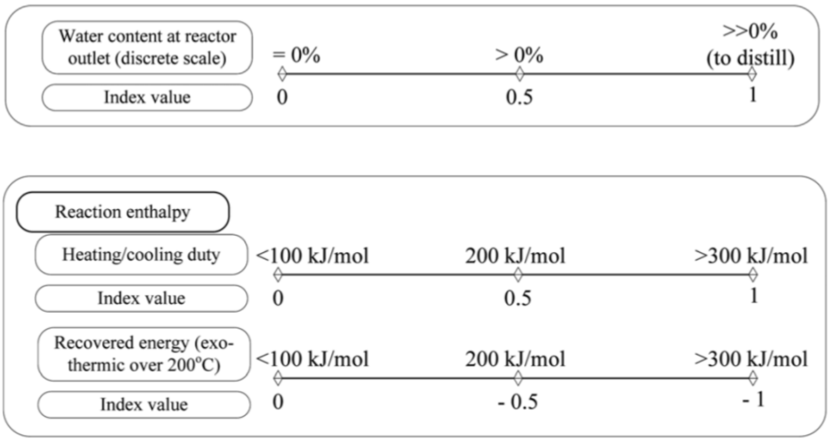
CatchBio ex-ante assessment methodology (2/2)

Examples



Patel, A.D. et al., Energy Environ. Sci, 2012;
partly based on Sugiyama, Ph.D. thesis, ETHZ, 2007

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Concluding remarks

Preliminary findings

- **Environmental assessment**
  - NREU and GHG emissions may be comparable for 1st and 2nd generation sugars
  - and consequently for bio-based chemicals derived from these
  - **Important opportunities for reducing NREU, GHG and land use**
  - **Drawbacks** for other impact categories
- **Economic assessment**
  - Techno-economic assessment indicates economic viability
  - But: Technical & economic risks (e.g. biomass prices), scale etc.
- **Overall**
  - A bio-based resource & material base without competition with food resources seems possible
  - R&D gaps and industry needs:
    - Smart feedstock/preteatment/product combinations for Switzerland
    - Swift and reliable screening methods
    - Demonstrate Smart value chains from Swiss biomass to end products with energy efficiency & closed loop

since June 2012:
Adjunct professor
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Full professor at University of Geneva
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