Friedrich-Schiller-University Jena
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Institute for Technical and Environmental Chemistry

Judging Renewables-based Products – LCA in Practice

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Outline

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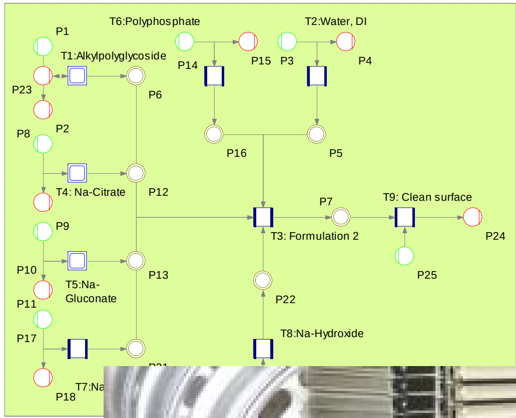
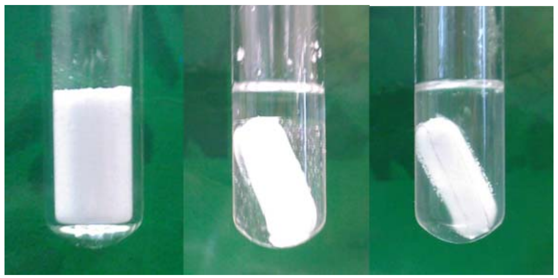
  - Selected examples from literature
- **Case example I**: industrial cleaner formulations for metals
- **Case example II**: Solvents in Diels-Alder reaction





Uni Regensburg

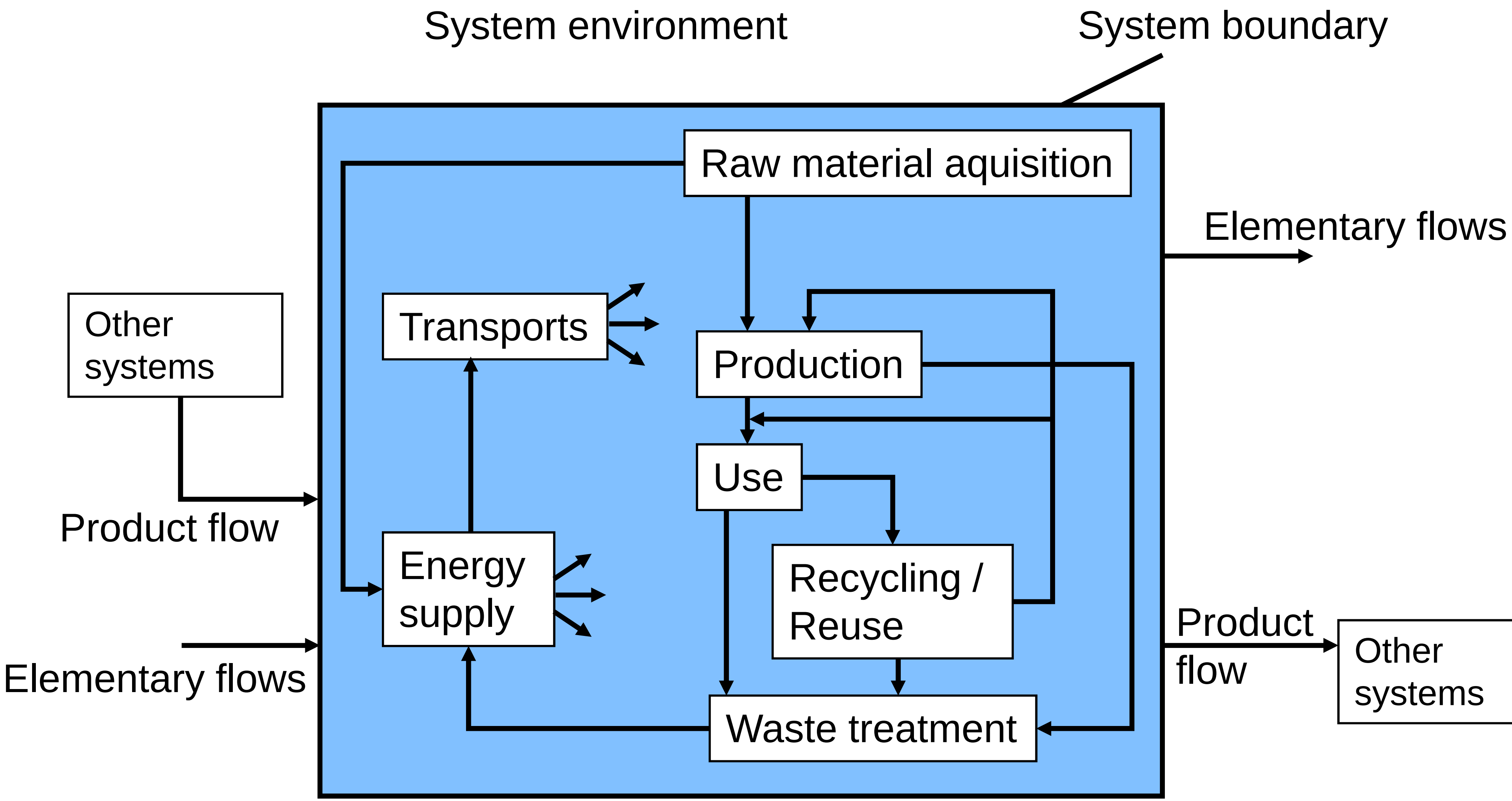
Life Cycle Assessment (LCA)

Methodological framework for estimating and assessing the environmental impact attributable to the life cycle of a product / process

Quelle: http://www.life-cycle.org/

- Avoids problem shiftings
- Makes the environmental impacts of different products or processes comparable
- Is standardised by DIN EN ISO 14040 and 14044

Life cycle inventory (LCI)



DIN EN ISO 14040 : 2006

Life cycle impact assessment (LCIA)

Material and energy flows → Environmental impact potentials

Impact categories considered*:

- Global warming (GWP)
- Abiotic recource depletion (ADP)
- (Stratospheric) ozone depletion (ODP)
- (Tropospheric) photochemical ozone creation (POCP)
- Acidification (AP)
- Eutrophication (NP)
- Human toxicity (HTP)
- Ecotoxicity (ETP)
- Land competition (LC)

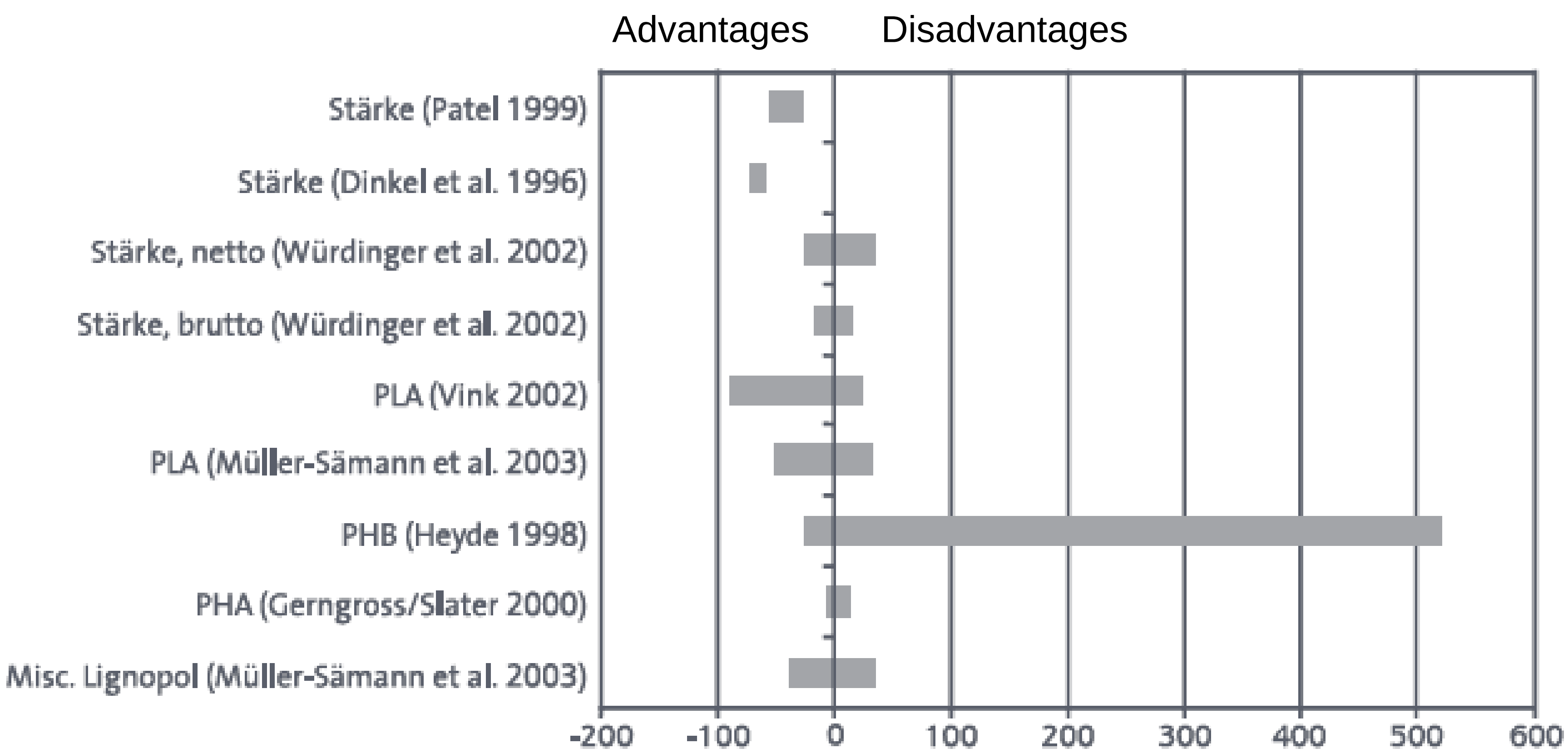
- Cumulative Energy Demand (CED)

$$IP = \sum_{i=1}^{n} m_i \cdot IF_i$$

m = mass
IF = impact factor

*Source: CML 2001

Range of differences between CED-values in various studies »RENEWABLE – FOSSIL« resource [MJ/kg]



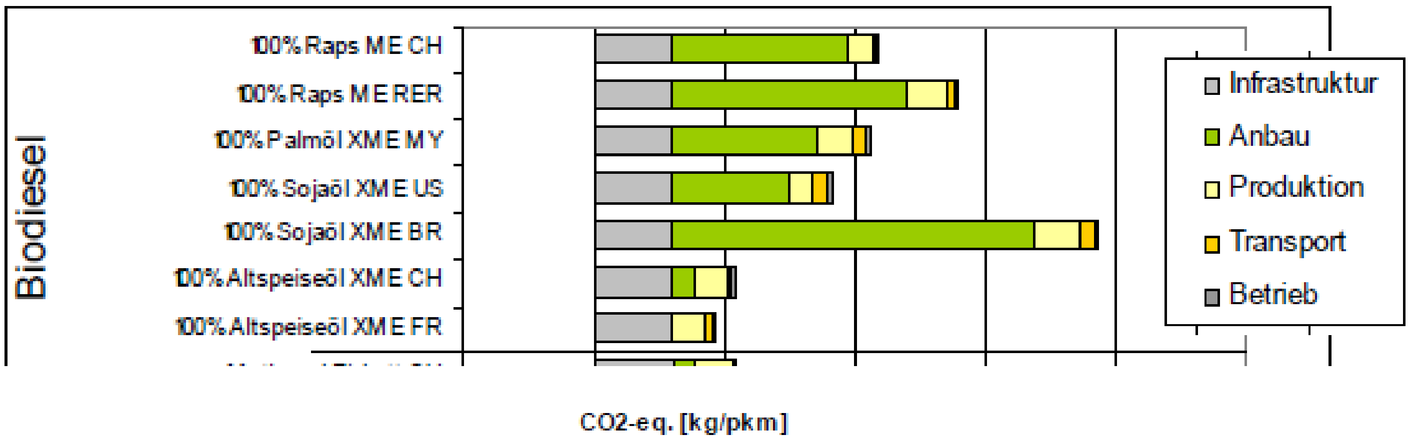
PHA = Polyhydroxyalkanoate
PHB = Polyhydroxybutyrate

In most cases no explicit advantages for renewable recources

Source: TFA, Nr. 114, 2007

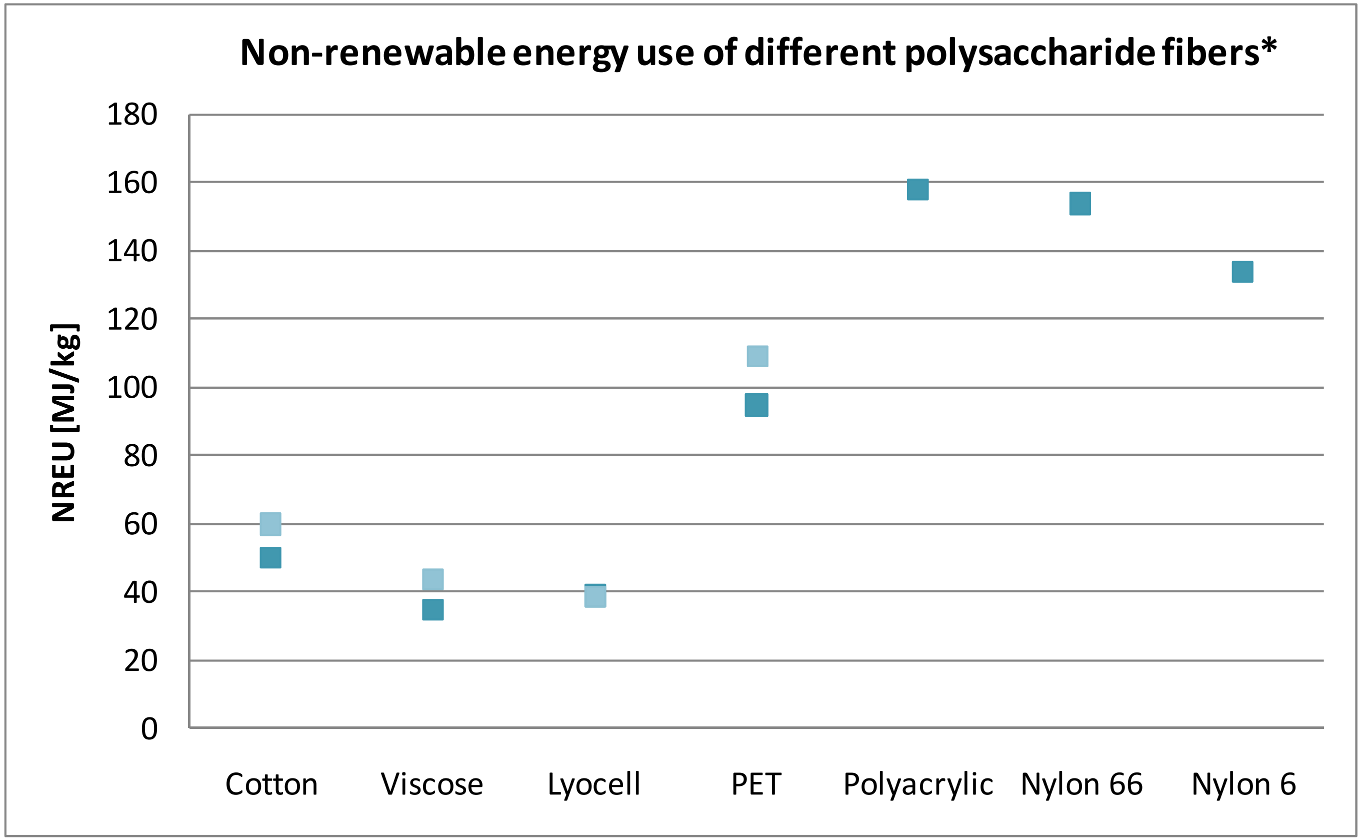
LCA of biofuels

- Holistic comparison of the environmental impacts of biofuels*
- Fuels examined → bioethanol, biomethanol, biodiesel and biogas
- "Most of the environmental impacts can be attributed to the agricultural cultivation of the respective raw materials", fuel processing and transportation less demanding
- Biogenic wastes ranging from grass to wood are pointed out as efficient solution to reduce the environmental impact compared with petrol



*Source: EMPA, 2007

Review of LCA studies of Polysaccharide Materials



*Source: L. Shen, M. Patel, J. Polym. Environ., 2008, 16:154–167

Impact categories considered within review:

Non-renewable energy use (NREU)

Greenhouse gas emissions (GWP)

"Polysaccharide-based end products show better environmental profiles than their conventional counterparts" (Exception: cotton)

Information about impacts related to 1 kg material not sufficient

Assessment of Renewable Raw Materials

Ideal approach:

Detailed „cradle to grave“ LCA for each alternative including all impact categories (e.g. suggested by CML)

Reality:

– Simplified LCA

– Evaluation at a more superficial level

- „cradle to gate“ approaches + concentration on selected impact categories e.g. energy demand and climate change

- Aspects like toxicity, eutrophication, acifidication and land competition → often not included

- Differences in material properties, e.g. higher material demand for the same application task or restricted recycling → not adressed

Sources:

PE International Report, 2007

TFA, Nr. 114, 2007

L. Shen, M. Patel, J. Polym. Environ., 2008, 16:154–167

Case Example I: Industrial Cleaners

Partners: Institute for Corrosion Protection, Dresden; NABU Oberflächentechnik GmbH, Stulln; FSU Jena

Project target: Ecological improvement of industrial cleaner formulations for aluminium surfaces

Industrial cleaners: Fluids used for cleaning and degreasing of metal surfaces before etching, metallisation and coating

Ecological evaluation: Accompanying LCA

System boundary: Cradle to use

DBU AZ 22446-31

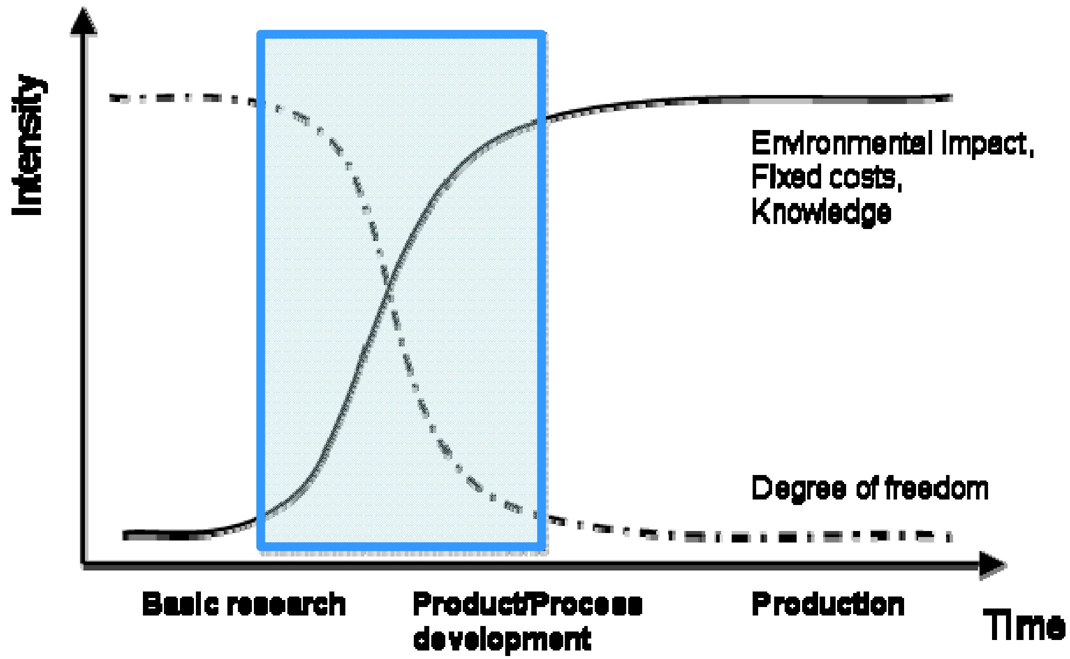
Strategy

Metal cleaner formulations for aluminium surfaces → focus upon compounds made from renewable resources

– Alkyl ethoxylate from petrochemical sources → alkyl polyglycosides from coconut oil

– Adaptation of additional components

– Two new cleaner formulations (formulation 1 and 2)



Accompanying assessment

– Ecological impact compared to a commercially available „state of the art“ reference formulation (reference)

– Impact on further product development

Life cycle inventory

Component	Formulation 1 [%]	Formulation 2 [%]	Reference
Alkyl polyglycoside (based on coconut oil)	4	4	-
Alkyl ethoxylate	-	-	+
Anionic surfactant	-	-	+
Na-Gluconate	2	5	+
Na-Citrate	2	3	-
Phosphonic acid	-	-	+
Polyphosphate	-	5	+
Na-Pyrophosphate	7	-	-
Na-Carbonate	7	5	-
Na-Hydroxide	3	3	+
Water	75	75	+

Specifications

FU = 1000 m^2 clean Al-surface

Cleaning process: immersion bath

Surface flow rate of the cleaning process:
1.25 m^2 Al-surface / L bath

Cleaner concentration:

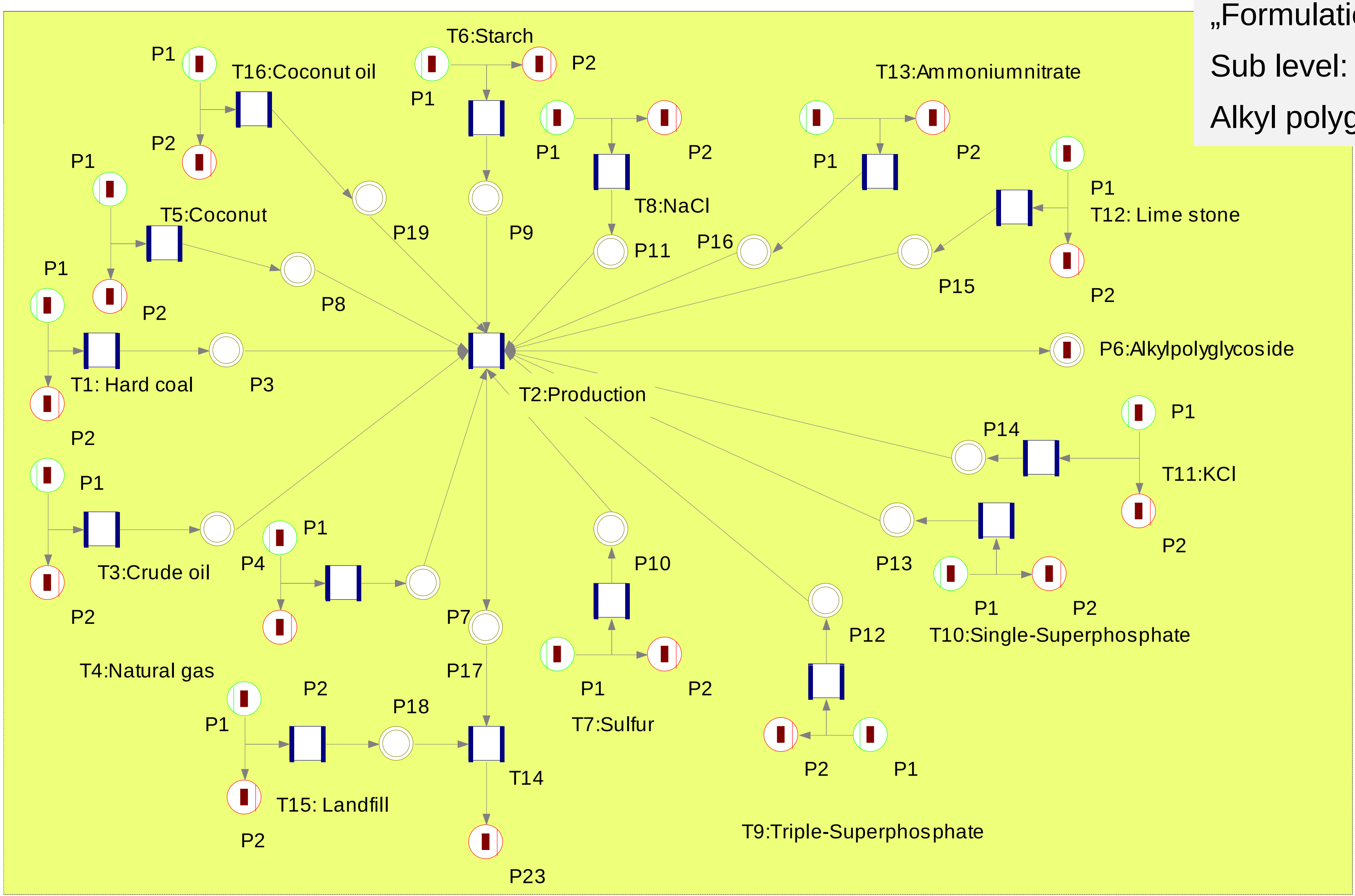
	Scenario 1	Scenario 2
Reference	50 g / L bath	30 g / L bath
Formulation 1	50 g / L bath	50 g / L bath
Formulation 2	50 g / L bath	30 g / L bath

Material and energy flow system

„Formulation 2“

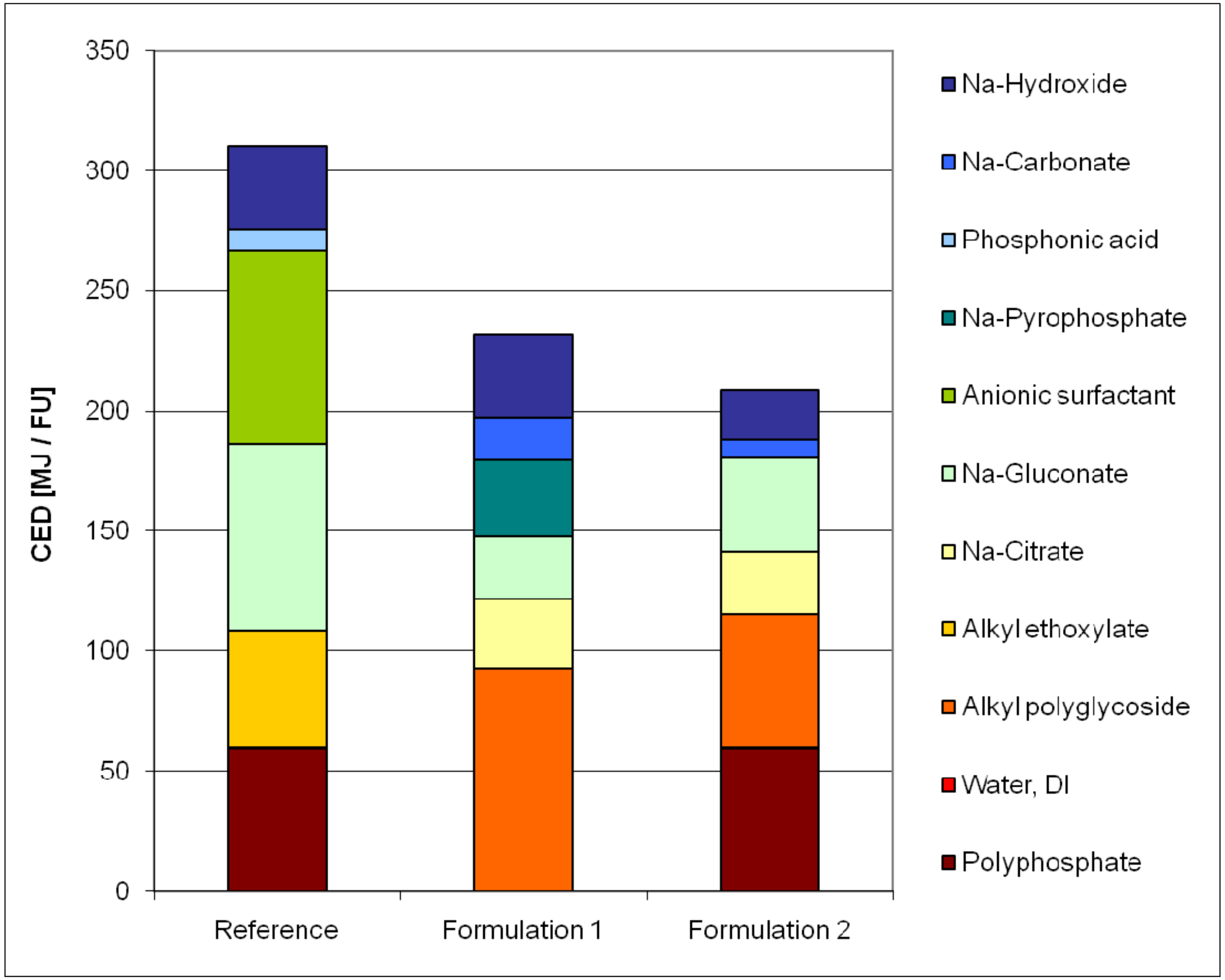
Sub level:

Alkyl polyglycoside



Umberto v. 5.1
Ecoinvent v. 1.2

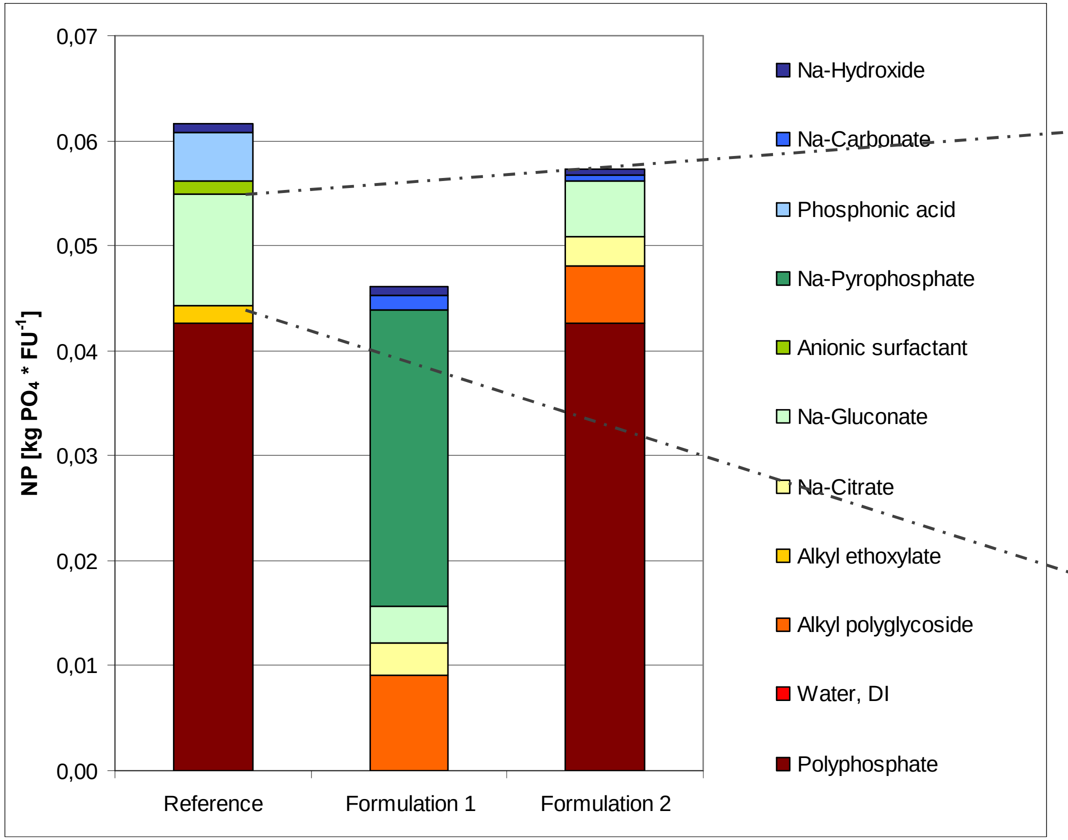
LCIA – Cumulative Energy Demand (CED)

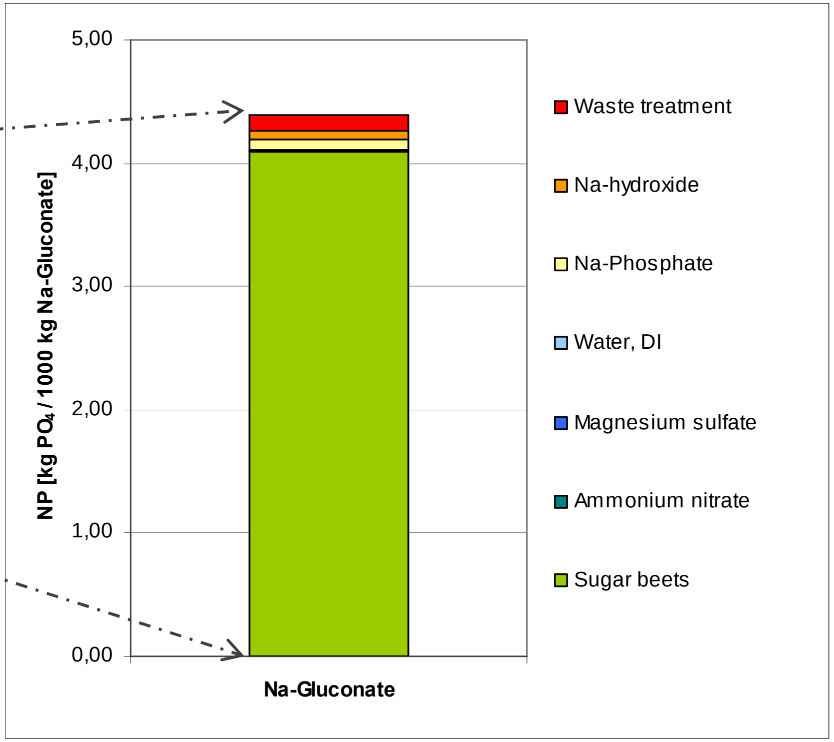


Scenario 2

- Most components significantly contribute to the overall impact
- Formulation 1 and 2 both can lead to a reduction of CED

Nutrification Potential (NP)

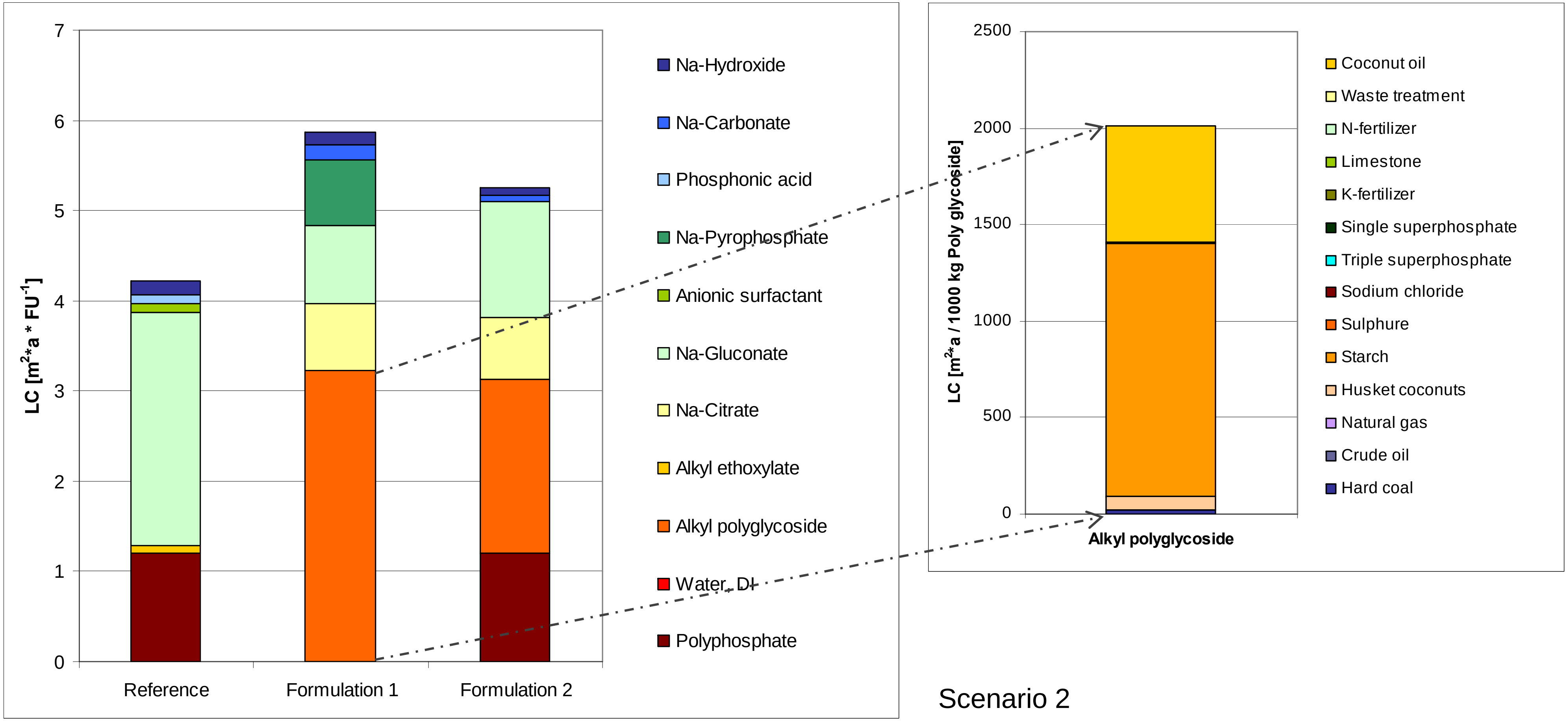




Scenario 2

- Main impact by the supply of the phosphates
- Supply of alkyl polyglycoside less relevant, but higher impact then alkyl ethoxylate + anionic surfactant
- NP of Na-gluconate (and also citrate) is dominated by the cultivation of sugar beets (raw material of the fermentative gluconate production)

Land Competition (LC)



Scenario 2

Main impact by the supply of alkyl polyglycosides and Na-gluconate caused by the cultivation of its renewable raw materials

Conclusions from case example 1

Results:

– Significant ecological advantages of the newly designed cleaner formulations based on renewable materials*
– Exception → impact category „land competition“
– Scenario 1 → formulation 1 ecologically favourable
– Scenario 2 → decision between Formulation 1 and 2 not explicitly feasible
– Impact of components significantly varies within the impact categories
– An exclusive consideration of selected impact categories → significantly distorts the results

*(*Impact categories considered:*
Cumulative energy demand, Global warming, Ozone depletion, Photochemical ozone creation, Acidification, Eutrophication, Human and Eco toxicity, Land competition)

Conclusions from case example 1

Optimisation strategy:

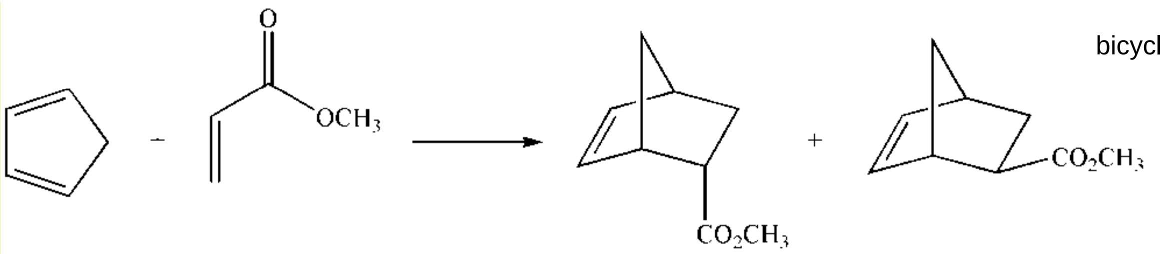
- Substitution of polyphosphate
- Reduction of Gluconate/Citrate fraction

Problems of performing LCA during process development:

- Great lack of LCI data for natural products
  → consideration of one newly developed formulation was hindered
- Unknown down-stream-processing
  → LCA restricted to a „cradle to use" approach
  → further advantages at the end of the life cycle not visible

D. Kralisch, G. Kreisel, U. Stieglitz, Ch. Ruhland. In *1st International IUPAC Conference on Green-Sustainable Chemistry*, Dresden, Germany, 10. - 15.09.2006

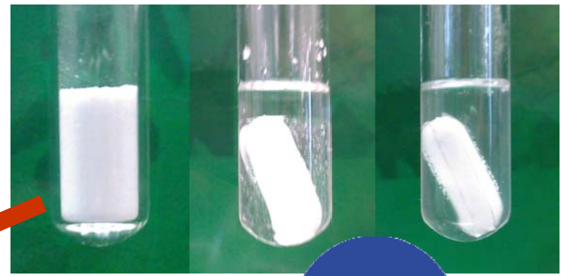
Case Example II: Solvents in Diels-Alder Reaction



bicyclo[2.2.1]hept-5-en-2-carboxylic acid methyl ester

Solvent	*T [°C]*	*Conversion methylacrylate [%]*		*Endo/exo-selectivity*
Methanol	25	48 h	95	4.9
Methanol/water (v/v 1:1)	25	48 h	98	5.5
Acetone	25	48 h	84	3.3
Cyclohexane	25	48 h	90	2.6
$[C_6MIM][BF_4]$	25	48 h	92	3.8
Dimethylurea/ citric acid (w/w 40/60)*	65	8 h	99	3.7
Solvent-free	25	48 h	98	2.9
$[C_6MIM][BF_4]$	65	8 h	98	3.3

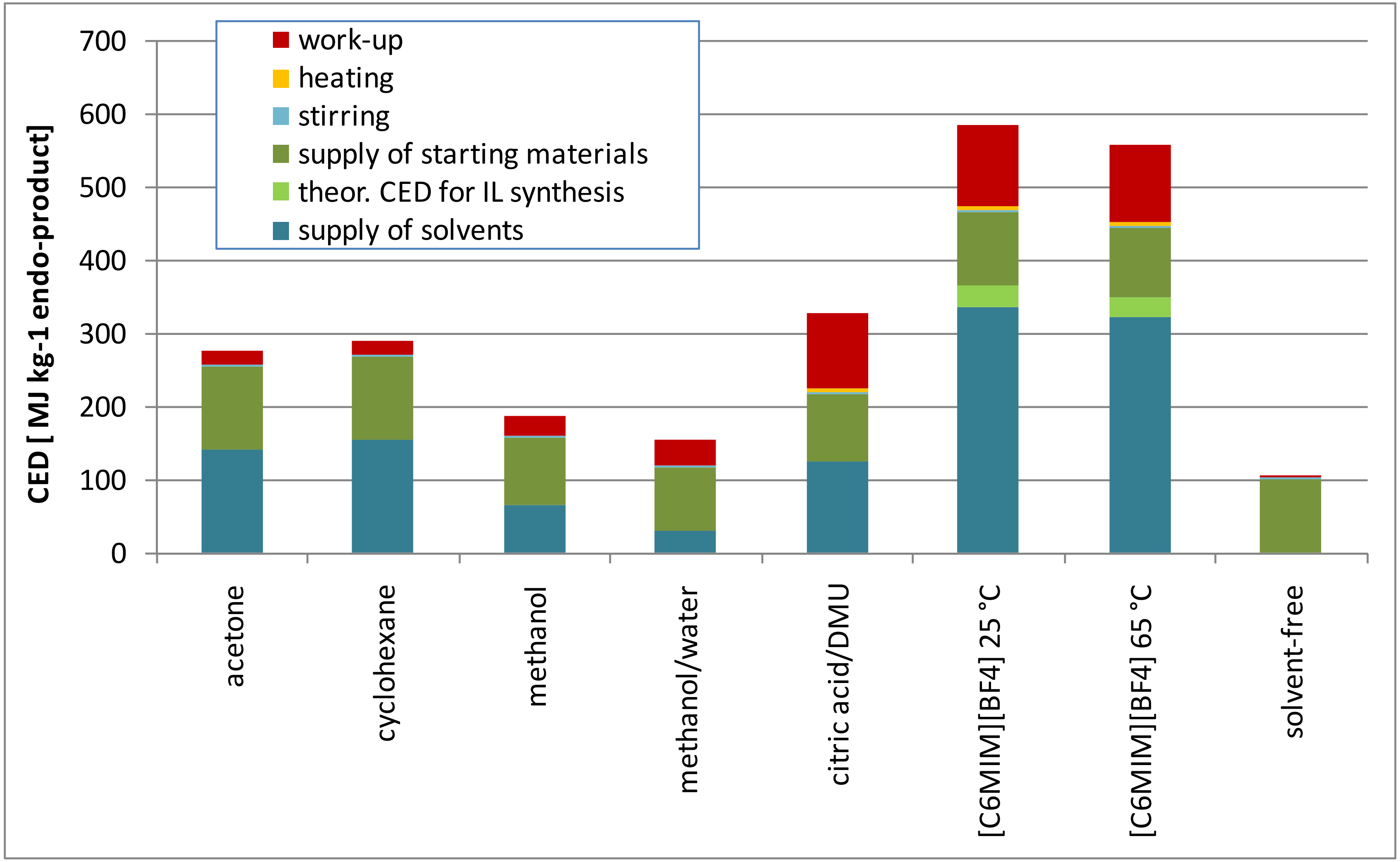
Non-volatile
Non-toxic



* G. Imperato, E. Eibler, J. Niedermaier, B. König, Chem. Comm. (Cambridge, United Kingdom) 2005, 1170.
D. Reinhardt, F. Ilgen, D. Kralisch, B. König, G. Kreisel, Green Chem., 2008, 10(11), 1170.

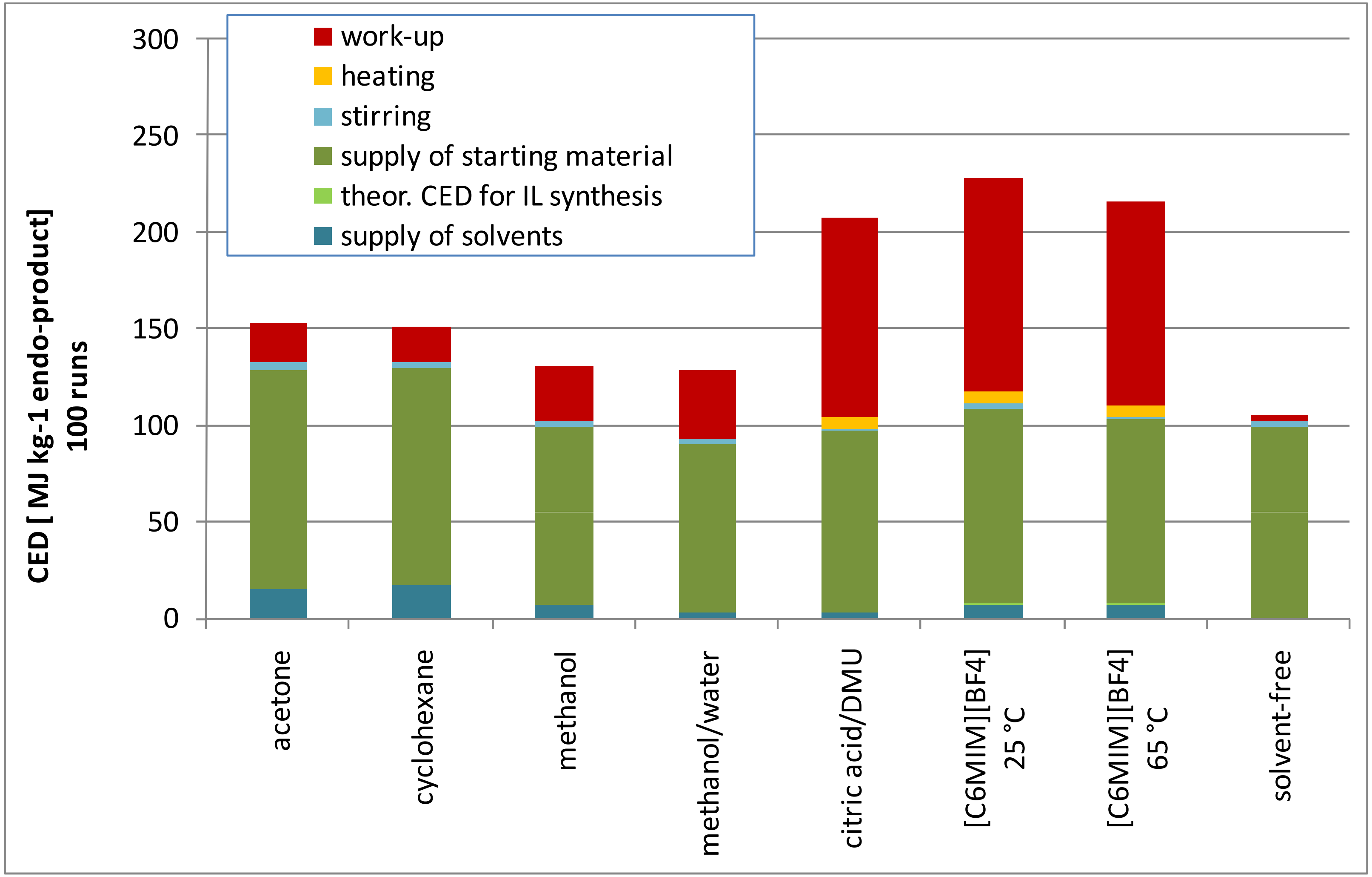
DBU AZ 20005/780

Cumulative Energy Demand



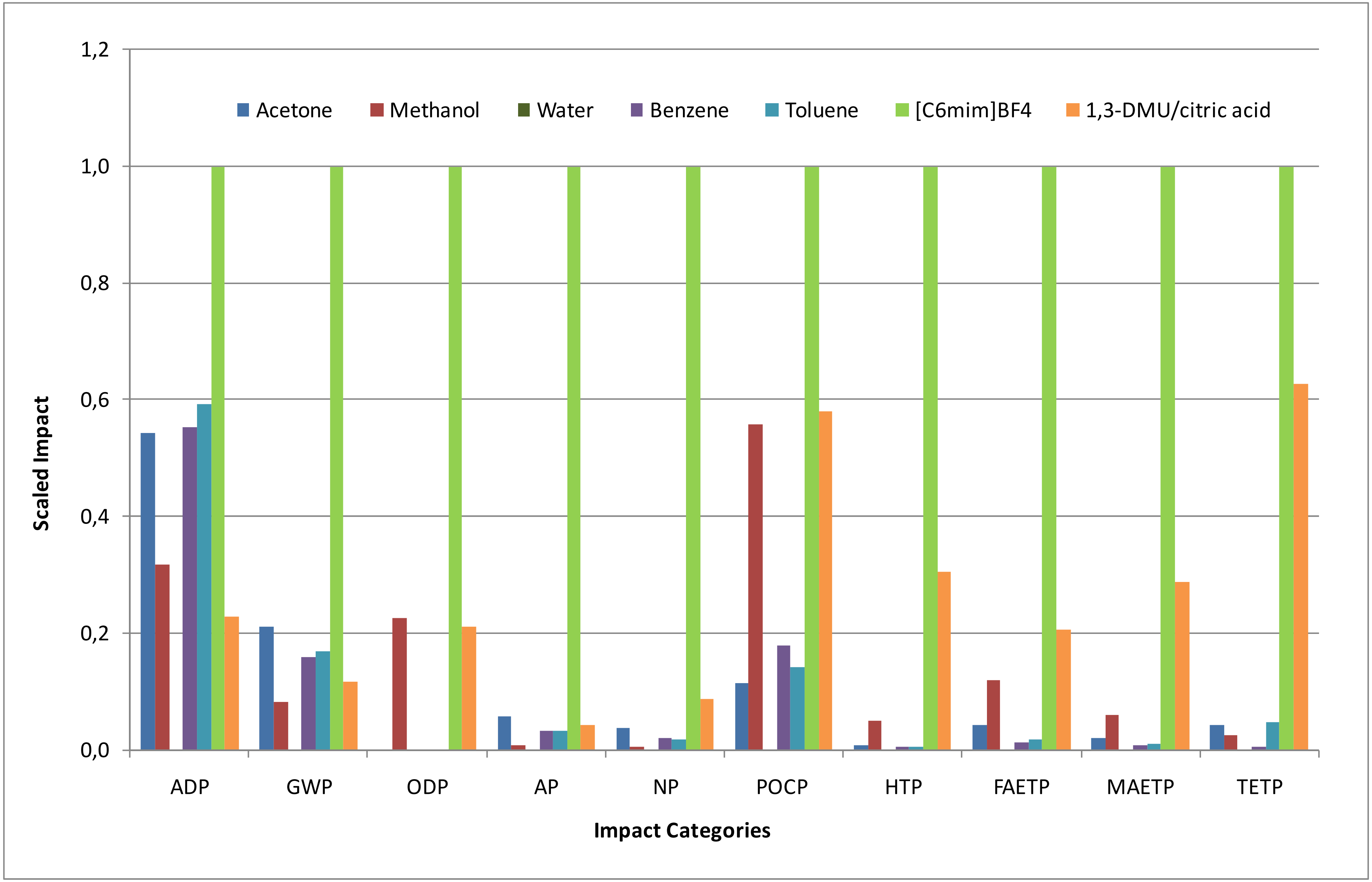
Efficient recycling strategy → CED ↓ ?

CED - Effect of Solvent Recycling

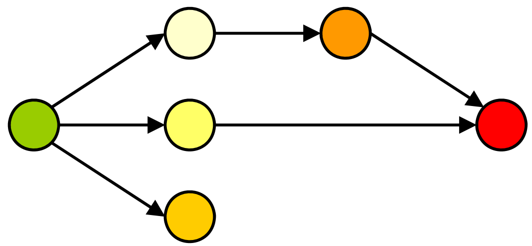


Low vapour pressure of solvents can be disadvantageous

LCIA: Supply of Molecular Solvents vs. Alternative Solvents



Conclusions from case example 2



Outranking of solvent alternatives concerning i) energy demand, ii) toxicity, iii) costs:

Solvent-free, methanol/water > methanol > acetone > cyclohexane > DMU/citric acid > [C_6MIM][BF_4]

Additional results of SLCA:

- Alternative Solvents as DMU/citric acid melts or IL are NOT a priori „green“

  → Significant improvements in performance
- Efficient recycling strategies → extraction more energy demanding then distillation
- SLCA helpful tool at early stages of R&D

  → Decision support tool for “green” product /process design

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Thank you for your attention!