



Deutsch-Brasilianische Wirtschaftstage 2008
Encontro Econômico Brasil-Alemanha 2008

Organization:



Cooperation:



Workshop (No. 3)
Renewable Raw Materials for Adhesives & Sealants
Opportunities for Innovations

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Henkel AG & Co. KGaA

Cologne, August 25, 2008



Adhesive Technologies



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Household/Office



- Small repair jobs
- Handcrafts

DIY



- Renovation
- Repairing, Mounting

Professional



- Professional and intensive usage
- Training of skills

Adhesive Technologies



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Industrial Businesses

Transportation



Electronics



Metal Industries



Durable Goods Sanicare Fast Moving Consumer Goods Packaging Materials



Maintenance, Repair & Overhaul



Bonding & Sealing Technology of the future



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	Industrial fasteners*, staples & tacks	Welding, soldering, brazing	Bonding & sealing
Reduction of vibration and tension			✓
No damage of material structure			✓
Volume & weight reduction		(✓)	✓
Even transfer of forces			✓
Joining of thin materials		✓	✓
Joining of heat-sensitive materials	✓	✓	✓
Joining of different materials	✓		✓
Joining	✓	✓	✓





Megatrends

Need for High Performance Adhesives & Sealants

- **Mobility**
 - New car concepts
- **Energy**
 - Fuel Cells
 - Wind Energy
 - Solar Energy
- **Communication**
 - Electronics
- **Sustainability**
 - CO2 footprint
 - Life cycle analysis



Henkel's Contributions to Sustainable Development



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Adhesives based on Renewable Resources



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1. Traditional Natural Adhesives

- **Starches & Dextrines** → paper & packaging, labelling, wallpaper
- **Cellulose ethers** → tiling, wallpaper adhesives
- **Caseins** → labelling, levelling compounds
- **Natural rubbers**

2. Additives, tackifiers

- **Colophonium derivatives, Terpene Phenolic resins ...**

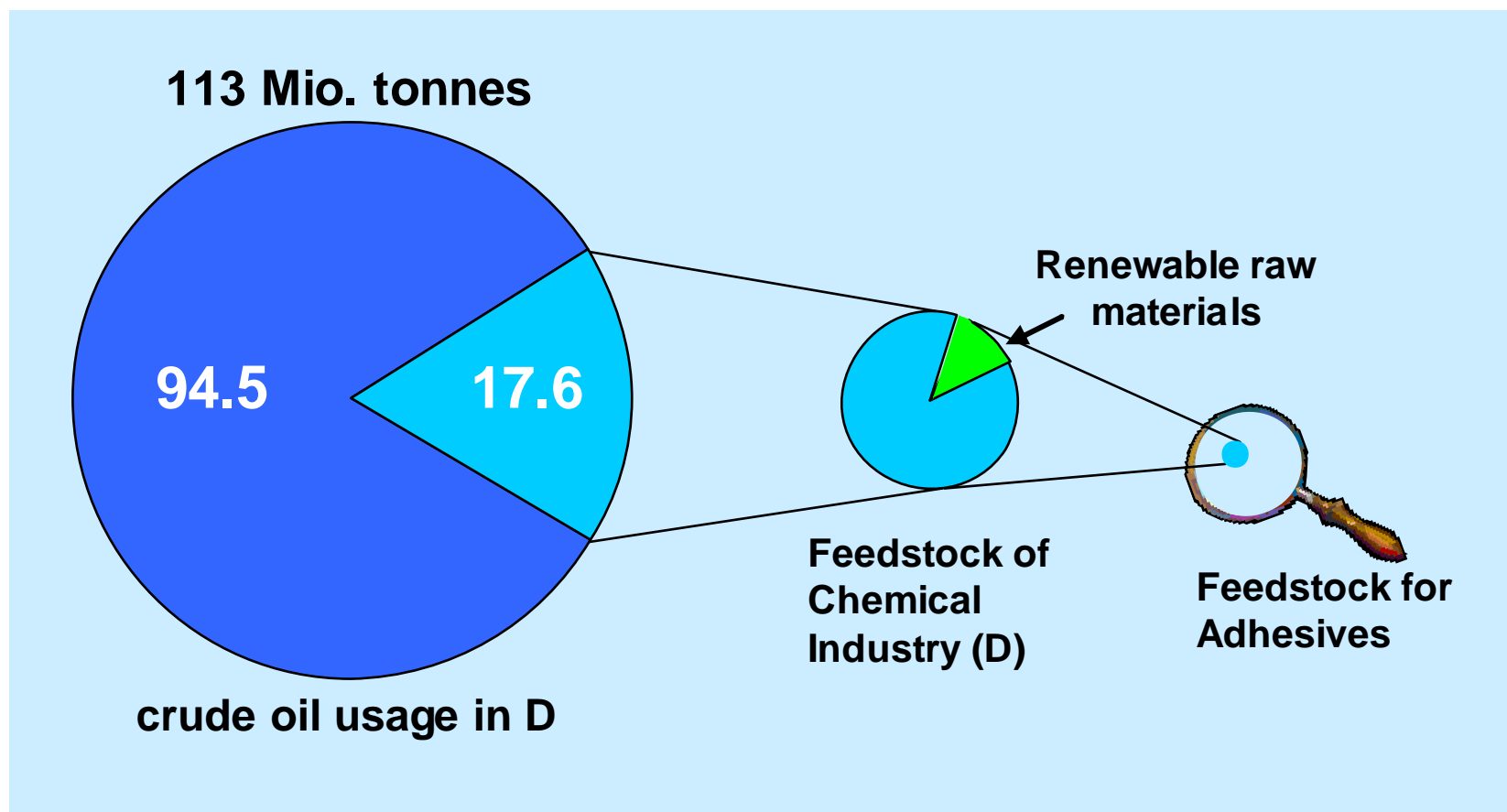
3. Synthetic adhesives with natural building blocks

4. Bio-Adhesives

Use of Petrochemicals vs. Renewable Raw Materials (2006)



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Renewable Raw for Synthetic Adhesives

Three ways to Chemical Feedstock



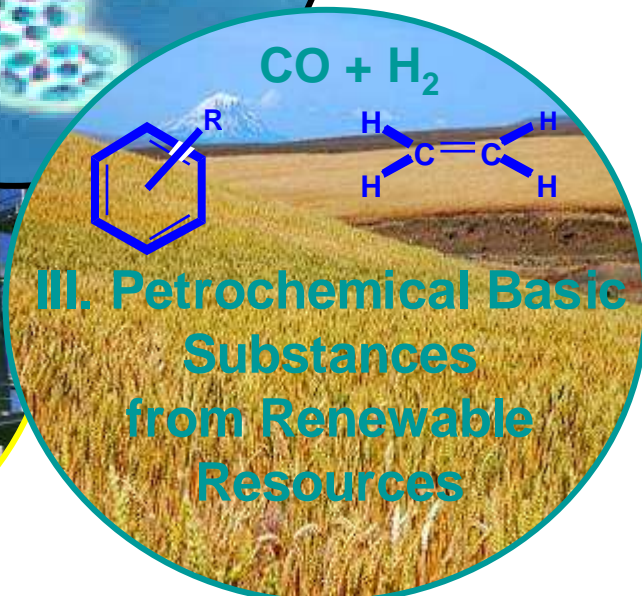
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I. Biotechnological Processes



II. Modification by Chemical Processes



$\text{CO} + \text{H}_2$



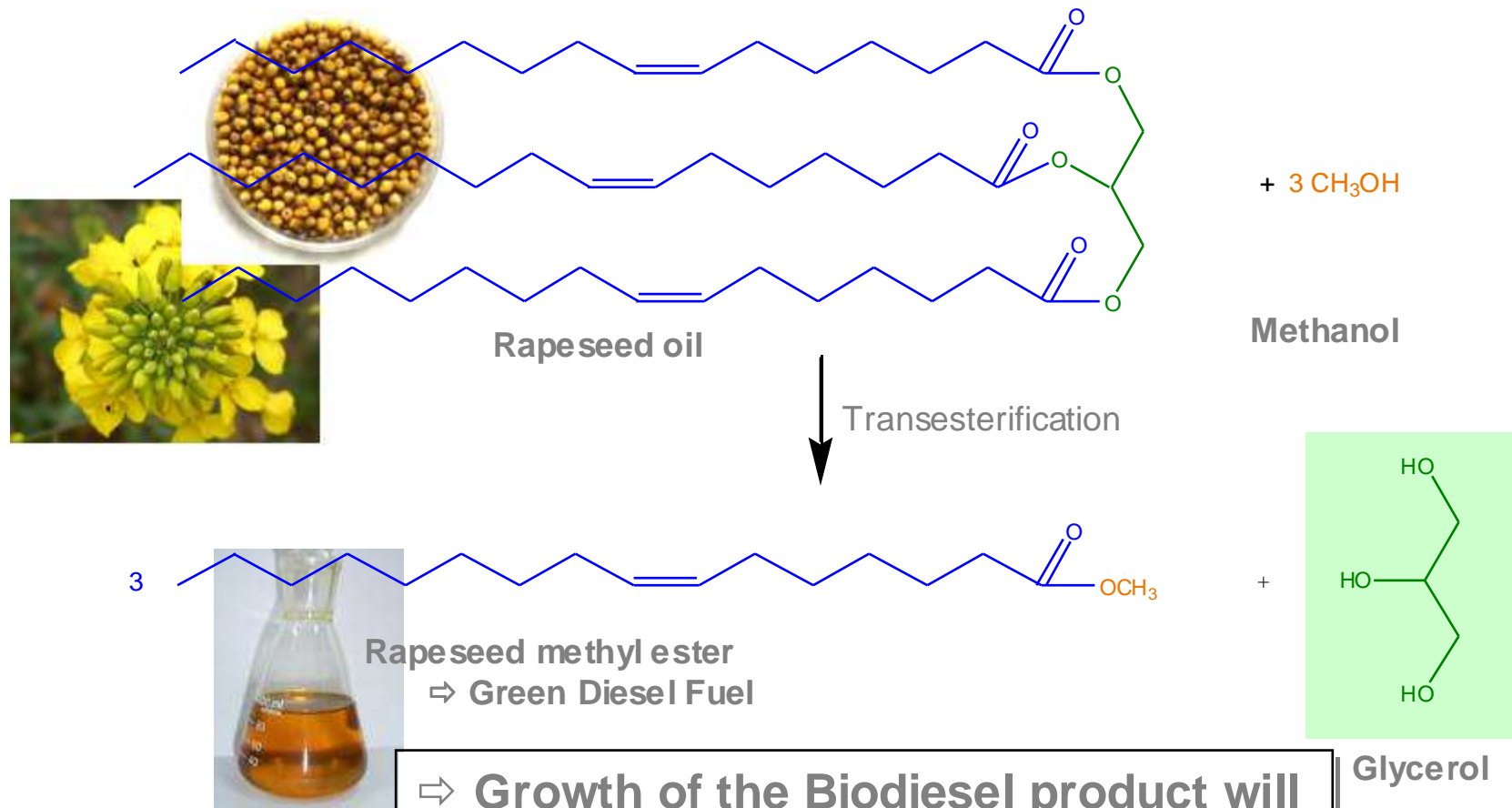
III. Petrochemical Basic Substances from Renewable Resources

Chemical Modification of Renewable Raw Materials



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Biodiesel production



⇒ Growth of the Biodiesel product will swamp the glycerol market

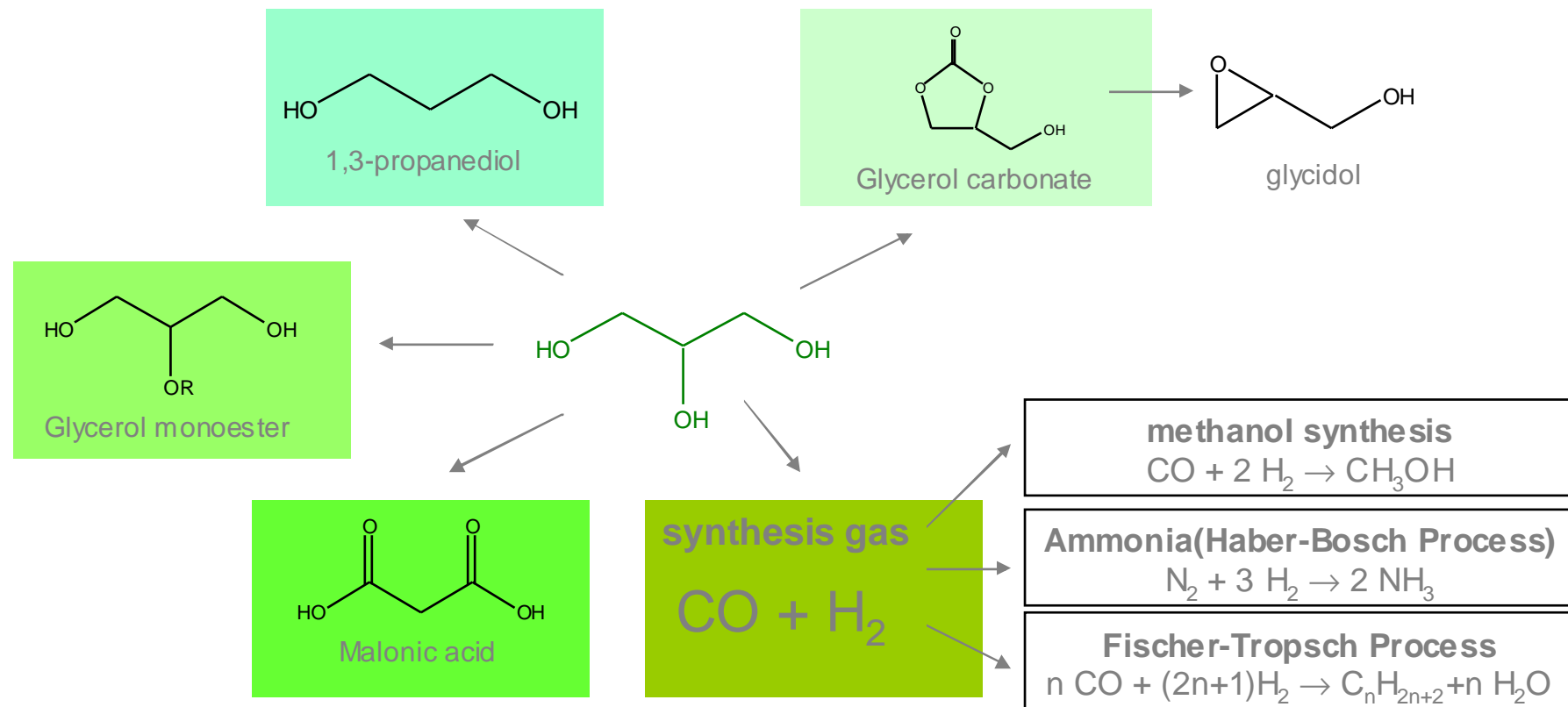


Platform Chemicals from Renewable Resources



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⇒ At prices approaching 0.75 US-\$/kg or less, glycerol could become a significant *platform chemical*



Renewable Raw Materials for Polyurethanes



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Diol / polyol components

- Castor oil
- Soybean oil
- Epoxidized methyloleat-based polyether polyol
- Sugar derivatives (e.g. isosorbide, manitol, sucrose)
- Polyester (e.g. 1,3-propanediol + succinic acid)
- Coconut diethanolamide

↓
All raws from renewable resources

Diisocyanates

- Methylene Diphenyl Diisocyanate (MDI)
- Toluene diisocyanate (TDI)
- Hexamethylene diisocyanate (HDI)

↓
All are petrochemical products

Only few examples for diisocyanates from renewable materials are known

- Furfuryl diisocyanate¹⁾
- Lysine ethylester diisocyanate²⁾

1) Hoflinger et al., J. Applied Polymer Science, Vol. 49, 337-344 (1993)

2) DE 19643816

Macroplast - Structural Adhesives



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- Castor oil is obtained from the castor oil plant (*Ricinus communis*)
- Applications: Truck and shipbuilding, filter, sports articles
- Reasons:
 - very hydrophobic
 - ⇒ avoids foam formation during the curing
 - ⇒ sticks better than polar polyols
 - good availability
 - defined composition



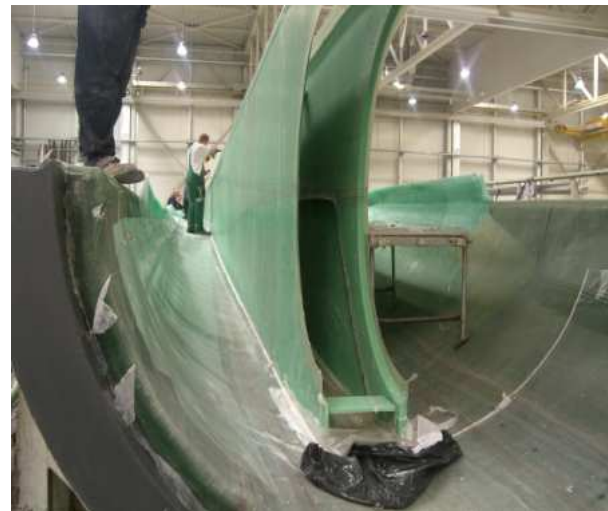


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High Performance 1 & 2 K PUR

Polyurethanes based on Renewable Polyoles

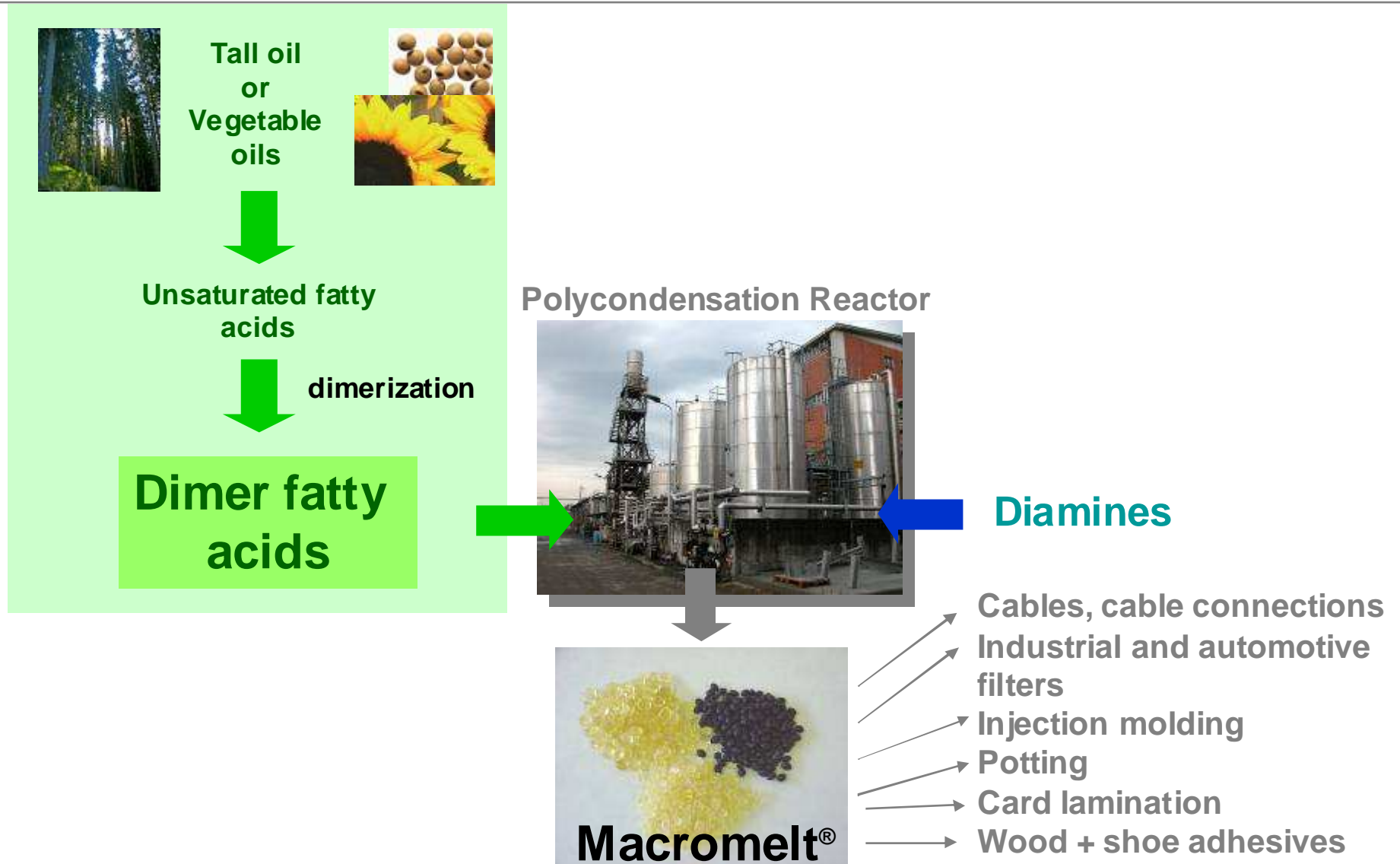
Half shell bonding of wind energy rotorblades



Macromelt® - Polyamide Hotmelts



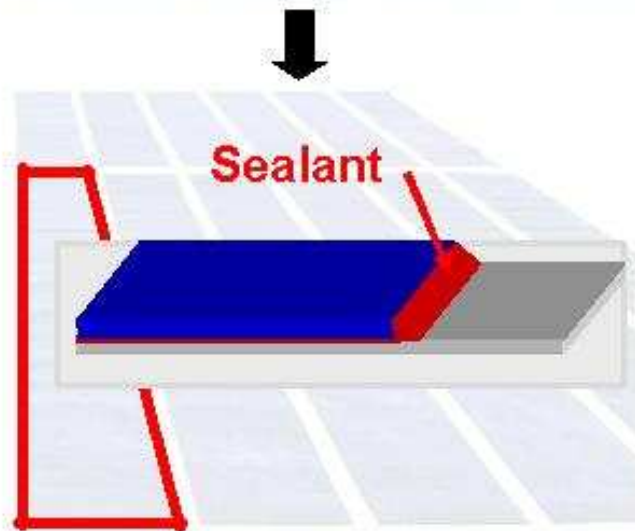
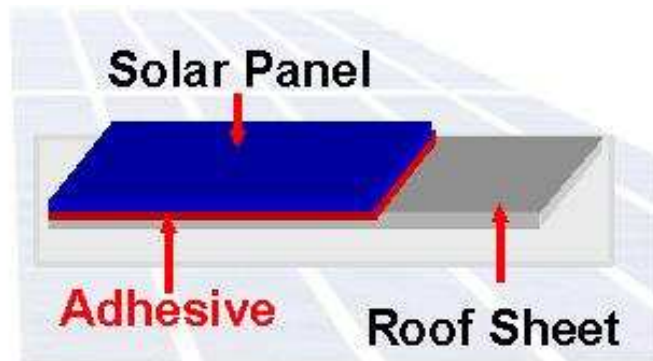
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High Performance Adhesives & Sealants for the Solar Industry



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SmartRoof!
Solar Roof from the
Coil

Energy & Climate: Adhesives and Sealants for Flexible Solar Cells



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- Contribution to the development of alternative energy sources
- Henkel hotmelts bond the solar cells on a roll and their electrical wiring to the roofing membranes
- Flexible solar cells can be simply rolled out on flat roofs



Materials & Waste

Using Renewable Raw Materials



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- Pritt stick has been free of solvents since its creation in 1969.
- In 2000, switch to a formulation based on renewable raw materials
- Renewable raw materials now account for 90 percent of its dry weight.



Learning from Nature

Biological Adhesives



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I. Adhesive secreted by Australian frogs



- Frogs produce a protein-based yellowish exudate that quickly cures to an elastic material
- 20 to 100 mg can be harvested from one frog once a month
- Focus on surgical adhesives

II. Bacterial exopolymer adhesives



- Biomass fermentation residues (e.g. from bioethanol production) could be potentially useful as wood adhesives

III. Holdfast proteins of mussels



- Mussel adhesive proteins have remarkable adhesion to all kinds of surfaces in the presence of water
- Complex biochemistry (protein deamidation, phosphorylation, Dopa chemistry)

Typical Characteristics of Biological Adhesives



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- Complex chemical structures and adhesion mechanisms, which are often only understood in a rudimentary manner
- Biodegradable / compatible with tissue and live systems
 - Perfect fit for medical applications
- Low – moderate adhesion on *most substrates*
- Interesting mechanisms for substrate recognition

Principle Chemistries and Comparison to Synthetic Adhesives



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Examples	Chemical structure	Structure of a synthetic adhesive
<p>Polysaccharides Bacterial Exopolysaccharides; Chitosan (from Chitin ⇒ crustaceans)</p>		<p>Diamine cross-linked epoxy resin</p>
<p>Phloroglucinol-based polyphenols Marine brown algae</p>		<p>Phenol Formaldehyde resin</p>
<p>Proteins Holdfast protein in mussels; Adhesive secreted by Australian frogs</p>		<p>Polyurethanes</p>
<p>Others Polyisopren (rubber); Tulipalin (tulips)</p>		<p>Acrylic resins</p>



Summary



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- Natural adhesives have a long tradition and count for about 15% of the worldwide adhesives consumption/ year
- High performance (structural) adhesives & sealants contribute essentially to the technical progress but are currently dominated by petrochemical resources
- It could be demonstrated that it is possible to develop high performance adhesives & sealants with building blocks based on renewable raws (top performance & sustainability)
- A further extension depends on how to overcome the limitations: low availability due to missing infrastructure/ platform, reproducibility and cost/ performance ratio
- The research into the structures and mechanism of adhesives excudated by living organism (biological adhesives) may offer exiting opportunities for the future