Potential of biobased polymers in pressure sensitive adhesives

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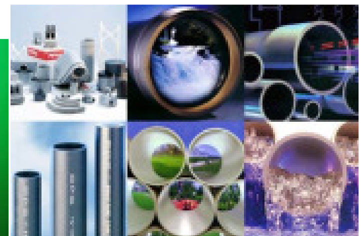
Biobased Products @ Food & Biobased Research

- Leading research group in the Netherlands
  - 90+ fte,
  - Confidential bilateral projects with multinationals, SMEs
  - Public-private sponsored projects
- BU comprises three interconnected Programmes:
  - Biorefinery & Sustainable Chains
  - Biobased Chemicals & Fuels
  - Biobased Materials
  - Algal and Microbial Technology
- Close link with Food Technology Centre

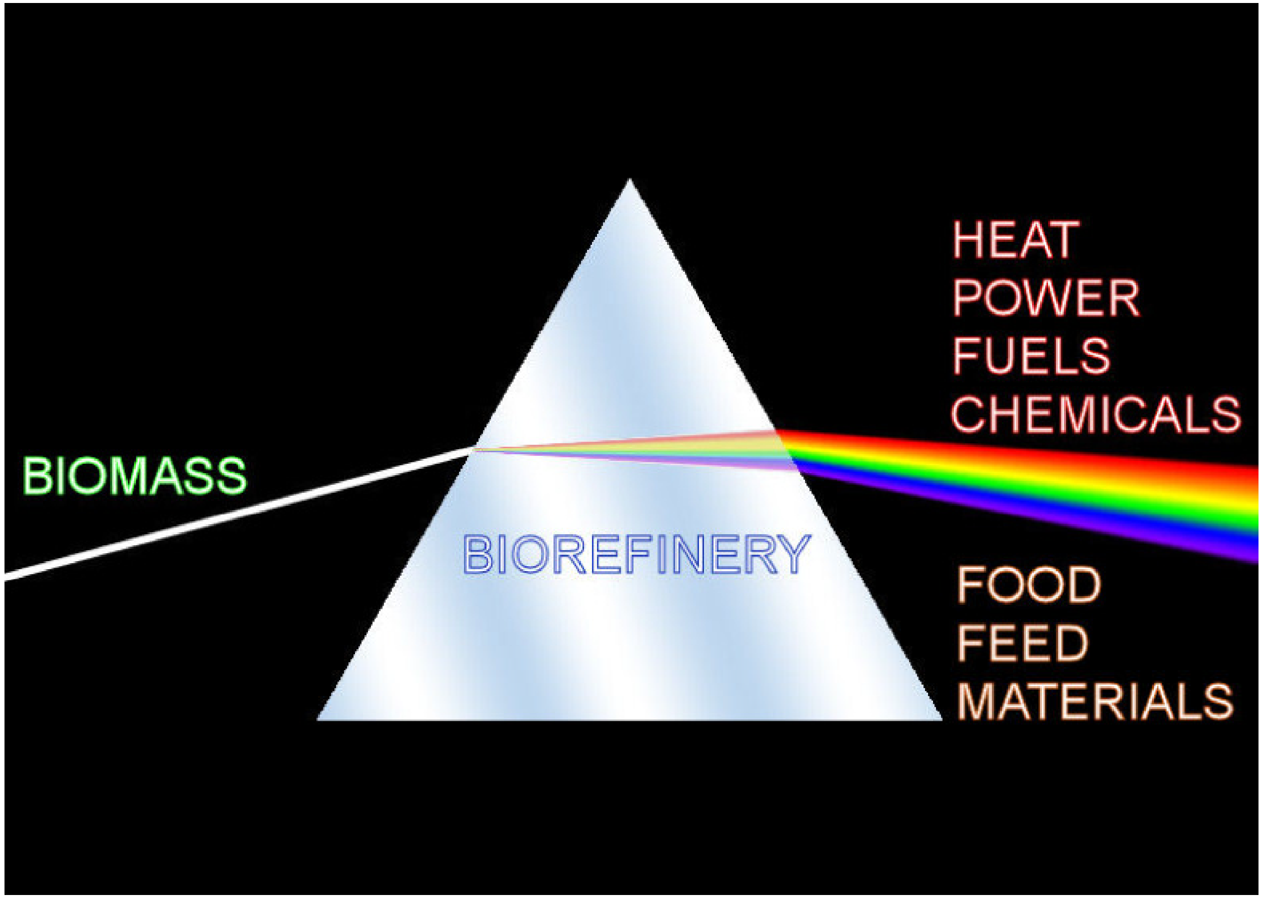


Biobased Chemicals & Fuels Programme WUR/FBR

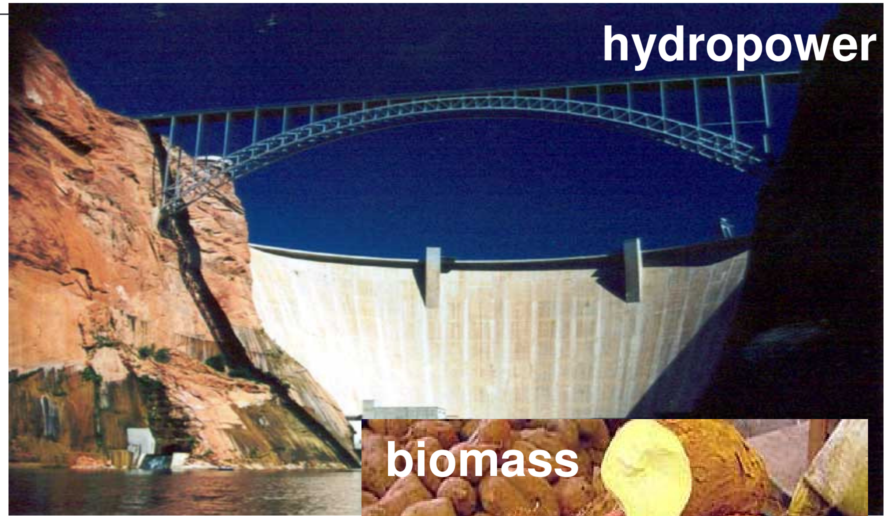
- Consists of over 40 projects in which biobased chemicals are one of the dominant aims
  - Confidential bilateral projects with international multinationals as well as SME' s.
  - Public private sponsored projects

  - Comprises 3 focus areas:
    - Carbohydrate based chemicals:
      - Furan platform
      - Isohexide platform
      - Sugar biotechnology platform
    - Lignin based chemicals
    - Vegetable oil and algae oil based chemicals
  - Internationally cooperates with numerous universities and institutes
  - Internally intensively cooperates with the bioenergy and biobased materials programme
  - Approximately 35 coworkers involved

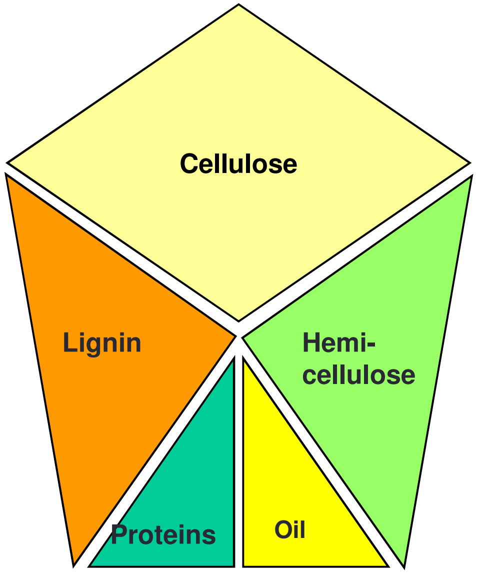
Existing and future biorefineries will refine biomass into a spectrum of products



Alternative sources of energy



General composition of biomass



Cellulose (circa 50%): polymer of β-(1,4)-glucan

Hemi-celllulose (circa 25%): short-chain branched, substituted polymer of sugars

Lignin (circa 25%): polymer derived from coniferyl, coumaryl and sinapyl alcohol precursors

Proteins (up to 10%, depending on the plant species): polymer of amino acids

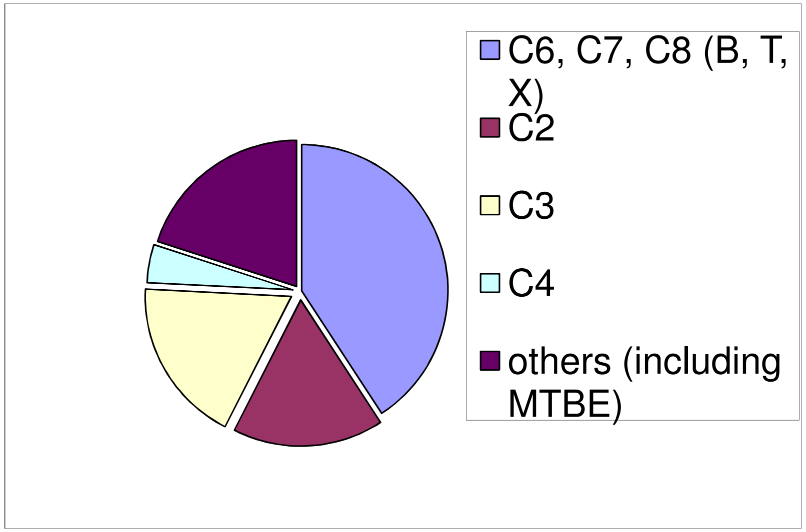
Oil (up to 10%, depending on the plant species): e.g. esters of glycerine and fatty acids

Usage of bulk (platform) chemicals

- Bulk chemicals are used as:
  - Solvents
  - Starting components for soaps, lubricants, additives (low molecular weight components)
  - Mostly as building blocks for polymers (high molecular weight components)
- Building blocks can be either aliphatic (flexible) or aromatic (rigid) nature

Up to 40% of basic chemicals produced in Port of Rotterdam is of aromatic nature

WUR/FBR and TNO are creating a shared Innovation programme on biobased aromatics



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IEA Bioenergy

Current Market Size

Fossil based Chemicals:

330 million tonnes

Main molecules:

methanol, ethylene, propylene, butadiene, benzene, toluene and xylene

Biobased Chemicals & Materials

50 million tonnes

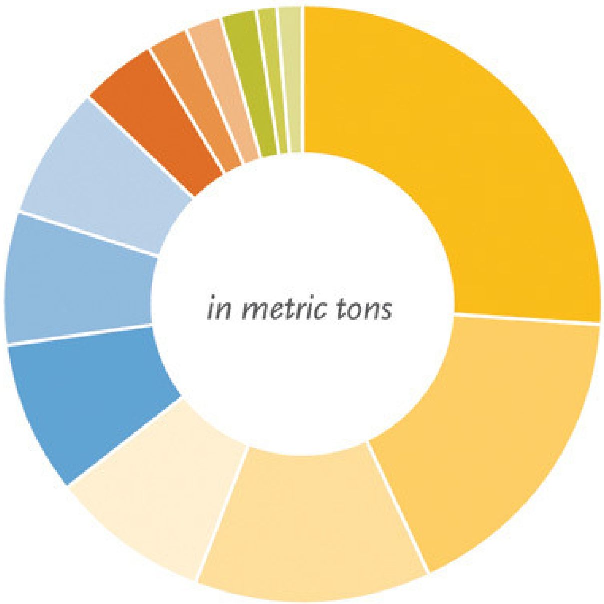
Main current biobased molecules:

Non-food starch, cellulose fibres/derivatives, tall oils, fatty acids and fermentation products

IEA Bioenergy

Biopolymer production capacity

Biopolymers production capacity 2015 (by type)



Bio-PE	450.000	26 %
Bio-PET	290.000	17 %
PLA	216.000	13 %
PHA	147.100	9 %
Biodegradable Polyesters	143.500	8 %
Biodegradable Starch Blends	124.800	7 %
Bio-PVC	120.000	7 %
Bio-PA	75.000	5 %
Regenerated Cellulose[1]	36.000	2 %
PLA-Blends	35.000	2 %
Bio-PP	30.000	2 %
Bio-PC	20.000	1 %
Others	22.300	1 %
Total	**1.709.700**	100 %

[1] *only hydrated cellulose foils*

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Plastics Europe anticipated biopolymer production capacity (tonnes) by 2015

IEA Bioenergy

Potential for GHG savings

Product	GHG savings ($t\ CO_2$/t of product)	Installed world capacity (million t/year)	Annual GHG savings (million tonne CO_2/year)[4]
Acetic acid	1.2	8.3	9.6
Acrylic acid	1.5	2.9	4.4
Adipic acid	3.3	2.4	7.9
Butanol	3.9	2.5	9.6
Caprolactam	5.2	3.9	20.0
Ethanol	2.7	2.6	7.1
Ethyl lactate	1.9	1.2	2.2
Ethylene	2.5	100.0	246
Lysine	3.6	0.6	2.3
Succinic acid	5.0	1.4	6.8
1,3-propanediol	2.9	-	-
PHA	2.8	57.0	160
PLA	3.3	11.1	36.5

Hermann, B.G., et. Al. 2007 *Environ. Sci. Technol*. 41, 7915-7921.

Drop-in versus Unique functionality

	Drop-in	Unique molecule
Market acceptance	↑↑	↓↓
Speed of introduction	↑↑	↓↓
Fit with existing infrastructure	↑↑ ↔	↔ ↓
Oil/Feedstock price sensitivity	↑↑↑	↑
Sustainability	↑ ↔ ↓	↑↑↑ ↔
Unique market space	↓↓↓↓	↑↑↑↑
Scalability	↑↑↑	↑ ↔ ↓
Legislation (e.a. REACH)	↑↑↑	↑↑↑↓↓↓

FBR; huge knowledge on biobased chemicals

Green building blocks
for
biobased plastics

PAULIEN HARMSEN AND MARTIJN HACKMANN

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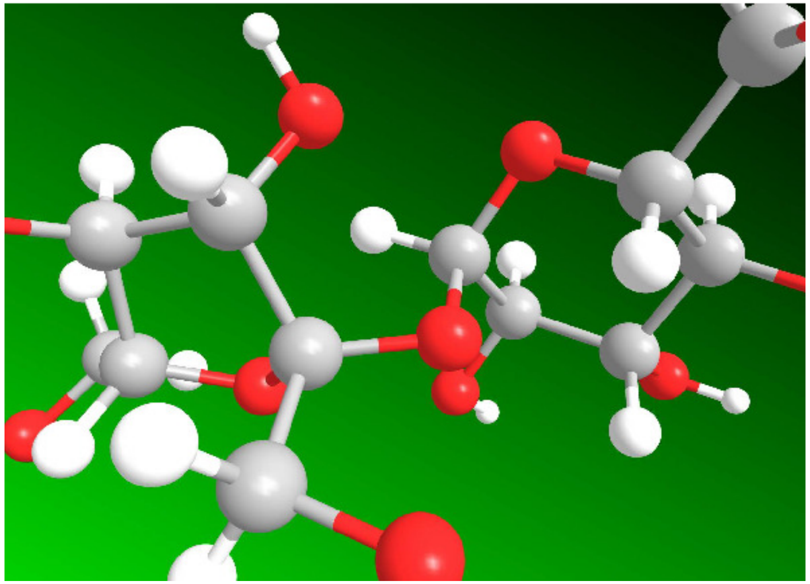
For quality of life



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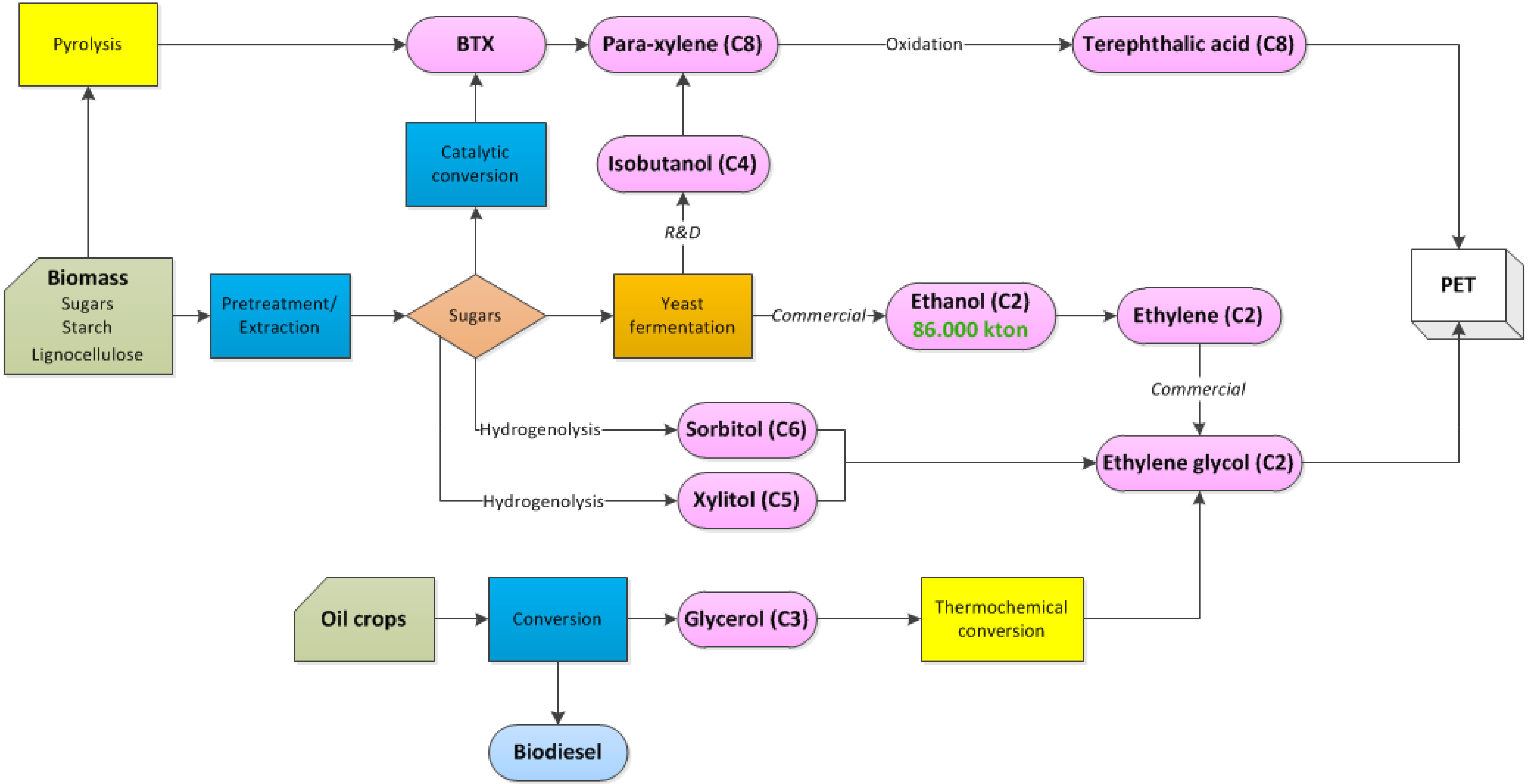
Polyesters: PET



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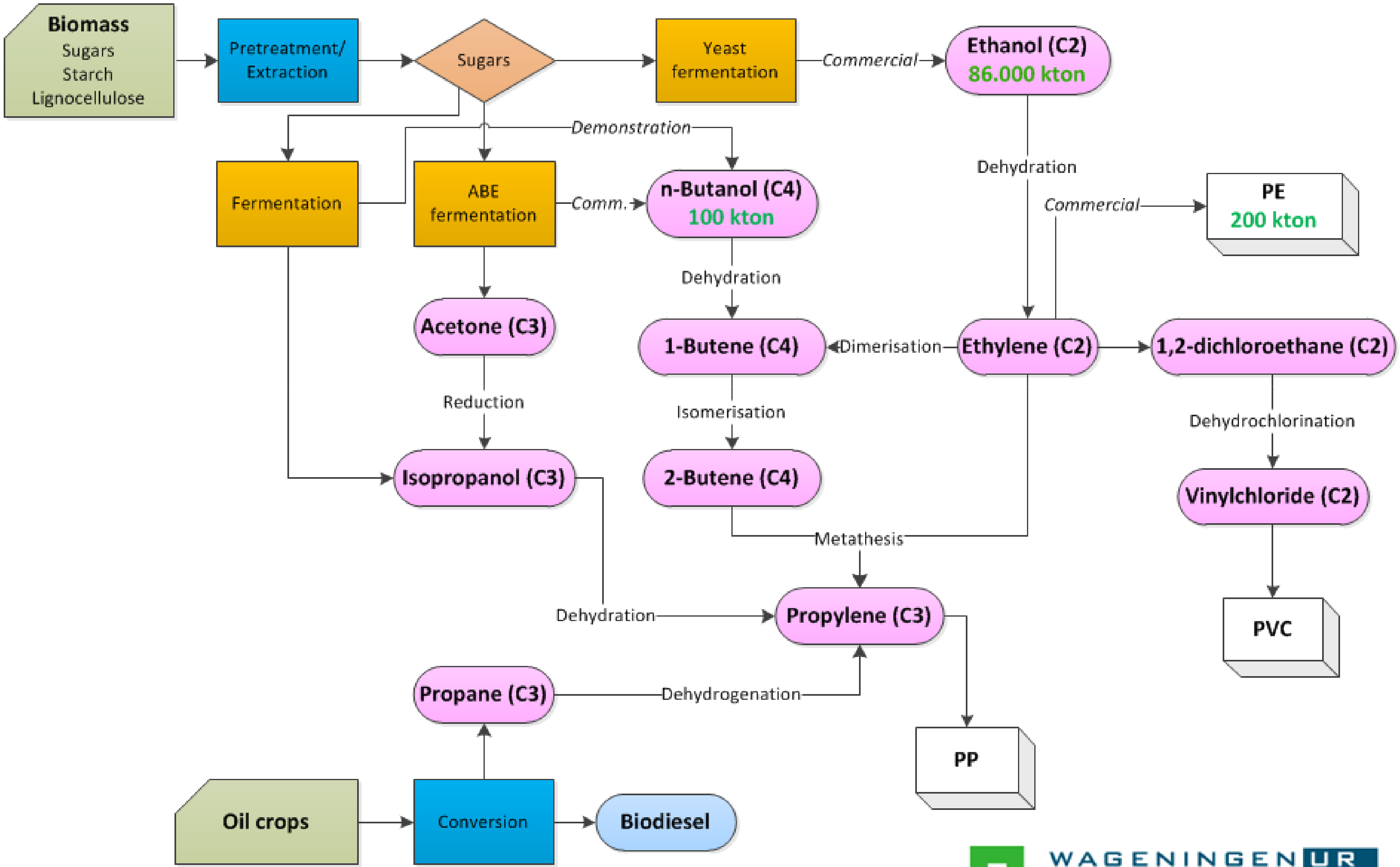
For quality of life

Source: P. Harmsen et al., *Green Building Blocks for Biobased Plastics* (WUR 2013)

Vinylpolymers: PE, PP and PVC



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Source: P. Harmsen et al., *Green Building Blocks for Biobased Plastics* (WUR 2013)

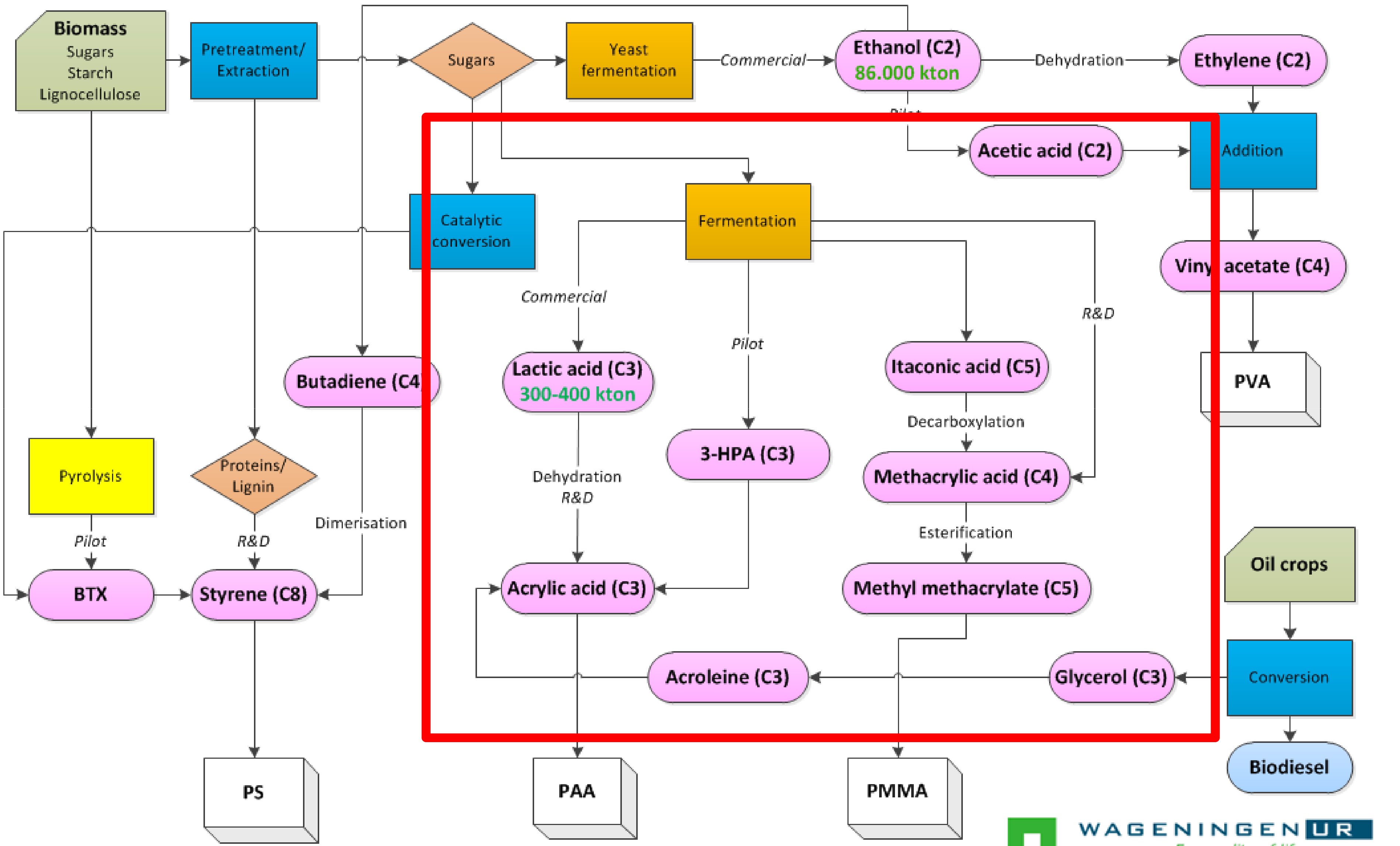
Pressure sensitive adhesives

- PSA's used in labels, tapes and protective films
- Binders PSA's most frequently based upon emulsion polymers
- Permanent tack requires low Tg polymers
- Combination of permanent tack, cohesive strength, peel strength and shear resistance required

- Most frequently used monomers:
  - Soft; acrylate esters e.g. butylacrylate, 2-EH acrylate
  - Hard; methylmethacrylate (MMA), vinylacetate, styrene
  - Polar; acrylic acid, methacrylic acid

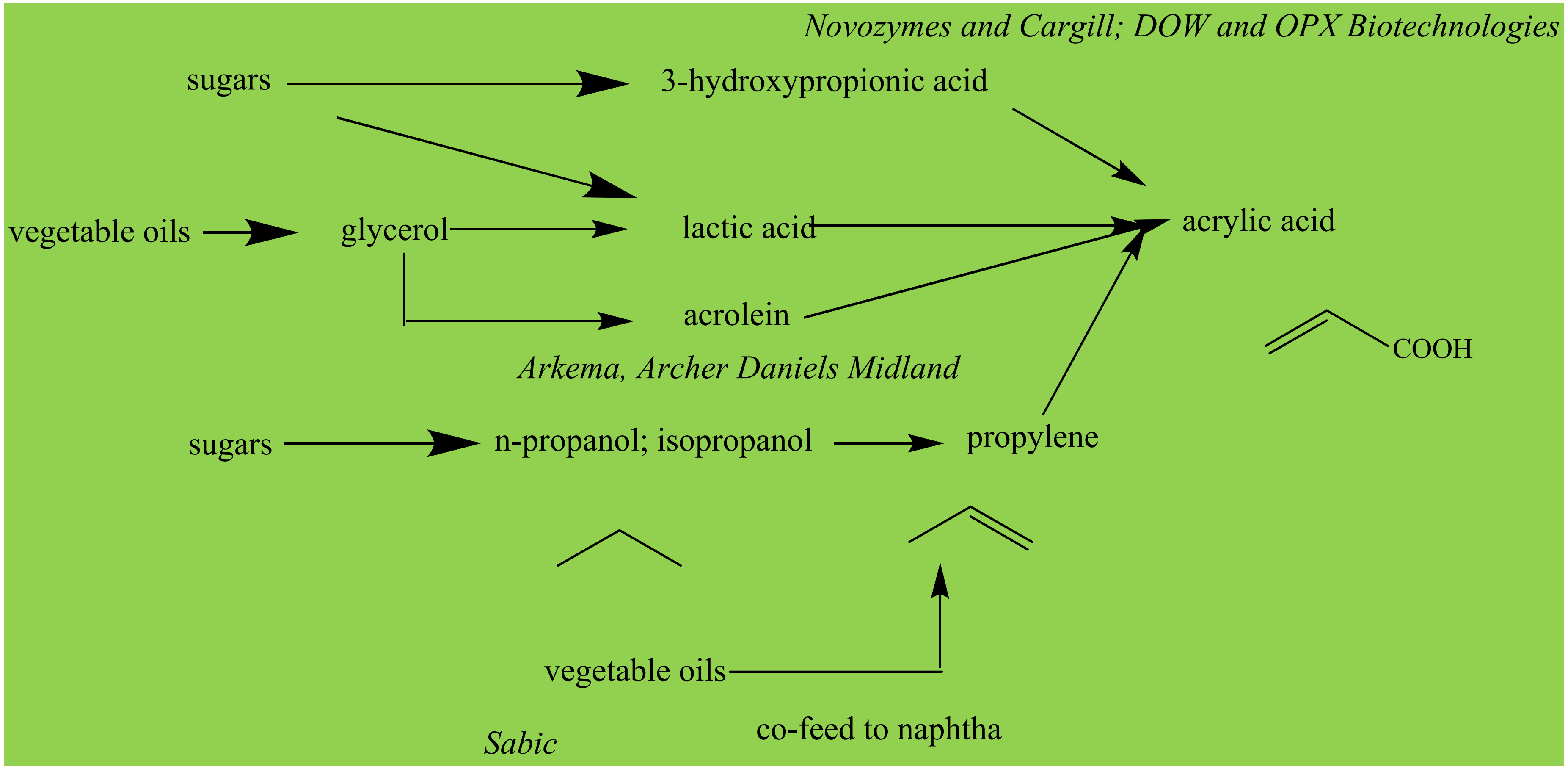
Ref; R. Jovanovic, M.A. Dube, Emulsion based Pressure Sensitive Adhesives, Journal of macromolecular science, Part C, 44:1 , 1-51, 2004.

Vinyl polymers: PS, PVA, PMMA and PAA

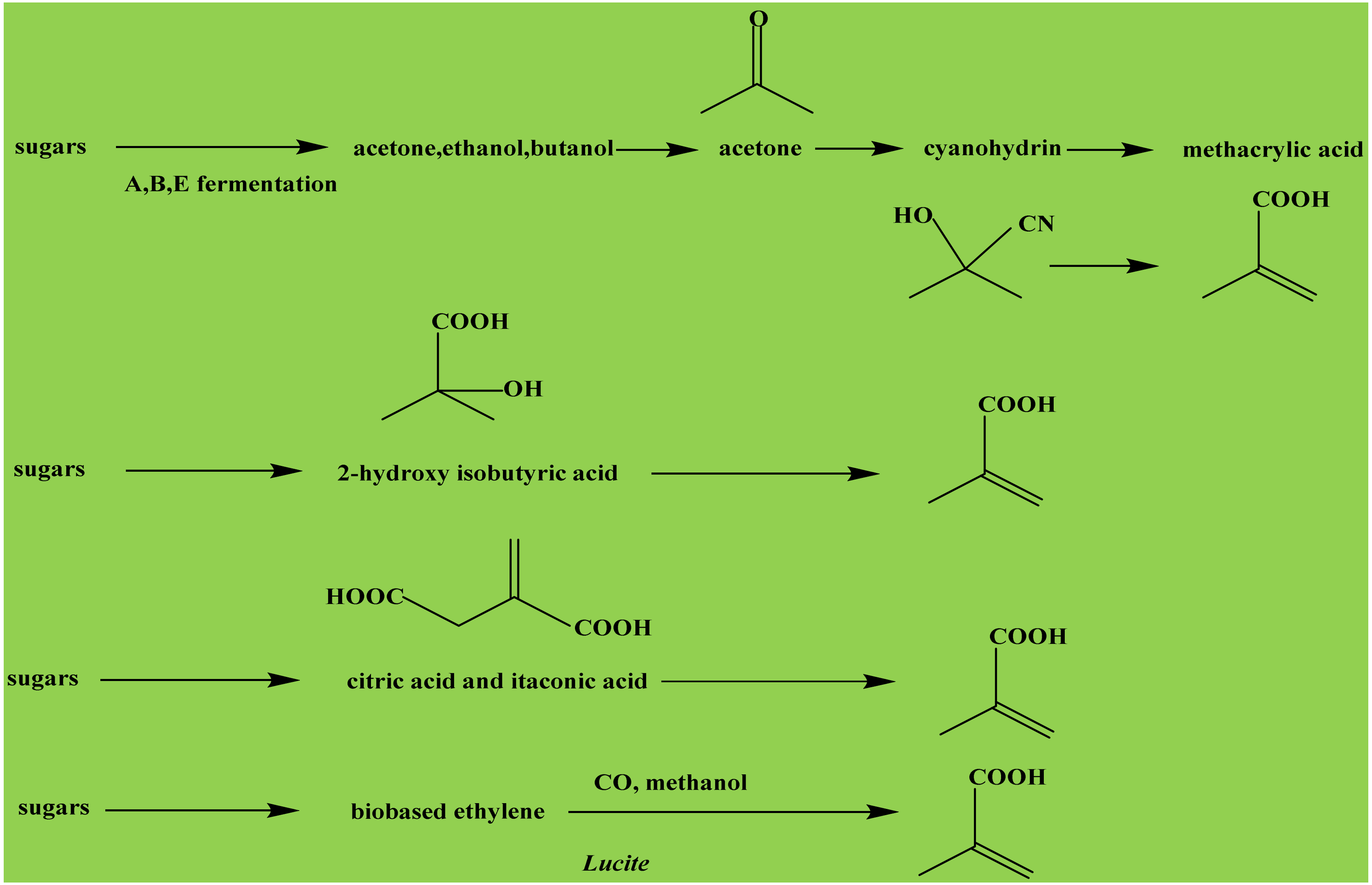


Source: P. Harmsen et al., *Green Building Blocks for Biobased Plastics* (WUR 2013)

Biobased routes to acrylic acid



Biobased routes to methacrylic acid



Bioroutes to n-BuOH and 2-EH

- Solvent-producing clostridia:
  - Anaerobic, spore-forming, Gram-positive
  - Utilize wide range of substrates (glucose, xylose, arabinose, starch, molasses..)
  - Produce:
    - Acids: butyric, acetic, lactic acids
    - Solvents: acetone, butanol (major product), ethanol
    - CO_2 and H_2

C. beijerinckii NCIMB 8052

Exponential growth phase

Stationary phase

n-butanol production

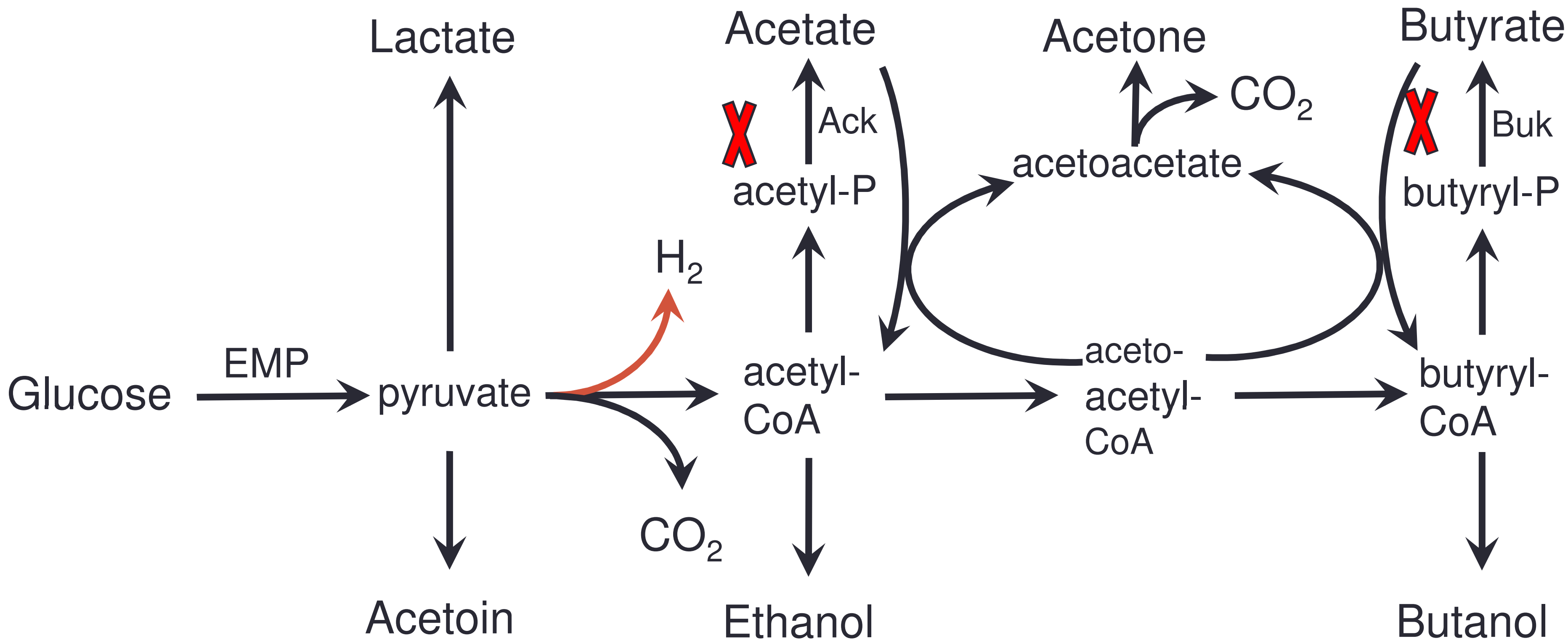
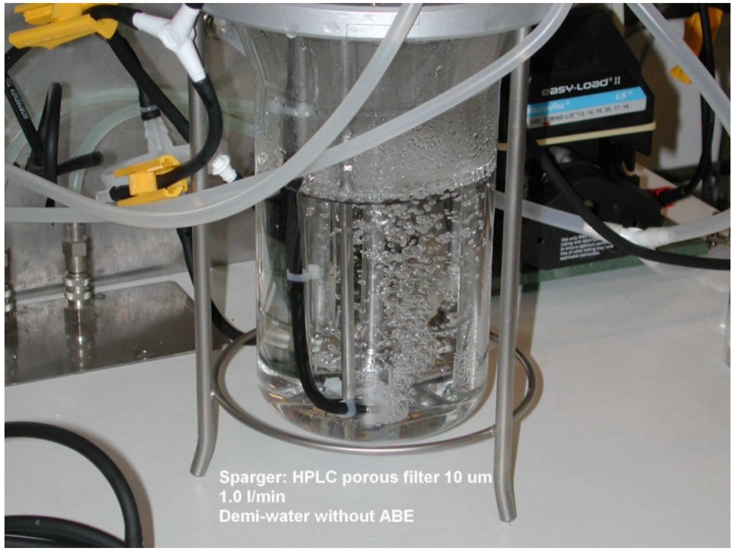


Fig.1 Simplified glucose metabolic pathway in *C. acetobutylicum*

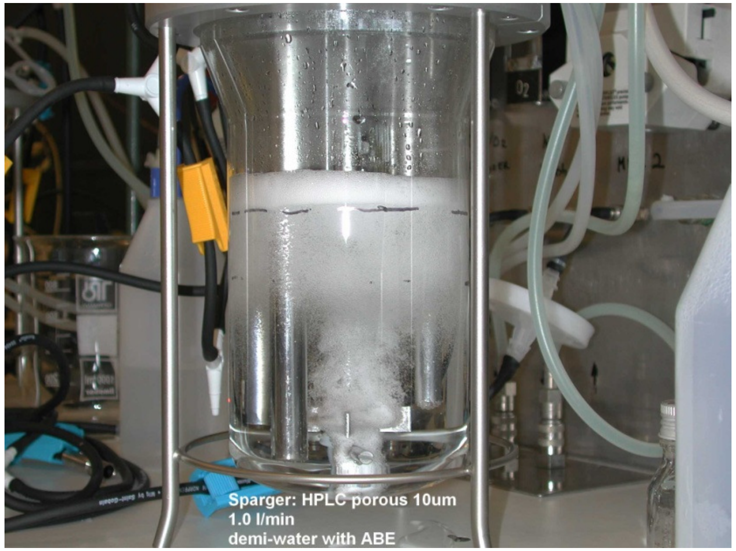
- Inhibition of acid production: No acetone production, Lower ATP yield

"in-situ"product removal n-butanol

- Example: Fermentation process with Gas stripping
  - Tested different spargers; Solvent filter, straight sparger,round sparger, ceramic sparger



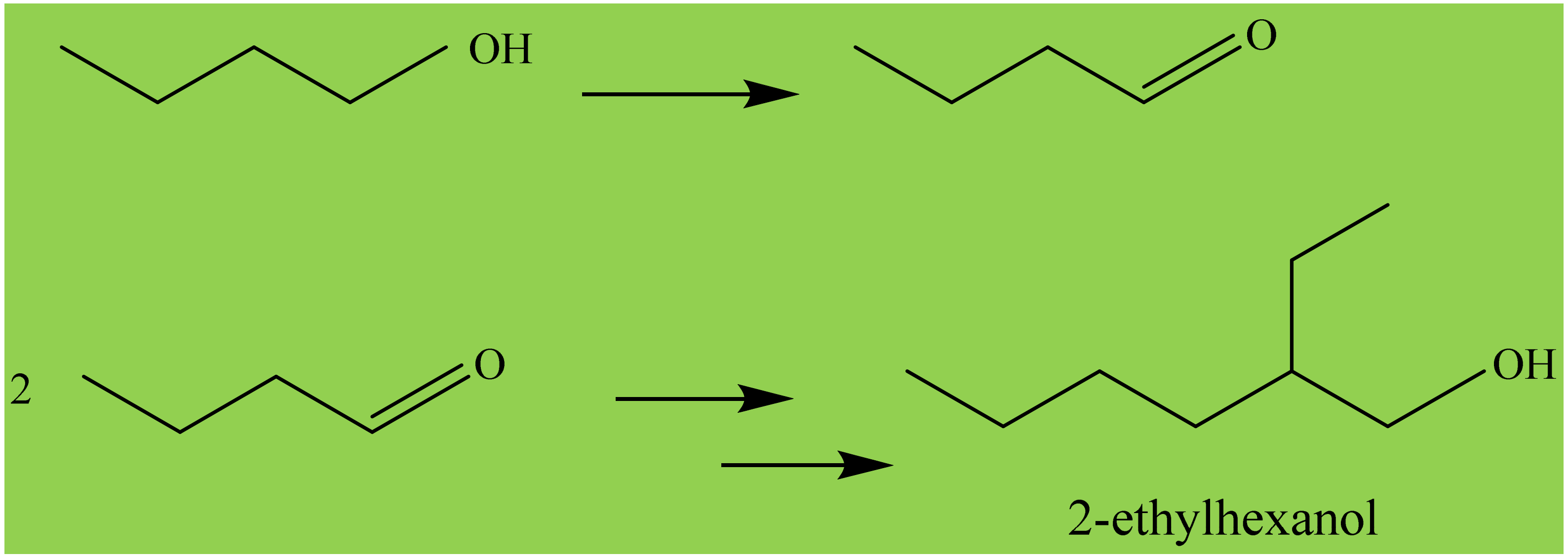
Solvent filter 10µm/demi water



Solvent filter 10µm/demi water+ABE

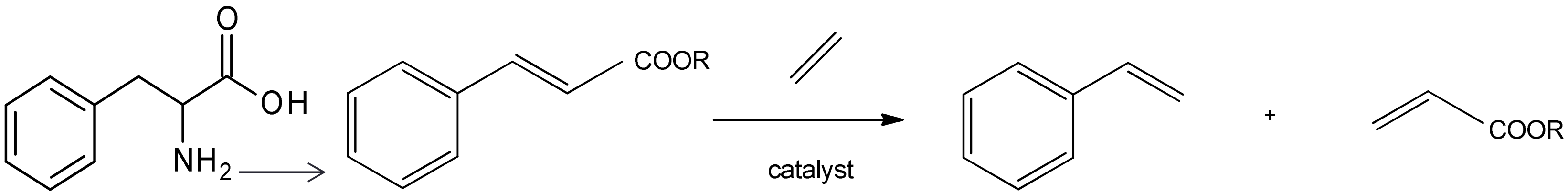
Bioroutes to n-BuOH and 2-EH

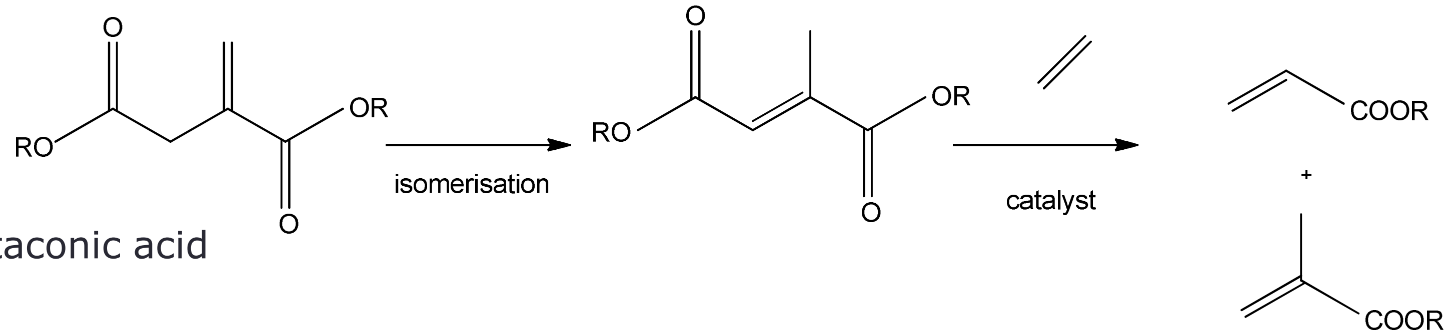
- Conversion of n-butanol into 2-ethylhexanol



Simultaneous production monomers

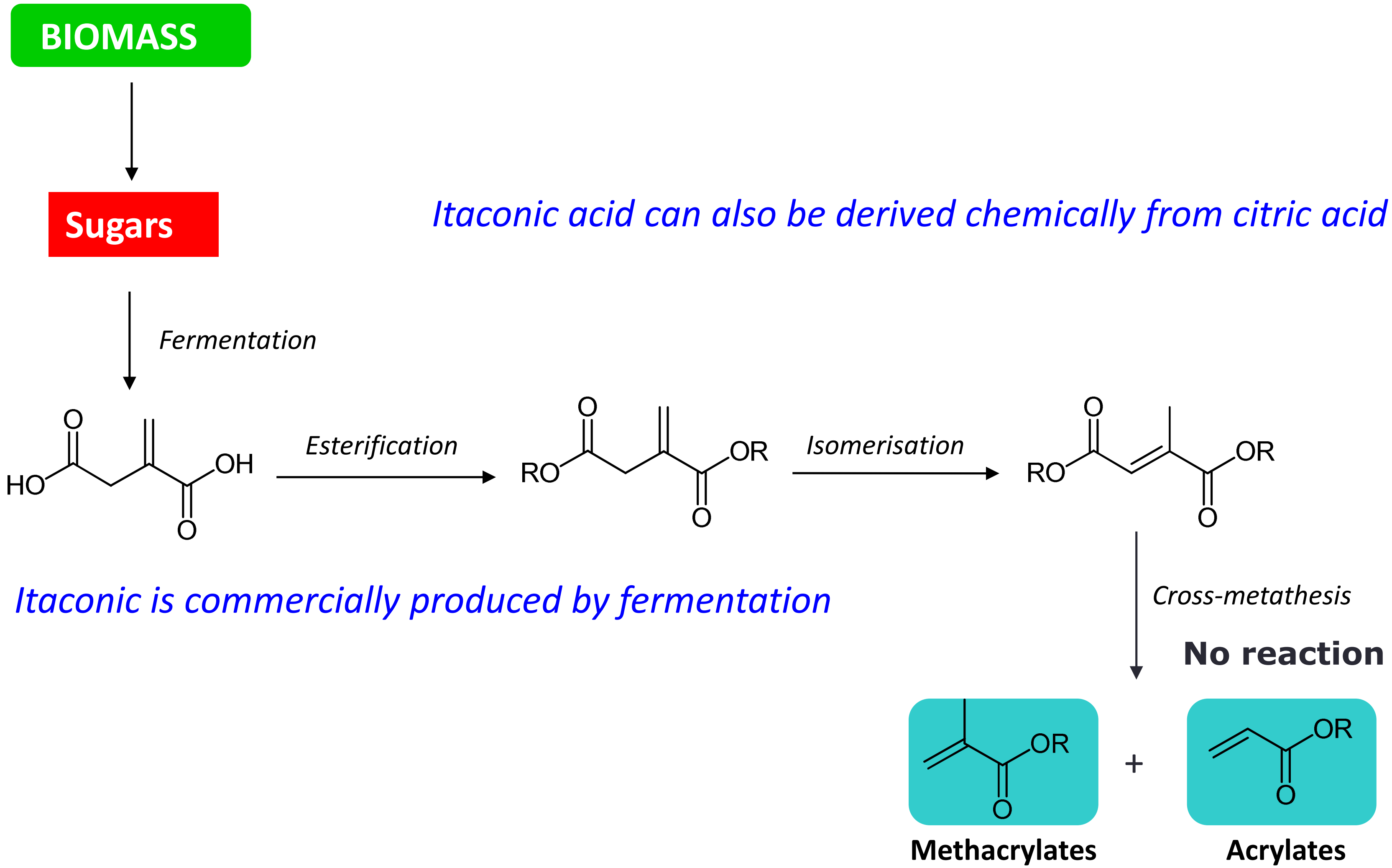
- Use a cross metathesis (ethenolysis) reaction to derive 2 biobased (bulk) chemicals at 100% atom efficiency





Itaconic acid

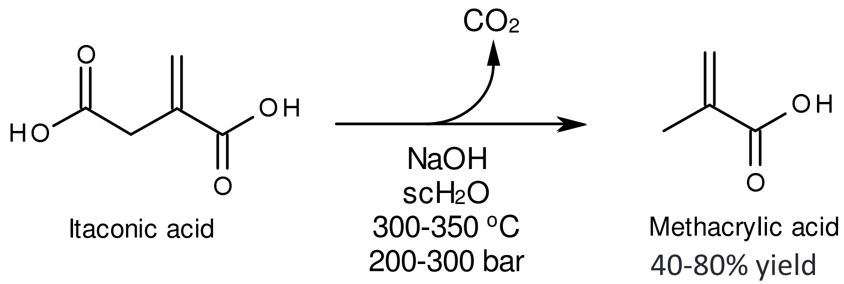
Biobased acrylic- and methacrylic acid



Biobased methacrylic acid; alternative approach

- Decarboxylation reaction of itaconic acid described in literature:

➔ Only 1 example, in supercritical water:



Carlsson *et al.*, *Ind. Eng. Chem. Res.* **1994**, *33*, 1989.

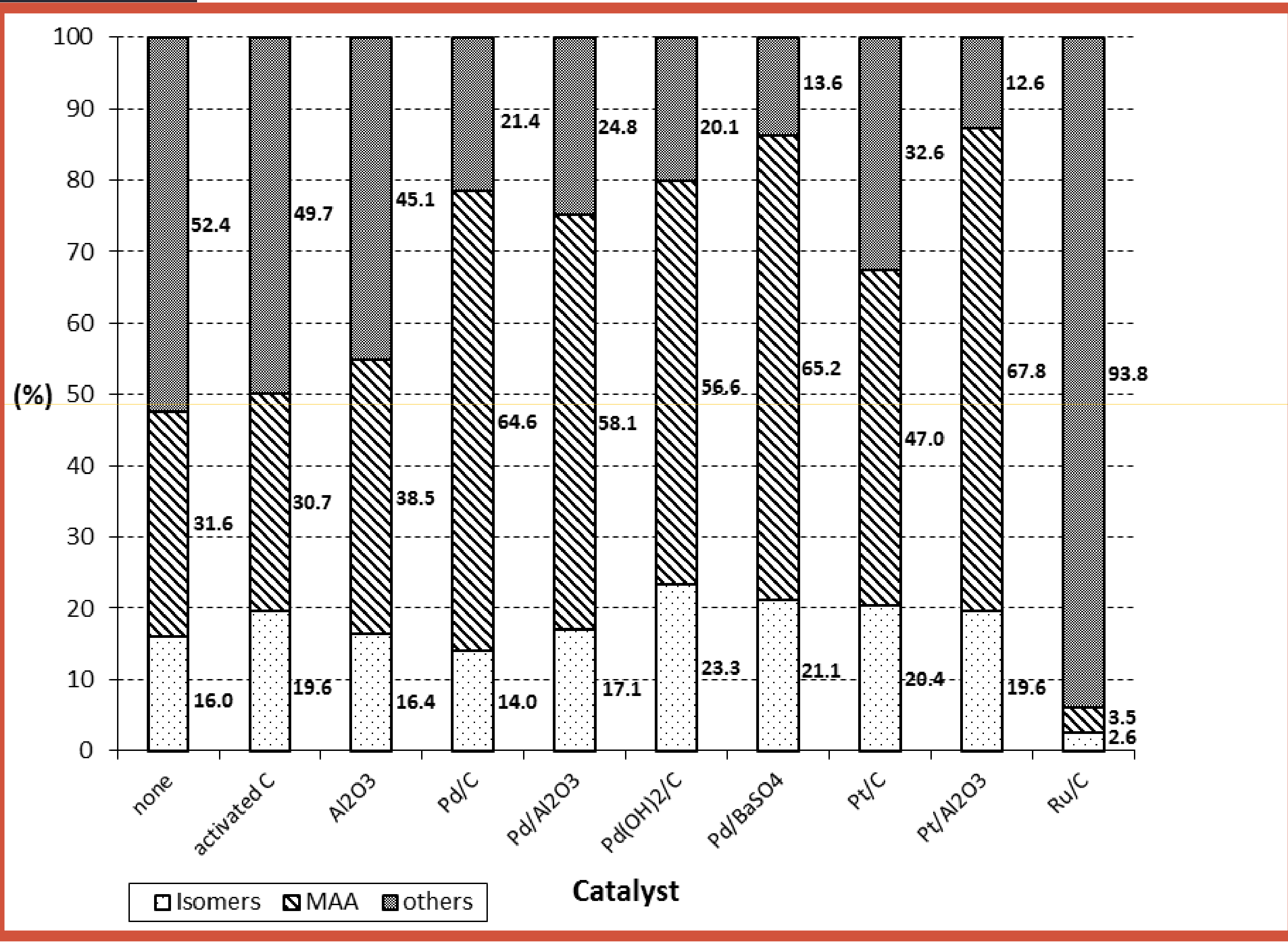
➔ Recent patent by Lucite Int. UK Ltd: WO2012/069812A1:

Continuous flow reactor at T = 250-350 °C and P = 200 bar
[itaconic acid] = 65 g/L
[NaOH] = 0.5 M
Reaction time < 10 min

➔ 19-58% yield

Biobased methacrylic acid form itaconic acid

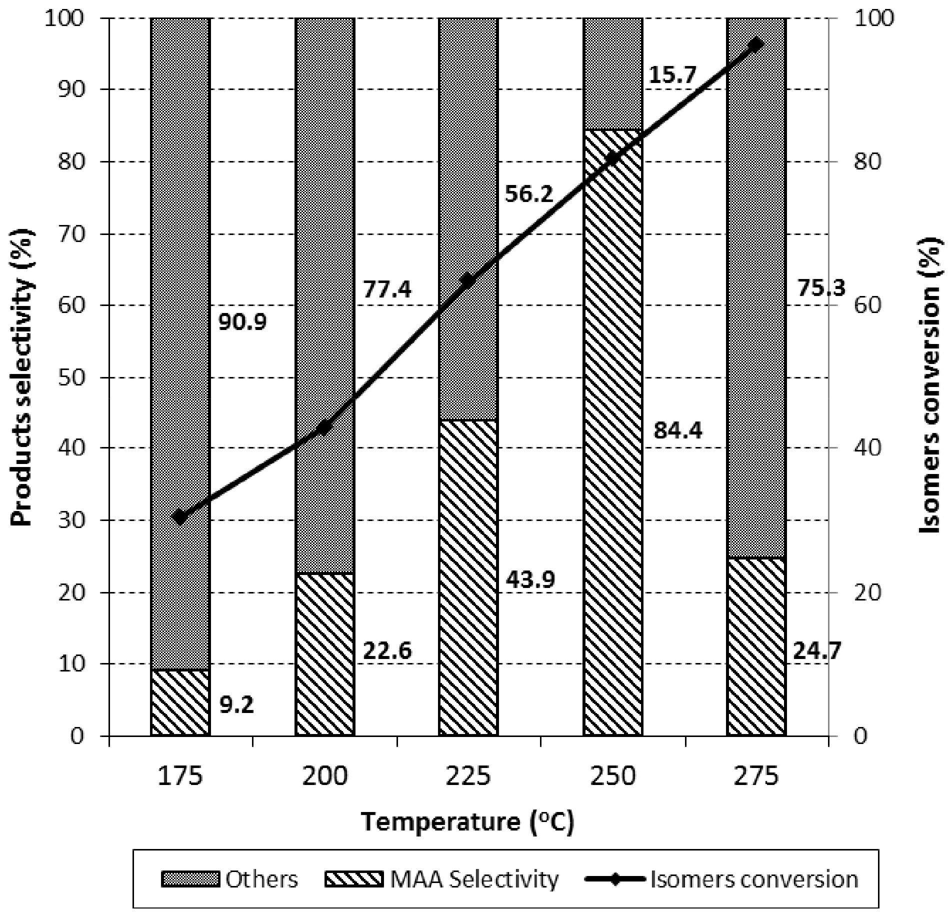
Catalyst screening:



Reaction conditions: itaconic acid (400 mg, 3.0 mmol), 0.15 M NaOH (20 mL), 250 °C (40 bar built-up pressure), 1 h.

Biobased methacrylic acid

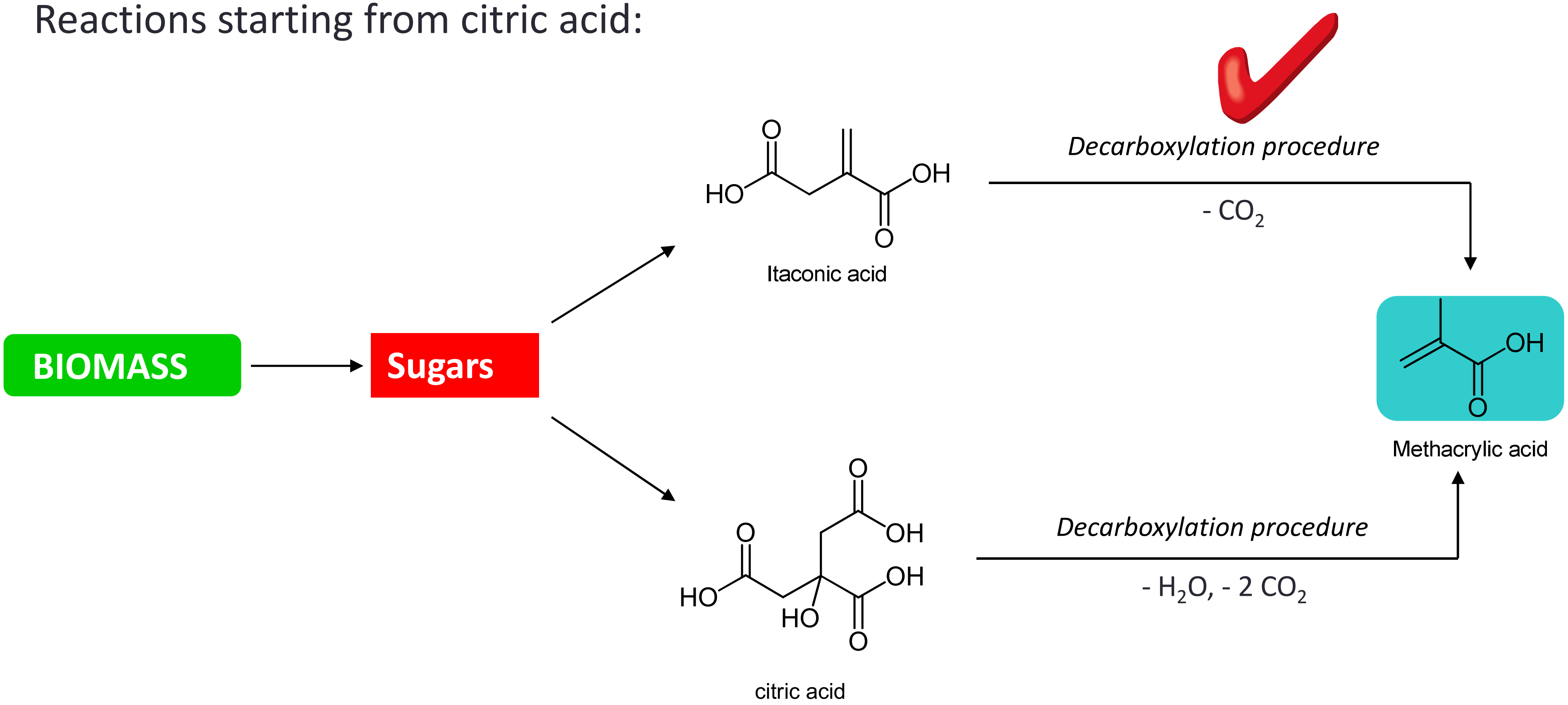
Reactions with Pt/Al_2O_3, effect of temperature:



Reaction conditions: itaconic acid (400 mg, 3.0 mmol), 0.15 M NaOH (20 mL), 1 h.

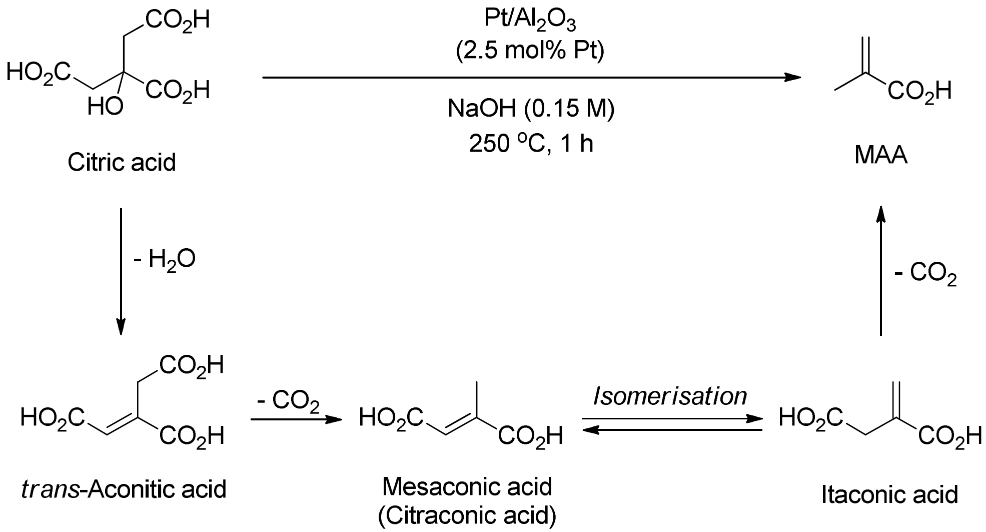
Biobased methacrylic acid

Reactions starting from citric acid:



Biobased methacrylic acid

Reactions starting from citric acid:



Conditions	Conversion citric acid	Itaconic acid	Mesaconic acid	Citraconic acid	Methacrylic acid	Others
Carlsson	100	35.0	16.0	25.0	6.0	18.0
WUR	99.6	4.0	10.5	4.5	41	46.1

- Carlsson *et al.*, *Ind. Eng. Chem. Res.* **1994**, *33*, 1989:
  NaOH, 320 °C, 200 bar, 1 min ➔ 100% conversion, 6% MAA selectivity
- WUR process:
  0.15 M NaOH, Pt/Al_2O_3 cat., 250 °C, 40 bar, 1 h ➔ 100% conversion, 41% MAA selectivity

Biobased pressure sensitive adhesives

- Literature describes various biobased approaches:

- Copolymers L-lactide, caprolactone with 2-hydroxyethyl methacrylate (HEMA) [Pu et al. 2012]
- Triblock copolymers comprising menthide and lactide [Shin *et al*. 2011]
- Sugar acrylates [patent to Ecosynthetix; 2013]
- Emulsion polymerisation of acrylated fatty acids [S. Bunker *et. Al*. 2003)

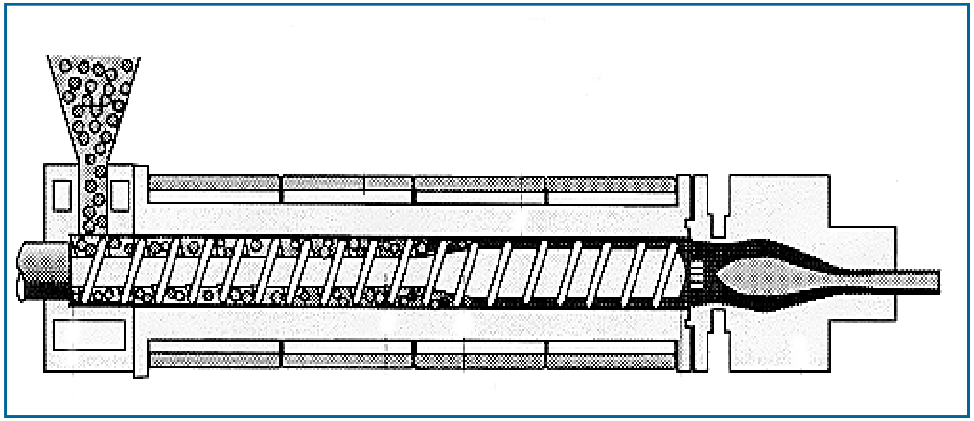
Previous adhesive research at FBR (2000-2010)

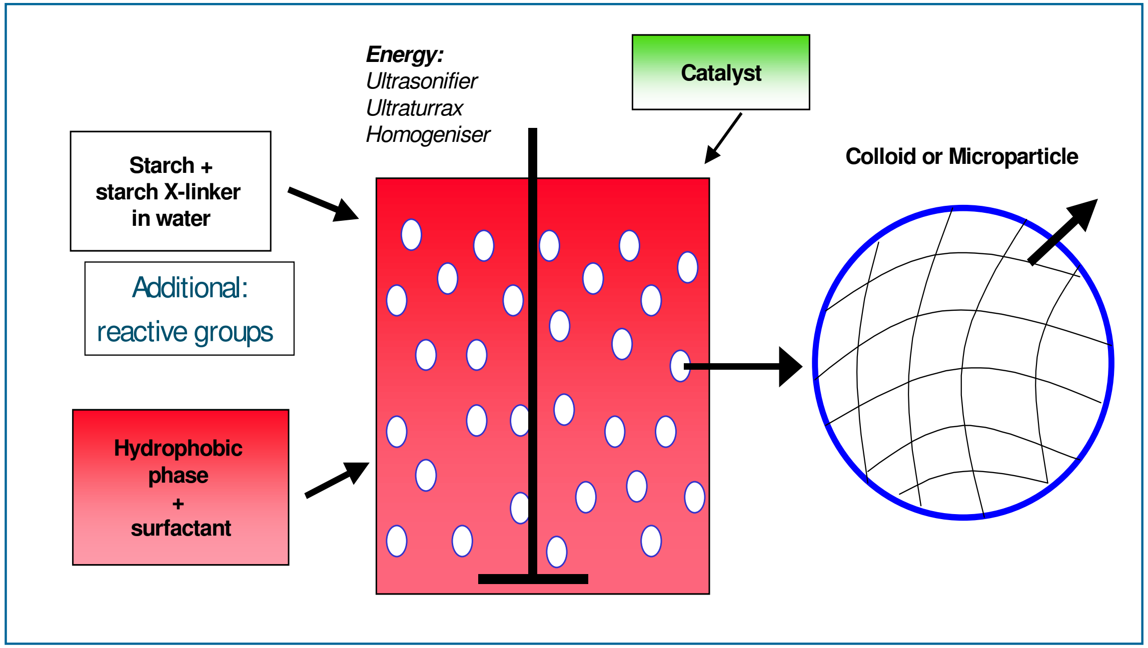
- Dispersion adhesives
  - Proteins
  - Colloïdal starch based systems
- Labelling adhesives
  - Replacement of caseïn; wheat gluten
- Hot melts
  - Proteins (gelatin, wheat gluten)
  - Dextrines, inulin
- Pressure sensitive adhesives based om mcl-polyhydroxyalkanoates
- Moisture curing adhesives
- Additives, including plasticisers
- Tackifiers

Starch microparticles or latex production routes

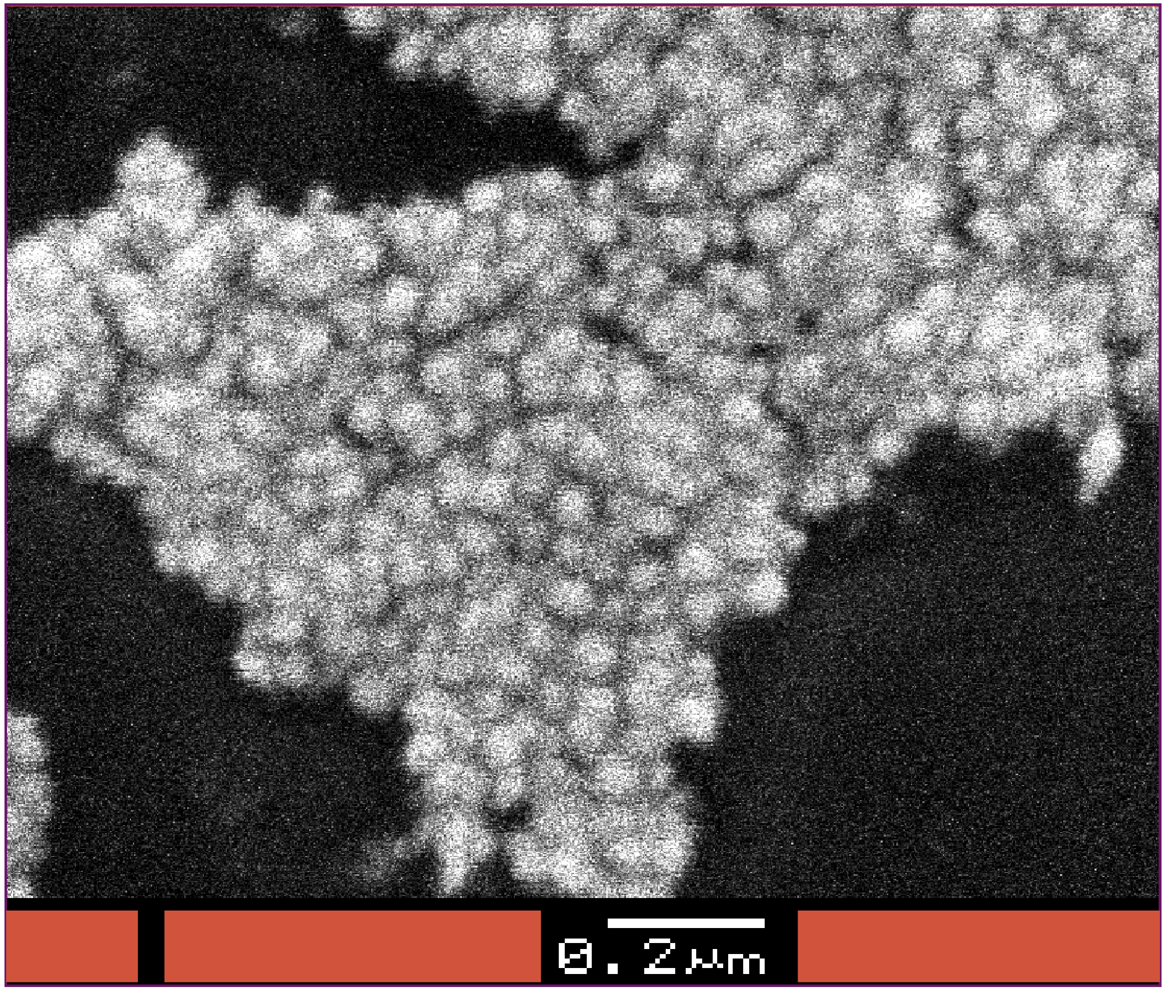
Novel routes

- emulsion X-linking *versatile*
- multiple emulsion *encapsulation*
- starch non-solvent *cheap, easy*
- extrusion *latex, cheap, large scale*





Starch microparticles

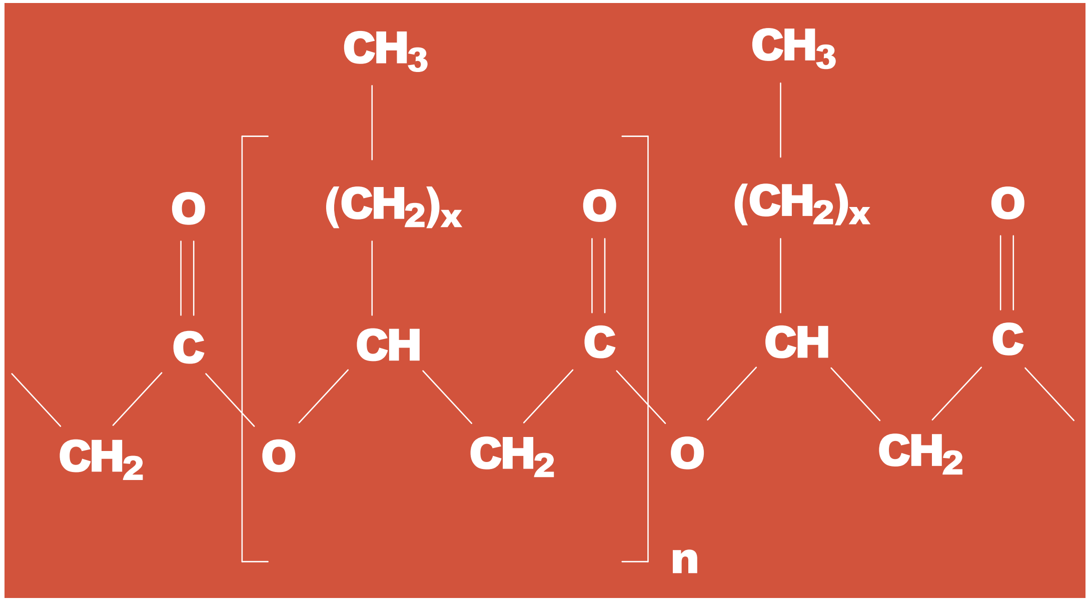


Applications of starch sub-micron particles

- Viscosity/rheology modifier
- Binder
- Dispersing agents
- Coatings
- Water binding polymer or hydrogel (>300 g water /g)
- High solid adhesives
- Matrix for encapsulation

Biotechnologically produced PHA’s

PHA$_{MCL}$ produced by *Pseudomonas putida*



n = 1000 - 3000 x = 0 - 1 , scl - PHAs (PHB, PHV)
x = 2 - 11, mcl - PHAs

- Very low Tg’s can be obtained

Options for biobased (PS) adhesives

- Emulsion polymerisation of renewable based vinylmonomers (drop-in as well as unique structure)
- Polysaccharide or protein based emulsion polymers;
  - Opportunities for using agricultural sidestreams
- Alternative biobased tackifiers (terpenes, lignin derivatives
- Alternatives for epoxy- and PUR-based adhesives
- Moisture curable adhesives; silyl-modified biobased molecules
- Biobased plasticisers

Conclusions

- Renewables offer opportunities for pressure sensitives adhesives:

  Via drop-in approach, or

  Making use of unique functionality present in biomass

- All main and additive components (latex binder, tackifiers, additives) potentially can be derived from renewables

Thank you

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