Chemical Modification of Renewables for Sustainable Chemicals Development

Cape Town, South Africa
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Leading edge research with governments and communities, industry and NGOs, to support innovation and sustainability in life sciences while managing and protecting natural and man-made

ECOSYSTEMS

Faculty of Bioscience Engineering
Ghent University - BELGIUM

FACULTY OF BIOSCIENCE ENGINEERING

- 100 Professors drive research across 16 departments
- 1,000 Academic staff
- 600 Peer-reviewed original publications
- Ranks in top five of the life sciences organizations in Europe
- Strong emphasis on external collaboration, internationally with over 300 organizations;
- Commitment to international education, FBE has set up the International Training Centre.

Department of Sustainable Organic Chemistry and Technology

6 professors; 60 PhD students; 30 specialising Master students

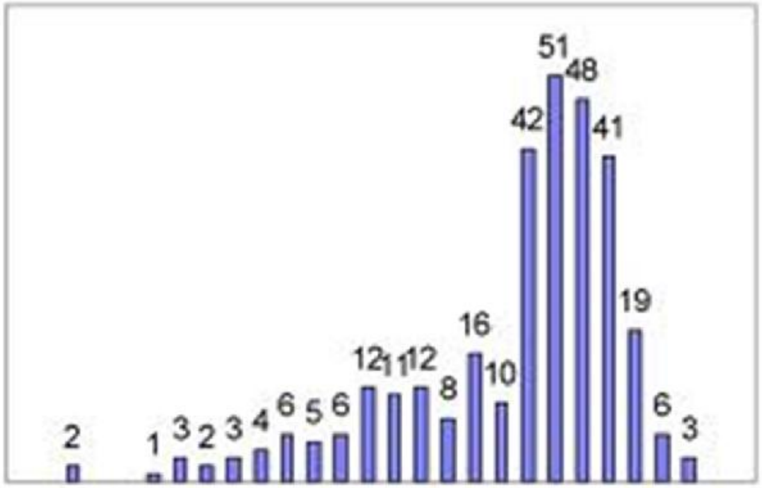
Lines of Research

Product and Methodology Oriented Synthesis

1. Heterocyclic Chemistry (N, P-chemistry)
2. Modification of Renewable Resources
3. Microreactor & Continuous Flow Technology

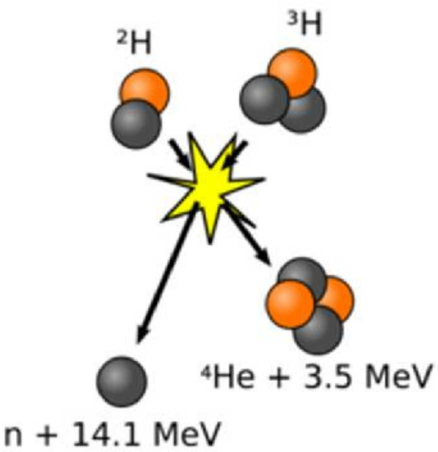
Interest in Renewables
Starting Point

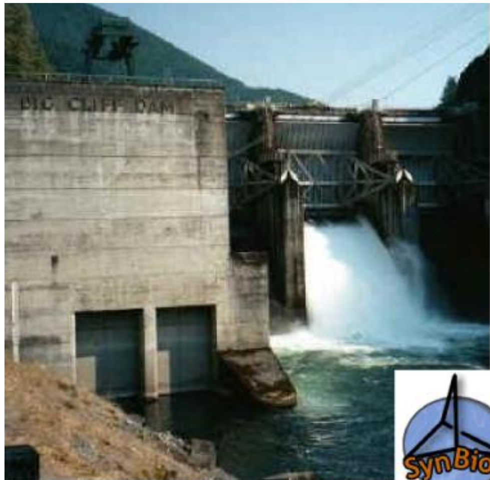
- Limited reserves of fossil fuels
- Strongly fluctuating prices
- Need for alternative energy sources (Biodiesel)
- Source for materials, chemicals



GIANT OIL FIELD DISCOVERIES, 1870-1995

Is energy the all time top priority?



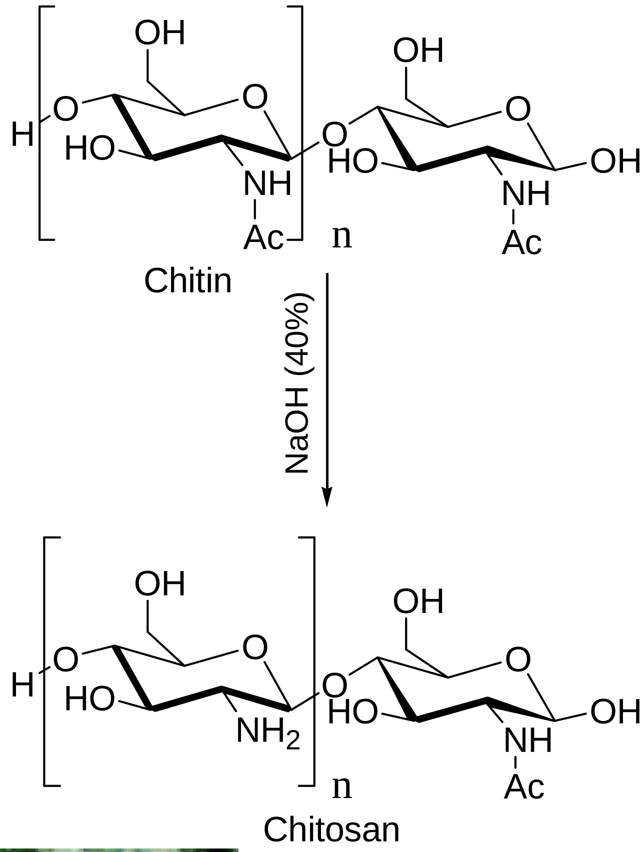


What about building blocks?

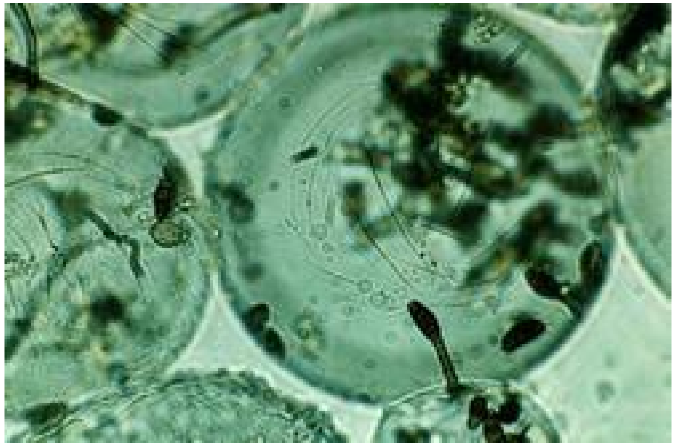
- 12 Rules of Green Chemistry

  (P. Anastas,1998); Try to incorporate renewable resources in industrial processes
- My Rule 14: Exploit the fantastic enzymatic systems of plants

Modification of Chitosan



- Chitosan = deacetylated chitin
  - residues of crustacea and cell wall of yeasts, Lentinus edodes, Absidia artrospora
- Biopolymer with interesting properties (waste product)
- Compatible with skin tissue
- Much modification research (increase of sollubility)



Esterification

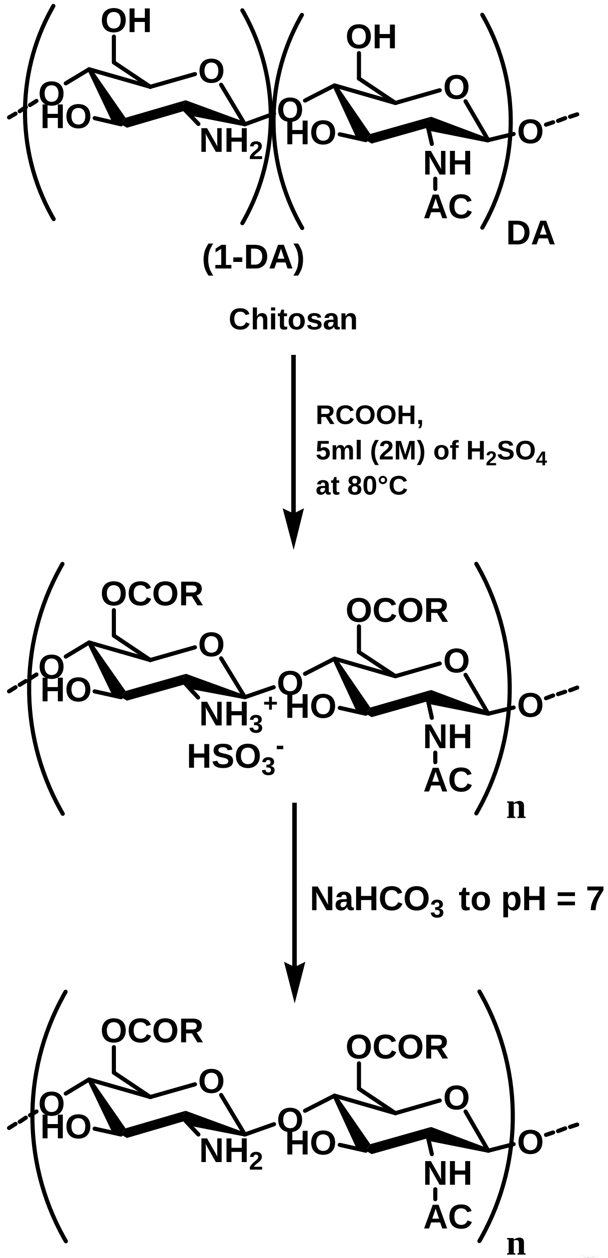
28 new chitosan alkanoates

ex.: chitosan butyrate (DS 0.28) at a mol ratio of (1:5) chitosan to butyric acid

insecticidal activity, at 0.5% (w/w) artificial diet, against cotton leafworm *Spodoptera littoralis*

larval growth inhibition at 0.5% (w/w)
58 (C4), 63(C5), 66(C7) and 69% (C10)

chitosan (3% inhibition) at the 4th day

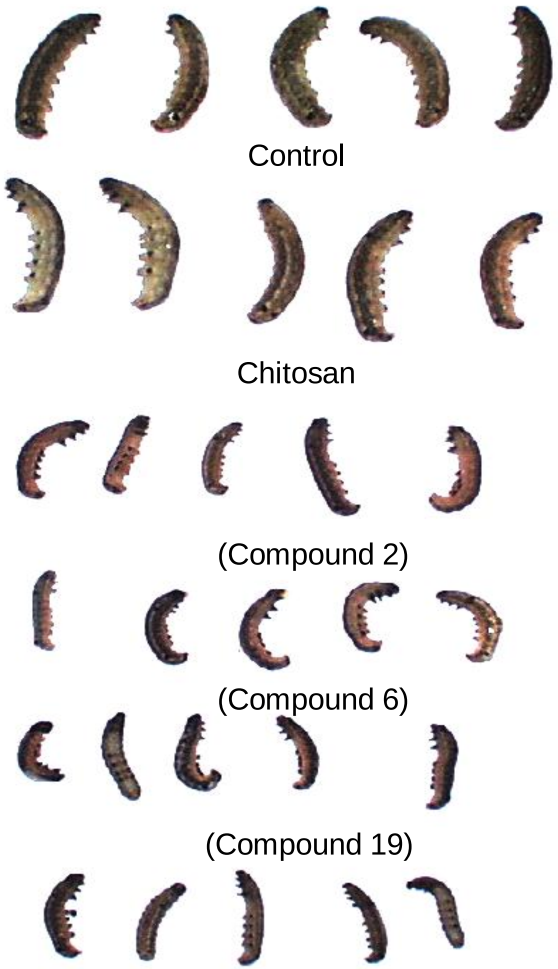


DA, degree of substitution
Ac = acetyl
R = alkyl chain

Spodoptera littoralis

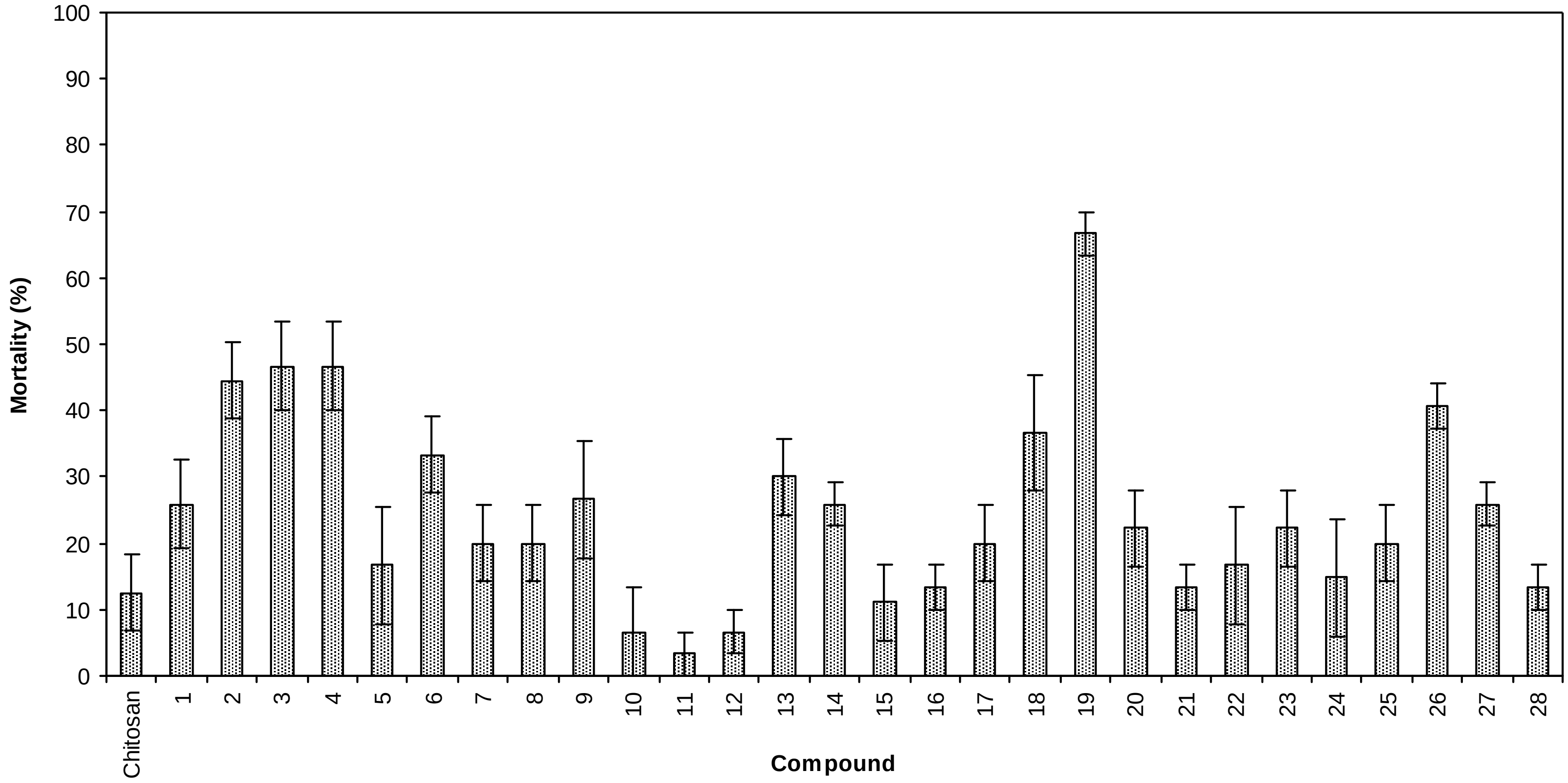
Cotton leaf worm
Severe harm to cotton,
Vegetables and ornamental crops

Inhibition of growth



	Larval length (mm± SEM)	
Control	(25.0± 0.11)	
Chitosan	(24.6± 0.10)	
(Compound 2)	(14.4± 0.07)	Butanoate
(Compound 6)	(12.0± 0.12)	Pentanoate
(Compound 19)	(12.6± 0.09)	Heptanoate
(Compound 26)	(11.4± 0.06)	Decanoate

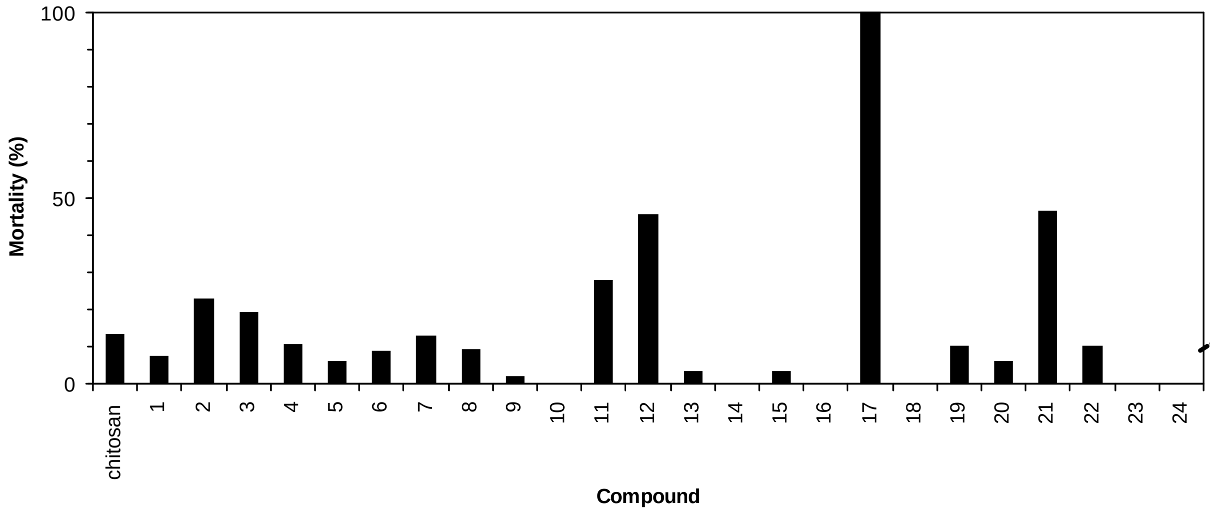
Mortality

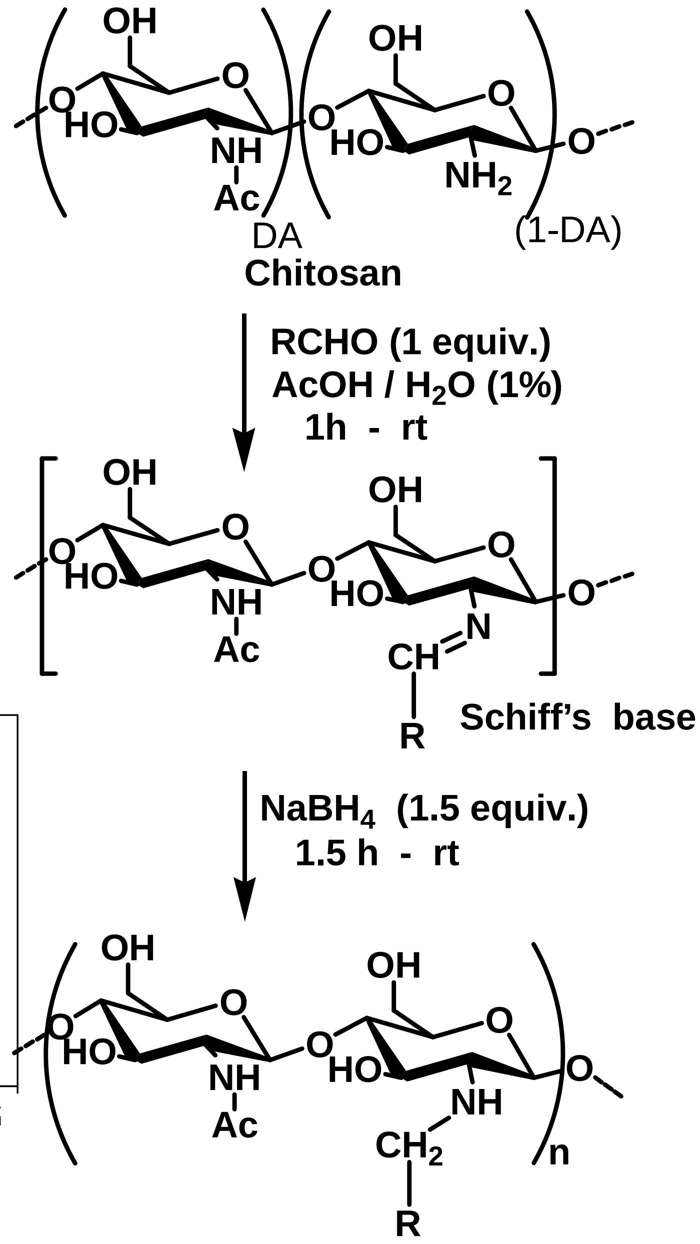


Mortality (%)
100
90
80
70
60
50
40
30
20
10
0
Chitosan
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
Compound

Reductive amination

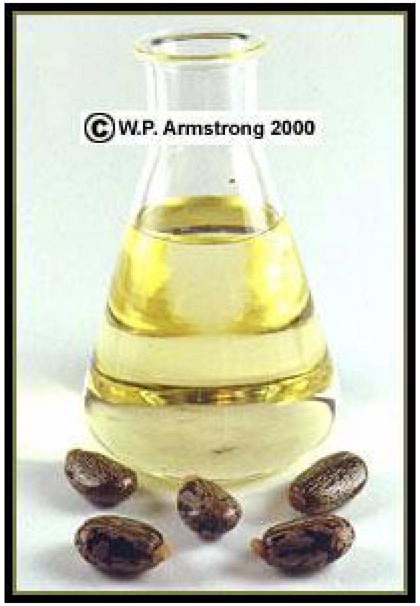
5 day feeding experiments (5g/kg) with S. littoralis
most active: *N*-(2-chloro-6-fluorobenzyl) chitosan
as total mortality was scored with concentrations
as low as 0.625 g kg-1 and the
LC50 was estimated 0.32 g kg-1.





Modification of Undecenoic Acid
Castor oil (Ricinus communis)

- Leading producing areas: India, China, Brazil and the former USSR
- Castor seed: between 40% and 60% oil which is rich in triglycerides, mainly ricinolein
- Currently, castor oil is imported by the EU



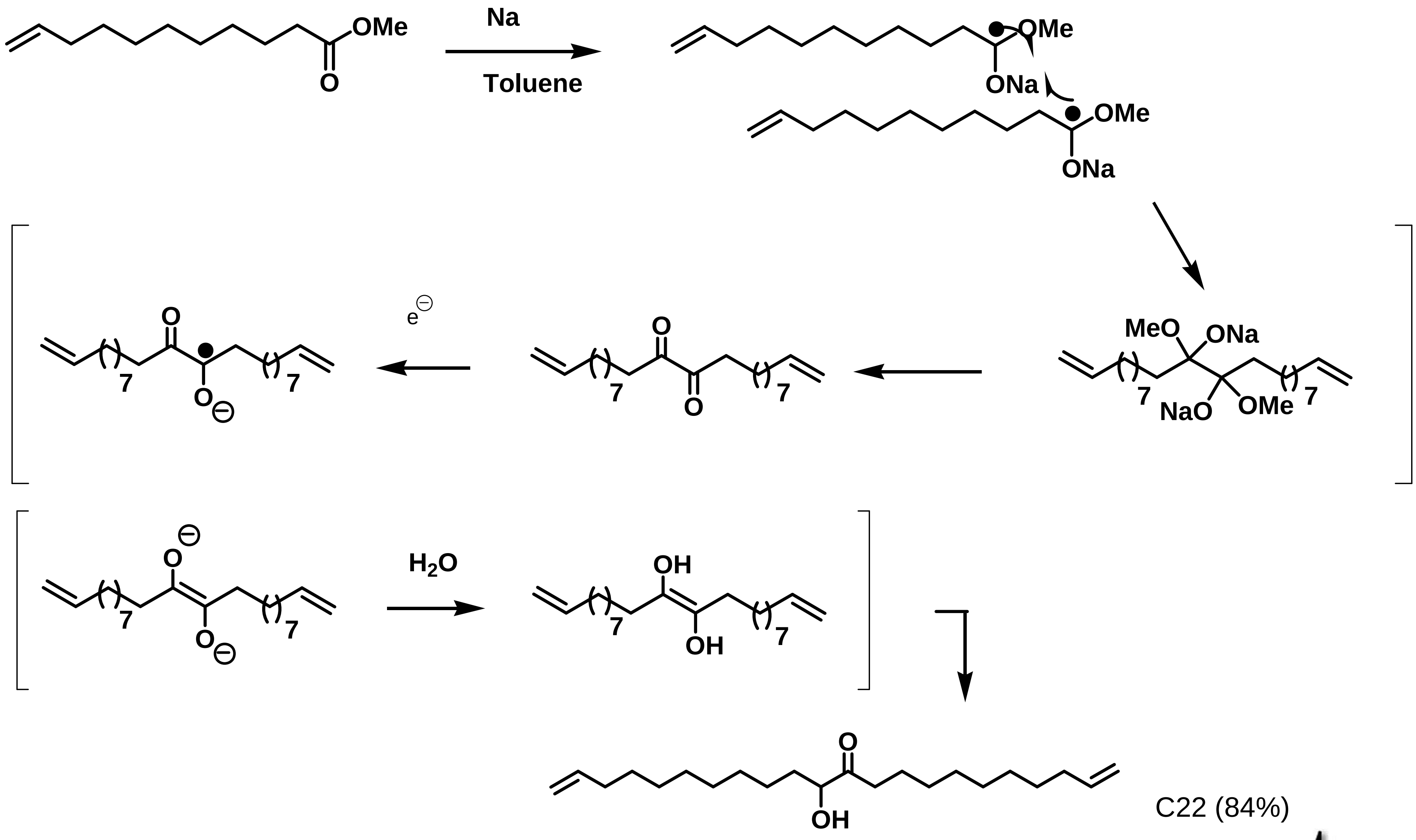
Production of fine chemicals from specific fatty acids

- Thermal cracking of ricinoleic acid

12-Hydroxy-9-octadecenoic acid

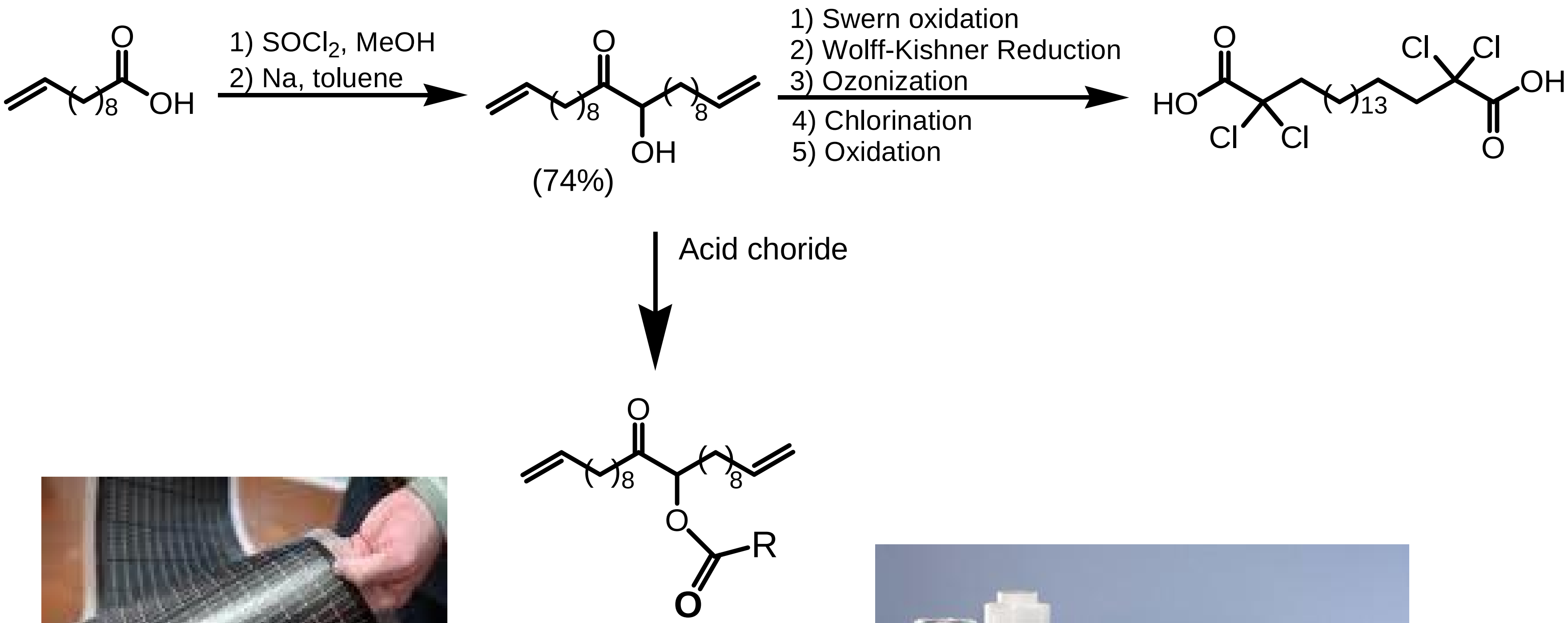
undecenoic acid - C11

Acyloin condensation



C22 (84%)

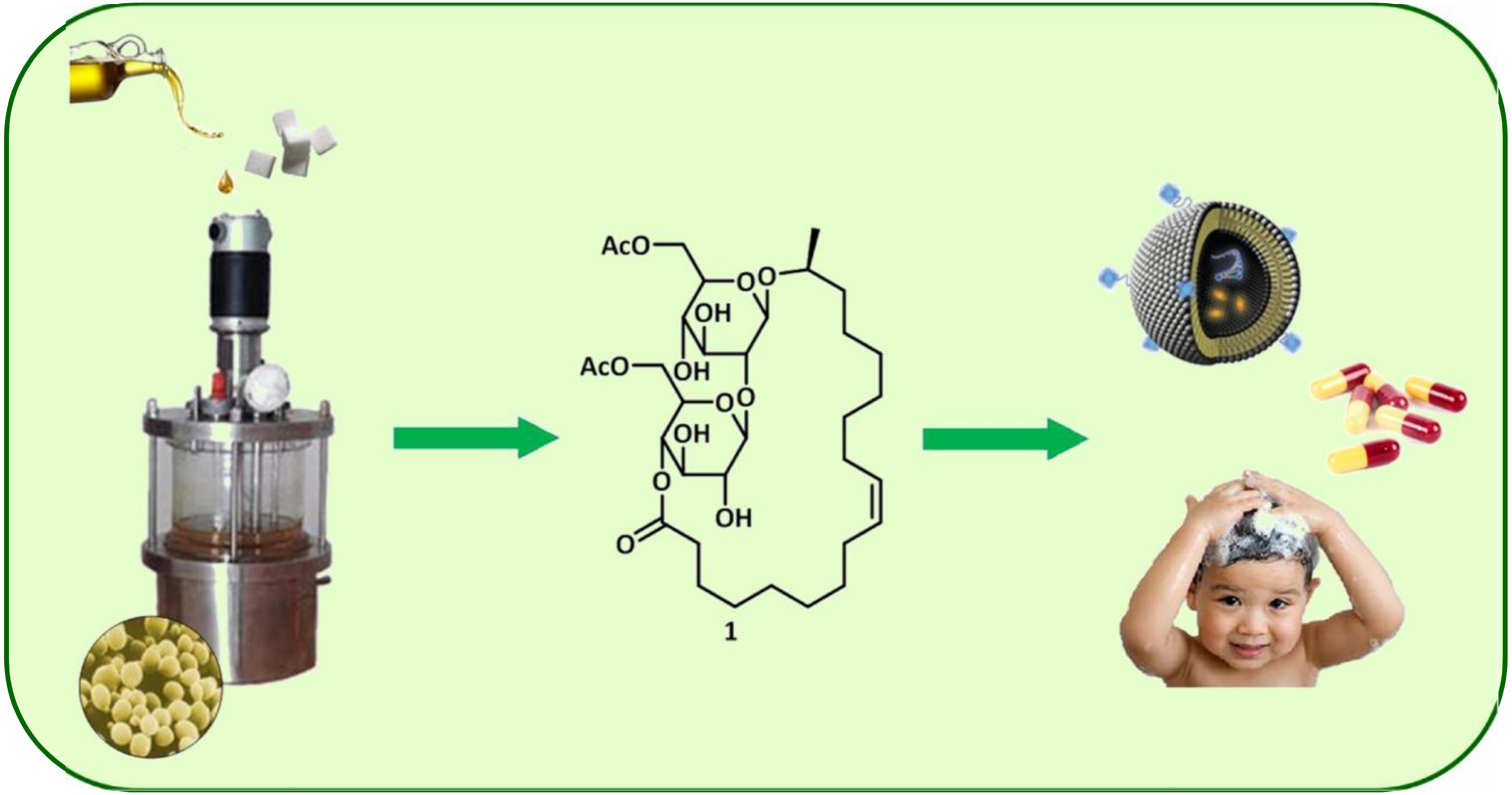
Acylation


1) $SOCl_2$, MeOH
2) Na, toluene
(74%)
1) Swern oxidation
2) Wolff-Kishner Reduction
3) Ozonization
4) Chlorination
5) Oxidation
Acid choride


John Moore/Getty Images

Sophorolipids

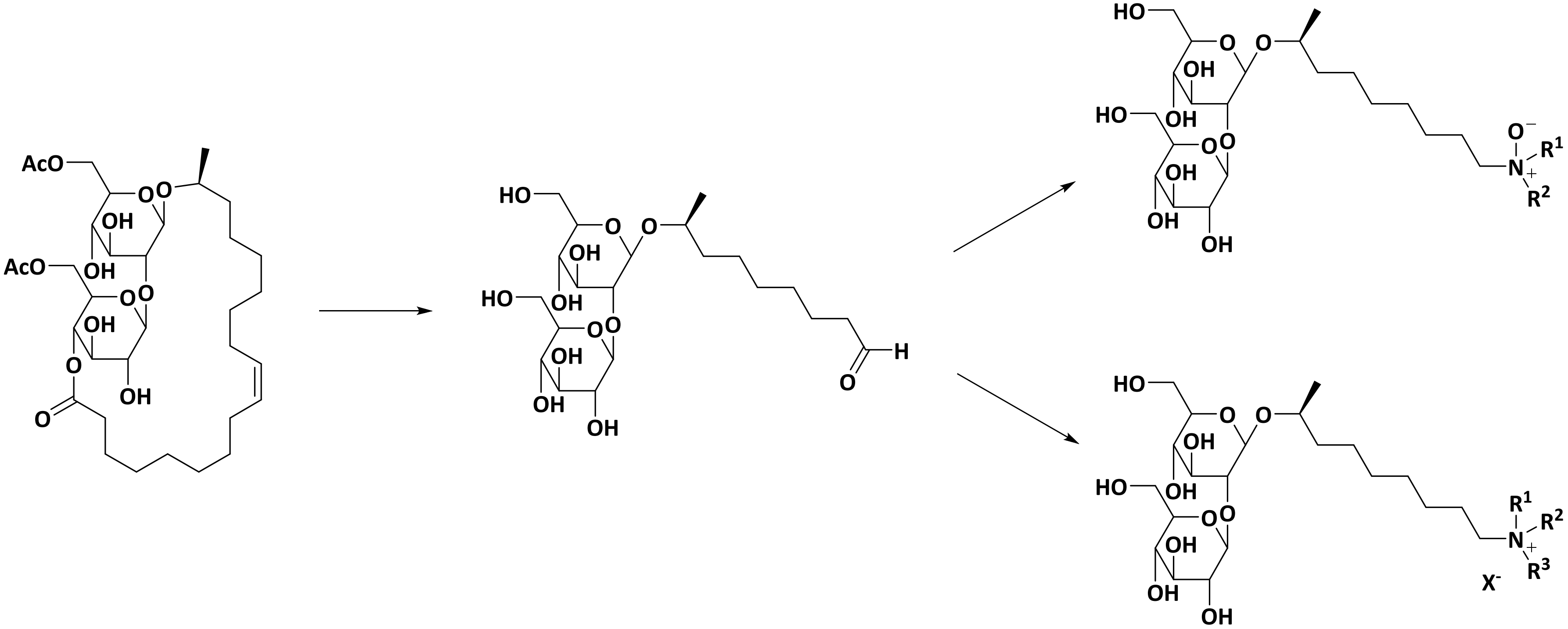
Chemical modification of microbial product:



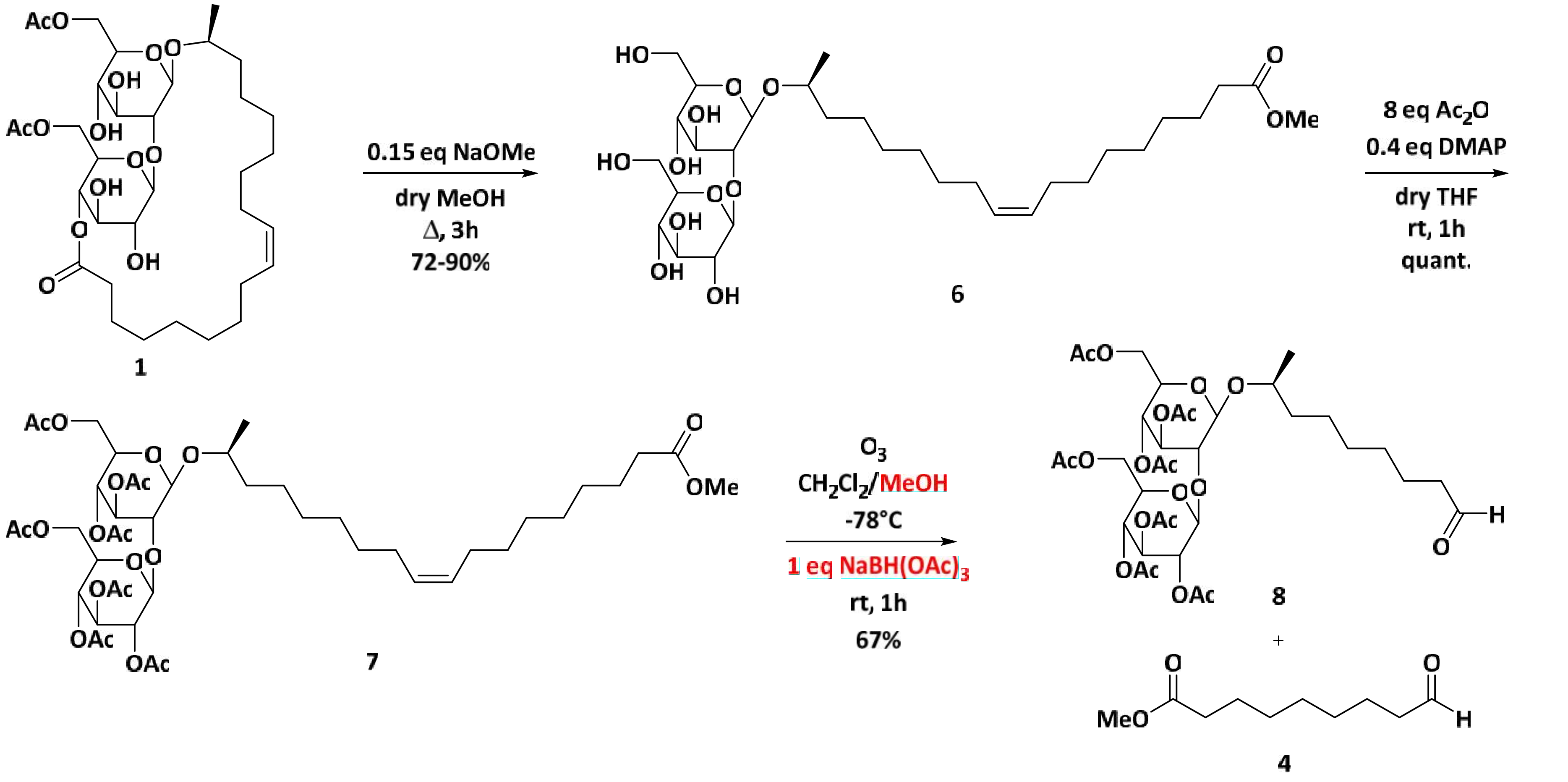
Goal

Chemical modification of microbial product:

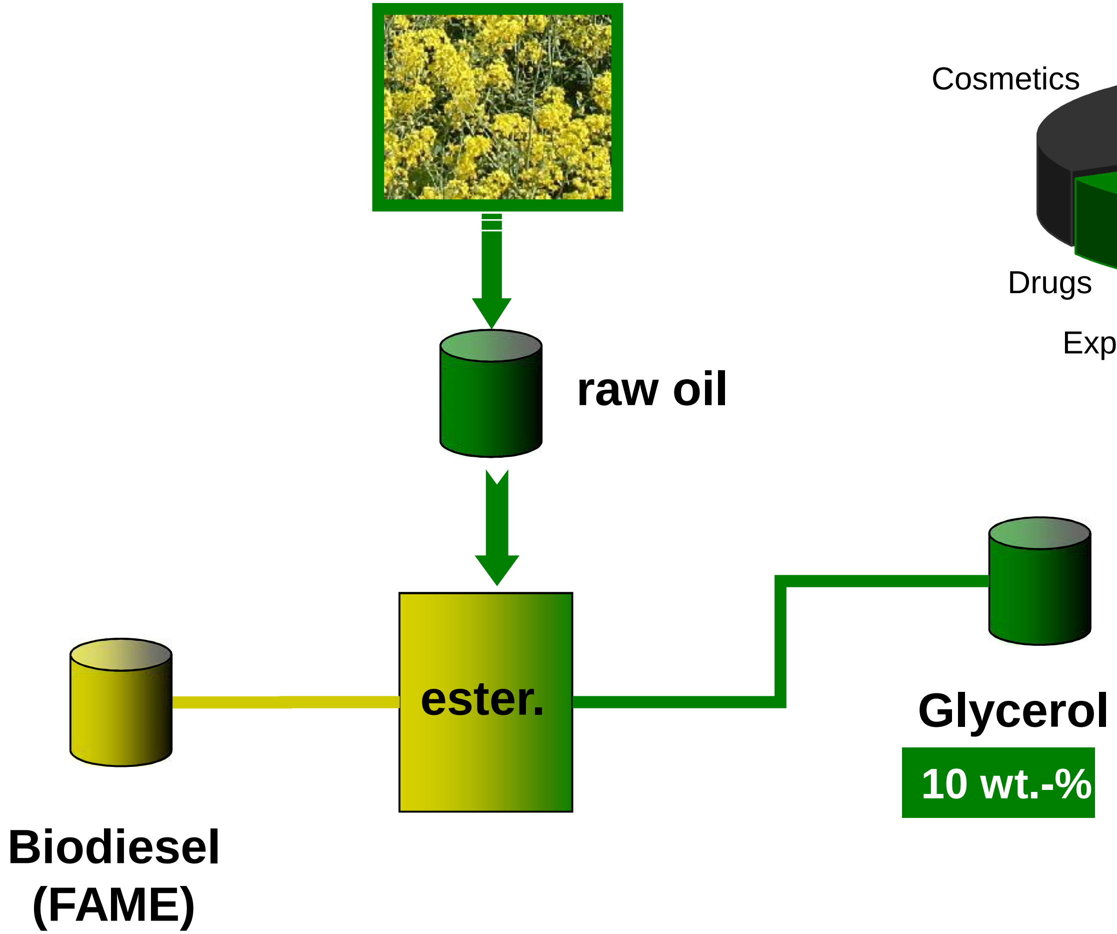
- Synthesis of aldehyde intermediate
- Modification towards amine oxides and quaternary ammonium salts

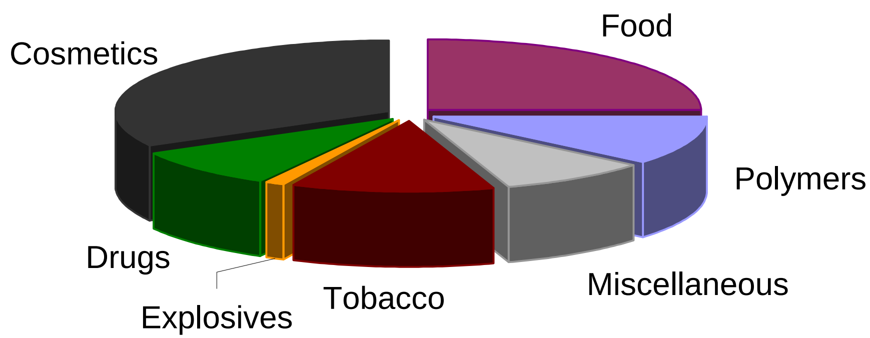


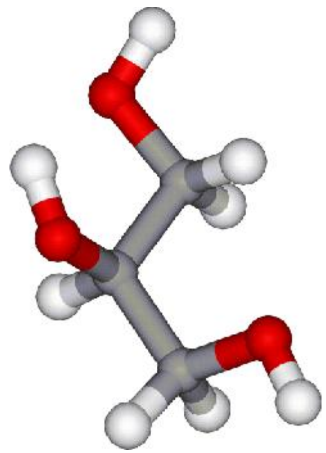
Synthesis of aldehyde intermediate



Glycerol: the bulky side of biodiesel





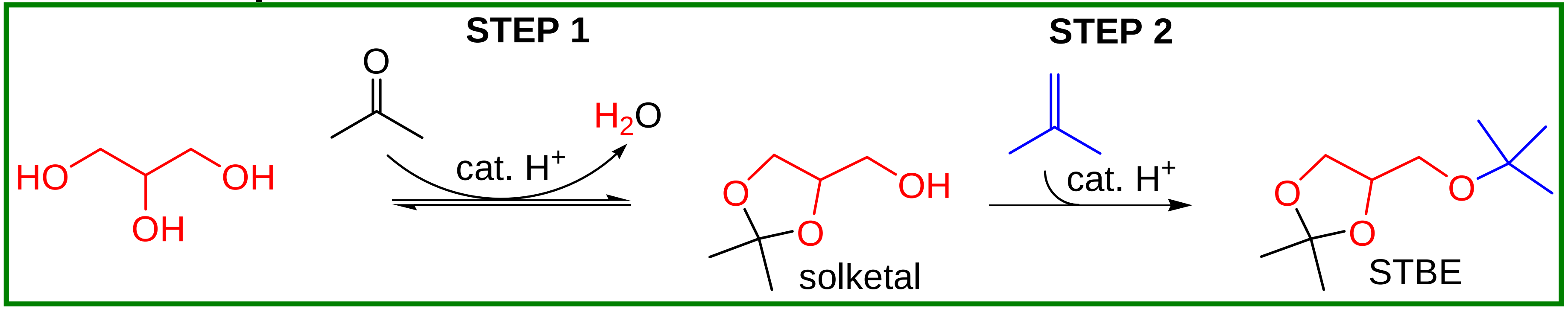


$C_3H_8O_3$
MW: 92.09

Chem. Rev. **2008**, *108*, 5253

Glycerol: a renewable building block

- Two steps to STBE



- STBE: a promising fuel additive
  - ➔ Significant reduction of small particles
  - ➔ Improved combustion/engine performances
  - ➔ Increased readiness for ignition

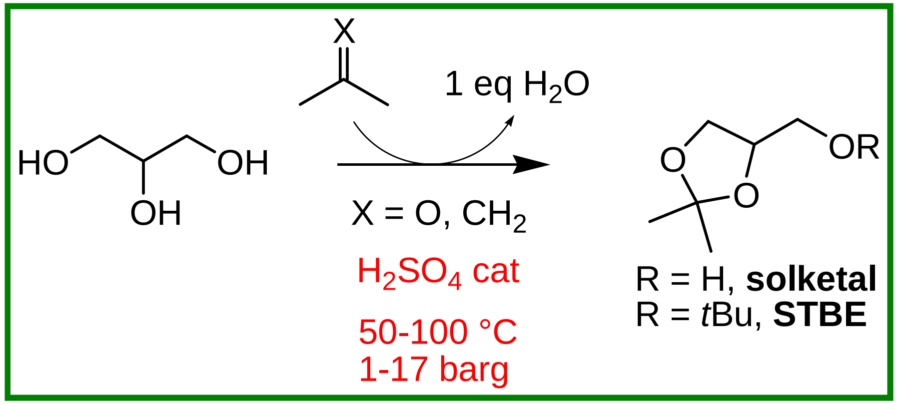
EP 1639061 (2004); CA 2530219 (2005); US 0270643 (2009)

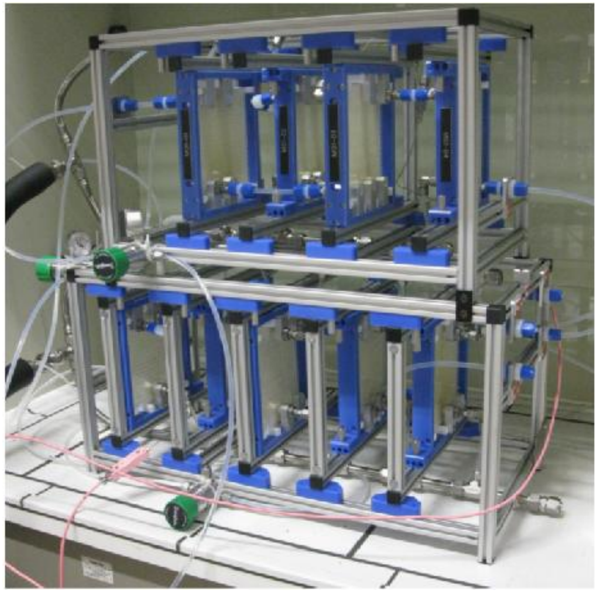
A flow process: the equipment

- The equipment adapts to the chemistry

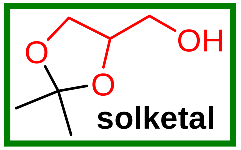
  … and to the lab !

CORNING

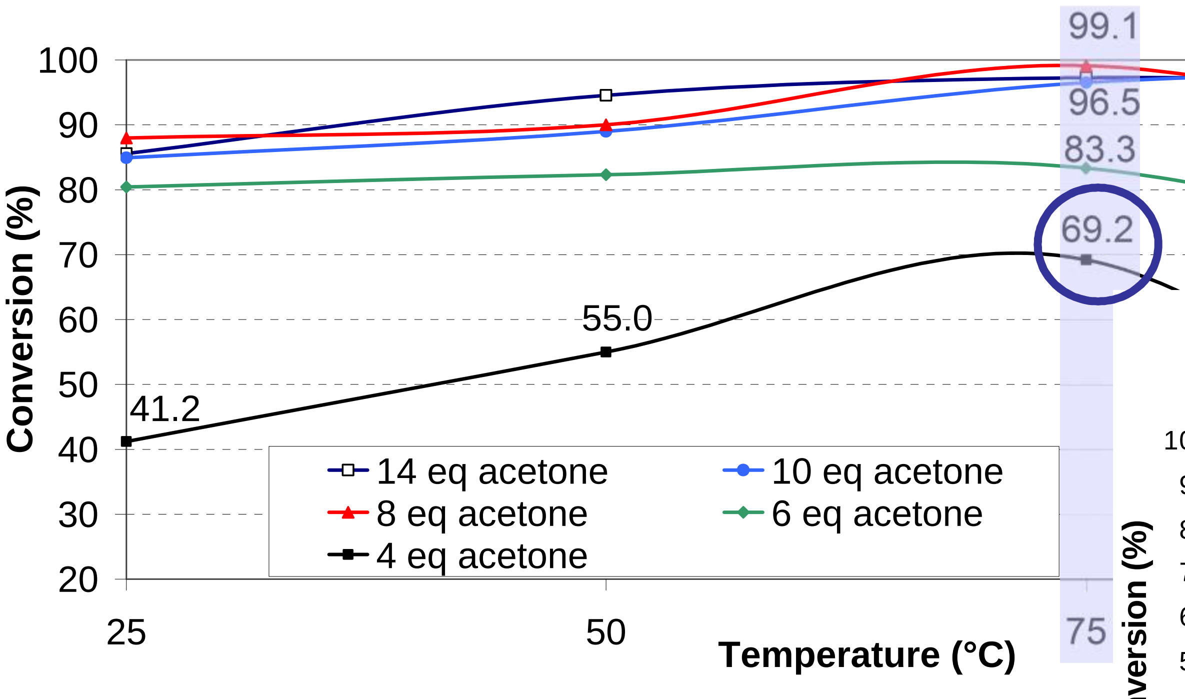




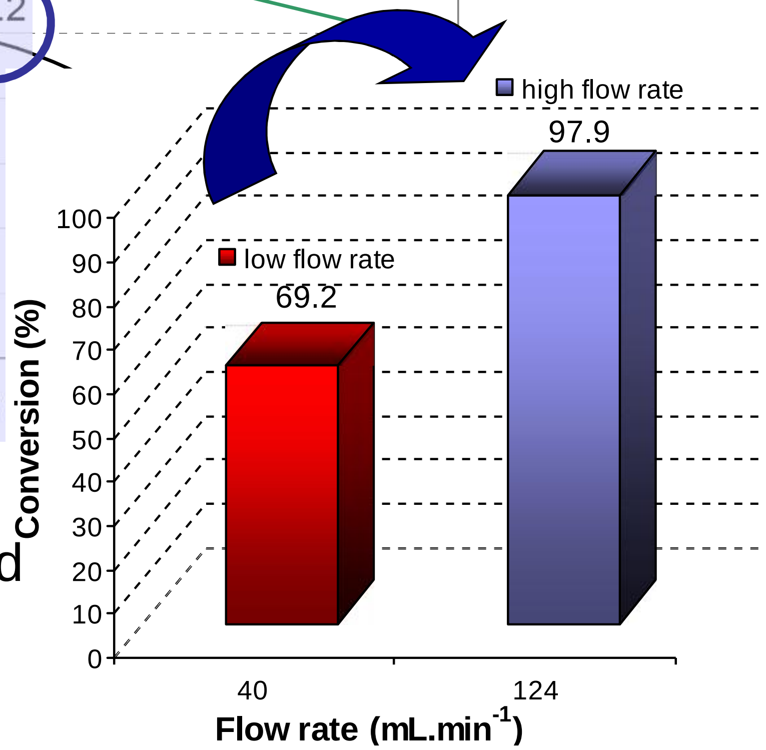
- Corrosive flow conditions ➔ **glass reactor, metal free/titanium, PFA**
- Handling of fluids with extremely different viscosities ➔ **appropriate auxiliaries**
- High temperatures, high pressure ➔ **sensors, automatisation**



Step 1: glycerol to solketal



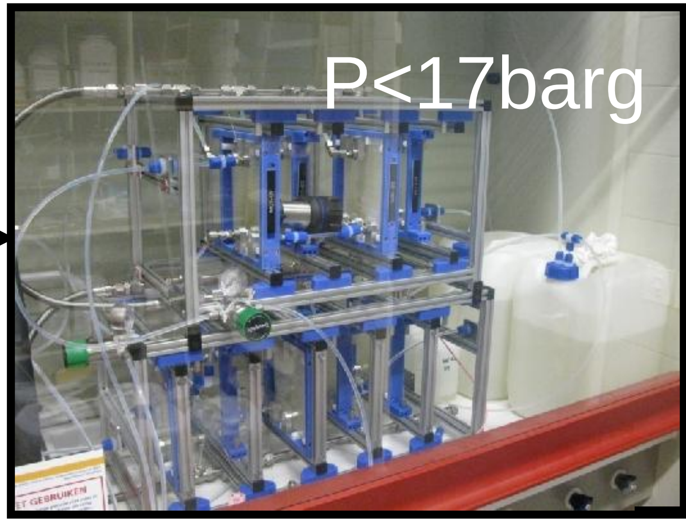
Flow x3 = ➚ conv.



- The higher the **excess**, the higher the yield
- **temperature**
- **flow**

Step 2: solketal to STBE

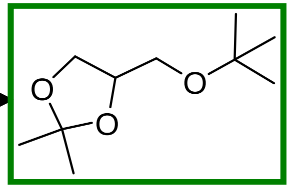
Isobutene



pumps

acid

- Slightly exothermic (MTBE)
- Irreversible reaction
- **Flash point -76.1°C !**
- **Polymerisation !**
- **Boiling point -7°C STP**



STBE

Flow production of STBE

- Step 1

➔ 11 kg/h throughput

➔ rt=26 s, selectivity > 98%, 4 eq acetone, 75 °C

➔ No solvent

Batch: 12 h, larger excess acetone, solvent

- Step 2

➔ 12 kg/h throughput

➔ rt=41 s, selectivity 95%, 1 eq *i*Bu, 90 °C, 17 barg

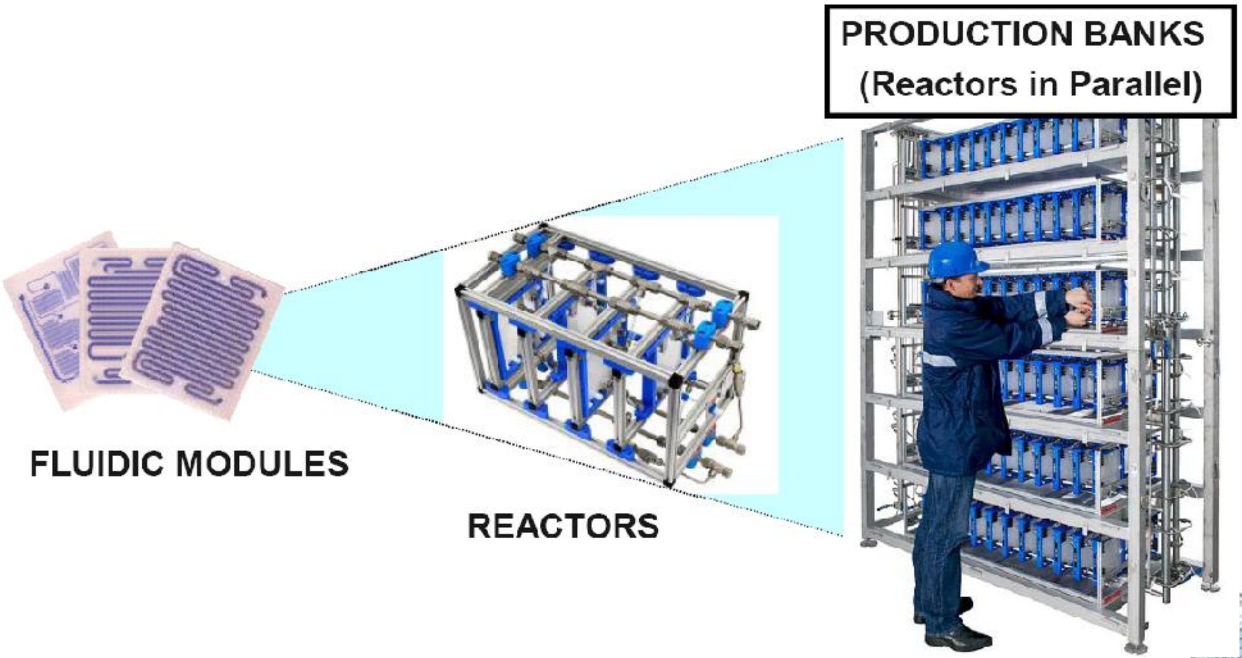
➔ No solvent

Batch: 12 h, > 2 eq *i*Bu, additives, 60 °C, 25 barg

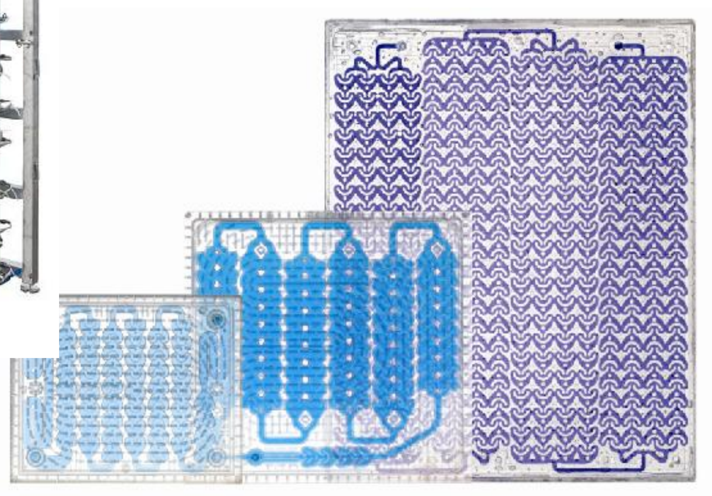
90 t/y Virtual production of STBE with 1 flow reactor !

Flow production of STBE

From 90 t/y to 1.2 10^4t/y STBE?

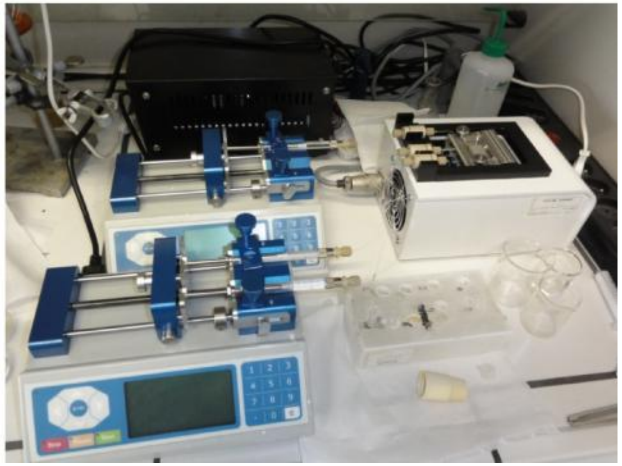


Copy and paste !



- X reactors in //
- Easy scale out

Platform of different systems



Research Group SynBioC (www.synbioc.ugent.be)

Conclusions

- Next to the attention that is actually paid to the development of biofuels,

  it is of crucial importance to develop

  bio-based building blocks for the chemical and applications industry using state of the art methodology
- The development of **bio-refineries** on the basis of **integral valorisation** of the renewable resources will be a major key in the transition to a bio-based economy

Acknowledgements

Green Chemistry in Belgium

- No formal society
- UGent Center of Renewable Resources (CoRR)
- Much industrial interest
- Sept. 2014: application for a academic scientific Working group on Sustainable Chemistry (catalysis, flow, renewables, microreactors, microwave, process intensification)

Green Chemistry
Centre of Excellence

UNIVERSITEIT GENT

International Conference on Renewable Resources and Biorefineries

RRB-11

York, June, 3-4-5 th 2015

RRB-10
RENEWABLE RESOURCES & BIOREFINERIES

UNIVERSITEIT GENT

Universidad de Valladolid

Always welcome to visit us in Belgium

And for good science we hope