Exploiting Nature's Diversity for the Development of Chemical Building Blocks

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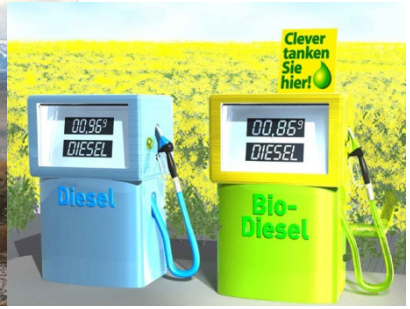
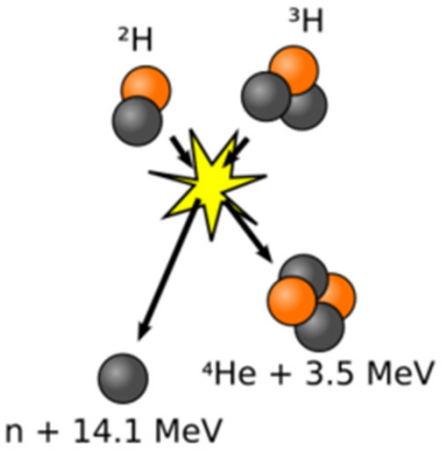
Departement of Sustainable Organic Chemistry and Technology

Is energy the all time top priority?





What about building blocks?

- « How about a thought from where the building blocks of organic chemistry will come from in the future? » (Foresight, Society of Chemical Industry, SCI, UK)
- 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

Strategic considerations

a ENZYMATIC EXPLOITATION

- use the powerful enzyme systems of plants to get complicated structures which would require a lot of synthetic steps (niche markets)

b DEGRADE – CONSTRUCT approach

- For compounds of lower complexity: it can be developed from a common general building block (economy of scale)

Renewable Topics at SynBioC

- Inulin (Chicory root), Chitosan (Crustaceae residu's)
- Undecenoic acid (Castor oil), Sophorolipids
- Flax modification
- Biodiesel, glycerol

Inulin

Reserve polysaccharide of different plant species

Present in e.g. dandelion, dahlia, Jerusalem artichoke, onion, garlic, …

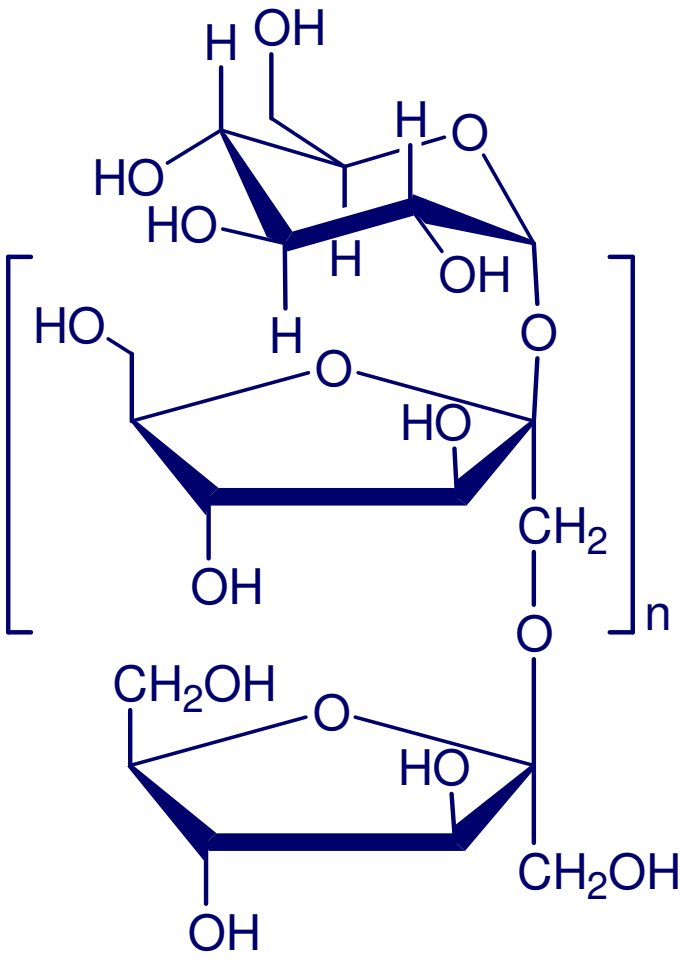
Polydisperse polyfructose

Industrially produced from chicory root (*Cichorium intybus*)

Chemical Properties of Inulin

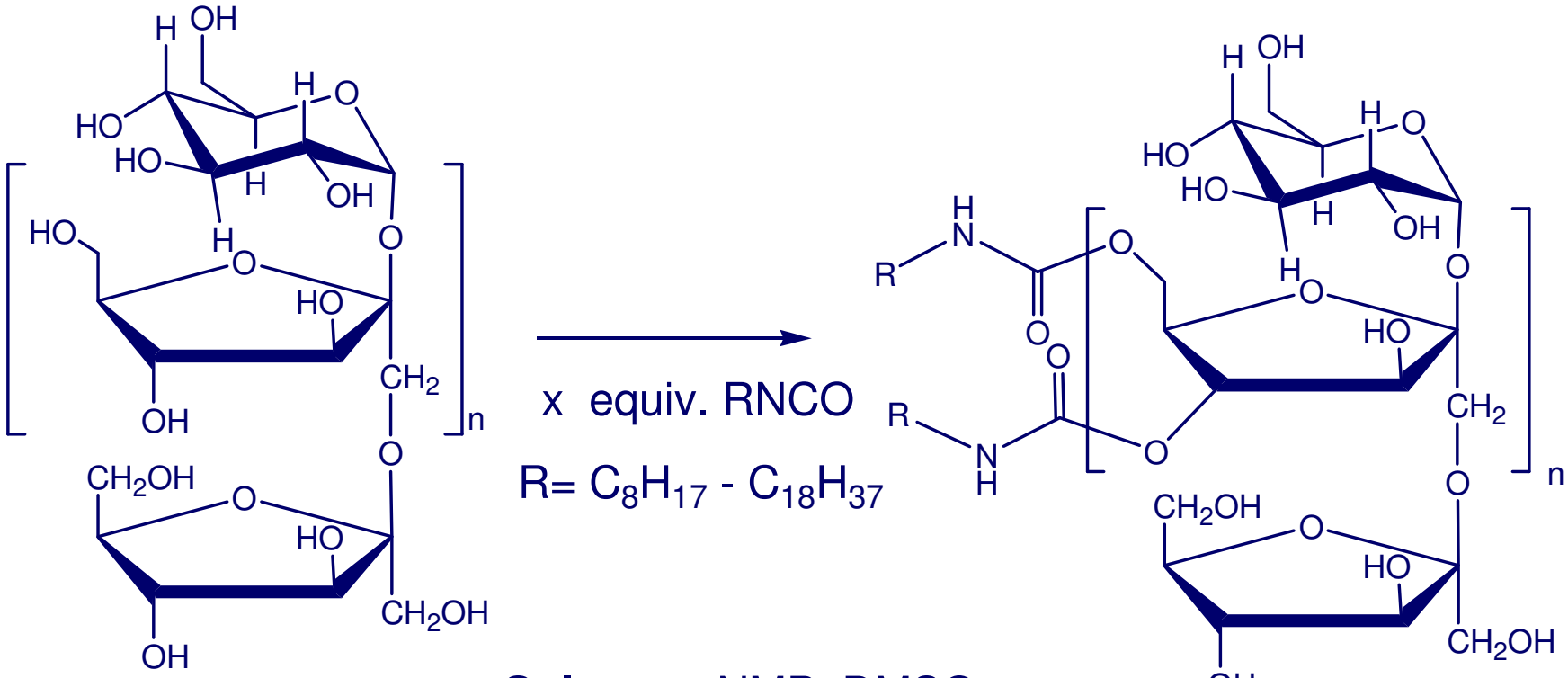
- Fructofuranose units linked via β(2→1)bonds
- Helicoidal linear carbohydrate
- Soluble in several polar organic solvents
  e.g. DMF, DMSO, pyridine, …
- Unique MW range when compared to cellulose or starch

DP: 3 – 60 fructose units
MW: 500 – 10000 g/mol



(GF_n)

Carbamoylation of Inulin

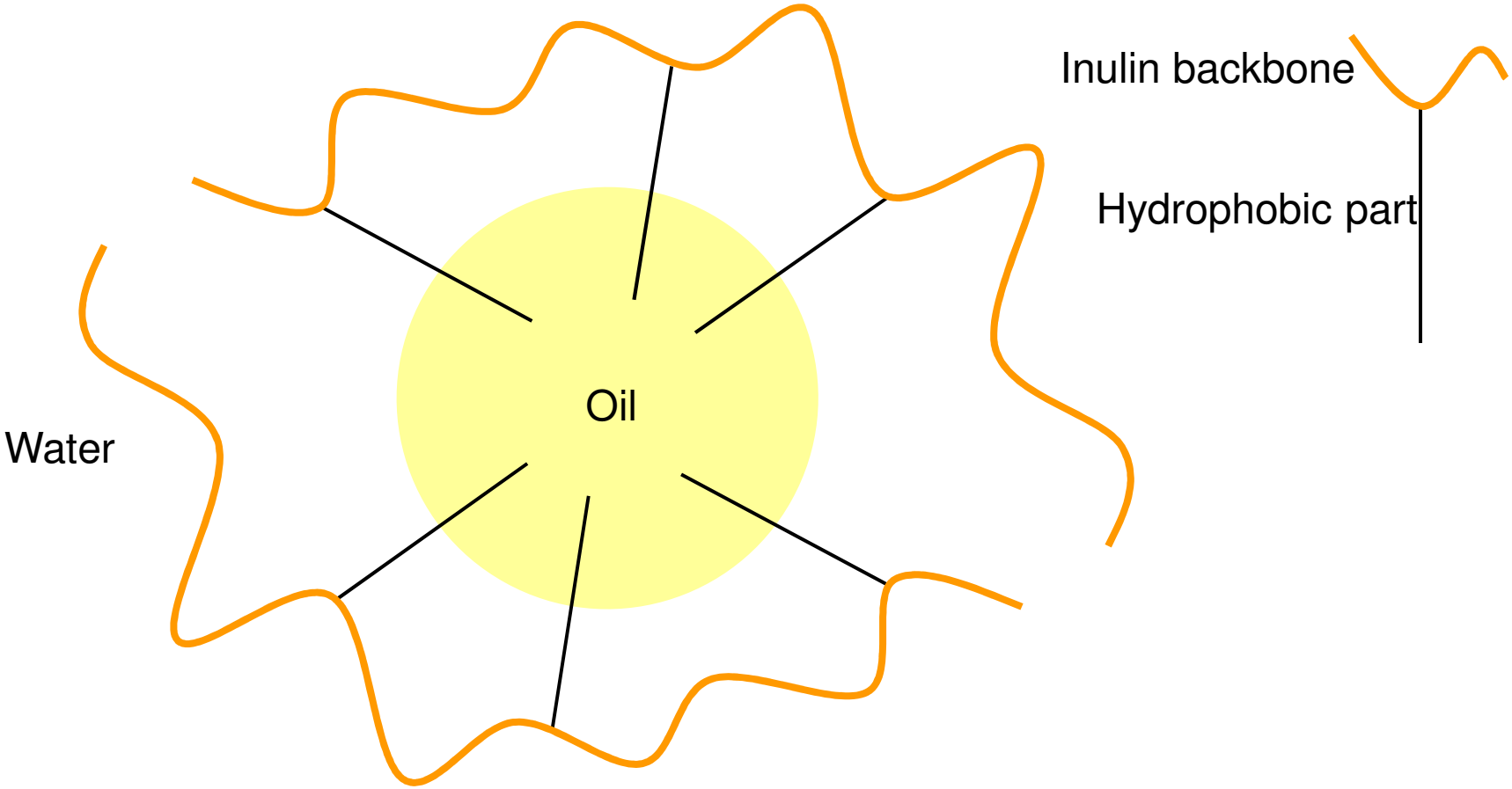


Solvents: NMP, DMSO

Reaction efficiency: 95 - 100 %

Stevens, C.V. et al, *Biomacromolecules*, 2, **2001**, 1256-1259.

Absorption of an inulin based surfactant on an oil droplet



Properties of Carbamoylated Inulin

50/50 O/W emulsions

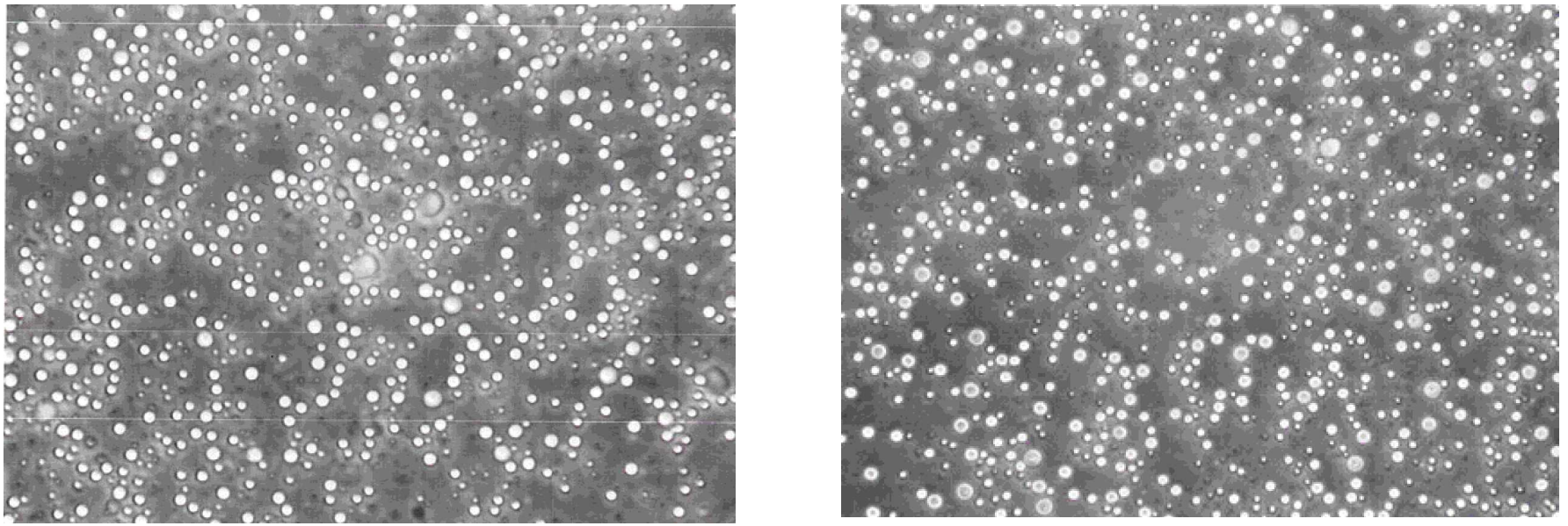
Oil separation →

Creaming →

← gently shaking redisperses the system

↑ "Stable emulsion"

Emulsion Stability



Optical micrograhs of diluted 50/50 IsoparM/water emulsions containing 2% INUTEC®SURFACTANTS that were stored at 50°C for a period of 1,5 (A) and 14 (B) weeks

No remarkable bigger bubbles during storage: no coalescence (no oil separation)

Creaming during the first days: gentle shaking leads to redispersion

Commercial products with Inutec

Advantages: 10 x less product needed to obtain stable emulsions
very stable emulsions with high salt concentrations

Modification of Chitosan

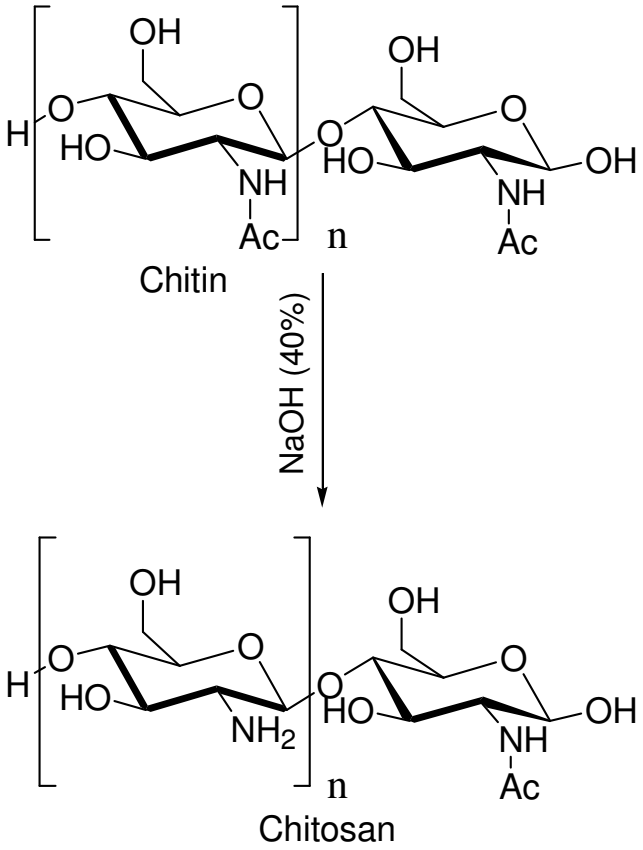
Chitosan = deacetylated chitin

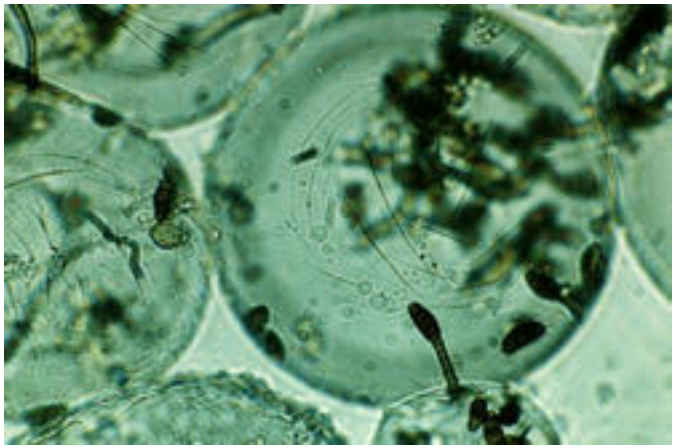
(component of residues of crustacea and cell wall of yeasts, Lentinus edodes, Absidia artrospora)

Biopolymer with interesting properties (waste product)

Compatible with skin tissue

Much modification research (increase of sollubility)





Esterification

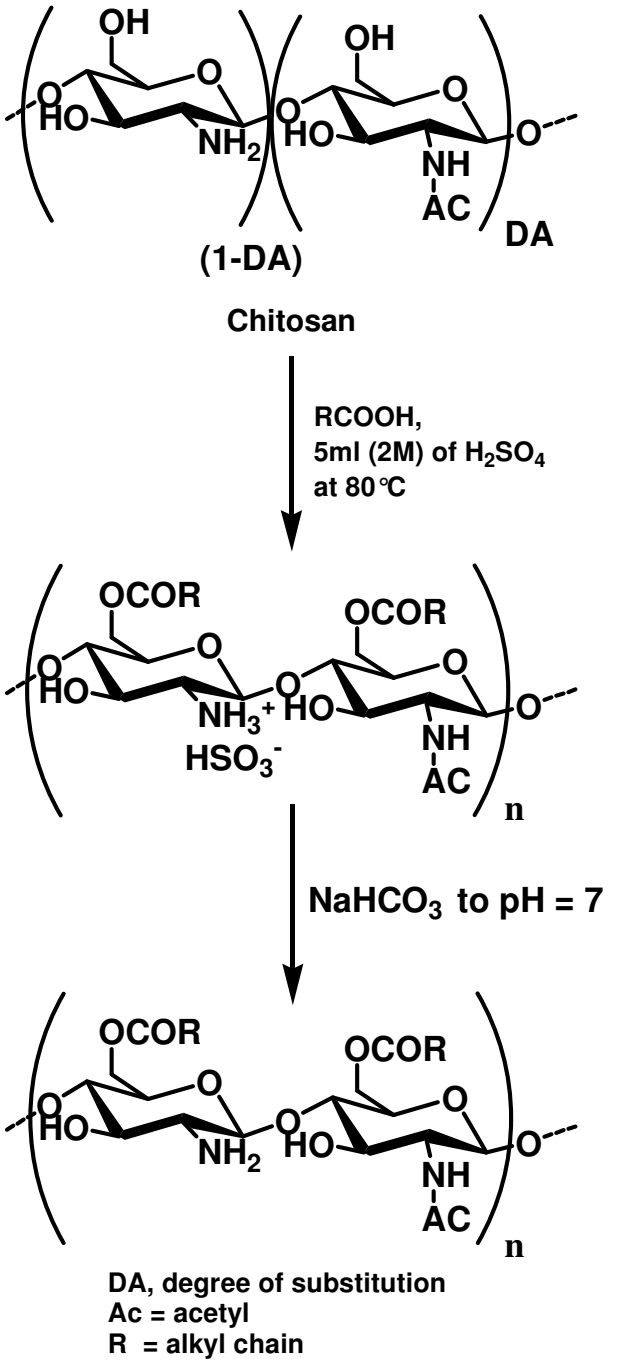
28 new chitosan alkanoates

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



Inhibition of growth

Control

Larval length
(mm± SEM)

(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)

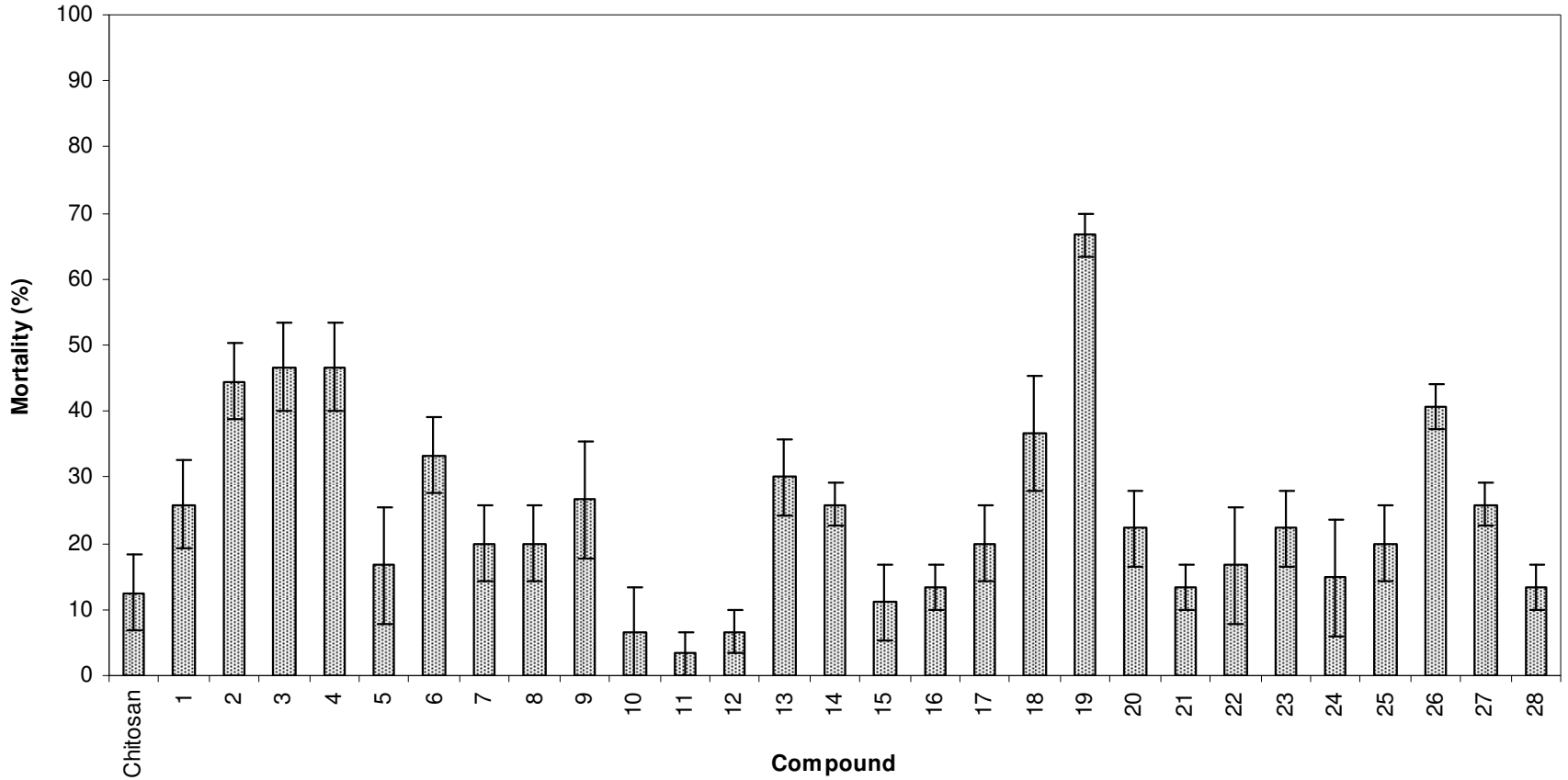
Heptanoate

(Compound 26)

(11.4± 0.06)

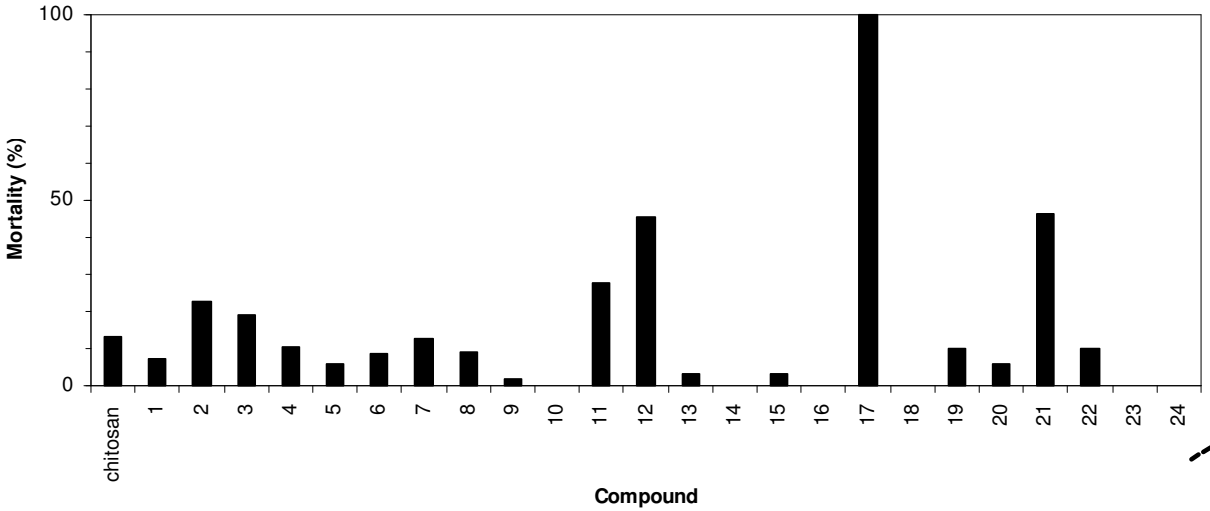
Decanoate

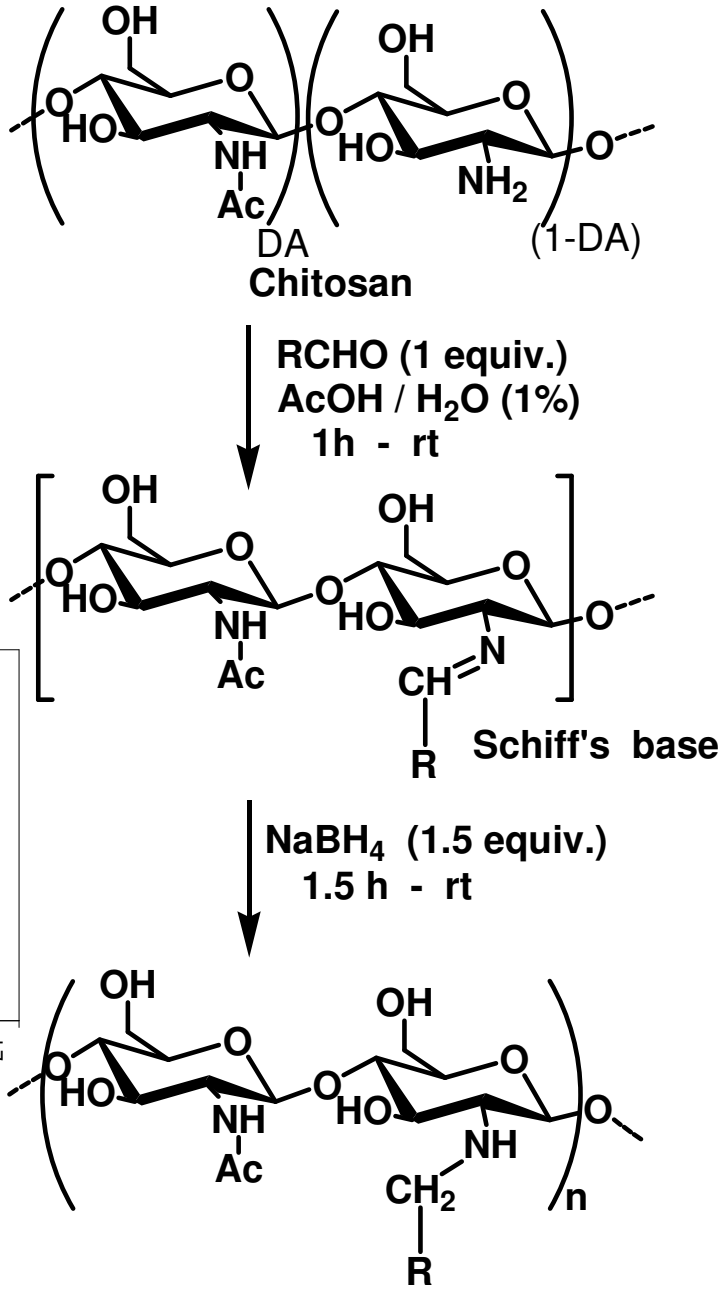
Mortality


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.

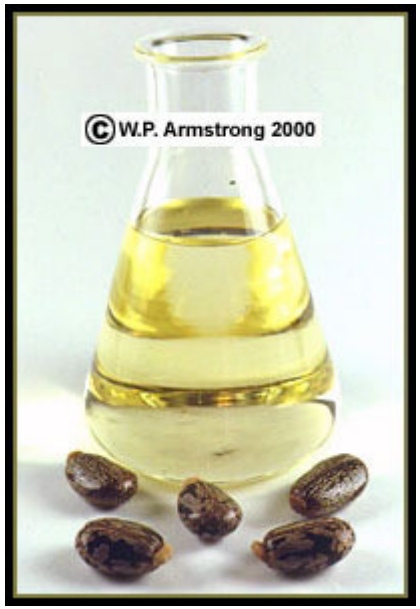




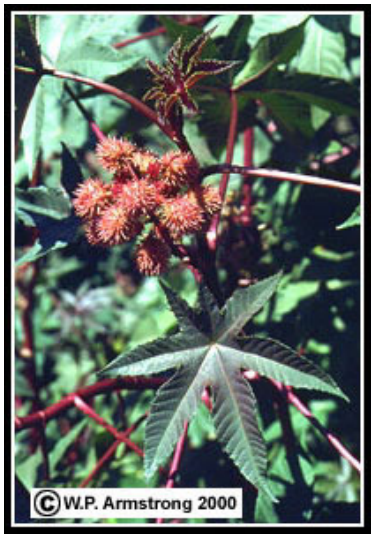
Modification of Undecenoic Acid

Castor oil (Ricinus communis)

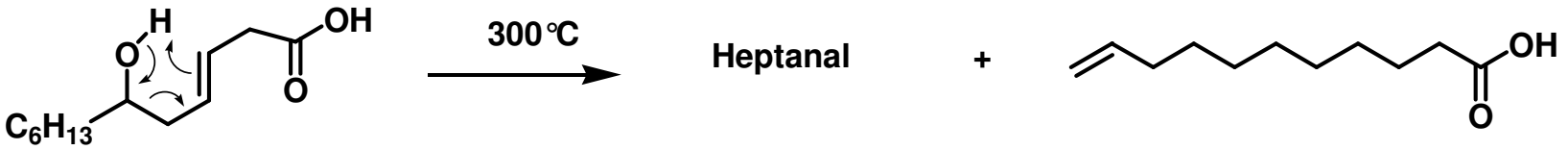
- Global castor seed production: 1 million tons per year.
- Leading producing areas: India, China, Brazil and the former USSR
- Castor seed: between 40% and 60% oil which is rich in triglycerides, mainly ricinolein
- Currently, 0.1 million tonnes of
- castor oil are imported by the EU



Production of fine chemicals from specific fatty acids



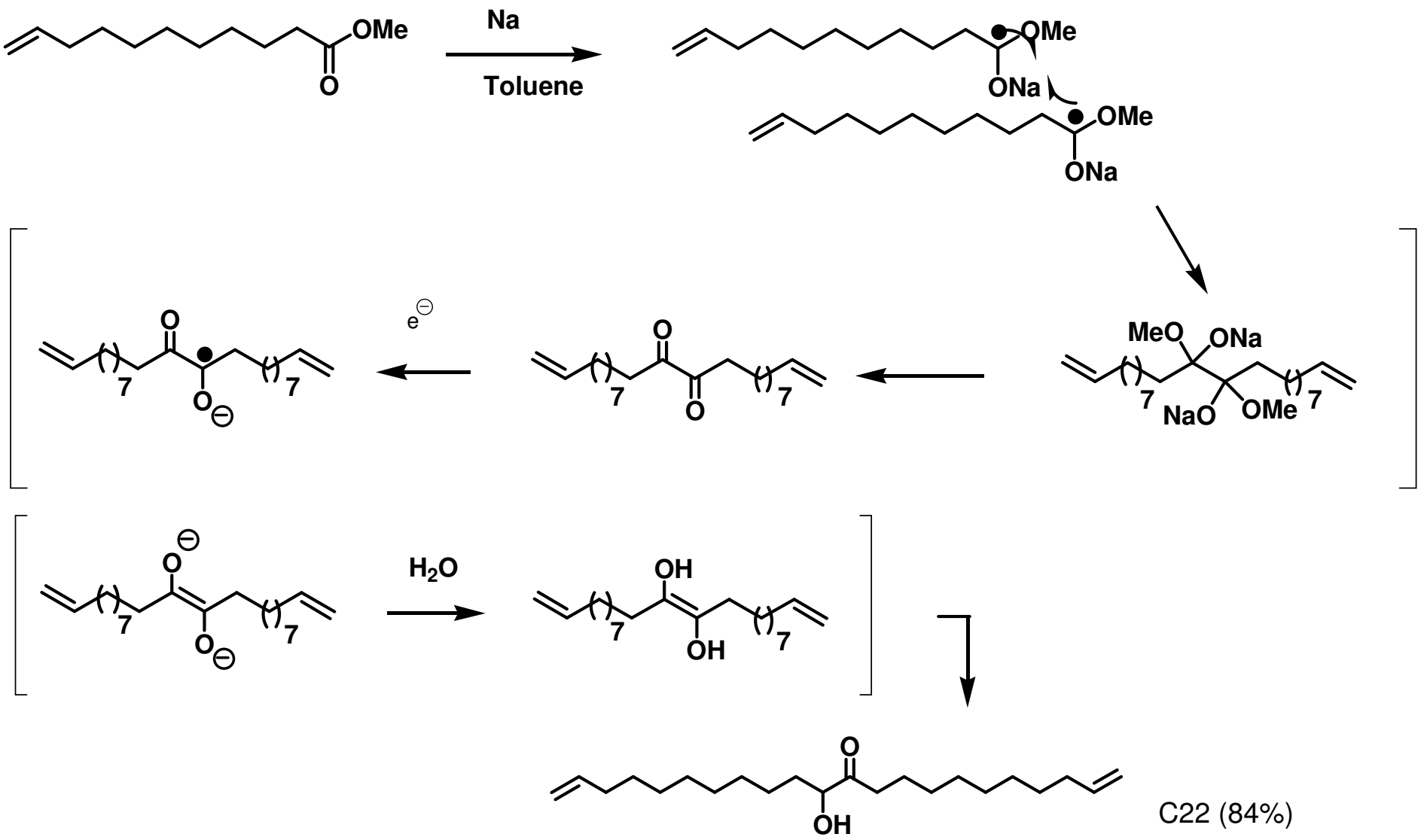
- Thermal cracking of ricinoleic acid



12-Hydroxy-9-octadecenoic acid

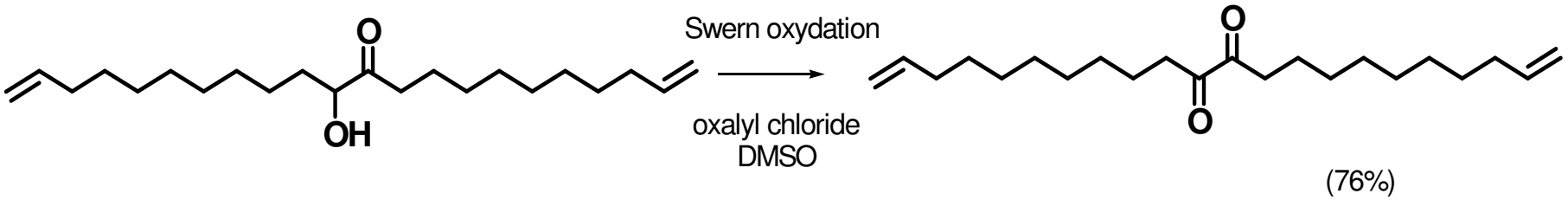
undecenoic acid - C11

Acyloin condensation



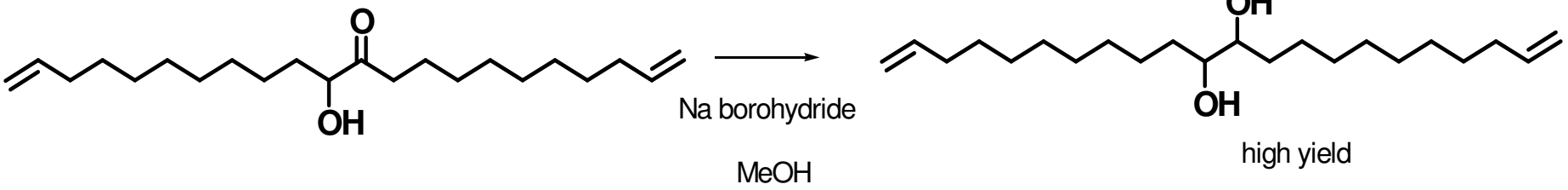
Hydroxyketon= C22-building block

OXYDATION



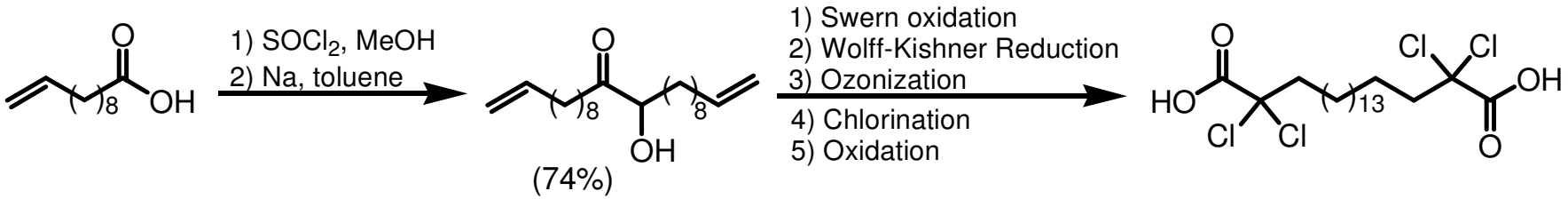
(76%)

REDUCTION



high yield

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

Glycerol: the bulky side of biodiesel

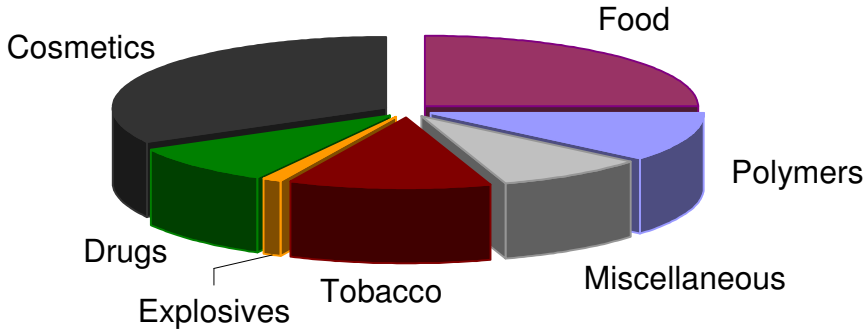
raw oil

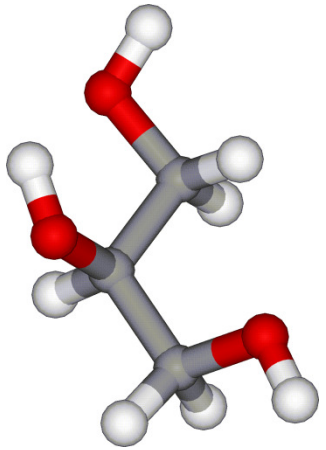
ester.

Biodiesel (FAME)

Glycerol

10 wt.-%



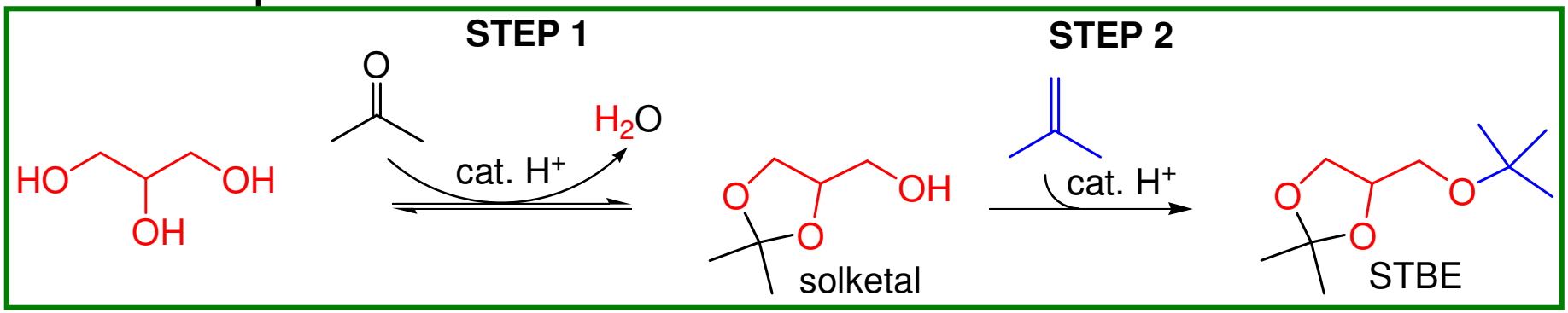


$C_3H_8O_3$
MW: 92.09

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

Glycerol: a renewable building block

- Two steps to STBE



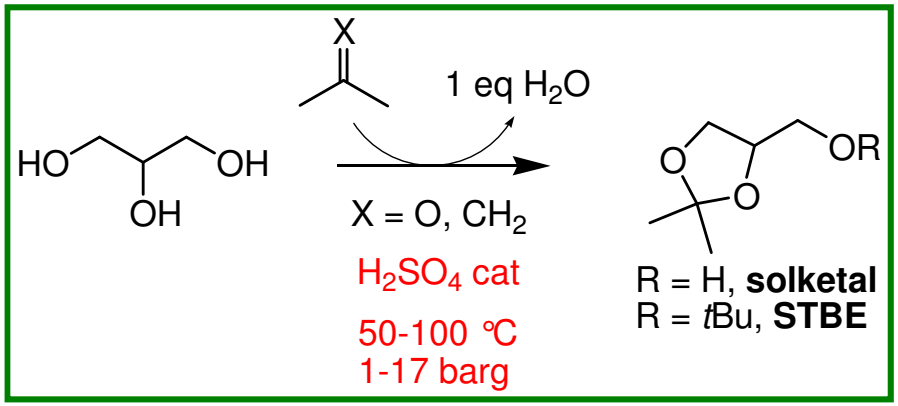
- STBE: a promising fuel additive
  - ➔ Significant reduction of small particles
  - ➔ Improved combustion/engine performances
  - ➔ Increased readiness for ignition

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

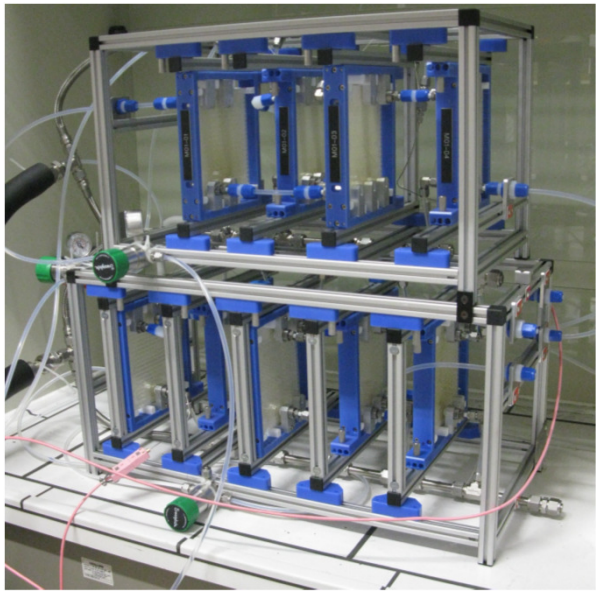
A flow process: the equipment

- 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**

Flow production of STBE: an overview

- 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

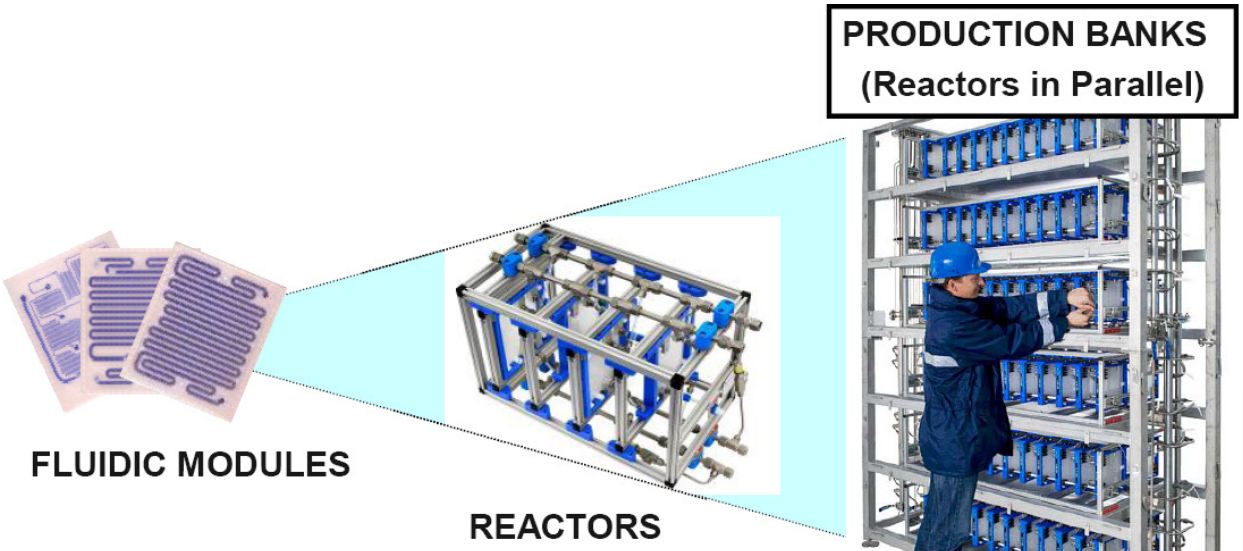
Batch: 12 h, > 2 eq *i*Bu, additives, 60 °C, 25 barg

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

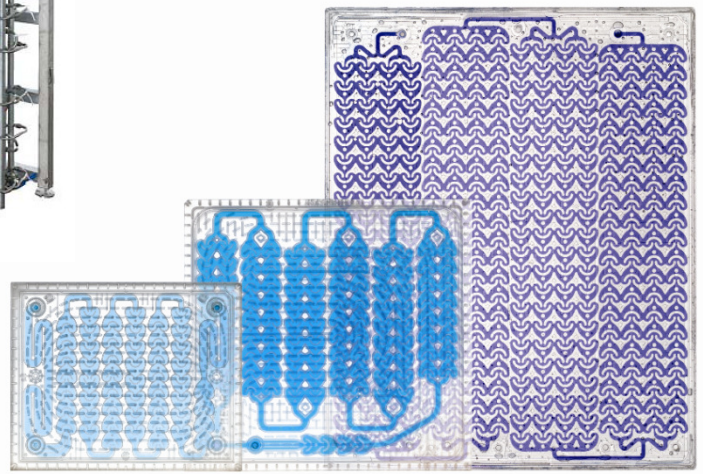
Flow production of STBE: an overview

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

Copy and paste



COURTESY OF CORNING



- X reactors in //
- Easy scale out

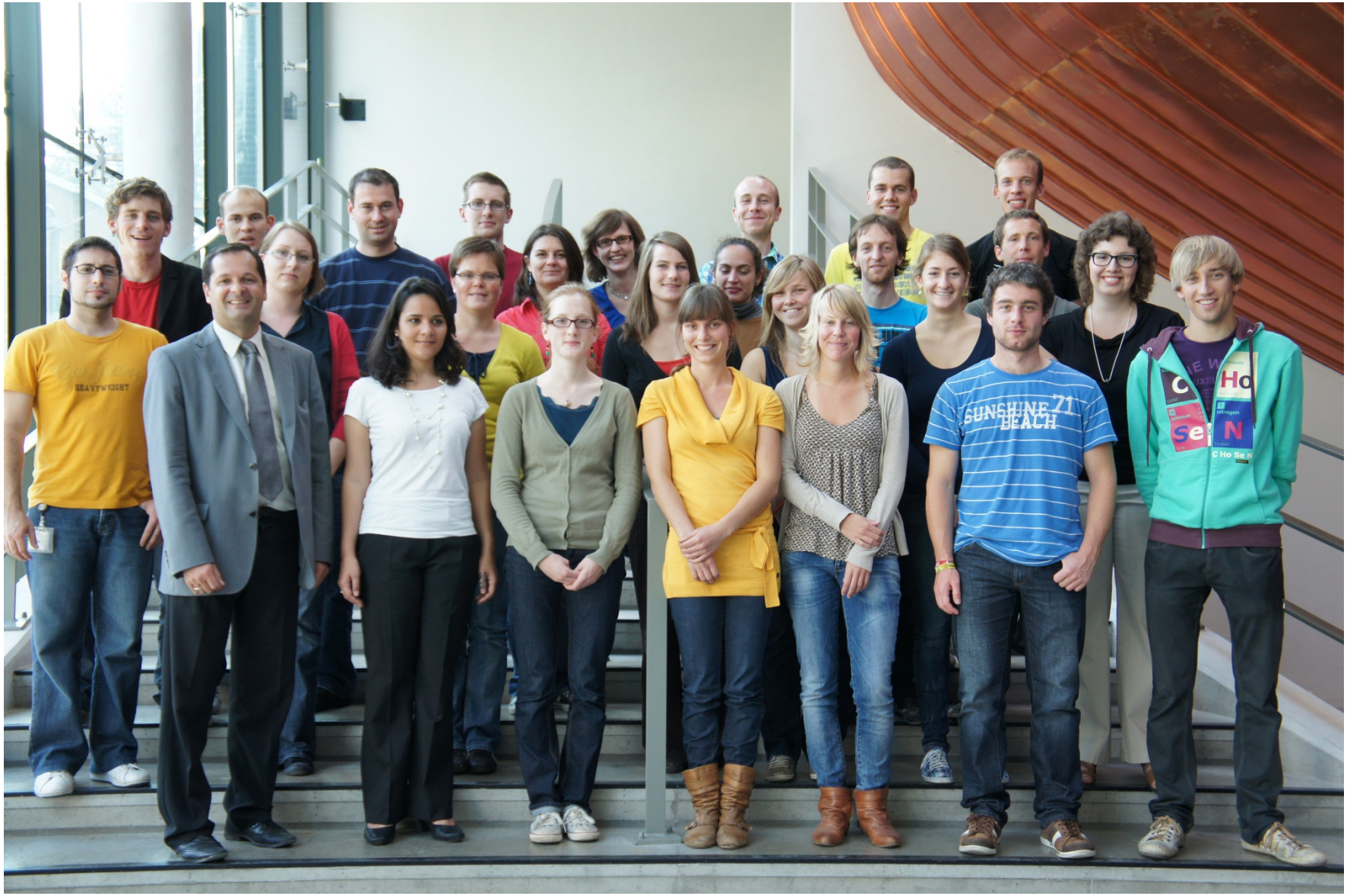
Conclusions

- 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



Always wellcome to visit Belgium