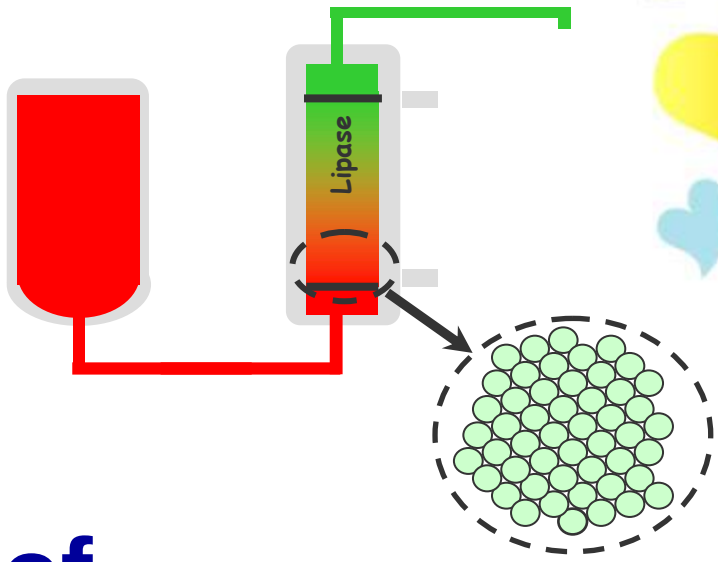

Processing aspects of enzymatic rearrangement

(for hardstock production)

R.M.M. Diks

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Contents

- Introduction
- Kinetics & deactivation
- Processing & reactor set-up

History ER process

- ‘33 earliest publication on (trans)esterification[1]
- ‘79 first patent (interesterification)[2]
- ‘83 first application in oils and fats modification[3]
- ‘85 publication on biocatalysis in organic media[4]
- ‘86 solvent free processing in PBR

……

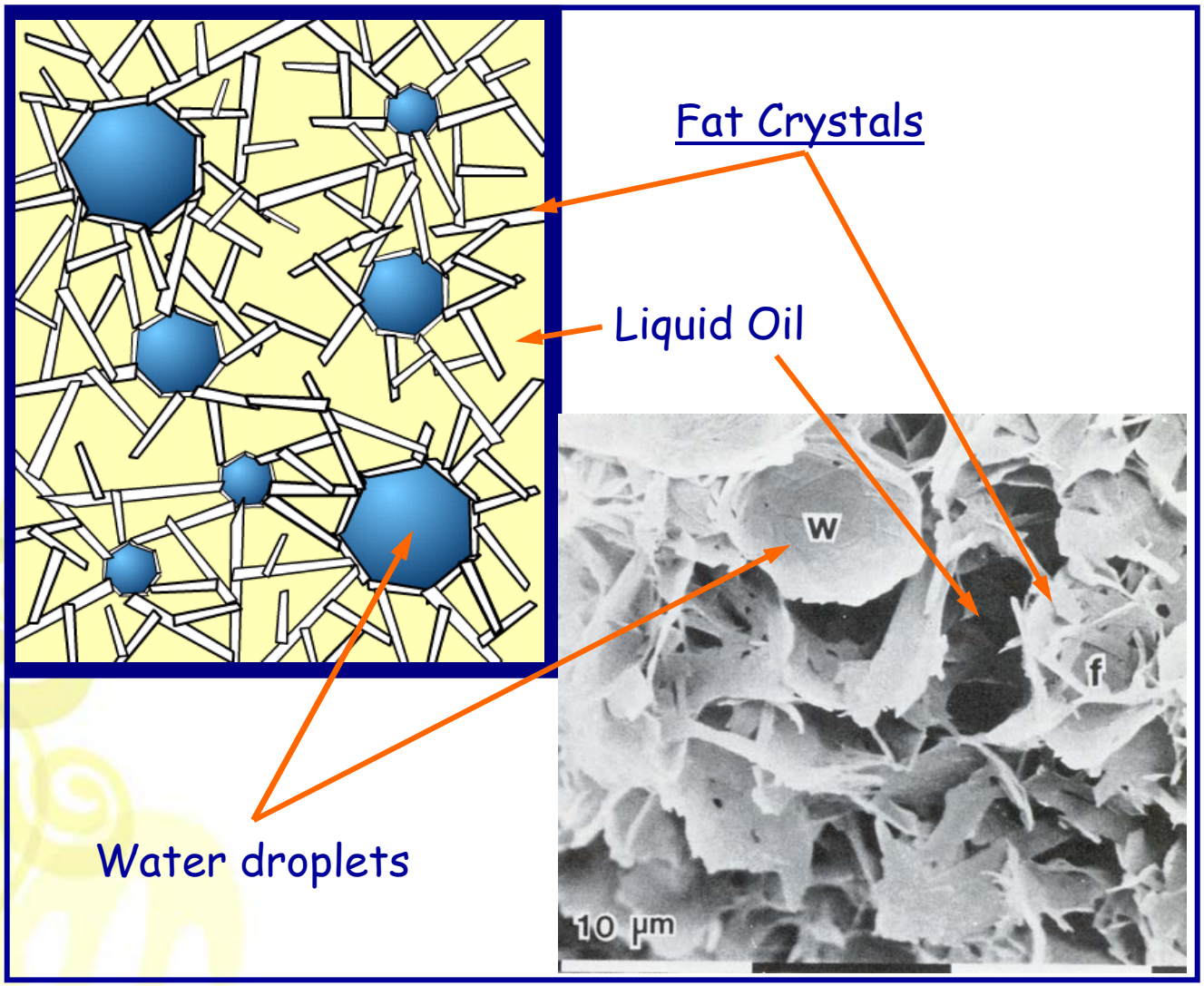
2004 First large scale plant hardstock production US

2007 First large scale plant hardstock production EU

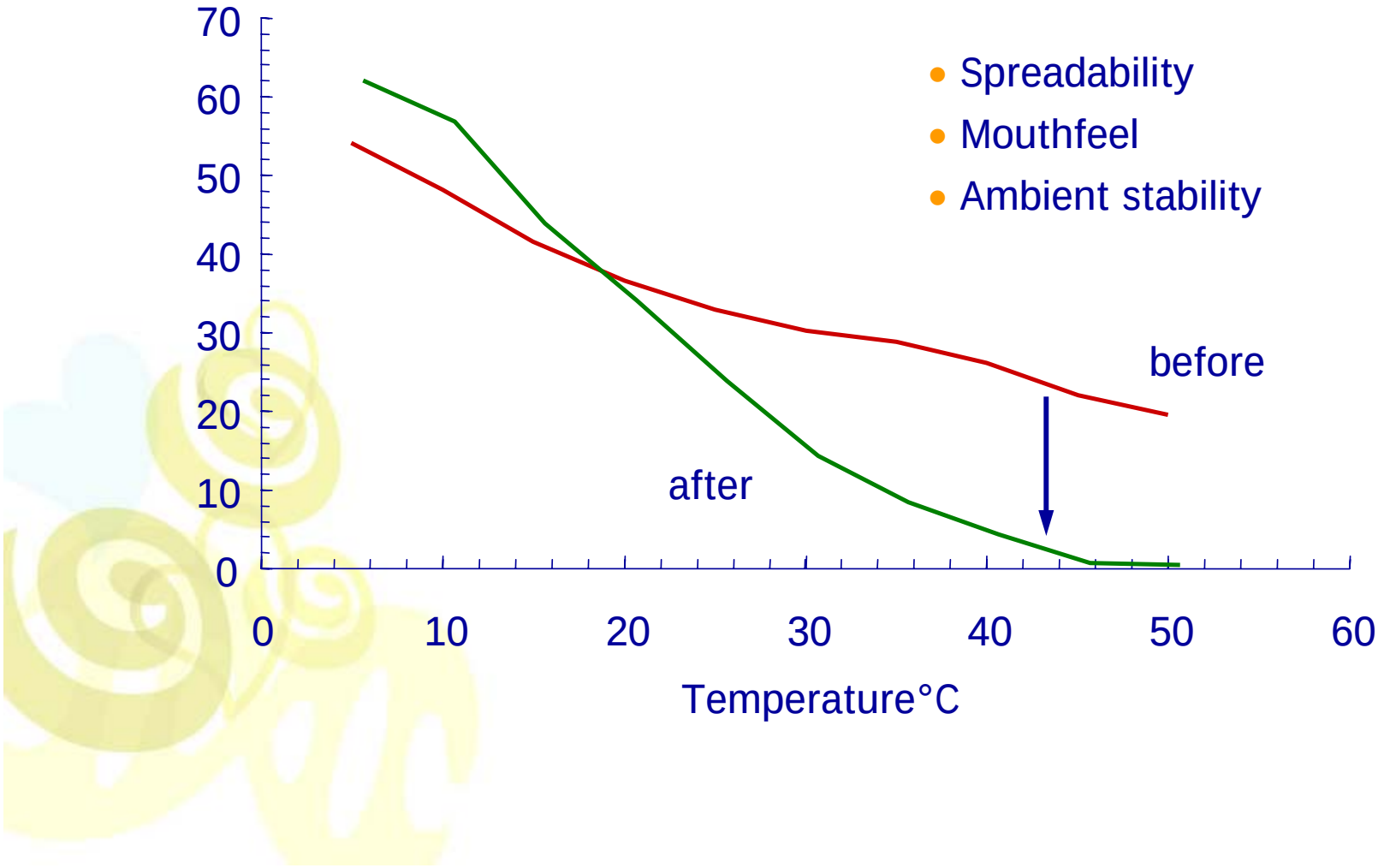
2011 ~ 300 kT capacity (EU)
~ 500 kT capacity (Global)

1. Sym E.A. (1933), Biochem. Z., 258, 304;
2. Coleman M.H., Macrae A.R. (1979), US Patent 4,275,081
3. Macrae A.R. (1983), JAOCS, 60, 2, 243.
4. Zaks A., Klibanov A.M. (1985), Proc. Natl. Acad. Sci, 82, 3192.
5. Hansen T.T., Eigtved P. (1986), World Conf. Oils Fats Ind.’, S. 365.

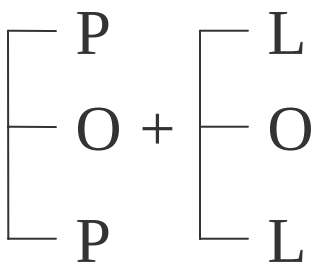
Structure of a fat continuous spread

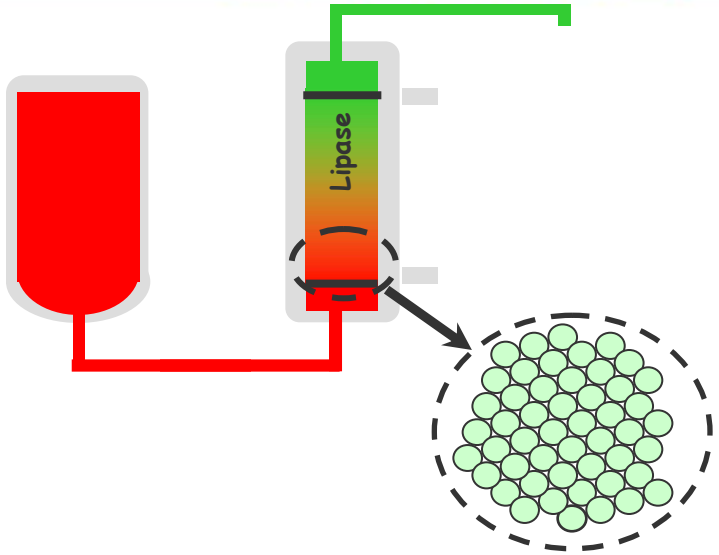


Fat melting properties

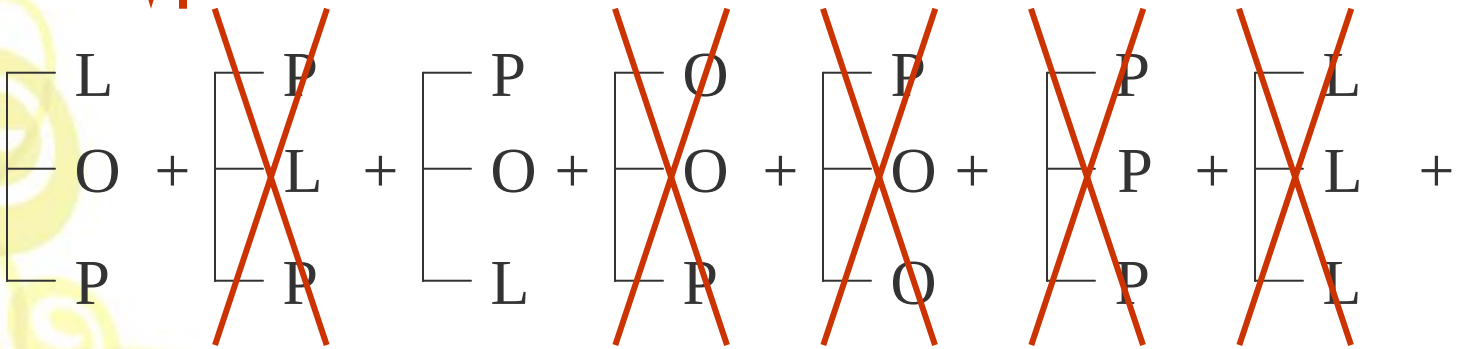


Enzymatic Rearrangement



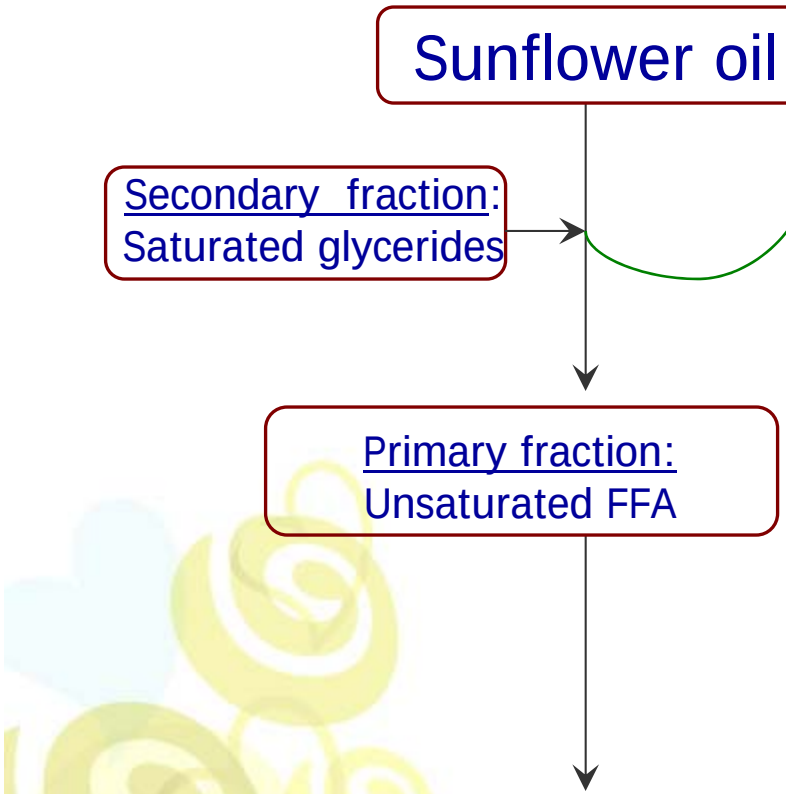


Lipase 60 °C

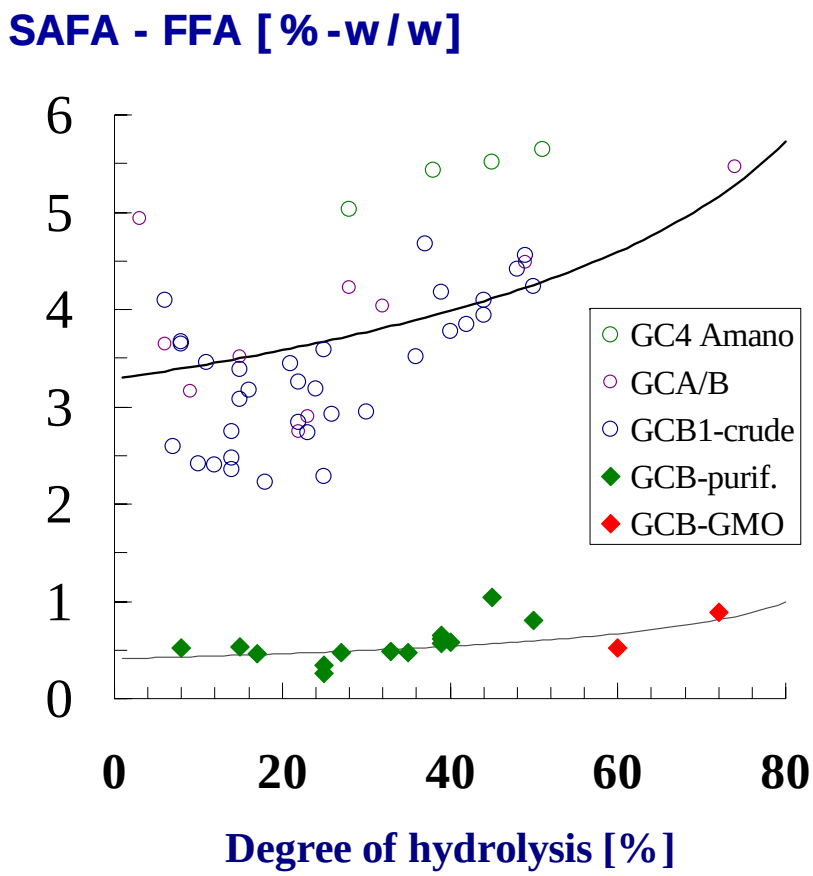


Lipases generally *sn*-1,3 specific ⟷ *acyl-migration* ⟷ catalyst random

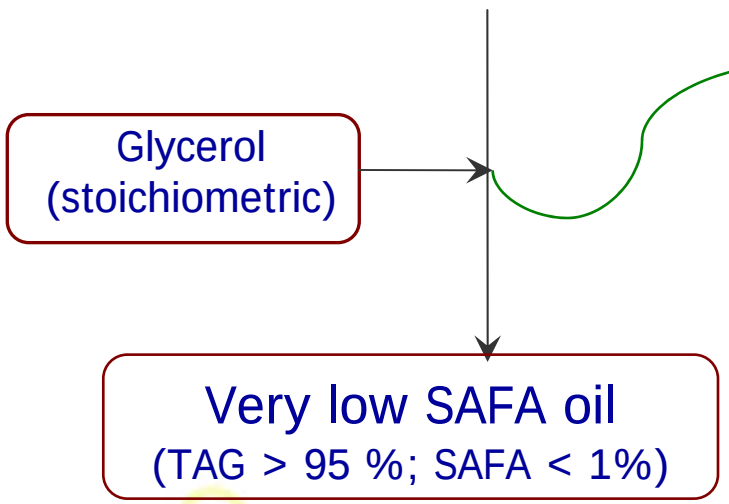
Cis-Δ9 fatty acid hydrolysis



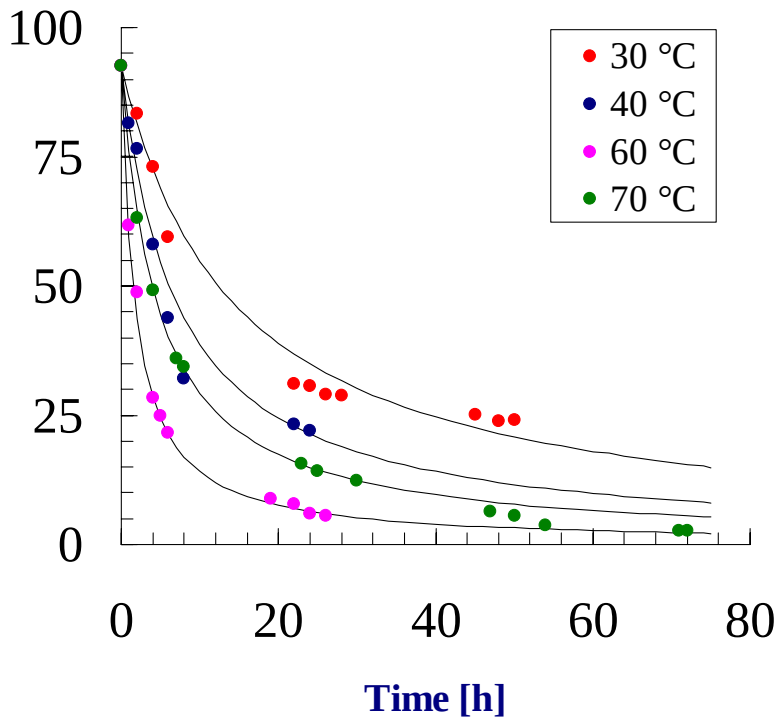
Geotrichum candidum B - 60 °C



Impact acylmigration



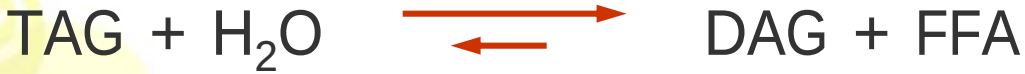
FFA content in fat phase [%-w/w]



ER kinetics

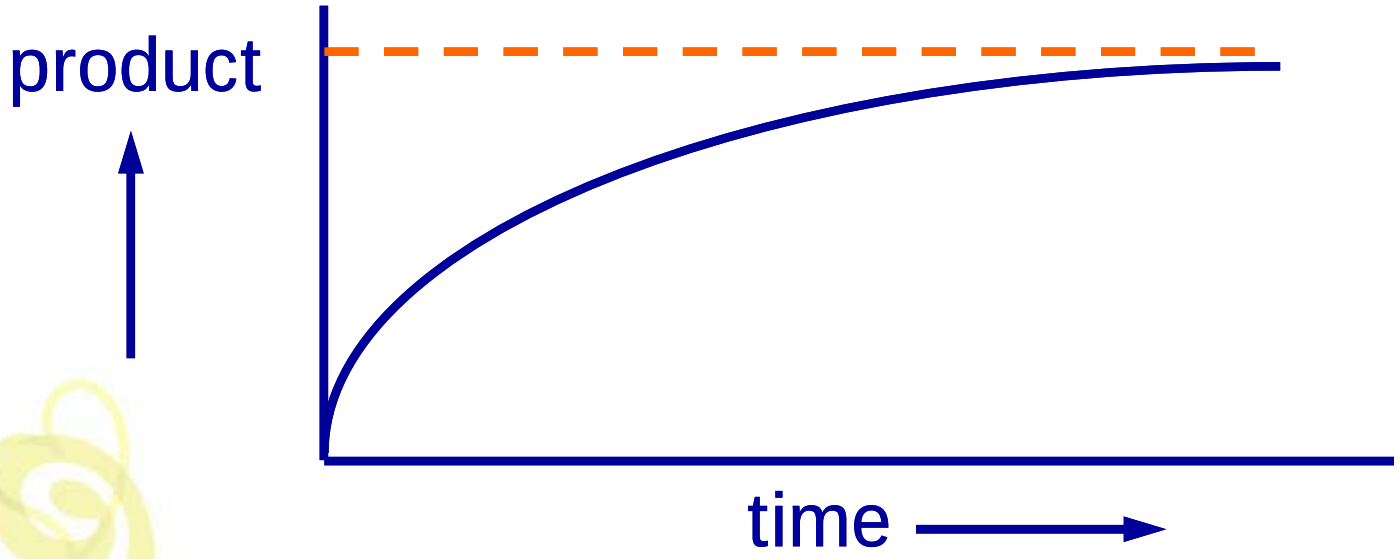
TAG Rearrangement (primary - slow)

Hydrolysis (secondary - quick)



Modeling - Pseudo 1st-order

"Just swapping the fatty acids..."

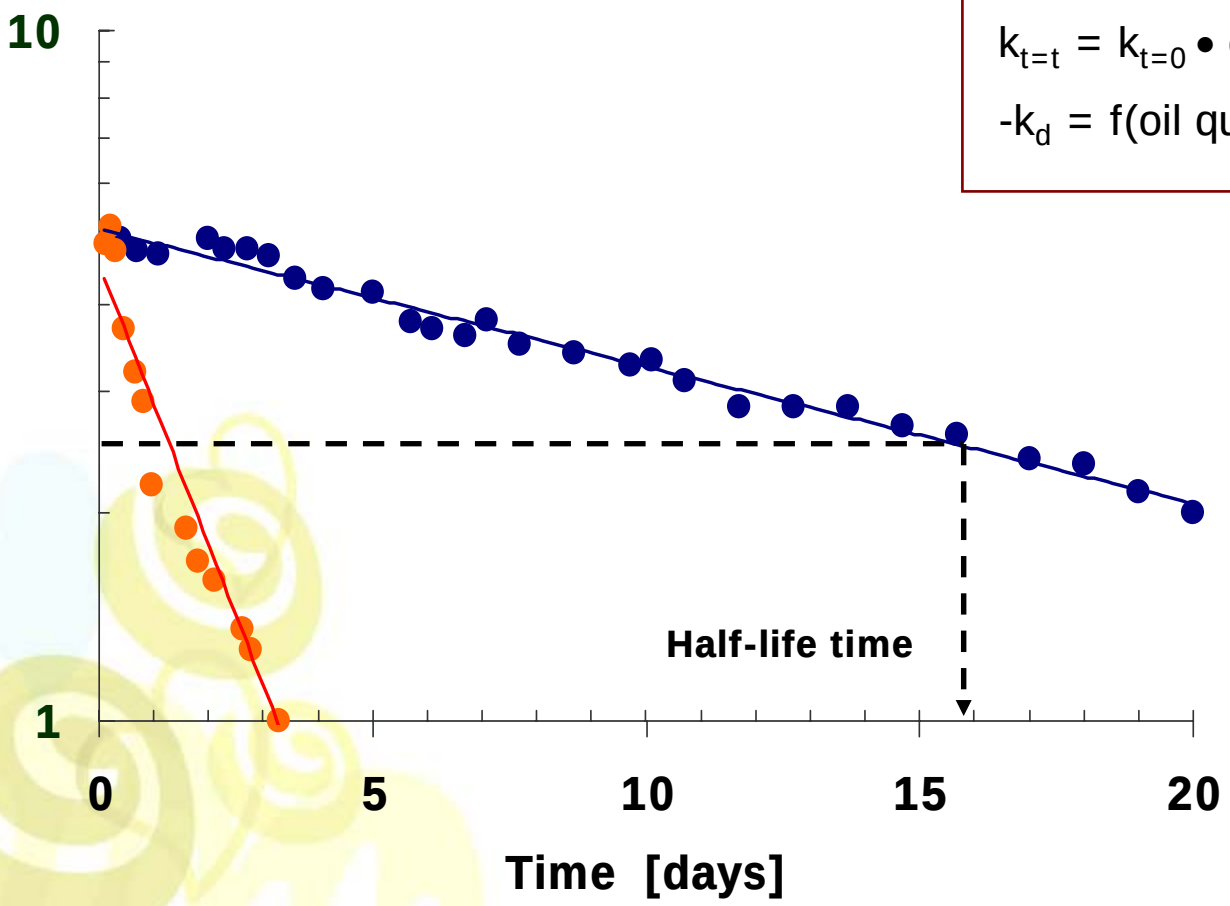


$k_{cat} \bullet C_{cat} \bullet t = - \ln (1-X)$

X = relative degree of conversion

(representative change between starting blend and product)

Catalyst deactivation (1st order)



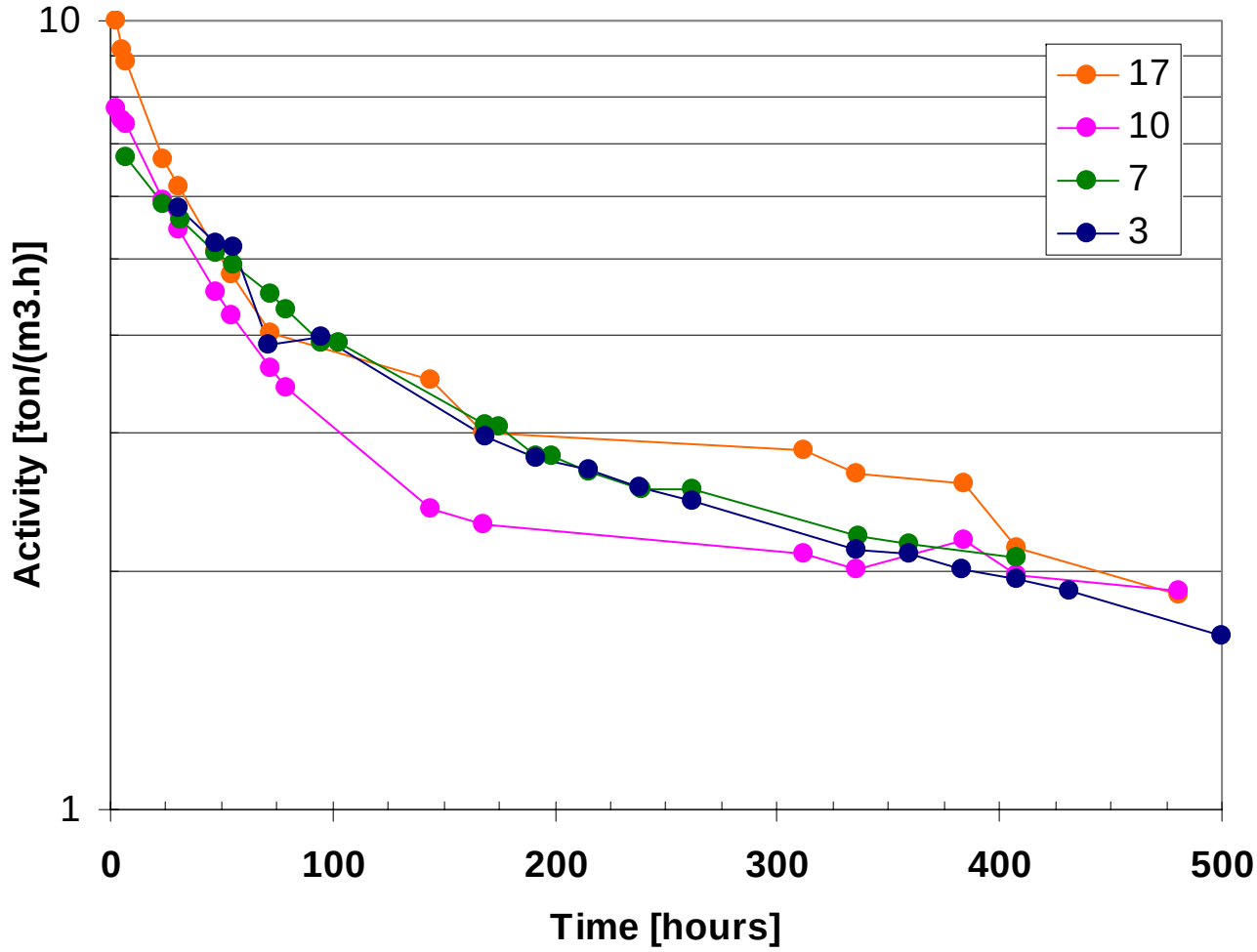
First-order deactivation kinetics:

$k_{t=t} = k_{t=0} \bullet e^{(-k_d \bullet t)}$

$-k_d = f(\text{oil quality}, T, a_w)$

R. oryzae **lipase / Accurel EP100**

Catalyst deactivation (2nd order)



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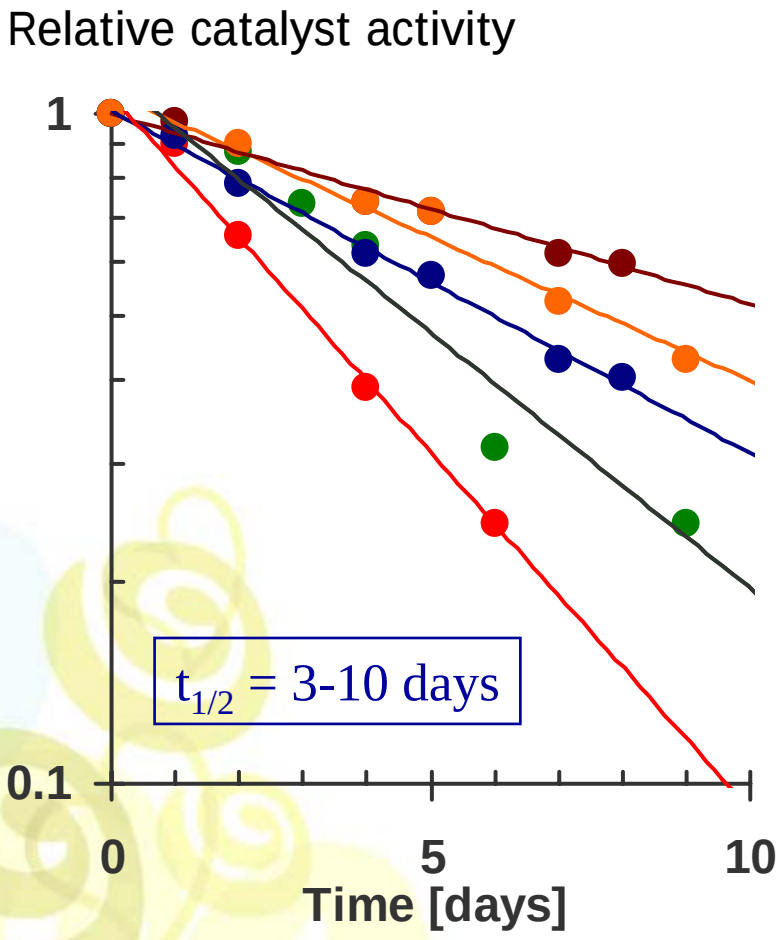
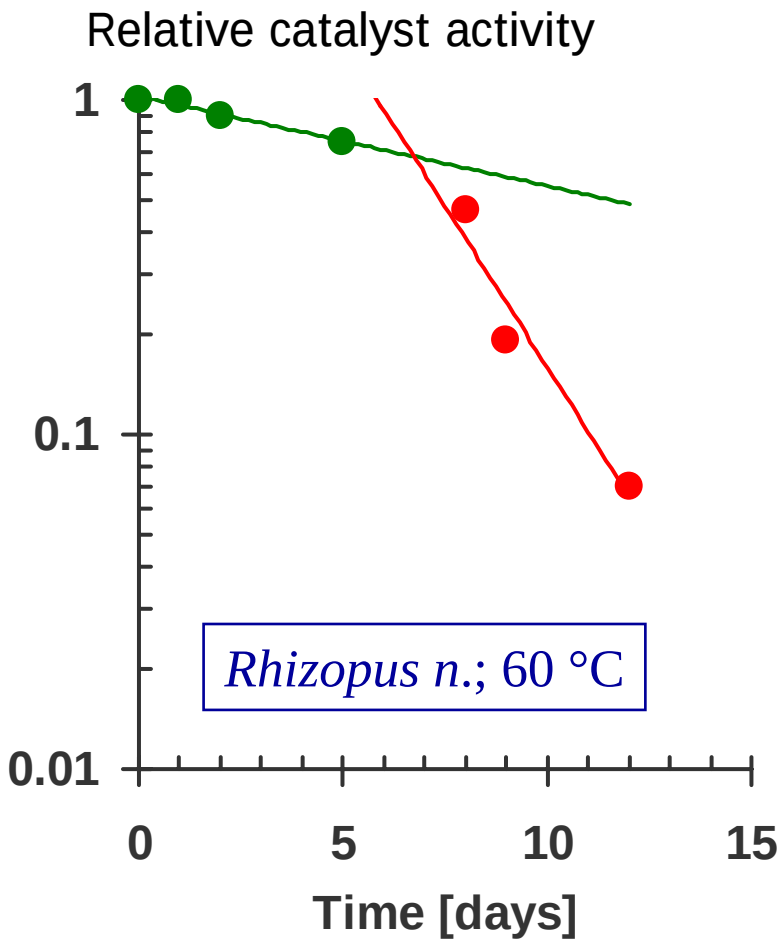
Effect of oil quality





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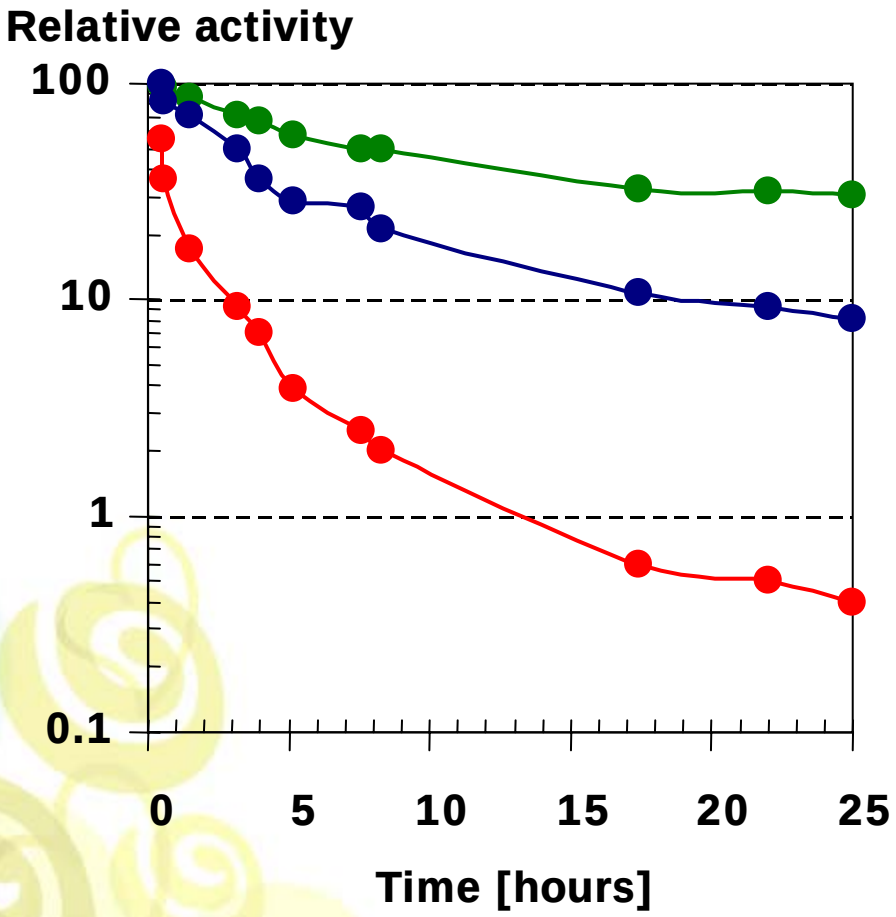
Deactivation mechanisms

- Thermal (denaturation)
- Fouling (apparent)
- Poisoning
  - hydroperoxides (POV)
  - secondary oxidation products (PAV)
  - metals
  - phospholipids
  - triterpenoids
  - acids
  - .....

Oxidation products



Fresh

Oxidised (POV=5)

Oxidised (POV=110)

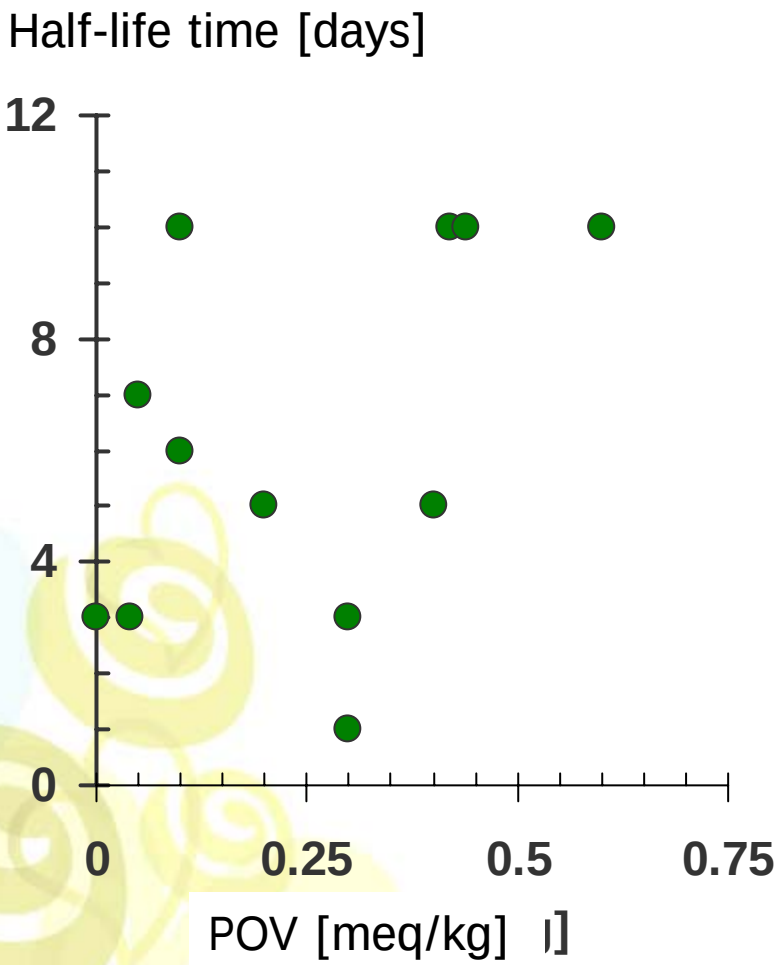
Lipozyme IM20

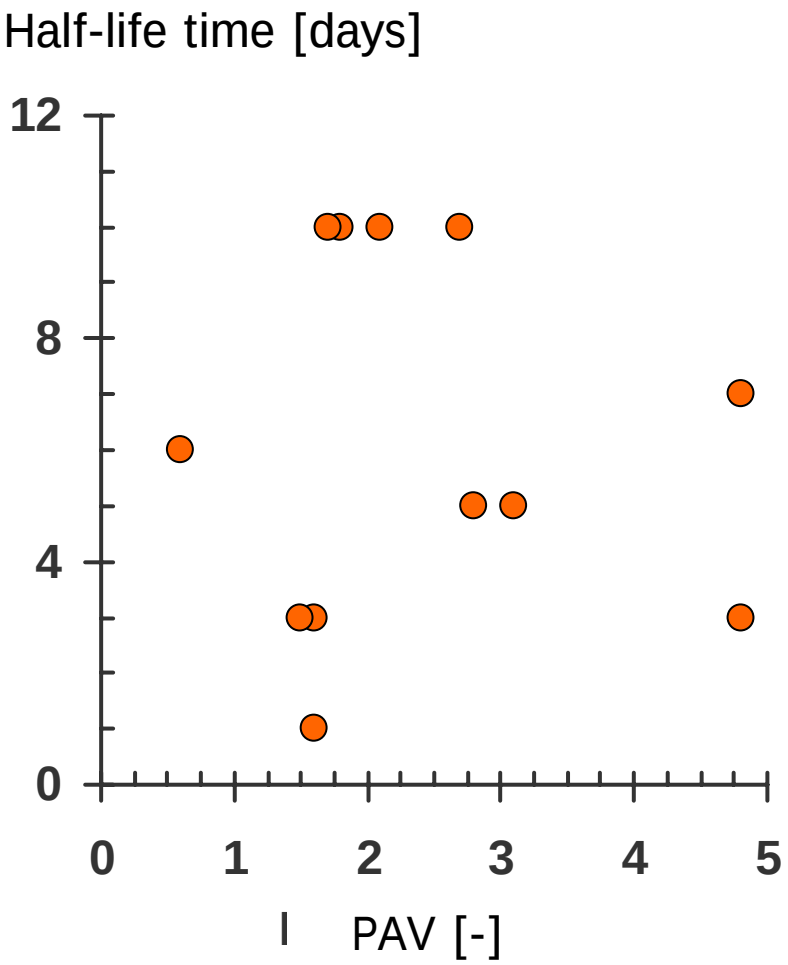
Butylether; 80 °C

$E_{state\ 1} \longleftrightarrow E_{state\ 2}$

Pirozzi D., Halling P. (1999), ICHEAP4 Conf., May 1999, Florence, Italy.

Oil quality parameters (2001)





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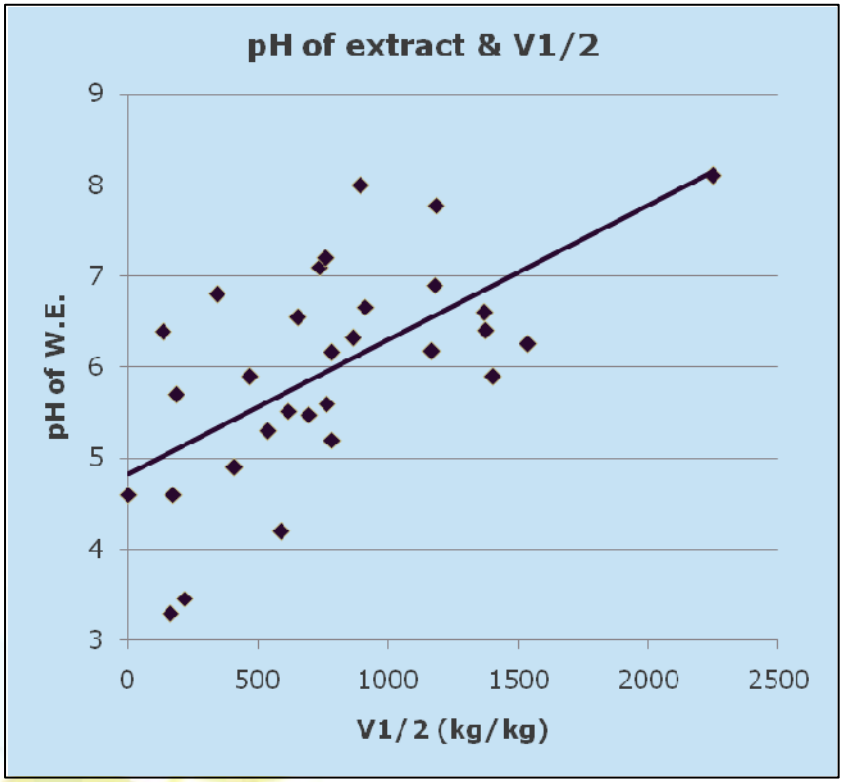
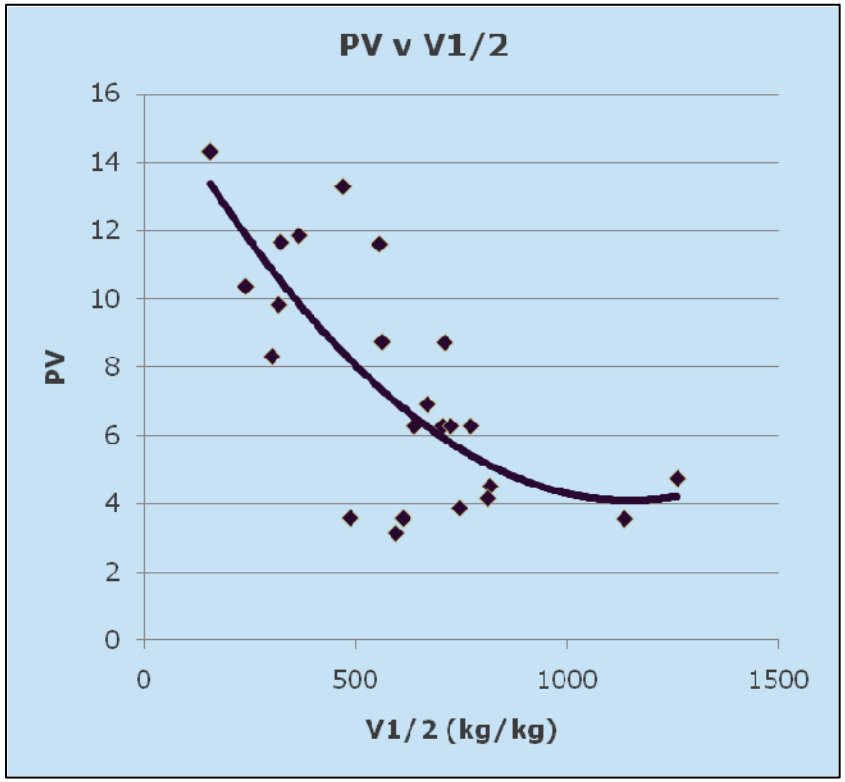
Oil quality parameters (2005)

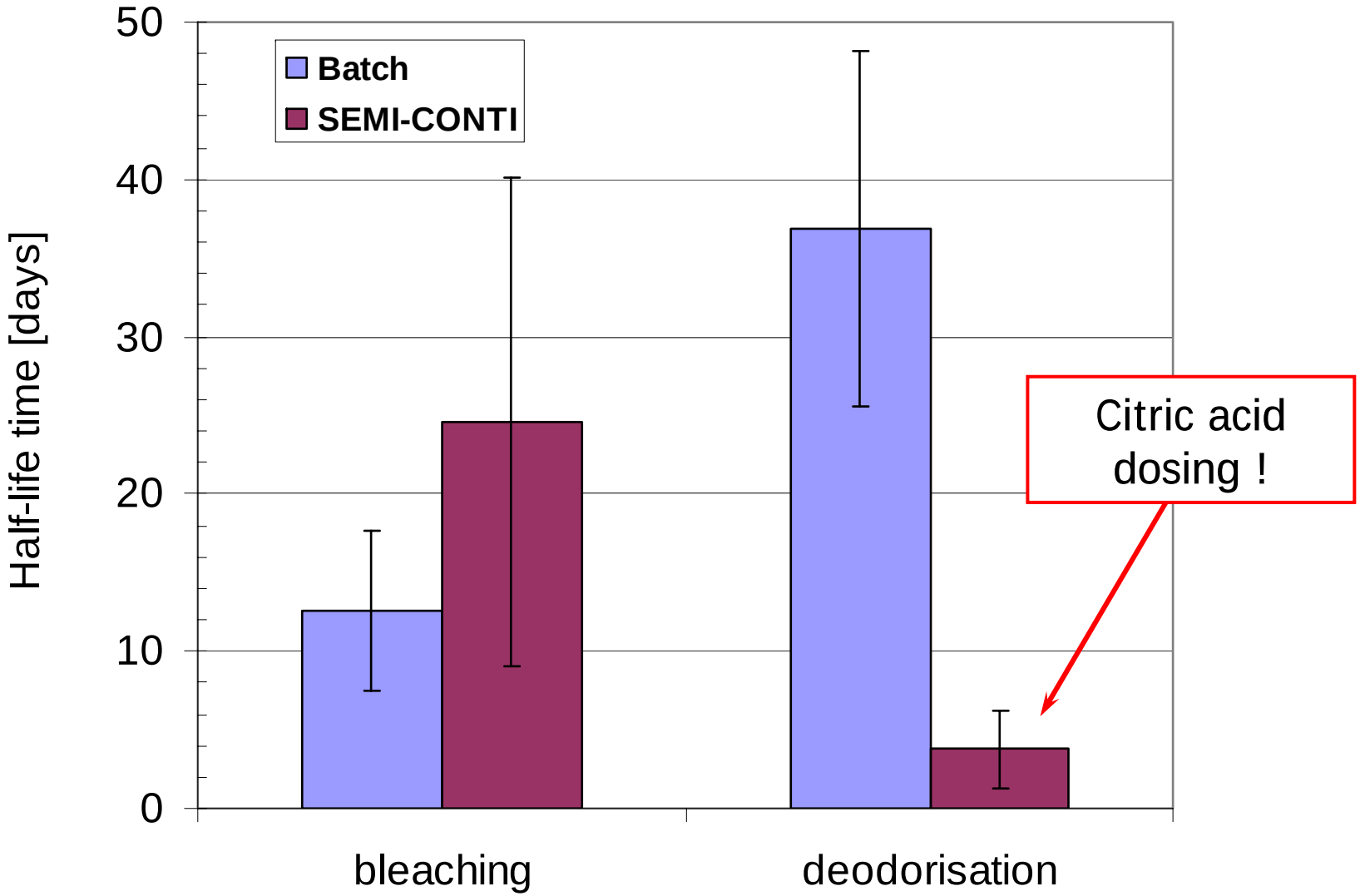




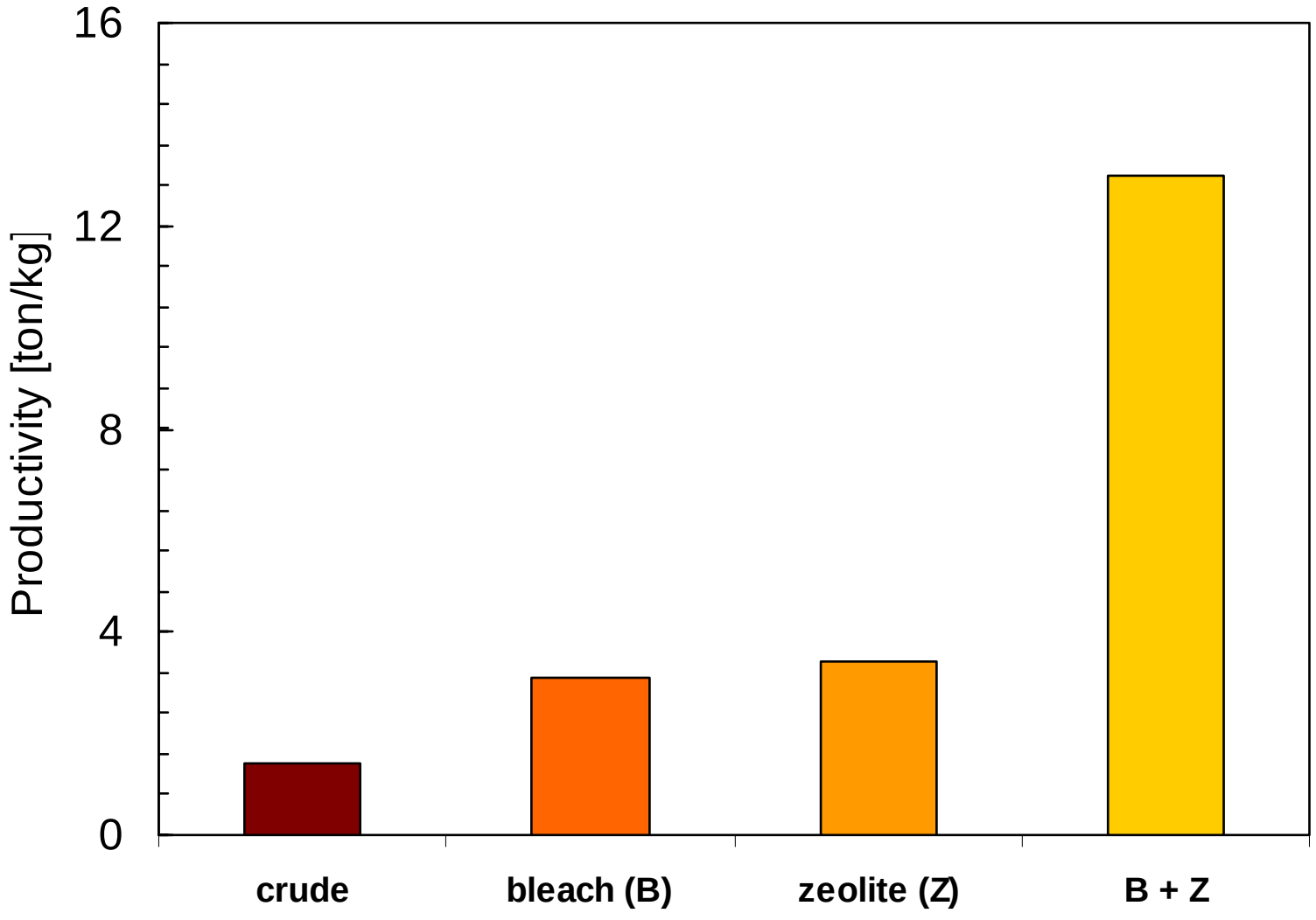
V1/2= the amount of oil processing when reaching half the initial activity

novozymes®

Pretreatment – processing



Pretreatment – silica /zeolites



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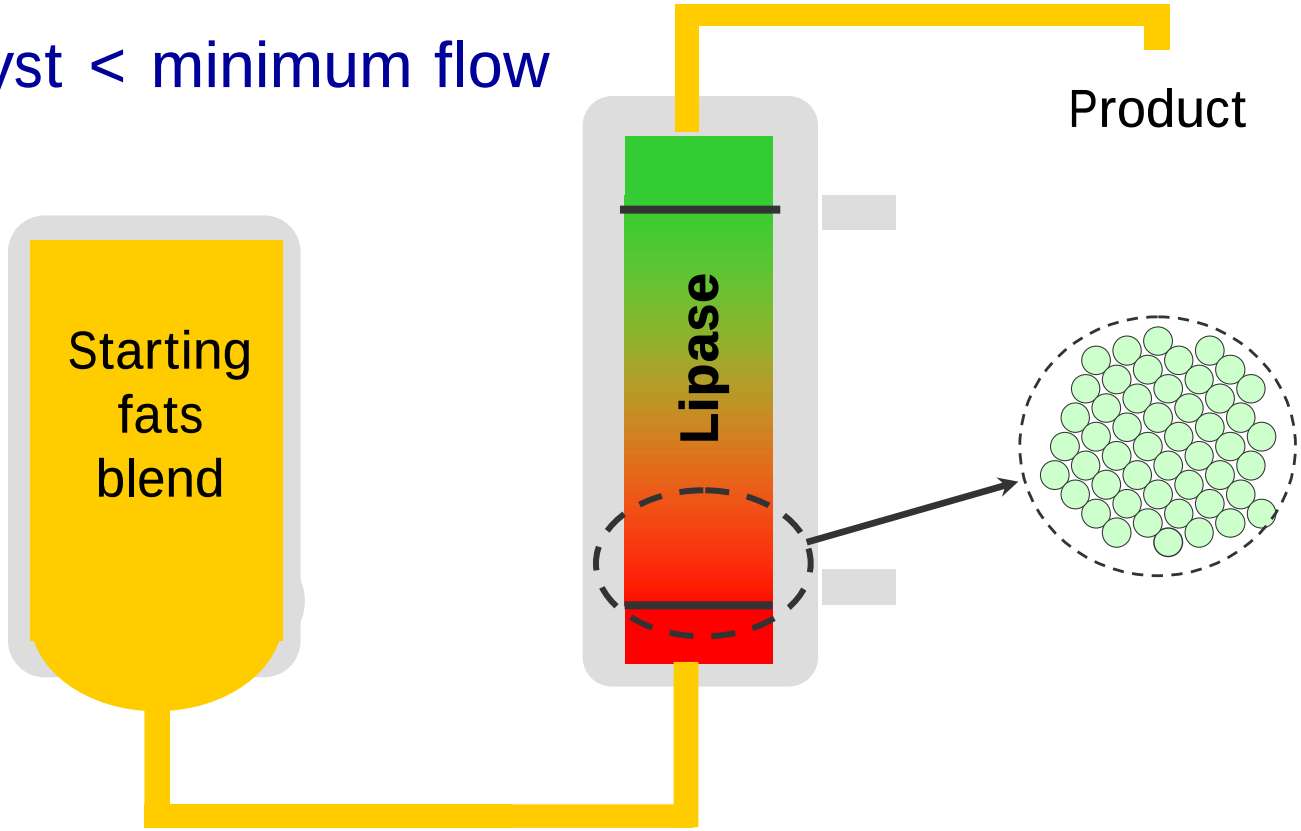
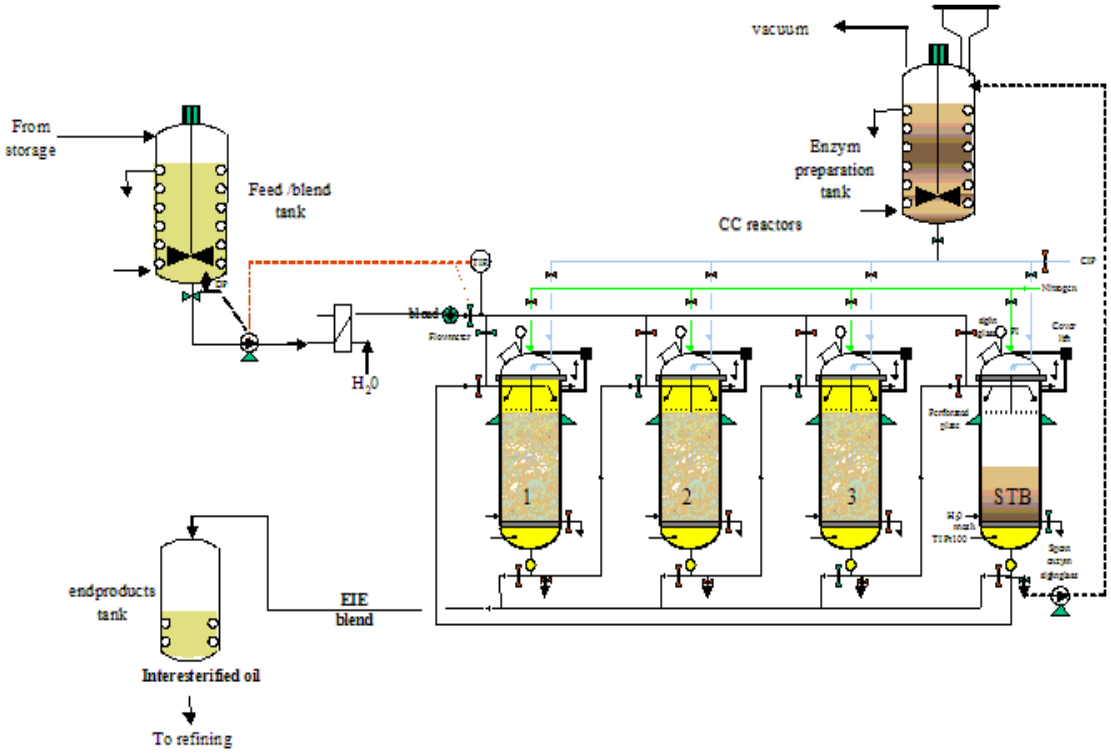
Single Packed Bed Reactor (PBR)

- How to deal with deactivation ?
  - Constant degree of conversion
  - Decreasing flow
  - Change catalyst < minimum flow



Series of PBRs

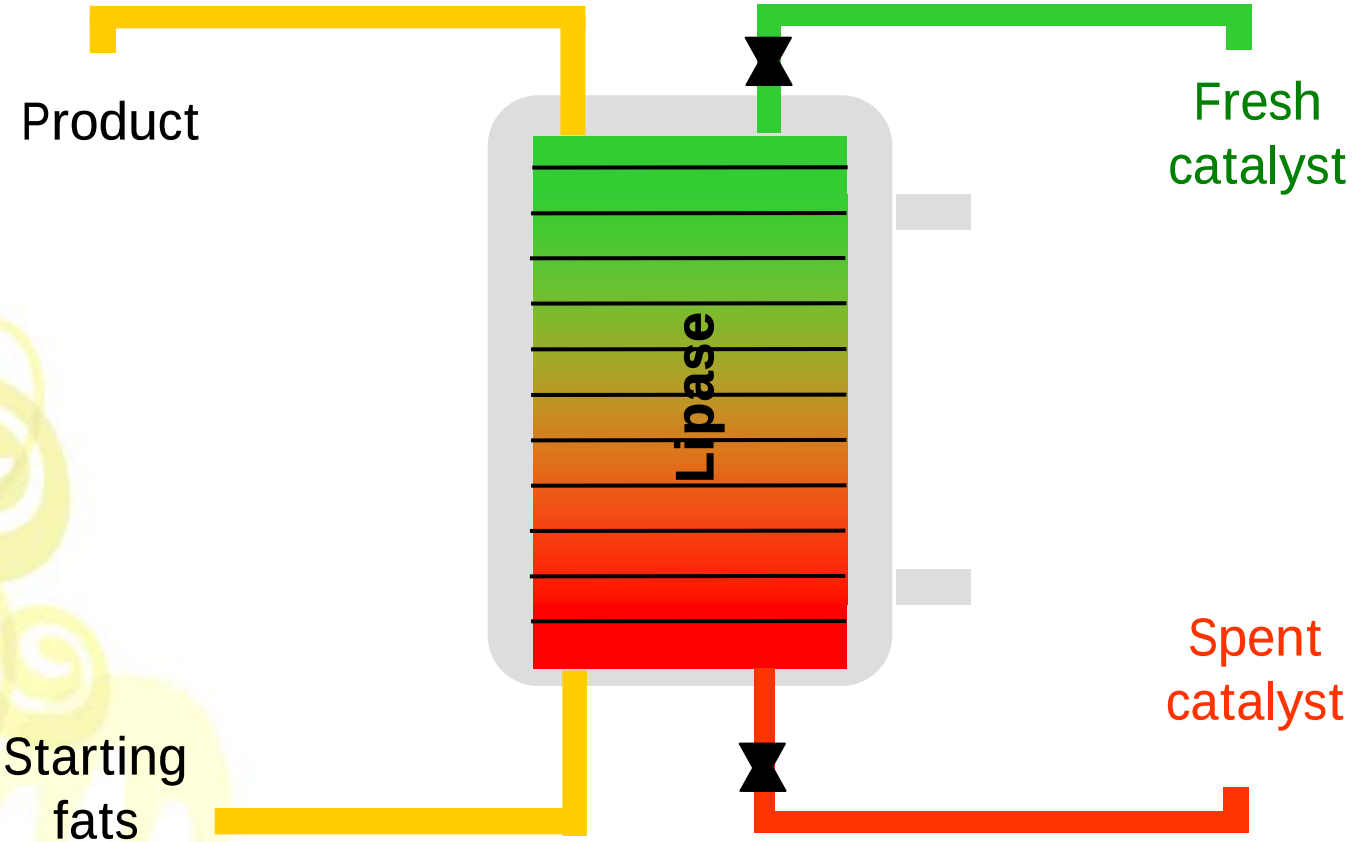
- Catalyst refreshment in the stand-by reactor



oils & fats
desmet ballestra

Semi-continuous PBR

- Semi-continuous catalyst refreshment
- Minimum catalyst exposure



Cargill patent - EP 1840 204 B1

Summary

- Enzymatic rearrangement has developed into a commercially viable alternative to chemical interesterification.

- The process kinetics can adequately be described using simple first-order modelling.

- Lipase deactivation:
  - seems mainly due to poisoning (oil quality & acids);
  - requires adequate pre-refining;
  - can be described by simple kinetics (enzyme specific).

- Several reactor systems have been developed to deal with catalyst deactivation.

Thank You !