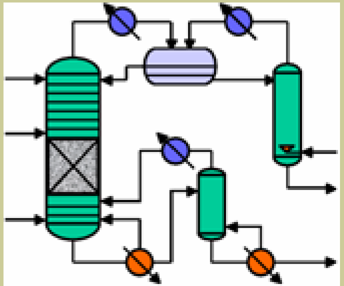
NWO/CW Project Nr. 700.54.653



Continuous Biodiesel Production

Reactive Distillation Makes It Happen

Tony KISS, A.C. Dimian, G. Rothenberg, F. Omota

UNIVERSITY OF AMSTERDAM
van ‘t Hoff Institute for Molecular Sciences
Nieuwe Achtergracht 166, 1018 WV Amsterdam
Tel.+31-20-525.6468, E-mail: *A.A.Kiss@uva.nl*
Web: *staff.science.uva.nl/~ktony*

NWO stw cognis OLEON uniqema SULZER Universiteit Twente de ondernemende universiteit

Acknowledgement

- **Jurriaan Beckers**

- Marjo C. Mittelmeijer-Hazeleger

- **STW – Dutch Technology Foundation**

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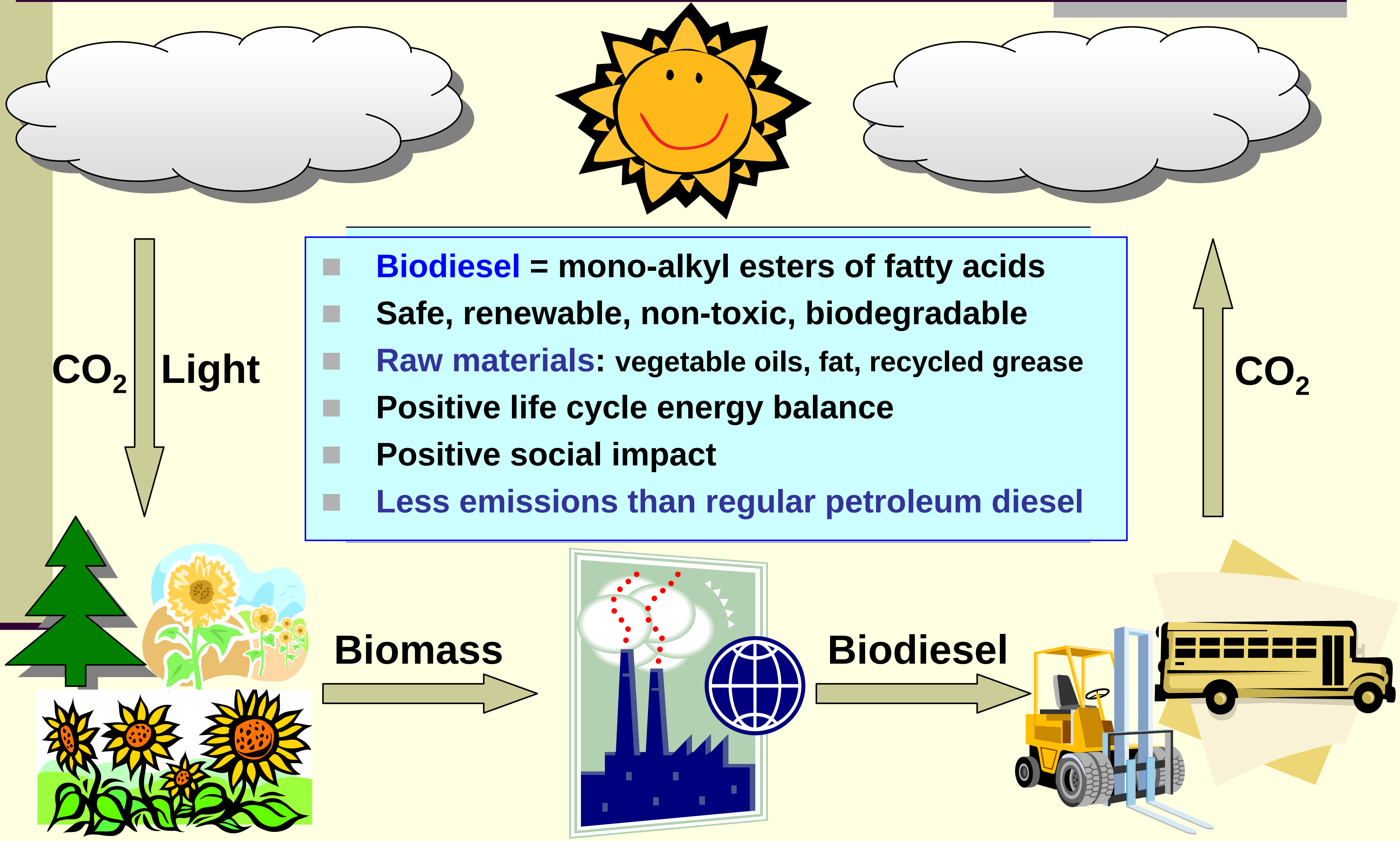
  Entrainer-Based Reactive Distillation

  for Synthesis of Fatty Acids Esters

- Cognis, Oleon, Sulzer and Uniqema

A.A.Kiss@*uva.nl*

Biodiesel = green energy



- **Biodiesel** = mono-alkyl esters of fatty acids
- **Safe, renewable, non-toxic, biodegradable**
- **Raw materials: vegetable oils, fat, recycled grease**
- **Positive life cycle energy balance**
- **Positive social impact**
- **Less emissions than regular petroleum diesel**

A.A.Kiss*@uva.nl*

Project goals

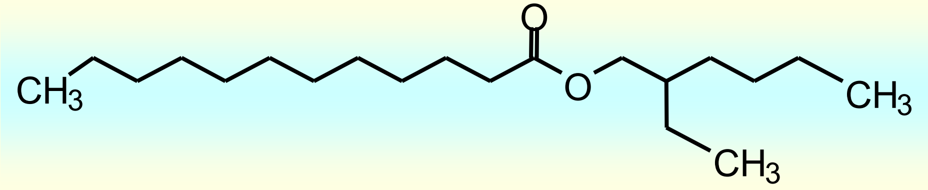
- Development of an active and selective solid acid catalyst for fatty acids esterification.
- Continuous biodiesel production process based on catalytic reactive distillation.

Catalyst requirements

- Water-tolerant
- Long life
- Inexpensive
- Active, selective, stable
- Easy to use
- Available on industrial scale

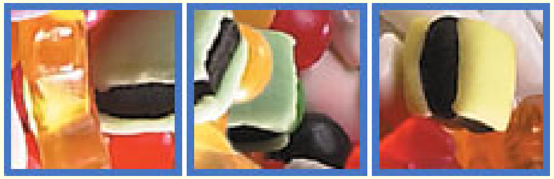
A.A.Kiss@*uva.nl*

Applications

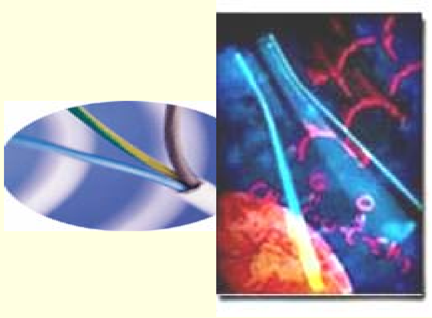


Cosmetics

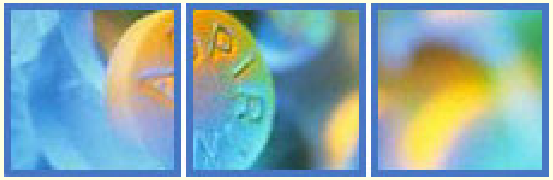
Food



- **Why fatty esters?**
  - **Food industry**
  - **Pharmaceuticals**
  - **Cosmetics**
  - **Plasticizers**
  - **Bio-detergents**
  - **Bio-diesel**



Pharmaceuticals



BioDiesel Limited

PACIFIC Biodiesel

Bio-stuff

BIO PAC
Cleaning Products
NOT TESTED ON ANIMALS

A.A.Kiss*@uva.nl*

Industrial key players

AKZO NOBEL

Henkel

PETER GREVEN

Partner der Industrie

penreco.

cognis.

BASF

The Chemical Company

uniqema

Crompton

NORFOX®

Lonza

FACI

OLEON

NOVANCE

Stepan Company

STEARINERIE-DUBOIS

PACIFIC Biodiesel

RIX

BioDiesel Limited

UNDESA

SUMITOMO CHEMICAL

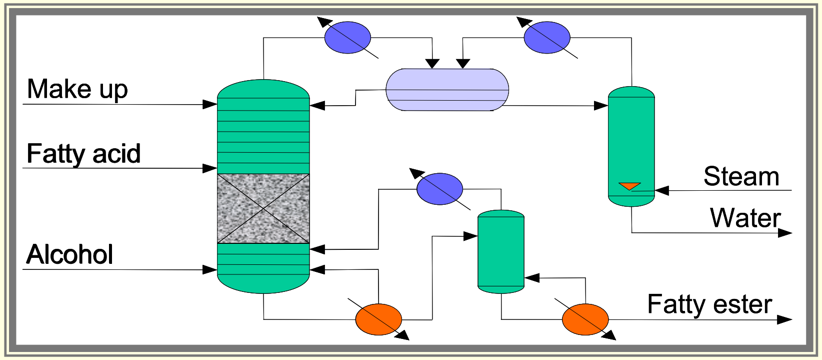
A.A.Kiss@*uva.nl*

Process comparison

- **Current process**
  - Batch esterification
  - High alcohol / acid ratios
  - Homogeneous catalysis
  - Difficult separation
  - Corrosive & toxic

- **Novel process**
  - Continuous esterification
  - Reactive distillation
  - Heterogeneous catalysis
  - Easy separation
  - Environmentally friendly

- Reduced investment costs
- Reduced energy consumption
- Increased process controllability
- Enhanced overall rates



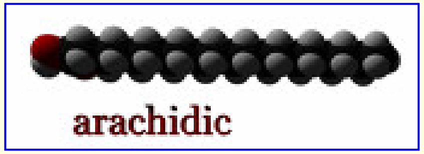
The key to success is an active & selective solid acid catalyst.

A.A.Kiss@*uva.nl*

Fatty acids & alcohols

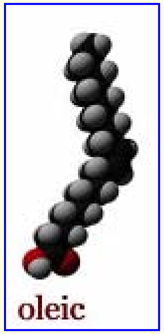
- **Saturated fatty acids**: $CH_3\text{-}(CH_2)_n\text{-}COOH$

Lauric acid	(n=10)
Myristic acid	(n=12)
Palmitic acid	(n=14)
Stearic acid	(n=16)
Arachidic acid	(n=18)



- **Aliphatic alcohols:**
  - Methanol
  - Ethanol
  - Propanol
  - …
  - 2-Ethyl hexanol

- **Unsaturated fatty acids**
  - Palmitoleic acid: $CH_3(CH_2)_5CH=CH(CH_2)_7COOH$
  - Oleic acid: $CH_3(CH_2)_7CH=CH(CH_2)_7COOH$



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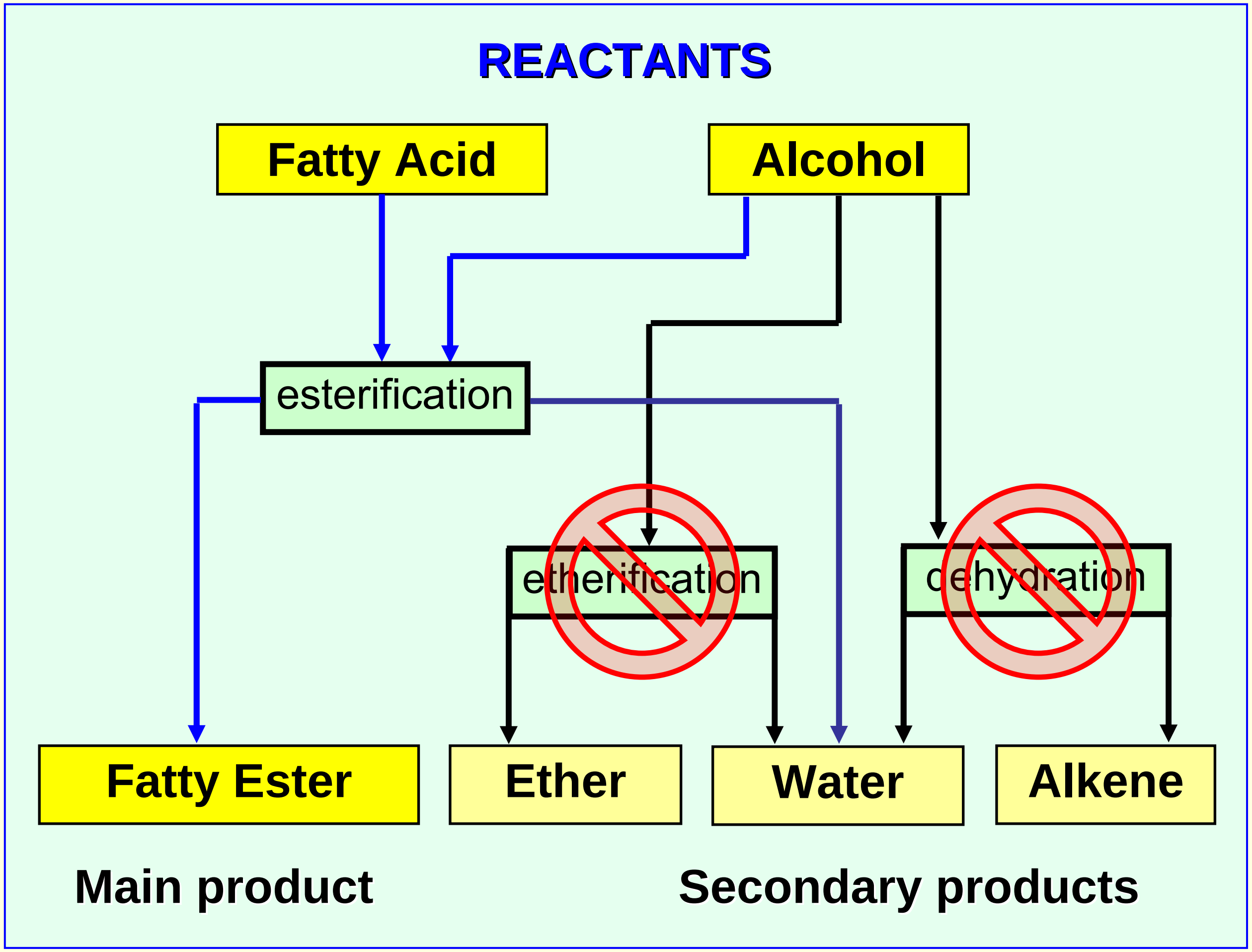
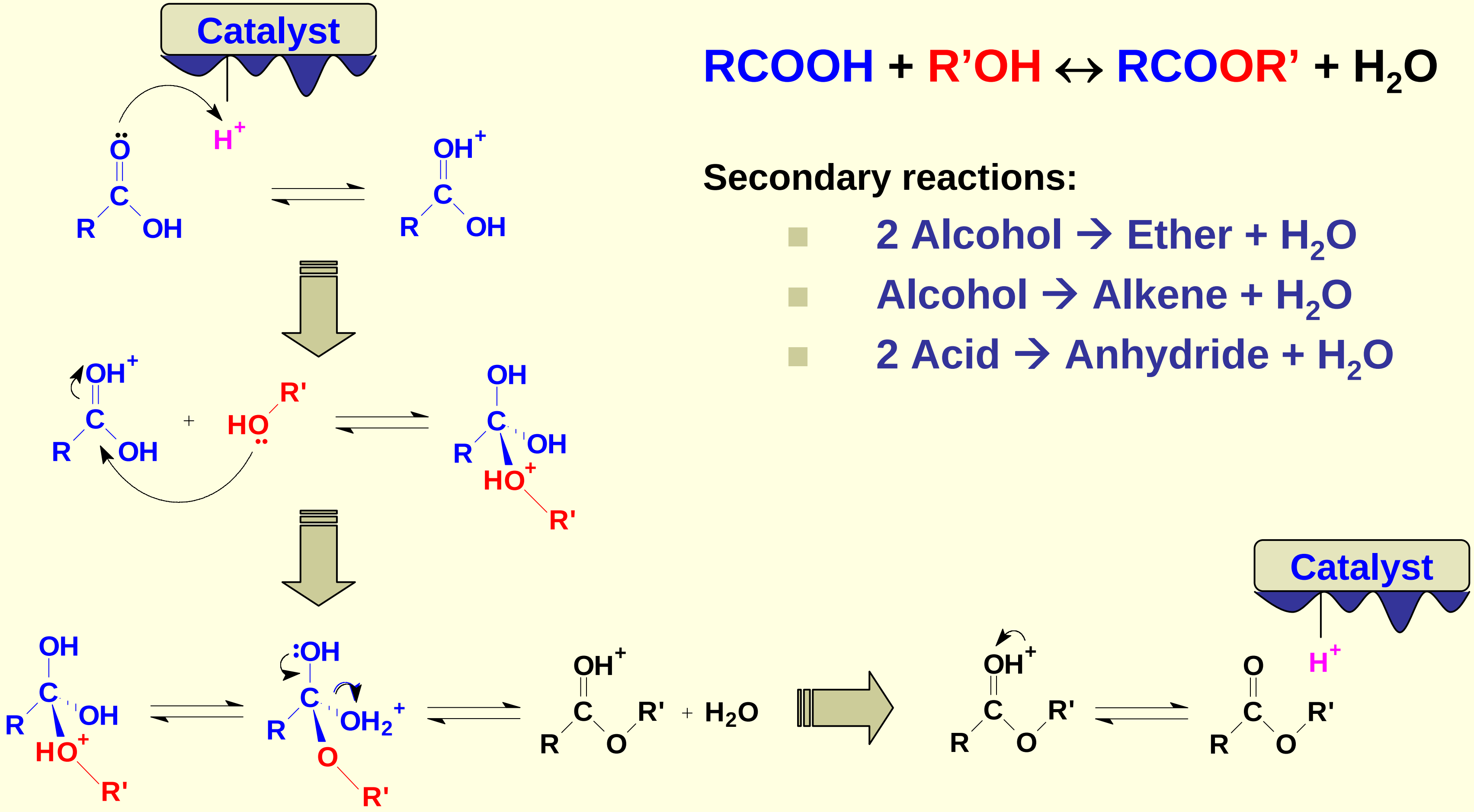
Reaction pathways



☑ **Excess of alcohol** ☑ **Water removal by distillation**

Reaction mechanism



$RCOOH + R'OH \leftrightarrow RCOOR' + H_2O$

Secondary reactions:

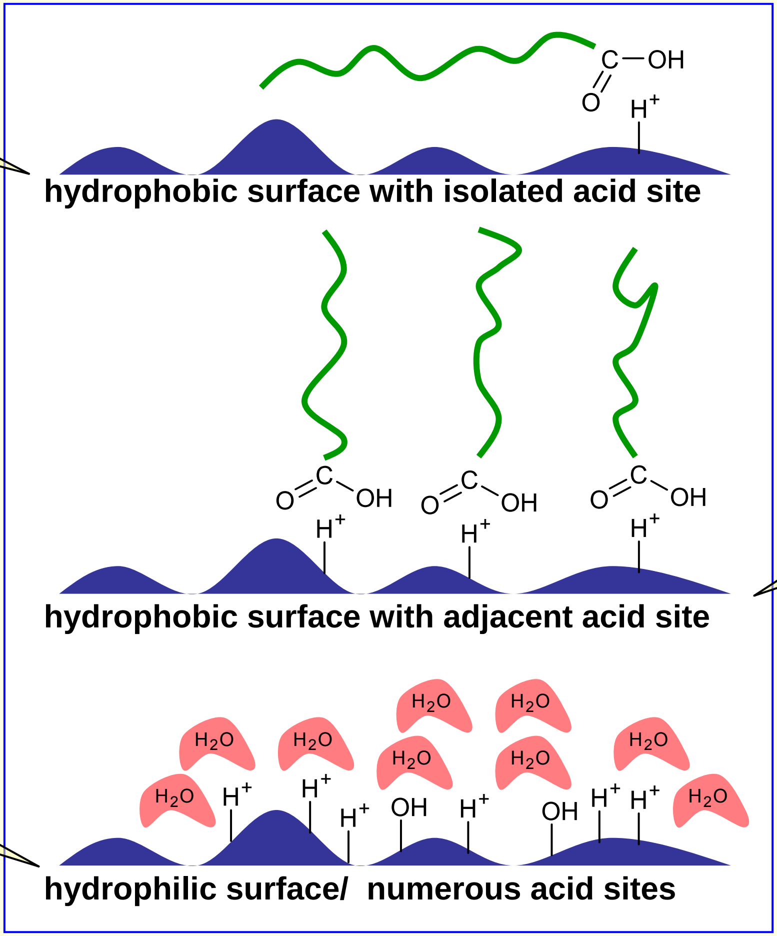
- 2 Alcohol → Ether + H_2O
- Alcohol → Alkene + H_2O
- 2 Acid → Anhydride + H_2O

Similar mechanism for hetero- and homogeneous catalysis.

A.A.Kiss@*uva.nl*

Surface hydrophobicity

Water tolerant.
Not enough acid sites.



hydrophobic surface with isolated acid site

hydrophobic surface with adjacent acid site

hydrophilic surface/ numerous acid sites

Proper trade-off
hydrophobicity-acidity.
Good catalytic activity.

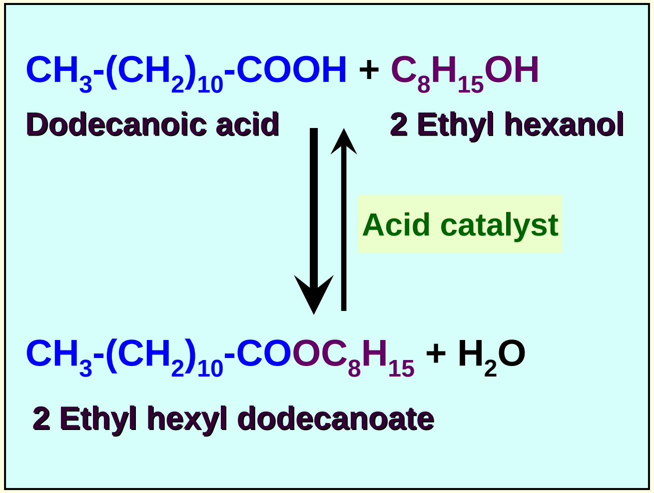
Water sensitive.
Easy deactivation.

Influence of surface hydrophobicity on catalytic activity.

A.A.Kiss*@uva.nl*

Solid acid catalysts

- Zeolites and clays
  - Beta, Y, MOR, ZSM-5
- HeteropolyAcids☒
- Oxides, sulphates
- Composite materials
  - Amberlyst
  - Nafion
- Carbon-based catalysts☒
  - Polysulfonated aromatics



$$CH_3\text{-}(CH_2)_{10}\text{-}COOH + C_8H_{15}OH$$

Dodecanoic acid **2 Ethyl hexanol**

$$\rightleftharpoons$$

Acid catalyst

$$CH_3\text{-}(CH_2)_{10}\text{-}COOC_8H_{15} + H_2O$$

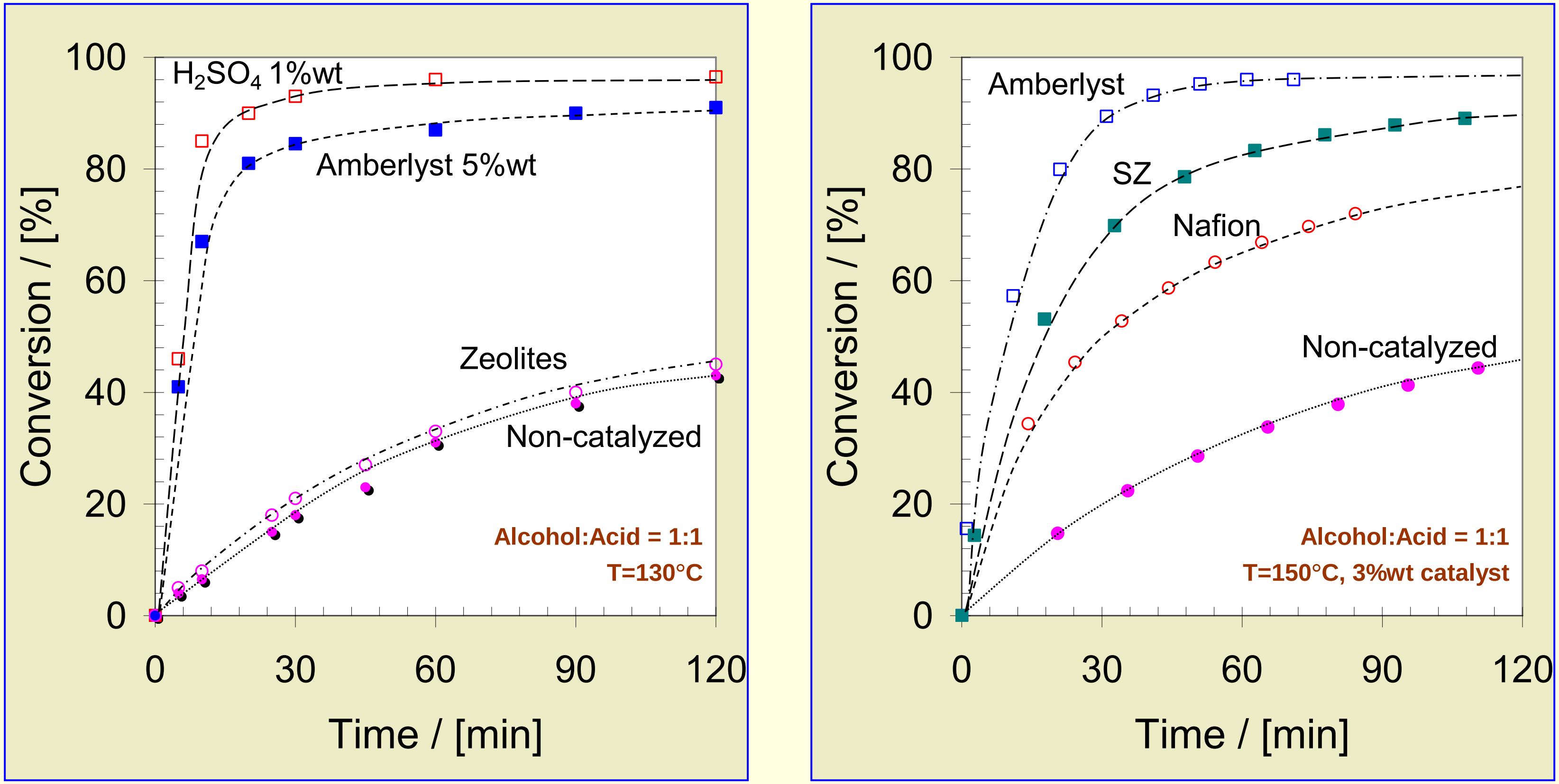
2 Ethyl hexyl dodecanoate

☒ = Not tested yet …

A.A.Kiss*@uva.nl*

Catalyst screening

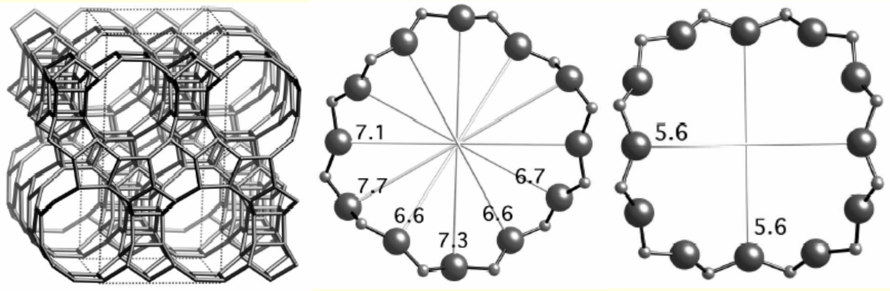
Reaction profiles for esterification of dodecanoic acid with 2-ethylhexanol



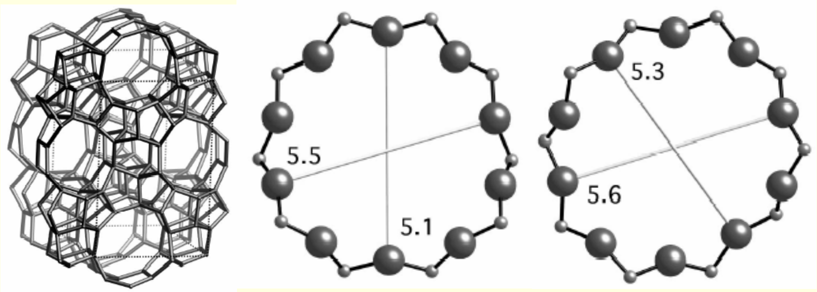
Organic resins are not thermo-stable. Zeolites have low activity.

A.A.Kiss*@uva.nl*

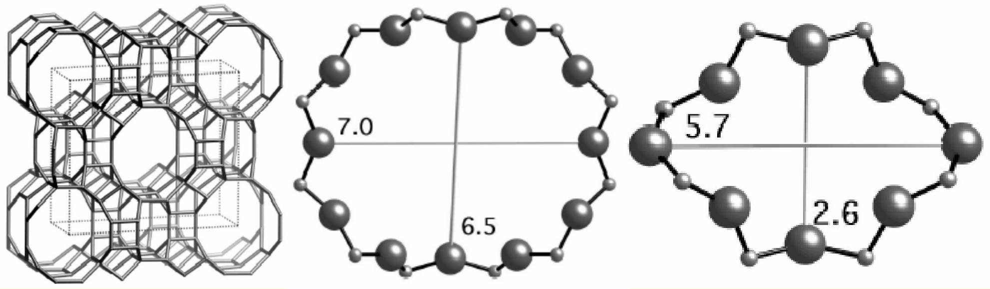
Zeolites – structure



***BEA** – Beta, tetragonal



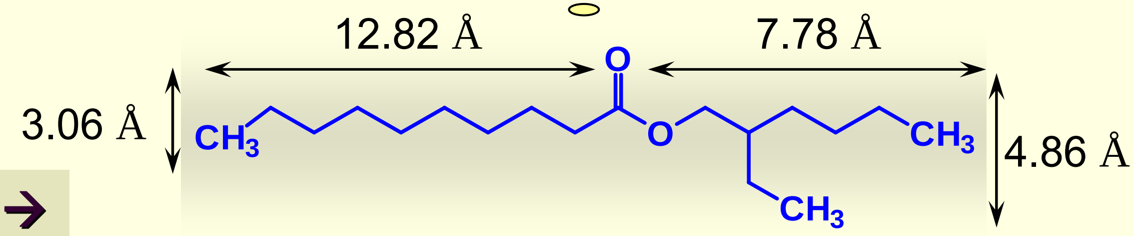
MFI – ZSM-5, orthorhombic



MOR – Mordenite, orthorhombic

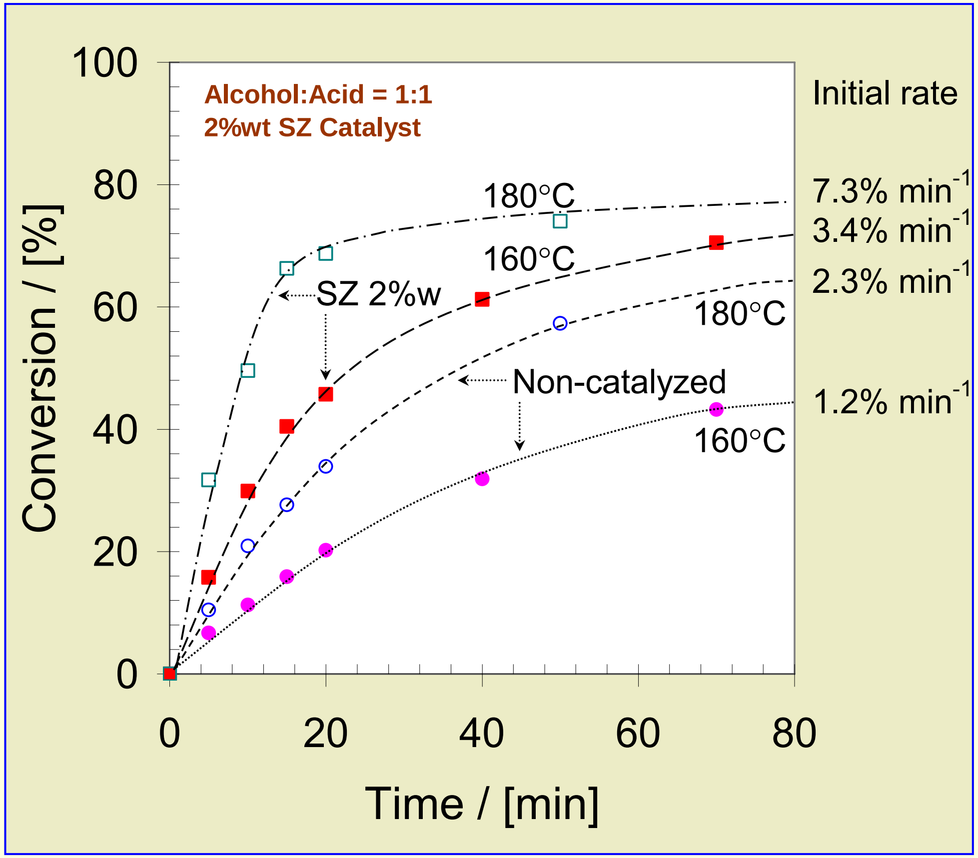
Diffusion limitations ?!

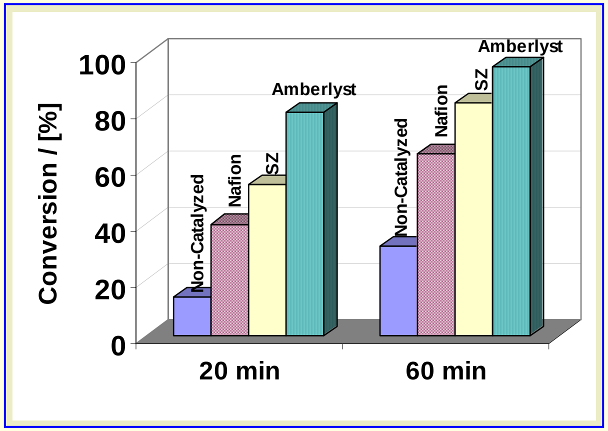
2-ethylhexyl dodecanoate →

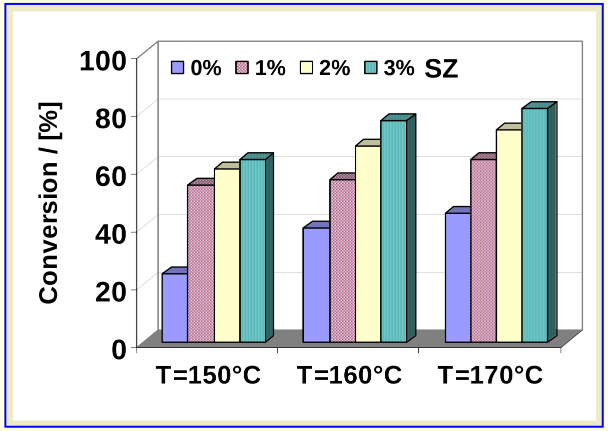


Sulphated zirconia

Reaction profiles for esterification of dodecanoic acid with 2-ethylhexanol





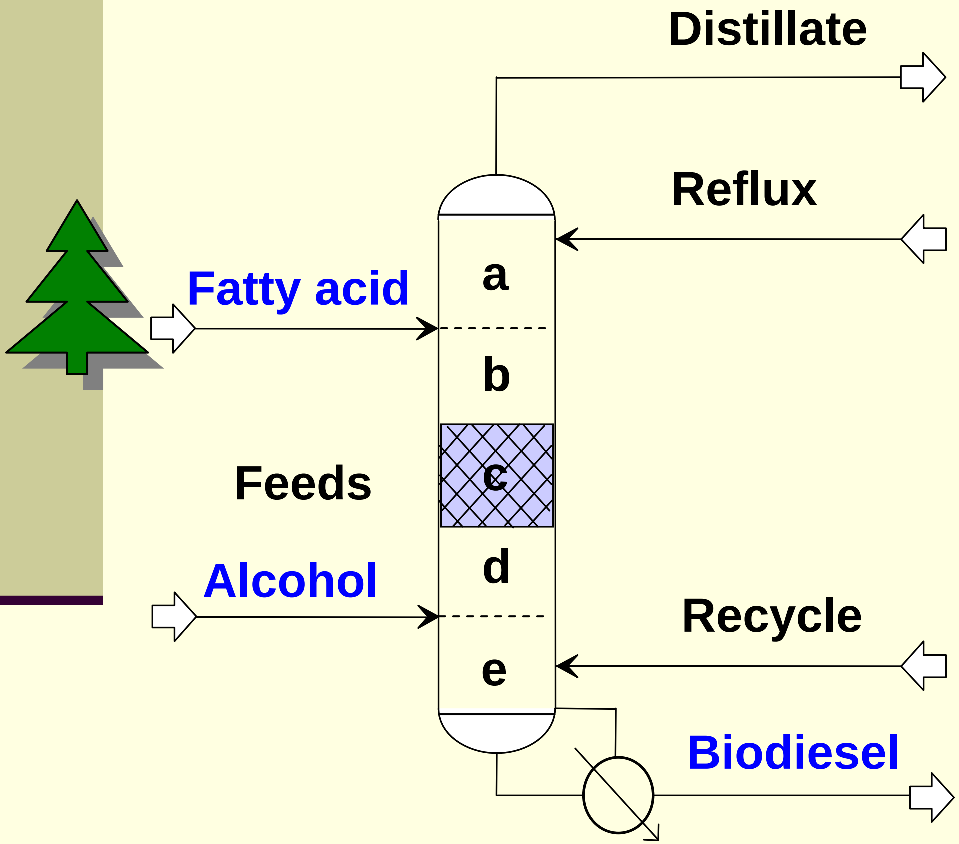


Similar activity for esterification with 1-propanol and methanol.

A.A.Kiss*@uva.nl*

Experiments + Simulations

- **Integration of experimental results with simulations of the reactive distillation (RD) setup, in AspenTech AspenPlus™**



RD column sections

a. **Rectifying section (water)**
b. **Recovery of alcohol**
c. **Reaction zone**
d. **Recovery of fatty acid**
e. **Stripping section (ester)**

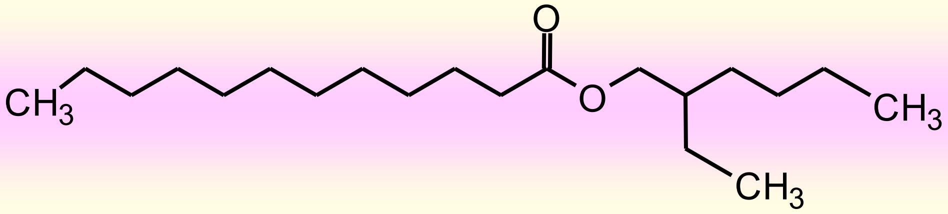
A.A.Kiss*@uva.nl*

Thermodynamic analysis

Water
T_b=100 ºC

Dodecanoic acid T_b=298 ºC

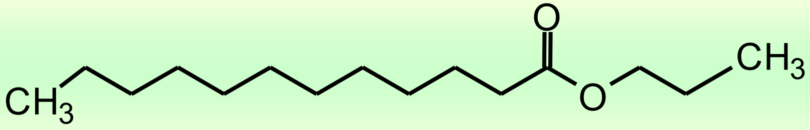
2-Ethylhexyl dodecanoate T_b=334 ºC



2-Ethylhexanol
T_b=186 ºC

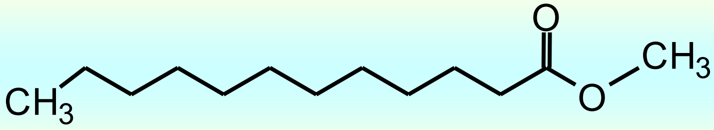
n-Propyl dodecanoate T_b=302 ºC

n-Propanol
T_b=97 ºC



Methyl dodecanoate T_b=267 ºC

Methanol
T_b=65 ºC



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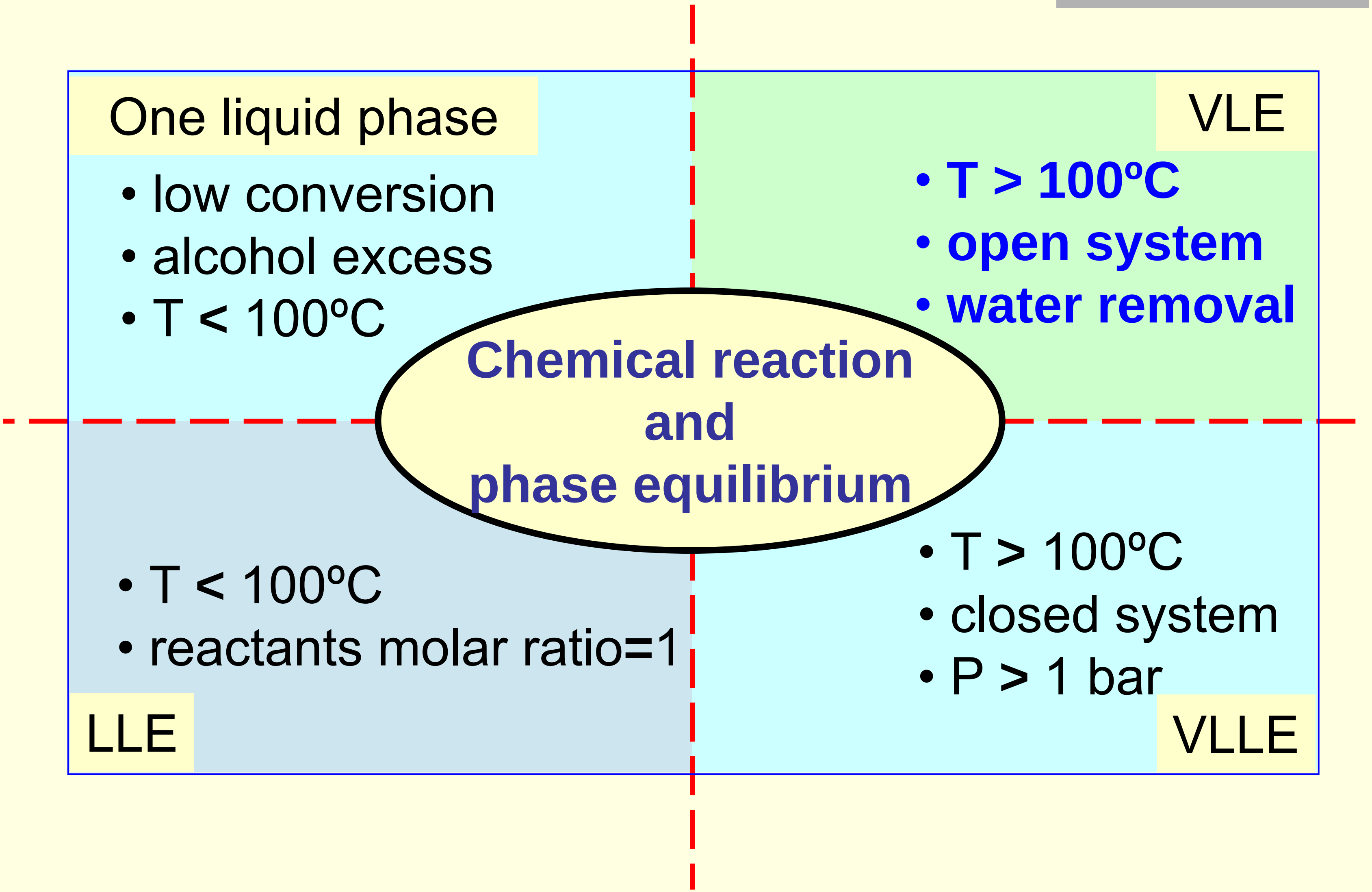
CPE analysis



One liquid phase

- low conversion
- alcohol excess
- T < 100ºC

VLE

- **T > 100ºC**
- **open system**
- **water removal**

Chemical reaction
and
phase equilibrium

- T < 100ºC
- reactants molar ratio=1

LLE

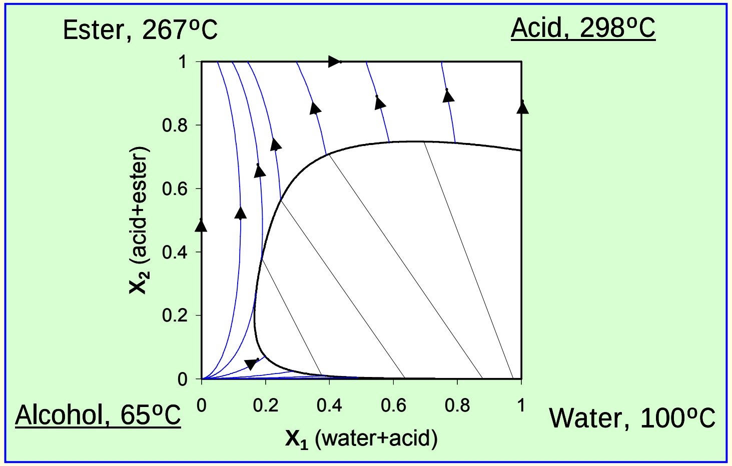
- T > 100ºC
- closed system
- P > 1 bar

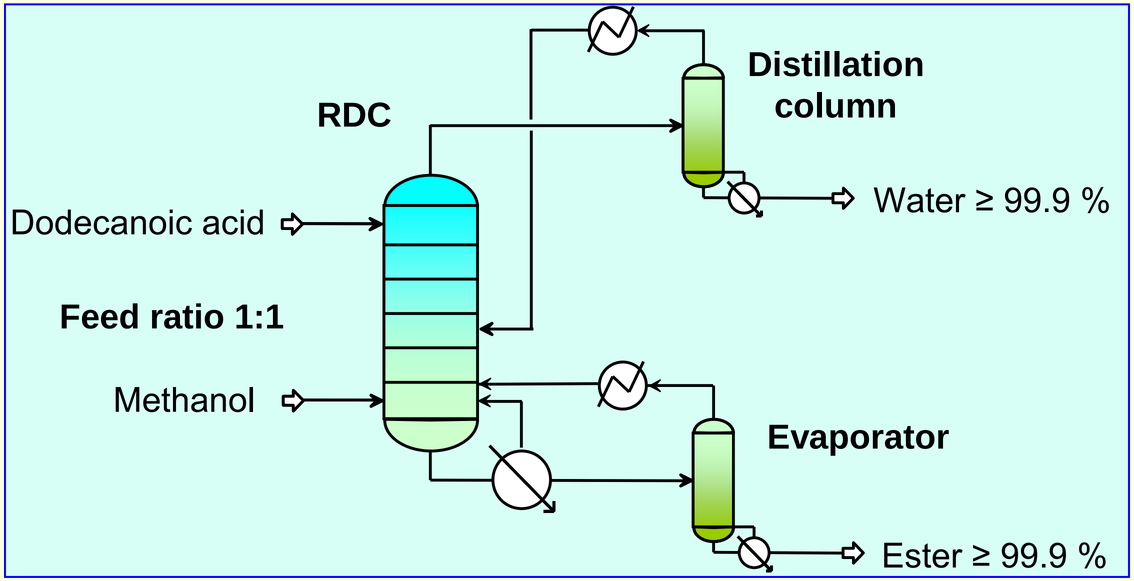
VLLE

A.A.Kiss*@uva.nl*

RD process – methanol

Feasible RD process.
High purity products.





RDC

Distillation column

Dodecanoic acid

Water ≥ 99.9 %

Feed ratio 1:1

Methanol

Evaporator

Ester ≥ 99.9 %

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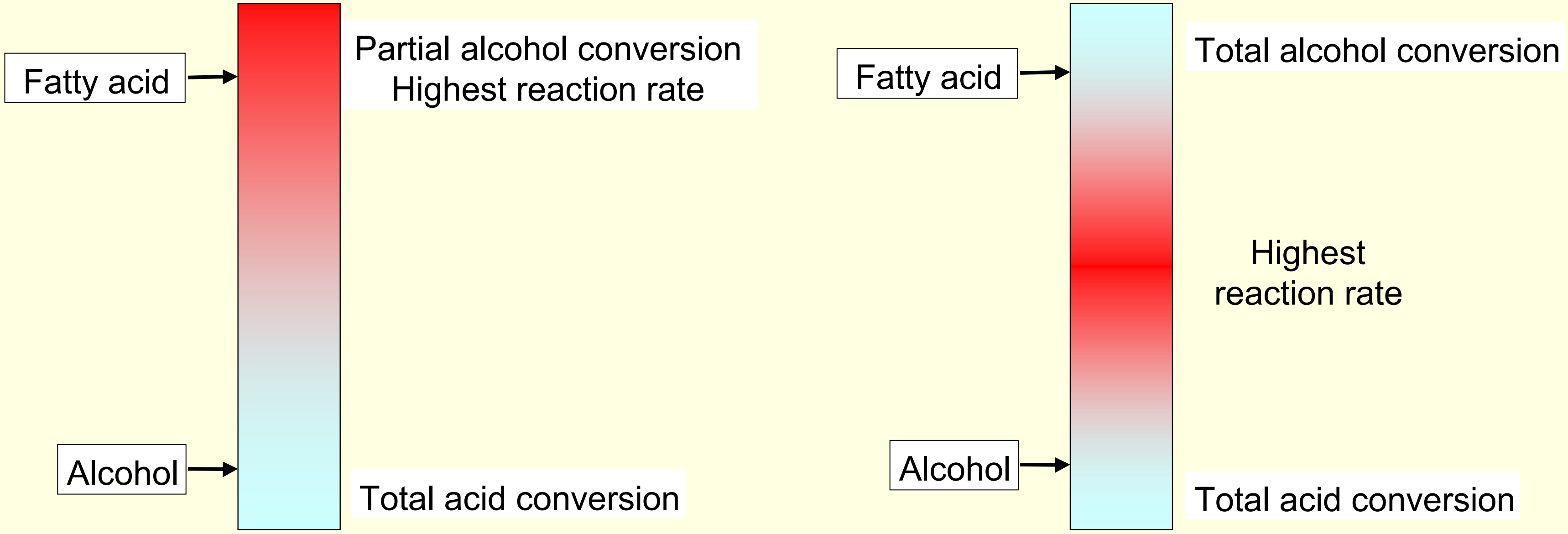
Effect of reflux ratio



Maximum reaction rate is located in the centre of RD column for an optimum reflux ratio

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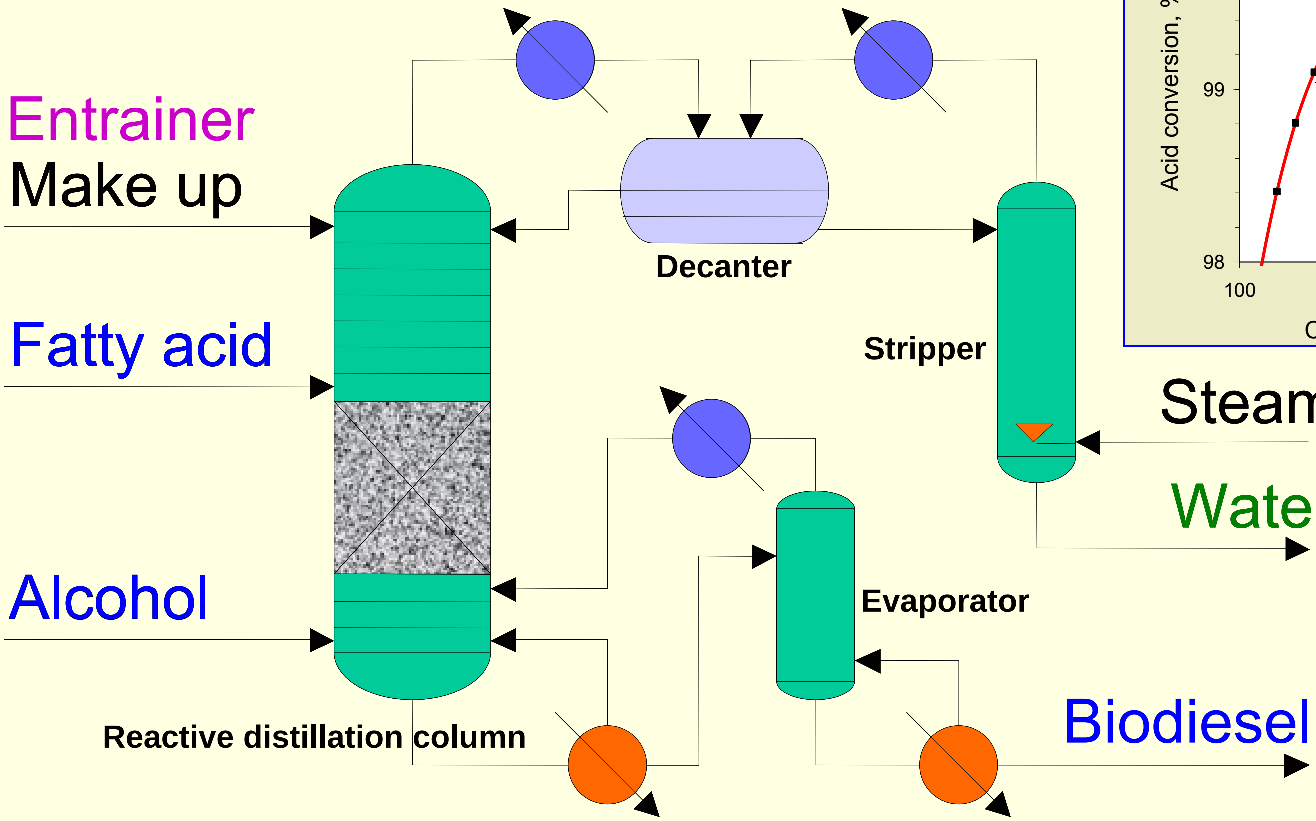
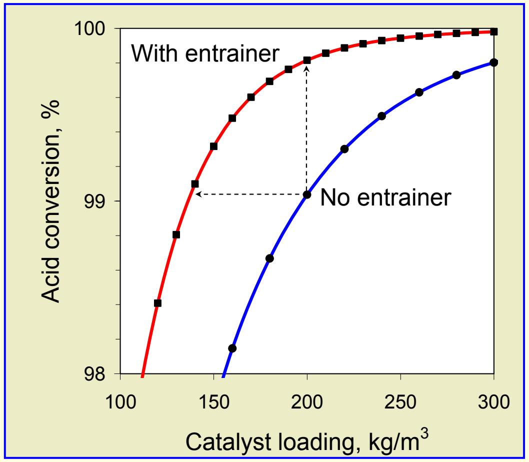
Entrainer-based RD flowsheet

Feasible process. High purity products >99.9%



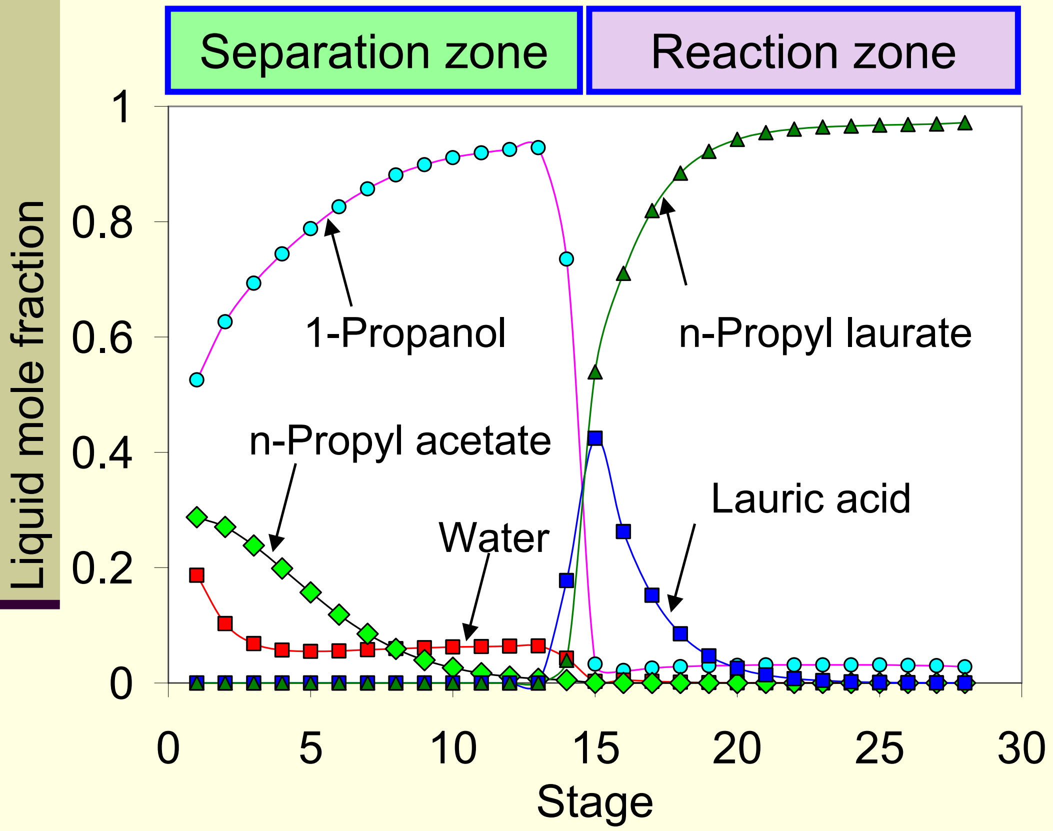


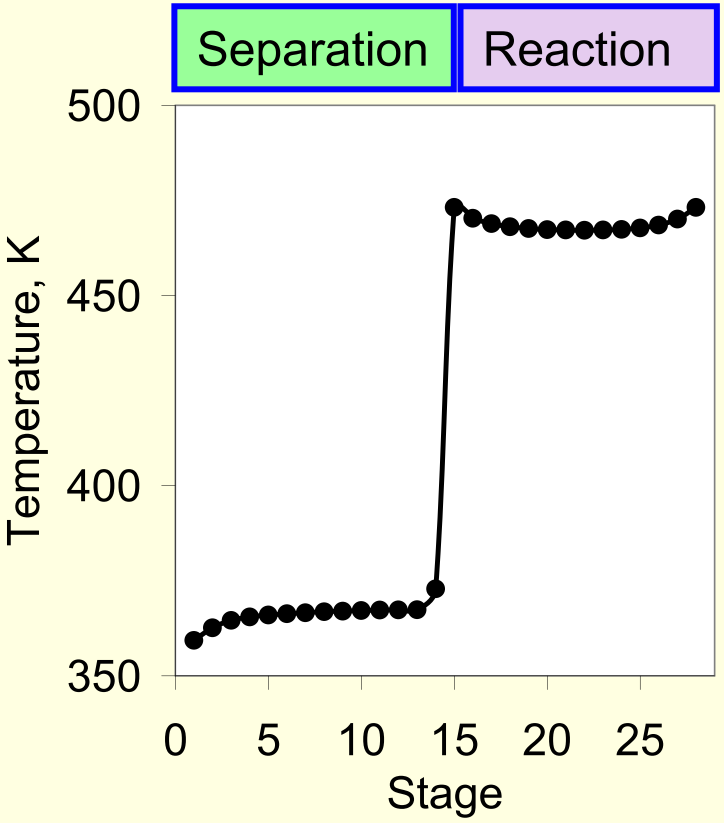
Enhanced mass transfer and reduced catalyst loading when entrainer is used.

A.A.Kiss*@uva.nl*

RDC profiles

Liquid composition and temperature profiles





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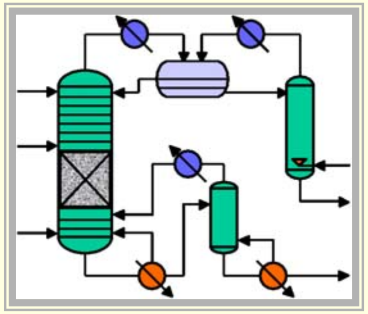
Reactive distillation – advantages

- No external recycles
- Reduced investment costs
- Reduced energy consumption
- Increased process controllability



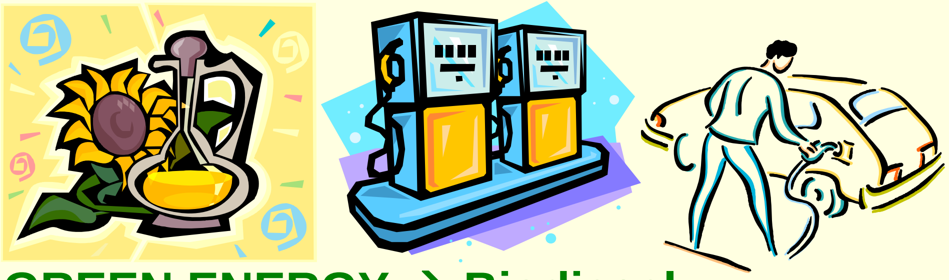
Reaction ⇄ Separation

- Equilibrium shifted to products
- Enhanced overall rates
- Improved selectivity
- Break azeotropes
- Handle difficult separations

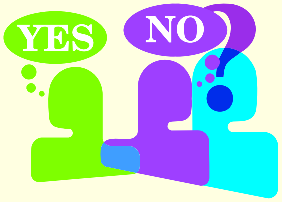
A.A.Kiss*@uva.nl*

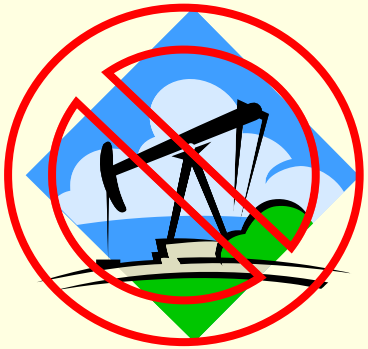
Conclusions

- **Surface hydrophobicity and acid sites density determines catalyst's activity & selectivity.**
- **Catalysts with small pores (*e.g.* zeolites) are not suitable. Resins are active but not thermally-stable.**
- **Sulphated zirconia is active, selective and stable.**
- **Biodiesel production by reactive distillation is feasible.**



GREEN ENERGY → Biodiesel





A.A.Kiss*@uva.nl*