Integrated synthesis and separation of oil derivatives by supercritical carbon dioxide

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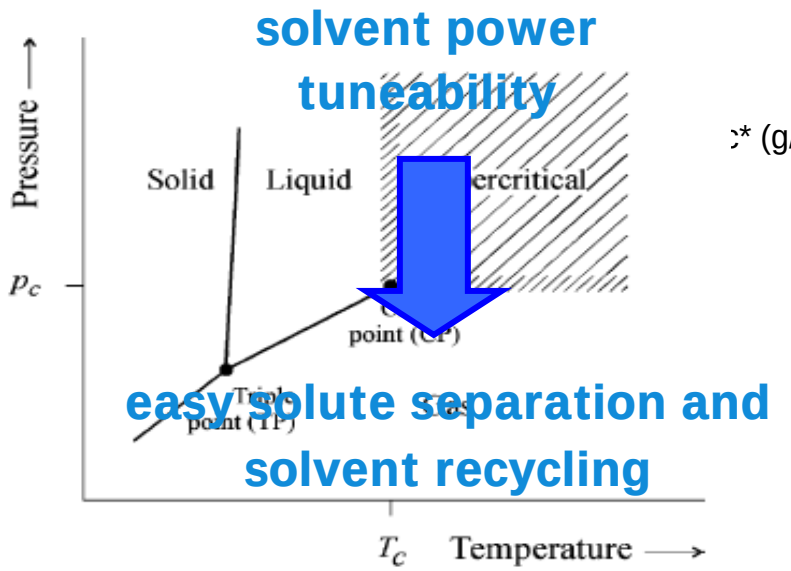
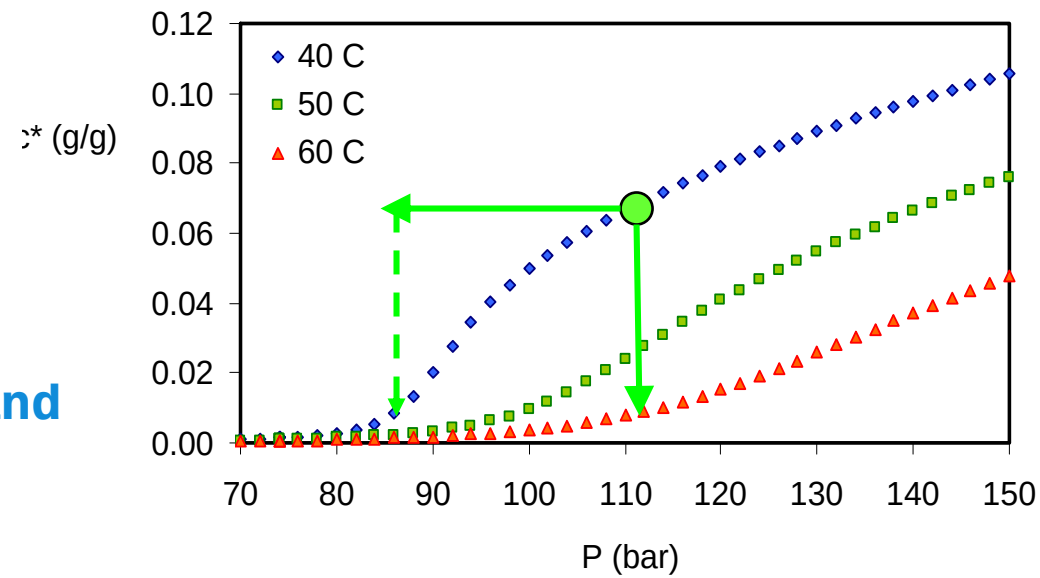
Supercritical fluids for lipid processing

- Extraction/fractionation of specialty oils
- Vegetable oil refining (deodorization, neutralization)
- Recovery/concentration of high-value bioactive lipids from refined oils and agricultural waste
- Transesterification of oils in supercritical alcohols

Supercritical fluids

- Strong dependence of fluid properties on P and T
- Liquid-like density, gas-like viscosity (high diffusion coefficients)
- Fluid density determines solvent power

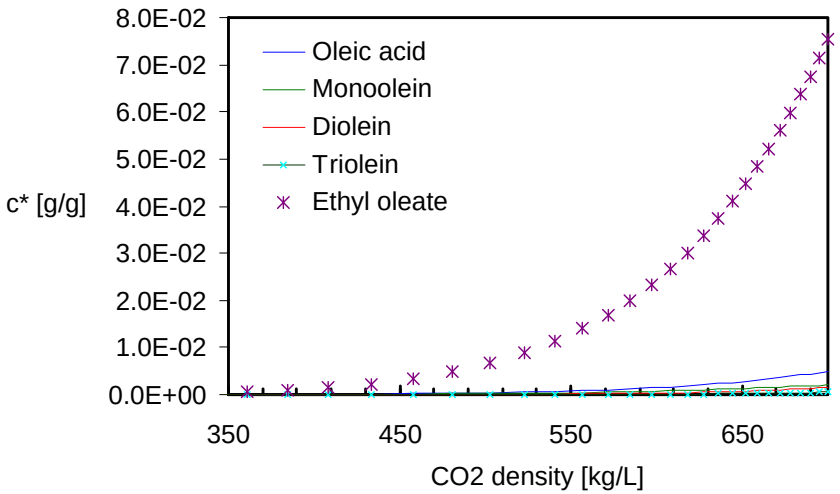




Supercritical carbon dioxide

- Non-toxic, “green” solvent → suitable for food processing
- Mild (super)critical conditions (74 bar, 31 C)

- Non-polar solvent
  - dissolves non-polar and slightly polar compounds
  - solvent power decreases with solute molecular weight



Guclu-Ustundag O. *et al*, Ind Eng Chem Res 39 (2000) 4756-4766

SC-CO_2 as process solvent

An integrated approach

Extraction

- Solvent power tuneability of SC-CO_2
- Well established technology

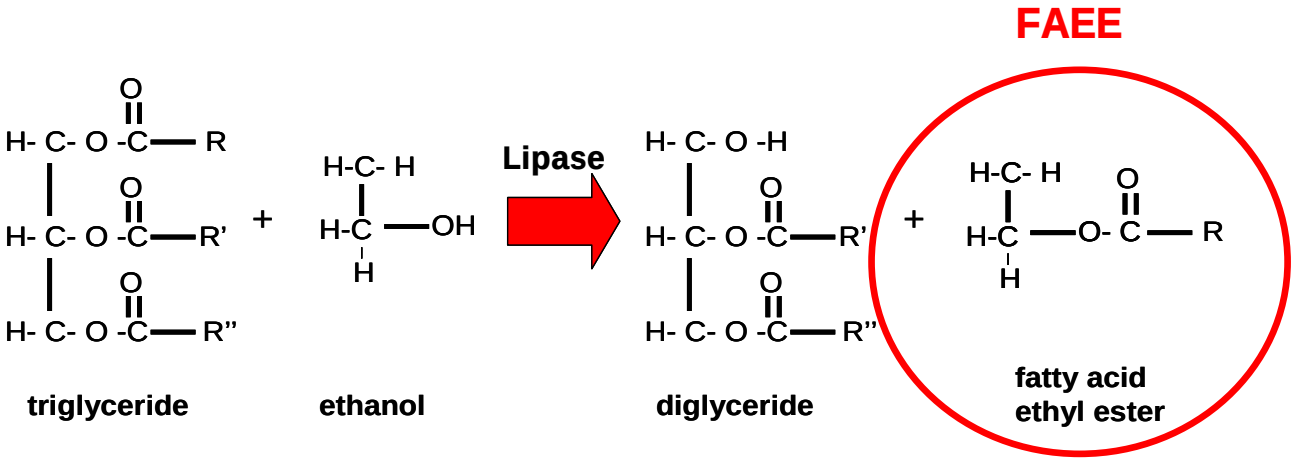
Integrated reaction-extraction

Reaction solvent or co-solvent

- Enhanced rates / reaction selectivity
- Extensive research
  - Possibility of integrating reaction with products separation

Oil ethanolysis

Simultaneous synthesis of partial glycerides and FAEE

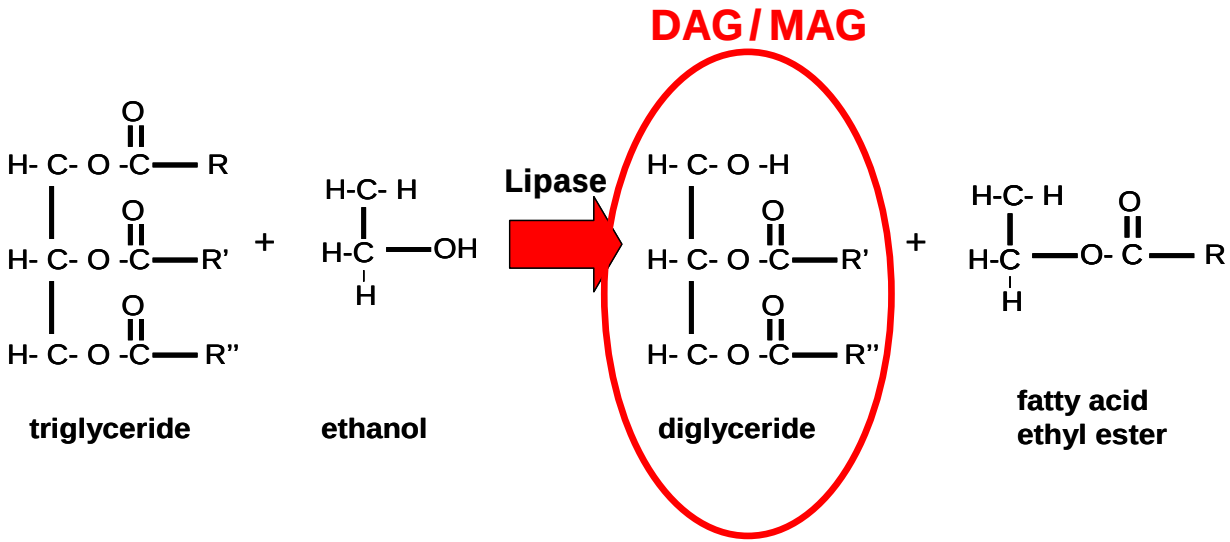


FAEE

- Functionality depends on chain length
- Additives in food / pharma / cosmetics
- Intermediates in the production of structured lipids

Oil ethanolysis

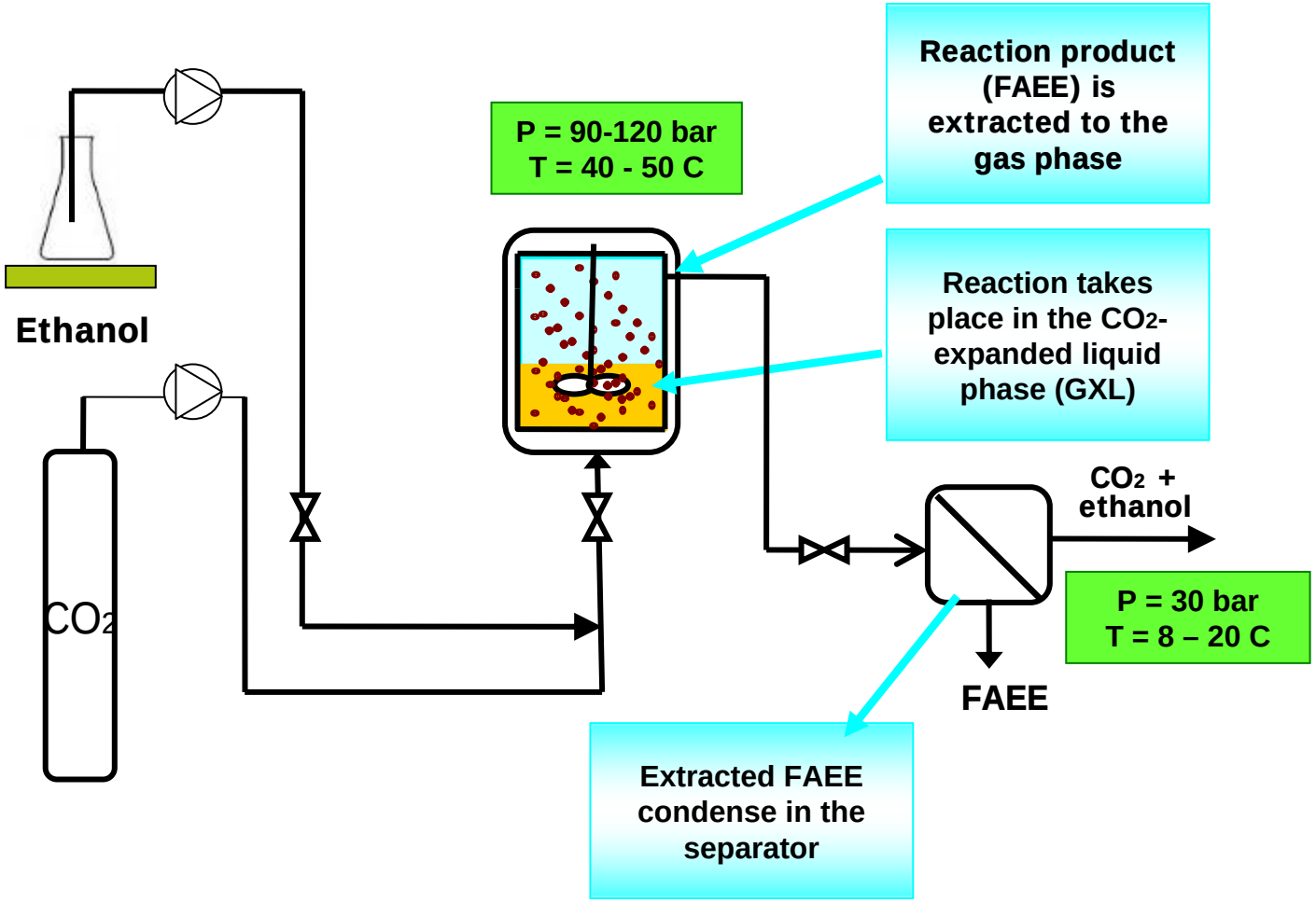
Simultaneous synthesis of partial glycerides and FAEE



DAG
- Food grade emulsifiers
- Novel dietary fat product

MAG
- Food grade emulsifiers

Experimental set-up



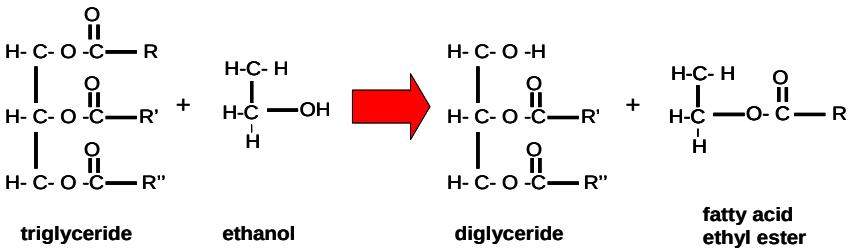
Lipases

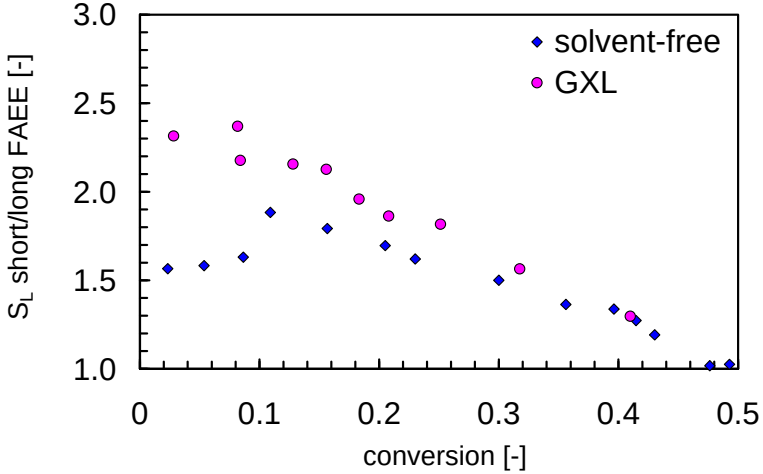
- Specificity/selectivity of lipases allows tailoring reaction products
- Green processing
- Immobilized lipases used:
  - *Candida antarctica* lipase B (Novozym 435 ®, Novozymes A/S)
  - *Pseudomonas fluorescens* lipase (Immozyme IMMAPF-T2, Chiral Vision)

Novozym 435 - results

Synthesis of FAEE from milk fat

- Reaction product composition
  - Lipase selective for short-chain fatty acids
  - Mixed DAG/MAG in partial glyceride product
- Effect of CO_2 on reaction rate and selectivity*
  - Enhanced lipase selectivity

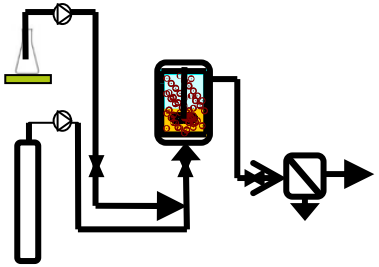




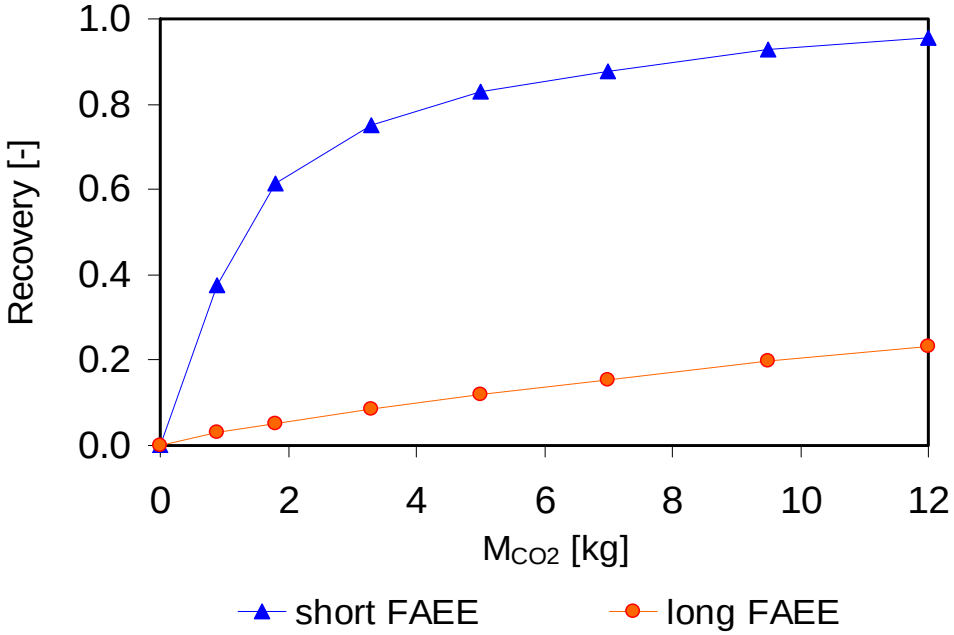
*Lubary M. *et al*, J Agric Food Chem 57 (2009) 116-121

Novozym 435 - results

Products separation by SC-CO_2

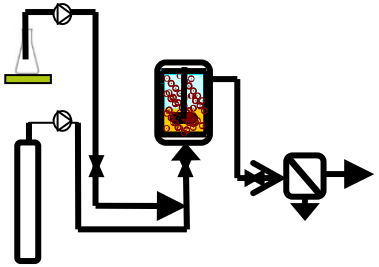


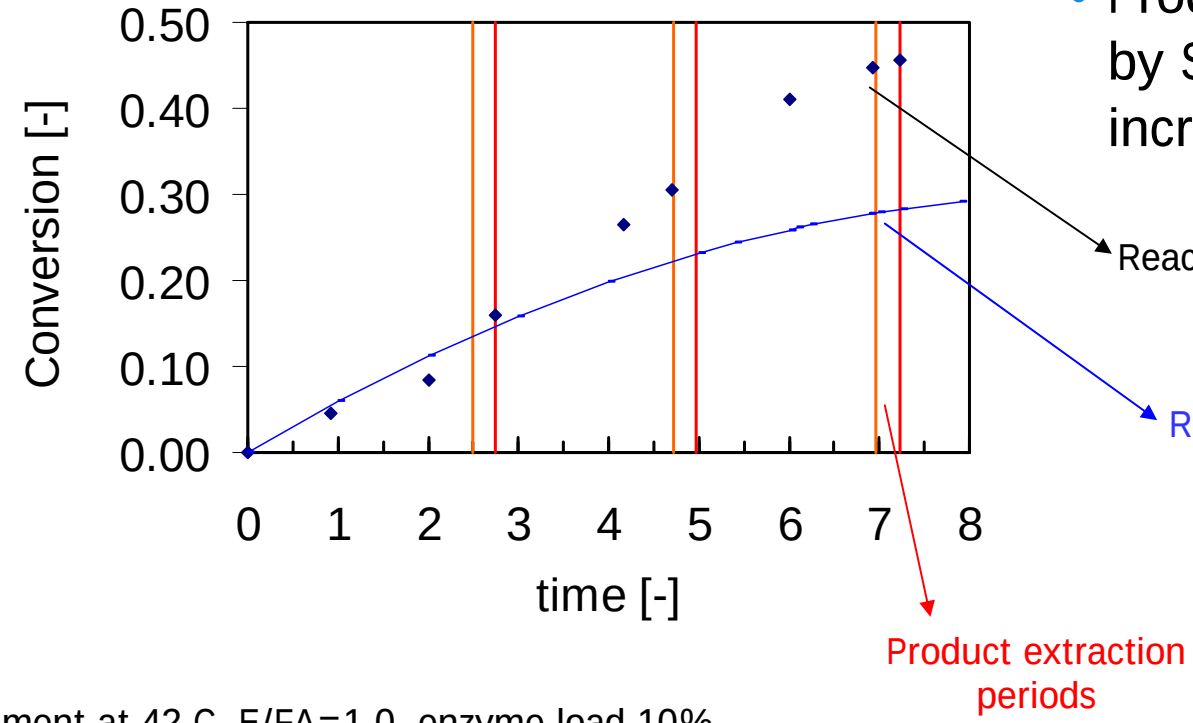
- High recovery of target product and good separation between short- and long- FAEE by SC-CO_2 extraction at 90 bar, 42 C



Novozym 435 - results

Integrated synthesis and extraction



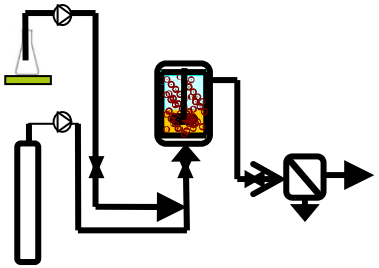


- Product removal (FAEE) by SC-CO_2 extraction increased conversion

Experiment at 42 C, E/FA=1.0, enzyme load 10%

Novozym 435 - results

Increased overall process selectivity



- Combination of
  - lipase selectivity
  - SC-CO_2 extraction selectivity

resulted in an improved separation between short- and long- FAEE

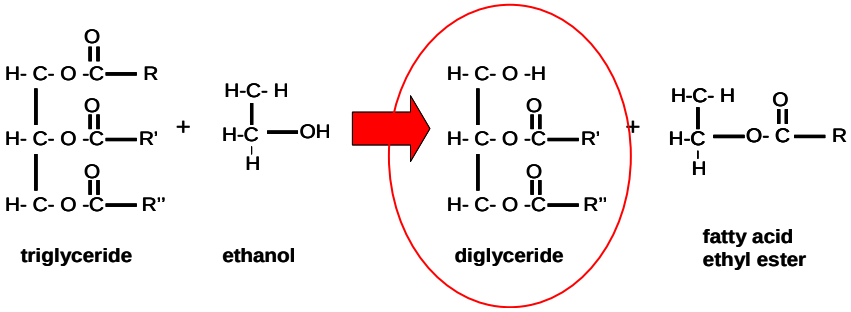
Raffinate
- **long FAEE**
- **MAG/DAG**

Extract
- **short FAEE**
- **Ethanol**

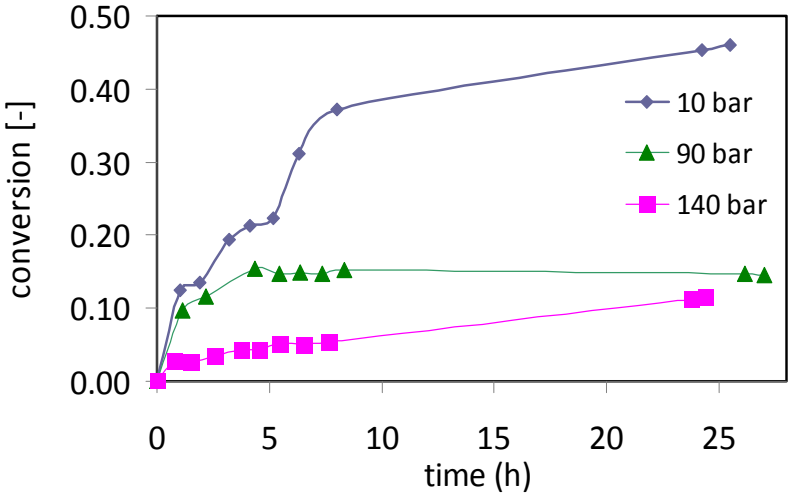
IMMAPF-T2 - Results

Synthesis

- Reaction product composition
  - Lipase produces DAG with high selectivity



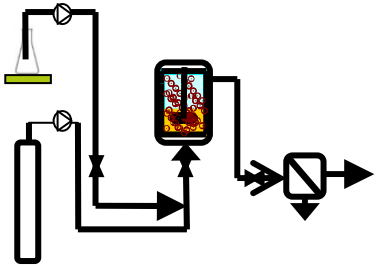
- Effect of SC-CO_2 on reaction rate → unfavorable



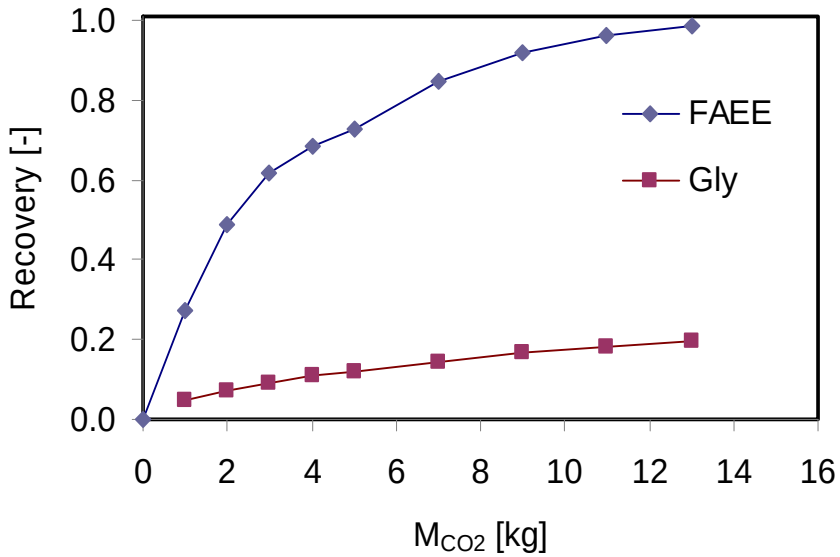
Experiments at 40 C, E/FA=0.5, enzyme load 5%

IMMAPF-T2 - Results

Products separation

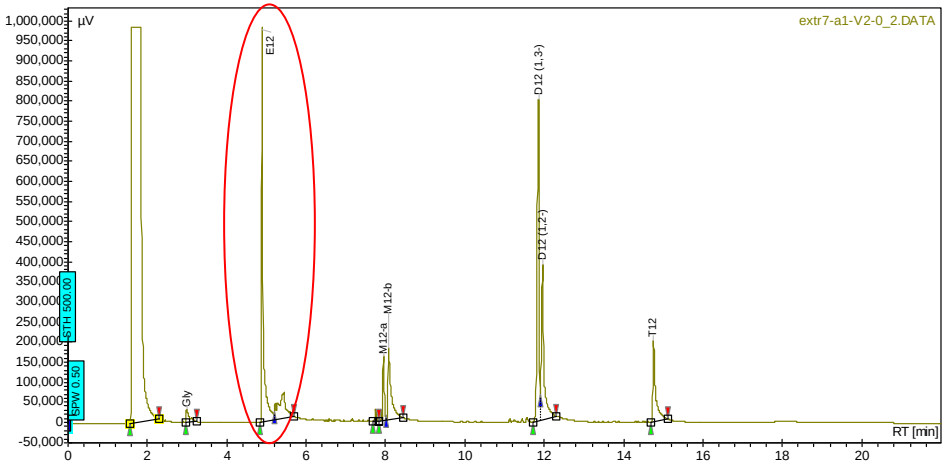


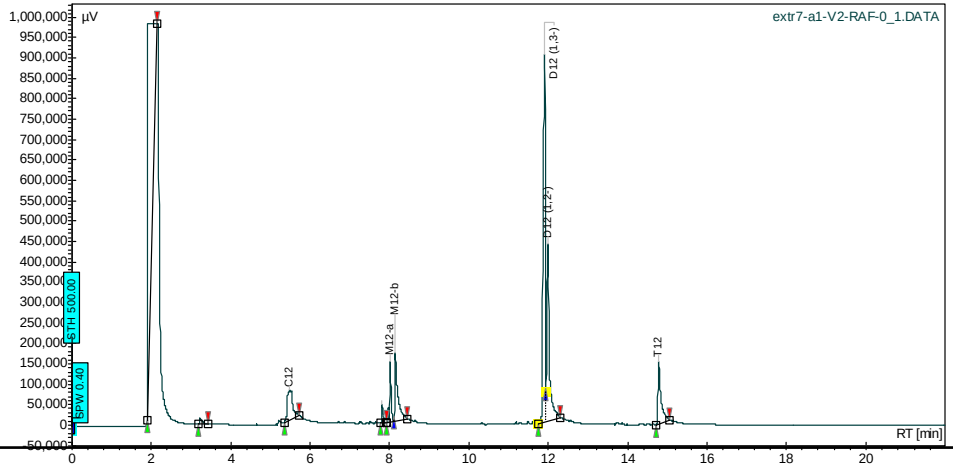
- Good separation between FAEE and glycerides at 110 bar and 40 C
- Reaction followed by extraction gives best result in this case



IMMAPF-T2 - Results

Products separation





- Complete removal of FAEE by SC-CO_2
- Raffinate composed primarily by DAG

Conclusion

- Synthesis and separation of edible oil derivatives was accomplished using immobilized lipases and SC-CO_2
  - Lipases allow tailoring reaction products
  - Efficient separation of FAEE results from SC-CO_2 extraction
- Lipase tolerance for high pressure/CO_2 presence determines the synthesis-separation integration possibilities
  - Novozym 435 produced a short-chain FAEE extract, and benefited from process integration
  - IMMAPF-T2 yielded a high purity DAG raffinate and a FAEE extract by ethanolysis and subsequent extraction

Acknowledgements

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