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FACULTY OF BIOSCIENCE ENGINEERING

Fat structuring with partial glycerides: effect on solid fat profiles

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Introduction and background

Importance of the solid fat content

- SFC-profile: guideline in judging the suitability of an oil/fat blend for a particular application
- Importance for chocolate: - hardness
  - fast melting and flavor release
  - mouth feel at higher temperatures
- Importance for margarine/spreads: - spreadability at 5°C
  - oil exudation
  - thickness and mouth feel
- Wassell and Young (2007): Use of SFC to select TFA-substitutes
- Several studies: link between SFC and macroscopic properties

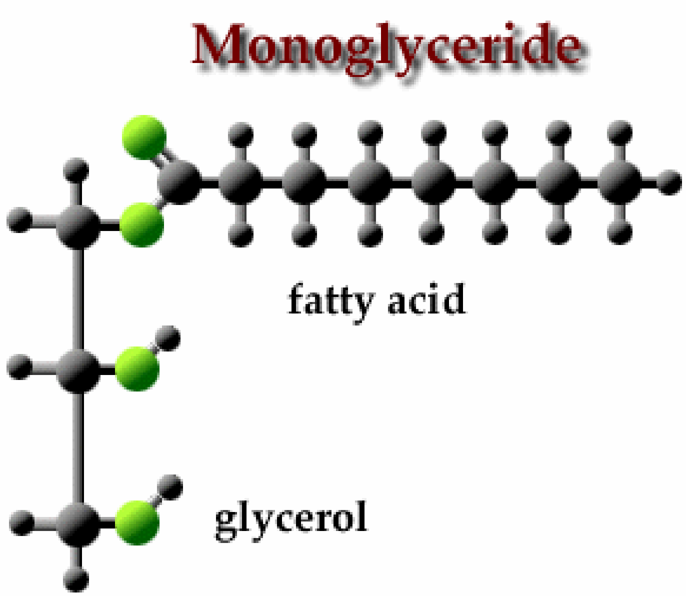
  => Fat structure based on SFC

Alternatives to crystalline fat

- In the past: fat structuring based on providing solid fat by regular vegetable oils and fats, especially palm oil fractions
- New trend: structuring of edible oils by alternatives to crystalline fat (Pernetti et al., 2007)
- Examples: - fatty alcohols
  - waxes
  - lecithin
  - sorbitan tristearate (STS)
  - phytosterols

=> totally different structure from regular triglycerides in fats and oils

Monoglycerides as solid fat providers



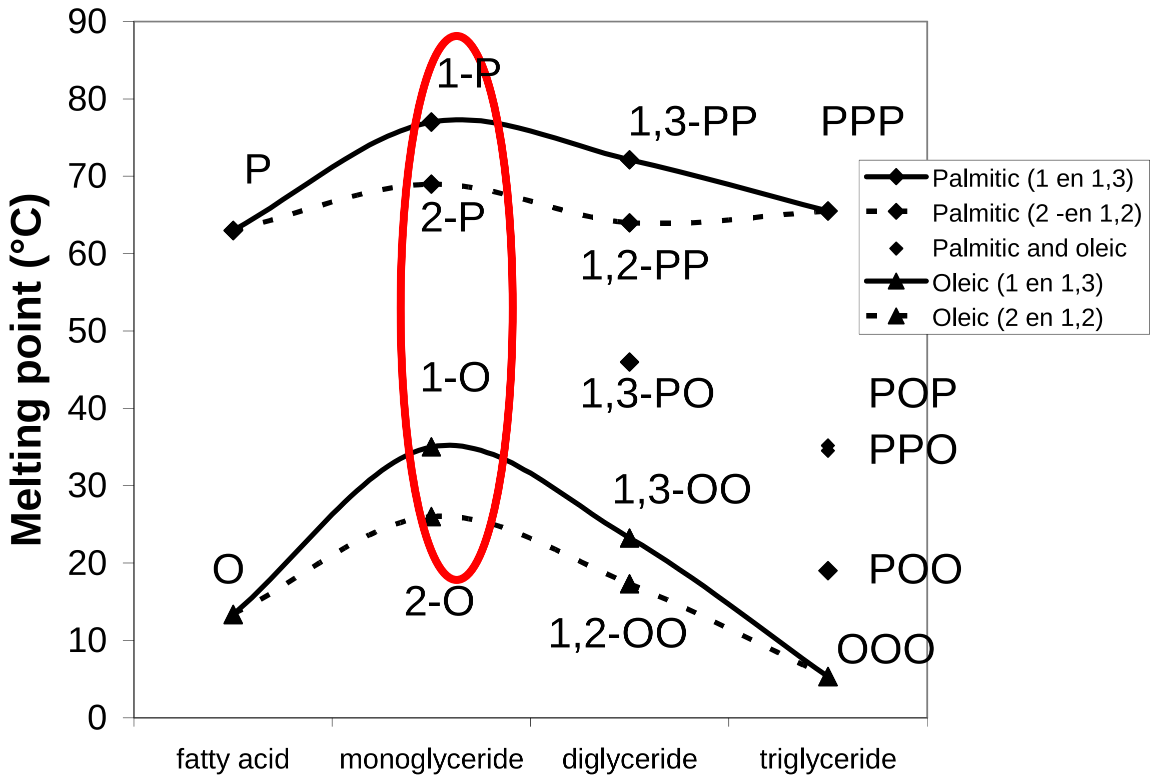
- One fatty acid on glycerol backbone
  ➔ amphiphilic neutral lipid molecule
- Generally known as emulsifiers in food products
- Other applications:
  - bread improver
  - antimicrobial agent
  - stabilization of foams
  - use in cosmetics

Monoglycerides as solid fat providers

- Some similarities between monoglycerides and triglycerides:
  - ➔ typical crystallisation and melting range
  - ➔ formation of a crystal network under certain conditions
  - ➔ characterized by a certain polymorphic behaviour
  - ➔ fysical properties governed by the fatty acid profile
- Monoglycerides could be used as solid fat providers
- Less difference with triglycerides than other alternatives to crystalline fat
- Important property: higher melting point compared to triglycerides

Monoglycerides as solid fat providers

- Monoglycerides: high melting point compared to triglycerides



Objective of the research

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- Study of the feasibility of monoglycerides as solid fat providers
- Investigation of the solid fat profile of different monoglyceride blends
  - ***Influence of the amount of saturated fatty acids***
  - ***Influence of the ratio of saturated fatty acids: palmitic/stearic, palmitic/behenic, stearic/behenic acid***
  - ***Influence of the ratio oleic/linoleic acid***
  - ***Influence of the amount of diglycerides***
- Selection of the right monoglyceride mixture to provide solid fat to triglyceride systems
- Investigation of the influence of the addition of water

Experimental setup

Investigated samples

- Use of commercial monoglycerides: produced by glycerolysis of vegetable oils and distillation to raise monoglyceride content (> 90%)
- SM90FHPos: based on fully hydrogenated palm stearin (saturated)
- SM90FHRso: based on fully hydrogenated rapeseed oil (saturated)
- SM90FHHer: based on fully hydrogenated high eruca rapeseed oil (saturated)
- UM90RRso: based on refined rapeseed oil (unsaturated)
- UM90RSfo: based on refined sunflower oil (unsaturated)

Investigated samples

- UM50HOSf: non distilled sample to study the effect of the amount of diglycerides
  - ***Based on high-oleic sunflower oil***
  - ***Contains around 30% DGL***
  - ***FA-profile: 81.20% oleic acid, 8.50% linoleic acid***

- UM90HOSf: based on refined high oleic sunflower oil (unsaturated)
  - ***To study the effect of the addition of water***

- Palm oil, palm stearin and rapeseed oil used as triglyceride providers

Performed analyses and methods

- Chemical analysis of commercial monoglycerides using:
  - FAME GC: Fatty acid profile
  - Carbon Number GC: Glyceride content
- Differential scanning calorimetry: reduction of the melting point of saturated monoglycerides in liquid oil
- pNMR: evolution of the solid fat content as a function of temperature
  - ➢ ***Determination of the solid fat profile***
- Pulsed field gradient NMR: determination of the complete relaxation curve
  - ➢ ***Study of the influence of the addition of water***

Results and discussion

Dilution of saturated monoglycerides with rapeseed oil

- Very high melting point of saturated monoglycerides compared to other glycerides
- Dilution of monoglycerides with rapeseed oil
- Analysis of the dilutions by DSC to derive the melting point of the system
- Ideal phase behaviour governed by the Hildebrand equation:

$$\ln(x) = \frac{\Delta H}{R}\left(\frac{1}{Tm} - \frac{1}{T}\right)$$

with x = mole fraction of the solid component in liquid oil

ΔH = melting enthalpy of the solid component

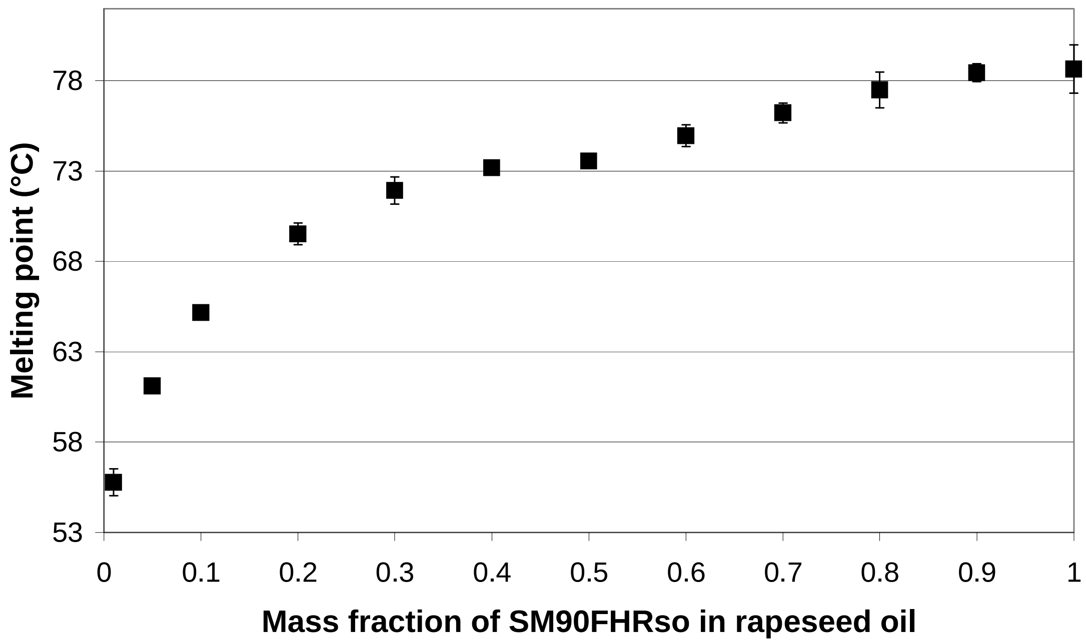
R = universal gas constant = 8.314 J/mol.K

T_m = melting point of the non diluted solid component

T = melting point of the diluted solid component

Dilution of commercial monoglycerides with rapeseed oil

SM90FHRso: distilled monoglycerides based on fully hydrogenated rapeseed oil



➔ Ideal phase behaviour following the Hildebrandt equation

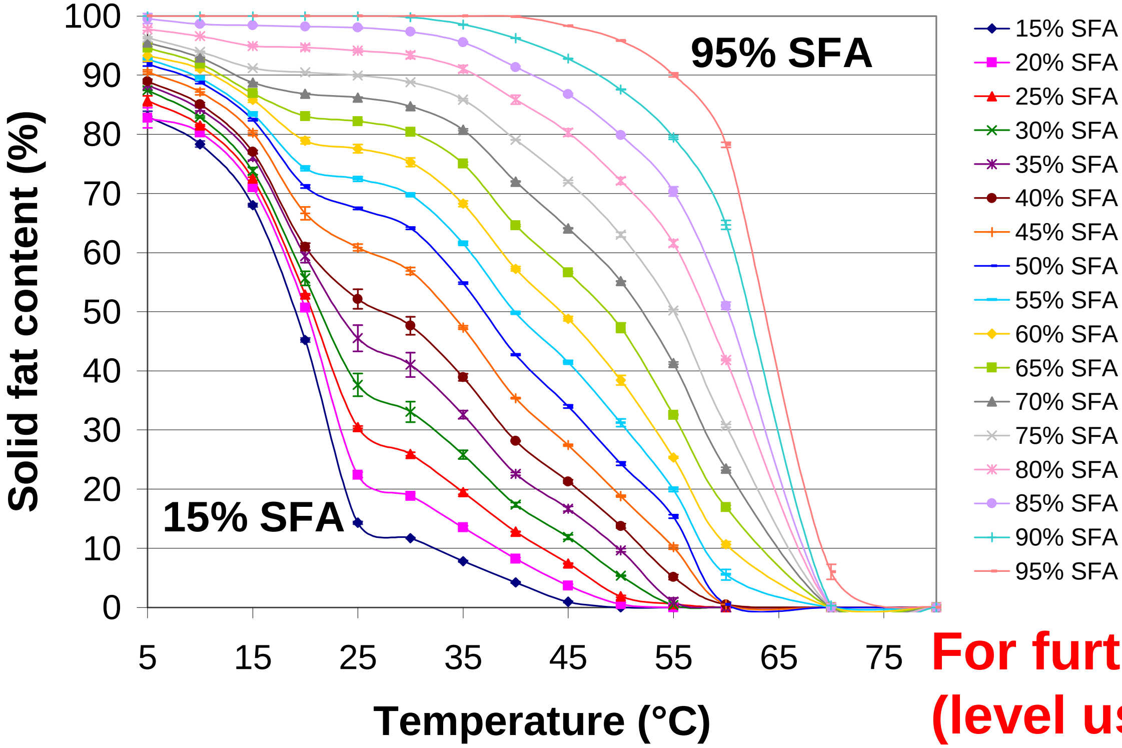
Fatty acid composition of the investigated samples

Fatty acid	SM90FHPos	SM90FHRso	SM90FHHer	UM90RRso	UM90RSfo
Palmitic (C16:0)	**58.64**	6.93	0.97	6.01	7.60
Stearic (C18:0)	39.03	**90.21**	4.17	1.71	4.71
Behenic (C22:0)	0.05	0.49	**84.54**	0.14	0.49
Oleic (C18:1)	0.00	0.06	0.06	**63.27**	22.41
Linoleic (C18:2)	0.00	0.06	0.00	17.79	**64.01**
SFA	99.79	99.67	97.98	8.80	13.18

=> Study of different effects, e.g. ratio P/S, by creating specific mixtures

Influence of SFA-content on solid fat profile

- Variation of SFA by mixing UM90RRso, SM90FHRso and SM90FHPos (ratio palmitic/stearic = 1)



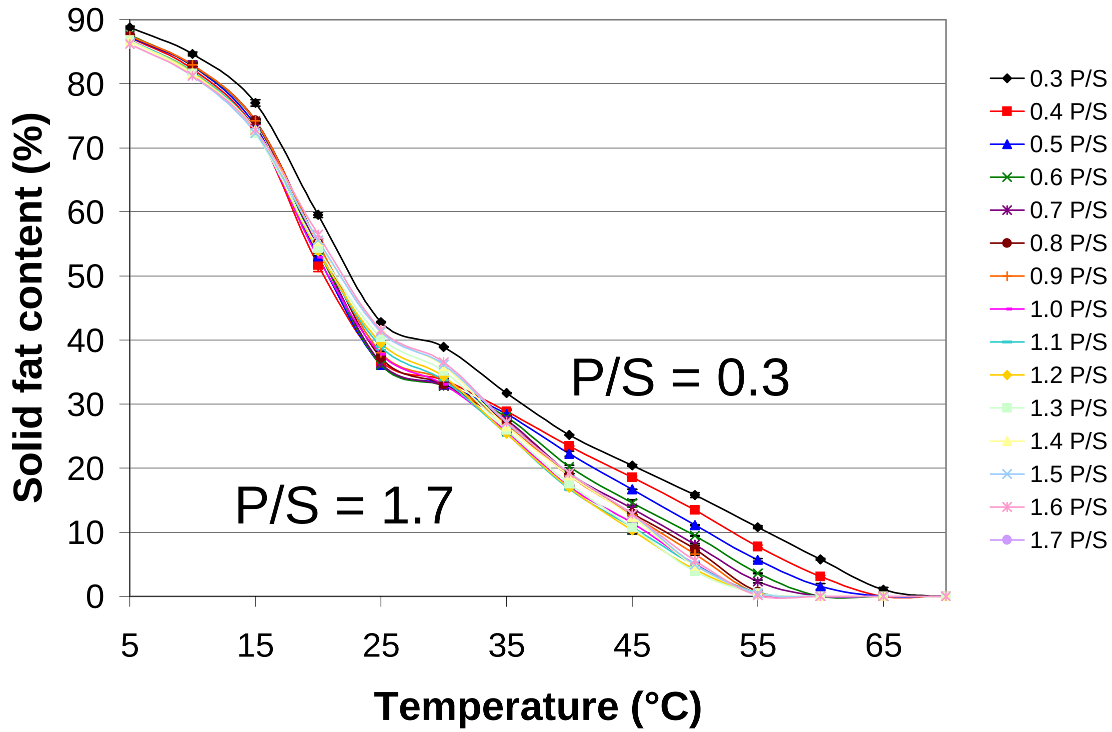
Different regions:

- below 15°C: small difference between different SFA-levels
- between 15°C and 25°C: huge reduction of SFC for low SFA levels (< 40%)
- above 25°C: gradual reduction of SFC for higher SFA levels

For further experiments: 30% SFA (level used by health organizations)

Influence of palmitic (P)/stearic (S) ratio on solid fat profile

- Variation of palmitic/stearic ratio by mixing UM90RRso, SM90FHRso and SM90FHPos (SFA-content = 30%)

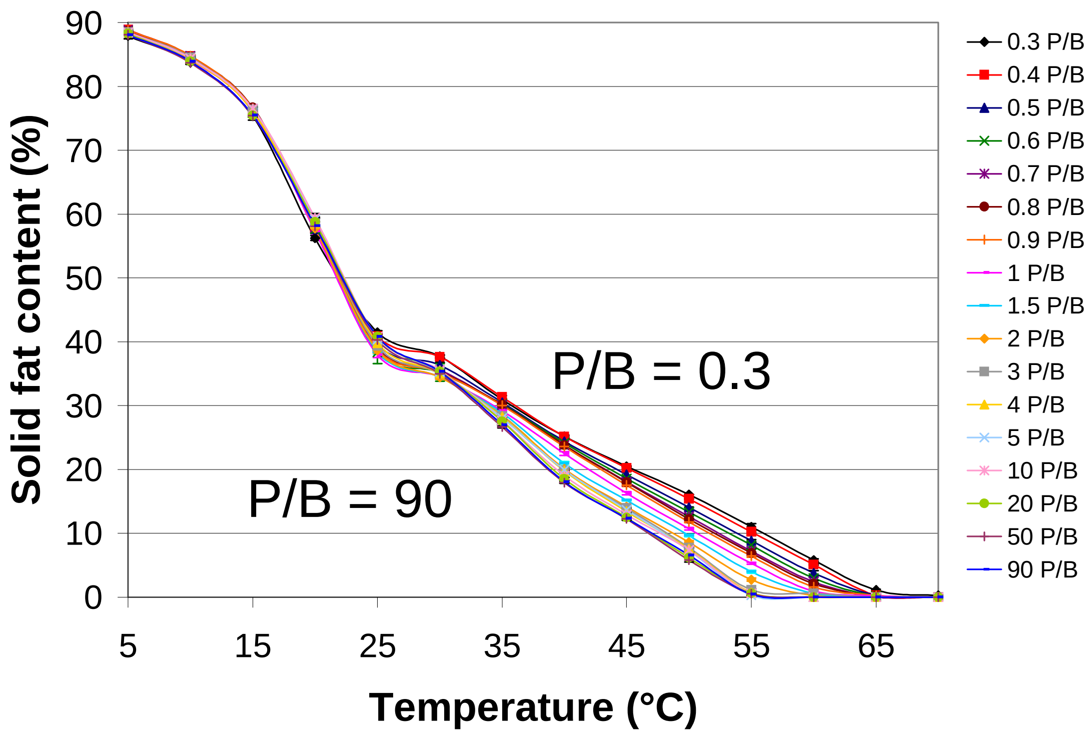


Effect at higher temperatures:

- lower SFC for higher ratios
- explanation: higher melting point of stearic acid compared to palmitic acid

Influence of palmitic (P)/behenic (B) ratio on solid fat profile

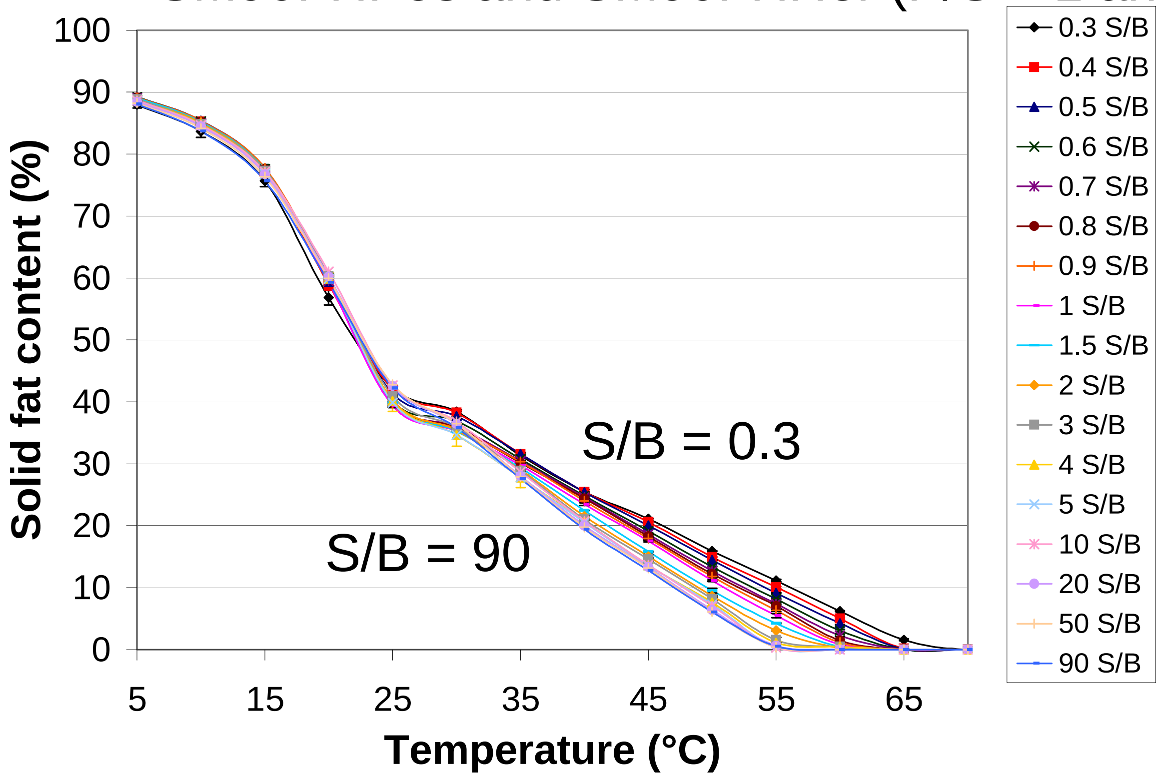
- Variation of palmitic/behenic ratio by mixing UM90RRso, SM90FHRso, SM90FHPos and SM90FHHer (P/S = 1 and SFA-content = 30%)



Same effect as for ratio P/S

Influence of stearic (P)/behenic (B) ratio on solid fat profile

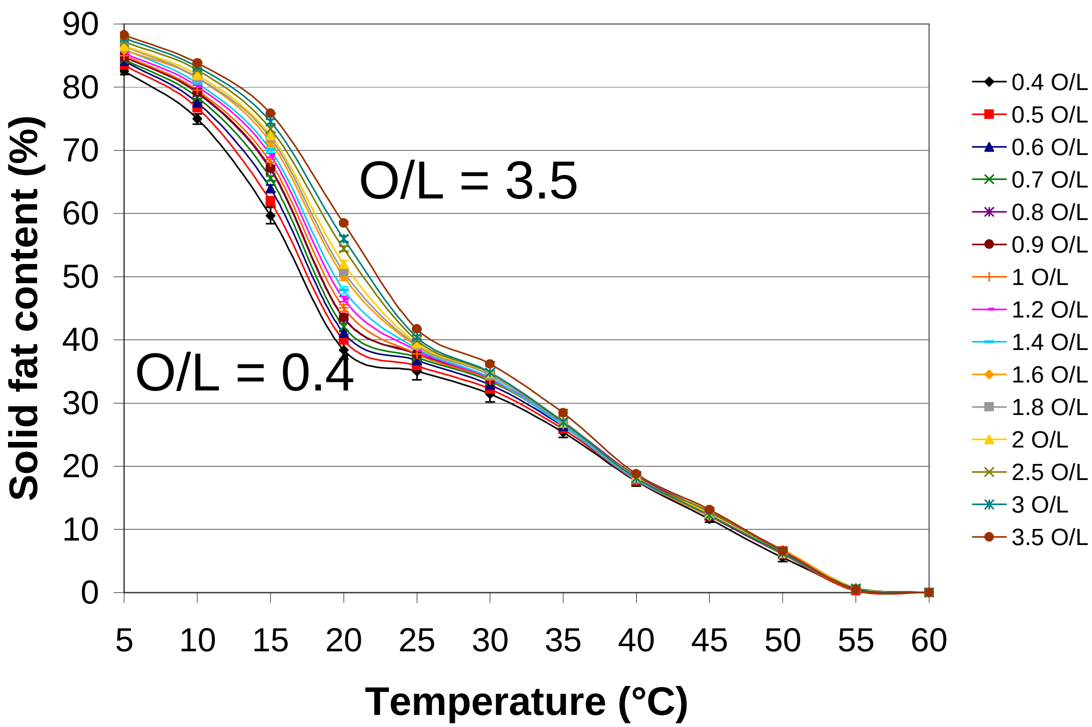
- Variation of stearic/behenic ratio by mixing UM90RRso, SM90FHRso, SM90FHPos and SM90FHHer (P/S = 1 and SFA-content = 30%)



Same effect as for ratio P/S and P/B

Influence of oleic (O)/linoleic (L) ratio on solid fat profile

- Variation of oleic/linoleic ratio by mixing UM90RRso, UM90RSfo, SM90FHRso and SM90FHPos (P/S = 1 and SFA-content = 30%)

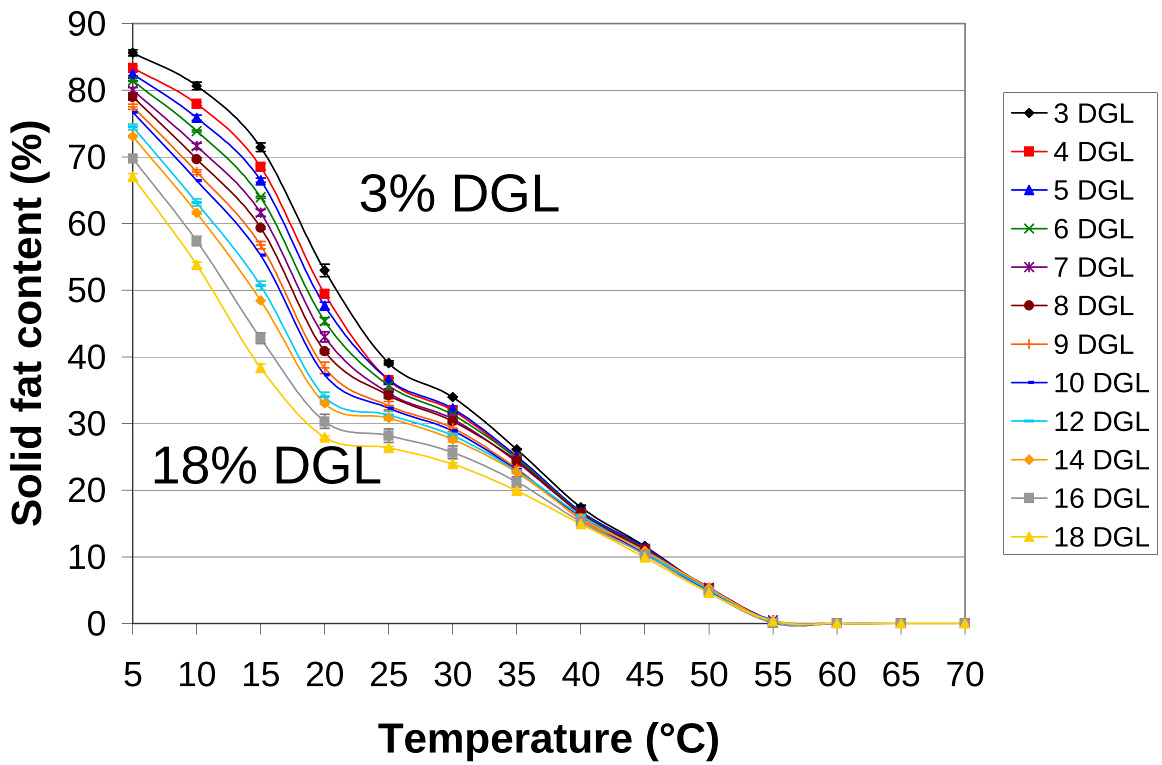


Effect at lower temperatures:

- lower SFC for lower ratios
- explanation: higher melting point of oleic acid compared to linoleic acid
- no difference at higher temperature because of same level and type of SFA

Influence of diglycerides (DGL) on solid fat profile

- Variation of diglyceride content by mixing UM50HOSf, UM90RRso, UM90RSfo, SM90FHRso and SM90FHPos (P/S = 1, O/L = 3 and SFA-content = 30%)



Effect at lower temperatures:

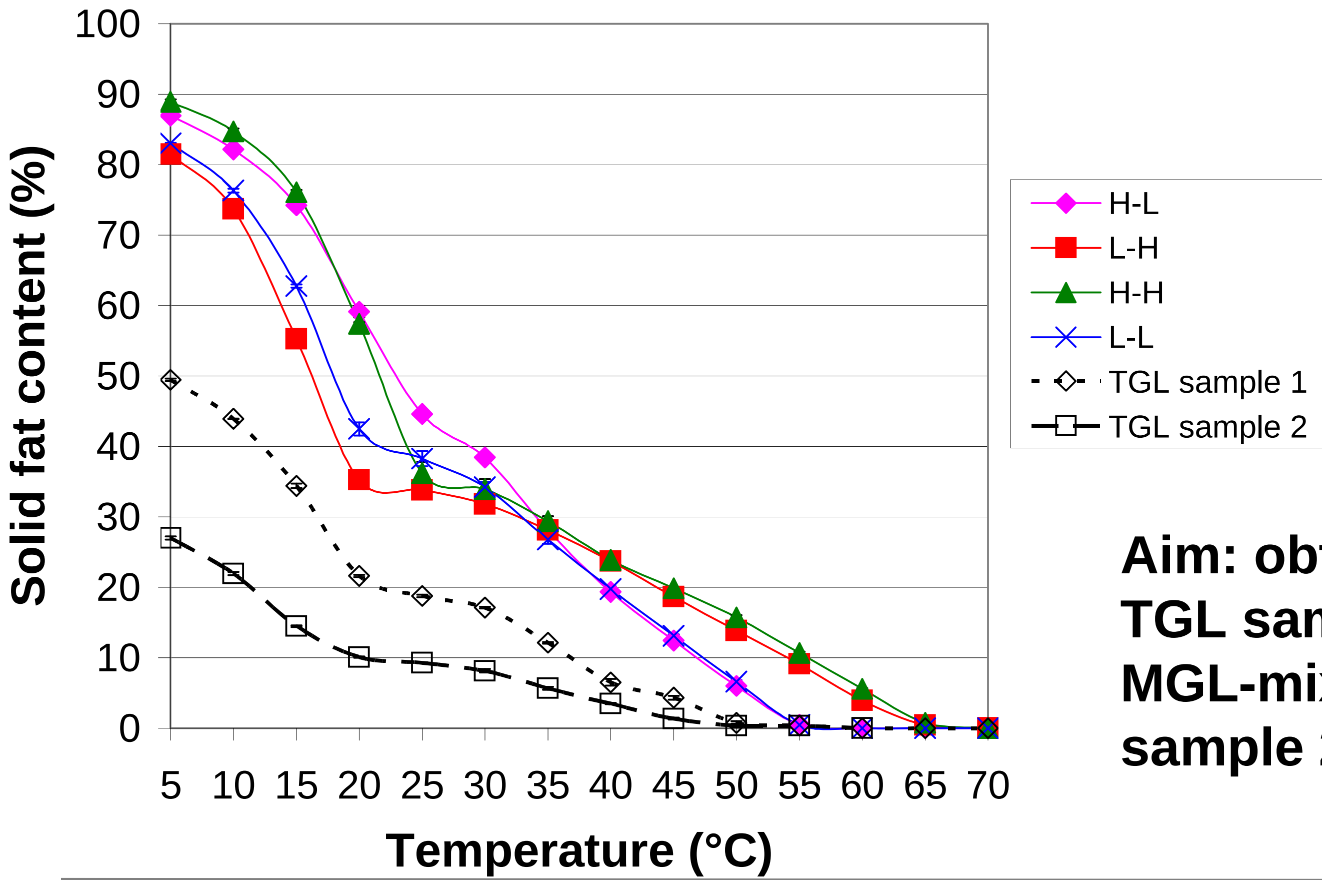
- lower SFC for higher DGL content
- explanation: lower melting point of DGL compared to MGL

Search for the desired SFC-profile

- Variation of SFC at high temperatures by varying P/S, P/B or S/B ratio
- Variation of SFC at low temperatures by varying O/L ratio

  => specific SFC-profile obtained by selection of the right ratio of P/S and O/L
- Investigation of 4 new mixtures of SM90FHRso, SM90FHPos, UM90RRso and UM90RSfo with SFA-content = 30%
- H-L: high SFC at low temperatures, low SFC at high temperatures
- L-H: low SFC at low tempertures, high SFC at high temperatures
- H-H: high SFC at low temperatures, high SFC at high temperatures
- L-H: low SFC at low temperatures, low SFC at high temperatures
- Comparison with two triglyceride samples:
  - TGL sample 1: 45% palm oil, 35% palm stearin, 20% rapeseed oil
  - TGL sample 2: 27% palm oil, 21% palm stearin, 52% rapeseed oil

Evolution of the SFC-profile of four extreme mixtures



Aim: obtain SFC-profile TGL sample 1 by adding MGL-mixture to TGL sample 2

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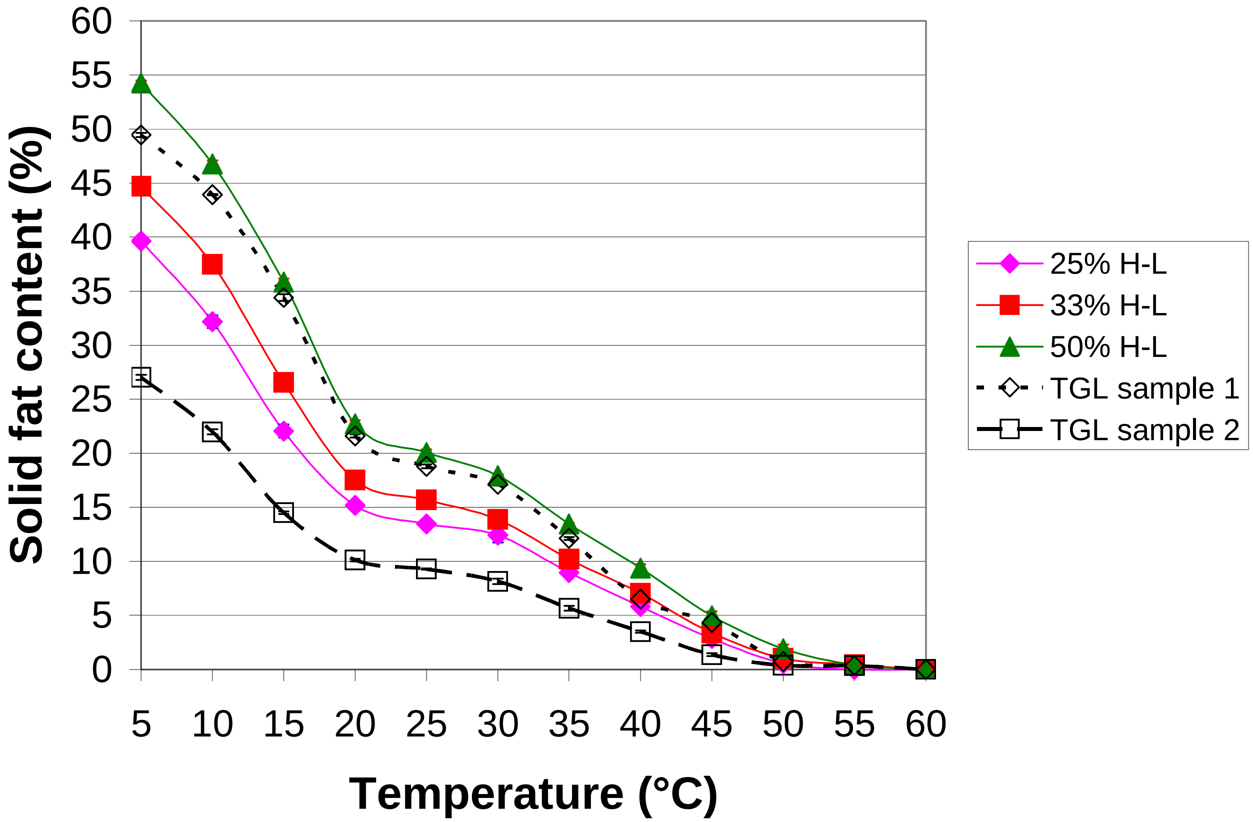
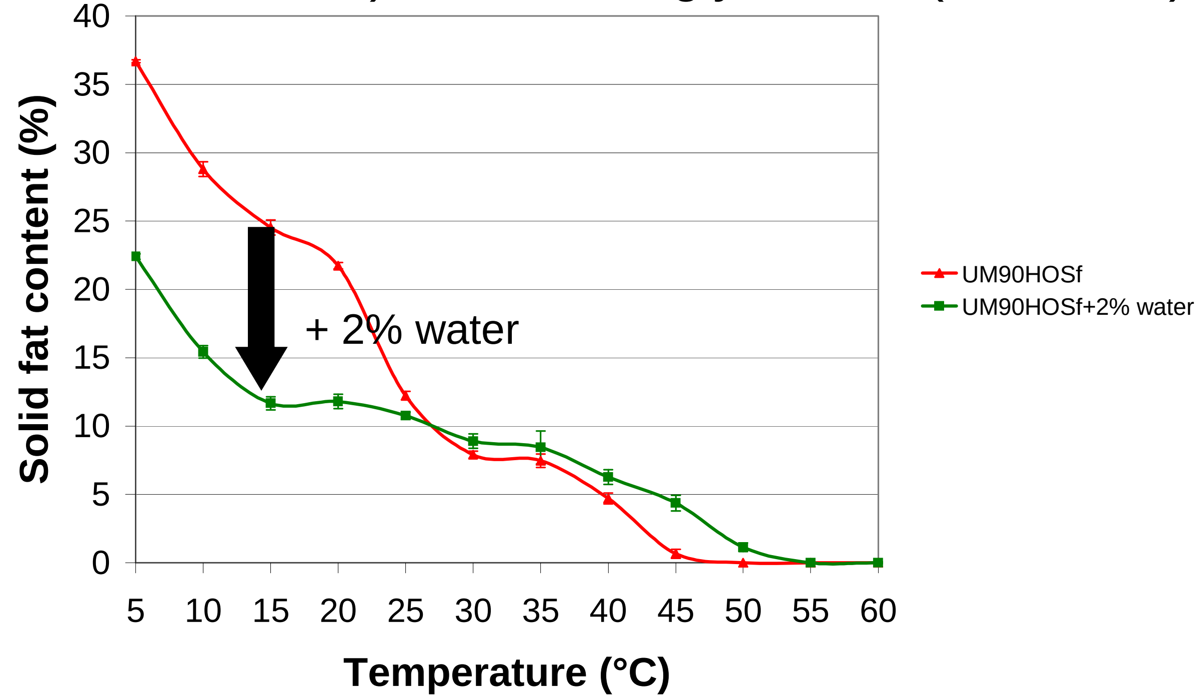
Monoglycerides as solid fat providers



Good correlation between TGL sample 1 and 50% mixture of H-L and TGL sample 2

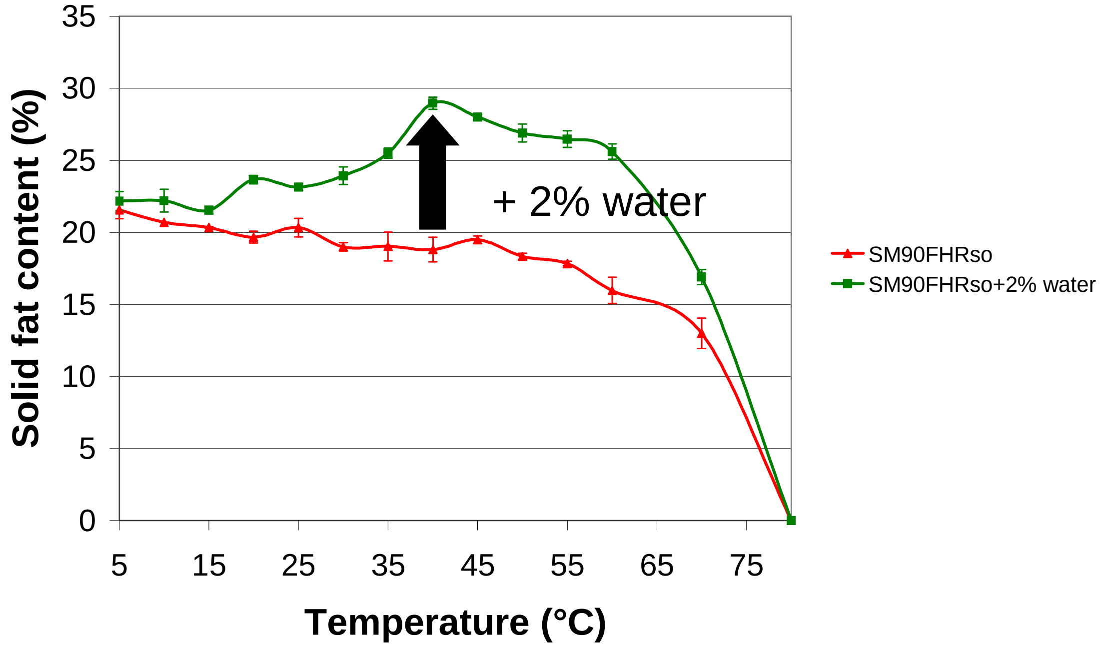
Influence of water on solid fat profile of monoglycerides

- Addition of 2% water to a system with 20%UM90HOSf (based on high oleic sunflower oil) and 80% triglycerides (30% SFA)



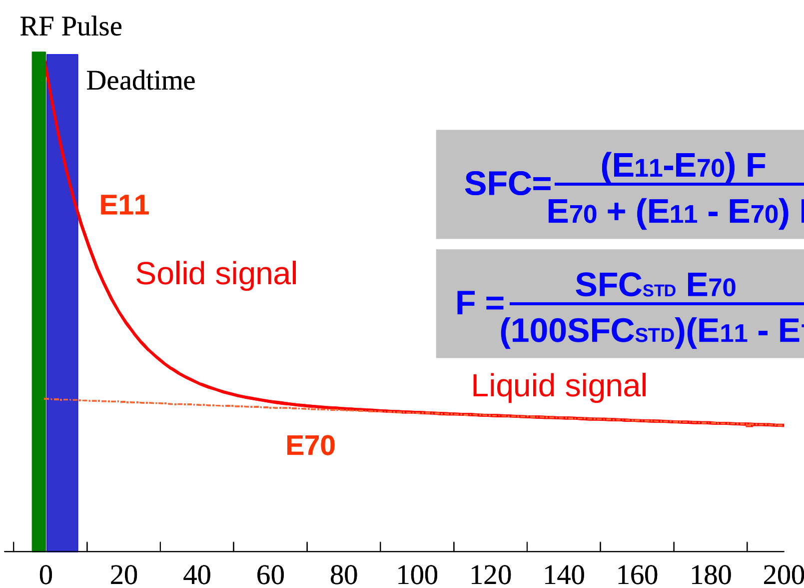
Influence of water on solid fat profile of monoglycerides

- Addition of 2% water to a system with 20% SM90FHRso and 80% triglycerides (30% SFA)



Influence of water: difference between saturated (SM90FHRso) and unsaturated (UM90HOSf) monoglycerides

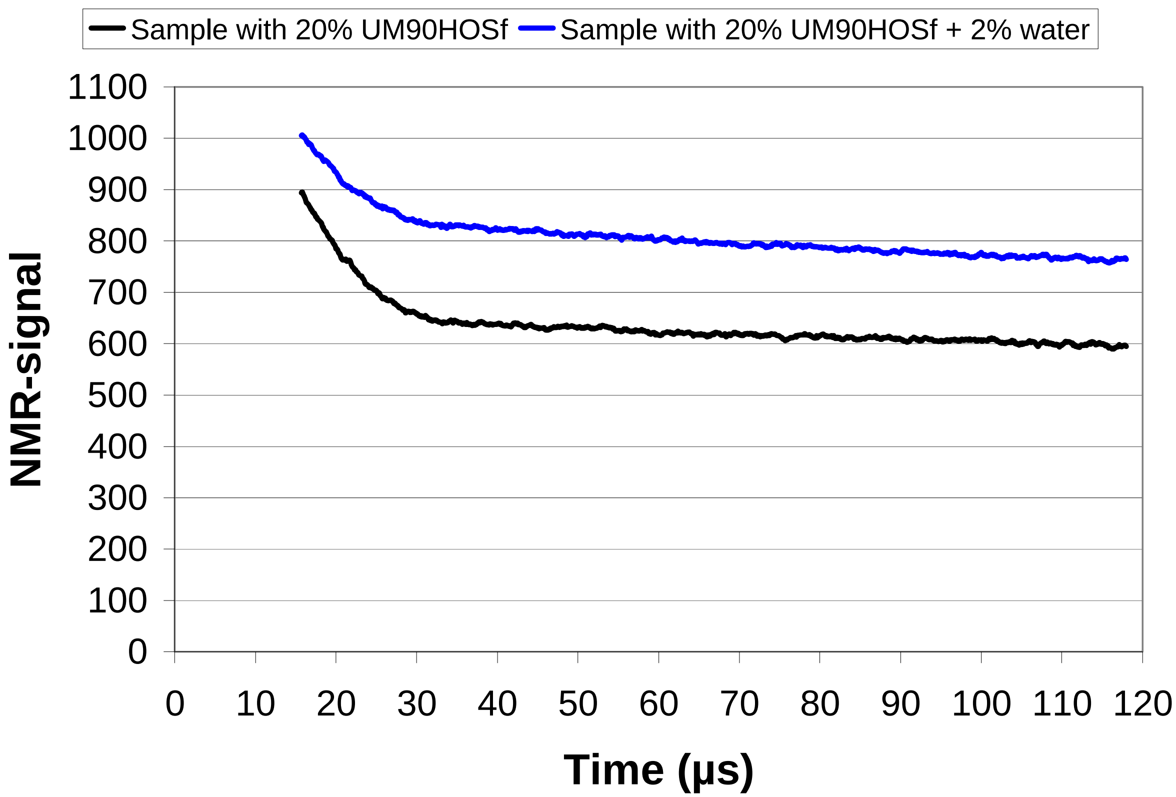
- Further investigation by a study of the complete relaxation curve (on which an SFC-measurement is based)
- Study at 4 temperatures: 5°C, 20°C, 35°C en 50°C



$$SFC = \frac{(E_{11} - E_{70})\,F}{E_{70} + (E_{11} - E_{70})\,F}$$

$$F = \frac{SFC_{STD}\,E_{70}}{(100SFC_{STD})(E_{11} - E_{70})}$$

Relaxation curve UM90HOSf-mixture at 5°C

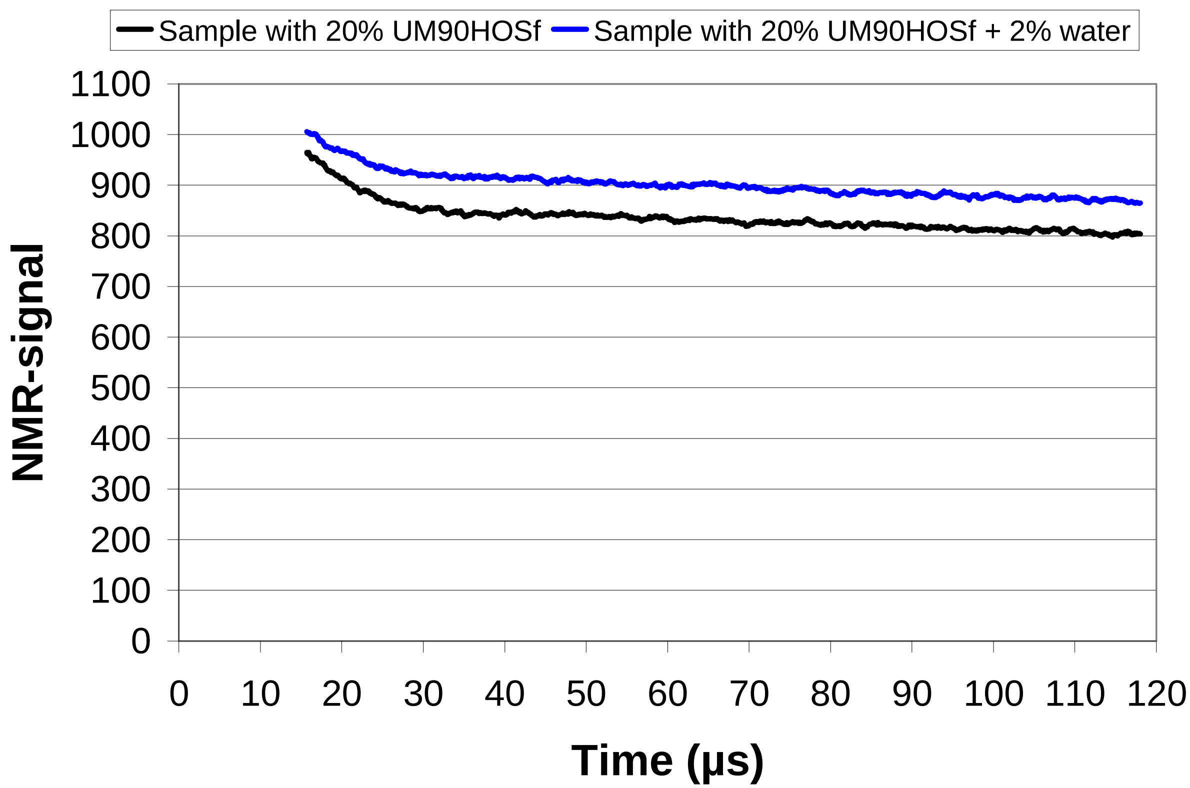


After addition of 2% water:

- Less strong solid signal
- Higher remaining liquid signal

⇒ more protons in the liquid state

Relaxation curve UM90HOSf-mixture at 20°C

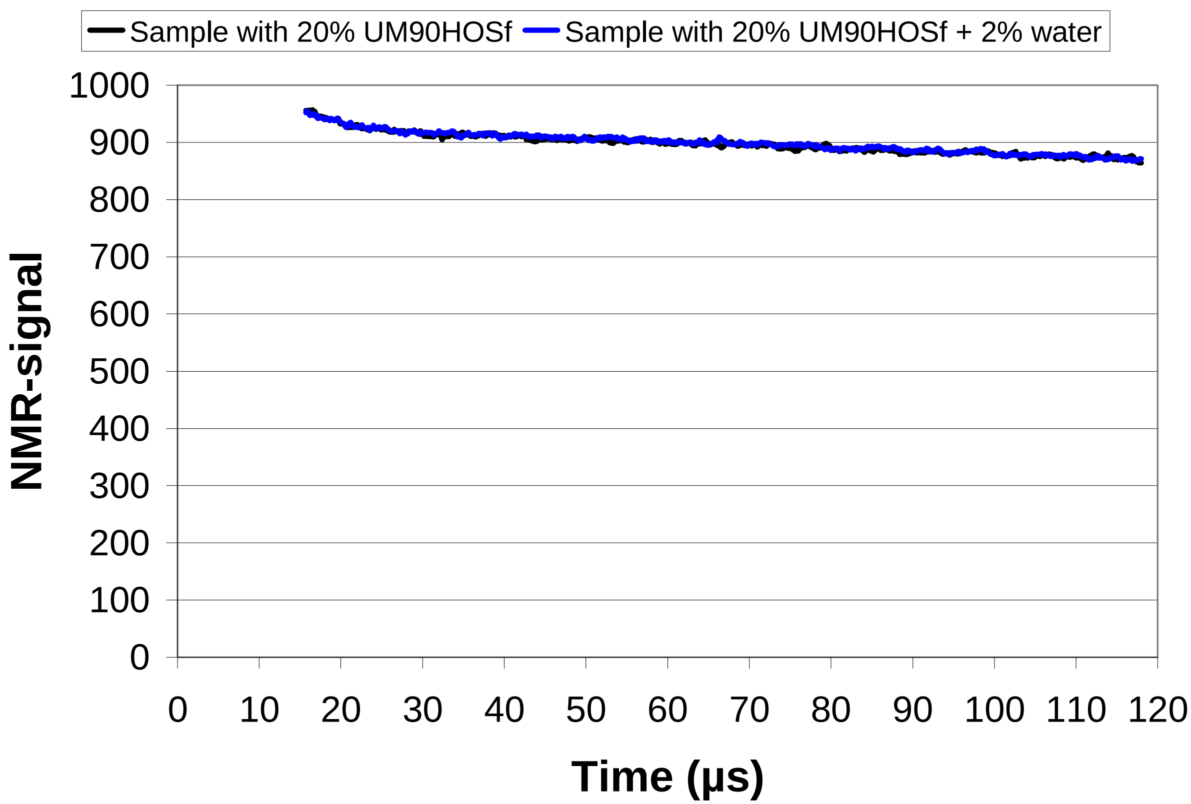


After addition of 2% water:

- Less strong solid signal
- Higher remaining liquid signal

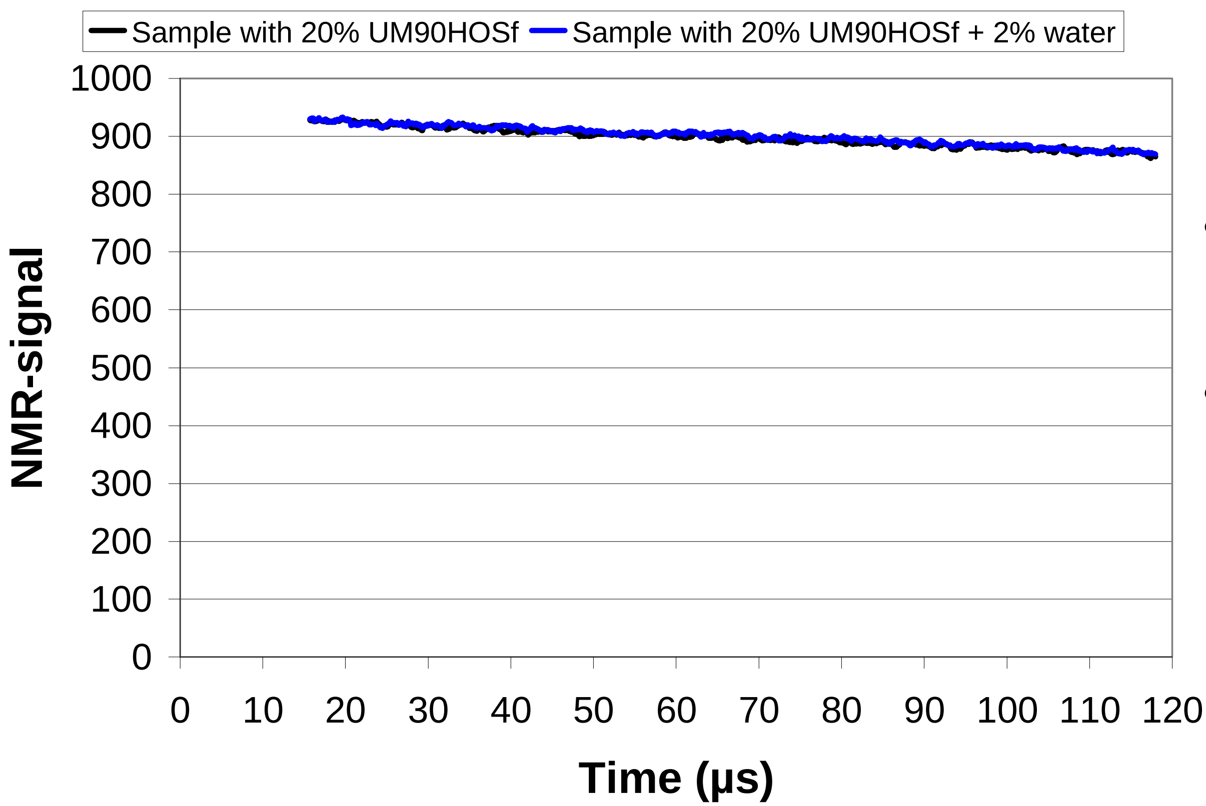
⇒ more protons in the liquid state

Relaxation curve UM90HOSf-mixture at 35°C



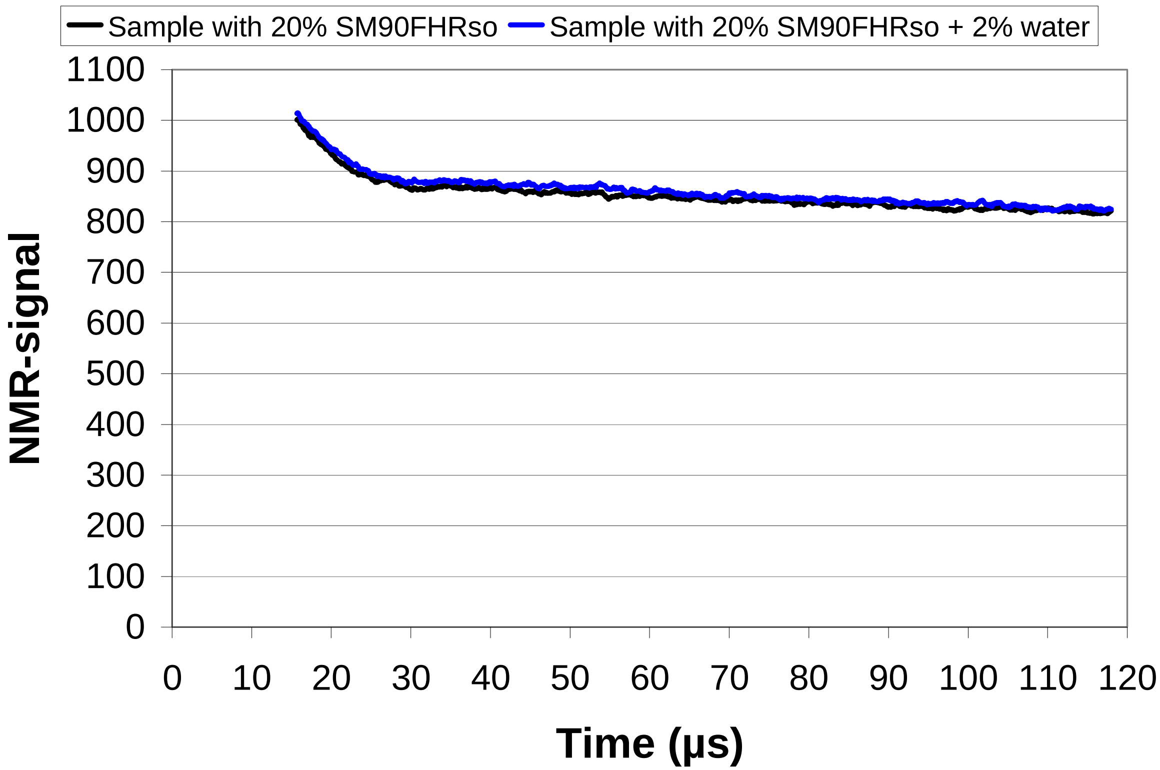
No difference after addition of 2% water

Relaxation curve UM90HOSf-mixture at 50°C



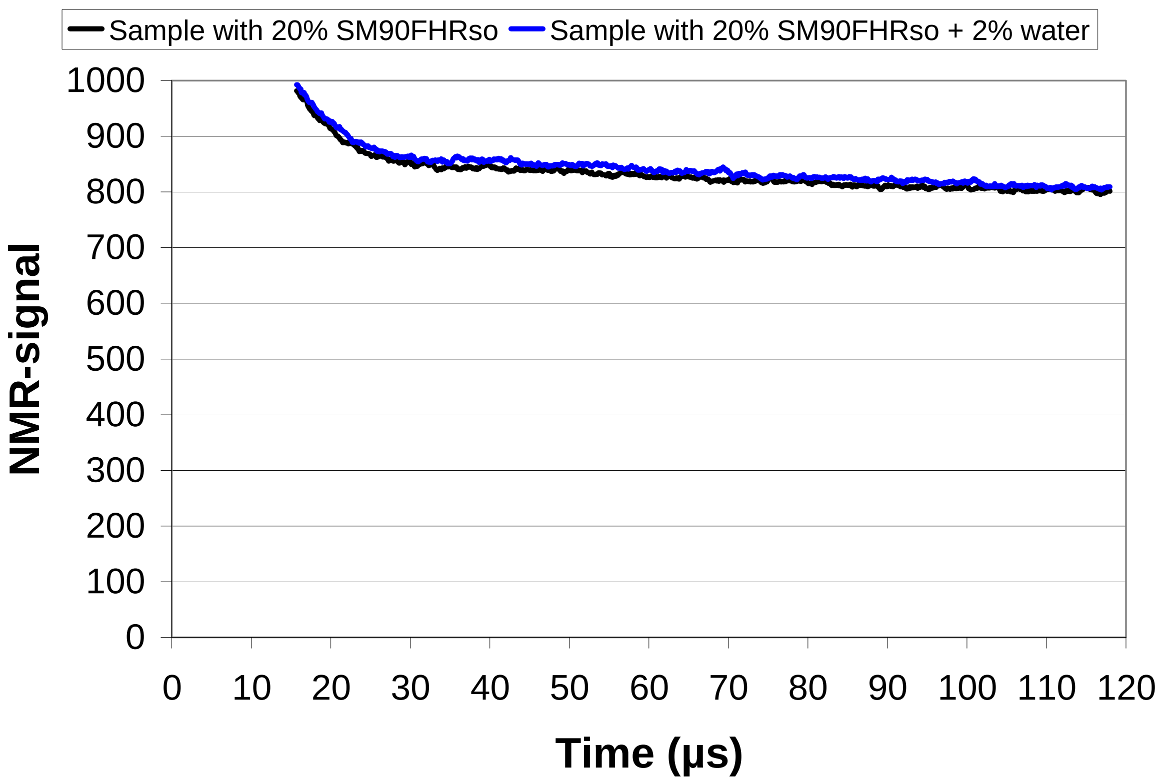
- No difference after addition of water
- No solid signal anymore

Relaxation curve SM90FHRso-mixture at 5°C



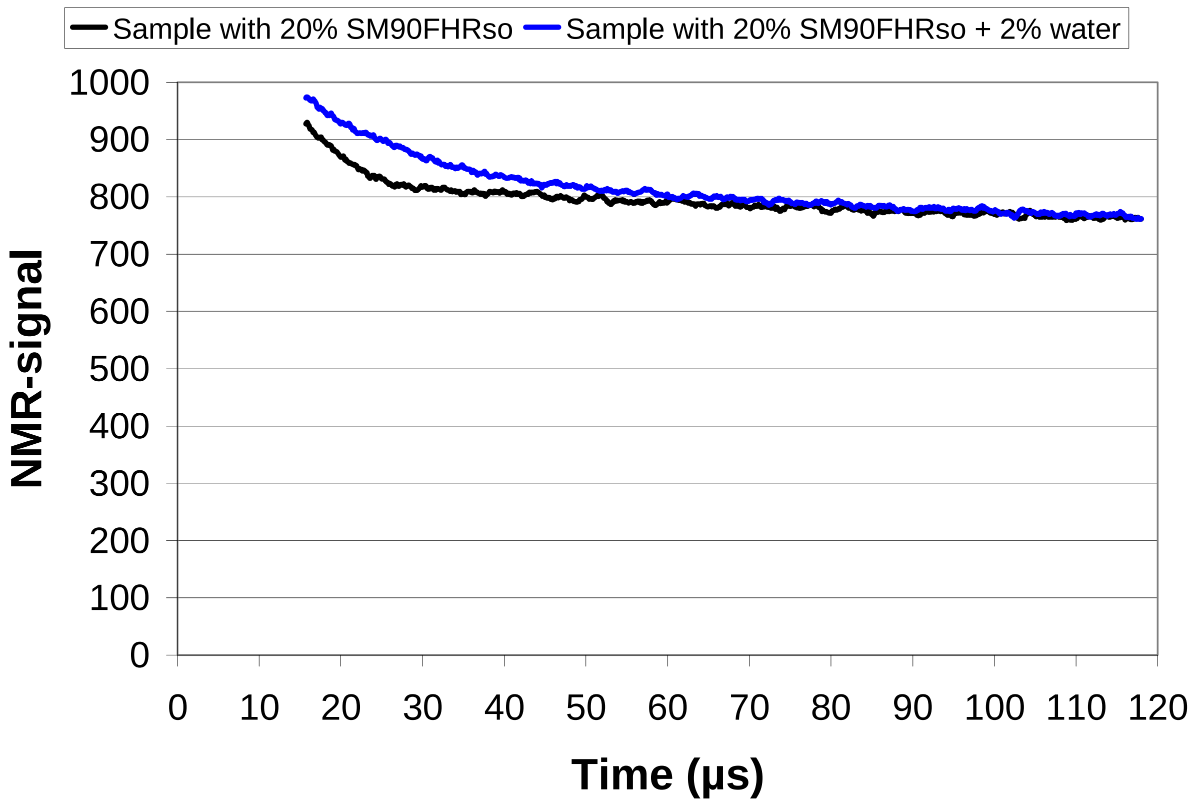
No difference after addition of 2% water

Relaxation curve SM90FHRso-mixture at 20°C



No difference after addition of 2% water

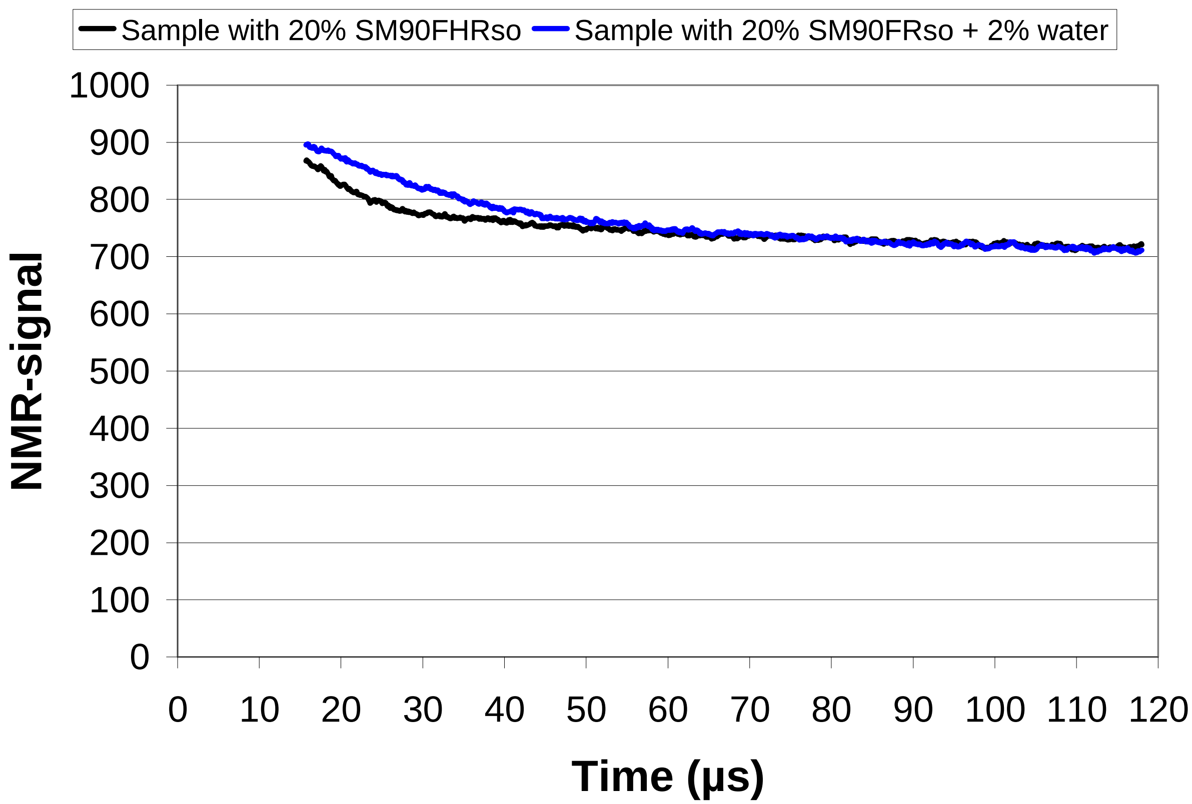
Relaxation curve SM90FHRso-mixture at 35°C



After addition of 2% water:

- Relaxation length of solid signal increased
- Protons in condition between solid and liquid state?
- Same liquid signal

Relaxation curve SM90FHRso-mixture at 50°C



After addition of 2% water:

- Relaxation length of solid signal increased
- Protons in condition between solid and liquid state?
- Same liquid signal
- Difference smaller as for 35°C

Conclusions

Conclusions

- Monoglycerides could be used as solid fat providers
- Modification of SFC-profile at high temperatures by varying ratio of saturated fatty acids, e.g. ratio P/S
- Modification of SFC-profile at low temperatures by varying ratio oleic versus linoleic acid or DGL-content
- Different signal when water is present
  - ***Reduction at low temperatures for unsaturated monoglycerides***
  - ***Increase at high temperatures for saturated monoglycerides***

Acknowledgements

- Vandemoortele N.V. is acknowledged for their scientific and financial collaboration and for providing the samples for this research
- Especially Wouter Meeussen, Ans Lesaffer and André De Laporte are acknowledged for their contribution to this research

vandemoortele

- Palsgaard is acknowledged for providing the sample UM90RRso

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Thank you for your attention!

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