Vegetable oil modeling applied for the formulation of structured lipids

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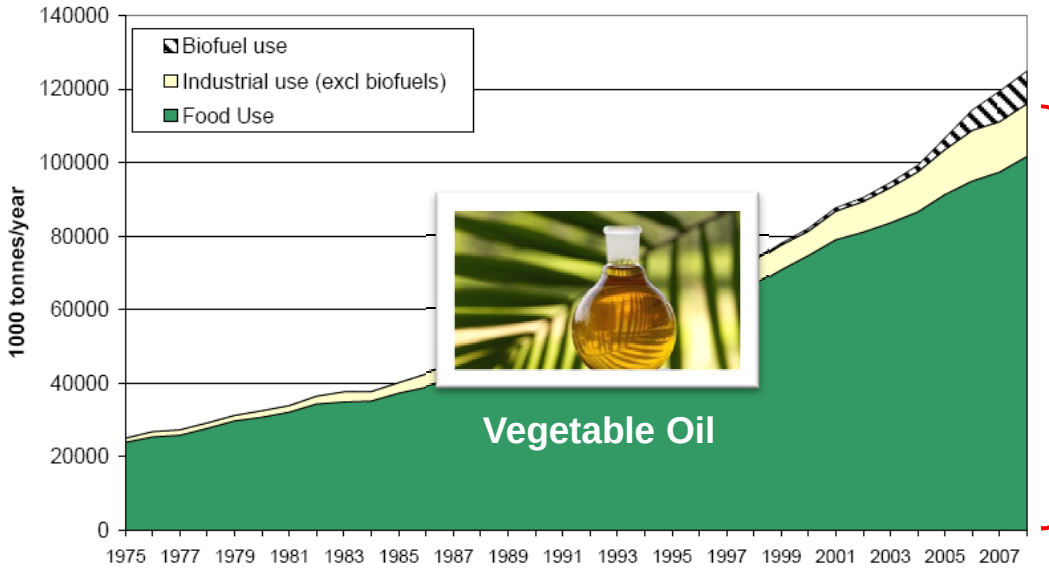
Journées Chevreul 2012 : chimie du végétal et lipochimie

Outline

- Motivations
- SFC : Solid fat content : the core property
- Vegetable Oil modeling
  - Analysis
  - Development
- Results
  - Binary TAGs mixture
  - Four TAGs mixture
  - Vegetable oil: 17 TAGs and more..
  - Oil blends, interesterified or not
  - Structured lipids application
- Conclusions

Motivations

- **Growing need for TAG based products = more systematic tools for their design**



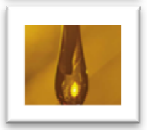
Our model concerns food & industrial uses


Solvents


Waxes


Cutting fluids


Cosmetics

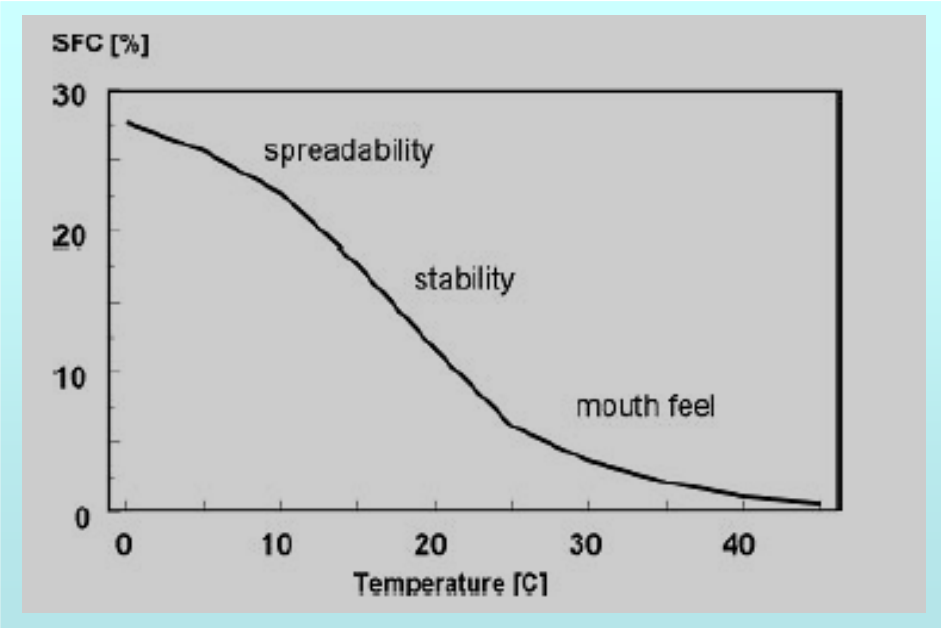

Lubricants


Foods

ROSILLO-CALLE, F. et al. A global overview of vegetable oils with reference to biodiesel. *Report for the IEA Bioenergy Task 40 (2009)*

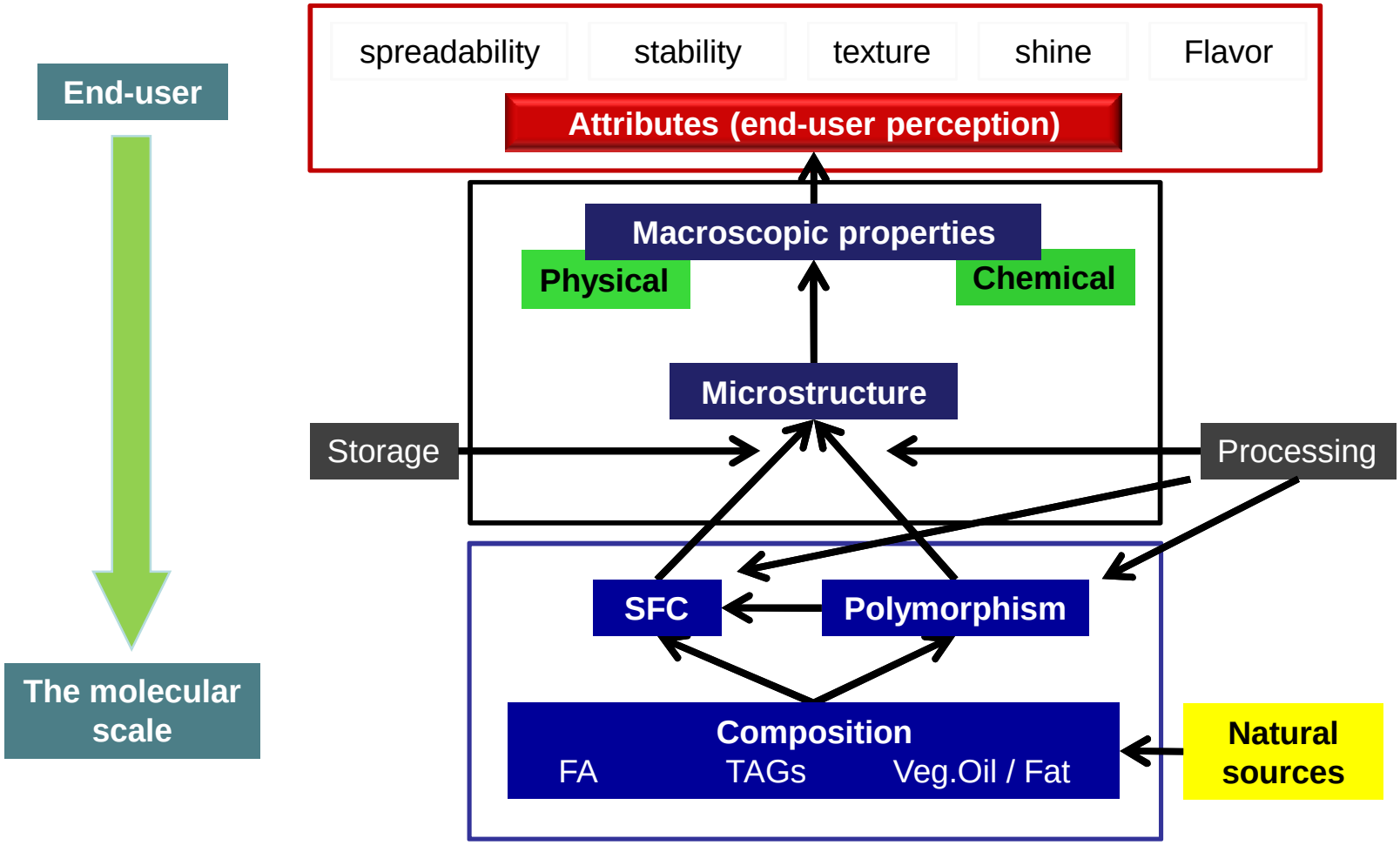
Solid Fat Content: the core property

- **Many evidences that end-user attributes are correlated with Solid Fat Content**



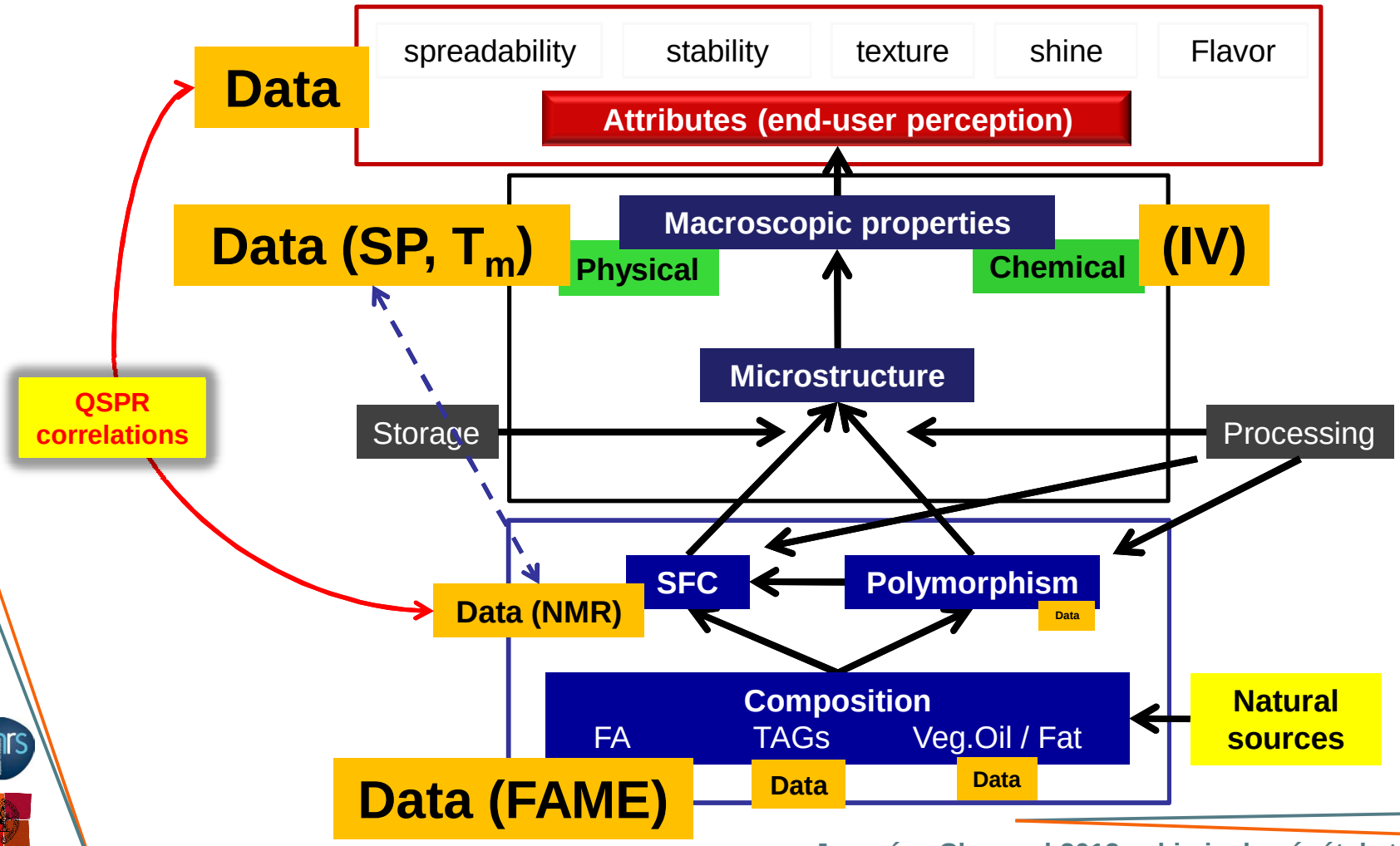
*Flöter**. The role of physical properties data in product development.** Eur. J. Lipid Sci. Technol. 2009, 111, 219–226*

Solid Fat Content: the core property



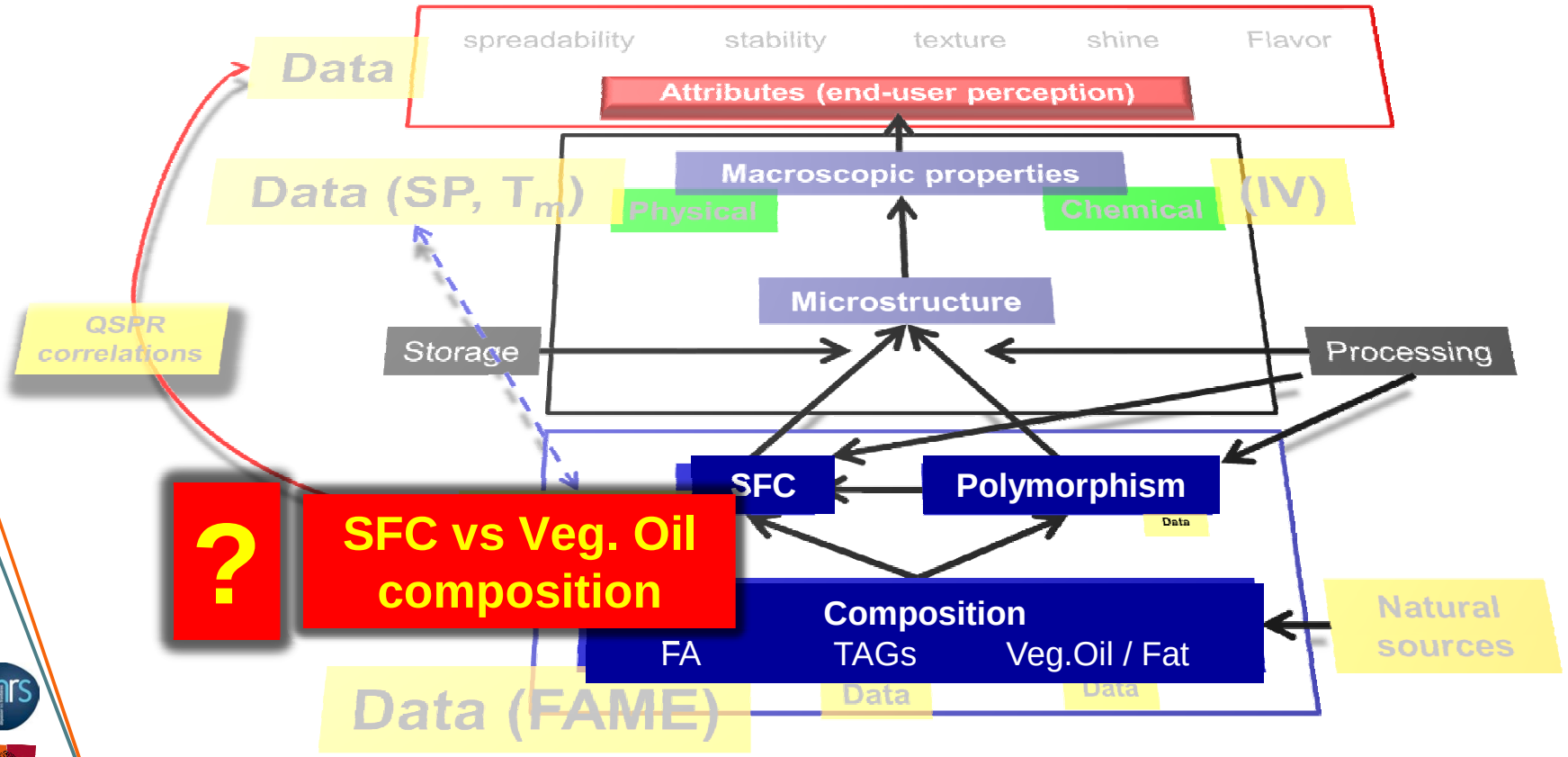
Vegetable Oil modeling

- Datas are not uniform and consistent across the scales.
- Predictive models did not exist so far.



Vegetable Oil modeling

- A predictive model for the missing links:
  - SFC vs Veg. Oil composition
    - *By using FA distribution or TAGs composition*



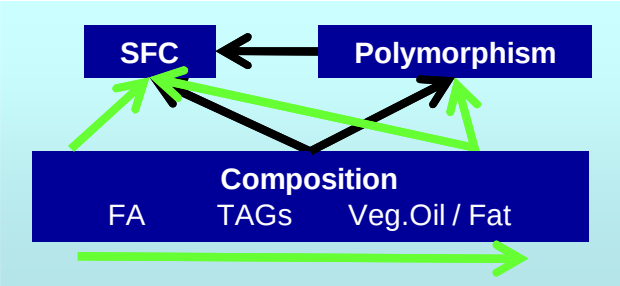
Vegetable Oil modeling

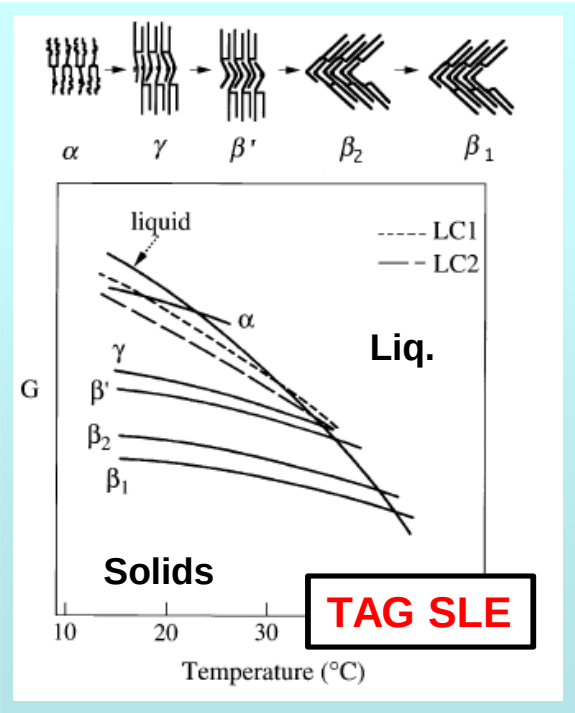
- **Model analysis**
  - **SFC calculation**
    - ***solid – liquid equilibrium (SLE)***
      - **Minimizing the gibbs free energy G**
  - **A very complex mixture pb**
    - ***Veg. Oils blends***

      m' Veg. Oils

      > 95% of n' TAGs

      combination of 3 FA
      - **Each scale give rise to phase diagrams, SFC, DSC**
  - **Polymorphism affects the SLE**



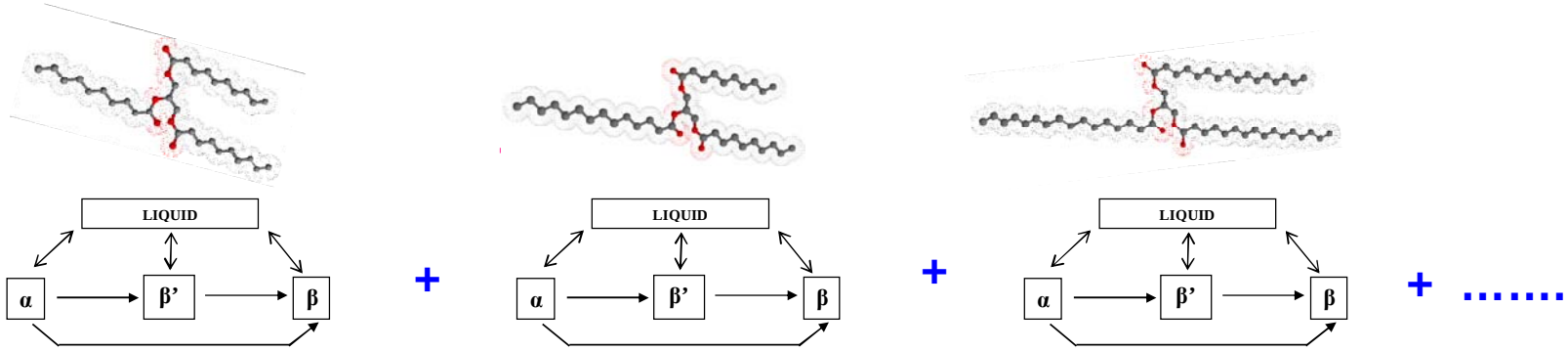


- **The final model must be predictive to help oil blend design**

The SLE model

- Model INPUT:

- **Veg. Oil considered as a mixture of *n'* TAGs**



- **Getting TAGs composition?**
  - ***(rare) from TAGs analysis***
  - ***(frequent) from FA distribution***
    - **from which we generate a probable TAGs distribution…**

- Model OUTPUT:

- **The TAGs distribution among the phases liquid and solids vs temperature**
  - ***Enable to compute SFC and DSC curves***

- Polymorphic solid(s) – liquid equilibrium

$$\min G(n) \quad with \quad G(n) = \sum_{i=1}^{nc} \sum_{j=1}^{np} n_i^j g_i^j(n)$$

$$g^{solid(j)} = RT \sum_{i=1}^{nc} x_i^{solid(j)} \left(\frac{\Delta H_{m,i}^{solid(j)}}{R} \left(\frac{1}{T_{m,i}^{solid(j)}} - \frac{1}{T} \right) + \ln\left(\gamma^{solid(j)} x_i^{solid(j)} \right) \right)$$

Predicted for each phase **Function of TAGs composition**

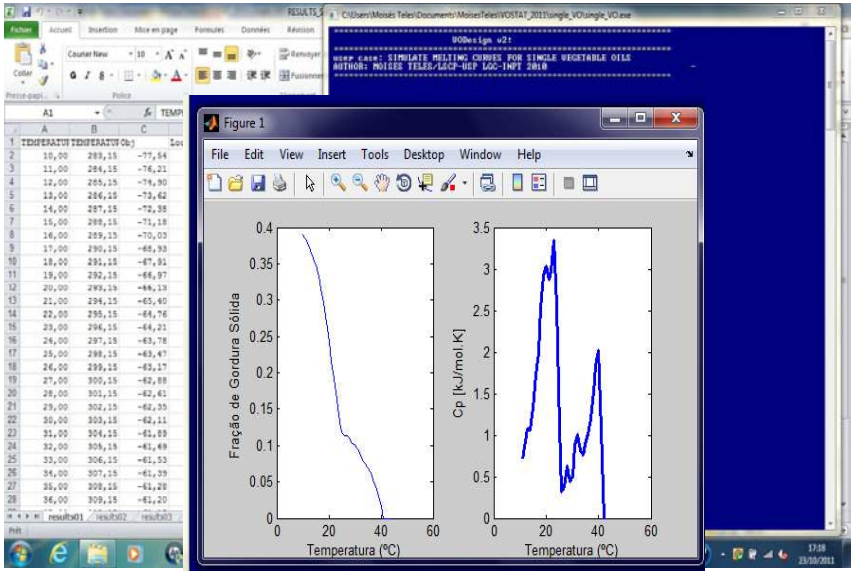
$$\Delta H_m \,\&\, T_m = f(polymorhic, FAtype, FA\ position)$$

$$g^{liquid} = RT \sum_{i=1}^{nc} (x_i^{liquid} \ln x_i^{liquid})$$

- Results:

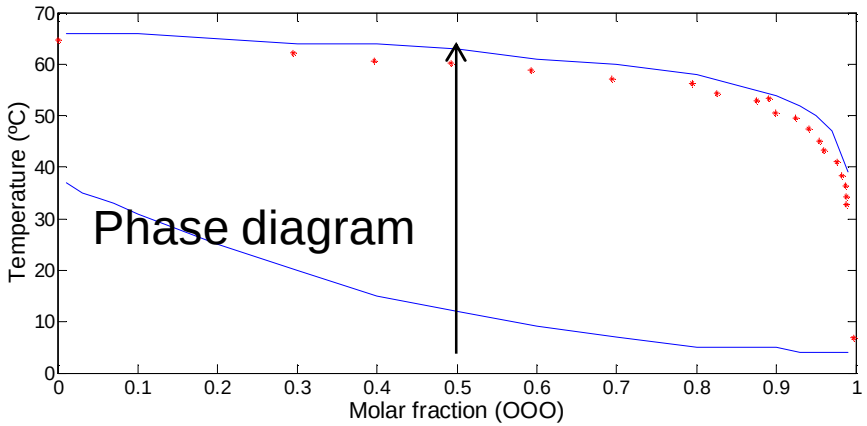
- **Solid Fat Content obtained directly from $n_{TAG}^{phase\ j}$**
- **(equilibrium) DSC curves from:**

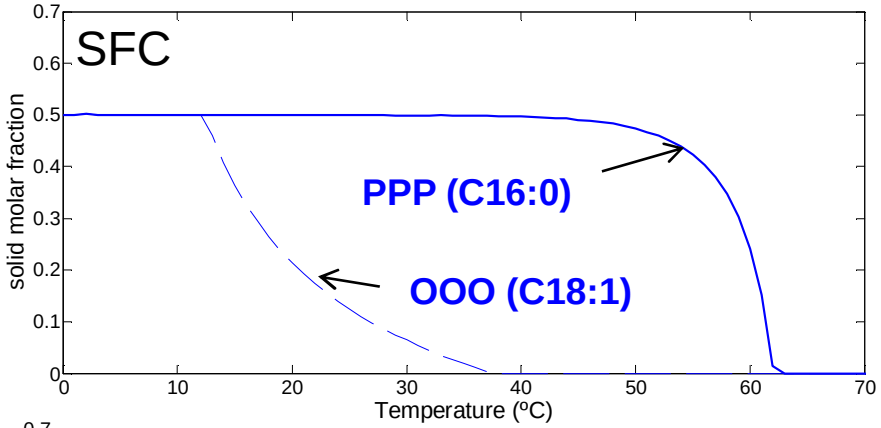
$$C_p^{app} = C_p + \frac{\partial G^E}{\partial T} + \sum_{j=1}^{np} \sum_{i=1}^{nc} \Delta Hm_i^j \frac{\partial n_j^i}{\partial T}$$



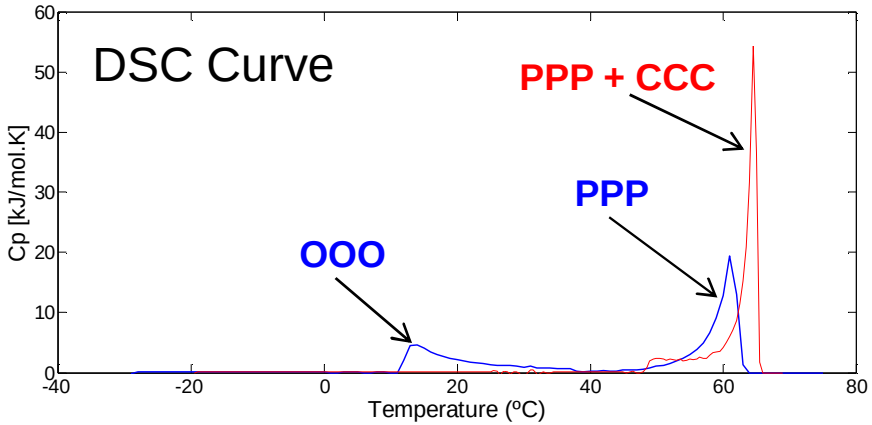
SLE Results: PPP/OOO vs PPP/CCC

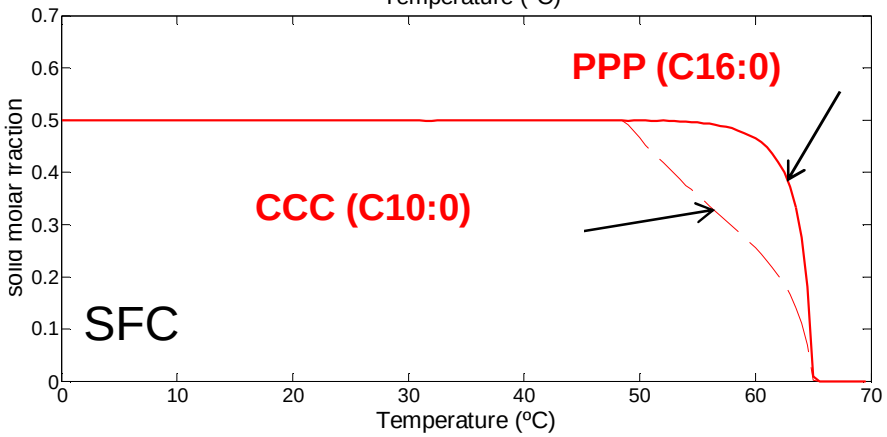
- Molecular size greatly affects crystal lattice and the SLE!





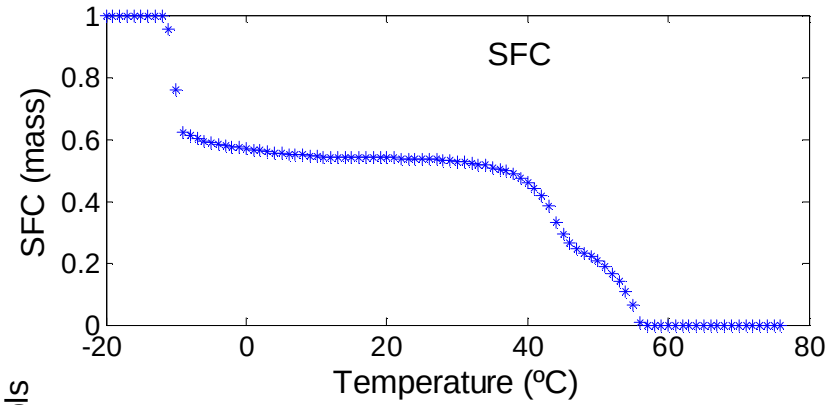
P: palmitic acid (C16:0) /
C: capric acid (C10:0) /
O: oleic acid (C18:1)

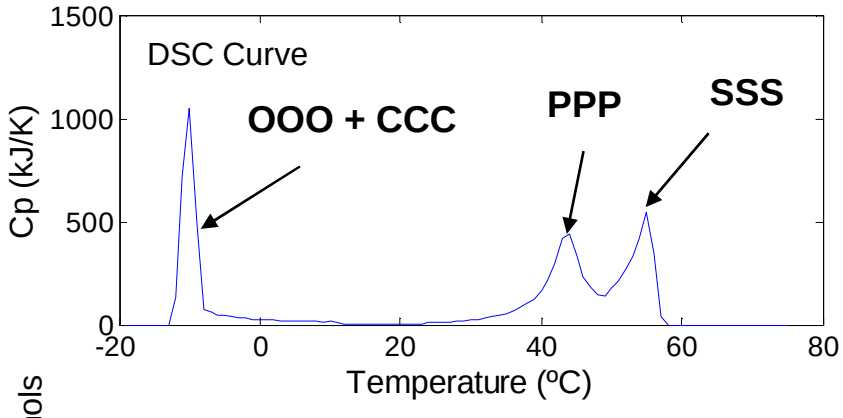


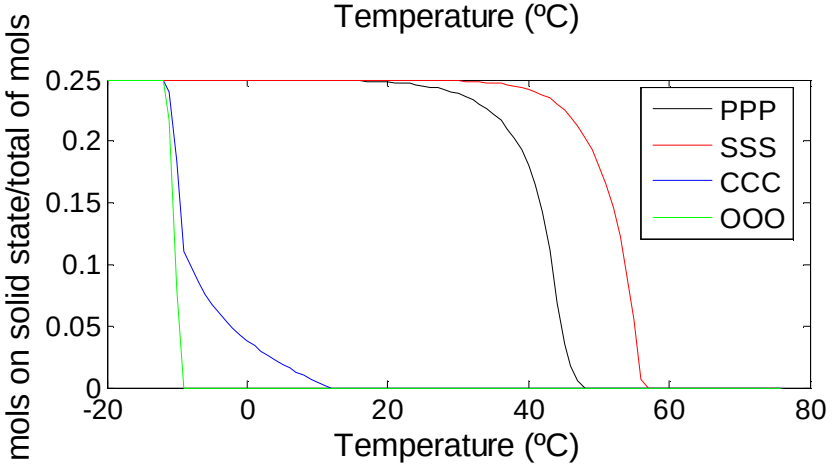


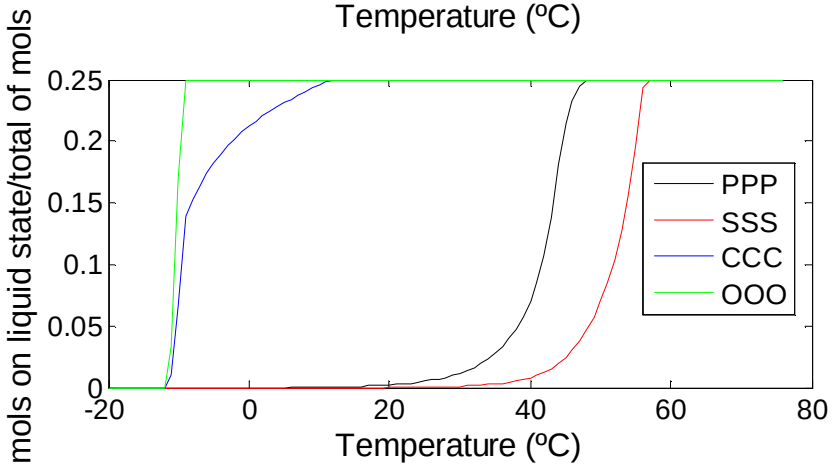
25% OOO 25% CCC 25% PPP 25% SSS mixture

- Capturing the complexity of TAG behavior in mixture







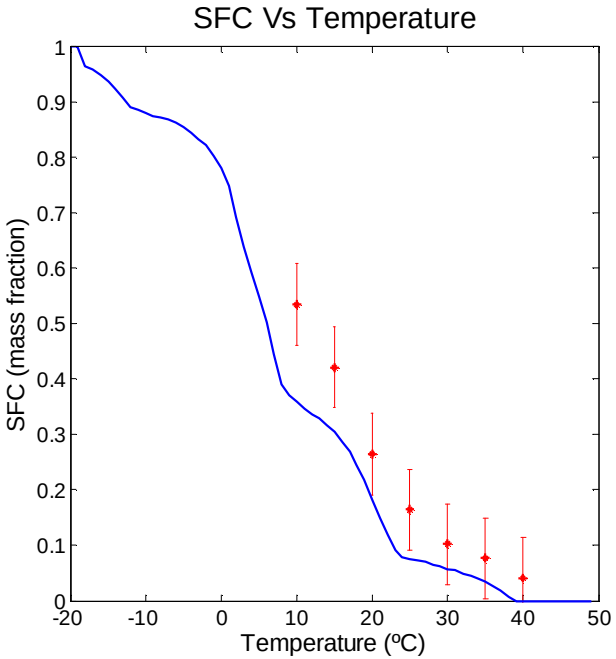


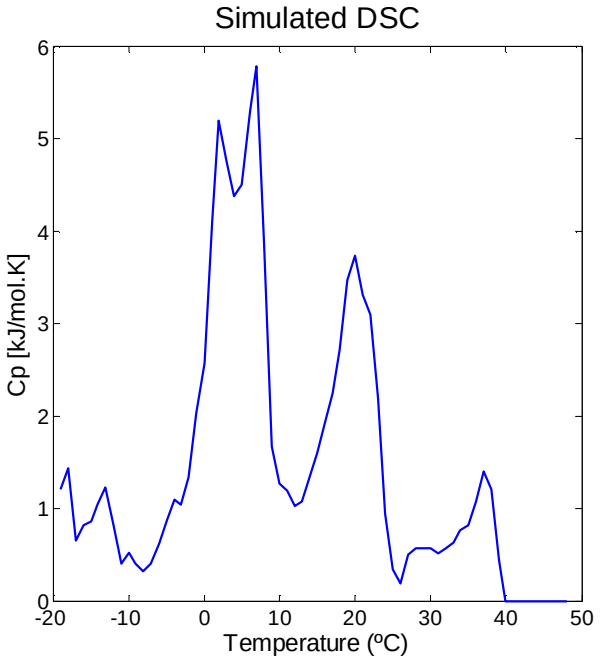
- **OOO and CCC melt together over the same T range**
- **PPP and SSS melt as pure compounds**

P: palmitic acid (C16:0) / S: estearic acid (C18:0) / C: capric acid (C10:0) / O: oleic acid (C18:1)

Veg. Oil: Palm oil

- Palm oil: 17 TAGs.



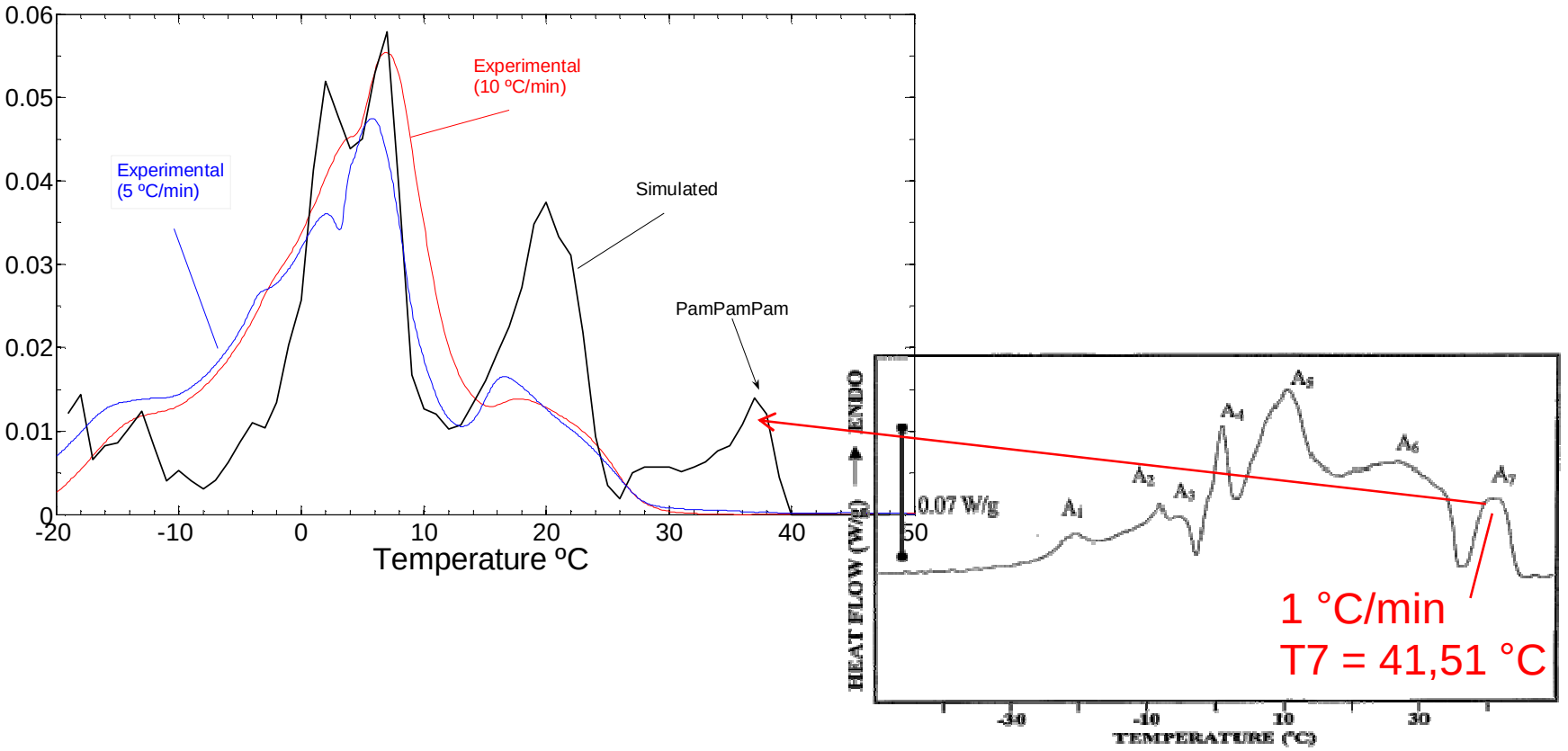


- **Melting Point correctly calculated**
- **Good SFC agreement, considering that we used two incoherent data sources**
  - ***Exp. Data: TAG composition from Sambanthamurthi R et al. (2000)***
  - ***Exp. Data: mean SFC from Lin, S.W. (2002)***

Veg. Oil: Palm oil

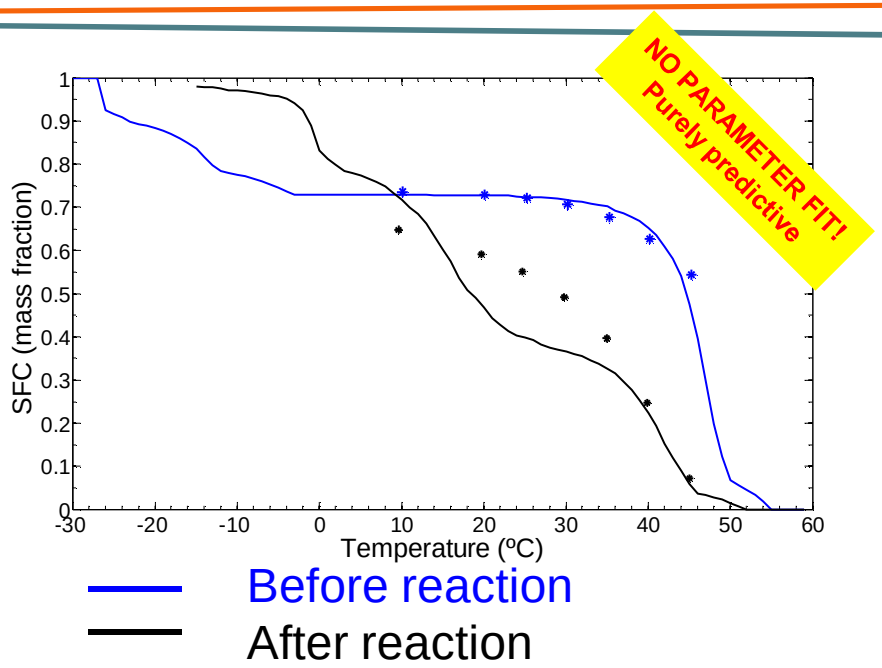
- DSC: temperature profile and main phase transitions

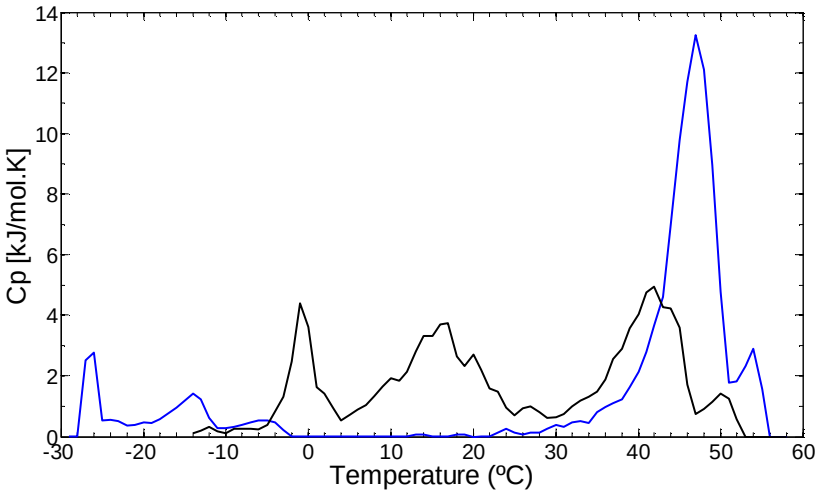
- **We solve S- L Equilibrium = we get equilibrium DSC**
  - ***= DSC with infinitely slow heating rate***



Oil blends and interesterified blends

- **Canola Oil (30%) – Fully Hydrogenated Palm Oil Stearin (70%)**
  - **No reaction:**
    - ***96 TAGs***
  - **After interesterification:**
    - ***162 TAGs***
- **Analysis:**
  - **Both physical & interesterified blends predictions agree with experimental data**
  - **Predicts the trend at lower temperature**
  - **Reaction makes peaks different and broader**





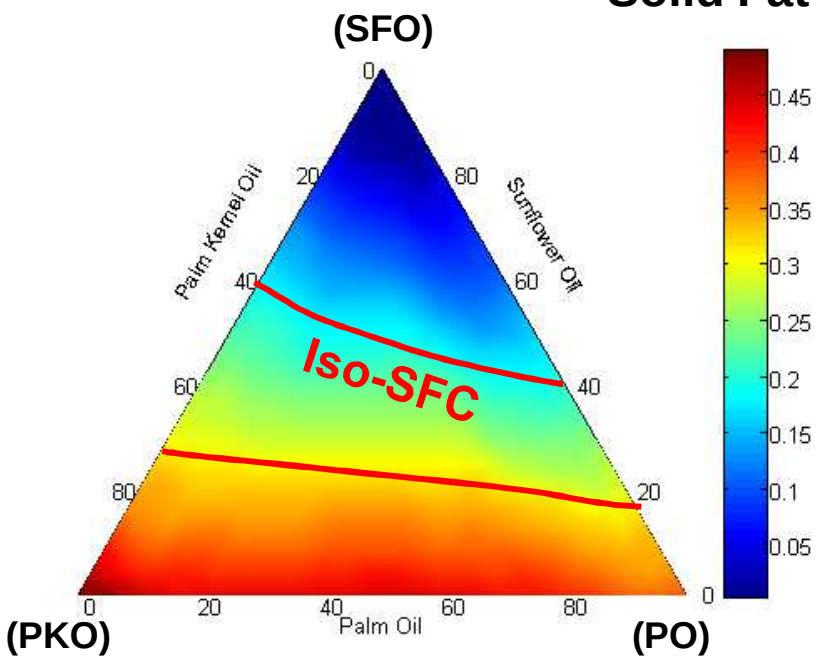
Ternary Veg. Oil blend

- Influence of interesterification

- **SFC is higher when SFO fraction is low**
- **Interesterification greatly reduces the SFC**

Palm Oil (PO)
Sunflower Oil (SFO)
Palm Kernel Oil (PKO)

Solid Fat Content

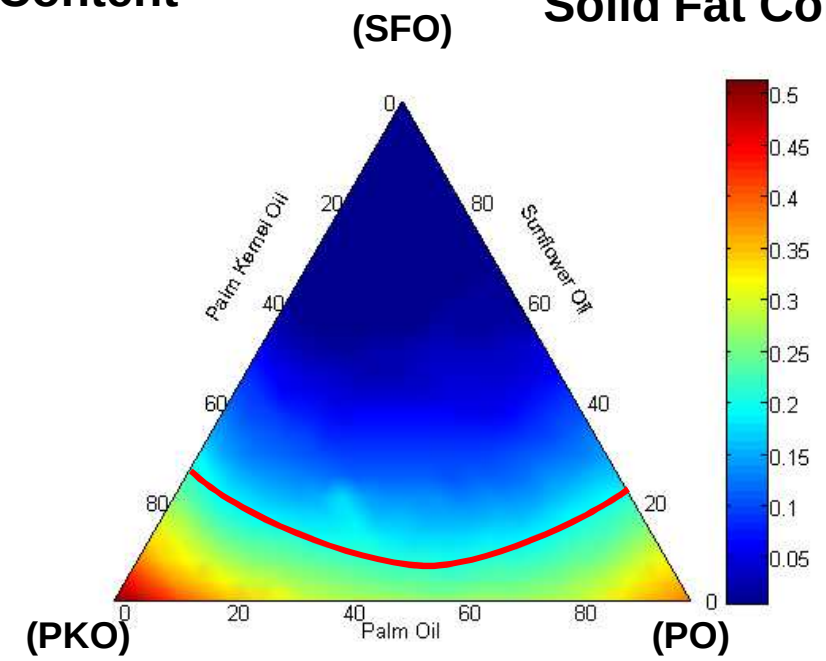


Not interesterified

PREDICTED in 2 hrs

T = 10 ºC

Solid Fat Content

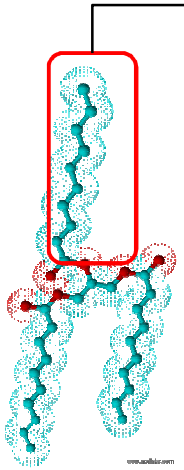


Interesterified

Structured Lipids Application

- Designing functional foods to get nutraceutical benefits

- **ex. DHA enhanced products**



sn2

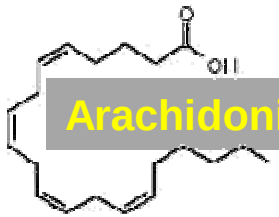
Medium FA

PUFA

Medium FA

	TAG1	TAG2	TAG3	TAG4
sn1	caprylic	caprylic	caprylic	caprylic
sn2	EPA Omega-3	DHA Omega-3	γ-LINOLEIC Omega-6	AA Omega-6
sn3	caprylic	caprylic	caprylic	caprylic

EPA C20:5



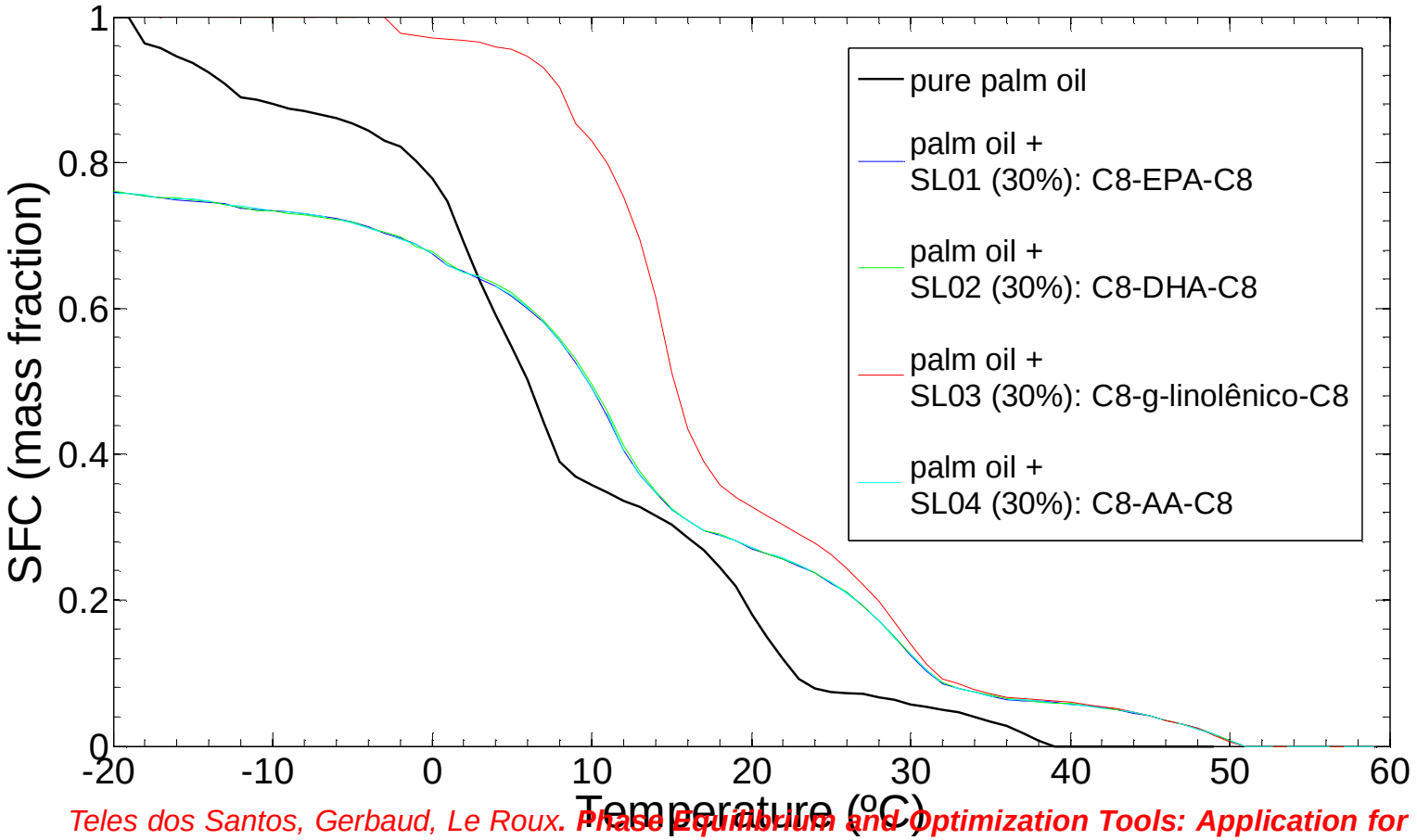
Arachidonic Acid C20:4

γ-linoleic C18:3

DHA C22:6

Structured Lipids Application

- High melting SL affects palm oil initial melting T

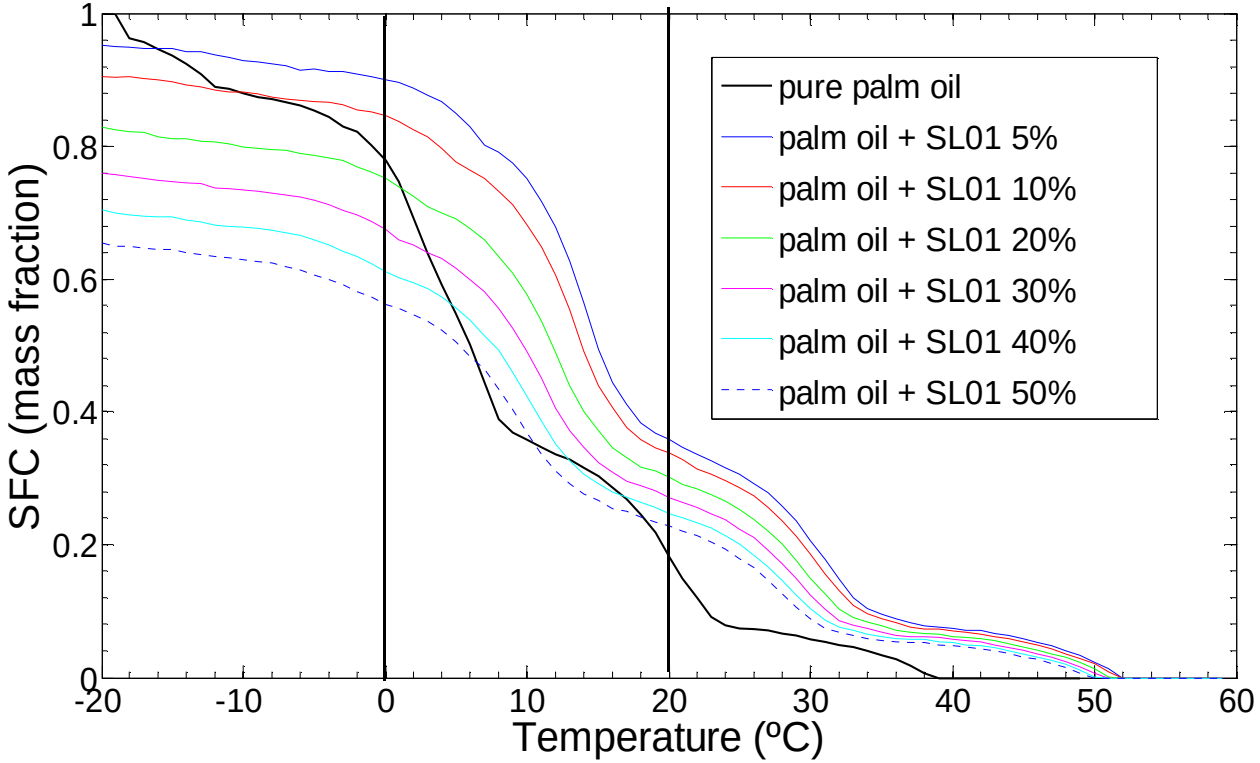


Teles dos Santos, Gerbaud, Le Roux. ***Phase Equilibrium and Optimization Tools: Application for Enhanced Structured Lipids for Foods.*** *J Am Oil Chem Soc (2011) 88:223–233.*

Structured Lipids Application

- The effect on SFC depends on the T range

- Palm oil + (Caprylic – EPA – Caprylic)



Teles dos Santos, Gerbaud, Le Roux. ***Phase Equilibrium and Optimization Tools: Application for Enhanced Structured Lipids for Foods.*** *J Am Oil Chem Soc (2011) 88:223–233.*

Conclusions

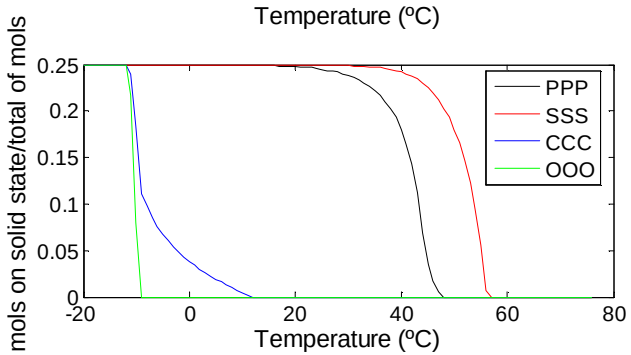
- Computer aided design of oil blends
  - Finding the blend that matches targeted SFC and DSC
  - Objective: to anticipate the most promising lab experiments

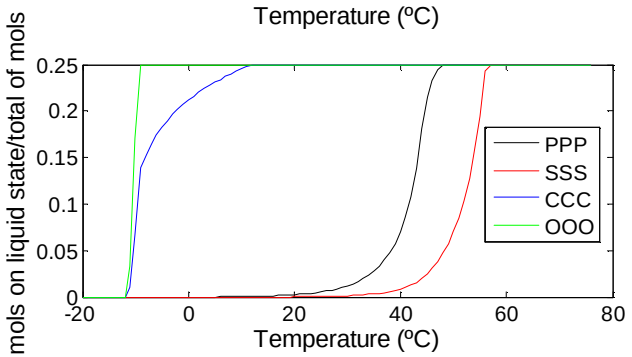
- A knowledge-based predictive model
  - Solid (multi) – liquid equilibrium based model
  - Uses FA distribution or TAGs composition data
    - ***FULLY PREDICTIVE model for SFC & equilibrium DSC curves***
  - Accuracy is good
    - We need coherent TAG & SFC data to prove that it could be even better…
  - Valid for any TAG mixture:
    - ***binary, ternary, vegetable oil, oil blend, interesterified oils blend***
  - Not valid for binary FA mixture

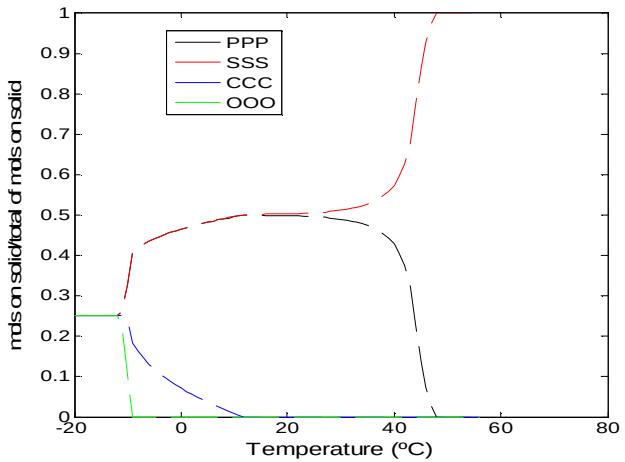
Teles dos Santos, Gerbaud, Le Roux. ***Phase Equilibrium and Optimization Tools: Application for Enhanced Structured Lipids for Foods.*** *J Am Oil Chem Soc (2011) 88:223–233.*

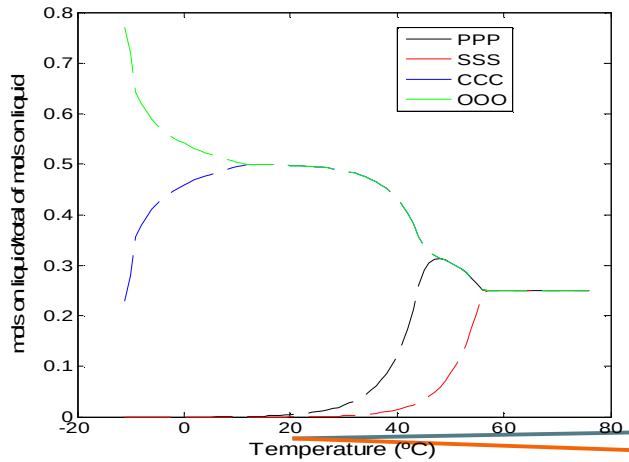
SLE Results: 4 TAGs mixture

- **Composition in each phase**
  - **Solid phase is gradually enriched with SSS;**
  - **OOO fraction gradually decreases in liquid phase**



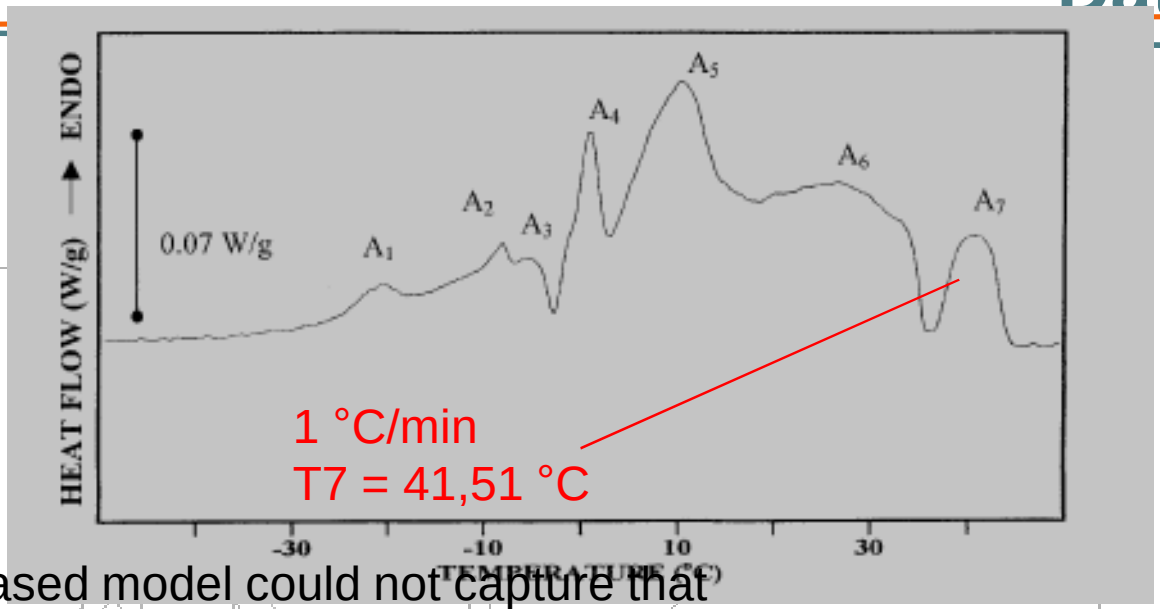






eg - DSC theoretical prediction Vs Experimental Data

- Palm Oil



A FA-based model could not capture that

C.P. Tan, Y.B. Che Man.
Differential scanning calorimetric analysis of palm oil, palm oil based products and coconut oil: effects of scanning rate variation.
Food Chemistry 76 (2002) 89–102

eq - DSC theoretical prediction Vs Experimental Data

	Transition Temperatures (ºC)									
	1		2		3		4		5	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
Peanut Oil	-51,7	nc*	-29,7	-28	-14,57	-11	0,83	2	8,26	7
Grapeseed Oil	-39,32	-40	-31,62	-30	-22,82	-21	-15,12	-15	-	-

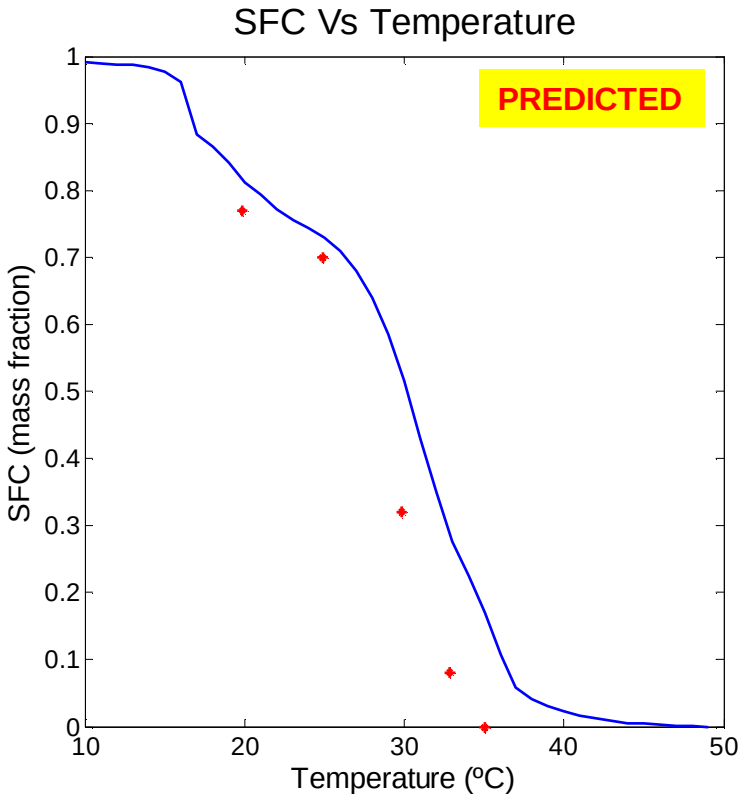
***Exp Data**.: C.P. Tan and Y.B. Che Man **.** Differential Scanning Calorimetric Analysis of Edible Oils: Comparison of Thermal Properties and Chemical Composition. JAOCS, Vol. 77, no. 2 (2000)*

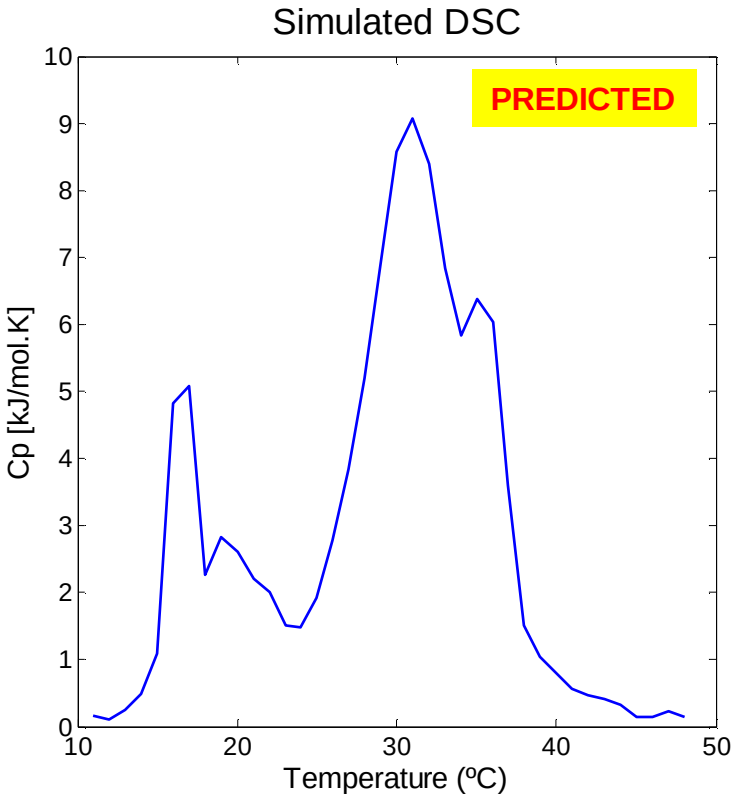
***Calc**.: calculated by VODesign*

**nc*: no convergence*

Single VO: Cocoa Butter

- **Cocoa butter: 12 TAGs.**
  - **High accuracy for lower temperatures**
  - **Shorter melting range corrected detected**
    - ***time elapsed: 26s***

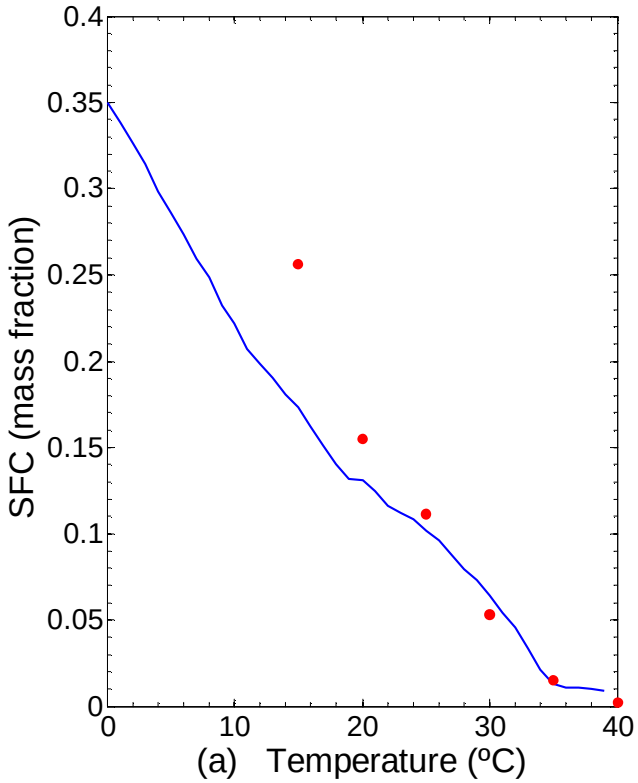


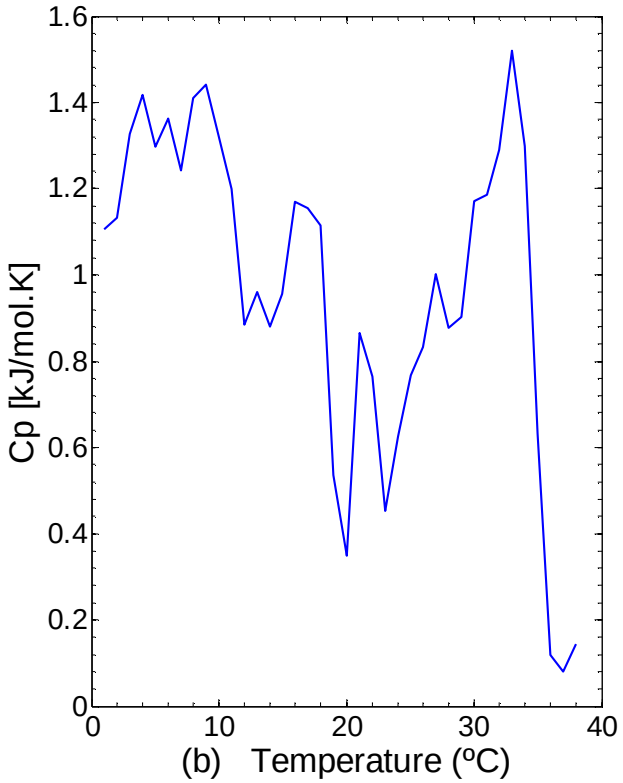


Exp. Data: WON, K. W. THERMODYNAMIC MODEL OF LIQUID-SOLID EQUILIBRIA FOR NATURAL FATS AND OILS. Fluid Phase Equilibria [S.I.], v. 82, p. 261-273, 1993.

Unconventional oils

- **Milkfat – corn oil (80-20) interesterified : 145 TAGs**
  - **Simulated and experimental results in agreement (T > 20 ºC)**
  - **Time: 15 min 37 s**



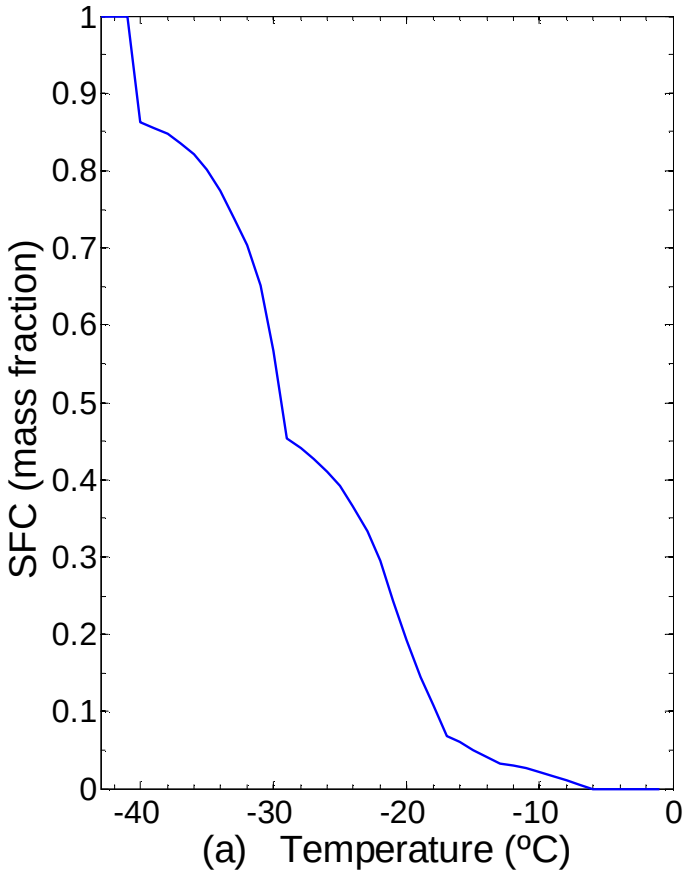


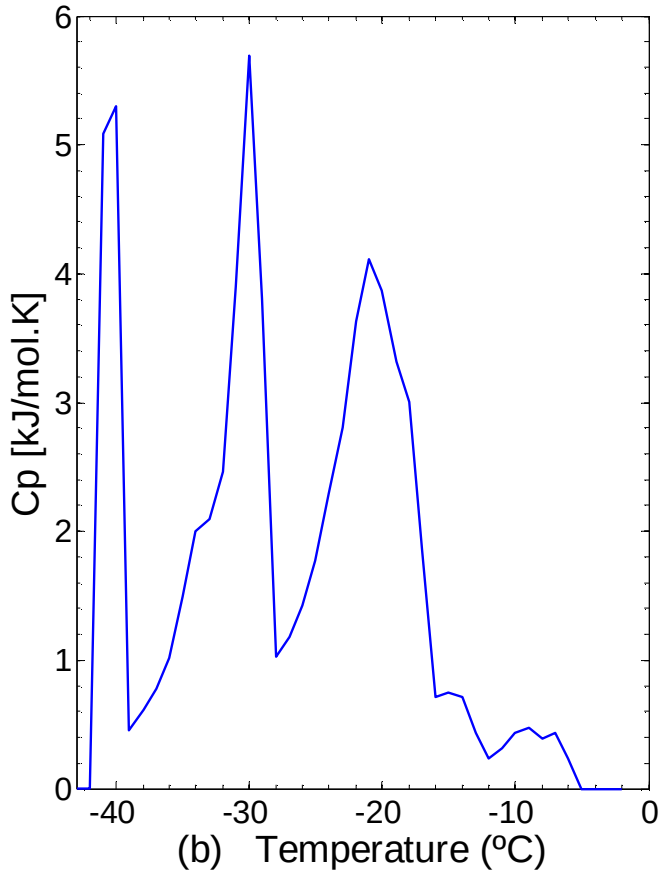
MilkCorn_8020.txt

Exp. Data: RODRIGUES, J. N.; GIOIELLI, L. A. Food Research International, v. 36, n. 2, p. 149-159, 2003.

- Theoretical prediction for value-added vegetable oil

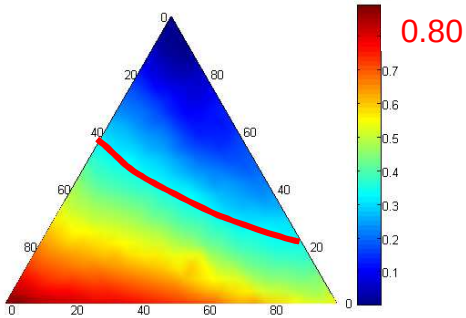
- **Grapeseed Oil: 10 TAGs**



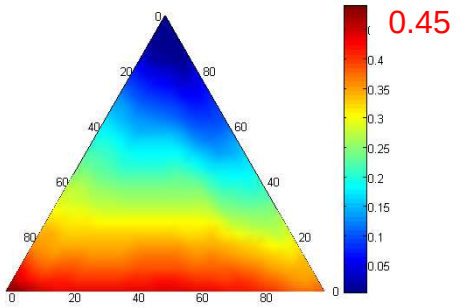


Influence of Temperature: ternary blend not interesterified

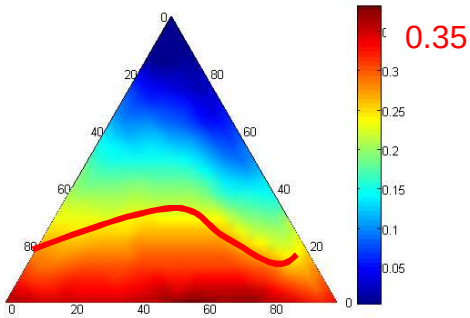
PO–SFO-



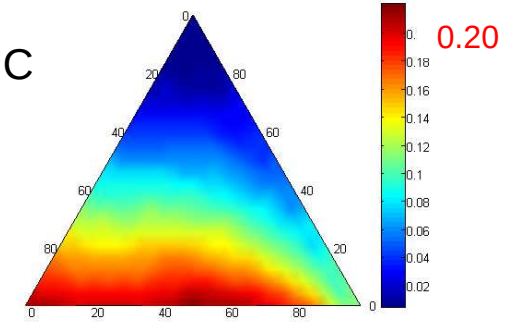
0 °C



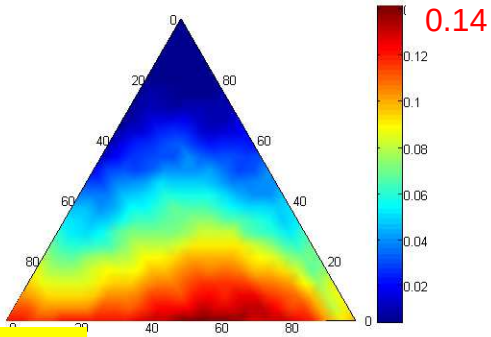
10 °C



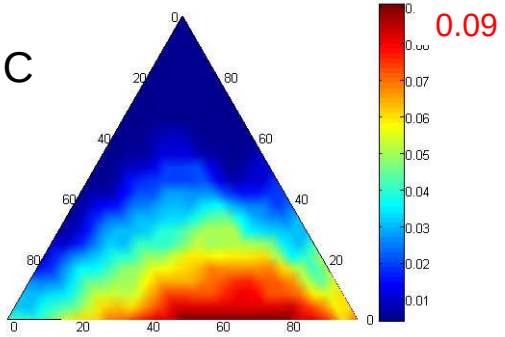
15 °C



25 °C



30 °C

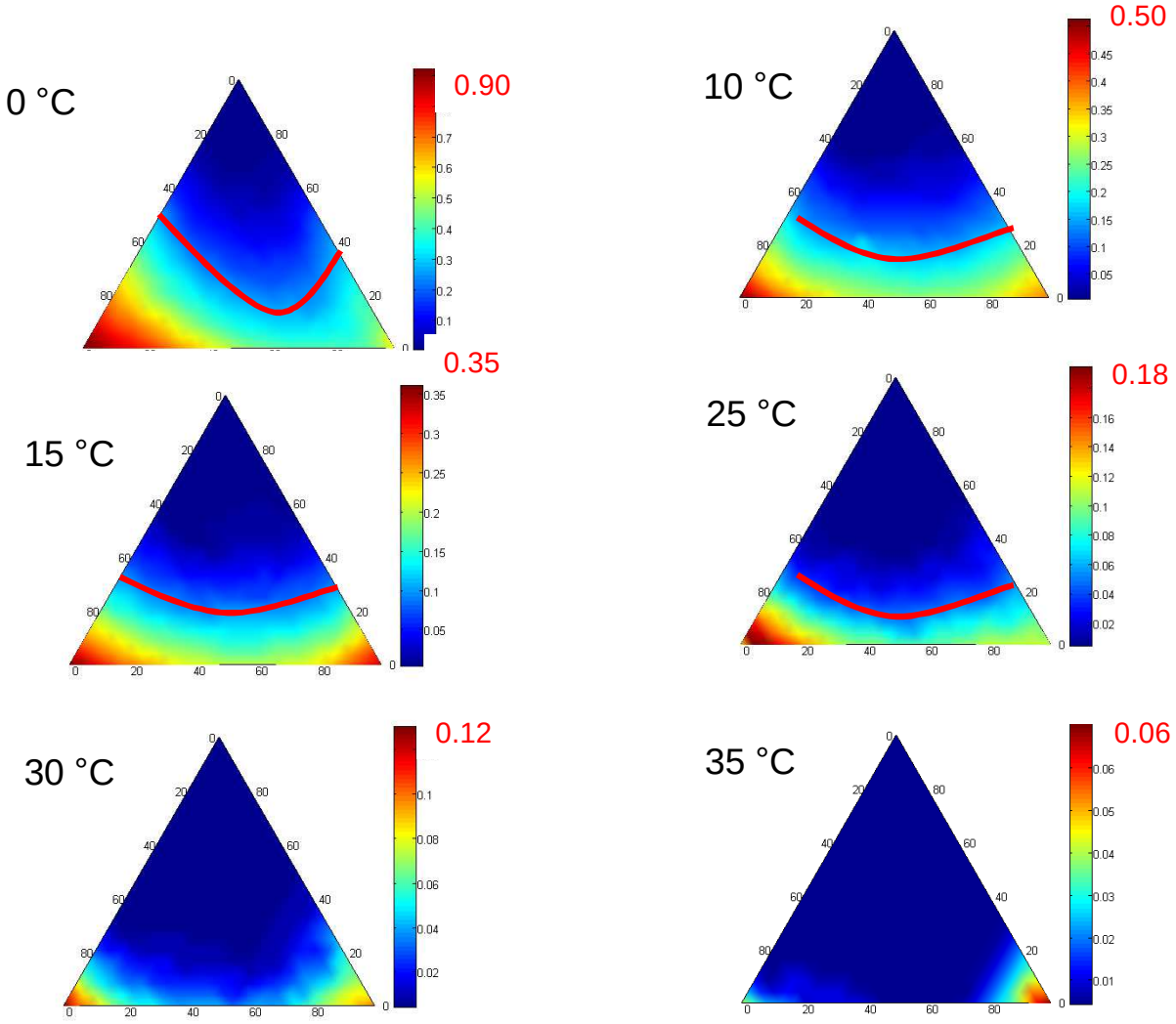


35 °C

PREDICTED

Influence of Temperature: ternary blend interesterified

PO–SFO–PKO



PREDICTED