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Vegetable oil modeling applied for the formulation of structured lipids

Vincent Gerbaud, Moises Teles dos Santos, Galo Carrillo Le Roux

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Vegetable oil modeling applied for the formulation of structured lipids

Vincent Gerbaud

Laboratoire de Génie Chimique, Toulouse



Moises Teles Dos Santos, Galo Carillo Le Roux

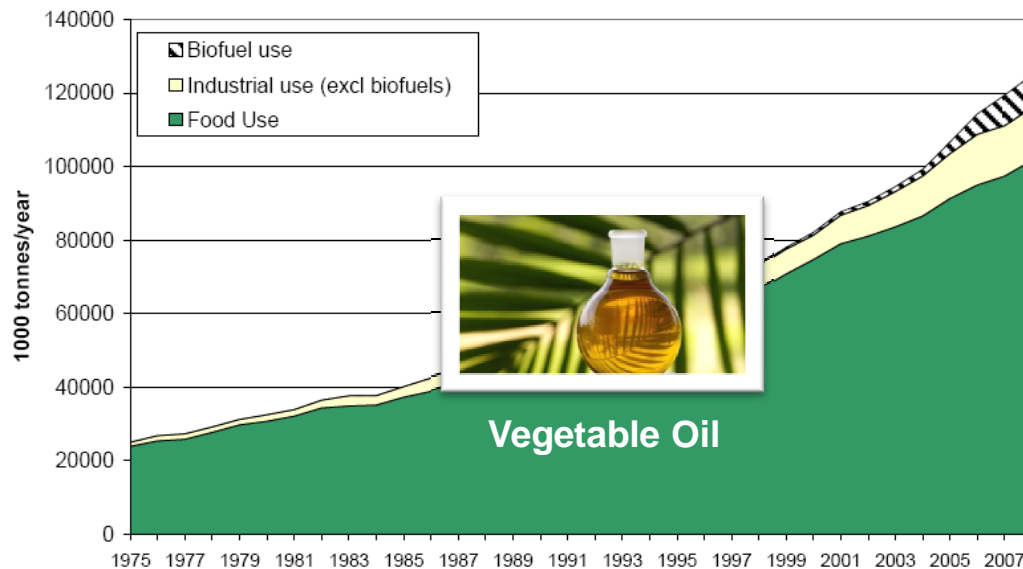
Universidade de Sao Paulo (Brasil)



Journées Chevreul 2012 : chimie du végétal et lipochimie

- 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

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



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

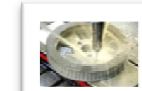
Our model concerns food & industrial uses



Solvents



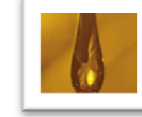
Waxes



Cutting fluids



Cosmetics



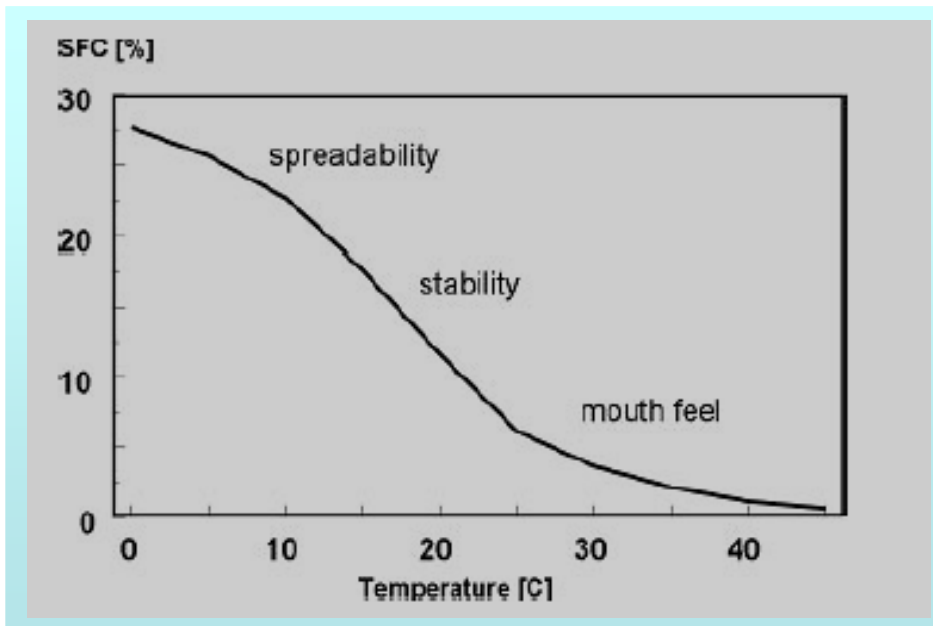
Lubricants



Foods

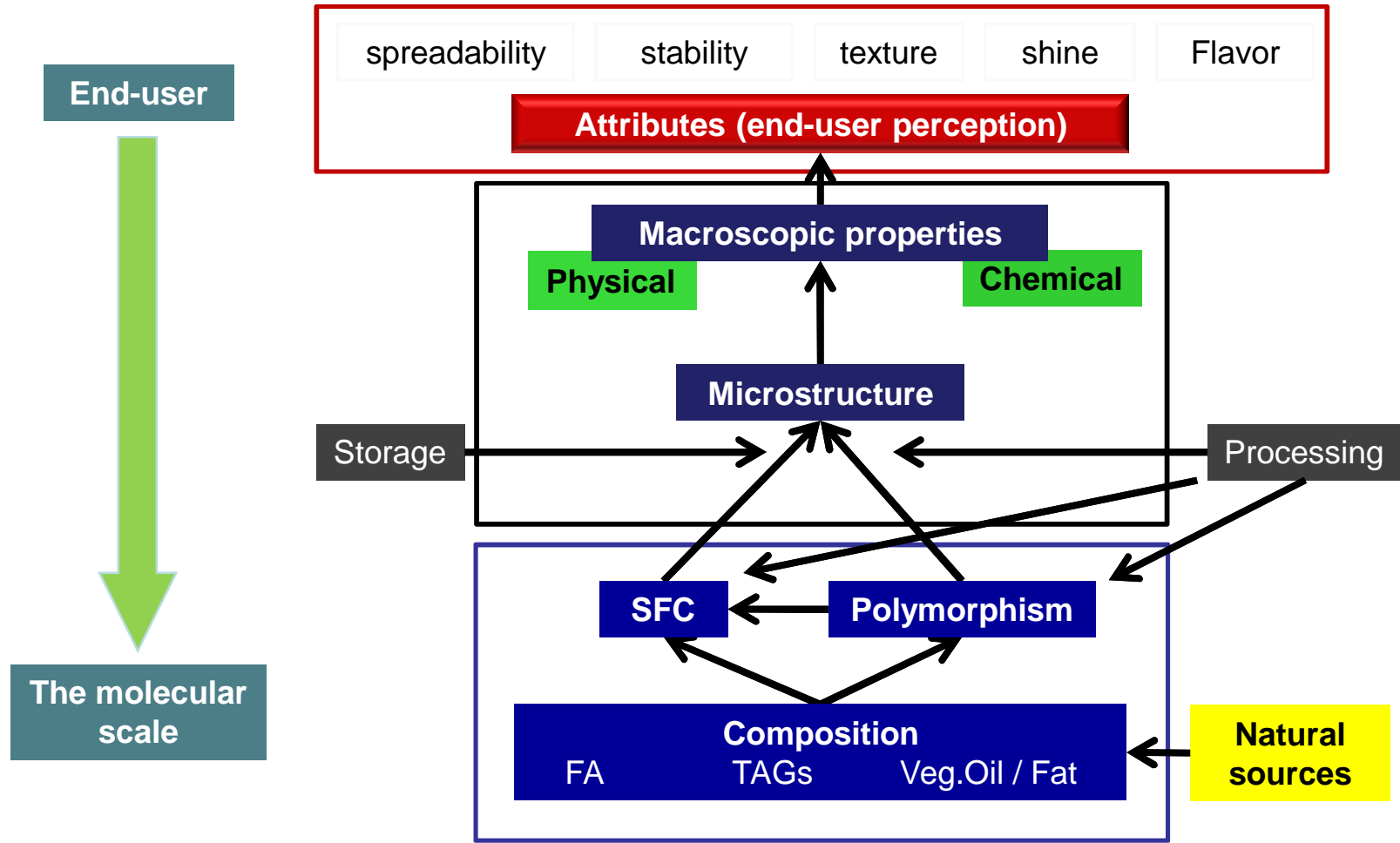
Solid Fat Content: the core property

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

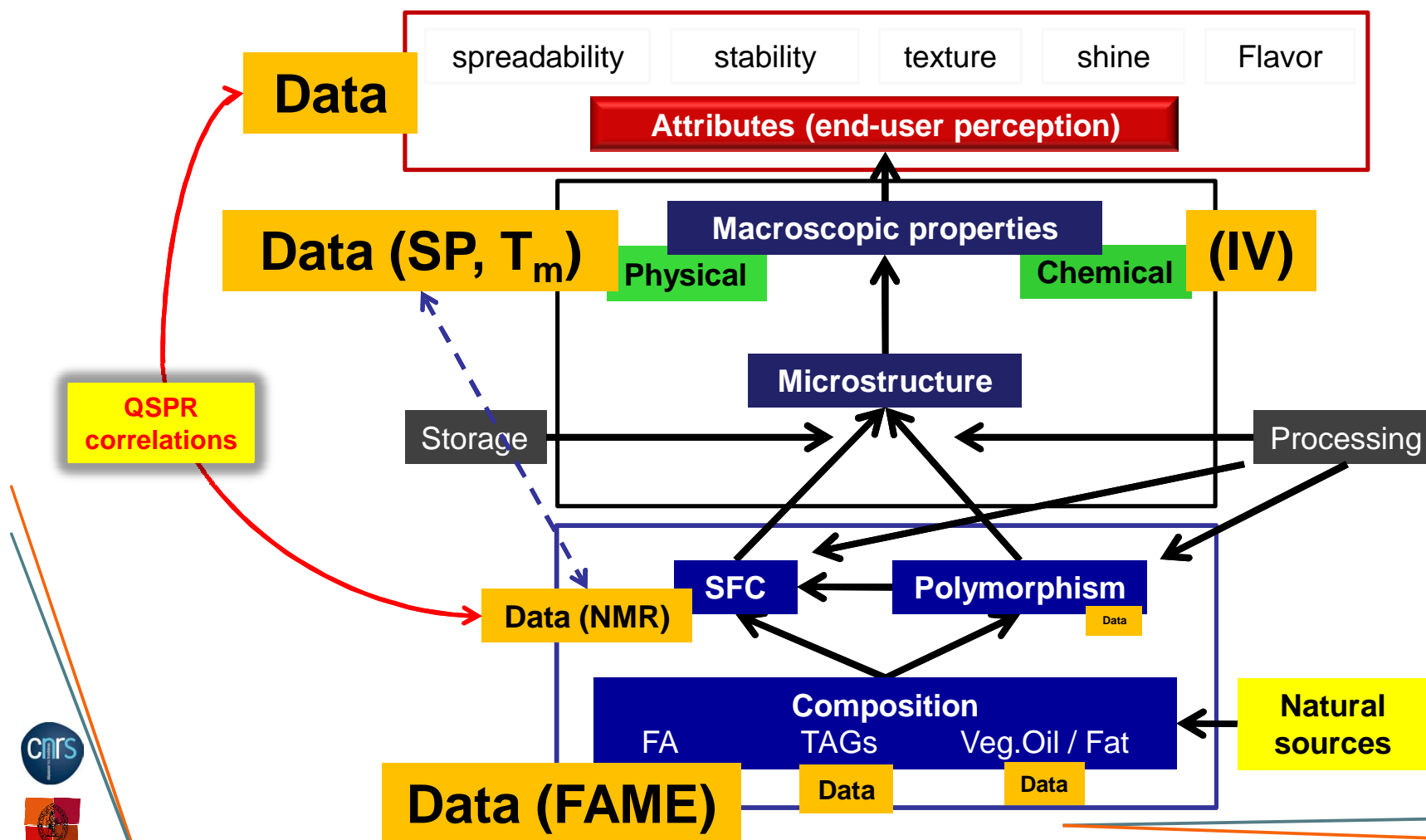


Flöter. The role of physical properties data in product development. Eur. J. Lipid Sci. Technol. 2009, 111, 219–226

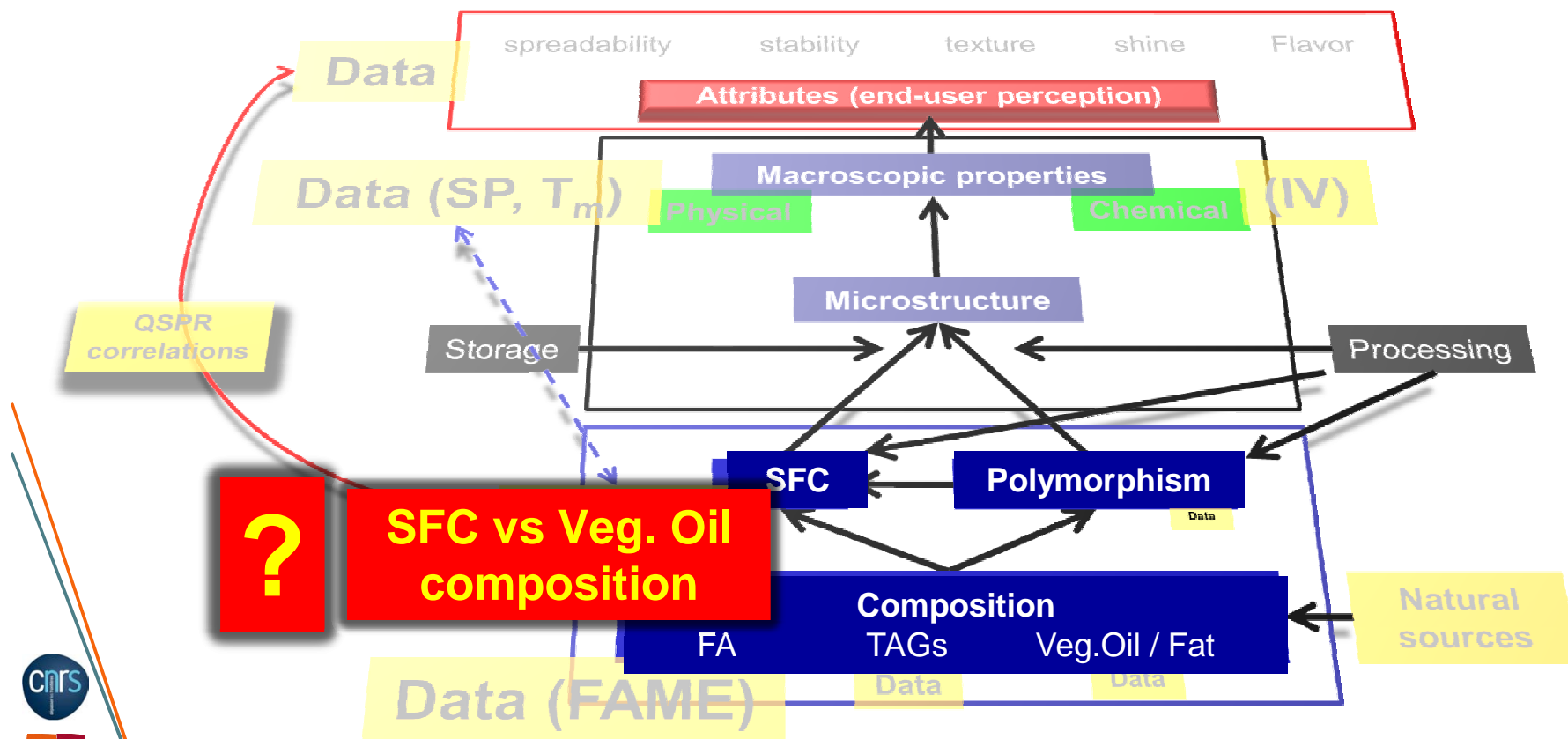
Solid Fat Content: the core property



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

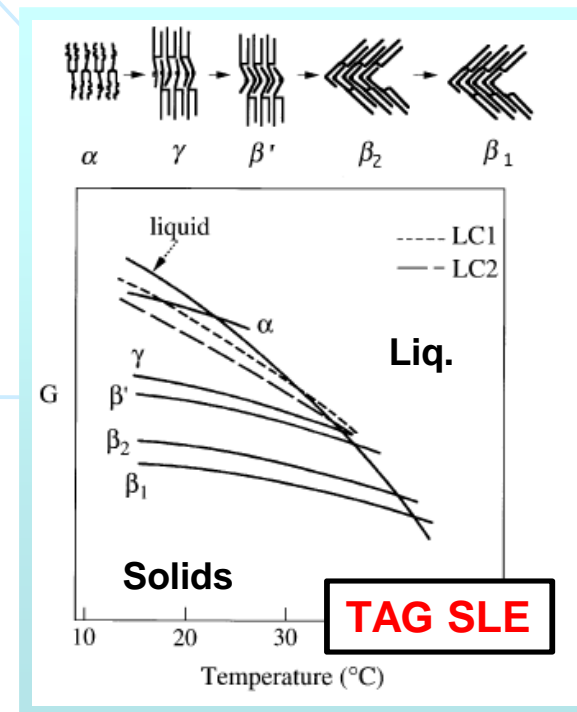
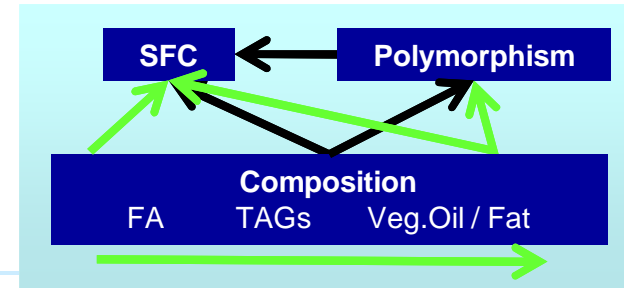


- - A predictive model for the missing links:
 - SFC vs Veg. Oil composition
 - *By using FA distribution or TAGs composition*



- 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

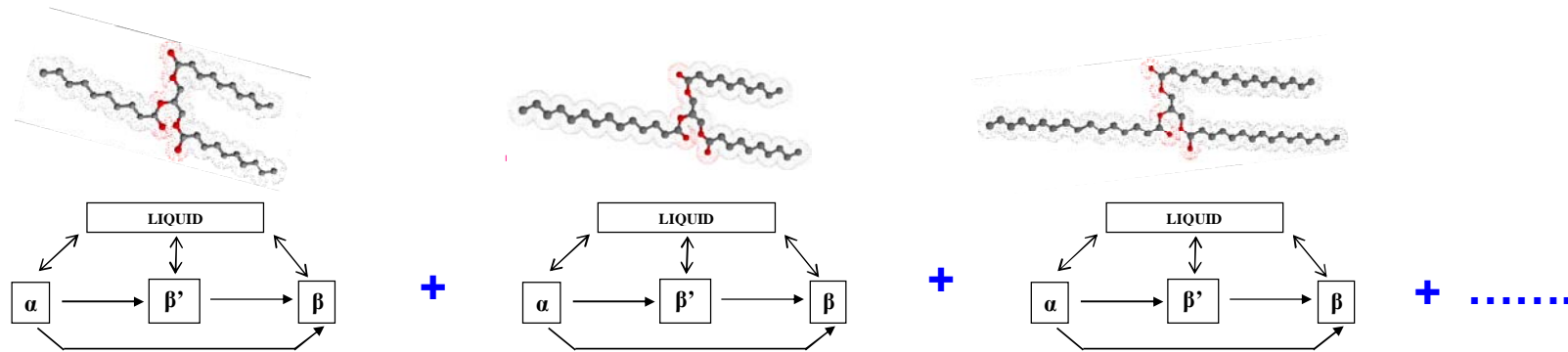


- **Polymorphism affects the SLE**

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

- 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

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

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

Predicted for each phase Function of TAGs composition

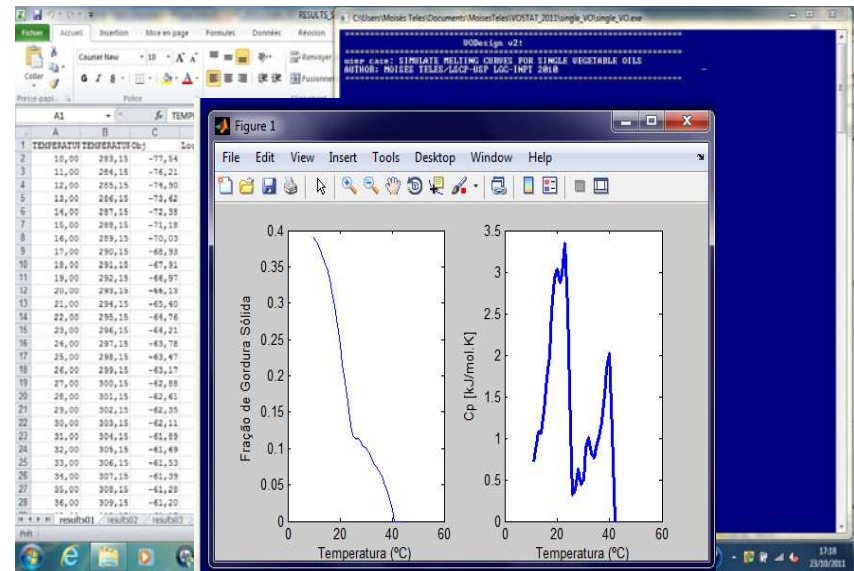
ΔH_m & $T_m = f(\text{polymorphic, FA type, FA position})$

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

Results:

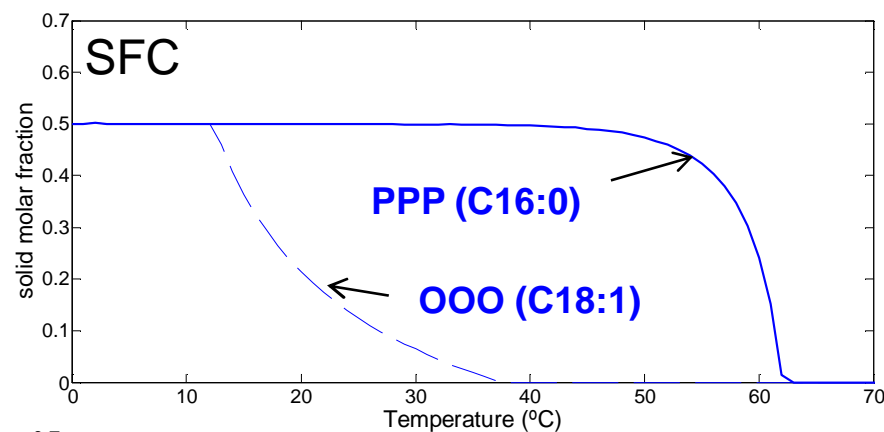
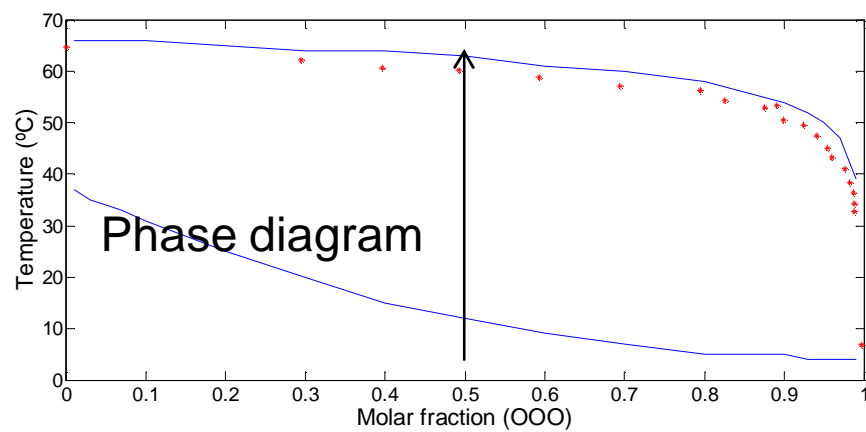
- Solid Fat Content obtained directly from $n_{TAG}^{phase j}$
- (equilibrium) DSC curves from:

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

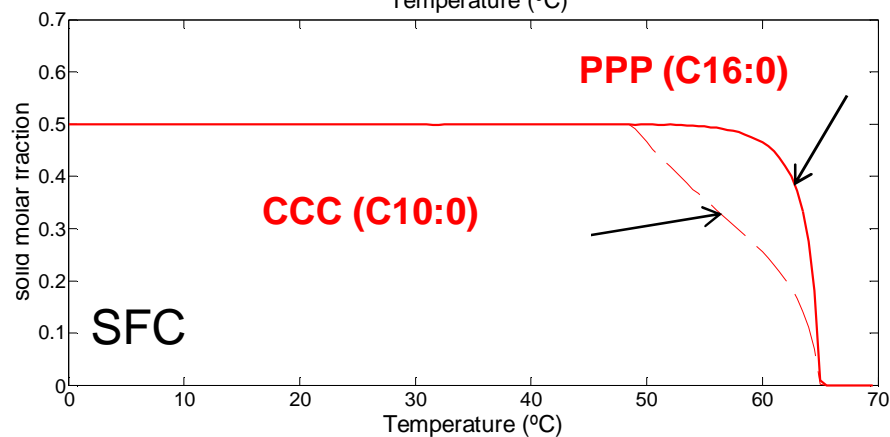
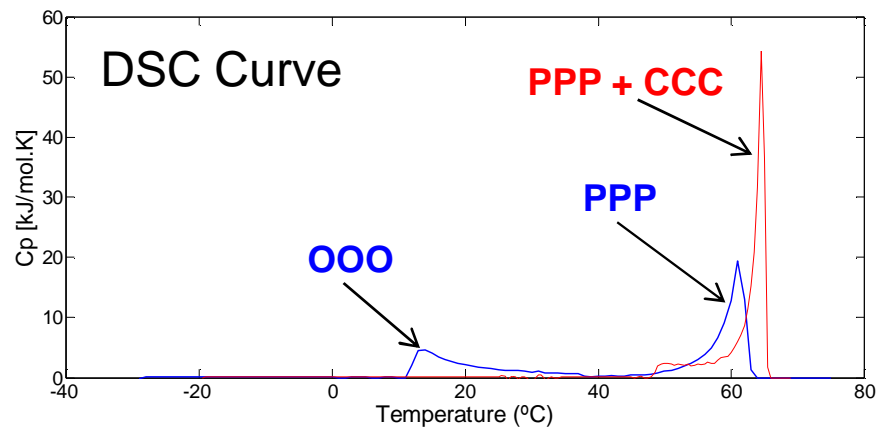


SLE Results: PPP/000 vs PPP/CCC

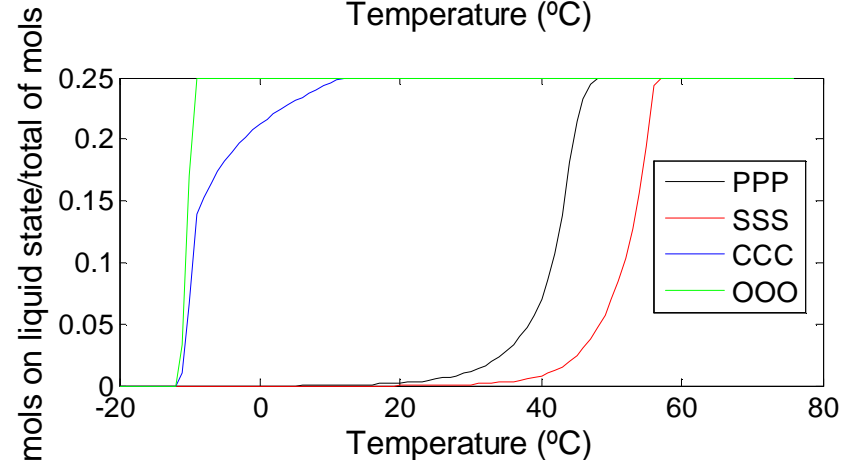
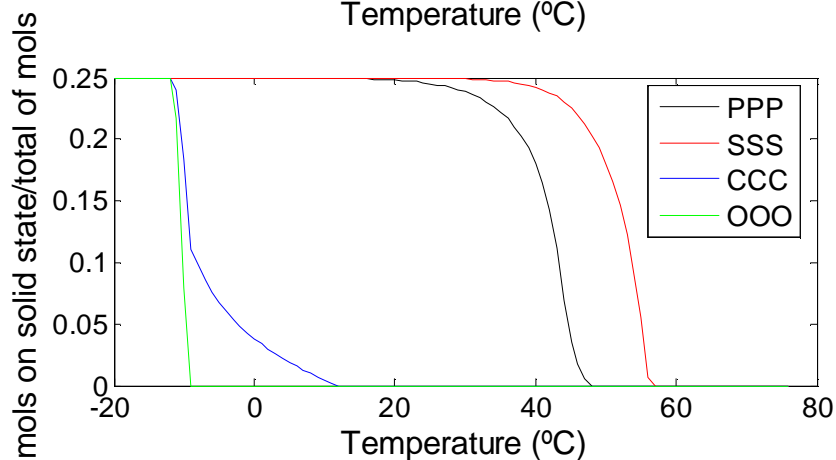
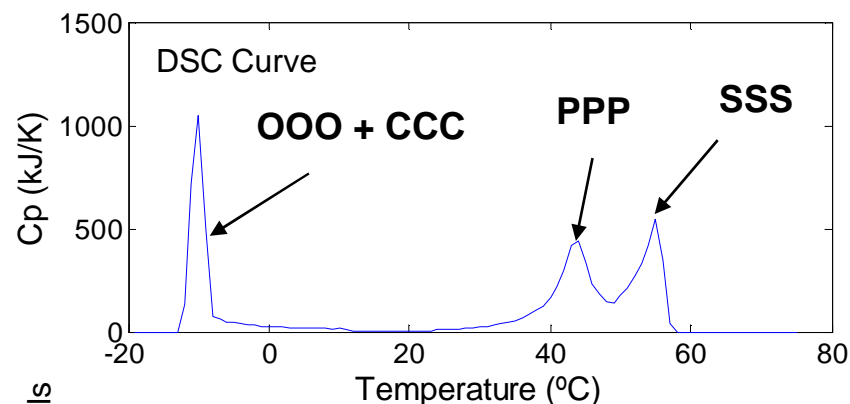
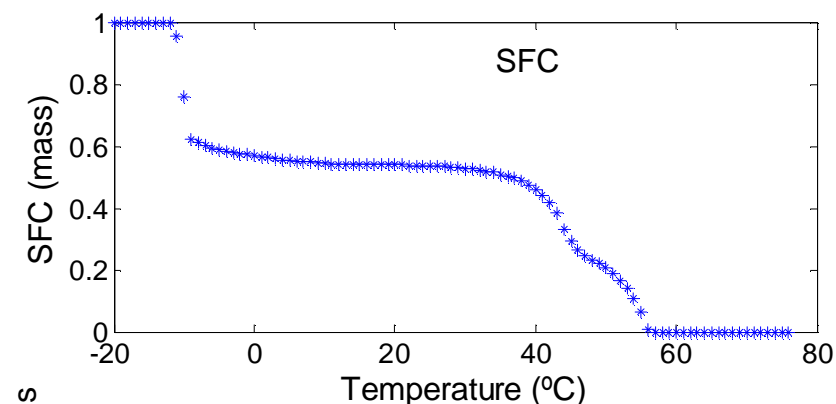
- Molecular size greatly affects crystal lattice and the SLE!



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



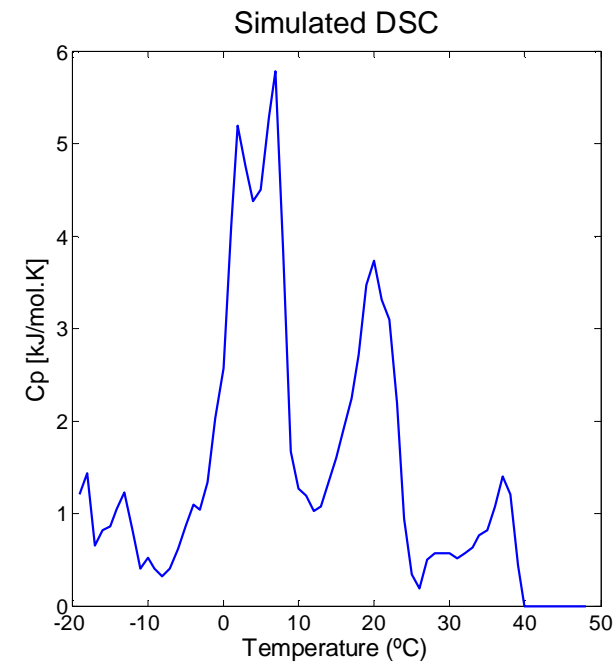
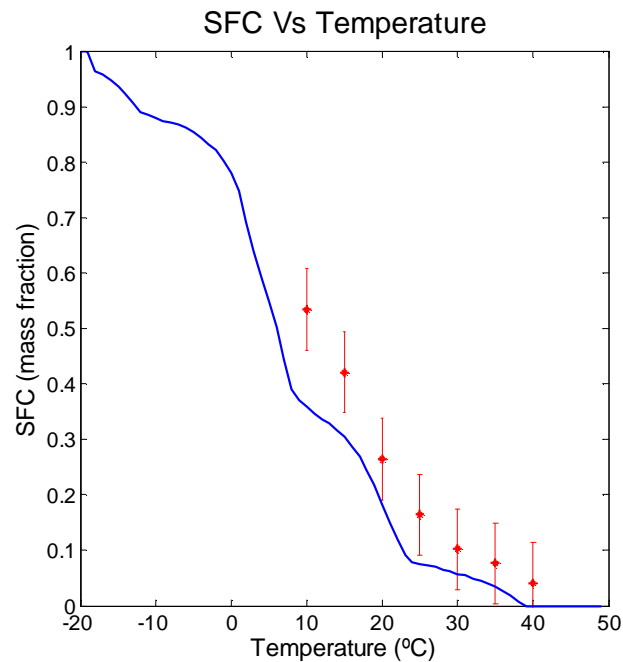
- Capturing the complexity of TAG behavior in mixture



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

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

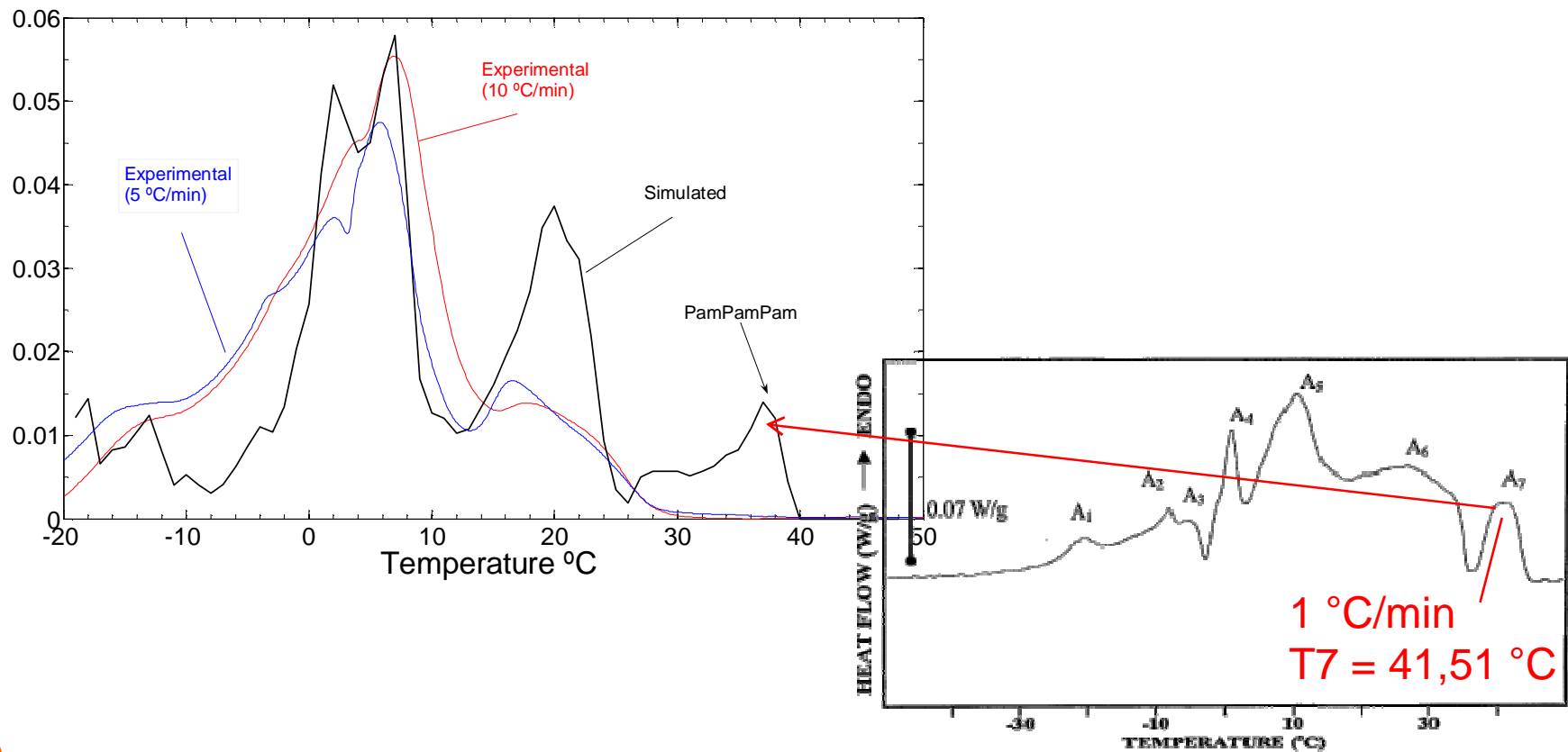
- Palm oil: 17 TAGs.



- **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)*

DSC: temperature profile and main phase transitions

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

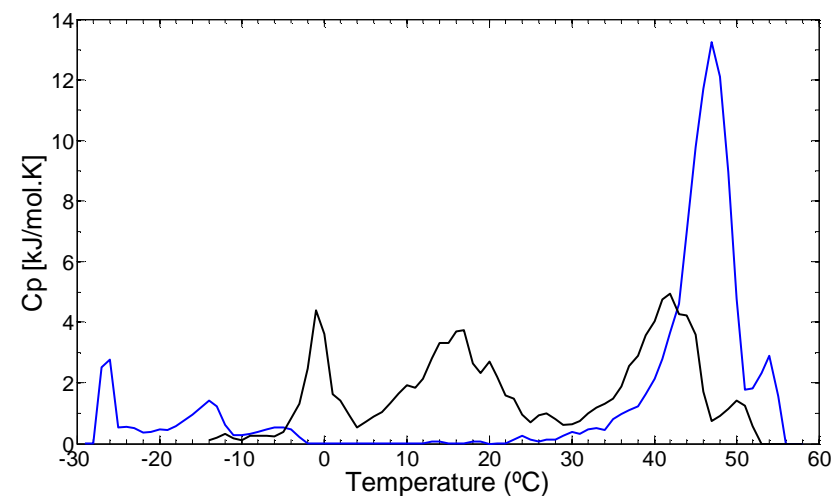
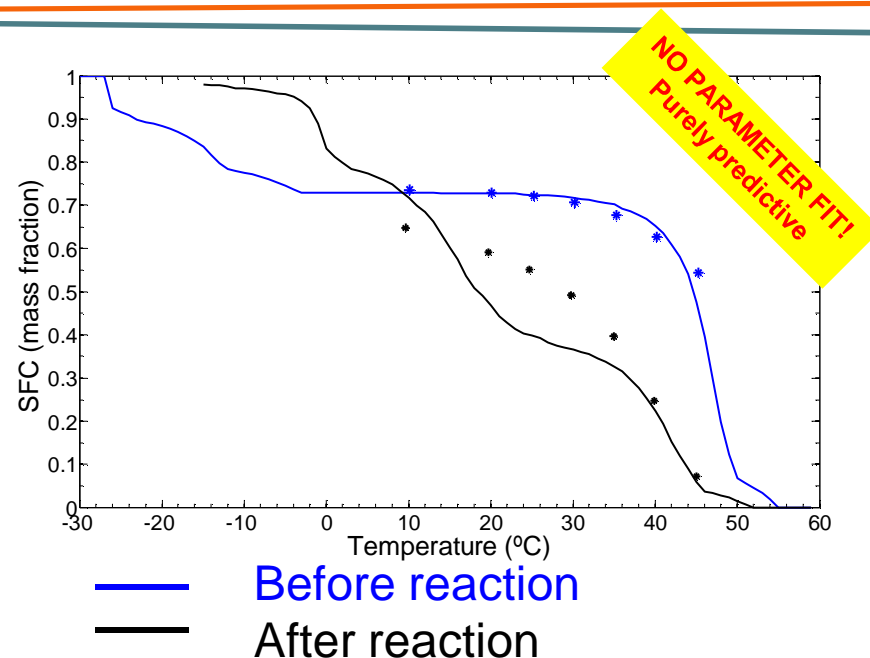


- Canola Oil (30%) – Fully Hydrogenated Palm Oil Stearin (70%)

- **No reaction:**
 - **96 TAGs**
- **After interesterification:**
 - **162 TAGs**

- Analysis:

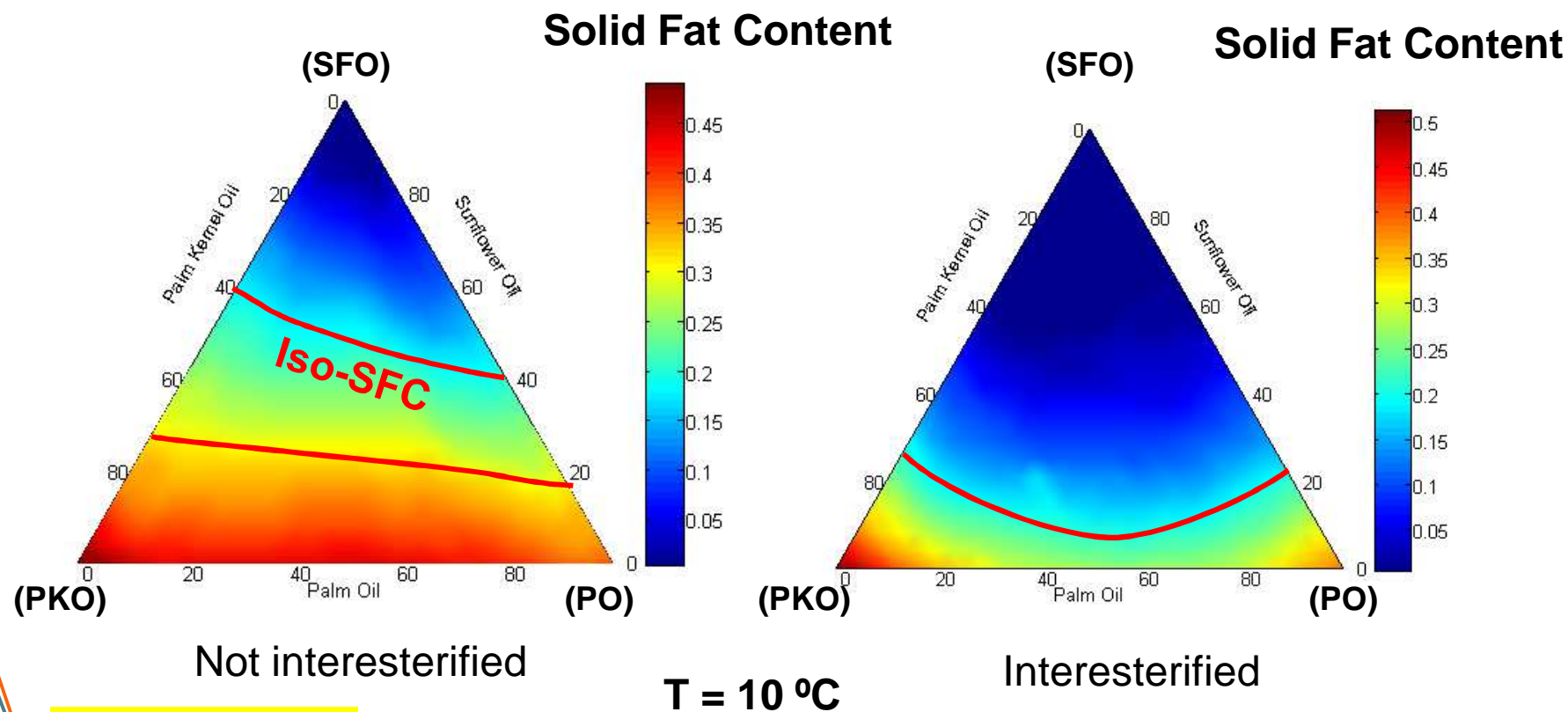
- **Both physical & interesterified blends predictions agree with experimental data**
- **Predicts the trend at lower temperature**
- **Reaction makes peaks different and broader**



- 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)

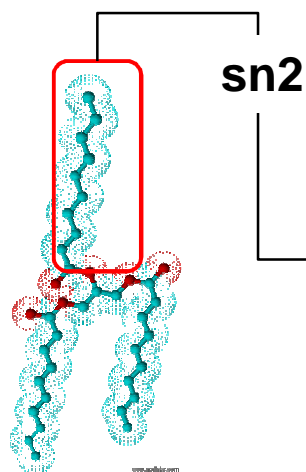


PREDICTED in 2 hrs

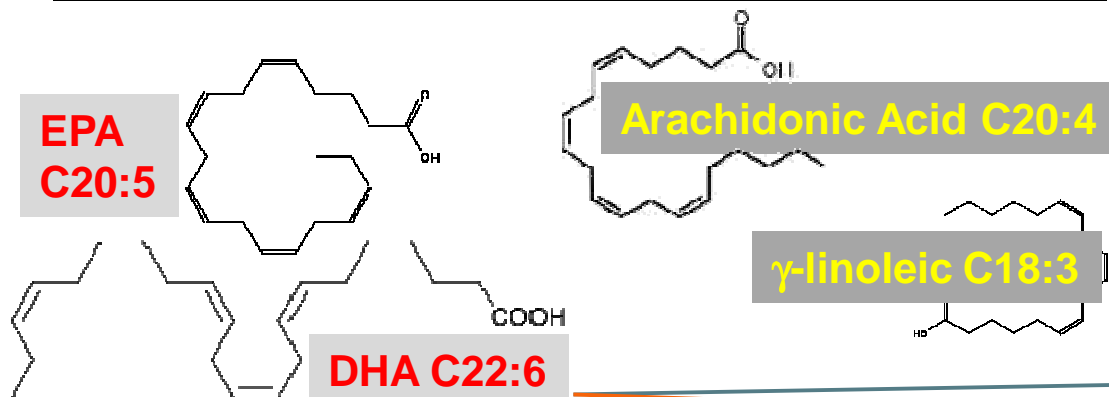
Structured Lipids Application

□ - Designing functional foods to get nutraceutical benefits

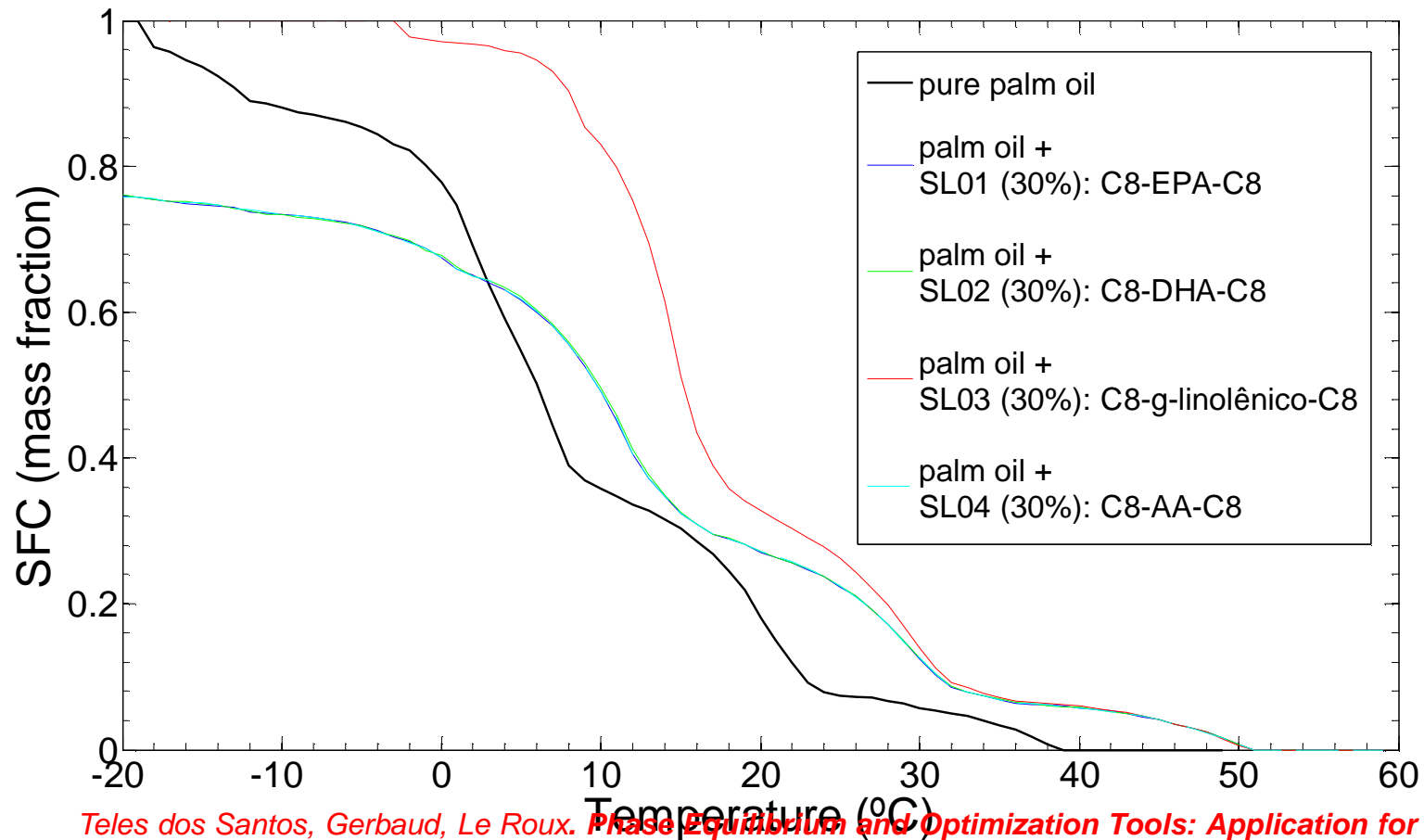
- ex. DHA enhanced products



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



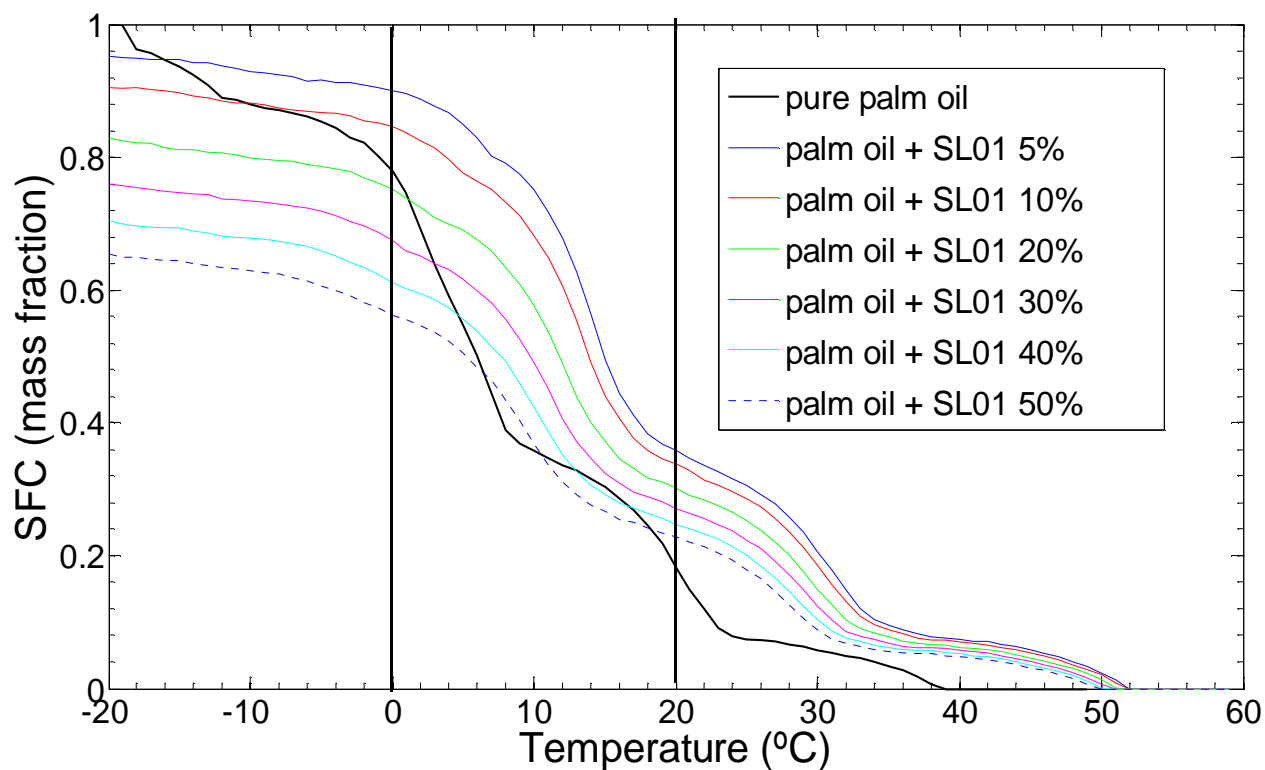
High melting SL affects palm oil initial melting T



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.

- 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.

- Computer aided design of oil blends

- Finding the blend that matches targeted SFC and DSC
- Objective: to anticipate the most promising lab experiments

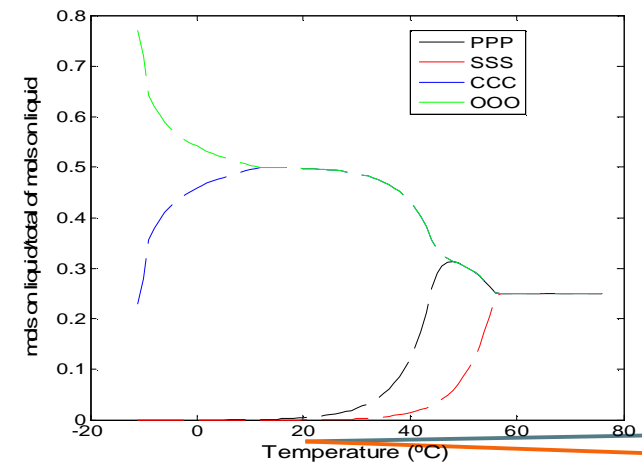
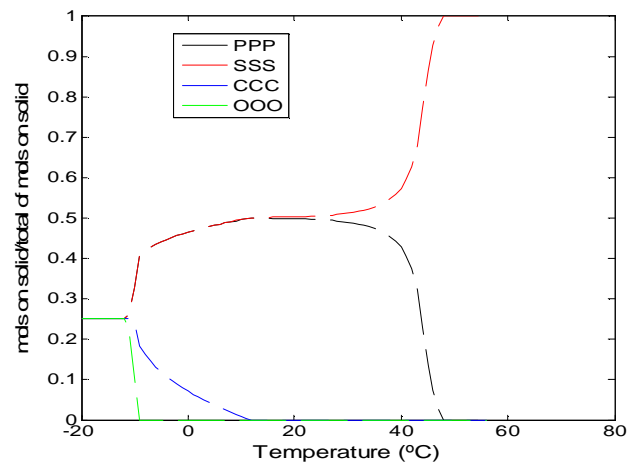
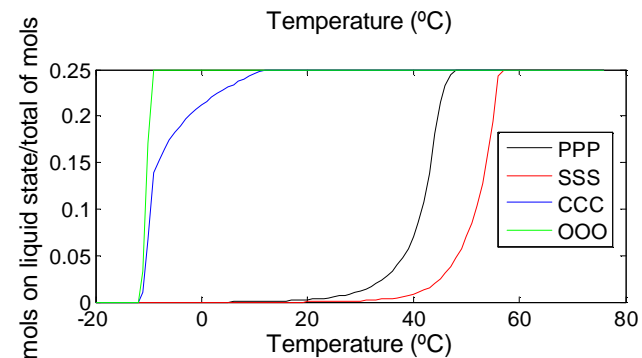
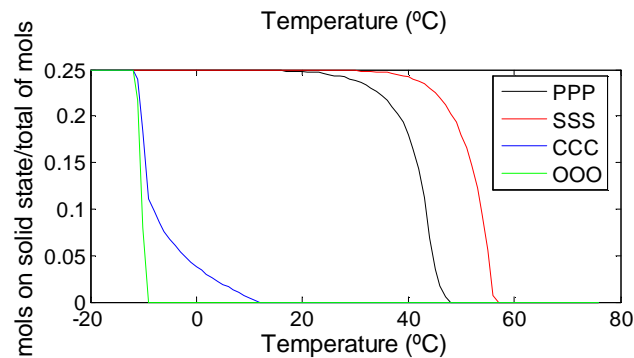
- A knowledge-based predictive model

- 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.

- Composition in each phase

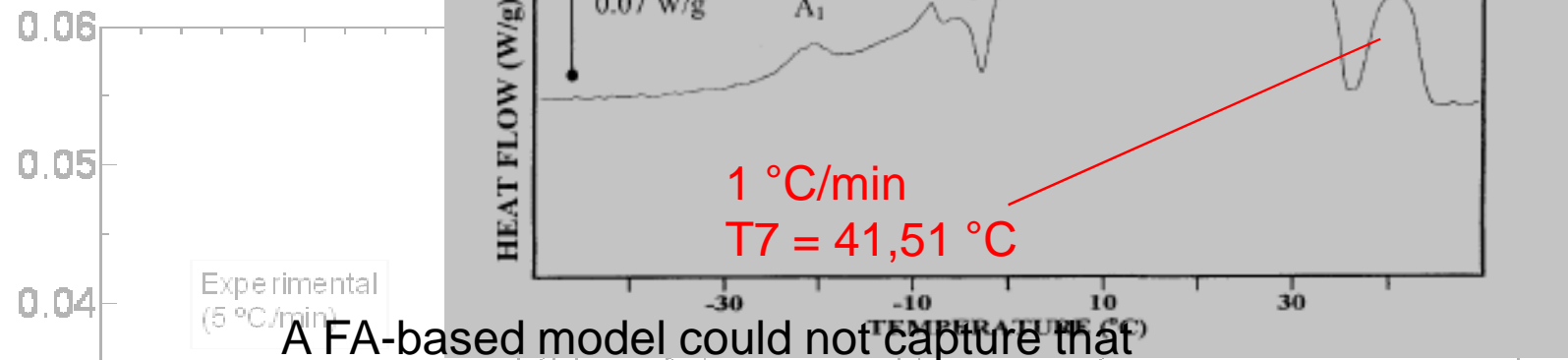
- Solid phase is gradually enriched with SSS;
- OOO fraction gradually decreases in liquid phase



eq - DSC theoretical prediction Vs Experimental Data

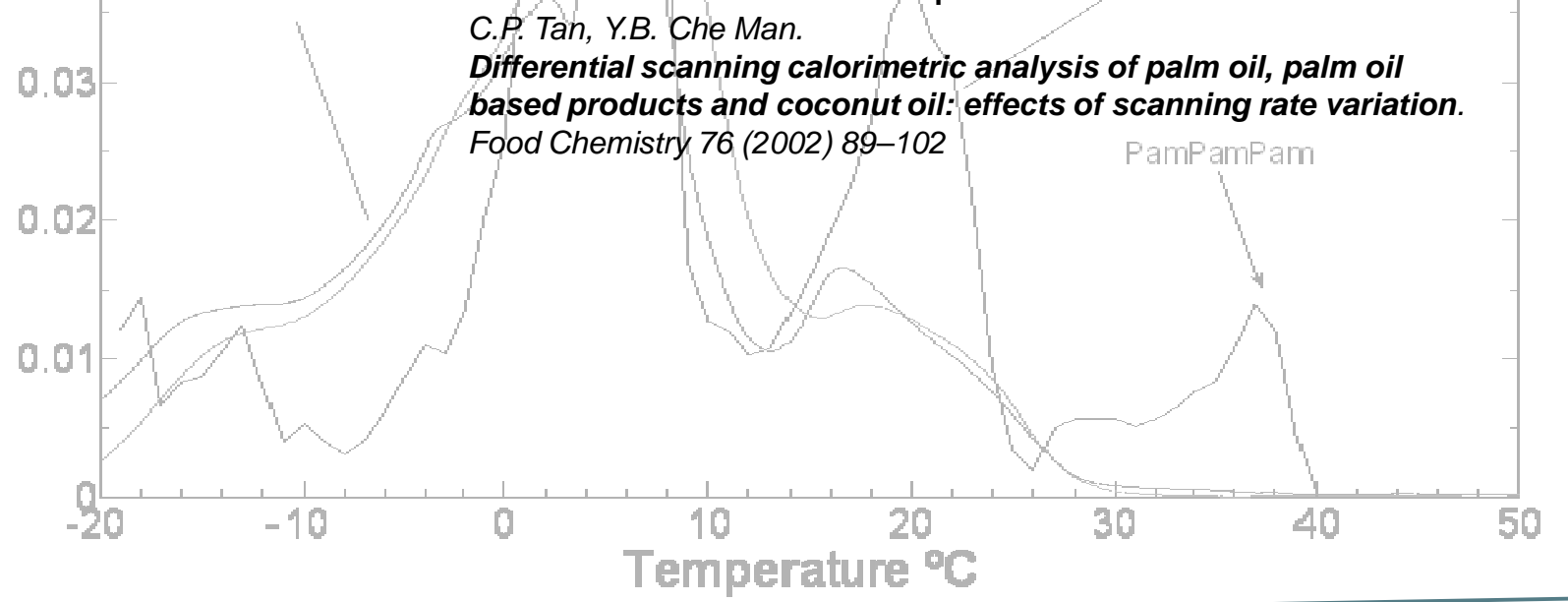


▪ Palm Oil



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 (°C)										
	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	-	-

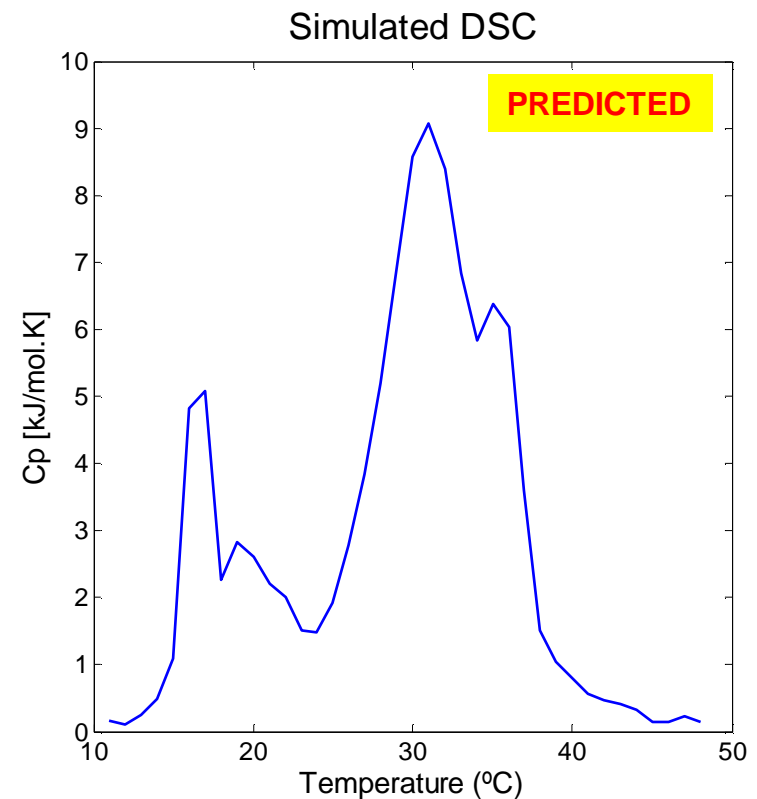
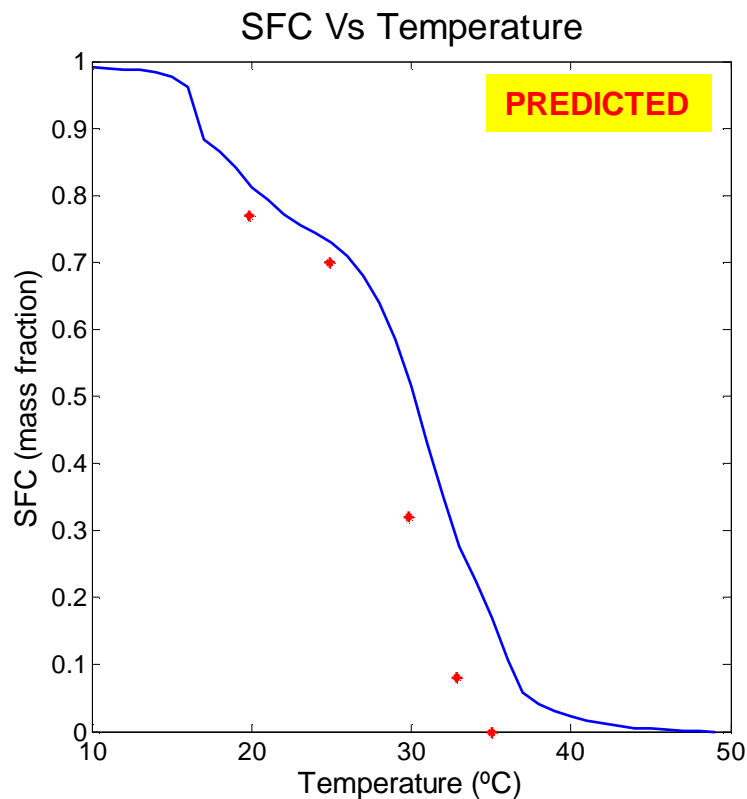
Exp Data.: C.P. Tan and Y.B. Che Man . *Differential Scanning Calorimetric Analysis of Edible Oils: Comparison of Thermal Properties and Chemical Composition. JAOCS, Vol. 77, no. 2 (2000)*

Calc.: calculated by VODesign

***nc:** no convergence

- Cocoa butter: 12 TAGs.

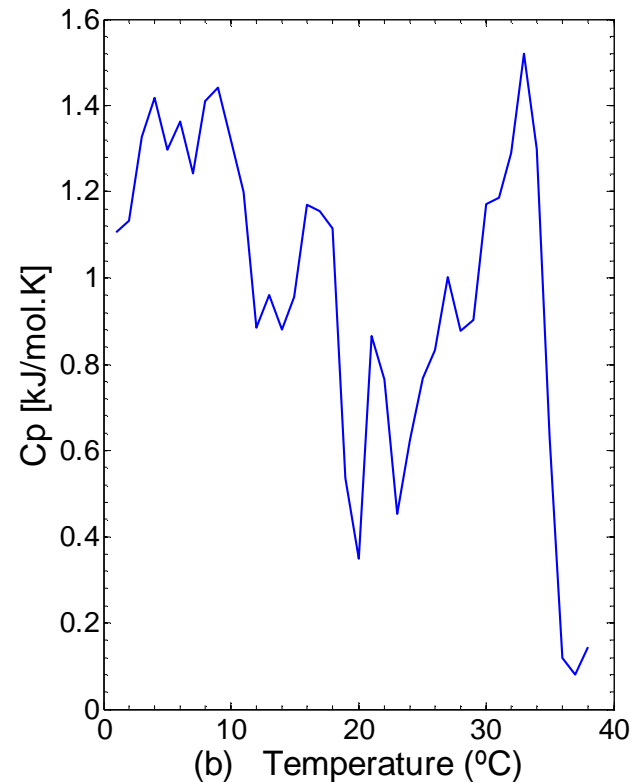
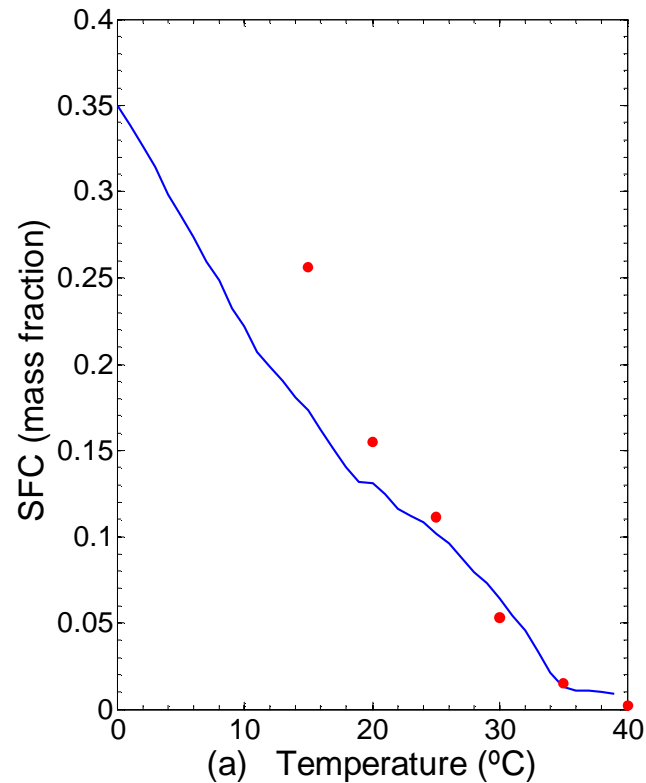
- High accuracy for lower temperatures
- Shorter melting range corrected detected
- **time elapsed: 26s**





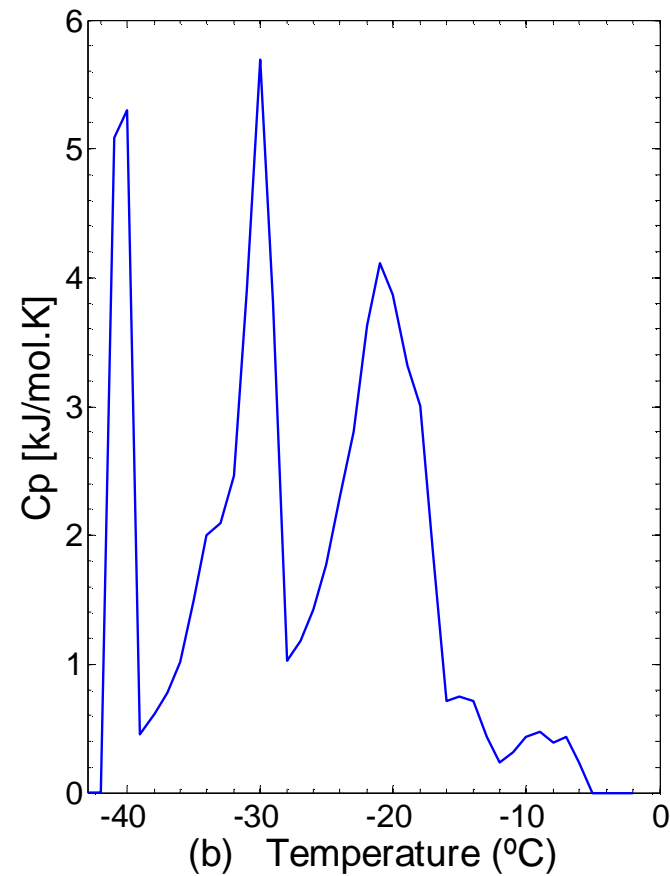
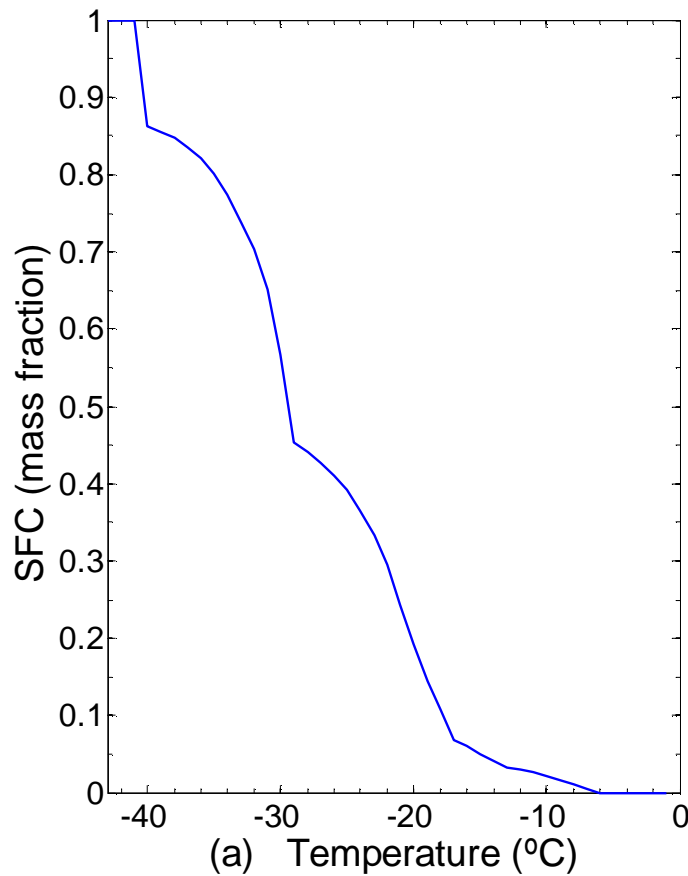
□ - Milkfat – corn oil (80-20) interesterified : 145 TAGs

- Simulated and experimental results in agreement ($T > 20\text{ }^{\circ}\text{C}$)
- Time: 15 min 37 s



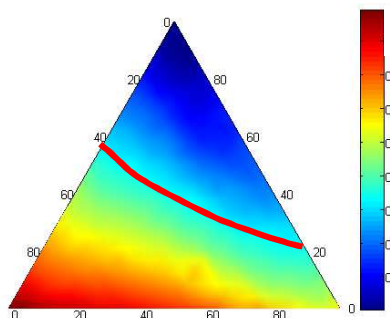
Theoretical prediction for value-added vegetable oil

- Grapeseed Oil: 10 TAGs



Influence of Temperature: ternary blend not interesterified

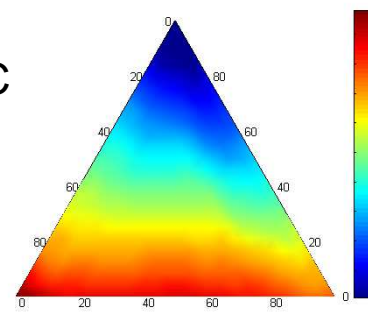
PO-SFO



0.80

0 °C

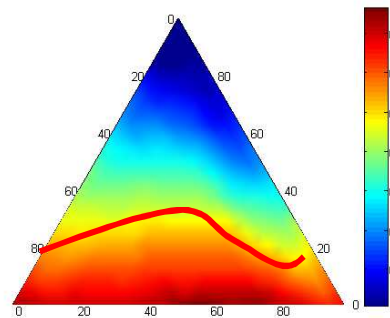
10 °C



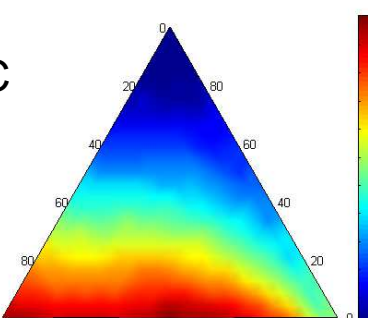
0.45

15 °C

25 °C



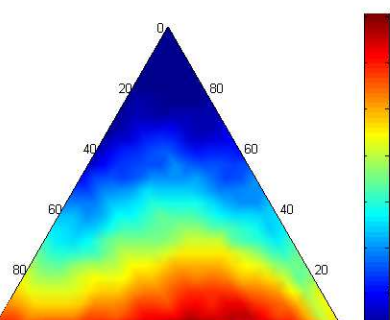
0.35



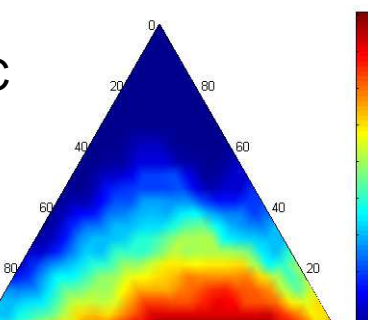
0.20

30 °C

35 °C



0.14



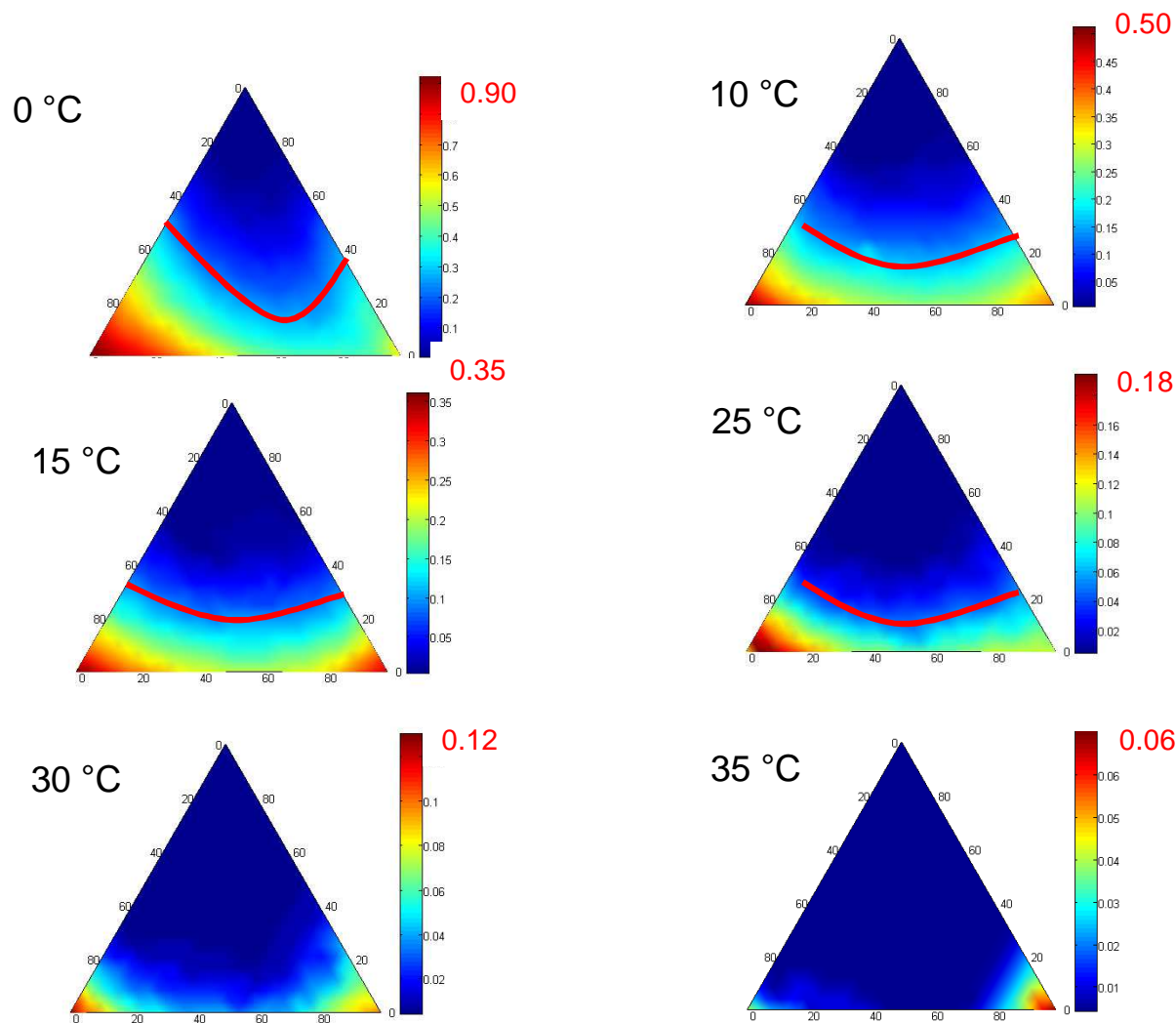
0.09

PREDICTED

Influence of Temperature: ternary blend interesterified



PO-SFO-PKO



PREDICTED

