# Influence of chemical composition on the isothermal cocoa butter crystallization

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# Overview

- Introduction and aim
- Materials and methods
- What happens during isothermal crystallization, cf. isosbestic point
- Influence of chemical composition on different crystallization parameters
- Take home message

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# Introduction

- CHEMICAL COMPOSITION of cocoa butter
- ~ growing conditions, plant age, cacao variety
- ~ production process, refining
- Influence on physical properties, e.g. crystallization kinetics
- => important e.g. for production of chocolate

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# Aim

- Chemical characterization of twenty cocoa butters
- Quantitative investigation of influence on isothermal, static cocoa butter crystallization described by model of Foubert et al. (2002)
- All different chemical composition variables in one study
- Using biological variability, not by adding chemical substances

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# Model of Foubert et al. (2002)

[redacted]

f(t): amount of crystallization [%]

h: fraction remaining crystallizable fat (0<h<1) [-]

$a_F$: value of f as t approaches infinity [%]

K: rate constant [$h^{-1}$]

n: order of the reverse reaction [-]

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# Model of Foubert et al. (2002)

- f(0) related to induction time
- physical interpretation of 'induction time' more straightforward + easier to extract from curve

  → represent as function of induction time
- $t\_ind_x$: time needed to reach e.g. 1% crystallization (x=0.01)

[redacted]

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# Materials and methods

- 20 different cocoa butters
- Isothermal crystallization at 20°C followed by DSC
- Chemical analyses: fatty acid profile, triglyceride profile, free fatty acids, phosphorus (~phospholipids), iron, traces of soap, unsaponifiable matter, peroxide value, diglycerides
- Principal component analysis: reduce dimensionality of fatty acid and triglyceride profile data
- Multiple linear regression to investigate influence of chemical composition on crystallization properties



# Isothermal crystallization at 20°C

- Two-step process
- From research with time-resolved X-ray diffraction (synchrotron radiation, ESRF Grenoble)
  - Occurence of isosbestic point in SAXS

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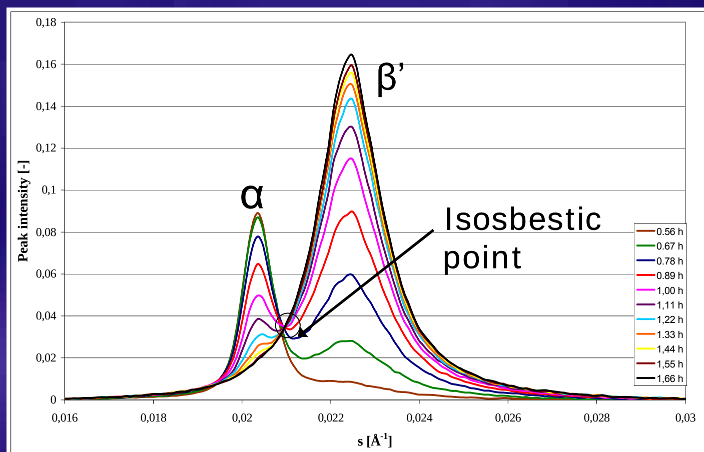
# Isosbestic point in SAXS





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# Isothermal crystallization at 20°C

- Occurence of isosbestic point in SAXS
  - The α structure is transformed into β’ without change of total volume
- End of β’ crystallization coincides with full disappearance of α crystals

→
  - First step: crystallization in α polymorph (kinetically favoured)
  - Second step: α mediated β’ crystallization
  - No direct β’ crystallization
- Increase in crystallinity during conversion: transformation of liquid-like layer in α


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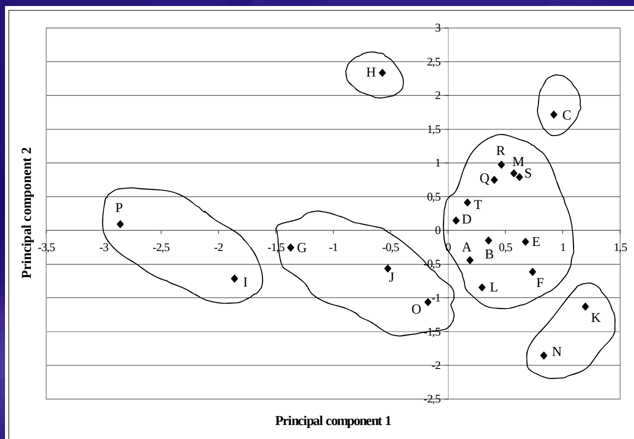
# Analysis of fatty acid and triglyceride profile




**PC1** ~ saturated(+) / unsaturated (-) fatty acids and mono-unsaturated (+) / di-unsaturated (-) triglycerides

**PC2** ~ PPP(+), MOP(+), PLP(-), PLS(-), SLS+OOO(-)

**PC3** ~ trisaturated triglycerides (+)

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# Influence on $a_F$

- Amount of crystallization in second step
  ~ equilibrium amount of solid fat
- Regression equation: $a_F$ = 6.2*PC1-8.2*FFA-6.8*DG+91
- + PC1 (Sat, SatUSat versus U, SatUU)
  matches results found in literature <= lower percentage of triglycerides that are able to crystallize
- - free fatty acids
- - diacylglycerols
  matches results found in literature on palm oil

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# Influence on $t\_ind_x$

- Induction time of second step
  ~ induction time for polymorphic transition
  BUT also growth rate (reverse influence as on K)
- Regression equation:
  $t\_ind_x$ = -0.2*PC1-0.06*PC3+0.006*P+0.17*FFA+0.17*DG-0.02



# Influence on $t\_ind_x$

- \- PC1 (Sat, SatUSat versus U, SatUU)
- \+ phosphorus
- \+ free fatty acids
- \- PC3 (SatSatSat)
- \+ diacylglycerols
- P, FFA + DG are known to retard polymorphic transition

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# Influence on K

- Rate constant
- Regression equation:

K = -1.3*FFA-2.2*DG-0.02*PO-3.8*UM-0.007*S-0.47*PC2+0.28*PC1+11

- \- diacylglycerols

  creation irregularities in packing
- \- soap

  influence known in chocolate industry

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# Influence on K

- \- free fatty acids
- \- PC2 (PPP, MOP, P versus PLP, PLS, SLS + OOO)
- \+ PC1 (Sat, SatUSat versus U, SatUU)

  only crystallization parameter for which not most important influence

  <= interference of extra oleate chain with molecular packing of mono-unsaturated triglycerides

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# Influence on n

- Order of reverse reaction (local remelting, redissolving of crystals or combination)

  ~ how long reverse reaction effects crystallization process: higher n, shorter influence
- Regression equation:

  n = 0.9*PC1+7.3*UM-0.4*Fe-0.39*DG+0.17*PO+0.02*P+1.9

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# Influence on n

- \+ PC1 (Sat, SatUSat versus U, SatUU)

  higher value => higher melting point => less effect of re-melting => higher n
- \- iron
- \+ unsaponifiable matter
- \+ peroxide value
- \+ phosphorus
- \- diacylglycerols

  promote nucleation => larger number of smaller crystals => redissolving promoted => lower n

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# Take home message

- Most important chemical characteristic with influence in crystallization
- ratio saturated versus unsaturated and mono-unsaturated versus di-unsaturated (except K)
- most important minor components: free fatty acids and diacylglycerols: negative influence on equilibrium amount of solid fat, growth rate and polymorphic transition
- Other: phospholipids + traces of soap

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# Acknowledgements

- DUBBLE
- Bart Goderis (KULeuven)
- FWO-Vlaanderen
- MSc students
- De Smet Engineering (P+Fe analyses)
- Barry Callebaut, ADM (providing samples)

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