Modelling multi-step processes in fat crystallization

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Introduction

- Crystallization kinetics
  - When and to what extent fat crystallizes
  - Important for controlling operations based on crystallization
  - Depends on chemical composition, crystallization conditions, …
- To quantify these effects => modelling crystallization kinetics
- Isothermal crystallization – one step process

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Model of Foubert et al. (2002)

$$\frac{dh}{dt} = K \times (h^n - h) \qquad h(t) = \frac{a_F - f(t)}{f(t)}$$

f(t): amount of crystallisation [%]

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)

$$f(t) = a_F\left[1-\left[1+\left((1-x)^{1-n}-1\right)\exp\left(-(1-n)\times K\times(t-t\_ind_x)\right)\right]^{\frac{1}{1-n}}\right]$$

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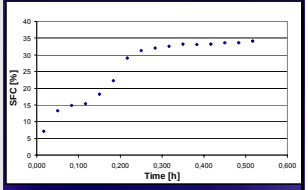
AIM

- Complexity of fats: crystallization = two-step process (polymorphism, fractional crystallization)
- Literature: fit with one step Avrami model
- Vanhoutte (2002): algebraic sum exponential equation + Gompertz model



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AIM

- Foubert model = differential equation: possibility to extend for more complex situations
- Model to describe two-step curve as a whole with physically meaningful parameters
- Simulation experiments: meaning of model parameters
- Parameter estimation on time-resolved XRD data

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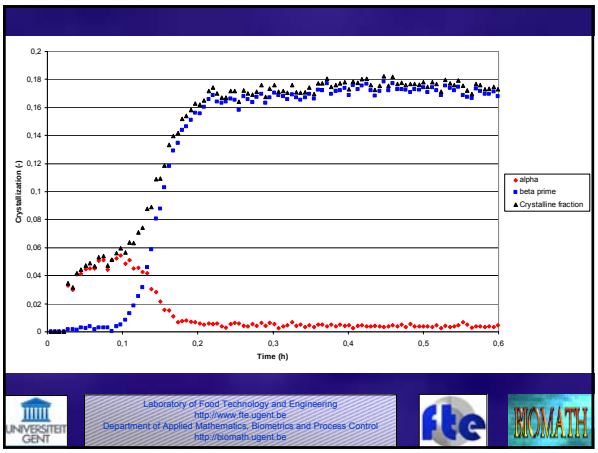
This research

- Isothermal crystallization at high supercooling (milk fat (fractions) and cocoa butter)
  - From research with time-resolved X-ray diffraction (synchrotron radiation, ESRF Grenoble)
  - Occurence of isosbestic point in SAXS
  - First step: crystallization in α polymorph
  - Second step: α mediated β' crystallization
  - No direct β' crystallization



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Fractional model: assumptions

- 1 α → 1 β' = only polymorphic transition, no extra material from the melt (cf. isosbestic point)
- Both steps: Foubert model
- First step: *n* is very large ≅ exponential function

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Fractional model

$$\frac{dfr_\alpha}{dt} = r_a - r_b$$

from melt to β'

$$\frac{dfr_{\beta'}}{dt} = r_b$$

from α

$fr\alpha$ and $fr\beta'$ = fraction of α and β' crystals
r_a = rate of α crystallization
r_b = rate of transformation to β'

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Fractional model

$$\frac{dh}{dt} = K * \left(h^n - h\right)$$

$$h = \frac{a_F - f}{a_F}$$

$$\frac{df}{dt} = k*(a-f) - a*k*\left(\frac{a-f}{a}\right)^n$$

reformulation

$$\frac{df}{dt} = k*(1-f) - 1*k*\left(\frac{1-f}{1}\right)^n$$

fractional: a = 1

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Fractional model

r_b: reformulated and fractional Foubert

$$r_b = k_{\beta'}*\left(1 - fr_{\beta'}\right) - 1*k_{\beta'}*\left(\frac{1-fr_{\beta'}}{1}\right)^{n\beta'}$$

r_a: idem BUT amount of fat available for α crystallization

$$r_a = k_\alpha*\left[1-\left(fr_\alpha + fr_{\beta'}\right)\right] - 1*k_\alpha*\left(\frac{1-\left(fr_\alpha + fr_{\beta'}\right)}{1}\right)^{n\alpha}$$

$k\alpha$ and $k\beta'$ = rate constants
$n\alpha$ and $n\beta'$ = order of reverse reaction

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Fractional model: initial conditions

$$fr_{\alpha}(0) = 1 - 1 * \sqrt[(1-n_{\alpha})]{1 + \frac{0{,}99^{(1-n_{\alpha})} - 1}{e^{((n_{\alpha}-1)*k_{\alpha}*tind_{\alpha})}}}$$

$$fr_{\beta'}(0) = 1 - 1 * \sqrt[(1-n_{\beta'})]{1 + \frac{0{,}99^{(1-n_{\beta'})} - 1}{e^{((n_{\beta'}-1)*k_{\beta'}*tind_{\beta'})}}}$$

$tind_{\alpha}$ = time needed to reach 1% of α crystallization
$tind_{\beta'}$ = time needed to reach 1% of β' crystallization

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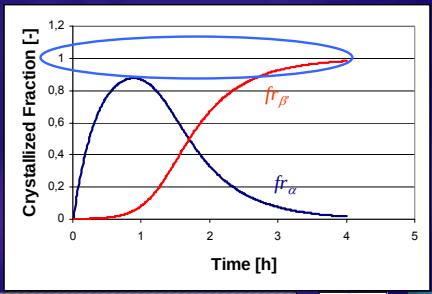
Fractional model



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Relation to data

$$f_{\alpha} = a_{\alpha} * fr_{\alpha}$$

$$f_{\beta'} = a_{\beta'} * fr_{\beta'}$$

$$f = f_{\alpha} + f_{\beta'}$$

a_{α} = max. amount of α crystallization [% or J/g]
$a_{\beta'}$ = max. amount of β' crystallization [% or J/g]
f = amount of crystallization [% or J/g]

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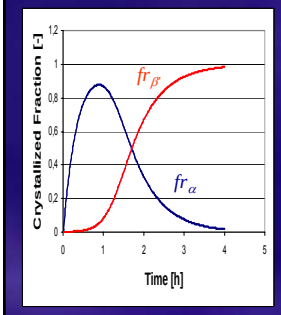

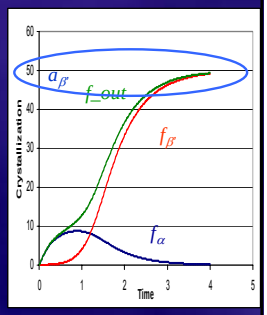

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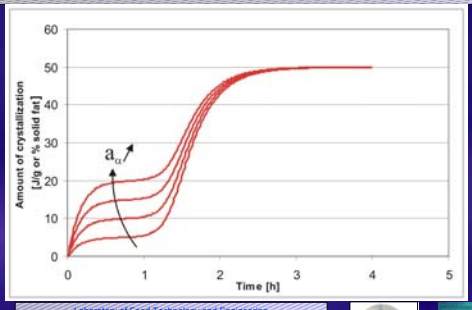
Two-step model: parameters



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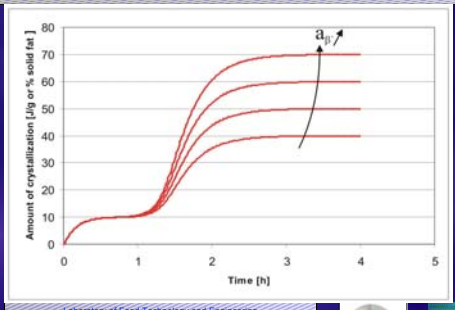

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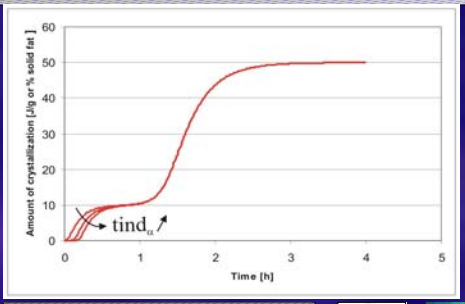

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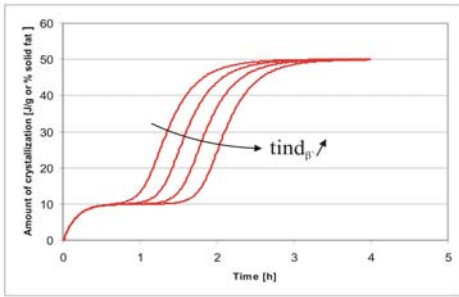

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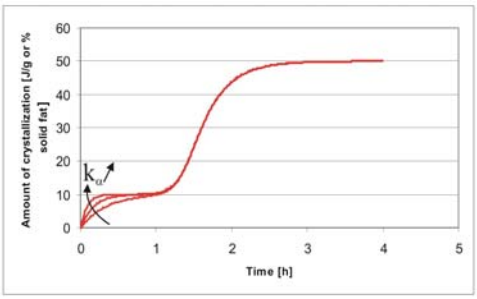

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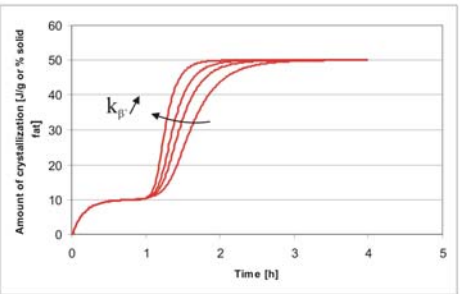

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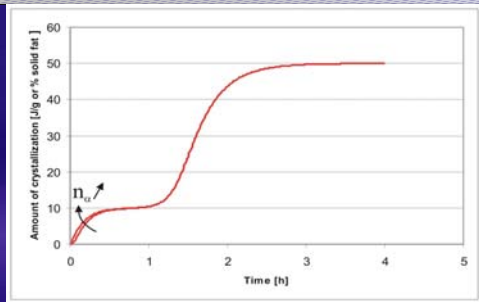

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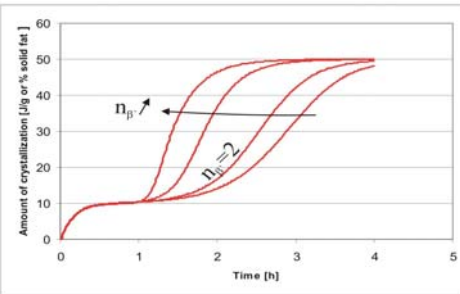

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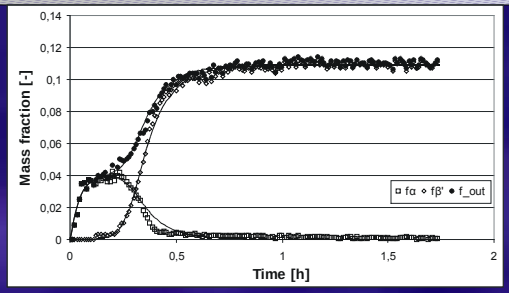
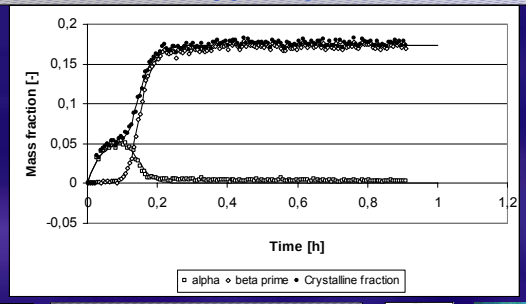
Parameter estimation: AMF at 19°C



Parameter estimation: AMF(HMF) at 24°C



Take home message

- Foubert model can be extended to describe two-step crystallization where:
  - Step 1: crystallization in α
  - Step 2: transformation to β'
- By changing assumptions + adapting equations: other type of two-step processes can also be described
- Future modelling work: non-isothermal crystallization, crystallization in emulsion, …

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