Modelling the temperature dependency of crystallization parameters in view of describing the non-isothermal crystallization process

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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
- Most simple case = Isothermal crystallization = one step process

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Model of Foubert et al. (2002)

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

$$h(t) = \frac{a_F - f(t)}{f(t)}$$

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)
- Advantage: differential equation

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Two step model of Foubert et al. (2006)

- Isothermal crystallization = two step process (cf. Dewettinck et al., 2004)
- First step: melt ➔ α
- Second step: α mediated β' crystallization
- Set of differential and algebraic equations
- Two-step model = 8 parameter model

$t\_ind_{\alpha}(=0)$, K_{α}, n_{α}, a_{α}

$t\_ind_{\beta'}$, $K_{\beta'}$, $n_{\beta'}$ en $a_{\beta'}$

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Aim

- Extension of Foubert model for crystallization under **non-isothermal conditions** (of cocoa butter) (cf. production of food products)
- How ?
  - Sensitivity analysis two step crystallization model
  - Optimisation of DSC method to obtain necessary data (2 step crystallization)
  - Effect of temperature on isothermal crystallization curves summarized by model parameters and development of secondary models to describe parameters as function of temperature
  - Combination of secondary models with two step model to describe non-isothermal crystallization
  - First validation using step function

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Sensitivity analysis

- How model output (f_out) changes as function of small changes in parameter values

➔ When does parameter have influence on f_out

➔ If two parameters have same influence on same moment in time = parameters cannot be estimated independently = identifiability problem = different combinations of parameters lead to identical model output

➔ Better to fix one parameter
  - ➔ Same degrees of freedom to estimate less parameters ➔ better parameter estimation
  - ➔ Better reproducibility

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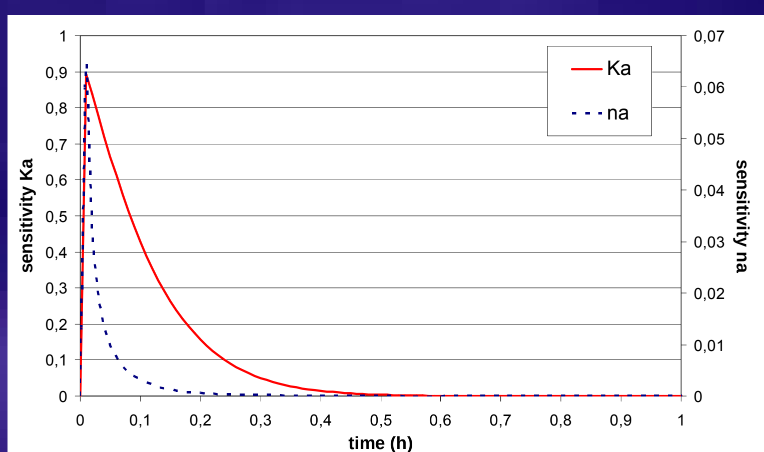
Sensitivity analysis



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Sensitivity analysis

- K_α and n_α describe the same (lower sensitivity for n_α)
- ➔ fix n_α to 100 (exponential curve)
- Analogous for $K_{\beta'}$ and n_β
- ➔ fix n_β' to 6 (mean value)
- No other identifiability problems
- ➔ 5 remaining parameters: K_α, a_α, $t\_ind_{\beta'}$, $K_{\beta'}$, $a_{\beta'}$

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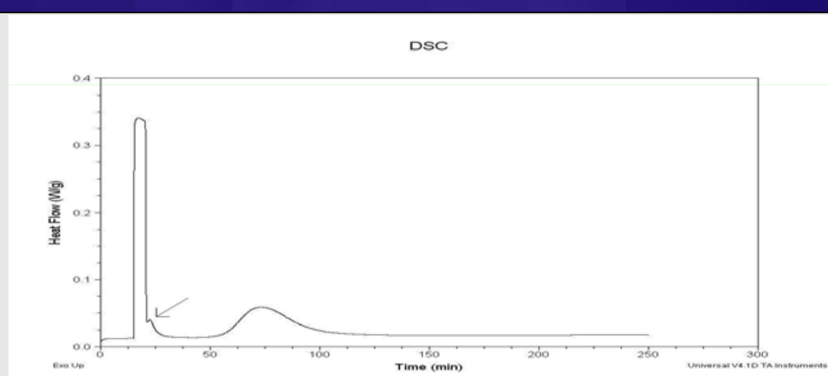
Isothermal DSC experiments



- Problem: melt -> α peak cannot be integrated
- Second step can be integrated

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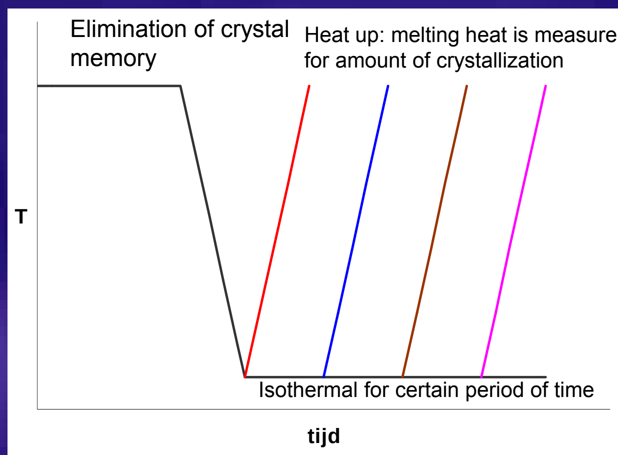
Solution: stop and return method



Disadvantage: long analysis time

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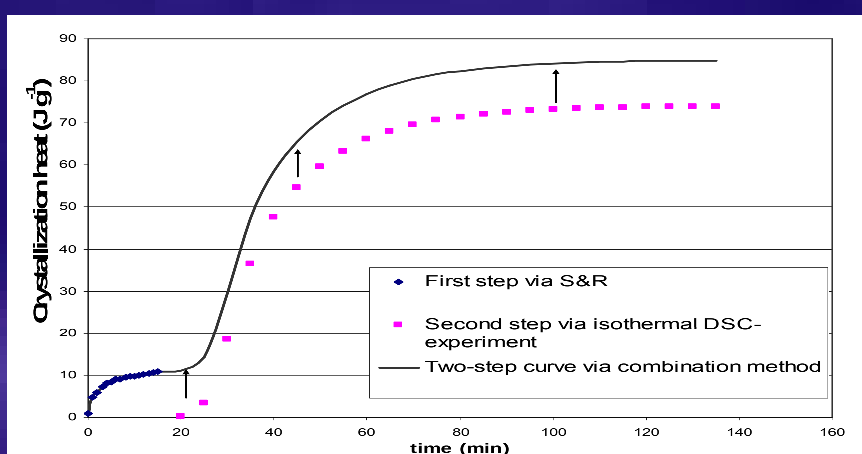
Combination method



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Materials and methods

- Isothermal crystallization curves using combination method
- Temperatures between 19°C and 23°C, 0.5°C interval
- 4 repetitions at each temperature
- Parameter estimation using WEST (Simplex algorithm) + errors on parameter estimates (Nelder & Mead algorithm)
- Model selection for secondary models: preferably physical background + criteria based on SSR and n° parameters (Vanrolleghem & Dochain, 1998)

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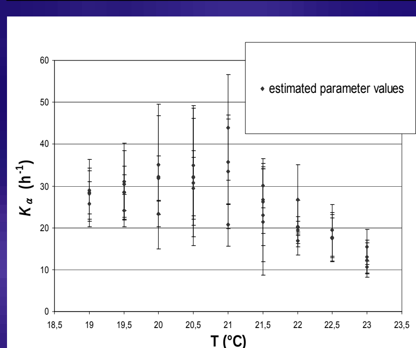
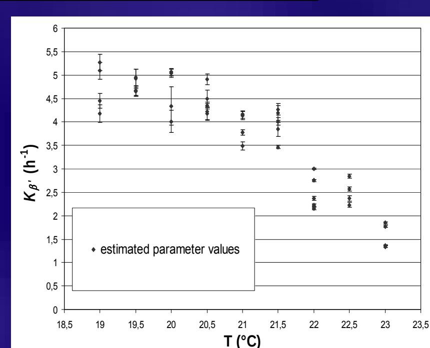
Temperature influence on model parameters

- K_{α} and $K_{\beta'}$ (rate constants of first and second step)





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Temperature influence on model parameters

- Influence T on rate constants:
  - Low T: increasing melt viscosity => slower diffusion => $K_{\alpha}\downarrow$ and $K_{\beta'}$ *rather constant*
  - High T: decreasing driving force, nucleation rate, crystal growth rate => K_{α} and $K_{\beta'}\downarrow$
- Lauritzen-Hoffman equation as secondary model for K_{α}:

$$K_{\alpha} = a_{LH} \times \exp\left[\frac{-b_{LH}}{T_K - c_{LH}}\right] \times \exp\left[\frac{-d_{LH} \times (T_K + T_{Km})}{2T_K^2 \Delta T}\right]$$

- Vogel-Fulcher equation as secondary model for $K_{\beta'}$:

$$K_{\beta'} = a_{VF} \times \exp\left(-\frac{E_{VF}}{R_g \times (T_K - T_0)}\right)$$

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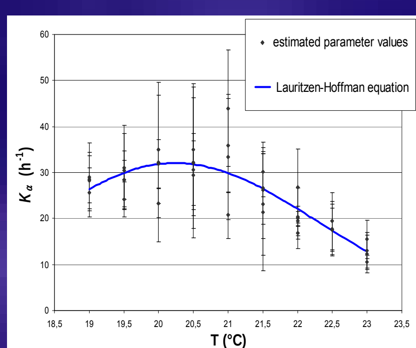

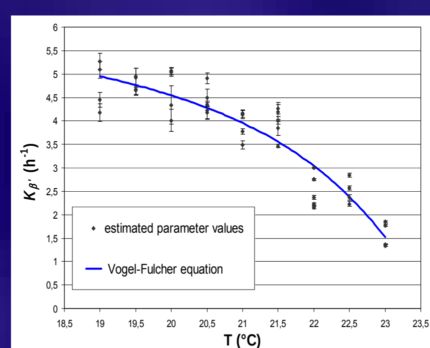

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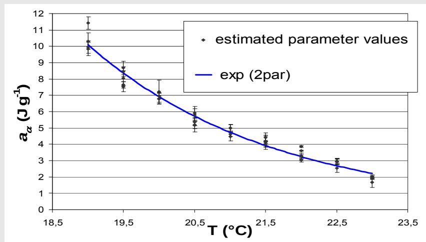
Temperature influence on model parameters

- Parameter a_α (maximum value of first step):



- Higher solubility at high T
- 2 parameter exponential as secondary model (better fit than Hildebrand)

$$a_\alpha = a_{E2} \times \exp\left(-b_{E2} \times T\right)$$

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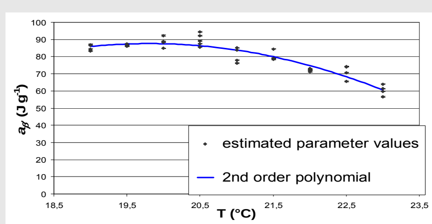
Temperature influence on model parameters

- Parameter $a_{\beta'}$ (maximum value of second step):



- Cf. SFC-curve
- 2nd order polynomial as secondary model

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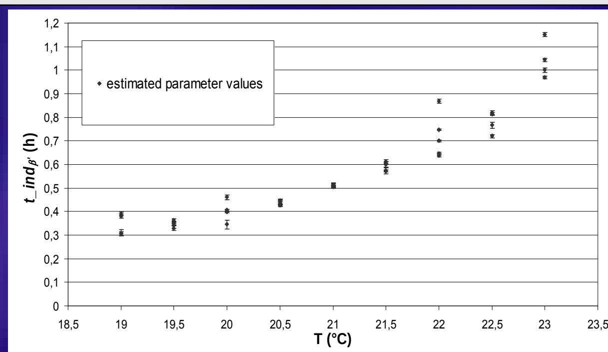
Temperature influence on model parameters

- $t\_ind_{\beta'}$ (induction time second step)
- Exponential increase with increasing T



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Temperature influence on model parameters

- Influence T on $t\_ind_{\beta'}$:
  - Induction time inversely proportional to nucleation rate (Turnbull-Fisher equation)
  - Same T influence for polymorphic transition
- Secondary model based on Turnbull-Fischer equation:

$$t\_ind_{\beta'} \cong \frac{1}{J} = \frac{a_{TF}}{T_K} \times \exp\left[\frac{b_{TF} \times T_{KM}^2}{\Delta T^2 \times T_K}\right]$$

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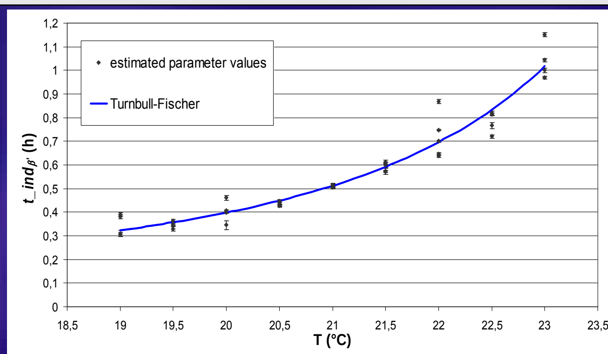
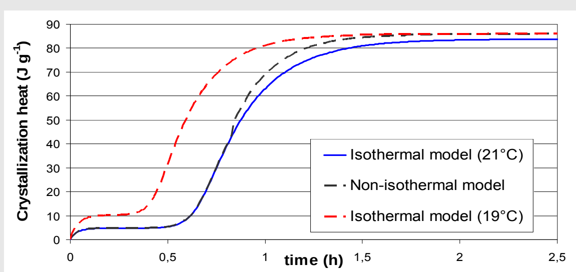
Temperature influence on model parameters

- $t\_ind_{\beta'}$ (induction time second step):



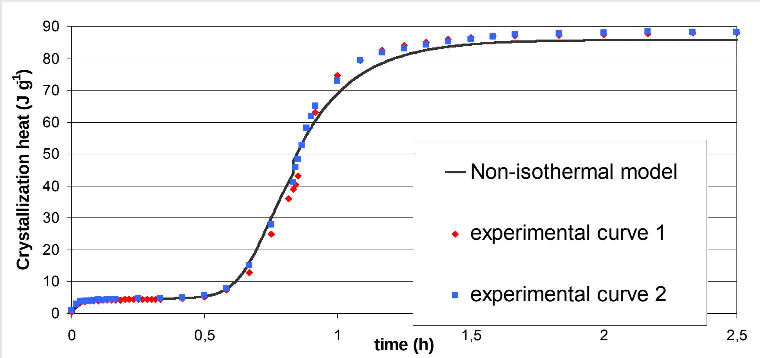
Non-isothermal Foubert model

- Combination of secondary models with two step model (parameters are variables as function of T)
- Validation: stepwise change of T
  - *50 min (0,83h) at 21°C*
  - *Next 100 min at 19°C*



Non-isothermal Foubert model

- Comparison of model output with experimental curve



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Take home message

- Important to develop non-isothermal model to describe crystallization during industrial production
- Big advantage of model written as differential equation, rather straightforward to extend to non-isothermal crystallization
- Combination method to obtain isothermal crystallization curves
- Sensitivity analysis: K and n have effect on same moment
  ➔ fix n values
- Development secondary models
- First validation showed potential of non-isothermal model
- Extension necessary for different cooling rates and temperature regions (take crystallization mechanism into account)

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