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Modelling of Crystallisation Kinetics of Cocoa Butter and Milk Fat

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Overview

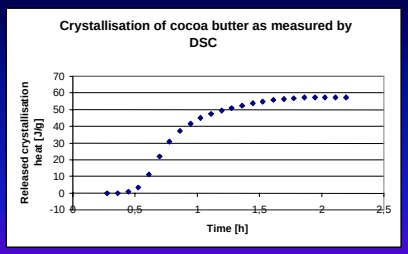
- why model crystallisation kinetics?
- existing models
- presentation of the new model
- model selection: which one gives the best fit?
- take home message

Why model crystallization kinetics?

- to gain insight in/quantify/predict effects of
  - fat composition
  - differences in fat origin
  - processing conditions
  - temperature (profiles)
  - additives / minor components
- our focus on:
  - milk fat
  - cocoa butter
  - Belgian chocolate

Why model crystallization kinetics?

Typical data set



Summarize in (small) number of characteristic numbers

Existing models: Avrami (Avrami, 1940)

$$f(t) = a_A \times \left(1 - \exp(-k \times t^m)\right)$$

t: time [h]

f(t): amount of crystallisation [% or J/g]

a_A: value of f as t approaches infinity [as f(t)]

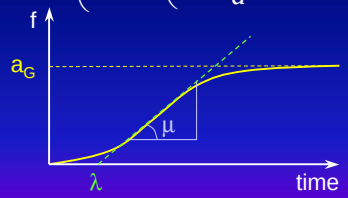
k: crystallisation rate constant [h^{-n}]

m: Avrami exponent [ ]

Existing models: Gompertz model

(Zwietering et al., 1990)

$$f(t) = a_G \times \exp\left(-\exp\left(-\frac{\mu \times e}{a} \times (t - \lambda) + 1\right)\right)$$



New model: background

(Foubert et al., accepted for publication Food Research International)

- (Wünderlich, 1990): phase transitions can be written in the form of a chemical reaction

  A (melt) ⇌ B (crystals)

  for kinetic description: same equations as for chemical reactions
- crystallisation process:

  first order forward reaction

  reverse reaction order n

New model: mathematical representation

$$\frac{dh}{dt} = K_n \times h^n - K_1 \times h \qquad h(t) = \frac{a_F - f(t)}{f(t)}$$

f(t): amount of crystallisation [% or J/g]

a_F: value of f as t approaches infinity [as f(t)]

h: relative remaining crystallisable fat (0<h<1) [ ]

K_i: rate constants [h^{-1}]

n: order of the reverse reaction [ ]

$h(t=0) = h_0$

New model: simplified version

parameter estimation studies:

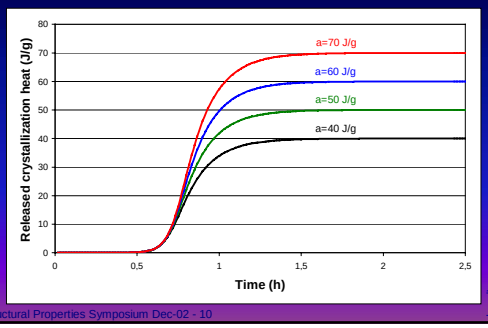
difference between K_1 and K_n is only 1.10^{-4} %

$$\frac{dh}{dt} = K \times (h^n - h) \qquad h(0) = \frac{a_F - f(0)}{f(0)}$$

quality of original model not significantly better than simplified version

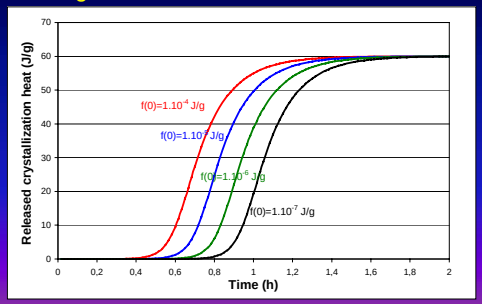
New model: the four parameters

- a: value as t approaches infinity
- f(0) = 1.10^{-5} J/g K = 6 h^{-1} n = 5



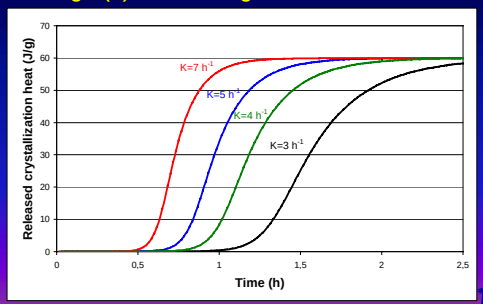
New model: the four parameters

- f(0) related to induction time
- a = 60 J/g K = 6 h^{-1} n = 5



New model: the four parameters

- K: rate of crystallisation, also of crystallisation start
- a = 60 J/g f(0) = 1.10^{-5} J/g n = 5



New model: the four parameters

- n related to degree of curve asymmetry
- definition of asymmetry:

$$asym = \frac{t_{90\%} - t_{50\%}}{t_{50\%} - t_{10\%}}$$ or equivalent

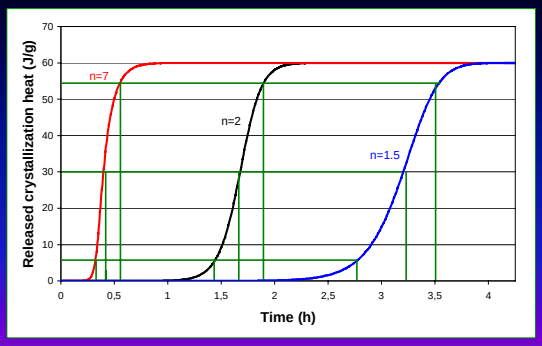
- relation between n and asym:

n = 2 asym = 1

n < 2 asym < 1

n > 2 asym > 1

New model: the four parameters



Advantages of differential equation

- easier to interpret mechanistically
- easier to make minor changes on basis acquired knowledge
- also useful for time-varying process conditions

e.g. non-isothermal processes

combination with secondary models (temperature dependency of model parameters)

BUT

parameter estimation not so straightforward

➡ also algebraic solution

New model: algebraic solution

- 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 x% crystallisation

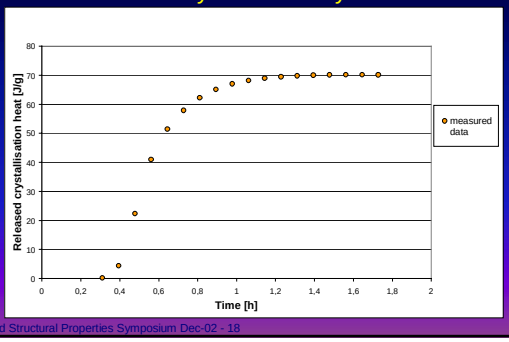
$$h = \left[1 + \left((1-x)^{1-n} - 1\right)\exp\left(-(1-n)\times K \times (t - t\_ind_x)\right)\right]^{\frac{1}{1-n}}$$

Model selection

- fit the three models to different data series (53)
- different samples (different cocoa butters + milk fat samples)
- different temperatures
- different measuring techniques (DSC + pNMR)
- visual model selection
- mathematical model selection

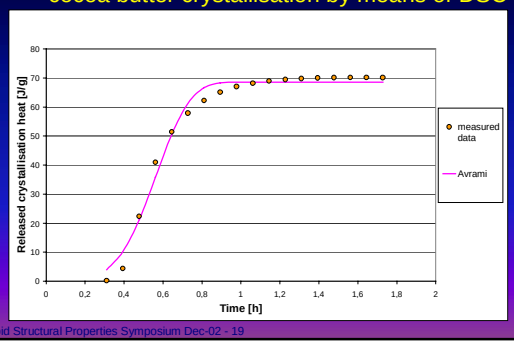
Model selection: visual

cocoa butter crystallisation by means of DSC



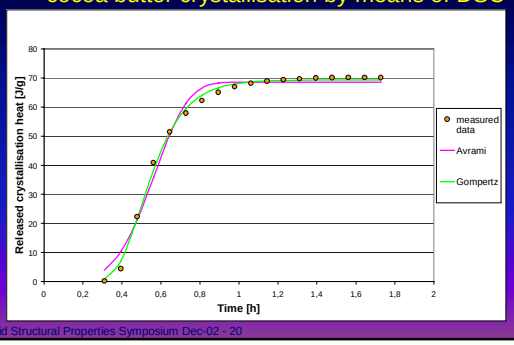
Model selection:visual

cocoa butter crystallisation by means of DSC



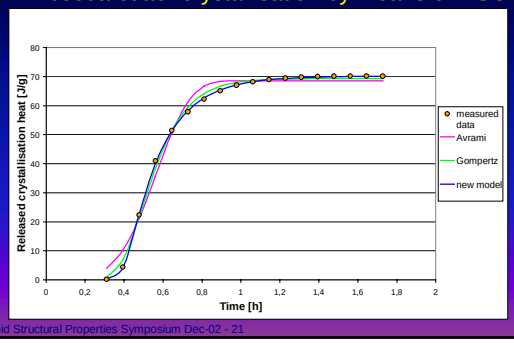
Model selection: visual

cocoa butter crystallisation by means of DSC



Model selection:visual

cocoa butter crystallisation by means of DSC



Model selection: mathematical

- four information criteria: based on sum of squared residuals (SSR) ➡ indication of how much predicted curve differs from measured curve, compensate in different ways for model complexity
- statistical F-test: is a more complex model significantly better than more simple model? (different number of parameters)
- analysis of residuals (measured – predicted value): should be random and independent: autocorrelation and run tests
- details: specialised textbook

Model selection: mathematical

	FPE	AIC	BIC	LILC	F-test	Run	Autocorr
ModelA	0%	0%	0%	0%	0%	0%	0%
ModelG	21%	23%	21%	17%	13%	8%	2%
ModelF	79%	77%	79%	83%	77%	87%	21%
ModelFG	0%	0%	0%	0%	10%	5%	21%
ModelAF	0%	0%	0%	0%	0%	0%	3%
All equal	0%	0%	0%	0%	0%	0%	53%

Model selection: mathematical

comparison of mean sum of squared residuals (MSR): model better if MSR is smaller

Gompertz: some very good fits, some significantly poorer fits

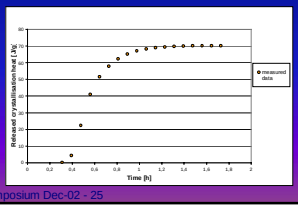
new model: more or less constant value, thus more flexible

Asymmetry of models

$$asym = \frac{t_{90\%} - t_{50\%}}{t_{50\%} - t_{10\%}}$$

- Avrami: asym depends on m

m values coincide with asym around 1 or smaller = start of crystallisation slower



Asymmetry of models

- Gompertz: asym = constant
  no flexibility concerning asymmetry
  explains why some very good fits and some significantly worse
- new model: asym depends on n

  n = 2 asym = 1

  n < 2 asym < 1

  n > 2 asym > 1

flexibility concerning asymmetry

Take home message

- new model to describe crystallisation kinetics of fats
  ADVANTAGES:
- differential equation ➡ time-varying conditions (e.g. non-isothermal crystallisation)
- algebraic solution for isothermal conditions: easy parameter estimation
- quality of fit always better than Avrami, better than Gompertz for majority of data series
- high flexibility: good fit for different samples, processing conditions, measuring techniques