A new dynamic model to describe the crystallization kinetics of fats

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OBJECTIVES

- create a new model able to better describe isothermal crystallization kinetics of fats
- compare the proposed model to the Avrami and Gompertz models

MODELS USED IN LITERATURE TO DESCRIBE ISOTHERMAL CRYSTALLIZATION KINETICS

AVRAMI MODEL

$$f(t) = a*\left(1-e^{-k*t^n}\right)$$

f(t): amount of crystallization at time *t* [J/g or % solid fat]

a: value for *f* as *t* approaches infinity [J/g or % solid fat]

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

n: Avrami exponent [-]

GOMPERTZ MODEL

$$f(t) = a * e^{-e^{\frac{\mu * e}{a}*(\lambda - t)+1}}$$

f(t): amount of crystallization at time *t* [J/g or % solid fat]

a: value for *f* as *t* approaches infinity [J/g or % solid fat]

μ: maximum increase rate [J/g h^{-1} or h^{-1}]

λ: induction time [h]

MATERIALS AND METHODS

- Isothermal crystallization at 20°C using DSC *(65°C for 15 min, cool at 8°C/min to crystallization temperature and hold until complete crystallization)*
- Thirteen cocoa butter samples
- For some samples: isothermal crystallization at 17°C to check the influence of crystallization temperature on the quality of the models
- Seven milk fat samples: crystallization using DSC to check the influence of the type of fat on the quality of the models
- Three milk fat fraction samples: crystallization using pNMR to check the influence of measuring technique (*samples were heated at 60°C for 1h and were then placed in a thermostated water bath, readings were taken at appropriate time intervals*)
- DSC curves were integrated using the apparatus' software. The data series were fitted by non-linear regression using Sigmaplot 2000

THE PROPOSED MODEL

- Written as a differential equation
- Written as function of *h*, the remaining crystallizable fat, = (*a*-*f*)/*a*
- Converted to algebraic solution

The fat crystallization process can be described as a forward first order reaction which is compensated by a reverse reaction of order n.

DIFFERENTIAL EQUATION

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

ALGEBRAIC SOLUTION

$$f(t) = a*\left[1-\left[1+\left(\left(1-\frac{f_0}{a}\right)^{1-n}-1\right)*e^{-(1-n)*K*t}\right]^{\frac{1}{1-n}}\right]$$

h: remaining crystallizable fat at time *t* [-]

f(t): amount of crystallization at time *t* [J/g or % solid fat]

a: value for *f* as *t* approaches infinity [J/g or % solid fat]

f_0: initially present amount of crystals [J/g or % solid fat]

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

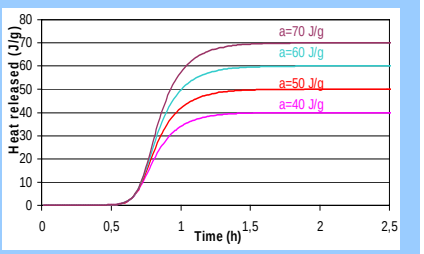
n: order of reverse reaction, linked to asymmetry of curve [-]

ADVANTAGES OF BOTH FORMS OF THE MODEL

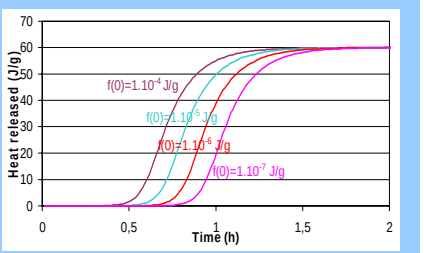
- Easier to interpret mechanistically
- Easier to modify on the basis of acquired knowledge
- By incorporation of secondary models for e.g. the temperature dependency of the parameters, the model can be used to describe non-isothermal crystallization kinetics
- Parameter estimation is easier because of more readily available software packages capable of non-linear regression of algebraic functions

INFLUENCE OF MODEL PARAMETERS ON CRYSTALLIZATION CURVE

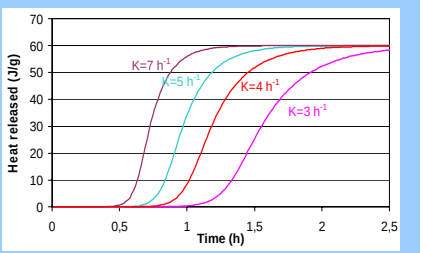
INFLUENCE OF *a* (f_0 = 1.10^{-5} J/g, *K* = 6h^{-1}, *n* = 5)



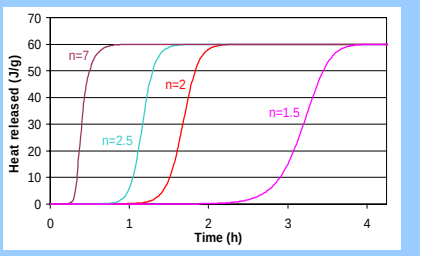
INFLUENCE OF f_0 (*a* = 60 J/g, *K* = 6h^{-1}, *n* = 5)



INFLUENCE OF *K* (*a* = 60 J/g, f_0 = 1.10^{-5} J/g, *n* = 5)

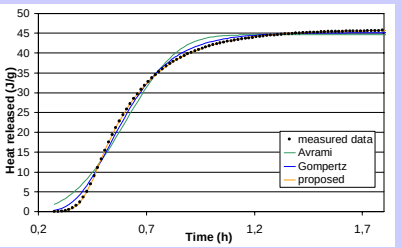


INFLUENCE OF *n* (*a* = 60 J/g, f_0 = 1.10^{-5} J/g, *K* = 6 h^{-1})

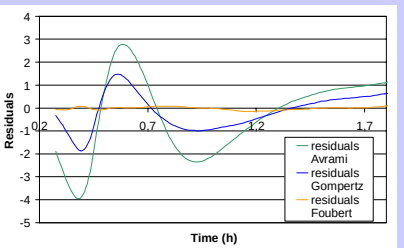


MODEL SELECTION

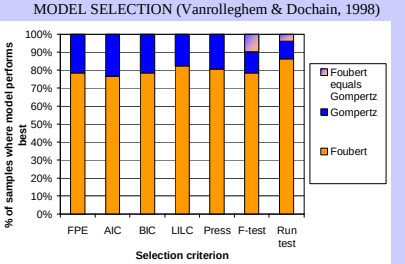
VISUAL REPRESENTATION OF QUALITY OF FIT



USE OF RESIDUALS TO COMPARE QUALITY OF MODELS



SEVEN DIFFERENT STATISTICAL METHODS FOR MODEL SELECTION (Vanrolleghem & Dochain, 1998)



Remark:since the Avrami model never performed best, this model was eliminated from the graph

CONCLUSIONS

- New model describes isothermal crystallization kinetics of fats much better than the generally used Avrami model
- Gompertz model already offers a big improvement compared to the Avrami model
- Proposed model performs even better than the Gompertz model in the majority of the cases.

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