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# MODELLING OF THE CRYSTALLIZATION KINETICS OF COCOA BUTTER

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## INTRODUCTION

The crystallization process consists of two steps: nucleation and crystal growth. However, before any crystallization can take place, supersaturation or supercooling of the mother phase must be achieved (Boistelle, 1988). The kinetics of fat crystallization, being dependent on the composition and on the processing conditions, is important for controlling operations in the food industry to produce the desired product characteristics (Metin & Hartel, 1998). In isothermal crystallization experiments the sample is quickly brought to a predetermined temperature at which the behavior of the system as a function of time is monitored.

Techniques used to monitor fat crystallization are differential scanning calorimetry (DSC), pulsed nuclear magnetic resonance (pNMR) and light-scattering techniques (Wright *et al.*, 2000).

The most generally used approach for the description of the isothermal phase transformation kinetics is the Avrami model developed in the 1940s (Avrami, 1940). This equation is given as:

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

where $f$ is the amount of solid fat at time $t$, $a$ is the value for $f$ as $t$ approaches infinity, $k$ is a crystallization rate constant and $n$ is the Avrami exponent.

Recently Kloek *et al.* (2000) used a modified Gompertz equation to describe the crystallization kinetics of fully hydrogenated palm oil in sunflower oil solutions. This equation is given by:

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

where $\mu$ is the maximum increase rate in crystallization and $\lambda$ is a measure for the induction time.

It is the aim of this paper to present a new model able to better describe the isothermal crystallization kinetics of fats. The quality of the proposed model will be compared to the quality of the Avrami and Gompertz models.

## MATERIALS AND METHODS

Different samples of cocoa butter were crystallized isothermally at 20°C (in threefold). Some were also crystallized at 17°C. Also some milk fat (fractions) were crystallized at two different temperatures. All these experiments were performed using DSC. The DSC crystallization curves were integrated to obtain the amount of heat released as a function of time. pNMR was used to record the isothermal crystallization kinetics of three milk fat fraction samples.
The data series were fitted to the different models by non-linear regression using the Sigmaplot 2000 software.

## RESULTS AND DISCUSSION

**The model (Foubert *et al.*, submitted for publication).** A new model, able to describe the isothermal crystallization kinetics of fats, was developed. The model was, in contrast to the Avrami and Gompertz models, written in the form of a differential equation. This type of equation has the advantage that it is often easier to interpret the equation mechanistically, it is easier to make minor changes to the equation on the basis of acquired knowledge and by incorporation of secondary models describing the temperature dependency of the parameters, the model can be used to describe non-isothermal crystallization kinetics. An algebraic solution however, offers the advantage that parameter estimation is easier because of more readily available software packages capable of non-linear regression of algebraic functions. Therefore both the differential equation and the algebraic solution are reported in this paper. The differential version of the equation can be written as

$$dh/dt = K * \left(h^n - h\right)$$

in which $h$ is the remaining crystallizable fat defined as

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

where $f$ is the amount of solid fat and $a$ is the value of $f$ for $t$ approaching infinity. The differential version of the equation shows that the fat crystallization process can be described as a forward first order reaction, which is compensated by a reverse reaction of the order $n$. To calculate the values of $h$ as a function of time according to this differential equation, the initial value for $h$, $h(0)$, needs to be specified. Via the definition of $h$ it can be seen that this value, $h(0)$, corresponds to the initially present amount of crystals $f(0)$. Thus, the proposed model contains a total of four parameters: $a$, the value of $f$ when $t$ approaches infinity, $K$, a rate constant, $n$, the order of the reverse reaction, which is also linked to the asymmetry of the curve and $f(0)$, the initially present amount of crystals. The algebraic solution of this differential equation is given as:

$$h = \left[1 + \left(h_0^{\,1-n} - 1\right) * e^{-(1-n)*k*t}\right]^{\frac{1}{1-n}}$$

**Model selection (Vanrolleghem & Dochain, 1998; Foubert *et al.*, submitted for publication).** Several methods exist to evaluate the quality of different models after fitting each model to the data. A first group are the information criteria: final prediction error (FPE), Akaike's Information Criterion (AIC), Bayesian Information Criterion (BIC) and LILC. Using these information criteria the proposed model appeared to be the best for 41 to 42 out of the 51 datasets (depending on the information criterion used), which means in 80 to 82% of the cases. For the other datasets the Gompertz model was the best.

The PRESS criterion (Predicted Residual Error Sum of Squares) is a criterion that gauges how well a regression model predicts new data. Using this criterion, the proposed model was the best in 42 cases (82%).

The statistical F-test is probably the most frequently applied method to decide whether the more complex model j is significantly better than model i. It appeared that in all cases the proposed model was better ($\alpha$ = 0.01) than the Avrami model and that in 41 cases the proposed model was better ($\alpha$ = 0.01 except for one case where $\alpha$ = 0.05) than the Gompertz model. In one case there was no significant difference between the two models.

The values of the mean sum of squared residuals (MSR) indicated that the proposed model is more flexible in describing the crystallization kinetics of fats. It gives a good fit for all the samples used, while the Gompertz model gives some very good fits, but also some significantly poorer fits.

The quality of the model can also be assessed by analysis of the properties of the calculated residuals (measured value minus predicted value) which need to be independent of each other. The run- and autocorrelation test can be used to check this. At first it seemed that none of the models satisfied the assumption of random and independent residuals. However, when the datasets were subsampled (only taking one data point each 5 minutes instead of each minute) this problem could be eliminated. When comparing the different models after subsampling, it appeared that the proposed model had a higher number of runs for 37 of the 43 cocoa butter samples (which equals 86%) and that the Gompertz and the proposed model had an equal number of runs for two samples. For the other samples the Gompertz model performed best taking this criterion into account. For the proposed model the autocorrelation test was satisfied in all cases, which was not the case for the other two models.

Apart from mathematical tools, one can also assess the quality of a model visually. Figure 1 shows the measured data points of one of the cocoa butter samples together with the predicted curves calculated with the Avrami, the Gompertz and the proposed model. Figure 2 shows the residuals for each of the models.

From the Figure it can be seen that the Gompertz and the proposed model are much closer to the data than the Avrami model. For this specific data sample the Gompertz model still deviates quite a lot from the measured data points.

**Evaluation of the models.** The newly developed model is capable of describing the isothermal crystallization kinetics of fats much better than the generally used Avrami model. The Gompertz model used by Kloek *et al.* (2000) already offers a big improvement when compared to the Avrami model. The proposed model, however, performs even better than the Gompertz model in the majority of the cases (Foubert *et al.*, submitted for publication).

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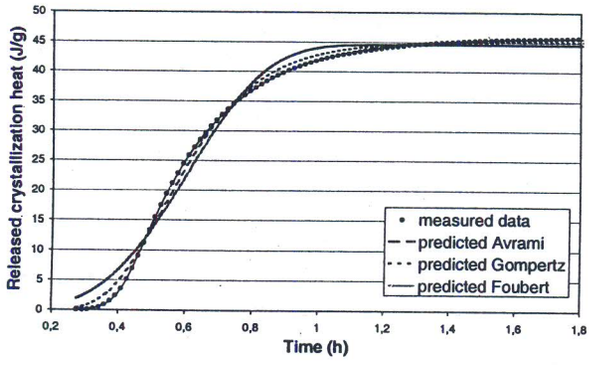


**Figure 1.** Visual representation of the quality of fit of the different models: measured data points and predicted curves for the three models.

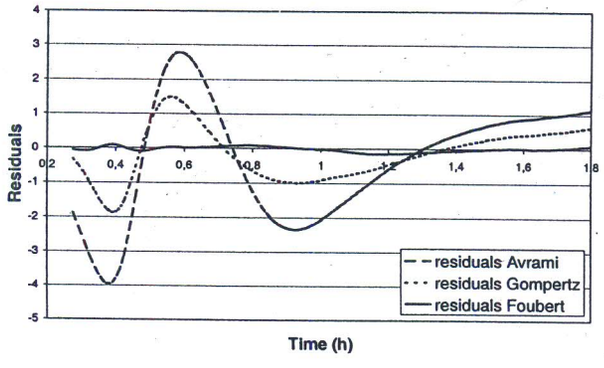


**Figure 2.** Visual representation of the quality of fit of the different models: residuals for the three models.

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