Monitoring Milk Fat Fractionation: Filtration Properties and Crystallization Kinetics

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ABSTRACT: The effect of fractionation temperature, residence time, and agitation rate on the chemical composition of the stearin and olein milk fat fractions was studied. During fractionation, filtration properties of the crystal suspension were monitored; crystallization kinetics was determined by ^{1}H NMR. Higher fractionation temperatures result in a lower stearin yield, more oil entrapment, and a lower final solid fat content of the crystal suspension. On the other hand, the chemical composition of the resulting fractions is not influenced. Longer residence times lead to longer filtration times and lower oil entrapment, whereas the yield is not affected. Longer residence times induce lower growth rates, but chemical composition is not influenced. Agitation rates varying from 10 to 15 rpm have no influence on the chemical composition of stearin and olein milk fat fractions. Higher agitation rates decrease the filtration quality and increase stearin yield, causing a softer stearin. In designing and monitoring milk fat fractionation, filtration experiments and the assessment of crystallization kinetics are valuable techniques, but compositional chemical analysis is not favorable.

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KEY WORDS: Agitation, filtration, kinetics, milk fat fractionation, residence time, statistical analysis, temperature.

Fractionation is a separation process that divides the fat into different fractions, each having its own physical and chemical properties. Industrially, three types of fractionation processes exist: dry, wet, and solvent fractionation (1). The latter is still used for special applications (cocoa butter substitutes from vegetable oils), but over time, the use of dry fractionation has progressively replaced solvent fractionation. In dry fractionation, crystals are formed by controlled cooling and agitation. The crystals in suspension are then separated by means of a rotary drum belt filter, a filter press, a centrifuge, or by means of an emulsifier followed by a centrifugation step. Fractionation of milk fat is extensively reviewed by Kaylegian and Lindsay (2) and more briefly by Deffense (3) and for edible oils in general by Hamm (4).

Fractionation compromises two process steps: the formation of a two-phase system by crystallization of the higher-melting TAG and subsequently a separation of those two phases (4). The latter is an important step since the amount of liquid fat entrapped in the filter cake will affect the physical properties of this fraction, called stearin, to a great extent. The entrapment of liquid fat is due to occlusion within the crystallized particles or aggregates as well as retention between the particles (4). The formation of mixed crystals in the form of agglomerated spherulites, which adsorb liquid within the crystals, depends to a considerable extent on the crystallization conditions employed (5,6). The amount of liquid oil remaining between the individual spherulite crystals in the filter cake is determined by the number, size, shape, and chemical composition of the crystals and the mechanism of filtration (6,7).

The crystal size and density have a major influence on the filtration time and the amount of filtrate (olein). These properties can be altered by the crystallization conditions and also by adding seed crystals (8). Dense crystals with an average diameter of more than 110 μm are easy to filter. Uniformly sized and shaped crystals will filter better than a suspension with a wide range of sizes (6). Black (9) studied the effect of crystallization parameters on filtration parameters. A crystal suspension that is easy to filter is produced by preheating the milk fat followed by a linear cooling, and a crystallization time of 8 h with slow agitation (10 rpm). Patience *et al.* (6) investigated the effects of agitation speed, diameter of impeller, and volume of crystallizer on the filtration resistance. It was found that as a function of tip speed, which is the speed at the extremities of the impeller, a minimum of filtration resistance was observed at low agitation (0.1–0.2 s^{-1} tip speed), while at lower and higher agitation speeds the suspension was more difficult to filter.

The chemical composition of milk fat fractions has been evaluated innumerable times. The differences in FA and TG compositions, based on carbon numbers, are small, especially compared to differences observed in the physical properties (3,10). Deffense (3) concluded that FA composition is not an appropriate tool to use to judge the selectivity of dry fractionation. Stereospecific distribution is a more important factor within the relationship between chemical composition and physical properties (11,12). The TG composition of milk fat can be based on M.W. (C-number) or carbon number combined with their degree of unsaturation. The latter is more closely related to the physical properties (3,11).

Static isothermal crystallization kinetics has been investigated quite often. However, few papers are available dealing with the kinetics of agitated isothermal systems. The Avrami equation is frequently used to study isothermal static crystallization. A disadvantage of this equation is that the Avrami exponent has little meaning in nonisothermal processes. The

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Gompertz equation, frequently used to describe microbial growth, is sometimes used as well (13).

The influence of process parameters such as fractionation temperature and agitation on the crystallization kinetics of milk fat was investigated by Grall and Hartel (14). This was done *via* microscopic analysis of samples taken during the fractionation process. As such, the induction time, nucleation rate, growth rate, and mass deposition rate were studied.

In this work the effect of three process parameters—fractionation temperature, agitation, and residence time—on the filtration properties, chemical composition, and crystallization kinetics is investigated. An alternative method is proposed to determine the oil inclusion by elaborating a small filtration experiment combined with a solid fat content (SFC) measurement. The oil inclusion is proportional to the ratio of mass fraction stearin to SFC of the crystal suspension.

EXPERIMENTAL PROCEDURES

Anhydrous milk fat (AMF). For each set of experiments, 25 kg of AMF from one batch was used to eliminate raw material variability. The AMF was supplied by Aveve Dairy Products (Klerken, Belgium).

Crystallization procedure. The pilot plant crystallizer was designed and built by Aveve Dairy Products. The fat was molten in a separate stainless-steel jacketed vessel at 60°C for at least 2 h. Molten fat was then transferred to the crystallizer, a stainless-steel jacketed vessel that was already heated to 60°C before transfer. During the crystallization procedure, the oil and water temperatures were measured on-line and further processed *via* Access (Microsoft). These measurements resulted in a typical time–temperature profile as displayed in Figure 1. The temperature profile of the water was altered in order to reach the desired oil temperature at the end of the fractionation experiment. Therefore, the oil-cooling curves depend on a predefined water-cooling profile. Conditions during the first 2 h of each experiment were identical. Hereafter, the fractionation temperature, the agitation rate, and the residence time (total time of the fractionation) were altered according to the central composite design.

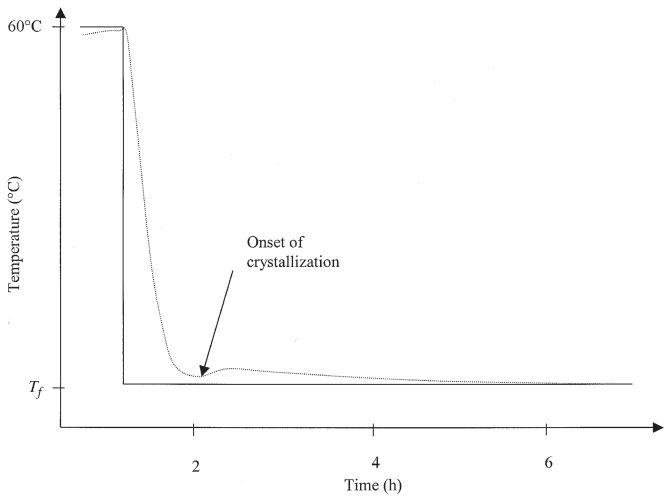

FIG. 1. Typical temperature profile for fractionation. T_f = oil temperature at the end of the fractionation; (····), oil temperature; (—), water temperature.

Filtration properties. At the end of the fractionation experiment about 400 g crystal suspension was vacuum filtered on a 0.1-m diameter filter. A filter cloth NKD 2396 (Marsyntex, Neumünster, Germany) with a porosity of 30 µm was used. The yields of stearin and olein were determined as weight fractions of the crystal suspension. Other parameters that were determined were the SFC of the slurry, the thickness of the filter cake, and the filtration time. These primary parameters were used to calculate some secondary parameters that were used to evaluate the filtration properties. The secondary parameters are:

$$\text{cake density} = \frac{\text{mass fraction stearin}}{\text{volume of the filter cake}} \quad [1]$$

$$\text{relative filtration time} = \frac{\text{filtration time}}{\text{amount of crystal suspension loaded on the filter}} \quad [2]$$

$$\frac{\text{yield}}{\text{SFC}} = \frac{\text{mass fraction stearin}}{\text{solid fat content of crystal suspension}} \quad [3]$$

$$= \frac{\text{g oil present in filter cake} + \text{g solid fat}}{\text{g solid fat}} \approx \text{oil inclusion} \quad [4]$$

FA composition. The FA composition was determined as methyl esters on a DB-Wax column (J&W Scientific, Folsom, CA; 30 m length, 0.32 mm i.d., 0.25 µm film thickness). The temperature program was 45°C (2 min), 10°C/min to 240°C, hold for 9 min. The injector and detector were held at 250°C.

TG composition. The TG composition was determined by injecting 1 µL of a solution of one fat droplet in 2 mL isooctane. A high-resolution GC column, DB-XLB (J&W Scientific; 2.5 m length, 0.25 mm i.d., 0.25 µm film thickness) was used. The temperature program was 110°C (0.5 min); 50°C/min to 265°C, hold for 3.6 min; 10°C/min to 280°C, hold for 0 min; 8°C/min to 345°C, hold for 5.1 min. The temperature of the injector was programmed as follows: 80°C (0.5 min), 200°C/min to 345°C hold for 16.4 min. The temperature of the detector was set to 345°C. A separation based on M.W. of the TG (C_{24} to C_{54}) was obtained.

Crystallization kinetics. Samples were taken during fractionation at intervals varying from every 10 to every 30 min. The SFC was determined in duplicate with ^{1}H NMR (pNMR) (Bruker PC20 series; Karlsruhe, Germany). The SFC was plotted against time, which resulted in a sigmoid curve (Fig. 2).

The Gompertz equation (13) was used to describe the crystallization process:

$$\text{SFC}(t) = \text{SFC}_{\max} \exp\left(-\exp\left\{\frac{(\mu e)}{\text{SFC}_{\max}}\left[(\lambda - t) + 1\right]\right\}\right) \quad [5]$$

This equation previously has been used to describe isothermal crystallization of fats (13). The parameter $\text{SFC}_{\max}$ (%) is related to the final SFC. The parameter µ (%·min^{-1}) is related to the maximal growth rate, whereas λ (min) is the induction time of crystallization.

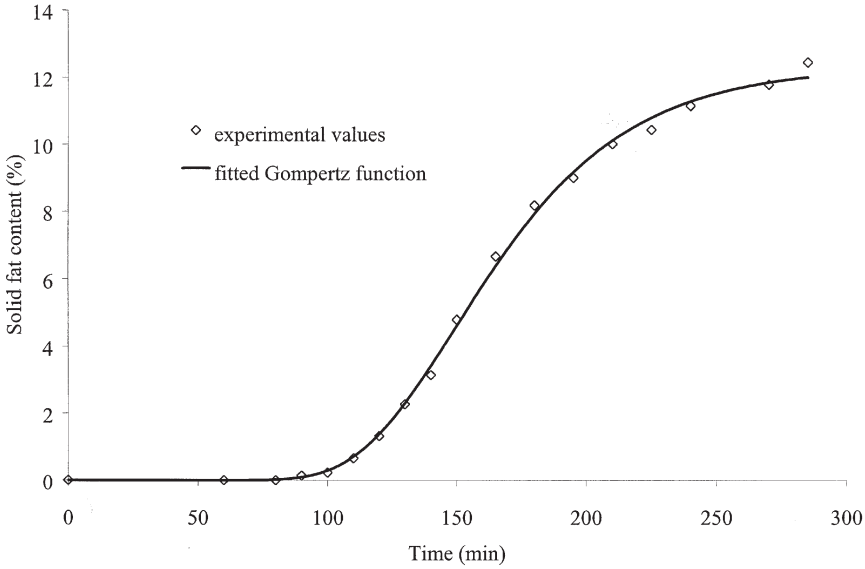

FIG. 2. Gompertz equation fitted to crystallization curve from fractionation; x-axis, residence time of milk fat in the crystallization vessel; y-axis, solid fat content of the crystal suspension in the crystallization vessel.

Parameter estimation was performed by nonlinear regression using the Sigmaplot 2000 software (SPSS Inc., Chicago, IL). This software uses the Marquardt–Levenberg algorithm to find the parameters that give the best fit between the model and the data.

Experimental design. The experimental setup was a central composite design. Two sets of 13 experimental combinations were chosen to obtain a relevant statistical survey of the effect of the process parameters. The center point was repeated five times (Fig. 3). In the first set, agitation and temperature were evaluated, and in the second set the effects of temperature and residence time were investigated. The software Design-Expert® 5.0 (Stat-Ease Inc., Minneaplis, MN) was used to fit polynomials to the responses such as crystallization parameters or filtration properties. The final result of these sets of experiments is a response surface within certain ranges of the process parameters. The response surface is described by an equation of the following form:

$$Y = aA + bB + cA^2 + dB^2 + eAB + f \qquad [6]$$

The parameter Y is a crystallization parameter or a filtration property, whereas A and B represent the coded process parameters agitation, temperature, or residence time. The value −1 in coded form is equal to the low level of the process parameter. The value +1 in coded form corresponds to the high level of the process parameter. For example, in the case of residence time the low level was 6 h, which corresponds to a coded residence time parameter −1, whereas the high level was 12 h, which corresponds to an coded residence time parameter +1. The coefficient f corresponds to the intercept discussed in the Results and Discussion section.

First, whether the variation of a response parameter could be explained as a function of process parameters was checked with an F-test. In this case, a P-value of 0.1 was the limit used to retain a parameter for further investigation. Second, whether the coefficients a to e were significantly different from zero was tested with a t-test. For example, when the coefficient a is significantly different from zero, there is a significant linear effect of the process parameter A. The coefficients a and b represent the linear effects of the process parameters, and c, d, and e represent the quadratic and interaction effects, respectively. The significance levels can be derived from the representation in the Tables 1 and 4 as follows: A coefficient with * as superscript is equal to a P-value between 0.01 and 0.05. A coefficient with ** as superscript is equal to a P-value smaller than 0.01. When the F-test did not detect any relationship between the process parameters and the Y response (a filtration property or a crystallization parameter), evaluating the significance level of each individual effect was not relevant.

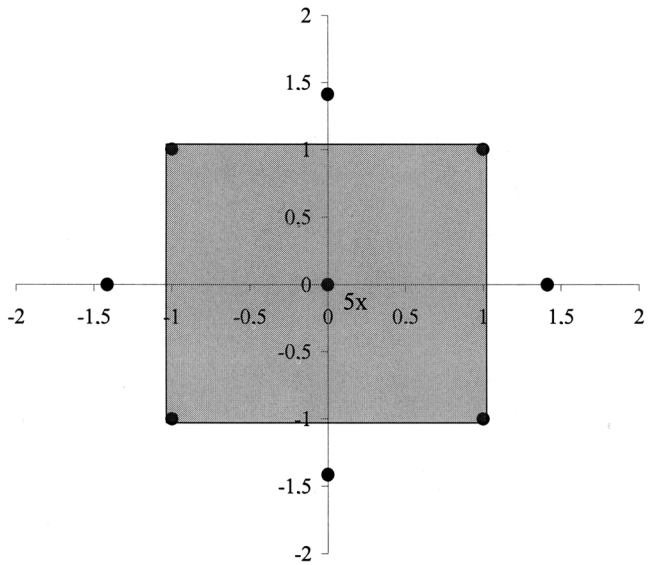

FIG. 3. Spatial distribution for data points of the coded factors A and B in a central composite design.

TABLE 1
Statistical Analysis of the Influence of Fractionation Temperature (A) and Agitation Rate (B) on Filtration Properties and Crystallization Kinetics[a]

Parameter	*P* value of *F*-test	Intercept	*A*	*B*	A^2	B^2	*AB*
Yield (*Y*)	<0.0001	44.4	–5.35**	NS	–1.73**	NS	NS
Y/final SFC	0.7586			Not relevant			
Rel. filtration time	0.1526			Not relevant			
Cake density	0.0183	0.75	–0.020	NS	–0.037*	NS	NS
SFC_{max}	<0.0001	12.49	–1.34**	0.37*	–0.54**	NS	NS
μ (growth rate)	0.0008	0.11	–2.981E – 3	NS	–0.014**	NS	NS
λ (induction time)	0.3809			Not relevant			

[a]*Y* = yield of stearin; SFC = solid fat content; NS = not significant = *P*-value *t*-test > 0.05. Not relevant = *t*-test not necessary if *F*-test is not significant ($P < 0.1$). *P-value *t*-test < 0.05. **P-value *t*-test < 0.01.

RESULTS AND DISCUSSION

Influence of fractionation temperature and agitation. In a first experimental central composite design, the process parameters fractionation temperature and agitation were investigated. Fractionation temperature and agitation rate ranged from 21 to 27°C and 11.5 to 14.5 rpm, respectively. Experimental combinations chosen within these ranges resulted in a crystal suspension with good filtration properties as determined in preliminary tests. The residence time of each fractionation was 6 h.

(i) Filtration properties. Oil entrapment previously was monitored by analysis of the carotene naturally present in milk fat in both fractions (6). In this study, a more direct measurement is used: the ratio yield to the amount of solid fat measured by pNMR. For example, if the crystal suspension contains 15% solids and the yield (*Y*) of stearin is 45%, the ratio *Y*/SFC is 3. This means that the filter cake contains one-third solid material and two-thirds liquid oil. An average value of 3.5 is observed. A value of 3 is observed as a minimum while proportions higher than 4 are related to poor filtration quality.

From Table 1 one can conclude that stearin yield is strongly dependent on the fractionation temperature. No effect of agitation was detected on yield, in contrast to the results published by Patience *et al*. (6). This is probably related to the rather small experimental range used for agitation rate. The parameter yield over SFC is not significantly affected by the process parameters, which means that no effect of oil inclusion is observed within the experimental ranges chosen. The same may be concluded for the filtration time.

The fractionation temperature influences the cake density to a certain extent, probably due to differences in crystal size and/or morphology. This was previously observed by Grall and Hartel (14): At 30°C more loosely packed crystal aggregates are formed, whereas at 20°C more compacted clumps of smaller crystals are observed.

To investigate a possible effect of higher agitation rates, experiments were performed at 13 and 25 rpm at fractionation temperatures of 20 and 28°C. Owing to more intense agitation, an increase in oil entrapment, a large increase in filtration time, and a denser filter cake were observed. These results can be

TABLE 2
Effect of Higher Agitation Rates on Filtration Properties[a]

T_f (°C)	Parameter	13 rpm	25 rpm
20	*Y*/final SFC	3.5	3.8
	Rel. filtration time	0.25	2.98
	Final SFC	13.7	13.9
	Cake density	0.69	0.80
	SFC at 20°C stearin	43.5	38.6
28	*Y*/final SFC	3.7	4.0
	Rel. filtration time	0.21	1.34
	Final SFC	9.8	10.2
	Cake density	0.67	0.77
	SFC at 20°C stearin	44.7	40.6

[a]T_f = fractionation temperature. For other abbreviations see Table 1.

TABLE 3
Average FA Composition of the Olein and Stearin Fraction of the First Central Composite Design[a]

	Olein		Stearin	
FA	Average	SD	Average	SD
4:0	4.3	0.1	3.3	0.1
6:0	2.9	0.1	2.2	0.1
8:0	1.6	0.06	1.3	0.1
10:0	3.5	0.1	3.1	0.2
10:1	0.32	0.02	0.26	0.02
12:0	3.7	0.4	3.7	0.3
14:0	11.0	0.4	11.9	0.4
14:1	1.22	0.07	0.95	0.04
15:0iso	0.25	0.02	0.26	0.02
15:0anteiso	0.54	0.03	0.47	0.03
15:0	1.04	0.03	1.14	0.03
16:0	30.7	0.4	35.1	0.5
16:1	2.0	0.1	1.54	0.06
17:0iso	0.38	0.05	0.45	0.06
17:0anteiso	0.41	0.02	0.45	0.03
17:0	0.48	0.05	0.55	0.05
17:1	0.31	0.03	0.24	0.02
18:0	7.3	0.4	9.2	0.5
18:1	20.7	0.6	16.7	0.6
18:2	2.8	0.1	2.4	0.1
18:3	0.32	0.04	0.24	0.02
18:2 (CLA)	0.52	0.04	0.39	0.05
SCFA	12.4	0.3	9.8	0.4
USFA	24.5	0.5	19.7	0.6
BCFA	1.58	0.07	1.62	0.09

[a]SCFA = short-chain FA (4:0–10:0); USFA = unsaturated FA (10:1–18:1, 18:2, 18:3, and CLA); BCFA = branched-chain FA (15:0–17:0 iso and anteiso).

TABLE 4
Statistical Analysis of Influence of Fractionation Temperature (A) and Residence Time (B) on Filtration Properties and Crystallization Kinetics[a]

Parameter	*P*-value of *F*-test	Intercept	*A*	*B*	A^2	B^2	*AB*
Yield	0.0232	0.43	–0.025*	NS	NS	NS	NS
Y/final SFC	0.0116	3.23	0.19*	–0.18*	NS	NS	NS
Rel. filtration time	0.0262	0.97	NS	0.42*	NS	NS	NS
Cake density	0.0465	0.75	NS	–3.46E – 03	NS	0.042*	NS
SFC_{max}	<0.0001	12.57	–1.42**	NS	NS	NS	NS
μ (growth rate)	0.0006	0.076	NS	–0.013**	NS	0.011**	NS
λ (induction time)	0.327				Not relevant		

[a]For abbreviations see Table 1. **P*-value *t*-test < 0.05. ***P*-value *t*-test < 0.01.

explained by higher shear rates, which break down crystal aggregates (Table 2). Besides a change in filtration properties, a softer stearin was produced as a result of more oil inclusion. By combining the data of the additional experiments with the data of the central composite design, similar responses are found as in Table 1, except that relative filtration time is significantly influenced by the process parameters. This could not be derived from the data of the central composite design. By variance analysis on the extended data set, the filtration time was found to increase with increasing fractionation temperatures and increasing agitation rates. Moreover, a significant interaction effect was found that demonstrates that the effect of agitation is smaller at higher fractionation temperatures.

(ii) FA composition. The FA composition is altered, as can be expected. The short FA up to 10:0, as well as unsaturated FA, are present in higher concentrations in the olein fraction (Table 3). For the branched-chain FA, a concentrating effect in the olein was only seen for 15:0 anteiso. Apparently, branching of saturated FA has little influence on their incorporation in a crystal habit (Table 3). Since rather small differences in FA composition between the experiments could be detected, no further statistical analysis was performed.

(iii) TG composition. The TG composition is altered, as can be expected. TG with carbon numbers from 24 to 40 are concentrated in the olein, whereas TG ranging from 44 to 52 are present in higher concentrations in the stearin (results not shown).

The influence of process parameters on the TG composition was rather small compared to the changes in physical properties and was not further investigated. Efforts to combine FA composition with TG composition by means of principal component analysis did not result in a better correlation with the process parameters.

(iv) Crystallization kinetics. The Gompertz equation described the crystallization curves adequately (R^2 = 0.997–0.999) as illustrated in Figure 2. The final or equilibrium solid fat content, SFC_{max}, is determined by fractionation temperature and agitation rate (Table 1). A higher fractionation temperature results in less solid fat. A higher agitation rate gives higher SFC_{max}, which can be explained by better diffusion, as this is one of the limiting factors during crystallization. This effect is quite surprising, since the final SFC is a thermodynamic parameter and the diffusion rate is suspected to be more related to the kinetic factor growth rate (μ).

The response of growth rate to variations in the process parameters is outlined in a perturbation plot (Fig. 4). The perturbation graph demonstrates the effect of changing one factor while holding the rest constant at the intermediate level. The effect of each individual process parameter is represented as a linear or quadratic function, depending of the selected model. The x-axis of this figure represents the coded parameters: −1 represents the low level of the range, 0 the intermediate or center point of the range, and +1 the high level of the process parameter. The growth rate is maximal at intermediate temperatures (24°C), probably caused by two adverse effects: a decrease in the temperature leads to a larger driving force for crystallization but lowers the diffusion rate as well (Fig. 4). The induction time is, as suspected, not influenced by agitation or fractionation temperature, as the start of the fractionation scheme is similar for all experiments (Table 1).

Influence of fractionation temperature and residence time. In a second central composite design, the process parameters fractionation temperature and residence time were investigated, and the agitation rate was held constant at 13 rpm. Fractionation temperature and residence time ranged from 21 to 27°C and 6 to 12 h, respectively.

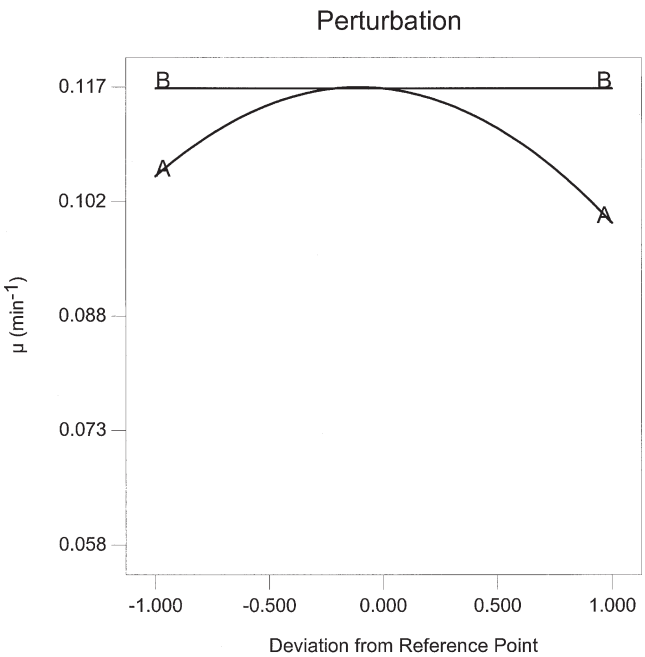

FIG. 4. Perturbation plot representing the effect of fractionation temperature (A) and agitation rate (B) on the growth rate (μ).

(i) Filtration properties. Only the fractionation temperature influences the yield significantly; the effect of longer residence time is not significant (Table 4). The effect of fractionation temperature is similar to that in the first central composite design.

The ratio yield/final SFC is determined by both process parameters. Low fractionation temperatures and longer residence times result in less oil entrapment, although longer filtration times can be expected (Table 4).

The effect of residence time on the relative filtration time is significant, but no influence is observed of the fractionation temperature (Table 4). At longer fractionation times, the final suspension is more difficult to filter. Longer stirring times damage the crystal aggregates, and at the end smaller crystals are obtained, probably with a broader size distribution.

(ii) FA composition. Similar trends are observed as in the previous central composite design: Short-chain FA (4:0–12:0) are decreased in the stearin (results not shown). Saturated long-chain FA are increased in the stearin, whereas long-chain unsaturated FA are decreased in the stearin (results not shown).

(iii) TG composition. Similar trends were observed as in the previous central composite design: low M.W. TG up to C_{42} are concentrated in the olein, and the amount of high-M.W. TG are increased in the stearin, except for C_{54} (results not shown).

(iv) Crystallization kinetics. The final SFC_{max}, as determined by parameter estimation, is influenced significantly only by fractionation temperature. Growth rate is strongly influenced by residence time in the range from 6 to 9 h, while at longer residence times this effect levels off (Fig. 5).

Gibon and Tirtiaux (15) showed that slower growth rates lead to a more selective crystallization. In this second central composite design, the residence time was changed, leading to slower growth rates. However, an effect on the crystal growth rate was observed only by extending the residence time from 6 to 9 h. From these data it can be concluded that for milk fat fractionation under the described conditions, residence times longer than 9 h are not effective to enhance the selectivity, as the growth rate is not influenced anymore. The only process that will occur after 9 h is the recrystallization of the crystal mass, also called segregation.

By a similar approach, the optimal residence time of an industrial plant can be determined as well. It is concluded that modeling crystallization kinetics of a fractionation process can be a useful tool for process design.

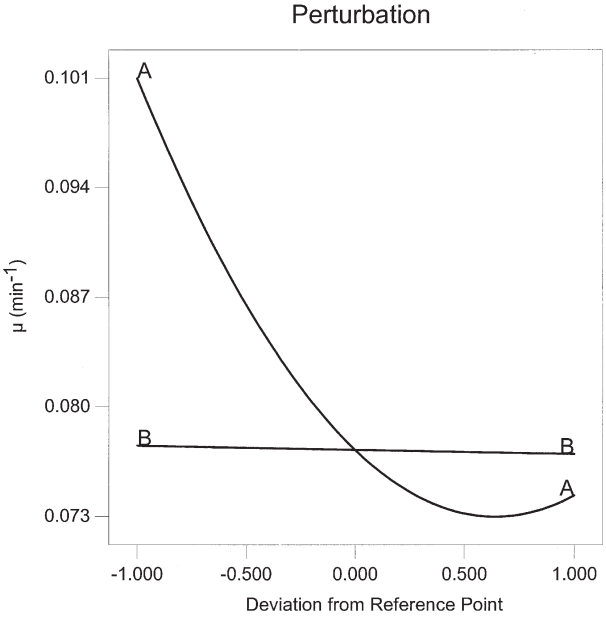

FIG. 5. Perturbation plot representing the effect of residence time (A) and temperature (B) on the growth rate (μ).

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