Available online at www.sciencedirect.com

SciVerse ScienceDirect

Procedia Engineering 42 (2012) 918 – 923

Procedia Engineering

www.elsevier.com/locate/procedia

20th International Congress of Chemical and Process Engineering CHISA 2012
25 – 29 August 2012, Prague, Czech Republic

Characterization of the stearin obtained by thermal fractionation of anhydrous milk fat

E. C. Bonomi[a] , V. Luccas[b], T. G. Kieckbusch[a] a*

[a]School of Chemical Engineering, University of Campinas, Campinas, SP, 13083-853, Brazil
[b]Cereal Chocotec, Institute of Food Technology (ITAL), P.O. Box 139, Campinas, SP, 13070-178, Brazil

Abstract

Thermal fractionation of anhydrous milk fat with high initial content of low molecular weight TAGs was performed based on a 2^2 factorial experimental design with three central and two axial points. The independent variables were the crystallization temperature and the cooling rate. A 2.0 L agitated glass reactor was used and the rotation was kept at 20 rpm. The filtration was performed under vacuum (500 mmHg), using a 14 μm average pore diameter filter paper. Curves of isothermal crystallization of the stearin fraction showed that increasing the crystallization temperature, increases the induction period and decreases the maximum solid content of stearin. An increase of the crystallization temperature resulted in an increase in solid fat content. All runs achieved an efficient fractionation using a single separation step and stearin with defined characteristics can be obtained adapting the process conditions.

Keywords: Butter oil, thermal fractionation, stearin

1. Introduction

Anhydrous milk fat (butter oil) is widely used as additive in high-quality foods in order to provide smooth taste and pleasant odor on the human palate. Butter oil is considered the most complex fat mixture found in nature, containing hundreds of lipidic components resulting in a large range of melting point and cross-crystallizations [1]. Milk fat contains about 65% saturated fatty acids (mainly C16:0, C18:0 and

* Corresponding author. Tel.: +55 19 35213930;
E-mail address: theo@feq.unicamp.br

1877-7058 © 2012 Published by Elsevier Ltd.
doi:10.1016/j.proeng.2012.07.484

C14:0) and about 35% unsaturated fatty acids (mainly C18:1). Samples of butter oil can vary in chemical composition and consequently in their physicochemical properties due to race and nutrition of the dairy cows as well as by seasonal and geographic factors [2]. Some of the functional characteristics of milk fat, like plasticity, hardness, and spreadability, can restrict its use in industrial scale.

Thus, many studies have been conducted in order to modify the milk fat chemical composition and therefore changing its chemical and physical properties. Thermal fractionation is the most recommended physical treatment, since it is a low cost process, not requiring solvents, uses simple equipments and retains most of the milk fat flavour [3]. In thermal fractionation the separation of the triacylglycerols (TAGs) is based on their melting points differences. The process consists of two main steps: crystallization and separation. Crystallization considers nuclei formation and crystal growth, and the separation is intended to remove the olein fraction (liquid part) from the stearin (crystallized fraction). A single stage of separation is usually adopted in order to obtain these fractions. The fractions have different physical and chemical properties and can be applied to different products depending on the purpose.

This study evaluates the characteristics of stearin obtained from brazilian samples of butter oil using an experimental design. The independent variables were the crystallization temperature (21°C to 27 °C) and the cooling rate (5 to 20 °C/hour). The stearin fractions were characterized by the TAGs composition and the solid fat content (SFC), measured by NMR. The difference between the solid fat content at 25 °C and at 35ºC ($\Delta S_{25°C-35°C}$) and the value of SFC at 25°C ($S_{25°C}$) were used as responses variables.

2. Materials and methods

2.1. Raw materials

The anhydrous milk fat used in the fractionation experiments was donated by Fonterra Brasil Ltda (Goiânia, GO, Brazil). At the time of use, the fat pails of 2 kg under refrigeration, was heated to 65°C.

2.2. Analytical Methodology

Triacylglycerol composition: determined using a capillary gas chromatograph Agilent 6850 (US), with a DB-17HT (50% methyl phenyl polysiloxan) 15 m column and internal diameter of 0.25 mm. Duplicate sample injections were performed, and the TAGs composition were calculated according to [4].

Solid fat content: SFC was determined by NMR, using a Bruker Minispec PC120 (Germany) and the direct method AOCS Cd 16b-93 [4].

Crystallization isotherms: samples were melted (100°C/15 min) and the increase in solid fat content as a function of the crystallization time was monitored by NMR Spectrometry, with the compartment stabilized at the pre-defined crystallization temperature [5].

2.3. Fractionation process

The fractionation was based on an experimental design with three central points and two axial points. The independent variables were the crystallization temperature (21, 22, 24, 26 and 27°C) and the cooling rate (5, 7.2, 12.5, 17 and 20°C/h). The conditions of each fractionation test are listed in Table 1.

The fractionation was performed in a system compose by two vessels, the crystallizer and the filtration device, both connected to a thermostatic bath. The crystallizer was a 2L jacketed glass reactor with a 20 cm anchor-paddle mechanical stirrer. Milk fat (2kg) was heated to 60°C for 15 minutes and then cooled at the previously defined rate, down to the crystallization temperature and maintained under agitation (20 rpm) for the pre-determined time. At the end of this step, a stopcock was opened and the product was transferred by gravity to the jacketed stainless steel receiving vessel of the filtration system. The mass

was filtered under vacuum through a filter paper (average pore diameter of 14 µm) supported by a perforated disc.

Table 1. Conditions of the experimental design and nomenclature

Independent variables	Thermal fractionation										
	F 1	F 2	F 3	F 4	F 5	F 6	F 7	F 8	F 9	F 10	F11
Crystallization temperature (ºC)	24.0	27.0	21.0	21.9	24.0	24.0	26.1	26.1	21.9	24.0	24.0
Cooling rate (ºC/h)	12.5	12.5	12.5	17.8	12.5	20.0	7.2	17.8	7.2	5.0	12.5

3. Results and discussion

Table 2 present the triacylglycerol composition of the stearin fractions obtained. The TAGs composition confirmed that the stearin fractions of all tests contain higher amount of long chain triacylglycerols (C42 to C54) if compared to the original butter oil. The values indicate that the tests F7 and F10, obtained stearin with the highest concentration of long chain triglycerides, about 67% and 65%, and the summation of short chain triglycerides is about 35% and 30% lower than that of the milk fat, respectively. These tests were performed under lower cooling rates.

Table 2. Triacylglycerol composition of the milk fat and in the stearin fractions obtained in the fractionation experiments

N° carbon	Milk fat	Stearin										
		F1	F2	F3	F4	F5	F6	F7	F8	F9	F10	F11
C 26	0.33	0.44	0.43	0.44	0.48	0.46	0.44	0.41	0.37	0.40	0.60	0.46
C 28	0.59	0.28	0.34	0.30	0.35	0.27	0.29	0.30	0.28	0.22	0.20	0.26
C 30	0.88	0.51	0.46	0.56	0.57	0.53	0.52	0.50	0.46	0.50	0.42	0.47
C 32	2.11	1.39	1.34	1.52	1.51	1.40	1.39	1.26	1.29	1.34	1.26	1.48
C 34	5.70	3.90	3.99	4.54	4.69	4.24	4.08	3.77	3.56	4.50	3.51	4.16
C 36	13.38	10.23	8.83	9.57	9.48	9.23	8.97	8.60	9.28	9.96	9.11	8.94
C 38	17.30	11.04	11.13	13.78	13.10	12.46	12.88	11.58	11.28	11.67	10.81	12.37
C 40	10.45	10.66	8.85	6.80	7.85	7.12	8.46	6.70	8.85	8.85	8.97	8.06
C 42	6.84	7.60	7.01	8.94	7.58	7.49	8.42	8.34	7.07	6.97	7.76	8.10
C 44	6.34	6.97	7.16	9.11	8.76	8.32	8.47	7.68	9.00	7.54	9.15	8.74
C 46	4.66	6.94	8.10	8.20	6.93	7.30	7.69	7.37	7.42	6.99	7.67	7.43
C 48	7.96	9.95	10.90	10.74	10.83	9.97	10.14	10.84	9.75	10.22	10.25	10.50
C 50	11.47	14.85	16.02	10.30	11.52	15.21	13.42	16.31	15.16	13.87	14.43	14.06
C 52	8.84	11.18	12.39	10.42	11.95	12.31	11.39	12.21	12.12	12.13	11.21	10.59
C 54	3.15	4.08	3.07	4.78	4.40	3.70	3.44	4.15	4.12	4.86	4.67	4.38
Σ C24 - C34	9.61	6.52	6.55	7.37	7.61	6.89	6.72	6.24	5.96	6.95	5.98	6.83
Σ C36 - C40	41.13	31.92	28.81	30.14	30.43	28.81	30.31	26.87	29.41	30.47	28.88	29.37
Σ C42 - C54	49.25	61.57	64.65	62.49	61.97	64.30	62.97	66.89	64.64	62.56	65.12	63.81
Total	100	100	100	100	100	100	100	100	100	100	100	100

Isotherm curves of the milk fat were obtained at the specified crystallization temperatures in order to compare behaviors and to estimate the time required to reach the maximum solids content in the process (Figure 1a). The curves show that increasing the temperature of crystallization of anhydrous milk fat increases the time of induction and decreases the maximum solids content. Inspection of the shape of the curves indicated the following time/temperature combinations for the fractionation runs: 90 min at 21°C; 100min at 21,9°C; 120 min at 24°C; 180 min at 26,1°C and also 27°C.

The solid fat content of the stearin fractions and of the original milk fat are shown in Figure 1b and the curves indicate that Test F7 and Test F10 obtained the largest $\Delta S_{25°C-35°C}$, around 20% and a SFC around 3% at 40°C. These are desirable requirements in chocolate manufacturing. Test F2 and Test F7, on the other end, obtained stearin fractions with approximately 32% of solid fat content at a temperature of 25°C. As expected, under the same cooling rate, an increase in the crystallization temperature resulted in an increase in solid fat content in the stearin fractions. A correlation of these data with the triacylglycerol composition (Table 2) shows that this Tests F7 and F10 are the ones with the higher amount of long chain triacylglycerols. This result is consistent, since the long chain TAGs have a higher number of carbon, a higher melting point and therefore a higher solid fat content.

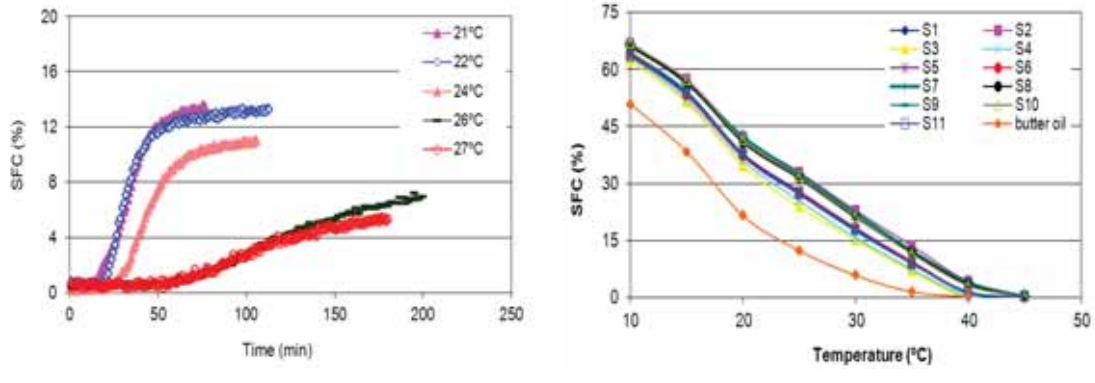
Table 2 shows the results of analysis of variance (ANOVA) for $\Delta S_{25°C-35°C}$ and for $S_{25°C}$ of the stearin fractions. The coefficient of determination of the model, R^2, is 0.94% for $\Delta S_{25°C-35°C}$ and 0.96% for $S_{25°C}$ and the percentage of variation explained by the model for the analyzed responses is high.

The value of F calculated (MQ_R/MQ_r) for $\Delta S_{25°C-35°C}$ and $S_{25°C}$ was 35.54 and 52.48, respectively. Since the value of $F_{0,95;3;7}$ (tabulated) is 4.35, that is 8 and 12 times smaller than F calculated, for the respective.

At 95% confidence the reason MQ_{lfit}/MQ_{pe} is less than the value of $F_{0,95;5;2}$. Therefore, the mathematical equations (Equations 1 and 2) obtained are considered valid and predictive, and the model is able to predict the responses in question.

$$\Delta S_{(25°C-35°C)} = 18,33 + 0,84 * T_{crist} - 0,47 * Tx_{resfr} + 0,51 * (Tx_{resfr})^2 \quad (1)$$

$$S_{25°C} = 27,91 + 2,97 * Tcrist - 1,12 * Tx\ resfr + 0,93 * (Tx\ resfr)^2 \quad (2)$$



(a) (b)

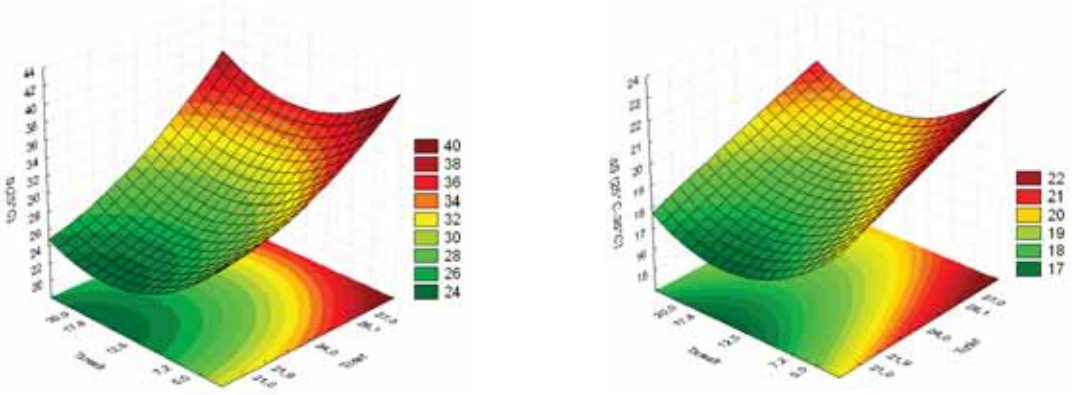
Fig. 1 (a) Crystallization isotherms of milk fat at test temperatures (b) Solid fat contents of the stearin fractions and butter oil

Table 2. ANOVA for the model adjustment represented by Equation 1 and 2.

Response	Source of variation	Quadratic sum	Nº de d.f.*	Quadratic mean	*F*
$\Delta S_{25°C-35°C}$	Regression (SQ_R)	9,01	3	3,00	35,54
	Residues (SQ_r)	0,59	7	0,09	
	Lack of fit (SQ_{lfit})	0,53	5	0,11	3,25
	Pure error (SQ_{pe})	0,07	2	0,032	
	Total (SQ_T)	9,60	10		
$S_{25°C}$	Regression (SQ_R)	85,61	3	28,54	52,48
	Residues (SQ_r)	3,81	7	0,54	
	Lack of fit (SQ_{lfit})	3,42	5	0,68	3,52
	Pure error (SQ_{pe})	0,38	2	0,19	
	Total (SQ_T)	89,42	10		

* d.f. (degrees of freedom)

Figures 2a and 2b show the relation between cooling rate and crystallization temperature and the responses $\Delta S_{(25°C-35°C)}$ and $S_{25°C}$ for the stearin fractions, respectively. As seen in Figure 2a, an increase in $\Delta S_{25°C\ -35°C}$ occurs with increasing T_{crist} (linear term) and with the decrease Tx_{resf} (linear term), indicating that the effect of crystallization temperature is higher than the cooling rate, 1.67% and 0.95% respectively. Figure 2b, shows that the increase in $S_{25°C}$ happens with the increase in T_{crist} and with decreasing Tx_{resf}. Similarly to the response of $\Delta S_{(25°C-35°C)}$, but at a more intense way, the effect of crystallization temperature is also higher than the cooling rate, 5.92% and 2.23% respectively.



(a) (b)

Fig. 2. Surface response to (a) $\Delta S_{(25°C-35°C)}$ and (b) $S_{25°C}$.

4. Conclusion

The isothermal crystallization of milk fat determined at the test temperatures provided the optimum time to achieve efficient fractionation. Statistical analysis revealed that the crystallization temperature has a greater effect than the cooling rate on thermal fractionation of milk fat, and provided a good model for

predicting the $\Delta S_{25°C-35°C}$ and $S_{25°C}$. The triacylglycerol composition for each sample was consistent with the results since the tests with the larger amount of long-chain triacylglycerol, contained the higher solid fat content. This simple thermal fractionation setup indicated the possibility of separating fat fractions, and to produce stearin with desired characteristics by changing process conditions.

References

[1] Lopez C, Bourgaux C, Lesieur P, Riaublanc A, Ollivon M. Milk fat and primary fractions obtained by dry fractionation 1. Chemical composition and crystallisation properties. *Chem Phys Lipids* 2006;**144**:17 – 33.

[3] Deffense E. Dry fractionation technology in 2000. *Eur J Lipid Sci Technol* 2000;**102**:234 – 236.

[4] Ribeiro APB, Claro da Silva R, Gioielli LA, Gonçalves MIA, Grimaldi R, Gonçalves LAG, Kieckbusch TG. Physico-chemical properties of Brazilian cocoa butter and industrial blends. Part I – Chemical composition, solid fat content and consistency. *Grasas y Aceites* 2012;**63**:79 – 88.

[5] Campos R. Experimental methodology. In: *Fat Crystal Networks*. Marcel Dekker, Marangoni AG (Ed), New York, 2005.