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Phase Composition During Palm Olein Fractionation and its Effect on Soft PMF and Superolein Quality

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Abstract Refined palm olein was dry fractionated via three different cooling programs on laboratory-scale fractionation equipment. The enrichment and depletion of the main triacylglycerols in the liquid and solid phase was plotted as a function of the crystallization degree of the oil. It was shown that for the given conditions and palm olein composition, the initial crystals mainly consisted of PPP, diacylglycerols, POP and PLP. At higher crystallization degrees, a sharp viscosity increase in the crystal suspension was primarily related to an obvious decrease of POP but also of POS in the recovered superolein, while the general crystallization rate of the system remained unchanged. Rather than a change in crystallization rate of POP, a change in the ratio between the crystallizing monounsaturated triacylglycerols is linked with the high viscosity of the crystal slurry. For a comparable degree of crystallization, the superolein of the more viscous crystal slurry, obtained through a membrane press filtration up to 15 bar, was more unsaturated than the superolein filtered from the less viscous slurry. Consequently, the high unsaturation in the corresponding soft palm mid fraction is only the result of an incomplete phase separation, and not due to an increased intersolubility of unsaturated triacylglycerols in the crystals.

Keywords Crystallization · Dry fractionation · Intersolubility · Palm olein · Superolein

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Introduction

Prior to its use in food, palm oil is often modified in order to improve or extend its applicability as an edible oil. In fact, the processing of the compositionally heterogeneous palm oil into well-defined fractions with a high added value has always been one of the main challenges of dry fractionation technology [1]. Basically, dry fractionation involves a fractional crystallization of the melt by controlled cooling, followed by a filtration process to separate the liquid "olein" from the solid crystals. Palm olein obtained in this manner can be further fractionated into a cold stable superolein and a steep-melting soft palm mid fraction (soft PMF). The latter fraction contains high levels of monounsaturated triacylglycerols (TAG) and can be further fractionated resulting in a mid olein and a hard PMF, which serves as a basis for cocoa butter equivalents (CBE). Such multi-stage routes are often used and improved in the industry to add value to palm oil [2–4].

The success of fat fractionation relies on the phase behavior of the constituent TAG. This concept of phase behavior not only refers to the melting point of a TAG or its polymorphic character, but also involves the mixing of different TAG in a liquid and solidified state, and it is found well described in various publications [5–7]. Such miscibility or intersolubility of the TAG in a solid form often presents problems in several fractionation processes, as the actual goal of fractionation is to separate different TAG. Intersolubility is determined by the nature of the TAG itself, the polymorphism and evidently, by the cooling regime applied to the oil. In general, a gentle, controlled cooling of liquid oil induces the crystallization of the more saturated compounds while the unsaturated TAG remain liquid. Polymorphism (which in its turn is also dependent on the cooling regime) affects intersolubility too, and it is

Table 1 Different cooling water programs for palm olein fractionation tests

	Program A	Program B	Program C
Step 1	Fast cooling, 1 h at 16 °C	Fast cooling, 1 h at 16 °C	Fast cooling, 1 h at 16 °C
Step 2	Fast cooling (−0.75 °C/h)	Slow cooling (−0.5 °C/h)	Slow cooling (−0.5 °C/h)
Step 3	2 h at 13 °C	2 h at 13 °C	2 h at 13 °C
Step 4	Slow cooling (−0.5 °C/h)	Slow cooling (−0.5 °C/h)	2 h at 13 °C
Step 5	3 h at 12 °C	3 h at 12 °C	3 h at 13 °C

generally assumed that the less stable crystal forms are associated with higher intersolubility [8]. Intersolubility can also explain why, in palm oil, rapid cooling could possibly cause the formation of mixed crystals that contain more unsaturated TAG, which lower the quality of the final solid product after filtration [9]. Furthermore, the separation stage is equally influenced by the preceding crystallization stage, as crystal composition and morphology affect the filtration efficiency too. Optimal separation of crystals from the liquid is generally achieved when crystals have a uniform size, morphology and composition [8, 10–12].

The present study aimed at gaining insight into the major relevant mechanisms of palm olein crystallization and their effect on the composition of the resulting superolein and soft PMF fraction obtained via membrane press filtration. Pilot scale fractionation tests and basic analytical techniques were used to follow the general behavior of TAG in palm olein to understand the crucial crystallization behaviour taking place, as well as to demonstrate the repercussions on process efficiency and soft PMF quality.

Materials and Methods

Materials

Refined palm olein was obtained from an industrial fractionation plant. Chemicals used were all either analytical or high-performance liquid chromatography grade (Acros Organics, Geel, Belgium).

Experimental Design and Analytical Methods

Fractionation Set-up

The fractionation trials were conducted in a laboratory fractionation crystallization unit with a capacity of 15 dm^3. The crystallizer consists of a tubular stainless steel double-jacketed vessel, connected to an external programmable waterbath for controlled cooling of the oil (setpoint ±0.1 °C). The agitation consists of a double bladed rotor over the complete height of the vessel. The temperature of the cooling water and oil are measured with temperature probes, installed 5 cm above the bottom of the vessel. Wizcon software was used to apply and control the time-temperature program and agitation.

Three different cooling programs A, B and C, based on temperatures and cycle times applied in industrial fractionation of palm olein, were used in the present study (Table 1). The start of the process, $t = 0$, is considered at the beginning the isothermal period (water temperature = 16 °C) in Step 1.

A small-scale polypropylene membrane press filter (internal cake volume: <1.5 dm^3, filter cloth oil permeability: 25 dm^3/dm^2 min) was used for the filtration of the crystal suspension. The filter was filled by applying a gently increasing pressure on the crystallizer (max. 2 bar). When the filter was filled, the connection to the crystallizer was closed and the pressure was slowly increased via deformation of the membrane (“squeezing”) up to a max pressure of 15 bar. The olein from the filling and squeezing stage and the final stearin cakes were collected separately for determination of the yield.

Viscosity

During the crystallization trials, the viscosity of the crystal suspension was measured with a Brookfield LV viscometer with matching spindle set (Brookfield Engineering Laboratories Inc., Massachusetts). Samples of 200 ml crystal suspension were drained from the crystallizer into a thermostated glass beaker. The appropriate spindle for the expected viscosity range (100–1,000 mPa s) was submerged in the suspension at 100 rpm and the viscosity was determined after 10 s, when a constant value was shown on the display. Additionally, the crystal suspension was filtered over a thermostated Büchner filter with a Watermark paper filter for 10 min.

Solid Fat Content

Samples (3–4 ml) of the crystal suspension were drained from the crystallizer unit into acclimatized 10-mm glass

Table 2 Chemical parameters and respective standard deviations of palm olein and produced fractions

	Palm olein	Soft PMF A	Soft PMF C	Superolein A	Superolein C
Yield (%)	–	40	30	60	70
Iodine value	56.4	46.8	41.7	63.3	62.9
Di- and triacylglycerol distribution[a] (%)					
DAG	7.03 ± 0.04	5.42 ± 0.09	4.20 ± 0.04	7.88 ± 0.07	7.97 ± 0.10
LLO	0.56 ± 0.04	0.41 ± 0.04	0.24 ± 0.04	0.60 ± 0.04	0.61 ± 0.04
PLL	2.69 ± 0.05	1.71 ± 0.07	1.01 ± 0.06	3.30 ± 0.04	3.22 ± 0.07
MLP	0.52 ± 0.06	0.77 ± 0.05	0.64 ± 0.07	0.81 ± 0.04	0.79 ± 0.10
OOL	2.01 ± 0.08	1.50 ± 0.06	0.87 ± 0.08	2.34 ± 0.07	2.31 ± 0.06
POL	11.60 ± 0.07	7.10 ± 0.05	4.58 ± 0.05	13.54 ± 0.11	13.27 ± 0.07
PLP	10.15 ± 0.09	9.67 ± 0.05	10.55 ± 0.08	10.08 ± 0.06	9.49 ± 0.07
OOO	3.68 ± 0.08	2.5 ± 0.09	1.7 ± 0.05	5.04 ± 0.06	5.03 ± 0.08
POO	24.68 ± 0.13	15.90 ± 0.12	11.67 ± 0.11	30.69 ± 0.10	30.20 ± 0.15
POP	27.32 ± 0.16	40.75 ± 0.18	48.90 ± 0.14	17.93 ± 0.04	18.34 ± 0.08
PPP	0.70 ± 0.05	1.49 ± 0.09	2.13 ± 0.04	0.05 ± 0.04	0.05 ± 0.04
SOO	2.86 ± 0.06	1.70 ± 0.04	1.26 ± 0.07	3.45 ± 0.05	3.39 ± 0.06
POS	4.79 ± 0.07	7.79 ± 0.08	8.46 ± 0.10	3.12 ± 0.06	3.67 ± 0.07
PPS	0.42 ± 0.05	1.01 ± 0.07	1.29 ± 0.07	0.26 ± 0.04	0.28 ± 0.04

[a] Standard deviations of triplicate analysis are reported

tubes. Consequently, the SFC was instantly analyzed without additional thermal pre-treatment, using pulsed nuclear magnetic resonance (p-NMR) by means of a Bruker Minispec mq 20 (Bruker, Germany) calibrated with three supplied standards (0, 31.4, 73.8%). The direct method was used (with *f*-factor = 1.501), the averages of duplicate analysis are reported.

TAG Distribution

The distribution of the triacylglycerols of the feedstock, vacuum and press filtered fractions was determined by HPLC, according to AOCS Official Method Ce 5b–89, with a differential refractometer as detector [13]. Minor practical adjustments to the flow rate and mobile phase composition were made in order to improve TAG separation, all in compliance with the said Official Method. All equipment—pump, column, autosampler and detector—was supplied by Waters (Zellik, Belgium). Analysis was done in triplicate, standard deviations are reported.

Calculation of the Actual Crystal Composition

Measurement of the actual crystal composition is not straightforward. The HPLC determination measures the compositions of the fractions. The composition of the olein then follows directly from the HPLC analysis. However, the composition of the solid fraction as measured is a mixture of the composition of the crystals and the composition of the residual olein trapped with the crystals. Thus the composition of the crystals is not given directly by the HPLC analysis. Isolating and washing the crystals with an organic solvent is often applied and can offer satisfying results for diverse fat matrices [14, 15], but this procedure inevitably involves the risk of dissolving the crystalline matter, and is less suitable for quantification. A theoretical, more elegant and reproducible method consists of the use of simple mass balances. Since the SFC of the crystal suspension can be continuously and reliably monitored during fractionation (with p-NMR), consistent information about the crystal content can be obtained using Eq. [1]:

$$\begin{aligned} \mathrm{TAG}_{\mathrm{feedstock}} \times 100 = {} & \mathrm{TAG}_{\mathrm{superolein}} \\ & \times (100 - \%\mathrm{SFC}_{\mathrm{suspension}}) + \mathrm{TAG}_{\mathrm{crystals}} \times \%\mathrm{SFC}_{\mathrm{suspension}} \end{aligned} \tag{1}$$

in which $\mathrm{TAG}_{\mathrm{crystals}}$ is the unknown, for each particular TAG. To estimate the absolute error on the calculated crystal contents, a standard deviation of 0.5% for the measured SFC of the crystal suspension and 0.2% for the measured TAG contents in the olein (Table 2) was taken into account.

Iodine Value

The IVs of the palm olein and fractionated products were determined using the AOCS officially recommended method Cd 1b–87.

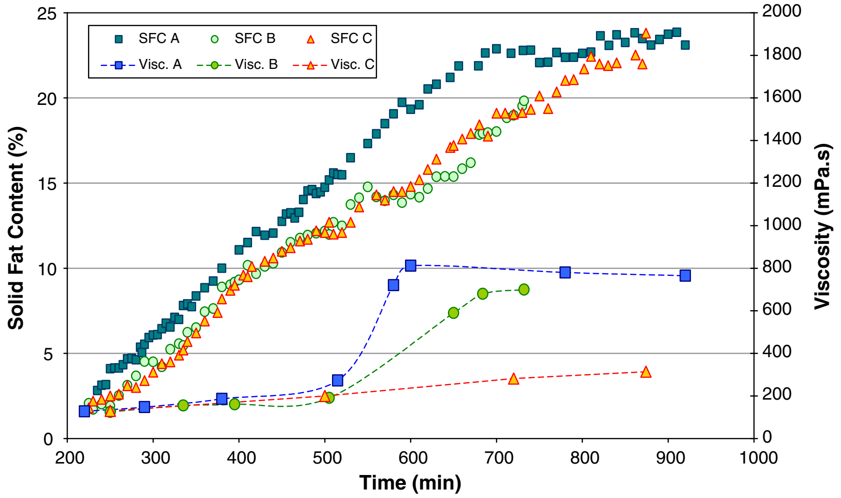


Fig. 1 Evolution of SFC and viscosity of palm olein under crystallization conditions of cooling program A, B and C (see Table 1 for cooling conditions)

Results and Discussion

Solid Fat Content and Viscosity

Figure 1 shows the evolution of SFC and viscosity during crystallization of palm olein via the three cooling programs mentioned (Table 1). The crystallization rate is the highest via cooling program A, yielding 20% solid fat after 10 h of cooling program while the programs B and C yield about 15% solid fat. This is a quite evident result of the slower cooling in step 2 for programs B and C, compared to program A. Overall, the viscosity rises with increasing crystal content, since the presence of substantial solid particles reduces the free flow of the residual olein. However, in program A, a large viscosity increase is observed after 550 min when the respective SFC is around 18%. A rather similar viscosity increase can be observed for program B, but the SFC is only about 15% at that moment. The viscosity in program C does not show such a sharp increase, although the evolution of the SFC is similar to program B. Moreover, under all cooling conditions, the crystallization rate seems not be drastically affected by the viscosity rise. Thus, the occurrence of a viscosity increase seems not so much correlated with the actual degree of crystallinity.

Phase Composition Analysis

Figure 2 shows the evolution of the most important TAG and the group of diacylglycerols (DAG) in the residual olein for the three cooling programs, as function of the crystallization degree. The contents are expressed in relative terms (so for each TAG, initial content in palm olein = 100%) in order to quantify the degree of depletion and enrichment of each separate TAG, regardless of their absolute content in the palm olein. Next to the diacylglycerols, the depicted triacylglycerols are chosen as to represent the respective TAG-classes (UUU, SUU, various SUS and SSS) and actually cover ca. 80% of the total palm olein composition.

In general, for all cooling programs, the following observations can be made. The curve of the DAG initially decreases below 100%, but then exceeds the original content as the crystallization degree reaches 10–15%. So although diacylglycerols are initially depleted from the liquid phase, they end up being concentrated in the liquid superolein after fractionation, which is indeed observed in the industrial palm olein fractionation. It has been demonstrated that the diacylglycerols have a retarding effect on nucleation and growth of TAG-crystals in palm olein [16]. Given their structural similarities (two aliphatic chains, yet one hydroxyl group) with triacylglycerols, these diacylglycerols thus interact at the surface of forming TAG-crystals and get depleted from the melt. They consequently inhibit or delay further crystallization with other TAG as a result of their partial structural incompatibility, which then lowers the growth rate. Taking place at the crystal surface, such interaction effects might partially explain the initial depletion at low crystallization degrees of the melt: when the system has a high surface-to-volume ratio, a lot of initial crystals (surfaces) are encountered with interfering DAG. When the crystallization of the TAG proceeds and each individual crystal grows and also agglomerates are formed, the surface-to-volume ratio will decrease. And with relatively less crystal surface being available, the DAG are therefore largely concentrated in the superolein. Also, the saturated DAG also could effectively crystallize in the given concentration and conditions [16], hence adding to the effect of depletion from the liquid.

Given the low melting points of such molecules, it is expected that OOO (representing the group of

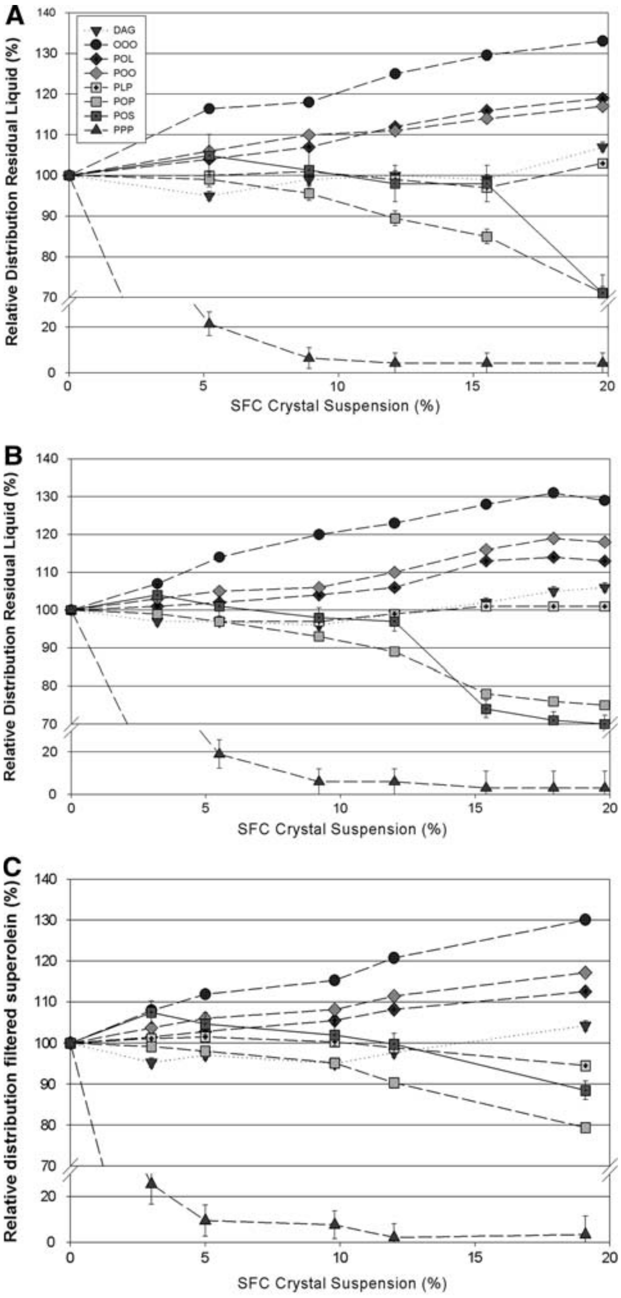


Fig. 2 Evolution of principal TAG and DAG in the vacuum filtered superolein as function of crystallization degree, for cooling program A (*above*), B (*middle*) and C (*below*)

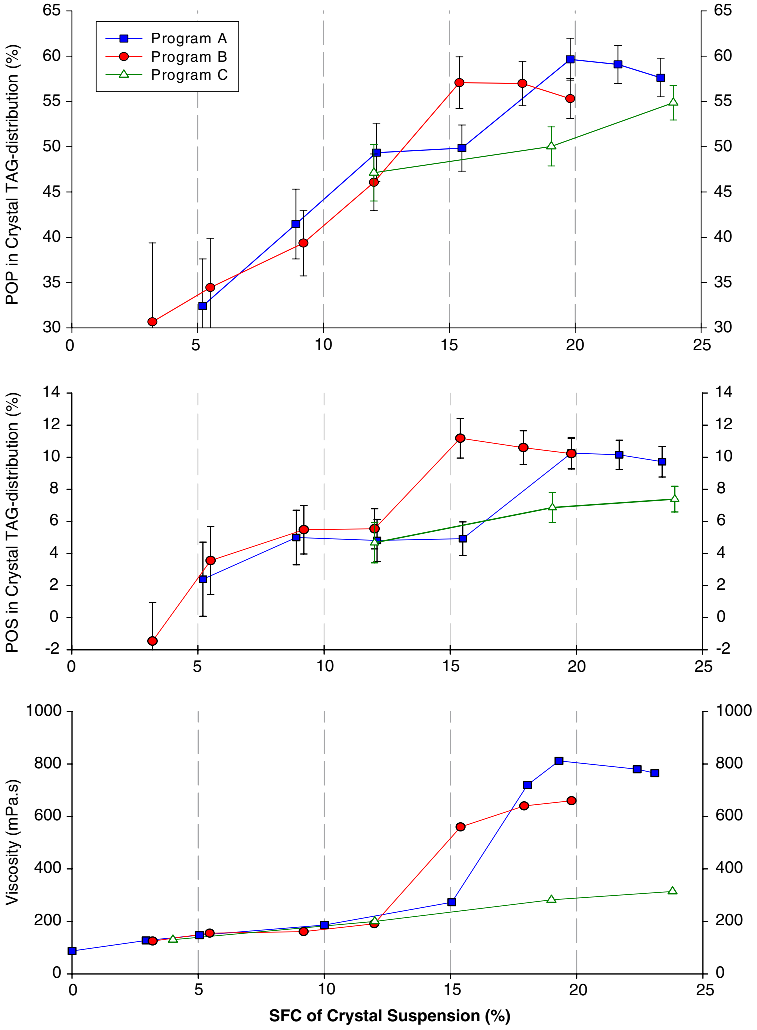
tri-unsaturated TAG) and POO (representing the group of di-unsaturated TAG) are continuously enriched in the liquid phase, as indeed was observed in the experiments. Similar behavior is observed for POL and SOO (not included in graph). The olein is initially quickly depleted from PPP, the main trisaturated TAG present in palm olein. It is, however, necessary to crystallize about 10% of this palm olein to produce a superolein containing less than 0.1% PPP. This is an important matter in view of the major impact trisaturated triacylglycerols have on the cold stability and cloud point of liquid palm fractions [17]. Even at elevated crystallization degrees (SFC > 15%), traces of PPP could still be found in the remaining olein. This is not likely to be a filtration effect (e.g., slight re-melting of crystals in filter or tiny crystal pieces coming through the filter membrane); at the given process temperatures, these low concentrations of PPP simply remain in solution.

In the group of mono-unsaturated TAG, at low crystallization degrees (<10% SFC), the most abundant component POP is readily depleting from the melt, while PLP and POS stay more or less equally distributed in melt and crystals. It has been stated by Déroanne et al. [14] that PLP crystallizes even preferentially to POP in palm oil, owing to a greater linearity of the linoleic acid chain in the 2-position. This study, however, suggests that this does not occur in palm olein, but indicates that both PLP and POS (a component that was actually not reported by Déroanne et al. [14]) display quite different crystallization behavior from POP in all three cooling conditions. Although POS in its most stable crystal form has the highest melting point of the three species discussed, it should be taken into account that the concentration of POS in the original melt is considerably lower than the POP and PLP concentration. So, lower temperatures might be needed to effectively crystallize POS, explaining the relatively slow depletion of POS from the olein.

At higher crystallization degrees (ca. 18% of solid fat) in program A, concomitant with the viscosity increase, the levels of POP and POS in the olein drop significantly when the SFC rises from 15 to 20%. Correspondingly in B, the POP and POS abruptly diminish in the olein around 15% of SFC, also when a sharp viscosity increase was observed. In program C, where the slurry maintains its fairly low viscosity at higher crystallization degrees, the depletion of the mono-unsaturated TAG shows a different pattern: the PLP-level drops well below 100% of its initial content, and conversely, a higher POS-level (approx. 88% of its initial concentration) is found in recovered olein. This suggests that in these last conditions of program C, the crystallization can be considered as being propelled by general supersaturation of the group of mono-unsaturated TAG, in which a high concentration will invoke a higher tendency to crystallize, rather than by the supercooling of each of the individual components, in which the order and amount of crystallization is more determined by the absolute melting point of each species. All observations strongly confirm that the viscosity change is associated with a shift in the composition of the crystallizing matter.

Figure 3 illustrates the evolution of the POP content and the POS content of the crystals and the viscosity as a

Fig. 3 Evolution of calculated POP and POS content in palm olein crystals and viscosity (*below*), for programs A, B and C



function of crystallization degree. Effectively, inversely to the depletion in the olein, Fig. 3 shows the parallel increased concentration of POP and POS in the crystals.

The TAG-analysis of the superolein fractions reveals that the crystals forming during the viscosity increase consist of POP, primarily, but also a considerable amount of POS. Additionally, solving the mass balance provides reliable quantitative results, which allows estimating the POP/POS ratio in the crystals during the crystallization stage. Just before the viscosity change, this ratio varied between eight and ten in cooling programs A and B, but readily dropped to values below six together with the viscosity rise. This means that for example in cooling program B, approximately one third of the 3% marginally crystallized material consists of POS. It is therefore suggested that the increase in viscosity is actually not induced by a too rapid crystallization of just POP, but rather by an uncontrolled co-crystallization of POP and POS.

Effect on Fraction Yield and Quality

At the point of filtration, the slurries produced via cooling programs A and C had an SFC, of respectively, 23.5 and 24%. These similar crystal concentrations permit to compare the filtration efficiency and fraction quality between a high-viscosity (A) and a low-viscosity slurry (C), independent of the concentration of crystals in the slurry. Therefore the effect of the crystal suspension viscosity on the product quality can be relevantly demonstrated in the distribution of the principal TAG of the final superolein and soft PMF, obtained by press filtration of the slurry (Table 2). It shows that the soft PMF produced with cooling program A contains significantly less monounsaturated triacylglycerols like POP, PLP and POS. Although this soft PMF is produced at a 10% higher yield, its low amount of POP can result in a too low solid fat content at room temperature for use in some food applications (like margarine). It also makes it a less suitable feedstock for further processing to a hard PMF [3, 4]. The higher degree of unsaturation of this particular soft PMF compared to the soft PMF of cooling program C can have two causes:

- the increased solidification of more unsaturated components during crystallization,
- the increased entrainment of olein during filtration.

These two phenomena are not mutually exclusive, but can be evaluated separately when taking the olein quality into account, which is rather independent of filtration efficiency. As the two considered crystal slurries contained a similar amount of crystals, the higher degree of unsaturation and lower amounts of POP and POS in the superolein of cooling program A demonstrates a better depletion of these two TAG from the liquid. These TAG are thus retained as solid fraction, and therefore a slightly “more selective” crystallization is observed for slightly faster cooling. This indicates that in the presented practical fractionation conditions, the effect of increased intersolubility of the unsaturated TAG in higher melting TAG as a result of faster cooling is quite negligible. Also, it convincingly shows that the inferior soft PMF quality is thus not due to the formation of mixed crystals containing elevated levels of SUU (solid solution), but should be fully attributed to insufficient phase separation. So, often indicated by the rapidly increasing viscosities, a change in crystal quality probably leads to an increased retention of (still liquid) SUU and UUU in the PMF cake. The discussed experiments moreover indicate that in palm olein fractionation, this change in crystal quality and consequent loss of soft PMF quality is caused by a subtle shift from a (primarily) POP–PLP co-crystallization to POP–POS co-crystallization, while the viscosity is not necessarily proportionally affected by the increase in solid fat content. The relative abundance of POS in the “viscous” crystals, quite disproportional to its level in the melt, then suggests that inappropriate supercooling of POS lies at the basis of this problem in palm olein fractionation.

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