Filtration in Hydrophobic Media: 2. A Triglyceride Partition Phenomenon as Observed by Tangential Filtration of Butter Oil

Salwa Bornaz, Jacques Fanni and Michel Parmentier*

Laboratoire de Physicochimie et Génie Alimentaires, Ecole Nationale Supérieure d'Agronomie et des Industries Allimentaires (ENSAIA), 54505, Vandoeuvre-les-Nancy, France

ABSTRACT: Having demonstrated a partition of a hydrophobic medium (butter oil) under crossflow filtration and having tentatively explained the phenomenon on stereochemical and saturation basis, the molecular partition was studied by tangential filtration. Under specific hydrodynamic conditions, a filtration phenomenon was demonstrated. The solid fat content (SFC) at 20°C of the fractions obtained was investigated accordingly. When the molecular partition takes place, an SFC divergency between the permeate and the retentate is observed. The amplitude of the divergency depends on experimental conditions. *JAOCS 72*, 1143–1148 (1995).

KEY WORDS: Butter oil, filtration, hydrophobic media, solid fat content, tangential filtration, triglycerides.

Among the multiple techniques used in the industry of oils and fats, energy-consuming cooling and heating processes are often repeated. In order to circumvent these economic disadvantages as well as the degradation of biomaterials, separative techniques using membranes have been assayed in the last decade, but no large-scale development has appeared from these trials. Some recent studies regarding filtration of fry oils, refining, extraction of solvents, deodorization, and decoloration have been made. Koseoglu and Engelgau (1) have made an exhaustive review on the application of membranes in this area and have concluded that such a methodology remains expensive and requires unusual cleaning procedures. Moreover, the flow decrease which occurs during the process requires several membrane changes. Others have shown that some chemical pretreatments of the membrane result in a flow increase, with the counterpart of a slight selectivity decrease (2,3).

An overview of the subject leads to the conclusion that further studies remain necessary to determine the proper strategy to be employed in each system where membrane techniques are envisaged. Such works could be extended to the study of surface phenomena, which could result in a better knowledge of membrane fouling and of the proper cleaning procedure.

*To whom correspondence should be addressed at Laboratoire de Physicochimie et Génie Alimentaires, Ecole Nationale Supérieure d'Agronomie et des Industries Allimentaires (ENSAIA), 2, Avenue de Fôret de Hayes, 54505, Vandoeuvre-les-Nancy, France.

To the best of our knowledge, it should be noted that most of the studies in this area have been done in the presence of a solvent, to induce a better mobility of the molecules. Some of the authors have made separation experiments using an oil/solvent solution, to extract some specific components such as phospholipids or sterols. For example, after having dissolved the oil in an organic nonacid/nonalcoholic solvent (mainly hexane), Sen Gupta (2) was able to separate phospholipids from neutral lipids through a silicone rubber ultrafiltration membrane.

Concerning the specific area of vegetable oils, several papers and patents deal with the problem of refining by membrane separation (1,4–6). According to Koseoglu and Engelgau (1), the use of a membrane technique could reduce by the yield loss 60% due to saponification of neutral lipids during chemical refining.

By using ultrafiltration to separate polar lipids from neutral lipids, Forsell *et al.* (7) demonstrated that the method is highly selective, but keeps a major disadvantage: the persistence of hexane smell in the final product. Elimination of the residual solvent is commonly done by evaporation; it is tough work for which membrane alternative techniques have been suggested (8). A number of reverse osmosis and ultrafiltration membranes have been assayed to check their resistance to refining solvents (ethanol, isopropanol, hexane) and their oil retention capacity (6). No oil or melted fat partition through a membrane has been described, and there is no report of hydrophobic interaction phenomenon, except when surface-active molecules in polar solvents are used (9).

In a previous paper, a selective partition through a hydrophobic membrane by crossflow filtration has been shown (10). The purpose of the present investigation is to confirm such a molecular partition by tangential filtration in hydrophobic media. The same approach was used, but such a design defines the limits of the phenomenon and some elements of interpretation. In addition, there exists no fat fractionation on a membrane in view of obtaining well-defined melting points. Because it is well known that a significant effect on the solid fat content (SFC) of butter or margarine induces a correlated effect on the stiffness of the final product, the effect of molecular partition of the collected fractions on the SFC at 20°C is also reported here. The use of tangential

filtration was justified because, in this design, monitoring of influent parameters such as flow rate and pressure is made easily. Moreover, the study was undertaken with a view to a future development of the process, since tangential filtration tends to replace crossflow filtration plants in many features.

MATERIALS AND METHODS

Materials. Butter oil was obtained by centrifugation of a commercial butter after melting at 60°C (Union Beurriere, Vesoul, France). A 316-L stainless-steel ultrafiltration unit Minitan System™ (15.2 cm × 11.6 cm × 10.8 em), supplied from Millipore (Millipore SA, Saint-Quentin-en-Yvelines, France), in line with a variable speed peristaltic pump and a manometer were used. The membrane was a 15.2 cm × 0.2 cm fritted 316-L stainless-steel rectangle with 0.5 μm pore size (Maagsa, Courbevoie, France). The active filtration surface was 60 cm^2.

Methods. Experiments were carried out on open loop. The permeate was continuously extracted, while the retentate was recirculated to the feed batch. The size of the feed tank was set at 10 L, in order to keep the feed composition steady. Because the sampling was done on the fluid outlets, the method allowed the possibility of discriminating the evolution of the triglyceride (TG) composition and of relative SFC at 20°C on both sides of the membrane. All experiments were carried out at 50°C and lasted up to 9 h.

Hydrodynamic conditions. The flow speed varied from 4 (low speed, LS) to 7 cm/s (high speed, HS), and the entering pressure from 0.45 10^5 (low pressure, LP) to 1.45 10^5 Pa (high pressure, HP).

Cleaning. All things considered, it can be assumed that clean stainless steel is neither hydrophilic nor hydrophobic. Nevertheless, during the very first minutes of the experiment, one can observe a slight flow rate drop, probably due to a thin hydrophobic material coating. In such an instance, the membrane surface is supposed to act as hydrophobic.

Under these conditions, the cleaning procedure must be done thoroughly as follows: (i) draining and circulation of a 0.05% (wt/vol) NaOH aqueous solution (2 L) on open loop; (ii) rinsing with hot distilled water (80°C); (iii) repetition of steps i and ii; (iv) circulation of a 0.05% (wt/vol) NaOH aqueous solution on closed loop for 20 min; (v) rinsing with 4 L of hot distilled water (80°C) on open loop; (vi) inversion of membrane position and repetition of steps iv and v; (vii) circulation of a tensio-active (Teepol® 1% wt/vol) for 15 min at 80°C; (viii) rinsing with hot distilled water; and (ix) drying the membrane for 14 h at 105°C.

SFC. The SFC of the crude product (I), the permeate (P), and the retentate (R) was determined with a Perkin-Elmer DSC4 (Norwalk, CT) according to Deroanne *et al.* (11).

TG composition. The TG composition was obtained on I, R, and P by high-performance liquid chromatography (HPLC) according to Bornaz *et al.* (12). Each experiment was done in triplicate with a variation coefficient of less than 5%.

Filtration performance indexes. Two filtration performance indexes expressed in % of P or R over I were calculated: (i) an absolute filtration performance index (λ), according to the following equation:

$$\lambda_{P,R}(\%) = \left(1 - \frac{P,R}{I}\right)100 \qquad [1]$$

where I = TG composition of the crude product and P, R = TG composition of the permeate or retentate. (ii) a relative filtration performance index $(\lambda^r_{i,j})k$, obtained by renormating in Equation 1 the filtration performance index λ_i for a TG group (j), with a given MW or theoretical carbon number (k), according to El-Hamdy and Perkins (13):

$$(\lambda^r_{i,j})^k = \frac{(\lambda_{i,j})^k}{\max(\lambda_{i,j})} \qquad [2]$$

where i = permeate, j = saturated, mono-, di-, and polyunsaturated TG, k = MW or TCN.

As gathered in a previous paper (12), the relative filtration performance index allows comparison between the behaviors of the different TG groups: S = saturated, M = monounsaturated, D = diunsaturated, and P = polyunsaturated TG, which correspond, in the same order, to the first, second, third, and fourth peaks of each quartet on the HPLC chromatogram. Such a subdivision is far from perfect, because the calculation of the TG proportion is based on a 1,2,3-random distribution of the fatty acids on the glycerol molecule. In such an instance, a representative average MW is calculated for each TG peak of the HPLC chromatogram.

RESULTS AND DISCUSSION

Permeation flow. Comparative P flow speeds vs. time in each experimental mode are displayed in Figure 1. The evolution of the P flow speed follows the general law of fouling. Obviously, a low speed and a high pressure are the conditions for an increase of permeation flow. Under these conditions, the filtration is not impaired by the fouling, which appears after several hours.

Influence of hydrodynamic conditions on the filtration performance index. The relative P/I composition profile was checked at 50, 110, 240, and 540 min. Because the retention phenomenon remained quite steady after 110 min, samples were taken at this moment. For example, Figure 2 displays the filtration performance index (P/I) of group S for two different couples of speed and pressure parameters. As observed in a previous study on crossflow filtration, the molecular behavior through the membrane depends on MW (10). However, the inversion MW point is clearly located at the same place whatever the flow speed might be.

Figure 3 shows the relative filtration performance index (P/I) under LS–HP conditions, for TG groups S, M, D, and P, respectively. Obviously, the curve profiles are similar. More-

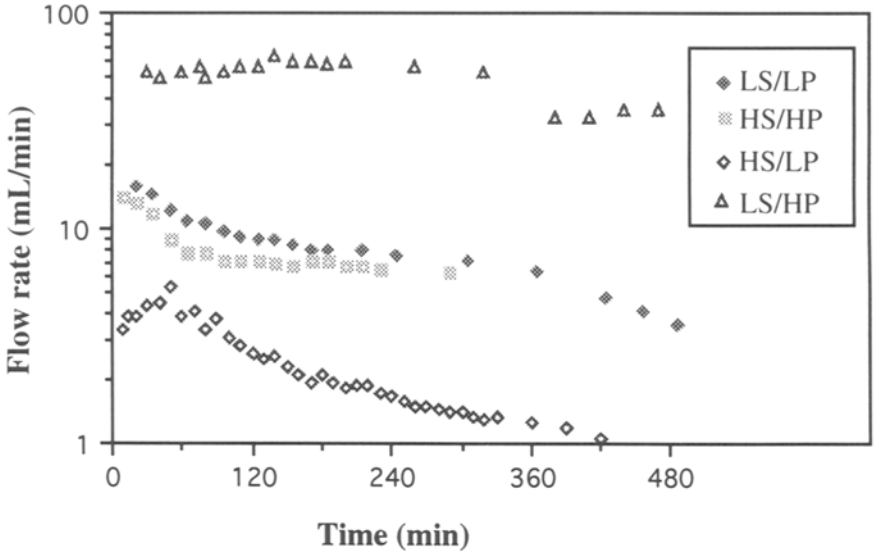

FIG. 1. Flow rates vs. time of melted butter oil under four experimental conditions high speed/low pressure (HS/LP); high speed/high pressure (HS/HP); low speed/low pressure (LS/LP); low speed/high pressure (LS/HP).

over, the partition phenomenon appears to be related with the TCN: the crossing of most of the molecules with TCN > 44 is impaired, whatever their saturation index might be, whereas the TG with a TCN < 44 cross the membrane more easily.

Comparison between the TG profiles of a P and its corresponding R. Under HS conditions, the composition profiles of P and its corresponding R do not diverge. Such an observation indicates that no filtration phenomenon is observed.

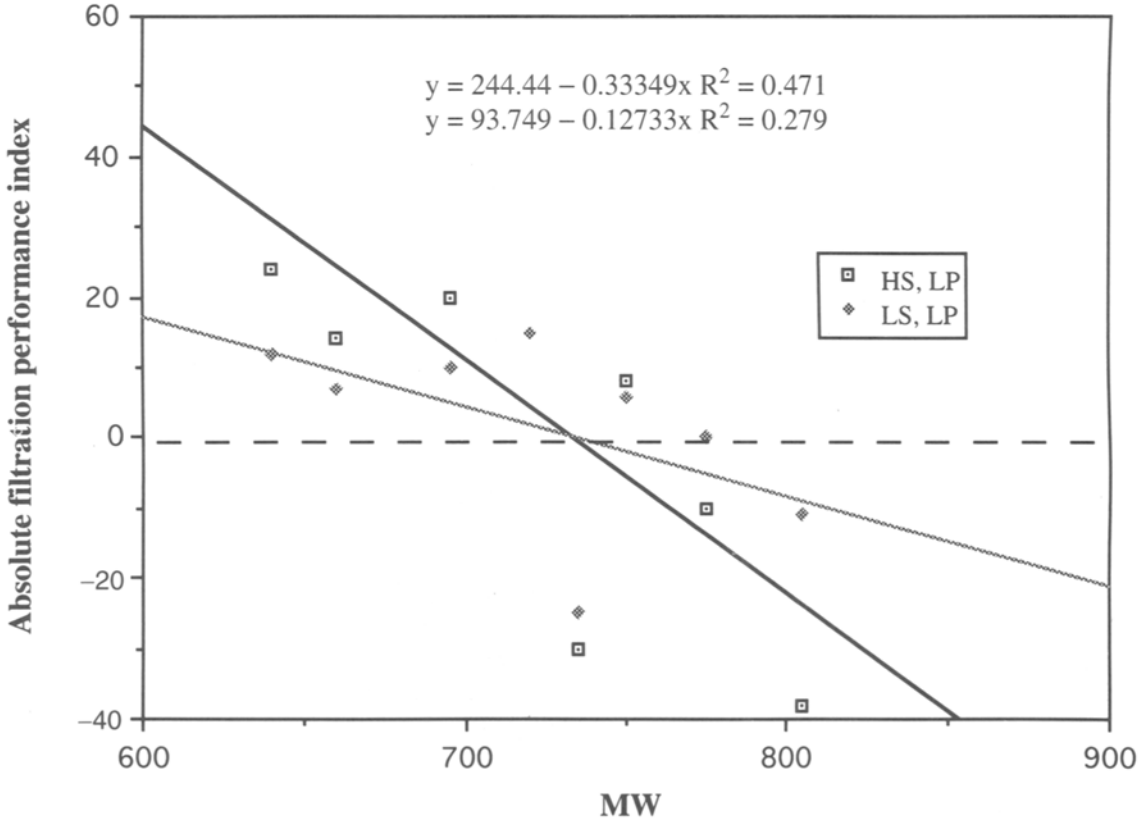

FIG. 2. Absolute filtration performance index (λ) of saturated triglycerides under HS/LP and LS/LP. See Figure 1 for abbreviations.

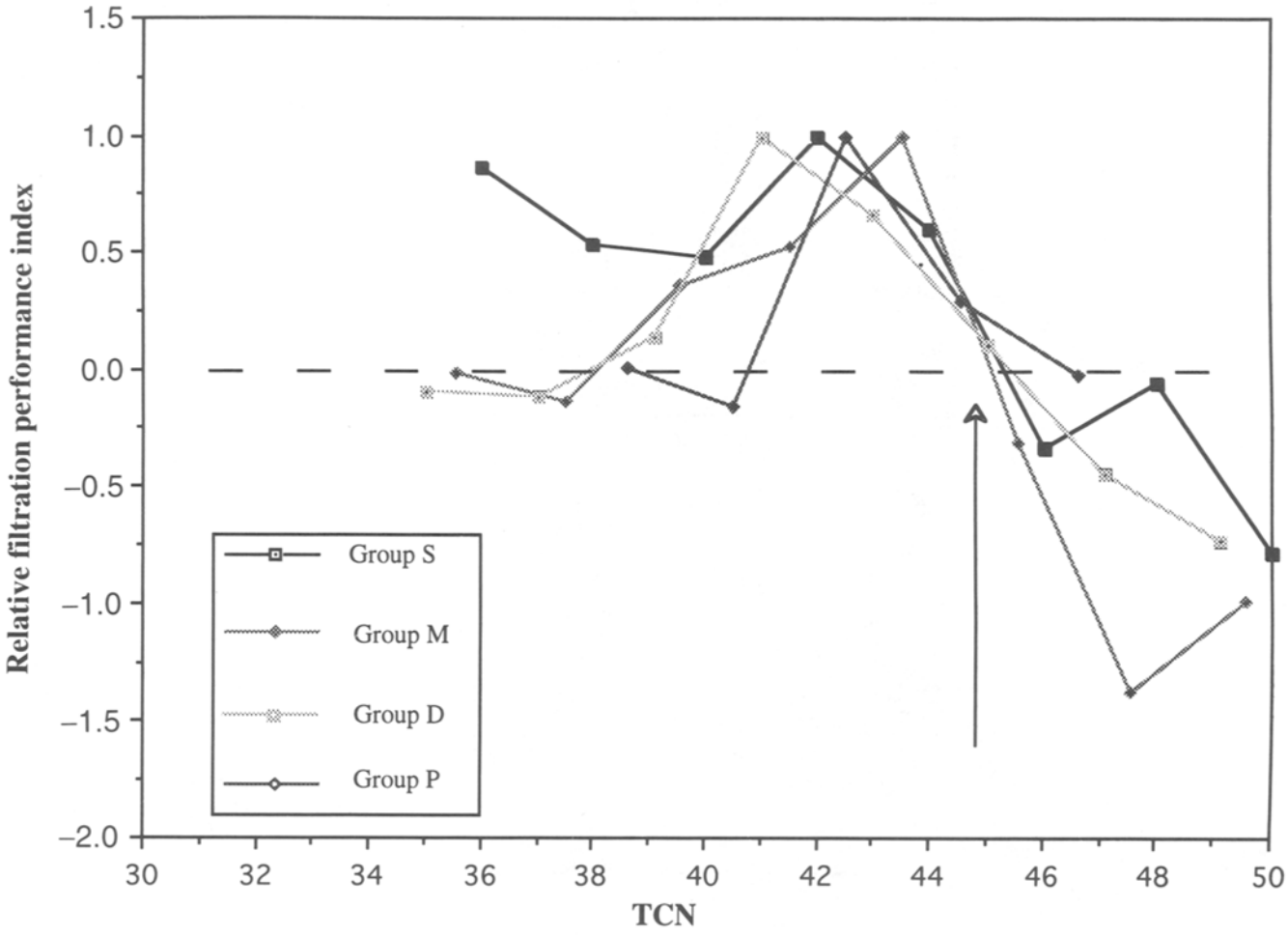

FIG. 3. Relative filtration performance index $(\lambda^{r}_{i,j})^{k}$, vs. theoretical carbon number (TCN) for each group of triglycerides (S = saturated; M = monounsaturated; D = diunsaturated; P = polyunsaturated) under LS–HP conditions. Arrow indicates TCN apparent inversion point. See Figure 1 for other abbreviations.

The variation of R/I or P/I composition observed in this case might be due to a preferential and selective adsorption of certain molecules onto the membrane. A strong divergency between P and R appears under conditions LS–LP and, more accurately, under LS–HP. For example, Figures 4 and 5 display the profiles R/I and P/I for TG-groups D and P. The quasi-symmetry observed clearly indicates that the phenomenon under consideration is a partition.

Influence of hydrodynamic conditions on the SFC of the fractions. In a first set of assays, the influence of pressure on the SFC of the fractions was investigated. Under LS–LP, the SFC of R remains quite steady and equal to I all along the filtration, although the SFC of P regularly decreases up to 360 min as shown in Figure 6. At this stage of the experiment, the discrepancy with R reaches 15% and slowly decreases down to 5% after 500 min, in relation with the fouling. Conditions LS–HP enhance this behavior: the SFC of both R and P highly diverge (+4% and −19% with respect to I), reaching maximum divergency after 50 min of filtration (Fig. 7). Under all these conditions, the evolution of the SFC is consistent with the foresaid divergency observed on TG composition.

HS conditions lead to a nonsignificant effect: the SFC of both the R and the P slightly decrease when compared to I. This observation outlines a nonfiltration phenomenon and should be related with the corresponding variation of TG composition (see above). In terms of SFC modification, the pressure parameter looks influent: the higher the pressure, the larger the divergency. Fouling occurs after a given time depending on hydrodynamic conditions, thus reducing both the flow rate and the separation efficiency.

However, a direct comparison between TG composition and SFC is not straightforward. Thus, the SFC discrepancy of the fractions cannot be explained *via* the slight difference observed on TG composition. The same observation can be made when comparing summer and winter butter spreadability: although the TG composition difference is slight, the SFC

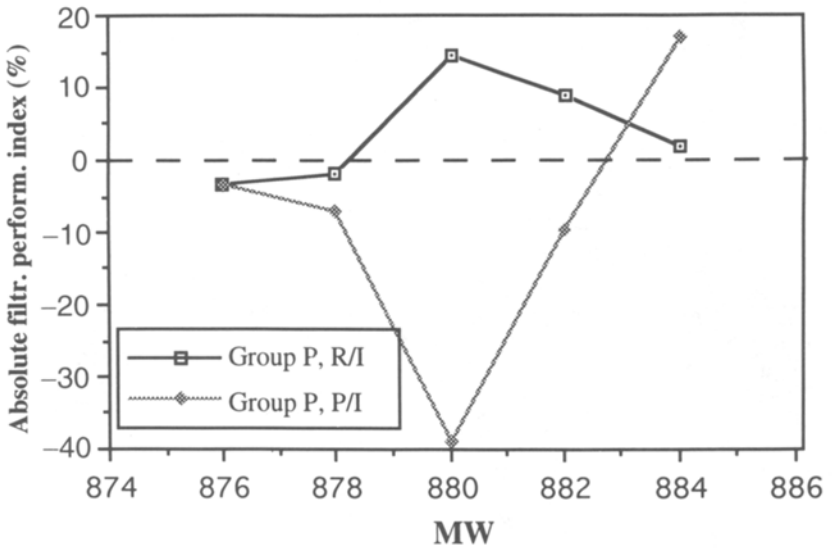

FIG. 4. Absolute filtration (filt.) performance (perform.) index (λ) vs. molecular weight (MW) for triglyceride group P showing partition between retentate/crude product (R/I) and permeate/crude product (P/I) under LS/LP. See Figures 1 and 3 for abbreviations.

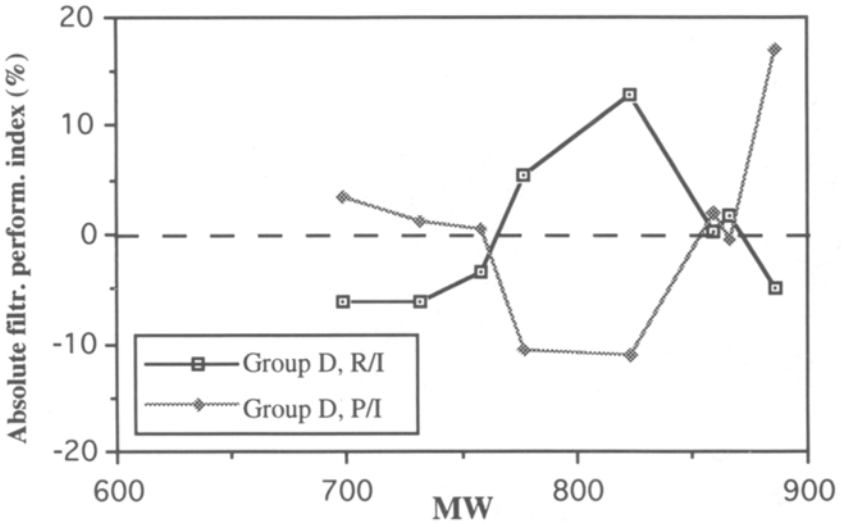

FIG. 5. Absolute filtration performance index (λ) vs. MW for triglyceride group D showing partition between retentate (R/I) and permeate (P/I) under LS/HP. See Figures 1 and 4 for abbreviations.

discrepancy goes larger, with a consequence on the texture of butter (14). That is not surprising since thermal and morphological parameters (and not only the composition) interfere with the solid or liquid state of such complex mixtures.

A partition between R and P through the membrane is confirmed by observing TG composition and SFC discrepancies under experimental conditions LS–HP which lead to the best result in terms of partition. Thus, a modification of the permeate and retentate TG composition, together with a significant SFC variation of the fractions, are clearly put into evidence. The amplitude of the divergency depends on speed and pressure conditions. Their relative effect should be specified for a better understanding of the entire phenomenon. This technique is an economic challenge, in terms of SFC modification of butter and vegetable oils (15). With a view to a future development, such a work is already set up in our laboratory.

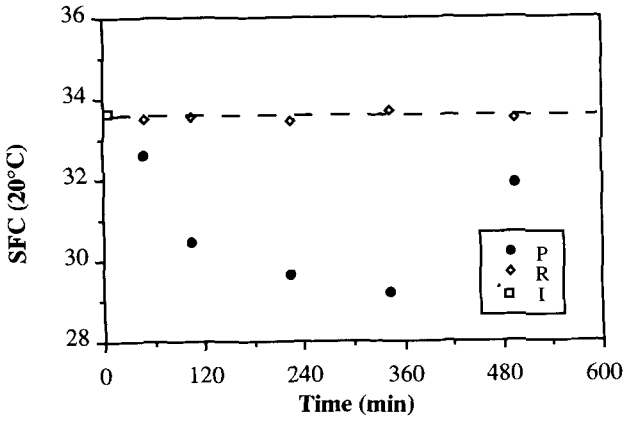

FIG. 6. Solid fat content (SFC) at 20°C vs. time of P, R, and I under LS/LP. See Figures 1 and 4 for abbreviations.

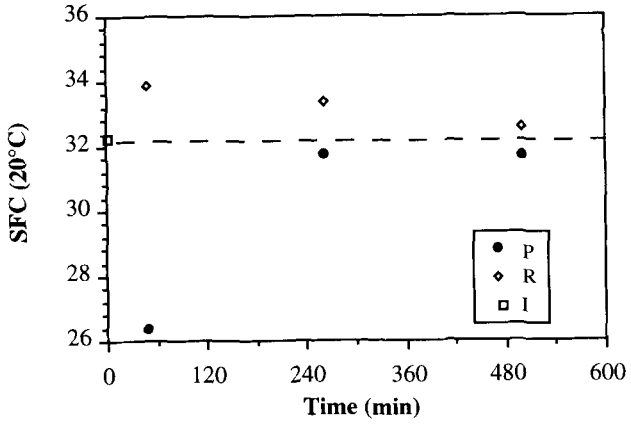

FIG. 7. SFC at 20°C vs. time of P, R, and I under LS/HP. See Figures 1, 4, and 6 for abbreviations.

REFERENCES

1. Koseoglu, S.S., and D.E. Engelgau, *J. Am. Oil Chem. Soc. 67*:239–249 (1990).
2. Sen Gupta, A.K., U.S. Patent 4,062,882 (1977).
3. Li, N.N., E.W. Funk, Y.A. Chang, S.S. Kulkarini, A.X. Swanikannu and L.S. White, *Membrane Separation Process in the Petrochemical Industry. Phase II*, Res. Cent. Signal, UOP, Inc., Des Plaines, report 1985 DOE/ID/12422-1.
4. Serafini, G., F. Camurati and E. Fedeli, *La Rivista Delle Sostanze Grasse 7*:65 (1988).
5. Koseoglu, S.S., *Oils and Fats International 7*:16–21 (1991).
6. Koseoglu, S.S., J.T. Lawhkon and E.W. Lusas, *J. Am. Oil Chem. Soc. 67*:315–322 (1990).
7. Forsell, P., M. Kervinen, MK. Alkio and K. Poutanen, *Fat Sci. Technol. 9*:355–358 (1992).
8. Kuk, M.S., R.J. Hron and G. Abraham, *J. Am. Oil Chem. Soc. 66*:1374–1380 (1989).
9. Faure, M., and M. Legault-Demar, *Bull. Soc. Chim. Biol. 32*:509 (1950).
10. Bornaz, S., J. Fanni and M. Parmentier, *J. Am. Oil Chem. Soc. 70*:1139–1142 (1995).
11. Deroanne, C., J.M. Marcoen, J.P. Wateleet and M. Severin, *J. of Therm. Anal. 11*:109–119 (1977).
12. Bornaz, S., G. Novak and M. Parmentier, *J. Am. Oil Chem. Soc. 69*:1131 (1992).
13. El-Hamdy, A.H., and E.G. Perkins, *Ibid. 58*:867 (1981).
14. Deroanne, C., *Lait 551/552*:39–55 (1976).
15. Parmentier, M., S. Bornaz and B. Journet, French Patent pending 93–15 023 (1993).

[Received July 19, 1994; accepted June 25, 1995]