A New Short-Path Distillation System Applied to the Reduction of Cholesterol in Butter and Lard

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A molecular distillation plant, built particularly to increase the separation efficiency and to obtain safer working conditions, was tested to remove cholesterol from anhydrous butter and lard. A preliminary experiment was carried out with butter to evaluate the fractionation obtained at temperatures between 190 and 250°C and residual pressures between 10^{-3} and 10^{-4} torr. A second experiment was carried out at 185°C and at the maximum operational vacuum, evaluating the fractionation achieved within a time scale between 30 and 180 min. Cholesterol was almost completely removed during the second hour with minimal loss of low-molecular weight triglycerides. An experiment was carried out with lard at 250°C and maximum achievable operational vacuum (10^{-4} Torr), lasting approximately 6 h, and cholesterol was removed almost completely during the second hour without significant modifications in the triglyceride composition. This situation remained constant throughout the duration of the test.

KEY WORDS: Cholesterol, distillation, fractionation, lard, milk fat, short path.

Molecular distillation is a well-known process; in principle, it consists of transferring molecules from the hot surface of an evaporating liquid to the cooled surface of a condenser through a short path, which, at the high operational vacuum levels, is of the same order of magnitude as the molecule's average path. A large amount of literature is currently available on theoretical principles, technology and conventional equipment (1,2).

Butter is an ideal experimental model for fractionation as a function of molecular weight by the proposed method because it is a heterogeneous mixture of triglycerides with a wide range of molecular weights (470–890). They provide differing volatilities and energies of molecular interaction. Furthermore, relatively volatile components, such as sterols, mono- and diglycerides, free fatty acids, vitamins A, E, K and D, and aroma compounds (aldehydes and lactones) (3) are present within butter. These compounds can be simultaneously separated during the distillation process. In practice, such separations have been the subject of numerous studies. Besides the reported stripping of vitamins A and E, sterols, mono- and diglycerides, free fatty acids and volatile components (4–7) from natural oils, molecular distillation has been applied to butter to recover volatile components (8,9), to reduce cholesterol content (10) and to obtain triglyceride fractions with altered compositions and physical characteristics (3). Hence, butter represents a primary reference substance for this study because the objectives of the study were to test the efficiency of a molecular distillation plant with innovative characteristics. The working conditions for the separation of cholesterol were studied from two different perspectives: (i) to obtain contemporary fractionations as a function of the triglyceride content and (ii) to obtain final products with a composition unchanged from that of the original butter.

Another fat examined in this study was lard, which, in terms of its narrow triglyceride molecular weight range, was examined solely for reducing cholesterol content without triglyceride fractionation.

The innovations of the plant used in this study are primarily the particular geometry of the feed system and microwave heating of the unit; other characteristics include the capacity to achieve low operational vacuum and the possibility of semiautomatic control of the unit.

EXPERIMENTAL PROCEDURES

Materials. Commercial anhydrous butter (Prealpi, Milan, Italy) and lard (Lipitalia, Turin, Italy) were used as received from producers.

Methods of analysis. Method NGD C10-1976 of the *Norme Grassi e Derivati* (NGD) (11) was used for free fatty acid determination. Fatty acid composition was determined by method NGD C42-1976 (11). For sterol content determination, method NGD C72-1989 (11) was used. *trans* Fatty acids were determined by method NGD C74-1991 (11). The following gas-chromatographic conditions were used for triglyceride analysis: SE52 capillary column, length 3 m, film thickness 0.1 μm, internal diameter 0.32 mm; oven temperature 120°C for 2 min, 8.5°C/min up to 350°C; injection system on column at 80°C; carrier gas hydrogen, flow rate at 5 mL/min.

Short-path distillation. The model presented in this paper (Fig. 1) is part of a new generation of plants, whose working criteria and technical characteristics have been presented previously (5,7). The product is put into tank 1. From tank 1 through pump 5, the product is recycled through the preheating component 6 up to a predetermined temperature and complete degassification and dehydration. From tank 1, through pump 5, the raw product is conveyed toward tank 3, through dosing pump 7 for further degassing. From tank 3, through dosing pump 7, the raw product is conveyed toward the distilling unit through preheating until 8. At the entrance to the distilling unit, through rotor 9, the product is distributed onto the whole circle of Pyrex glass unit 10, which forms the internal wall of the evaporator. The Pyrex glass body is inserted into a cavity equipped with a microwave generator. The latter heats the liquid film product, which is uniformly spread by rotating unit 11 and also gives the film a helical movement toward the lower part of the evaporator. At a given distillation temperature, the light fractions vaporize and condense on the walls of condenser 12 and are collected by gravity flow at the lower end of the unit. The distilled liquid is evacuated through tube 13 in the direction of collecting tank 2 and then discharged through tube 14. At the same time as the distillation of the light fractions, the nonvolatile residue follows a path along the wall of the distiller and is conveyed downward into a peripheral container. The residue is evacuated from the distiller into collecting tank 4 and then discharged. In

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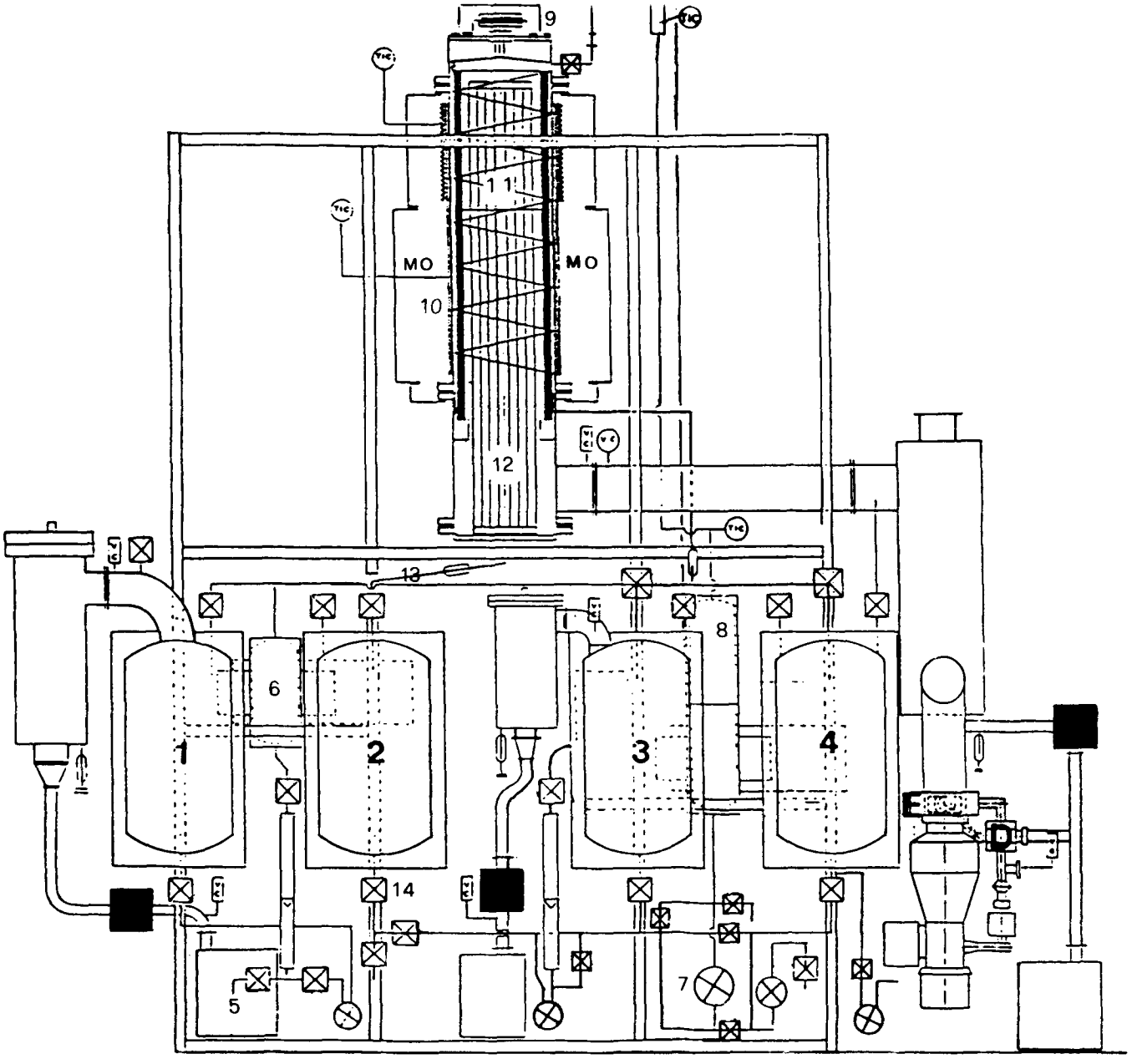

FIG. 1. Flow sheet of short-path distillation plant. 1, Preliminary degassing unit; 2, distillate discharge; 3, crude and degassed product tank; 4, residue tank; 5, volumetric pump; 6, microwave preheater; 7, feeding volumetric pump; 8, microwave preheater; 9, rotor; 10, evaporator; 11, rotating unit; 12, condenser; 13, distilled product exit pipe; 14, distillate discharge.

practice, the product is recycled from tank 3, through dosing pump 7, to the distiller for a second pass to obtain higher levels of the volatile fraction before being discharged into tank 4.

Working method for butter. The first test was carried out with successive distillations over the temperature range of 180–250°C. The working conditions are described in Table 1. A second test was carried out with a single distillation temperature of 185°C. The latter conditions are described in Table 2.

Working method for lard. A first test was carried out with two successive distillations at 200 and 240°C, respectively. Exact conditions are described in Table 3. A second test was carried out with a single isothermal distillation at 250°C with intermittent sampling (conditions are listed in Table 4).

RESULTS AND DISCUSSION

To achieve the separation of cholesterol and selective fractionation of triglycerides, anhydrous butter was molecularly distilled at temperatures of 190, 210, 230 and 250°C. The material balance, cholesterol content, free fatty acid content and fatty acid compositions of triglyceride fractions were carried out on the distilled fractions and residues (Table 5). Fractions distilled at 190 and 210°C

TABLE 1

Milk Fat Distillation—Experiments Carried Out at Different Temperatures (processed quantity = 11.5 kg)

	I	II	III	IV
Evaporator temperature (°C)	190	210	230	250
Condenser temperature (°C)	75	75	75	75
Recycle (L/h)	56	48	48	40
Rotor speed (rpm)	75	75	75	75
Distillation time (min)	75	90	120	150
Residual pressure				
Initial (torr × 10^{-4})	31	13	18	9
Final (torr × 10^{-4})	11	10	12	7
Residence time (s)	4.8	4.8	4.8	4.8

TABLE 2

Milk Fat Distillation—Experiment Carried Out at a Constant Temperature (processed quantity = 10 kg)

	I	II	III	IV	V	VI
Evaporator temperature (°C)	185					
Condenser temperature (°C)	75					
Recycle (L/h)	65					
Rotor speed (rpm)	70					
Sampling intervals (min)	30	60	90	120	150	180
Residual pressure						
Initial (torr × 10^{-4})	37	13	8	6	6	6
Final (torr × 10^{-4})	12	10	7	6	6	6
Residence time (s)	5.1					

TABLE 3

Lard Distillation—Experiments Carried Out at Different Temperatures (processed quantity = 9.9 kg)

	I	II
Evaporator temperature (°C)	200	240
Condenser temperature (°C)	75	75
Recycle (L/h)	20	20
Rotor speed (rpm)	120	120
Distillation time (min)	60	120
Residual pressure		
Initial (torr × 10^{-4})	8	7
Final (torr × 10^{-4})	7	6
Residence time (s)	3	3

TABLE 4

Lard Distillation—Experiment Carried Out at a Constant Temperature (processed quantity = 10.5 kg)

	I	II	III	IV	V	VI
Evaporator temperature (°C)	250					
Condenser temperature (°C)	80					
Recycle (L/h)	20					
Rotor speed (rpm)	120					
Sampling intervals (min)	60	120	150	240	300	360
Residual pressure	6	6	6	6	6	6
Residence time (s)	3					

represented 3.43 and 3.99% of the initial mass and contained >93% of the total cholesterol. This means that, under these conditions, it was possible to achieve an almost complete removal of cholesterol to satisfy dietary goals. It is suggested that the nondistillable cholesterol may be bound by lipid structures with high molecular weights. At these temperatures, more than 60% of the free fatty acids are removed. From the data presented in Table 5, the varying content (in terms of mass fractions with respect to initial) for individual triglycerides present in each distillate, from C28 to C46, was calculated at the different temperatures (Figs. 2,3). At the initial temperature of 170°C, shown in Figures 2 and 3, no distillation of triglycerides occurred. One can observe from the patterns of molecular weight distribution of the triglycerides that, by interpolation, it is possible to select an optimal temperature condition for obtaining a selectively enriched triglyceride fraction.

With the aim of evaluating, apart from the physical losses, potential isomerization of fatty acids, both the

TABLE 5

Milk Fat Distillation—Experiments Carried Out at Different Temperatures (mass balance and fractions composition)

Fraction[a]	SM	d190	r190	d210	r210	d230	r230	d250	r250
Mass (kg)	12.7	0.4	12.3	0.5	11.8	0.8	11.0	0.9	10.1
Cholesterol (ppm)	3472	66953	1217	24038	234	481	216	342	205
FFA (as % butyric acid)	0.09	2.10	0.02	0.13	0.01	0.10	0.01	0.09	0.01
Fatty acid composition									
4:0	4.1	7.9	4.0	10.8	3.7	0.1	3.3	0.2	2.9
6:0	2.2	5.4	2.1	3.6	2.0	2.4	2.0	2.7	1.9
8:0	1.3	3.2	1.2	2.6	1.1	1.0	1.1	1.7	1.0
10:0	2.8	5.3	2.7	3.4	2.6	3.1	2.5	3.2	2.5
12:0	3.2	0.0	3.4	6.6	3.2	5.1	3.1	4.2	3.0
14:0	10.0	0.0	10.4	4.9	10.6	13.5	10.4	12.4	10.2
16:0	27.0	0.0	27.9	12.7	20.6	28.7	28.6	29.4	28.5
18:0	8.4	0.0	8.7	20.6	8.1	0.5	8.7	1.0	9.4
18:1	19.7	0.0	20.4	4.6	21.0	8.8	21.9	9.1	23.0
18:2	2.1	0.0	2.2	1.2	2.2	2.0	2.2	2.1	2.2
18:3	0.6	0.0	0.6	0.2	0.6	0.4	0.6	0.3	0.5
Others	18.7	78.2	16.6	28.8	16.0	24.7	15.4	24.7	14.6

[a]SM, starting material; d°C, distillate obtained at °C; r°C, residue obtained at °C; FFA, free fatty acid.

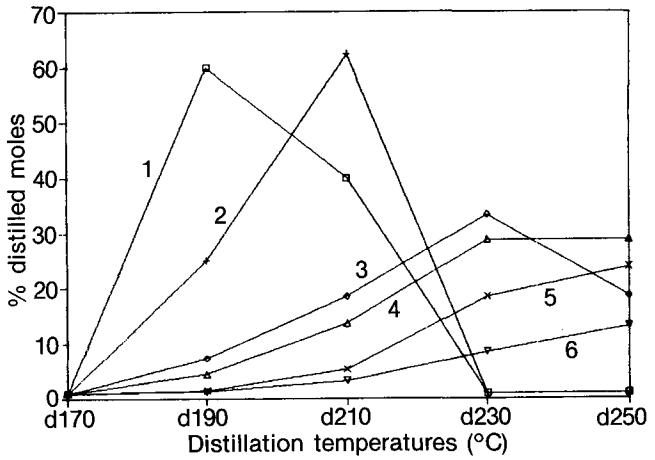

FIG. 2. Changes in triglyceride content (as 100 × distilled moles/initial moles) at different distillation temperatures. 1, C_{28} triglycerides; 2, C_{30} triglycerides; 3, C_{32} triglycerides; 4, C_{34} triglycerides; 5, C_{36} triglycerides; 6, C_{38} triglycerides.

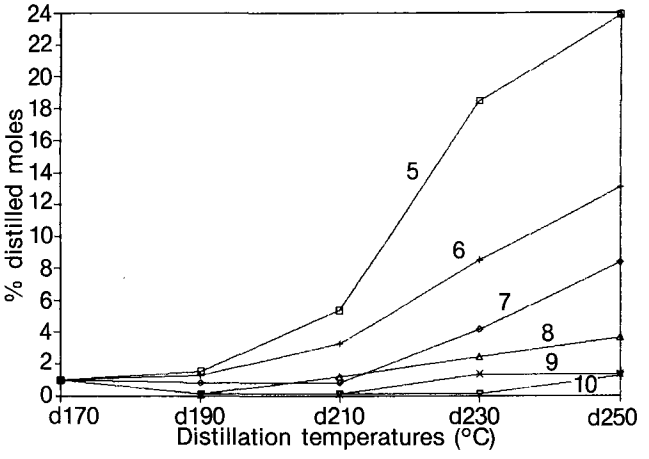

FIG. 3. Changes in triglyceride content (as 100 × distilled moles/initial moles) at different distillation temperatures. 5, C_{36} triglycerides; 6, C_{38} triglycerides; 7, C_{40} triglycerides; 8, C_{42} triglycerides; 9, C_{44} triglycerides; 10, C_{46} triglycerides.

starting butter and the triglyceride fraction at 250°C were analyzed for *trans* fatty acids. Gas-chromatographic analysis showed the presence of C_{18} *trans* fatty acids at 0.3% in the starting sample and 0.5% in the final residue fraction. This small increase in *trans* isomers shows that the operating conditions used do not produce major degradation problems.

As to separating the cholesterol without significantly changing the butter triglyceride composition, the anhydrous butter was repetitively distilled at 185°C. The composition of each residue fraction after 30, 60, 90, 120, 150 and 180 min of the distilled liquid, as well as of starting buffer is given in Table 6. The cholesterol separation was satisfactory after the fourth pass (2 h) through the distillation unit. At this point, and after the sixth pass (3 h), variations in the triglyceride composition of the residue fraction were minor compared to the initial composition. In Table 7, changes in triglyceride composition during distillation and the removal of cholesterol are described. The table expresses the values as a relationship between the mass of glycerides present in the sample with that of the initial sample. Glycerides with the highest molecular weight, not distilled except at a trace level, are considered to be unchanged and do not appear in the table. These results lead to the conclusion that, for butter, the plant would appear to be suitable for cholesterol removal.

With regard to the aroma compounds (methyl ketones, lactones, aldehydes and others) although as well as lipid-soluble vitamins (A, E, K, D), not examined in this study,

TABLE 6

Milk Fat Distillation—Experiments Carried Out at a Constant Temperature of 185°C (mass balance and fractions composition)

Fraction[a]	SM	r30	r60	r90	r120	r150	r180	dtot
Mass (kg)	9.1	9.0	8.9	8.9	8.7	8.5	8.5	0.6
Cholesterol (ppm)	3737	3074	2341	1619	440	400	350	50123
FFA (as % butyric acid)	0.12	0.04	0.02	0.01	0.01	0.01	0.01	1.53
Fatty acid composition								
4:0	4.4	4.4	3.8	3.8	3.3	3.6	2.4	8.1
6:0	2.7	2.8	2.5	2.5	2.2	2.4	1.9	4.6
8:0	1.6	1.6	1.5	1.6	1.3	1.4	1.6	3.4
10:0	2.4	3.6	3.5	3.5	2.9	3.0	2.7	6.2
12:0	3.7	3.9	3.9	3.9	3.4	3.4	3.3	5.9
14:0	11.0	11.3	11.7	11.7	10.9	11.0	10.9	11.8
14:1	0.4	0.4	0.3	0.3	0.3	0.3	0.3	0.2
16:0	27.6	27.7	28.5	28.5	29.0	28.6	29.3	18.6
16:1	1.7	1.7	1.8	1.7	1.8	1.8	1.8	0.9
18:0	10.2	9.7	9.8	9.8	10.6	10.6	11.2	3.3
18:1t	1.7	1.7	2.0	2.0	2.1	2.1	2.3	0.5
18:1	18.3	17.9	18.1	19.4	21.0	19.6	21.8	7.1
18:2	2.0	1.9	2.0	2.1	2.2	2.1	2.3	1.0
18:3	0.5	0.5	0.5	0.6	0.6	0.5	0.7	0.2
Others	10.7	10.8	10.2	8.5	8.4	9.4	7.6	28.1

[a]SM, starting material; rmin, residue obtained after minutes; dtot, pooled distilled fractions; FFA, free fatty acids.

TABLE 7

Milk Fat Distillation—Mass Changes of Different Glycerides and Cholesterol as a Function of Processing Time[a]

	Processing time (min)						
Triglyceride	0	30	60	90	120	150	180
C_{28}	100	103	101	91	52	39	31
C_{30}	100	103	103	99	78	65	51
C_{32}	100	102	103	103	93	84	79
C_{34}	100	102	103	103	97	93	90
C_{36}	100	103	102	102	100	98	94
C_{38}	100	102	101	102	101	100	96
C_{40}	100	102	101	102	101	101	97
Cholesterol	100	81	61	42	11	10	9

[a]Results reported as % in residue with respect to the initial mass. Distillation carried out at a constant temperature of 185°C.

TABLE 8

Lard Distillation—Experiments Carried Out at Different Temperatures

	Starting material	Distillate 200°C	Residue 200°C	Distillate 240°C	Residue 240°C
Mass (kg)	9.93	0.28	9.65	0.01	9.71
Cholesterol (ppm)	1167	13520	806	484700	304

it is almost certain that these compounds will be concentrated in the fractions distilled at the lower temperatures, based on volatility data reported in the literature (3). Attention should be given to these fractions in the interest of recovering them for eventual dietary purposes.

Regarding anhydrous lard, the level of removal of cholesterol was studied initially at successive temperatures of 200 and 240°C. In Table 8, the material balance of distilled fractions and residues are presented along with cholesterol content. It seems that distillation at the higher temperature, to shorten processing time, did not result in significant change in the total mass of lard. Therefore, a second test of distillation at 250°C for 6 h was carried out, with samples taken hourly. The results are described in Table 9. There was a significant reduction in the cholesterol content in the residues, from an initial value of 988–156 ppm after the first hour and 105 ppm after 2 h, after which further reduction was minor. For an industrial application, the distillation time at 250°C could be limited to 2 h to reduce cholesterol to an acceptable nutritional level.

The working conditions for molecular distillation are nondestructive. Hickman and Embree (12) introduced the concept of "risk of decomposition," Dh, from the expression:

$$D\text{h} = \log D \qquad [1]$$

where D = t (s) × P (mmHg). For example, pure vitamin D has a Dh > 1, crude and refined oils have Dh > 3 and Dh > 4, respectively. With particular reference to triglycerides, in all experiments discussed here, they were held well under their decomposition temperature. In the case of lard, where the distillation was carried out at 250°C for long periods of time (up to 6 h), it was necessary to check by analyzing the composition for *trans*-isomer fatty acids that could have formed during the thermal treatment.

TABLE 9

Lard Distillation—Experiments Carried Out at a Constant Temperature of 250°C (mass balance and cholesterol content)

Product	Distillation time (h)	Mass (kg)	Cholesterol (ppm)
Starting material	0	10.36	988
Distillate	1	0.30	2888
Residue	1	10.06	156
Distillate	2	$5e^{-4}$	10^6
Residue	2	10.06	105
Distillate	3	$1e^{-4}$	10^6
Residue	3	10.06	80
Distillate	4	$6e^{-4}$	10^6
Residue	4	10.06	80
Distillate	5	$3e^{-5}$	10^6
Residue	5	10.06	70
Distillate	6	$3e^{-5}$	10^6
Residue	6	10.06	70
Pooled distillates		0.30	31333

The results are described in Table 10. A modest increase in *trans*-isomers is evident after 6 h but was negligible for the first 3 h. Therefore, in the case of lard, the molecular distillation plant used in this study is suitable for the preparation of commercial products with low cholesterol content.

The experiments carried out allow us to demonstrate the technological possibility of reducing cholesterol in butter and lard, working under safe conditions that do not result in undesirable modifications of the lipid matrix. In fact, as shown in Tables 1–4, the contact time of the product in the evaporator at high temperature is limited to a

TABLE 10

Lard Distillation at a Constant Temperature of 250°C (effect of processing time on *trans* fatty acids formation)[a]

Processing time (h)	0	1	2	3	4	5	6
trans Oleic	0.27	0.29	0.30	0.30	0.32	0.33	0.33
trans Linoleic	0.12	0.14	0.16	0.16	0.14	0.22	0.23
trans Linolenic	0.02	0.07	0.07	0.08	0.09	0.12	0.13

[a]Results expressed as % m/m on total fatty acids.

few seconds. The reduction in cholesterol content was always greater than 90%. Further reduction would not appear feasible without seriously affecting the quality of the end product. The cholesterol ester fraction, amounting to about 10% of the total in both fats, cannot be distilled under the experimental conditions used. As far as the two fats examined are concerned, lard can be treated at raised temperatures for relatively short periods of time, based on the difference in volatility between free cholesterol and triglycerides. The opposite is true for butter, where particular care must be taken to minimize the distillation of the low-weight triglyceride fraction, whose distillation curve tends to overlap that of cholesterol.

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