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PREPARATION OF HARD BUTTER FROM PALM AND SAL 'OLEIN MIXTURE'

Keywords: cocoa butter substitute; palm olein and sal fat

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Olein mixtures {[POo:SLo]} obtained from the acetone fractionation (at 10°C) of palm olein (POo) and sal fat (SL) blends {[POo:SL(70:30)]o, [POo:SL(55:45)]o, and [POo:SL(40:60)]o} were hydrogenated at: temperature, 200°C; pressure, 7 psi; and stirring rate, 500 rpm, using 0.1% catalyst (Nysel SP-7, G-15 Flakes or Resan-22). The physicochemcial changes in the olein mixtures during hydrogenation were studied by determining their slip melting points, iodine values, hardness and DSC melting curves. These studies revealed that the use of [POo:SL (70:30)]o, Nysel SP-7 catalyst and a hydrogenation time between 1.0 and 1.5 hr was suitable for the preparation of cocoa butter substitute.

INTRODUCTION

The process of co-fractionating palm olein and sal fat blends during the preparation of cocoa butter equivalent (Md. Ali *et al.*, 1990) (*Figure 1*), produces a by-product called 'olein mixture', which may be hydrogenated to make cocoa butter substitute (CBS). Currently, the market for CBS is independent of that for cocoa butter. In the present work, olein mixtures were prepared using blends of palm olein and sal fat in various ratios, and hydrogenated using three types of commercially available catalyst. It was found that, generally, the hydrogenation process would be feasible if the ratio of palm olein in the substrate could be increased, if the process could be completed in a short time, and if the quality of the hydrogenated product was maintained.

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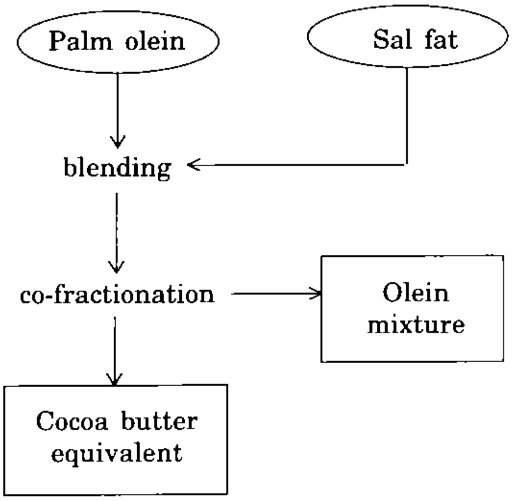

Figure 1. Preparation of CBE from palm olein and sal fat.

MATERIALS AND METHODS

Olein mixtures {[POo:SL]o} obtained from the acetone fractionation at 10°C of palm olein (POo) and sal fat (SL) blends in the ratios of 70:30, 55:45 and 40:60 were hydrogenated at 200°C, 7 psi pressure, and 500 rpm stirring rate, using 0.1% catalyst (Nysel SP-7, G-15 Flakes or Resan-22). Samples were taken at every 30 min for 3 hours. Slip melting points and iodine values were determined according to the AOCS (1964) method Cc 33-25 and method Cd 1-25 respectively. Hardness was measured by using a penetrometer with a 2.460 g, 15° needle. Before the measurement, a 30 ml sample in a 50 ml sample jar was melted at 60°C for 30 min before cooling to 0°C and holding there for 90 minutes. The fat was then stabilized at 23±0.5°C for a week prior to hardness measurement at the same temperature. Melting behaviour was studied by using a Mettler DSC Model FP80 (Switzerland), equipped with a Mettler FP84 TA microscopy cell and Mettler FP89AT System Software running on an IBM PC. A sample of about 4 mg of fat was precisely weighed (±0.005 mg) in the DSC pan, then melted and stabilized in a manner similar to that used for the hardness measurement described above. In addition, the stabilized sample was again held at 0°C for 5 min on the DSC head before the measurement. The DSC melting thermogram was recorded at a heating rate of 10°C/min from 0°C to 50°C. The triglyceride composition of unhydrogenated olein mixtures was analysed on HPLC (Waters Associates, Milford, MA) according to the reported method (Md. Ali *et al.*, 1991). The fatty acid composition of a selected hydrogenated oil was determined after conversion to fatty acid methyl esters (FAME) (Timms, 1978) by using GLC (Perkin Elmer, Sigma 2B), according to a method based on that of Tan (1991). The FAME mixture was injected at 290°C, separated on a 60 m × 0.25 mm i.d. fused silica capillary column coated with SP2340 (Supelco, USA) at an isothermal temperature of 180°C, and detected with FID at 290°C.

RESULTS AND DISCUSSION

Table 1 shows that the olein mixtures {[POo: SL]o} obtained from the fractionation of palm olein and sal fat blends consisted of about 22.5% to 28.2% mono-unsaturated triglycerides (*i.e.* POP, 15.9% to 22.4.9%; POS, 4.9% to 5.5%; and SOS, 0.9% to 1.1%). Most of the remainder were di- and poly-unsaturated triglycerides, mainly POO, SOO and PLO. However since their iodine values were very close (between 53.7 and 55.1) the variations in triglyceride composition had only a small effect on the melting points of the unhydrogenated olein (substrates), which were within the narrow range of 10.2°C to 11.5°C (*Table 2*). During high selectivity hydrogenation, POO, SOO, PLO and some other unsaturated triglycerides could be transformed from the usual *cis* to a *trans* configuration. A high content of such glycerides in the end products is important in the preparation of non-lauric hard butter since it provides good hardness with a sharp melting profile at body temperature (37°C).

The data in *Table 2* show that catalyst activity during hydrogenation (as indicated by the decrease per minute in iodine value) was highest using Resan-22 (0.28 IV per min,

TABLE 1. TRIGLYCERIDE COMPOSITION OF OLEIN MIXTURE BEFORE HYDROGENATION

Triglycerides	[POo:SL(70:30)]o	[POo:SL(55:45)]o	[POo:SL(40:60)]o
OOL	0.6	0.4	0.6
PLL/MOL	2.1	1.9	1.7
OOL	1.9	1.0	1.9
PLO	10.5	9.3	8.2
OOO	4.7	5.5	5.6
PLP	7.4	8.6	6.2
POO	25.9	25.1	21.9
SOO	8.8	12.3	18.0
POP	22.4	20.1	15.9
POS	4.9	5.1	5.5
SOS	0.9	0.9	1.1

*P = palmitic acid
L = linoleic acid
M = miristic acid
S = stearic acid
O = oleic acid

TABLE 2. EFFECT OF CATALYST AND SUBSTRATE ON PHYSICO-CHEMICAL CHANGES IN OLEIN MIXTURES DURING HYDROGENATION

Time (hours)	[POo:SL(70:30)]o			[POo:SL(55:45)]o			[POo:SL(40:60)]o		
	IV	m.p.(°C)	D(cm)	IV	m.p.(°C)	D(cm)	IV	m.p.(°C)	D(cm)
					Nysel SP-7				
0	55.1	10.2	> 3	54.7	11.3	> 3	53.7	11.5	> 3
0.5	53.7	30.0	> 3	52.5	32.4	> 3	52.2	28.3	> 3
1.0	50.7	36.2	1.12	51.2	35.0	2.10	50.6	34.1	2.55
1.5	50.1	37.8	0.87	50.1	37.5	0.96	49.9	35.5	1.32
2.0	49.3	38.9	0.74	49.8	37.5	0.86	49.2	36.4	0.94
3.0	48.1	40.0	0.66	48.9	39.1	0.63	48.7	37.6	0.64
				G-15 Flakes					
0	55.1	10.2	> 3	54.7	11.3	> 3	53.7	11.5	> 3
0.5	50.3	31.9	> 3	51.3	33.8	> 3	52.8	26.0	> 3
1.0	45.5	38.4	1.85	43.8	36.9	1.65	48.2	34.5	> 3
1.5	41.8	41.3	1.04	42.2	38.7	1.08	44.2	36.0	1.48
2.0	37.8	44.4	0.71	39.8	41.2	0.86	41.9	39.6	1.07
3.0	37.1	45.8	0.54	38.2	44.0	0.68	38.6	43.9	0.70
				Resan-22					
0	55.1	10.2	> 3	54.7	11.3	> 3	53.7	11.5	> 3
0.5	35.0	45.6	0.62	34.2	45.0	0.60	33.7	44.5	0.53
1.0	22.0	52.4	0.32	23.0	52.0	0.34	24.3	51.0	0.36
1.5	13.3	55.9	0.27	12.1	56.0	0.27	11.4	56.4	0.26
2.0	8.7	57.1	0.20	6.4	57.5	0.22	5.5	58.0	0.24
3.0	2.8	58.8	0.18	3.2	58.0	0.20	2.9	59.0	0.22

IV = iodine value;
m.p. = melting point;
D = penetration depth

followed by G-15 Flakes (0.09 IV per min) and Nysel SP-7 (0.03 IV per min). A similar pattern was found in the effect of the catalysts on slip melting point. After 3 hours of hydrogenation using Resan-22, G-15 Flakes and Nysel SP-7, the slip melting points of the fats were > 50°C, > 40°C and ≤ 40°C respectively. Catalytic activity which is too high is unfavourable (as is low selectivity) since it limits the geometrical isomerization which is a necessity for the formation of unsaturated *trans* fatty acids in the glycerides. The penetration test showed that fats obtained by hydrogenation using Resan-22 were the hardest. However, the hardening was related to saturation, and thus after 0.5 hour of hydrogenation, even though their hardness was close to that of Malaysian cocoa butter (penetration depth 0.62 cm) their melting points were too high (> 40°C) to allow their use as CBS. The results also showed that the hardness of a fat also increases with increasing palm olein content in the substrates.

The data in *Table 2* show that the use of [POo:SL (70:30)]o, Nysel SP-7 catalyst and a hydrogenation time between 1.0 and 1.5 hour was suitable for the preparation of cocoa butter substitute. DSC analysis (*Figure 2*) showed that hard butter obtained after 1.5 hour of

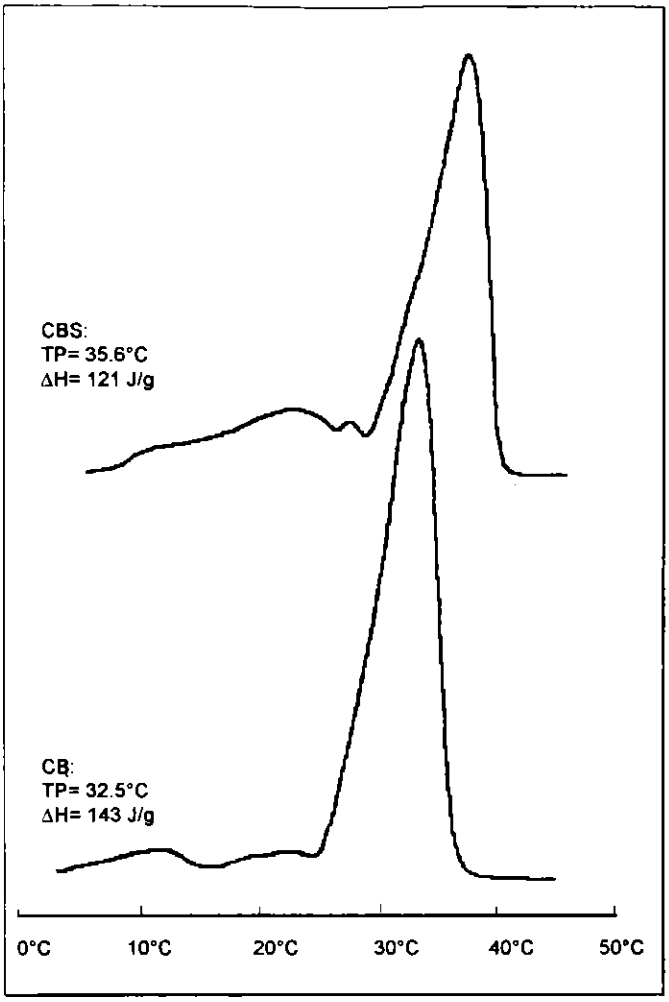

Figure 2. DSC melting endothermograms of non-lauric cocoa butter substitute (CBS) and cocoa butter (CB).

hydrogenation (CBS) had a melting curve quite similar to that of cocoa butter (CB). GLC analysis showed that this fat consisted of 16:0 (30.6%), 18:0 (12.5%), $18{:}1^t$ (30.3%), $18{:}1^c$ (19.7%), and isomers of 18:2 (7.0%).

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