NEW NON-LAURIC COCOA BUTTER SUBSTITUTES FROM PALM OLEINS

Keywords: Non-lauric cocoa butter substitute; Palm olein; Palm super-olein; Hydrogenation; Fractionation; Solid fat content

LEONG WAN LEONG AND OOI TIAN LYE *

Fairly good linoleic selectivity was obtained on the hydrogenation of palm olein products in a laboratory Parr Reactor at 180°C, using Nysel SP7 (0.06% as Ni) as catalyst, a pressure of 25 psig and a stirring speed of 600 r.p.m. When palm oleins with iodine values of 57, 62.5 and 66 respectively were hydrogenated to give products with a slip melting point of 34°C - 35°C, these products were soft as defined by their solid fat content (SFC) profiles. However, fractionation of these hydrogenated products gave various stearin fractions with a slip melting point of 38.5°C and yields varying from 55% to 85 percent. The SFC profiles of these stearins were comparable to those in commercial specifications for chocolate coating fat. When palm olein with IV 66 was hydrogenated to a slip melting point of 39°C, the SFC of the product was also comparable to that required for a commercial coating fat. However, dry fractionation could not remove the waxy tail from the product effectively.

INTRODUCTION

Palm oil has been identified as a valuable starting material for producing all types of cocoa butter alternatives. It is a source of symmetrical triglycerides containing about 28% of palmitic-oleic-palmitic (POP) and 5% of palmitic-oleic-stearic (POS) triglycerides (Defense, 1985). An enriched symmetrical triglyceride fraction can be produced by fractionation and used in the formulation of cocoa butter equivalent fats (CBE) by blending with other symmetrical triglycerides such as Illipe and Shea nut fats. However CBE fats are normally very expensive and offer limited cost savings compared with cocoa butter. Non-lauric cocoa butter substitutes (CBS)

---

* Palm Oil Research Institute of Malaysia,
P O Box 10620,50720 KUALA LUMPUR.

Original manuscript received on 15 October 1991

TABLE 1. FATTY ACID COMPOSITIONS (%) OF OLEIN AND SUPER OLEIN

Material	C12	C14	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	OTHERS
Olein (IV-57)	0.3	1.15	39.5	0.25	4.1	42.9	10.8	0.5	0.4
Super-olein (IV-62.5)	0.4	1.14	34.5	0.3	3.4	47.8	11.5	0.5	0.3
Super-olein (IV-66)	0.3	1.1	33	0.1	3.5	48.5	12.5	0.7	0.4

which can be produced by hydrogenation or by hydrogenation and fractionation of oils are usually a cheaper alternative although their degree of compatibility with cocoa butter is limited (Pease, 1985). In the United States, the predominant oils used for producing non-lauric CBS are those from soya bean and cottonseed. However, some of the liquid products from the fractionation of palm oil could also be valuable source materials.

Hydrogenation of oils is normally carried out in a heterogeneous system containing the solid catalyst, the liquid oil and hydrogen gas. In partial hydrogenation, hydrogen atoms are added to some of the double bonds of unsaturated fatty acids in the triglyceride molecules, eliminating them, while a proportion of the remaining double bonds are isomerized through *cis/trans* conversion and positional shift along the fatty acid chain (Larsson, 1983). As a result of these chemical changes, the melting range is shifted to higher temperatures and the stability to oxidation and resistance to flavour deterioration are improved.

With non-lauric oils, the properties of the hydrogenated products will depend on selectivity. Ideally, a reaction of high selectivity should be achieved, so that hydrogenation proceeds stepwise and polyunsaturated acids are gradually converted into oleic or *trans*-oleic (elaidic) acid with minimum formation of positional isomers. The increase in stearic acid should also be minimal. Selectivity is dependent on the type and quantity of catalyst used, the temperature, the level of agitation and the pressure. Many publications have indicated that high linoleic and linolenic acid selectivity in a hydrogenation reaction can be achieved if nickel and poisoned catalyst, medium to high temperature (150°C - 200°C), low pressure (1-3 bar) and mild agitation are used (Grothues, 1985; Allen, 1981;

TABLE 2. PHYSICAL PROPERTIES OF HYDROGENATED PALM OLEIN AND SUPER-OLEINS

Hydrogenated products	S.M.P (°C)	IV	SFC (%)							IV before hydrogenation
			10°C	15°C	20°C	25°C	30°C	35°C	40°C	
HPO$_o$-1	35.0	47.5	62.0	47.4	31.0	18.2	11.1	4.6	-	57.0
HPO$_o$-2	35.4	54.2	68.9	53.0	41.0	25.5	14.5	8.2	1.8	62.5
HPO$_o$-3	33.7	55.1	69.3	54.0	36.8	22.9	13.3	4.5	-	66.0
HPO$_o$-4	36.5	55.1	79.0	70.5	56.0	40.3	24.0	9.1	-	66.0
HPO$_o$-5	39.0	51.0	87.4	82.0	67.0	54.7	34.1	19.1	2.0	66.0

TABLE 3. FATTY ACID COMPOSITIONS (%) OF HYDROGENATED PALM OLEIN

Hydrogenated products	C12:0	C14:0	C16:0	C16:1	C18:0	C18:1 t	C18:1 c	C18:1 isomers	C18:2 tt	C18:2 tc	C18:2 ct	C18:2 cc	C20:0	Other
HPO_o-1	0.2	1.1	41.9	0.1	7.0	5.1	36.1	2.1	0.2	0.3	0.3	4.9	0.4	0.3
HPO_o-2	0.3	1.0	34.9	0.1	5.3	13.7	36.8	0.9	0.6	1.3	1.2	1.8	0.4	2.0
HPO_o-3	0.2	1.2	34.5	0.1	6.2	15.6	34.5	1.5	0.5	1.6	1.8	1.5	0.4	0.8

TABLE 4. FRACTIONATION OF HYDROGENATED PALM SUPER-OLEIN

Fractionation products	SMP (°C)	IV	Yeild %	SFC (%) 10°C	15°C	20°C	25°C	30°C	35°C	40°C	Cooling Programme
HPO_o-2(S)	38.5	47.5	55.0	82.2	-	63.0	46.6	31.8	20.3	3.1	50°–17°C
HPO_o-3(S)	38.7	48.5	58.5	83.6	74.7	60.5	46.5	31.6	14.9	2.5	50°–17°C
HPO_o-4(S)	38.5	50.0	84.0	85.2	76.5	63.5	49.8	33.0	16.3	2.0	50°–16°C
HPO_o-5(0)	38.0	51.0	95.0	87.0	79.6	68.9	54.4	35.7	17.4	2.9	50°–33°C

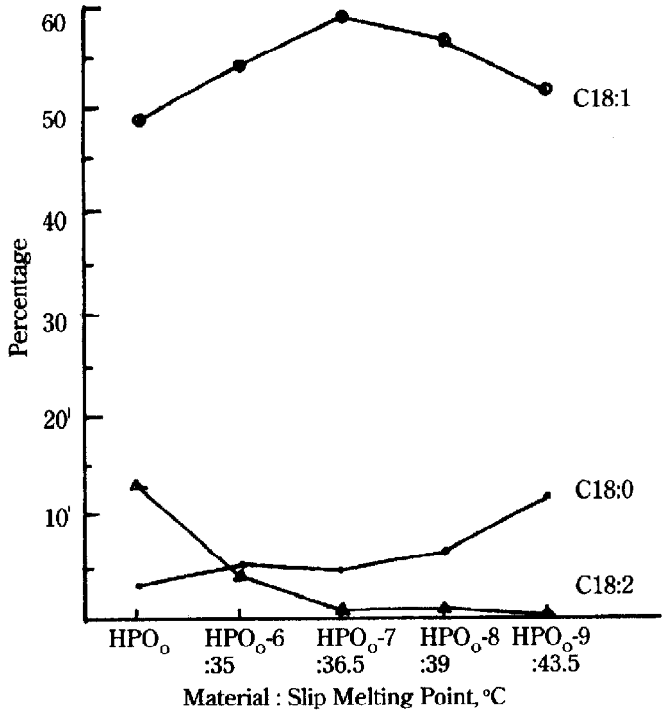

Figure 1. Change of C18:0, C18:2 during Hydrogenation of Palm Superolein (IV66)

Coenen, 1976 and Beckmann, 1983). Proper control of the selectivity of hydrogenation gives a mixture of triglycerides with the right oleic, elaidic, stearic and palmitic acid composition *i.e.* a mixture with a narrow melting range at around 37°C (body temperature); such a product may be suitable for use as a cocoa butter substitute. However, in view of the many parameters involved in the hydrogenation process, it is not easy to control selectivity. Consequently most hydrogenated products have a 'waxy tail' in their solid fat content profile; this is partly due to the presence of an excess of higher-melting triglycerides largely made up of elaidic and stearic acids resulting from the conversion of unsaturated acids during hydrogenation. However, it is believed that the waxy tails could be removed or minimized by submitting the hydrogenated product to a crystallization-filtration process.

The object of this paper is to present some experimental data on the possibility of producing non-lauric CBS by partial hydrogenation (or hydrogenation and fractionation) from palm oil liquid fractions particularly super-olein.

EXPERIMENTAL

Materials

Refined, bleached and deodorized palm olein (one sample) and super-olein (two samples), with IV values of 57, 62.5 and 66 respectively were used for the experiments. The fatty acid compositions of the materials are shown in *Table 1.*

Hydrogenation

A Parr hydrogenator with a capacity of 700 grams of oil was used. It was equipped with a speed-controlled agitator, a pressure gauge, a temperature indicator and the necessary safety features. Heating of the oil was electrical and indirect, on the external surface of the reaction vessel.

A fixed procedure was followed for all the hydrogenation experiments. The optimum conditions for hydrogenation which were determined from the results of a number of preliminary experiments were as follows:

Catalyst	:	Nysel SP 7
Quantity	:	0.06% as Ni
Temperature	:	180°C
Pressure	:	25 psig
Stirring rate	:	600 r.p.m.

Hydrogen gas was supplied from a cylinder and the experiments were controlled by monitoring the change of slip melting point on samples taken at ten-minute intervals. When the slip melting point of a sample reached the predetermined value, the experiment was complete.

Fractionation

Fractionation experiments involve two stages; crystallization and filtration. The crystallization of oil samples was carried out by passing cold or chilled water through the jacket of a 1-litre vessel equipped with a glass stirrer and a low speed motor. A programmable controller directly controlled the temperature of cold or chilled water and hence the rate of cooling. Filtration of the crystallized oil was conducted by using a jacketed stainless steel filter and Whatman paper under vacuum.

Analysis

The fatty acid composition of oil samples, and the percentage of *cis-*, *trans-* and positional isomers were determined with a Shimadzu GC-9APTF using a 3-metre x 5 mm I.D. packed column of 10% SP-2340, and a 50-metre SP2340 capillary column, respectively. The solid fat content of oils was determined by NEWPORT wideline NMR based on a standard PORIM procedure, which consisted in heating the sample to 70°C and maintaining it there for 30 minutes. The sample was then cooled to 0°C and kept it at that temperature for 90 minutes before the measurement with the NMR instrument was carried out. PORIM standard methods (PORIM, 1983) were also used for determining iodine values and slip melting points. The slip melting point analysis used for process control during hydrogenation was done with a quick method based on 10 minutes tempering time.

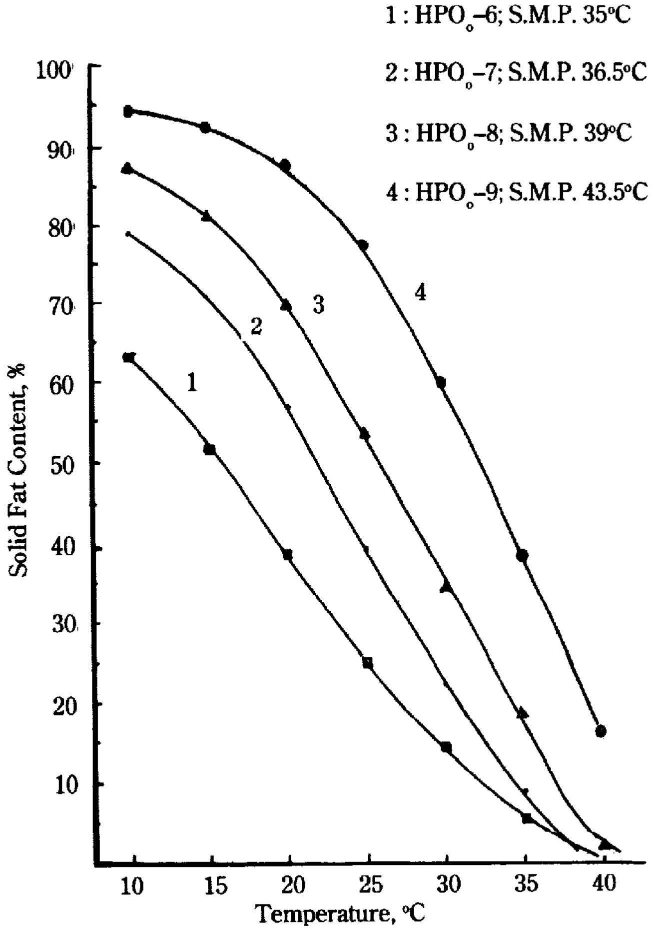

Figure 2. Solid Fat Contents of Hydrogenated Palm Superoleins

RESULTS AND DISCUSSION

The selectivity of hydrogenation using Nysel SP 7 and the conditions set out above is shown by the change in the percentages of the fatty acids 18:0, 18:1 and 18:2 during the progressive hydrogenation of palm super-olein (IV 66) to slip melting points of 35°C, 36.5°C, 39°C and 43.5°C (*Figure 1*). When hydrogenation started, the percentage of 18:2 declined while that of 18:1 increased. As the slip melting point increased to above 36.5° C, 18:2 had declined to a minimum, while 18:1 was starting to decline and 18:0 to increase. The increase of 18:0 was small until the slip melting point of the hydrogenated palm super-olein exceeded 39°C. The linoleic acid selectivity was considered adequate. The results discussed in this paper are all from experiments using the same hydrogenation conditions.

HPO$_0$-1, HPO$_0$-2 and HPO$_0$-3 were the respective products from the hydrogenation of palm olein (IV 57) and super-oleins (IV 62.5 and 66) to a slip melting point of around 34°C - 35°C (*Table 2*). (The fatty acid compositions and the percentage of *cis-* and *trans-* isomers in HPO$_0$-1, HPO$_0$-2 and HPO$_0$-3 are shown in *Table 3*). The SFC analysis of these products indicates that none of them was suitable for use as cocoa butter substitute. They were too soft at temperatures between 10°C and 30°C. The comparatively low SFC of the products could be due to the fact that the polyunsaturated fatty acid content in the starting materials was too low. The iodine values of HPO$_0$-1, HPO$_0$-2 and HPO$_0$-3 were 47.5, 54.2 and 55.1 respectively, and the reduction from the IV values of the starting materials before the slip melting point exceeded 34°C was only 7 - 11 IV units. This small reduction indicates that hydrogenation was mild and hence the products were soft. There was also little difference in SFC between HPO$_0$-1, HPO$_0$-2 and HPO$_0$-3 at different temperatures, mainly because the percentage of 18:2 in their respective starting materials differed only slightly.

The solid fat contents of the products (HPO$_0$-3 to HPO$_0$-9) of hydrogenation of palm super-olein of IV 66 to higher slip melting points are shown in *Table 2* and in *Figure 2*. In general, the SFC between 10°C and 40°C increased as the slip melting point of the product increased. Neither HPO$_0$-3 nor HPO$_0$-4 was good enough for use as CBS because the solid fat contents were low at low temperatures and the products were soft. However HPO$_0$-5 (SMP 39°C) seemed to be acceptable as CBS for use as chocolate coating fat when its properties were compared with the commercial specifications from a Malaysian specialty fat manufacturer. If the waxy tails at 35° and 40°C were removed and the SFC at 25° and 30°C were higher, it could be used as CBS in chocolate manufacturing. This might be achieved by a fractionation process.

Fractionation can produce a stearin with a higher SFC at temperatures between 10° and 30°C. *Figure 3* shows the SFC profile of HPO_o-3 and the stearin fraction obtained from it, HPO_o-3(S). The results from the fractionation of other hydrogenated palm super-oleins are shown in *Table 4*. HPO_o-2(S), HPO_o-3(S) and HPO_o-4(S) were the stearin fractions from HPO_o-2, HPO_o-3 and HPO_o-4 at fractionation temperatures of 17°, 17° and 16°C respectively and 7 hours of crystallization time; the product yields were 55%, 58.5% and 84% respectively. The respective slip melting points were 38.5°, 38.7° and 38.5°C. The SFC patterns for the three stearin fractions between 10° and 40°C were identical, and comparable to the commercial specifications of CBS coating fat. All three stearin fractions also exhibited waxy tails at 40°C. They might be used as coating fats but are not good enough as fine chocolate fat.

HPO_o-5, a hydrogenated palm super-olein with a slip melting point of 39°C was fractionated at 33°C, with the aim of removing the waxy tail. The properties and product yield of the olein fraction, (HPO_o-5(0)), are also shown in *Table 4*. It was found that there was no significant difference in SFC profiles between HPO_o-5(0) and HPO_o-5 although both products could meet the commercial specifications for chocolate coating fat in terms of SFC, slip melting point and IV. The waxy tail was still present, as evident by the SFC at 40°C. This could be due to the limitations of dry fractionation, which cannot normally provide sharp separation of solid stearin and liquid oleins owing to the aggregation of liquid and solid during the long hours of crystallization: filtration by the more common techniques, mainly vacuum or pressure, is difficult. This affects the triglyceride compositions of the olein and stearin fractions. Consequently the SFC of HPO_o-5(0) at 35° and 40°C were still high and the SFC at 25° and 30°C were not significantly increased. Perhaps solvent fractionation could do a better job of obtaining an olein fraction with a minimum of waxy tail, or none.

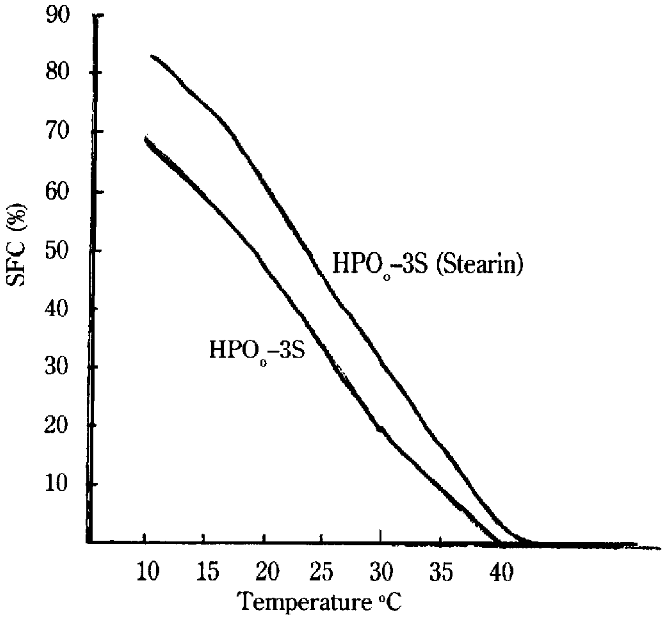

Figure 3. Solid Fat Contents (SFC) of Hydrogenated Palm Super-Olein and its Stearin Fraction

CONCLUSION

- It was possible to achieve reasonably high linoleic acid selectivity when palm oleins were hydrogenated in a laboratory scale Parr reactor at 180°C, using Nysel SP7 (0.06% as Ni) as catalyst, a pressure of 25 psig, and a stirring speed of 600 r.p.m.

- Hydrogenation of palm olein and super-oleins with iodine values of 57, 62.5 and 66 respectively to slip melting points of around 34°C-35°C did not produce satisfactory non-lauric CBS, as shown by the SFC profiles between 10° and 40°C. However, if palm super-olein with an IV of 66 was hydrogenated to a slip melting point of 39°C, the product was found to have a SFC profile comparable to that of a commercial non-lauric CBS, and it could be traded as a chocolate coating fat.

- Fractionation of hydrogenated palm super-oleins with slip melting points of 34° to 36°C was found effective in producing stearin fractions yield varying from 55% to 85%, whose properties were comparable to the commercial specifications of non-lauric CBS.

- The dry fractionation process was not effective in removing the waxy tail of a hydrogenated product.

Other approaches such as solvent fractionation or detergent fractionation should be tried.

ACKNOWLEDGEMENT

The authors wish to thank Mr Flingoh Oh of PORIM for his assistance in conducting solid fat content analyses, the Director of Chemistry and Technology for his valuable comments, and the Director-General of PORIM for the permission to publish this paper.

REFERENCES

ALLEN, R R (1981). Hydrogenation, *J. Am. Oil Chem. Soc.*, 166 - 169.

BECKMANN, H J (1983). Hydrogenation Practice. *J. Am. Oil Chem. Soc.*, *60*, 234A - 242A.

COENEN, J W E (1976). Fats and Oils Modification. *J. Am. Oil Chem. Soc.*, *53*, 382 - 389.

DEFENSE, E (1985). Fractionation of palm oil. *J. Am. Oil Chem. Soc.*, *62*, 376 - 385.

GROTHUES, B G M (1985). Hydrogenation of palm and lauric oils *J. Am. Oil Chem. Soc.*, *62*, 390 - 399.

LARSSON, R (1983). Hydrogenation theory: some aspects. *J. Am. Oil Chem. Soc.*, *60*, 227A; 275 - 281.

PEASE, J J (1985). Confectionery fats from palm oil and lauric oil. *J. Am. Oil Chem. Soc.*, *62*, 426 - 430.

PORIM Test Methods for Palm Oil and Palm Oil Products. Palm Oil Research Institute of Malaysia, May 1983.