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FORMULATION OF *TRANS*-FREE MARGARINES USING HYDROGENATED AND INTERESTERIFIED PALM OLEIN

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ABSTRACT

Palm olein (POL) was studied as a material for the formulation of trans*-free margarines (TFM) having less than 1% of* trans *fatty acid content. To achieve this aim, hydrogenation and interesterification reactions were performed using POL to obtain fats having desirable melting properties. Samples from the early stages of hydrogenation and after interesterification were analysed for their melting behaviour and* trans *contents. During hydrogenation, the iodine value of POL was reduced from 55.2 to 46.0 while* trans *fatty acid (TFA) content and slip melting point (SMP) increased from 0% to 7.15% and from 24.0°C to 37.8°C, respectively. The results show that slightly hydrogenated POL had low* trans *content and appropriate melting ranges for TFM formulations. Interesterification increased both SMP and solid fat contents (SFC) at all measuring temperatures. In conclusion, a combination of POL and its hydrogenated and interesterified forms within certain ranges can be used for the preparation of* trans*-free base stocks for stick type margarines. The optimum ranges were determined as 40%-50% for interesterified, 10%-30% for hydrogenated and 30%-40% for natural POL.*

Keywords: palm olein, hydrogenation, interesterification, melting behaviour, *trans*-free margarine.

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INTRODUCTION

Margarine is produced as a butter-like product from edible fats and oils using hardening techniques such as hydrogenation, interesterification and fractionation which increase the solid content, and improve resistivity to thermal and atmospheric oxidation as well as the plasticity of the products.

Hydrogenation reduces the relative unsaturation of the oils as well as promotes geometric and positional isomerisation (Erickson and Erickson, 1995). *Trans* fatty acids (TFA) form during hydrogenation, then increase and decrease after reaching their maximum point (Musavi *et al*., 2008). They affect the physical and chemical properties of the final products because they have higher melting points and greater stability than *cis* fatty acids (Lo and Handel, 1983).

Over the years, the *trans*-free trend has forced margarine manufacturers to use different techniques to obtain *trans*-free base stocks with desirable melting properties. Use of partial hydrogenation has been widespread to obtain hard stocks for margarines. The fact that TFA increases the risk of cardiovascular disease (Lichtenstein, 1998) makes hydrogenation an undesirable process because of its *trans* production potential. Thus, there are two ways to obtain low *trans* partially hydrogenated oil: at the early and late stages of hydrogenation.

Interesterification is an alternative reaction in oil modification. Fatty acids are randomly replaced in triacylglycerol (TAG) as a result of intra- and intermolecular exchange of the acyl groups in TAG molecules during the reaction. Interesterification of vegetable oils also has an important impact on the melting behaviour of fats, like plasticity and consistency (List *et al*., 1977;

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Marangoni and Rousseau, 1995). When vegetable oil blends are used as starting material, saturated fatty acids (SFA) mainly in the 1,3-positions of TAG shift to the 2-position, and the reaction reaches its equilibrium when each fatty acid is equally present in all positions (Lo and Handel, 1983). Interesterification of liquid vegetable oils alone does not give any benefit because only small amounts of SFA are involved in the reaction; however, various fat phases can be obtained by randomisation of the liquid oil with highly saturated fats like palm stearin or fully hydrogenated soyabean oil. Palm olein (POL) is a product of the fractionated crystallisation process which has widespread use as a frying oil. Despite having 46% SFA, POL has only 13.7% SFA at the 2-position of TAG (Siew and Minal, 2007). Thus, it has good hardening potential after the hydrogenation and/or interesterification processes.

Some studies have been done on hardening POL to use it with other vegetable oils for the formulation of margarine hard stock. Yap *et al.* (1989) hydrogenated POL with an iodine value (IV) of 57, using 0.2% commercial nickel catalyst (with 25% Ni) at 175°C, 103 kPa hydrogen pressure and 850 rpm agitation rate. At the point of 40.7 IV, the *trans* content of the hydrogenated POL was above 20%; it then reached its maximum point of 24% with 31 IV, and declined to 10% with 6 IV. POL was chemically interesterified for preparing low-*trans* vanaspati, and considerably higher solid fat contents (SFC) at all measuring temperatures were obtained (Farmani *et al*., 2006). Also, the melting point rose from 17.9°C to 38.1°C. Soares *et al*. (2009) who obtained similar results explained these increases in solid contents or melting points by the changes in the TAG structure after interesterification. They observed an increase in trisaturated (SSS) and triunsaturated (UUU) TAG but a considerable decrease in disaturated-monounsaturated (SSU) as well as a slight decrease in saturated-diunsaturated (SUU) TAG.

The aim of this work was to obtain suitable fat phases for *trans*-free margarines (TFM) having less than 1% of *trans* isomers, using lightly hydrogenated and randomly interesterified POL.

MATERIALS AND METHODS

Materials

Commercial POL with 55.2 IV was hydrogenated in an industrial type reactor (DeSmet, Belgium). Nysosel 820 (22% Ni on SiO_2) was purchased from Engelhard (Iselin, NJ) and used in all the reactions. Dry sodium methoxide used in the interesterification reactions was purchased from Merck (Germany).

A mixture of 37 fatty acid methyl esters (C4-C24), methyl esters of *cis*-11-vaccenic acid and a *cis-trans* isomer mixture of linoleic acid were purchased from Supelco (Bellefonte, PA). Methyl esters of *trans*-11-vaccenic acid, *cis*-12-oleic acid, CLA and *cis-trans* isomers of linolenic acid were purchased from Sigma-Aldrich (St. Louis, MO). All reagents were of analytical grade.

Methods

Hydrogenation. Hydrogenation reactions in seven separate runs were carried out at 180±2°C, 2 bar H_2 pressure and 115 rpm stirring speed. Refined, bleached and deodorised POL was used as the material for each run, and hydrogenated from 55.2 IV to seven different IV. The oil was introduced into the reactor and heated under vacuum (40 mbar) with agitation for 1.5 hr. After reaching 180°C, 0.002% of the catalyst and a calculated amount of hydrogen were introduced into the reactor. The samples were then withdrawn at the end of the reactions after the reactor pressure was reduced to the starting pressure. The oil was filtered to remove the catalyst and then subjected to analysis.

Interesterification. Interesterification of POL was performed in a laboratory-scale reactor using dry sodium methoxide. To remove moisture from the oil, 200 g of POL was heated under vacuum at 500 rpm agitation speed at 110°C for 30 min, and then cooled to 95°C. After that, 0.3% of sodium methoxide was immediately introduced into the system, and the reaction was continued for 1 hr under constant conditions. To stop the reaction, 25% phosphoric acid was added and mixed in for 20 min. The filtered oil was then heated to 110°C, mixed for 2 min with 0.5% bleaching earth to remove colour and soap residues. The interesterified POL was filtered in the presence of anhydrous sodium sulphate to remove moisture, and kept at 4°C for analysis.

Fatty acid composition and iodine value. The methyl esters of the fatty acids and their isomers were prepared according to IUPAC methods (Anon., 1987), and analysed using a Shimadzu GC-2010 model gas chromatograph (Japan) equipped with a DB23 column (60 m, 0.25 mm i.d., 0.25 mm film thickness; J&W). The injector, column and detector temperatures were 230°C, 195°C, and 240°C, respectively. The split ratio was 1:80. The carrier gas was helium at a flow rate of 0.3 ml min^{-1}. The IV of the samples was calculated from the fatty acid compositions using the AOCS Official Method Cd 1c-85 (Anon., 2003a).

Solid fat content. SFC of the samples was measured by a low-resolution pulsed NMR using a Maran

SFC (Resonance Instrument Ltd., Witney, UK), according to the AOCS Official Method Cd 16b-93 (Anon., 2003b).

Slip melting point. Slip melting point (SMP) was determined in triplicate according to the AOCS Official Method Cc 3-25 (Anon., 2003c).

RESULTS AND DISCUSSION

Lightly hydrogenated POL has an important place in the margarine industry because of its low *trans* content. Certain hydrogenation degrees and usage ratios are applicable for TFM solutions. Besides that, lower hydrogen amounts are required making the process much cheaper than other liquid oil hydrogenations. In contrast to partial hydrogenation, the interesterification of POL produces oil with increased SFC at 35°C or higher temperatures.

In this study, randomly interesterified and lightly hydrogenated POL with a narrow IV range were blended with POL in various proportions to determine the possibility of preparing hard stock for TFM having less than 1% total *trans* content. To achieve this aim, POL was hydrogenated in seven separate runs, from 55.2 to 46.0 IV, and data on the melting behaviour of the samples withdrawn at the end of the reactions are presented in *Table 1* and *Figure 1*. Meanwhile, POL was also interesterified, which increased SFC of the fat at all the measuring temperatures as indicated in *Figure 1* as well. The findings on SFC of interesterified POL were similar to those reported by other researchers (Berger and Idris, 2005; Farmani *et al*., 2006; Soares *et al*., 2009). SMP of POL was also raised from 24.0°C to 39.4°C after interesterification which is common for vegetable oils after interesterification (Sonntag, 1982), due to the formation of saturated and unsymmetrical TAG which melt at higher temperatures than their symmetrical counterparts (List *et al*., 2000) when they have the same polymorphic form.

As shown in *Table 1* and *Figure 1*, SMP and SFC increased with reduced IV by hydrogenation. SMP of POL increased from 24.0°C to 37.8°C after hydrogenation when IV was reduced to 46.0. Although obtaining steeper curves, SFC values of the hydrogenated samples at high measuring temperatures increased with hydrogenation, which adversely affects the mouth feel properties of fat. Similarly, interesterified POL has higher SFC values at high measuring temperatures as well in spite of no change in saturation. Total *trans* and stearic acid contents were also increased from 0% to 7.15% and 3.92% to 7.18%, respectively (*Table 1*), on hydrogenation. It was concluded from these data that both hydrogenated and interesterified POL had some disadvantages when they were used in high ratios for the formulation of TFM. Hydrogenated POL increased the *trans* content of the final product while interesterified POL decreased taste and melting quality in the mouth because it has high SFC at 35°C or higher temperatures.

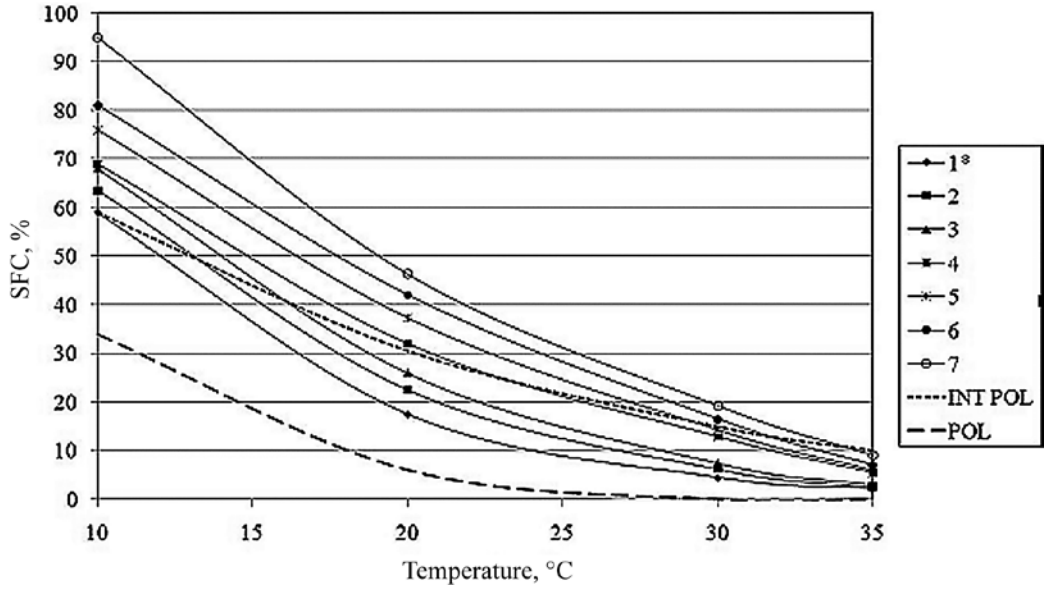
In Turkey, a spreads/margarine codex was issued by the Ministry of Agriculture and Rural Affairs in 2008 in accordance with the regulation of the EC, No. 2991/94. Spreads/margarines, or their blends with butter, can be produced in the fat range from 10% to 99%, and all terms existing in the EC regulation such as three-quarter fat, half fat, low fat, reduced fat or fat spread X % can be used in the product labels. *Trans* content is strictly controlled and has to be declared on the label in cases where it is higher than 1% in the product.

Using the findings on *trans* content and melting behaviour, it is possible to obtain *trans*-free

TABLE 1. FATTY ACID COMPOSITION (%), IODINE VALUE AND SLIP MELTING POINT OF HYDROGENATED PALM OLEIN

Fatty acid	Palm olein	Hydrogenated palm olein						
		1	2	3	4	5	6	7
C16:0	42.48	42.48	42.42	42.10	42.45	42.63	42.67	41.50
C18:0	3.92	4.02	4.16	4.38	5.20	5.39	6.14	7.18
C18:1 *tr*	ND	1.09	1.94	3.29	3.57	4.90	5.63	6.25
C18:1 *cis*	42.20	42.31	42.29	42.08	41.44	41.48	40.14	39.93
C18:2 *tr*	ND	0.37	0.54	0.83	1.44	1.01	1.00	0.90
C18:2 *cis*	9.37	7.92	6.70	5.42	4.23	2.68	2.24	1.77
Total *trans*	ND	1.46	2.48	4.12	5.01	5.91	6.63	7.15
SFA	48.03	48.19	48.28	48.16	49.23	49.73	50.91	51.06
IV	55.2	54.3	53.0	52.1	50.6	48.4	47.0	46.0
SMP (°C)	24.0	28.0	29.8	31.7	33.4	34.7	37.0	37.8

Note: ND: not detected, SFA: saturated fatty acids, IV: iodine value, SMP: slip melting point.



Note: *1-7 are the samples from early stages of POL hydrogenation as indicated in *Table 1*.
INT POL = interesterified palm oil olein. POL = palm olein.

Figure 1. Changes in solid fat content (SFC) during hydrogenation and interesterification at varying temperatures.

TABLE 2. FATTY ACID PROFILE, *TRANS* CONTENT AND SLIP MELTING POINT OF *TRANS*-FREE MARGARINE BASE STOCK FORMULATIONS

Composition	Formulation No.				
	F 1	F 2	F 3	F 4	F 5
	30% POL 40% INTPOL 30% HPOL 2	40%POL 40% INTPOL 20% HPOL 3	30% POL 50% INTPOL 20% HPOL 3	35% POL 50% INTPOL 15% HPOL 4	40%POL 50% INTPOL 10% HPOL 7
SFA (%)	48.0	48.0	48.0	48.2	48.3
UFA (%)	52.0	52.0	52.0	51.8	51.7
MUFA (%)	43.69	43.71	43.71	43.48	43.50
PUFA (%)	8.31	8.29	8.29	8.30	8.32
TFA (%)	0.72	0.80	0.82	0.80	0.70
SMP (°C)	35.3	35.2	35.8	36.0	35.1

Note: SFA: saturated fatty acids, UFA: unsaturated fatty acids, MUFA: monounsaturated fatty acids, PUFA: polyunsaturated fatty acids, TFA: *trans* fatty acids, SMP: slip melting point, POL: palm olein, INTPOL: interesterified POL, HPOL: hydrogenated POL.

base stocks having desirable melting behaviour by blending POL, hydrogenated POL and interesterified POL in certain ratios. *Trans* contents of the hydrogenated samples and SFC values of interesterified POL above 35°C were the main factors for determining these ranges. In addition, SFC values of POL and hydrogenated POL were also important. Some fat phases for stick margarine formulations were then prepared, and their SFC and fatty acid profiles were measured as presented in *Table 2*. As may be seen in *Table 2*, the optimum range for using interesterified POL varied between 40% and 50%, while it was 10% to 30% for using hydrogenated POL having IV between 55.2 and 46.0. Unmodified POL was used in the range of 30%-40% in all the formulations.

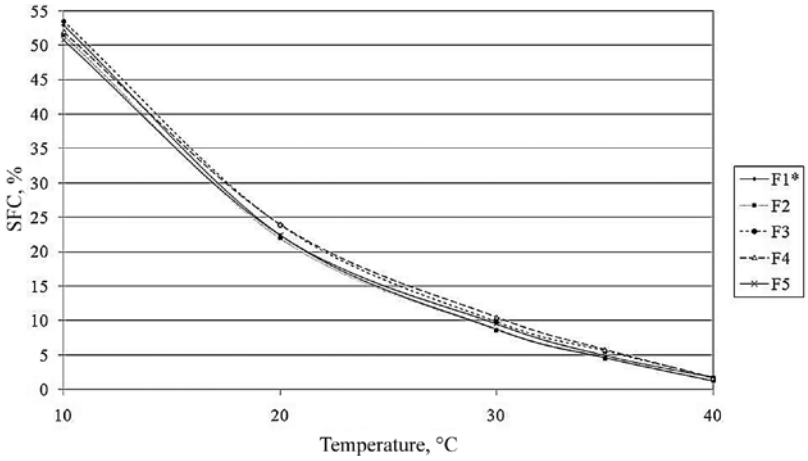
Fatty acid composition as well as SFC value (*Figure 2*) of the formulations were very similar to each other, while their SFA level was similar to that of POL. This situation can be explained by the fact that interesterification brought no change to the fatty acid composition of the oil, and that only slightly hydrogenated fats were used in formulations. Therefore, SFA, unsaturated fatty acids (UFA), monounsaturated fatty acids (MUFA) and polyunsaturated fatty acids (PUFA) in the blends were only changed slightly and the *trans* content was less than 1%, which is in the suitable range for the production of TFM.

SMP and SFC of 13 different stick margarines marketed in Turkey were analysed and their SFC data are presented in *Figure 3*. SMP of these

margarines were found to be between 34.7°C and 38.5°C, while that of the selected blends varied between 35.1°C and 36.0°C.

SFC of the selected blends in *Figure 2* were within the range of SFC values of the 13 different stick margarines marketed in Turkey. SFC values of the selected blends were 50.8%-53.5% at 10°C, 22.0%-24.0% at 20°C, 8.70%-10.50% at 30°C, and 4.60%-5.80% at 35°C, while those of the stick margarines marketed in Turkey ranged from 45.0%-55.0% at 10°C, 22.5%-28.2% at 20°C, 9.50%-13.8% at 30°C and 3.2%-7.3% at 35°C. SFC of the blends were not too high at 10°C and lowered to about 20% at 20°C, which shows that they were not too firm and had reasonable spreadability. Other factors such as crystal structure, cooling or conditioning may influence the spreadability. SFC at 20°C and 30°C indicates oil-off resistance or the stability of the products, while at 35°C, the mouth feel properties. SFC of the blends at 20°C and 30°C show that they were suitable in stability because they were within the SFC ranges of stick margarines sold in Turkey. As may be seen in *Figure 2*, SFC values of the blends at 35°C were about 5%, which may be reduced by blending in liquid oils in order to get a more pleasant mouth feel. These results suggest that the melting behaviour of *trans*-free blends prepared from certain proportions of modified and unmodified POL at elevated temperatures were very similar to those of stick margarines marketed in Turkey.

In conclusion, POL plays an important role in margarine production. Hydrogenation and interesterification of this oil produces very suitable base stocks especially for *trans*-free stick margarine production. Certain ranges of these base stocks can be used in preparing TFM having desirable melting behaviour.



Note: *F1-F5 are the formulations as indicated in the *Table 2*.

Figure 2. Solid fat content (SFC) of the selected blends of natural, hydrogenated and interesterified palm olein at varying temperatures.

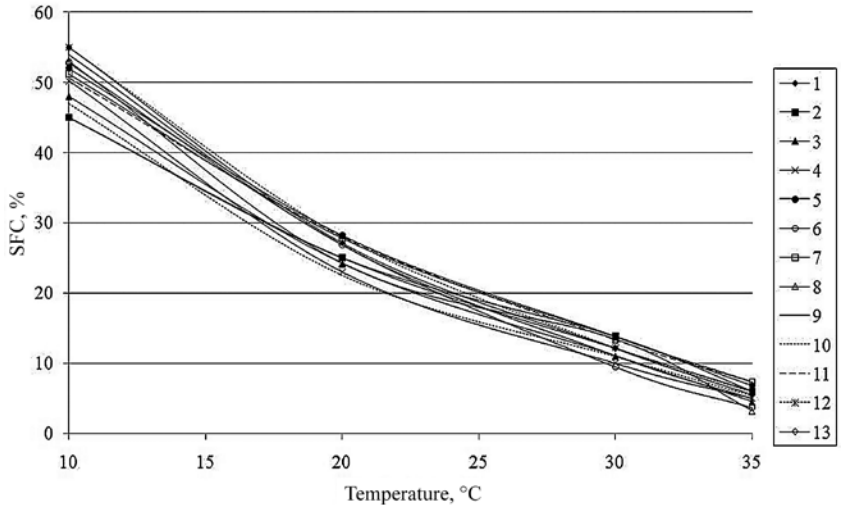


Figure 3. Solid fat content (SFC) of Turkish stick margarines in relation to temperature.

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