

Preparation of modified fats from vegetable oil and fully hydrogenated vegetable oil by randomization with alkali catalysts

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Randomization of fat blends, formulated by mixing vegetable oil with fully hydrogenated vegetable oil in various ratios, using alkali catalysts, have been investigated. The relationship between the structure and physical properties was examined. The fatty acid and triacylglycerol composition of each original fat blend and the randomization products together with the physical properties such as melting, crystallization characteristics and solid fat content were correlated. The differences in the exothermic and endothermic peak temperatures, melting points and solid fat content among the fat blends showed the effects of the composition on the physical properties. Copyright © 1996 Elsevier Science Ltd.

INTRODUCTION

Vegetable oils have been modified for many years by hydrogenation. This reduces double bonds to single bonds, thereby increasing both melting point and stability of the oil (Gray & Russel, 1979). However, the partial hydrogenation also results in the formation of positional isomers with double bonds in positions other than 9-, 12- and 15-, and geometric isomers in the *trans*- rather than *cis*- configuration found in most vegetable oils (Lo & Handel, 1983). The partially hydrogenated oils contain *trans*-unsaturated fatty acids, positional isomers and conjugation structures that are not naturally occurring in vegetable oils. The physical properties of these fatty acids are altered and also appear to be different (Gavriilidou & Boskou, 1991).

An alternative to isoselective hydrogenation is random interesterification to obtain fats with desired physical and nutritional properties. Interesterification, in comparison with hydrogenation, does not produce *trans* unsaturated fatty acids, these fats and oils do not lose their biological value. The randomization of low nutritional value fully hydrogenated fats with vegetable oils can produce valuable fat blends with good consistency

and with reduced or zero *trans*-isomers of unsaturated fatty acids suitable for margarines.

This paper investigates the randomization of fat blends formed from vegetable oils and fully hydrogenated vegetable oils in various ratios to produce fats with desired texture and melting characteristics suitable for using in margarines. The randomization fat blend was determined by means of high performance liquid chromatography (HPLC). The physical and thermal characteristics were studied by pulsed nuclear magnetic resonance (p-NMR) and differential scanning calorimetry (DSC).

MATERIALS AND METHODS

Materials

Commercially refined and bleached vegetable oil (VO), composed of a mixture of sunflower and rapeseed oil, was obtained from industrial sources (Palma-Tumys a.s., Bratislava). Fully hydrogenated vegetable oil (FHVO) was prepared from the same VO in a laboratory reactor. All solvents and chemicals were of analytical grade. HPLC solvents of acetonitrile and acetone were distilled and degassed before usage.

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Methods

Preparation of interesterification catalysts

Sodium hydroxide catalyst solution was prepared as 30% NaOH in distilled water. Sodium methoxide catalyst solution (20% MeONa in anhydrous methanol) was prepared by dissolving small bright pieces of metallic sodium in anhydrous methanol.

Intesterification procedures

Samples (120 g) of vegetable oil–hydrogenated vegetable oil in various mixing ratios (w/w) were interesterified for 60 min at 120°C with 1% w/w of sodium hydroxide catalyst per fat blend, or 30 min at 90°C with 0.5% w/w of sodium methoxide catalyst per fat blend. Each fat blend was placed into a clean, dry 250 ml round-bottom flask, heated for 30 min at 90°C under vacuum and nitrogen atmosphere to remove traces of moisture. The fat mixture was then heated to 120°C, followed by the addition of NaOH catalyst or MeONa catalyst at 90°C. The reaction was carried out under vacuum in an atmosphere of nitrogen with continuous stirring for 1 h with NaOH catalyst or for 30 min with MeONa catalyst to achieve complete randomization. The reaction was then stopped by addition of 100 ml hot distilled water containing dilute phosphoric acid. The interesterified blend was washed with hot distilled water until neutral and then dried over sodium sulphate and filtered through Whatman 30 filter paper at 80°C.

Hydrogenation

The laboratory hydrogenation was carried out in a Parr 4563 Mini Reactor (USA) with a 600 ml bomb and a charge of 400 g VO. Operating temperature was 180°C with hydrogen pressure at 200 kPa. An axial flow turbine operated at 1000 rpm. The Süd-Chemie Ni catalyst KE-NF 20 was used at a level of 0.5% by weight of the VO. The mixture of fully hardened oil and catalyst was immediately filtered and blended with unhydrogenated VO.

Analytical methods

The original fat blends and interesterified products were analyzed as follows: melting points were obtained by the capillary tube method (AOCS, 1973a) and were calculated as an arithmetic mean of the readings from three samples. Acid values were determined by the AOCS (1981) and iodine values were determined by the Hanuš method (ČSN, 1965). *Trans* isomers were determined by infrared spectrophotometry (Specord 71 IR Carl Zeiss, Jena) (AOCS, 1973b) using trielaidin as a standard.

The fatty acid compositions of the VO, FHVO and their original and interesterified fat blends were determined by gas–liquid chromatography (GLC) of the fatty acid methyl esters (FAME), prepared by the Christopherson–Glass method (Christopherson & Glass, 1969). Fat samples were analyzed in a Hewlett–Packard Research Gas Chromatograph 7620A with a flame ionization detector. A 2-m glass column packed

with Chromaton N-AW (Lachema Brno, CS) coated with 10% DEGS was used in this analysis. The column was run isothermally at 180°C, the carrier gas was nitrogen. The fatty acids were identified by comparing their retention times with those of known standard mixtures of saturated and unsaturated fatty acids (Sigma, USA). The chromatograms were recorded and integrated on the HP-3380 integrator. Fatty acid compositions of the different fat samples were calculated (percentage by weight) from the peak areas.

The original fat blends and the samples after interesterification were monitored by non-aqueous reverse-phase high-performance liquid chromatography (RP-HPLC). The triacylglycerol samples were analyzed in a liquid chromatograph (Lab. přístroje Praha, CS), on a Separon SGX C-18 (5 μ m, 150 \times 3 mm) column (Tessek Praha, CS) with acetone–acetonitrile (65:35, v/v) as the eluent, at a flow rate 0.5 ml/min, and a refractive index detector RIDK 101 (LP Praha, CS). Fat samples (50 mg) were dissolved in acetone (1 ml) and 20 μ l injected (Rheodyne loop injector Model 7010, USA). The chromatograms were plotted on a TZ 4620 recorder and integrated using a CI 100 integrator (LP Praha, CS).

Differential scanning calorimetry (DSC) was performed in a Perkin–Elmer DSC-7 Thermal Analysis System, with ΔH calculated by the instrument software (Norwalk, Connecticut, USA). A 6–9 mg fat sample was hermetically sealed into aluminium DSC pans. Analysis began at a sample temperature of 0°C. The sample was then heated at a rate of 5°C/min to 70°C (first heating), then cooled at 5°C/min to 0°C. The sample was again heated at 5°C/min to 70°C (second heating). Prior to DSC analysis, the fat samples were stored at 5°C for 7 days.

Solid-fat content (SFC) was determined with a pulsed nuclear magnetic resonance pNMR (Bruker Minispec PC 120 s pulsed NMR instrument, Germany). Dried fat samples were subjected to the following thermal treatment: NMR tubes each containing 2.5 ml fat sample were melted at 80°C, then held at 60°C for 5 min, at 0°C for 60 min and at each of the temperatures (0, 10, 20, 30 and 60°C) for 30 min. The spin–spin relaxation signal was measured 15 and 70 μ s after irradiation with radio frequency radiation. The instrument was calibrated using a stable reference standard whose solid content was accurately known. The solid fat content was calculated by the instrument software, the SFC-application.

RESULTS AND DISCUSSION

The physical and chemical characteristics, involving the major fatty acid profiles of the original vegetable oil, hydrogenated vegetable oil and their fat blends, are displayed in Table 1. Vegetable oil was hydrogenated to an iodine value of 1.3. Stearic acid was the main fatty acid (92.2%) in the FHVO, and by increasing the percentage of FHVO more stearic acid was incorporated into the original and interesterified blend (from 20 to 30%). Because the overall fatty acid composition did not

Table 1. Chemical and physical characteristics of vegetable oil, fully hydrogenated vegetable oil and their fat blends in various mass ratios

Fatty acid (wt %)	VO:FHVO (w/w)					
	VO	FHVO	2:1	2.2:1	2.6:1	3:1
16:0	6.4	7.8	6.9	6.8	6.8	6.7
18:0	1.9	92.2	30.9	29.2	26.9	23.8
18:1	34.2	0	23.1	24.4	25.2	25.9
18:2	55.1	0	37.4	37.9	39.3	41.8
18:3	2.4	0	1.7	1.7	1.8	1.8
IV (cgI ₂ /g)	124.4	1.3	85.1	87.25	93.1	94.55
MP (°C)	< 10	67.9	61.2	60.9	60.1	59.1
AV (mg KOH/g)	0.13	0.69	0.28	0.27	0.24	0.21

IV = iodine value. MP = melting point. AV = acid value. VO = vegetable oil.

FHVO = fully hydrogenated vegetable oil. 16:0 = palmitic acid. 18:0 = stearic acid. 18:1 = oleic acid. 18:2 = linoleic acid. 18:3 = linolenic acid.

Table 2. Fatty acid profiles of TAG fat blends of VO:FHVO (w/w) in various ratios before and after randomization

Fatty acid (wt %)	VO:FHVO (w/w)											
	2:1			2.2:1			2.6:1			3:1		
	before	after	PU/S	before	after	PU/S	before	after	PU/S	before	after	PU/S
16:0	6.9	6.8		6.8	6.8		6.8	6.8		6.7	6.8	
18:0	30.9	31.1		29.2	29.1		26.9	27.2		23.8	23.6	
18:1	23.1	23.3		24.4	24.6		25.2	25.1		25.9	25.9	
18:2	37.4	37.2		37.9	37.8		39.3	39.2		41.8	41.8	
18:3	1.7	1.6	1	1.7	1.7	1.1	1.8	1.7	1.2	1.8	1.9	1.4

VO = vegetable oil.

FHVO = fully hydrogenated vegetable oil.

PU/S = polyunsaturated/saturated acid ratio.

16:0 = palmitic acid. 18:0 = stearic acid. 18:1 = oleic acid. 18:2 = linoleic acid. 18:3 = linolenic acid.

Table 3. The TAG group composition of VO:FHVO in various mass ratios before and after randomization with NaOH determined by RP-HPLC and a comparison of interesterified fat blends determined by RP-HPLC and calculated according to random distribution

ECN	VO:FHVO (w/w)											
	2:1			2.2:1			2.6:1			3:1		
	NaOH			NaOH			NaOH			NaOH		
	origin	exp.	theor.	origin	exp.	theor.	origin	exp.	theor.	origin	exp.	theor.
42	24.2	7.9	6.9	23.8	8.2	7.2	23.4	8.6	8.4	23.1	9	9.2
44	34.7	15.2	15.3	34.6	15.7	16.4	34.3	17.4	17.5	33.8	19.7	19.7
46	24.3	25.4	25.1	24.3	26.6	26.1	24.2	26.7	26.4	24.1	28.2	27.5
48	13.4	25	24.9	13.5	24.6	24.9	13.7	24.3	24	13.9	24.3	23.6
50	2.7	19.1	19.2	2.9	18.1	17.9	3.4	17.1	16.8	3.6	14.3	14.6
52	0.7	7.4	8.6	0.9	6.6	7.5	1.2	6.1	6.9	1.5	4.5	5.4

origin = TAGs group composition of original fat blends determined by RP-HPLC (area %).

exp. = TAGs group composition of interesterified fat blends with NaOH determined by RP-HPLC (area %).

theor. = TAGs group composition of randomized fat blends determined by calculation according to random distribution (mol %).

change after the randomization (Table 2), the high linoleic acid (18:2) content of the vegetable oil was also present in the randomization products (from 37 to 41%). From the nutritional point of view, the high content of essential linoleic acid enhances the biological value of fatty food products such as margarine.

The randomization was followed by changes in the triacylglycerol (TAG) group composition of the initial blends and their corresponding randomized products. These changes in the triacylglycerol group composition of the initial blends and their corresponding randomized products were analysed by RP-HPLC and the results

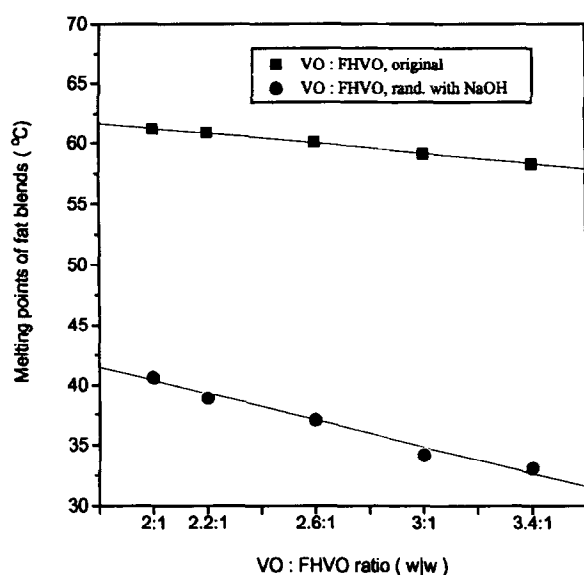


Fig. 1. Melting behaviour of binary blends of vegetable oil (VO)–fully hydrogenated vegetable oil (FHVO) in various mass ratios and changes obtained after randomization reactions catalysed with 1% NaOH in the form of 30% water solution.

are displayed in Table 3. The identification of triacylglycerol groups was based on the concept of equivalent carbon number ECN (Shukla, 1988).

The randomized products analyzed by RP-HPLC were compared with TAG group composition calculated according to random distribution. TAG group compositions of the randomized products were similar to the TAG group compositions which were calculated according to random distribution (Table 3).

The altered triacylglycerol composition of the randomized fat blends was also reflected in the melting point and the solid fat content of the fat blends. The melting points of various mixtures of vegetable oil and fully hydrogenated vegetable oil, before and after randomization with NaOH, are shown in Fig. 1. A decrease in the melting point of each examined fat blend was detected after the randomization reaction. The randomized products have melting points of 34.2–40.6°C. The difference obtained by randomization, seen as a reduction of the transition points after randomization, is related to the presence of the melting trisaturated triacylglycerols of FHVO. The reduction of melting point achieved by randomization of vegetable oil and hydrogenated vegetable oil depended on the mass ratios of the original fat blends. With a fat mixture consisting mostly of FHVO (FHVO:VO=2:1), the melting point reduction was approximately 20°C. The highest reduction of the melting point, i.e. 25°C, was obtained when the FHVO:VO mass ratio was 1:3.

The solid fat content (SFC) of the original and randomized fat blends is shown in Fig. 2. As in the case of the melting points, a decrease in the solid fat content was detected after randomization of fat blends. These decreases in melting points and SFC are due to a decrease in the proportion of higher melting triacylglycerols (mainly trisaturated triacylglycerols, SSS) as a

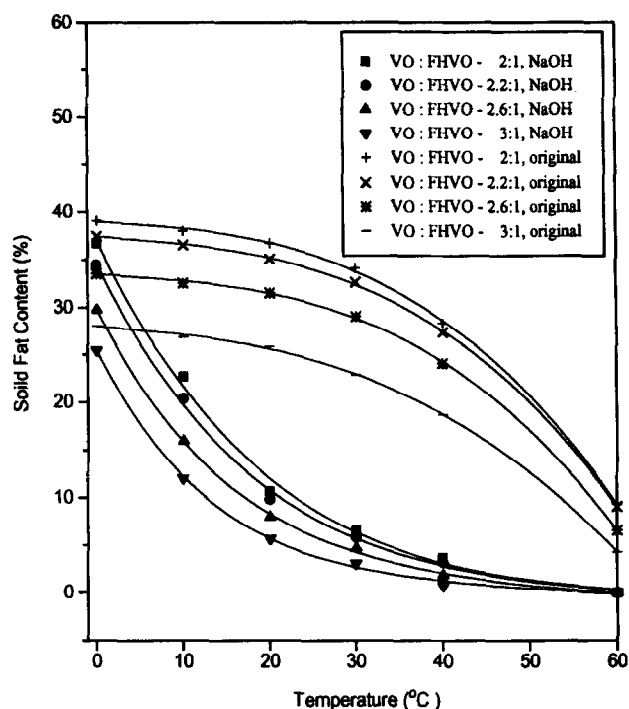


Fig. 2. Effect of NaOH catalysed randomization reactions on solid fat content (SFC) values of various mixtures of vegetable oil (VO) and fully hydrogenated vegetable oil (FHVO).

result of randomization. The *trans*-fatty acid content of the fat blends (below 5%), derived from FHVO, was not affected by randomization.

Polyunsaturated to saturated (PU/S) fatty acid ratios are reported in Table 2. The PU/S ratio (calculated from the fatty acid data) for the experimental fat blends was from 1.0 to 1.4. The experimental blend did conform to the recommendation of the American Medical Association (List *et al.*, 1977) of a PU/S ratio of 1.2.

Differential scanning calorimetry (DSC) of the fat blends was also used to determine whether any changes in the physical structure of the fat blends had resulted from the randomization process. The DSC heating and cooling curves in the constant-temperature time studies of the randomized blends stored for 7 days at 5°C, and DSC heating curves of these randomized blends after cooling, exhibited more than one peak in all blends compared with one endothermic peak (or one–two exothermic peaks) for each original fat blend. The DSC melting thermograms exhibited six endothermic peaks for randomized fat blends and the DSC crystallizing thermograms for each randomized blend exhibited three exothermic peaks (Table 4). There were differences among the randomized fat blends in the endothermic and exothermic peak temperatures and total ΔH of crystallization (Table 4). These differences indicate the effect of mass ratio of each of the fat blends on the melting and crystallization behaviour of the randomized fat blend. This effect is related to the differences in the TAG composition of the fat blends. The randomized fat blends exhibited six endothermic peaks, clearly showing the effect of randomization on melting characteristics. Zeitoun *et al.* (1993) also showed the

Table 4. Differential scanning calorimetry melting and crystallization characteristics of initial and randomized fat blends of VO with FHVO in various ratios (w/w)

VO:FHVO (w/w)	Heating		Cooling		
	Peak temp. (°C)		Peak temp. (°C)	Total ΔH (J/g)	<i>n</i>
	1 st heating	2 nd heating			
2:1, origin	63.5	63	40	-27	—
2:1, NaOH	9,16,22,40,49,59	9,15,21,33,49,60	5,14,29	-7	0.7
2.2:1, origin	62.5	62	40	-25	—
2.2:1, NaOH	9,15,21,40,45,58	9,15,20,33,45,58	5,13,29	-7	0.7
2.6:1, origin	62.5	62	28,39	-22	—
2.6:1, NaOH	9,15,21,38,44,57	9,14,19,33,43,57	5,12,28	-6	0.6
3:1, origin	61.5	61.5	26,38	-19	—
3:1, NaOH	10,13,19,35,42,57	9,13,18,32,42,57	5,11,25	-4	0.6

n = reaction rate.

Table 5. Chemical and physical characteristics of randomized fat blend of VO:FHVO (2:1, 2.6:1) with 1% NaOH (as a 30% water solution) and 0.5% MeONa (as a 20% methanolic solution)

TAG group composition	VO:FHVO (w/w)					
	2:1			2.6:1		
	NaOH	MeONa	theor.	NaOH	MeONa	theor.
ECN	(area %)	(area %)	(mol %)	(area %)	(area %)	(mol %)
42	7.9	7.9	6.9	8.6	8.9	8.4
44	15.2	15.6	15.3	17.4	17.3	17.5
46	25.4	25.1	25.1	26.7	26.2	26.4
48	25	24.4	24.9	24.3	23.6	24
50	19.1	19.7	19.2	17.1	17.2	16.8
52	7.2	7.3	8.6	6.1	6.8	6.9
MP (°C)	40.6	37.8	—	37.1	34.3	—
AV (mg KOH/g)	7.6	0.89	—	7.4	0.83	—

MP = melting point.

AV = acid value.

VO = vegetable oil.

FHVO = fully hydrogenated vegetable oil.

ECN = equivalent carbon number determined by RP-HPLC.

NaOH = randomized fat blends with 1% NaOH (as a 30% water solution).

MeONa = randomized fat blends with 0.5% MeONa (as a 20% methanolic solution).

theor. = TAG group composition of randomized fat blends determined by calculated according to random distribution (mol %).

effect of interesterification on melting characteristics. Differences were noted in the randomized fat blends of the same mass ratio in the endothermic and exothermic peak temperatures, in the number and shape of the peaks. Differences were also observed in the endothermic and exothermic peak temperatures, in the number and the shape of peaks. The difference between the DSC heating and DSC cooling curves of the same fat blends is caused by the different physical parameter-temperature behaviour of melting and crystallization.

DSC is a useful technique for the investigation of the transition of crystal forms during melting of fats (Zeitoun *et al.*, 1993). It is recognized that when the fat is heated it can exhibit multiple melting phases. Each recrystallization step represents a transition of the polymorphic form from its less stable form to a more stable one (Wilton & Wode, 1963; Hoerr & Paulicka,

1968). Because the more stable crystal form has a higher melting point, transition peak temperature can serve as an important indicator of the polymorphic form of the crystals (Zeitoun *et al.*, 1993). The DSC was used to demonstrate recrystallization (at a heating rate of 5°C/min) of the stored randomized fat blends after 7 days at 5°C and immediately cooled randomized fat blends. Differences in DSC heating curves among the randomized blends with the same mass ratio after 7 days at 5°C (first heating) and the heating curves of these fat blends after cooling (second heating) were observed. A shift to higher peak temperatures in the DSC heating curves of the stored randomized fat blends, and changes of the shape and area, were observed (Table 4).

The improved melting characteristics of the randomized samples confirm their functionality in producing fat blends suitable for margarine production. The

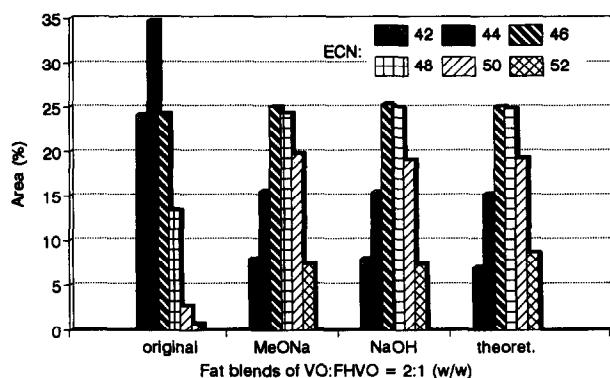


Fig. 3. Effect of randomization with 1% NaOH and 0.5% MeONa on ECN values of vegetable oil (VO)-fully hydrogenated vegetable oil (FHVO) blends in 2:1 mass ratios.

randomized fat blends of melting range 34–37°C (the 2.6:1 or 3:1 vegetable oil-hydrogenated vegetable oil blends) would be useful in the preparation of various types of *trans*-isomer free margarines where the high polyunsaturated fatty acid content is desired for possible health reasons. The products of a melting point between 38 and 42°C (the fat blends of VO:FHVO = 2:1 or 2.2:1) could be used as an alternative to lard in frying media (good cooking fats) but with a higher essential linoleic acid content. These products would also be suitable for the bakery and confectionery industry.

The randomization of the fat blends (VO:FHVO = 2:1 and 2.6:1) with 1% NaOH as a 30% water solution and by 0.5% MeONa as a 20% methanolic solution, which is currently used as a catalyst for chemical randomization, are compared. Table 5 and Fig. 3 show that the fat blends randomized by NaOH or MeONa have similar physical characteristics (the melting points and SFC) and also TAG group composition. The lower melting point in fat blends interesterified by methanolic MeONa is very likely to be caused by the presence of the by-products, such as fatty acid methyl esters. The NaOH randomization catalyst has been shown to be suitable for this purpose. Catalyst NaOH, compared with MeONa, is safer, cheaper, easy to prepare and store. The disadvantage of NaOH catalyst is that it results in high acid values in fats compared with MeONa (Table 5), owing to greater hydrolysis of TAGs by the water solution of NaOH.

In conclusion, the present work shows that the randomization using NaOH catalyst (as a 30% water solution) can be used to produce fat blends from vegetable oil and fully hydrogenated vegetable oil suitable for margarine production with a *trans* fatty acid content below 5%.

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