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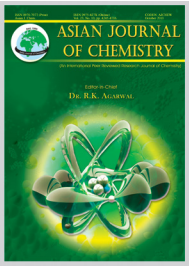

Catalytic Interesterification of Different Oils and Fats Using Lipozyme TL IM

YOUSEF FAZLI* and PARISA KERMANI

Department of Chemistry, Faculty of Science, Arak Branch, Islamic Azad University, Arak, Iran

*Corresponding author:Fax: +98 861 3670017; Tel: +98 861 3670017; E-mail: y-fazli@iau-arak.ac.ir; yousef.fazli@gmail.com

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Lipozyme TL IM was used to catalyze the interesterification reaction of different oils and fats (sunflower, soybean, corn, canola, palm super olein, palmolein and palm oil) at 70 ºC. The solid fat content of the resulting fats and oils was determined at different temperatures. Moreover, the melting profiles of them were investigated by differential scanning calorimetry. The solid fat content of the liquid oils increased at 0 ºC and solid fat content of the palm oil and palmolein decreased at 0 ºC and 10 ºC and increased at 20, 30 and 40 ºC. The solid fat content of palm super olein increased at all temperatures. Differential scanning calorimetry result shows a shift in peak after interesterification compared to before interesterification for soybean oil but in corn and sunflower oils no considerable change were found before and after interesterification, while there is a new peak in addition to the shifted peak for cottonseed and palm super olein. For palm oil and palmolein, shifted peak occurs just after interesterification

Key Words: Differential scanning calorimetry analysis, Solid fat content, Sunflower, Soybean, Corn, Palm oil, Palmolein, Palm super olein, Cottonseed interesterification.

INTRODUCTION

The development of methods to improve the nutritional and functional properties of fats and oils is of great interest in food processing. The molecular weight, unsaturation and positional distribution of fatty acid residues on the glycerol backbone of triacylglycerols are the principal factors determining the physical properties of fats and oils[1,2]. The possible application of enzymatic interesterification for the production of non special oils and fats such as margarine hard stocks and cooking oils have been investigated by several groups[3]. This process is used for the manufacture of shortenings, margarines and spreads to improve their properties, modify their melting behaviour and enhance stability[4,5]. Due to inherent advantages associated with the enzymatic processes, research efforts have been directed towards the substitution of chemical interesterification applications by enzymatic interesterification. Enzymatic reactions are more specific, require less severe reaction conditions and produce less waste. Also, when immobilized, enzymes can be reused, thereby making them economically attractive[6]. If region or stereo specific lipases are used to interesterify oil blends, formed products are different from those obtained by chemical interesterification and they can have better functional properties. Enzymatic interesterification is accomplished using lipases enzymes obtained predominantly from bacterial yeast and fungal sources[7]. Lipozyme TL IM is an immobilized lipase from termomyces lanuginosus on porous silica granulates. (Lipozyme TL IM is commercial lipase from Novozym company).

EXPERIMENTAL

Refined, bleached and deodorized sunflower, corn, soybean, cottonseed, palm oil, palmolein and palm super olein oils were prepared from Industrial Company (Tehran, Iran). Commercial lipase, lipozyme TL IM was obtained from Bagsvaerd, Denmark. Filter paper whatman 91 was purchased from Maidstone, England. All other used chemicals and solvents were of the highest purity available.

Interesterification reaction: The enzymatic reactions were carried out by adding 8 g lipase to 100 g of the mentioned oils or fats and mixing the blend with a mechanical stirrer in a 200 mL beaker at 70 ºC, at 200 rpm. Reaction samples were filtered using filter paper to separate the enzyme from the oils or fats.

Acidity: The amount of free fatty acid was determined by ISO 660:1996[8]

Solid fat content: The applied instrument was a Bruker Minispec mq 20 MHZ NMR spectrometer. Calibration was performed by standards provided by Bruker.

The solid fat content for palm oil, palmolein and palm super olein were determined according to AOCS official method Cd 16b-93[9]. The fat samples were melted and kept at 100 ºC for 15 min thereafter at 0 ºC for 1 h and finally maintained for 30-35 min at each chosen measuring temperature.

The solid fat content for the oils (sunflower, corn, cottonseed and soybean) was determined at 0 ºC. Prior to analysis the oils were heated and kept at 70 ºC for 15 min thereafter at 0 ºC for 16 h.

Thermal analysis: Thermal analysis was performed using DSC (DSC: Metler Toledo 822e). Metler Toledo 822e differential scanning calorimetry was used to obtain thermograms. Calibration was done with Indium. About 10 mg of each sample was placed inside an aluminum pan.

Crystallization profiles: Palm oil, palmolein, palm super olein and cottonseed samples were held for 5 min at 70 ºC then cooled to -10 ºC and the related thermograms were recorded at the heating rate of 5 ºC/min. For the cooling scan, the sunflower and corn samples were first held at 70 ºC for 5 min before being cooled at 5 ºC/min to -20 ºC. Soybean sample was cooled from 40 ºC (after holding for 5 min) at 5 ºC/min to 80 ºC.

Peroxide value: The peroxide value was determined according to AOCS official method Cd 8b-90[9].

Iodine value: The iodine value was determined according to AOCS official method Cd 1b-87[9].

RESULTS AND DISCUSSION

Solid fat content by NMR: The solid fat content of the samples, measured by NMR technique is shown in Table-1. This clearly indicates that the solid content of palm oil is reduced about 12 % and 4 % at 0 ºC and 10 ºC respectively and increased about 2, 4 and 0.1 % similar to the one at 20, 30 and 40 ºC respectively. In the palmolein, reduction of solid content was approximately such as palm oil but the increase at 20 and 30 ºC were more (about 11 % and 7 % respectively). Furthermore, the solid content of palm super olein increased completely after interesterification but the increase at 0, 10, 20 and 30 ºC are about 3, 8, 10 and 3 % respectively. It shows that the amount of triacylgliceride with higher melting point, palmolein and palm super olein increases after interesterification. The solid content of soybean, corn and sunflower oils at 0 ºC increased 5 %, 3 %, 2 %, while the solid content for cottonseed oil increased 6, 5 and 1.5 % at 0, 10 and 20 ºC. The changes in solid fat content are because of the shifts in saturated and unsaturated fatty acid of triacylglycerol chain.

Chemical properties: Acid value of all the oils and fats increased by 1.5 % and the iodine value was approximately constant. The peroxide value increased but it was different in oils and fats. The acid, peroxide and iodine values are shown in Table-2. In fact, enzymatic interesterification process causes the breakdown of fatty acids in 1,3-triacylglycerol position so fatty acids position change accordingly, so some fatty acid and diacylglycerol were produced at the end of interesterification. Due to no changes of fatty acid type, iodine value is constant. Due to reaction temperature at 70 ºC for 2 h, an increase in peroxide value increasing was detected which will be different based on oil type and saturated, unsaturated fatty acid composition.

TABLE-1
SOLID FAT CONTENT (SFC) OF TRANSESTERIFIED AND NONTRANSESTERIFIED

Sample		SFC[1]	SFC				
		-	0 ºC	10 ºC	20 ºC	30 ºC	40 ºC
Palm oil	A[2]	-	69.92	55.67	26.29	8.89	2.96
	B[3]	-	57.82	51.68	28.28	12.7	3.05
Palmolein	A	-	57.05	41.88	6.59	0.0	0.0
	B	-	44.22	39.02	17.39	6.61	0.0
Palm super olein	A	-	28.12	20.31	0.53	0.0	0.0
	B	-	31.45	28.50	10.58	3.30	0.0
Cottonseed oil	A	-	6.74	0.33	0	0.0	0.0
	B	-	12.94	5.22	1.52	0.0	0.0
Sunflower	A	0.01	-	-	-	-	-
	B	1.70	-	-	-	-	-
Soybean	A	0.0	-	-	-	-	-
	B	4.6	-	-	-	-	-
Corn	A	0.01	-	-	-	-	-
	B	3.31	-	-	-	-	-

[1]SFC: SFC after keeping 16 h at 0 ºC; [2]A: Before interesterification; [3]B: After interesterification

Thermal analysis by DSC: The influence of cooling rate on the DSC scan of palm oil, palmolein and palm super olein samples (before and after interesterification) is shown in Figs. 1-3. Crystallization curves of oil and fat samples (before and after interesterification) are illustrated in Figs. 4 and 5 (soybean oil and cottonseed oil) respectively.

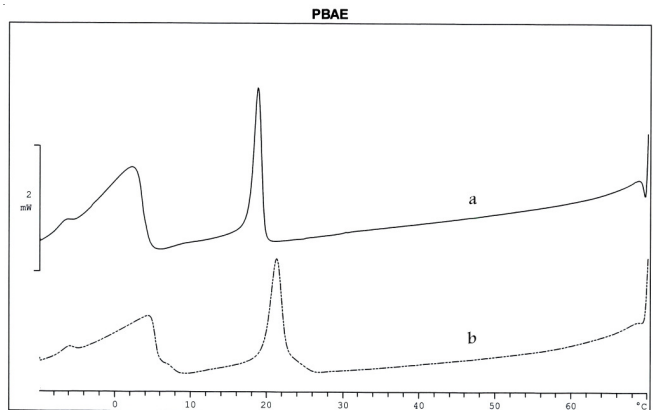

Fig. 1. Cooling thermogram of transesterified and non transesterified of palm oil (a) before esterification, (b) after esterification

Before interesterification: Based on palm and palmolein oil thermograms (Figs. 1 and 2 Curve a), palmolein thermogram curve is simple with two complete separated exotherm peaks. For palm oil, thermogram is the same as palmolein but

TABLE 2
IODINE VALUE, ACID VALUE AND PEROXIDE VALUE

Test	Sunflower		Corn		Cottonseed		Soybean		Palm		Palmolein		Palm super olein	
	A[a]	B[b]	A	B	A	B	A	B	A	B	A	B	A	B
IV	122.2	122	122.6	122	110.8	109	124.5	123.8	52.4	52.3	59.9	58.7	69.1	69.2
AV (%)	0.05	1.4	0.06	1.9	0.38	2.1	0.07	0.154	0.28	1.49	0.1	1.52	0.045	1.34
PV (meq/Kg)	0.4	5.0	0.2	5.0	0.4	6.0	0.4	4.0	0.2	5.0	0.2	4.6	0.4	5.0

[a]A : Before interesterification; [b]B : After interesterification

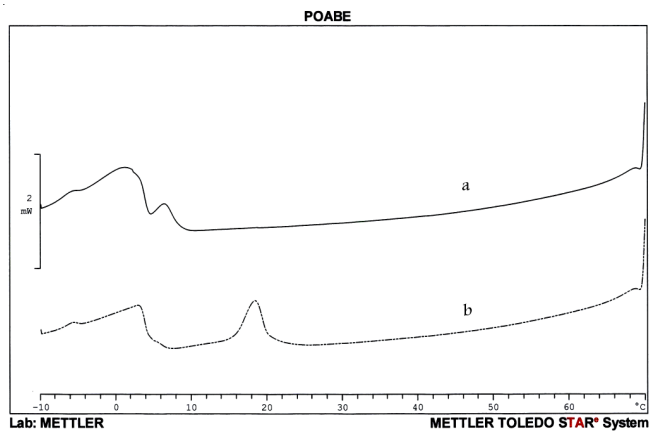

Fig. 2. Cooling thermogram of transesterified and non transesterified of palmolein (a) before esterification, (b) after esterification

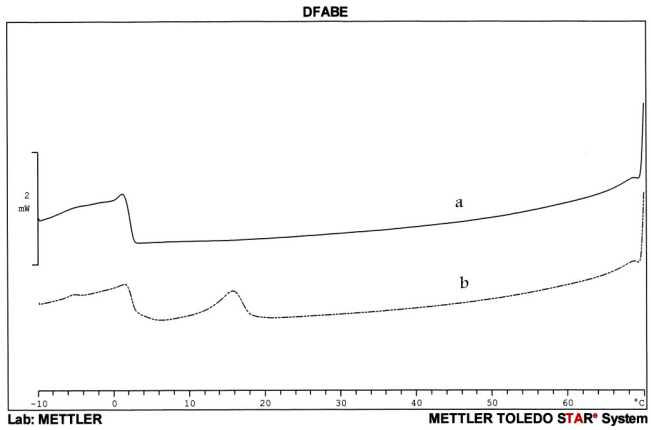

Fig. 3. Cooling thermogram of transesterified and non transesterified of palm super olein (a) before esterification, (b) after esterification

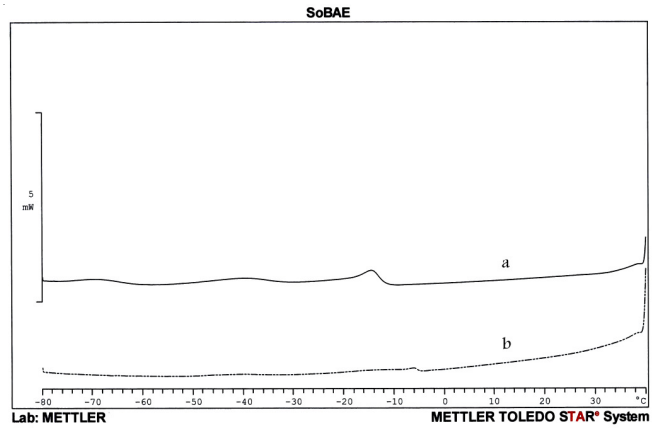

Fig. 4. Cooling thermogram of transesterified and non transesterified of soybean oil (a) before esterification, (b) after esterification

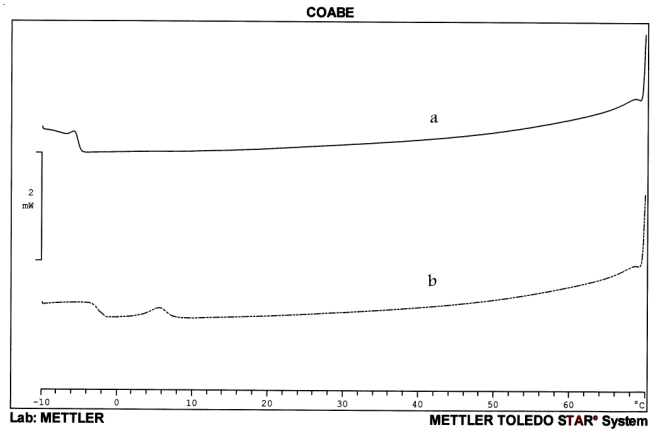

Fig. 5. Cooling thermogram of transesterified and non transesterified of cottonseed oil (a) before esterification, (b) after esterification

one of the peaks is shown at higher temperature (High-T Peak), which is related to saturated triacylglycerol. Due to fractionation in palmolein, the hard content is separated, so palm super olien oil is produced. Curve a of Fig. 3 related to palm super olein shows the elimination of peak in higher temperature, so there is just one peak in low temperature. According to the curves (Figs. 1-3 Curve a) related to palm oil, palmolein and palm super olein, Peak position in low-temperature is constant and due to decreasing saturated triacylglycerol in palmolein and palm super olein, peak position of palmolein in high temperature tend to shift to peak in low temperature position and in palm super olein peak in high temperature eliminated. These results show peaks in low and high temperature are because of saturated triacylglycerol and unsaturated ones. Also, there is just one wide peak on thermogram curves of soybean and cottonseed (Figs. 4 and 5, curve a).

After interesterification: Fig. 3 curve b shows that the high temperature peak appeared in the crystallization curve of palm super olein. In crystallization curve of palm oil and palmolein, both peaks are observed. Although the high temperature peak in palm oil was apparently the major feature (Figs. 1 and 2, curve b). The distance between two peaks in palmolein is much and the two peaks are completely separate and the higher temperature exotherm tends to shift up far from the low-temperature peaks (Fig. 2, curve b). Although the thermogram of soybean oil (Fig. 4, curve b) is relatively simple, there is considerable broadening in the cooling thermogram. Fig. 5 curve b shows in cottonseed curve two separated exothermic peaks (high and low temperature peaks) based on saturated triacylglycerol are recognized. A complete comparison of transition temperatures for crystallization curves before and after interesterification are clearly indicated and summarized in Table-3. Regarding Table-3, esterification of palm, palmolein and palm super olein not only causes a shift in the peak of low-temperature and high-temperature to higher temperature but also separates the two peaks from others. However, two peaks in the palm oil have shifted about 2 ºC toward high temperature and distance between them is 0.58 more than before esterification. Higher-temperature shift for palmolein is higher (about 12 ºC) however low-T shift is about 1 ºC. Therefore, separation of two peaks in palmolein is more than palm oil. For palm super olein, there is one peak before esterification which converts to two peaks (low and high-temperature) after esterification. The distance between two peaks is 14 ºC which is more than the one between palm and palmolein. In fact, interesterification counteracts the effect of fractionation that causes shifts in fatty acids sites. As a result, the behaviour of palm super olein shifts to palmolein and there will be two parts (hard and soft). This effect is more obvious for palm super olein than the others which are shown in their solid fat contents in Fig. 6. In the esterification of palm and palmolein, solid fat content decreases at 0 and 10 ºC and increase at 20

TABLE-3
COMPARISON OF DIFFERENTIAL SCANNING CALORIMETRY-MEASURED TRANSITION TEMPERATURE FOR CRYSTALLIZATION CURVES OF FAT AND OIL SAMPLES[a]

Sample	Condition	Transition temperature (°C)		
		1	2	Peaks distance
Palm oil	A[b]	2.58	18.75	16.17
	B[c]	4.50	21.25	16.75
Palmolein	A	2.17	6.50	4.33
	B	3.08	18.42	15.34
Palm super olein	A	1.25		0.00
	B	1.67	15.75	14.08
Cottonseed oil	A	-5.67	-	0.00
	B	-3.33	5.67	0.00
Corn oil	A	-17.00	-	0.00
	B	-13.17	-	0.00
Sunflower oil	A	-15.92	-	0.00
	B	-11.83	-	0.00
Soybean oil	A	1.00	-	0.00
	B	1.00	-	0.00

[a]Each value in the table represents the means for four determinations. SD of the reported results is in the range of 0-1.1 ºC; [b]A: Before interesterification; [c]B: After interesterification

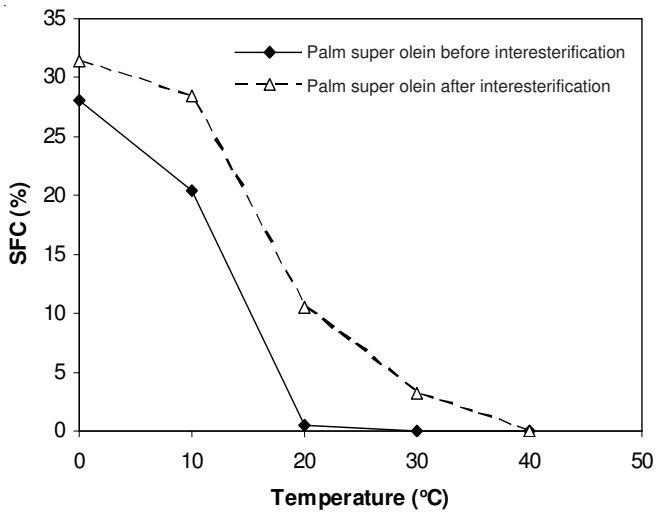

Fig. 6. Solid fat content (SFC) of transesterified and nontransesterified palm super olein

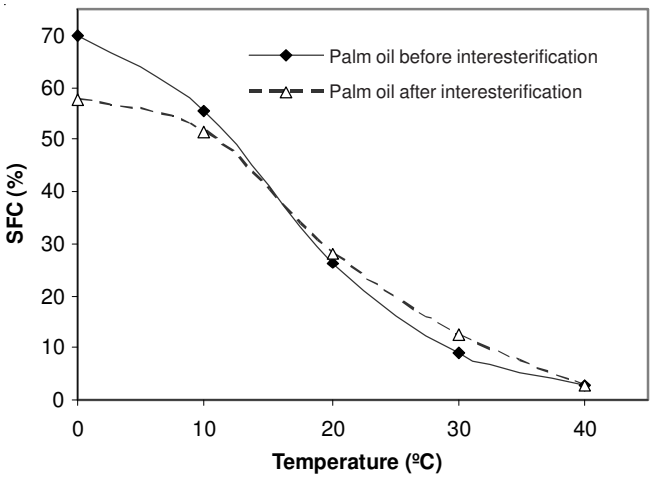

Fig. 7. Solid fat content (SFC) of transesterified and nontransesterified palm oil

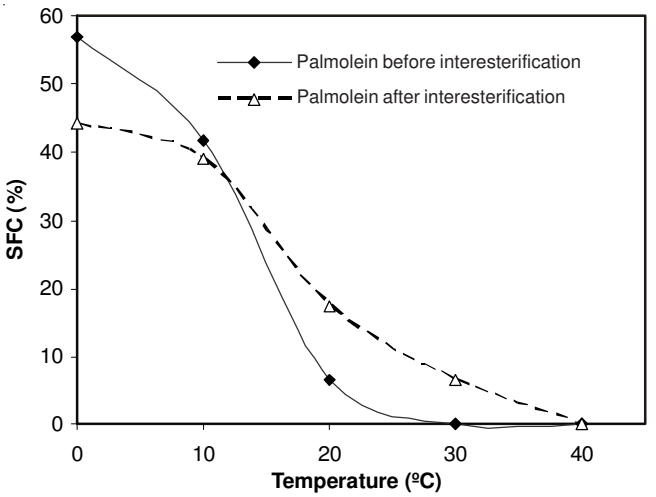

Fig. 8. Solid fat content (SFC) of transesterified and nontransesterified palmolein

and 30 ºC and the slope of solid fat content decreases (Figs. 7 and 8). For cottonseed oil, there is one peak before esterification at 5.67 ºC but after esterification two peaks appear at 3.37 ºC and 5.67 ºC, which change the solid fat content (Table-1). For soybean, esterification causes peak shifting to higher temperature and peak expanding. No detectable changes were found in therograms of corn and sunflower oils before and after interesterification. There is a little change in interesterification of triacylglycerols of sunflower and soybean and corn oils that causes an increase in turbidity at 0 ºC.

Conclusion

Regarding the results, it is indicated that interesterification of sunflower, Soybean, cotton seed, Palm super olein causes an increase in solid content as well as cloudiness which is not suitable for liquid oil but after interesterification of palm & palmolein, solid content curve has a gentle slope compared to before interesterification which are useful for preparing margarine and shortening oil.

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