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EFFECT OF CHEMICAL INTERESTERIFICATION ON PHYSICAL AND CHEMICAL CHARACTERISTICS OF SUNFLOWER OIL AND TALLOW BLENDS

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ABSTRACT

Sunflower oil and tallow were interesterified in different ratios (1:9, 2:8 and 4:6 w/w), at various degrees of temperature, for many periods of time. Using sodium methoxide (0.3% w/w) and sodium hydroxide: glycerol: water (1:2:3 w/w) as catalysts. Acid value, iodine value, peroxide value and melting point of interesterified and non-interesterified (control) blends were analysed. Solid fat content, trans fatty acids and fatty acid compositions of selected interesterified blends were determined. Iodine values of all blends with all conditions were more or less equal to iodine values of their control samples, while acid values of interesterified samples were decreased relative that of control sample. Interesterified samples which obtained using sodium hydroxide: glycerol: water (1:2:3 w/w) gave preferable peroxide value more than that using sodium methoxide(0.3% w/w).Trans fatty acids of selected interesterified samples using sodium hydroxide: glycerol: water (1:2:3 w/w) were better than those selected interesterified samples using sodium methoxide (0.3% w/w).

Keywords: Chemical interesterification, blend, sunflower oil, tallow, sodium methoxide, sodium hydroxide: glycerol: water, fatty acid compositions, solid fat content, melting point, trans fatty acids.

INTRODUCTION

Most vegetable oils in their native state have only limited applications due to their specific chemical compositions. To widen their use ,vegetable oils are modified, either chemically by hydrogenation or interesterification, or physically by fractionation(Petrauskaite *et al.*,1998). Interesterification is one of the most important process for modifying the physicochemical characteristics of oils and fats (Noor Lida *et al.*,2002). During interesterification, fatty acids (FAs) are exchanged within (interesterification) and among (interesterification) triacylglycerols (TAGs) until a thermodynamic equilibrium is reached (Rodríguez *et al.*, 2001). Interesterification of solid fats and vegetables oils can produce a fat blend with optimum characteristics.

Rearrangement or randomization of acyl residues in triacylglycerols has provided fats or oils with new physical properties (Zeitoun *et al.*, 1993). In most oils and fats, unsaturated fatty acids preferentially occupy the 2-postions of the triacylglycerol molecules. Fatty acids are distributed in a random manner among the triacylglycerol molecules by chemical interesterification. The degree of unsaturation or isomeric state of the fatty acid does not change (Noor Lida *et al.*,2002).

However, during partial hydrogenation, some cis double bonds are isomerised into their trans former. In the past few years, several nutritional studied have suggested a direct relationship between trans fatty acids and increased risk for coronary heart diseases (Karabulut *et al.*, 2004).

Chemical interesterification has long been used to modify oils and fats into functional products. It modifies the physical properties of oils by rearranging the distribution of fatty acids on the glycerol backbone without changing their chemical composition. With the rising concerns over the nutritional impact of trans fatty acids on health, interesterification has become more popular for the preparation of low or zero trans functional plastic fats (Norizzah *et al.*, 2004)

In interesteritication, fatty acids are exchanged within (interesterification) and among (interesterification) triacylglycerols until a thermodynamic equilibrium is reached [Rousseau *et al.*(1996), and Konishi *et al.* (1993)]. The objective of this study was to manufacture shortening by chemical interesterification (IT) of tallow-sunflower oil mixtures and to evaluate the physical, thermal, chemical, and textural properties for the purpose of finding a replacement for hydrogenated fish oil (Rodríguez *et al.*, 2001).

The aim of this work is to assist in the proper choice of oils, catalyst and conditions including temperature and time to produce a large variety of plastic lipid blends of various melting point ranges which can be used in many segments of the food industry with zero trans hard phase having good physical and chemical characteristics to use it in manufacturing margarine, vanaspati and shortenings.

MATERIALS AND METHODS

Materials :

1-a- Refined, bleached and deodorized sunflower oil was obtained from local supermarket.

2-b- Tallow was obtained from a local butcher.

3-c- Sodium methoxide was purchased from Electro Sciente Company 4-d- Sodium hydroxide and glycerol were purchased from El-Nasr Pharmaceutical Chemicals Company.

5-e- Sunflower oil: tallow blends were prepared with ratios (1:9, 2:8 and 4:6 w/w).

All used chemicals and solvents were of highly pure grade.

Methods:

- Interesterification Process:

Portions (100g) of each blend was heated under the selected temperatures (60, 80 and 135°C) using periods of time (0.5, 1, and 1.5h). When the blend had reached the reaction temperature, the catalyst [0.3% of sodium methoxide or 0.6 ml. of sodium hydroxide: glycerol : water (1:2:3 w/w)] was added while the blend was vigorously stirred. To end the reaction, an excess of citric acid was added to neutralize the catalyst. The excess of citric acid and sodium methoxide was removed with warm water washes

three times. Residual water was removed with an excess of anhydrous sodium sulfate, followed by decantation.

Finally, the interesterified blends were analyzed for determination of chemical analysis (Iodine value, Acid value, Peroxide value , Fatty acid compositions, Trans fatty acids) and physical analysis (Melting point, Solid fat content).

- Determination of iodine value (IV), acid value (AV) and peroxide value (PV) were carried out according to AOCS Official Methods (1996).

-Determination of fatty acid composition:

Preparation of fatty acid methyl esters:

About 0.2 gm of the non-interesterified and some selected interesterified samples were mixed with 30 ml sulfuric acid : methanol (4 : 96 v/v) in a 250 ml round bottom flask. The contents were then heated under reflux for about three hours. The methyl esters were thrice extracted with petroleum ether (40 - 60°C) then it was washed several times with distilled water till the washings were neutral to phenol phthalein. The combined fatty acids methyl esters layers were dried over anhydrous sodium sulfate and filtered. The petroleum ether was then removed using a rotary evaporator and an aliquots of the fatty acid methyl esters were analyzed by gas chromatography (Farag 1994).

- Gas liquid chromatographic analysis of fatty acids methyl esters:

The identification of the components of fatty acids methyl esters was done using gas liquid chromatography on a Hewlett Packard Model 6890 chromatograph equipped under the following conditions:

- Separation was done on an INNO wax (polyethylene glycol) Model No. 19095 N-123, 240°C maximum, capillary column 30.0 m x 530 μm x 1.0 μm, nominal flow 15 ml / min. with average velocity 89 cm / sec. and pressure 8.2 psi.
-Column temperature was 240°C with temperature programming : Initial temperature 100 °C to 240°C maximum with 10 °C rising for each minute and then hold at 240°C for ten minutes.
- Injection temperature 280°C, back inlet, with split ratio 8:1, split flow 120 ml / min., gas saver 20 ml / min.
- Carrier gas was nitrogen with flow rate 15 ml / min.
- Flame ionization detector temperature 280°C.
- Hydrogen flow rate 30 ml / min.
- Air flow rate 300 ml / min.
- Determination of Melting Point

Melting point was determined to non and interesterified blends by electeric melting point apparatus (Electrothermal 9100) according to AOCS Official Method (1996).

-Determination of Solid Fat Content

SFC was measured using pulse NMR (Nuclear Magnetic Resonance), apparatus model Moran SFC. Company Oxford (England). SFC was measured in temperature range 10°C - 40°C, calibration and verification by standard tubes (0, 29.65, 70.3)% according to AOCS Official Method (1996).

- Determination of Trans Fatty Acids:

Analysis using Fourier Transform Infra Red (FTIR) instrument:

Non-interesterified and some selected interesterified samples were subjected to FTIR analysis on a Nexus 670 Fourier Transform Infra Red spectrometer, Thermo Nicolet, USA. The FTIR spectra were analyzed using "Omnic 5.2a" software. A fixed sample volume (5µl) of each sample was carefully and homogeneously spread between two KBr disks of fixed weights. The samples were referenced to their own blank KBr disks. For collection of the data, a DTGS detector and KBr beam – splitter were used. The measuring at wave length 850-1150 µ. According to AOCS Official Methods (1996).

RESULTS AND DISCUSSIONS

The determined properties of interesterified sunflower oil : tallow blends of three different ratios 1:9; 2:8; 4:6 w/w, at temperatures 60°, 80° and 135°C for different times (0.5 hr , hour and 1.5 hr) using sodium methoxide (0.3% w/w) and sodium hydroxide : glycerol : water (1:2:3 w/w) catalysts, were acid value, iodine value, peroxide value and melting point value. All result were comparable to that of fresh sunflower-tallow blend (control).

A-1- Acid value of the interesterified sunflower oil - tallow blends

Acid values of interesterified sunflower oil – tallow blends samples are illustrated in figures (1-6). Concerning of acid value of the interesterified samples at different temperatures using both catalysts decreased from control sample and the maximum decrease got by using sodium hydroxide: glycerol : water (1:2:3 w/w) catalyst for interesterified blend of sunflower oil – tallow blend with 4:6 ratio at 60°C for 1.5 hr and at 135 °C for 1 hr.

A-2- Iodine value of the interesterified sunflower oil - tallow blends

These iodine values are shown in figures (7-12). Regarding these values the interesterified samples using both catalysts for different times and at different degrees of temperature of all blends ratios were more or less equal to iodine values of their control samples.

A-3- Peroxide value of the interesterified sunflower oil - tallow blends

Peroxide value of all interesterified samples, are drawn in figures (13-18). It is clear that interesterified samples obtained using sodium hydroxide: glycerol : water (1:2:3 w/w) catalyst gave preferable peroxide value more than that of using sodium methoxide (0.3 % w/w) especially of the interesterified samples of all ratios at 60°C and at 135°C for all time periods.

A-4- Melting point of the interesterified sunflower oil - tallow blends

The melting point of the interesterified samples of sunflower oil : tallow blend are reported in figures (19-24). We can notice that using sodium methoxide catalyst during interesterification at 60 °C, the melting point of the interesterified sunflower oil - tallow blend with ratio (2:8) for one hour was less than that of the other samples. While at 80°C the least melting point for the same ratio was happened in 0.5 hr interesterification and at 135°C the lowest melting point was got with the interesterified sunflower oil : tallow ratio (4:6 w/w) for 1 hour.

Concerning sodium hydroxide : glycerol : water (1:2:3 w/w) catalyst the melting point of the interesterified sunflower oil : tallow blend samples at different temperatures for different ratios in different time periods were more or less the same.

A-5- Solid fat content of selected interesterified sunflower oil - tallow blends

Solid fat indices of the control and interesterified sunflower oil : tallow blend samples (1:9 w/w) ratio using sodium methoxide (0.3% w/w) catalyst at 80°C and 135°C shown in figures (25-26) and these using sodium hydroxide: glycerol : water (1: 2: 3 w/w) catalyst at 60°C and 135°C recorded in figures (27-28). It is clear that the preferable sample was the interesterified sunflower oil : tallow at 60°C using sodium hydroxide: glycerol : water catalyst for one hour.

A-6- Trans fatty acids of selected interesterified sunflower oil - tallow blends

It is clear from figures (29-30) that trans fatty acid of four selected interesterified sunflower oil: tallow blend (1:9 w/w) ratio at 60°C using sodium hydroxide: glycerol : water (1:2:3 w/w) catalyst for one hour and that at 135°C using the above catalyst for half hour gave the preferable trans fatty acids in interesterified blend those that of interesterified blend using sodium methoxide (0.3% w/w).

A-7- Fatty acid compositions of selected interesterified sunflower oil - tallow blends

These values are represented in figures (31-34). Interesterification of sunflower oil: tallow (1:9 w/w) blend using sodium methoxide (0.3% w/w) catalyst caused reduction of unsaturated fatty acid and increasing of saturated fatty acid percentages. While interesterified using sodium hydroxide: glycerol : water (1:2:3 w/w) catalyst increased unsaturated fatty acid and decreased saturated fatty acid percentages. Interesterified sunflower oil: tallow (1:9 w/w) blend at 60°C and 135°C using sodium hydroxide: glycerol : water (1:2:3 w/w) for one hour and half hour gave blends have unsaturated fatty acids about 40% of total fatty acids.

The changes in triacylglycerol profiles were reflected in the solid fat content profiles of the blends (Noor Lida *et al.*, 2007)

Forssell *et al.* (1993), the melting point reduction achieved by interesterification was depend on the mass fractions of the substrate the lower the mass fraction of tallow, the larger the reduction of the melting point.

It has been found that after interesterification the concentrations of free fatty acids and partial acylglycerols increased. On the other hand the slip melting temperatures and solid fat contents in triacylglycerols isolated from interesterified fats and their oxidative stability were lower if compared with non-interesterified, initial blend (Kowalski *et al.*, 2004).

1-6

J. Agric. Sci. Mansoura Univ., 33 (5), May, 2008

7-12

13-18

J. Agric. Sci. Mansoura Univ., 33 (5), May, 2008

19-24

25-28

J. Agric. Sci. Mansoura Univ., 33 (5), May, 2008

29-30

31-34

The interesterification increased both free fatty acids and polar fraction contents and the increases were higher in chemical interesterified fat mixtures (Brys *et al.*, 2004).

The acidity and content of polar fractions were increased after interesterification. (Kowalska *et al.*, 2005).

These finding more or less agree with the results got in this piece of work.

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تأثير الأسترة الكيميائية علىالصفات الطبيعية والكيميائية لخلطات زيت عباد الشمس والشحم الحيوانى

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تم اجراء عملية الأسترة الكيميائية لمخاليط زيت عباد الشمس و الشحم الحيوانى بنسب مختلفة وهى (١:٩ ،٢:٨ ، ٤:٦وزن/وزن) عند درجات متباينة (٦٠، ٨٠ و١٣٥° م) وأزمنة مختلفة(٣٠، ٦٠ و٩٠ دقيقة) فى وجود ميثوكسيد الصوديوم ٠,٣% وهيدروكسيد الصوديوم: جلسرول: ماء بنسبة (١:٢:٣) كعوامل مساعدة.

تم قياس التحاليل الكيميائية والطبيعية على المخاليط المؤسترة وهى كالآتى: الرقم اليودىورقم البيروكسيد و رقم الحموضة و درجة الانصهار.

وأجري قياس نسبة صلابة الدهن الى سيولته عند درجات حرارة مختلفة والأحماض الدهنية العكسية ومكونات الأحماض الدهنية لبعض المخاليط المختارة .

وقد وجد من النتائج أن الرقم اليودى لجميع العينات تحت كل ظروف التفاعل يزيد اويقل قليلا عن عينات الكنترول. بينما رقم الحموضة أقل فى العينات التى تم لها الأسترة الداخلية بالنسبة لعينات الكنترول. أما العينات التى أجريت لها الأسترة والناتجة من استخدام هيدروكسيد الصوديوم: جلسرول: ماء بنسبة ١:٢:٣ (وزن/ وزن) أعطت قيم للرقم البيروكسيدى أفضل من الناتجة من استخدام ميثوكسيد الصوديوم(٠,٣% وزن/وزن). الأحماض الدهنية العكسية للعينات المختارة باستخدام العامل المساعد هيدروكسيد الصوديوم: جلسرول: ماء بنسبة ١:٢:٣ (وزن/ وزن) أفضل من الناتجة من استخدام ميثوكسيد الصوديوم(٠,٣% وزن/وزن) كعامل مساعد.