HUNGARIAN UNIVERSITY OF AGRICULTURE AND LIFE SCIENCES

EFFECT OF FULLY HYDROGENATED COCONUT OIL ON THE PHYSICAL PROPERTIES OF NON-HYDROGENATED COCONUT OIL

DOI: 10.54598/005860

The Thesis of the PhD dissertation

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Budapest
2023

Doctoral School

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1. INTRODUCTION

Food is an essential aspect of human function, existence, and experience and often, diverse and distinct social problems come together around food (Thompson, 2015). Food industries are looking for how they will secure and provide plentiful, healthy and nutritious food for all while addressing the multiple burdens of undernutrition, overweight and obesity and micronutrient deficiencies. Fat is an important part of a healthy diet as it is a great source of energy, and supplies essential fatty acids and fat-soluble vitamins. An estimated 80% of the total fat produced is used for food; this highlights the importance of fats in food products.

Fats and oils are very important raw materials and functional ingredients for several food products such as confectionery, bakery, ice creams, emulsions, and sauces, shortenings, margarine, and other specially tailored products. Lipids also hugely contribute to the desired texture of end products, impart a characteristic flavour and act as a delivery system for fat soluble ingredients and vitamins. They confer desirable characteristics on several foods, contribute to tenderness to shortened cake, and by aerating batter, fats aid in establishing texture in cakes; they also add flavour to foods and influence the order in which components of flavour are released when foods are eaten, besides having a lubricating effect and producing a sensation of moistness in the mouth. Many fat-based food products require solid fats to interact with other ingredients in order to provide the desired structure and to offer oxidative stability.

Most natural oils and fats have only limited application in their original state, due to their particular fatty acid and triacylglycerol composition (Chiu, et al., 2008). The best-known modification processes applied today in the edible oil industry are hydrogenation, interesterification (chemical or enzymatic) and fractionation. The main purpose of these processes is to change the physicochemical properties of the oil or fat, by reducing the degree of unsaturation of the acyl groups (hydrogenation), by redistributing the fatty acids chains (interesterification) or by a physical separation of the triacylglycerol's through selective crystallization and fractionation. The partial hydrogenation method results in a substantial formation of trans fatty acids, compounds that act as coronary artery disease risk factors by modulating the synthesis of cholesterol and its fractions and acting on the eicosanoids. However, the development of the hydrogenation technique transformed the shortening industry and promoted the use of fully hydrogenated vegetable oil for its increased stability, health benefit and no-trans configuration. The interesterified fats can be used in various applications by replacing the partially hydrogenated fats; consequently, interesterification can successfully

substitute the partial hydrogenation process. Saturated fats are the only viable sources of the required high-melting (solid) fats as a use of its alternative, trans fats has been phased out or banned in some cases such as in Denmark, and New York City.

In the food industry, physical properties of fat play a significant role in two major areas: (a) optimization and controlling the processing of end products such as chocolate, butter, margarine, ice-cream, whipped cream among others and (b) purification of oils and fats into fractions with specific properties and functionalities. Also, the crystal network of fat plays a key role in the development of specific structure with desired physical, textural and sensorial properties of most lipid-based food products that are consumed on a regular basis. Therefore, a fundamental understanding of this phenomenon is necessary to assist food researchers to characterize the properties of food products and optimize the processing parameters in order to control the characteristics of final products as well as to lay a platform for future development of newer food products with added functionality. In previous research, some group studied the thermal and rheological properties of ternary blends of coconut oil (CO) and palm stearin (PS), with either partially hydrogenated soybean oil (PH-SBO) or refined soybean oil (trans-free-SBO) crystallized under quiescent conditions. Recent research showed that, compared to other fats, the composition and the phase behaviour of coconut oil are relatively simple which is widely used in various food application because of physiological properties of lauric acid in the metabolism and in health issues such as cholesterol and fat accumulation and storage. Miscibility of coconut oil with different oils is hardly limited. In this study, we used fully hydrogenated coconut fat to find the appropriate melting and solidification properties as well as texture profile of fat blends. Fully hydrogenated oil does not contain trans isomers, therefore, its suitable substitute of the partly hydrogenated oil. The several studies have focused on the influence of blending, enzyme-catalysed transesterification and hydrogenation of oils on their chemical composition, thermal and structural properties (Baltork et al., 2001 Kovács et al., 2008., Solymosi, et al., 2011). Also determination of solid fat content and melting point of blends of coconut oil and anhydrous milk fat gave scientific results to food industry (Soos et al., 2014).

In European countries, coconut fats are one of the major ingredients in snacks and confectionary industries. Due to its melting and crystallization characteristics, margarine and shortening production, as well as the confectionary industry, consider coconut oil as a basic material in product formulations. Coconut oil is extensively used in the food industries as a confectionary fat particularly in the preparation of ice creams. Coconut oil (CNO) contains about 90% saturated fatty acid (SFA), that do not get oxidized, including medium chain fatty

acids (60–66%) which are nutritionally important (Mensink and Katan 1990). MCFA have several desired features such as high oxidative stability (due to their saturation), low viscosity and melting points and high solubility in water. Coconut oil is one of the widely used edible oils in the diet because it contains lauric acid (C12) as its major fatty acid, accounting for 45–53 % of the overall fatty acid composition. MCT are digested more easily and absorbed rapidly by the body than other fats. When non-hydrogenated coconut oil supplements have been provided, studies often find evidence for modest benefits of coconut oil consumption on lipid profiles. Animal studies have shown that coconut oil in particular lowered total cholesterol, lipoproteins, and phospholipids. It has been reported that despite the high consumption of coconut as saturated fats, the ratios of total cholesterol to HDL-cholesterol, and LDL-cholesterol to HDL-cholesterol were lower, thus lowering cardiovascular disease (CVD) risk in rural males with a high degree of physical activity, subsisting on a diet consisting mainly of plant food. Coconut oil which is rich in lauric acid has less effect on total cholesterol and LDL-c and is a better alternative to butter and hydrogenated vegetable fats.

2. OBJECTIVES OF THIS RESEARCH WORK

1. To study the effect of fully hydrogenated coconut oil on physical properties (crystallization and melting) of non-hydrogenated coconut oil by using Nuclear Magnetic Resonance Spectroscopy(pNMR) and Differential scanning calorimetry (DSC).
2. To study the effect of fully hydrogenated coconut oil on rheological and textural properties of non-hydrogenated coconut oil.
3. To study microstructural changes in crystals of coconut blends by using polarized light microscopy.

3. MATERIALS AND METHODS

3.1 Materials

In this study, we used Barco coconut oil as the initial non-hydrogenated coconut oil (NHCO) which was kindly provided by Mayer's Kft from Budapest. The fully hydrogenated coconut oil (FHCO) was obtained from a local industry in Hungary. The oils and fats were stored at 0°C before use. All the chemicals used were either analytical or high-performance liquid chromatography (HPLC) grade.

1. Sodium hydroxide solution 50%
2. Sodium acetate, For HPLC, ≥99.0%,

3.2 Methods

3.2.1 Preparation of oil blends

The blends were prepared for study in the proportions of 25:75 (Blend 1), 50:50 (Blend 2), 75:25 (Blend 3) (w/w%) non-hydrogenated coconut oil: fully hydrogenated coconut oil (Fig 4.1). The total volume of blend were 200 gram. Materials were melted at 100 °C and homogenized for 10 min in order to destroy the crystal structure completely. All blends and pure fat samples were stored in a refrigerator at 10 °C until use.

3.2.2 Fatty acid composition

Fatty acid composition of pure fats was analysed by means of gas chromatograph HP 5890 GC System type following standard methods of ISO 5508:1990 and ISO 5509:1990).

4.2.3 Slip melting point (SMP)

Slip melting point (SMP) was measured under the regulation of the standard: MSZ EN ISO 6321:200 (Animal and Vegetable Fats and Oils to establish the melting point of the fats by open capillary method (slip melting point))

3.2.4 Solid fat content (SFC) analysis by pNMR

Solid fat content analysis was carried out in two ways: as a function of time and as a function of temperature, to get solid fat profiles of oils by using pulsed Nuclear Magnetic Resonance spectrometer (pNMR). Samples were melted (100°C/ 15min) and kept in a high precision dry bath at 80°C for the complete destruction of their crystal history. Solid fat content

(SFC) was measured at 10±1°C, 15±1°C and 18±1°C. The analyses of samples were performed in triplicate for each temperature.

The melting profile of the fats was studied by measuring the solid fat content (%) at 5±1°C, 10±1°C, 15±1°C, 20±1°C, 25±1°C and 30±1°C respectively by the same NMR Analyzer. The fat was melted at 80°C by using a water bath and placed in a refrigerator (0°C) for 60 min before the first SFC measurement. Afterward, the SFC was determined at temperature ranges of 5 to 30 °C (with 5 °C intervals) through equilibrating the NMR tubes in these temperatures for 30 min before measurement. Determinations were done in triplicate.

3.2.5 Crystallization and melting characteristics by DSC

For DSC analysis, a Perkin–Elmer differential scanning calorimeter, DSC-7 equipped with a thermal analysis data station (Perkin–Elmer Corp., Norwalk, CT, USA) was used. This DSC was available at Department of Refrigeration and Livestock Products Technology for measurement. The data processing software used was Pyris Series Thermal Analysis System. Samples were subjected to the following temperature programme as follows: Fat sample were heated to 80 °C to remove crystallization history. Then samples were cooled to 0°C and kept at this temperature for 10 min. Heating was performed from 0°C up to 80°C. Samples were kept at this temperature for 30 min, and then the cooling program was applied at 1 °C min^{-1} to –20°C and kept under this condition for 10 min. Finally, the samples were heated up to ambient temperature. Measurements were done during the constant speed heating and cooling processes. All DSC values reported are the average of three scans.

3.2.6 Texture profile analysis:

A spreadability test was performed to determine the textural properties of the formulations using a Texture analyser (TA-TX Plus, Stable Micro System, UK) equipped with a 2 kg load cell. An analytical probe was twice penetrated into each fat sample to a defined depth (15 mm) and at a defined rate (2 mm/s). Any excess of sample was scraped off with a knife. Experiments were carried out at least five times.

3.2.7 Rheology measurements:

This study is divided into two sections where the first section discusses the effect of temperature on viscoelastic properties and the second section discusses the effect of shear rate and shear stress on oil viscosity.

Oscillatory rheology:

Rheological measurements were performed by a controlled stress-strain rheometer (MCR 301, Physica/Anton Paar, Ostfildern Germany–Europe) connected to a circulating water bath for the temperature control.

The small-amplitude oscillatory shear test were performed. The viscoelastic behaviour of the samples was evaluated from 10°C to 25°C by using a parallel plate (diameter: 50 mm) and a gap distance of 2 mm. Excess sample protruding from the edge of the sensor was trimmed off carefully with a thin blade. In our measurement, an oscillatory shear strain was applied to the sample at constant frequency of 10 rad/sec and a constant strain amount of 0.1 %, which satisfies the linear viscoelastic condition. The values of shear storage modulus (G′) and shear loss modulus (G″) were obtained from Rheoplus software.

Dynamic viscosity tests:

Dynamic viscosity tests were conducted by using a rotational rheometer with a coaxial cylindrical measurement system. The tests were carried out at different temperatures respectively 30°C, 40°C, 50ºC, 60ºC, 70ºC and 80°C respectively.

3.2.9 Polarized light microscopy measurements (PLM):

Crystal morphology was recorded during crystallization. Polarised light microscopy was used to visualise the microstructure of the fat crystal networks.This analysis was done in Energy research centre, Institute of Technical Physics and Materials Science, Budapest. A drop of sample was taken and placed between a slide and a cover-slide to evaluate crystals microstructure. Images were taken using a Canon 1000D DSLR camera mounted on an SP300F polarised light microscope obtained from Brunel Microscopes Ltd., Chippenham, UK. A minimum of six images were taken of each sample. A photomicrograph was obtained at 100× magnification.

Statistical Analysis

All samples oil were submitted to one-way analysis of variance (ANOVA). This analysis of the data from the NHCO & FHCO was used to study the differences between 3 blends. The significances of all terms in the polynomial were judged statistically by computing the F-value

at probability (p) of 0.05. The statistical analysis was performed using Statgraphics Plus V5.1 software (StatpointTechnologies, Warrenton, VA)

4. RESULTS

The addition of FHCO to NHCO had shown some diversity in fatty acid composition. The increment and decrement of fatty acids can lead to changes in physicochemical and functional properties of the fat blends. The results from this study, showed that the percentage of the total saturated fatty acid (SFA) ranged from 92.90% for FHCO:NHCO (75:25) to 97.25% for blend of FHCO:NHCO (25:75), with the predominant presence of lauric acid (C12:0) and myristic acid (C14:0). These fat blends showed a significant difference in fatty acid composition, in comparison to non-hydrogenated coconut oil.

Fully hydrogenated coconut fat induced dramatic changes in crystallization behaviour (SFC max values) of non-hydrogenated coconut oil. All fat samples showed sigmoidal curves for temperatures of 10±1 and 15±1 °C. Crystallization was very fast and the equilibrium SFC was constant as the crystallization time increased. As the temperature was increased to 18±1 °C, all fat samples showed sigmoidal curves.

The differences in the crystallization behaviour of fat samples at different temperatures are demonstrated by the linearized Avrami lines. These straight lines were fitted to the values of $\ln[-\ln[1-SFC(t)/SFC(\infty)]]$ against $\ln(t)$.

The crystallization curves of non-hydrogenated coconut oil and fully hydrogenated coconut oil as well as their blends were similar, showing only one exothermic peak between 11.11 °C and 16.67 °C.

The crystallization of the non-hydrogenated coconut oil, fully hydrogenated coconut oil and blends showed that peak crystallization temperature increased with the increase in the proportion of fully hydrogenated coconut fat in blends.

SFC profiles of fat blends with proportion of 75:25, 50:50 and 25:75 (w/w) FHCO:NHCO were significantly different from each other, increasing with an increasing proportion of FHCO in the blend ($p<0.05$). The SFC values of all samples decreased with increasing temperature.

The melting behaviour of original oils and blends was characterized by only one endothermic peak.

The Melting profile results showed NHCO started melting first when compared to other samples due to a higher content of unsaturated triglyceride. The addition of fully hydrogenated coconut oil in non-hydrogenated coconut oil did not change the melting behaviour but as the content of FHCO was increased, the melting peaks of blend shifted towards the high temperatures.

We observed that the addition of FHCO to non-hydrogenated coconut fat at different concentrations leads to an increase in values of textural parameters, proportional to the increase in FHCO concentration.

In our study, we observed that during the heating process, crystallized coconut fat showed a viscoelastic crystalline structure with G'> G". But above a certain temperature, the coconut fat melted quickly to a liquid state and the value of G' and G" decreased drastically. On the other hand, G' and G" of fully hydrogenated coconut fat decreases linearly with increasing temperature until it reaches 22 ºC and it showed a viscoelastic solid structure as a result

The fat samples shown Newtonian behaviour at high temperatures 60 ºC,70 ºC & 80 ºC whereas gel-like behaviour at 30 ºC, 40 ºC, and 50 ºC.

Coconut oil crystals were spherulites consisting of fine needle-like crystals radiating and branching outward from densely-packed central cores.

5. NEW SCIENTIFIC FINDINGS

My research experiment included mixing of non-hydrogenated and fully hydrogenated coconut fats which showed the following new scientific findings:

1. The equilibrium SFCmax values were directly proportional to the blending ratio and temperature gradients.
2. Based on the parameters of the AVRAMI model, the behaviour of solidification with instantaneous nucleation and one-dimensional focal growth was determined.
3. Mixing the material did not modify the single peak thermograph of the solid.
4. The blending of fats did not change the cooling profile, whereas peak crystallization temperature increased with an increase in the proportion of fully hydrogenated coconut fat in non-hydrogenated coconut fat.
5. The results proved that the addition of FHCO to NHCO at different concentrations leads to increased hardness, and therefore serves as a hardening agent.
6. The rheological results proved that as the concentration of FHCO increased in NHCO, the linear viscoelastic region of rheological graphs slightly increased with an increase in relative temperature.
7. The blend showed a large number of small crystals which modifies the spreadability of fats.

6. SCIENTIFIC CONTRIBUTION AND PUBLICATION

Publications

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