

Sains Malaysiana 41(7)(2012): 871–877

Emerging Trends in Modification of Dietary Oils and Fats, and Health Implications - A Review

(Tren Baru dalam Pengubahsuaian Lemak dan Minyak Diet serta Implikasi Kesihatan)

PRADEEP PULIGUNDLA, PRASAD SHEKHAR VARIYAR, SANGHOON KO*,
VIJAYA SARATHI REDDY OBULAM

ABSTRACT

In recent years, issues regarding safety and wellness of dietary oils and fats have received major attention. This is particularly so in the case of structured modified fats, which are being used extensively to meet the product-specific demand primarily in bakery industry as shortenings, cocoa butter substitutes in confectionary industry, and in margarine preparation, as butter substitute. During modification stages, native oils and fats are subjected to different physical and chemical treatments such as fractionation, hydrogenation and interesterification in order to produce fats with desirable physical as well as functional properties. Numerous studies have demonstrated the adverse health effects of these modified oils and fats, especially trans fatty acids, using animal models as well as human volunteers. Consequently, the decades-old process of partial hydrogenation of oils has been abandoned in most nations. However, alternative technologies to hydrogenation are on rise, creating new trends in modified oils and fats synthesis to cater food industry needs that may have unforeseeable consequences on human health.

Keywords: Hydrogenation; interesterification; oils and fats modification; structured lipids; trans fats

ABSTRAK

Sejak beberapa tahun kebelakangan ini, isu keselamatan dan kebaikan minyak dan lemak dalam diet telah mendapat perhatian. Ini terutamanya dalam kes lemak terubahsuaikan berstruktur, yang digunakan secara meluas untuk memenuhi permintaan khusus, terutamanya sebagai lemak dalam industri bakeri, pengganti mentega koko dalam industri gula-gula dan sebagai pengganti mentega dalam penyediaan marjerin. Semasa peringkat pengubahsuaian, minyak dan lemak asli melalui perubahan sifat kimia serta fizikal berbeza seperti pemeringkatan, penghidrogenan, interesterifikasi dan sebagainya bagi menghasilkan lemak dengan ciri fizikal serta ciri berfungsi yang baik. Banyak kajian ke atas haiwan serta manusia telah menunjukkan kesan buruk minyak dan lemak yang terubahsuaikan kepada kesihatan, terutamanya asid lemak trans. Ini menyebabkan proses penghidrogenan separa minyak yang telah digunakan bertahun-tahun lamanya tidak diteruskan di kebanyakan negara. Walau bagaimanapun, penggunaan teknologi alternatif kepada penghidrogenan semakin meningkat, mewujudkan trend baru dalam minyak terubahsuaikan dan sintesis lemak untuk memenuhi keperluan industri makanan yang mungkin mempunyai kesan yang tidak dapat diramalkan ke atas kesihatan manusia.

Kata kunci: Interesterifikasi; lemak terstruktur; lemak trans; minyak dan lemak terubahsuaikan; penghidrogenan

INTRODUCTION

Oils and fats represent one of the major and important constituents of our diet. They are relatively high energy yielders (9 kcal/g) upon oxidation when compared to carbohydrates and proteins (4 kcal/g). Oils and fats are carriers of the oil-soluble vitamins A, D, E and K. Fatty acids (FAs) namely linoleic acid, linolenic acid are considered as essential FAs (EFAs) because mammals lack the ability to introduce double bonds in FAs beyond carbon 9 and 10 (Bhalla et al. 2009). Almost all the polyunsaturated fats in the human diet originate from essential FAs. Dietary fats and closely related oils consist of FAs linked with glycerol via ester linkages to form triacylglycerol (TAG) or triglyceride (TG). The characteristics of fats and oils

are related to the properties of the FAs that they contain. Glyceride molecules in fat and oil can be either made up of a single FA species or any combination of up to three different FAs. Most naturally occurring fat and oil molecules contain a combination of FAs.

Physical properties of fat are based on their FAs composition, which in turn related to the number of carbon atoms, unsaturation and conformation of the FAs. Fats are classified as saturated or unsaturated according to the nature of the FAs present. Saturated fats have long hydrocarbon chains (C-C) packed closely together which increases the van der Waals' forces and, therefore, have more solid nature and higher melting points than unsaturated fats. On the other hand, unsaturated fats, also known as oils,

contain one or more C=C bond in *cis* configuration. This configuration introduces 'kink' into the hydrocarbon chain that restricts rotation around this bond. Hence there exists a weak intermolecular force which impairs close packing of chains. They thus are liquids and have lower melting points than saturated fats at room temperature.

The rearrangement or structural alteration (modification) of the FAs in native oils and fats is commonly used in the fat industry to produce plastic fats, margarine fat, vanaspati substitute, and novel fat products like cocoa butter substitute (CBS). The modification can be accomplished by different processes such as hydrogenation, interesterification, etc.; and these can also be used for improving the stability of fat and fat products (De & Patel 2010). Modified native oils and fats are extensively used in modern food applications. The modified fats can provide distinct taste, texture, and other characteristics such as modified (desirable) melting point and crystal behavior, increased shelf life etc. Besides, in certain circumstances, they may also contribute nutritional, cost, and additional functionality benefits. From a health viewpoint, over consumption of fats is directly related to ailments such as cardiovascular diseases, cancer, and diabetes, and has been declared one of the major dietary health concerns all over the world, especially in U.S. and other developed countries (Trivedi & Singh 2005). Over a long period of time the modified fats, especially partially hydrogenated oils, have been greatly criticized and now banned in most countries as a consequence of well documented adverse health effects shown by trans FAs they contain. Trans FAs are defined as all unsaturated FAs that contain one or more isolated double bonds in trans configuration. This excludes FAs with conjugated double bonds. Unlike the *cis* forms, in trans FAs, the unsaturated chains are virtually straight, resembling saturated FAs, and thus display higher melting points. Trans FAs have been convincingly associated with the risk of heart disease based on epidemiologic and clinical studies. Food products containing partially hydrogenated oils constitute the major source of trans FAs. Unhealthy image associated with trans FAs has prompted food manufacturers to evaluate their products and seek more healthful alternatives. Accordingly, recently there have been several reports on the production of genetically modified oils and fats as well as low-calorie modified fats with self-proclaimed superior health benefits. The present review highlights the emerging technologies and trends in oil and fat modification that are being employed in most industries for improvement of their functionality and processability in food.

DIETARY FAT MODIFICATION

The production of some novel and value added products from the native oils are the prime objectives of modification (De & Patel 2010). In native form, certain vegetable oils have only limited applications in the food products due to presence of polyunsaturated FAs with very low melting points. Unsaturated FAs of oils are often unstable at higher

temperatures like frying. Products prepared from these oils are easily susceptible for rancidity due to atmospheric oxygen, reducing greatly product shelf life. Therefore, processes such as the hydrogenation of oils have been used in order to increase their plasticity (stiffness) at room temperature. Chemically, the hydrogenation of oils is the reduction of double bonds to single saturated bonds, by the reaction of hydrogen gas in the presence of metal catalyst. Reduction of only a fraction of the double bonds results in partially hydrogenated fats. These partially hydrogenated oils can be used for frying and in processed foods. Thus, products made from hydrogenated oils have relatively long shelf life.

From an economic point of view, the central problem in fat processing is to make products of constant and stable characteristics at a fixed price from a raw material supply that fluctuates in composition and price. In such a situation, flexibility in raw material choice is of high importance. Such feasibility is enhanced by fat modification techniques (Coenen 1976). For e.g. margarine based on partially hydrogenated oil is less expensive to produce and have higher melting points, longer shelf life and improved organoleptic properties compared to butter or lard. Likewise, cocoa butter substitutes (CBS) have been produced from lipase catalyzed reaction between palm oil mid fraction and stearic acid. Cocoa butter has a unique crystallization behavior and melts between 25–35°C imparting the desirable "mouth feel". However, high cost and price fluctuations motivated the search for cheap alternatives or substitutes.

Fatty acids distribution in the TG molecules affects the physical properties of a fat, in addition to their molecular nature (i.e. chain length and unsaturation). Industrial applications of some natural fats are limited due their unique FA distribution. Processes such as interesterification involving an exchange of acyl group among TGs can be applied to improve the consistency and usefulness of such fats.

PROCESSES EMPLOYED FOR FATS MODIFICATIONS FRACTIONATION

Fractionation is the process of cooling the oil slowly to yield solidified fat at various temperatures. The oil is initially heated and held at its melting point in order to erase the crystal memory, and then allowed to slowly cool resulting in crystallization of higher melting TGs. Solid fat portion can be separated out by filtration. The fractionation is generally done by either of dry type, detergent based, and solvent based methods. Each results in similar end products. Palm oils is generally fractionated to produce palm olein or liquid fraction (melting point around 18–20 °C) which is desirable for applications such as cooking, and palm stearin or hard fraction (melting point around 48–50 °C) that is generally blended with oils for margarine and spreads applications (Gunstone & Norris 1983). For example, milk fat lacks the appropriate plasticity and hardness for use in pastries, its melting profile results

in poor spreadability of butter and promotes softening in chocolate (Versteeg et al., 1994). To overcome the limitation, dry fractionation (crystallization from the melt) of milk fat has been performed that allows the separation of TG in fractions with different melting ranges and physical properties that are suitable for a variety of food and pharmaceutical products (Lopez & Ollivon 2009). Fractionation however creates two problems. If the value of secondary fraction is below that of the process feedstock viability of the process becomes important. A second disadvantage is the incomplete phase separation or “entrainment” particularly in solid-liquid equilibrium. Some of the current fractionation methods that hold promise are the counter-current crystallization and supercritical fluid extraction.

HYDROGENATION

Hydrogenation of vegetable oils is one of the earliest and most common commercial modification methods. The process reduces the unsaturated FAs content of TGs by attaching hydrogen atoms at the points of unsaturation. Oils are allowed to react with hydrogen gas under pressure, at high temperature (120 to 210 °C) in the presence of metal catalysts such as nickel/platinum/copper for 6 to 8 h. Hydrogenation not only affects the functionality of oils, but also enhances the oxidative stability (shelf life) of the food product (O’Brien 2009). Hydrogenation raises the melting point of fats and retard rancidity. Oils can be hydrogenated to varying degrees. Partial hydrogenation or brush hydrogenation hardens oils (semi-solid form) but does not make them fully solid. Full hydrogenation requires complete conversion of liquid oil into a solid fat at room temperature (22 °C). Fully hydrogenated products are virtually completely saturated and do not contain trans fats. Fully hydrogenating the oils will make them too solid, and do not have the desired functionality of partially hydrogenated oils (O’Brien 2009), which makes them difficult to use for cooking.

ADVERSE EFFECTS OF PARTIALLY HYDROGENATED OILS

During catalytic hydrogenation, trans FAs are formed as side products. In general, if unsaturated FAs leave the metallic catalyst surface too rapidly (short retention time), the hydrogenation reaction is not complete and the double bonds may be shifted, the cis configuration (kink nature) of unsaturated FAs is converted to trans form (less kink

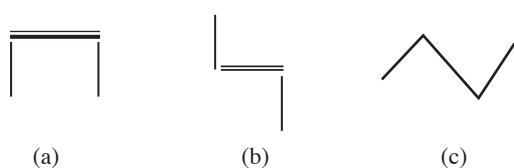


FIGURE 1(a). Cis (bent form) of unsaturated FA, (b) Trans (straight form) of unsaturated FA and (c) Saturated FA (straight form)

structure) and hence is called trans FAs (Figure 1). Trans fat is less likely to occur in nature. Shortenings made from vegetable oils, margarine are rich sources of trans FAs. Additionally, the hydrogenation process destroys ω -3 essential FAs very rapidly.

Generally nickel catalyst, particularly Rayney’s Nickel, is used in hydrogenation. It is a mixture of 50% nickel and 50% aluminum. Remnants of both metals remain in products containing hydrogenated or partially hydrogenated oils and ultimately enter in foodstuffs prepared from those fats. Nickel is one of the known potential carcinogens. Trans fat is known for its ability to increase low-density lipoproteins (LDL), and decrease good high-density lipoproteins (HDL). Studies have demonstrated that the adverse effect of trans FAs is significantly higher than that of saturated fat as assessed by the ratio of total to HDL cholesterol (Mensink & Katan 1990; Zock & Katan 1992). They tend to congregate at adipose tissue sites, and are difficult to excrete from the body. They are also known for altering effect on the cell membranes integrity (Hernandez et al. 2007) by competitively inhibiting the essential FAs incorporation into membrane phospholipids.

Several epidemiological studies supported the increased risk of coronary disease with intake of partially hydrogenated fats. Intake of partially hydrogenated fats has paralleled the rise in coronary artery disease (CAD) mortality in the United States and other countries (Booyens et al. 1988). In a case-control study, a positive association between intake of trans FAs and risk of myocardial infarction was observed among men and women (Ascherio et al. 1994). Additional side effects of trans FAs include allergic reactions, arteriosclerosis, increased risk of cancer, decrease in insulin response, and slight immune dysfunction (Hui 2006).

EMERGING TECHNOLOGIES TO MINIMIZE/ELIMINATE TRANS FATS

CATALYTIC TRANSFER HYDROGENATION

The catalytic transfer hydrogenation (CTH) is a safe, simple, and eco-friendly promising alternative technique that offers selective hydrogenation of edible oils with lower *trans* isomer FAs, compared to conventional catalytic hydrogenation (Naglic et al. 1998; Smidovnik et al. 1994; Tike & Mahajani 2006). The CTH technique eliminates conventional high-pressure operation, and handling of highly flammable hydrogen gas (elaborate precautionary methods), when replaced with a hydrogen donor. The commonly used hydrogen donors are cyclohexene, cyclohexadiene, phosphinic acid, hydrazine, formic acid, sodium or ammonium formate, and sodium hypophosphite (Banik et al. 1999). Use of conditioned nickel catalyst selectively prevents formation of *trans*-stereoisomers (Higgins 2007). Procedure for hydrogenation of soybean oil in supercritical carbon dioxide, hydrogen and nickel catalyst with minor formation of trans FAs have been

reported (King et al. 2001). Electrochemical hydrogenation of oils at low temperature (70 °C) in the presence of formate as electro-catalyst with nickel and palladium has also been demonstrated to produce significant amount of hydrogenated FAs with a low content of trans FA isomers (< 10%).

INTERESTERIFICATION

Interesterification is a catalyst assisted process of reorganization of FA groups between glyceride molecules in oil, known since 1920s. The distribution among TG molecules may be random (random interesterification) or conforms to some special pattern (directed interesterification). The interesterification process leads to formation of different combinations and yields more desirable physical properties (Strayer et al. 2006). The process involves blending high saturated hard fats (e.g., palm oil, palm stearin and fully hydrogenated vegetable oils) with liquid edible oils to produce fats with intermediate characteristics. Procedures involving chemical and nonspecific enzyme methods result in randomized distribution of triglycerides. Chemical catalysts such as sodium methoxide or ethoxylate are generally employed. The catalyst is neutralized at end of the process, and later the oil undergoes a clean-up stage of washing, bleaching, and deodorization (Strayer et al. 2006). A substantial oil loss (approx. 30%) occurs due to the formation of soap and fatty acid methyl esters (FAME). Enzymatic interesterification is specific and uses a 1,3-specific lipase enzyme under mild reaction conditions that preserves one of the three positions creating an end product more like natural fat (Dian et al. 2006). Other advantages include fewer process steps, lower investment costs, no requirement for post-treatment cleanup stages, and maintain tocopherol concentration in the product. Expensive biocatalyst long reaction time and higher sensitivity to reaction conditions (e.g., pH and temperature) are the hindering factors for commercial application of the enzymatic process.

The interesterification process has been used in the production of spreads with specific physical properties such as having a desired melting point, slow rancidification, and also for TGs production possessing specific compositions and nutritional properties (Gibson & Williams 2003). Chemical and enzymatic interesterification has been specially employed in the formulation of margarines and shortenings with no trans FAs while still maintaining physical properties, taste and stability (List et al. 1997). The vegetable oils including corn, palm, peanut, cottonseed, canola, and sunflower oils can be randomly interesterified with fully hydrogenated soybean oil or fully hydrogenated cottonseed hard fats to produce desirable fat compositions for margarines and shortenings (List et al. 1995). The margarine manufacturers are employing interesterification technique and various degrees of oil blending to achieve the regulatory bodies' criteria-like the US Food and Drug Administration's (FDA) criteria for foods containing zero *trans* fat (<0.5 g of *trans* fat

per serving). The health effects of interesterified fats, however, need to be investigated. 'Don't ignore the hidden danger'; it's a warning message from a recent human volunteers participated study on metabolic effects of interesterified fats in diets. We are well aware that the trans fat negatively affect LDL and HDL cholesterol, likewise, interesterified fats have shown a relatively weak impact on cholesterol. However, an intriguing result of this study is that the deleterious effect of interesterified fat on blood glucose is more pronounced than that of trans fat, raising glucose levels by 20 % within a month (Sundram et al. 2007). In contrast, a recent study showed the no effects of interesterification on fasting levels of blood lipids, glucose and insulin (Berry et al. 2007), wherein, a comparison was made between shea butter (3% C18:0 on the 2-position) and interesterified shea butter (23% C18:0 on the 2-position).

INNOVATIVE PRODUCTS BASED ON NEW TECHNOLOGIES GENETICALLY MODIFIED OILSEED VARIETIES/ DESIGNER OILS

A number of genetically modified oilseed varieties have been introduced during past several years. They contain saturated FAs, palmitic and stearic acids, at varying levels. The sequence of a gene can be altered by conventional breeding or by using recombinant DNA technology. It is possible to improve the composition and properties of oils from different plants through genetic alterations. For instance, the first genetically modified vegetable oil had a high proportion of lauric acid that is desirable for many food and nonfood applications. Recently, genetically modified soybean oil has been introduced that eliminates the need for hydrogenation to be used in bakery goods and for frying. The oil also has a healthier FA composition. High-oleic sunflower oil having better oxidative stability in deep frying applications and extended shelf life compared to traditional sunflower oil has been developed using selective breeding and mutagenesis (Fick 1983). Other example includes canola oil seed mutants with low linolenic/ high oleic acid content (Przybylski & Mag 2002). Some reported benefits of genetically modified oils include high oxidative stability, zero trans fat and low saturated FAs, non-hydrogenated, high oleic content, liquid at room temperature, and excellent taste and flavor (Orthofer 2006). Transgenic strategies and plant breeding have led to a number of high stearate germplasms from soybeans (Bubeck et al. 1989; Liu et al. 1997), sunflower (Osorio et al. 1995), and canola (Facclotti et al. 1999).

STRUCTURED LIPIDS

Structured lipids are TGs containing short chain FAs and/ or medium chain FAs, and long chain FAs. Structured lipids are prepared by chemical and enzymatic synthesis or random transesterification (Akoh 1998). Structured lipids are developed for specific purposes, such as reducing the amount of fat available for metabolism and, potentially, caloric value (Lucca & Tepper 1994). Medium chain TGs

such as acrylic and caproic TGs have also been produced by interesterification and are reported to deliver nutritional and health benefits as partially hydrogenated oils and have recently been marketed by several companies under various brands such as Enova, Neobee and Vivola.

LOW-CALORIE STRUCTURED LIPIDS

Salatrim is the acronym for short- and long-chain acyl triglyceride molecules. Salatrim is a 'family' of structured lipids produced by the interesterification of triacetin, tripropionin, or tributyrin, or their mixtures with either of the hydrogenated canola, soybean, cottonseed, or sunflower oil. Triglycerides with three short-chain FAs are removed in the process. The different salatrim types differ in the content of short-chain FAs; some contain all 3FAs, others only 2 FAs, and some just 1 FA. The calorific value and energy (kilojoules) yield per gram, of salatrim is lower than that of traditional fat due to presence of the high amounts of short-chain FAs (Finley et al. 1994). According to US and EU reports, Salatrim is estimated to deliver around 21-25 kJ/g of energy compared to 38 kJ/g traditional fat, depending on the specific type of Salatrim. Their functional properties and presence of fully saturated FAs make them an attractive option to replace partially hydrogenated oil and thus reduce overall trans FAs in products.

STRUCTURED TRIGLYCERIDES HAVING POLYUNSATURATED FATTY ACIDS

The nutritional and medical significance of polyunsaturated fatty acids (PUFAs) such as eicosapentaenoic acid (EPA, 20:5n-3) and docosahexanoic acid (DHA, 22:6n-3) has led to synthesis of structured TGs having high proportions of these essential PUFAs. The ω -3 fatty acids (ω -3 FAs) have been shown to have numerous beneficial effects. Majorly, they help prevention or treatment of arteriosclerosis, thrombosis, inflammatory diseases and high blood pressure (Akoh et al. 1995; Yamane 2000). PUFAs are most efficiently absorbed as TGs. However, due to their labile nature, at elevated temperatures and extremes of pH during chemical processes, side reactions such as oxidation, cis-trans isomerization or double bond migration in PUFAs can occur (Haraldsson et al. 1993). In contrast, lipase mediated synthesis of PUFA containing TGs is a favored process. Lipase from *Geotrichum candidum* is most commonly used for *cis* Δ 9 bond. *Rhizomucor miehei* lipase (RML) is used for incorporating EPA/DHA in soybean oil to a final content of 10.5 to 34.7% (Huang & Akoh 1994).

COCOA BUTTER SUBSTITUTES (CBS)

Cocoa butter contains 1, 3 disaturated -2-oleylglycerides predominantly, in which palmitic, stearic and oleic acid account for more than 95% of total FAs. Synthesis of CBS from palm oil midfraction and stearic acid by 1, 3 specific lipases was initially patented by Unilever (Coleman & Macrae 1977) and Fuji Oil (Matsuo et al. 1981a, 1981b). Later on, lipase catalyzed synthesis of CBS has

been reported by numerous researchers by reformulated vegetables oils such as hydrogenated cotton seed oil, olive oil and subsequent fractionation (Sridhar et al. 1991). The CBS produced by microbial lipases has been given GRAS status.

EDIBLE OIL ORGANOGELS

Liquid edible oil, which is organic by nature, can be entrapped within a thermo-reversible, three-dimensional gel network. These structures are formed upon self-assembly of a relatively low concentration of surfactant-like small molecules (organogelators) into crystalline fibres, which eventually lead to gelation of oil to form organogels (Hughes et al. 2009). Different organogelators are known, however, 12-hydroxystearic acid is commonly used; ricinelaic acid or mixtures of β -sitosterol and γ -oryzanol are also used. Organogels have the ability to cater different functionalities in food products including oil mobility and migration restriction, replacement of saturated and trans fat, emulsions stabilization, and the controlled release of nutraceuticals. The structured food oils with an organogel network shown to have the health benefits, a lower mean postprandial TG levels, compared to commercially available butter and margarine spreads. Therefore, the organogels could be used as a substitution of conventional spreads.

POTENTIAL OF LIPASES IN UPGRADATION

In modification of fats and oils, i.e. for position-specific and acyl-group specific modifications, lipases play an important role biotechnologically. Microbial lipases have gained importance because of their multifold properties, easy extraction procedures and unlimited supply (Saxena et al. 1999; Yadav et al. 1998), though they can be obtained from animals and plants. Lipases mediate structured lipids synthesis either by transesterification or interesterification reactions (Basheer et al. 1995; Gupta et al. 2003). Potential 1, 3 position-selective microbial lipases are available commercially; produced by *Mucor*, *Rhizomucor*, *Penicillium* and *Candida* spp. These lipases act regioselectively, i.e. selective hydrolysis of TGs, result in 2-monoglyceride and a mixture of FAs. On the other hand, non-specific lipases act randomly at TG molecule and, therefore, least significant in fats and oils modification.

IMPLICATIONS OF TRANS FATS REPLACEMENT

Evaluation of health implications of trans FAs replacement by alternative fats needs careful attention. Many trans FA alternatives contain saturated FAs (SFA), in particular, tropical fats such as those derived from coconut, palm and palm kernel. Control feeding studies of palm oil (containing 50% SFA) have shown no detrimental effects on blood lipid profiles (Ong et al. 1995). In some cases a slight positive effect on HDL cholesterol and lipoprotein was noted. Palm oil has also been shown to have antithrombotic activity similar to those exerted by PUFAs (Ong 1994).

Individual SFA have been however suggested to affect blood lipid profiles differently. Lauric acid rich palm kernel and coconut oil are still better alternatives to trans FA for products that require solid fats for texture. These oils are also a basic source of medium chain TGs (8:0 to 10:0) and hence are also used in various low-energy and health products. Trans FAs do not provide any known nutritional benefits. As trans FA have apparent unfavorable health effects, its replacement with SFA can provide relative improvement in the dietary quality of processed food. However, potential consequences of increased SFA in place of trans FA need to be carefully assessed. Further, the use of alternative fats containing enhanced-oleic acid content produced through plant breeding or genetic modification may possibly have negative health effects by reducing intake of essential FAs like linoleic (n-6) and linolenic (n-3) acids.

CONCLUSION

In this review, an attempt has been made to provide information on the current and emerging methods of modified oils and fats production, and their impact on human health. Modification of native oils and fats is primarily intended to meet the challenges in bakery and food industry as the chemical-modification to their FAs backbone imparts new physical and functional properties to them. Hydrogenation process has been introduced to increase melting temperature of oils; thereby most vegetable oils can be made suitable for applications such as bakery shortenings and frying fats with improved heat stability. Nowadays, considering the adverse health effects of trans FAs, the partial hydrogenation practice is abandoned in most nations, and is being replaced by alternate hydrogenation methods. Given the increased use of trans FA alternatives, there is a clear need for ongoing sampling and analysis of foods to generate accurate, comprehensive and publicly available food composition databases. This can be used to track dietary intake of trans FA and other FAs, and to study associations between the expected reductions in trans FA intake and health risk factor. Thus, more studies are needed to evaluate the pros and cons of dietary modified oils and fats produced through alternative hydrogenation practices as there is scarce information on their long-term health effects.

ACKNOWLEDGEMENT

This work was supported by the National Research Foundation of Korea (NRF) grant funded by Korean government (MEST) (No. 2009-0067290).

REFERENCES

Akoh, C.C. 1998. Fat replacers. *Food Technol.* 52: 47-52.
 Akoh, C.C., Jennings, B.H. & Lillard, D.A. 1995. Enzymic modification of trilinolein: incorporation of n-3 polyunsaturated fatty acids. *J. Am. Oil Chem. Soc.* 72: 1317-1321.

Ascherio, A., Hennekens, C.H., Buring, J.E., Master, C., Stampfer, M.J. & Willett, W.C. 1994. Trans fatty acids intake and risk of myocardial infarction. *Circulation* 89: 94-101.
 Banik, B.K., Barakat, K.J., Wagle, D.R., Manhas, M.S. & Bose, A.K. 1999. Microwave-assisted rapid and simplified hydrogenation. *J. Org. Chem.* 64: 5746-5753.
 Basheer, S., Mogi, K.I. & Nakajima, M. 1995. Interesterification kinetics of triacylglycerides and fatty acids with modified lipase in n-hexane. *J. Am. Oil Chem. Soc.* 72: 511-518.
 Berry, S.E., Miller, G.J. & Sanders, T.A. 2007. The solid fat content of stearic acid-rich fats determines their postprandial effects. *Am. J. Clin. Nutr.* 85: 1486-1494.
 Bhalla, R., Singh, A.K., Pradhan, S. & Unnikumar, K.R. 2009. Lipids: Structure, Function and Biotechnology Aspects, In *A Textbook of Molecular Biotechnology*, edited by Chauhan, A.K. & Varma, A. pp. 173-209. New Delhi: I.K. International Pvt. Ltd.
 Booyens, J., Louwrens, C.C. & Katzeff, I.E. 1988. The role of unnatural dietary trans and cis unsaturated fatty acids in the epidemiology of coronary artery disease. *Med. Hypotheses* 25: 175-182.
 Bubeck, D.M., Fehr, W.R. & Hammond, E.G. 1989. Inheritance of palmitic and stearic acid mutants of soybean. *Crop Sci.* 29: 652-656.
 Coenen, J.W.E. 1976. Hydrogenation of Edible oils. *J. Am. Oil Chem. Soc.* 53: 382-389.
 Coleman, M.H. & Macrae A.R. 1977. Rearrangement of fatty acid esters in fat reaction reactants. German Patent DE 2705608.
 De, B.K. & Patel, J.D. 2010. Modification of palm oil by chemical and enzymatic catalysed interesterification. *J. Oleo Sci.* 59: 293-298.
 Dian, N.L.H.M., Sundram, K. & Idris, N.A. 2006. DSC study on the melting properties of palm oil, sunflower oil, and palm kernel olein blends before and after chemical interesterification. *J. Am. Oil Chem. Soc.* 83: 739-745.
 Facclotti, M.T., Bertain, P.B. & Yuan, L. 1999. Improved stearate phenotype in transgenic canola expressing a modified acyl-acyl carrier protein thioesterase. *Nat Biotechnol.* 17: 593-597.
 Fick, G.N. 1983. Genetics and breeding of sunflower. *J. Am. Oil Chem. Soc.* 60: 1252-1253.
 Finley, J.W., Klemann, L.P., Leveille, G.A., Otterburn, M.S. & Walchak, C.G. 1994. Caloric availability of salatrim in rats and humans. *J. Agric. Food Chem.* 42: 495-499.
 Gibson, G.R. & Williams, C.M. 2003. *Functional Foods: Concept to Product* Cambridge, England: Woodhead Publishing Limited.
 Gunstone, F.D. & Norris, F.A. 1983. *Lipids in Foods: Chemistry, Biochemistry and Technology*. Elmsford, New York: Pergamon Press.
 Gupta, R., Rathi, P. & Bradoo, S. 2003. Lipase mediated upgradation of dietary fats and oils. *Crit. Rev. Food Sci.* 43: 635-644.
 Haraldsson, G.G., Gudmundson, B.O. & Almarsson, O. 1993. The preparation of homogeneous triacylglycerides of eicosapentaenoic acid and docosahexaenoic acid by lipase. *Tetrahedron Lett.* 34: 5791-5794.
 Hernandez, J.R., Alvarado, E.D., Charó-alonso, M.A. & Toro-vazquez, J.F. 2007. Physicochemical and rheological properties of crystallized blends containing trans-free and partially hydrogenated soybean oil. *J. Am. Oil Chem. Soc.* 84: 1081-1093.

- Higgins, N.W. 2007. Low trans-sterioisomer shortening systems. Patent No. US 7,169,430 B2
- Huang, K.H. & Akoh, C.C. 1994. Lipase-catalyzed incorporation of n-3 polyunsaturated fatty acids into vegetable oils. *J. Am. Oil Chem. Soc.* 71: 1277–1280.
- Hughes, N.E., Marangoni, A.G., Wright, A.J., Rogers, M.A. & Rush, J.W.E. 2009. Potential food applications of edible oil organogels. *Trends Food Sci. Tech.* 20: 470–480.
- Hui, Y.H. 2006. *Fats Hydrogenation in Food Processing. Handbook of Food Science, Technology and Engineering.* Vol. 4, 156, Fla: CRC Press, Taylor and Francis group.
- King, J.W., Holliday, R.L., List, G.R. & Synder, J.M. 2001. Hydrogenation of vegetable oils using mixtures of supercritical carbon dioxide and hydrogen. *J. Am. Oil Chem. Soc.* 78: 107–113.
- List, G.R., Mounts, T.L., Orthoefer, F. & Neff, W.E. 1995. Margarine and shortening oils by interesterification of liquid and trisaturated triglycerides. *J. Am. Oil Chem. Soc.* 72: 379–382.
- List, G.R., Mounts, T.L., Orthoefer, F. & Neff, W.E. 1997. Effect of interesterification on the structure and physical properties of high-stearic acid soybean oils. *J. Am. Oil Chem. Soc.* 74: 327–329.
- Liu, K., Corliss, G., Orthoefer, F.T. & Brown, E.A. 1997. Properties and applications of specially bred soybean oil. *Paper presented at the 88th American Oil Chemists' Society Annual Meeting and Expo.* Seattle, WA, May 11–14.
- Lopez, C. & Ollivon, M. 2009. Triglycerides obtained by dry fractionation of milk fat: 2. Thermal properties and polymorphic evolutions on heating. *Chem. Phys. Lipids* 159: 1–12.
- Lucca, P.A. & Tepper, B.J. 1994. Fat replacer and the functionality of fat in foods. *Trends Food Sci. Tech.* 5: 12–19.
- Matsuo, T., Sawamura, N., Hashimoto, Y. & Hashida, W. 1981a. Method for producing cocoa butter substitute. U.S. Patent 4,268,527.
- Matsuo, T., Sawamura, N., Hashimoto, Y. & Hashida W. 1981b. The enzyme and method for enzymatic transesterification of lipid. Eur. Patent No.0035883.
- Mensink, R.P.M. & Katan, M.B. 1990. Effect of dietary trans fatty acids on high-density and low-density lipoprotein cholesterol levels in healthy subjects. *New Engl. J. Med.* 323: 439–445.
- Naglic, M., Smidovnik, A. & Koloini, T. 1998. Kinetics and catalytic transfer hydrogenation of some vegetable oils. *J. Am. Oil Chem. Soc.* 75: 629–633.
- O'Brien, R.D. 2009. *Fats and Oils: Formulating and Processing for Applications.* 3rd ed. Boca Raton, Fla.: CRC Press, Taylor and Francis Group.
- Ong, A.S.H. 1994. Nutritional aspects of palm oil: An introductory review. *Asia Pac. J. Clin. Nutr.* 3: 201–206.
- Ong, A.S.H., Choo, Y.M. & Ooi, C.K. 1995. Developments in palm oil. In *Developments in Oils and Fats*, edited by Hamilton, R.J. pp. 153–191. Glasgow, UK. Blackie Academic and professional.
- Orthoefer, F. 2006. Global Fats and Oils. *IFT Annual Conference + Food Expo*, Orlando, Florida.
- Osorio, J., Fernandez-martinez, J., Mancha, M. & Garces, R. 1995. Mutant sunflowers with high concentration of saturated fatty acids in the oil. *Crop Sci.* 35: 739–742.
- Przybylski, R. & Mag, T. 2002. Canola/rapeseed oil. In *Vegetable oils in Food Technology*, edited by Gunstone, F.D. pp. 98–127. Boca Raton, USA: CRC press LLC.
- Saxena R.K., Ghosh, P.K., Gupta, R., Davidson, W.S., Bradoo S. & Gulati, R. 1999. Microbial lipases: potential biocatalysts for the future industry. *Curr. Sci. India* 77:101–115.
- Smidovnik, A., Kobe, J., Leskovsek, S. & Koloini, T. 1994. Kinetics of catalytic transfer hydrogenation of soybean oil. *J. Am. Oil Chem. Soc.* 71: 507–511.
- Sridhar, R., Lakshminarayana, G. & Kaimal, T.N.B. 1991. Modification of selected Indian vegetable fats into cocoa butter substitutes by lipase catalyzed ester interchange. *J. Am. Oil Chem. Soc.* 68: 726–730.
- Strayer, D., Belcher, M., Dawson, T., Delaney, B., Fine, J., Flickinger, B., Friedman, P., Heckel, C., Hughes, J., Kincs, F., Liu, L., Mcbrayer, T., Mccaskill, D., Mcneill, G., Nugnet, M., Paladini, E., Rosegrant, P., Tiffany, T., Wainwright, B. & Wilken, J. 2006. *Food Fats and Oils*, 9th ed, Institute of Shortening and Edible Oils. Washington, D.C.
- Sundram, K., Karupaiah, T. & Hayes, K.C. 2007. Stearic acid-rich interesterified fat and trans-rich fat raise the LDL/HDL ratio and plasma glucose relative to palm olein in humans. *Nutr. Metab.* 4:3 doi: 10.1186/1743-7075-4-3.
- Tike, M.A. & Mahajani, V.V. 2006. Studies in catalytic transfer hydrogenation of soybean oil using ammonium formate as donor over 5% Pd/C catalyst. *Chem. Eng. J.* 123: 31–41.
- Trivedi, R. & Singh, R.P. 2005. Modification of oils and fats to produce structured lipids. *J. Oleo Sci.* 54: 423–430.
- Versteeg, C., Thomas, L.N., Yep, Y.L. & Papalois, M. 1994. New fractionated milk fat products. *Aust. J. Dairy Technol.* 49: 57–61.
- Yadav, R.P., Saxena, R.K., Gupta, R. & Davidson, W.S. 1998. Lipase production by *Aspergillus* and *Penicillium* spp. *Folia Microbiol.* 43: 373–378.
- Yamane, T. 2000. Lipase-catalyzed synthesis of structured triacylglycerols containing polyunsaturated fatty acids: Monitoring the reaction and increasing the yield, In *Enzymes in Lipid Modification*, edited by Bornscheur, U.T. pp. 148–169. Wiley-VCH Verlag GmbH, D-69469 Weinheim (FRG).
- Zock, P.L. & Katan, M.B. 1992. Hydrogenation alternatives: effects of trans fatty acids and stearic acid versus linoleic acid on serum lipids and lipoproteins in humans. *J. Lipid Res.* 33: 399–410.
- Pradeep Puligundla & Sanghoon Ko*
Department of Food Science and Technology
Sejong University
98 Gunja-dong, Gwangjin-gu
Seoul 143-747, Korea
- Prasad Shekhar Variyar
Food Technology Division
Bhabha Atomic Research Centre
Mumbai 400 085, India
- Vijaya Sarathi Reddy Obulam
Department of Biochemistry
Sri Venkateswara University
Tirupati 517 502, India

*Corresponding author: email: sanghoonko@sejong.ac.kr

Received: 14 December 2011

Accepted: 30 January 2012