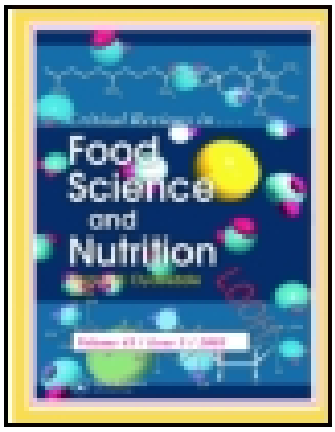

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Edible Lipids Modification Processes: A Review

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Edible Lipids Modification Processes: A Review

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Abstract

Lipid is the general name given to fats and oils, which are the basic components of cooking oils, shortening, ghee, margarine, and other edible fats. The chosen term depends on the physical state at ambient temperature; fats are solids and oils are liquids. The chemical properties of the lipids, including degree of saturation, fatty acid chain length and acylglycerol molecule composition are the basic determinants of physical characteristics such as melting point, cloud point, solid fat content, and thermal behavior. This review will discuss the major lipid modification strategies, hydrogenation and chemical and enzymatic interesterification, describing the catalysts used mechanisms, kinetics, and impacts on the health-related properties of the final products. Enzymatic interesterification will be emphasized as method that produces a final product with good taste, zero trans fatty acids, and a low number of calories, requires less contact with chemicals, and is cost efficient.

Keywords: Hydrogenation, *trans* fatty acids, cardiovascular, Chemical interesterification, enzymatic interesterification, lipase, selectivity, structured lipids, polyunsaturated.

Introduction

Triglycerides (TAGs) are the main constituents of most natural oils and fats. The molecular structures of TAGs are of great importance in food chemistry and technology because of their correlation with the physiochemical properties of the food. TAGs consist of saturated, mono-unsaturated, and poly-unsaturated fatty acids, the basic units of most lipids, which are attached to the three positions of the glycerol backbone. Important physical characteristics of oils and fats, such as thermal behavior, elasticity, melting point and viscosity, are all considerably dependent on the crystal structure of the fat(Kaneko 2001), and these characteristics are influenced by the chemical composition of the TAG(Andrikopoulos 2002). Triacylglycerols can exist in multi-crystalline phases, and the presence or absence of one polymorph depends heavily on the composition of the fatty acids and their distribution among the three glycerol positions(Foubert, Dewettinck et al. 2007). Technologies that can create the desired fat in a solid state, such as blending two or more types of fatty intermediates, hydrogenation, fractionation of oil constituents, enzymatic interesterification, and chemical interesterification(Husum., Pedersen. et al. 2004), are of great importance in the lipid modification field.

Lipid Modifications

1- Hydrogenation

Margarine and shortening manufacturing requires a hard stock fat with high plasticity and high oxidative stability. Hydrogenation technology can be used to achieve this goal, converting liquid

or semi-solid lipids to solids by fully or partially saturating the double bonds. This technique was first discovered by Sabatier and Senderens (1897), who evaporated the organic compounds from a fat and allowed it to react with hydrogen gas on a metal catalytic surface (nickel).

Whale oil hydrogenation was the first industrial use of this technology (W.Norman 1903). Then, in 1939, a patent describing the novel production of plastic fats through the hydrogenation of liquid oil triacylglycerols was issued to Kaufmann; this procedure reduced the dependence on limited types of available fats to make margarine and shortening. The hydrogenation process opened up the market to marine animal oils, oils with high unsaturated fatty acid contents, which typically deteriorate rapidly due to the absence of a natural stabilizing compounds, and also for novelty products such as trans isomer-rich (CBSs) cocoa butter substitutes and partially hydrogenated margarine hard stock (Dijkstra 2007, 2010 and Knothe 2010).

This process is carried out by reacting hydrogen gas with the active sites within liquid fats, i.e., the mono, di, tri, and tetra double bonds of the fatty acids (Fig 1) under controlled pressure, temperature, agitation speed, and catalyst quality and quantity in a hydrogenation reactor, usually the batch type to produce less trans isomer (Gabrelia 2008). The product yielded by this process has two important properties. First, it has a greater stability of flavor due to minimizing oxidation reactions and second, it has characteristics and functionalities that are desirable for specialty fat applications, such as steep melting properties, cooking stability, creaming ability, and pleasant appearance (O'Brien 2009).

Catalyst

Homogeneous and heterogeneous catalysts for the reaction of hydrogen with double bonds have been reported in the literature (Frankel and Little 1969; Veldsink, Bouma et al. 1997), but homogeneous catalysts are not commonly utilized in the industry due to their low activity, low cost efficiency, toxicity, and difficulties in catalyst recovery (Schoon 1995; Islam, Mondal et al. 2010).

Nickel catalysts, especially Raney nickel, have been used widely to catalyze the hydrogenation of edible lipids under hydrogen gas at high pressure and elevated temperatures. The nickel catalyst is usually prepared by the reduction of a nickel salt and supported on an inert solid and/or flaked support in hard fat (Jowett 1991). Other types of catalysts have been utilized as lipid hydrogenation catalysts, such as ruthenium (Mendes 2001) and palladium-ruthenium (Gabriela et al. 2005). This catalyst converts linolenic fatty acid to linoleic fatty acid very selectively, but its poor activity and sensitivity to inactivation has limited its application to small (lab)-scale uses (Hubaut, Bonnelle et al. 1989;Liaw and Chen 2000). The use of precious metals as hydrogenation catalysts has been another excellent approach (Schneider, Lara et al. 2010), since the catalyst is effective at relatively low temperatures (60°C) compared to those required higher temperature namely (130-140°C) for nickel catalysts, therefore, the content of *trans*-isomers in the acquired hydrogenated lipids should be lower (Haumann 1994; Savchenko and Makaryan 1999). Although experiments have demonstrated that ruthenium is a much more effective as hydrogenation catalyst than nickel (Mäki-Arvela 2008, ũ ervenr̃ 1989), the commercial application of this catalyst group is still limited by its low cost efficiency and handling difficulties (Gray and Russell 1979; Mun Yhung and David 2005).

The advent of gas liquid chromatography (GLC), pulse nuclear magnetic resonance (P-NMR), and extensive research on the catalyst quality and quantity have permitted a decreased catalyst dosage and improved the reliability of the product quality and characteristics, lowering the number of poor quality batches.

Mechanism and Kinetics

The catalyzed hydrogenation reaction is one of the most complex and significant reactions applied to modify the properties of fats and oils. A complex mixture of products are formed by the various chemical reactions that occur simultaneously, as presented in Fig 2, whereas the process involves: (1) double bond reduction (major reaction), (2) *trans*-isomerization formation, and (3) double bond location shifts (positional isomerization) (Bernas 2009, 2010 and Wong 2011).

The first report on hydrogenation mechanism was published by Horiuti and Polanyiin in 1934 (Doyle, Shaikhutdinov et al. 2003). This mechanism is the foundation of the current model and suggested that the two hydrogen atoms required to saturate the double bond must react sequentially; therefore, a semi-hydrogenated intermediate can return to its initial state. The stability of this intermediate is dependent on the number of double bonds in the initial state.

The most recent hydrogenation mechanism was proposed by Dijkstra (Dijkstra 2006) based on an interpretation of the observations made in his previous works (Dijkstra 1997). He proposed an explanation on the relationship between hydrogen concentration and reaction selectivity, isomerization, and the preferred final product. This model provides a good explanation of the difference in reaction rates of *cis/trans* isomers and the effect of catalyst type on promoting

trans-isomer formation. The proposed mechanism stated the reaction is initiated by the adsorption of molecular hydrogen on the surface of the catalyst, noted by asterisk (*) in Fig 3, to be followed by the separation of the atoms in two rapid reversible reactions (1) and (2).

In steps (3), (6) and (8), the diene fatty acids *cis,cis*(c,c-D), *cis,trans*(c,t,D), and *trans,trans*(t,t-D) are adsorbed in a reversible manner on the catalyst surface, giving rise to the prediction that a higher concentration of these fatty acids increases the rate of the adhesion. The two fatty acids (c,t-D) and (t,t-D) were formed by the dissociation of the fatty acids formed in steps (5) and (7) (Dijkstra 2010).

The first hydrogen atom is added either to the *cis* double bond in reactions (4) and (7) or to the *trans* bond in reactions (5) and (9) to produce the two major half-hydrogenated intermediates (c-DH*) and (t-DH*), which can either revert to their previous states and then be dissociated or continue the reaction in the primary saturation state by reacting irreversibly with a second hydrogen atom in steps (10) and (11) to form two monoenes (c-M) and (t-M) (Horiuti and Polanyi 1934).

In steps (12) and (13), the monoene re-attached itself to the catalyst surface and reacts with the hydrogen atom adsorbed on the same surface with a previously mentioned sequence of reversible reactions to reach a fully saturated fatty acid. The overall rate of reaction is administrated by two factors, the hydrogen concentration and the catalyst quality and quantity in the oil. The hydrogen concentration reflects the balance between the demand and supply, which is itself a consequence of the hydrogen solubility and is determined by the system pressure, oil temperature, and the design of the stirring system. Eventually, the catalyst may deactivate and leading to decreases the

concentration of the adsorbed hydrogen atoms [H*] due to the reduction in active site concentration, which makes reactions (14) and (15) preferred over reaction (16).

The activity of the mixture reaction is decreased during the reaction run, which translates to an increase in hydrogen atom concentration [H*], making the series of reactions (14), (15), and (16) more favorable than the reaction with diene acid. This selectivity occurs due to the stronger dependence of this reaction series on hydrogen atom [H*] concentration.

Health Aspects

Cardiovascular disease (CVD) studies have focused intensively on the control of nutrition as a means as to lower the ratio of plasma cholesterol (Onyeneke and Alumanah 1991). The type and ratio of lipids present in a diet are essential factors that affect the incidence of hypertension (Gemma 2008). Dietary saturated fats and *trans*-isomer content have a major effect on the concentration of the cholesterol in the plasma and connective tissue of the arterial walls, which are major factors in atherosclerosis, high blood pressure, and coronary heart disease (CHD) (Mutanen, Kleemola et al. 1992; Sundram, Karupaiah et al. 2007).

High and low density lipoprotein (HDL and LDL), two of the four major types of lipoprotein(W.Christie 2012), have been shown to have opposing effects on coronary risk. While HDL is able to reduce coronary risk (Barter and Rye 1996; Nichols, Vupputuri et al. 2011), LDL has an inverse effect, predisposing middle-aged individuals to CHD(Tan, BETTERIDGE et al. 1993; Briel, Ferreira-Gonzalez et al. 2009). The transported cholesterol, particularly LDL, is the main cause of the progression of atherosclerosis. Fats that are rich in *trans* and saturated fatty

acids elevate the levels of LDL, increasing the risk of CHD and simultaneously negatively impacting the HDL level (Sundram, Karupaiah et al. 2007;Brouwer, Wanders et al. 2010).

2- Interesterification (IE)

Interesterification, or fatty acid exchange, is a process during which fatty acid esters exchange positions either within the same glyceride backbone or with the other glyceride molecules. This alters the chemical composition of the fats, resulting in changes in the physical properties of the fats. This reaction can be described simply as a random or direct attack on the fatty acids joined to the glycerol backbone, leading to the breakage of the bond between these fatty acids and glycerol backbone, after which the released fatty acid is mixed with other free fatty acids in the pool and the vacant glycerol position is re-occupied by another randomly selected free fatty acid (O'Brien 2009).

Interesterification Types

There are three different types of interesterification process, classified according to the substances included in the reaction:

a) Acidolysis

Acidolysis is a reaction in which an acyl group is transferred between the triglyceride molecules and the free fatty acids [Fig 4]. This catalyzed process occurs in the presence of an acid-base catalyst to form monoglycerides (MAGs) and diglycerides (DAGs) from the partial hydrolysis of the fatty acid esters in the TAG molecules. New TAGs are formed when the hydroxyl group of the MAG or DAG reacts with a free fatty acid (Marangoni and Rousseau 1995).

In practicality, this reaction is inefficient due to the high cost of fatty acids and final separation of large amounts of FFAs, but it is considered an effective method for the incorporation of novel fatty acids to improve the nutritional properties of specific TAGs (Namal Senanayake and Shahidi 1999).

b) Glycerolysis

In this reaction, an alcoholysis reaction is initiated when one mole of TAG reacts with three moles of alcohol in the presence of either a strong alkali or acid (Senanayake and Shahidi 2005), or a lipase enzyme (Ergan, Trani et al. 1991), generating a mixture of glycerol and alkyl esters. This process is consecutive and reversible until equilibrium is reached.

The glycerol molecules formed in the first step mix extensively with TAGs to exchange acyl groups until equilibrium is reached in what is known as glycerolysis to produce MAGs and DAGs [Fig 5] (Gunstone 2004).

c) Trans-esterification

Trans-esterification is a molecular rearrangement process in which the fatty acids are shuffled within one TAG molecule (interesterification) and among the other TAG molecules after random breakage until equilibrium is achieved among all possible combinations (Sreenivasan 1978). The first step in trans-esterification is the cleavage of the ester bonds linking glycerol to the fatty acyl residues; in the second step, the liberated fatty acids are re-attached to a new position either on the backbone of same glycerol or on another glycerol molecule (Rousseau and Marangoni 1998).

Interesterification Methods

Presently, the interesterification of triglycerides is carried out either chemically or enzymatically. In chemically process, fatty acids are exchanged among acylglycerols randomly to produce a predetermined TAG composition with complete positional randomization. This reaction is generally catalyzed by metal alkoxides, which are relatively cheap and readily available (Mangos, Jones et al. 1999). Enzymatically, this process takes advantage of the regiospecificity of lipases toward both acylglycerol parts and fatty acids, and this selectivity can be exploited to synthesize structured lipids that cannot be obtained via conventional chemical interesterification.

1) Chemical Interesterification (CIE)

This process is the most commonly industrially implemented method of interesterification. It can modify the physical properties of a fat or oil (Ribeiro, Basso et al. 2009) by either random or directed fatty acid interchange within and among the triglycerides. Randomized CIE lipids can be obtained when the radicals of the fatty acids shift liberally among TAG molecules until reaching equilibrium; the equilibrium is highly dependent on the input materials and can be predicted based on probability laws (Derick and Alejandro 2002).

In directed CIE, the reaction occurs under relatively low temperatures with the aim of removing the saturated TAGs from the reaction medium; therefore, the temperature of the reaction is kept below the melting point of the desired TAGs while the interesterification process takes place under this condition. As the saturated TAGs are crystallized, the reaction equilibrium is pushed toward generating more of these TAGs. A continuous process is preferable due to the difficulties of controlling batch processes, and the most suitable catalysts are those with the high activity at low temperature, such as sodium/potassium alloys (Laning 1985; Alejandro and Dérick 2008).

Mechanism and Kinetics

In 1948, Eckey observed that FAMEs are formed in an equivalent quantity to TAGs in oil when a sodium methanolate (sodium methoxide) catalyst is added. Baltes found that sodium diacylglycerolate is formed after adding the catalyst, and he suggested a mechanism in which this compound serves as an active intermediate of the interesterification reaction (Dijkstra 2008).

In 1961, Weiss observed that the activation energy required for the formation of the catalytically active intermediate is higher than that of the interesterification reaction itself and accordingly suggested that the true intermediate is an enolate anion. More recently, Liu proposed a complementary interpretation for the formation of long chain ketones formed from ß-keto esters (Liu 2004).

An enolate mechanism that has been suggested by Dijkstra (Dijkstra 2004; Dijkstra, TŖke et al. 2005) incorporates all of these earlier suggestions and observations and provides an adequate explanation and illustration of these data as presented in [Fig 6]. The first step of this mechanism is the abstraction of Ŭ-hydrogen by means of strong alkali to form an enolate anion. At the second step, the generated enolate anion react with the hydroxyl group, resulting in an ester interchange to form a glycerolate anion, in which the hydroxyl group comes from partial glycerol or alcohol and the enolate is regenerated by the subsequent abstraction of Ŭ-proton from a fatty acid moiety.

Health Aspects

Chemical interesterification has gained an advantage over hydrogenation due to the increasing concerns about the effects of hydrogenated fats on health and nutrition. Although the effect of stereospecificity on the biological activities of fatty acid is not well defined (De Schrijver, Vermeulen et al. 1991; Berry 2009), it has been proven that the nutritional value of the unsaturated fatty acid dose not affected by the randomization process (Alfin-Slater, Aftergood et al. 1966). Furthermore, the metabolic response to randomized and natural lipids was examined in rats (Kritchevsky 1988) fed with animal, vegetable, or marine fats. These experiments showed that the absorption of polyunsaturated fatty acids is not related to the fatty acid profile of the dietary fat. Further tests showed no symptoms in rabbits fed chemically randomized oils reported to be atherogenic (Kubow 1996).

A comparison between interesterified and nonesterified soya-butter fat feeding in human and rats found that interesterified fats give a significan reduced influence on serum cholesterol compared to noninteresterified fats (Mukherjee and Sengupta 1981).

In contrast, a study on the effects of the chemical interesterification of partially hydrogenated fats on the levels of lipids in rat tissues and on cholesterol absorption showed that *trans* fatty acids tend to increase hypercholesterolemia (Koga, Yamato et al. 1995).

2) Enzyme-Catalyzed Interesterification

Enzyme-catalyzed interesterification is a process in which an enzyme is introduced to catalyze the glyceride backbone rearrangement reaction. This biochemical reaction is executed by lipases acquired from either fungal or yeast bacterial sources that excrete these enzymes into their environment for lipid digestion (Macrae 1983). Lipases are the general catalysts of TAG

hydrolysis and FA interesterification and can be defined as carboxyl bonds hydrolyses (EC 3.1.1.3) due to their functions in attacking the glycerol esters in the glyceride molecule. The strong attraction of lipases toward hydrophobic surfaces allow them to be adsorbed from aqueous media by long-chain TAG (Desnuelle 1972).

Lipases obtained from plants have a limited interest due to their specificity toward triacylglycerols of the species from which they were isolated. Lipases obtained from different plants have diverse substrate specificity, hydrophobicity, optimum PH, and subcellular location (Huang, Lin et al. 1988).

The most thoroughly studied lipases from an animal source are the pancreatic lipases, which are responsible for breaking down approximately 50% of the dietary triacylglycerols; the remaining 50% are broken down by lingual, pharyngeal, and gastric lipases (Carrere, Gargouri et al. 1994). The versatility, availability, and cost efficacy of microbial lipases and developments in genetic engineering and modern processing technology (Vulfson 1993) have increased the attention paid to these lipases. However, only 25% of screened microbial lipases were active (Hou and Johnston 1992), and few organisms can produce a mixture of extracellular lipases that are generally compatible with human pancreatic lipase (Baillargeon, Bistline et al. 1989).

Specificity

The specificity of some lipases presents a unique advantage in catalyzed lipid modification relative to chemical interesterification. This specificity allows the conversion of lipids to more valuable products such as esters (Li, Tianwei et al. 2003), organic synthesis (Gotor-Fernández

and Vicente 2007), and biodiesel (Bajaj, Lohan et al. 2010). Lipases can be classified according to their functionality into four types [Table 1]:

I) Non-specific

Non-specific lipases interact with any fatty acid ester at any location within the TAG molecule. *Candida cylindraceae* and *Staphylococcus aureus* are two non-specific lipases that produce a completely randomized product, similar to that produced by CIE process (Macrae 1983; Villeneuve and Foglia 1997). A comparison between a 1,3-specific lipases from microbial sources and none-specific enzyme on the transesterification of palm olein has been reported by Ghazali 1995.

II) Regeo-specific

Another class of lipases are *sn-1,3* regeo-selective lipases, such as *Aspergillus niger* and *Rhizopus arrhizus***,** which have the ability to react with the ester bonds of the fatty acids located at position 1 and 3 of TAG but not with esters located at the *sn-2* position, due to the steric hindrance (Macrae and How 1988). Other lipases, i.e., the lipase from *Candida parapsilosis,* hydrolyze the fatty acid acyl group of the *sn-2* position more rapidly than that of the *sn-1* or *sn-3* under specific conditions (Riaublanc, Ratomahenina et al. 1993).

III) Stereo-specific

This type of lipase has a stereospecific ability to hydrolyze esters located at *sn-1* and *sn-3* at different rates. The origin of the acyl group, lipase source, fatty acid chain length, and substrate concentration are all determinants of stereospecificity (Lavayre, Verrier et al. 1982;Uzawa,

Nishida et al. 1990). Some examples of this type of lipase are *Pseudomonas fluorescens* and *Humicola lanuginosa* lipases, which have *sn-1* specificity, and *C. antarctica* B and human *lingual*, which have *sn-3* specificity (Jensen, Dejong et al. 1982; Rogalska, Cudrey et al. 1993).

IV) Fatty acid-specific

This type of lipases is specific toward one class of fatty acids. These lipases will hydrolyze the esters of the intended fatty acid during the enzymatic reaction regardless of their position. The *Geotrichum candidum* lipase, for example, is specific towards fatty acids that contains a double bond at cis-9 (Jensen 1983) and *Penicillium roquefortii* lipase is specific toward short-chain fatty acids (Mase, Matsumiya et al. 1995).

Mechanism and Kinetics

The interesterification of lipids using lipase as a catalyst is a multisubstrate reaction (glycerides, water, and fatty acids) that follows the Ping-Pong Bi-Bi mechanism. This reaction is initiated by the hydrolysis of the fatty acid moiety of the acylglycerol to be sequenced through an esterification reaction until equilibrium is reached (Malcata, Reyes et al. 1992, Reyes and Hill 1994).

Interesterification involves acylation and deacylation of the substrate in the active site of the lipase (Miller, Prausnitz et al. 1991). The acylation reaction begins when the serine amino acid in the active site makes a nucleophilic attack on the substrateôs carbonyl carbon, forming a covalent acyl-enzyme complex. The presence of histidine and aspartic acid residues make the serine a stronger nucleophile. The negative charge of the glutamic acid or aspartic acid residues stabilizes

the positively charged histidine imidazole ring after protonation. The subsequent reaction forms a tetrahedral that will be stabilized by forming two hydrogen bonds with the oxyanion-stabilizing residues (Jaeger, Ransac et al. 1994). During this reaction, the alcohol is released through a breakage of the carbon-oxygen bond within the ester, and the catalytic triad (three amino acid residues) to forms a covalent bond with the acylglycerol.

The leaving alcohol and the serine residue then are bonded to the hydrogen in the histidine. A tetrahedral intermediate is formed by the addition of a hydroxyl group to the carbonyl carbon through a nucleophilic attack by water or an alcohol, resulting in the release of the modified glyceride and regeneration of the active site serine (Wong 1994; Marangoni and Rousseau 1995) [Fig 7].

Health Aspects

Structured lipids, or structured triglycerides, are able to precisely modify fats and oils either by interchanging the fatty acids type and location to those with the desired physical properties, or by increasing the polyunsaturated fatty acid or short and medium chain fatty acid contents to provide more nutritive value. Therefore, the catalyst used must be specific to direct this modification accurately and prioritize lipase-catalyzed interesterification; these characteristics cannot be produced using chemical methods. Medically structured lipids are produced to nourish patients that require a special diet.

Caproic, octanoic, and capric fatty acids are not incorporated into the lipoprotein groups in our bodies; therefore, they can be used to produce medical SLs by interchanging them with FAs on the TAG backbone. These medical SLs are easily oxidized in the liver of premature babies and

malabsorption patients, allowing them to be used as an important source of energy (Jandacek, Whiteside et al. 1987; Gandhi 1997). Other medical SLs generated by structuring marine oils with MCTs can be used to reduce tumor protein synthesis (abnormal swelling) and decrease weight in rats, in comparison to LCTs (Ling, Istfan et al. 1991).

The nutritional properties of lipid TAGs can be improved impressively by structuring with PUFAs and MCFAs because TAGs with PUFAs at the *sn*-2 position and MCFAs at the *sn*-1,3 positions are hydrolyzed rapidly by pancreatic lipase in the intestines (Quinlan and Moore 1993). Human milk fat substitute, one of the greatest nutritionally improved products, is produced by interesterifying a blend of vegetable oils and marine oils enzymatically modified (Karabulut, Turan et al. 2007)

Conclusion

The growing global concern about *trans*-fats, poly-unsaturated fats, and eco-friendly processes has increased the demand for novel technologies that address these concerns and at the same time are cost effective and versatile for manufacturers.

EIE technology is currently the preferred process because developments in lipase immobilization technology have improved the enzyme stability and tempered the conditions of the overall process.

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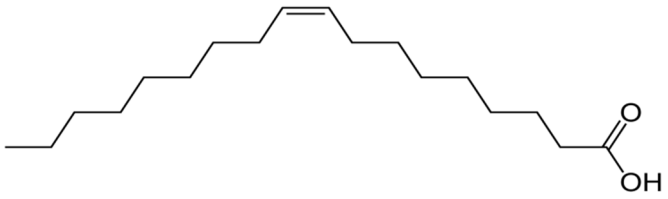
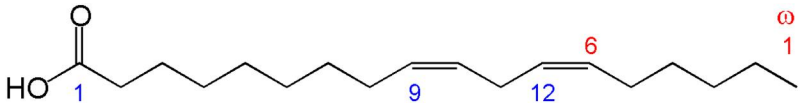
Table.1: Lipases and their industrial applications (Lian at al. 2004).

Lipase	Specificity (remarks)	application
Candida cilyndracae	M<S, L sn-1,2,3	EMC Pharmaceutical ingredient
Mucor javanicus	sn-1,3	In Dairy, oil & fats products
Rhizopus arrhizus	sn-1,3 (phospholipase A1 activity)	Oleochemistry Dairy flavor
Aspergillus niger, *Rhizopus javanicus*, *Rhizopus niveus*	sn-1,3	In Dairy, oil & fats products Pharmaceutical products
Pseudomonas sp	Non-specific	Synthesis of lipophilic antioxidants PUFA production
Candida rugosa	Non-specific	Chiral esters
Thermomyces lanuginosus	sn-1,3	Oil interesterification
Rhizomucor miehei	sn-1,3 S > M , L	Food Surfactants

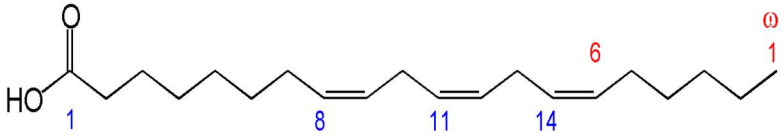
Candida antarctica	sn-3	Food flavors Cosmetic components
Geotrichum candidum	cis-ϕ[9]	Food supplements ɔ-linolenic acid (GLA)



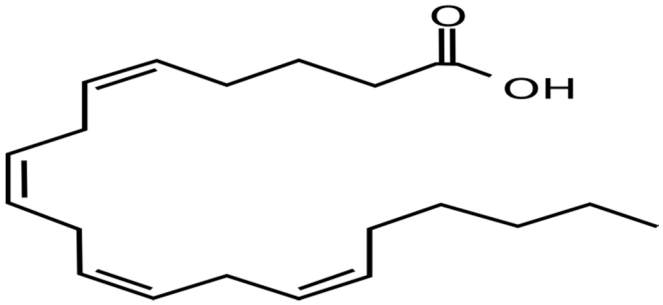
Oleic acid, ((9*Z*)-Octadec-9-enoic acid) IUPAC



18:2n-6 Linoleic acid (Cis isomer), ((9*Z*,12*Z*)-9,12-Octadecadienoic acid) IUPAC



Gamma cis linolenic acid 18:3n-6, (all-*cis*-6,9,12-octadecatrienoic acid) IUPAC



Arachidonic acid 20:4n-6, ((5*Z*,8*Z*,11*Z*,14*Z*)-5,8,11,14-Eicosatetraenoic acid) IUPAC

Figure 1: Chemical formula of some natural unsaturated fatty acids (*cis* isomers).

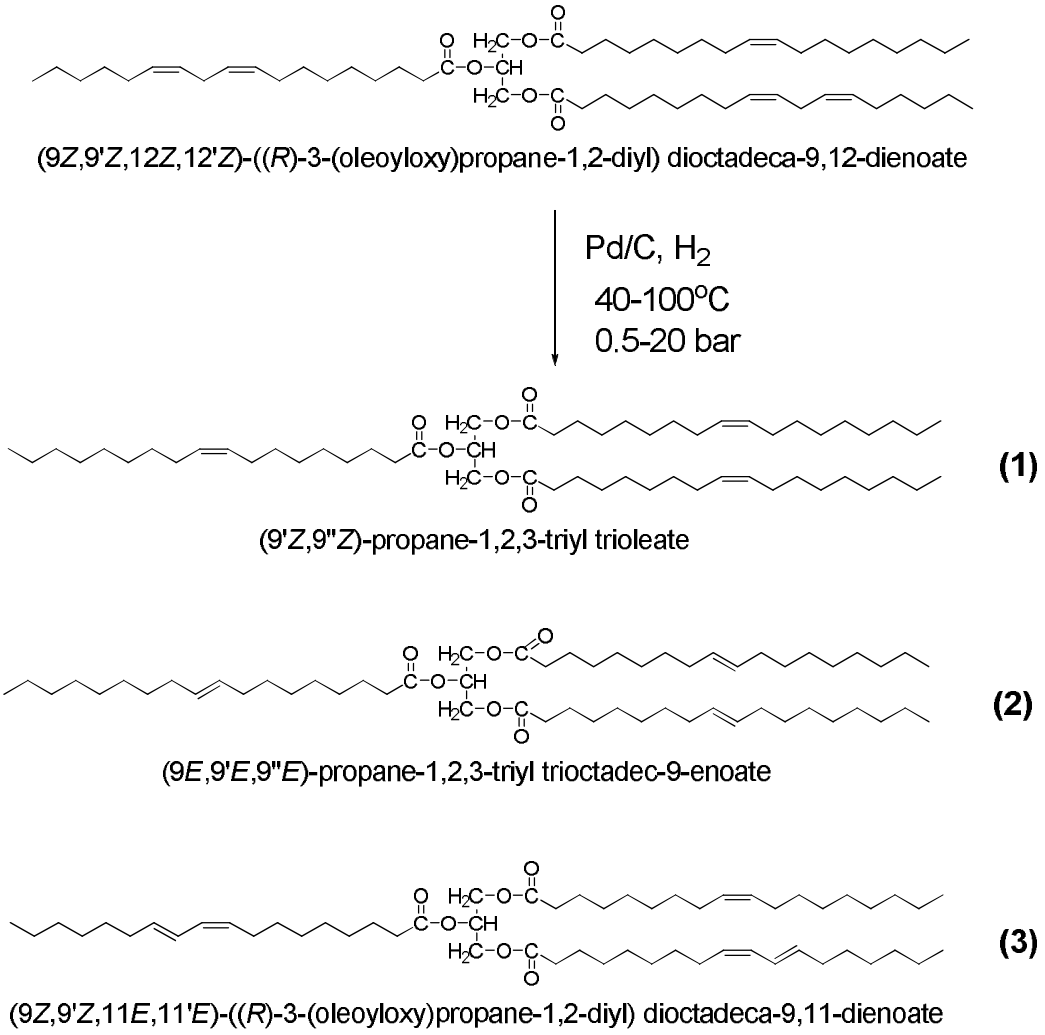


Figure 2: Major and minor hydrogenation products.

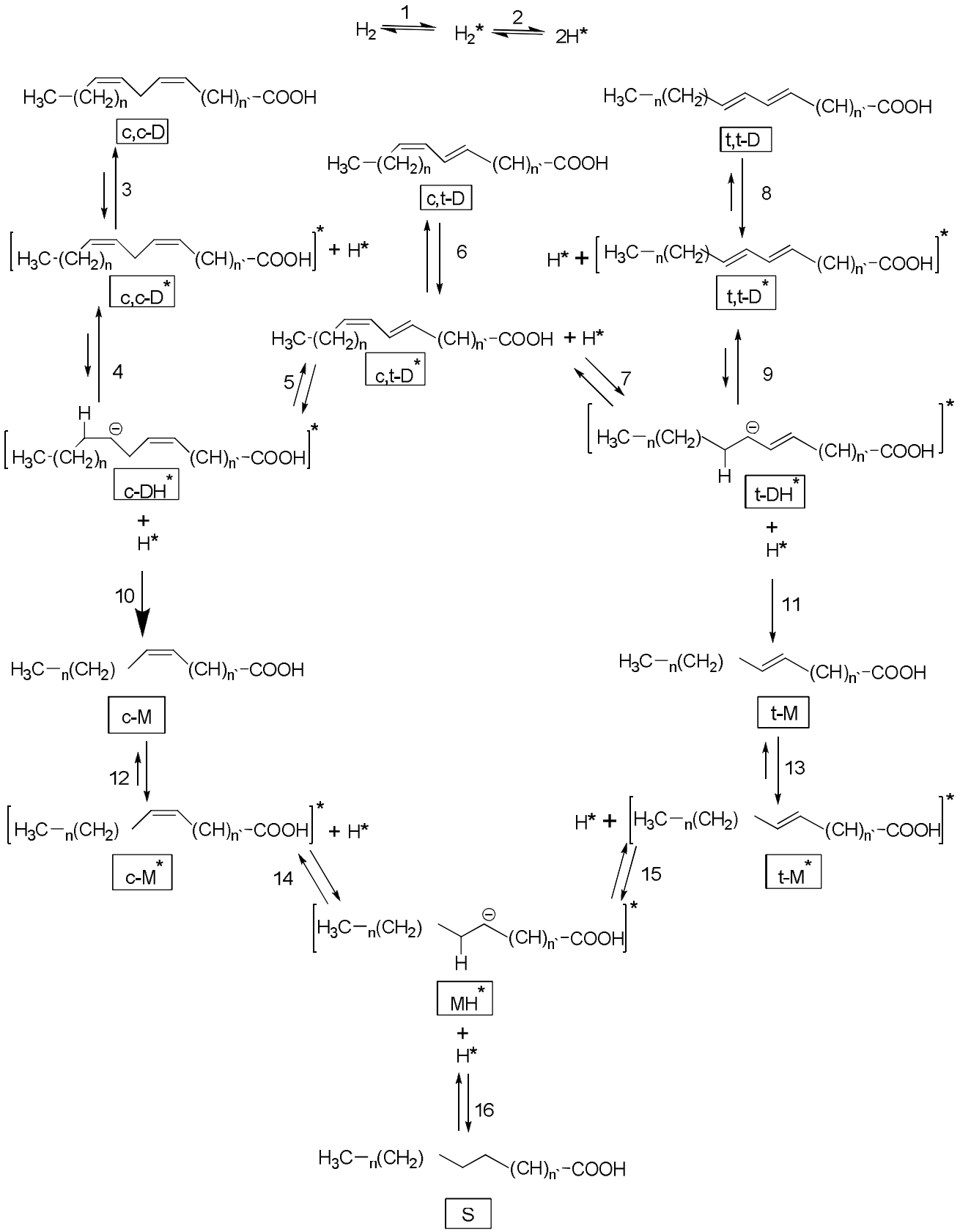


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Fig 3: Hydrogenation mechanism as reported in reference Dijkstra A.J. 2006.

*, c, t, D, M, S stands for; adsorption, cis, trans, diene, monoene, and saturated fatty acid respectively.

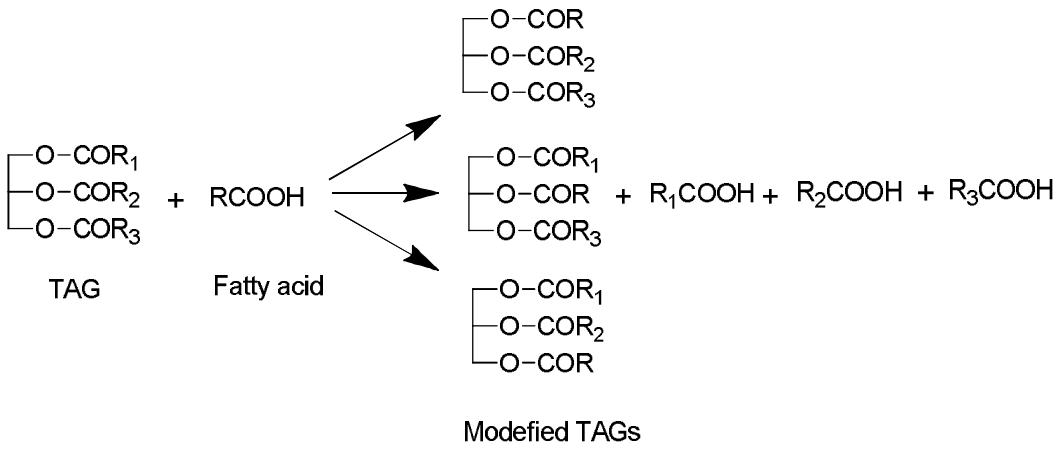

Figure 4: Acedolysis reaction of fatty esters with fatty acid.

** (R = CH_3-$(CH_2)_n$)

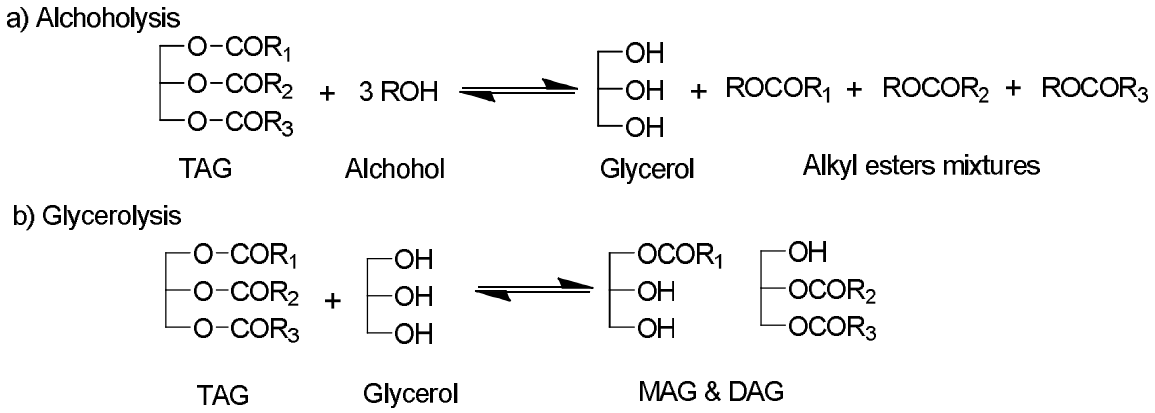

Figure 5: Glycerolysis and Alcoholysis process.

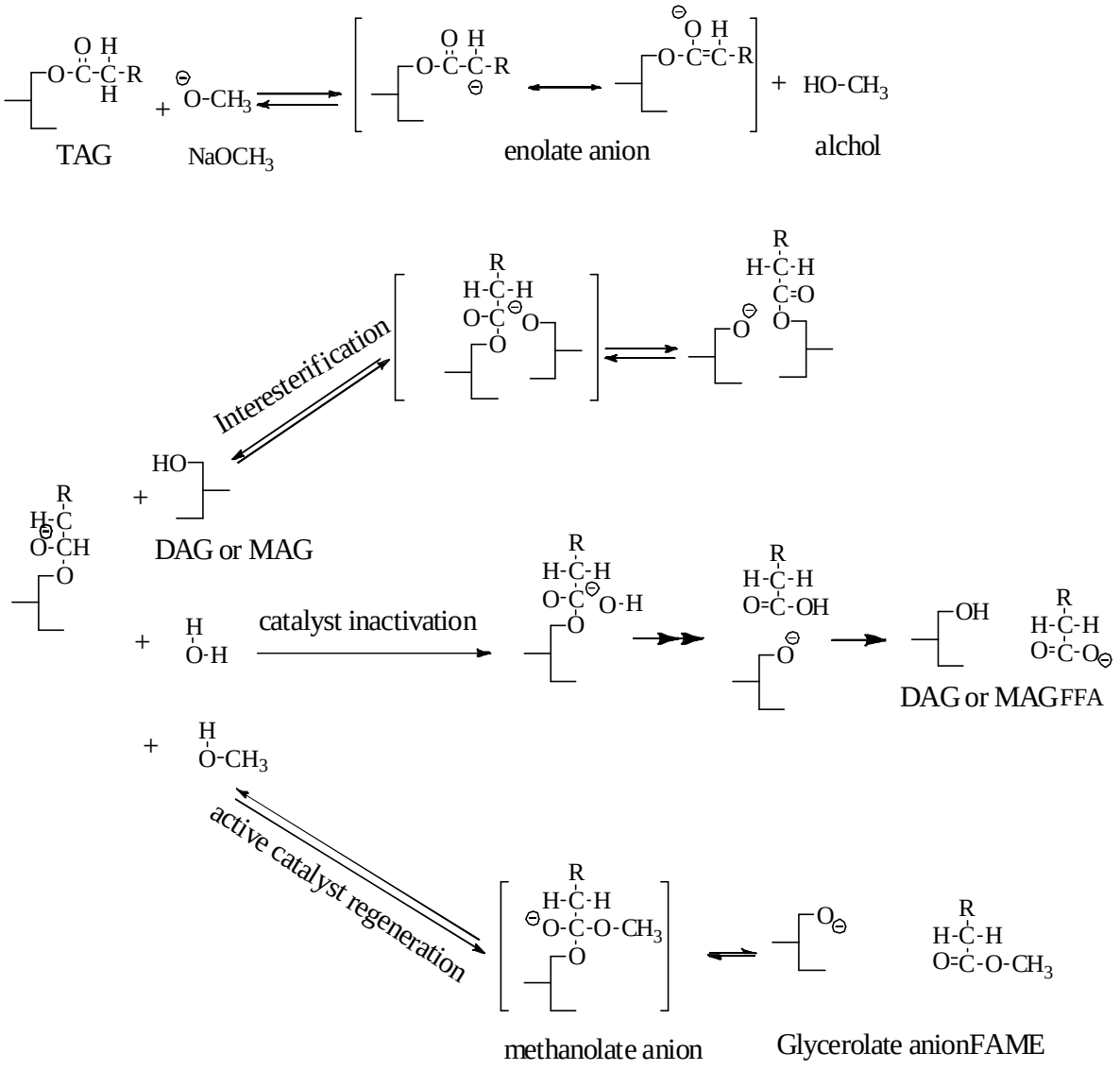

Figure 6: Mechanism of chemical interesterification (adapted from Dijkstra and TR, ke. 2005)

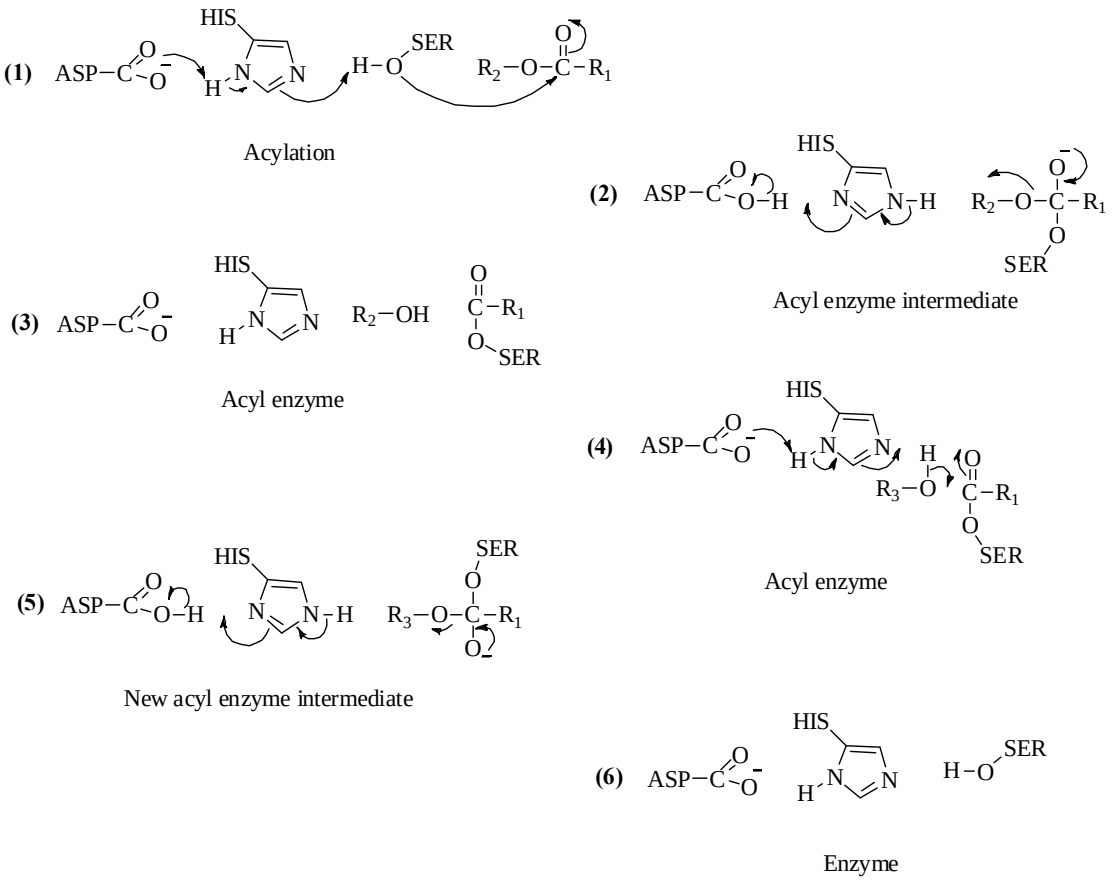

Figure 7: Lipase catalytic mechanism of lipids. (Maragoni and Rousseau 1995).