Chapter 3

CHEMICAL MODIFICATION OF OILS AND FATS

From the fats and oils obtained from natural resources, the majority of them are used directly or just after refinement. While the others are used after modification by chemical process. This chapter lists some typical modifications of fats and oils by chemical means.

3-1 Alkaline Hydrolysis

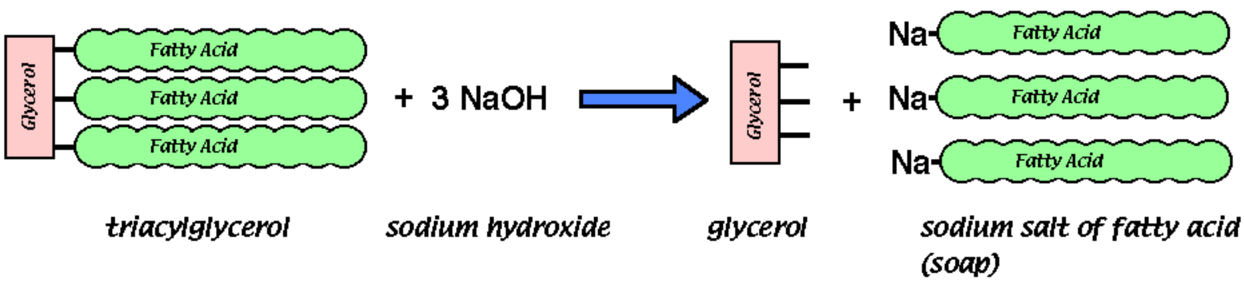

Figure 3-1-1: Alkaline hydrolysis (saponification) of oil to make soaps.

There are many methods for hydrolysis of triacylglycerol molecule. The most common method is alkaline hydrolysis. Heating (around 100 ℃) triacylglycerols with aqueous solution of sodium hydroxide results in glycerol and alkaline salt of fatty acid (i.e. soap) (Figure 3-1-1). This is called saponification, and used for production of soap.

3-2 Hydrogenation

Number of double bonds in oils and fats affects physical property such as melting point, crystallinity. Generally, double bonds reduce the oil's melting point. Therefore, oils rich in unsaturated fatty acids are liquid, while ones with small amount of unsaturated fatty acids are solid or semi-solid.

Hydrogenation is a process to add hydrogen atoms into double bonds of unsaturated fatty acids (Figure 3-2-1). As the result of hydrogenation, liquid oil becomes solid or semi-solid. A typical example of hydrogenation is in the process of margarine and shortening production. Vegetable oil is hydrogenated with gaseous H_2 in the presence of a metal catalyst (usually nickel catalyst). If the hydrogenation is completely performed, all the double bounds are

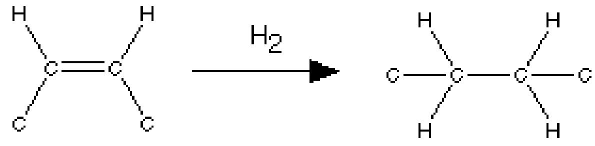

Figure 3-2-1: Hydrogenation.

converted to the saturated ones with the same carbon number. For example, complete hydrogenation of linoleic acid (18:2 ω-6) generates stearic acid (18:0) (Figure 3-2-2).

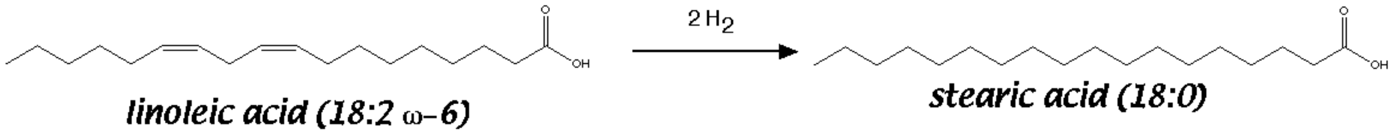

Figure 3-2-2: Complete hydrogenation of linoleic acid, giving stearic acid.

Vegetable oil is too soft for margarine or shortening because it is liquid. Saturated fat obtained by complete hydrogenation is too hard. Margarine requires something in the middle, i.e. not too hard but not too soft. Margarine and shortening makers "partially hydrogenate" their product. They only add hydrogen atoms until the oil is at the desired consistency. During the hydrogenation process, hydrogen atoms are inserted in no particular order. When they stop the incomplete hydrogenation process, unsaturated fatty acids are in varying stages of hydrogenation. Some molecules are mostly hydrogenated, while others are not. And the double bonds have often shifted to unnatural positions, resulting in the generation of *trans* fatty acids or *trans* fat, which is thought to increase risk of coronary heart disease.

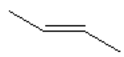

Figure 3-2-3: *Trans*(or *E*) double bond structure of *trans* fatty acids.

In 2003, Food and Drug Administration (FDA) in USA issued a regulation requiring manufacturers to list *trans* fat, on the Nutrition Facts panel of foods and some dietary supplements (Figure 3-2-4). With this rule, consumers have more information to make healthier food choices that could lower their consumption of *trans* fat as part of a heart-healthy diet.


Nutrition Facts
Serving Size 1 cup(228g)
Serving Per Container 2

Amount Per Serving		
Calories 260	Calories from Fat 120	
		% Daily Value*
Total Fat 13g		**20%**
Saturated Fat 5g		**25%**
Trans Fat 2g		
Cholesterol 30mg		**10%**
Sodium 660mg		**28%**
Total Carbohydrate		**10%**
Dietary Fiber 0g		**0%**
Sugars 5g		
Protein 5g		
Vitamin A 4%	•	Vitamin C 2%
Calcium 15%	•	Iron 4%

* Percent Daily Values are based on a 2,000 calories diet. Your Daily Values may be higher or lower depending on your calories needs:

	Calories:	2,000	2,500
Total Fat	Less than	65g	80g
Sat Fat	Less than	20g	25g
Cholesterol	Less than	300mg	300mg
Sodium	Less than	2400mg	2400mg
Total Carbohydrate		300g	375g
Dietary Fiber		25g	30g

Calories per gram:
Fat 9 • Carbohydrate 4 • Protein 4

Figure 3-2-4: Nutrition Facts panel of a food indicating the *trans* fat content

3-3 Transesterification

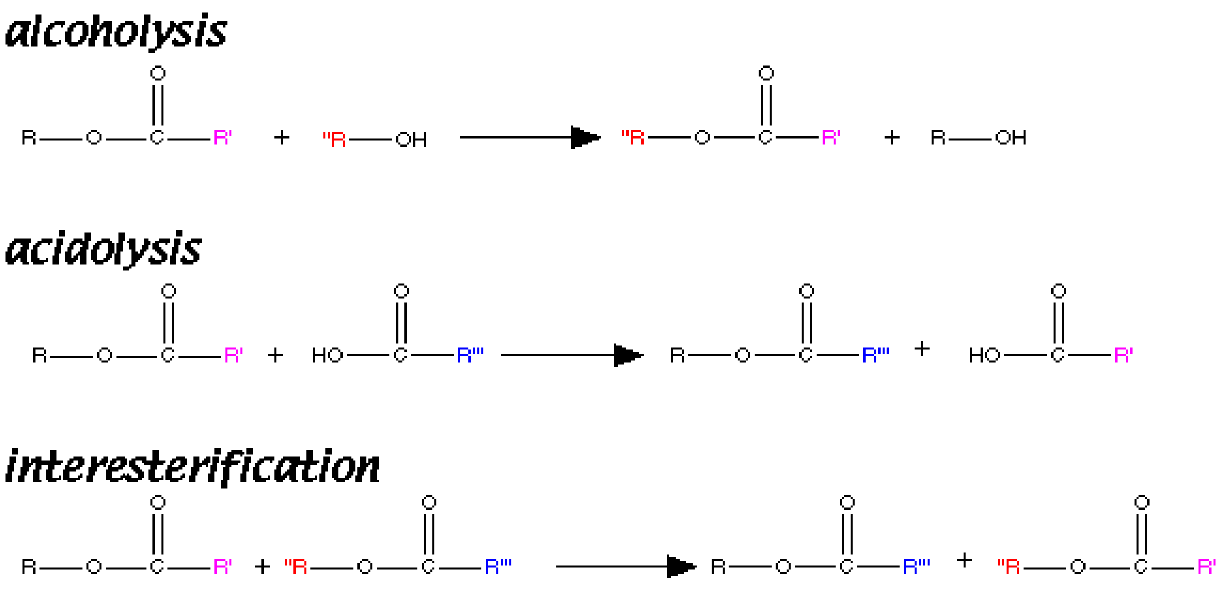

Figure 3-3-1: Transesterification.

Transesterificaton includes chemical reactions where an ester is reacted with alcohol (alcoholysis), acid (acidolysis), or another ester (intereseterification or ester exchange), to generate a new ester (Figure 3-3-1).

3-3-1 Alcoholysis

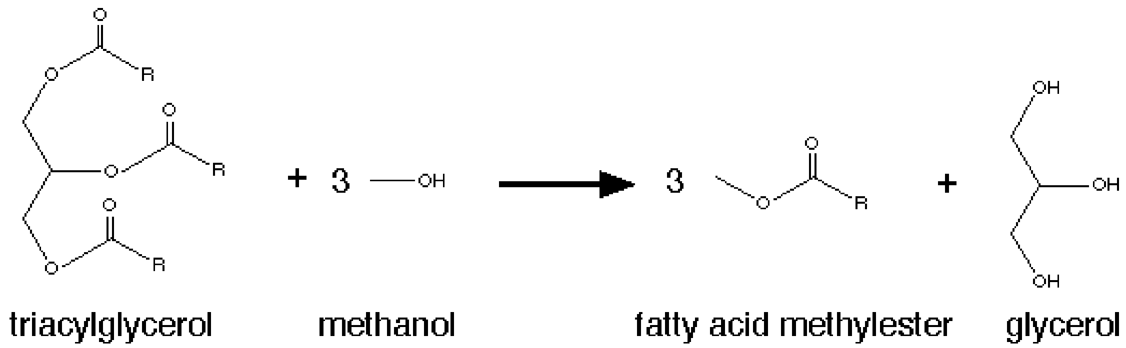

Figure 3-3-2: Methanolysis of oil for the production of fatty acid methylester.

When methanol is used in alcoholysis, the reaction is called methanolysis, in which fatty acid methyl ester and glycerol are generated (Figure 3-3-2). Fatty acid methyl esters can be used as an alternative fuel for diesel engine (biodiesel). Biodiesel is a substitute or extender for traditional petroleum diesel. It can be used in conventional diesel engines, and the use of biodiesel is advantageous for reducing emission of CO_2, CO, SO_2 and particle materials. Biodiesel is now spreading world wide. For example, in France, all the diesel fuel marketed contains 5% of biodiesel.

Another example of alcoholysis is glycerolysis, where triacylglycerol is reacted with glycerol (alcohol) in the presence of alkaline catalyst to form partial glyceride such as monoacylglycerol. A mixture of triacylglycerol and glycerol are heated at 200-250 ℃ in the presence of sodium hydroxide. The resulting main product is monoacylglycerol, which is used as food emulsifier after purification by molecular distillation.

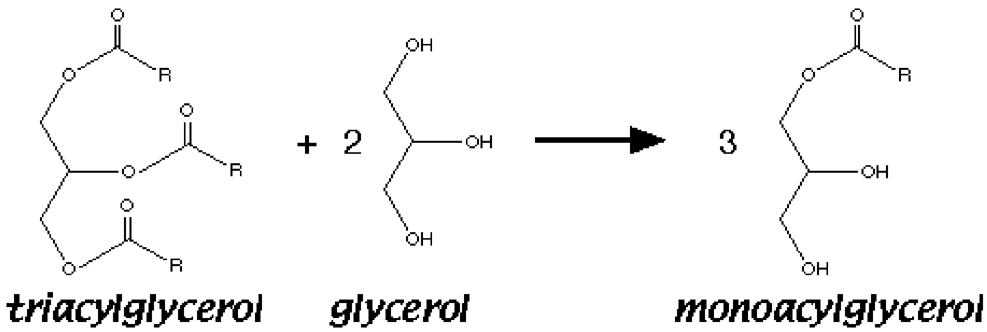

Figure 3-3-3: Glycerolysis. In practical process, the product is a mixture of mono- and diacylglycerols.

3-3-2 Acidolysis

An industrial application of acidolysis is production of long chain fatty acid vinylesters from vinylacetate (this is obtained by chemical reaction of ethylene and acetic acid) and fatty

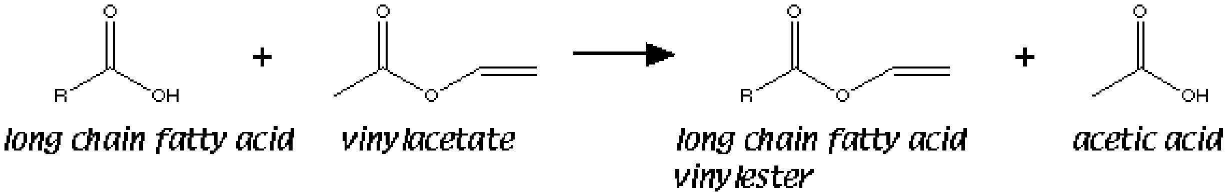

Figure 3-3-4: Production of fatty acid vinyl ester by acidolysis.

acids. Long chain fatty acid vinyl esters are industrial raw material for making plastics (Figure 3-3-4).

3-3-3 Interesterification

Interesterification of oil changes its molecular composition. Oils or fats are mixture of various triacylglycerol molecules having different fatty acids and positional distribution. Treating oils and fats with sodium methoxide as a catalyst at 80 ℃ causes intermolecule ester exchange, changing the molecular composition, while leaving the fatty acid composition unchanged. As a result, the oil changes its physical properties such as melting point and consistency.

An important application of interesterification is improvement of natural lard (pig fat). Natural lard tends to form a rough crystal, which is difficult to handle, during storage. This is because 64% of palmitic acid is attached to 2nd position of triacylglycerol molecules. Randomizing the positional distribution of fatty acids of natural lard by interesterification improves its physical property, making it a smooth "rearranged lard".

Another example of interesterification is in the field of margarine production. Interesterification of soybean oil and completely hydrogenated soybean oil provides a material for margarine. This rearranged oil has an advantage that it does not contain *trans* fatty acid, because it is not made through partial hydrogenation.

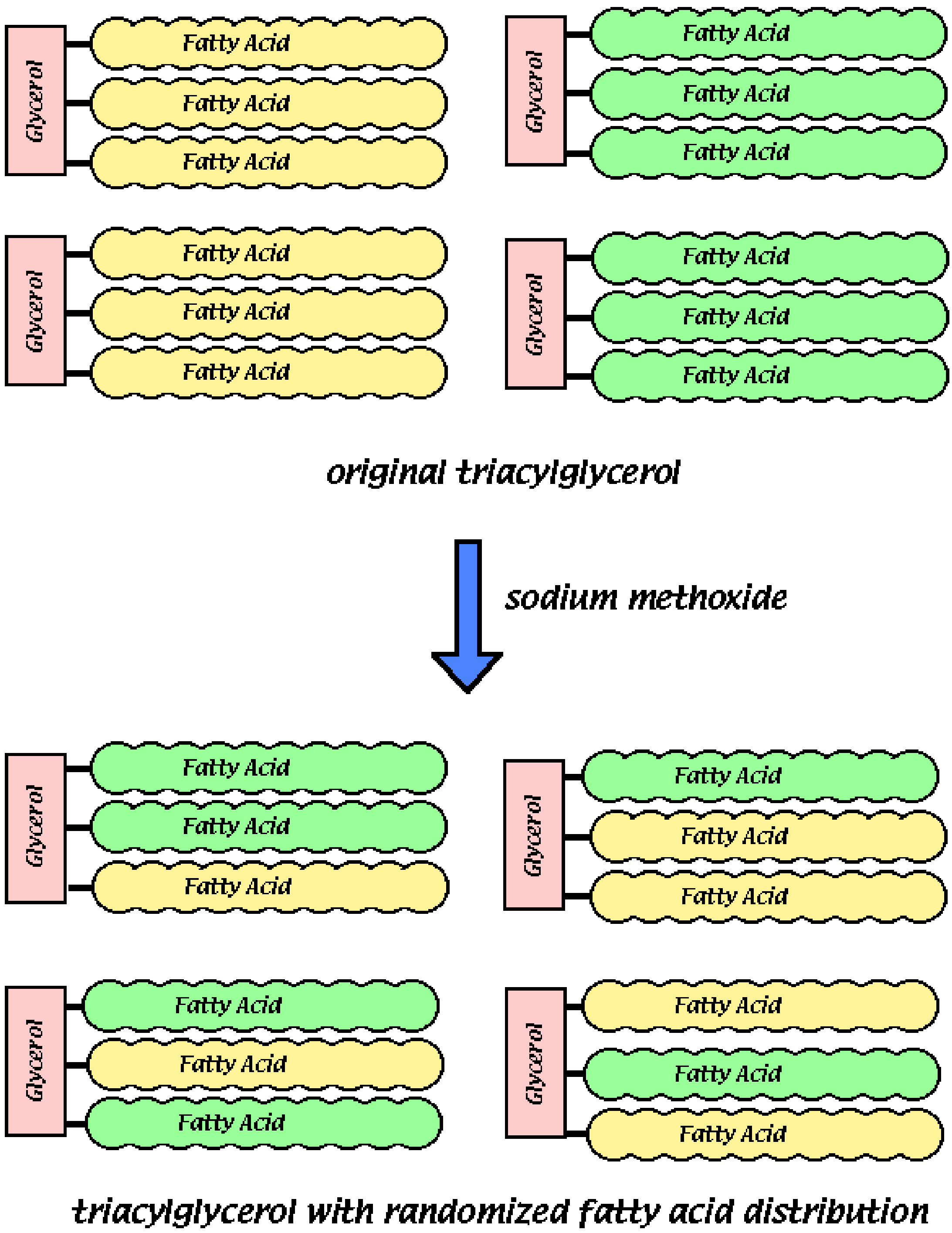

Figure 3-3-5: Interesterification of triacylglycerol molecules. Fatty acid distribution is randomized, resulting in the change of the physical property of the oil.