

Chapter 1

General Introduction

In recent years, functional and nutritional oils and fats have commercial interest. Polyunsaturated fatty acids, like eicosapentaenoic acid (EPA) and docosahexenoic acid (DHA) have been reported to have beneficial and nutritional effects. EPA and DHA reduce the level of low-density lipoprotein in human⁷⁹⁾. And it was also determined that EPA and DHA have several medical benefits for allergies, diabetes and cancer^{9,33,91,95)}. Medium chain fatty acid triglycerides (MCT) composed of caprylic acid and capric acid are known to have nutritional function. MCT are more rapidly absorbed and utilized for energy than long chain fatty acid triglycerides (LCT). MCT is commonly used in the diets of patients with pancreatic deficiency, premature infants and surgery patients⁷⁰⁾. Betapol is the human milk fat substitute produced by Unilever. In human milk, palmitic acid is the most abundant saturated fatty acid and about 70% of palmitic acid is positioned at the *sn*-2 position of the glycerol backbone. Therefore, the main composition of fat of Betapol is the triglyceride, which consists of palmitic acid at *sn*-2 position and unsaturated fatty acids in *sn*-1 and 3 positions. It was indicated that Betapol leads to improve bone mineral density in infants³⁸⁾. In foods area, cacao butter equivalent (CBE) and low calorie fats are well known as functional oils. CBE has been studied in several years to modify physical properties of conventional fats to utilize as chocolate fat. Low calorie fats like Salatrim and Caprenin are already used for confectionery industries. Salatrim was developed by Nabisco Foods Group. The structure of Salatrim is triglycerides constituting mixtures of long chain (C18:0) and short chain (C3:0 and C4:0) fatty acids randomly esterified to glycerol. Caprenin was developed by Procter & Gamble. The structure of Caprenin is a randomly structured lipid containing behenic acid (C22:0) obtained from hydrogenated rapeseed oil and two medium chain fatty acids (C6:0 and C8:0) from coconut and palm kernel oils. Both fats provide 5 Cal/g, which is very low compared with typical fats (9 Cal/g)³⁸⁾.

These physical and nutritional properties of fats and oils are related to the fatty acid composition and positional distribution of the acyl groups bonded to the glycerol.

It means triglycerides quality can be improved by controlling their fatty acid composition. Interesterification is one of the methods to improve triglycerides quality. Interesterification is the exchange of acylgroups, between an ester and an acid (acidolysis), an ester and an alcohol (alcoholysis), or an ester and an ester (transesterification). Chemical interesterification catalyzed by alkali metals or alkali metal alkylates requires high temperatures. By this process, the fatty acids in the triglycerides are exchanged randomly, and side reaction takes place⁸⁷⁾. Enzymatic processing with lipase is a useful technique for the production of functional valuable fats and oils, because of their specificity and high activity at low temperatures, having many advantages compared to conventional chemical processing⁹²⁾. Several methods for interesterification using lipase have been studied, and lipase modification by polyethylene glycol^{46,102)}, covalent attachment of fatty acid⁷⁵⁾, and immobilization on anion exchange resins⁷⁶⁾ were developed. However, in many cases, reaction rate is not sufficient, and side reaction products (diglycerides and monoglycerides) are produced due to addition of water. In the last few years, researchers have studied surfactant-modified lipase, which is a complex of lipase and surfactant⁸²⁾. The surfactant-modified lipase was obtained by the aggregation of lipase and surfactant in water. It was assumed that the hydrophilic radicals of the surfactant attached to the lipase surface and the hydrophobic radicals arranged themselves on the outer side of the lipase. By this modification, the lipase becomes soluble or well dispersed in the organic solvent and can have a high activity in the organic solvent. Modified lipase had interesterification activity at low water content, then, the side reaction was limited. The modification process was very simple, special equipment and facilities were not required to produce. To consider foods application, the raw materials for modification and immobilization have to be desirable foods grade. The surfactant-modified lipase would be made with foods grade lipase and surfactant. Further in my previous study, the surfactant-modified lipase showed a much higher interesterification activity than the original lipase and surfactant mixture. The surfactant-modified

lipase may have a lot of benefits for food application, then, the characteristics and the activity of the surfactant-modified lipase have been studied.

In this thesis, the interesterification activities of modified lipase in organic solvent for various kinds of lipases and surfactants were investigated. The best combination for a surfactant-modified lipase to reach the highest activity and protein recovery is proposed. And to optimize reaction condition, specificity and activity of the modified lipase and the effect of water content in the reaction system on the activity were investigated. To evaluate and simulate modified lipase activity, interesterification kinetics of fatty acids and triglycerides and interesterification kinetics of triglycerides were studied. To develop practical production process, the continuous membrane reactor system for the interesterification between triglyceride and fatty acid was proposed. Furthermore, a non-solvent system is very useful for the commercial production of functional fats and oils, since it is safe, cost effective and environmental friendly. The interesterification between triglycerides in a non-solvent system with surfactant-modified lipase was investigated.