Introduction

The fatty acid glycerylesters are one of the most important class of food additives used as emulsifiers. The term emulsifier is often used interchangeably with surface active agent or surfactant. Most of the food emulsifiers are esters or modified esters formed by the combination of polyalcohols with edible fatty acids or fats.Food emulsifier serves many additional functions, besides affecting solubility and miscibilty behavior. There is a limited number of natural emulsifiers which are used in food as such or after modification. On the other hand the emulsifiers used are mostly synthetic. These are usually made by either alcoholysis or direct esterification. When glycerol is used, the process is called glycerolysis. Mono-and diglycerides are the most commonly used food emulsifiers.

Emulsifiers perform one or more functions in a specific system. In many cases, it is necessary to combine two or more emulsifiers to accomplish the desired effect. Often an emulsifier may perform one function at one level and a completely opposite function at another level. In many cases, it becomes necessary to combine the functions of two or more emulsifiers in order to obtain the desired effect in the food . Mono-and diglycerides are used as emulsifiers in a great number of food products such as bread, cakes, cake mixes and also frozen desserts. There are three physical forms of the mono-and diglycerides: hard, soft, and liquid, depending on the type of fatty acid and percentage of monoglyceride content. However, these three types fall under the category of "generally recognized as safe food emulsifiers " "GRAS" .

The ethoxylated esters are a group of emulsifiers, the use of which has grown in the last several years. Ethoxylated mono-and diglycerides are reaction products of 20 moles of ethyleneoxide with mono-and diglycerides. They are used as dough conditioners in yeast-raised baked products in amounts not exceeding 0.5% by weight of the flour used.

Different fatty acid esters, such as glycerol mono stearate, 20 and 40 etho-stearic acid were tested in starch jellies and in high-and low-cook caramels.

Review of Literature

The literature concerning the preparation, stability, estimation and application of edible fatty acid glyceryl esters is quite voluminous . The following is an attempt to summarise the most important literature concerning the mono and diglycerides used as emulsifiers .

Preparation of Partial Glycerides:

Edible fatty acid glyceryl esters are usually made by direct esterification, alcoholysis or enzymatic method. In the direct esterification, fatty acids and polyalcohols are reacted together under controlled conditions to form esters. In alcoholysis, fats are reacted with polyalcohols to make analogous products. For example , the process is called glycerolysis when shortening is reacted with glycerine to form mono-and diglycerides.

1- Direct esterification:

Fatty acid glyceryl esters as edible emulsifiers can be obtained by a synthetic procedure in which the glycerol and fatty acid or fatty acid derivatives are the reactants. It is important to start with pure materials. The presence of saturated acids permits purification of the resulting derivatives by crystalization.

The early attempts for producing emulsifiers containing a high proportion of monoglycerides have been carried out by Hilditch and Rigg (1) in which glycerol was esterified with one or more fatty acids such as stearic, oleic or palmitic in a solvent medium composed of one or more monohydric mononuclear phenols such as phenol or p-cresol in the presence of camphor-B- sulphonic acid as catalyst. As the temperature, the time and the quantity of catalyst increase, the total yield of the reaction product increases and the percentage of monoglycerides falls slightly.

Christensen (2) reported that a mixture of higher fatty acids such as stearic and a glycerate of an alkali-forming metal such as sodium glycerate having at least one free hydroxyl group reacts at about 100-200°C to form mono-and diglycerides.

Kawai (3) reported that lauric, stearic and oleic acids react with glycerol at 170-180° and 230-240°C. Glycerides formed from lauric and oleic acids consisted cheifly of mono-and diglycerids with some amount of triglyceride but those from stearic acid consisted mainly of di-and triglycerides. Glycerides obtained by prolonged heating at 170-180° contained less mono-and diglycerides than those obtained by heating at 230-240°C for a short time.

Blagonravova (4) indicated that in the esterification of oleic acid with glycerol, the use of catalyst (toluene sulphonic acid) is necessary only when low temperature (140°C) is used.

Nakamori (5) has made a fundamental study on glycerides indicating that in the reaction between glycerol and acetic acid, monoacetin is formed first, then diacetin. Also monostearin is formed in the reaction between stearic acid and glycerol (1 : 1.4 mole ratio) at 240-250°C. The reaction mechanism between stearic acid and glycerol in heterogeneous system was discussed and it was concluded that the esterification does not progress at the interface but in the acid layer.

Partial esterification of glycerol with pure oleic, linoleic, linolenic and ricinoleic acids by Wachs and Heine (6) gave glyceride mixtures which upon molecular distillation yielded 40% monoester concentrates.

Chaudhury (7) used NaOH catalyst at 180°, six hours. The ratio of fatty acid to glycerol was 1 : 3. In other experiments he used excess glycerol and a yield from 55 to 60 % was obtained .

Fatty acids used were stearic, palmitic, myristic, lauric, oleic and linoleic. Also he found that monoglyceride could be extracted from an acid free and glycerol free glyceride mixture by the use of 60 % ethyl alcohol and petroleum ether. According to the separation scheme of Buch and Densen (8), the alcohol layer contained monoglycerides, the hydrocarbon layer contained the di-and triglyceries.

Demarq (9) studied the partial esterification of fatty acids. The influence of catalysts, quantity of reagents and temperature were discussed. In 12 analogous tests only 23.2-61.5% of monoglyceride could be obtained from 100 - 200 g. of glycerol for 100g. of stearic acid at 110-225° for 7 hours and varing quantities of $SnCl_2$, H_2SO_4, NaOH or camphor sulphonic acid as catalysts. Two tests with dioxane, as solvent, produced 33.7 and 39.4% of monoglyceride. The best but uneconomical yields were obtained with pyridine as solvent.

Feuge (10) prepared monoglyceride azeotropically by continuous removal of water of esterification using p-toluene sulphonic acid as catalyst. The effect of variables on the composition and yield of glycerides was observed. The yield of esterification with stearic acid was up to 70.1 % monoglyceride, at 100°C. Azeotropic distillation took place with aliphatic hydrocarbon solvents.

Shrivastova and Mehtaa (11) esterified oleic, lauric, myristic and palmitic acids, with glycerol using 0.1 % NaOH as catalyst in presence of an inert CO_2 atmosphere. The glycerol esters thus obtained were fractionated by the method of liquid-solid counter-current distribution of urea adducts.

Hartman (12) studied the esterification rates of the saturated C_8, C_{10}, C_{12}, C_{14}, C_{16}, C_{18}, oleic and linoleic acids at 180°C , with equivalent and equimolar amounts of glycerol with and without a co-solvent. The esterification with equivalent amounts of glycerol without co-solvent followed second order kinetics and proceeded at a similar rate for all acids examined . Esterification with equimolar amounts of glycerol was kinetically complex and the rate depended on the solubility of glycerol in individual fatty acids.

Lazer (13) prepared glycerol mono-oleate by direct esterification of oleic acid. Changes in electric conductance of the reaction were possibly correlated with monoglyceride formation and could be used for automated process control. Direct reaction of fatty acid and glycerol was examined for the preparation of monoglycerides. Effects of different factors, namely, catalyst, time, temperature and reaction solvent on the yield of monoglycerides were investigated.