

RESPONSE SURFACE ANALYSIS OF HIGH FRUCTOSE CORN SYRUP CAKES
EMULSIFIED WITH
SUCROSE ESTERS AND MONO- AND DIGLYCERIDES

by

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(ABSTRACT)

Cakes were formulated with high fructose corn syrup (HFCS) as a replacement (0, 50, and 100% based on weight) for sucrose, and corn oil as a total replacement for hydrogenated vegetable shortening. Two different emulsifiers were used: sucrose esters (SE) or mono- and diglycerides (MDG). Nine different treatment variations were evaluated, which differed according to the level of HFCS (0, 50, and 100%) and the choice of emulsifier (none, MDG, and SE). Objective tests were performed on the cake batters, and both objective and sensory tests were applied to the baked cakes. Microscopic examination of the batter and cake supported the starch gelatinization observed by differential scanning calorimetry (DSC) and the differences in dispersion of the oil phase with and without emulsifiers. Response surface methodology (RSM) was employed to predict

the levels of HFCS required with and without emulsifiers to produce cakes of relatively high volume, moistness, tenderness and low aftertaste.

Cakes prepared with HFCS as a partial or complete replacement for sucrose had acceptable objective and sensory characteristics when sucrose esters were used as the emulsifier and corn oil was used as the lipid source. RSM analysis predicted that a high-volume, moist, tender, and low-aftertaste cake would result if prepared with 3 g SE emulsifier and HFCS at a level of 0 to 38%. In an SE-emulsified cake having total replacement of sucrose by HFCS, RSM predicted a high-volume, moist, and tender cake but with increased aftertaste. However, aftertaste may not be perceptible with the addition of a suitable flavoring to the cake formula.

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I. INTRODUCTION AND OBJECTIVES

Cakes are baked products of sugar, egg, flour, and fat. Each component plays a functional role in determining structure and flavor of the cake. The fat, egg, flour components and the minor ingredients such as emulsifiers and leavening agents contribute to structure formation (Shepherd and Yoell, 1976). Fat acts as a tenderizer, as does sugar, which also serves as a sweetener. Fat also acts to increase the amount of air incorporated into the batter, and fat distribution can be improved by the use of emulsifiers.

A cake batter is a complex emulsion system. In the most common types of cake batters, plastic hydrogenated shortenings are used, and disperse in the aqueous phase as irregularly-shaped particles. Dissolved egg proteins and sugar are present in the batter aqueous phase in which flour particles are suspended. Air bubbles whipped into the batter during preparation are held in the fat phase of the batter until heated to approximately 37°C, whereupon the air passes from the fat to the aqueous phase. During baking, the cake batter expands with the increase in size of air cells, and the structure of the cake heat sets as egg protein coagulates and wheat starch partially gelatinizes. The finished baked cake is a heat-set foam with a light, aerated structure (Shepherd and Yoell, 1976).

Cakes may also be shortened by liquid fat (oil) although oils do not aerate batters very effectively. However, oil-containing batters have been improved with regard to aeration by use of emulsifiers. Emulsifiers function as useful additives in cake formulations and can provide for: greater cake specific volume, improved eating quality due to increased moistness and a more rapid flavor release, better crumb structure, and greater crumb softness (Shepherd and Yoell, 1976). Emulsifiers have been shown to stabilize egg white proteins, but may also influence starch granule swelling or coalescence by complexing with amylose (Cloke, Gordon, and Davis, 1983). Thus, emulsifiers can delay starch gelatinization. It is believed that a high quality cake is produced when starch gelatinizes and protein is denatured at the same temperature (Donovan, 1977). Emulsifiers are known to improve layer cake quality by enhancing air incorporation and shortening dispersion (Ebeler and Walker, 1984). A blend of mono- and diglycerides emulsifiers (MDG) have been used extensively in the food industry, and is the most commonly used emulsifier (Dziezak, 1988). Sucrose ester emulsifiers (SE) have improved high-ratio white layer cake volume and softness (Ebeler and Walker, 1984).

High fructose corn syrup (HFCS) can be used as a replacement for sucrose in cakes (Thompson et al, 1980;

Saussele et al, 1983; Koepsel and Hosenev, 1980; Coleman and Harbers, 1983; McCullough et al, 1986). Corn syrups are currently used to replace sucrose in many bakery products. The use of corn syrups in cakes has not been as successful as in other products (Koepsel and Hosenev, 1980). Some of the problems associated with cakes formulated with HFCS as a partial (25% or greater) replacement for sucrose include: decreased volume, dark color of crust and crumb, loss of tenderness, and coarse texture (Koepsel and Hosenev, 1980; Volpe and Meres, 1976; Coleman and Harbers, 1983). Henry (1976) reported the influence of sugars on decreasing cake volume due to delaying starch gelatinization. Starch gelatinization is an important event occurring during processes such as the baking of cakes. The onset and temperature of starch gelatinization play an important role in determining the final structure of a baked cake and the final volume.

Response surface methodology (RSM) is a statistical technique useful in the food industry. It has been applied to optimizing one or more parameters in a food system as a function of several variables at combinations of levels .

The overall objective of this study was to investigate the interaction of HFCS, corn oil, and added emulsifier in a cake and to optimize the product via Response Surface Methodology (RSM). To accomplish this objective, a

preliminary (pilot) study was conducted to examine whether HFCS and corn oil acted independently in contributing to cake objective and sensory parameters. Also, the level of emulsifier (MDG and SE) required to produce an optimum cake formulated with HFCS and corn oil was determined. Then, the effects of HFCS and the emulsifier on certain objective and sensory cake parameters were studied. RSM was used to predict the levels of HFCS with and without emulsifier required to satisfy a set of simultaneously optimized response variables.

II. REVIEW OF LITERATURE

Functions of Cake Ingredients

The ingredients in a standard shortened cake include wheat flour, sugar, shortening, liquid, egg, and leavening (Bennion, 1985). Both the cake batter and the baked cake can be viewed as foams, one mobile and the other rigid (Charley, 1970). Ingredients can serve as one or more of the following: tougheners, tenderizers, moisteners, driers, and flavorers (Pyler, 1973). Success in cake making depends on the formula, the quality of the ingredients, the mixing method, and the baking procedure (Griswold, 1960).

Flour: Flour Protein.

For cakes, short patent "soft" wheat flours of low protein content are used. Short patent flours yield a soft gluten on hydration which does not toughen during mixing, yet possess enough strength to form the fine foam cake structure (Pyler, 1973). Such flours are marketed as "cake flours". Cake flours, because of small flour particle size yield cakes with small cells which contributes to the formation of a fine, even grain and velvety texture. Cakes made from cake flour also have greater moisture-absorbing capacity than those made from all-purpose flour (Griswold, 1960). Flour is a source of protein, starch, and some

lipid, all of which contribute to cake structure and provide calories and nutrients. The gelatinized starch is probably more important to structure than the small amount of gluten developed by the flour. Flour starch and proteins are moisture binders and are classified as driers or tougheners (Paton et al, 1981). Cake flours are usually bleached with a high dosage of chlorine gas. Chlorinated flour produces a cake of increased cake volume and may alter some of the flour lipids (Bennion, 1985). Volume increase may be due to increased soluble protein content (Shepherd and Yoell, 1976).

Flour: Starch.

Starch is the major component of wheat flour, and its properties greatly influence the outcome of baked goods including cakes (Hoseney et al, 1983). Starch in cake acts as a water binder to help set the final baked structure. Since starch, protein, and sugar all compete for water, formula balance between liquid and dry ingredients is critical. Complex chemical and physical interactions can occur with starch in-food systems. Texture, viscosity, and stability are known to be influenced by the percent and molecular weight of the starch components amylose and amylopectin (Luallen, 1988).

During baking, starch undergoes a process called gelatinization, wherein the organized granule structures are disrupted (Zobel et al, 1988). The starch source, its environment (presence of water, sugar, emulsifiers) and treatment (temperature, pH) all can affect its gelatinization characteristics which in turn affects the baked product (Glover et al, 1986). Unaltered, native wheat starch granules are required for optimal results in cake baking (Howard et al, 1968) because treatments such as heat-moisture application can cause granule damage (Kulp and Lorenze, 1981). The ability of starch to produce a viscous paste when heated in water is its most important practical property (Swinkels, 1985).

Sucrose/High Fructose Corn Syrup

Sucrose (Figure 1a) not only provides sweetness and calories in a cake but influences texture and volume. It interferes with gluten development from the flour proteins and weakens (tenderizes) the cake structure. Most likely this is due to the attraction of sucrose for water, which otherwise would be absorbed by the gluten proteins (Bennion, 1985). Sucrose elevates the temperature at which egg proteins coagulate during baking and also the temperature at which starch gelatinizes (Charley, 1970). Sucrose also allows for the incorporation of air into fats as they are

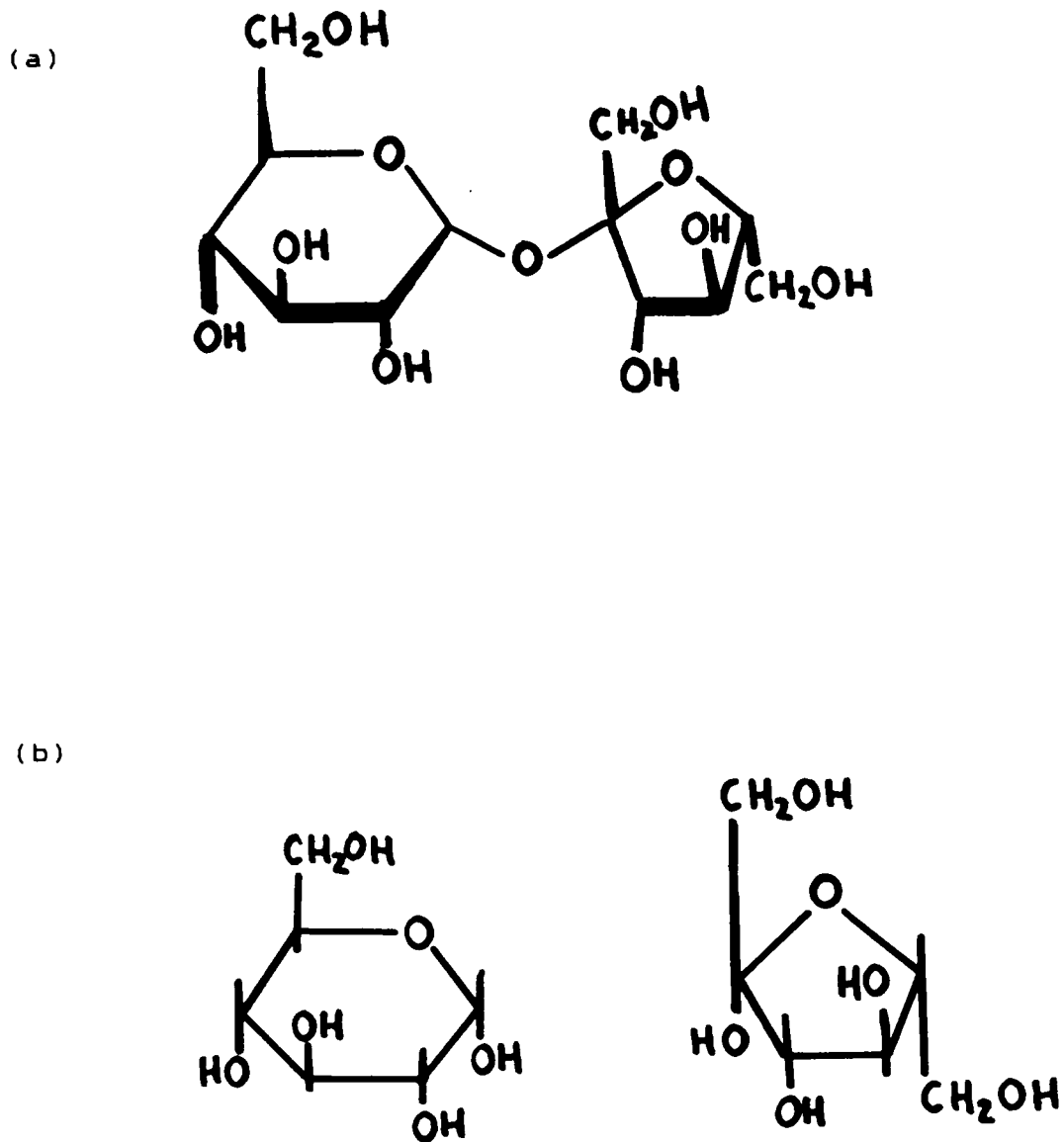


Figure 1. Structures of saccharides.

- (a) sucrose, a disaccharide
 (b) component monosaccharides of HFCS: glucose and fructose

creamed. Sugars must be in crystalline form to accomplish this, as the air which is generated during mixing adheres to faces of the sugar crystals and is introduced as small bubbles ("cells") into the fat (Griswold, 1960).

During baking, sucrose decreases the cohesive forces in batter allowing it to move more freely, and increasing the volume of the cake (Bennion, 1985). The cohesive force results from the opposing action of toughening ingredients (flour, egg white) and tenderizing (sugar and shortening) ingredients (Paton et al, 1981).

When heated, saccharides are involved in reactions which result in browning of the cake crust. The caramelization reaction occurs as sugars are heated, dehydrated, and melted into a colorless liquid that develops a brown color. Maillard reactions require reducing sugars which contain a carbonyl group and a free amine group and occur at lower temperatures than caramelization (Shelton and D'Appolonia, 1985).

Saccharides in the form of sucrose also act as flavor enhancers and shelf-life extenders (Ash, 1979). The high osmotic pressure of the sugar in solution lowers the water activity and is a major factor in suppressing microbiological spoilage (Shepherd and Yoell, 1976). The intensity of flavor contribution is determined by the kind of sugar (sucrose, glucose, fructose, lactose, etc.).

High fructose corn syrup (HFCS) (Figure 1b) is called a high dextrose equivalent (DE) sweetener. HFCS possesses functional properties that differ from those of sucrose. HFCS is the sweetest of the corn syrups although the intensity of its sweet taste is variable and depends upon the temperature, concentration, and pH (Horn, 1981). The presence of fructose in HFCS produces high hygroscopicity, or the tendency to absorb and retain moisture. Humectancy, which Horn (1981) defines as the resistance to change in moisture content, is a property of low DE corn sweeteners. Because HFCS contains molecules in solution, it exhibits the colligative properties of freezing point depression, boiling point elevation, and osmotic pressure.

The monosaccharides in HFCS (Figure 1b) are directly fermentable by microbes. The rapid reactivity of HFCS to browning is a consequence of the monosaccharide content of HFCS and has been documented by many researchers (Coleman and Harbers, 1983; Harris and Johnson, 1987; Koepsel and Hosney, 1980; and Saussele et al, 1983). Maillard browning, a nonenzymatic reaction, forms hexose-amines, which subsequently rearrange to high molecular weight pigments (Figure 2). Caramelization, a dehydration reaction previously mentioned will result after heating. Either browning reaction produces a vast array of end products, the mechanisms leading to their formation still largely unknown

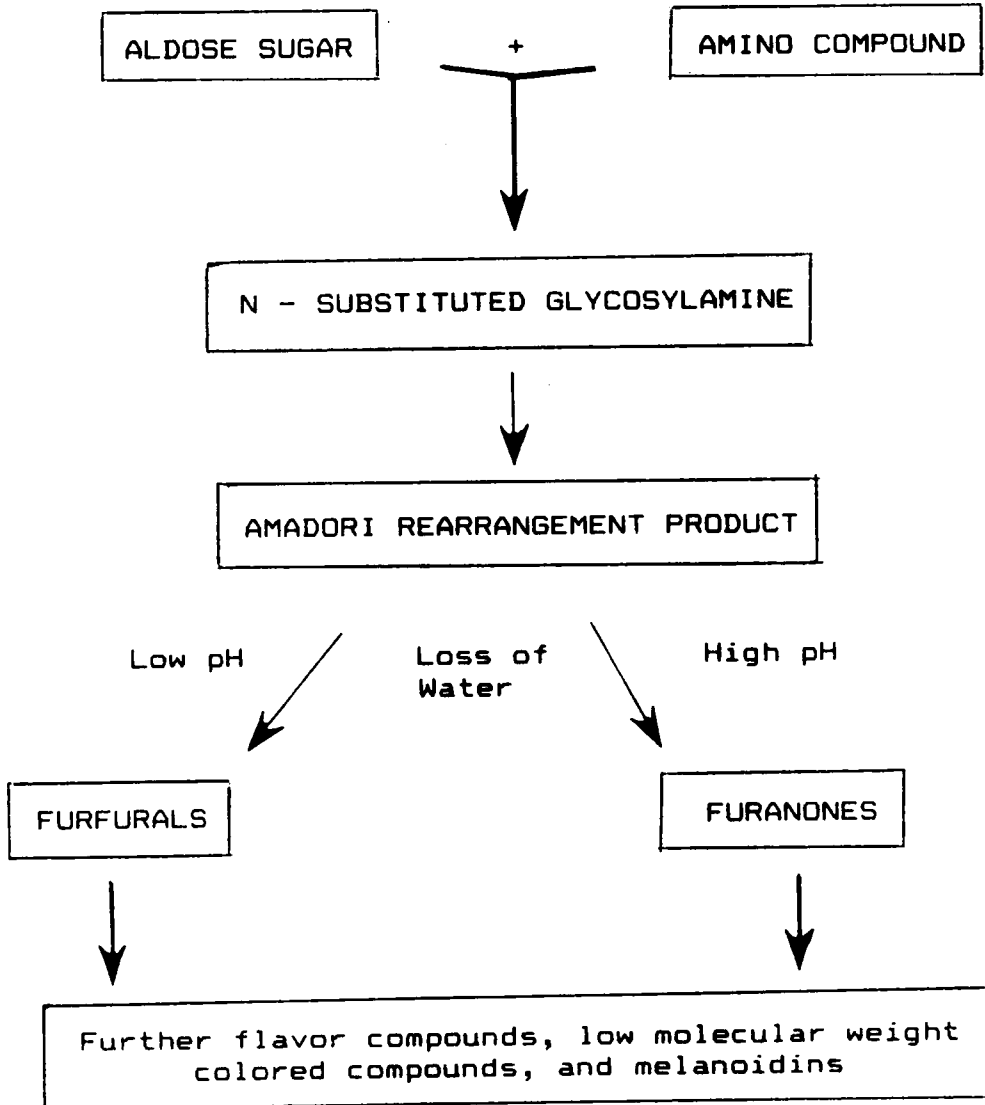


Figure 2. Outline of the Maillard reaction.

(Horn, 1981).

High fructose corn syrup supplies the same energy as sucrose, and has been applied as direct and total replacement for sucrose in many instances. The higher DE corn syrup HFCS has been utilized in products such as beverages, fillings and icings, soft candies and confectionary (Luallen, 1988).

Shortening/Oil

Shortening is a hydrogenated fat, which may be of a plant source or a combination of plant and animal lipid. Hydrogen is reacted with a nickel catalyst to create a semisolid, plastic fat. According to Pyler (1973) fat in cake performs three basic functions: air entrapment during creaming, lubrication of protein and starch causing crumb "shortness" or tenderness, and the emulsification and holding of liquids in the baking cake, thereby increasing its softness. Fat-enclosed air cells collect water vapor and carbon dioxide released during baking, which expand to produce the volume and cell structure of the baked cake. Thus, fat acts as a leavening agent, a tenderizer, and an emulsifier ingredient. Fats also serve as mediums for heat transfer during baking (Bennion, 1985). They supply calories, improve moistness, and extend shelf-life.

The ability of a shortening to aerate the batter is related to its crystalline form (Painter, 1981). Fats can occur in several crystalline forms: alpha, beta prime, intermediate, and beta (Birnbaum, 1978). The crystalline form most suitable for cakemaking is the beta prime, because of the oil absorbing capability of these small rosette-like crystals, which alternate in rows of opposing orientation when depicted in cross-section (see Figure 3 from Birnbaum, 1978). Thus, the beta prime shortenings have been characterized as being smooth and creamy with excellent aerating capabilities (Hartnett, 1977).

Cakes prepared with lard compare unfavorably with those made with hydrogenated vegetable shortening. This is due to its inability to hold air, a consequence of the stability of the large beta crystal form. A disadvantage of using butter for the fat source is the narrow plastic range (Charley, 1970). The difference in plastic range of butter versus other fats is related to the fatty acid composition and the fact that shortening is composed of liquid oil and fat crystals only, while butter contains liquid oil, fat crystals, and water droplets (Juriaanse and Heertje, 1988). Hydrogenated vegetable shortenings maintain desirable plasticity over a wide temperature range, and butter either hardens or softens excessively within a relatively narrow temperature span.

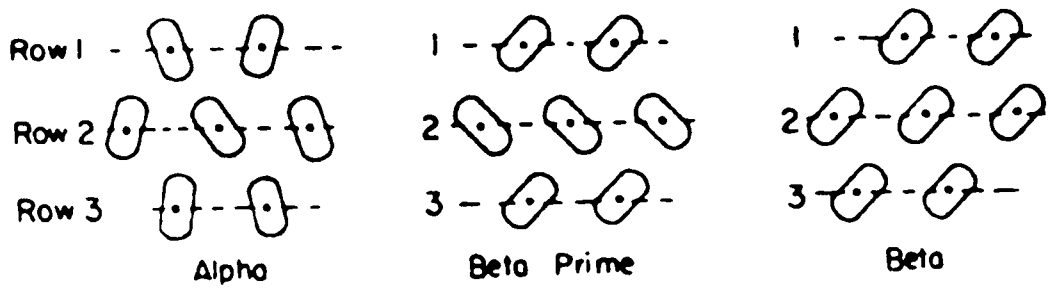


Figure 3. Cross-section of three common fat crystals (from Birnbaum, 1978).

Regarding the use of an oil or a liquid fat as the shortening ingredient in plain cakes, it has been generally accepted that oil produces a cake of poor quality (Ohlrogge and Sunderlin, 1948). Vegetable oils do not hold air during creaming (Griswold, 1960; Hartnett and Thalheimer, 1979) and result in cakes with poor volume and harsh crumb (Vaisey-Genser and Ylimaki, 1989). However, if the mixing procedure used is the muffin method (Griswold, 1960) or conventional sponge method wherein the egg whites are whipped separately and added last, a satisfactory cake can result (Ohlrogge and Sunderlin, 1948).

In addition, there has been an increase in the usage of fluid or liquid shortening in cakes with the advent of emulsifier technology (Baldwin et al, 1972; Hartnett, 1977; Hartnett and Thalheimer, 1979). Rasper and Kamel (1989) found that emulsifiers overcame the negatives associated with the use of oil in cakes, and that emulsifiers reduced the amount of oil required in a cake formula.

Butter with and without emulsifier (mono- and diglyceride) was studied for its ability to function in plain cake as a shortening by Hunt and Green (1955). They reported that fat was well-dispersed, interfaces between fat and aqueous phases were distinct, and air bubbles were more evenly distributed with added emulsifier. The mono- and diglycerides were added to butter at a level of 3.5%.

Emulsified batters were of thinner consistency and higher specific gravity than butter-only controls, indicating that less air was incorporated. However, the average cake cross-sectional areas were obtained with the emulsified cake batters.

Guy and Vettel (1973) examined cakes prepared with butter, commercial cake shortening, and a 50/50 blend. A 2.5% level (basis flour) of Atmul 80/Atmul 84 emulsifier blend was added or left out of some butter formulations. Butter cakes had 5 to 10 percent lower volumes than cakes made with shortening, but volumes were equal or greater than shortened controls if emulsifier was added. Additionally, flavor and softness were superior in all the butter cakes. Since the cakes containing a blend of butter and shortening more closely matched the all-shortening cakes, the authors recommended use of all-butter (emulsified) to produce a superior quality cake.

In a study of emulsified vs. unemulsified beef tallow as a shortening, Bundy and co-workers (1981) found that beef tallow plus emulsifier could be substituted for vegetable shortening in white layer cake without adverse effects. No significant differences were found for volume, compressibility, tenderness, and sensory evaluation. However, the unemulsified tallow cakes were of inferior quality.

According to Knightly (1981), the use of oil as a shortening replacer in cakes offers too many advantages to be ignored. These include: (1) oil readily blends cold into powders or fluid batters; (2) oil can be transported, stored and pumped without using costly heating or agitation equipment; (3) lower usage levels result in significant cost reductions; and (4) vegetable oil appeals to the nutrition-conscious consumer as it is polyunsaturated and cholesterol-free.

Vaisey-Genser et al (1987) successfully replaced hydrogenated shortening in layer cakes with canola oil. Multiple contour maps derived through response-surface methodology showed optimum levels of water, oil, and emulsifier. Water levels had to be adjusted because the fat level was manipulated to suit the emulsifier. The emulsified oil cakes were fragile to handle, but possessed improved volume and moistness. All canola oil cakes were successful with 16.9% of water and 9.5% emulsifier with 10.5% oil (flour basis). Increasing the oil level was disadvantageous to volume, flavor, and specific gravity.

In a later paper, Vaisey-Genser and Ylimaki (1989) reiterated the need for careful balancing of oil, water, and surfactant system in reduced-fat cake systems, which can be developed into "lite" cake formulations. Rasper and Kamel (1989) tested several emulsifiers at the 3% level (flour

basis) with corn or canola oil reduced as low as 6% in reduced-calorie cake formulation. Sucrose (30%) was replaced with either sorbitol or polydextrose. Water content had to be increased to 120%, but at that level 6% oil cakes emulsified with a combination of sodium stearoyl lactylate, sorbitan monostearate, and Polysorbate 60 compared favorably with plastic shortening controls in volume, crumb firmness, and moisture.

Eggs

Eggs function in various ways to contribute to cake structure and quality. According to Pyler (1973), these include: (1) binding action of egg white proteins and egg yolk proteins which are able to whip into foams and also coagulate into structural networks during baking; (2) leavening action of the foam, wherein air bubbles entrapped during whipping expand during heating, which increases the volume of the foam; (3) tenderizing action of egg yolk lipids with lecithin as an emulsifying agent; (4) flavor; (5) color; and (6) calories.

Eggs are approximately two-thirds egg white and one-third yolk. Taken separately, egg whites are tougheners, while egg yolks are tenderizers. Egg white is mostly water plus 12% solids, mainly protein. The major protein fractions are ovalbumin (54%), conalbumin (13%), ovomucoid

(11%), globulin (8%), lysozyme (3.5%), and ovomucin (1.5%). It is believed that the globulin fraction produces foam, ovomucin helps stabilize the foam, and ovalbumin and conalbumin provide the necessary heat-setting proteins (Shepherd and Yoell, 1976).

The egg white proteins are denatured and coagulated by both the mechanical forces of beating and by heating to stabilize the foam that beaten egg whites produce (Bennion, 1985). When beaten egg whites or whole beaten eggs are added at the end of the mixing process to a batter, the quality of cakes made with oil can be improved (Ohlrogge and Sunderlin, 1948).

Fresh eggs are preferable to older eggs since the whites are thicker and a more stable foam is produced. The cohesive forces in a baking cake batter increase as egg white is added in increasing amounts, but decrease as more yolk is added (Paton et al, 1981). The size of eggs used in a formula therefore affects the outcome of the cake. For this reason, in experimental work the amount of whole egg or its components are always weighed or measured (Charley, 1970).

Fresh egg whites, having a moisture content of 85 percent, serve as moisteners, whereas egg yolk is only 49 percent moisture but 32 percent fat and 16 percent protein (Pyler, 1973). Egg yolk contains two lipoprotein classes

and a mixture of globular proteins called livetins. Yolk is also composed of phospholipid, triglyceride, and cholesterol; yolk performs both batter emulsification and aeration (Shepherd and Yoell, 1976).

Emulsifiers

Emulsifying agents in cake batter have several functions, as listed by Dziezak (1988): (1) to promote emulsion stability, stabilize aerated systems, and control agglomeration of fat; (2) to modify texture, shelf life, and rheological properties by complexing with starch and protein components; and (3) to improve the texture of fat-based foods by controlling the polymorphism of fats. The choice of selecting a particular emulsifier for an application is made based on its solubility in the continuous phase of the emulsion.

According to Pyler (1973), hydrophilic (water soluble) emulsifiers in general prove more effective overall when used in cake shortenings than will lipophilic (fat soluble) emulsifiers. Lipophilic emulsifiers may inhibit water absorption by flour protein and starch by forming a moisture barrier coating around them (Garti et al, 1981). Also, classes of emulsifiers which are so-called alpha-tending, are thought to prevent oil or shortening-induced destabilization of the protein foam formed during the mixing

of a cake batter (Wootton et al, 1967).

Howard and co-workers (1966) showed that emulsifiers exhibit polymorphism, the ability to exist in different crystal forms. They found that emulsifiers of the alpha-tending variety acted to enhance air incorporation into batters by increasing the strength of the interfacial films formed due to their presence.

The amount of emulsifier added to shortening is often minute, a fraction of a gram being sufficient in some batters. Cakes baked with properly selected emulsifiers can have improved volume, grain, texture, moistness, and shelf-life compared to non-emulsified cakes.

Leavening Agents

Cakes attain their light texture through the formation of many gas bubbles throughout the batter. These gas bubbles or cells eventually become the grain of the baked cake. Baking powders are leavening agents used to release carbon dioxide gas (CO_2). Common reactions are a combination of an acid salt and bicarbonate to release CO_2 . Carbon dioxide must be released at just the right time during batter preparation and subsequent baking to ensure the desired quality of the cake. Because of the expansion of the gas bubbles during baking, most of the carbon dioxide should be released before crumb structure is set by protein

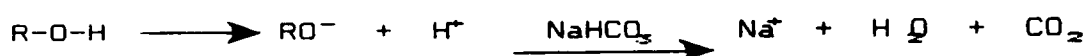
coagulation and starch gelatinization (La Baw, 1982).

Different baking powders (tartrate, phosphate, and combinations) can be grouped according to how fast they release CO_2 . Fast-acting powders such as tartrate and phosphate release most of their gas volume upon contact with liquid; slow-acting powders such as sodium aluminum sulfate (SAS) require oven heat to cause evolution of CO_2 ; and combination or double-acting powders react partly at low temperatures but require elevated temperatures for complete reaction (Pyler, 1973).

Phosphate baking powders contain either calcium phosphate, $\text{Ca}(\text{H}_2\text{PO}_4)_2$ or disodium pyrophosphate, $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$. Tartrate baking powders contain cream of tartar, which is potassium acid tartrate, $\text{KHC}_4\text{H}_4\text{O}_6$, plus tartaric acid, $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$. SAS baking powders contain sodium aluminum sulfate (alum), $\text{NaAl}(\text{SO}_4)_2$. The aluminum ion hydrolyzes on contact with water to form a hydronium ion:



The phosphate and tartrate acid leaveners also react to provide the hydrogen ions necessary to generate CO_2 release from bicarbonate (Meyer, 1960).

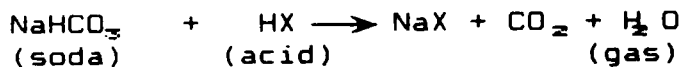


Combination powders which include a fast leavening acid such as monocalcium phosphate (MCP) or sodium acid pyrophosphate (SAPP) in conjunction with a slowly reacting leavening agent such as SAS or dicalcium phosphate dihydrate (DCP) often are best for cake baking (La Baw, 1982). The faster acting leavening acid begins to react almost immediately with the sodium bicarbonate in the baking powder, which increases the density and viscosity of the cake batter. The slower leavening acid reacts with the remaining bicarbonate to further increase cake volume and maintain it as the structure sets during baking.

Cream of tartar (COT) was the first chemical leavener used and dates back to the 1830's (La Baw, 1982). The rate of the evolution of CO_2 is very fast with COT and bicarbonate when compared to other leaveners. In cakes, COT produces a more tender and whiter crumb, enhances sweetness, prevents shrinkage, diminishes Maillard browning, and stabilizes egg white foam to allow for adequate protein coagulation during baking (Bennion, 1985). These functions relate to the acid nature of cream of tartar, which imparts its acidity to the batter.

Water/Liquid

Liquid in cake batter dissolves sugar and makes possible this reaction of soda and acid in the baking powder (La Baw, 1982):



In addition, liquid disperses the fat and the flour particles and hydrates the protein and starch (Charley, 1970). This allows for gluten formation and starch gelatinization. Liquid also provides steam which aids in the leavening process.

Whole milk may be used, or water plus nonfat dry milk. Milk solids provide structure, flavor, crust color, and tolerance to ingredient variations (Ash, 1979). They also serve as driers (Pyler, 1973).

According to Leung (1981), water may be associated with food components as (1) strongly bound water; (2) water adsorbed onto hydrophilic sites by weak hydrogen bonding; (3) structural water in solution, gel, or suspension held by weak physical forces; and (4) water in solutions containing small solutes such as sugar and salt, which depress the activity of water. The water content of a food is also important in determining its shelf-life since the rates of chemical change and microbial activity are directly

dependent on the molecular mobility of partially hydrated and soluble solute molecules.

The level of liquid in a batter affects volume, crumb structure, moistness, and top contour of the cake (Wilson and Donelson, 1963). According to Gaines and Donelson (1982), cake batter viscosity is affected by the liquid level. In their study, as the liquid level was increased from 110% to 170%, the batter viscosity fell by a factor of 15.

Formula Balance

Howard (1972) has expressed the importance of balance in describing layer cake formulations as the balancing of the functional properties of each essential ingredient present. Concurrent with this is the need to balance proportions of ingredients in a cake formula.

A proven, satisfactory plain standard cake has, by measure, one third as much fat as sugar, two thirds as much milk as sugar, and about three times as much flour as liquid (Table 1a, from Bennion, 1985).

The proportion of sugar may be increased to equal or exceed flour by weight, as in high-ratio formulas. This, in turn, requires an alteration in the liquid content to preserve the ratio of liquid to sugar, which influences the setting temperature of the batter (Charley, 1970). Pyler

Table 1.

- (a) Standard Cake Formula (from Bennion, 1985)
 (b) Standard Cake Formula (from Pylar, 1973)

(a)

<u>Ingredient</u>	<u>Amounts</u>
Sugar	1 1/2 c
Fat	1/2 c
Milk	1 c
Flour	3 c
Eggs	2
Baking Powder	3 t
Salt	1/2 t
Flavor	1 t

(b)

<u>Ingredient</u>	<u>% by weight of flour</u>
Sugar	29.8%
Flour	21.2%
Fat	11.6%
Whole eggs	12.6%
Milk	22.2%
Baking Powder	1.3%
Salt	0.8%
Flavor	0.5%

(1973) established that the amount of sugar could actually be as high as 140 percent that of flour, so long as the combined liquid content was not exceeded. Once the flour:sugar ratio is chosen the other formula ingredients must be adjusted. Also, Miller et al (1967) found that gummy layers may develop in cakes if too high a liquid level is used. This raises an important point: when the proportion of any one essential cake ingredient is altered by more than 25 percent without a compensatory decrease or increase in another ingredient, the quality of the cake is likely to be poor (Charley, 1970).

According to Pyler (1973), three rules of formula balance are: (1) the sugar weight should not exceed flour weight; (2) the egg weight should exceed the shortening weight; (3) the liquid weight (eggs, milk, water) should exceed slightly the sugar weight. A representative yellow cake (high ratio) is given in Table 1b (Pyler, 1973).

In terms of under- or over-additions of ingredients, Bennion (1985) noted the following: (1) excess sugar causes the cake to fall and produces a coarse texture, a brown and gummy crust, a gummy crumb, and thick cell walls; (2) excess egg gives a rubbery, tough crumb; (3) excess fat weakens cake structure and decreases its volume; (4) too little baking powder gives a compact, heavy cake while too much causes a harsh, gummy crumb, coarse texture, and volume

decrease; (5) too little flour weakens cake structure and makes for a coarse texture; excess flour produces a dry, compact cake which may develop tunnels; and (6) too much liquid produces a moist cake of low volume.

The use of emulsified shortenings in cakes permits higher levels of sugar and water to be used (King and Olejko, 1989). However, too much emulsifier can be disastrous in cakes. For example, with an excess of mono- and diglycerides in shortening, a reversal is noted. Batter viscosity drops and cake volume shrinks because the crumb structure is weakened by too fine a dispersion of shortening with excess emulsifier (Birnbaum, 1978)

With proper formula balance, and the aid of artificial sweeteners, high fructose corn syrup, milk replacers, microcrystalline cellulose, and emulsifiers, shortening-free, low-calorie and low-cholesterol cakes are being currently developed in response to consumer preference (Kamel and Washnuik, 1983; Smith, 1984; Waring, 1988).

Emulsions, Emulsifiers, and Emulsion Stability

Emulsions

When two immiscible liquids such as oil and water are mixed together, the mixture readily separates into the individual components. However, mayonnaise, which contains oil, water, and additional ingredients, can be stable over months. The difference is that in mayonnaise is an ingredient which stabilizes the emulsion formed -- known as a stabilizer, surfactant, or emulsifier.

The class of baked foods called cakes may include foam types, those leavened principally with air, those chemically leavened, and other variations (Campbell et al, 1979). They may be either shortened or non-shortened. Cakes are a result of baking the principal raw materials in cake batters: flour, fat, sugar, and egg. Each ingredient plays an important functional role in the structure and eating quality of the cake (Shepherd and Yoell, 1976).

Cakes are considered, in the initial batter phase, to be a complex fat-in-water emulsion system; the aqueous phase containing dissolved sugar and suspended flour particles plus an emulsion of fats or oil (Pohl, 1968). In many cake emulsion systems air bubbles formed during mixing are located in the fat phase instead of the water phase. But during heating of batters, the air bubbles transfer to the

aqueous phase, and by the intermediate stage of baking all the air is held in the aqueous phase foam. The batter expands with the air cells due to thermal expansion and uptake of carbon dioxide (CO_2) from leavening agents. Cake batters depend also on another source of gas for leavening: whipped-in air. Emulsifiers can improve the amount of air that can be whipped into the batter by reducing the surface tension of the aqueous phase. Incorporation of air (aeration) into batter is important in achieving effective utilization of CO_2 and producing baked cake grain uniformity (Handleman, 1961).

In the final stages of baking, the structure of the cake is heat set as the egg protein coagulates and wheat starch undergoes partial gelatinization. The finished baked cake is a heat-set foam with a light, aerated structure with a regular cell structure. The fat, egg, flour components, emulsifiers, and leavening agents all contribute to structure formation (Shepherd and Yoell, 1976). The foam cell walls are due to proteins in batter and it is the integrity of these protein-film walls which determines cake volume and uniformity of appearance. Shortening (fat or oil) in the cake recipe is an antifoam and acts to disrupt foam cells. Emulsifiers can coat the exterior of fat particles to prevent disruption to the protein film (Wootton, 1967).

The cake crumb structure consists of starch and sugar held in a network of flour and egg proteins. Emulsifiers can improve crumb softening and extend shelf life of cakes by their ability to reduce the surface tension of fats and oils and, provide a better dispersibility of the fat phase (Krog, 1983). Crumb softening in cakes also involves retention of moisture, and the rupture of too many starch granules, which may collapse the cake.

In summary, good quality cakes, as defined by Ebeler and Walker (1984), should have the combination of a large volume, a fine grain, and a moist and tender crumb. Emulsifiers act to improve cake quality by enhancing air incorporation and shortening dispersion and by stabilizing protein films. They aid in producing cakes with tender crumb, improved eating quality, higher degree of symmetry, and extended shelf life.

Emulsifiers

Emulsifiers or surfactants are amphiphilic substances which according to their chemical structure possess both hydrophilic and lipophilic properties. Different solubility tendencies thus exist within the same molecule and are responsible for incomplete solubility in both water and oil. Emulsifiers, in fact, orient themselves at air-water or oil-water interfaces, a phenomenon called interfacial

absorption. A consequence of this is to reduce the interfacial tension between the different phases (Krog, 1977).

Del Vecchio (1975) classified emulsifiers according to four factors: the charge that these molecules carry in solution, the degree of their solubility in various solvents, the HLB value, and the nature of functional groups making up the emulsifier. Emulsifiers, classified by charge, are termed anionic, cationic, or nonionic. If a surfactant or emulsifier is classified as anionic, the anion which is formed in water is the surface active agent. For a cationic emulsifier, the cation formed in water is the surface active agent. Nonionic surfactants carry no charge in aqueous systems.

Solubility of emulsifiers in water and oils is the basis of the second classification scheme. Hydrophilic surfactants are water soluble, that is dispersible in water and insoluble in oil, while hydrophobic surfactants are the reverse.

The third classification is the hydrophile-lipophile balance method (HLB). Simply stated, HLB relates the molecular weight of the hydrophilic portion of the surfactant molecule to the molecule's total molecular weight. The HLB of a surfactant may be calculated from the equation:

$$\text{HLB} = a/b \times 20$$

where a is the molecular weight of the hydrophilic portion of the molecule and b is the total molecular weight. From the equation, HLB values may vary from zero to 20. A molecule with an HLB value of 20 is 100 percent hydrophilic and zero percent lipophilic; theoretically, it is not surface active. On the other hand, an HLB value of 10 is 50 percent hydrophilic and 50 percent lipophilic.

The HLB of a surfactant is often determined experimentally by actually preparing emulsions using materials of known HLB values and comparing the unknown material to those emulsions under similar conditions for a comparison of stability. Those which impart similar stability have similar HLB values. The HLB value determines the application of the emulsifier (Table 2). Other methods of determining HLB values depend upon chemical analysis to determine the average composition of the molecule, calculating the HLB value according to the ratio of molecular weights.

A fourth technique for classifying surfactants consists of an equation and "hydrophilic group numbers" which are assigned to various functional moieties which commonly appear in emulsifiers (3). The agreement between this

Table 2. Application of emulsifiers according to HLB values (from Del Vecchio, 1975).

<u>HLB Range</u>	<u>Application</u>
3- 5.6	water-in-oil emulsifier
7- 9	wetting agent
8-18	oil-in-water emulsifier
13-15	detergent
15-18	solubilizing agent

technique and the experimental determination of HLB is very similar, but the technique itself is not often used.

Figure 4a presents a diagrammatic representation of an amphiphathic emulsifier, depicted as a match stick, the head of which is the hydrophilic portion and the tail of which is the hydrophobic portion. When added to water, the emulsifier molecules orient themselves at the surface as depicted in Figure 4b.

As more emulsifier is added, a monolayer will eventually cover the water's surface, with the hydrophilic portions oriented toward the water and the lipophilic (hydrophobic) portions repelled into the air. The result is an oil surface on the water, and is the basis of one of the useful properties of surfactants: their ability to decrease the surface tension of water. If greater amounts of emulsifier are added to the system, they are forced into the aqueous phase and orient themselves to the most stable configuration -- the micelle (Figure 4c).

In a system containing water, oil, and an emulsifier, the type of emulsion formed will depend upon the nature of the surfactant itself, the HLB value, and the relative phase volumes of water and oil. According to Bancroft's rule, the type of emulsion is determined by the differing solubilities of the emulsifier in the phases (Birnbbaum, 1978). The rule states that the phase in which the emulsifier is more

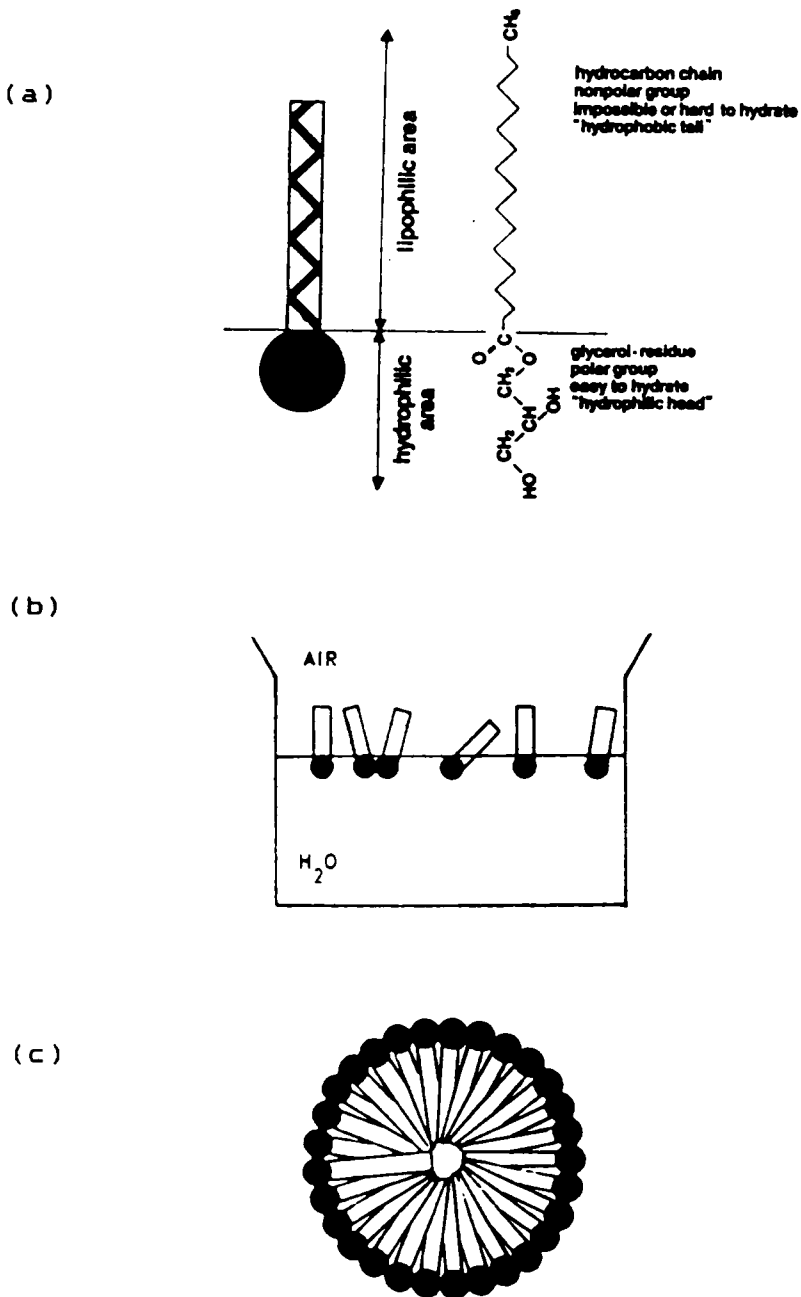


Figure 4. Diagrammatic representations of emulsifiers.

- (a) Representation of an emulsifier molecule (from Shuster and Adams, 1984).
- (b) Orientation of emulsifier at air-water interface (from Del Vecchio, 1975).
- (c) Micelle (from Del Vecchio, 1975).

soluble becomes the outer (continuous) phase (Schuster and Adams, 1984). Figure 5a shows an oil droplet which is stabilized as the discontinuous phase of an emulsion by a surfactant. The surfactant molecules orient themselves so their lipophilic portions are directed toward the oil droplet and their hydrophilic portions are oriented toward the water.

A water-in-oil emulsion wherein a water droplet is similarly stabilized by a surfactant is given in Figure 5b. The hydrophilic moieties of the emulsifier are oriented toward the water droplet while the lipophilic portions are oriented to the oil phase.

Surfactants play a variety of roles in food applications. Functions include emulsification, solubilization (the ability of a surfactant to carry and disperse an oil-like material into aqueous solution or suspension), complex formation (many surfactants can complex with molecular species such as sugars, starches, and proteins), crystal modification (surfactants are able to change crystal properties, entering into actual crystal structures and modifying them), and wetting, dispersing, and foaming (Birnbäum, 1978; Del Vecchio, 1975; Painter, 1981; Shuster and Adams, 1984). A mixture of surfactants may give better stabilization to an emulsion than would a single emulsifier at the same concentration. According to Parker

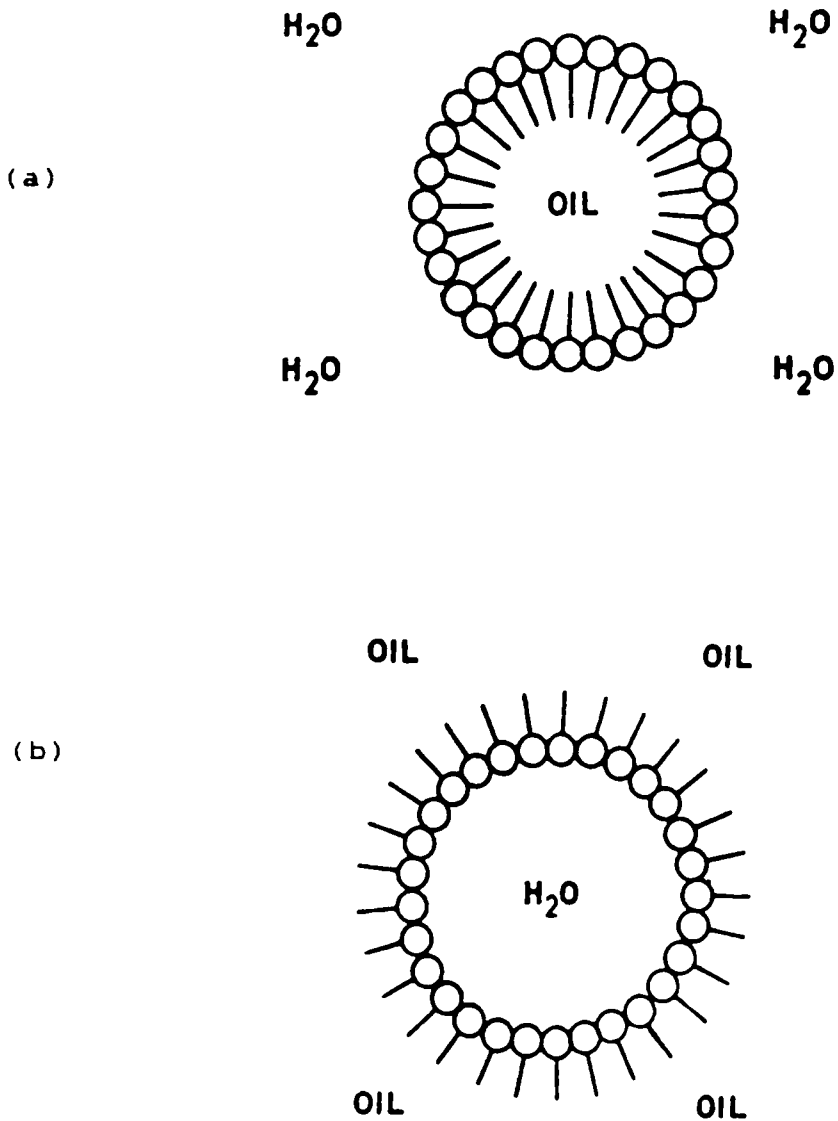


Figure 5. Kinds of emulsions (from Del Vecchio, 1975).

- (a) Oil-in-water type.
- (b) Water-in-oil type.

(1987) this can be attributed to (1) better packing of the molecules in the adsorbed layer, (2) formation of a mixed crystal phase at the interface, or (3) formation of a two-dimensional, visco-elastic "skin", all of which strengthen the adsorbed layer. However, under baking conditions, some combinations will prove detrimental, often due to excessive aeration (Kamel and Rasper, 1988).

There are a limited number of emulsifiers which either occur naturally or are approved for use by the Food and Drug Administration (FDA, 1987). FDA approves emulsifiers to be used in conjunction with good manufacturing practices; or at levels required to achieve the desired effect. Emulsifiers can be used in all foods unless the standard of identity of the food precludes such use (ex: acetylated monoglycerides, hydroxylated lecithin, fatty acid esters, polyglycerol esters, propylene glycol mixed esters).

Emulsifiers: Sucrose Fatty Acid Ester Emulsifiers

Sucrose fatty acid esters are nonionic surfactants made from the reaction of sucrose with fatty acids (Ebeler and Walker, 1984). They are obtained by the esterification of the sugar hydroxyl groups with fatty acids as shown in Figure 6.

Depending on the conditions of the esterification reaction, mixtures containing mono-, di-, or triesters of sucrose can be obtained, with HLB values ranging from low to high (HLB 1 - 15). This series is a result of varying the degree of fatty acid substitution on the sucrose molecule (Breyer and Walker, 1983).

Pomeranz et al. (1969) first reported the use of sucrose esters in bread. Chung et al. (1981) reported that sucrose esters completely replaced the function of natural free lipids of flour in breadmaking. The investigators also found that the more hydrophilic sucrose esters gave better bread loaf characteristics than did hydrophobic esters. Watson and Walker (1986) observed the effects of sucrose ester emulsifiers on bread dough mixing characteristics using the Brabender Farinograph and the National Mixograph. The time to peak of the Farinogram was reduced by the addition of sucrose esters, which also increased Mixogram optimum mix times. Sucrose ester emulsifiers were used to

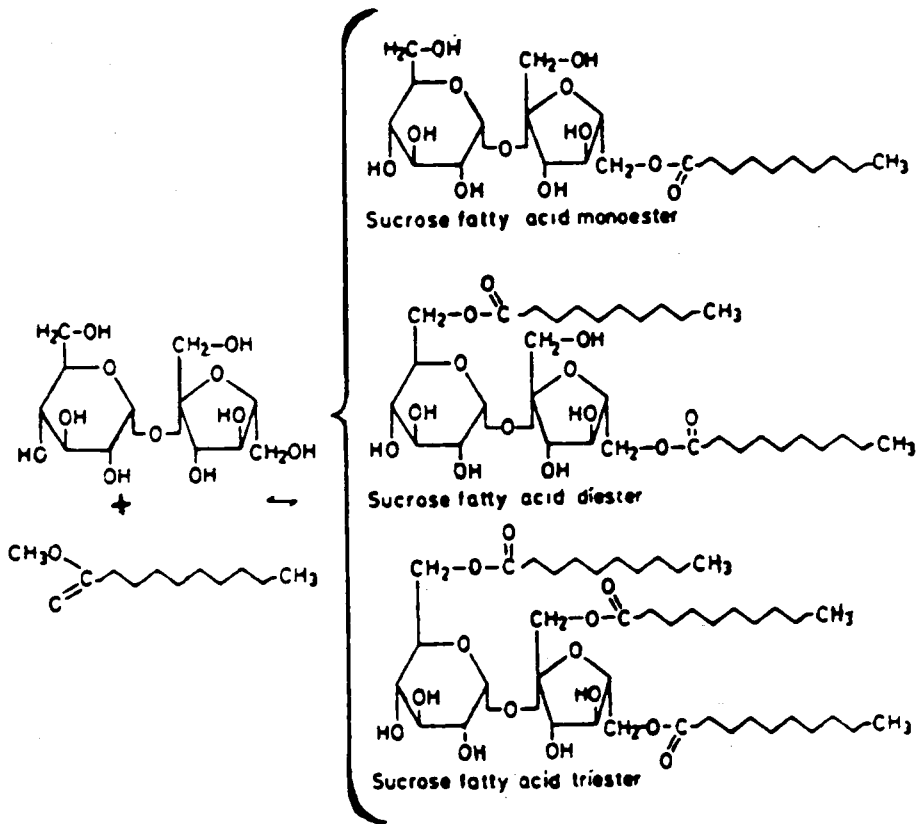


Figure 6. Synthesis of sucrose esters by transesterification of fatty acid methyl esters (from Falbe, 1986).

control cookie spread and as stabilizers in ice cream (Breyer and Walker, 1983; Buck, Walker, and Pierce, 1986).

Ebeler and Walker (1984) used sucrose esters of various HLB values in white layer cakes and found improvements in cake volume and softness as HLB increased. Visual observations, amylograph data, and microscopic studies indicated that sucrose esters delayed the pasting and gelatinization of the starch granules. Authors Ebeler, Breyer, and Walker (1986) compared batter emulsion characteristics of alpha-mono- di-glyceride emulsified batters with sucrose ester emulsified batters. The latter exhibited pseudoplastic viscosity characteristics intermediate to those of nonemulsified and alpha-mono- di-glyceride emulsified batters. Cake volume was increased when emulsifier was used, but the sucrose ester emulsified cakes shrank from the edge of the pan and collapsed upon cooling.

The effects of sucrose esters of differing HLB values were studied by Pierce and Walker (1987). A plastic mono- and diglyceride (MDG) emulsifier with 52% active alpha-monoglyceride content was used as a reference emulsifier. Batter specific gravity increased as the amount of reference emulsifier added increased, indicating a decrease in the amount of air entrapped in the batter. Dry sucrose esters produced a slight decrease in batter specific gravity, but

prehydration of the more polar, high HLB esters F-110 and F-160, resulted in significant decreases in specific gravity.

Batter flow rate was measured, with a low flow rate corresponding to a more viscous batter with more air incorporation. As the concentration of the reference MDG emulsifier increased from 0 to 2.5%, so did the batter flow rate, indicating a decrease in air incorporation (Pierce and Walker, 1987). On the other hand, prehydration of the sucrose esters resulted in decreased batter flow rate (increased viscosity) especially at the higher HLBs. As the specific gravity decreased, flow rate decreased, indicating that the amount of air incorporated into the batter did increase with the use of sucrose esters.

Low HLB esters produced cakes of equal volume to control (non-emulsified) cakes. The reference cakes with MDG decreased in volume as the amount of mono- and diglyceride added was increased. When added as a prehydrate, the high HLB esters, especially F-110, increased cake volume from 20 to 160 cm³. No statistical correlations were found between HLB or concentration with pH, moisture, or gelatinization of starch. The authors concluded that the HLB F-110 and HLB F-160 esters could be useful in sponge cake production (Pierce and Walker, 1987).

Sucrose esters are produced commercially in several countries for use in foods. The Codex Alimentarius

Committee Of the Food and Agriculture Association of the World Health Association set an acceptable daily intake of 0-2.5 g for sucrose esters of fatty acids (Lauridsen, 1976). Sucrose esters are a dry powder and are conveniently added to formulations such as cakes. Theoretically, the low HLB esters offer fat solubility and are compatible with water-in-oil (w/o) emulsions; high HLB esters are water soluble and are compatible with oil-in-water (o/w) emulsions (Dziezak, 1988).

Food-grade sucrose esters are manufactured in Japan under license by Dai-Ichi Kogyo Seiyaku Co., Ltd. of Kyoto. The process is patented by the State of Nebraska, Department of Economic Development, and licenses are available for use in the United States and other countries (Breyer and Walker, 1983). Sucrose esters have been approved for use as emulsifiers or stabilizers in baked food and in baking mixes (Anonymous, 1983) and are listed under section 172.859 of the Code of Federal Register (USFDA, 1987) to be used in accordance with current good manufacturing practice and in an amount not to exceed that reasonably required to accomplish the intended effect of an emulsifier, texturizer, or protective coating of fruits to retard ripening and spoilage.

Higher esters (hexa, hepta, and octa; Figure 7) have been developed which can totally replace fats and oils in

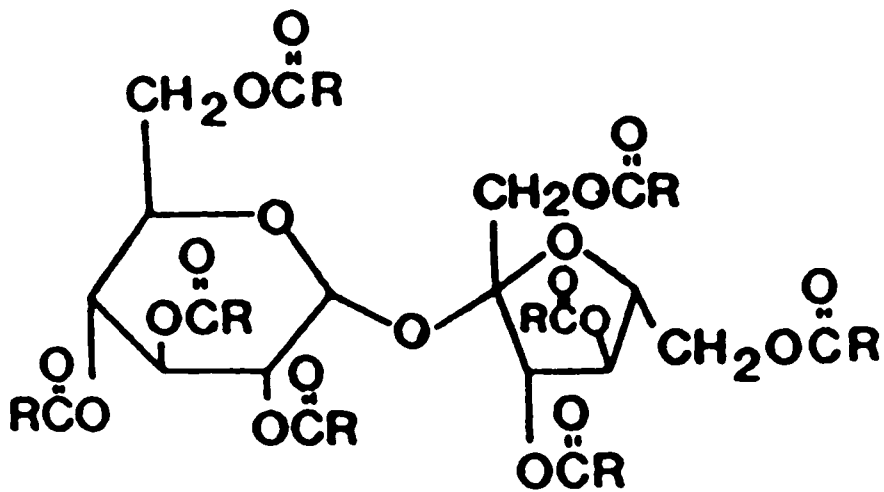
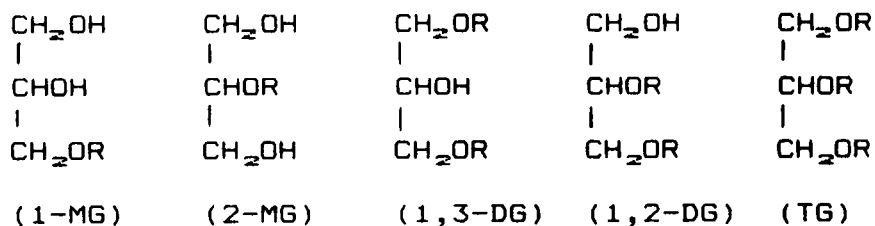


Figure 7. Structure of sucrose octaester. R = fatty acid.
(From Harrigan and Breene, 1989).

frying and as shortening. Olestra[®], a sucrose polyester product by Procter & Gamble, is pending FDA approval (Harrigan and Breene, 1989). The high esterification levels make the compound less sugar-like, more fat-like, less hydrophilic, and not digestible or absorbable.

Emulsifiers: Mono- and Diglyceride Emulsifiers

Mono- and di-glycerides (MDG) have been among the most extensively used surfactants in the baking industry. Surfactant consumption in the U.S. for 1982 was 240 million pounds, with mono- and diglycerides accounting for 80 percent (192 million pounds) of the total (Dziezak, 1988). According to Harris et al. (1941), MDG (Figure 8) were the first emulsifiers used in the preparation of cakes. They came into use in the 1930's incorporated into special fats called superglycerinated fats, as esters of glycerol or glycerin (a trihydric alcohol) and fatty acids, designated by R (Pyler, 1973):



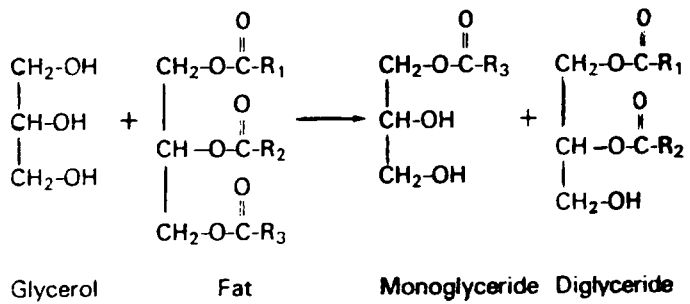


Figure 8. Formation of mono- and diglycerides.

The 1-MG and 2-MG are referred to as alpha- and beta-monoglycerides, respectively. Monoglycerides can be prepared either by direct esterification of fatty acids or by interesterification or glycerolysis of fats (MacDonald, 1968). The resulting reaction represents a mixture consisting of approximately 50% MG, 30-40% DG, and the remainder triglycerides, unreacted glycerol, and free fatty acids. In baked products, the functionally important components are the alpha-monoesters (Ofelt et al., 1958).

Many derivatives of MDG are commercially available, each offering a different functionality (Dziezak, 1988). These include ethoxylated mono- and diglycerides (EMG), succinylated monoglycerides (SMG), and diacetyl tartaric acid esters of monoglyceride (DATEM). Mono- and diglycerides can also be differentiated as being hard or soft. Hard, highly-saturated MDG (low iodine value) are superior to soft MDG (high iodine value) in the degree of starch complexing, which affects product texture and shelf life (Norris and Carlyle, 1973). Soft MDG, because of their unsaturation and reduced melting point, are more suitable for the development of a low viscosity fluid system (Norris and Carlyle, 1973).

Mono- and di-glycerides strengthen cake batters by aiding in finely distributing air during mixing. Optimal improvement occurs at a critical emulsifier concentration.

This is related to a particular air bubble size and quantity in the batter, beyond which quality loss occurs (Birnbaum, 1978).

Jooste and Mackey (1952) reported a finer dispersion of fat and air with increasing MG emulsifier and stated that the improved cake volumes obtained were due to improved gas retention at the time of protein coagulation during baking. The air incorporating ability of the emulsifiers was also observed by Wootton and co-workers (1967). They postulated that the emulsifiers concentrate at the fat-liquid and air-liquid interfaces, reinforcing these films which can then stretch with the expanding gas without rupturing.

Ebeler et al. (1986) prepared white layer cakes using a commercial grade plastic alpha-MDG emulsifier (62% total MG, 52% alpha MG content) at 0.5%, 1.0%, and 1.5% of flour weight. Batters appeared very smooth and were quite fluid compared to thick, curdled non-emulsified controls. The specific gravity was increased, in contrast to what other researchers have reported. The resulting cakes had high volumes, indicating that the MDG had stabilized the air cells, preventing their coalescence and escape from the system.

Emulsion Stability

Emulsion stability (ES) has frequently been assessed in terms of the quantity of oil and/or cream that separates from an emulsion over a fixed period of time at a specified temperature (Parker, 1987). An emulsion is a dispersion of one liquid phase in a continuum of another liquid phase in which the droplets do not mix. The reason the two phases separate so quickly after being shaken together is related to Van der Waals forces. The droplets of the dispersed phase bear Van der Waals forces of attraction for each other, and are pulled together until they coalesce (Parker, 1987).

Emulsion stabilizers (emulsifiers) work to delay the attraction between the droplets of the dispersed phase by either forming a barrier to coalescence or by introducing a repulsive force between approaching droplets. Also, the lifetime of an emulsion can be extended by slowing the rate of drainage of the continuous phase by either increasing its viscosity or by making the interface between the phases rigid (Parker, 1987).

InKlaar and Fortuin (1969) described a method to evaluate the emulsion stabilizing activity of protein meat additives. Samples were dispersed in water and soybean oil was added to the dispersed protein with stirring at 1,000 rpm. Contents were kept in a centrifuge tube placed in an

85°C water bath for 15 minutes. The tube was cooled under running tap water for 15 minutes and then centrifuged at 3,000 rpm for 15 minutes. The amount of oil separated was recorded after two centrifugation cycles, and calculated as a percentage of the total amount of oil added.

The stability of oil-in-water emulsions containing meat proteins was studied by Acton and Saffle (1970). An emulsion stability test to determine the extent of moisture homogeneity between samples was devised, which measured changes in moisture rather than oil separation after 24 hours. Stability of emulsions was according to the equation

$$SR = \frac{100 - M_{\text{test}}}{100 - M_{\text{original}}} \times 100$$

where SR is stability rating, M_{test} the percent moisture of the bottom 5 ml of sample stored at 37°C for 24 hours, and M_{original} the initial percent moisture of the sample.

The emulsion stability of simple systems with added soy protein isolates or concentrates was investigated by Hutton and Campbell (1977). Samples were prepared and stored overnight in centrifuge tubes at 4°C and were then held at either 4 or 90°C for one hour prior to equilibration to ambient temperature in a water bath. Samples were then centrifuged at 873 x G for 30 minutes and the volume of

separated liquid was read directly from the graduated centrifuge tubes and expressed as a percentage of total volume.

Stone and Campbell (1980) prepared emulsions of distilled water (240 g), soy protein isolate (13.28 g), salt, starch, and corn oil (66.2 g). Thirty-five gram samples were held for 15 minutes in a shaker water bath at either 4°C or ambient temperature. The amount of oil that did not separate out after centrifuging for 30 minutes at 1,500 x G was determined and calculated as grams oil per gram of soy isolate ("emulsified oil").

The method of Acton and Saffle (1970) presented earlier was modified by Aoki et al (1981) in determining emulsion stability. Soybean oil and a 0.2% protein solution were homogenized at a volume ratio of 35:65 at 16,000 rpm for one minute. Ten grams of emulsion were immediately placed into a 15 x 150 mm test tube and percent moisture of the bottom 5 grams of emulsion initially and after 30 minutes at room temperature were determined. By using the following equation, emulsion stability (ES) was calculated:

$$ES = \frac{100 - M_{\text{test}}}{100 - M_{\text{original}}} \times 100\%$$

High Fructose Corn Syrup

Sucrose is an extremely important food ingredient consumed in amounts totalling billions of pounds in the United States. Much sugar is consumed directly and in the form of soft drinks, baked goods, and other prepared foods (Long, 1986).

According to Casey (1977), enzymatic technology for producing crystalline dextrose was first commercialized in 1958 using acid hydrolysis followed by enzyme (glucoamylase) hydrolysis. Subsequently a combination of a starch liquefying enzyme (alpha amylase) and a starch saccharifying enzyme (glucoamylase) was developed, and made crystalline dextrose an attractive product for replacement of sucrose. However, dextrose and corn syrups suffered in comparison with sucrose because of their lower sweetness value (0.74 times that of sucrose).

The starch industry sought to develop new sweetened products in order to expand their markets in sweetened foods. Isomerization of glucose to fructose was considered due to the fact that fructose possesses roughly twice the sweetness value of glucose (Casey, 1977).

High fructose corn syrup (HFCS) of recent innovation is an enzymatically produced product, made possible by the discovery of ketol isomerase, an enzyme that catalyzes the rearrangement of a sugar molecule in an equilibrium reaction

(Casey, 1977):

aldose form \longleftrightarrow ketose form

In the commercial process, isomerization of glucose (an aldose) to fructose (a ketose) reaches an equilibrium of approximately 50-50.

Casey (1977) stated that the enzymatic process at first seemed to most U.S. technologists a scientific curiosity rather than a commercially promising process. An interest in glucose isomerizing enzymes in Japan in the 1960's led to the realization that a technique of using bacterial cells containing the immobilized enzyme as the isomerizing agent rather than using cell-free extracts of the enzyme could be implemented. Once the essential technology for producing HFCS on an economical basis had been demonstrated by the Japanese, one U.S. company, Standard Brands, Inc., purchased the right to license the Japanese process in America (Casey, 1977).

At first the isomerization process was a batch operation using soluble enzyme, but in 1972 it was converted into an immobilized enzyme system using a continuous process. The technique was eventually automated with a sophisticated control system. Enzyme suppliers and HFCS producers began to focus on process improvements and patents

for them, such as new bacterial strains for producing enzyme, new techniques for immobilization of the enzyme, and changes in isomerizing conditions for converting sucrose to fructose.

There are regulations governing the manufacture/safety of HFCS, including:

- (1) HFCS must conform to the Standards of Identity for corn syrup (21 CFR 168.120)
- (2) 42% HFCS is listed as a GRAS substance (21 CFR 182.1866)
- (3) Glucose isomerase enzymes have been affirmed as GRAS (21 CFR 184.1372)
- (4) Alpha amylases from Bacillus licheniformis has been affirmed as GRAS (21 CFR 184.1027)
- (5) Glucoamylases from Aspergillus niger are considered GRAS, with a petition filed by the Enzyme Technical Association (Long, 1986)

In the United States, HFCS is made from corn starch (Figure 9). The 42% fructose syrups which result from commercial processing typically have a profile of 71% total solids, 29% moisture, a pH value of 4.0, 50% glucose, 42% fructose, and 8% other sugars (Inglett, 1981). There are two major products, a 42% fructose syrup, and a 55% fructose syrup. The generic name "corn sweetener" is applied to nutritive carbohydrates prepared from the hydrolysate of

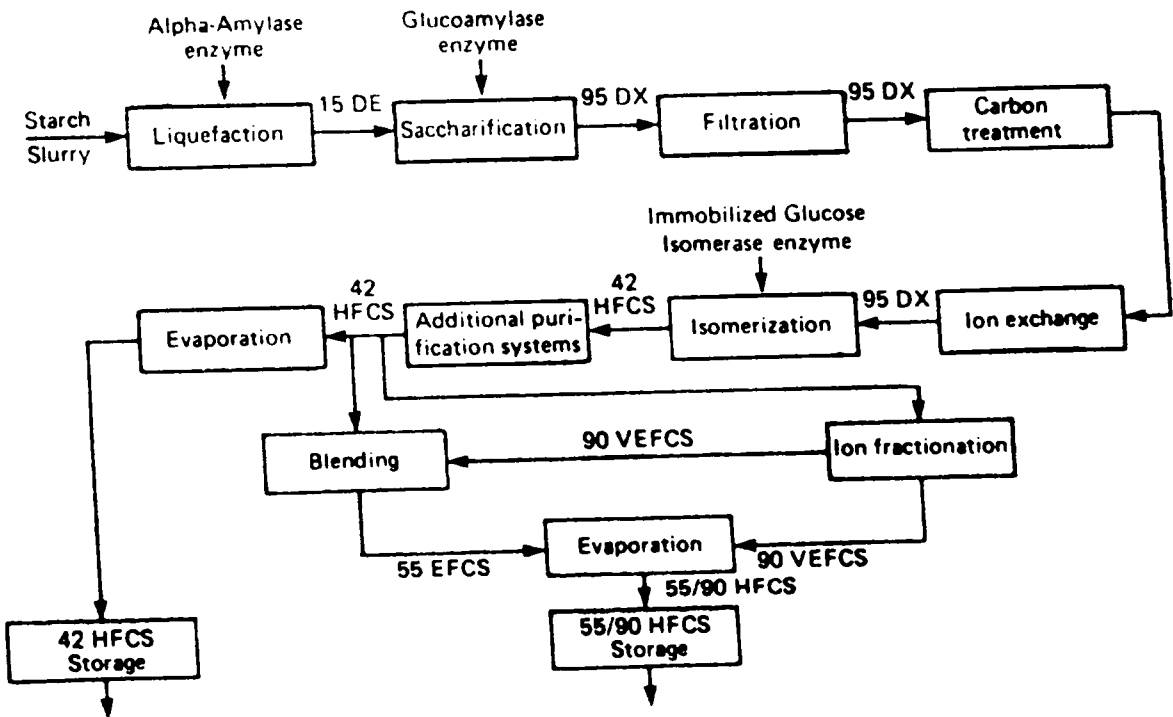


Figure 9. Flow sheet of production process of HFCS from corn starch slurry (from Van Tilburg, 1985).

corn starch (Horn, 1981). Commercial use of HFCS has increased in the past two decades due to its lower expense. In fact, liquid corn syrups represent the largest volume of sales for carbohydrates in the food industry (Luallen, 1988).

The use of HFCS has increased because of economics, quality of the product, and ease of handling (Long, 1985). In 1977, mass production of the 55% fructose syrup began, and since 1982 the market division between the 42% and 55% HFCS has shifted to the latter. Since 1984, all cola beverages use 55% HFCS at a 100% sucrose replacement level. The nonbeverage industries use primarily the 42% HFCS.

HFCS has found wide application as an alternative to sucrose in food products where the main function of the sugar is to provide sweetness (Inglett, 1981). Although not identical in other functional properties, HFCS is theoretically equivalent to sucrose in sweetness.

In 1972, a fructose-containing corn syrup was first introduced to the baking industry (Redfern and Hickenbottom, 1972). Today high fructose corn syrups have been used in the production of breads, cookies, sweet doughs, and cakes. Cakes do present a difficult application of HFCS. Thompson et al. (1980) studied the flavor acceptance and taste perception of butter cakes prepared with sucrose or HFCS. The flavor acceptabilities were equivalent, although some

panelists described a sharpness or tartness to the flavor of the HFCS cake crusts.

Saussele and coworkers (1983) used HFCS as a replacement for some of the sucrose in a variety of cake formulations and noticed an adverse effect on both crust and crumb color when HFCS replaced 25 percent of the sucrose. This confirmed the known tendency of fructose, as a reducing sugar, to participate readily in browning reactions with amino groups present in flour proteins. Koepsel and Hosney (1980) found that layer cakes made with HFCS had excessive browning while Volpe and Meres (1976) noted an undesirable sourness in the crumb of white layer cakes in which 60% of the sucrose was replaced by HFCS. These investigators attributed the sour flavor to the high-acid leavening system ($\text{pH} < 5.7$) used and believed that the sourness might be masked by a flavoring system different from vanilla. The leavening system did reduce crust browning and crumb yellowing, however, to an acceptable level.

Thompson and co-investigators (1980) reported that although volume of butter cakes with HFCS were lower than that of sucrose cakes, the cakes were equally tender. Koepsel and Hosney (1980) found that replacement of 100% of sucrose with HFCS in high-ratio white layer cakes resulted in greatly reduced cake volume and open grain. Coleman and Harbers (1983) used HFCS to replace 25, 50, 75 or 100% of

the sucrose in angel cakes. The replacement with 50% or more HFCS resulted in foams of lower specific gravities, cakes with lower and decreased sweetness, while 25% replacement did not greatly alter the physical measurements or sensory characteristics under study.

McCullough and co-researchers (1986) prepared shortened cakes with HFCS at 0, 50, and 75% replacement for sucrose. Objective measurements revealed the HFCS cakes to be of lower volume, darker crust and crumb, and equivalent in moisture when compared to sucrose cakes. Sensory panelists judged the HFCS cakes to be more moist, yet no different in crumb color. The 75% HFCS cakes were rated as sweeter than the sucrose or the 50% HFCS cakes.

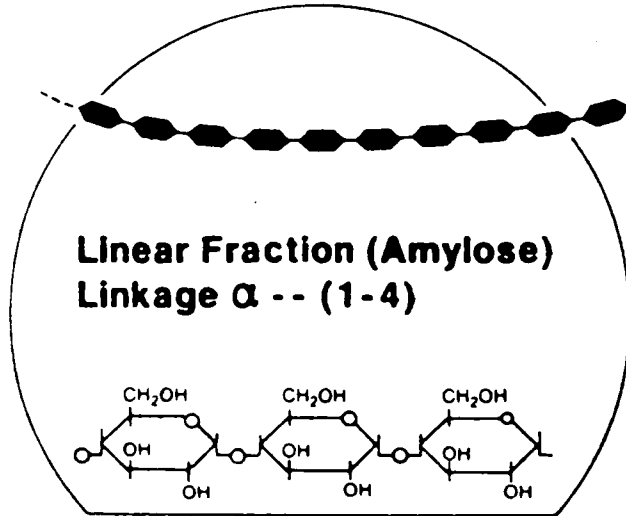
Starch, Starch Gelatinization, and Analysis

Starch is a carbohydrate occurring as discrete granules in the organs of plants, such as wheat and corn (Lineback, 1984). Starch is a condensation polymer of glucose, and is in fact synthesized in plants from sugars (Swinkels, 1985). There are two kinds of glucose polymers: amylose, a linear chain molecule, and amylopectin, a branched chain molecule (Figure 10). Starch granules are dominated by the amylopectin fraction (Luallen, 1988).

When starch is heated in the presence of water beyond a critical temperature, starch granules swell markedly and irreversibly. This phenomenon is called gelatinization. The gelatinization process occurs over a temperature range and is associated with a rise in viscosity of the starch suspension. This viscous mass resulting from the swelling of starch in water is termed starch paste (Olkku, 1978).

On a molecular level, starch is comprised of various crystalline (primarily amylopectin) and amorphous (primarily amylose) regions. This has been shown by x-ray crystallography or diffraction. Prior to gelatinization, crystalline specimens yield reflections from crystal planes, but after melting, change from a crystalline to an amorphous state (Zobel et al, 1988). This is indicative of a breakdown of granule structure. According to Pravisani et

(a)



(b)

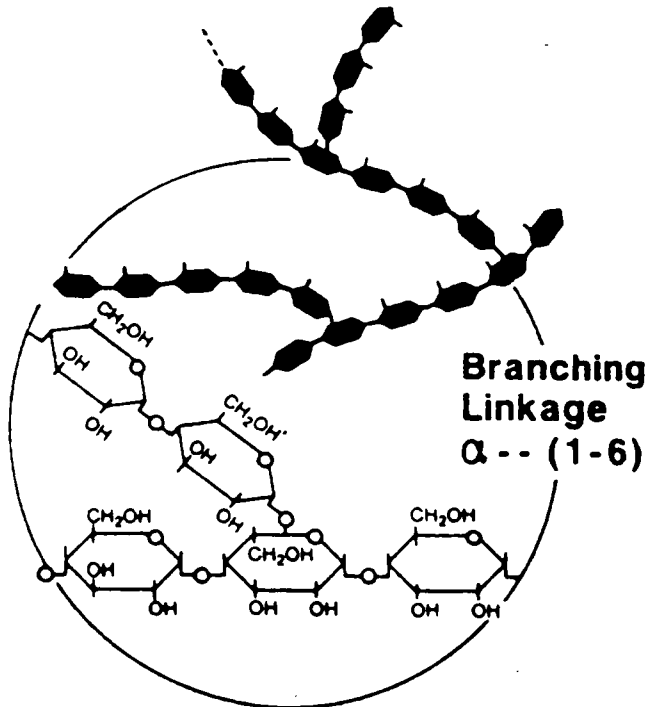


Figure 10. Molecular structures of the component fractions of starch (from Shuster and Adams, 1984).

- (a) linear amylose
- (b) branched amylopectin

al (1985), gelatinization involves simultaneous loss of birefringence and x-ray diffraction pattern, heat absorption, hydration of the starch granule with accompanying expansion, and a decrease in the relaxation time of the water molecules. They term the reaction mechanism for gelatinization "a semi-cooperative process where the gelatinization of the amorphous regions of the granule behave as a reaction promoter of the crystalline zones", which was evidenced by experiments conducted above and below a critical temperature of 67.5°C.

During gelatinization, some of the starch amylose can diffuse into the surrounding aqueous environment, which contributes to the rise in viscosity (Ghiasi et al, 1982d). Later, when the granules have fully swollen, some of the soluble amylose may diffuse back into the granules. The mixture, upon cooling, forms a paste-like mass or gel. This process is termed retrogradation, and signifies a return to an aggregated and associated state from a dissolved and dissociated one (Swinkels, 1985). In contrast to native starch granules, wherein mainly amylopectin constituted the crystalline regions, the retrograded crystalline starch material is composed mainly of amylose. In food processing, retrogradation of starch, represented by skin formation on puddings and weeping in pie fillings, is undesirable (Olkku, 1978).

Several methods have been employed in the study of starch gelatinization. These include viscoamylograph analysis of heated starch slurries, determinations of swelling, viscosity, loss of birefringence, enzymatic digestion, differential scanning calorimetry, scanning electron microscopy, and x-ray diffraction.

Sullivan and Johnson (1964) detected a close relationship between the susceptibility of various starches to enzymatic digestion (beta amylase) and the observed loss of birefringence. Gelatinized starch was more susceptible to enzyme attack. They equated a 50% loss of birefringence by the starch granules to the production of 5 mg of maltose after incubating 40 ml of a 1% starch suspension with purified beta-amylase enzyme.

Researchers at Kansas State University (Shetty et al, 1974) used the enzyme glucoamylase followed by glucose oxidase to measure the amount of glucose released after digestion. They found excellent agreement between theoretical percent gelatinization and actual gelatinization calculated by their procedure.

An increase in viscosity of heated starch slurries has been attributed to the friction between swelling starch granules as they imbibe large amounts of water. However, Miller et al (1973), using an amylograph method plus light micrographs and scanning electron micrographs, showed

granule swelling to be due to formation of an exudate which is released from the starch granules. It was noted that viscosity always increased sharply after most of the granule swelling ceased.

Ghiasi et al (1982a) discovered that both amylose and amylopectin leach out into the exudate of a heated starch slurry but do so differentially. Amylose is leached out at lower temperatures, amylopectin at higher temperatures. The molecular size of the carbohydrates leached from starch was investigated by gel filtration, and was ascribed to a high iodine-affinity branched amylose fraction, not amylopectin. Another study by Ghiasi et al (1982d) showed that several factors, including the presence of soluble starch and its increasing concentration in a decreasing water environment as starch granules bind the solvent water, are involved in the viscosity question.

Direct microscopic observation of starch in limited water systems was performed by Derby and co-workers (1975). Limited water was chosen as a more accurate reflection of the situation in baking. With this consideration, the structural change of starch as it was heated and the application to baking conditions was demonstrated. Photomicrographs of starch granules obtained from white layer cake batters prepared with 80% and 120% of normal water level heated to 96°C in a Farinograph showed

substantial size differences. Not only were starch granules larger in the presence of 120% water, but the volume of these baked cakes was 1000 cc, compared to 600 cc when 80% of normal water level was used. This contradicted Miller et al (1973) who concluded that a correlation between starch paste viscosity and granule size was almost nonexistent. Unfortunately, no viscosity data of the cake batters containing 80% and 12% water were provided by Derby et al (1975).

Kubota et al (1979) used a capillary tube viscometer to measure gelatinization rates of rice and potato starches. The gelatinization rates were equated to the flow behaviors of heated starch suspensions at various temperatures and potato starch granules expanded more than rice starch granules. Using the Arrhenius equation, the equivalent values of the activation energies for rice and potato starches were about 14 and 230 kcal/g-mol respectively. The gelatinization temperature range for potato starch was lower than that for rice; thus the rate of gelatinization was higher for potato starch solutions.

Scanning electron microscopy was used to reveal the proportion of folded and deformed starch granules in various baked goods, indicating the extent of gelatinization. Hosney et al (1977) found the appearance of starch extracted from different baked products to differ widely.

The extent of gelatinization and the subsequent number of folded or collapsed granules varied from relatively few in pie crust and sugar cookies to nearly 100% in angel food cake.

Lineback and Wongsrikasem (1980) confirmed a low (4%) gelatinization of starch isolated from baked sugar cookies and a high (97%) gelatinization of starch from angel food cake, with intermediate levels of gelatinization for cinnamon rolls, cake doughnuts, and white bread. They also noted the granule damage and folding in angel food cake starch, but remarked that such an observation is not easily quantified.

A study by Wooten and Chaudhry (1980) was performed to expand the range of products for which gelatinization data was available and to examine influencing factors. Because of limited water-to-starch ratios, little if any gelatinization occurred in shortbread, hard sweet cookies, or soda crackers, as evidenced by in vitro starch digestibility and iodine complexing as measured spectrophotometrically. Other baked products, with higher (0.7 and above) water/flour ratios, displayed gelatinization and in-vitro digestibility. Discrepancies, when they occurred, were attributed to the effects of ingredients such as sugar. More gelatinization was seen in white bread and cake, but less in cookies and crackers.

Starch gelatinization was analyzed using Differential Thermal Analysis (DTA) by Wada and co-workers (1979). This technique involved the heating of starch or food samples, and measured transition temperatures and endothermic peaks coinciding with the loss of birefringence of the starch granules.

Differential scanning calorimetry (DSC), according to Donovan (1977), is particularly well-suited for the study of starch gelatinization. DSC measures the heat flow into a sample as a function of temperature as the components of the sample are heat-denatured. In addition, interaction of components in a food system such as cake batter can be conveniently and rapidly observed on very small samples. As such, information about the heat stabilities of proteins and starch alone or in the presence of other components is easily obtained.

Donovan (1977) studied the baking of angel food cake via DSC and concluded that, in the presence of sucrose used in a lean (no fat) batter, both starch and major egg white proteins were denatured near 95°C. This simultaneity he postulated as a requisite for cake structure formation and achievement of maximum cake volume.

Mizukoshi et al (1979) followed the starch gelatinization and protein coagulation in a model sponge cake. They discovered that starch gelatinized between 79

and 88°C and that egg protein coagulated between 82 and 96°C. Coincidental were changes in light transmission, viscosity, and loss of birefringence under polarized light. In agreement with Donovan (1977) was the observation of near-simultaneous starch and protein denaturation.

DSC was used by Biliaderis et al (1980) to study gelatinization of various cereal and legume starches. DSC transition temperatures were compared to characteristic gelatinization temperatures obtained by loss of birefringence of the starch granules and visco-amylograph viscosity. A schematic representation of the interrelationships between amorphous and crystalline regions of heated starch was proposed (Figure 11).

The investigators remarked on the important role of water to assist the heat-induced melting of the starch crystallites, in going from the ordered crystalline conformation (stabilized by hydrogen bonding) to the random conformation. According to the authors, it was not possible to make direct correlations between DSC endotherms and either loss of birefringence or pasting (viscosity) temperatures, due to their dependence on experimental parameters such as heating rate and thermal lags in the equipment.

Ghiasi et al (1982c) reported the effects of high (2:1), equivalent (1:1) and low (1:2) water-to-starch ratios

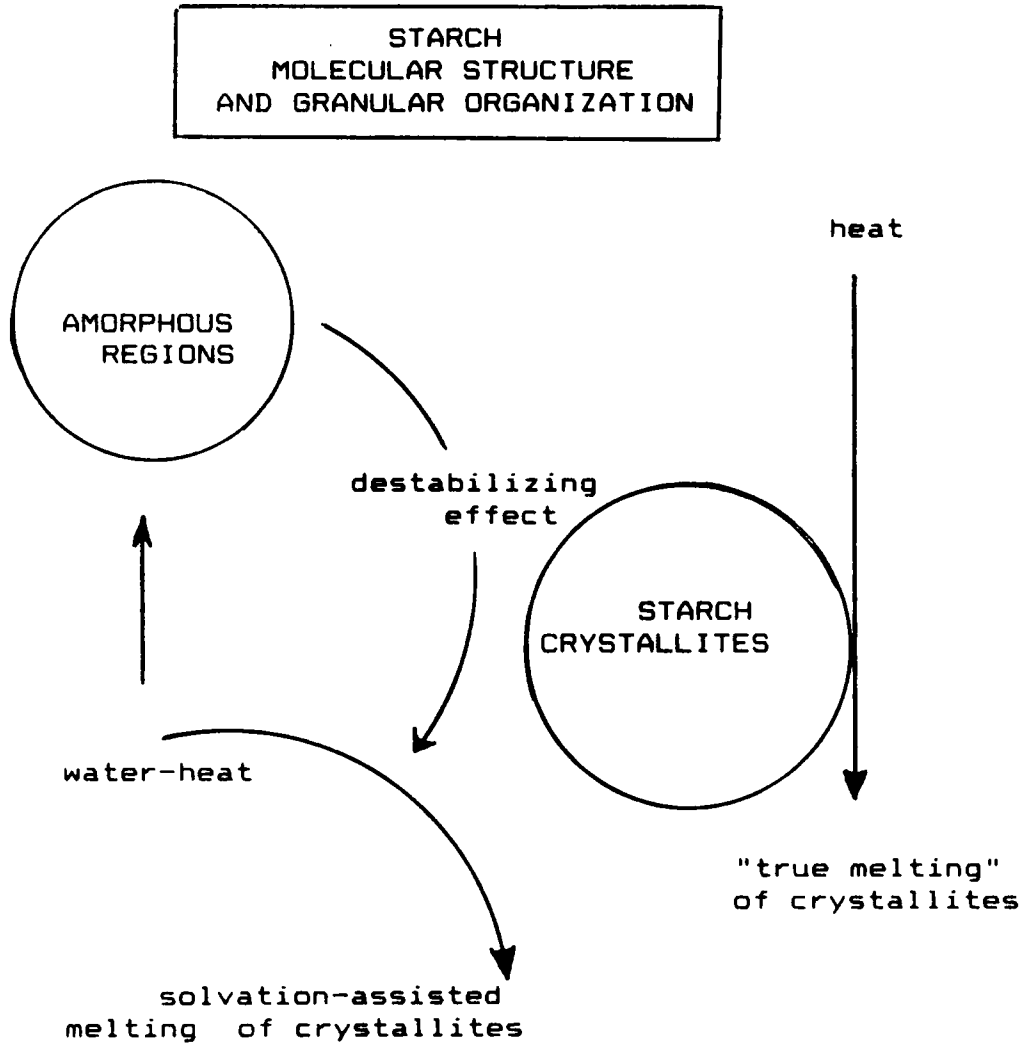


Figure 11. Possible interrelationships among parameters involved in heated starch phase transitions (from Biliaderis et al, 1980).

on DSC thermograms of wheat starch. At the high water level, only a single endotherm occurred, with an onset temperature of 57°C and a peak of 64°C. At the water-to-starch ratio of 1:1, the size of the endotherm decreased and developed a trailing shoulder. At low water ratios, the second endotherm shifted to higher temperatures.

Micrographs of starch heated in the DSC showed an effect of water content upon loss of birefringence (an indicator of starch gelatinization taking place). At the high water-to-starch ratio, birefringence was completely lost and granules were extensively swollen and deformed, whereas at the low water-to-starch ratio, there was incomplete loss of birefringence and lack of extensively swollen or deformed granules. The authors commented that low water content restricts swelling and deformation, and increases the temperature range (30°C compared to 7°C for high water content) for birefringence loss to occur.

Gorton (1984) has reported on the use of the DSC to study how cookie dough reacts to heat. In agreement with others, it was found that very little starch gelatinizes during the baking of cookies. Three endothermic peaks were generated, corresponding to fat melting, sugar dissolving, and starch gelatinization. The endotherms for starch gelatinization exceeded the interior temperature of a baking cookie.

DSC thermoanalytical studies of cookie dough by Abboud and Hosney (1984) of cookie dough also showed the same three endotherms, with starch gelatinization occurring above 100°C. Enthalpy differences between raw cookie dough and baked cookies supported the conclusion of little or no starch gelatinization in sugar cookies.

The fact that sugar increases the temperature at which starch gelatinizes has been often reported. Bean and Osman (1959) studied the effect of ten different sugars on the hot-paste viscosity attained during gelatinization of corn starch paste. Disaccharides were more effective than monosaccharides in inhibiting gelatinization, but all did delay gelatinization. At sugar concentrations of less than 20%, there was an increase in hot-paste viscosity, but at concentrations of 20% or more of the sugars, viscosity decreased.

Bean and co-workers (1978) presented direct microscopic evidence of the effects of sucrose, glucose, and fructose on starch gelatinization. The loss of birefringence showed that sucrose more than glucose, and glucose more than fructose, raised the initial gelatinization temperature of wheat starch in solution. This is the same as saying that the starch gelatinization event was delayed by all three sugars, and the most by sucrose. They also investigated substituting either monosaccharide for sucrose in a layer

cake formula and found that in order to obtain optimum contour and volume, a certain sugar-water ratio to permit starch gelatinization at approximately 90°C was necessary. This required higher glucose levels and even higher fructose levels as compared to sucrose in the formula.

Sugar/water ratios are very important in balancing cake formulations, as shown by Kissell (1959; 1962) and by Miller and Trimbo (1965). These ratios may be affecting cake quality through their effects on starch gelatinization temperatures.

Spies and Hosney (1982) found that as the concentration of sugar in sugar-flour-water solutions was increased, starch gelatinization temperature also increased. This they explained by the fact that sugar lowered the A_w (water activity) when present in a starch/water system, which would increase the energy requirement for reactions involving water hence a higher gelatinization temperature for starch. They also proposed that starch-sugar interactions might take part in delaying starch gelatinization, with sugar stabilizing starch chains in the amorphous region of the starch granule, thereby increasing the energy required for gelatinization.

Ghiasi et al (1983) investigated the effect of various ingredients including sucrose on the water available to starch for gelatinization. Sucrose increased the initial

DSC deviation (gelatinization) temperature to 98°C in heated doughs having a 1:1 ratio of sugar to flour within a range of 22°C. The researchers commented that more water was apparently available to the starch when high sugar levels were present. They stated that sucrose, although initially able to bind more water at room temperature than other dough ingredients (flour proteins and starch), loses this ability as the temperature increases. This allows the water to be available for starch gelatinization.

Starch also interacts with emulsifiers, which in turn affects the rate of gelatinization, the gelatinization temperature, the gel strength, peak viscosity, and complex formation by starch molecules (Schuster and Adams, 1984). An early concept that starch, in reacting with iodine, formed a complex in which iodine molecules become enclosed in a linear row along the axis of a starch helix, is believed to result from starch-surfactant interaction. The amylose and not the amylopectin portion of starch binds with iodine.

Osman et al (1961) investigated the ability of eighteen surfactants to bind with the amylose fraction of starch as evidenced by their interfering with amylose-iodine complexing. All but one of the emulsifiers greatly reduced the iodine affinity of amylose, and this ability was related to the size of the hydrocarbon portion of the surfactants.

The longer and more hydrophobic the fatty acid portions of the emulsifiers, the greater the competition with iodine for binding sites on amylose.

There is disagreement, however, as to whether formation of emulsifier-starch complexes could affect starch gelatinization. Longley and Miller (1971) of General Mills investigated the effectiveness of a series of saturated monoglycerides to retard soft wheat starch gelatinization as measured by a light transmission technique. They found that monoglycerides derived from long chain (greater than twelve carbons) fatty acids affected starch gelatinization. The authors believed the effect was due either to a reaction of starch with emulsifier within the swelling granules or through reduced water absorption by the monoglyceride-treated starch.

Other investigators (Ghiasi et al, 1982b) studied starch-surfactant interactions using x-ray diffraction. They found that both sodium stearyl lactylate (SSL) and monoglycerides (MG) formed strong complexes with amylose at 60, 70, or 80°C. The existence of such complexes at 60°C was believed to be due to the surfactant molecules having to enter the starch granules to complex with amylose, since at that low temperature gelatinization has not started and starch solubles had not yet begun to leach out. MG was found to form a stronger, more stable complex with starch

than SSL, and it was demonstrated that iodine and SSL compete for the same binding sites on starch.

These same researchers (Ghiasi et al, 1982d) in another experiment investigated the effect of MG and SSL on amylograph viscosity of wheat starch heated in aqueous suspensions. Both emulsifiers reduced the first-stage viscosity of the paste and delayed the increase of second-stage viscosity, which the scientists felt was due to starch-surfactant complexing. Also, both emulsifiers affected amylograph viscosity equally; the authors concluded that amylose viscosity therefore did not depend entirely on starch solubility, but on several factors. The factors are that during starch gelatinization, starch granule volume increases as more water is bound. Also, soluble starch increases viscosity as a function of its concentration. The bound water is no longer free to behave as a solvent, and as more is bound, the soluble starch concentration in the remaining unbound water increases greatly increasing viscosity.

Differential scanning calorimetry was used by another group (Cloke et al, 1983) to measure enthalpies of starch transformation and saturated monoglyceride (SMG) and unsaturated monoglyceride (USMG) phase transitions in a lean cake batter over the range of 40-120°C. The emulsifiers in batter were found to produce relatively small effects on

starch phase transitions. The researchers commented that sucrose in the batter might delay formation of amylose-emulsifier complexes, and that during baking, the emulsifiers might play a greater role in the later stages of batter development rather than in the initial phase transitions.

According to Varriano-Marston (1977), light microscopy can provide information about starch particle size, starch gelatinization (as measured by loss of birefringence) and the homogeneity of food material. Cake batters have been studied by placing a drop between a microscope slide and cover slip. Information about gas-cell number, distribution, and size -- factors known to affect cake crumb structure and texture -- can be provided (Varriano-Marston, 1981).

Davis et al (1986) examined model starch systems heated in the DSC using ordinary and polarized light microscopy. The systems contained oils of differing saturation plus starch and water. Enthalpies were lower for samples containing saturated oil or those with intermediate unsaturation. Starch from the saturated oil (coconut) samples were less swollen and retained more birefringence, indicating a delayed gelatinization, as compared to the most polyunsaturated (safflower) oil. But the corn, soybean, and cottonseed oil group, which contain both polyunsaturated,

mono-unsaturated, and saturated fatty acids, were most effective in limiting the first phase transition and granule swelling. The researchers concluded that the lipids, especially those that were highly saturated, might interfere with water diffusion or transport from one region of the sample to the other in systems of oil, starch, and water.

Scanning electron microscopy (SEM) produces dramatic three-dimensional images of structures such as the starch granule, and cereal scientists have largely abandoned light microscopy techniques in favor of SEM (Varriano-Marston, 1981). However, SEM only provides information about topological relationships, not the intricacies of internal structure. Varriano-Marston believes that scientists should not overlook the importance of light microscopy or transmission electron microscopy (TEM) in answering research questions. Also, due to the high sugar and fat content of cake batters, they are not amenable to SEM analysis (Varriano-Marston, 1981). Dehydration, a necessary step for SEM, grossly distorts the batter structure. Freeze-etching and TEM techniques, however, have been successfully used with cake batters.

Pohl and co-workers (1968) reported on a method for freeze-drying cake batter for microscopic study. Following rapid freezing to immobilize the structural elements in the batter and to remove water, osmium tetroxide (OsO_4) vapors

fixed the fat, which was accompanied by dark staining of fatty constituents. Upon dehydration and fat fixation, batter was infiltrated with paraffin and sectioned for microscopic study.

Upon microscopic examination, batter was seen as an emulsion of fat in an aerated aqueous phase. The irregular globular fat particles were dispersed throughout the aqueous starch-protein system. Air bubbles were not incorporated into the fat particles, but were distributed throughout the aqueous phase. Such an arrangement, the investigators felt, could explain how moisture and carbon dioxide might migrate readily into the air bubbles for expansion during baking.

The applicability of cryofixation freeze-etch methods integrated with TEM as an alternative to the above strategy was studied by Hsieh et al (1981). Cake batter containing corn oil without added emulsifiers was rapidly frozen (at minus 160°C) and fractured. Prior to viewing under TEM, specimens were etched and shadowed with platinum and carbon. The authors remarked that the method was able to show the changes in starch granules and oil dispersion as well as the development of new interfaces when heated. After heating to 102°C, oil pools were closely associated with starch granules.

Researchers from the University of Minnesota (Cloke et al, 1982) also used the cryofixation freeze-etch technique

to study cake batter structure before and after heating. Batters were prepared with and without saturated and unsaturated monoglycerides in corn oil. They found that the morphology of the starch granules changed during heating. Cross-fracture for starch granules was difficult to obtain in unheated batter, but by 87-91°C, were frequent, due to granule expansion. This temperature (at which cross-fractures became obvious) was altered (increased) by the presence of emulsifier. Unemulsified granule surfaces were also more layered and smoother, and their cross-fractures showed distinct rims. The batter matrix between starch granules was more clearly defined in unsaturated monoglyceride (USMG) containing cakes. USMG appeared to be less effective than saturated monoglyceride (SMG) in delaying starch granule swelling, possibly because of decreased complexing with amylose.

Fretzdorf and co-workers (1982) performed a freeze-etch study on the ultrastructure of dough and bread. They found that water was distributed in dough in three forms: as a coating around starch, as droplets, and as larger pools. Protein development progressed from a protein network in flour-water dough to a sheetlike protein in a complete dough. Protein-starch interaction was clearly visible, and in bread crumb, protein and starch were tightly connected.

Pomeranz et al (1984) employed SEM to observe changes in various doughs during mixing, fermentation, and baking. Samples of dough, bread crumb and crust, were air-frozen at -20°C and freeze-dried. The freeze dried pieces were fractured to expose interior surfaces and sputter coated with gold. In white bread dough, the structure was seen to be formed by a protein matrix that becomes more finely distributed during fermentation with small vacuole formation. In the crumb, considerable interaction between proteins and swollen-modified starch occurred. There was a greater interaction of large starch granules than small starch granules with protein. In baked wheat bread the structure involved primarily interaction of denatured gluten with large starch and small starch granules that were strung together.

Model cake systems containing different emulsifiers as well as unemulsified corn oil and shortening (HVS) controls were studied by Hsu and co-researchers (1980) using SEM. Water loss rates were followed, and were found to be depressed in the temperature ranges associated with starch gelatinization, and were related to the type of emulsification system used. Oil cakes lost water more rapidly than did shortening cakes. The rate at which water was lost varied according to emulsifier, with diacetylated tartaric acid ester of monoglyceride (DATEM) showing higher

losses than those for any other system tested, including saturated and unsaturated monoglycerides, succinylated monoglycerides, and a blend of distilled monoglycerides with water.

Cross-sectional cake areas measured for an index to volume, showed the unemulsified oil cakes to be significantly smaller than either cakes made with HVS or emulsified oil cakes. Crumb structure with unemulsified oil was the most compact. SEM of crumb in HVS cakes showed a veil of matrix covering swollen granules. In oil cakes, the matrix assumed irregular shapes around the starch granules or as small discrete droplets.

Granules in emulsified oil cakes were more frequently disc-shaped whereas those in HVS cakes were oval and football shaped. This suggested less extensive granule swelling in HVS cakes. In emulsified oil cakes, a variety of discrete granule forms were seen, including doughnut shapes and partially folded discs. It was expected that starch granules from cakes made with saturated monoglycerides would be less swollen since Krog (1977) and others have reported high amylose-complexing for these emulsifiers and corresponding inhibition of granule swelling. However, such differences were not observed via SEM by Hsu et al, who felt that starch-emulsifier complexes were observable as a variation in the distribution of the

matrix material in the cake crumb examined. The matrix composition could not be defined via SEM but the authors surmized its composition to be proteins from flour, lipids, and solubilized starch.

SEM and TEM studies of ice cream emulsions and peanut oil/casein emulsions were performed by Liboff et al (1988). SEM emulsions of ice cream proved unsatisfactory, with the main difficulty being obstruction of the fat globules by a proteinaceous precipitate. However, SEM samples of peanut oil/casein emulsions mixed with warm 4% agar, fixed in 4% glutaraldehyde and postfixed in 1% osmium tetroxide yielded well-preserved fat globules with round, regular shapes. Such a preparation procedure might be applicable to the study of cake batter via SEM, which hitherto has not been succesful (Varriano-Marston, 1981).

Cake Baking Technology

Cake History

The art of cake baking has probably existed for centuries, yet recently, with the advent of experimental foods research in general, and cereal science in particular, baking a cake derives from the realm of science and technology.

It is known that the manner in which cake ingredients are combined, mixed, and baked plays an important role in the outcome of the baked cake. In this section, the commonly used cake mixing methods will be presented. This will be followed by a discussion of the stages of cake baking, including the current state of knowledge regarding the chemical and physical changes that occur as wet and dry ingredients are mixed into a batter and are heated in such a way so as to produce the final baked product.

Cake Mixing Methods

The purpose of cake mixing is to create an extensive, homogeneous dispersion of ingredients with a maximum incorporation of air and a minimum development of gluten from the flour. A variety of methods are commonly employed for the combining of cake ingredients. These will be given as presented by Bennion (1985) and Pyler (1973).

The conventional or creaming method requires first a plastic fat to be creamed with sugar. Then, eggs or egg yolks are added to the fat-sugar mixture and blended until the batter becomes very light. The dry ingredients are sifted together and added in alternate small portions with the liquid to assure a more homogenous mixture. Egg whites may be beaten separately and added at the end of mixing.

The conventional sponge method is used for lean mixtures containing insufficient fat to produce the light creamed texture of the fat-sugar mixture. About half of the sugar is beaten with the fat and the remainder is reserved to be beaten with the eggs to a stiff consistency. The liquid and dry ingredients are added alternately to the sugar-fat mixture prior to folding in the stiff egg-sugar mixture. A successful oil cake can be made with this method.

The quick-mix or single stage method requires that more liquid and sugar be used than for the conventional method. An emulsified shortening should also be used. A creaming stage is not required for emulsified shortenings due to their ability to incorporate air on their own (Birnbaum, 1978). The mixing occurs in two stages. First, all dry ingredients are sifted into the mixing bowl; fat, part of the liquid and flavoring are added and beaten for a specified time. Second, unbeaten eggs or egg whites plus

remaining liquid are beaten for a specified time and added to the mixture.

Thorough ingredient mixing is necessary, but either too much or too little mixing will adversely affect the outcome of the cake, according to Bennion (1985). Excessive stirring produces compact, low-volume cakes, which are heavy and soggy, while under-stirring results in a coarse, thick cell walls in crumb. Optimum mixing gives the best volume and the most uniform texture, with small, thin cell walls. It should be noted that optimum mixing varies with the proportion of the ingredients and the quantity of batter. The mixed batter should be baked without delay, as loss of CO₂ can occur, resulting in a low-volume cake.

As with mixing, the optimal baking temperature varies according to the cake formula, batter quantity, moisture content, and the type and size of the baking pan used. Pyler (1973) stated that lean cake mixtures bake well at temperatures ranging from 350-400°F, while batters high in sugar require lower (325-350°F) temperatures. Both white and yellow cakes bake well in the 350-360°F range.

The Stages of Cake Baking

Howard (1972) defined a properly mixed cake batter as a "fat-in-water emulsion in which there are four bulk phases (aqueous, fat, vapor, and solid starch granules) and at least six different interfaces at which both physical and chemical interactions can occur." In an earlier paper he divided the mechanism of layer cake baking into three stages: (1) initial batter aeration; (2) thermal stability of fluid batter; and (3) thermal setting of batter to form a rigid and porous expanded structure at the conclusion of the baking cycle (Howard et al, 1968).

In the first (aeration) stage, the shortening more than the emulsifier is thought to be important for air incorporation. Upon creaming of shortening with sugar, the air is mainly contained in the fat phase. Initially, the batter is a water-in-fat emulsion which changes to a fat-in-water emulsifier after the addition of the remaining liquid ingredients. Soluble milk and egg proteins were found to be essential for proper aeration in batters made with fluid shortenings containing surface-active lipids and alpha-tending emulsifiers (Howard et al, 1968). These emulsifiers formed tough films around the dispersed oil droplets and prevented the fat phase from interfering with the foaming properties of the soluble proteins.

During stage two, the early baking stage, the fat phase (if a hydrogenated shortening is used) begins to melt and release air bubbles into the aqueous phase. With proper stabilization the air cells are uniformly distributed, and expand along with CO_2 which results from the action of leavening agents. There is also diffusion of water into the vapor phase which continues to expand the batter until the starch gelatinization temperature is reached.

The batter stability afforded by the emulsifier film surrounding the oil droplets is replaced by the stabilization due to polyvalent cations (such as calcium), unhydrolyzed protein, and surface-active lipids such as stearic acid. The reason the emulsifier alone cannot maintain batter stability is that during baking, the melting point of the emulsifier film is reached and exceeded (Howard, 1972). The role of starch in maintaining batter emulsion stability has been attributed to the increase in viscosity of the batter due to granule swelling and concomitant water absorption (Howard et al, 1968).

The third stage is called the thermal setting or gelation stage. During this late baking stage, the fluid, aerated batter emulsion changes state to a solid, porous structure. Most of the water present in the system has been absorbed by competing ingredients, namely starch, protein, sugar, and thickening agents. The gelatinization properties

of the starch granules control the final physical properties of the baked cake. The extent of water absorption by starch must be sufficient to convert the aqueous fluid phase to a solid, porous structure that will not collapse late in baking or during cooling.

Shepherd and Yoell (1976) have also divided cake making into three distinct phases: (1) batter preparation and the early part of baking; (2) intermediate baking stage; and (3) structure development. The three stages are described as follows.

After the initial mixing of ingredients, air bubbles are in the fat phase, flour particles are suspended in the aqueous phase, and the fat is dispersed throughout the batter. During the first stage there is little apparent change in the mixed batter until a temperature of 37 to 40°C, whereupon the fat in the batter melts. Then, irregularly-shaped fat particles become spherical droplets, the batter becomes completely an oil-in-water emulsion, and air bubbles are released into the aqueous phase from the fat phase.

The intermediate stage is defined as the period between the final melting of fat and the start of cake formation. Cake batter undergoes bulk flow in the pan due to convection currents up the sides and down through the center. Creamed-in air bubbles act as nuclei for the whole batter expansion

by the movement of water vapor and carbon dioxide into the air cells. For a given batter type and pan, the amount of bulk flow will depend on the batter viscosity, which is temperature dependent, and the temperature differential between various regions of the batter. The lower the viscosity, the greater the amount of convection flow.

The final stage in cake making is the development of the finished baked cake structure. The cake owes its structure to the partial gelatinization of flour starch plus the coagulation of egg and wheat protein during the final minutes of baking, when internal cake temperatures reach 100°C. Due to bulk movements of batter, the structure sets up throughout the cake at different times. The crust receives maximum heat and sets first. The last part of the structure to set is the central region of the cake. Removal of a cake too soon from the oven results in a collapse of the crust over the as yet unbaked region.

Shepherd and Yoell (1976) stated that the importance of heat setting of egg proteins (ovalbumin, conalbumin, plus yolk protein) and starch gelatinization to a cake's final structure is unquestionable. The former process actually involves three separate stages: protein denaturation, aggregation, and gelation. As the batter temperature rises and flour absorbs more water, the effective protein concentration increases, which lowers the setting

temperature of the proteins. This is offset, however, by the effect of sugar and some emulsifiers, which can delay (increase) the setting temperature.

Shepherd and Yoell (1976) have postulated a "bricks-in-mortar" structure for baked cake, in which starch granules are held together by strands of protein. Partial gelatinization rather than complete gelatinization ensures a stable structure that will not collapse.

Response Surface Methodology

Giovanni (1983) defined response surface methodology (RSM) as a statistical technique that uses quantitative experimental data to determine and simultaneously solve multivariate equations which can be graphically represented as response surfaces. RSM allows the researcher to: (1) describe how the test variables affect the response; (2) determine the test variable interrelationships; (3) describe the combined effects of all test variables on the response.

In food product development, the goal is product optimization. Walker and Parkhurst (1984) noted that many investigators still attempt to achieve this by changing one variable (factor) at a time or to study all variables in all possible combinations. These approaches are inefficient, as stated by Giovanni (1983), for several reasons: (1) much time and money is spent on performing a large number of experiments; (2) the product optimum may be missed because the researcher must guess in specifying the various ingredient levels to test; (3) it is difficult to quantify interactions among variables; and (4) neither approach establishes the relationship between the variables and responses via a mathematical model.

In the language of RSM, factors are the variables which researchers can manipulate in their experiments; for example, the kind of sweetener used in a formula. The

factor levels would refer to the amount used, such as the percent sweetener in a formula. The response is the variable which the researcher wishes to optimize. It is dependent upon the effect of different (independent) factor variables under investigation; for example, cookie sweetness as a function of sweetener and sweetener level used.

RSM has been used increasingly by food scientists since the early 1970's, although Kissell and Marshall (1962) and Kissell (1967) published earlier papers utilizing so-called Box-Wilson multiple-response surface designs. In these studies, main and interaction effects of ingredient variations upon white layer cake quality were investigated. Multiple regression equations and response surface drawings were presented, which defined the relationships between the ingredients and the responses of interest.

Henselman et al (1974) optimized both physical properties and sensory attributes of an experimental high protein bread, using a response surface computer program. The scientists commented enthusiastically about the application of RSM in conjunction with consumer sensory acceptance panels for such an experiment.

Three-dimensional response surface plots were a feature of a study conducted by Hutton and Campbell (1977) regarding the emulsifying and thickening function of soy protein concentrates and isolates. Response surfaces were generated

for emulsified oil (g oil/g sample) as a function of pH and temperature.

Lah and co-workers (1980) reported on the value of rapid RSM analysis in determining optimum conditions for whipping a full-fat soy protein product in which seven variables were considered. They concluded that it would have been very difficult to investigate such a problem without using RSM, due to the complexity of the chemistry and physics involved and the number of interrelated variables being investigated.

Computer analysis of a response surface experimental design was employed by Min and Thomas (1980) as a statistical method to find the relationship between ingredients and physical characteristics of a whipped topping. It was also a means to optimize the ingredient levels of fat, corn syrup solids, and stabilizer needed to produce a satisfactory, freezable dairy whipped topping.

The authors presented computer-generated response surface plots for overrun and firmness and the associated model equations. The latter were found to account for the majority of the variation in the two responses and indicated that each ingredient acted independently in contributing to each response.

Johnson and Zabik (1981) used response surface methodology to simultaneously optimize foaming index and

volume of angel food cakes according to the levels of various albumin proteins. That this was accomplished with six different variables and a limited number of experiments attests to the value of RSM.

An RSM computer program written in BASIC and compatible with Apple systems was developed for personal computing by Walker and Parkhurst (1984). The response program was designed to print contour maps, generate models, and predict the experimental conditions required for response optimization.

The textural optimization of reduced-calorie cakes using RSM was carried out by Neville and Setser (1986). The authors found the end result of their optimization procedure to be the development of a sucrose-free, shortening-free cake prepared with N-Flate, a matrix system of emulsifier blended with guar gum and pregelatinized starch, and polydextrose.

SENSORY EVALUATION

Sensory evaluation is an experimental tool used by investigators seeking to identify and describe qualitative and/or quantitative aspects of foods and beverages. According to Sidel and Stone (1976) the primary purpose of sensory evaluation is to provide information regarding the effect of specific experimental treatments upon a particular population. The accuracy of the information obtained by a sensory study depends on the selection of an appropriate experimental design and appropriate analysis of the data (Sidel and Stone, 1976). Additionally important are the selection, training, and use of judges if descriptive work is to be done (Zook and Wessman, 1977) and adequate preparation for the evaluation itself (Larmond, 1977). The latter includes:

- (1) proper testing facilities; the testing environment should be quiet, comfortable, odor-free, with suitable lighting and separate test booths with facilities for rinsing the mouth between samples.
- (2) having a testing schedule that is known to the panelists.
- (3) preparing test samples in advance with an attempt made to ensure uniform sample quantity, temperature, and appearance.

- (4) selecting and using an appropriate sample coding and order of presentation (from Larmond, 1977).

Pangborn (1984) has differentiated between the analytical (laboratory) methods of measuring sensory attributes and the consumer measurement of sensory attributes. Analytical methods include threshold and difference testing, quantitative testing such as ranking, magnitude estimation and time-intensity duration, and qualitative testing, such as quantitative descriptive analysis (QDA) and the texture profile. Consumer or affective testing include acceptance, preference, and hedonic test.

Quantitative descriptive analysis is a statistical approach developed by Stone at the Tragon Corporation. In its original form, highly trained judges developed descriptive terms for the test samples as a group, then assigned intensities individually on unstructured, non-numerical scales. Repeated judgments were collected from each panelist and the data was analyzed (ANOVA, correlation, etc.) by a computer package provided by Tragon (Pangborn, 1986). QDA configurations describing the products were prepared. Typical configurations had lines radiating outward from a central point, each line representing a particular descriptive term. The average intensity for each

term was plotted on its line, and the average intensities for all the terms provided a product profile (Zook and Wessman, 1977).

QDA data has several potential uses, according to Zook and Wessman (1977):

- (1) as an aid in product development
- (2) as an aid in the maintenance or improvement of an established product
- (3) as a diagnostic tool in product problem-solving
- (4) as a quality control measure

Although more time consuming, expensive, and requiring complex statistical analysis to establish significance of results than do instrumental food analyses, sensory panels can give sensitive, reliable results (Pangborn, 1976).

III. METHODOLOGY

Objectives

The overall goal of this research was to study the interaction of HFCS, corn oil, and added emulsifier in a cake system and to optimize the product by RSM.

A. Pilot Study

There were two objectives to the pilot study:

(1) To determine if HFCS and corn oil act independently on objective and sensory cake interactions. This was investigated by measuring the effects of three levels (0, 50, and 100%) of corn oil (CO) substituted by weight for a plastic unemulsified vegetable shortening upon cake volume and cake deformation, and three sensory attributes (sweetness, tenderness, and aftertaste). Response surface analysis (RSM) was used to generate equations and plots showing how HFCS and CO contributed to cake volume and deformation (tenderness) and to predict the levels of HFCS and CO required to produce optimally tender, high-volume cakes.

(2) To determine the level of emulsifier required to produce an optimum cake using HFCS and corn oil. The effects of two different emulsifiers (mono- and diglycerides, a low HLB emulsifier and sucrose esters, a

high HLB emulsifier) upon cake volume in corn oil-shortened HFCS cakes were measured. Response surface analysis was used to predict the levels of each emulsifier required to produce the optimum cake volumes over all levels of HFCS.

B. Research Problem

There were two objectives to the research problem:

(1) To employ RSM (response surface methodology) to predict the levels of HFCS with and without MDG or SE (at levels determined in the pilot study) required to produce optimally moist, tender, high-volume cakes lacking objectionable aftertaste.

(2) To study the effect of HFCS and emulsifiers on certain interactions such as starch gelatinization and protein denaturation of a food system.

The objectives were investigated by:

(a) examination of the effects of three levels (0, 50, and 100%) of HFCS with and without mono- and diglycerides (MDG) or sucrose esters (SE) upon batter characteristics: pH, specific gravity, flow, and emulsion stability.

(b) examination of the effects of three levels (0, 50, and 100%) of HFCS with and without MDG or SE upon starch gelatinization and egg white protein denaturation in model systems and cake batter.

(c) examination of the effects of three levels (0, 50, and 100%) of HFCS with and without MDG or SE upon specific objective cake parameters: volume, deformation, percent moisture, crust and crumb color.

(d) examination of the effects of three levels (0, 50, and 100%) of HFCS with and without MDG or SE upon specific sensory parameters: cell size, cell uniformity, crumb color, sweetness, moistness, tenderness, aftertaste.

(e) examination of the microstructure of the HFCS cake batters and cake crumbs with and without MDG or SE.

Experimental Designs

A. Pilot Study

Cakes were prepared using 0, 50, and 100% HFCS substituted for sucrose by weight of sugar and 0, 50, and 100% corn oil substituted for solid vegetable shortening by weight of fat. Nine treatment variations resulted, with two factors (HFCS and corn oil) each at three levels (0, 50, and 100%). This represented a 3^2 factorial design (Table 3a). The baking schedule followed an incomplete block design (Table 3b). Each treatment variation was baked four times. In all, 36 cakes were baked over a four week period.

Two different emulsifiers (MDG = mono- and diglycerides and SE = sucrose esters) were separately incorporated into

Table 3.

- (a) Experimental design for testing corn oil and HFCS in 9 cake formula variations.
- (b) Baking schedule of pilot study in which corn oil and HFCS content differed for 9 variations.

(a)

		HFCS replacement for sucrose		
		0%	50%	100%
Corn oil	0%	1	4	7
replacement	50%	2	5	8
for	100%	3	6	9
solid shortening				

(b)

		<u>Variations</u>
WEEK ONE	<u>Day 1</u>	6, 4, 5
	<u>Day 2</u>	9, 7, 8
	<u>Day 3</u>	9, 8, 7
WEEK TWO	<u>Day 1</u>	1, 3, 2
	<u>Day 2</u>	3, 1, 2
	<u>Day 3</u>	5, 4, 6
WEEK THREE	<u>Day 1</u>	4, 1, 7
	<u>Day 2</u>	8, 2, 5
	<u>Day 3</u>	9, 6, 3
WEEK FOUR	<u>Day 1</u>	3, 9, 6
	<u>Day 2</u>	7, 4, 1
	<u>Day 3</u>	2, 8, 5

0, 50, and 100% HFCS cake formulations shortened with corn oil. MDG was added to the batter at 1, 2, and 3% of flour weight, and sucrose esters were added to the batter at 1, 2, 3, and 4% of flour weight. Cake volumes were recorded and compared to unemulsified controls.

B. Research Problem

Cakes were prepared using 100% corn oil as the only fat source and 0, 50, and 100% HFCS substituted by weight for sucrose. In addition, either sucrose ester emulsifier, mono- and diglyceride emulsifier, or no emulsifier was incorporated into the formulations. The amount of each emulsifier added was determined experimentally. As before, nine treatment variations resulted in a 3² factorial design, according to the level of HFCS and the emulsifier chosen (Table 4a). Baking was in the form of a randomized, balanced incomplete block design (Table 4b).

Ingredients and Supplies

Cake ingredients were purchased in advance from local supermarkets and stored in their containers at room temperature (22-25 degrees C) until use. These included SoftaSilk cake flour (General Mills, Inc., Minneapolis, MN), Hearth Club double-acting baking powder (Rumford Co., Terre Haute, IN), Crisco corn oil (Procter & Gamble, Cincinnati,

Table 4.

- (a) Experimental design of research problem. HFCS vs. sucrose - unemulsified controls vs. emulsified (MDG and SE).
- (b) Baking schedule for research problem presented as a randomized balanced incomplete block design.

(a)

		HFCS replacement for sucrose		
		0%	50%	100%
Emulsifier	NONE	1	4	7
	MDG	2	5	8
	SE	3	6	9

(b)

		<u>Variations</u>
WEEK ONE	<u>Day 1</u>	5, 4, 6
	<u>Day 2</u>	9, 7, 8
	<u>Day 3</u>	2, 3, 1
WEEK TWO	<u>Day 1</u>	4, 7, 1
	<u>Day 2</u>	6, 9, 3
	<u>Day 3</u>	2, 8, 5
WEEK THREE	<u>Day 1</u>	3, 7, 5
	<u>Day 2</u>	9, 2, 4
	<u>Day 3</u>	8, 6, 1
WEEK FOUR	<u>Day 1</u>	2, 6, 7
	<u>Day 2</u>	9, 1, 5
	<u>Day 3</u>	8, 3, 4

OH), and Richfood nonfat dry milk (Richfood, Richmond, VA).

Sucrose was obtained from the bulk supply of the General Stores of Virginia Polytechnic Institute and State University. High fructose corn syrup (Invertose high fructose corn syrup 2643) containing 42.0% fructose, 53.0% glucose, and 5.0% other sugars was obtained from CPC International, Inc. (Summit-Argo, IL.). Sucrose ester emulsifier (DK Ester F-110 sucrose fatty acid ester) was provided by Dai-Ichi Kogyo Seiyaku Co., Ltd. of Tokyo, Japan. Mono- and diglyceride emulsifier (Panalite 50 SVK #510) with 52% minimum alpha monoglyceride content was obtained from ADM ARKADY, Olathe, Kansas. The emulsifier, and Kroger brand fresh whole eggs, were kept refrigerated until use, at which time they were brought to room temperature.

Cake Procedure

The cake formulas are listed according to treatment in Tables 5a and 5b. The basic HFCS cake formulations were adapted from those of Volpe and Meres (1976). Cakes were mixed by a modified conventional method (Campbell et al, 1979) using a Kitchen-Aid model K-5A mixer (Hobart, Troy, OH) connected to a power source through a Gralab laboratory timer (Gralab, Dayton, OH). This method consisted of creaming the sweetener with the fat, and then adding the egg

Table 5. Pilot study cake formulae.

- (a) HFCS vs. sucrose; corn oil vs. vegetable shortening
 (b) HFCS vs. sucrose; emulsified (MDG and SE) vs. unemulsified

(a) Formula for HFCS/sucrose cakes

Ingredient (g)	Replacement level of HFCS for sucrose		
	0%	50%	100%
Cake flour	200	200	200
Egg yolk	57.2	57.2	57.2
Sucrose/HFCS	240/0	120/169	0/338
Fat (shortening or oil)	108	108	108
Egg white	82.8	82.8	82.8
Nonfat dry milk	20	20	20
Baking powder	10	10	10
Cream of Tartar	3	3	3
Distilled water	149	99	50

(b) Formula for HFCS/sucrose cakes

Ingredient (g)	Replacement level of HFCS for sucrose		
	0%	50%	100%
Cake flour	185	185	185
Egg yolk	57.2	57.2	57.2
Sucrose/HFCS	240/0	120/169	0/338
Corn oil	81	81	81
Egg white	82.8	82.8	82.8
Nonfat dry milk	20	20	20
Baking powder	10	10	10
Cream of Tartar	3	3	3
Distilled water	149	99	50
MDG emulsifier	"	"	"
SE emulsifier	"	"	"

" MDG = 0, 1, 2, 3%

" SE = 0, 1, 2, 3, 4%

yolks to the fat-sugar system. The dry ingredients were sifted together and added alternatively with the water. The egg whites were whipped separately and quickly folded into the batter by hand (60 strokes). When required, mono- and diglyceride emulsifier was added warm to blend with the corn oil, while sucrose ester emulsifier was hydrated with part of the formula water and added with it. For each cake, six hundred and thirty grams of batter were poured into a 20x20x5 cm cake pan and baked at 350 degrees F for 34 minutes in a Westinghouse household type oven. The cakes were allowed to cool one hour before objective measures were taken, and were kept wrapped 24 hours in polyvinyl plastic prior to sensory evaluation.

Objective Analyses

A. Pilot study

Cake Volume: Volume was determined by two methods, rapeseed displacement (Campbell et al, 1979) and the AACC template method (AACC, 1968).

Instead of using a volumeter, which caused excessive cake flattening and consequent volume loss because of the amount of seed required to pour onto a cake, a simple apparatus, amounting to a cake pan side-wall extender, was devised (Figure 12). The extender did not require nearly as many seeds be poured into it. It was designed to fit

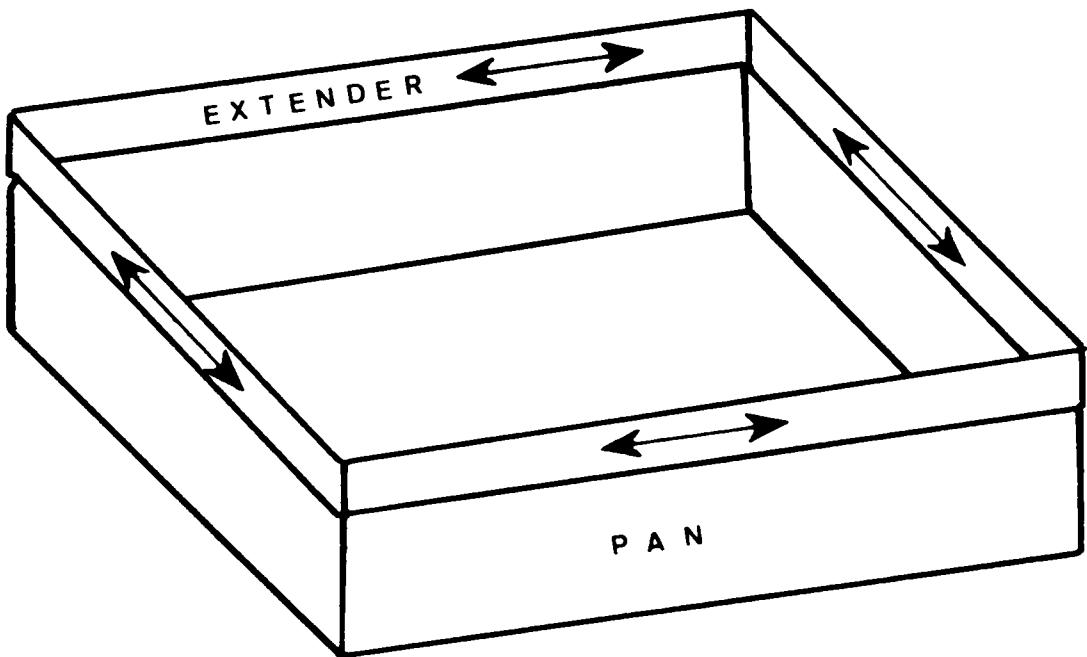


Figure 12. Cake pan side wall extender.

squarely onto the perimeter of a cake pan, being just taller than the cakes being measured. In order to calculate cake volume, the cake was left in the pan, the extender was attached to the pan, and just enough seeds were poured to cover the cake; excess seed was scaled off across the top of the extender. The weight of seed that covered the cake was then measured, and was equated to a definite volume (cm^3), since the weight of seed per unit volume (100 cm^3) had already been ascertained in g/cm^3 . This led to a formula for cake volume by seed displacement:

$$\text{Cake Vol} = (\text{Vol}_{\text{pan}}) + (\text{Vol}_{\text{extender}}) - (\text{Vol}_{\text{seed}})$$

$$\text{Cake Vol} = (19.6 \times 19.6 \times 4.9 \text{ cm}) + (960) - (\text{Vol}_{\text{seed}})$$

$$\text{Cake Vol} = (2842) - (\text{Vol}_{\text{seed}})$$

The AACC template can be used to obtain a "volume index" which is a sum of the three center heights at cross-section, $B + C + E$ (Figure 13). However, it was discovered that an approximation of the seed volume, with consistently 5% error or less, could be determined by using the following formula:

$$\text{Cake Volume} = \left(\frac{B + C + D}{3} \right) \times s^2$$

where s^2 = length x width of the square pan

Template for Method 16-01

©1982, 1972, American Association of Cereal Chemists, Inc.

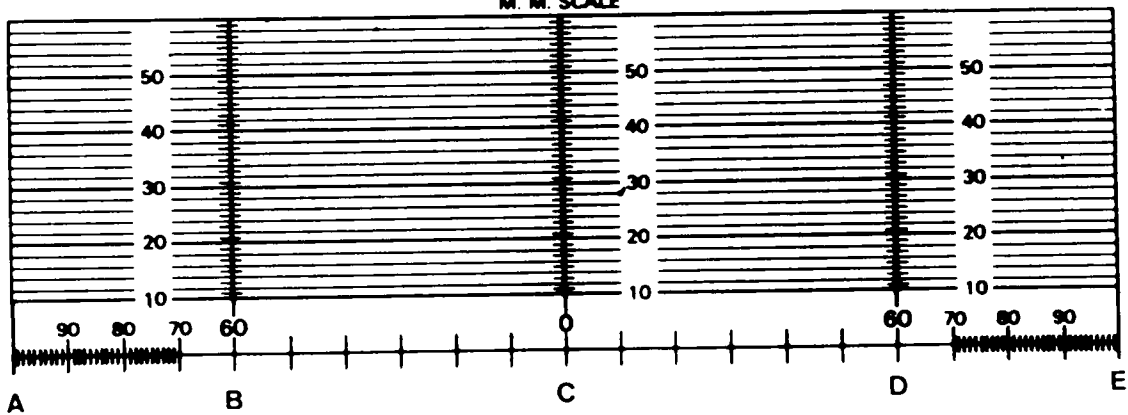
LAYER CAKE MEASURING CHART
M. M. SCALE

Figure 13. AACC layer cake measuring template (reduced from full size).

A third method was created which made use of integral calculus. The volume of revolution of any number of shapes including discs and domes are given by specific formulas in calculus. A typical cake resembles a rectangular base with a domed top (Figure 14). The total volume is calculated as follows:

$$V_{\text{total}} = V_{\text{base}} + V_{\text{dome}}$$

where the V_{base} (a "flattened cube") = $l \times w \times h$ and V_{dome} of radius r and height y is given by:

$$V_{\text{dome}} = \pi \int_0^h (r - y^2)^2 dy$$

in our case, $r = 9.8$, and thus:

$$V_{\text{dome}} = \pi \int_0^h (96.04 - 19.6y^2 + y^4) dy$$

$$V_{\text{dome}} = \pi \left(96.04y - \frac{19.6y^3}{3} + \frac{y^5}{5} \right) \Bigg|_0^h$$

substitute height value for y (using C of template - h) and solve for V_{dome} . Although it was fun to visualize the cube + dome nature of a cake and to have an opportunity to apply advanced mathematics to create an alternative volume determination, the calculus volumes differed for the rapeseed volumes by as much as 10%.

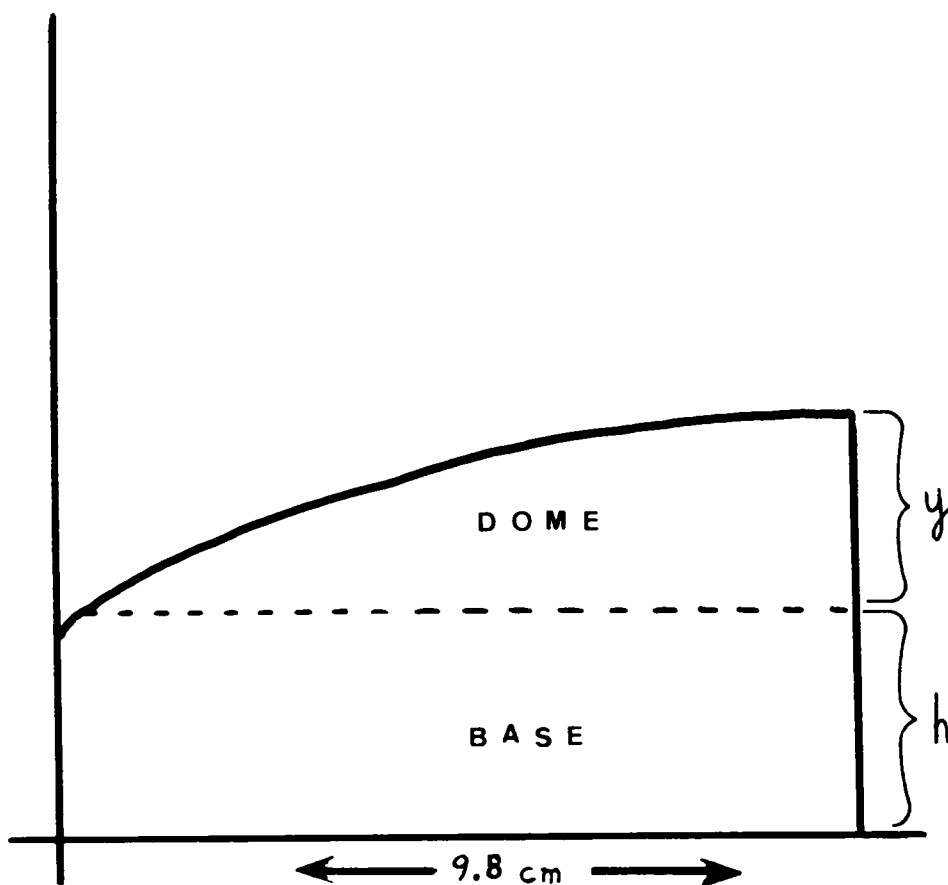


Figure 14. Cross-section of half a cake section, showing rectangular base and domed top.

This discrepancy presumably was due to the fact that the dome is not a good enough approximation of the upper surface of a cake, plus the cake contours and symmetries are often quite variable.

In all cases where cake volumes are reported, they are the rapeseed volumes using the extended side.

Deformation: As an index of tenderness, a Hi-accuracy Penetrometer (Lab-Line Instruments; Melrose Park, IL) with a 50 g weight attachment was used to compress cake samples. Three cake mini-sections, approximately 3 x 3 x 5 cm each, were cut from the center of the cakes, and the readings (force required for compression) were averaged. A Baker compressimeter (F. Watkins Corp., West Caldwell, NJ) was used to confirm the compression required, and since a strong correlation ($r = 0.8$) existed, the penetrometer, which was simple to operate, was used throughout the study.

B. Research Problem

Volume: The volume was determined as described in the pilot study.

Deformation: The deformation was determined as described in the pilot study.

Color: Both cake crust and cake crumb color were measured using a Hunter Labscan Spectrocolorimeter with cathode ray tube display (Hunter Associates Laboratory, Reston, VA). Cakes were sectioned and color analyzed 24 hours after baking. The instrument displayed the L, a, b, and ΔE color values according to the specifications of the CIE (Commission Internationale d'Eclairage). The "L" value is a measure of lightness, 0 = black, 100 = white. The "a" value measures green (-) to yellow (+). The relationship between L, a, b and ΔE (Figure 15) is given by the following formula:

$$\Delta E = \sqrt{L^2 + a^2 + b^2}$$

Moisture: Moisture analysis was performed on 24-hour cooled cakes that had been wrapped in air tight polyvinyl film by oven-drying using a Brabender Model SAS-692 (South Hackensack, NJ) moisture tester. Duplicate 10.0 g samples of cake crumb from as near to cake center as possible were dried for 2 hours at 155°C.

pH: pH of freshly-made batter was determined with a Corning Model 5 pH meter (Corning, NY) calibrated to pH 7.0 at 22°C.

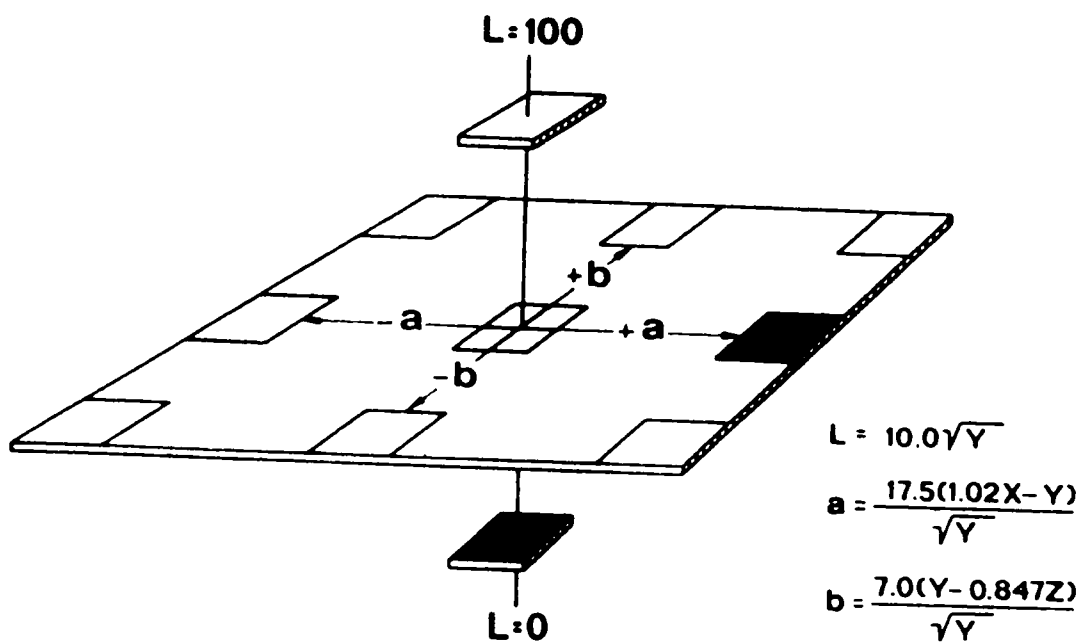


Figure 15. The L, a, b Hunter color solid (from Hunter Lab, Reston, VA).

Specific Gravity: Batter specific gravity was determined by filling a 50 ml container with fresh batter, recording the weight, and dividing that by the weight of the same container filled with water.

Flow Rate: Batter flow rate was measured by pouring fresh batter fully into a 6.5 cm diameter funnel, which was set directly over a 25 ml graduated cylinder. The batter was released and allowed to flow freely into the cylinder, and the amounts obtained after $t = 30$ seconds and $t = 45$ seconds were recorded and averaged to give a flow rate in ml/sec.

Emulsion Stability: A method was developed which involved preparing batter with a lipophilic dye (Oil-Red-O, No. 0625, Sigma Chemical Co., St. Louis, MO) added, placing 10 ml of the dyed batter into a test tube, and measuring the absorbance of the bottom 5 ml immediately and at timed intervals ($t = 30$ min, 1 hr, 2 hr) in cuvette. The dye imparted a red color to the batter, which was measured in a spectrophotometer. If the emulsion became unstable (ie: the oil and water phases separated) the dye would reside in the upper oil phase and be absent from the bottom aqueous phase, resulting in a drop in absorbance.

Sensory Evaluation

A. Pilot Study

Sensory evaluation of the cakes was completed within 24 hr of each baking session by an 8-member volunteer panel of 6 graduate students and one technician from the Department of Human Nutrition and Foods (6 female, 1 male) and one graduate student (male) from the Department of Food Science and Technology. Panelists received one training session to explain the attributes to be evaluated (sweetness, tenderness, and aftertaste). The panelists were seated at partitioned gray sensory booths, received 6 samples (approximately 3 x 3 x 4 cm) per session, and were given fresh water ad libitum.

A simple ranking for sets of 3 samples (done in duplicate at each session) was performed. Samples were presented with a code of randomly chosen letters and placed on white paper plates. Six different sets of 3 samples were evaluated in all, corresponding to the three rows and the three columns of the experimental design (Table 3a) as the 0, 50, and 100% HFCS column groups and the 0, 50, and 100% corn oil row groups. An example of the score sheet is given in Appendix A.

B. Research Problem

Sensory evaluation of the cakes was completed within 24 hr of each baking session (Table 4b) by an 8-member volunteer panel of 6 female graduate students, 1 male graduate student, and one female technician, all from the Department of Human Nutrition and Foods at Virginia Polytechnic Institute and State University. A modified Quantitative Descriptive Analysis (QDA) method was used (Stone and Sidel, 1985). Panelists received two training sessions, with the investigator serving as panel leader. Score sheets were prepared using the terminology the panel members developed. The panelists discussed the terms for clarification so that all would feel comfortable with the descriptive terms decided upon. The terms were tested by the panelists with trial samples.

Ingredients in the samples were not identified, as they might influence the panelists' expectations. The descriptive terms which evolved from the training sessions were: cell size, cell uniformity, crumb color, sweetness, moistness, tenderness, and aftertaste. Six samples were presented to the panelists at each taste session in private sensory booths as before. Cake samples (approximately 3 x 3 x 4 cm in size) were coded with three-digit numbers and placed on white napkins. The panelists marked on a nonnumerical, unstructured 15 centimeter horizontal line

their impressions of each sample according to the descriptive anchor words. The length of each marked line segment was measured and recorded as a score, according to the QDA method of Stone and Sidel (1985). A sample score card is given in Appendix A.

Differential Scanning Calorimetry

A Perkin-Elmer DSC-4 Differential Scanning Calorimeter with microprocessor controller and data handling (Perkin-Elmer Corp., Norwalk, CT) was used to analyze starch gelatinization of cake batter and ovalbumin denaturation and starch gelatinization in model systems. Samples were weighed on a Perkin-Elmer AD-6 computerized micro balance. Indium was used as a standard for calibrating temperatures.

A. Model System: Ovalbumin Denaturation

Fresh egg white and water with or without added emulsifiers (4% w/w basis) and sweeteners (0%, 50%, or 100% HFCS on a 50% w/w basis) were heated from 0 to 120°C at a scan rate of 10 deg/min in large volume aluminum DSC pans. The capsules were sealed with a press and heated in the DSC apparatus, with an empty pan as a reference. The DSC thermograms (plots of heat flow as a function of temperature) for egg white showed two major endotherms, at roughly 65°C and 85°C, due to the denaturation of conalbumin

and ovalbumin. The T_{onset} and T_{max} were recorded and averaged for comparison among the 9 variations (Figure 16).

B. Model System: Starch Gelatinization

Wheat starch in water (1:3 ratio) with or without added emulsifiers (10% of starch weight) and sweetener (0, 50, and 100% HFCS added at 100% starch weight) were sealed into standard aluminum DSC pans and heated from 0 to 120°C at 10°C per minute. The major endotherm which resulted represented starch gelatinization, and the onset and maximum temperatures were recorded and averaged for comparison among the 9 variations (Figure 16).

C. Cake Batter

The gelatinization of starch from flour present in the cake batters was measured. Each batter variation was prepared and a small aliquot (approximately 50 mg) was weighed into the DSC pan. The samples were heated from 40 to 140°C at a scan rate of 10°C per minute. The sensitivity was set at 5 mcal/sec and rescaled to 1.5 mcal/sec. The reference material was an empty pan.

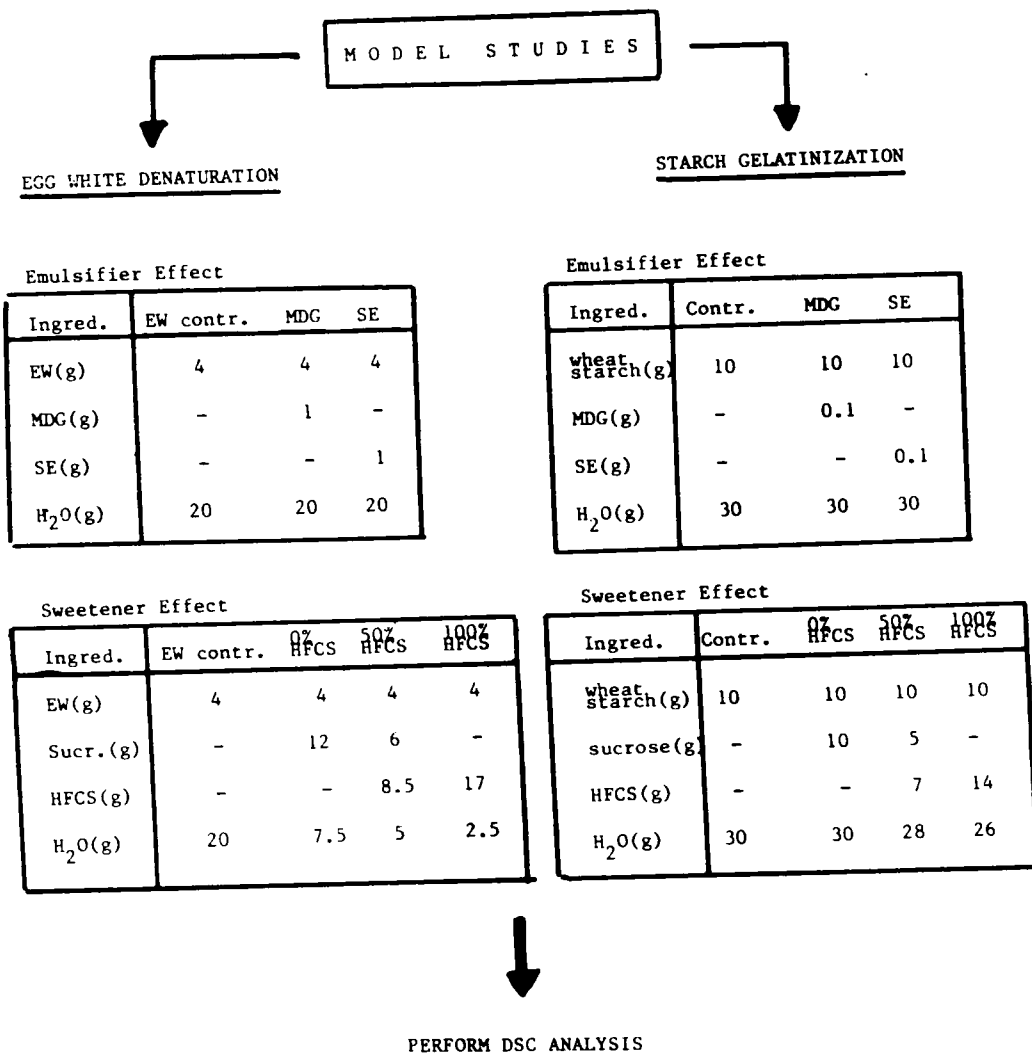


Figure 16. Flow chart for determining egg white protein denaturation and starch gelatinization in model systems.

Microscopy

A. Light Microscopy (LM)

1. Cake batter smears were made by placing 50 g of fresh batter into a beaker, adding one drop of a hydrophilic dye (Fast Green FCF, #F7258, Sigma Chemical Co., St. Louis, MO) plus three drops of Oil-Red-O (#O-0625, Sigma Chemical Co., St. Louis, MO) which is a lipophilic dye. One drop of stained batter was placed on a microslide and a plastic cover slip was placed over it. A Vanox Brightfield Microscope Model AHBT (Olympus Optical Co., Tokyo, Japan) was used to view the batter smears at 250x magnification. Photographs were taken of the batters, with black-and-white Kodak Tri-X pan 400 film.

2. Thick TEM cake sections were viewed at 250, 500, and 1000x magnification using the Vanox microscope. The sections had been fixed in a general purpose fixative, embedded in Polybed 812 resin, and stained in Safranin red and Toluidine blue (see following section). Black-and-white photographs were taken as before.

B. Transmission Electron Microscopy (TEM)

Cake crumb samples were cut into approximately 5 mm square blocks. These were fixed in 5% glutaraldehyde and 3% formalin in 0.05 M Na cacodylate buffer, pH 7.3 overnight. Post-fixation was accomplished on washed samples using 2%

osmium tetroxide in 0.1 M Na cacodylate. Dehydration was in graded alcohols, 15, 30, 50, 70, 95, and 100% for 15 minutes each. Samples were then held in propylene oxide for another 15 minutes, and infiltrated in pure resin overnight.

Thick sections (0.2 to 0.5 mm trapezoidal-shaped) of prepared samples were cut under a dissecting microscope and stained with 0.5% Safranin red and 1.0% Toluidine blue. The stained thick sections were examined using light microscopy (see previous section) to identify subsections for ultrathin sectioning. The ultrathin sectioning was performed with an ultramicrotome. Ultrathin ribbon sections of cake crumb approximately 20 microns in length were stained with Reynold's lead citrate (Stevens Metallurgical Corp., NY) and 2% uranyl acetate. The stained ribbons were then applied to 200 mesh copper hexagonal grids and viewed at 4800x and 10,000x magnification in a JEOL JEM-100 CX II TEMSCAN (JEOL USA Inc., Medford, MA) electron microscope.

C. Scanning Electron Microscopy (SEM)

Heated (to 95°C in a water bath) and unheated cake batters were spray-dried in a Buchi 190 Mini Spray Dryer (Buchi Instruments, Flawis, Switzerland) which was operated at maximum aspiration with an inlet temperature of 182°C and an outlet temperature of 110°C. Drying is a critical specimen preparation step for samples to be analyzed via

SEM. The spray-dried samples were stored in a dessicator prior to viewing.

The dried batter samples were affixed to specimen stubs using a silver adhesive paint and then coated in a thin carbon base followed by gold using an SPI Sputter Coater (Structure Probe, Inc., West Chester, PA). The coated stub samples were examined at various magnifications (2000-4000x) using a JEOL JSM-35C (JEOL USA, Inc., Medford, MA) scanning electron microscope operated at an accelerating voltage of 10 or 15 kV. Black and-white photographs were taken using Polaroid Type 55 P/N film.

Statistical Treatment of the Data

The experimental design of the research problem was a balanced incomplete block (BIB) design. In such a design, t treatments are distributed over b blocks, each of size k , where $k < t$, such that each treatment occurred in r blocks, no treatment occurring more than once in a block, with each pair of treatments occurring in y blocks.

The research study's BIB design had parameters treatments $t = 9$, $b = 12$, $k = 3$, $r = 4$, and $y = 1$.

For objective and sensory data having replications in triplicate or quadruplicate, standard statistical analyses

were performed. These included calculating the mean, standard deviation, and range for each data set. The analysis of variance (ANOVA) technique was used to estimate the variation in the data. ANOVA compared means from different sample groupings and tested whether they were the same or whether significant ($p < 0.05$) or marginally significant ($p < 0.10$) differences existed. The ANOVA F test identified situations when means were statistically different from each other (thereby rejecting the null hypothesis, the hypothesis of no difference) but a further test was required to identify which means differed from which other means. This was accomplished by a specific multiple comparison test method: Duncan's Multiple Range Test. The Duncan test was performed at the $p < 0.05$ level of significance.

The Pearson product-moment correlation (r), when used, measured the closeness of a linear relationship between two variables. A correlation of zero would mean that each variable had no predictive ability for the other, whereas this ability would increase as the correlation approached a value of positive one or negative one. Customarily, a correlation is significant if the r value of the data exceeds the highest correlations obtainable by chance as presented in statistical tables for critical values of r for a given number of degrees of freedom. The coefficient of

determination r^2 provided an easily understood measure of the degree of association between variables. When r exceeded 0.7, then the majority of the variation of one variable was explained by the variation in the other variable. Correlation did not imply causality, but it might provide a clue to causality.

Kramer's statistical test for ranked data is based on a table of critical values. The sensory averages of the pilot study were tested for significant differences at the $p < 0.05$ level using the table values.

Coefficient of variation (Cv) was used to examine the intra-individual consistency of the sensory panelists. As such, it was used as an index of performance in each panelist's evaluation of the nine cake variations of the research problem.

Response surface methodology (RSM) was used to test the effects of several variables on different responses. It is a statistical method that used quantitative data from the experimental design and determined and simultaneously solved multivariate equations. These equations were graphically represented as response surfaces. The response surfaces were used to pictorially describe how the test variables affected the response, either singly or in combinations.

IV. RESULTS AND DISCUSSION

Objectives

The overall goal of this research was to study the interaction of HFCS, corn oil, and added emulsifier in a cake system and to optimize the product by RSM.

A. Pilot Study

There were two objectives to the pilot study:

(1) To determine if HFCS and corn oil act independently on objective and sensory attributes of cake. This was investigated by measuring the effects of three levels (0, 50, and 100%) of high fructose corn syrup (HFCS) substituted by weight for sucrose and three levels (0, 50, and 100%) of corn oil (CO) substituted by weight for a plastic unemulsified vegetable shortening upon cake volume and cake deformation, and three sensory attributes (sweetness, tenderness, and aftertaste). Response surface analysis (RSM) was used to generate equations and plots showing how HFCS and CO contributed to cake volume and deformation (tenderness) and to predict the levels of HFCS and CO required to produce optimally tender, high-volume cakes.

(2) To determine the level of emulsifier required to produce an optimum cake using HFCS and corn oil. The

effects of two different emulsifiers (mono- and diglycerides, a low HLB emulsifier and sucrose esters, a high HLB emulsifier) upon cake volume in corn oil-shortened HFCS cakes were measured. Response surface analysis was used to predict the levels of each emulsifier required to produce the optimum cake volumes over all levels of HFCS.

B. Research Problem

There were two objectives to the research problem:

(1) To employ RSM (response surface methodology) to predict the levels of HFCS with and without MDG or SE at levels determined by the pilot study required to produce optimally moist, tender, high-volume cakes lacking objectionable aftertaste.

(2) To study the effect of HFCS and emulsifiers on certain interactions such as starch gelatinization and protein denaturation of a food system.

The objectives were investigated by:

(a) examination of the effects of three levels (0, 50, and 100%) of HFCS with and without mono- and diglycerides (MDG) or sucrose esters (SE) upon batter characteristics: pH, specific gravity, flow, and emulsion stability.

(b) examination of the effects of three levels (0, 50, and 100%) of HFCS with and without MDG or SE upon starch

gelatinization and egg white protein denaturation in model systems and cake batter.

(c) examination of the effects of three levels (0, 50, and 100%) of HFCS with and without MDG or SE upon specific objective cake parameters: volume, deformation, percent moisture, crust and crumb color.

(d) examination of the effects of three levels (0, 50, and 100%) of HFCS with and without MDG or SE upon specific sensory parameters: cell size, cell uniformity, crumb color, sweetness, moistness, tenderness, aftertaste.

(e) examination of the microstructure of the HFCS cake batters and cake crumbs with and without MDG or SE.

The results and discussion are presented in two sections. The first section is related to the objectives of the pilot study while section two is related to the objectives of the research problem.

For ease of discussion the terms 0, 50, and 100% HFCS cakes refer to the level of replacement of HFCS for sucrose in the cake formula. The terms 0, 50, and 100% corn oil refer to the level of replacement of corn oil for hydrogenated vegetable shortening.

I. Pilot Study

In the pilot study, results are grouped according to whether they relate to objective testing of batter and cake or to sensory testing of cake.

OBJECTIVE MEASURES

Batter Specific Gravity: Mean specific gravity of the cake batters ranged from 0.75 to 0.81 but were not significantly different at the 0.05 level (Appendix B).

Cake Volume: The mean values for cake volume are reported in Table 6a. Greatest cake volumes were obtained with the 50% level of HFCS substitution for sucrose. Lowest cake volumes were obtained with the 100% level of HFCS substitution for sucrose. The effect of HFCS on cake volume was significant at the 0.05 level (Table 6b). These

Table 6.

- (a) Mean and RSM-predicted values for cake volume as a function of high fructose corn syrup (HFCS) and corn oil (CO).
- (b) Effects of various factors upon the response variable cake volume

(a)

Actual Data			Predicted Volume ⁴
\bar{x} volume (cm ³) ¹	HFCS(%) ²	CO(%) ³	(cm ³)
1980.5	0	0	1964.41
1951.0	0	50	1987
2029.0	0	100	2009.08
1989.0	50	0	1993.08
2030.3	50	50	2014.41
2023.5	50	100	2035.25
1882.8	100	0	1894.75
1935.0	100	50	1914.83
1926.3	100	100	1934.41

¹ Mean of 4 replications.² % HFCS replacement for sucrose.³ % CO replacement for hydrogenated vegetable oil.⁴ Predicted by RSM (SAS, 1985).

(b)

<u>Day effect</u>	<u>HFCS effect</u>	<u>CO effect</u>	<u>HFCS*CO effect</u>
none	significant	marginal	none
F = 1.13	F = 15.46	F = 2.60	F = 1.45
p = 0.3991	p = 0.0001	p = 0.093	p = 0.2445

HFCS = high fructose corn syrup

CO = corn oil

findings are in general agreement with published results. Volpe and Meres (1976) found that volumes of white layer cakes prepared with HFCS substituted for sucrose 60% by weight exceeded those of 100% sucrose control cakes. Koepsel and Hoseney (1980) reported decreased volumes of high-ratio white layer cakes when 100% of the sucrose was replaced by HFCS. They attributed the volume reduction to decreased air incorporation during mixing and premature starch gelatinization during baking of the 100% HFCS cakes.

Cakes prepared with corn oil replacing solid vegetable shortening 100% by weight showed marginally significant ($p < 0.1$, Table 6b) volume increases at all levels of HFCS when compared to the all-vegetable shortened cakes and those shortened with a blend of corn oil and vegetable shortening (Table 6a).

Cake Tenderness (deformation): The mean values for cake tenderness, as measured by deformation, are reported in Table 7a. The effect of corn oil on cake tenderness was significant ($p < 0.05$, Table 7b). Cakes prepared with solid vegetable shortening (0% corn oil) were significantly less tender than the 100% corn oil cakes. Since liquid corn oil does not have the ability to exert a true shortening effect, this was unexpected.

HFCS also significantly affected cake tenderness (Table 7b), 50 and 100% HFCS cakes were significantly less tender

Table 7.

- (a) Mean and RSM-predicted values for cake deformation as a function of high fructose corn syrup (HFCS) and corn oil (CO).
- (b) Effects of various factors upon the response variable cake deformation

(a)

Actual Data			Predicted Deformat. ⁴
\bar{x} deformation (0.1mm) ¹	HFCS(%) ²	CO(%) ³	(0.1mm)
106.0	0	0	91.85
131.1	0	50	147.25
126.3	0	100	124.38
72.0	50	0	93.23
172.3	50	50	154.33
140.4	50	100	137.17
66.5	100	0	59.35
124.3	100	50	126.15
109.4	100	100	114.68

¹ Mean of 4 replications.² % HFCS replacement for sucrose.³ % CO replacement for hydrogenated vegetable oil.⁴ Predicted by RSM (SAS, 1985).

(b)

<u>Day effect</u>	<u>HFCS effect</u>	<u>CO effect</u>	<u>HFCS*CO effect</u>
none	significant	significant	significant
F = 0.42	F = 15.51	F = 7.52	F = 8.76
p = 0.9279	p = 0.0001	p = 0.0001	p = 0.0001

HFCS = high fructose corn syrup

CO = corn oil

than 0% HFCS cakes. Coleman and Harbers (1983) also detected a decrease in tenderness as HFCS substitution for sucrose in angel food cakes increased from 50 to 100%. Mean cake volume and deformation for each variation of the pilot study are presented as bar graphs in Figure 17.

VOLUME AND DEFORMATION

Pilot Study Experimental Design

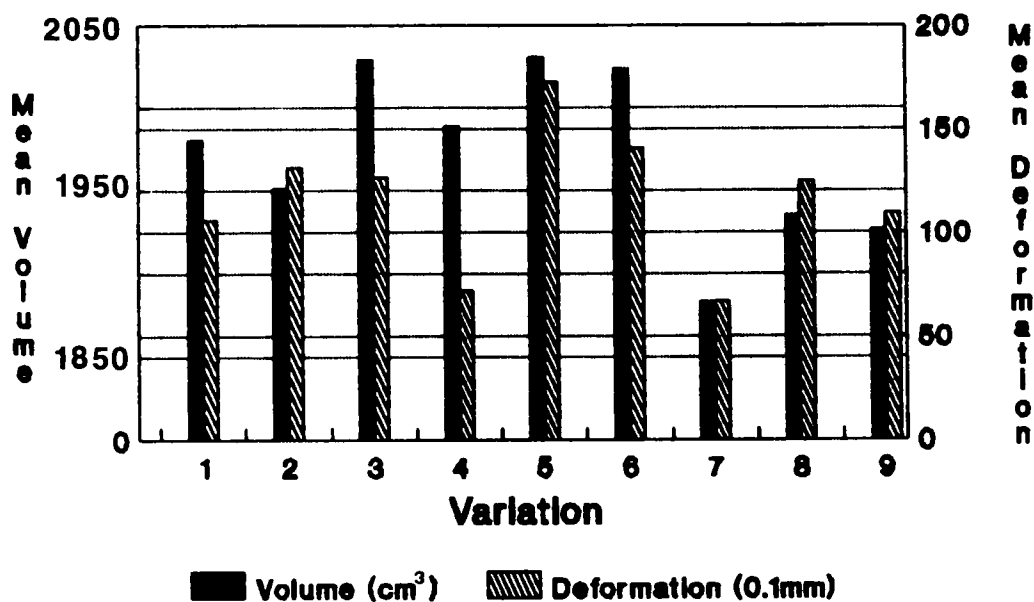


Figure 17. Mean cake volume and deformation for variations 1-9 of pilot study experimental design. Variations 1-3 were 0% HFCS cakes; 4-6 were 50% HFCS cakes; and 7-9 were 100% HFCS cakes. Variations 1, 4, 7 were shortened with unemulsified vegetable shortening (Creamtex, Durkee Industries); variations 2, 5, 8 were shortened with a 50:50 blend of Creamtex and corn oil; and variations 3, 6, 9 were shortened with corn oil.

(HFCS = high fructose corn syrup)

SENSORY MEASURES

The sensory panelists ranked the sweetness, tenderness, and aftertaste of the cake variations. Six different cake variation groupings were evaluated in all. The objective was to compare across three levels (0, 50 and 100%) of HFCS while holding % corn oil constant, and vice-versa (Tables 8a and 8b). The average rankings of four replicates per grouping were tested for significant differences using the rank statistical chart of Kramer et al, 1974). Significance was at the 5% ($p < 0.05$) level.

As the level of HFCS increased within corn oil groups (Table 8a), aftertaste increased. The formation of undesirable flavor components can be a result of the non-enzymatic browning reactions of the fructose and glucose components of the HFCS. HFCS did not affect either tenderness or sweetness.

As the level of corn oil increased within the HFCS groups (Table 8b), tenderness decreased while sweetness and aftertaste were unchanged. Cakes prepared with 100% corn oil were judged to be marginally ($p < 0.1$) less sweet and with less aftertaste than cakes prepared with all vegetable shortening and those containing 50% corn oil. Regarding the effect on aftertaste, possibly corn oil batters, being more fluid than vegetable shortening batters, presented less of a barrier to volatile escape. As off-flavor compounds were

Table 8.

- (a) Results of sensory evaluation by grouping according to % corn oil (CO)
- (b) Results of sensory evaluation by grouping according to % high fructose corn syrup (HFCS)

(a)

<u>Group</u> ¹	<u>Variations Tested</u> ²	<u>Significant Findings (0.05 level)</u> ³
0% CO	1, 4, 7	Variation 7 had greatest aftertaste
50% CO	2, 5, 8	Variation 8 had greatest aftertaste
100% CO	3, 6, 9	Variation 3 had least aftertaste

¹ % replacement of hydrogenated vegetable oil.

² Variations 1, 4, 7 = no emulsifier; variations 2, 5, 8 = mono- and diglycerides as emulsifier; variations 3, 6, 9 = sucrose ester as emulsifier.

³ Rank statistic (Kramer, 1974).

(b)

<u>Group</u> ¹	<u>Variations Tested</u> ²	<u>Significant Findings (0.05 level)</u> ³
0% HFCS	1, 2, 3	Variation 3 was least tender
50% HFCS	4, 5, 6	Variation 6 was least tender
100% HFCS	7, 8, 9	Variation 8 was least tender

¹ % replacement for sucrose.

² Variations 1, 4, 7 = no emulsifier; variations 2, 5, 8 = mono- and diglycerides as emulsifier; variations 3, 6, 9 = sucrose ester as emulsifier.

³ Rank statistic (Kramer, 1974).

formed, more may have been released before becoming entrapped in the cake crust layer. The corn oil/HFCS mixture may have allowed for greater dispersion and effective separation of the reactants involved in non-enzymatic browning as well.

There was disagreement between objective and sensory results regarding cake tenderness. Cakes containing no corn oil (variations 1, 4 and 7) were lowest in deformation (objective tenderness) but highest in sensory tenderness. Cakes containing only corn oil (variations 3, 6 and 9) were high in deformation but were ranked by the sensory panelists as being low in tenderness.

RESPONSE OPTIMIZATION

The RSM program (Mursac Package, Barnard and Batson, Inc., Huntsville, AL) generated equations or models showing the influence of HFCS and corn oil acting as independent variables upon the dependent variables cake volume (Figure 18a) and cake tenderness (Figure 18b). Three-dimensional response surface plots were predicted on the basis of these equations (Figures 19 and 20) for both response variables.

RSM also predicted values of HFCS and corn oil needed for maximum cake volume and tenderness based upon objective measurements (Table 9).

(a)

Equation: $\text{Volume} = 1964.417 + 1.843 (\text{HFCS}) + 0.457 (\text{CO}) + (4.999 \times 10^{-4})(\text{HFCS} \times \text{CO}) + (-0.025)(\text{HFCS}^2) + (-9.999 \times 10^{-5})(\text{CO}^2)$

Coefficient of determination (R^2) = 0.524
 Coefficient of multiple correlation = 0.724
 Standard error of estimate = 47.381

Equation coefficients: constant, 1964.417; HFCS, 1.843; CO, 0.457 (-4.999×10^{-4} , -0.025 , -9.999×10^{-5})

(b)

Equation: $\text{Deformation} = 91.856 + 0.380 (\text{HFCS}) + 1.890 (\text{CO}) + (2.280 \times 10^{-3})(\text{HFCS} \times \text{CO}) + (-7.053 \times 10^{-3})(\text{HFCS}^2) + (-0.016)(\text{CO}^2)$

Coefficient of determination (R^2) = 0.750
 Coefficient of multiple correlation = 0.866
 Standard error of estimate = 18.104

Equation coefficients: constant, 91.856; HFCS, 0.380; CO, 1.891 (2.280×10^{-3} , -7.053×10^{-3} , -0.016)

Figure 18. RSM equation and associated statistics for:

- (a) volume as a function of HFCS and corn oil
- (b) deformation as a function of HFCS and corn oil

CAKE VOLUME AS A FUNCTION OF HFCS AND CORN OIL

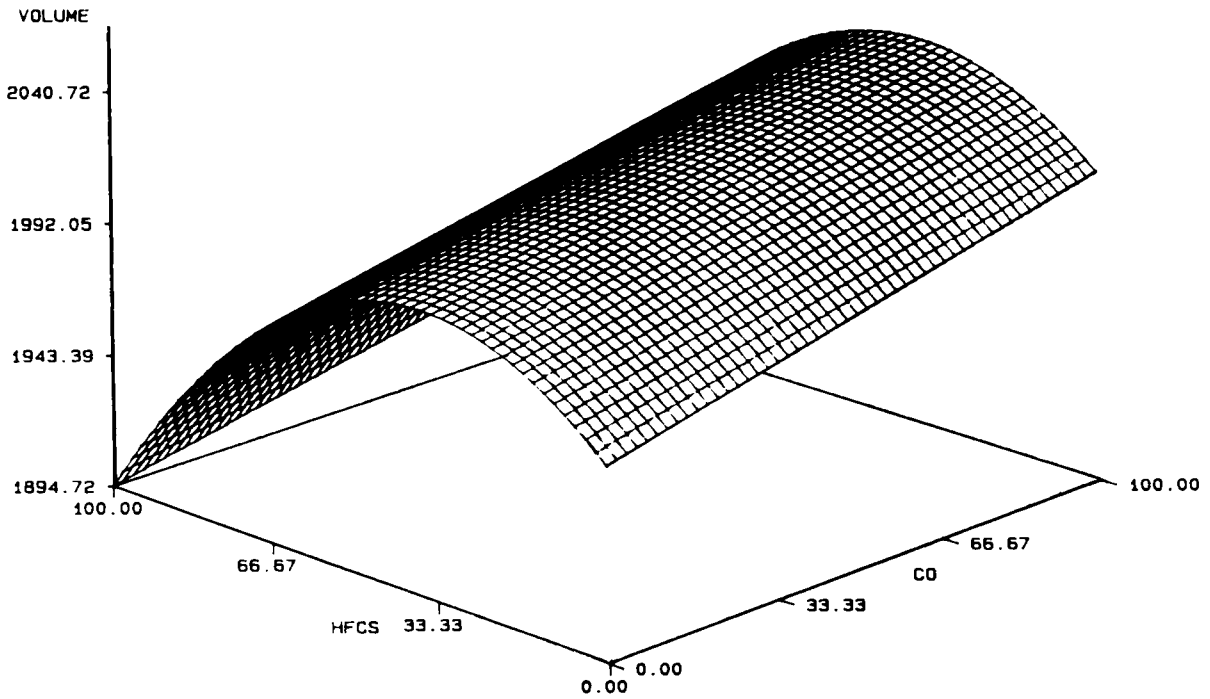


Figure 19. Predicted response surface for cake volume as a function of HFCS and corn oil.

CAKE TENDERNESS AS A FUNCTION OF HFCS AND CORN OIL

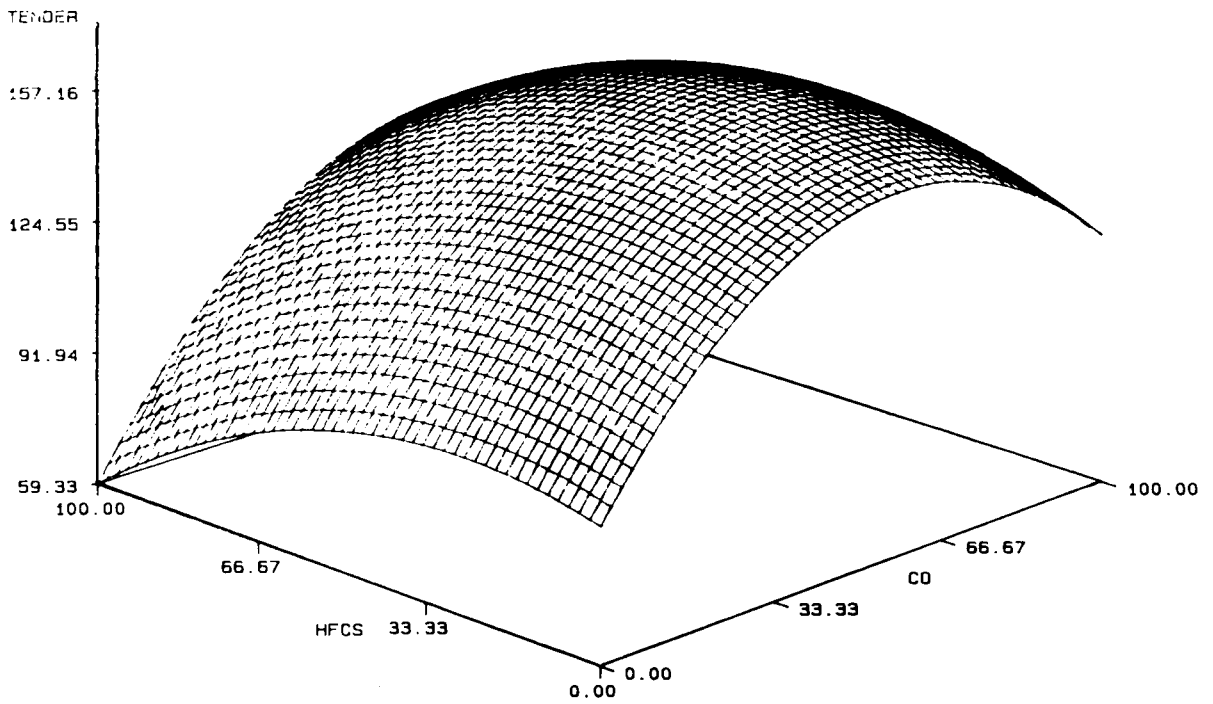


Figure 20. Predicted response surface for cake tenderness (deformation) as a function of HFCS and corn oil.

Table 9. Dependent variables (volume and deformation) maximized via RSM according to percentage HFCS and corn oil.

<u>Maximized Dependent Variable</u>	<u>%HFCS</u>	<u>%CO</u>
volume (2041 cm ³)	35	100
tenderness (15B 0.1mm)	41	64

Cake volume was increased when corn oil was substituted 100% weight for hydrogenated vegetable shortening. Since the addition of an emulsifier to the batter might also improve volume, a further objective of the pilot study was to investigate using an emulsifier in the cake formulations. Both a low HLB emulsifier (MDG = mono- and diglycerides) and a high HLB emulsifier (SE = sucrose esters) were tested. In addition, the corn oil content of the batters with and without emulsifiers was reduced by 25% based upon reports in the literature which mentioned lower requirements for liquid shortening levels (Knightly, 1981; Rasper and Kamel, 1989) as compared to hydrogenated shortenings.

Adding an emulsifier also allowed for an increase in water content of batter. Since corn oil caused decreased sensory tenderness, the flour content of the batters (flour is a toughener) was decreased 7.5% to 185 grams. This also increased the hydration of the dry ingredients, effectively increasing water content.

The level of MDG added to batter was 1.0, 2.0 and 3.0% based upon flour weight. RSM program (RSReg, SAS Institute, Cary, NC) generated the model for cake volume as a function of HFCS and MDG (Figure 21a), predicted volumes for any level of HFCS and MDG (Figure 21b) and generated the three-dimensional fitted response surface (Figure 22). Any level of MDG used caused cake volume to decrease at all HFCS

(a)
$$\text{Volume} = 2010.06 + (7.843)\text{HFCS} + (-26.956)\text{MDG} \\ + (-7.9 \times 10^{-2})\text{HFCS}^2 + (-2.04 \times 10^{-1})\text{HFCS} \times \\ \text{MDG} + (-39.417)\text{MDG}^2$$

(b)

<u>% MDG</u>	<u>Predict. Vol.</u>	<u>% HFCS</u>
0	2010.06	0
0.5	1986.73	0
1.0	1943.69	0
0	2205.50	50
0.5	2177.08	50
1.0	2128.94	50
0	2007.52	100
0.5	1974.01	100
1.0	1920.79	100

Figure 21:

- (a) RSM model for volume as a function of HFCS and MDG.
 (b) RSM predicted values for volume as a function of HFCS and MDG.

PLOT OF THE FITTED RESPONSE SURFACE

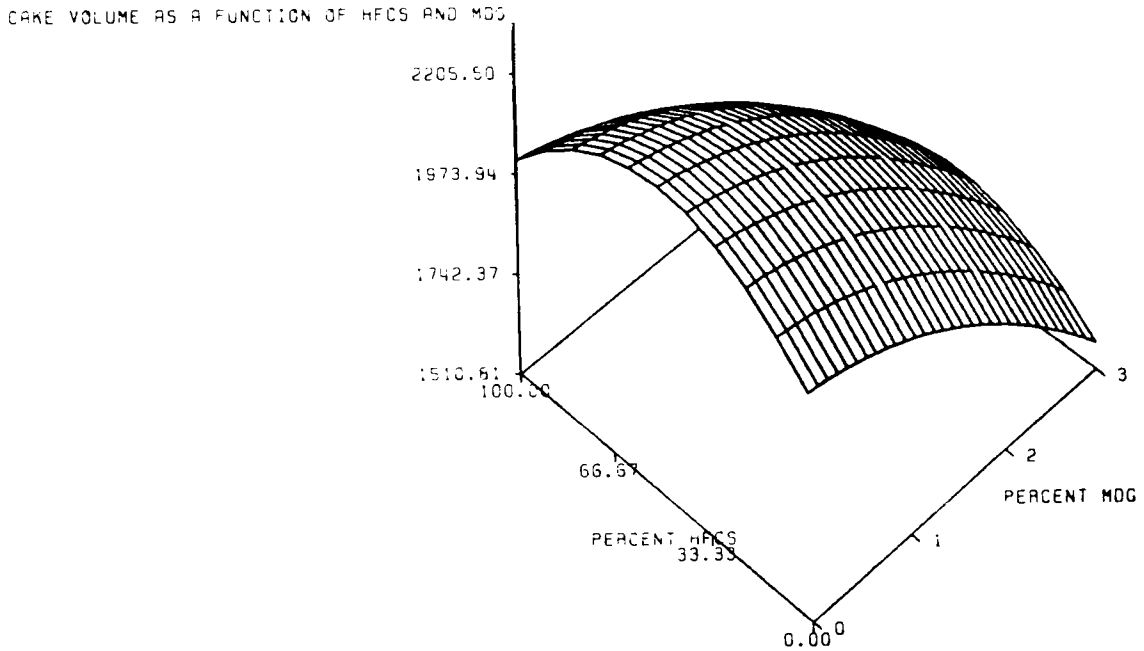


Figure 22. Plot of the predicted response surface for the variable cake volume as a function of the levels of HFCS (high fructose corn syrup) and MDG (mono- and diglycerides) shown.

levels. An increase in sensory tenderness did appear to occur, however. The level of 0.5% MDG (approximately one gram) was chosen as a compromise between volume and tenderness effects for use in the research problem.

The level of SE added to batter was 1.0, 2.0, 3.0, and 4.0% based upon flour weight. The SAS RSM program generated the model for cake volume as a function of HFCS and SE (Figure 23a), predicted volumes for any level of HFCS and SE (Figure 23b), and generated the three-dimensional fitted response surface (Figure 24). Optimum volume occurred in the range of 1.3 - 2.1% SE and depended upon the level of HFCS used. The level of 1.7% SE (approximately 3 grams) was chosen as a compromise over the HFCS levels for use in the research problem.

SUMMARY OF PILOT STUDY

Shortened yellow cakes were prepared using 0, 50, and 100% HFCS substituted for sucrose by weight of sugar and 0, 50, and 100% corn oil substituted for hydrogenated vegetable shortening by weight of fat. This resulted in nine treatment variations. The amount of HFCS used had a significant effect on both the volume and deformation of the cakes. Corn oil significantly affected deformation only. There was a marginally significant trend in volume increase as percent corn oil increased. RSM showed that HFCS and

(a)
$$\text{Volume} = 2030.68 + (3.011)\text{HFCS} + (14.680)\text{SE} + (-3.07 \times 10^{-2})\text{HFCS}^2 + (-5.67 \times 10^{-2})\text{HFCS} \times \text{SE} + (-3.450)\text{SE}^2$$

(b)

<u>% SE</u>	<u>Predict. Vol.</u>	<u>% HFCS</u>
1.7	2045.66	0
2.1	2046.29	0
2.6	2045.52	0
1.2	2113.75	50
1.7	2114.67	50
2.3	2113.50	50
0.5	2028.52	100
1.3	2030.76	100
2.1	2028.59	100

Figure 23:

- (a) RSM model for volume as a function of HFCS and SE.
 (b) RSM predicted values for volume as a function of HFCS and SE.

PLOT OF THE FITTED RESPONSE SURFACE

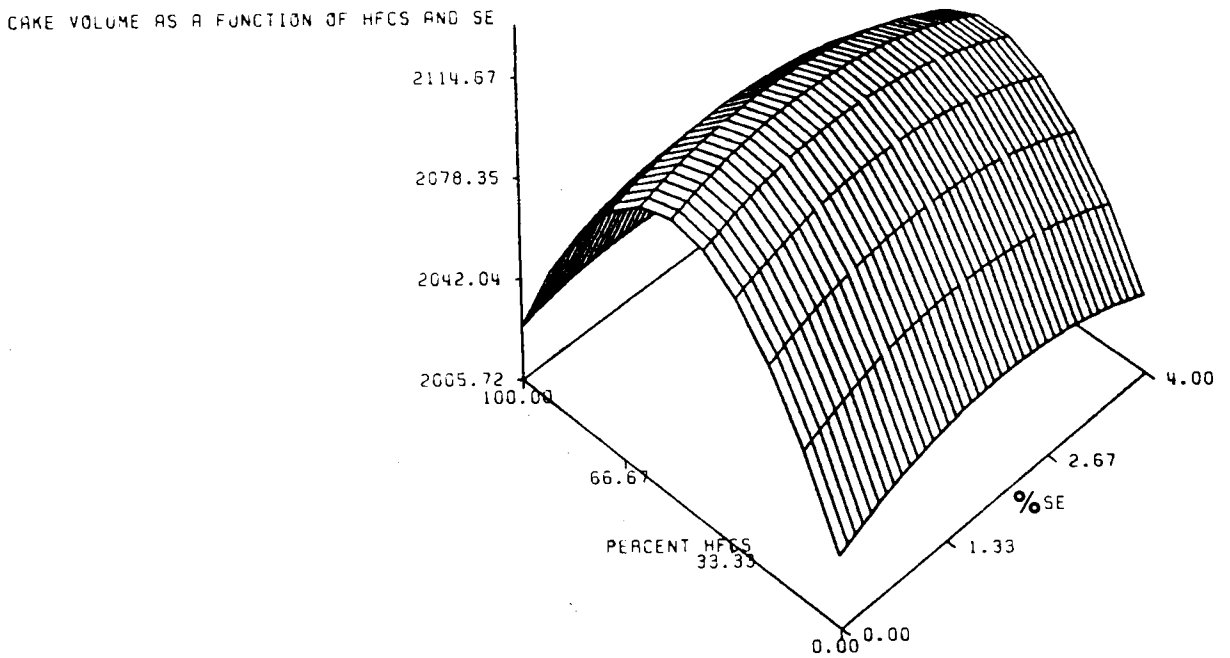


Figure 24. Plot of the predicted response surface for the variable cake volume as a function of the levels of HFCS (high fructose corn syrup) and sucrose ester (SE) emulsifier shown.

corn oil acted independently in affecting cake volume and tenderness. The levels of HFCS and corn oil predicted by RSM to produce optimally tender cakes were 41% and 64% respectively, and to produce optimal volume: 35% HFCS and 100% corn oil. Two emulsifiers, one a low HLB and one a high HLB (MDG and SE, respectively) were incorporated into the HFCS-corn oil cake formulations at levels of 1.0 and 3.0 grams per total batter weight based upon preliminary baking data of 0, 50, and 100% HFCS cakes analyzed by RSM.

II. Research Problem

For the research problem, results will be presented under five main headings, in the manner of the objectives: (1) batter characteristics, (2) cake characteristics, (3) sensory parameters, (4) microstructure, and (5) response surface methodology.

BATTER CHARACTERISTICS

The mean values for batter pH, specific gravity, and flow rate are reported in Table 10.

pH: High fructose corn syrup (HFCS) had a statistically significant effect on batter pH (Table 11a). Batters prepared with sucrose only were significantly higher in pH than either the 50% or 100% HFCS batters (Table 12a).

Table 10. Mean¹, standard deviation, and range values for batter pH, specific gravity (SG), and flow rate (FLOW).

- (a) values per cake variation
(b) values overall

VARIABLE	N	MEAN	STANDARD DEVIATION	MINIMUM VALUE	MAXIMUM VALUE	STD ERROR OF MEAN
----- VARI=1 -----						
PH	4	6.88750000	0.04787136	6.85000000	6.95000000	0.02393568
SG	4	0.76850000	0.00680686	0.75900000	0.77500000	0.00340343
FLOW	4	0.20125000	0.05567989	0.15900000	0.27900000	0.02783994
----- VARI=2 -----						
PH	4	6.98750000	0.08539126	6.90000000	7.10000000	0.04269563
SG	4	0.77825000	0.03111672	0.75600000	0.82400000	0.01555836
FLOW	4	0.25025000	0.05239195	0.19100000	0.31800000	0.02619598
----- VARI=3 -----						
PH	4	7.01250000	0.11086779	6.90000000	7.15000000	0.05543389
SG	4	0.75525000	0.03575262	0.72200000	0.80600000	0.01787631
FLOW	4	0.13975000	0.02581182	0.10700000	0.17000000	0.01290591
----- VARI=4 -----						
PH	4	6.75000000	0.07071068	6.65000000	6.80000000	0.03535534
SG	4	0.75350000	0.04667976	0.71000000	0.80100000	0.02333988
FLOW	4	0.22650000	0.09872014	0.12900000	0.35000000	0.04936007
----- VARI=5 -----						
PH	4	6.88750000	0.08539126	6.80000000	7.00000000	0.04269563
SG	4	0.75525000	0.02390781	0.77900000	0.83700000	0.01195390
FLOW	4	0.33550000	0.04619163	0.29200000	0.40000000	0.02309581
----- VARI=6 -----						
PH	4	6.86250000	0.06291529	6.80000000	6.95000000	0.03145764
SG	4	0.77325000	0.00865544	0.76200000	0.78100000	0.00432772
FLOW	4	0.18500000	0.05760208	0.10100000	0.23000000	0.02880104
----- VARI=7 -----						
PH	4	6.82500000	0.05000000	6.75000000	6.85000000	0.02500000
SG	4	0.76125000	0.01317510	0.74900000	0.77500000	0.00658755
FLOW	4	0.23850000	0.04891830	0.16900000	0.27900000	0.02445915
----- VARI=8 -----						
PH	4	6.82500000	0.08460254	6.75000000	6.95000000	0.04330127
SG	4	0.82700000	0.02408319	0.80400000	0.86000000	0.01204159
FLOW	4	0.40525000	0.01894310	0.37700000	0.41700000	0.00947255
----- VARI=9 -----						
PH	4	6.83750000	0.08539126	6.75000000	6.95000000	0.04269563
SG	4	0.77575000	0.00758837	0.76500000	0.78200000	0.00379418
FLOW	4	0.20375000	0.01800694	0.18200000	0.22000000	0.00900347

¹ Mean of 4 replications.

(b) VARIABLE	N	MEAN	STANDARD DEVIATION	MINIMUM VALUE	MAXIMUM VALUE	STD ERROR OF MEAN
PH	36	6.87500000	0.10453981	6.65000000	7.15000000	0.01742330
SG	36	0.77761111	0.03230770	0.71000000	0.86000000	0.00538462
FLOW	36	0.24286111	0.09015737	0.10100000	0.41700000	0.01502623

Table 11. Effects of high fructose corn syrup (HFCS) and emulsifier on batter characteristics.

- (a) pH
- (b) specific gravity
- (c) flow rate

(a)

<u>HFCS Effect</u>	<u>Emulsifier Effect</u>	<u>HFCS X Emuls. Effect</u>
significant	marginal	none
F = 11.20	F = 4.16	F = 1.03
p = 0.0003	p = 0.1053	p = 0.4088

(b)

<u>HFCS Effect</u>	<u>Emulsifier Effect</u>	<u>HFCS X Emuls. Effect</u>
none	significant	none
F = 1.95	F = 6.83	F = 1.39
p = 0.1625	p = 0.0514	p = 0.2634

(c)

<u>HFCS Effect</u>	<u>Emulsifier Effect</u>	<u>HFCS X Emuls. Effect</u>
significant	significant	none
F = 8.07	F = 19.65	F = 1.39
p = 0.0018	p = 0.0085	p = 0.2640

Table 12. Results of Duncan's Multiple Range Test for batter variables pH, SG, flow rate according to:

- (a) HFCS
(b) emulsifier.

(* denotes significant differences at 0.05 level).

(a)

<u>HFCS</u>	<u>Mean pH</u>	<u>Mean SG</u>	<u>Mean Flow</u>
0	6.9625*	0.7673	0.1971*
50	6.8333	0.7775	0.2490
100	6.8292	0.7880	0.2825

(b)

<u>Emul.</u>	<u>Mean pH</u>	<u>Mean SG</u>	<u>Mean Flow</u>
0	6.821	0.7611	0.2221
MDG	6.900	0.8037*	0.3303*
SE	6.904	0.7681	0.1762

This disagrees with the results of Coleman and Harbers (1983), who reported no significant pH differences in 0, 50, and 100% HFCS cakes. Corn syrups, however, are among the ingredients that decrease batter pH (Ash and Colmey, 1973). High fructose corn syrup has been shown by Volpe and Meres (1976) to reduce the pH of batters. Neither mono- and diglyceride (MDG) emulsifier nor sucrose ester (SE) emulsifier significantly affected batter pH.

Specific gravity: Specific gravity measurements give information about the amount of air incorporated into batter. Increasing specific gravity in batter represents a decrease in the amount of air incorporated (Pierce and Walker, 1987). The means for specific gravity are shown in Table 10. There were no significant differences in specific gravity as the HFCS content of the batters increased from 0 to 100%. The specific gravity did increase with increased HFCS levels, however, which is in agreement with other data (Volpe and Meres, 1976; McCullough et al, 1986; and Coleman and Harbers, 1983). However, the variable emulsifier significantly affected batter specific gravity (Table 11b). MDG significantly increased batter specific gravity over both unemulsified and SE emulsified batters (Table 12b). This is in agreement with the findings of Ebeler et al (1986), who reported that MDG batters had the highest specific gravity, unemulsified batters the lowest, and SE

batters intermediate specific gravity in white layer cake batter.

Flow rate: Flow rate gives an indication of the fluidity or viscosity of batter (Ebeler et al, 1986). There was a significant HFCS effect upon batter flow rate (Table 11c). Zero percent HFCS batters were significantly lower in flow rate compared to 50% and 100% HFCS batters (Table 12a). Volpe and Meres (1976) reported HFCS cake batters to be less viscous than sucrose cake batters.

The choice of emulsifier also had a statistically significant effect on batter flow rate (Table 11c). MDG batters had significantly increased flow rates compared to either unemulsified or SE batters (Table 12b). The latter produced slight but not significant decreases in batter flow rates. The sucrose esters were added as a prehydrate in 10 ml of formula water, which was allowed to stand 3 minutes prior to addition. During this time, the SE solution became a viscous paste. It may be that the high HLB emulsifier (SE), being hydrophilic, swelled as it attracted batter water, which resulted in a thicker (more viscous) batter.

The low HLB emulsifier (MDG), being lipophilic, may cause egg foam destabilization, causing break down of aerated foam somewhat, resulting in a thin (less viscous) batter. Norris and Carlyle (1973) discussed the use of MDG in developing low viscosity batters. Ebeler et al (1986)

reported that unemulsified control batter had a low flow rate which increased slightly with sucrose esters added and markedly with mono- and diglycerides. Pierce and Walker (1987) showed that as the concentration of MDG increased from 0 to 2.5% in cake batter, so did batter flow rate, whereas sucrose esters, added dry, resulted in slight but not significant decrease in batter flow rate.

In terms of batter viscosity, a lower batter flow rate indicates a more viscous batter with more air incorporation. Figure 25 shows a plot of flow rate versus specific gravity for the unemulsified, MDG-emulsified, and SE-emulsified batter. Flow rate was significantly correlated with specific gravity ($r = 0.775$). Pierce and Walker (1987) also reported a correlation between batter flow rate to specific gravity in a study of emulsified sponge cake batters.

Emulsion Stability: The mean values for the emulsion stability of model emulsion systems as measured by turbidity are reported in Table 12-1. Absorbance values ranged from 0.152 for the unemulsified control to 1.827 for the SE-emulsified model system. After vortexing for 60 seconds, the unemulsified control almost immediately separated into the oil and water phases. The bottom layer showed no turbidity and gave an absorbance reading similar to that of the water blank. The addition of emulsifiers, however, increased the turbidity of the model emulsion system. SE-

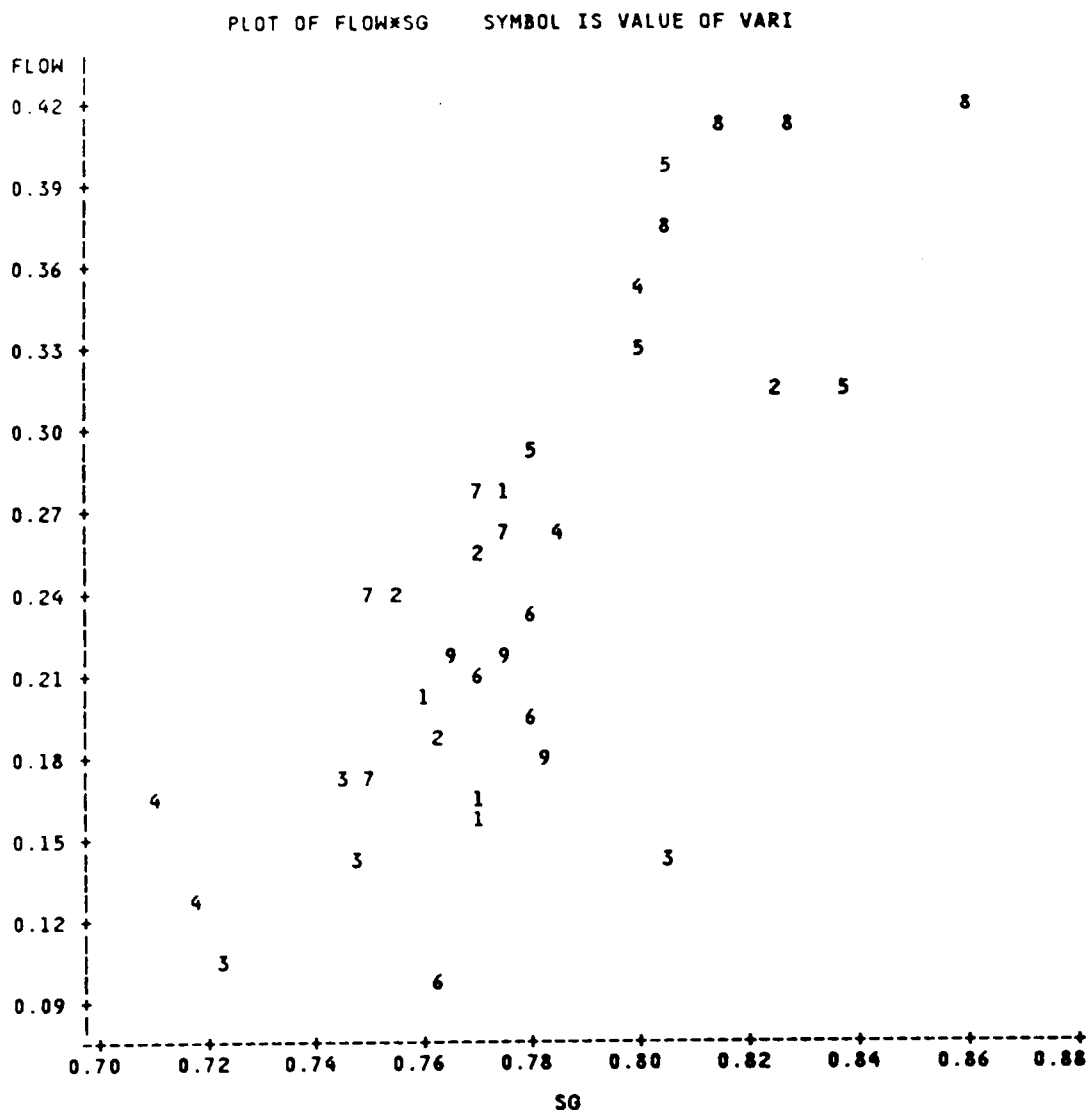


Figure 25. Plot of flow rate (FLOW) versus specific gravity (SG) for batters prepared with no emulsifier (variations 1, 4, 7), MDG (variations 2, 5, 8) and SE (variations 3, 6, 9). The Pearson correlation coefficient (r) was 0.775.

MDG = mono- and diglyceride
SE = sucrose ester

Table 12-1. Mean[±] absorbance values of model emulsion systems with and without emulsifiers.

<u>System</u>	<u>\bar{x} absorbance @ 660 nm (t=10 min)</u>
blank (H ₂ O)	0.000
control (H ₂ O + CO)	0.160
H ₂ O + CO + MDG	1.138
H ₂ O + CO + SE	1.807

[±] Mean of four replications.

CO = corn oil

MDG = mono- and diglycerides

SE = sucrose esters

emulsified mixtures were much more turbid (visually and as measured spectrophotometrically) than MDG-emulsified mixtures ten minutes after vortexing. The cloudy white emulsion separated into an opaque lipid layer and a slightly turbid aqueous layer in the MDG-emulsified system, while the SE-emulsified system retained its high turbidity throughout and did not separate into distinct phases. Therefore, the sucrose esters imparted emulsion stability to the system and mono- and diglycerides did not.

Differential Scanning Calorimetry (DSC):

A. Model Systems

The heat denaturation of the component proteins in egg white were studied by DSC. At a heating rate of 10°C/min egg white showed two major endotherms, in agreement with Donovan (1977) (Figure 26). The maxima of the endotherms occurred at 70.0 and 84.5°C, corresponding to the denaturation of conalbumin and ovalbumin, respectively. The temperatures (onset, peak or maximum, and average) of thermal denaturation of the samples are reported in Table 13.

Added sucrose, high fructose corn syrup (HFCS), and a 50:50 blend of both sweeteners increased the ovalbumin denaturation temperatures, which is a shift to the right. The effect differed according to the level of HFCS. The 50:50 blend of HFCS and sucrose (50% HFCS) caused the

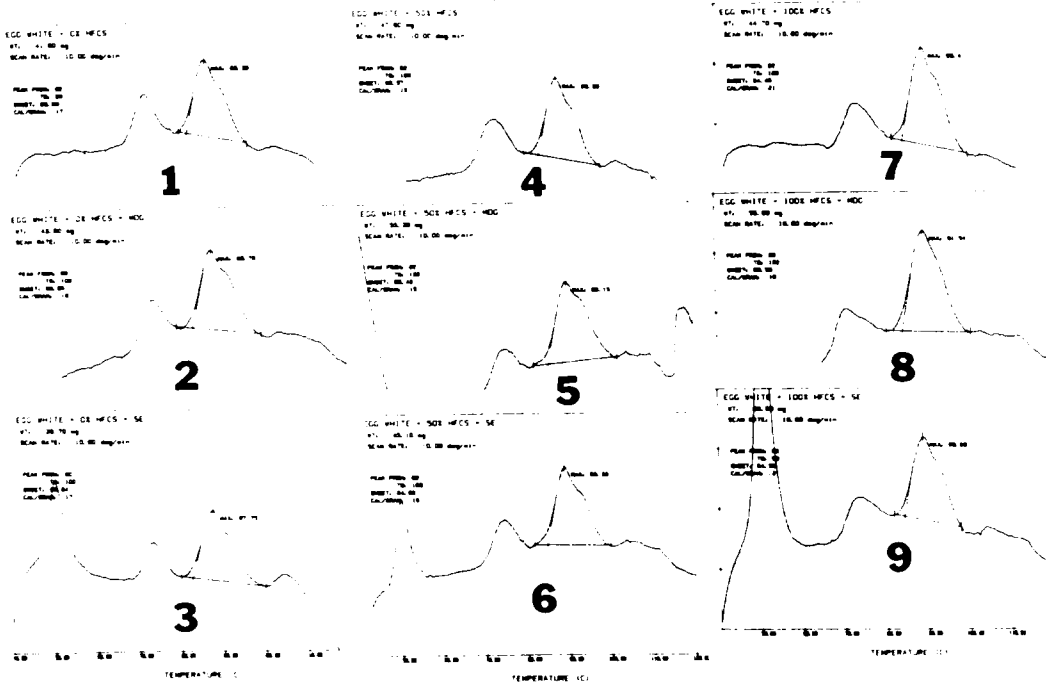
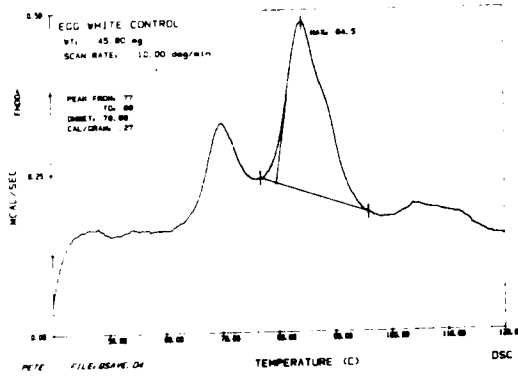


Figure 26. Thermograms of heat denaturation of egg white control and 9 treatment variations.

Variation

- | | | |
|-------------------|--------------------|---------------------|
| 1 = 0% HFCS | 4 = 50% HFCS | 7 = 100% HFCS |
| 2 = 0% HFCS + MDG | 5 = 50% HFCS + MDG | 8 = 100% HFCS + MDG |
| 3 = 0% HFCS + SE | 6 = 50% HFCS + SE | 9 = 100% HFCS + SE |

Table 13. Ovalbumin denaturation in model systems.

	<u>T_{onset}</u>	<u>T_{maximum}</u>	<u>T_{average}</u>
Egg white (EW) control	79.68	84.50	82.09
EW + sucrose	83.69	88.33	86.01
EW + sucrose + MDG	83.85	88.79	86.32
EW + sucrose + SE	82.64	87.75	85.20
EW + 50% HFCS	85.57	89.86	87.72
EW + 50% HFCS + MDG	85.43	90.15	87.79
EW + 50% HFCS + SE	84.93	89.39	87.16
EW + 100% HFCS	84.45	89.41	86.93
EW + 100% HFCS + MDG	86.55	91.54	89.05
EW + 100% HFCS + SE	84.32	89.08	86.70

denaturation temperature to increase 4.3°C over the egg white control. This was 0.5°C more than the effect of all HFCS (100% HFCS) and 1.5°C more than the effect of all sucrose (0% HFCS). According to Donovan et al (1975), a 2°C shift in a thermogram corresponds to a sevenfold decrease in the rate of egg white protein denaturation. Donovan et al (1975) demonstrated this with a 10% addition of sucrose to egg white, and attributed the temperature shift to increased stabilization of the egg white proteins by sucrose, with an increase in heat capacity of the solution.

Emulsifiers affected the denaturation thermograms of ovalbumin too. Mono- and diglycerides (MDG) caused a further shift to the right (0.3 to 2.1°C), indicating a further stabilization of the egg proteins. Sucrose esters (SE), on the other hand, caused a slight shift to the left to lower temperatures (by 0.3 to 0.6°C) compared to unemulsified controls. In other words, SE functioned to counteract the stabilization of egg white proteins afforded by the sweeteners sucrose and HFCS. Whether these effects are due to reactions of each emulsifier in competing with protein for water or directly with the egg proteins are unclear.

Starch also undergoes phase transitions, and these were measured in the DSC. A high water-to-starch (3:1) model system was used (Figure 16), with saccharides present at

100% of starch weight. A single endotherm similar to that of Ghiasi (1982c) was obtained for the thermal denaturation of wheat starch, as shown in Figure 27. The endotherm occurred (T_{max}) at 69.0°C and represented the gelatinization of starch.

The effect of added saccharides (sucrose, 50% HFCS, and 100% HFCS) on starch gelatinization is presented in Table 14. The different sweeteners delayed gelatinization but to different extents. One-hundred-percent HFCS delayed the gelatinization T_{max} less (27.8°C) than did all sucrose/0% HFCS (39.16°C) and the blend of HFCS with sucrose, 50% HFCS (33.08°C). Donovan (1977) reported a 30°C increase in starch gelatinization when sucrose is present. HFCS, a mixture of the two monosaccharides glucose and fructose (Figure 1), delayed gelatinization less than the disaccharide sucrose. The differences attributed to mono- and disaccharides was in agreement with Koepsel and Hosney (1980) and Spies and Hosney (1982), who stated that in general monosaccharides delay gelatinization less than disaccharides.

Spies and Hosney (1982) explained that longer chain saccharides may lower the water activity and interact with starch chains to stabilize the amorphous (non-crystalline) areas of the granule. Longer sugar molecules bridge more gaps between chains, form links, restrict flexibility, and

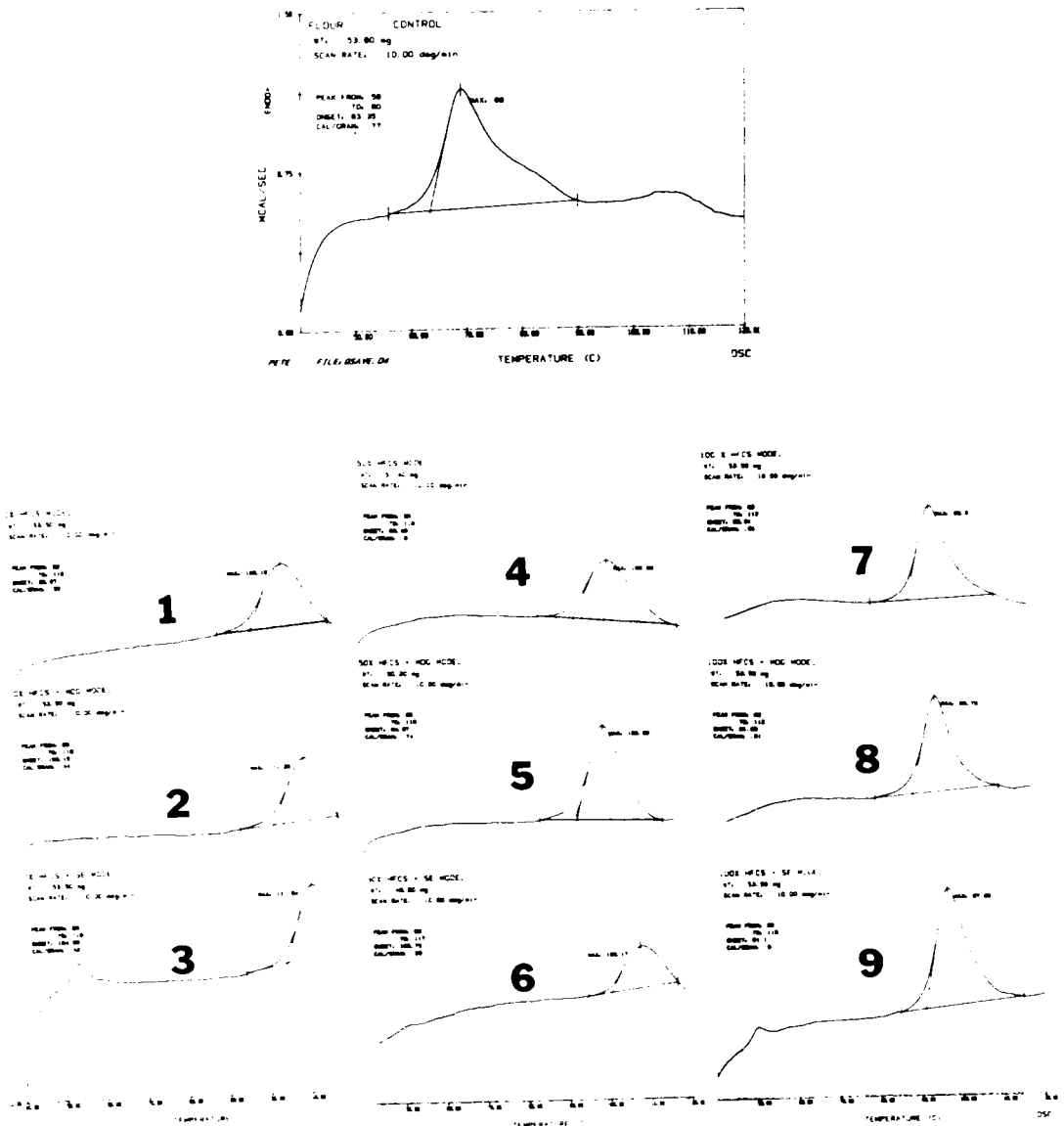


Figure 27. Thermograms of starch gelatinization of flour control and 9 treatment variations.

Variation

- | | | |
|-------------------|--------------------|---------------------|
| 1 = 0% HFCS | 4 = 50% HFCS | 7 = 100% HFCS |
| 2 = 0% HFCS + MDG | 5 = 50% HFCS + MDG | 8 = 100% HFCS + MDG |
| 3 = 0% HFCS + SE | 6 = 50% HFCS + SE | 9 = 100% HFCS + SE |

cause an increased energy requirement (higher gelatinization temperature) to pull apart the starch crystallites.

The emulsifiers also affected starch gelatinization in the model systems. The starch gelatinization temperatures (T_{onset} , T_{max} , $T_{average}$) of wheat starch with and without the added emulsifiers are shown in Table 14. In the presence of sucrose (0% HFCS), both MDG and SE delayed starch gelatinization 3°C. However, in the presence of HFCS (100% HFCS), neither MDG nor SE greatly affected gelatinization according to T_{max} . This may be due to the nature of the monosaccharides in HFCS being less able than sucrose to stabilize the amorphous (amylose) regions of the starch, which subsequently denature even in the presence of emulsifiers. The situation of emulsifier effect at 50% HFCS was ambiguous; MDG caused a later onset temperature but an earlier maximum and average temperature of starch gelatinization. SE caused nearly a 6°C delay in starch gelatinization.

Emulsifier-starch complexes are known to form, and are based upon competition for iodine binding sites on the amylose fraction of starch (Figure 28). MDG-starch complexes have been reported by Norris and Carlyle (1973). According to Ghiasi et al (1982b) when a surfactant enters the starch granule it immediately forms the helical complex with amylose. Ghiasi et al (1982d) reported on the ability

Table 14. Wheat Starch denaturation (gelatinization) in model systems.

	<u>T_{onset}</u>	<u>T_{maximum}</u>	<u>T_{average}</u>
Wheat Starch (WS) control	63.35	69.00	66.18
WS + sucrose	99.97	108.16	104.07
WS + sucrose + MDG	103.15	111.25	107.20
WS + sucrose + SE	104.88	111.64	108.26
WS + 50% HFCS	93.49	102.08	97.79
WS + 50% HFCS + MDG	94.07	100.83	97.45
WS + 50% HFCS + SE	100.75	108.17	104.46
WS + 100% HFCS	90.91	96.80	93.86
WS + 100% HFCS + MDG	91.08	96.73	93.91
WS + 100% HFCS + SE	91.10	97.08	94.09

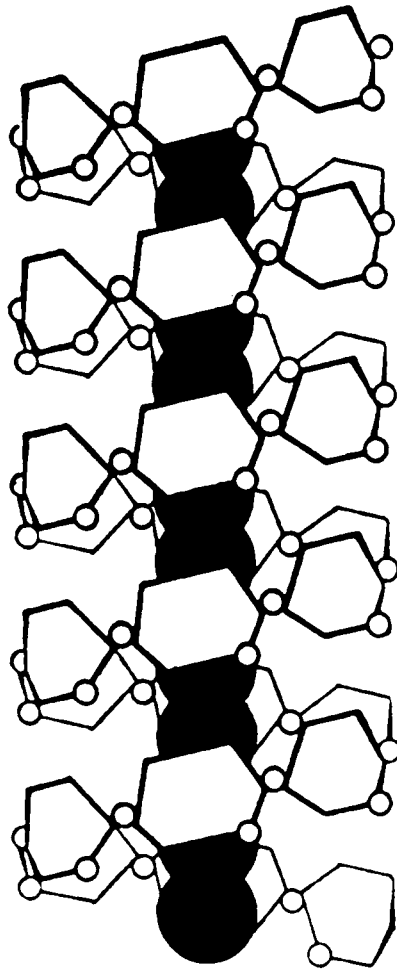


Figure 28. Structure of the amylose-iodine complex (from Schuster and Adams, 1984).

of the surfactant monoglyceride (MG) to accomplish this with the MG-amylose complex remaining stable to 95°C. The emulsifier-starch complex may cause a delay in starch gelatinization if the hydrophobic portion of the emulsifier is greater than twelve carbons in length (Longley and Miller, 1971). Osman et al (1961) postulated that the structures of the hydrophilic moieties of emulsifiers might also be important in starch-emulsifier interactions. The more hydrophilic sucrose esters may delay starch gelatinization in another way: by competing with starch for available water. This would effectively increase the starch concentration in the decreasing amount of solvent, which would necessitate more energy input into the system to cause starch gelatinization.

Ebeler and Walker (1984) hypothesized that sucrose esters altered the starch gelatinization of cakes baked in their study based upon their appearance. No DSC data was reported, but starch isolated from sucrose ester emulsified cupcakes remained birefringent longer than unemulsified controls, indicating a delay in gelatinization. They postulated that the high number of hydroxyl groups on the SE molecule may bind water and that therefore insufficient water was available for starch gelatinization to occur. Hsu et al (1980) reported that some emulsifiers can affect water loss rates in cakes, which in turn affects starch

gelatinization.

B. Cake Batter

The denaturation of complete cake batter as studied by DSC is reported in Table 15 and the DSC thermograms are presented in Figure 29. As with the model systems, a trend was apparent regarding sweetener effect on starch gelatinization.

Sucrose more than HFCS delayed starch endothermic transitions in batter, as was the case in the model systems. Emulsifiers in batter did not greatly affect starch gelatinization, possibly due to the fact that they were present in lower concentrations than in the model systems, and that more interactions between them and other batter components were possible. In one batter variation (number 2, 0% HFCS + MDG) however, the gelatinization temperature was delayed 3°C. This was similar to the effect of MDG on starch gelatinization in the model system. It is possible that the particular batter aliquot in the DSC pan had a greater concentration of MDG compared to the other two MDG variations, possibly due to uneven distribution of emulsifier in the batter. Cloke et al (1983) found that T_{onset} varied more for non batter (model) systems because individual components could not be directly weighed into sample pans but instead had to be added pre-mixed.

Table 15. Denaturation temperatures (starch gelatinization) of cake batter variations 1-9.

	<u>T_{onset}</u>	<u>T_{maximum}</u>	<u>T_{average}</u>
0% HFCS	94.41	99.80	97.11
0% HFCS + MDG	97.52	102.95	100.24
0% HFCS + SE	93.66	98.86	96.26
50% HFCS	91.34	97.00	94.17
50% HFCS + MDG	90.89	96.20	93.55
50% HFCS + SE	91.78	96.86	94.34
100% HFCS	88.88	93.83	91.36
100% HFCS + MDG	88.78	93.84	91.31
100% HFCS + SE	88.11	93.03	90.57

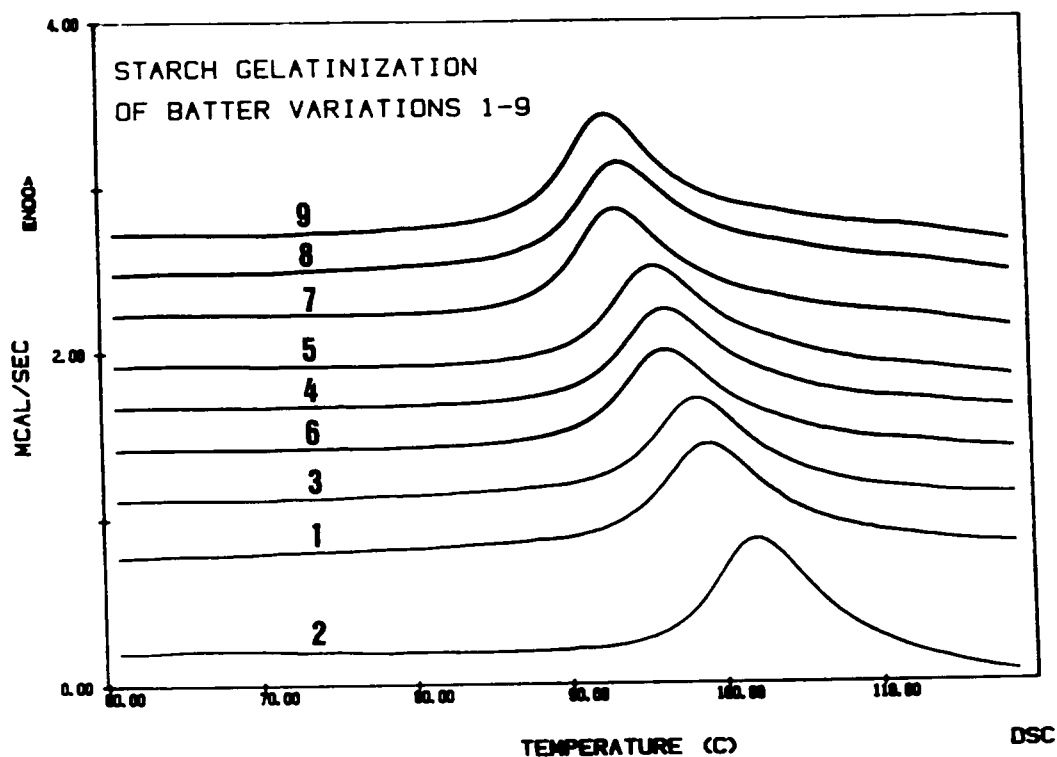


Figure 29. DSC thermograms of batter variations 1-9 showing starch gelatinization peaks. Variations 1-3 were 0% HFCS cakes; 4-6 were 50% HFCS cakes; and 7-9 were 100% HFCS cakes. No emulsifier was used in variations 1, 4, 7; mono- and diglycerides were used in variations 2, 5, 8; and sucrose esters were used in variations 3, 6, 9.

(HFCS = high fructose corn syrup)

The DSC results show that both the denaturation of egg white proteins and the denaturation (gelatinization) of starch can be delayed by saccharides and some emulsifiers as well. The disaccharide sucrose was more effective than HFCS in delaying starch gelatinization in model systems and in cake batter, while the monosaccharide-containing HFCS was more effective than sucrose in delaying egg white protein (ovalbumin) denaturation. MDG emulsifier caused delayed ovalbumin denaturation in model systems and in one instance in batter, while SE emulsifier caused a slight decrease in the thermal stability of ovalbumin. Although neither emulsifier greatly affected starch gelatinization in batter, SE rather than MDG had the potential to do so based upon the results in model systems.

The importance of both protein denaturation and starch gelatinization in relation to cake baking was discussed by Donovan (1977). Cake structure was defined as a composite, similar to bricks in mortar. The starch grains being the "bricks" and the ovalbumin, a major protein of "mortar". The mortar functions to cement the bricks in place. During denaturation, the starch granule swelling produces bricks rather than pebbles, and the outcome is a high-volume cake. Too much starch denaturation would be undesirable, as the bricks would "deflate". On the other hand, if substances in the composite cause too drastic a delay (i.e.: above 100°C)

in starch gelatinization, the structure will not set during baking (Bean et al, 1978).

According to Donovan (1977) the processes of protein denaturation and starch gelatinization should occur in the same temperature range if a cake is to have adequate structure. Since sucrose and HFCS affected both processes differently it is likely that distinct optimum sets of starch gelatinization and protein denaturation temperatures exist for 0, 50, and 100% HFCS cakes.

CAKE CHARACTERISTICS

Cake Volume: The mean values for cake volume as measured by rapeseed displacement are reported in Table 16. High fructose corn syrup (HFCS) had a statistically significant effect on cake volume (Table 17a). Cakes prepared with 50% HFCS were significantly greater in volume than the 0 and 100% HFCS cakes (Table 18a; see discussion of HFCS and cake volume in pilot study results and discussion section). There was a marginally significant overall effect of emulsifiers on cake volume (Table 17a). MDG-emulsified cakes were significantly decreased in volume compared to unemulsified cakes, while SE-emulsified cakes were significantly increased over unemulsified controls. The top contours of the MDG cakes were more peaked whereas the SE cake contours were flatter. Figure 30 presents mean cake volume per variation as a function of HFCS and emulsifier in bar graph form.

At comparable levels, sucrose ester emulsifiers were shown by Breyer and Walker (1983) to improve bread loaf volume compared to sodium stearoyl-2-lactylate and mono- and diglycerides. Ebeler and Walker (1983) reported that MDG-emulsified layer cakes had high contours and that SE cakes were relatively flat. Ebeler et al (1986) confirmed the flat profiles of SE-emulsified cakes. MDG-emulsified cakes were reported to decrease in volume as the concentration of

Table 16. Mean, standard deviation, and range for cake volume (VOL), deformation (DEF), percent moisture (MOIST), crust color (CRUST), and crumb color (CRUMB).

(a) values per cake variation
 (b) values overall

VARIABLE	N	MEAN	STANDARD DEVIATION	MINIMUM VALUE	MAXIMUM VALUE	STD ERROR OF MEAN
----- VARI=1 -----						
VOL	4	2054.250000	37.51777357	2011.000000	2093.000000	18.7588868
DEF	4	147.250000	16.76056880	135.000000	172.000000	8.3802844
MOIST	4	38.375000	1.21757957	36.800000	39.700000	0.6087898
CRUST	4	47.175000	0.60423505	46.480000	47.880000	0.3021175
CRUMB	4	80.475000	2.46531269	77.650000	83.580000	1.2326563
----- VARI=2 -----						
VOL	4	2027.500000	32.91909274	1984.000000	2060.000000	16.4595464
DEF	4	133.500000	33.04037934	111.000000	181.000000	16.5201897
MOIST	4	39.150000	0.75055535	38.200000	39.800000	0.3752777
CRUST	4	46.785000	1.97999158	45.110000	49.650000	0.9899958
CRUMB	4	80.205000	4.68935319	76.190000	85.580000	2.3446766
----- VARI=3 -----						
VOL	4	2093.750000	74.62964112	1998.000000	2167.000000	37.3148206
DEF	4	171.250000	18.90987396	152.000000	197.000000	9.4549370
MOIST	4	38.175000	1.69582821	36.100000	40.100000	0.8479141
CRUST	4	48.957500	1.86485701	46.550000	51.010000	0.9324285
CRUMB	4	81.402500	2.29606003	79.320000	84.470000	1.1480300
----- VARI=4 -----						
VOL	4	2133.750000	47.62614828	2087.000000	2198.000000	23.8130741
DEF	4	133.750000	15.67174702	124.000000	154.000000	6.8358735
MOIST	4	36.000000	9.67160793	21.500000	41.100000	4.8358040
CRUST	4	44.832500	2.92899727	41.880000	48.420000	1.4644986
CRUMB	4	80.572500	1.79079824	78.940000	82.730000	0.8953991
----- VARI=5 -----						
VOL	4	2084.500000	57.92236183	1998.000000	2121.000000	28.9611809
DEF	4	164.250000	21.97536500	134.000000	186.000000	10.9876825
MOIST	4	40.500000	0.37416574	40.000000	40.900000	0.1870829
CRUST	4	41.127500	2.57585423	37.600000	43.300000	1.2879271
CRUMB	4	79.510000	0.54467115	78.720000	79.940000	0.2723356
----- VARI=6 -----						
VOL	4	2106.500000	56.33530569	2044.000000	2177.000000	28.1676528
DEF	4	127.000000	27.39829678	102.000000	166.000000	13.6991484
MOIST	4	40.100000	0.21602469	39.900000	40.400000	0.1080123
CRUST	4	45.835000	2.18512393	43.970000	48.690000	1.0925620
CRUMB	4	82.440000	2.14320632	80.620000	85.280000	1.0716032
----- VARI=7 -----						
VOL	4	2013.250000	38.34383914	1969.000000	2058.000000	19.1719196
DEF	4	139.000000	19.27001124	119.000000	156.000000	9.6350056
MOIST	4	40.725000	0.41129876	40.200000	41.100000	0.2056494
CRUST	4	48.627500	2.43816017	46.060000	51.800000	1.2190801
CRUMB	4	81.015000	2.67657119	78.260000	83.330000	1.3382856
----- VARI=8 -----						
VOL	4	1984.000000	21.83269719	1957.000000	2010.000000	10.9163486
DEF	4	108.750000	10.50000000	94.000000	118.000000	5.2500000
MOIST	4	40.475000	0.78049130	39.800000	41.600000	0.3902456
CRUST	4	45.405000	1.61725075	43.510000	46.900000	0.8086254
CRUMB	4	80.155000	2.27334555	77.400000	82.080000	1.1366728
----- VARI=9 -----						
VOL	4	2057.500000	48.84328681	1988.000000	2094.000000	24.4216434
DEF	4	132.250000	15.90335394	110.000000	147.000000	7.9516770
MOIST	4	40.900000	0.64807407	40.200000	41.700000	0.3240370
CRUST	4	46.652500	1.62762352	44.700000	48.420000	0.8138118
CRUMB	4	81.565000	1.90109618	78.800000	83.010000	0.9505481

(b)

VARIABLE	N	MEAN	STANDARD DEVIATION	MINIMUM VALUE	MAXIMUM VALUE	STD ERROR OF MEAN
VOL	36	2061.666667	62.57840796	1957.000000	2198.000000	10.4297347
DEF	36	139.666667	25.78593193	94.000000	197.000000	4.2976552
MOIST	36	39.377778	3.31085756	21.500000	41.700000	0.5518096
CRUST	36	46.155278	2.87973559	37.600000	51.800000	0.4799559
CRUMB	36	80.815556	2.37392074	76.190000	85.580000	0.3956535

Table 17. Effects of high fructose corn syrup (HFCS) on cake characteristics.

- (a) volume
- (b) deformation
- (c) percent moisture
- (d) crust color
- (e) crumb color

	<u>HFCS Effect</u>	<u>Emulsifier Effect</u>	<u>HFCS*Emul. Effect</u>
(a)	significant F = 9.89 p = 0.0006	marginal F = 5.36 p = 0.0739	none F = 0.59 p = 0.6749
(b)	significant F = 3.79 p = 0.0353	none F = 0.12 p = 0.5164	significant F = 3.49 p = 0.0202
(c)	none F = 1.53 p = 0.2351	none F = 0.78 p = 0.5164	none F = 0.91 p = 0.4720
(d)	significant F = 10.90 p = 0.0003	marginal F = 4.27 p = 0.1017	none F = 1.47 p = 0.2380
(e)	none F = 0.02 p = 0.9772	none F = 2.88 p = 0.1680	none F = 0.37 p = 0.8291

Table 18. Results of Duncan's Multiple Range Test for cake variables volume (VOL), deformation (DEF), percent moisture (MOIST), crust color (CRUST), and crumb color (CRUMB) according to:

- (a) HFCS
(b) emulsifier (EMUL)

(* denotes significant differences at 0.05 level)

(a)

HFCS	mean VOL	mean DEF	mean MOIST	mean CRUST	mean CRUMB
0	2058.50	150.67*	38.57	47.64	80.69
50	2108.25*	141.67	38.86	43.93*	80.84
100	2018.25	126.67*	40.70	46.90	80.91

(b)

EMUL	mean VOL	mean DEF	mean MOIST	mean CRUST	mean CRUMB
0	2067.08	140.00	38.37	46.88	80.69
MDG	2032.00*	135.50	40.04	44.44	79.96*
SE	2085.92*	143.50	39.73	47.15	81.80*

VOLUME AND DEFORMATION

Research Problem

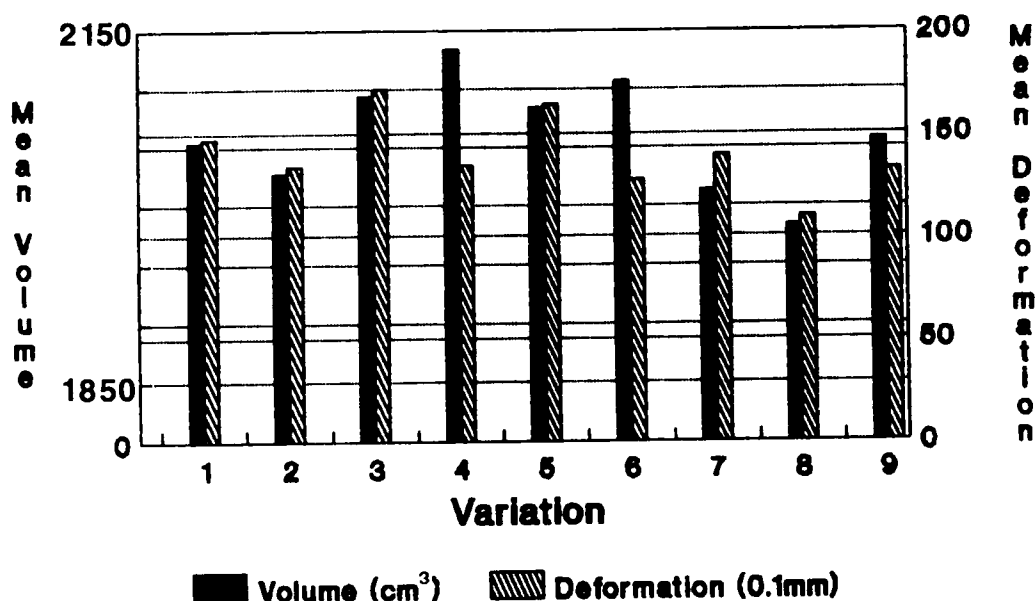


Figure 30. Mean cake volume and deformation for variations 1-9 of the research problem using various levels of HFCS plus corn oil with and without mono- and diglycerides (MDG) or sucrose esters (SE). Variations 1-3 were 0% HFCS cakes; 4-6 were 50% HFCS cakes; and 7-9 were 100% HFCS cakes. Variations 2, 5, 8 were emulsified with MDG, and variations 3, 6, 9 were emulsified with SE. No emulsifier was added to variations 1, 4, 7.

(HFCS = high fructose corn syrup)

that emulsifier was increased whereas SE-emulsified cakes were increased in volume over controls and MDG cakes (Pierce and Walker, 1987).

It is interesting to note the effects obtained by varying the amount of corn oil used in preparing 0, 50, and 100% HFCS unemulsified oil cakes. A bar chart depicting the mean cake volumes obtained from the pilot study (using hydrogenated vegetable shortening = 0 g corn oil vs. 108 g corn oil) and research problem (using only 81 g corn oil) is shown in Figure 31. The mean cake volumes for each level of HFCS substitution for sucrose were increased when all corn oil was used as the shortening, at a reduced concentration (80 vs. 108 g = 25% reduction).

Cake Deformation: The mean values for cake deformation (tenderness as measured by the Penetrometer device) are reported in Table 16. The effect of HFCS on tenderness was significant (Table 17b). Cakes prepared with sucrose (0% HFCS) were significantly more tender than 50% HFCS cakes, and the 100% HFCS cakes were least tender overall. The fact that the sucrose cakes deformed the most is attributable to its greater tenderizing effect on cake structure as compared to that of HFCS. This results is in agreement with the findings of the pilot study regarding cake deformation and HFCS level.

VOLUME AND DEFORMATION

Effect of corn oil

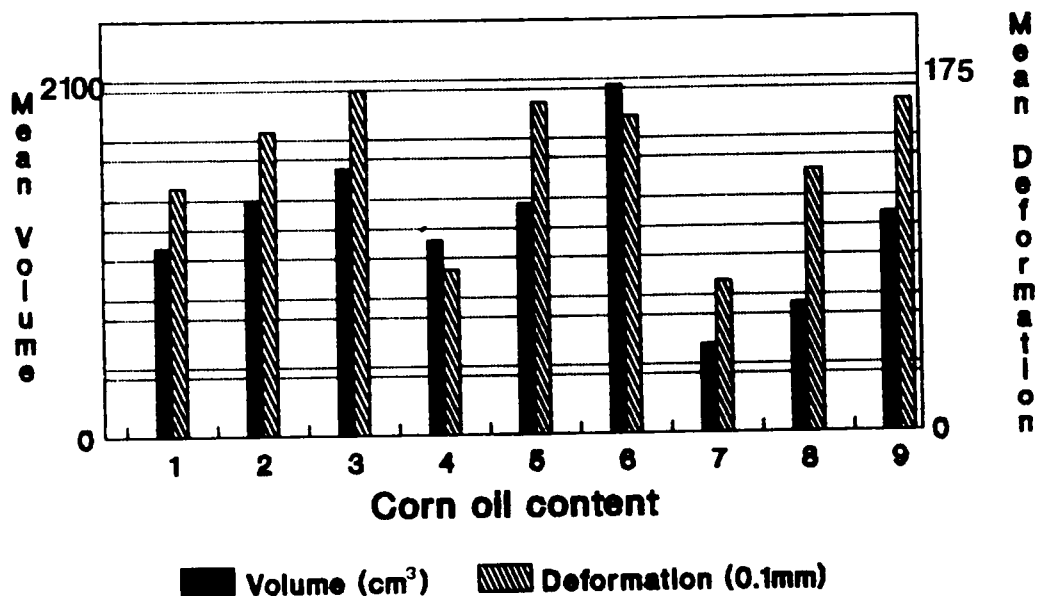


Figure 31. Effect of varying the corn oil content upon mean cake volume and deformation in cakes prepared with 0% HFCS (variations 1, 2, 3), 50% HFCS (variations 4, 5, 6), and 100% HFCS (variations 7, 8, 9). No corn oil was used for variations 1, 4, 7 (a plastic unemulsified vegetable shortening, Creamtex); 108 grams of unemulsified corn oil were used in formulating variations 2, 5, 8; and 81 grams of unemulsified corn oil were used in formulating variations 3, 6, 9.

(HFCS = high fructose corn syrup)

The addition of emulsifiers did not significantly affect cake tenderness at the 0.05 level, although SE-emulsified cakes deformed the most, indicating increased tenderness over control and MDG-emulsified cakes. Mean cake deformation values according to cake variation are represented as bar graphs in Figure 30. The decreased concentration of corn oil (81 g) used in the research problem cake formulations produced increased deformation compared to when only vegetable shortening or 108 g of corn oil were used (Figure 31).

Cakes with increased tenderness were reported by Ebeler and Walker (1984) when sucrose esters rather than mono- and diglycerides were used as the emulsifier, as indicated by Instron data. The Instron device measured a decreased force required to compress 2 cm thick SE cake samples compared to MDG and control cake samples.

Cake Moistness: The mean values for cake percent moisture as measured by the Brabender Moisture Tester are reported in Table 16. As the level of HFCS substitution for sucrose increased, the percent moisture also increased, but this effect was not significant at the 0.05 level. No significant emulsifier effect on moistness occurred (Table 17c) although improving moisture retention is a function of emulsifiers. However, the mean moisture values for emulsified cakes (both MDG and SE) were increased somewhat

over the unemulsified controls (Table 18c).

McCullough et al (1986) reported no significant moisture differences among 0, 50, and 75% HFCS cakes. Coleman and Harbers (1983) reported mean percentage moisture values for HFCS cakes. In their study, 50 and 100% HFCS cakes averaged 40.07 and 40.50 percent moisture, which were slightly but not significantly increased over 0% HFCS controls (30.06 percent moisture).

Cake Crust Color: The mean ΔE values for cake crust color as measured by the Hunter Colorimeter are reported in Table 16. The effect of HFCS on crust color was significant. The ΔE values relate to the lightness of the color, the higher the ΔE , the lighter the color. Fifty percent HFCS substitution for sucrose produced significantly darker (lower ΔE values) crusts compared to controls. The crust color of cakes baked with 100% HFCS were darker than controls but slightly lighter than 50% HFCS crusts (Figure 32).

Coleman and Harbers (1983) also reported that crust color in angel food cakes was significantly affected by replacement of sucrose with HFCS, although in their study the 100% HFCS cakes were darkest. McCullough et al (1986) noted darker crust colors when HFCS replaced sucrose at 50 and 75% levels. They commented that the crust darkening due to HFCS was consistent with the reactivity of the

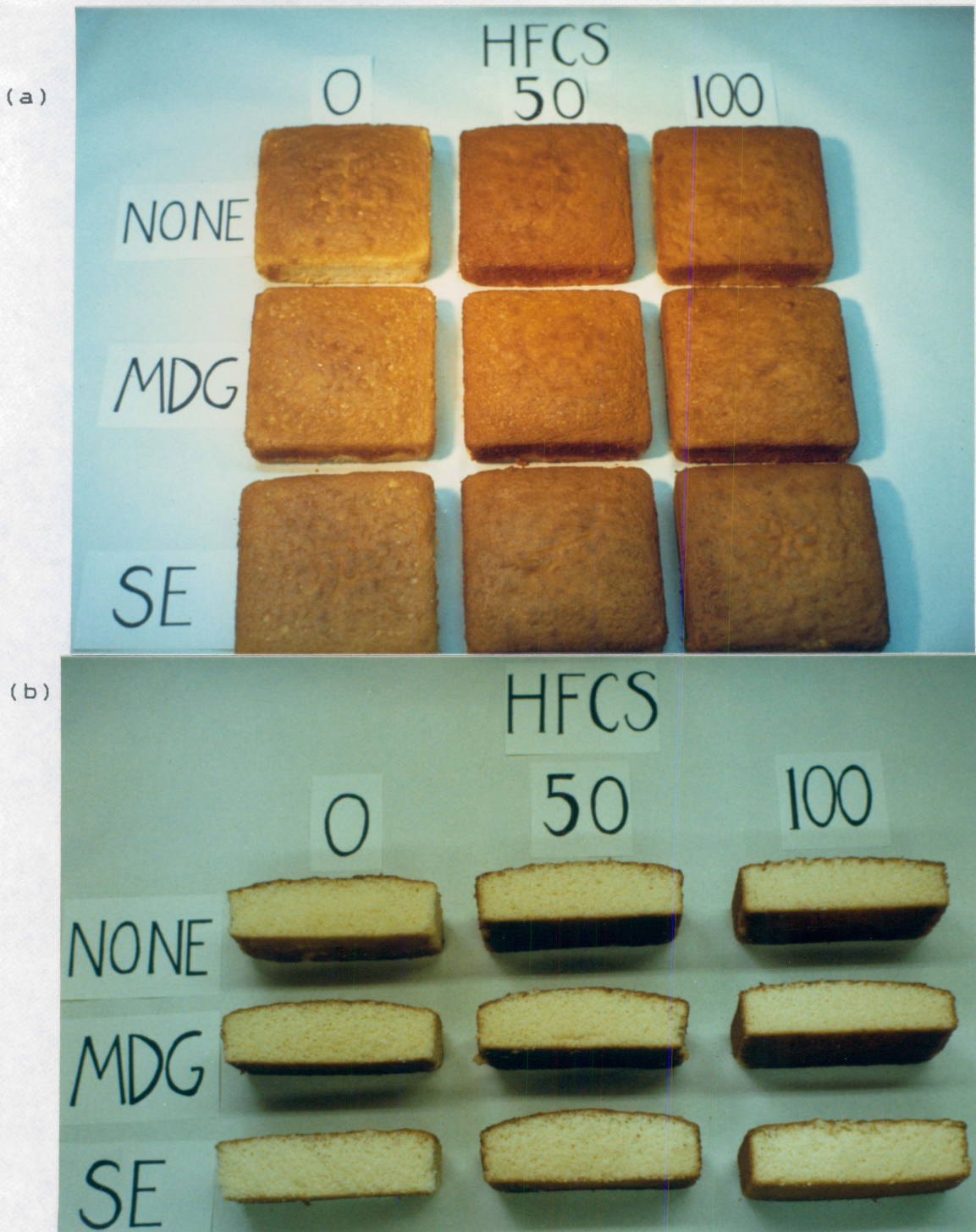


Figure 32. Color photographs of cakes baked for the research problem showing comparative:

- (a) top crust color
- (b) cross-section height and contour

for the nine cake variations.

monosaccharides present in HFCS in carbonyl-amine browning reactions (Figure 2).

There was a marginally significant effect of emulsifier on crust color (Table 17d). MDG cake crusts were darkest, unemulsified cake crusts were intermediate, and SE cake crusts were lightest (Table 18). The reason might be due to an inhibitory effect on the Maillard reaction, although by some unknown mechanism. It was clearly not due to any effect on batter pH (Table 12b), which is known to cause diminution of browning at low pH.

Cake Crumb Color: The mean ΔE values for cake crumb color as measured by the Hunter colorimeter are reported in Table 16. Neither HFCS nor emulsifier significantly affected crumb color (Table 17e). Lightness of crumb color increased in mean value as the level of HFCS was increased but these differences were not significant at the 0.05 level (Table 18). Emulsified crumb lightness values were significantly different from each other, with SE crumb lighter than MDG crumb (Table 18).

Ash and Colmey (1973) discussed the role of the Maillard and caramelization reactions on crust and crumb colors as being very pH dependent. Low pH inhibits the Maillard reaction, whereas alkaline pH enhances it, darkening both crust and crumb. Volpe and Meres (1976) reported that in HFCS cakes, as the pH of the crumb

decreased, the lightness increased, but McCullough et al (1986) found darker crumb colors with increased levels of HFCS substitution for sucrose. This would seem to indicate that pH values increased with HFCS, although no pH data were reported. A darker (more yellow) crumb was also reported by Coleman and Harbers (1983) with increased HFCS levels in cakes, but lightness (ΔE) values were not significantly different at any level of HFCS substitution for sucrose.

SENSORY ANALYSIS

Crumb Color: The mean values for cake crumb color as evaluated by the sensory judges (panelists) are reported in Table 19. The effect of HFCS on crumb color was significant (Table 20a). Judges rated the crumb of cakes prepared with all sucrose to be the most yellow in crumb color compared to the crumb of cakes prepared with 50% HFCS (Table 21). In comparison, the sensory results supported the trend of lighter crumb with increasing levels of HFCS replacement for sucrose as measured using the Hunter Colorimeter.

Emulsifiers also significantly affected the sensory judges' perception of crumb color (Table 20a). Judges rated MDG-emulsified crumb least yellow in color compared to SE-emulsified and unemulsified crumb (Table 21). This is contrary to results obtained for crumb lightness as measured

Table 19. Mean, standard deviation, and range for cake sensory parameters: CRUMB (crumb color), SIZE (cell size), UNIF (cell uniformity), SWEET (sweetness), MOIST (moistness), TEND (tenderness), and AFTER (aftertaste).

VARIABLE	N	MEAN	STANDARD DEVIATION	MINIMUM VALUE	MAXIMUM VALUE	STD ERROR OF MEAN
----- VARI=1 -----						
CRUMB	36	8.08888889	1.96756235	4.40000000	11.70000000	0.32792786
SIZE	36	8.33611111	2.61371687	1.90000000	13.20000000	0.43561948
UNIF	36	8.16277778	2.99012528	2.80000000	13.30000000	0.49835421
SWEET	36	6.92777778	2.94362373	1.80000000	13.50000000	0.49860395
MOIST	36	5.79722222	2.85491917	1.50000000	11.60000000	0.47581986
TEND	36	6.30000000	2.77560804	2.60000000	13.10000000	0.46260134
AFTER	36	9.95277778	2.31707773	5.40000000	12.90000000	0.38617962
----- VARI=2 -----						
CRUMB	36	8.67500000	2.02150934	3.80000000	11.60000000	0.33691822
SIZE	36	8.58611111	2.59154149	2.80000000	12.60000000	0.43192358
UNIF	36	8.46944444	2.46968123	2.30000000	12.20000000	0.41161354
SWEET	36	7.14444444	2.77658006	1.60000000	12.20000000	0.46276334
MOIST	36	6.31388889	3.05550115	1.00000000	12.30000000	0.50925019
TEND	36	7.33611111	2.81730903	1.90000000	12.30000000	0.46955150
AFTER	36	8.81666667	3.06896911	2.90000000	13.30000000	0.51149485
----- VARI=3 -----						
CRUMB	36	9.98611111	2.12322568	5.00000000	14.00000000	0.35387095
SIZE	36	8.31666667	2.48038016	2.40000000	12.10000000	0.41339669
UNIF	36	7.26166667	2.73165308	1.90000000	12.90000000	0.45527551
SWEET	36	7.71944444	2.47288286	3.00000000	12.40000000	0.41213381
MOIST	36	8.14722222	2.76089904	3.10000000	12.10000000	0.46014984
TEND	36	9.03333333	2.45178495	3.80000000	12.30000000	0.40861749
AFTER	36	9.84444444	2.84780060	1.90000000	13.30000000	0.47463343
----- VARI=4 -----						
CRUMB	36	8.95555556	1.71555011	5.10000000	12.10000000	0.28559168
SIZE	36	8.80833333	2.58195662	3.40000000	12.70000000	0.43032610
UNIF	36	7.96666667	2.68328157	3.10000000	12.10000000	0.44721368
SWEET	36	7.71388889	2.79674840	1.60000000	13.10000000	0.46612473
MOIST	36	6.28888889	2.93128717	2.00000000	12.70000000	0.48856786
TEND	36	7.22222222	2.74164821	3.50000000	12.90000000	0.45694137
AFTER	36	7.27500000	3.32018717	1.20000000	13.50000000	0.55336453
----- VARI=5 -----						
CRUMB	36	6.82500000	2.64492776	1.00000000	12.30000000	0.46082129
SIZE	36	8.27222222	2.62140759	3.20000000	12.40000000	0.43698127
UNIF	36	7.73333333	2.87034095	3.00000000	12.30000000	0.47839016
SWEET	36	7.18888889	2.83466075	3.20000000	12.00000000	0.47246346
MOIST	36	7.56666667	2.55667194	2.20000000	12.20000000	0.42611199
TEND	36	7.53888889	2.62420358	2.80000000	13.60000000	0.43736726
AFTER	36	8.03333333	2.86715389	2.30000000	12.60000000	0.47785898
----- VARI=6 -----						
CRUMB	36	9.08055556	2.19164901	5.60000000	14.00000000	0.36527484
SIZE	36	8.46944444	2.48904106	2.40000000	11.70000000	0.41484018
UNIF	36	7.85000000	2.51015082	3.20000000	11.60000000	0.41835847
SWEET	36	8.50833333	2.61712765	3.50000000	12.00000000	0.43618794
MOIST	36	8.46388889	2.95530059	3.00000000	13.20000000	0.49255010
TEND	36	9.03055556	2.84291796	3.80000000	13.80000000	0.47381966
AFTER	36	6.95833333	2.88734925	1.90000000	11.60000000	0.48122488
----- VARI=7 -----						
CRUMB	36	8.23333333	2.02188031	3.90000000	11.90000000	0.33698005
SIZE	36	8.97777778	2.74529323	2.90000000	13.20000000	0.45754887
UNIF	36	7.84722222	2.98543953	2.80000000	13.00000000	0.49737326
SWEET	36	7.48055556	2.86743484	1.70000000	12.80000000	0.47790581
MOIST	36	7.34166667	3.20395960	1.40000000	12.40000000	0.53399327
TEND	36	8.98611111	2.70419281	2.40000000	13.70000000	0.45069880
AFTER	36	6.21111111	3.09329023	1.10000000	12.00000000	0.51554037
----- VARI=8 -----						
CRUMB	36	6.68055556	2.40972072	3.60000000	11.80000000	0.40162012
SIZE	36	9.32500000	2.80054842	2.40000000	12.70000000	0.46675807
UNIF	36	8.20833333	2.99059239	1.00000000	13.00000000	0.49843207
SWEET	36	7.71944444	2.95855365	2.10000000	13.60000000	0.49309227
MOIST	36	7.07222222	2.86943065	2.60000000	12.40000000	0.47675844
TEND	36	8.53611111	2.88158218	3.60000000	14.00000000	0.48026370
AFTER	36	5.62500000	3.10044928	1.00000000	13.90000000	0.51674155
----- VARI=9 -----						
CRUMB	36	9.41666667	2.27752999	4.00000000	14.00000000	0.37958833
SIZE	36	9.13055556	2.16950547	4.70000000	11.80000000	0.36158424
UNIF	36	7.68055556	2.71365009	1.90000000	12.10000000	0.45227302
SWEET	36	8.33888889	2.70800694	3.20000000	12.70000000	0.45133449
MOIST	36	8.48611111	3.04641736	3.50000000	13.10000000	0.50773623
TEND	36	9.23055556	2.87281042	4.00000000	14.00000000	0.47880174
AFTER	36	4.97500000	2.52296594	1.00000000	12.40000000	0.42049432

Table 20. Effects of high fructose corn syrup (HFCS) and emulsifiers on cake sensory parameters.

- | | |
|---------------------|----------------|
| (a) crumb color | (e) moistness |
| (b) cell size | (f) tenderness |
| (c) cell uniformity | (g) aftertaste |
| (d) sweetness | |

	<u>HFCS Effect</u>	<u>Emuls. Effect</u>	<u>HFCS*Emuls. Effect</u>
(a)	significant F = 4.13 p = 0.0170	marginal F = 5.90 p = 0.9930	significant F = 4.30 p = 0.0021
(b)	marginal F = 2.39 p = 0.0931	none F = 0.01 p = 0.9930	none F = 0.35 p = 0.8416
(c)	none F = 0.03 p = 0.9718	none F = 1.90 p = 0.2631	none F = 0.58 p = 0.6784
(d)	none F = 1.47 p = 0.2306	significant F = 11.24 p = 0.0228	none F = 0.28 p = 0.8886
(e)	marginal F = 2.71 p = 0.0678	significant F = 13.85 p = 0.0159	none F = 0.87 p = 0.4792
(f)	significant F = 7.07 p = 0.001	marginal F = 5.35 p = 0.074	marginal F = 1.92 p = 0.1072
(g)	significant F = 49.57 p = 0.0001	none F = 0.55 p = 0.6168	marginal F = 1.81 p = 0.1269

Table 21. Results of Duncan's Multiple Range Test for cake sensory parameters crumb color (CRUMB), cell size (SIZE), cell uniformity (UNIF), sweetness (SWEET), moistness (MOIST), tenderness (TENDER), and aftertaste (AFTER) according to:

- (a) HFCS
- (b) emulsifier

(* denotes significant differences at 0.05 level)

	HFCS			Emulsifier		
	0	50	100	0	MDG	SE
CRUMB	8.92	8.29	8.11	8.43	7.40	9.50
SIZE	8.42	8.58	9.15	8.71	8.73	8.71
UNIF	7.94	7.85	7.91	7.97	8.13	7.59
SWEET	7.26	7.80	7.85	7.37	7.35	8.19*
MOIST	6.75*	7.44	7.63*	6.48	6.98	8.37*
TEND	7.56*	8.10	8.92*	7.50	7.80	9.10*
AFTER	9.54*	7.42	5.61*	7.81	7.49	7.26*

by the Hunter Colorimeter, which did not detect significant differences in crumb color according to emulsifier. Lack of agreement between objective and sensory results of color measurement has occurred. McCullough et al (1986) reported that sensory panelists were unable to detect the differences in crumb color measured by the Hunter Colorimeter in their study with HFCS cakes. It should be noted that those cakes were formulated with egg whites in place of whole eggs. No studies were found testing effects of emulsifiers on cake crumb color. A significant interaction occurred between HFCS with emulsifiers, and this explained part of the differences in crumb color (Table 21).

Cell Size: The mean values for cake cell size as evaluated by the sensory judges are reported in Table 19. The effect of HFCS on cell size was marginally significant, whereas emulsifier had no effect on cell size (Table 20b). Judges rated the cake crumb of cakes prepared with 100% HFCS as having significantly larger cell size compared to the crumb of cakes with 0 and 50% HFCS. This is surprising in light of the fact that large cell size has been associated with large volume (Ash and Colmey, 1973). One-hundred-percent HFCS cakes therefore would be expected to have small rather than large cell size. However, in their study of white layer cakes, Volpe and Meres (1976) reported that cakes prepared with HFCS always gave acceptable sensory

grain (cell size) scores in comparison with sucrose controls.

Cell Uniformity: The mean values for cake cell uniformity as evaluated by the sensory judges are reported in Table 19. There were no significant effects of HFCS, emulsifier, or interaction on cell uniformity (evenness of grain; Table 20c). Sucrose ester emulsified batters produced cakes with the least cell uniformity, while MDG emulsified batters produced cakes with the most cell uniformity. The MDG cakes also were the lowest in volume. No studies were found reporting the effects of emulsifiers on crumb cell uniformity in cakes prepared with HFCS.

Cell Sweetness:, The mean values for cake sweetness as evaluated by the sensory judges are reported in Table 19. There were no significant effects of HFCS on cake sweetness (Table 20d). However, the judges rated the cakes with 50 and 100% HFCS as being slightly sweeter than sucrose controls (Table 21). Emulsifier had a significant effect on cake sweetness. Sucrose ester-emulsified cakes were judged to be sweeter than the MDG and unemulsified cakes (findings were significant at 0.05 level). No studies on the influence of emulsifiers on sweetness in HFCS cakes were found.

Cake Moistness: The mean values for cake moistness as evaluated by the sensory judges are reported in Table 19.

Marginally significant effects of HFCS on cake moistness and significant effects of emulsifier on cake moistness were found (Table 20e). Cakes prepared with 100% HFCS cakes were rated as significantly more moist than sucrose controls, and SE-emulsified cakes were judged to be more moist than MDG and unemulsified cakes (Table 21).

McCullough et al (1986) also reported that sensory moistness was greater in cakes prepared with 50 and 75% HFCS compared to sucrose controls. They commented that the humectant properties of HFCS appeared to create a moist mouthfeel. Both Henry (1976) and Sausselle et al (1976) suggested that HFCS may contribute to moisture retention in baked products to a greater extent than does sucrose. No studies were found that reported the effects of emulsifiers on moistness in HFCS cakes. The sensory findings of increased moistness with increased HFCS content agreed with the percent moisture data obtained with the Brabender Moisture Tester.

Cake Tenderness: The mean values for cake tenderness as evaluated by the sensory judges are reported in Table 19. The effects of both HFCS and emulsifier plus their interaction on cake tenderness were marginally significant (HFCS was significant at $p = 0.001$; Table 20f). The most tender cakes were judged to be the cakes prepared with 100% HFCS, which were significantly more tender than the sucrose

controls (Table 21). The SE-emulsified cakes were significantly more tender than the MDG-emulsified and unemulsified cakes (Table 21). Previously, cake deformation was found to be significantly affected by both HFCS and emulsifier (Table 17), with SE cakes having the greatest deformation values (compressed), indicating highest tenderness. However, the results for the effect of HFCS on cake deformation were opposite to the sensory results: 0% HFCS (sucrose control) cakes were significantly more tender than cakes prepared with 100% HFCS (Table 18).

No sensory tenderness differences were found among cakes prepared with all sucrose or HFCS at 50 and 75% replacement levels by McCullough et al (1986). Coleman and Harbers (1983) reported that sensory tenderness scores increased as HFCS levels increased from 0 to 100% substitution for sucrose in angel cakes. Volpe and Meres (1976) found that sucrose layer cakes were rated as more tender than HFCS layer cakes in which 60% of the sucrose was replaced with HFCS.

Pierce and Walker (1987) reported that MDG-emulsified cakes were less tender than SE-emulsified cakes as determined by an Instron Universal testing machine. No sensory evaluations of sucrose ester emulsified cakes were found in the literature.

Cake Aftertaste: The mean values for cake aftertaste as evaluated by the sensory judges are reported in Table 19. The effect of HFCS on aftertaste was significant, and emulsifier caused a marginally significant effect (Table 20g). Zero-percent HFCS cakes (sucrose controls) had significantly less aftertaste than the HFCS cakes, and the 100% HFCS cakes had the most aftertaste (Table 21). The emulsifiers caused a slight increase in the perception of aftertaste over unemulsified controls (Table 21). Coleman and Harbers (1983) reported that six out of ten panelists detected bitterness in some of the HFCS cakes evaluated. The authors mentioned that undesirable flavor compounds can be produced by caramelization of sugars and by aldosome reactions. No mention of the effects of emulsifiers on the sensory perception of aftertaste in cakes was found in the literature. A more alkaline cake crumb can potentiate formation of off-flavors due to enhancement of the Maillard reaction, but such was not the case here.

QDA Analysis of Cake Sensory Parameters: QDA (Quantitative Descriptive Analysis) configurations for the seven sensory attributes of crumb color, cell size, cell uniformity, sweetness, moistness, tenderness, and aftertaste were generated using an adaptation of a SAS Star Chart procedure (SAS Institute, Cary, NC). Typical "spiderweb" sensory profiles resulted and are presented by variation

(Figures 33-41). The mean intensities for the attributes were generated on lines radiating outward from a value of zero at the center point to a value of ten at the outer perimeter. These radial lines corresponded exactly in centimeter length with each parameter mean as calculated directly from the sensory scorecards, which contained lines 15 cm in length. Ten centimeters out of a possible 15 cm was the maximum value obtained for each of the seven sensory parameters. Therefore, the QDA radial lines were not based on any sensory extreme.

Figure 42 allows for direct comparison of the polygons generated by each variation's component attribute mean intensities. The score cards were designed so that increasing intensities corresponded to the desired direction of intensity (i.e.: high mean values for moistness corresponded to increased moistness; high mean values for aftertaste corresponded to lack of undesirable aftertaste). Therefore, the variation with a polygon most completely filling its surrounding circle was judged to be the most successful sensorally (although it might be argued that yellow vs. white crumb color and more sweet vs. less sweet taste as the desirable direction is debatable).

By summing the areas ($A = 1/2 bh$) of the seven triangles which made up a polygon, the total polygon area was obtained. A quantitative comparison was then made among

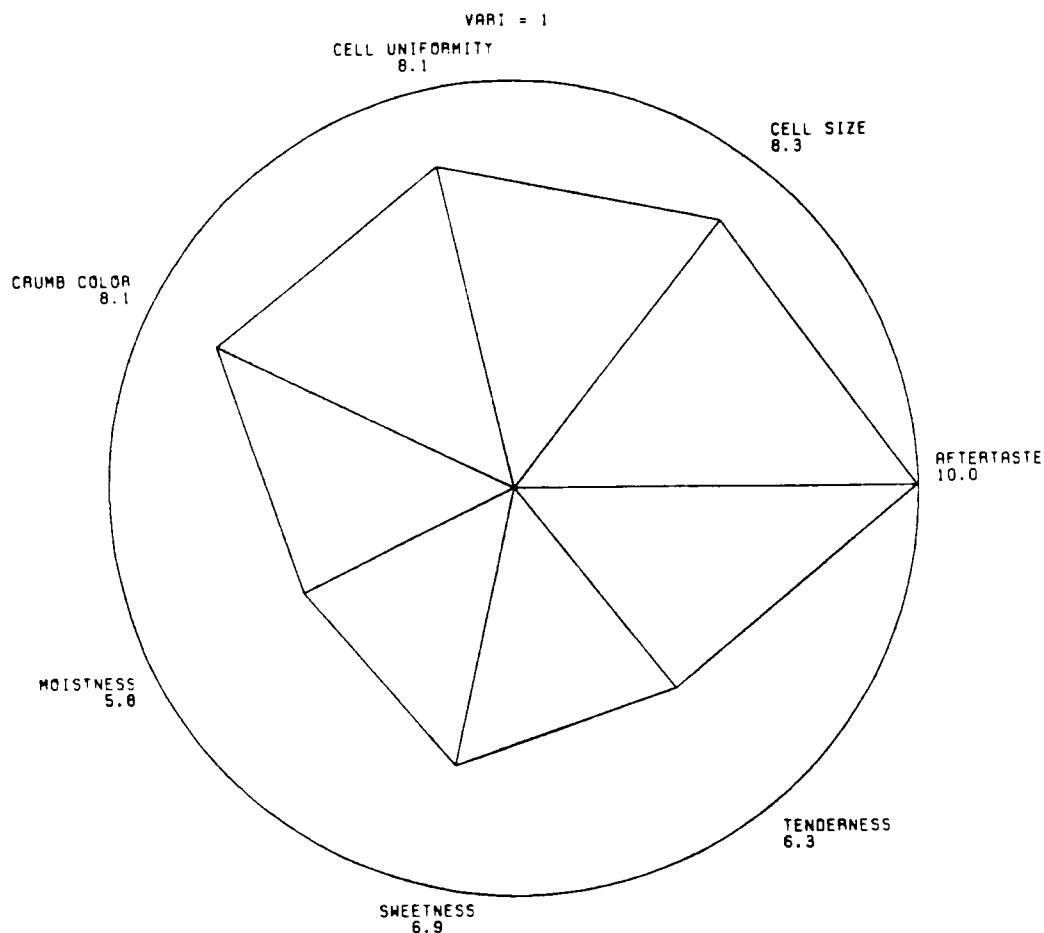


Figure 33. GDA profile depicting the mean sensory scores for cake variation 1 (0% HFCS, sucrose control, without emulsifier). Values are represented as follows: cell size 0 = large, 10 = small; aftertaste 0 = most, 10 = least; tenderness 0 = least, 10 = most; sweetness 0 = least, 10 = most; moistness 0 = least, 10 = most; crumb color 0 = dark yellow, 10 = light yellow; cell uniformity 0 = uneven, 10 = even.

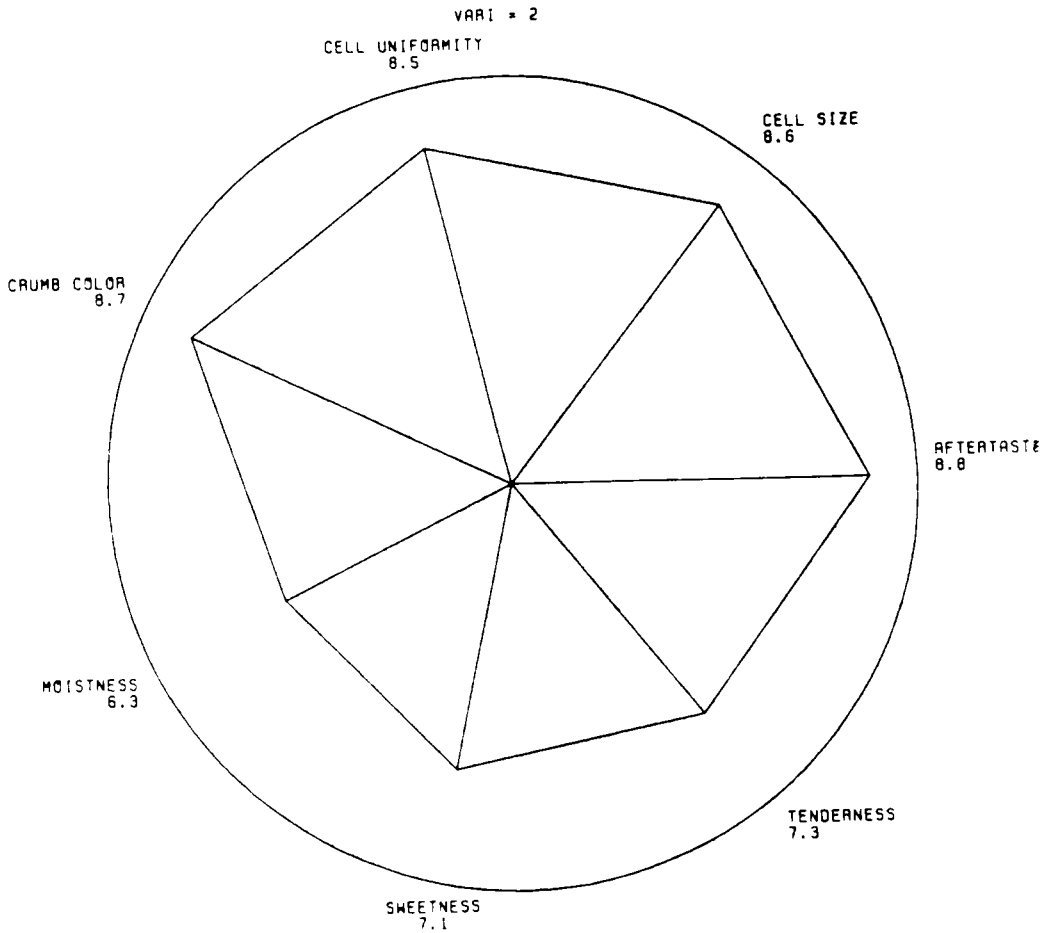


Figure 34. QDA profile depicting the mean sensory scores for cake variation 2 (0% HFCS with added mono- and diglycerides). Values are represented as follows: cell size 0 = large, 10 = small; aftertaste 0 = most, 10 = least; tenderness 0 = least, 10 = most; sweetness 0 = least, 10 = most; moistness 0 = least, 10 = most; crumb color 0 = dark yellow, 10 = light yellow; cell uniformity 0 = uneven, 10 = even.

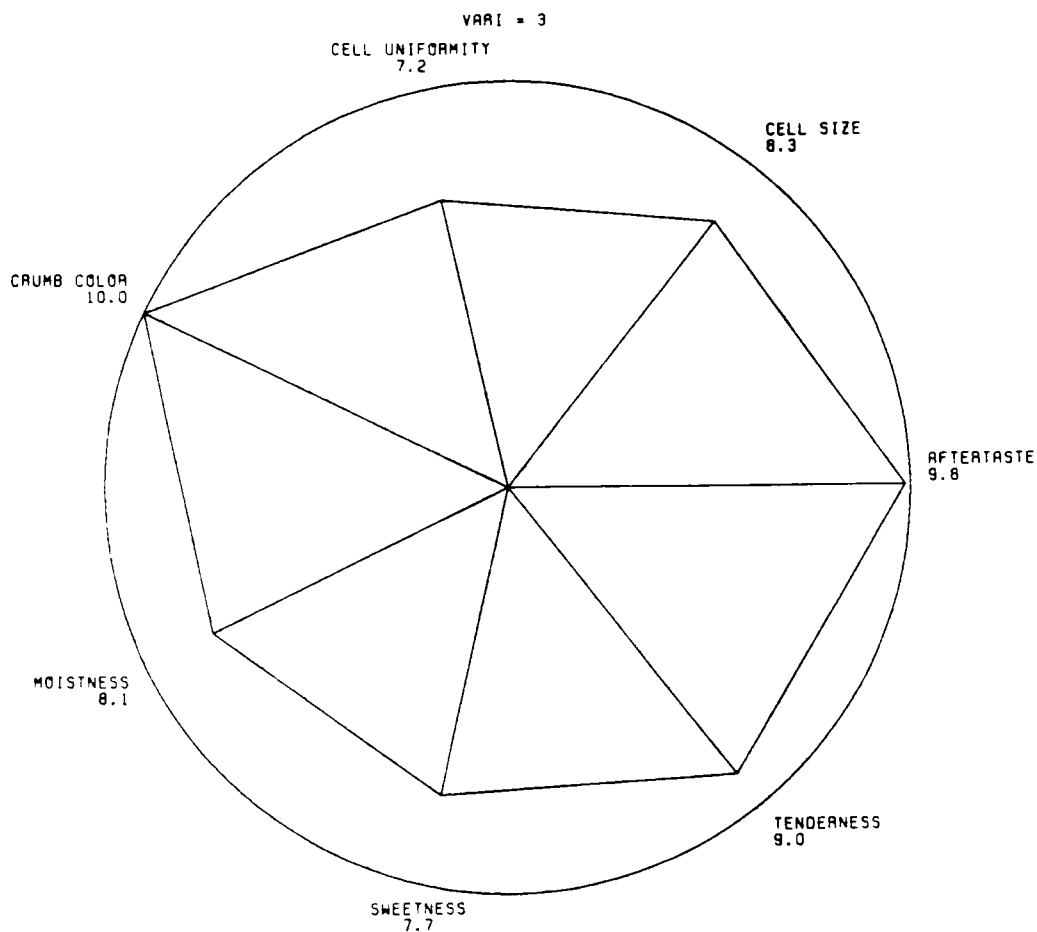


Figure 35. QDA profile depicting the mean sensory scores for cake variation 3 (0% HFCS with added sucrose esters). Values are represented as follows: cell size 0 = large, 10 = small; aftertaste 0 = most, 10 = least; tenderness 0 = least, 10 = most; sweetness 0 = least, 10 = most; moistness 0 = least, 10 = most; crumb color 0 = dark yellow, 10 = light yellow; cell uniformity 0 = uneven, 10 = even.

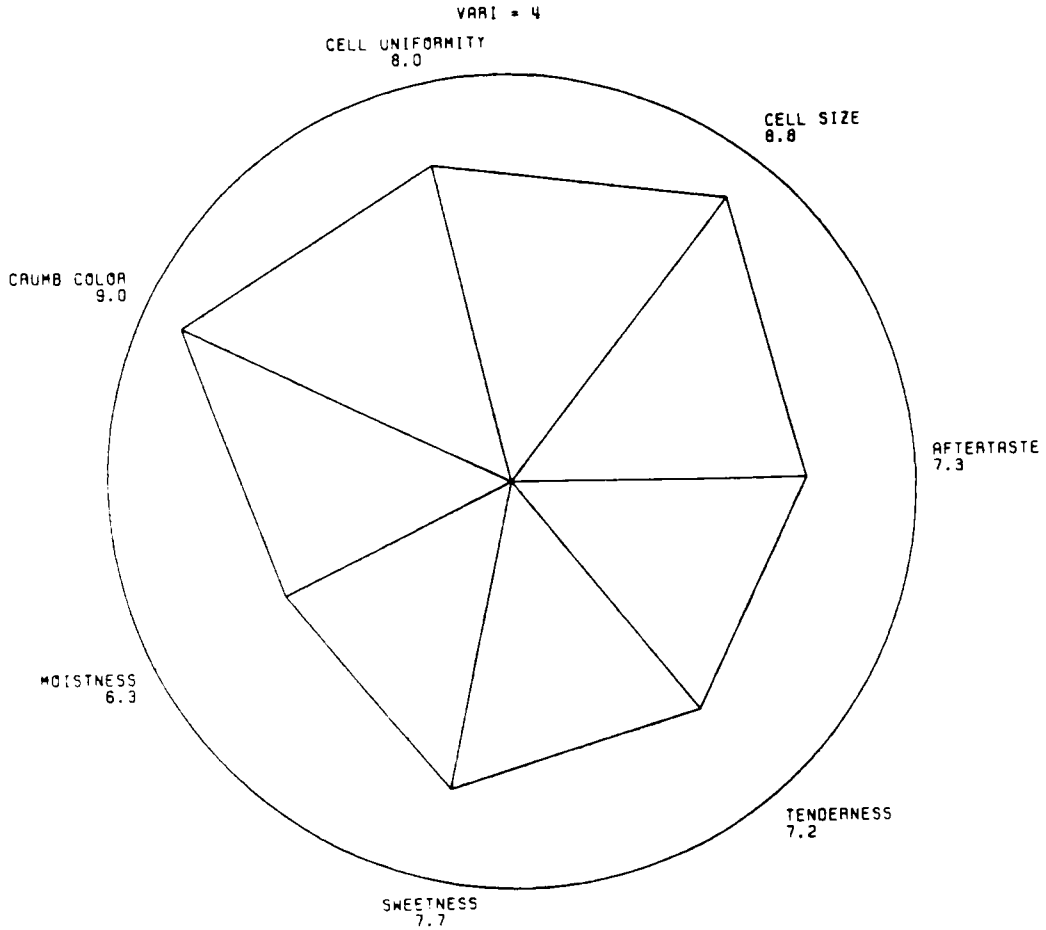


Figure 36. QDA profile depicting the mean sensory scores for cake variation 4 (50% HFCS without emulsifier). Values are represented as follows: cell size 0 = large, 10 = small; aftertaste 0 = most, 10 = least; tenderness 0 = least, 10 = most; sweetness 0 = least, 10 = most; moistness 0 = least, 10 = most; crumb color 0 = dark yellow, 10 = light yellow; cell uniformity 0 = uneven, 10 = even.

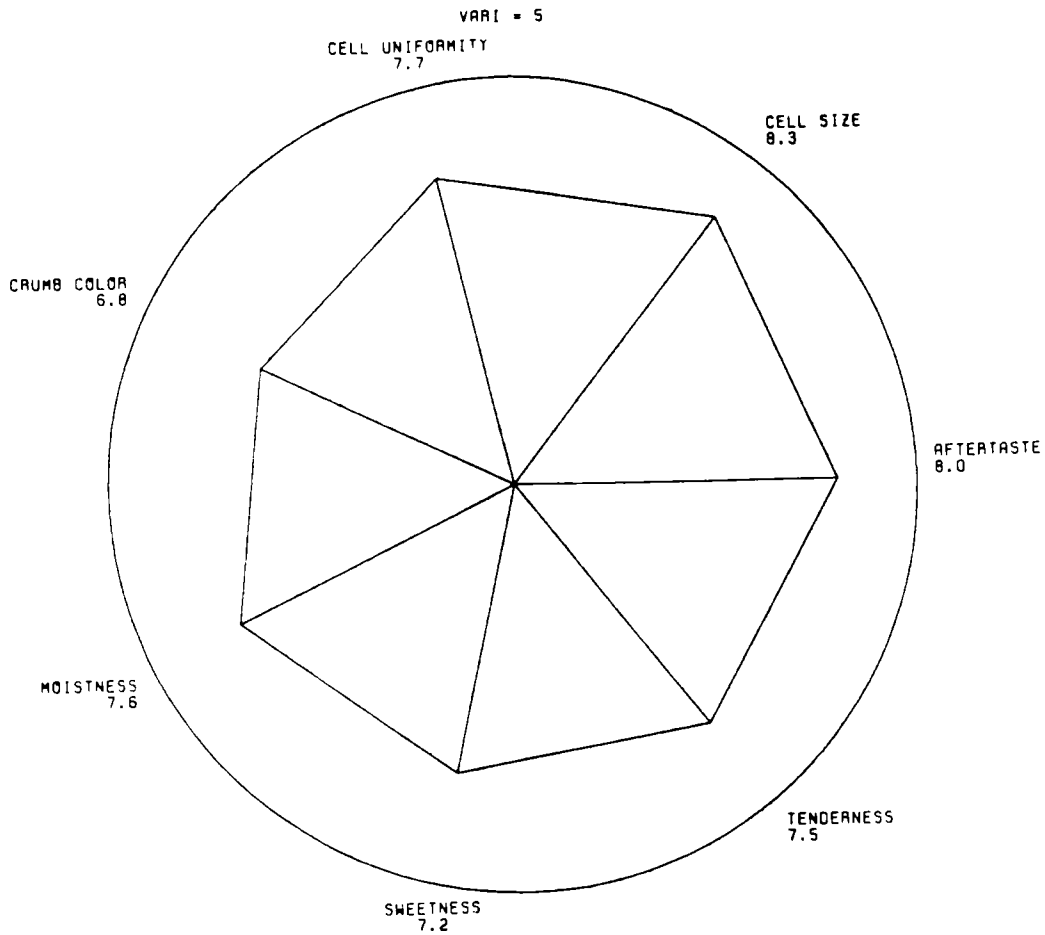


Figure 37. QDA profile depicting the mean sensory scores for cake variation 5 (50% HFCS emulsified with mono- and diglycerides). Values are represented as follows: cell size 0 = large, 10 = small; aftertaste 0 = most, 10 = least; tenderness 0 = least, 10 = most; sweetness 0 = least, 10 = most; moistness 0 = least, 10 = most; crumb color 0 = dark yellow, 10 = light yellow; cell uniformity 0 = uneven, 10 = even.

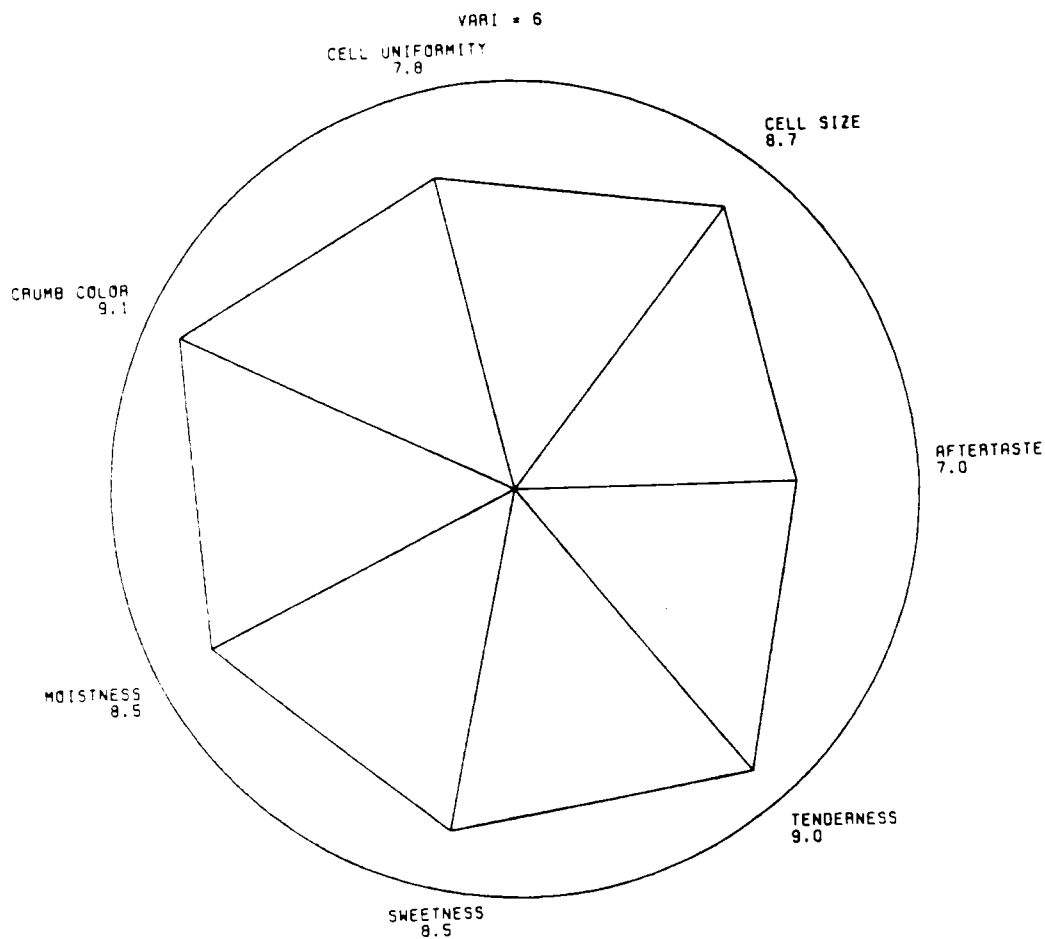


Figure 38. QDA profile depicting the mean sensory scores for cake variation 6 (50% HFCS emulsified with sucrose esters). Values are represented as follows: cell size 0 = large, 10 = small; aftertaste 0 = most, 10 = least; tenderness 0 = least, 10 = most; sweetness 0 = least, 10 = most; moistness 0 = least, 10 = most; crumb color 0 = dark yellow, 10 = light yellow; cell uniformity 0 = uneven, 10 = even.

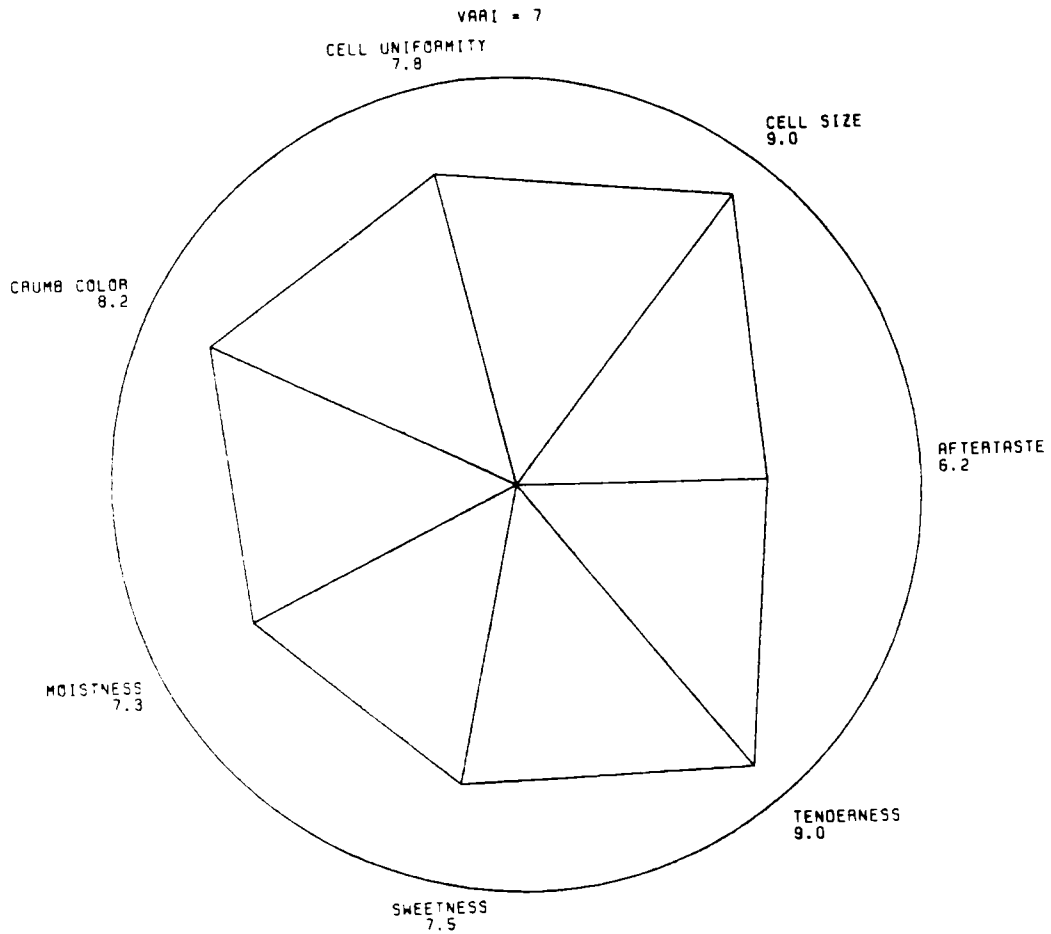


Figure 39. QDA profile depicting the mean sensory scores for cake variation 7 (100% HFCS without emulsifier). Values are represented as follows: cell size 0 = large, 10 = small; aftertaste 0 = most, 10 = least; tenderness 0 = least, 10 = most; sweetness 0 = least, 10 = most; moistness 0 = least, 10 = most; crumb color 0 = dark yellow, 10 = light yellow; cell uniformity 0 = uneven, 10 = even.

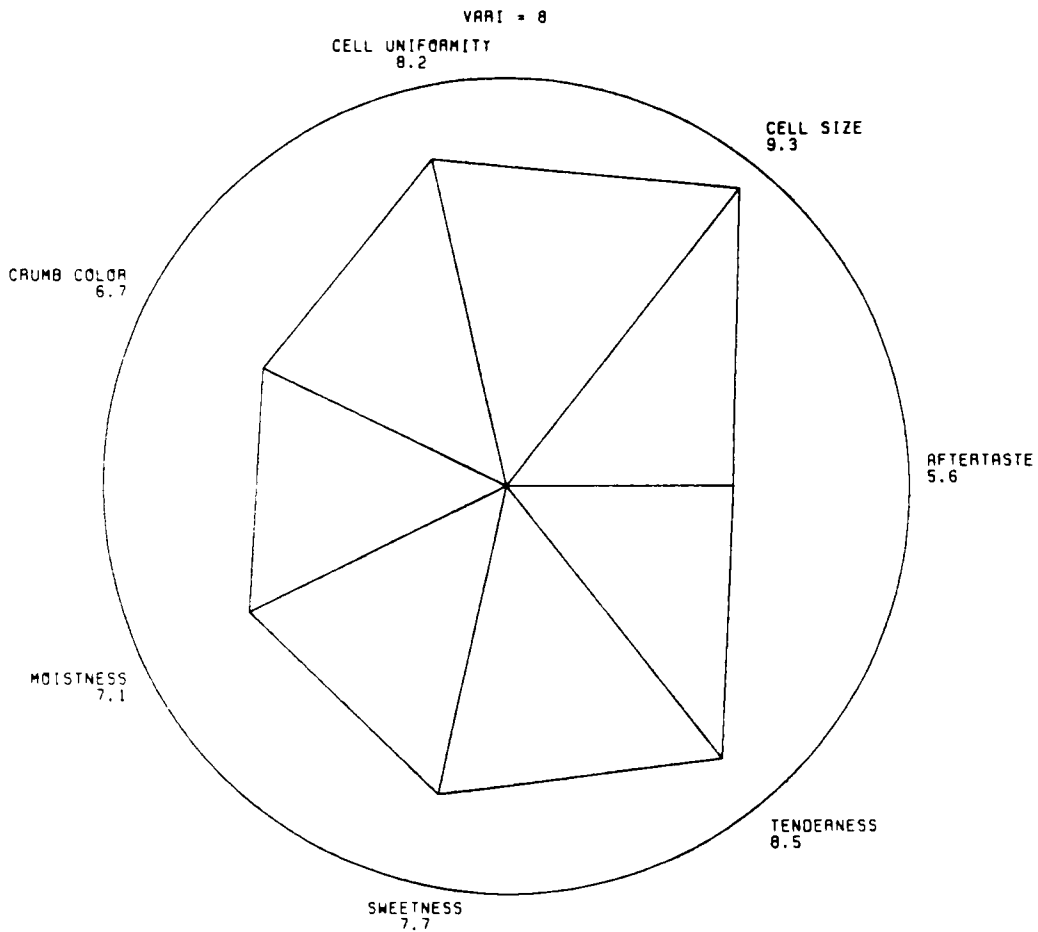


Figure 40. QDA profile depicting the mean sensory scores for cake variation 8 (100% HFCS emulsified with mono- and diglycerides). Values are represented as follows: cell size 0 = large, 10 = small; aftertaste 0 = most, 10 = least; tenderness 0 = least, 10 = most; sweetness 0 = least, 10 = most; moistness 0 = least, 10 = most; crumb color 0 = dark yellow, 10 = light yellow; cell uniformity 0 = uneven, 10 = even.

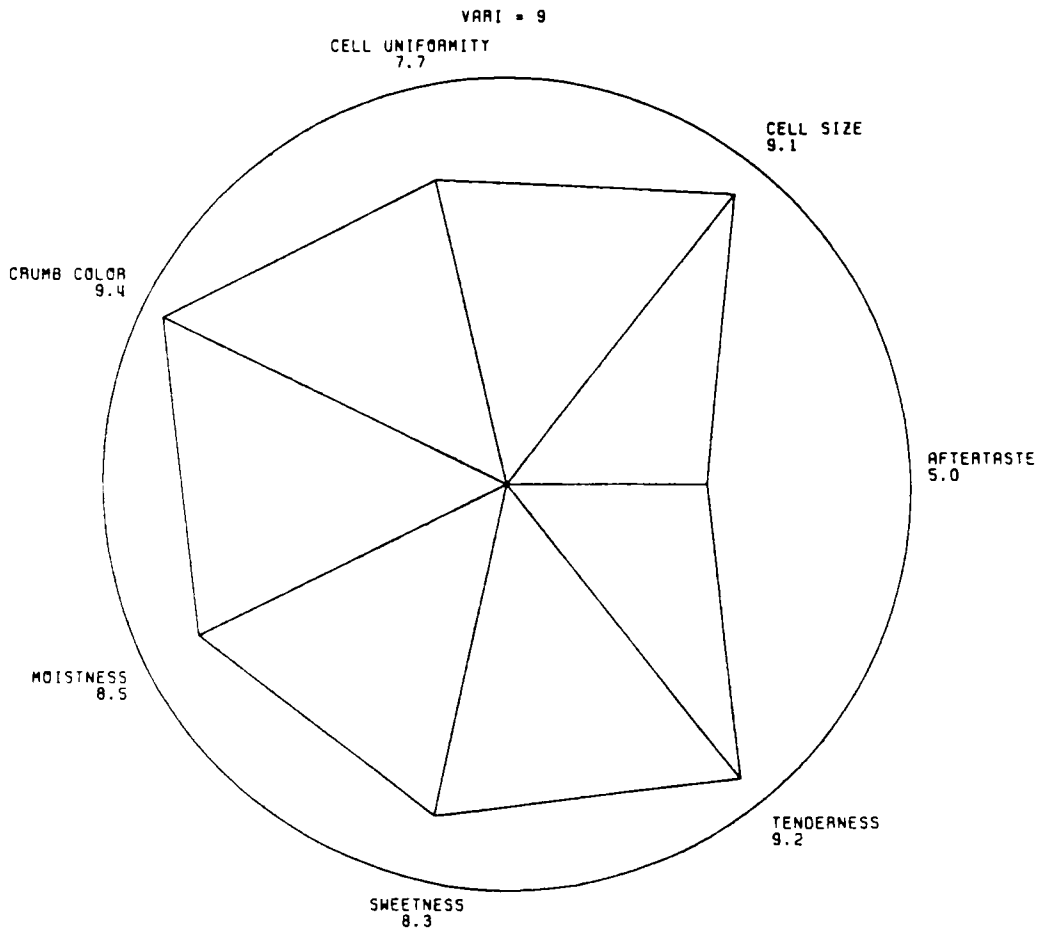


Figure 41. QDA profile depicting the mean sensory scores for cake variation 9 (100% HFCS emulsified with sucrose esters). Values are represented as follows: cell size 0 = large, 10 = small; aftertaste 0 = most, 10 = least; tenderness 0 = least, 10 = most; sweetness 0 = least, 10 = most; moistness 0 = least, 10 = most; crumb color 0 = dark yellow, 10 = light yellow; cell uniformity 0 = uneven, 10 = even.

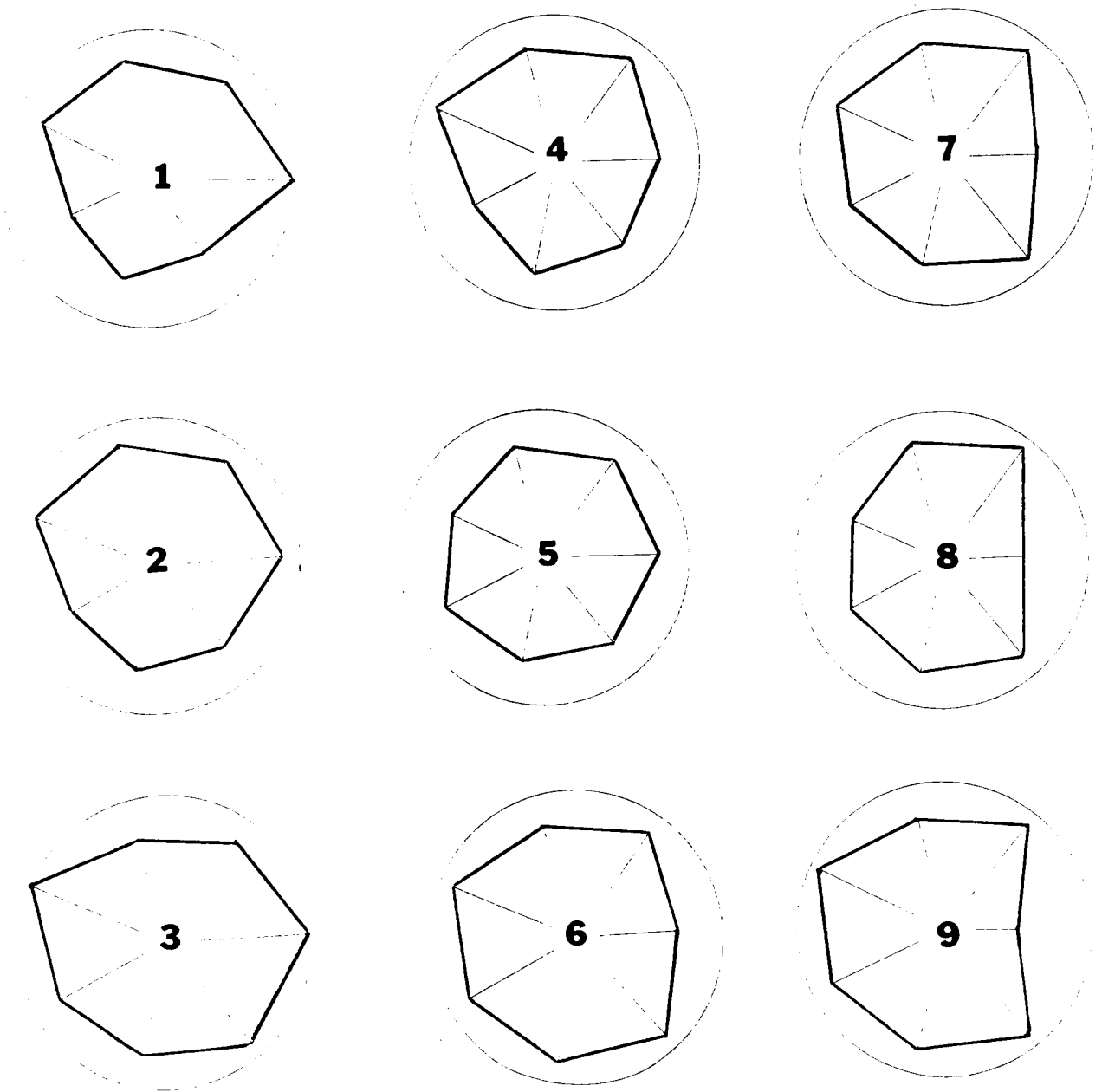


Figure 42. QDA configurations for cake variations 1-9 to compare polygon sizes as a function of the mean sensory scores for each variation. Variation 1 = 0% HFCS unemulsified; 2 = 0% HFCS + MDG; 3 = 0% HFCS + SE; 4 = 50% HFCS unemulsified; 5 = 50% HFCS + MDG; 6 = 50% HFCS + SE; 7 = 100% HFCS unemulsified; 8 = 100% HFCS + MDG; 9 = 100% HFCS + SE.

the polygons based on area. In Table 22a the complete polygon areas are reported. From these, the ranking of cake variation from most successful from a sensory standpoint to least was as follows:

0% HFCS + SE > 50% HFCS + SE > 100% HFCS + SE >
 100% HFCS unemulsified > 50% HFCS unemulsified >
 0% HFCS unemulsified > 50% HFCS + MDG > 100% HFCS
 + MDG

In recognizing that three of the sensory parameters were visual (crumb color, cell size, cell uniformity) and that the remaining four were related to the sensation of taste and mouthfeel (sweetness, moistness, tenderness, aftertaste), the areas of polygons associated with the latter four only were calculated (Table 22b) and compared. The most successful from a taste and mouthfeel standpoint:

0% HFCS + SE > 50% HFCS + SE > 100% HFCS + SE >
 100% HFCS unemulsified > 50% HFCS + MDG > 100%
 HFCS + MDG > 0% HFCS + MDG > 50% HFCS unemulsified
 > 0% HFCS unemulsified

The important result from this analysis was that the best cakes from a sensory standpoint were sucrose ester

Table 22. Areas of QDA polygons by cake variation.

- (a) for complete polygon, including all seven sensory parameters
 (b) for limited polygon, including four (sweetness, moistness, tenderness, and aftertaste) sensory parameters

Variation	(a)	(b)
	Polygon Area (cm ²)	Polygon Area (cm ²)
0% HFCS	120.78	44.92
0% HFCS + MDG	127.52	47.09
0% HFCS + SE	149.49	64.20
50% HFCS	121.74	45.69
50% HFCS + MDG	116.05	48.72
50% HFCS + SE	140.23	61.03
100% HFCS	123.36	51.20
100% HFCS + MDG	114.58	48.23
100% HFCS + SE	133.01	55.43

emulsified, regardless of the level of HFCS.

Evaluation of Sensory Judge Performance: The performance of each of the seven sensory judges who participated in the sensory evaluation of the nine cake variations of the research problem was analyzed using the statistical coefficient of variation determination (Cv). Cv related the mean of each judge's four observations per cake to its standard deviation. For example, if the mean of four observations was 10 with a standard deviation of 2, the Cv = 0.20 or 20%. As such, the Cv measured intra-individual consistency for a judge by cake variation.

The results are reported in Table 23. Judges were called subjects, and each sensory parameter evaluated was designated as a single letter of the alphabet. Where a blank occurred in the table, the subject's own intra-individual variation was below 50%, which was arbitrarily chosen as the critical level of performance. Therefore, subjects with consistent performance for any attribute of any cake variation were depicted by a blank. Where performance was poor (intra-individual variation was increased, meaning a Cv > 0.50), the sensory attribute causing the inconsistency was identified within the table followed by the Cv in parentheses.

Two subjects (judges), subjects 7 and 8, had the most consistent performance according to this criteria, having Cv

Table 23. Intra-individual consistency per variation using (CV) coefficient of variation.

CAKE VARIATION

Subject	1	2	3	4	5	6	7	8	9
1	M(75.5)	M(54.7) T(58.9)	M(63.3)						T(58.2)
2	T(58.2)	M(56.7) T(52.7)		M(65.7) T(58.3)	A(59.9)		M(53.8) A(61.1)		A(53.9)
3									M(54.6) T(54.2)
4	M(55.4)	Z(60.5)		Z(55.0) A(60.9)		A(53.8)	S(50.0)	M(52.4)	
5	S(94.6) M(55.2)	M(54.9) T(67.4)		M(52.1)	C(54.8) M(60.0) T(54.2) A(62.4)	M(60.4) A(67.8)	A(64.5)	A(62.4)	U(54.2) A(74.4)
6	M(52.6) U(69.6)	S(60.8) M(62.8)	U(63.1)	S(54.4)	C(61.0) S(51.5)		U(52.4) S(55.9)	S(66.4) U(66.6) A(72.1)	U(56.7) A(77.6)
7									
8									
9	U(55.6)	M(85.8)	A(52.9)	M(57.4)			A(65.1)		A(53.6)

M = moistness
T = tenderness
S = sweetness
A = aftertaste

C = crumb color
Z = cell size
U = cell uniformity

< 0.50 for all seven sensory parameters for each of the nine cake variations; one (subject 3) was consistent for eight of the cakes, and inconsistent cake variation 9 for the parameters moistness and tenderness; and so on.

A performance rating or score was developed based on the frequency of having $Cv < 0.50$, weighting "scores" using an arbitrary scheme. For example, each time a subject achieved a consistent performance, 10 points were assigned, giving a maximum performance score of 9 variations \times 10 cakes = 90. A specified point value of two points, was deducted each time a $Cv > 0.50$. Following through with this scheme produced the results given in Table 24. The mean score for the group was 33.5 points total. Four judges exceeded the mean, and five fell below it. There were high and low extremes that rather balanced out (two judges with positive consistency scores, two judges with negative scores). Without those extremes, the mean was consistent, at 32.4.

The panel of judges, then, consisted of three "outstanding" judges (subjects 3, 7, and 8), one "very good" one (subject 1), three "mediocre" judges (subjects 2, 4, and 9) and two "poor" judges (subjects 5 and 6). Judges may be screened beforehand by simple and rapid discrimination and threshold testing, such as the triangle test (Zook and Wessman, 1977). Judges may receive solid training and

Table 24. Overall performance score totals for the nine sensory judges (subjects) based on Cv. (note: highest score = 90 and represents perfect intra-individual consistency).

<u>Subject</u>	<u>Performance Total</u>
1	40
2	12
3	76
4	16
5	-20
6	-20
7	90
8	90
9	18

appear to fully understand what information is required of them in sensory testing. However, certain individuals are less discriminating in one or more sensory areas, and the administration of an appropriate screening test could be a valuable tool to identify those judges and eliminate them from consideration regarding serving on the sensory panel.

MICROSCOPY

Light Microscopy of Cake Batter

Cake batter smears were photographed as shown in Figures 43-45. The batters were seen to be emulsions of oil dispersed in the aqueous phase, which contained a matrix of starch and protein. Larger, more irregularly-shaped droplets were characteristic of the unemulsified batters (Figures 43a, 44a, and 45a) whereas the emulsified batters showed an increased dispersion of smaller, spherical oil droplets. The batter matrix was more dense in the unemulsified batters.

Light Microscopy of Cake Crumb

Light micrographs (Figures 46-50) of cake crumb sections show the structural contributions of starch and protein in baked cake. Protein was closely associated with starch in forming a matrix framework wherein starch was observed to be in various stages of folding

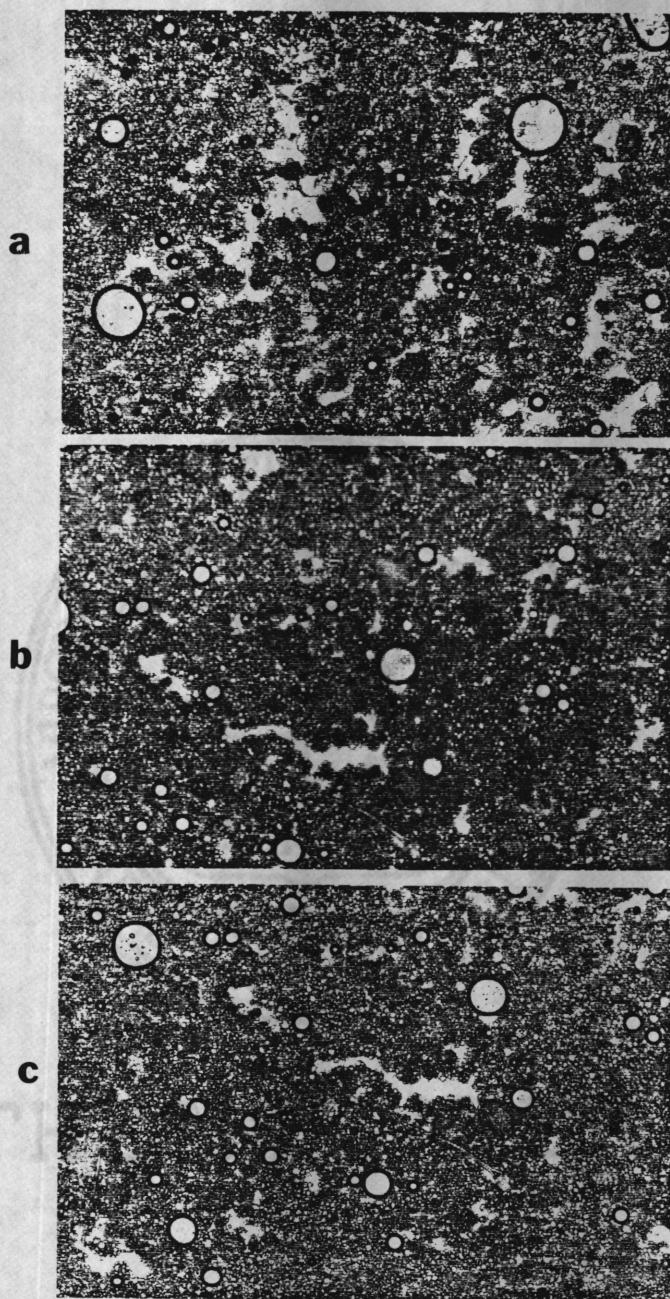


Figure 43. Light micrographs of cake batter.

- (a) variation 1 (0% HFCS, no emulsifier)
- (b) variation 2 (0% HFCS, MDG emulsifier)
- (c) variation 3 (0% HFCS, SE emulsifier)

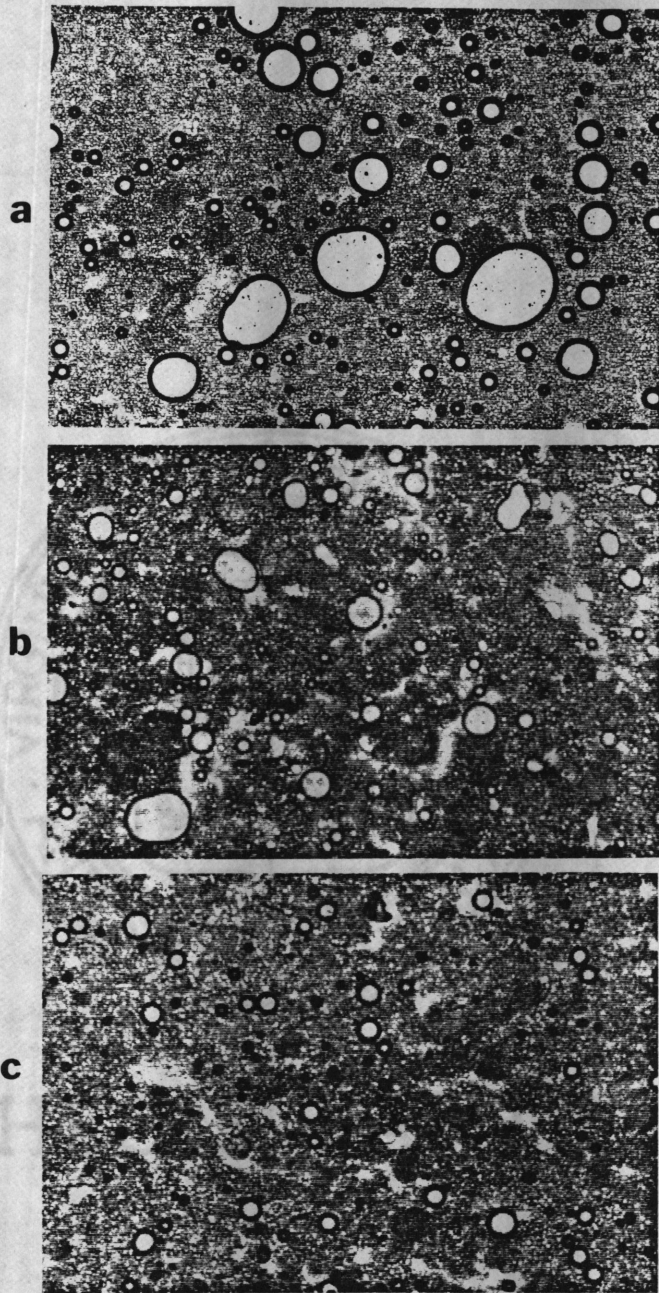


Figure 44. Light micrographs of cake batter.

- (a) variation 4 (50% HFCS, no emulsifier)
- (b) variation 5 (50% HFCS, MDG emulsifier)
- (c) variation 6 (50% HFCS, SE emulsifier)

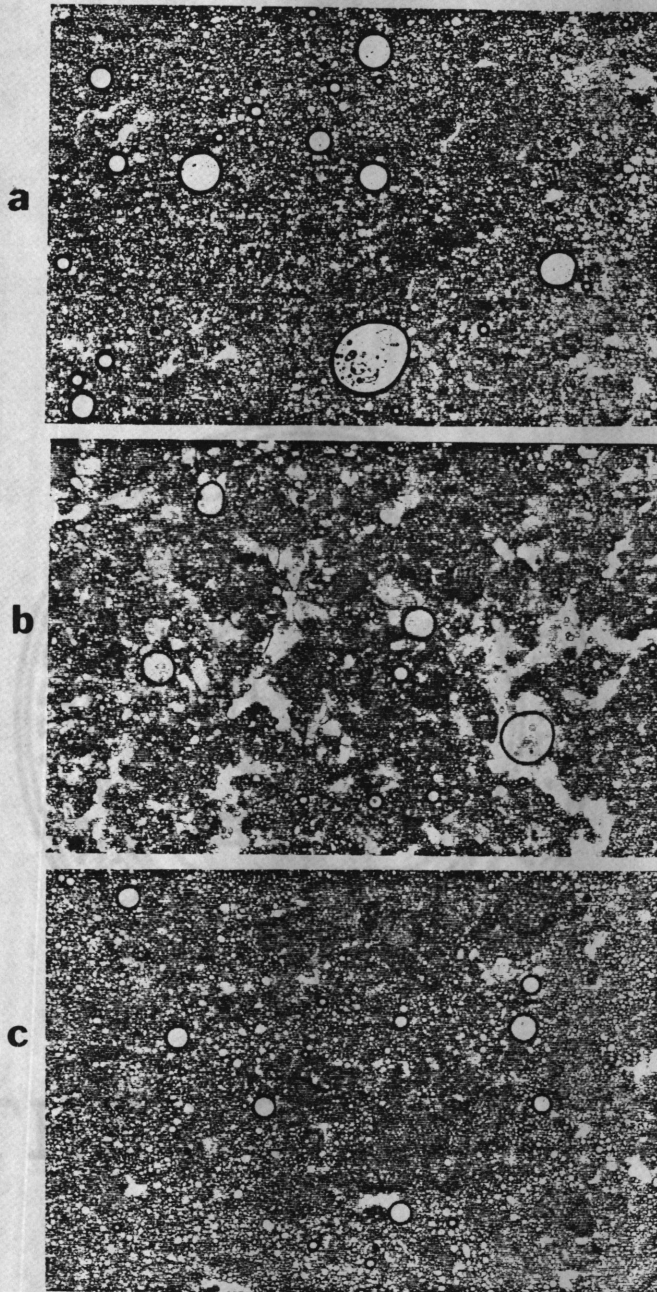


Figure 45. Light micrographs of cake batter.

- (a) variation 7 (100% HFCS, no emulsifier)
- (b) variation 8 (100% HFCS, MDG emulsifier)
- (c) variation 9 (100% HFCS, SE emulsifier)

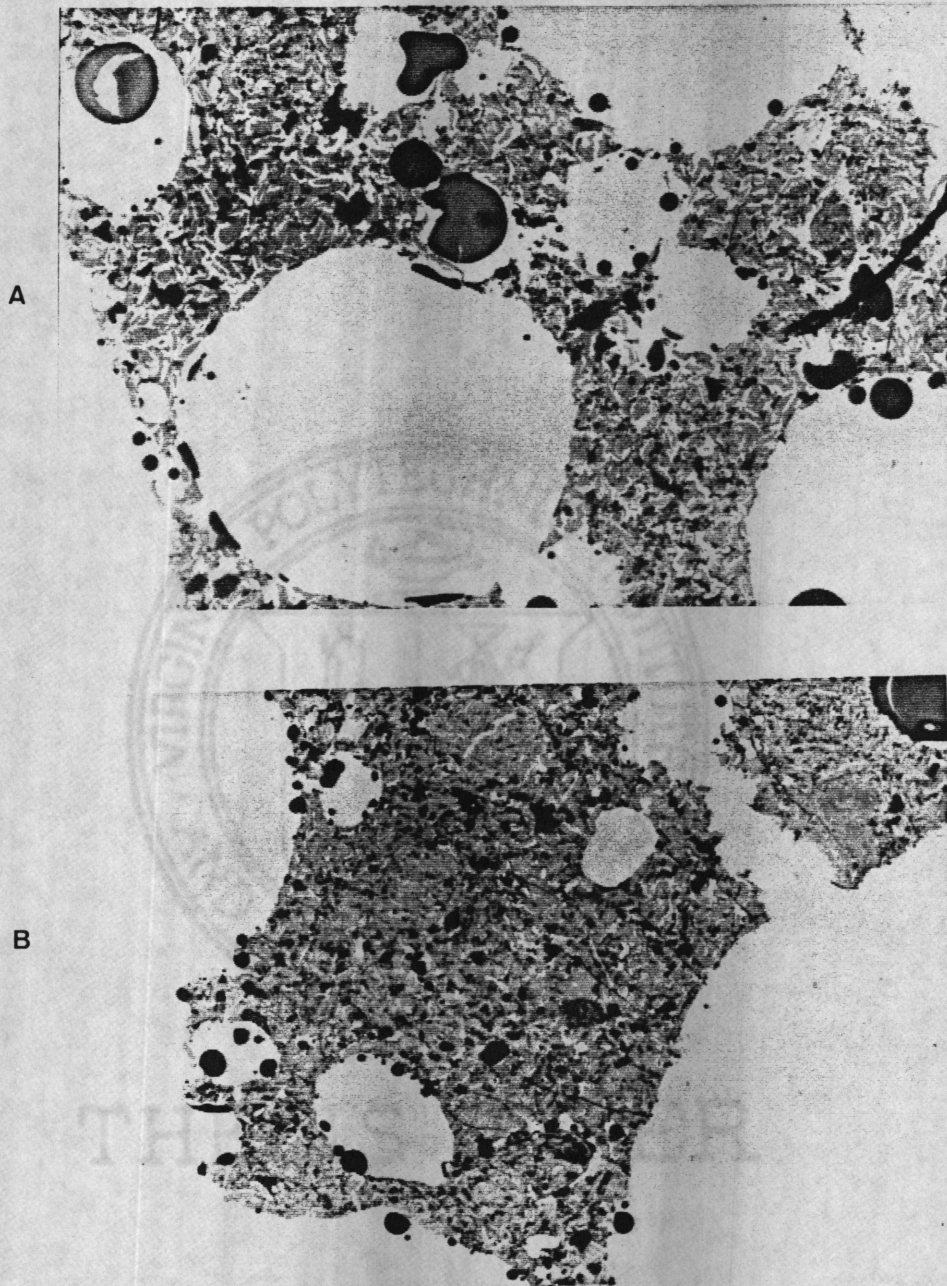


Figure 46. Light micrographs of (a) unemulsified and (b) mono- and diglyceride emulsified cake crumb sections viewed under low (250X) magnification.

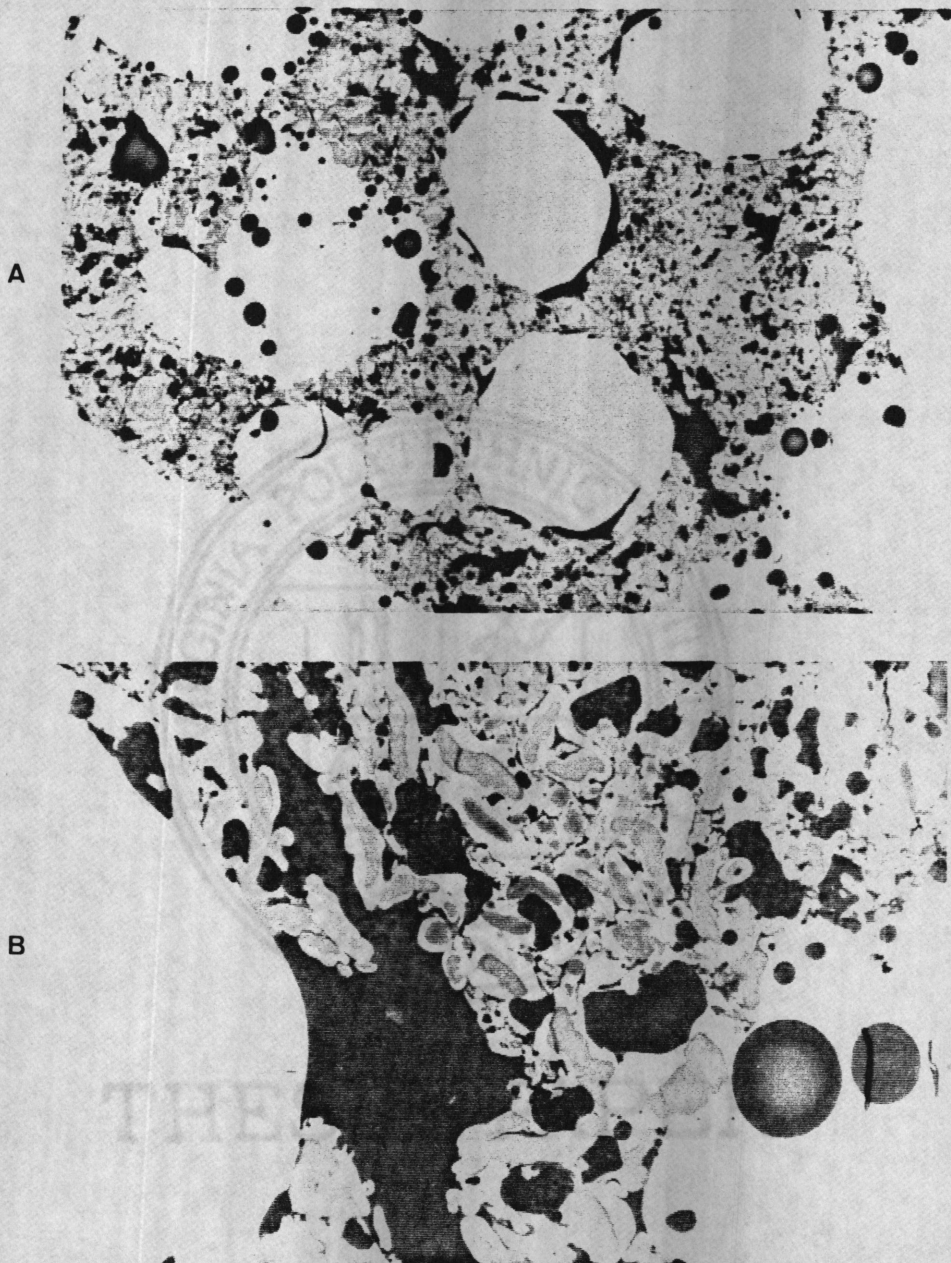


Figure 47. Light micrographs of cake crumb sections emulsified with sucrose esters (a) at low magnification (250X) and (b) high magnification (1000X) showing arrangement of lipid at the rim of an air vacuole.

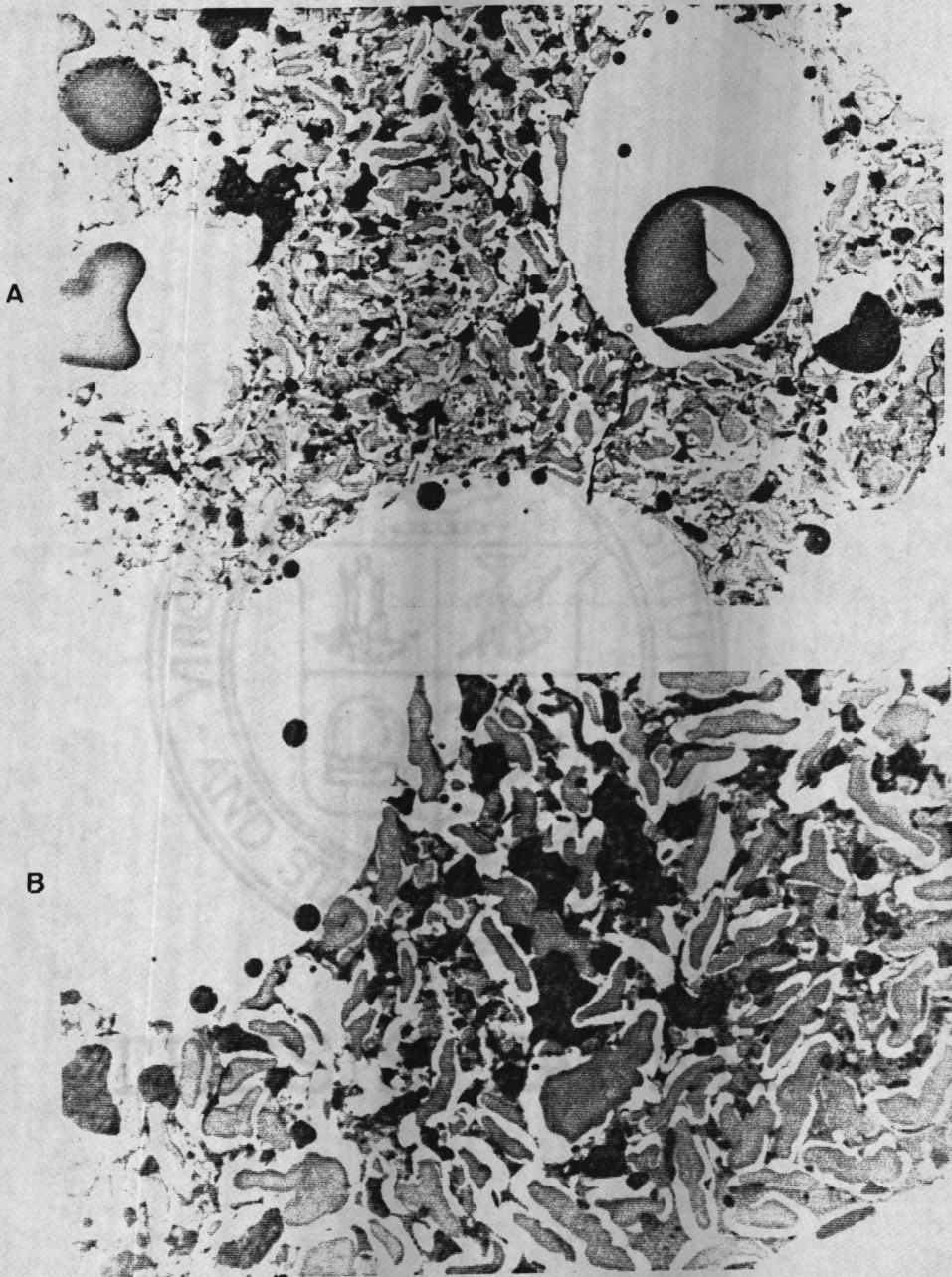


Figure 48. Light micrograph of unemulsified cake batter showing arrangement of protein, starch, and lipid around air vacuole at (a) 500X magnification and (b) 1000X magnification.

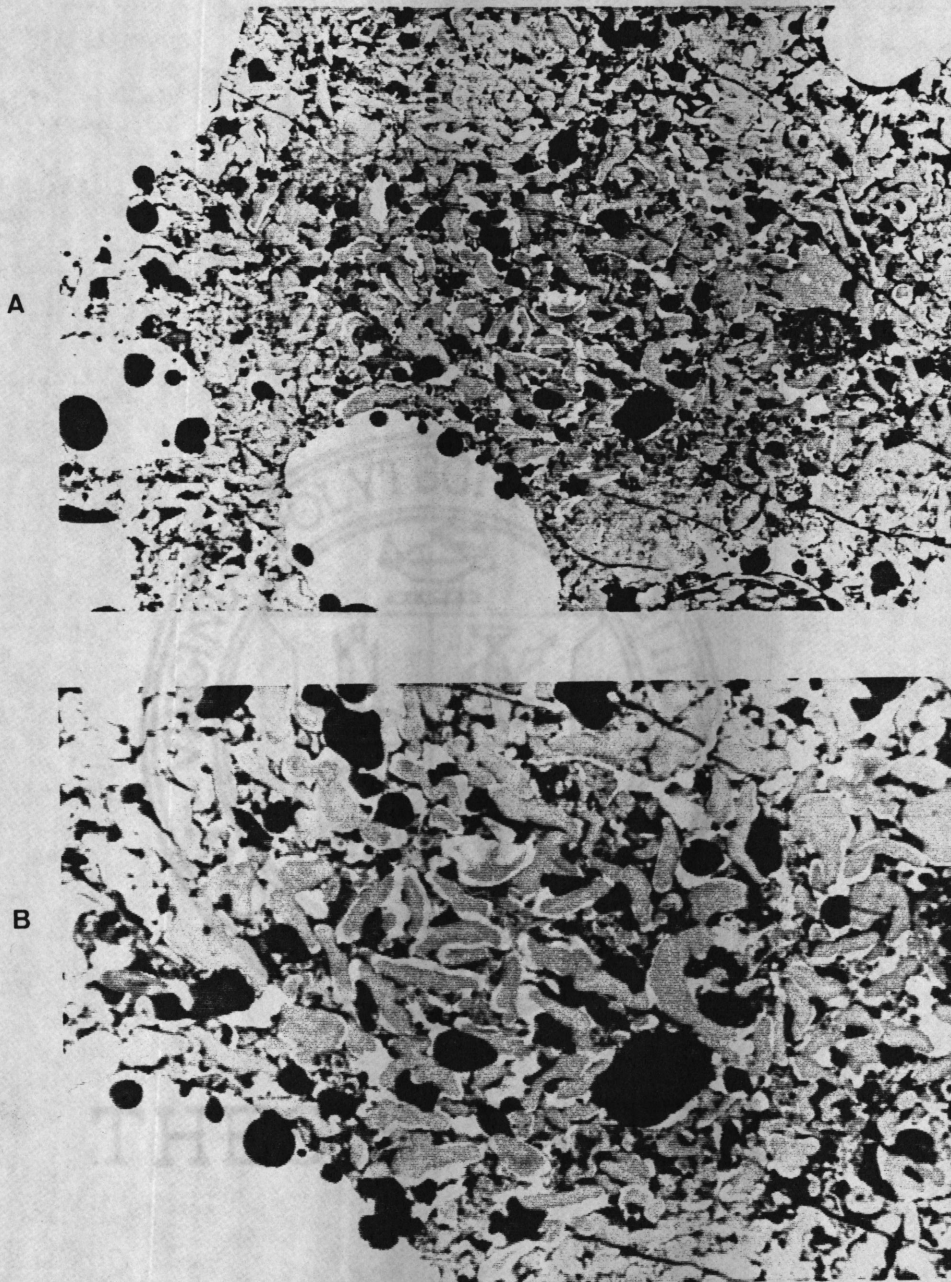


Figure 49. Light micrographs of mono- and diglyceride emulsified cake crumb sections showing arrangement of protein, starch, and lipid around air vacuole at (a) 500X magnification and (b) 1000X magnification.

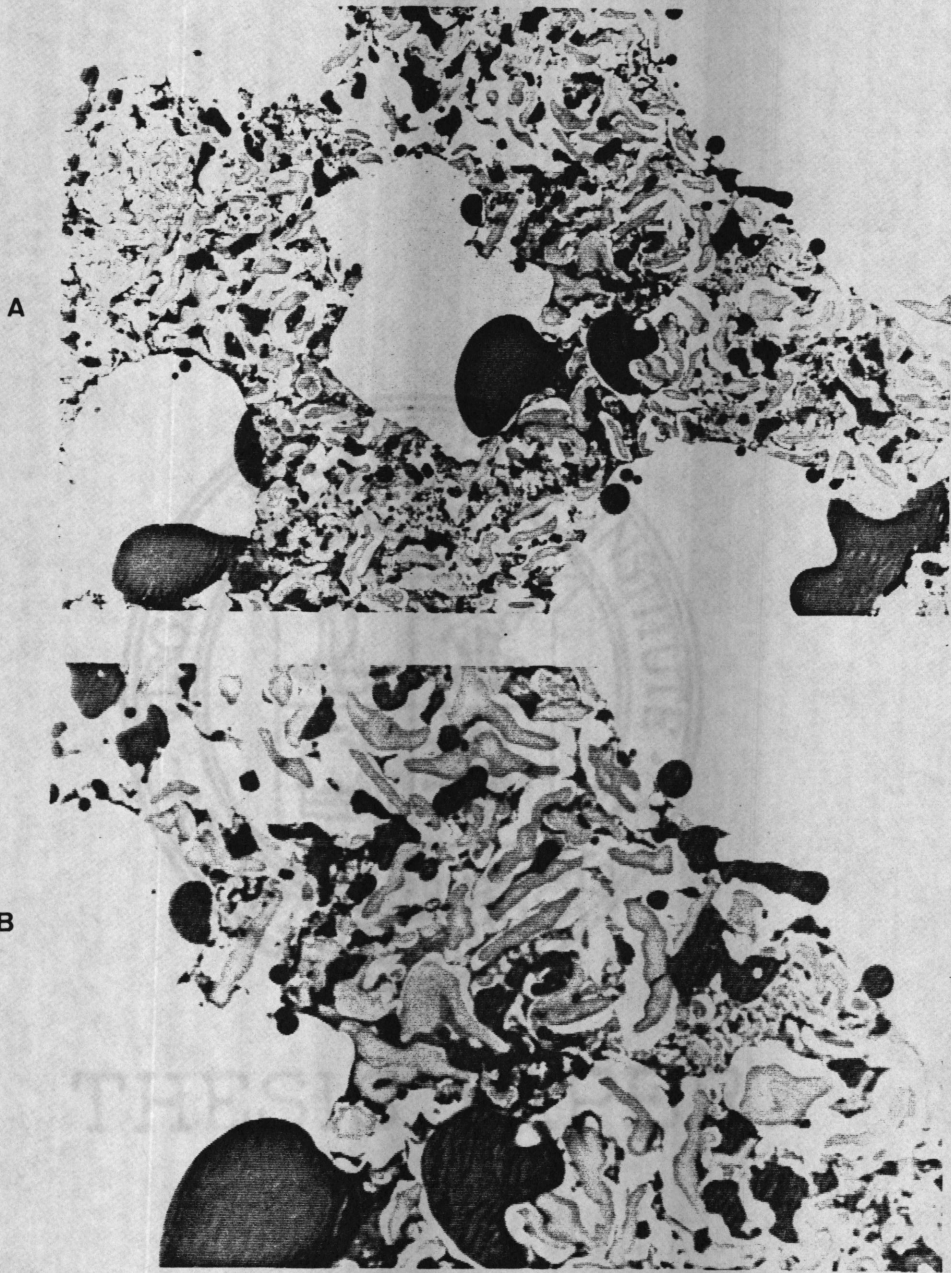


Figure 50. Light micrographs of sucrose ester emulsified cake crumb sections showing arrangement of protein, starch, and lipid around air vacuole at (a) 500X magnification and (b) 1000X magnification.

(gelatinization). Air/gas vacuoles occurred within the matrix and were often rimmed by lipid (Figure 47). Lipid also was observed to be situated adjacent to starch in many instances (Figures 46, 49, and 50).

Scanning Electron Microscopy of Cake Batter

Scanning electron micrographs of heated and unheated batter samples from each cake variation are shown in Figures 51-53. An attempt was made to photograph isolated starch granules in order to compare their morphologies upon heating in the presence of increasing levels of HFCS and according to the presence or absence of emulsifier. In general, unheated granules (Figures 51a, 52a, and 53a) were small, round, and unfolded. With heating, the granules expanded and deformed to various degrees. In agreement with Pomeranz et al (1984), some small starch granules were seen in clusters around large granules (Figure 52b). Since the heated batter samples had been heated to above the onset starch gelatinization temperature, it was expected that folding of the granules would be apparent. The 50 and 100% HFCS series (Figures 52 b-d, and 53 b-d) that had been heated showed more extensive swelling or folding due to the lower gelatinization temperatures than the 0% HFCS series (Figure 51 b-d). Some heated granules were doughnut-shaped, others were disc-shaped. According to Hsu et al (1980), the latter situation is indicative of more extensive swelling.

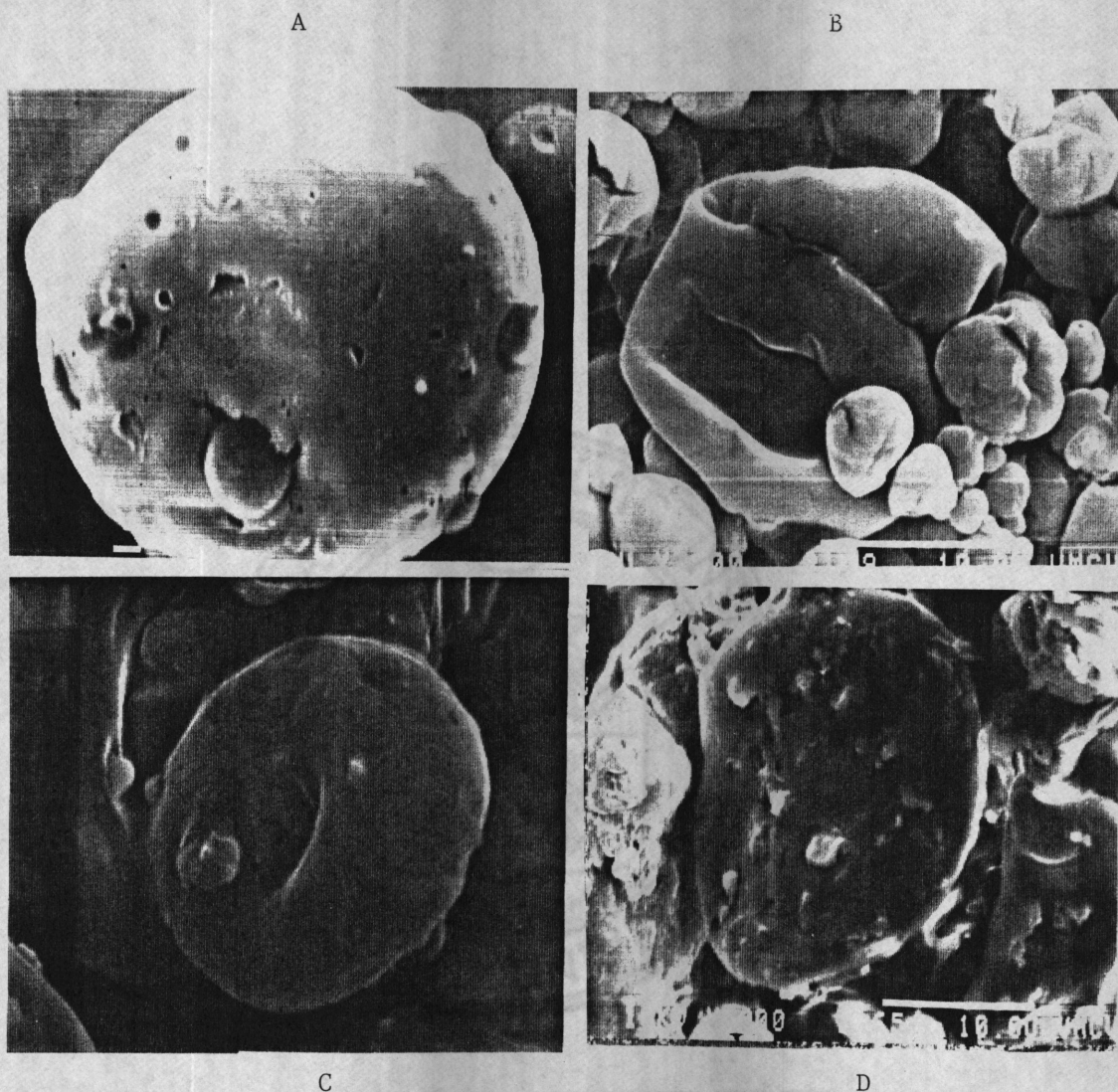


Figure 51. SEM micrographs of starch granules from spray-dried 0% HFCS cake batters with and without added emulsifiers.

- (a) no emulsifier, unheated
- (b) no emulsifier, heated to 95°C
- (c) MDG emulsifier, heated to 95°C
- (d) SE emulsifier, heated to 95°C

MDG = mono- and diglycerides
SE = sucrose esters

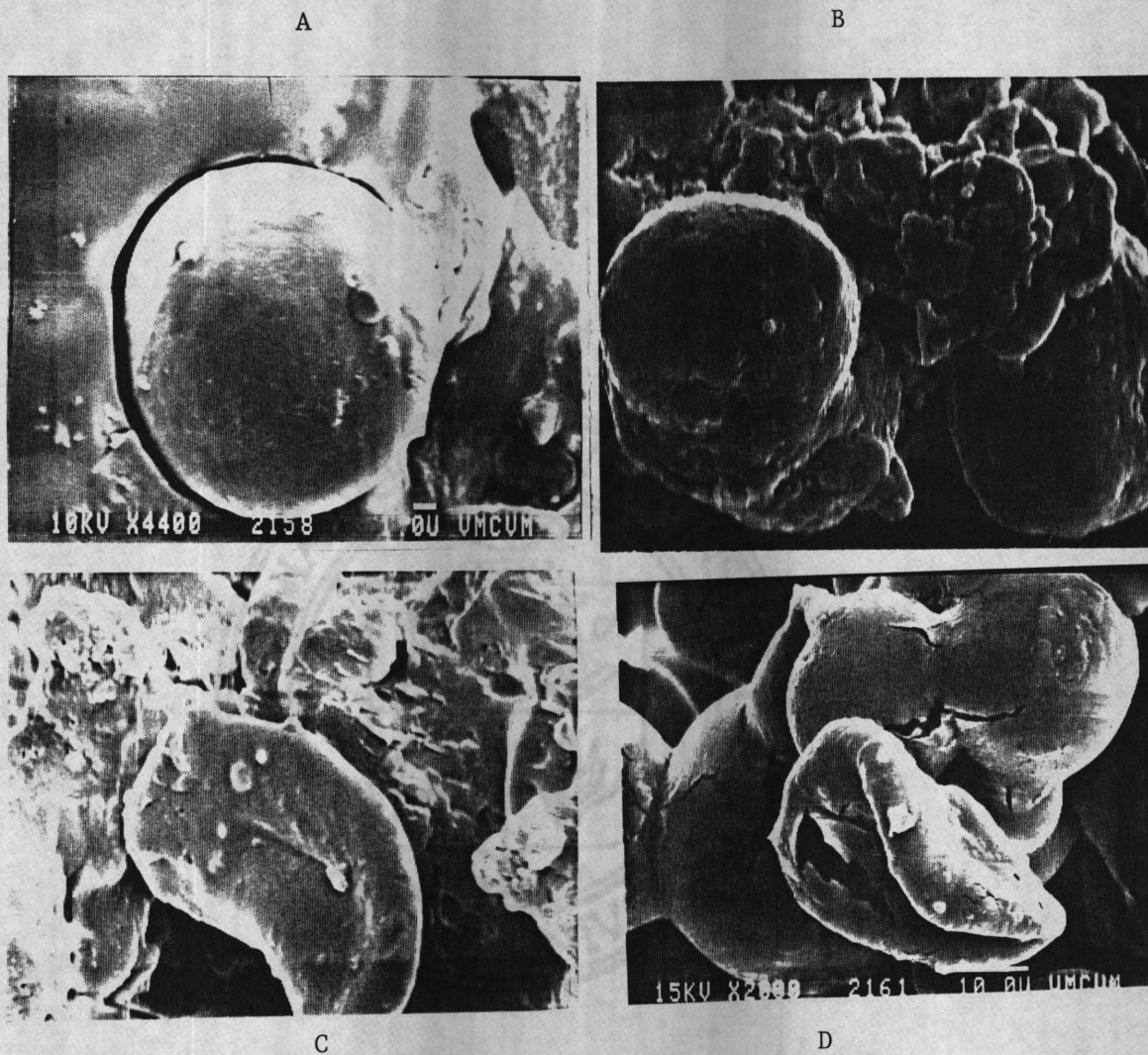


Figure 52. SEM micrographs of starch granules from spray-dried 50% HFCS cake batters with and without added emulsifiers.

- (a) no emulsifier, unheated
- (b) no emulsifier, heated to 95°C
- (c) MDG emulsifier, heated to 95°C
- (d) SE emulsifier, heated to 95°C

MDG = mono- and diglycerides
SE = sucrose esters

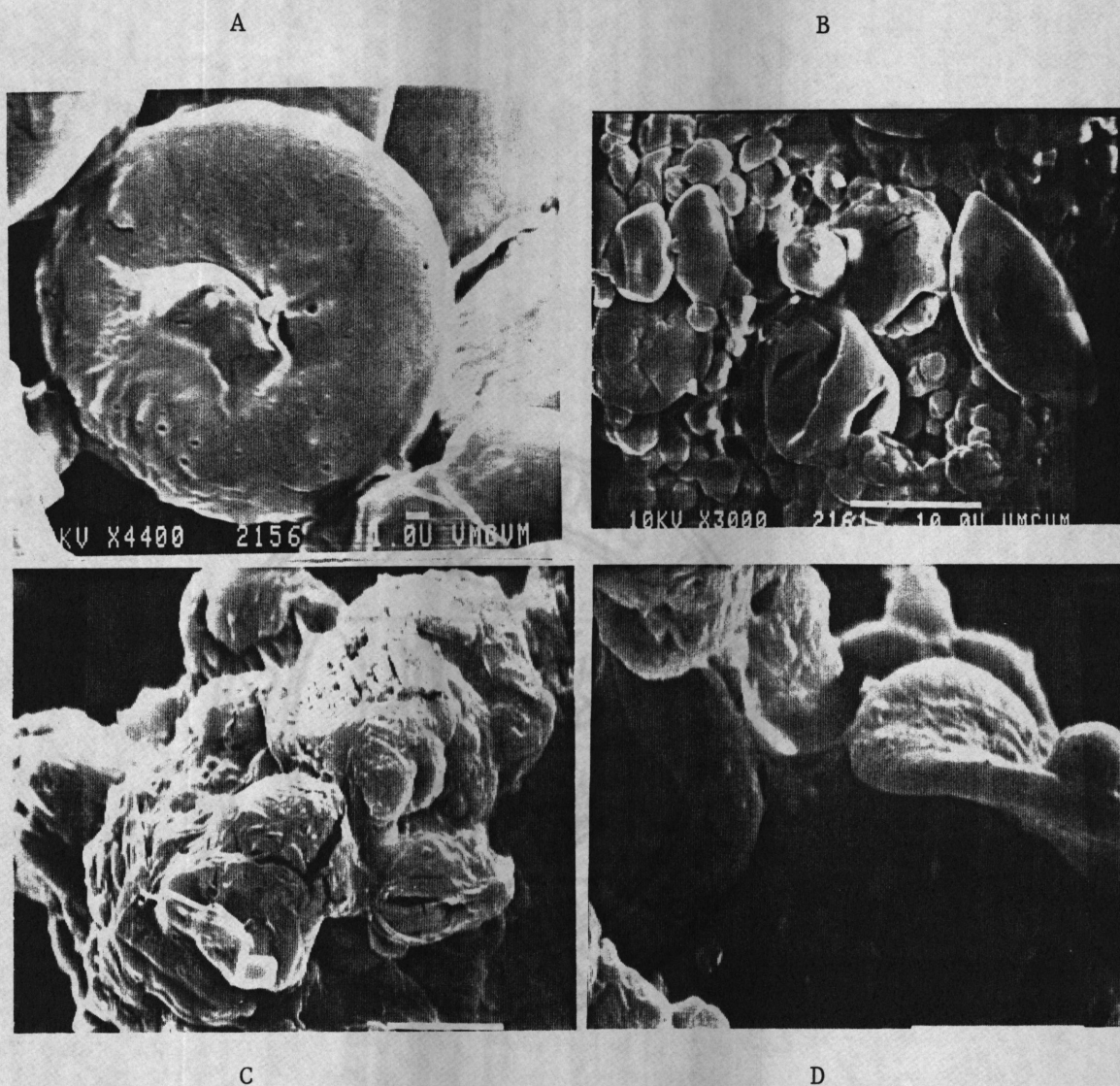


Figure 53. SEM micrographs of starch granules from spray-dried 100% HFCS cake batters with and without added emulsifiers.

- (a) no emulsifier, unheated
- (b) no emulsifier, heated to 95°C
- (c) MDG emulsifier, heated to 95°C
- (d) SE emulsifier, heated to 95°C

MDG = mono- and diglycerides
SE = sucrose esters

The emulsifiers appeared to affect granule morphology somewhat, although in all cases the granules did retain a discrete structure. This is believed to be essential for the development of normal cake crumb (Howard et al, 1968; Shepherd and Yoell, 1976). Granule deformation is thought to reflect the relative extent of starch gelatinization but cannot be quantified easily (Hsu et al, 1980; Lineback and Wongsrikasem, 1980).

Transmission Electron Microscopy of Cake Crumb

The ultrastructure of cake crumb was studied with the transmission electron microscope. Cake crumb appeared as a composite of protein, starch, and lipid (Figures 54-63). Lipid appeared as spherical bodies in cross-section (Figures 54 and 59) either as large lakes or as associated with starch or protein (Figures 60, 61, 63). Protein formed channels or strands which bounded starch granules (Figures 55, 56, 59, 60, 62). It is possible that the size and integrity of the protein surrounding the starch, as well as the amount of associated lipid, would affect the tenderness of the cake crumb (Bechtel et al, 1978). None of the constituent macromolecular components of the crumb appeared to vary greatly in morphology among treatments.

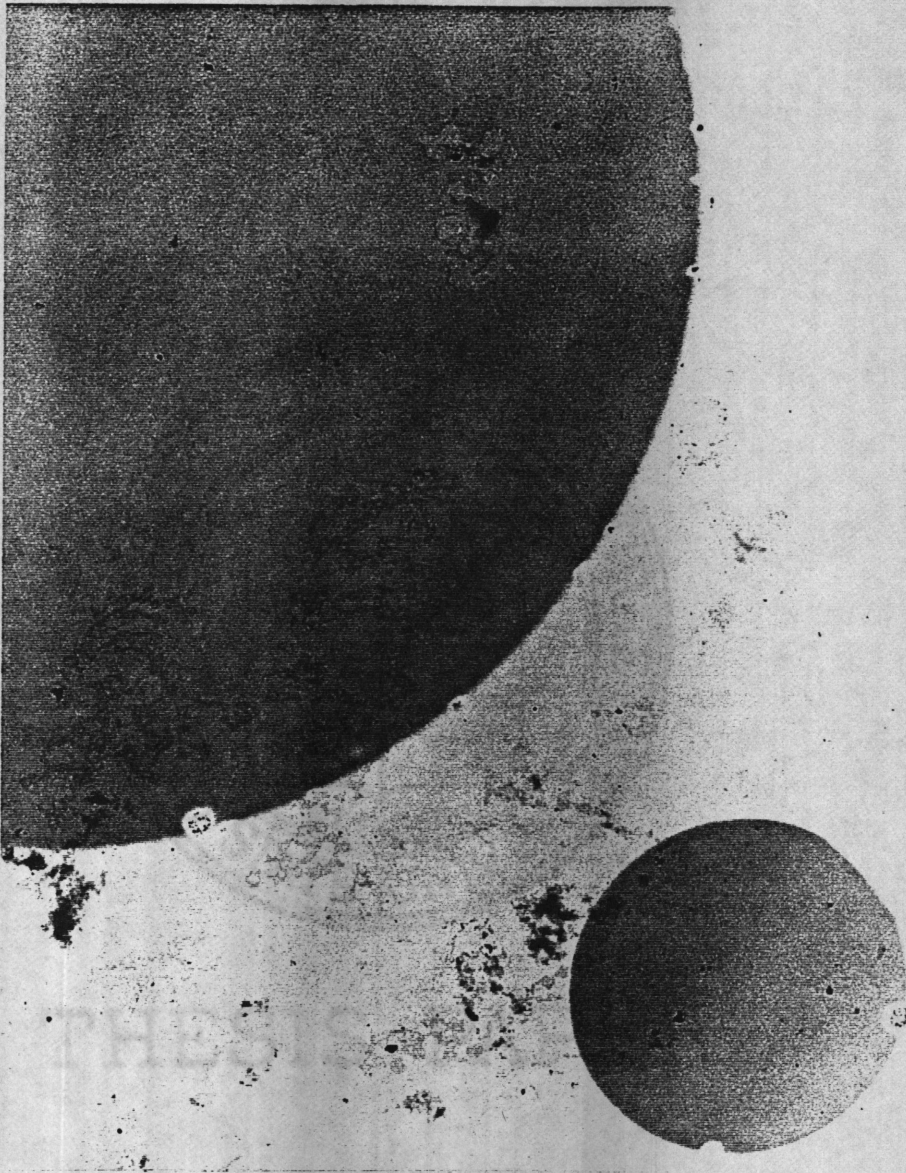


Figure 54. TEM micrograph of cake crumb showing lipid (magnification = 14,160X).

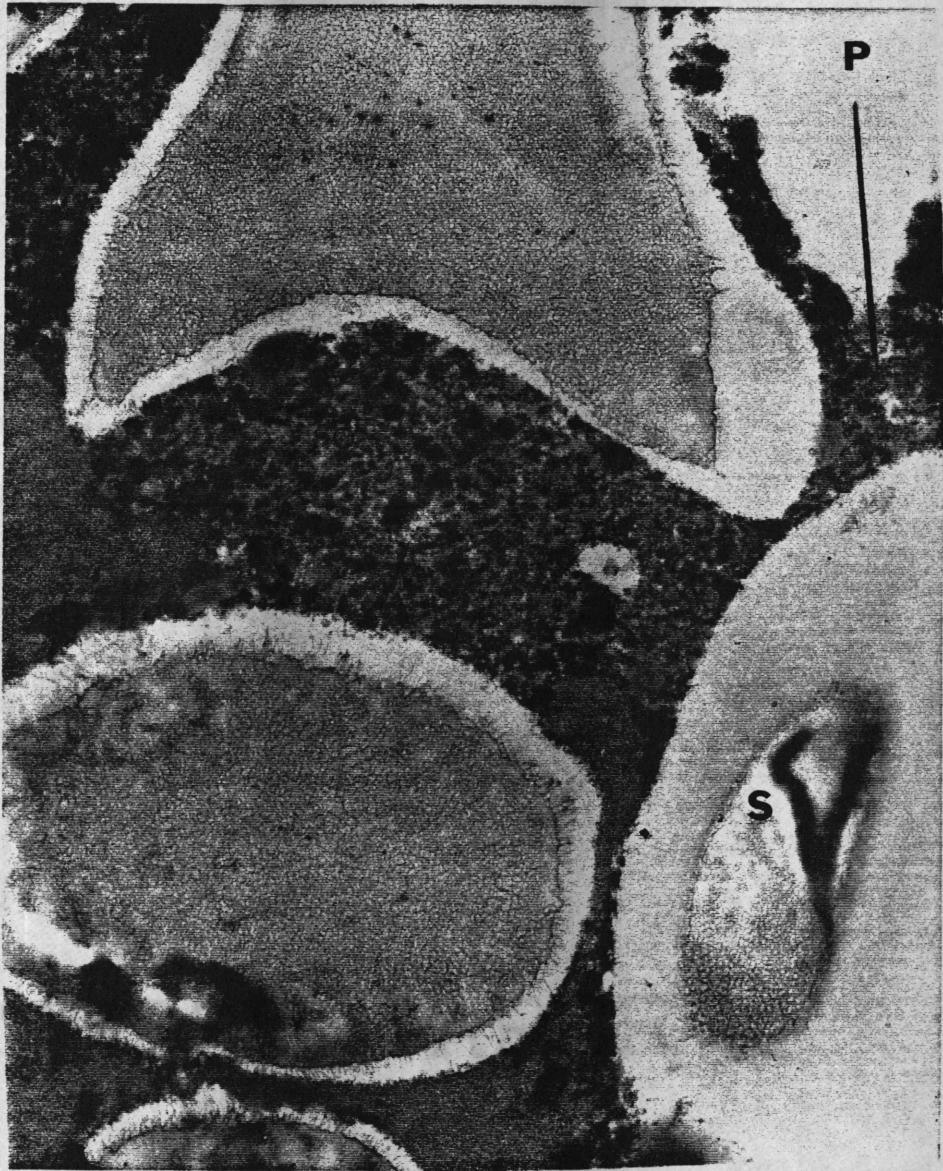


Figure 55. TEM micrograph of cake crumb (variation 1, 0% HFCS without emulsifier).

S = starch, P = protein.
Magnification = 29,500X.

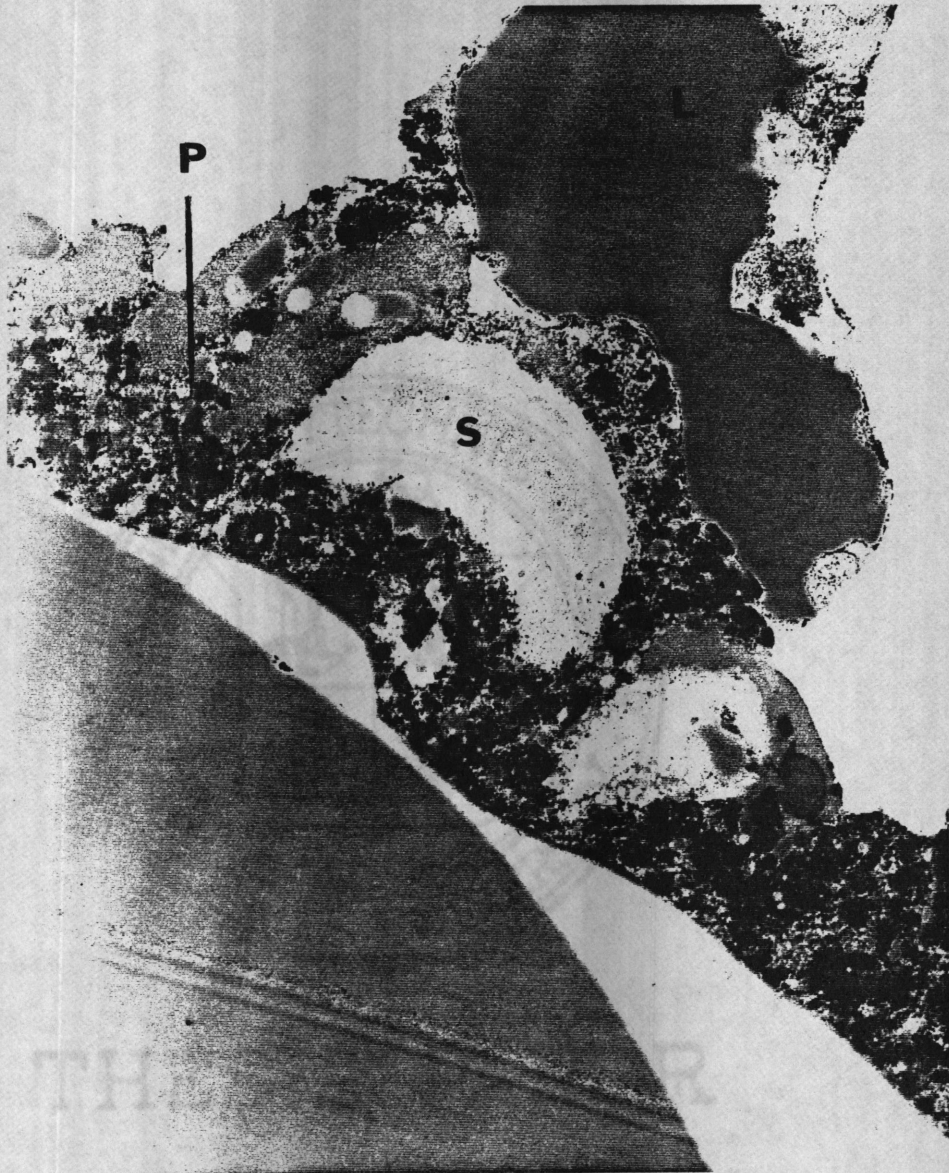


Figure 56. TEM micrograph of cake crumb (variation 2, 0% HFCS with MDG emulsifier).

S = starch, P = protein, L = lipid.
Magnification = 14,160X.



Figure 57. TEM micrograph of cake crumb (variation 2, 0% HFCS with MDG emulsifier).

S = starch, P = protein.
Magnification = 29,500X.

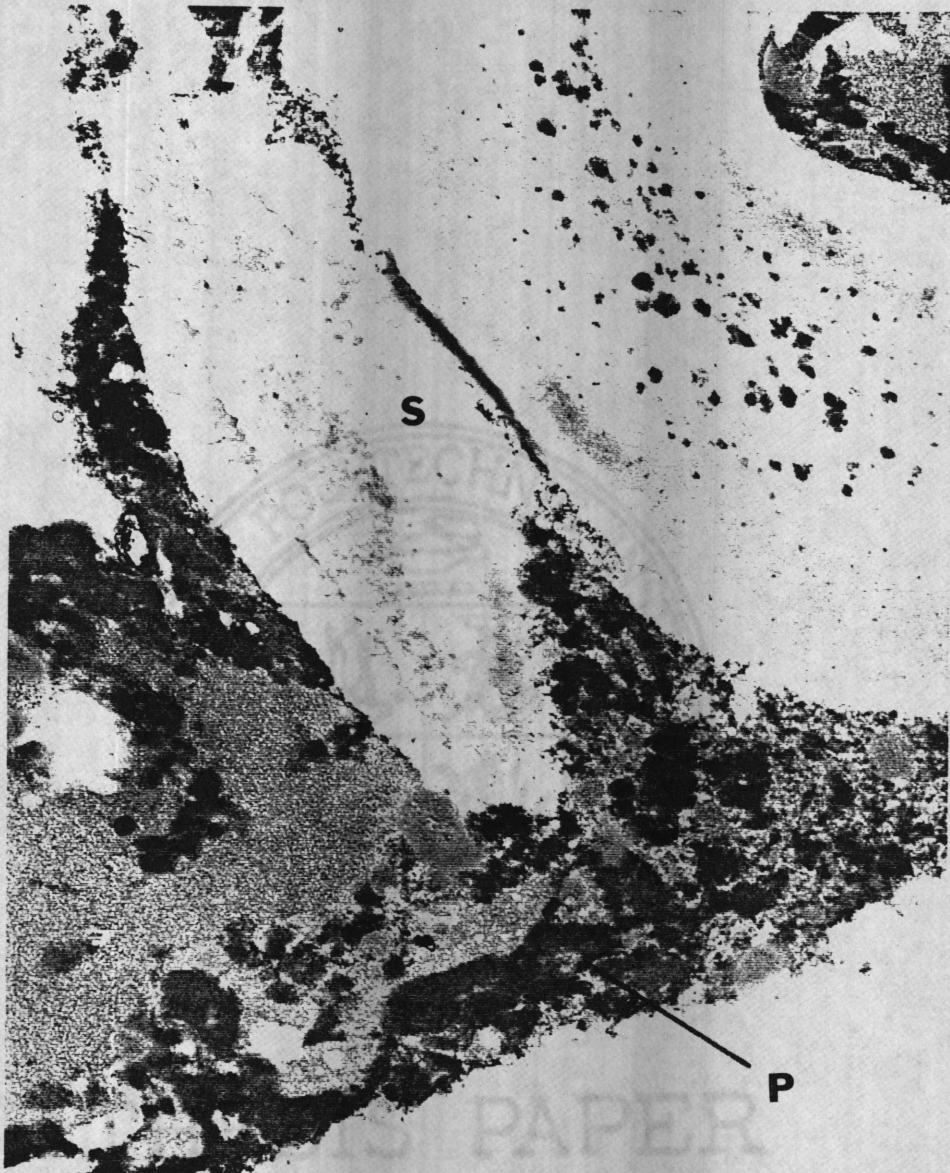


Figure 58. TEM micrograph of cake crumb
(variation 3, 0% HFCS with SE emulsifier).

S = starch, P = protein.
Magnification = 29,500X.

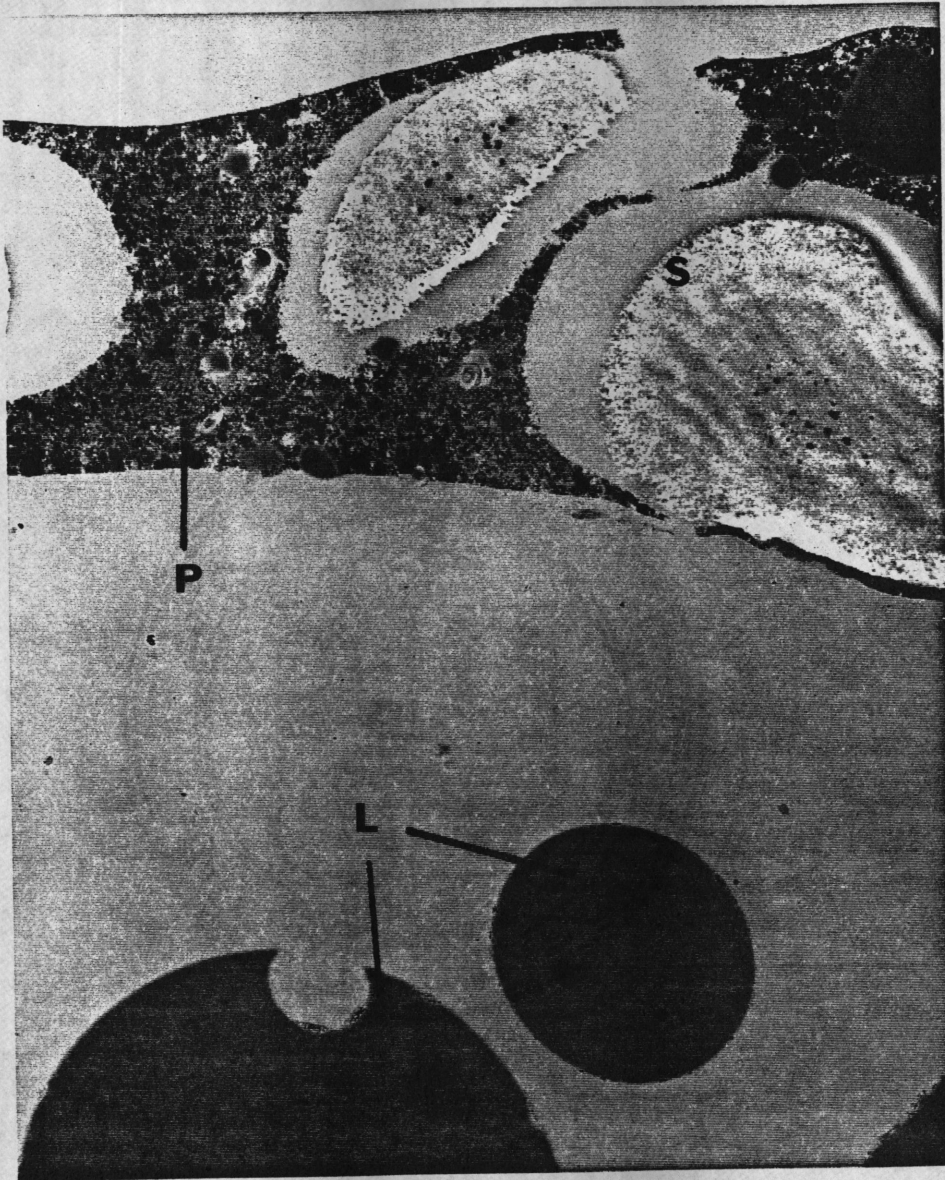


Figure 59. TEM micrograph of cake crumb
(variation 4, 50% HFCS without emulsifiers).

S = starch, P = protein, L = lipid.
Magnification = 14,160X.

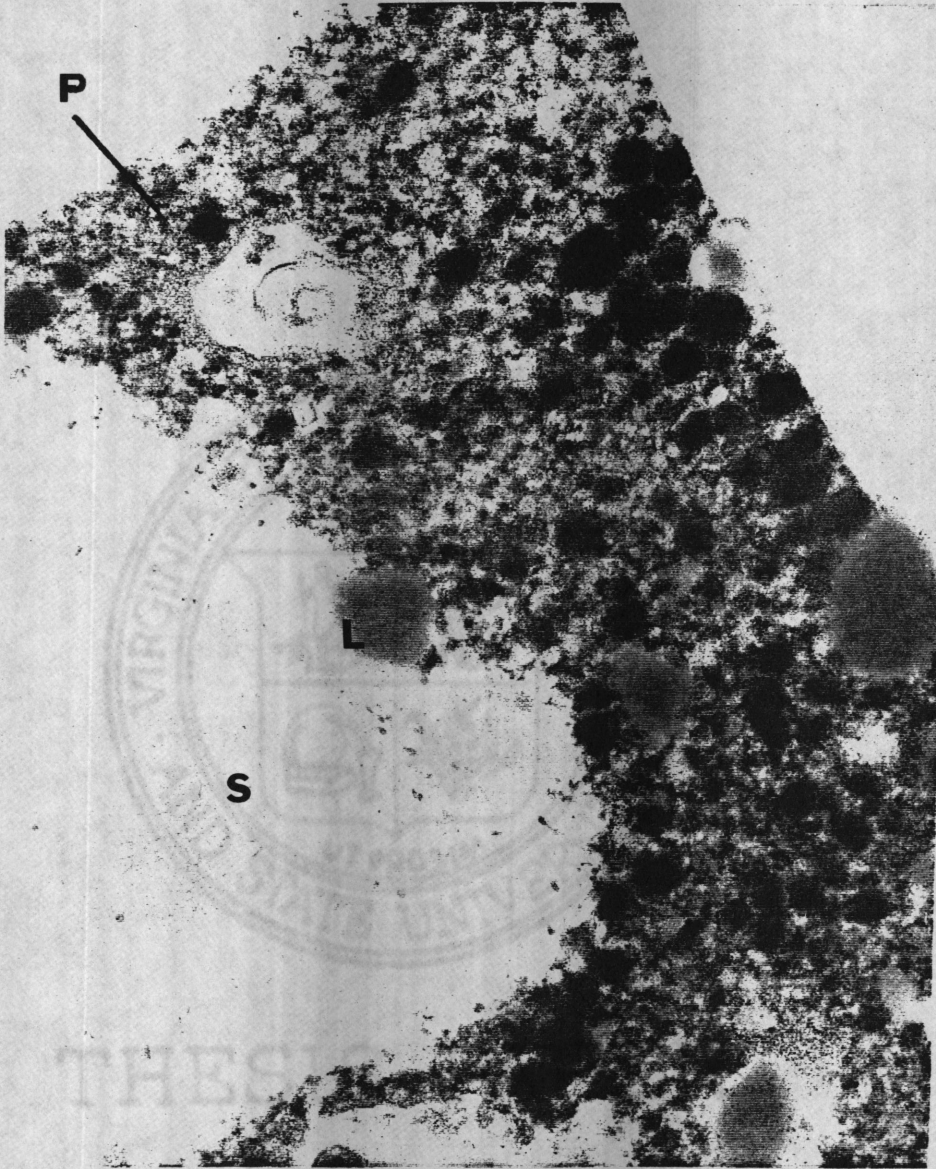


Figure 60. Highly magnified TEM micrograph of cake crumb (variation 4, 50% HFCS without emulsifiers) showing protein-starch interface.

S = starch, P = protein, L = native lipid.
Magnification = 56,050X.



Figure 61. TEM micrograph of cake crumb (variation 7, 100% HFCS without emulsifier).

S = starch, P = protein, L = lipid.
Magnification = 29,500X.

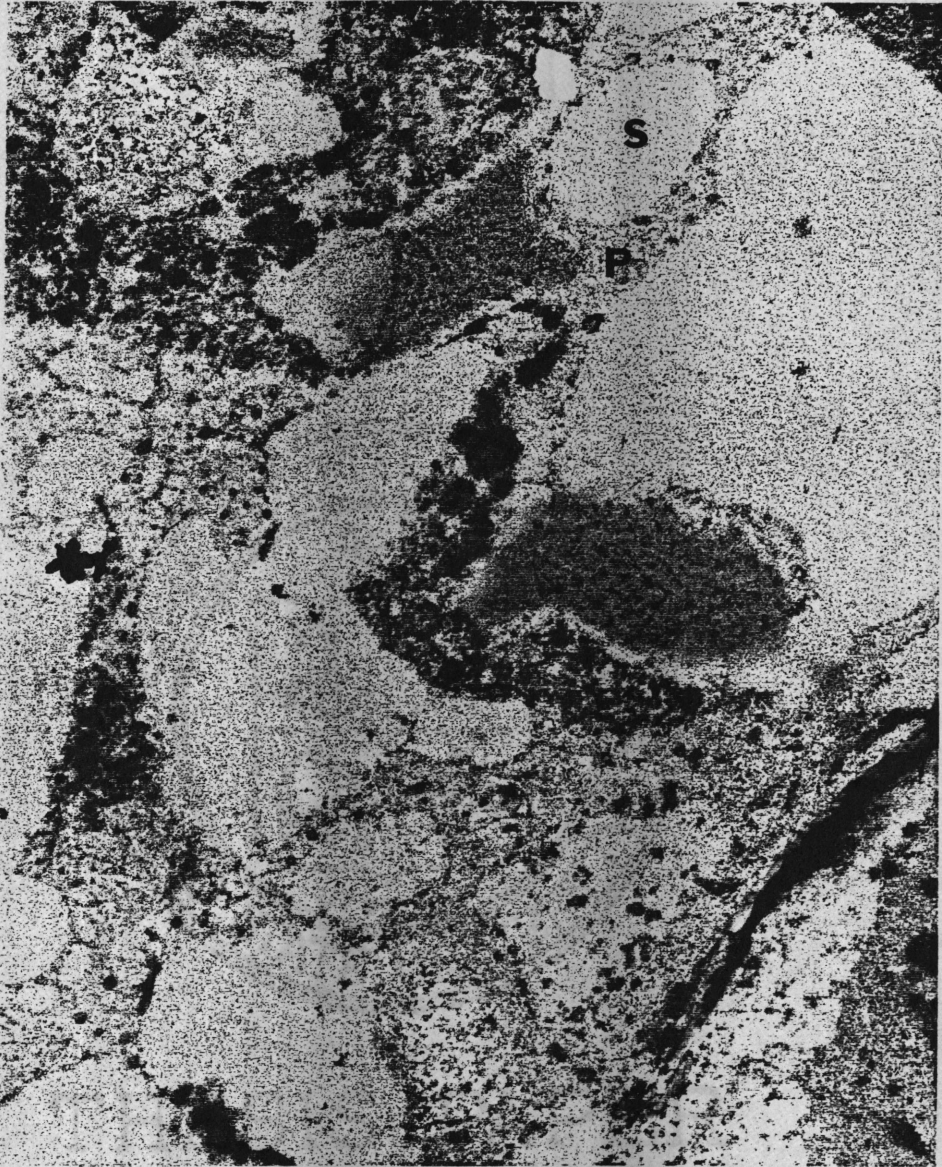


Figure 62. TEM micrograph of cake crumb (variation 8, 100% HFCS with MDG emulsifier) showing interaction of protein and starch.

S = starch, P = protein.
Magnification = 29,500X.

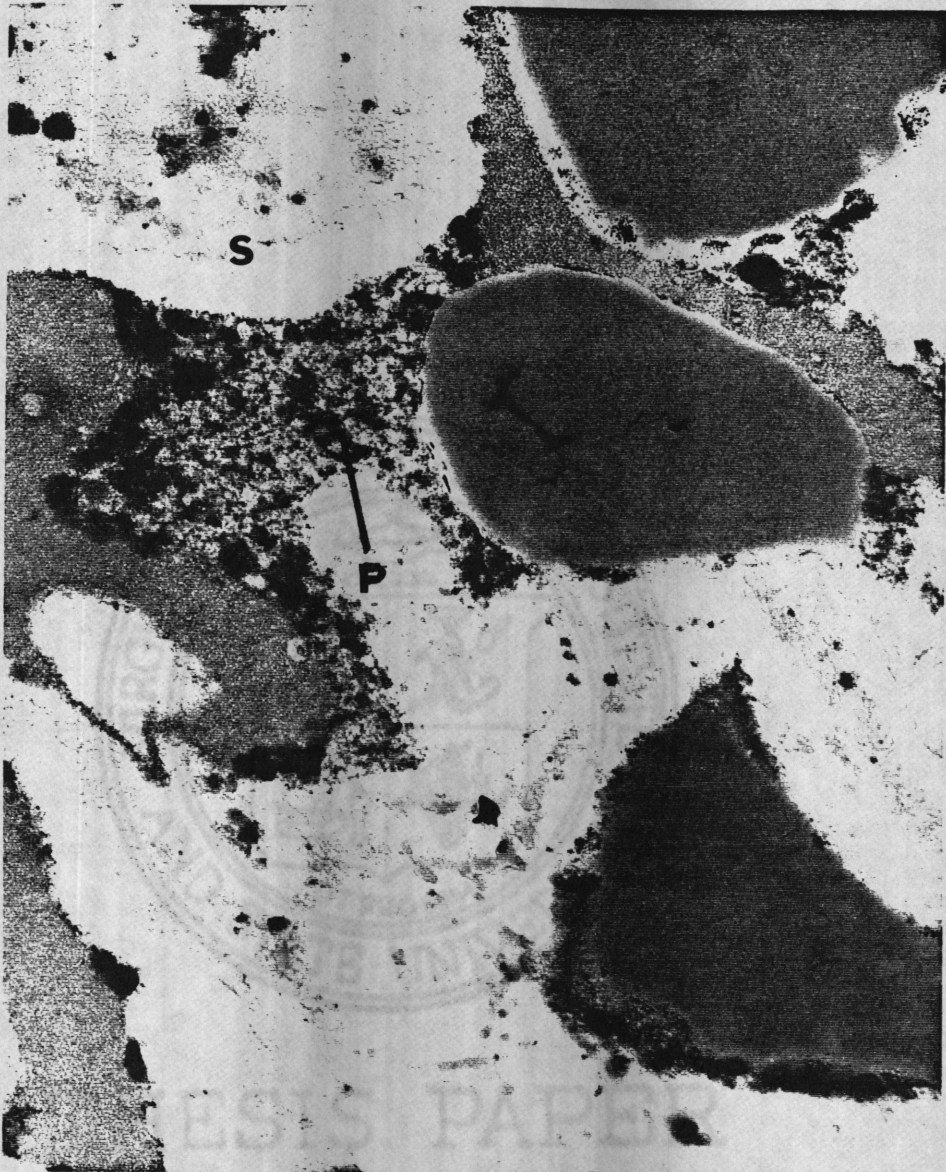


Figure 63. TEM micrograph of cake crumb
(variation 9, 100% HFCS with SE emulsifier).

S = starch, P = protein.
Magnification = 29,500X.

SIMULTANEOUS RESPONSE OPTIMIZATION

Four cake attributes, one physical (volume) and three sensory (moistness, tenderness, and aftertaste) were simultaneously optimized by RSM. The factor levels (percent HFCS substitution for sucrose and choice of emulsifier) were found that would simultaneously satisfy the following set of desired specifications:

- (1) volume > 2062 cm³ (from rapeseed displacement)
- (2) sensory moistness > 7.28 cm (from sensory scorecard)
- (3) sensory tenderness > 8.13 cm (from sensory scorecard)
- (4) sensory aftertaste > 7.52 cm (from sensory scorecard)

The desired specifications were simply taken as exceeding the overall mean values for each parameter or attribute listed. It was hypothesized that if this was simultaneously accomplished, a quality cake with good volume and sensory characteristics would result. The limitation of this procedure is that the optimization was based on the sensory mean data of this particular experiment. True optimization would require the panelists to evaluate product acceptability in addition to the other sensory qualities.

The fitted response surfaces of volume, sensory moistness, sensory tenderness, and sensory aftertaste are

shown as two-dimensional plots in Figures 64-67. From these figures one can predict the response optima for any combination of HFCS and emulsifier. By applying the specification restrictions to each response surface, contour maps from which optimum levels of HFCS in emulsified and unemulsified cakes could be identified were produced (Figures 68-71).

Optimum Volume: In unemulsified cakes, a range of 3-83% HFCS met the volume specification, with an optimum volume obtained with 47% HFCS. In MDG-emulsified cakes, a range of 17-65% HFCS met the volume specification, with optimum volume obtained with 42% HFCS. In SE-emulsified cakes, a range of 0-100% HFCS met the volume specification, with optimum volume obtained with 39% HFCS.

Optimum Moistness: In unemulsified cakes, no value of HFCS used could meet the moistness specification, although the 100% HFCS level came closest. In MDG-emulsified cakes, a range of 31-88% HFCS met the moistness specification, with optimum moistness obtained with 58% HFCS. In SE-emulsified cakes, a range of 0-100% HFCS met the moistness specification, with optimum moistness obtained with 75% HFCS.

Optimum Tenderness: In unemulsified cakes, a range of 79-100% HFCS met the tenderness specification, with optimum tenderness obtained with 100% HFCS. In MDG-emulsified

FITTED RESPONSE SURFACE OF VOLUME

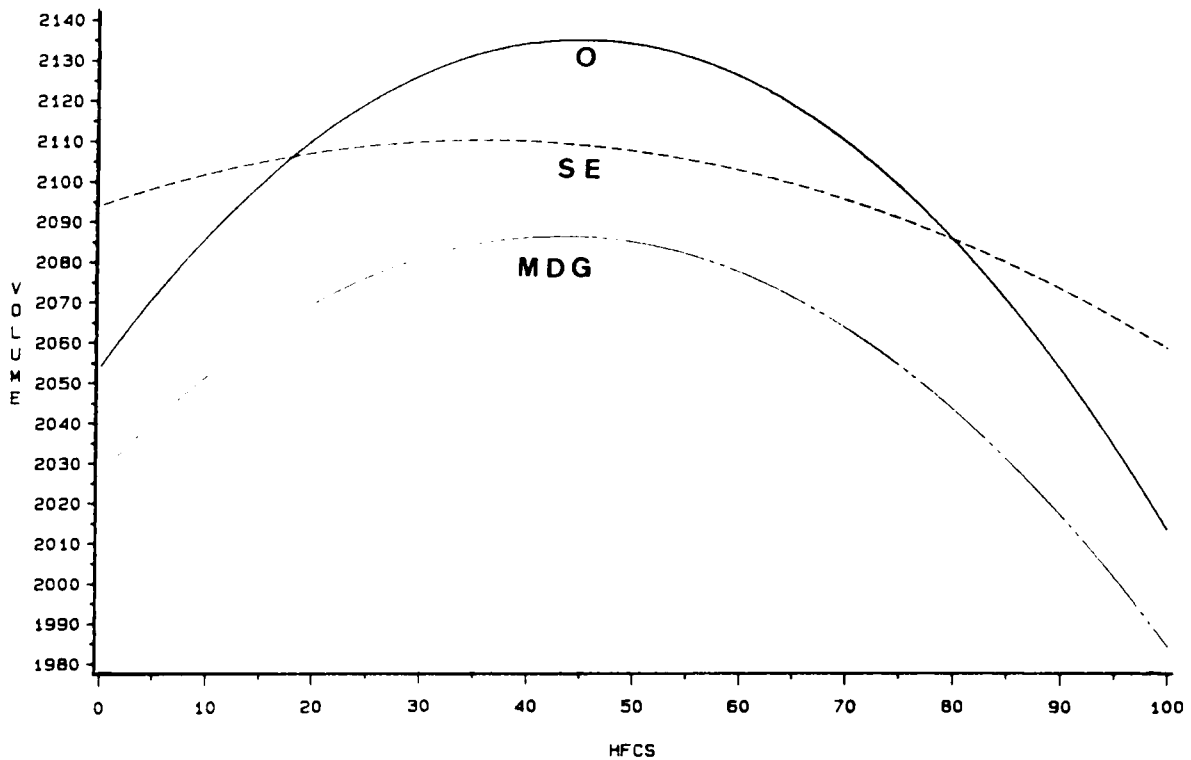


Figure 64. Fitted response surfaces of cake volume for unemulsified (curve o), mono- and diglyceride emulsified (curve MDG), and sucrose ester emulsified (curve SE) cakes predicted over all levels of HFCS (high fructose corn syrup).

FITTED RESPONSE SURFACE OF MOISTNESS

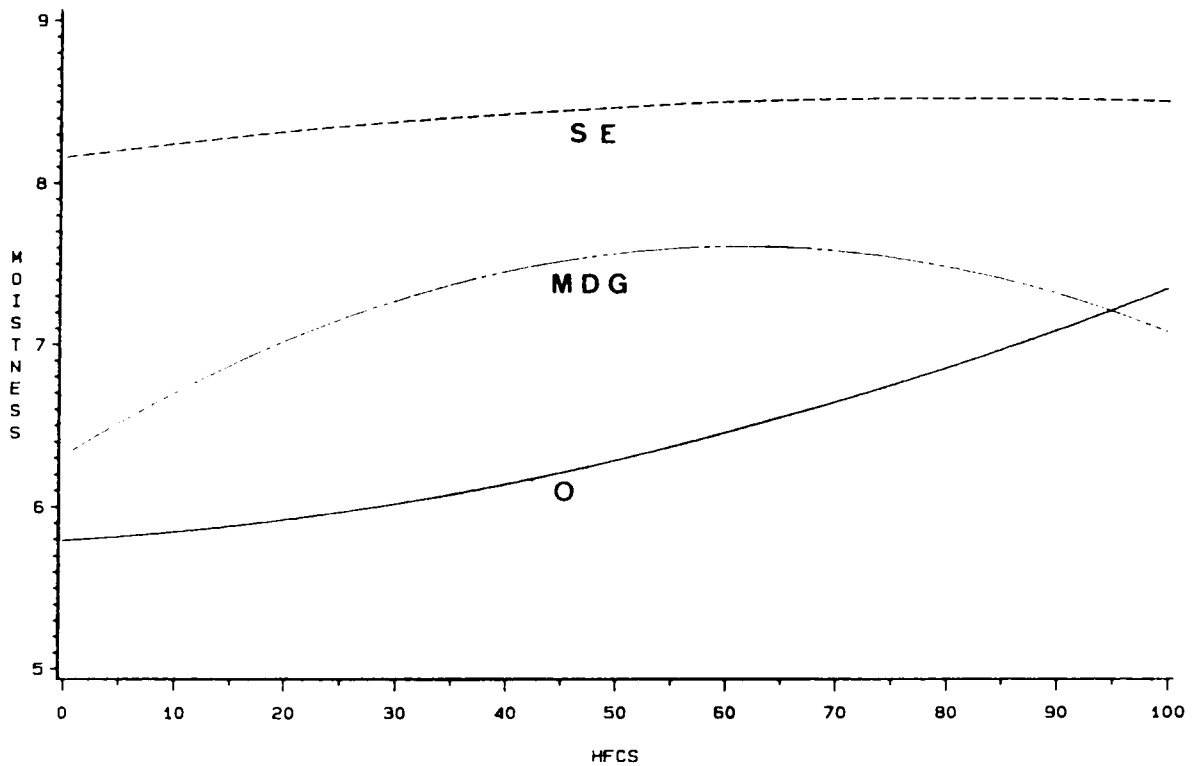


Figure 65. Fitted response surfaces of sensory moistness for unemulsified (curve O), mono- and diglyceride emulsified (curve MDG), and sucrose ester emulsified (curve SE) cakes predicted over all levels of HFCS (high fructose corn syrup).

FITTED RESPONSE SURFACE OF TENDERNESS

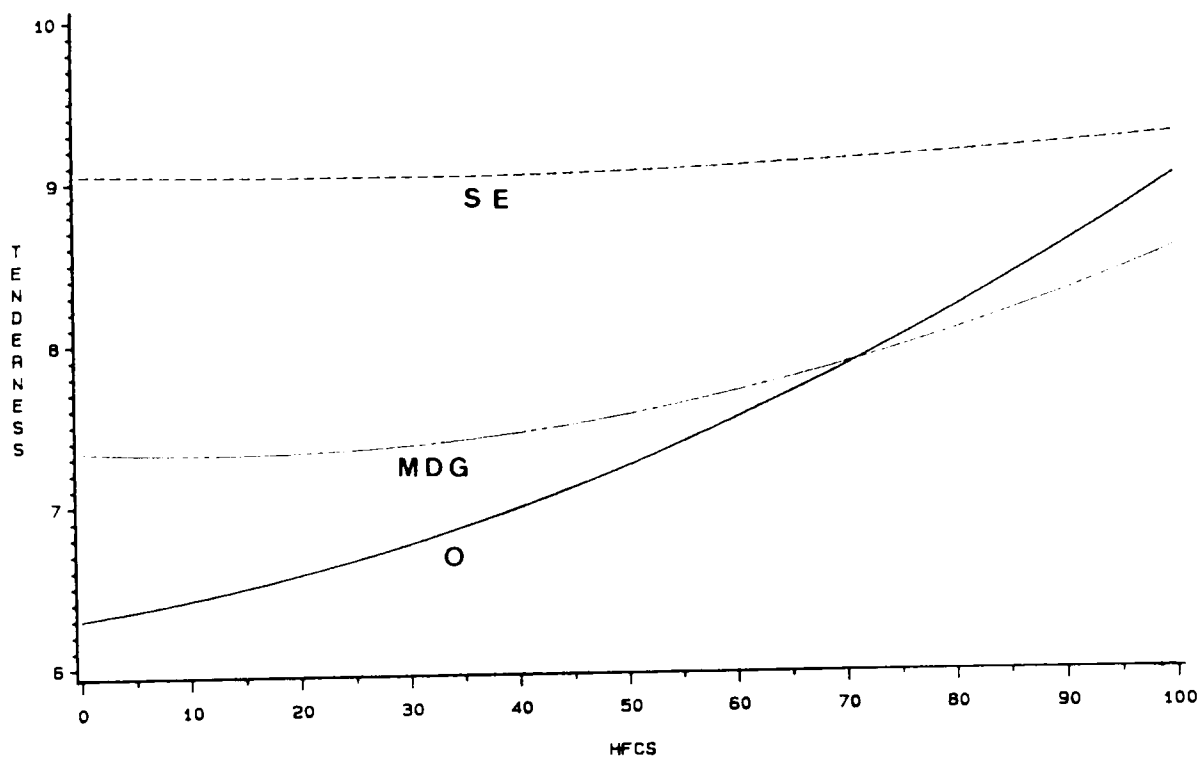


Figure 66. Fitted response surfaces of sensory tenderness for unemulsified (curve O), mono- and diglyceride emulsified (curve MDG), and sucrose ester emulsified (curve SE) cakes predicted over all levels of HFCS (high fructose corn syrup).

FITTED RESPONSE SURFACE OF AFTERTASTE

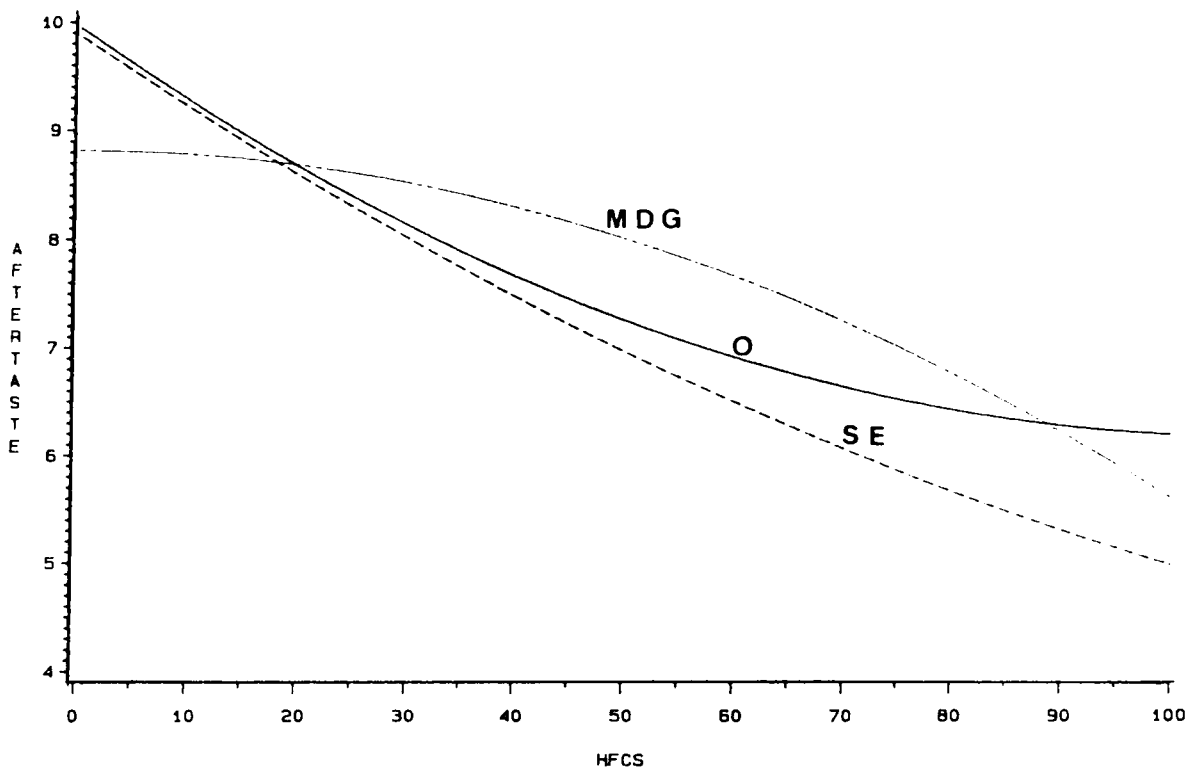


Figure 67. Fitted response surfaces of sensory aftertaste for unemulsified (curve o), mono- and diglyceride emulsified (curve MDG), and sucrose ester emulsified (curve SE) cakes predicted over all levels of HFCS (high fructose corn syrup).

FITTED RESPONSE SURFACE OF VOLUME

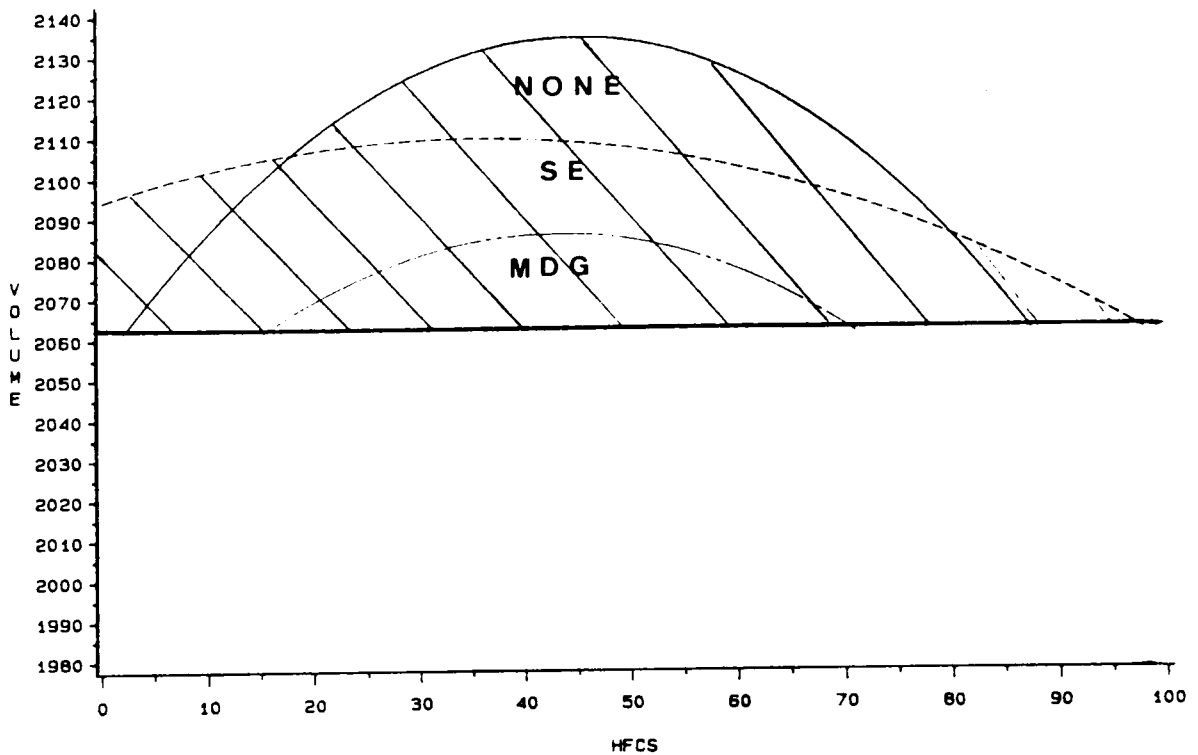


Figure 68. Response surface contours of cake volume for unemulsified (none), mono- and diglyceride emulsified (MDG), and sucrose ester emulsified (SE) HFCS cakes predicted to satisfy optimization specification volume > 2062.

FITTED RESPONSE SURFACE OF MOISTNESS

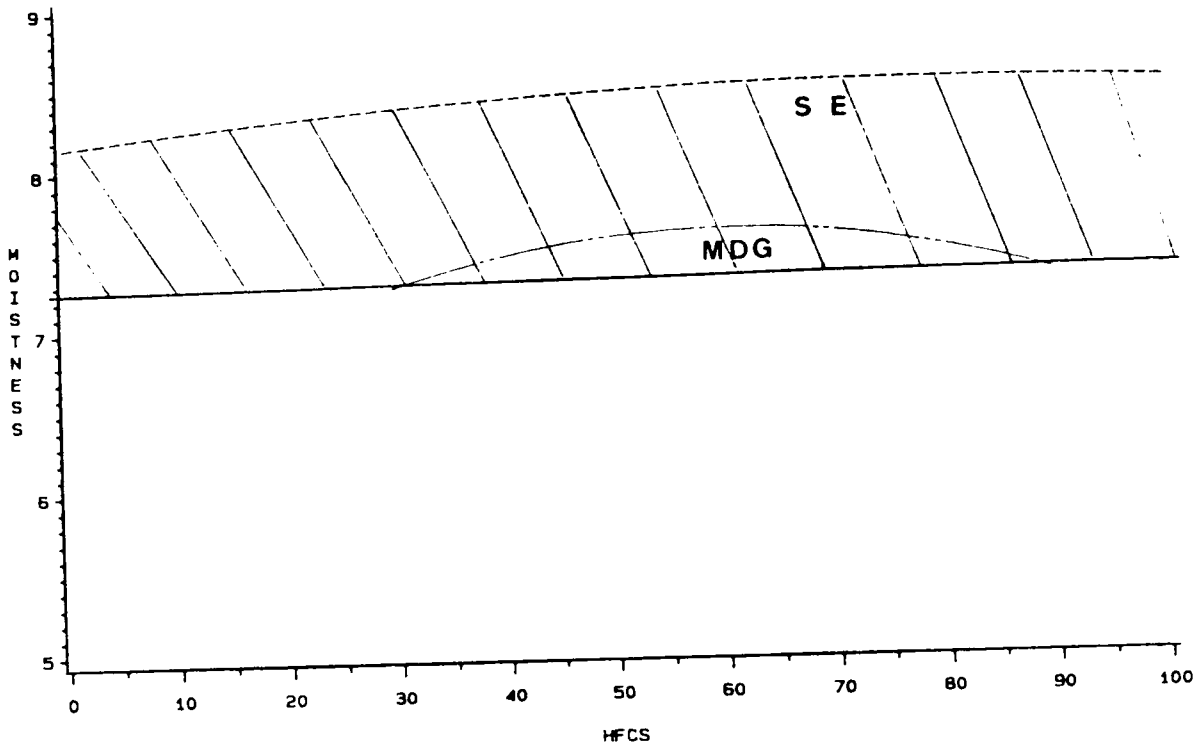


Figure 69. Response surface contours of sensory moistness for mono- and diglyceride emulsified (MDG), and sucrose ester emulsified (SE) HFCS cakes predicted to satisfy optimization specification moistness > 7.28 .

FITTED RESPONSE SURFACE OF TENDERNESS

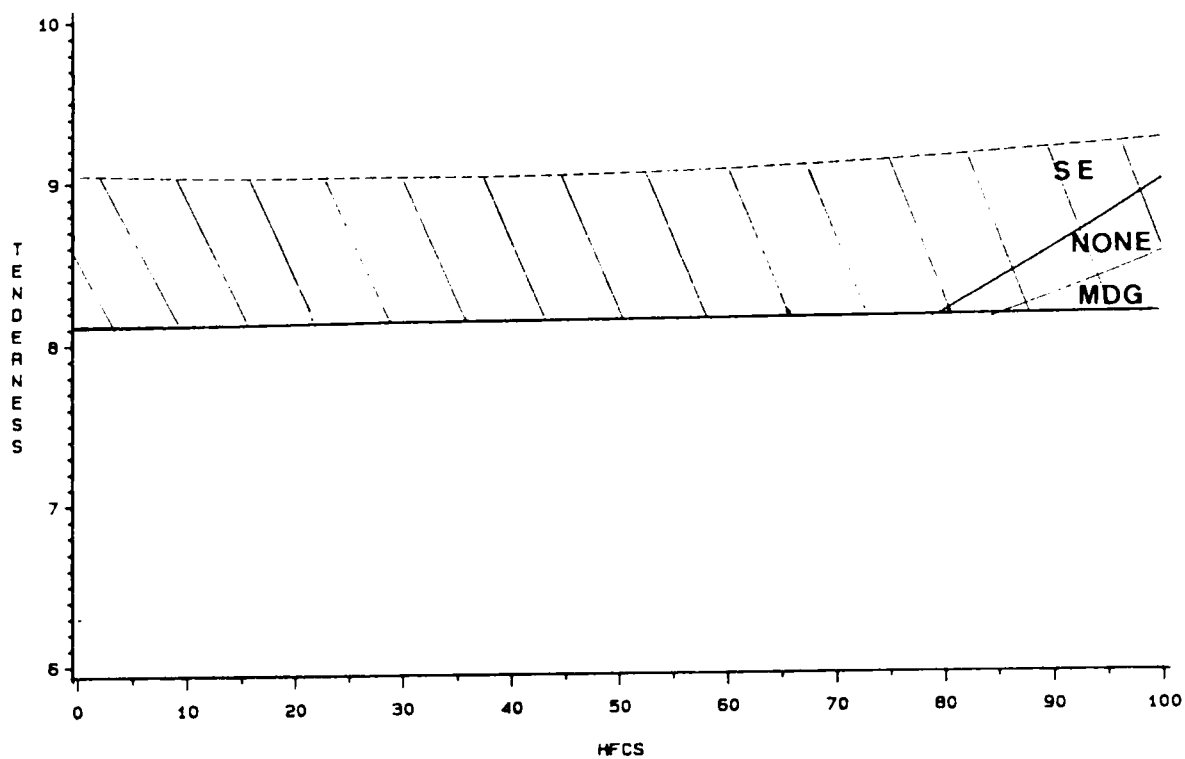


Figure 70. Response surface contours of sensory tenderness for unemulsified (none), mono- and diglyceride emulsified (MDG), and sucrose ester emulsified (SE) HFCS cakes predicted to satisfy optimization specification tenderness > 8.13.

FITTED RESPONSE SURFACE OF AFTERTASTE

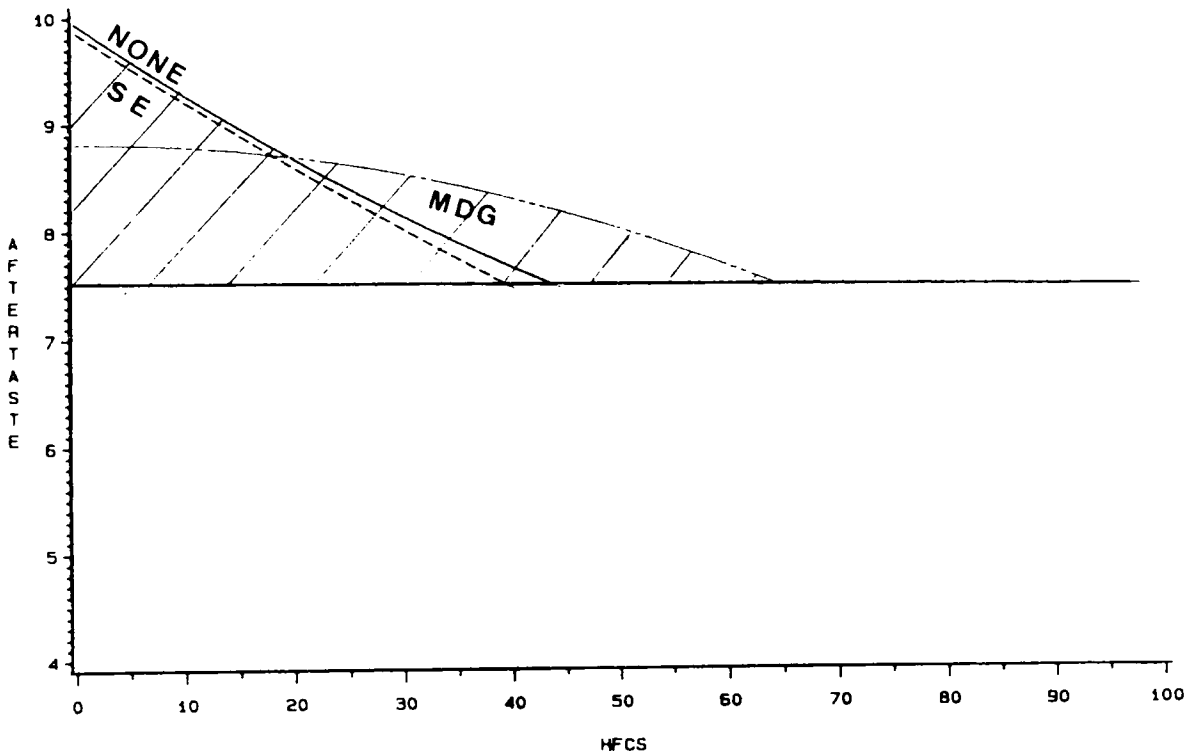


Figure 71. Response surface contours of sensory aftertaste for unemulsified (none), mono- and diglyceride emulsified (MDG), and sucrose ester emulsified (SE) HFCS cakes predicted to satisfy optimization specification aftertaste > 7.52.

cakes, a range of 85-100% HFCS met the tenderness specifications, with optimum tenderness obtained with 100% HFCS. In SE-emulsified cakes, a range of 0-100% HFCS met the tenderness specification, with optimum tenderness obtained with 100% HFCS.

Optimum Aftertaste: In unemulsified cakes, a range of 0-43% HFCS met the aftertaste specification, with optimum aftertaste obtained with 0% HFCS. In MDG-emulsified cakes, a range of 0-65% HFCS met the aftertaste specification, with optimum aftertaste obtained with 0% HFCS. In SE-emulsified cakes, a range of 0-38% HFCS met the aftertaste specification, with optimum aftertaste obtained with 0% HFCS.

From the results, it was concluded that an optimally moist and tender high volume unemulsified HFCS cake with acceptable aftertaste cannot be produced because it would lack sensory moistness. Also, if 0-43% HFCS is used, only volume and aftertaste will be acceptable; if 43-83% HFCS is used, only volume and tenderness will be acceptable. With MDG as the emulsifier, an optimally moist, high volume cake with acceptable aftertaste could be produced but the tenderness specification would not be met. However, with 31-65% HFCS the other three specifications would be satisfied. Finally, using SE as the emulsifier, a cake which simultaneously satisfies all four parameters is

possible if 0-38% HFCS is used. Furthermore, 38-100% HFCS can be employed with only aftertaste being adversely affected. Aftertaste may not be a real problem in actual commercial production of HFCS cakes if flavorings such as vanilla and almond are used in the formulations.

Characteristics of Optimized 100% HFCS Cakes: A profile of 100% HFCS cakes was made possible by the RSM optimization analysis. Unemulsified 100% HFCS cakes are tender but reduced in volume and in moisture, and possess increased aftertaste; MDG-emulsified 100% HFCS cakes are tender, but have reduced volume, moistness, tenderness and increased aftertaste; SE-emulsified 100% HFCS cakes are moist, tender and of good volume but with increased aftertaste. However, as noted above, the aftertaste can be masked with a suitable flavoring or combination of flavorings, meaning that production of an acceptable 100% HFCS cake is possible with sucrose esters as the emulsifier.

V. SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

Cakes were prepared with high fructose corn syrup (HFCS) as a replacement for sucrose, corn oil (CO) as a replacement for hydrogenated vegetable shortening, and sucrose esters (SE) and mono- and diglycerides (MDG) as emulsifiers. Nine cake variations made up the experimental design of the research problem, varying according to the level of HFCS used (0, 50, and 100% substitution for sucrose) and the choice of emulsifier (none, MDG, and SE). The batters were evaluated by objective testing, and the cakes were evaluated by both objective and sensory testing. Results were analyzed using analysis of variance (ANOVA) and Duncan's Multiple Range Test. Response surface methodology (RSM) was used to examine the effects of HFCS, CO, MDG, and SE on cake volume, and to simultaneously optimize volume, sensory moistness, sensory tenderness, and sensory aftertaste as a function of HFCS and emulsifier. In a pilot study, corn oil was successful as a replacement for hydrogenated vegetable shortening, slightly increasing the volume and lightening the crust color of HFCS cakes.

Four batter characteristics, pH, specific gravity, flow rate, and thermal denaturation were examined. In general, the pH of HFCS batters was decreased, and the flow rates were increased compared to sucrose batters. Starch

gelatinization was delayed more in the sucrose batters than in the HFCS batters. The emulsifiers did not significantly affect pH or starch gelatinization, but MDG-emulsified batters had higher specific gravity and flow rate than SE-emulsified and unemulsified batters.

Cake characteristics were examined by four objective tests: volume was measured by rapeseed displacement; moisture was measured by an oven drying moisture tester; deformation was measured by a penetrometer; and crust and crumb color were measured by the Hunter Colorimeter. In general, cakes prepared with HFCS deformed less and were darker in crust color than sucrose control cakes. Volume decreased in 100% HFCS cakes compared to controls but increased in 50% HFCS cakes. HFCS did not significantly affect moistness or crumb color. SE-emulsified cakes increased in volume compared to unemulsified controls, while MDG-emulsified cakes decreased in volume. Emulsifiers did not significantly affect the other cake characteristics.

An eight-member taste panel evaluated the cakes for seven attributes: crumb color, cell size, cell uniformity, sweetness, moistness, tenderness, and aftertaste. Crumb color, sweetness, moistness, and tenderness were found by the panel to differ significantly among treatments. In general, cakes prepared with HFCS had lighter crumb color, were equal in sweetness, were more moist, more tender, and

possessed more aftertaste when compared to the sucrose control cakes, according to the panelists. The SE-emulsified cakes were more sweet, more moist, and more tender than MDG-emulsified and unemulsified cakes.

Quantitative descriptive analysis (QDA) of the sensory data, which included a comparison of each cake variation's unique QDA profile, showed that the most satisfactory cakes from a sensory standpoint were the sucrose ester emulsified cakes and those prepared with the higher levels of HFCS.

Microscopic examination of the cake batters showed that the corn oil was more finely distributed as oil droplets when MDG and SE emulsifiers were used. The specific gravity of MDG batters was significantly increased, indicating less air incorporation than with sucrose esters. Since batter aeration was probably due mainly to the whipping of the egg whites and not the creaming of the corn oil with the HFCS, it is hypothesized that the MDG destabilized the batter, which resulted in the low volumes obtained in MDG-emulsified cakes. The emulsion stability data supports the notion that MDG destabilized the batter.

Cake structure is achieved by the association of starch and protein components of the batter, as seen in light micrographs and transmission electron microscopy (TEM) micrographs. Both protein and starch were found to denature in roughly the same temperature range (88.07-93.03°C mean

onset temperature) in model systems. Starch in batter also denatured (gelatinized) over a similar range (88.59–95.20°C mean onset temperature). The cakes with the smallest volumes (100% HFCS, mean volume = 2018 cm) also had the earliest starch gelatinization (88.59°C) while the cakes with the largest volumes (50% HFCS, mean volume = 2108 cm) showed an intermediate (91.34°C) gelatinization temperature compared to sucrose control cakes. The latter had the highest starch gelatinization temperature (95.20°C) and intermediate volume (2059 cm). It is possible that an optimum starch gelatinization temperature exists for each level of HFCS, and that volumes of 100% HFCS cakes might be improved with formula manipulations that change the gelatinization temperature of starch in 100% HFCS batter in the direction of the optimum. From the DSC results, the hypothetical optimum starch gelatinization temperature (temperature associated with the highest cake volume) is most likely greater than 90°C.

Starch gelatinization of heated samples of emulsified and unemulsified 0, 50, and 100% HFCS batters was observed via the scanning electron microscope (SEM) and to a degree by the light microscope. In general, the results of the SEM analysis confirmed the DSC analysis in that the starch granules in heated batter showed definite evidences of gelatinization (swelling, folding, etc.) at 95°C compared to

the starch in unheated batter. If DSC analysis had shown the onset of starch gelatinization to occur at temperatures above 95°C, then SEM would not have shown any morphological changes in the starch granules.

RSM analysis of the effects of HFCS level and emulsifier showed, in agreement with the QDA results, that only cakes prepared with sucrose esters could simultaneously be optimized for volume, moistness, tenderness, and aftertaste. These parameters were predicted to be met at levels of HFCS ranging from 0-38% substitution for sucrose. A 100% HFCS cake emulsified with sucrose esters was predicted to meet all of the parameters except aftertaste, which could be discounted with the addition of a suitable flavoring agent.

In conclusion, both corn oil and high fructose corn syrup were successfully integrated into a cake formula. The use of a high HLB emulsifier (sucrose esters) further improved the volume and eating qualities of the cake. Significant differences were found in specific objective and sensory analysis of nine cake variations according to the level of HFCS and choice of emulsifier. The extent of starch gelatinization played an important role in determining cake volume. HFCS caused premature starch gelatinization, which decreased cake volume. Corn oil and sucrose ester emulsifiers partially compensated for the

volume-lowering effect of HFCS, probably through mechanisms other than those affecting starch gelatinization.

In this study, the corn oil and HFCS, both being liquids, provided for the easy mixing of the dry cake ingredients, while the SE emulsifier increased batter viscosity and stabilized the batter emulsion. The addition of separately whipped egg whites (the major source of air cells in the batter) at the end of the mixing procedure probably prevented excessive foam destabilization and volume loss.

The overall objective of this study was to investigate the interaction of HFCS, corn oil, and added emulsifier in a cake system and to optimize the cake by response surface methodology. This objective was accomplished by the preliminary pilot study and the research study combined. Contributions of this research were as follows:

- (1) 100% HFCS cakes were produced with acceptable volume, moistness, and tenderness using corn oil and sucrose ester emulsifiers.
- (2) a calculus and template method were created to measure cake volume.
- (3) creation of a cake pan sidewall extension to measure cake volume via rapeseed displacement.
- (4) the utility of a high hydrophile-lipophile balance (HLB) emulsifier vs. a low HLB emulsifier in HFCS

cake baking.

- (5) application of the spray-drying technique to batter for SEM microscopic analysis.
- (6) development of models to predict the effects of variables in HFCS cake baking performance.
- (7) development of a simple method to estimate emulsion stability.
- (8) adaptation of the SAS graph Star Chart procedure for QDA application; a comparison of the method using areas of QDA-generated polygons to obtain a sensory ranking of evaluated cakes.

Further avenues for investigation include the following:

- (1) repeat the conditions of the research experiment but use a substituted mono- and diglyceride (MDG) emulsifier in place of unsubstituted MDG.
- (2) perform shelf-life testing of the cakes prepared in this experiment.
- (3) investigate the use of blends of MDG and sucrose ester (SE) emulsifiers of varying HLB content in HFCS cakes.
- (4) investigate the use of a pregelatinized starch in the formula to improve cake moistness.
- (5) perform volatile analysis of the baking cake and of the baked crust, investigate the timing of volatile production and escape as a function of

key ingredients; relate to sensory aftertaste.

- (6) determine whether the spray-drying of batter for scanning electron microscopy (SEM) analysis generates the exudate (Miller et al, 1973) of the freeze-drying process.
- (7) bake HFCS cake with microwave energy and use SEM to evaluate the starch in the crumb.
- (8) develop reduced-calorie emulsifier/oil system or a low calorie total-fat substitution system for HFCS cakes.
- (9) develop a spray-dried 100% HFCS cake mix that only requires the addition of oil, egg, and water to produce a quality cake.
- (10) use response surface analysis to optimize cake volume as a function of HFCS and the onset temperature of starch gelatinization as measured by differential scanning calorimetry (DSC).
- (11) repeat the conditions of the research experiment but include flavorings in the cake formulations and investigate the effects on sensory aftertaste and product acceptability. Optimize product via RSM.

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Appendix A
Scorecards.

YELLOW CAKE SCORECARD

Judge I.D.

Directions: Evaluate each sample for the listed characteristics, and mark the corresponding line with a vertical slash according to your impression, with the sample number above.

- 1. CRUMB COLOR
dark yellow ----- light yellow
- 2. CELL SIZE
large ----- small
- 3. CELL UNIFORMITY
uneven ----- even
- 4. SWEETNESS
less ----- more
- 5. MOISTNESS
less ----- more
- 6. TENDERNESS
less ----- more
- 7. AFTER TASTE
more ----- less

Appendix A (continued)

Scorecards.

CAKE SCORECARD

Instructions: RANK CAKE SAMPLES FROM MOST TO LEAST ACCORDING TO 3 CHARACTERISTICS (tenderness, sweetness, aftertaste).

- ① For tenderness, gently pull each sample in half and decide which sample was most tender, least tender, and in-between.
- ② For sweetness, you must take the bottom half of each sample and chew it.
- ③ For aftertaste, you must take the top half of each sample, chew + swallow it. Wait several seconds before scoring.

SAMPLE SETRANKING (MOST TO LEAST)

K P B

Tenderness _____

Sweetness _____

Aftertaste _____

X F N

Tenderness _____

Sweetness _____

Aftertaste _____

Appendix B

Mean¹ specific gravities of the nine cake batter variations of the pilot study.

<u>Treatment</u>	<u>Mean SG of batter</u>
0% HFCS + 0% CO	0.75
0% HFCS + 50% CO	0.76
0% HFCS + 100% CO	0.78
50% HFCS + 0% CO	0.77
50% HFCS + 50% CO	0.78
50% HFCS + 100% CO	0.79
100% HFCS + 0% CO	0.77
100% HFCS + 50% CO	0.80
100% HFCS + 100% CO	0.81

¹ Mean of four replications.

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