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Influence of Process Parameters in the Manufacture of Cottage Cheese Curd from Ultrafiltered Skim Milk

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INFLUENCE OF PROCESS PARAMETERS IN THE MANUFACTURE OF COTTAGE CHEESE CURD FROM ULTRAFILTERED SKIM MILK

by

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True confessions should preface acknowledgments in order to tune perspective. This thesis has only taken eight years to finish since I left school to work in the food industry--without it. My determination to complete the thesis seemed evenly balanced at times with my fear of realizing I could never really do it. We cannot face some struggles without the support of others. Because of the tolerance and generosity of such friends, I have traversed to the endpoint. Overcoming the obstacles has proved the veracity of the exercise for me. Now I feel great relief and appreciation as this effort finally resolves itself into its personal and tangible forms.

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A processing procedure for the manufacture of directly acidified cottage cheese curd from 16% total solids ultrafiltered retentate was developed. The effects of preacidification of skim milk before ultrafiltration and heat treatment of retentate were investigated to improve the functional and sensory qualities of retentate curd.

Retentate directly acidified with phosphoric acid and glucono-delta-lactone to pH 4.7 formed a dense, rubbery curd that could not be handled well in a vat. A heat treatment of 71.1°C for 30 min applied to the retentate resulted in a curd with acceptable handling properties. However, this heat treatment caused the curd to shift in pH, become translucent in appearance, and have a pasty texture. Preacidification of the skim milk to pH 5.8 12 h prior to ultrafiltration, and a less severe heat treatment of 71.1°C for 6 min made a stable curd with good sensory quality.

A 3 x 4 x 3 randomized split block design experiment was done to test the effects of preacidification and heat treatment on the properties of retentate curd. Skim milk was pasteurized at 62.8°C for 30 min and split into three lots which were unacidified, phosphoric acid added to pH 6.2, and phosphoric acid added to pH 5.85. The three lots of skim milk were ultrafiltered at 54.4°C to 16% total solids. Each lot was divided into four treatments which were unheated, heated to 71.1°C for 7 s, 76.7°C for 7 s, and 82.2°C for 7 s. Each vat was replicated three times. Cottage cheese pH, total solids, and six sensory attributes were measured. Finished cottage cheeses were evaluated by an expert panel of five judges. Total solids, protein content, and fines content of the whey were also measured. Preacidification treatment at pH 6.2 enhanced curd structure, which increased solids recovery, reduced fines, and improved curd appearance, firmness, and texture. Heat treatments caused softening of the curd and increased moisture content in the curd. Excessive heat treatment caused shattering, fines, and mealiness. The best curd from the experiment was produced from pH 6.2 retentate heat treated at 71.1°C for 7 s. Whey proteins decreased in wheys from retentates heat treated at 76.7°C for 7 s and 82.2°C for 7 s. The effects of heat treatment were more pronounced with increasing acidification. (103 pages)

GENERAL INTRODUCTION

Cottage cheese is a fresh, unripened cheese which evolved in rural American homes or cottages, hence, the popular name. The curd is formed by acid coagulation of skim milk, using either lactic acid fermentation or direct acidification. The curd is cut, cooked in its own whey, drained, rinsed, and blended with a salted cream dressing. Composition of cottage cheese is defined in the United States Code of Federal Regulations to contain not less than 4% milkfat and not more than 80% moisture in the finished food (CFR 21:202).

Ultrafiltration (UF) is a fluid fractionating process in which a colloidal suspension or emulsion passes across a semi-permeable membrane, under a pressure gradient. When milk is ultrafiltered, water and dissolved low molecular weight components such as lactose and mineral salts pass through the membrane, while larger molecules such as protein and fat are selectively retained.

The review of the literature discusses the chemistry of milk and retentate systems, the physicochemical effects of partial acidification and heating on those systems, and the chemistry of acid coagulation of milk and retentate.

The goal of this research was to develop a pilot process to manufacture UF cottage cheese curd and measure the yield compared to the conventional method. Previous research at Utah State University had shown that acceptable curd could not be made from 3-fold concentrated retentate

(16% total solids) without some modification of the retentate.

The first part of the research, conducted at Utah State University, centered on developing treatments to change the curd-forming ability of skim milk retentate. The process treatment developed in modifying retentate involved vat heating of the retentate prior to curd making.

The second part of the research, conducted at Dairymen, Inc. (Louisville, KY) and the University of Kentucky, utilized HTST treatment of retentates. The effect of pre-acidification (three levels) and heat (four treatments) on retentate were measured in the functional characteristics and sensory quality of UF cottage cheese.

The thesis reports the project in two parts, as described, followed by a general summary.

PART 1. CHEMISTRY OF MILK SYSTEMS IN THE MANUFACTURE OF COTTAGE CHEESE CURD FROM ULTRAFILTERED RETENTATE: A REVIEW

ABSTRACT

Cottage cheese curd is the product of applied treatments on the acid coagulation of skim milk. Ultrafiltration used in cheesemaking is the selective concentration of milk proteins and fat through membrane separation technology. The chemistry of skim milk and the effect of various treatments which alter milk components, such as partial acidification, ultrafiltration, heat treatment, and acid coagulation, are reviewed in this paper. The principal steps of cottage cheese manufacture are outlined and briefly described.

CHEMISTRY OF SKIM MILK

Major Components

Milk is the liquid food produced and secreted by the mammary gland for the nourishment of the newly born. Bovine milk contains approximately 87% water, 4.9% lactose, 3.5 to 3.7% fat, 3.5% protein, and .7% ash (31). Cottage cheese is made from skim milk which is practically free from fat and has two phases. The aqueous phase of milk is composed of water in which carbohydrate, protein, minerals, and water-soluble vitamins are dissolved. The colloidal phase is dispersed through the aqueous phase and is composed of aggregates of casein proteins to which is bound undissolved mineral.

Casein Proteins

The fundamental chemistry of milk proteins has been reviewed in detail by Walstra (54) and Whitney (57). Casein may be simply defined as the protein precipitated by acidifying skim milk to pH 4.6 at 20° C and is the raw material from which cottage cheese curd is manufactured. Casein comprises the principal proteins of milk, occurring mostly as particles of macromolecular size, generally termed "micelles." A speculative calculation given the size and composition of monomers known to form the micelle would estimate the aggregate to comprise at least 25,000 casein monomers. Casein micelle population is estimated to be approximately 10^{14} particles per milliliter in bovine milk.

There are four principal casein proteins, classified α_{s1}-, α_{s2}-, β-, and K-casein (54, 57). These proteins are distinct in their amino acid sequences, structure, and functional properties. Genetic variants of each of these proteins have been identified. Ninety percent of casein protein in cow's milk exists as α_{s1}-, β-, and K-casein in a ratio of about 3:2:1. α_{s1}-, α_{s2}- and β-casein are highly phosphorylated proteins possessing a net negative charge and are insoluble under normal milk conditions of pH, ionic strength, and temperature. K-casein is known to stabilize the insoluble caseins of the micelle. K-casein is a glycoprotein and is soluble over a broad range of calcium concentrations. K-casein can be enzymically split by chymosin into two fractions known as macropeptide and para-K-casein. The macropeptide contains bound carbohydrate and is hydrophilic. Para-K-casein comprises two thirds of the K-casein molecule, is not soluble, and is hydrophobic in nature.

Casein Micelle

Structure and function of casein micelles have been reviewed by McMahon (35) and Walstra (53). Electron microscopy of casein micelles shows rough-surfaced porous spheres with a typical diameter of 100 to 200 nm. Molecular weight measurements of the micelle range from 10^8 to 10^9 daltons. The casein micelle is commonly theorized to be randomly constructed of spherical subunits aggregated into a loose micellar structure (46, 47). Electron microscopy measures subunit size at 10 to 30 nm. Micellar calcium phosphate (MCP) forms salt linkages between subunits and holds the micelle intact. Removal of MCP from the micelle with EDTA causes disintegration of the micelle into submicellar particles. Subunits are believed to be internally stabilized by hydrophobic bonding and calcium caseinate bridges. Subunits on the surface of the micelle possess the majority of the K-casein found in the micelle, which makes the micelle exterior hydrophilic in nature. Micelles hold about 1.5 grams of water per gram of protein.

A different theory (26, 51) proposes the micelle to be a continuous network structure of proteins with a skeleton framework composed primarily of α_{s1}-casein and MCP. A hydrophobic core composed of α_{s1}-, α_{s2}- , and β-casein is surrounded by a layer containing a high proportion of K-casein.

Several forces contribute to overall stability within casein micelles (20). Hydrophobic interactions occur with nonpolar residues in the interior of the molecule. Electrostatic interactions occur as ionic sidechains of polypeptides meet the solvent and other proteins to form ionic bonds. Hydrogen bonding promotes secondary and tertiary structures in the caseins. Disulfide bonds stabilize preformed intra- and intermolecular conformations.

Environmental conditions such as pH and temperature affect the dissociation of caseins from the micelle (10, 12). The highest rate of dissociation occurs at low temperatures (4°C) and low pHs (< pH 4.9), with β-casein being the predominant casein liberated.

Micellar Calcium Phosphate

Minerals of the casein micelle are primarily calcium and inorganic phosphate which occur in a molar ratio of about 1.6 to 1.8 $Ca:PO_4$ (11, 28, 50, 54). Milk serum is saturated with calcium and phosphate due to several species of undissolved calcium phosphate deposited as MCP. Approximately 68% of the total calcium and 47% of the phosphate of milk are bound to protein and MCP. Small amounts of citrate, Mg, K, Na, and trace minerals are also associated with the micelle.

The dynamic concentration of salt species of calcium and inorganic phosphate that make up MCP contributes to the high buffering capacity of milk and controls the pH and functionality of the micelle (54). Citrate content in milk also affects the composition of MCP since citrate strongly binds and solubilizes Ca (2).

The exact makeup of MCP in the micelle is not known since calcium phosphates occur in different compositions and forms, both amorphous and crystalline. Holt et al. (28) suggested the primary makeup of MCP is acidic amorphous calcium phosphate, similar to brushite, tied to phosphorylated loop regions in Ca^{++} sensitive caseins. McGann et al. (34) described MCP as a basic tricalcium phosphate, which forms salt bridges across the micelle.

An equilibrium between MCP and dissolved molecules in a double ionic layer exists as a function of pH and temperature (20). As the pH is lowered, dissolution of MCP occurs and ionic concentrations of Ca^{++} and phosphates increase (2, 11, 50, 51). Demineralization of the micelle adversely affects its stability, causing micellar volume to expand (1, 50, 52), migration of caseins out of the micelle (12, 15), and micellar disintegration into subunit particles (11, 27, 45).

Warming milk causes a shift in the solubility equilibrium, which favors less soluble species of calcium phosphate and reduces ionic calcium (20, 37). Storage of milk at 5° C increases ultrafilterable Ca and P. The solvation of MCP is reversed in milk by raising the temperature back to 20° C and holding for 12 h (13).

Severe heating of milk (15 min at 100° C or 4 h at 50° C) transforms MCP into insoluble calcium salts such as crystalline hydroxy apatite (51) or a complex of dicalcium phosphate and tricalcium citrate (43). The formation of insoluble salts in heated milks occurs more readily at neutral pH (51).

Phosphate in MCP binds to casein protein via phosphoserine and phosphothreonine esters (20, 54).

Carboxyl groups on casein may also provide calcium binding sites (4). Polylysine in a model system promotes formation of calcium phosphate precipitate and is theorized to contribute mineral binding sites onto casein (51).

Serum Chemistry

Milk serum is the continuous phase of milk which occupies space between micelles and around the subunits of the micelle (54). Serum components include water, lactose, serum proteins, dissolved mineral, non-protein nitrogen, and water-soluble vitamins.

Lactose is the distinctive carbohydrate of milk. Lactose is a reducing disaccharide composed of glucose and galactose and is present in skim milk at approximately 4.9% (31). Biological oxidation of lactose is the principal carbon source for fermenting microorganisms used in cultured milk products. Conversion of lactose into lactic acid by selected cultures in cottage cheese manufacture provides the chemical mechanism for acid coagulation of casein. Generally, lactose is not a concern in cottage cheese production and is largely disposed of in the whey and rinse waters (19).

Serum proteins account for about 20% of the proteins found in milk. The major non-casein serum proteins are β-lactoglobulin, α-lactalbumin, serum albumin, and the immunoglobulins. Milk contains about 5% non-protein nitrogen (54, 57).

β-lactoglobulin makes up about 50% of the serum proteins. It is a globular protein with well defined secondary, tertiary, and quaternary structure, which makes it susceptible to heat denaturation. β-lactoglobulin preferentially complexes with K-casein upon heating (14, 39, 48).

Interaction between whey proteins and casein micelles with heating is enhanced at pH 6.4 or lower or with addition of Ca^{++} ion to the serum (15, 30, 51). High heating of skim milk to co-precipitate serum proteins has been explored as a method to increase cottage cheese curd yields (18, 56).

Serum caseins account for 3 to 10% of the total milk protein in warm milk, but may rise to 20% in cold milk (54). β-casein exhibits endothermic self-association, solubilizes, and migrates from the micelle when milk is cooled (12, 15, 42). Serum caseins are implicated in the destabilization of the micelle and coagulation of milk (26).

Minerals in solution exist as free ions which associate with other ions of opposite charge to form ion pairs (20, 54). Ionization of acids and bases is dependent on the pH of the system. Solubility of mineral salts is determined by temperature, pH, and ionic strength of the solution (2, 51). The ionic composition of the aqueous phase changes rapidly because of the formation of different ion pairs governed by solubility equilibrium established between the ionic layer and the colloidal state. Approximately 31% of the calcium in milk is diffusible by dialysis, i.e., not directly bound to the micelle. However, only 10% of the calcium in milk is ionized. About 53% of the phosphorus of milk is inorganic phosphate dissolved in the milk serum.

CHEMISTRY OF ULTRAFILTERED SKIM MILK

Colloidal Phase

Membrane fractionation of skim milk selectively concentrates molecules larger than the molecular weight cutoff of the membrane (58). Milk is also filtered by a deposition of protein and mineral, termed the gel concentration boundary layer, which collects on the surface of the polymer membrane (22). The rate of permeation or flux through the membrane is dependent on the pressure difference between sides of the membrane and the hydraulic resistance of the gel layer. Resistance is determined by the thickness and porosity of the gel layer, which is a function of the average fluid velocity, temperature, pH, and concentration level of the retentate (58).

Ultrafiltration selectively concentrates casein micelles, but does not change casein micelle structure or size (23). Serum proteins are retained in the retentate during UF. No denaturation of serum proteins occurs during UF concentration. Retention of Ca, Mg, phosphate, citrate, trace minerals, and water soluble vitamins depends on the proportion bound to protein (23, 44). The ratio of total Ca and P to total protein decreases with the partitioning of soluble Ca and P in the permeate, but does not significantly reduce the MCP content of the micelle.

The buffering capacity of a milk system can be expressed as a dB/dpH calculation and graphed over a range of pH values (8, 49). The buffering capacities of retentates rise exponentially with increasing total solids. Increased buffering capacity of retentate is the result of selective concentration of proteins and attached MCP. Retentate, concentrated five-fold, displays a dB/dpH at pH 5.1 seven times greater than the original skim milk.

Aqueous Phase

Volume of the aqueous phase in retentate decreases with UF concentration, but the chemical characteristics do not change (2). The composition of the aqueous phase is essentially the same in permeate, retentate, and the milk from which it is processed. Equal concentration of mineral salts, lactose, and other low molecular weight components are maintained in the serum on both sides of the membrane during processing, regardless of colloidal mineral load (3). Concentration by UF does not change the saturation equilibrium of the retentate's aqueous phase, and pH remains constant. This differs from concentrates produced by evaporation or reverse osmosis where only water is removed from the system, and the aqueous phase is concentrated.

Diafiltration (DF), the addition of water during UF, dilutes the ionic strength of the aqueous phase (9). Lactose and dissolved minerals are washed from the aqueous phase during DF. Minerals not associated with MCP, such as soluble Ca^{++} and phosphate ions, and monovalent ions are significantly reduced during DF. Slow equilibrium times between the colloidal and aqueous states prevent rapid dissolution of MCP during DF. Total calcium and phosphate content in DF retentate lowers only slightly because most of these minerals are undissolved and attached to MCP (49).

Equilibria Changes During UF

Interactions between soluble minerals and insoluble minerals associated with casein micelles in retentate are dependent on physicochemical influences like pH, temperature, citrate level, and ionic strength, but not on UF concentration (2, 23). Composition, pH, and temperature of the aqueous phase controls the deposit of calcium phosphates of varying solubilities in the micelle (28, 42, 50, 51). As volume reduction occurs in the aqueous phase, the net effect of physicochemical influences diminishes (2).

Treatment of the aqueous phase of milk prior to UF by citration or partial acidification shifts the mineral equilibrium towards the aqueous phase and acts to dissolve MCP (23). Ultrafiltration of such treated milks results in partitioning greater amounts of dissolved mineral in the permeate (49).

The effect of temperature on the mineral balance in retentate is approximately the same as it is in milk (2). Formation or dissolution of calcium salts occurs in retentate as the temperature is raised or lowered (13).

CHEMISTRY OF ACID COAGULATED CURD

Mechanism of Coagulation

Several phenomena irreversibly change the physical characteristics of the casein micelle as the pH of milk is lowered by acidification. Reducing the pH increases the solubility of MCP, causing demineralization of the micelle (2, 51). Complete removal of inorganic phosphate and over 80% of the calcium in the micelle occurs by pH 5.2 (11, 26, 50). Demineralization weakens micelle structure, and micellar volume expands (1, 21, 52). Increased levels of soluble caseins, especially β-casein and K-casein, dissociate from the micelle (12).

Micelles possess a net negative charge that results in electrostatic repulsion of other micelles and colloidal dispersion throughout the aqueous phase of milk (20, 54). Casein micelles are coated with a diffuse "hairy layer" which aids steric repulsion (53). Collapse of the hairy layer covering the micelle surface occurs as the net negative charge of the protein is neutralized by H_3O^+ ions (1). Aggregation of individual micelles follows as repulsive forces are eliminated.

Milk gel formation viewed with scanning electron microscopy and transmission electron microscopy show micelles join into chains and clusters of chains which crosslink until a continuous network of aggregated micelles, or milk gel, is formed (21). Structure formation of acid milk gels viewed with freeze-fracture electron microscopy shows micelles break apart into smaller particles with removal of MCP at pH 5.2 (26). A loose submicellar aggregate is formed that later reassociates and contracts into a porous gel as the pH drops below 4.8 (38).

Factors Affecting Coagulation

Concentrations of colloidal and ionic calcium modulate coagulation reactions (5). Addition of Ca^{++} stimulates milk coagulation and gel strength, while depletion of Ca^{++} inhibits it. Treatments that affect mineral balance in milk, such as preacidification or precitration, along with UF or DF, have been used to manipulate curd formation (24, 25, 29).

Heat treatment of milks prior to gelation results in reduced curd firmness (14, 32). Preheating milk above 80°C prior to acidification induces protein-protein network between β-lactoglobulin and K-casein (30, 48) which enhances onset of gelation (26). Heated skim milk gels consist of finer (less coarse) protein network that retains moisture more effectively than unheated skim milk gels (24). However, the number or strength of elastically effective bonds is reduced, resulting in a reduction of curd firmness (32).

Acid coagulation reactions in milk are concentration sensitive. Coagulation rates are faster with increasing concentration of casein micelles in the aqueous phase, due to more frequent collision of particles (33, 36). The rate at which casein aggregation occurs affects the structure and coarseness of the curd (5, 24). Strength and density of gels increase with increasing concentration.

Syneresis

Cutting the coagulum disrupts the gel and initiates syneresis, or the release of whey from the curd (55). The rate of syneresis is dependent upon a pressure gradient exerted on the whey trapped in the porous network and the resistance of flow through the network. Pressure results from internal and external forces such as shrinkage of the gel as protein strands contract, break, and rearrange due to cooking, gravity, mechanical pressure from agitation, and heat. Flow resistance depends on the permeability of the network.

Volume reduction of the aqueous phase by UF limits the amount of whey released by UF curd (24). Rate of syneresis in rennet-coagulated curd is not significantly affected by UF concentration (40).

COTTAGE CHEESE MANUFACTURE

The manufacturing steps for producing cottage cheese curd are described in detail by Emmons and Tuckey (19). Milkfat is separated from the milk serum to $\leq$ .10%, and the resulting skim milk is pasteurized at a minimum temperature (62.8°C/30 min or 72.2°C/16 s) to meet legal requirements. Skim milk for cottage cheese manufacture may receive various pre-treatments such as fortification, high heating, addition of calcium salts, partial acidification, and enzyme coagulators (17, 18, 56).

Skim milk is quiescently acidified either by lactic fermentation or direct acidification (6) to form a milk gel. The gel should be cut at the isoelectric point of the casein, generally at pH 4.65 to 4.75. Pre-treatments, such as those mentioned above, may shift the isoelectric point of casein and the pH at which the milk coagulates (17). The pH at cutting determines the physical characteristics of the curd (16, 41). Curd cut at pH values above 4.80 is initially fragile, but with applied heat, cooks out overly firm and high in total solids. Curd cut at pH values below 4.60 cooks out too soft, disintegrates into excessive fines, and results in high curd moisture content.

After the milk gel is cut, it is allowed 20 to 30 min to synerese (19). The resulting whey provides a medium in which curds may be agitated while heat is applied, until a desired curd firmness and total solids are achieved. The cooked curd is drained and rinsed with water to cool the curd and remove excess acid and lactose. After the final rinse and drain, the dry curd is creamed with a salted dressing and packaged. Each of these steps plays a significant role in determining the physical characteristics of the curd during production, curd yield, and the quality of the finished food (7).

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PART 2. PROCESS DEVELOPMENT OF COTTAGE CHEESE FROM ULTRAFILTERED SKIM MILK USING PRE-ACIDIFICATION AND VAT HEATING

ABSTRACT

A processing procedure for the manufacture of cottage cheese curd from 16% total solids ultrafiltered retentate was developed. Efforts to use lactic culture as the acid source were unsuccessful. Retentate was directly acidified with phosphoric acid and glucono-delta-lactone to pH 4.7. The retentate formed a dense, rubbery curd that would not handle well in a vat. A heat treatment of 71.1°C for 30 min applied to the retentate resulted in a curd with acceptable handling properties. However, it caused the curd to rise in pH during storage, become translucent in appearance, and have a pasty texture. Preacidification of the skim milk to pH 5.8 12 h before ultrafiltration, combined with a less severe heat treatment of 71.1°C for 6 min, produced a stable curd with good sensory quality.

INTRODUCTION

Ultrafiltration (UF) applied to cheesemaking has been reviewed by Jensen et al. (10) and Lelievre and Lawrence (13). Several researchers have investigated UF for cottage cheese manufacture as a means of increasing yield (5, 11, 12, 15). Matthews et al. (15) made good quality cottage cheese from 12 to 13% total solids (TS) retentate, but did not show any yield advantage. Cottage cheese produced from 20% TS retentate by Covacevich and Kosikowski (5) improved yields, but the resulting curd was gelatin-like and would not absorb cream properly. Preliminary yield trials by Narasimhan (18) with 16% TS retentate indicated 12.4% and 15.3% increased yield for cultured and direct acid UF cottage cheeses over conventional cultured cottage cheese. However, Narasimhan directly acidified cold retentate, warmed it electostatically to form a curd, and cut it at the proper temperature and pH. This method is not practical for commercial processes.

The goal of this project was to develop a commercially adaptable method to manufacture UF cottage cheese curd. Many treatments were investigated to form a retentate curd structure with desirable functional and sensory qualities. This paper outlines the development of process treatments which were found necessary to manufacture directly acidified cottage cheese curd from skim milk retentate when batch heating was used.

MATERIALS AND METHODS

Preparation of Milk and Retentates

Milk. Raw whole milk was obtained from the Utah State University dairy farm. The milk was separated to ≤ .10% milkfat, and the skim milk was pasteurized at 63°C for 30 min, then cooled to 3°C until used.

Preacidification. Pasteurized skim milk at 3°C was acidified with food grade 85% liquid phosphoric acid (Vitex® 750, Bunge Foods, Atlanta, GA) to pH 5.8 and held 12 h or longer before UF.

Ultrafiltration. Ultrafiltration was by a batch method using an Abcor HFK-130 (Koch Membranes, Wilmington, MA) single stage, spiral wound, polysulfone membrane with a molecular weight cutoff of 10,000 daltons with 5 m^2 of filtering surface. Temperature was kept at 54.4° ± 1.1°C. An inlet pressure of 420 kPa (60 psi) and outlet pressure of 280 kPa (40 psi) were used throughout the process. Pasteurized skim milk and preacidified skim milk were concentrated to about 17% TS and standardized to 16% TS by adding permeate from the same milk.

Heat Treatment of Retentates. Retentates were batch heated to temperatures ranging from 68.3 to 76.7°C and held 6 to 30 min. Typically 30 kg of retentate was weighed into a 38 L milk can, heated in a hot water bath (90°C) to the desired temperature, held for the desired time, and then cooled in a cold water bath.

Cheese Making Procedure

Acidification. Cottage cheese was manufactured using two-stage direct acidification (4). Lots of skim milk retentate (10 to 15 kg) were weighed into rectangular stainless steel vats (20 cm x 40 cm x 30 cm). The cold retentate (3°C) was acidified with 85% aqueous phosphoric acid, diluted three times with water, and stirred continuously while slowly warmed .6°C/min to 32.2°C in a warm water bath. Glucono-delta-lactone (GDL) (Vitex® 850, Bunge Foods, Atlanta, GA) was added to the warm retentate as a 20% slurry in ice water and then stirred vigorously for 1 to 2 min to dissolve throughout the vat. The retentate was left undisturbed to quiescently acidify at 32.2°C for 60 to 80 min before cutting.

Handling the Curd. Retentate curd was cut at various pH's ranging from 4.6 to 5.0 with 0.64 cm curd knives and allowed to heal for 10 to 15 min. An equal amount of permeate (10 to 15 kg) obtained from the same lot of milk was warmed to 35°C, acidified to pH 4.7, and added to the vat as a cooking vehicle.

Various heating profiles were investigated to determine their effect on curd properties. Cooking temperatures of 46.1 to 60.0°C were used at an average heating rate of 1°C for 5 min to give heating times of 90 to 120 min. Curd was held at the final cook temperature for 10 min, drained, and washed with two rinses of water (32 and 4°C). Amount of rinse water used was equal to the amount of permeate added. Rinses were held 15 to 20 min, and the final drain allowed 20 to 30 min.

Creaming the Curd. A low solids (16.5% TS) cream dressing containing 11.0% milkfat and 2.5% salt was prepared according to Manus (14). The dressing was designed to yield 20% TS, 4% milkfat, and 1% salt in the finished product when added at a ratio of 60:40 (curd to dressing). Creamed cottage cheese was packaged in .5 kg plastic containers and stored at 4°C for evaluation 2 to 5 d later.

Composition Analysis

Moisture. Moisture (21) was determined on 2 to 3 g of skim milk, retentate, permeate, or curd. Duplicate samples were weighed in aluminum pans, evaporated on a steam bath, and dried for 3 h at 100°C in a forced draft oven (Thelco model 28, GCA Precision Scientific). Samples were cooled in a glass desiccator before determining final weight. Samples exhibiting discrepant results were repeated until close agreement was obtained.

Calcium. Calcium (1) in retentate and retentate curds was determined by atomic absorption (AA) spectrometry, using a Model 457 AA/AE spectrophotometer (Instrumentation Laboratory, Inc.). Samples were ashed in a muffle furnace at 550°C using 16 *M* nitric acid as an oxidizing agent to aid in ashing. Ash was dissolved in 5 ml 6N HCl, transferred to a volumetric flask, and diluted to 100 ml with deionized water. The samples were diluted with 1000 ppm lanthanum oxide solution to bring the calcium concentration into the linear range of the spectrophotometer and reduce AA interference.

Acidity. The pH of skim milk was determined before and 12 h after preacidification. The pH of retentate and permeate before and after acidification, rinse water, curd, and finished cottage cheese was also determined. A glass electrode and potentiometer (Model 811, Orion Research, Cambridge, MA) were used for pH measurements.

RESULTS AND DISCUSSION

Establishing Process Parameters

Lactic Fermentation. Initial work in establishing a pilot process for manufacturing UF cottage cheese included an investigation of lactic fermentation of retentate as recommended by Narasimhan (18). Trials using 16% TS skim milk retentate demonstrated long set times (10 to 12 h), even with a double inoculum (5.0%) of pH-controlled starter. Long set times were reported by Narasimhan (18) and Mistry and Kosikowski (16). Uneven coagulation in the vat was observed on the surface of the retentate, i.e., a top layer (.5 to 1.0 cm) of retentate would not coagulate and was consequently lost in the whey. The curd shattered excessively and was mealy in texture. Because of these problems associated with using lactic culture, further effort was directed to develop a directly acidified curd.

Direct Acidification. Skim milk retentate was acidified at 3°C and then gently warmed until a clot formed. Retentate acidified with phosphoric acid coagulated at high pH (pH 5.5) when warmed to 37°C. However, when the retentate was acidified with lactic acid, coagulation did not occur above pH 5.0. This is consistent with observation of previous culture set vats which were uncoagulated at pH 4.80 at 32.2°C. The effect of increasing amounts of 85% phosphoric acid added to 16% TS retentate on pH and the temperature of coagulation is shown in Table 1.

TABLE 1. Relationship between pH of acidified 16% TS skim milk retentate and the temperature at which it clotted.

% Vitex® 750* (w/w)	pH	Clot Temperature (°C)
.40	5.74	--
.50	5.50	37
.60	5.37	27
.76	5.20	25
.84	5.12	24
.90	5.06	23
1.00	5.00	21

* 85% phosphoric acid, Bunge Foods, Atlanta, GA

Cottage cheese manufacture requires a quiet state for a curd matrix to form (8). A commercially available technology for directly acidified cottage cheese (4) uses a two-stage process where cold skim milk is first acidified with phosphoric acid, then gently warmed and, secondly, acidified by slow hydrolysis of GDL into gluconic acid in quiescent skim milk at 32.2°C. Following this procedure, a level of Vitex 750 was determined to acidify the retentate without initiating the onset of coagulation at 32.2°C. Further studies determined the proper amount of GDL necessary to obtain a desired pH in retentate at cutting. The levels of phosphoric acid and GDL used in various experiments are shown in Table 2. Retentate (16% TS) acidified with phosphoric acid to pH 5.5 and GDL to pH 4.7 resulted in a curd that was dense and rubbery and could not be cut by conventional .64 cm curd knives. This agrees with

TABLE 2. Levels of added 85% phosphoric acid (H_3PO_4) and glucono-delta-lactone (GDL) and their effect on average pH values in various types of 16% TS retentate.

RETENTATE TYPE	% H_3PO_4 added	pH after adding H_3PO_4	% GDL added	Average pH at cutting	Number of Trials
Unmodified 16% TS retentate	.475	5.52	2.20	4.76	3
Unmodified 16% TS retentate	.475	5.52	2.25	4.63	3
Heat treated @ 71.1°C/30 min	.425	5.57	1.75	4.96	8
Heat treated @ 71.1°C/30 min	.425	5.57	2.00	4.87	9
Heat treated @ 71.1°C/30 min	.425	5.57	2.25	4.83	4
Heat treated @ 71.1°C/30 min	.425	5.57	2.50	4.78	4
Preacidified to pH 5.80 Heat treated @ 71.1°C/6 min	.200	5.48	1.65	4.83	11
Preacidified to pH 5.80 Heat treated @ 71.1°C/6 min	.200	5.48	1.80	4.78	8

observations of Casiraghi et al. (3) and Green (9) who attributed increased firmness to a denser casein network and a high level of ionic calcium solubilized by pH reduction. Retentate curd was high in total solids when cooked and had an undesirable mealy texture. Depending on the final cook temperature, the total solids content of retentate curds from various process treatments ranged from 22.7 to 29.8%.

Heat Treatment. It was anticipated that thermal modification of the retentate would overcome the tough curd problem by reducing curd strength (6) and allow conventional handling of the curd. A batch heat treatment of the retentate at 71.1°C for 30 min resulted in curd that cut and handled well in the vat. Slight differences in the temperature to which the retentate was heated significantly affected the quality of the UF curd. Curd made from retentate heated to 69.7°C for 30 min was tough to cut. Retentate heated to 72.5°C for 30 min resulted in curd that was soft, broken up, and mealy. Retentate heated to 76.7°C for 30 min did not form a curd. The AC endpoint (8), which is the pH when milk first begins to clot, was observed to shift upwards to around pH 5 as a result of the heat treatment. Curds with acceptable cutting and the best finished texture were cooked to a final temperature of 46.1°C in a whey-permeate blend, drained, rinsed, and creamed in the usual manner.

Translucency Defect. A serious defect was repeatedly observed in cottage cheese where heat treatment was applied to the retentate. After 2 to 3 d of storage, the cottage cheese significantly deteriorated in appearance and mouthfeel, becoming translucent and pasty. This may have been similar to the "gelatin-like" UF curd reported by Covacevich and Kosikowski (5). The pH of the UF cottage cheese rose from around pH 5.0 to pH 5.2 or higher. This was attributed to high buffer capacity (2, 16) in the curd and the slow rate at which equilibrium of the calcium phosphate was achieved in heat-treated retentate curd (17). Formation of less soluble calcium salts, such as hydroxyapatite (24) or tricalcium citrate (20), has been reported in heat-treated milks with neutral pH. Insoluble calcium salts must have remained in the curd throughout the acid coagulation (pH at cutting = 5.0) of the retentate and subsequent cook and rinses. It was theorized that the slow upward pH shift in the UF cottage cheese to pH 5.2 to 5.3 caused solubilization of the casein from the curd matrix (25) and resulted in a reduction in curd opacity and texture.

Several manipulations of the process were attempted to stop the translucency defect. Acidified rinses and dressings lowered the pH of the finished cottage cheese somewhat, but did not halt the shift in pH or the curd's dissolution. Raising the final cook temperature from 46.1°C to 54.4°C increased total solids content in the curd, as expected, but did not improve curd stability. Single strength rennet (.025 mL rennet/.454 kg retentate TS) slightly improved cutting and handling of curd, but caused tighter shrinking during cooking, resulting in higher total solids and increased mealiness. Rennet did not prevent translucency in curds made from heat-treated retentate.

Lowering the pH at cutting had the greatest effect on curd stability. Curd translucence did not develop when the curd was cut at pH $\leq$ 4.8. The increased acidic environment at this pH shifted the solubility equilibrium to dissolve more mineral from casein micelles, which resulted in lower buffer capacity in the curd (2, 23). Unfortunately, retentate coagulum cut at this pH produced inferior cheese curd which was soft, shattered, and mealy. Such defects are typical of curd cut below the AC endpoint (7, 19).

Preacidification. Micellar calcium phosphate in UF retentate was reduced by acidification of the skim milk before ultrafiltering. Preacidification of cold skim milk with phosphoric acid to pH 5.8, 12 h before UF, resulted in a curd which contained less calcium and did not shift in pH. Calcium content of cottage cheeses made from heat-treated retentates cut at various pH levels and from preacidified retentate is shown in Table 3. The calcium level in preacidified retentate curd approached the average Ca^{++} content of .158% (dry basis) for conventional cottage cheese curd (22).

Preacidified retentate (pH 5.8) formed a softer curd than pH 6.7 retentate, but still required heat treatment to make a curd which cut and handled well in the vat. Reducing the duration of heat treatment at 71°C from 30 to 6 min resulted in a UF curd with acceptable cutting properties.

TABLE 3. Effect of pH at cutting on calcium content of curd from heat-treated and preacidified 16% TS skim retentate.

Retentate Type	pH at cutting	%Ca (dry basis)
Heat treated *	4.90	.616
Heat treated *	4.95	.752
Heat treated *	5.03	.930
Preacidified **	4.84	.164

* Heated at 71.1°C for 30 min
** Preacidified to pH 5.8

Process Parameters

Good quality UF cottage cheese curd was successfully produced from preacidified (pH 5.8) skim milk, ultrafiltered to 16% TS, heat treated at 71.1°C for 6 min, cut at pH 4.8, and cooked to 51.7°C. The retentate curd had good texture and was stable during storage. Total solids of the dry curd by this UF method were about 10% higher than conventional methods (22% TS versus 20% TS). Total solids in the cottage cheese were adjusted to 20% TS by use of a low solids (16.5% TS) cream dressing.

CONCLUSION

A pilot scale process using conventional equipment for manufacturing directly acidified cottage cheese curd from 16% TS skim milk UF retentate was developed.

Retentate curd structure was softened by heat treating the retentate to 71.1°C and holding for 30 min. However, this heat treatment increased the curd buffering capacity and caused the pH of the finished curd to rise during storage. Curd made from this heat-treated retentate was not stable, and it acquired a translucency defect with storage. Lowering the cutting pH was the only parameter that had any effect on eliminating the translucency defect, but this resulted in mealiness when the curd was cooked.

Preacidification of skim milk to pH 5.8 before UF resulted in less calcium in the curd and corrected the translucency defect. Preacidification enhanced the effect of heat treatment, so the amount of heat needed to obtain a curd with acceptable handling properties was reduced. Preacidification to pH 5.8 coupled with a heat treatment of 71.1°C for 6 min resulted in a curd that cut easily and had good sensory quality after cooking.

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PART 3. PROCESS DEVELOPMENT OF COTTAGE CHEESE FROM ULTRAFILTERED SKIM MILK USING PRE-ACIDIFICATION AND HTST HEATING

ABSTRACT

The effect of two processing parameters, acidification of skim milk before ultrafiltration, and heat treatment of retentate, were investigated to improve the functional and sensory qualities of the curd.

Skim milk was pasteurized at 62.8°C for 30 min and split into three lots which were unacidified, phosphoric acid added to pH 6.2, and phosphoric acid added to pH 5.85. The three lots of skim milks were ultrafiltered to 16% TS, and each lot was divided into four treatments which were unheated, heated to 71.1°C for 7 s, 76.7°C for 7 s, and 82.2°C for 7 s. Cottage cheese pH, total solids, and six sensory attributes were measured. Finished cottage cheeses were evaluated by an expert panel consisting of five judges. Total solids, protein content, and fines content of the whey were also measured.

Preacidification to pH 6.2 enhanced curd structure, which increased solids recovery, reduced fines, and improved curd appearance, firmness, and texture. Heat treatments caused softening of the curd and increased moisture content. Excessive heat treatment caused shattering, fines, and mealiness. The best curd from the experiment was produced from pH 6.2 retentate, heat treated at 71.1°C. More whey proteins were incorporated in cheese curd made from retentates heated to 76.7°C and 82.2°C. The effects of heat treatment were more pronounced as acidification increased.

The translucency defect previously observed when cottage cheese was made from UF retentate that had been vat-heated to 71.1°C for 30 min did not occur in this experiment. This was attributed to the use of HTST heating of the retentate, compared to batch heating used in the previous trials.

INTRODUCTION

A previously developed process for manufacturing cottage cheese curd from batch heat-treated 16% total solid (TS) ultrafiltered (UF) skim milk retentate showed preacidification of skim milk and heat treatment of retentate play a significant role in determining curd acceptability. Recently, Ocampo (14) reported good quality cottage cheese from 16% TS retentate with 2.24% yield increase, but the curd was high in total solids.

Another experiment was designed to test the effect of various levels of skim milk acidification prior to UF and increased HTST heat treatments of retentate on finished product attributes. Treatments were selected to optimize a procedure for making cottage cheese curd with suitable strength, texture, total solids, and storage stability.

MATERIALS & METHODS

Experimental Design

A randomized split block design was used to determine the effects of acidification of skim milk and heat treatment of UF retentate on the functional characteristics of cottage cheese curd and overall sensory quality. Pasteurized skim milk was split into three aliquots, two of which were acidified (pH 6.20 and pH 5.85), with the control milk having a pH of 6.7. After the treated skim milks were concentrated by ultrafiltration, the retentates were split into four fractions, three of which were given additional heat treatments (Figure 1).

Skim Milk

Approximately 1500 L (400 gallon) of whole raw milk were drawn from a 1,135,000 L (30,000 gallon) bulk silo at a Dairymen, Inc. (Louisville, KY) receiving station. This milk was previously tested by Dairymen, Inc. according to standard methods (17) and had a direct microscopic count of < 40,000, a standard plate count of < 25,000 cfu per ml, 12.6% TS, and 3.55% milkfat. The milk was warmed to 43°C and mechanically separated with a pilot size DeLaval® (Kansas City, MO) centrifugal separator to ≤ .10% milkfat. The skim milk was vat-pasteurized at 62.8°C for 30 min, cooled, and divided into three lots.

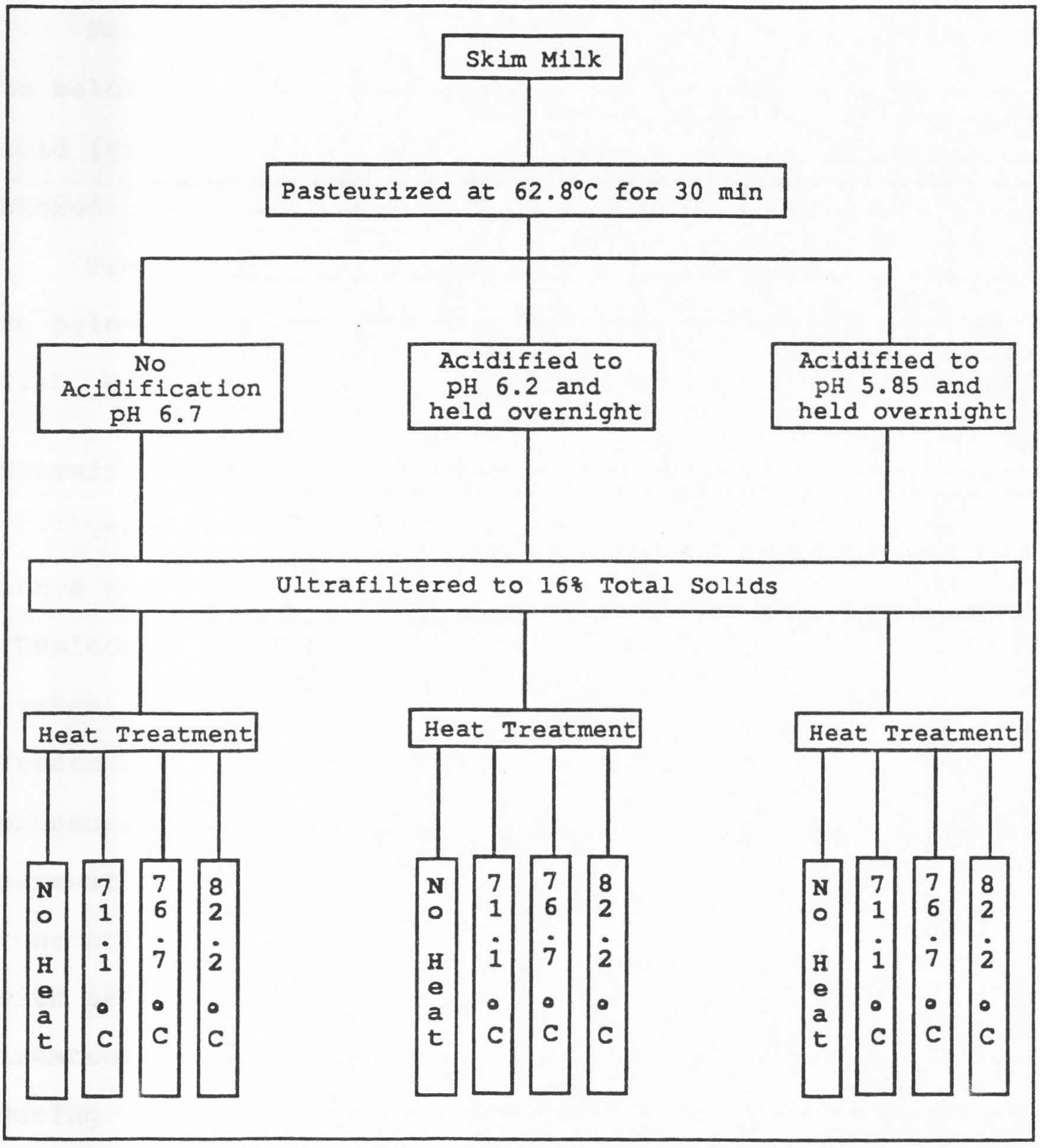

Figure 1. Schematic of process treatment design.

Preacidification

Treatment 1. Pasteurized skim milk (390 kg) was used as a control and was transferred directly for UF.

Treatment 2. Pasteurized skim milk (390 kg) was cooled to below 4°C, acidified with .07% w/w 85% aqueous phosphoric acid (Vitex® 750, Bunge Foods, Atlanta, GA) to pH 6.2, and stored overnight.

Treatment 3. Pasteurized skim milk (390 kg) was cooled to below 4°C, acidified with .155% w/w phosphoric acid to pH 5.85, and stored overnight.

Ultrafiltration

The three treatments of pasteurized skim milk described above were ultrafiltered using a pilot scale Romicon® (Romicon Corp., Woburn, MA) tubular polysulfone membrane system, with 6.1 m^2 of membrane surface. Skim milk treatments were warmed to 55°C and recirculated under a pressure gradient (inlet 210 kPa, outlet 60 kPa) to draw off permeate until the retentate exceeded 16% TS (approximate 3x concentration). Retentate was standardized to 16.0 ± .1% TS with permeate taken from the same lot. Permeate from each treatment was then cooled to below 4°C and stored until used during cheesemaking.

Heat Treatment

Retentates were heat-treated using an Alfa-Laval® (Kansas City, MO) pilot scale Steri-Therm™ high temperature short time (HTST) plate heat exchanger. The retentates from each preacidification treatment received either no additional heat, or were heated to 71.1°C for 7 s, 76.7°C for 7 s, or 82.2°C for 7 s. They were then rapidly cooled to below 4°C. One lot at pH 5.85 (Treatment 3) gelled in the HTST heat exchanger when heated to 82.2°C and was discarded. Therefore, eleven lots of retentate were used for making cottage cheese. The retentate and permeate were transported to the University of Kentucky for cheesemaking.

Manufacture of Cottage Cheese

The pilot scale production of cottage cheese curd from retentate is shown in Figure 2. Each lot was replicated three times, which resulted in thirty-three vats of cottage cheese being produced. The length of storage time between heat treatment and cheesemaking was accounted for by using retentate age as a covariant in the statistical analysis of the data.

Acidification. Retentate (4.5 kg) was weighed into 8 L stainless steel cylindrical vats and acidified at 4°C with diluted phosphoric acid to pH 5.5. Four to six vats were placed in a recirculating warm water bath, and the retentate was gently warmed under constant and equal agitation to 32.2°C. Glucono-delta-lactone (GDL) (Vitex® 850, Bunge Foods, Atlanta, GA) was added to the warm retentate as a 20% slurry in ice water and agitated vigorously for 2 min to insure complete dissolution and

Skim milk retentate at 4°C
4.5 kg retentate in 8000 ml cylindrical vat
Add phosphoric acid to pH 5.5

↓

Warm retentate to 32°C
Add glucono-delta-lactone to slowly acidify
Allow quiescent coagulation for 60 min
Cut coagulum at pH 4.7 to 4.8

↓

Add 2.5 kg permeate at pH 4.7, 32°C
Allow 10 to 15 min of healing time
Begin heating with equal and constant agitation

↓

Cook curd in permeate to 52°C in 75 to 90 min
Hold curd at final cook temperature for 10 min

↓

Drain curd in cheesecloth
Collect whey sample

↓

1st rinse at 32°C, held 10 min
2nd rinse at 4°C, held 20 min
Final drain for 20 min
Weigh dry curd

↓

Blend curd with salted cream dressing
(60:40 curd to dressing ratio)
Store cottage cheese at 4°C

↓

Hold 5 to 7 d
Judge by expert panel

Figure 2. Schematic diagram of manufacture of cottage cheese curd from 16% TS skim milk retentate.

distribution throughout the vat. The vats were left undisturbed for 60 min to quiescently acidify the retentate to pH 4.78 ± .02. The two-stage acidification rates used with the various treatments are shown in Table 4.

TABLE 4. Quantities of 85% phosphoric acid required to acidify 16% TS skim milk retentate to pH 5.50 ± .02, and glucono-delta-lactone (GDL) to further acidify it to pH 4.78 ± .02.

Treatment	Phosphoric acid added (w/w)	GDL added (w/w)
No preacidification	.460 %	2.111 %
Preacidified to pH 6.20	.356 %	1.956 %
Preacidified to pH 5.85	.204 %	1.800 %

Monitoring the Curd. A curd tension monitoring device (CEM Corp., Mountain Home, NC) was used to measure the onset of coagulation and development of curd firmness in retentate treatments. Measurements in millivolts were made with a strain gauge relating resistance of the coagulating milk to an oscillating disc suspended in the vat. These millivolt readings were used to express relative curd firmness. The apparatus, described by Ustunol and Hicks (21), was set at an oscillating speed of 12 cycles per min, with a stroke depth of 1.1 cm.

Handling the Curd. Vats were cut with specially designed .64 cm stainless steel wire knives. Permeate

(2.5 kg) from the same preacidification treatment, adjusted to pH 4.7 at 32.2°C, was added to the vats to facilitate cooking. Vats were allowed to heal for 10 to 15 min. All vats were cooked to 51.7°C in 75 to 90 min, according to Table 5, and held at the final cook temperature for 10 min.

TABLE 5. Cooking schedule used in manufacture of cottage cheese curd from 16% TS skim retentate.

Time (min)	Temperature * (°C)	Rate of Increase (°C/5min)
0:00 → 0:30	31.1 → 37.2	1.0
0:30 → 1:00	37.2 → 44.5	1.2
1:00 → 1:30	44.5 → 51.7	1.2

* Temperature values averaged from eight trials.

Curd was recovered from the cheese vats using wire mesh strainers lined with two layers of cheese cloth. Whey from each vat was collected and stirred, and a 200 mL sample was drawn and retained for pH, TS, protein, and fines analysis. After draining the whey, the curd was washed with 3.0 kg acidified rinse water (pH 4.0 at 32.2°C) for 10 min. A second 2.0 kg acidified rinse (pH 4.0 at 4°C) was applied to the curd and held for 20 min. The curd was drained for 20 min in cheese cloth and the net contents were weighed.

Creaming the Curd. Retentate curd was blended 60:40 (curd to dressing) with HTST pasteurized low solids cream dressing. The dressing (18.3% TS, pH 5.7) was composed of water, cream, buttermilk, salt, and stabilizer. The dressing was designed to produce a finished product with 20.0% TS, 4.0% milkfat, and 1.0% salt. Creamed cottage cheese was packaged in .25 kg plastic containers and stored at 4°C for 5 to 7 d until evaluated.

Composition Analysis

Moisture. Total solids were determined on 2.0 to 3.0 g of skim milk, permeate, retentate, whey, dressing, and blended cottage cheese. Total solids of the dry curd were calculated by use of the equation:

$$\%\ \text{TS dry curd} = \frac{\%\ \text{TS creamed curd} - .4(\%\ \text{TS dressing})}{.6}$$

A model AVC-80™ (CEM Corp, Mountain Home, NC) microwave drying oven standardized to a vacuum drying oven (1) was used for moisture determination. A representative sample was evenly spread over two fiberglass pads and microwaved at 90% power for 4 min. Moisture assays were determined in duplicate. Samples exhibiting discrepant results were repeated until close agreement was obtained.

Fat. Fat was determined in duplicate by the Babcock method (17) using 9.0 g of whole raw milk in an 8% certified test bottle, and 9.0 g of skim milk in a .5% certified test bottle.

Protein. Nitrogen was estimated by the semi-micro Kjeldahl procedure (8). Samples of skim milk (5 g), retentate (2 g), permeate (10 g), and decant from centrifuged whey (10 g) were analyzed for nitrogen. Determinations were in triplicate and protein content was calculated by multiplying the nitrogen content of the sample by a factor of 6.38.

Acidity. The pH of skim milk was determined before and 12 h after acidification. The pH of retentate, permeate, dressing, and blended cheese was also determined. An Orion® Model 901 potentiometer (Orion Research, Cambridge, MA) was used for pH measurements.

Whey Fines. The percent fines in cottage cheese wheys (whey and permeate) was estimated from the pellet weight of a centrifuged sample as a fraction of the total sample weight (about 38 g). A CR-6000 refrigerated centrifuge (International Equipment Company, Needham Heights, MA) set at 4200 rpm for 15 min was used for the fines determination.

Sensory Evaluation

Sensory quality of cottage cheese samples was judged by a five-member expert panel. Samples were evaluated in random order with identity of the treatment withheld from the judges. Judges evaluated the cottage cheese on six attributes relating to appearance, texture, and flavor. A sensory score sheet (Figure 3) was designed to find subtle differences among treatments of curd. A 10 cm line for each attribute was drawn, with the midpoint being the point at which an attribute was judged acceptable or unacceptable.

JUDGE: ______________________________

SAMPLE: ______________________________

INSTRUCTIONS: Score the following attributes in cottage cheese by placing a bold mark across the line at the point which corresponds to the acceptability of the sample. The midpoint indicated on the line represents the point at which an attribute becomes acceptable.

```
APPEARANCE  |------------------|------------------|

ABSORBANCE  |------------------|------------------|

OPAQUENESS  |------------------|------------------|

FIRMNESS    |------------------|------------------|

MEALINESS   |------------------|------------------|

FLAVOR      |------------------|------------------|
            Extremely      Acceptable      Extremely
            Poor                                Good
```

COMMENTS:

Figure 3. Sensory score sheet for judging UF cottage cheese samples.

Sensory scores were quantified by measuring the distance in centimeters along the response line to where a mark was made across the line.

Statistical Analysis

All data were analyzed using a SAS® General Linear Model procedure (20). Objective measurements (TOTSOL, PH, WHEYTS, WHEYFN, WHEYPRT) from the experiment were analyzed using a model with the dependent variables of

TRT + TEMP + AGE + REP

where

TOTSOL = Total Solids of the Retentate Curd
PH = pH of the Cottage Cheese at 5 d
WHEYTS = Total Solids of the Whey
WHEYFN = Whey Fines
WHEYPRT = Whey Protein
TRT = Preacidification Treatment of Retentate
TEMP = Heat Treatment of Retentate
AGE = Age of Retentate (Covariant)
REP = Replicate

Sensory measurements (APPEAR, ABSORB, OPAQUE, FIRM, MEALY, FLAVOR) from the experiment were analyzed using a model with dependent variables of

TRT + TEMP + JUDGE + AGE + REP

where

APPEAR = Appearance of Cottage Cheese
ABSORB = Absorbance of Cream Dressing in Cottage Cheese
OPAQUE = Degree of Whiteness in Cottage Cheese
FIRM = Firmness of Cottage Cheese
MEALY = Mealiness of Cottage Cheese
FLAVOR = Flavor of Cottage Cheese
JUDGE = Panel Member

Curd firmness measurements (TIME, CURD) from the experiment were analyzed using a model with dependent variables of TRT + TEMP + AGE + REP

where

TIME = Time of Observation
CURD = Curd Firmness Measurement (mV).

RESULTS AND DISCUSSION

Preparation of Retentates

Gelation of the pH 5.85 retentate at the highest heat treatment level (82.2°C) is consistent with results reported by Green (7). Casein micelles undergo demineralization of micellar calcium phosphate (MCP) at pH less than 6.0 (22). pH reduction induces casein migration from the micelle (5). Reduced structural integrity within micelles, increased levels of serum caseins, and elevated serum Ca^{++} contribute to the instability of the system when subjected to heat. Adherence of β-lactoglobulin to casein micelles with high heat (> 80°C) occurs at pH 6.4 or lower (10, 15). Large increases in retentate viscosity were observed in preacidified HTST-treated retentates. The pH 5.85 retentate became so thick with the highest heating level that forward flow through the HTST unit was eventually stopped.

Cottage Cheese Manufacture

Cottage cheeses manufactured from all eleven combinations of treatments were generally similar in character, being overly firm and high in TS. Retentate curds were dense, yet fragile at the onset of cooking, and the agitation speed required by the stirring mechanism to keep the curd from matting was destructive to curd identity. This was especially noticed with retentate that produced softer curds. Shattered curd was one of the most common visual defects noted by the judges.

Retentate curds from the eleven combinations of treatments were randomly manufactured and replicated three times during 3 d. A faster rate of coagulation was observed as the age of the retentate increased. Because of this, age was entered as a covariant into the General Linear Model for statistical analysis of the data. Retentate age was found to significantly (*P* < .01) lower finished product pH, reduce TS of the curd, and increase protein content of the whey.

Curd Recovery

Recovery of TS in retentate curd was calculated as a percentage of the TS in the vat prior to acidification. The percent curd recovered from retentates is shown in Figure 4.

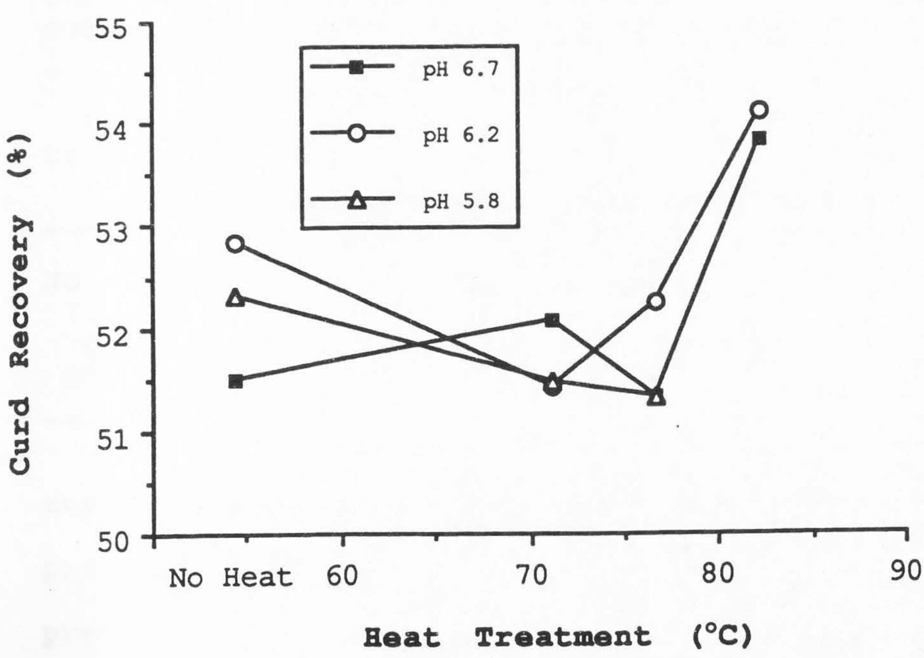

Figure 4. Effect of preacidification treatments and heat treatments on % curd recovery means; LSD = .8%, *P* < .05.

Means of % curd recovered in Table 6 demonstrate there was a greater recovery of solids in preacidified retentates. Highest recovery of solids occurred in pH 6.2 retentate.

TABLE 6. Effect of preacidification on percent of total solids recovered as retentate curd.

pH of Retentate	TS recovered (%)	Comparison of all treatments: *P* > *F*		
		6.7	6.2	5.8
6.7	51.97	---	.0001	.0150
6.2	53.02		---	.0174
5.8	52.51			---

The effect of heat treatment on recovery of solids is given in Table 7. The significant increase in recovery from

TABLE 7. Effect of heat treatment on percent of total solids recovered as retentate curd.

Heat treatment (°C)	TS recovered (%)	Comparison of all treatments: *P* > *F*			
		No heat	71.7°C	76.7°C	82.2°C
No heat	51.8	---	.0066	.0006	.0001
71.7	51.2		---	.4805	.0001
76.7	51.0			---	.0001
82.2	53.5				---

the highest heat application, along with a decrease in the protein content of centrifuged whey, demonstrates that whey proteins were complexed to casein and incorporated in UF curd. Emmons et al. (6) reported 10% increased yield of curd made from skim milk heated at 79.4°C for 30 min.

Curd Firmness

The strain gauges failed during the experiment, so not all vats were monitored for curd strength. One to three measurements were made for each treatment. Development of curd firmness in skim UF retentate was significantly affected (*P* < .01) by preacidification of skim milk before UF and also by heat treatment. Typical curd firmness versus time after adding GDL is shown in Figure 5.

Analysis of curd firmness data for the effect of preacidification, comparing all heat treatments, is shown in Table 8. The pH 6.2 retentates had the highest curd

TABLE 8. Effect of preacidification on curd firmness.

pH of Retentate	Curd firmness (mv)	Comparison of all treatments: *P* > *F*		
		6.7	6.2	5.8
6.7	123	---	.0001	.0001
6.2	166		---	.0001
5.8	71			---

firmness when averaged across all heat treatments, which may have contributed to the best percent curd recovered for the experiment. Casiraghi et al. (3) reported curd firmness was directly related to ionic calcium concentration and demonstrated increased curd firmness with rennet-coagulated 2.3x retentate acidified to pH 6.3. Other researchers (9, 12) have also shown that increased ionic calcium content increased curd firmness. Decreased curd firmness with pH

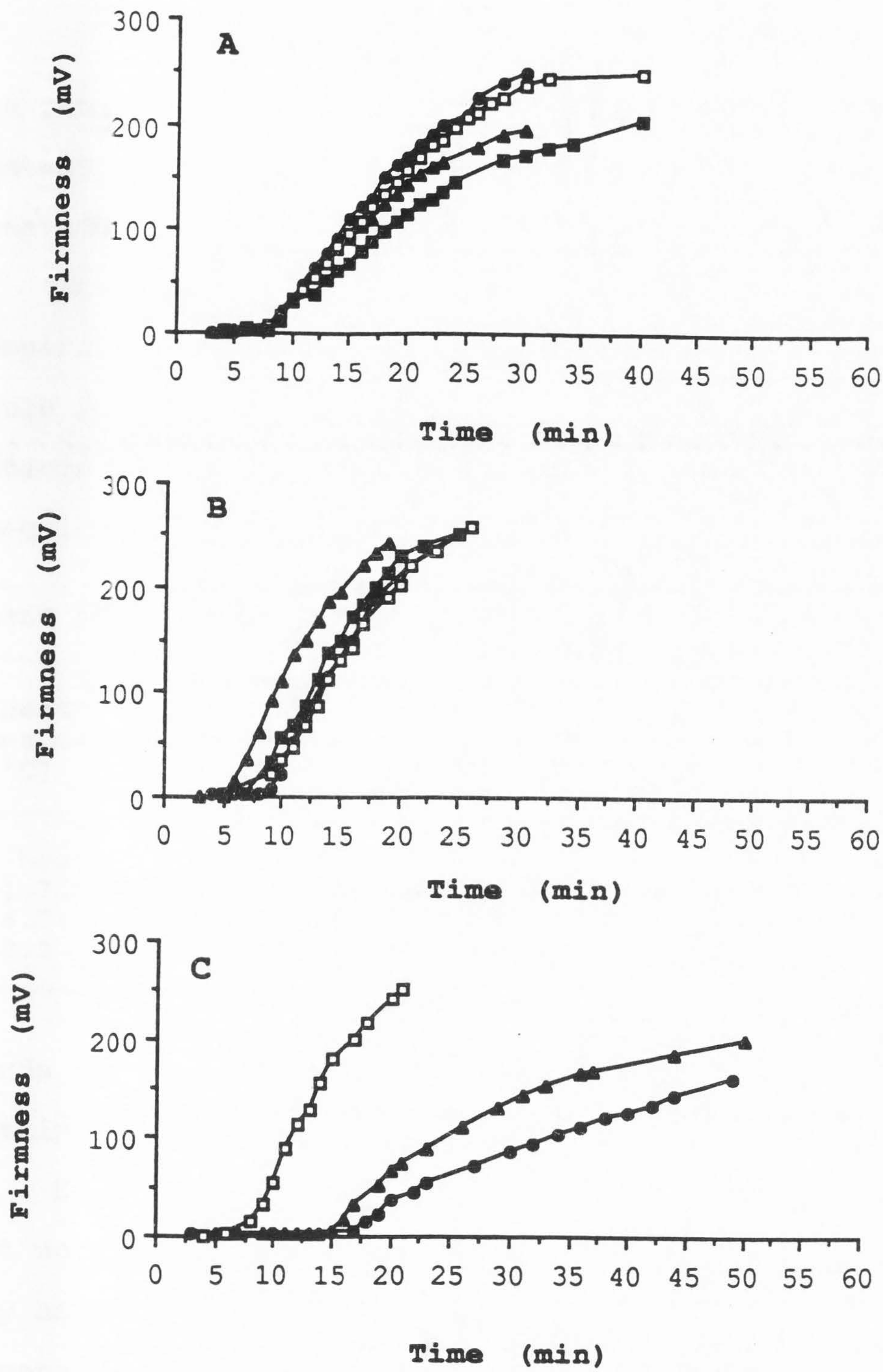

Figure 5. Typical curd firmness versus time after adding glucono-delta-lactone to 16% total solids UF retentate:
A. Retentate from non-acidified skim milk (pH 6.7)
B. Retentate from skim milk pre-acidified to pH 6.2
C. Retentate from skim milk pre-acidified to pH 5.8;
□ Not heated, ▲ 71.1°C, ● 76.7°C, ■ 82.2°C.

5.8 retentate is thought to be the result of reduced MCP content (7) and pH-accentuated heat denaturation in heat-treated samples (4, 22).

The effect of heat treatment on curd firmness, comparing all preacidification treatments, is given in Table 9. As expected, heat denaturation of whey proteins interfered with curd formation, slowing the onset of coagulation and greatly reducing curd strength (12, 15).

TABLE 9. Effect of heat treatment on curd firmness.

Heat treatment (°C)	Curd firmness (mv)	Comparison of all treatments: $P > F$			
		No heat	71.7°C	76.7°C	82.2°C
No heat	165	---	.0001	.0001	.0001
71.7	128		---	.0002	.0001
76.7	98			---	.2528
82.2	88				---

Curds from 82.2°C heat-treated retentate were much softer at cutting, tended to shatter more easily, and were more mealy.

Non-heated retentates were somewhat difficult to cut, but not as tough as the curds in the previous study. This may have been affected by different UF membrane systems, vat dimensions, and curd cutting apparatus.

Cheese pH

The effect of treatments on cottage cheese pH is shown in Figure 6. The pH means of 5 d old cottage cheese shown in Table 10 were significantly ($P < .05$) influenced by

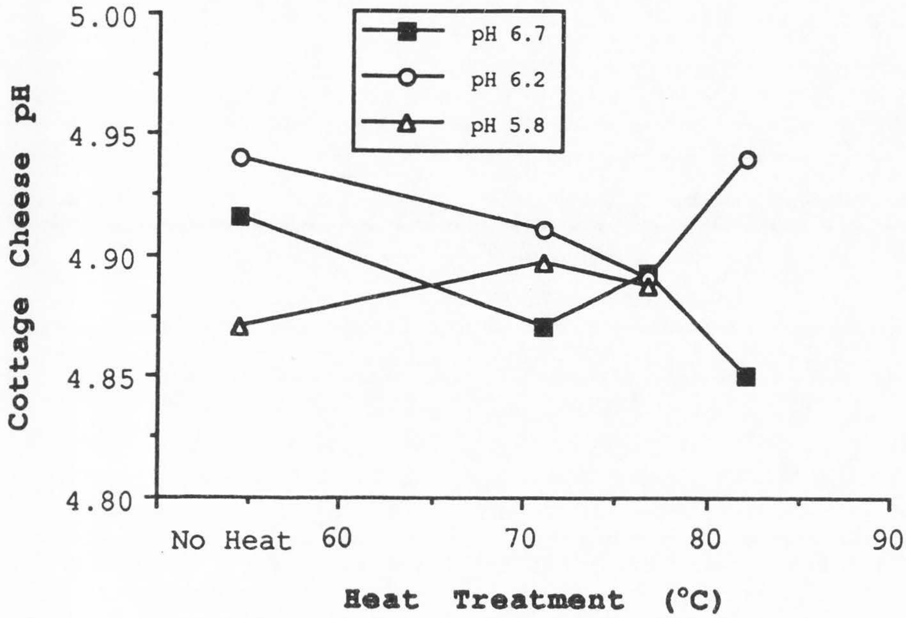

Figure 6. Effect of preacidification treatments and heat treatments on cottage cheese pH means; LSD = .04, $P < .05$.

TABLE 10. Effect of preacidification on cottage cheese pH.

pH of Retentate	pH after 5 d	Comparison of all treatments: $P > F$		
		6.7	6.2	5.8
6.7	4.90	---	.0111	.0490
6.2	4.93		---	.0001
5.8	4.88			---

preacidification treatment. Cutting pH's ranged between 4.78 and 4.80 for all treatments. The increased pH mean with curd from pH 6.2 retentates may be explained by increased solubilized calcium phosphate at this pH (5).

Heat treatment in this experiment did not significantly affect finished product pH. Curds from pH 6.7 heat-treated retentates were expected to have the highest buffering capacity and highest finished product pH, as was realized in previous trials using batch-heated retentate. However, curd produced from pH 6.7 HTST heat-treated retentates did not develop the translucency defect, as was previously observed.

The difference in curd stability between the two experiments may be explained by changes in heat treatment. The duration of the heat treatment was reduced from 30 min for the batch method to 7 s in the HTST method. Several researchers (2, 13, 16, 22) have demonstrated a rise in insoluble calcium phosphate complex with high heat treatment and extended time. The HTST heat treatment used in this experiment denatured whey proteins and affected cuttability, but may not have provided sufficient time to form insoluble calcium phosphates. Absence of insoluble calcium salts in HTST heat-treated retentate would account for the lack of a pH rise in UF curd during storage in this experiment.

Curd Moisture

A trend of increasing moisture in cottage cheese with increasing heat treatment applied to retentates can be seen in Figure 7. Curd solids means as affected by heat treatment are shown in Table 11.

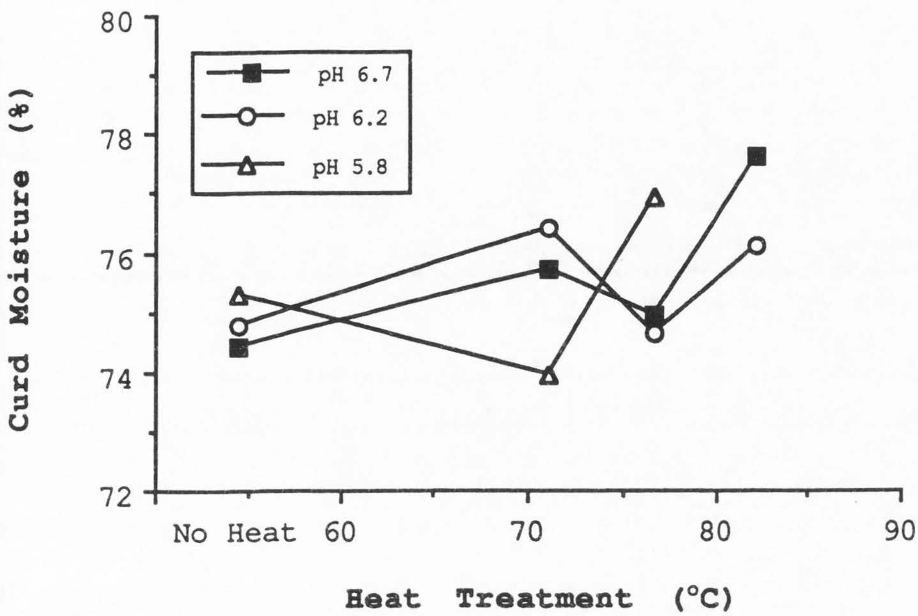

Figure 7. Effect of preacidification treatments and heat treatments on curd moisture means; LSD = 1.0%, *P* < .05.

TABLE 11. Effect of heat treatment on total solids of retentate curd.

Heat treatment (°C)	TS curd (%)	Comparison of all treatments: *P* > *F*			
		No heat	71.7°C	76.7°C	82.2°C
No heat	25.07	---	.0467	.2162	.0001
71.7	25.68		---	.0009	.0001
76.7	24.71			---	.2528
82.2	23.15				---

Preacidification of retentate to pH 5.8 significantly affected (*P* < .02) the moisture content of cottage cheese. A trend toward higher moisture with increasing acidification is indicated by the means for curd TS shown in Table 12.

TABLE 12. Effect of preacidification on total solids of retentate curd.

pH of Retentate	TS curd (%)	Comparison of all treatments: $P > F$		
		6.7	6.2	5.8
6.7	25.3	---	.5788	.0080
6.2	25.2		---	.0247
5.8	24.6			---

Denaturation and complexation of whey proteins onto casein are enhanced as pH declines (10, 22). Heat denaturation of milk protein is known to increase the water-binding capacity of acid coagulated curd (11).

Whey Measurements

Whey Total Solids. Total solids in wheys from retentate curds remained mostly constant regardless of treatment. Figure 8 shows the effect of the various treatments on % TS in the wheys.

The effect of heat treatment on whey total solids is presented in Table 13. Whey total solids followed a decreasing trend as heat treatment increased. Whey total solids would be expected to decrease as heat treatment increased, due to denatured whey protein complexing with casein (7, 15).

A slight rise in whey total solids in the 82.2°C treatment reflects an increased fines content. Curd produced from retentates heated to 82.2°C disintegrated with

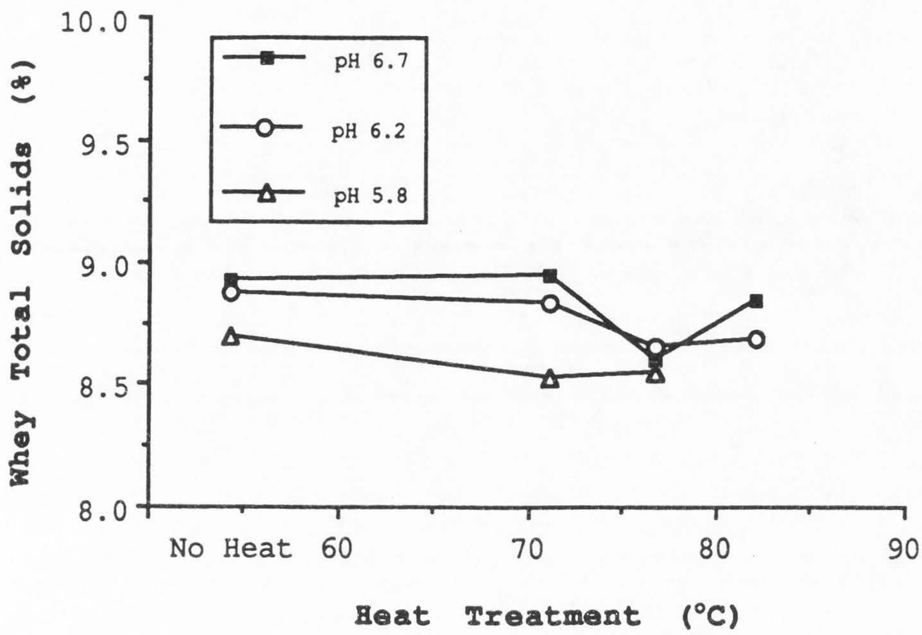

Figure 8. Effect of preacidification treatments and heat treatments on whey total solid means; LSD = .11%, $P < .05$.

TABLE 13. Effect of heat treatment on whey total solids.

Heat treatment (°C)	Whey TS (%)	Comparison of all treatments: $P > F$			
		No heat	71.7°C	76.7°C	82.2°C
No heat	8.38	---	.0070	.0001	.0003
71.1	8.29		---	.0002	.3280
76.7	8.11			---	.0006
82.2	8.25				---

stirring in the vat. Fines were extremely small in these vats and were able to pass through the cheesecloth more readily than fines from other wheys.

Preacidification treatment means of total solids measured in wheys drained from retentate curd are shown in Table 14. A significantly lower mean was observed in the pH

TABLE 14. Effect of preacidification on whey total solids.

pH of Retentate	Whey TS (%)	Comparison of all treatments: *P* > *F* 6.7	6.2	5.8
6.7	8.74	---	.4752	.0001
6.2	8.72		---	.0001
5.8	8.52			---

5.8 treatment. This effect is probably the result of reduced serum protein content (4, 22) and lower fines content, as shown in Table 15.

Whey Fines. The % fines in whey, as measured by centrifuged plug weight, is represented in Figure 9. The low mean for fines from the pH 5.8 treatment conflicts with observations noted during the trials and curd firmness data. Retentates preacidified to pH 5.8 produced softer curds and

TABLE 15. Effect of preacidification on whey fines.

pH of Retentate	Whey fines (%)*	Comparison of all treatments: *P* > *F* 6.7	6.2	5.8
6.7	5.12	---	.1583	.0001
6.2	4.88		---	.0001
5.8	4.00			---

* % Whey fines = plug weight / whey sample weight x 100

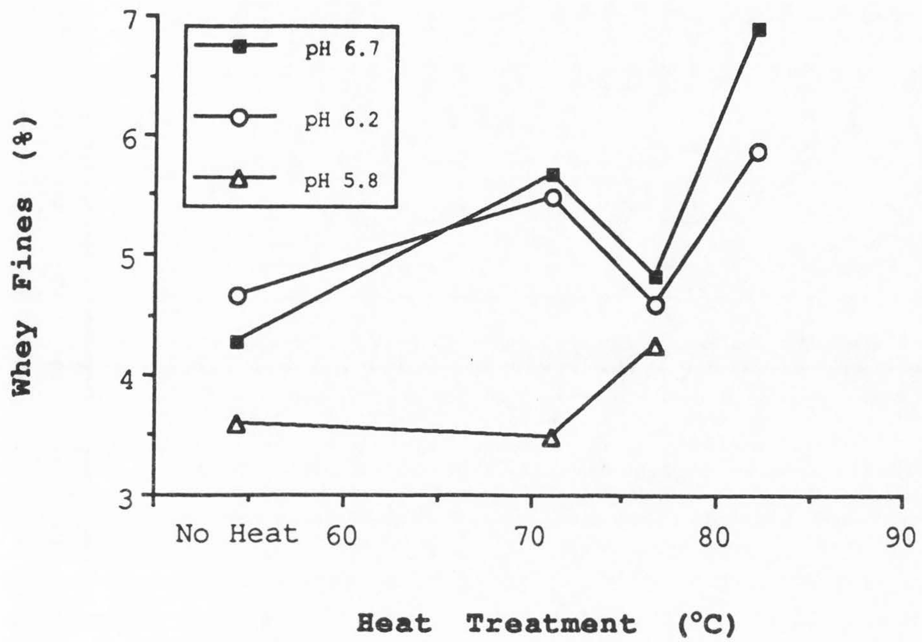

Figure 9. Effect of preacidification treatments and heat treatments on whey fines means; LSD = .54%, $P < .05$.

were more given to shattering and fines, particularly as heat treatment increased. The fines mean for pH 5.8 retentate is much lower than observed because curd fines clogged the cheesecloth and acted as an additional filter. This observation was also reported by Riddell-Lawrence and Hicks (18).

Whey Protein. Total protein was measured in centrifuged whey as an indicator of whey protein denaturation. The effect of treatments on % protein in centrifuged whey is shown in Figure 10.

No significant overall effect from preacidification was observed. However, this may have been obscured by the lack

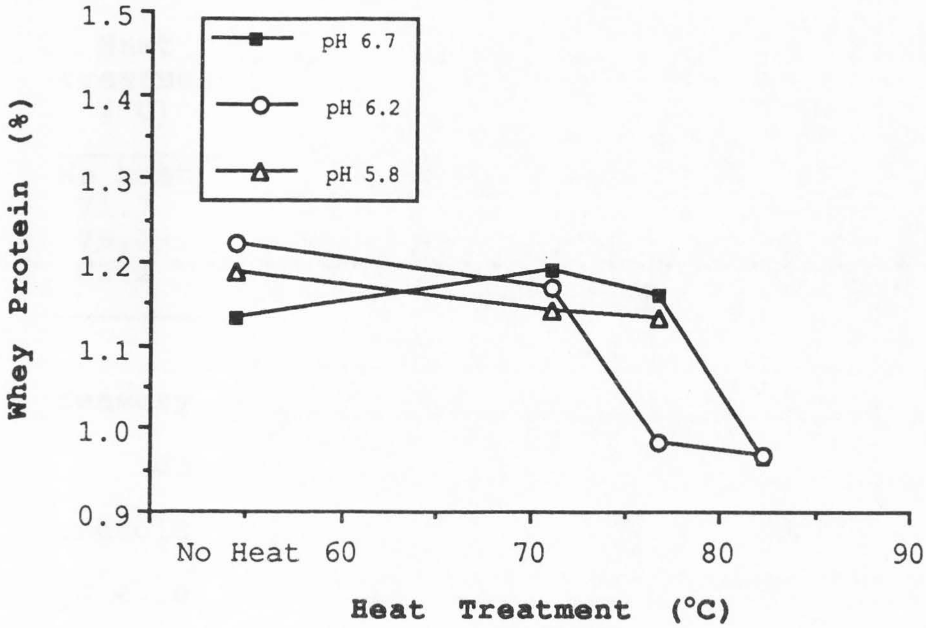

Figure 10. Effect of preacidification treatments and heat treatments on means of total protein in centrifuged whey; LSD = .06%, $P < .05$.

of results from the missing treatment cell. Green (7) reported that retentates preacidified to pH 6.4 and 6.0 were more susceptible to heat damage. Also, whey proteins were less denatured with HTST treatment versus vat heating (7).

Total protein means in centrifuged whey, shown in Table 16, were significantly lower for the 76.7° and 82.2°C heat treatments. Ruegg et al. (19) reported denaturation of ß-lactoglobulin commenced at 73°C.

TABLE 16. Effect of heat treatment on total protein in centrifuged whey.

Heat treatment (°C)	Total proteins (%)	Comparison of all treatments: *P* > *F*			
		No heat	71.7°C	76.7°C	82.2°C
No heat	1.10	---	.9714	.0001	.0001
71.7	1.10		---	.0001	.0001
76.7	0.99			---	.0001
82.2	0.88				---

Sensory Measurements

Cottage cheese appearance was significantly affected by preacidification level ($P < .0001$), heat treatment ($P < .0119$), and age of the retentate ($P < .0001$). The effect of treatments on appearance is shown in Figure 11.

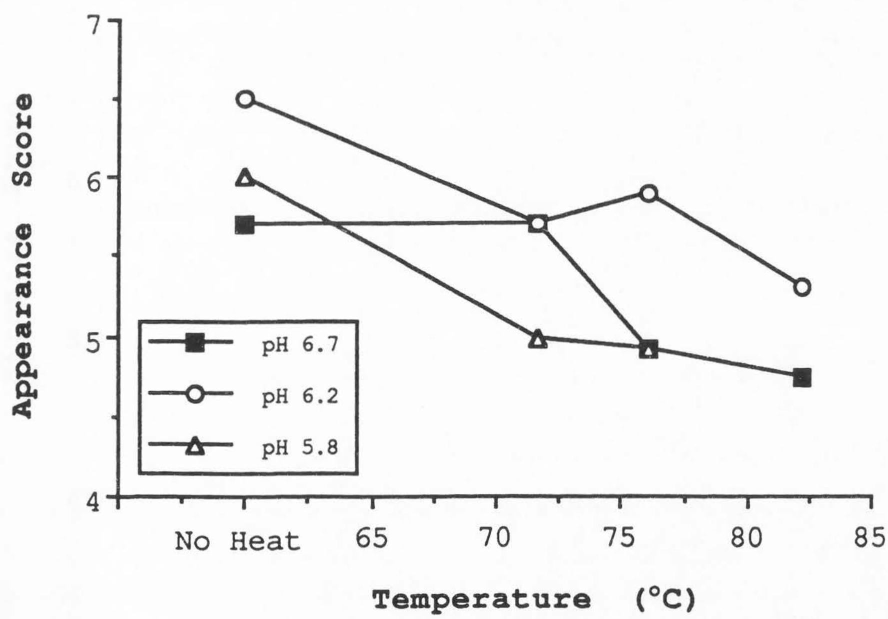

Figure 11. Effect of preacidification treatments and heat treatments on appearance scores by expert panel; LSD = .8, $P < .05$.

Absorption of cream dressing by retentate curds was acceptable and not significantly affected by any treatment. Mean scores for absorption ranged from 6.5 to 7.1 on a ten-point hedonic scale.

The degree of white opaqueness exhibited by UF cottage cheese was normal and not significantly affected by any treatment. Mean scores for opaqueness in cottage cheeses of all treatments ranged from 8.4 to 8.6.

Firmness scores for UF cottage cheeses were significantly affected by preacidification level ($P < .0776$) and heat treatment ($P < .0440$). The effect of treatments on firmness is shown in Figure 12. Acceptability scores

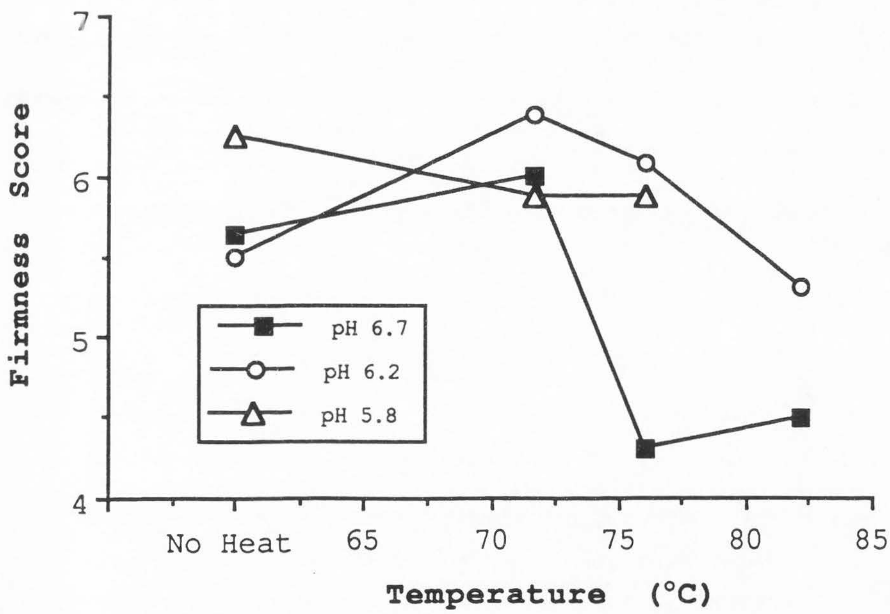

Figure 12. Effect of preacidification treatments and heat treatments on firmness scores by expert panel; LSD = 1.3, $P < .05$.

declined with heat treatments beyond 71.1°C. This related to curds which were too firm. Cottage cheese curd with the most desirable firmness was produced from pH 6.2 retentate heat-treated at 71.1°C.

Mealiness scores for UF cottage cheeses were not significantly affected by any treatment. All cottage cheeses manufactured in the experiment were generally mealy in texture, as indicated by the low mean scores given by the judges. A trend of greater acceptability was demonstrated in the average means of the three preacidification treatments. Curds from pH 6.7, 6.2, and 5.8 retentates scored 4.8, 5.3, and 5.5 for mealiness.

Flavor scores for UF cottage cheeses were not significantly affected by any treatment. Flavor of the various treatments was judged mostly acceptable with mean scores ranging from 5.7 to 6.2. Flavor criticisms noted by the judges were flat, metallic, and slightly bitter.

CONCLUSION

The treatments of preacidification of skim milk before UF, and heat treatment of UF retentates were shown to have significant effect on the composition and sensory qualities of UF cottage cheese. Curd structure and total solids recovery were enhanced by preacidification to pH 6.2. Heat treatment of UF retentates decreased curd firmness and increased the moisture content of curd. Treatments had a combined effect on milk protein denaturation, i.e., increasing preacidification and heat treatment caused softer curd formation and reduced protein content in centrifuged whey. Retentates which had been denatured beyond an optimal level produced curds which were shattered and mealy in texture. Curd with the most desirable appearance, texture, and firmness was manufactured from retentate which had been preacidified to pH 6.2 and heat treated at 71.1°C for 7 sec.

By using HTST processing, the translucency defect in curds made from pH 6.7 heat-treated retentates was avoided. Presumably, HTST heating does not allow sufficient time to form insoluble calcium phosphates to the same extent as batch heating of retentates.

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GENERAL SUMMARY

Process parameters for making cottage cheese curd from vat- and HTST-heated 16% TS retentate were developed using a two-stage direct acidification process. An unusual translucency defect was observed in curd from vat-heated retentate. The defect was eliminated by pre-acidifying the milk to pH 5.8 prior to UF. Pre-acidification reduced the amount of heat required to produce curd with sufficient strength for handling in the vat. Good curd was made from pH 5.8 retentate vat heated to 71.1°C for 6 min. Curd made from HTST-treated retentates was generally too firm and high in total solids. Curd with the most acceptable appearance and texture was manufactured from pH 6.2 retentate heat treated at 71.1°C for 7 s. The HTST-heated retentate did not exhibit the translucency defect.

Curd strength and moisture content of UF curd were significantly altered by pre-acidification level and amount of heat treatment. Denaturation of milk protein by heat treatment reduced curd firmness, increased curd moisture, and reduced the protein content of centrifuged whey. Pre-acidification was shown to have a complementary influence on protein denaturation and its effect on curd strength.

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