AN ABSTRACT OF THE THESIS OF

Won Byong Yoon for the degree of Master of Science in Food Science and Technology presented on July 9, 1996. Title: Use of Linear and Nonlinear Programming to Optimize Surimi Seafood.

Abstract approved: ______________________________

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Least cost formulations for surimi seafood were studied by linear programming (LP) and nonlinear programming (NLP). The effects of water and starches on functional properties of Alaska pollock and Pacific whiting surimi gels were investigated. Six starches (modified potato starch, potato starch, modified wheat starch, wheat starch, modified waxy corn starch, and corn starch) and their mixtures were used as ingredients. Mixture and extreme vertices design were used as experimental designs. Canonical models were applied to the optimization techniques. Blending different kinds of surimi showed linear trends for each functional property, so that LP was successfully employed to optimize surimi lots. Strong interactions were found between surimi and starch or in starch mixtures. Two optimum solutions, obtained from LP and NLP, were compared in this study. Corn starch and modified waxy corn starch greatly improved the functional properties.

Use of Linear and Nonlinear Programming to Optimize Surimi Seafood

by

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A THESIS

submitted to

Oregon State University

in partial fulfillment of the requirements for the degree of Master of Science

Completed July 9, 1996
Commencement June 1997

Master of Science thesis of Won Byong Yoon presented on July 9, 1996.

APPROVED:

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I understand that my thesis will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my thesis to any reader upon request.

Won Byong Yoon, author

ACKNOWLEDGEMENTS

I would like to express my heartily appreciation to my major professor, Dr. Jae W. Park, for his valuable guidance, encouragement, and support during my study. My sincere gratitude goes to Dr. Michael T. Morrisey, Dr. Edward Kolbe, Dr. Skip Rochefort, Dr. Thomas Seymor, Dr. Haejung An, Dr. Nahm G. Lee, Dr. John Lin, and Dr. Jirawat Yongsawatdigul for their invaluable advice and instruction. I greatly appreciate Young-Ki Lee for his inspiration and friendship. Many thanks to all seafood lab family and all of my friends in Korea for their kindness, support, and unforgettable companionship. Appreciation is especially extended to my forever advisor Dr. Byoung-Yong Kim for giving me a great opportunity in my life.

Finally, I would like to express my deep appreciation to my brother, sister, mother, and father with God, who always support me with their love from my lovely home country, Korea.

To the God.

To the Soul of Korean Marine Corps.

Once Marine, Forever Marine.

CONTRIBUTION OF AUTHORS

Dr. Jae W. Park was involved in the design, analysis, and writing of each manuscript. Dr. Byoung-Yong Kim was involved in the analysis of this study.

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Chapter 1. INTRODUCTION

Surimi, stabilized fish myofibrillar proteins, is commonly used as a major ingredient for a variety of surimi seafood, such as crab meat. Surimi seafood plays an important role in the U.S. seafood market with annual consumption of near 160 million lbs in 1994 (Park, 1995). The success of surimi seafood is based on better utilization of raw materials, longer shelf life of frozen surimi, and variety and consistent quality (Okada, 1992). The gel functionality, i.e., texture and color, of surimi seafood has been considered the most important aspect of product quality. Textural properties of surimi seafood, due to the gel-forming ability of surimi, are most commonly characterized by failure shear stress and strain value (Lanier, 1992). Blending various grades of surimi lots was suggested as a method to maintain the consistent functionalities and minimize the cost of surimi seafood (Park, 1992). Starch was reported as a major ingredient to control the functionalities and cost of the surimi seafood (Okada, 1963). The surimi gel matrix becomes more compact and firm as starch granules bind water in protein gel matrix (Kim and Lee, 1987).

Optimization methods have contributed to solving engineering problems in the food industry; such as, evaporator system (Beesley and Rhinesmith, 1980), dehydration system

(Mishikin et al., 1982), heat processing (Lund, 1982), and operations of processing plants, to determine a management policy to minimize (or maximize) cost (or profit). With respect to finding an optimum state of food formulations, several methods such as a response surface methodology and linear programming have been used to develop new food formulations, especially for least cost, of several products such as meat, beer, ice cream, and cereal products as an optimization method (Evans, 1982; Arteaga et al., 1994). Moreover, the solution of LP gives useful information, such as, inventory control and purchasing decision from sensitivity analysis, as well as least cost formulation (Eppen et al., 1993). When an objective function indicates to minimize or maximize a response obtained from experiments, the objective value of LP can predict a response satisfying with other given constraints or boundary conditions. The effects of ingredient interaction on protein functionality was investigated by LP and forplex methods (Arteaga et al., 1993). When there were interactions between ingredients, more accurate optimum solutions could be obtained from forplex methods. For surimi seafood, the optimum use of LP formulation was allowed to select different levels and types of functional ingredients in addition to surimi, such as starch (Park, 1992).

Researches have determined the effect of ingredients on surimi gel functional properties (Lee et al., 1992; Park, 1994a). However, neither the interaction effect of starch nor desirable experimental design in mixture experiments was considered. In this study, our overall goal was to develop an optimization method for surimi seafood at minimum cost while maintaining the consistent quality of products. Specific objectives were to investigate the functional properties of each ingredient in mixture formulations and to develop mathematical models to determine the optimum formulation of surimi seafood. In addition, the optimization procedures for surimi seafood, such as experimental design, modeling, and data analysis, were established.

Chapter 2. LITERATURE REVIEW

FISH MYOFIBRILLAR PROTEINS (SURIMI) AND GELATION OF SURIMI

The muscle proteins can be classified into three groups; sarcoplasmic, myofibrillar, and stroma proteins (Hultin, 1985). Only myofibrillar protein, contributing the gelation of surimi, remains after washing and refining. The myofibrillar protein is composed of myosin (55-60%) and actin (15-30%).

The most important textural property of fish mince is the gelling property. Mulvihill and Kinsella (1987) defined protein gels as three dimensional matrices or networks in which polymer-polymer and polymer-solvent interactions occur in an orderly manner resulting in the immobilization of large amounts of water by a small portion of protein. The setting ability of fish pastes and development of elasticity in the heat-set gel are direct results of the thermodynamic requirement that entropy tends to increase (Niwa, 1992).

Fish myofibrillar proteins form a strong and elastic gel upon the heating of surimi gels. The microstructure of myofibril disappears by comminution with salt. The disappearance of this structure is caused by the dissolution of myofibrillar proteins in water with the aid of salt. Simultaneously, dissolved myosin combined with actin filaments yield macromolecular actomyosin. Both myosin and actomyosin have dominant roles in surimi gelation and show species specificities with regard to gelation properties (Numakura et al., 1985). The gelling characteristics of actomyosin are largely derived from the myosin portion of the molecule. The species-specificity of the myosin is inherent in the heavy-chain portion of the molecule (Niwa et al., 1980).

There are four types of bonds which contribute to the building of a network structure during the gelation of a surimi paste: salt linkage, hydrogen bonds, disulfide bonds, and hydrophobic interactions (Niwa, 1992; Lanier, 1996). The intermolecular salt linkages, which occur between charged amino acids of the protein chain, may play an important role in stabilization of the network structure of various food gels.

Hydrogen bonds are important in the stabilization of bound water within the hydrogel. A large amount of water molecules are hydrogen bonded to the polar amino acid residues, which are abundantly exposed on the molecular surface of the proteins. An intermolecular disulfide (SS) bond is formed by the oxidation of two cysteine residues. The formation of SS bonds is more intensive in carp (Itoh et al., 1979) and Atlantic croaker actomyosin (Liu et al., 1982) at the higher temperature (at 80°C or above) than at the lower temperatures at which setting occurs. This suggested that the unfolding of myofibrillar proteins is more intense at higher temperatures and the partly hydrophobic cysteine residues are more exposed. The hydrophobic bond is formed by heating protein. This bond is generally considered a hydrophobic interaction because it is formed, not by the spontaneous neutral action between the hydrophobic residues themselves, by the influence of the water. The major role of hydrophobic interactions in the setting of surimi paste at low temperatures was first suspected due to the fact that such setting is suppressed by sucrose and also by protein denaturatants such as concentrated urea and guanidine hydrochloride (Okada, 1963; Niwa and Miyake, 1971).

Cohesiveness, which is an indicator of gel deforming ability, of surimi gels was better than that of other food protein and hydrocolloid (Lanier, 1986). This cohesiveness is dependent on the quantity and quality of myosin in surimi (Nishioka et al., 1990). Gelation of fish mince is thermo-irreversible (Lanier, 1996).

The gel forming ability of fish myofibrillar protein is greatly improved through a low temperature setting (Montejano et al., 1984). The physical properties of surimi paste can change without heating. A low temperature setting enhances gelation of surimi (Niwa, 1992) by creating covalent bonds which affects the elastic and cohesive nature of gels (Lanier, 1986). The proper setting temperatures are most likely dependent on the fish inhabitant temperature (Kamath et al, 1992). The optimum setting temperature was 25°C for Alaska pollock surimi and Pacific whiting surimi (Howe et al., 1994).

Ohmic heating to cook surimi paste has been suggested due to its ability to control the heating rate (Yongsawatdigul and Park, 1996). Slow heating using ohmic heating improved shear stress but did not affect shear strain of pollock gels. Analysis showed that the increase of shear stress was due to the cross-link of myosin heavy chain through covalent bonds. Pacific whiting, containing an endogenous proteolytic enzyme, had lower shear stress and shear strain values upon slow heating rates.

TORSION TEST OF SURIMI GELS

The Japanese folding test has long been used for surimi gel texture assessments due to its simplicity and no need for a specific equipment, however, its results provide more subjective values of gels. Textural properties are expressed by some fundamental unit from standard tests, such as compressive test, tensile test, and torsion test. These tests can be executed with large or small deformation. Normally, small shear strain and compression moduli have not been consistent predictors of sensory texture (Hamann and Webb, 1979; Szczesniak, 1985). The compressive test is widely accepted as a measurement of strength. One of problem with testing surimi gels in axial compression is that required strains can be so large as to make material failure impossible (Hamann, 1983).

Torsion tests are widely used to evaluate the rupture properties of surimi gels because of failure shear stress and failure shear strain which showed strong relationships with sensory properties of food (Hamann, 1992) and its mechanical merits. Mechanical merits of torsion tests are that (1) there is no volume change during measurement, (2) pure shear stress and pure shear strain values can be obtained, and (3) tensile force, compression force and shear force are applied equally during measurement (Kim, 1996).

To determine the mechanical properties of solid food materials in terms of pure shear, the materials were assumed to be elastic. On the basis of the assumption, the theoretical equation to describe the rupture properties from the torsion tests were derived. The assumption is acceptable unless the viscoelasticities are mainly considered during measurement. Conditions and justifications for the assumption of elasticity in solid food have been discussed by Hamann (1983). A pure shear stress can be obtained using a torsion test where twisting moments are applied about a central axis. In order to minimize undesirable stress concentrations at the locations where the twisting moments are physically applied, torsion test specimens are milled to have a minimum diameter at midsection. The maximum shear stress occurs at the boundary of the minimum cross section for this specimen geometry (Kim, 1996).

EXPERIMENTAL DESIGN AND OPTIMIZATION

Experimental design in formula optimization

Experimental designs are currently viewed as a quality technology to achieve product excellence at the lowest possible overall cost (Joglekar and May, 1990). For certain problems, it may be that experimental points should evaluate all possible formulations. In a practical situation, several problems are created in terms of time and cost to conduct the experiment. It is designed to find a suitable experimental design in order to optimize food formulations.

Several experimental methods are widely accepted to optimize food formulations. They are full-factorial designs, fractional factorial designs (Taguchi's orthogonal arrays), response surface methodology, and mixture design. A full-factorial experimental design is used to investigate the response at all factor-level combinations of the independent variables. It is applied when the number of factors are very low and when the complete interactions between factors are needed. A fractional factorial design is used when many factors are considered and some key factors need to be determined. This technique is not used to optimize formulation, but it is used as a screening technique to select from a large number of factors (e.g., ingredients and processing factors) affecting a response (Arteaga et al., 1994). Response surface methodology (RSM) is currently the most popular optimization technique in food science, especially for food formulation and processing conditions, because of its comprehensive theory, reasonably high efficiency and simplicity (Box and Draper, 1987; Khuri and Cornell, 1990; Arteaga et al., 1994). RSM encompasses a group of techniques used to study the relationship between one or more responses and input variables.

In mixture experiment, the factors are the proportion of ingredients in a mixture and their levels are not independent of (Cornell, 1990). In most experiments, the response is assumed to depend on relative proportions of the ingredients forming the mixture. For n ingredients, the basic constraint in mixture experiment is:

$$\sum x_i = x_1 + x_2 + . . . + x_n = 1.0$$

where x_i represents the proportion of the i th component in the mixture. This constraint makes mixture experiments different from other factorial experiments.

A coordinate system for mixture design is called a simplex coordinate. If three ingredients are considered as factors, a triangular coordinate system defines the experimental space. There are two types of mixture designs. The first can be applicable when the formula being developed is composed of individual ingredients as well as mixtures of ingredients. The experimental design for these types of problems covers the entire simplex area. Several experimental designs have been developed for such problems: the most common ones are the simplex-lattice designs, the simplex-centroid designs, and the augmented simplex-centroid designs (Cornell, 1990). In a simplex-lattice designs, the experimental points are spread evenly over the whole simplex factor space (Hare, 1974; Park, 1994b). Simplex-centroid designs are composed of lattice designs with a centroid point (Park, 1994b). Cornell (1986) suggested an innovative design to improve fitting responses, which is called an augmented simplex-centroid design. This design supports the use of complex models such as the special quadratic model, and is especially useful for situations where the shape of the response surface is unknown. The augmented simplex-centroid design was used to study interaction effects in protein functionality (Arteaga et al., 1993).

In formulation development, constraints must be placed on the allowable minimum and maximum proportion of some or all of the components making up the mixture. Such mixture problems are termed constraint mixture problems. Extreme-vertices designs were suggested to solve these problems (McLean and Anderson, 1966; Hare, 1974). These designs include vertices, which are defined as combinations of limits of the ingredients (i.e., extreme vertices) and face, edge, and overall centroids. Because the values of the constraints determine the final experimental design, it is important to make sure that no conflict occurs among them.

The concept of optimization in food

In today's highly competitive and ever-changing market place, product development is essential for most food industries. It is necessary to create an efficient product development technique, for food formulation. Optimization is the best choice for an alternative from a specified set of choices (Arteaga et al., 1994). Therefore, optimization needs to describe potential alternatives and a way of deciding which alternative is best (Norback and Evans, 1983; Arteaga et al., 1994). Thus, formula development is essential prior to solving an optimization problem. Once the concept for a new food product is established, technical and marketing constraints must be considered to clearly estimate the technical feasibility of the concept. Once the model products have been formulated from the concept description, the next step is to optimize the new prototype product (Meyer, 1984). In optimization, the meaning of 'best' could have different meanings for different products. In one case, the best formulation could be the least expensive one satisfying certain limits, whereas other products qualities, such as, physical or chemical properties, could be used to define the best formulation. In formula optimization, the main objective is to find the best level for each key component or ingredient: in addition, the levels for critical processing variables may also be optimized. The dependent variables or response is the entity to be optimized (i.e., maximized or minimized). When several response are involved in an optimization problem, the multiresponse optimization technique can be applied. An important element of the food product optimization problem is the constraints. Constraints may limit the values of factors or response (Arteaga et al., 1994).

Optimization theories are broadly applied in food manufacturing as well as development of new formulations. Lund (1977) reviewed the principles involved in maximizing thermal processing for nutrient retention, and Ohlsson (1980 a, b) performed similar research maximizing the sensory quality in canned foods. Teixeira et al. (1969) demonstrated by simulation that thermal gradients in conduction-heating foods in containers gave rise to an optimum retort time/temperature treatment for maximizing nutrient retention. Teixera et al. (1969) reported the code for calculating the optimum thermal process with constant retort method for performing the calculation. Those were accomplished by Thijssen et al. (1978) in a short-cut method for calculating sterilization conditions for optimum quality retention.

Linear programming

There is a need to use the optimization technique to determine the optimum formula. Linear programming (LP) is widely used in formula development. LP is a mathematical technique to optimize problems involving a linear objective function with linear constraints on the variables. LP is mainly used to find least-cost formulations that meet specific linear constraints (Norback and Evans, 1983; Park, 1992). There are strong limitations for the use of LP in the optimization of food product, due to its proportionality, additivity, divisibility, and certainty (Hiller and Lieberman, 1990). Chan and Kavanagh (1976) reported the use of a fractional factorial design and LP in the optimization of light-duty liquid detergent. Their research demonstrated that the formulation could be optimized by LP although some properties are nonlinear. Linear programming (LP) has been used to develop new food formulations, especially in terms of least cost, for several products such as meat, beer, ice cream, and cereal products as an optimization method (Evans, 1982; Arteaga et al., 1994).

Many examples using LP in the food system, especially for food formulation, were reviewed and explained (Norbak and Evans, 1983). Blending of meat was used as a good example of LP to determine an optimum blending ratio of frankfurters, bologna, sausage, etc (IBM, 1966). Another food product which has been successfully formulated in industry using LP is icecream (IBM, 1964; Singh and Kalra, 1979). A detailed example in the Danø (1974) reference illustrates the value of LP in finding the optimal formulation of icecream from an overwhelming number of alternatives. A major concern in cereal-based foods is that adequate levels of protein be present in the formulation. Inglett et al. (1969) used LP to find the essential amino acid pattern of a cereal-based food which showed a similar pattern to hen's egg. Cabins et al. (1972) used LP to formulate a least cost cereal-based food. The protein quality was controlled by setting both lower and upper limits on each essential amino acid in terms of its percent of total essential amino acid content. Wadsworth et al. (1979) described the formulation of a cereal-based product using an indirect approach which can be solved by LP. Hsu et al. (1977a,b) studied the blending of a wide range of plant and animal protein sources in formulation for bread, pasta, cooking an extruded corn-meal snack, and sausage. Constraints of LP were used to control both the nutritional and functional properties. LP was also fully applied for beer-blending problem (Danø, 1974). Bender et al. (1976) introduced LP to control the level of a low cholesterol, low fat beef stew. The objective was to minimize cost while enforcing nutritional constraints based on the recommendations for fat-modified and low cholesterol diets.

For the surimi seafood, the use of LP has been applied in blending various kinds of surimi lots. Texture and color properties in blended surimi products were an approximate linear function of the mass of each surimi lot added to the formulation (Lanier and Park, 1989).

Nonlinear programming

Response surface methodology (RSM) is widely applied in the food system when the response showed nonlinearity (Moquet et al., 1992). Daley et al. (1978), optimizing a sausage product from minced fish using RSM, showed that the relationship between texture properties and ingredient levels were nonlinear. Pearson et al. (1962) described the application of RSM to determine the optimum levels of salt and sugar in cured ham. Their objective was a taste-panel score. Smith and Rose (1963) investigated the effect of various levels of flour, shortening, and water on the quality of a pie crust. Quality was evaluated based on flakiness, gumminess, and specific volume. Kissell (1967) reported on the formulation of a white layer cake improved varying the level of seven ingredients. The cakes were evaluated on the basis of volume, top-contour shape, and internal score. Henika (1982) described the application of RSM to sensory data to guide the formulation of products. Hasting and Currall (1989) also showed significant interactions between ingredients and the texture of cod surimi gels. Chen et al. (1993) demonstrated the advantage of use of RSM compared with LP in terms of optimization of surimi seafood textural properties because of the nonlinear properties of additives. The nonlinear effect of protease inhibitors and gel strength enhancers on Pacific whiting surimi gels were studied by Hsu (1995). The strong nonlinear effect of beef plasma protein (BPP) as a protease inhibitor was determined.

Theory of Derringer and Suich methodology

The desirability function approach is an analytical technique for optimization of multiresponse-multifactor systems. It was first developed by Harrington (1965) and later modified and extended by Derringer and Suich (1980). The method calculates individual and overall desirabilities associated with each response and the whole system, respectively. It simply permits subjective judgement on the importance of response variables, but it has very few applications to optimize biological systems or food processes (Guillou and Floros, 1993).

When several response variables y_1, y_2, . . . , y_m have been represented by fitted equations Y_1, Y_2, . . . , Y_m based on the same set of coded input variables x_1, x_2, . . ., x_k, the equation often arises of where in the x space the best overall set of response values might be obtained. When there are only two or three important input variables, it is possible to solve this problem by superimposing at the response contours for the different fitted responses Y_1, Y_2, . . . , Y_m simultaneously by overlaying of various contour diagrams, When the problem can be expressed as one of maximizing or minimizing one response subject to constraints in the others linear programming methods can sometimes be used advantageously. A different approach is to introduce an overall criterion of desirability (Derringer and Suich, 1980). Suppose we choose, for each response, levels $A \leq B \leq C$ such that the product is unacceptable if $Y < A$ or $Y > C$ so that the desirability (d) of the product increases between A and B and decrease between B and C. When the responses are out of range, d = 0. Overall desirability is defined as $D = (d1, d2, d3 \, .. dm)^{1/m}$, where di is the desirability function for the i th response, i = 1,2,...,m. The maximum of D can be sought to give the most desirable point for all responses simultaneously. Box and Drapper (1987) mentioned that great caution is needed in the application of these methods. If used mechanically, they can sometimes lead to unanticipated conditions that are not practically desirable.

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Chapter 3.

Linear Programming in Blending Various Components of Surimi Seafood

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Submitted to Journal of Food Science,
Institute of Food Technologist, Chicago, Illinois
1996

II. Linear Programming in Blending Various Components of Surimi Seafood.

ABSTRACT

Shear stress, shear strain, and whiteness of surimi gels made with high and low grades of Alaska pollock and Pacific whiting were investigated to determine linearity. A canonical form of least square linear model in mixture design showed a greater linearity (r^2=0.99) for blending high and low grade surimi lots. Due to their linearities without interaction ($p<0.001$), a least cost linear program provided optimum blending for surimi lots based on cost, constraints, and decision variables. However, the use of the linear program to determine an optimum formulation of surimi with various starches and water content was not feasible due to the interaction between surimi and starch, or starch and water.

Key words: optimization, linear programming, mixture design, surimi

INTRODUCTION

Surimi, stabilized fish myofibrillar protein, is commonly used as an ingredient of surimi seafood. Surimi seafood plays an important role in the U.S. seafood market with an annual consumption of 160 million lbs in 1994 (Park, 1995a). The success of surimi seafood was based on better utilization of raw materials, longer shelf life of frozen surimi, and variety and consistent quality (Okada, 1992). The gel functionality of surimi seafood, such as texture and color, is the most important aspect of product quality. Textural properties of surimi seafood are most accurately characterized by failure shear stress and strain value (Lanier, 1992). Blending various grades of surimi maintained the consistent functionalities and minimum cost of surimi seafood (Lanier, 1988; Park, 1992). Starch is the main ingredient in controlling functionalities and cost of surimi seafood (Okada, 1963). The surimi gel matrix becomes more compact and firm as starch granules bind water in the protein gel matrix (Kim and Lee, 1987).

Although linear programming (LP) has limitations, such as, proportionality, additivity, divisibility, and certainty (Hiller and Lieberman, 1990), it has been used to develop new food formulations (Arteaga et al., 1994). To determine a least cost formulation, LP was applied to several food products, such as, meat, beer, ice cream, and cereal products as an optimization method (Evans, 1982; Arteaga et al., 1994). LP can predict a minimized (or maximized) objective function with a response satisfying other given constraints as well as high and low limitations. The solution of LP could provide inventory control and purchasing decisions from sensitivity analysis, as well as least cost formulation (Eppen et al., 1993). The LP formulation for the surimi seafood can be successfully used if interactions between different levels of ingredients are not allowed (Park, 1992). Chen et al. (1993) reported that both LP model and response surface methodology (RSM) could be used to find the optimum gel strength of surimi mixed with starch and egg white. The effects of ingredient interaction on protein functionality were investigated by LP and forplex methods (Arteaga et al., 1993). Compared to LP, the forplex method provided more accurate optimum solutions to detect the interaction effect of ingredients.

Factors affecting functionality are represented as proportions of components with levels dependent upon each other. Therefore, it is a basic constraint that the sum of all ingredients functions must be 1 (or 100%) (Hare, 1974; Cornell, 1981). To determine the effect of each factor in a formulation, a mixture design is commonly used for an experimental design. The method is employed when the fraction range of each component is from 0 to 100%.

Objectives of this study were to develop an optimization method of surimi seafood at a minimum cost with consistent quality, and to investigate the possible application of linear programming in blending various components of surimi seafood.

MATERIALS & METHODS

Surimi and starch

A high grade (FA) of surimi from Alaska pollock (Arctic Storm, Seattle, WA) and Pacific whiting (Point Adams Packing Co., Hammond, OR) were used to evaluate gel functional properties. Four blocks (10 kg each) of surimi were cut into small pieces (~1000 g each) and randomly stored, to eliminate the statistical difference of each block, in the freezer at -25°C. Low grade surimi was prepared by thawing (48 hrs at 25°C) and refreezing the high grade surimi. The surimi was stored at -25°C. The moisture content of pollock and whiting surimi was 75% (±0.5) and 74.5% (±0.5), respectively, according to the AOAC method (1990). Surimi gels were prepared with different moisture contents at 75, 77.5, 81, 83, and 85.5%. Six commercial starches [wheat starch (W) and modified wheat starch (MW) (Midwest Grain, Atchison, KS), corn starch (C) and modified waxy corn starch (MWC) (American Maize, Hammond, IN), and potato starch (P)and modified potato starch (MP) (Roquette, Keokuk, IA)] were used for the study. Effects of each component on functional properties of surimi gels were investigated.

Surimi gel preparation

Partially thawed surimi tempered at room temperature for 2 hr was chopped in a food processor (Stephan Machinery Corp., Columbus, OH) at low speed for 1.5 min. Salt was added to extract salt soluble proteins and chopping was continued for 0.5 min. Other ingredients, such as starch and water were added into the paste and chopped for 1 min. For surimi gels with starch, the level of salt and moisture content was standardized at 2 and 75 %, respectively. Chopping continued for 3 min at high speed with vacuum (0.6-0.7 bar). The chopping temperature was controlled, not to exceed 8°C, using a refrigerated circulator (NesLab, Portsmouth, NH) containing a solution (50:50) of ethylene glycol and water (50:50). A sausage stuffer (The Sausage Maker, Buffalo, NY) was used to stuff raw paste into stainless steel tubes (ID = 1.9 cm, length = 17.5 cm) with screw caps. The interior wall of the tubes was coated with cooking oil spray. The tubes were submerged in a 90°C water bath simultaneously and cooked for 15 min. Cooked gels were cooled in ice water, and a refrigerated for 24 hr for analysis of functional properties.

Functional properties of surimi gels

To measure the textural functionality, cooled gels (5°C) were held at room temperature for 2 hr (Howe et al., 1994). Ten gels were milled into dumbbell geometry (length = 2.9 cm, end diameter = 1.9 cm and minimum diameter = 1.0 cm), and then was tested to measure the failure shear stress and failure shear strain using a torsion gelometer (Gel Consultants, Raleigh, NC). Five samples from each treatment were chosen for color analysis using a Minolta CR300 colorimeter (Osaka, Japan). CIE L*, a*, b* values were measured and whiteness was calculated by the equation, L* - 3b* (Park, 1994; 1995b).

Experimental design and modeling

An optimization procedure for surimi blending is illustrated in Fig. 3.1. Data analysis and optimization were accomplished using spread sheet software, Quattro Pro (Novell, Inc., Orem, UT). Mixture design was used to determine the ratios between high and low grade surimi lots.

In a mixture design, the fractions of components are correlated with each other and a least square linear regression model is not applicable because of the correlation of independent variables (Cornell, 1981). Thus, the linear regression model include only n-1 terms of coefficient when the number of components is n (Eq. 3.1):

$$Y = \beta_1 X_1 + \beta_2 X_2 + \ldots + \beta_{n-1} X_{n-1} + \beta_0 \qquad \text{(Eq. 3.1)}$$

where X represents the fraction of each component, and n, β_n and β_0 are the number of components, coefficient of the n^{th} component, and intercept term, respectively. This equation indicated that the coefficients (β) of independent variables in the model have a limitation to express the effects of all components in the mixture. However, these limited coefficients, of all components, should be available to compose an LP model and to obtain a feasible solution.

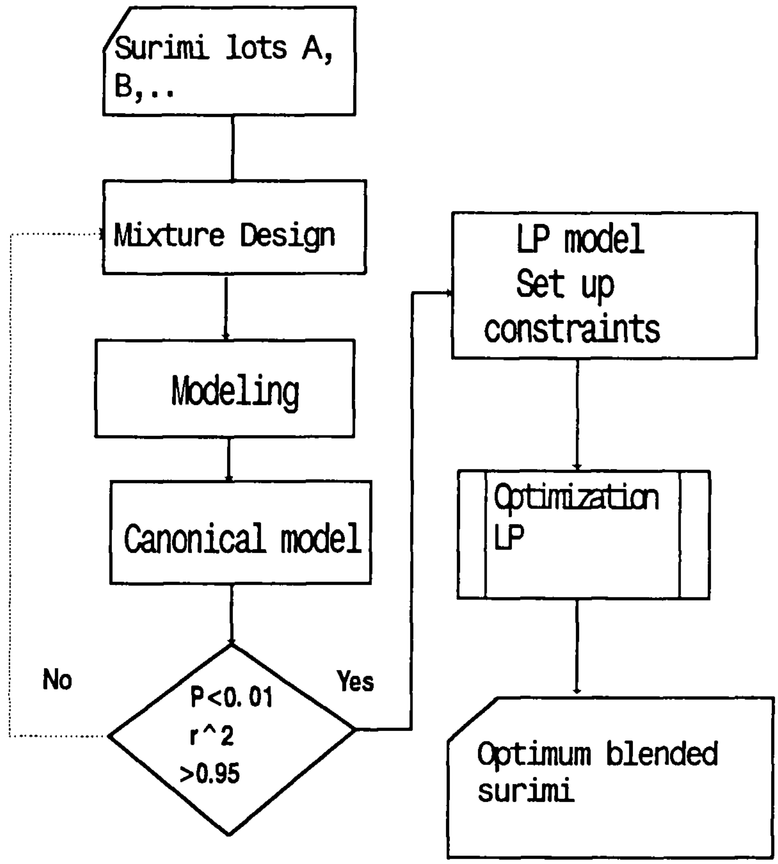

Fig. 3.1. Optimization outline for surimi seafood using linear programming (LP)

A canonical form of a least square linear model is composed of the coefficients of all components (Eq. 3.2). Instead of using an intercept term, a canonical model contains the new coefficient term which is not shown in a least square regression model.

$$Y = \beta_1 X_1 + \beta_2 X_2 + \ldots + \beta_{n-1} X_{n-1} + \beta_n X_n \qquad \text{(Eq. 3.2)}$$

This canonical form demonstrates the effects of all components to provide a feasible solution in the LP model. In this study, linear models with canonical form were built by modified least square regression (Cornell, 1981) and evaluated in terms of F-test for model and regression coefficient (r^2).

Least cost linear programming model for surimi blending

The least cost linear programming (LCLP) model including an objective function, decision variables, and constraints for surimi blending, are summarized in Table 3.1. The coefficients of the objective function of LCLP were the cost of each variable ($0.75-1.25/lb) depending on quality and species of surimi. The value of the objective function, the cost, was set to be minimized to obtain a least cost formulation.

To formulate an LCLP model for the surimi seafood, shear stress, shear strain, and whiteness of various grades of surimi lots were used as decision variables. The first order canonical models were employed for LCLP to represent the activity of each decision variable.

Table 3.1. Least cost linear programming model.

Objective function (Cost: $/lb)	*X_1 X_2 X_3 X_4	1.25 0.80 1.05 0.75
Canonical form for decision variables	Shear stress Shear strain Whiteness	** $\alpha_1X_1 + \alpha_2X_2 + \alpha_3X_3 + \alpha_4X_4$ $\beta_1X_1 + \beta_2X_2 + \beta_3X_3 + \beta_4X_4$ $\gamma_1X_1 + \gamma_2X_2 + \gamma_3X_3 + \gamma_4X_4$
Target Constraints	Shear stress Shear strain Whiteness Weight ($\sum Xi$)	$\geq$ 38 kPa $\geq$ 2.5 $\geq$ 70 = 1
Limitation of each component	Upper Lower	1 0

* X_1: Pollock high grade, X_2: Pollock low grade, X_3: Whiting high grade, X_4: Whiting low grade.

** α, β, and γ represent the coefficient of each canonical model to express each response, respectively.

As indicated in Table 3.1, target constraints for shear stress, shear strain, and whiteness were set at ≥38kPa, ≥2.5, and ≥70, respectively (Park, 1990). The optimization procedures of the LCLP for surimi blending were executed using Quattro Pro (Novell, Inc., Orem, UT).

RESULTS & DISCUSSION

Blending different grades of surimi

Blending different grades, such as, high (H) and low (L), of pollock and/or whiting surimi in different proportions showed the linearities of shear stress, shear strain, and whiteness (Fig. 3.2,3&4). There was no interaction between different grades of surimi lots (H*L) in blending as shown in high r^2 (>0.99) and low p-value (<0.001). According to Hare (1974), the minimum experimental point is two for a linear model when the number of components is two. However, in this study, the number of experimental points was set at three to determine an interaction between H and L grade surimi. Different ratios of high to low grade were used, such as, 1:0, 0.5:0.5, and 0:1, respectively. Since the linear effect of blending surimi on each functionality was determined in the range of 0-100%, the first order canonical model was developed and employed for an LP model. The linearity of blending different grades of surimi existed in all ranges of independent variables (Fig. 3.2,3&4). The functionality of each surimi was individually measured, before blending and the coefficient of each variable in canonical form of linear regression model was calculated. The final equation for the optimum formulation was developed as follows (Eq. 3.3):

Functional property of the blend

= [(% surimi 1) x (functional property of 1) +

(% surimi 2) x (functional property of 2) + ...

+ (% surimi n) x (functional property of n)]

= Σ [(% surimi i) x (functional property of i)] (Eq. 3.3)

The stress values of blended pollock H and L at any proportion were estimated by the following canonical model form: Stress of the blend = 64.5 x (% of high grade) + 28.24 x (% of low grade), where 64.5 and 28.24 represented the stress values of 100% pollock H and L grade, respectively (Fig. 3.2).

Since the functionalities of blended surimi showed a linear relationship and proportionality to the quantity of each surimi, blending surimi from 4 different lots (H and L grade of pollock and whiting) was optimized using LCLP, based on the cost and constraint variables (Table 3.1) and decision variables (Table 3.2). Decision variables were quite different depending on quality and species of surimi: shear stress (23.5-64.5 kPa), shear strain (0.85-2.75), and whiteness (63-85).

The optimum blending for the least cost was 39% H grade pollock, 12% L grade pollock, 49% H grade whiting, and 0% of L grade whiting (Table 3.3). This blending formulation with different levels of surimi not only exceeded the target

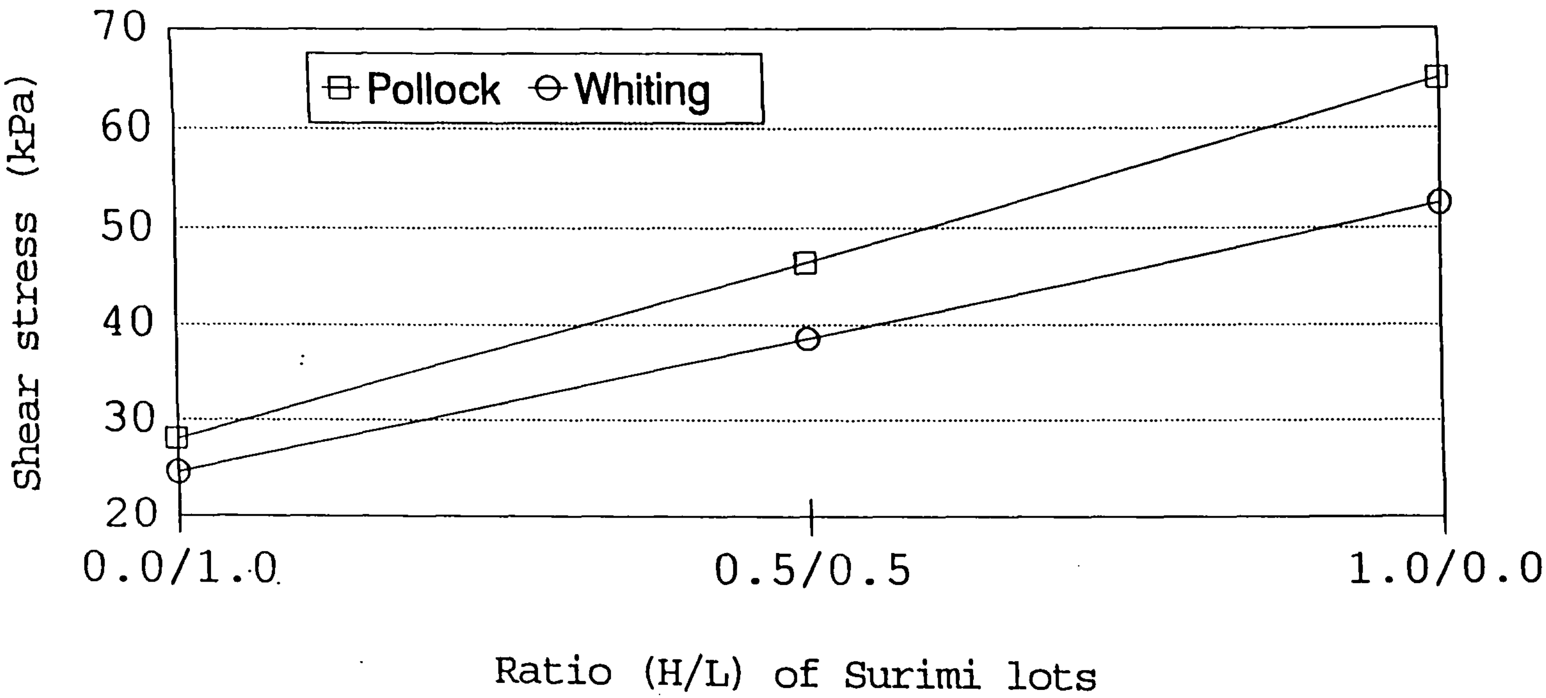

Fig. 3.2. Effect of blending surimi lots on the failure shear stress. The linearity of blending various gades of surimi lots was proved by their $r^2 > 0.99$ and $p < 0.0001$ (H: high grade, L: low grade of surimi)

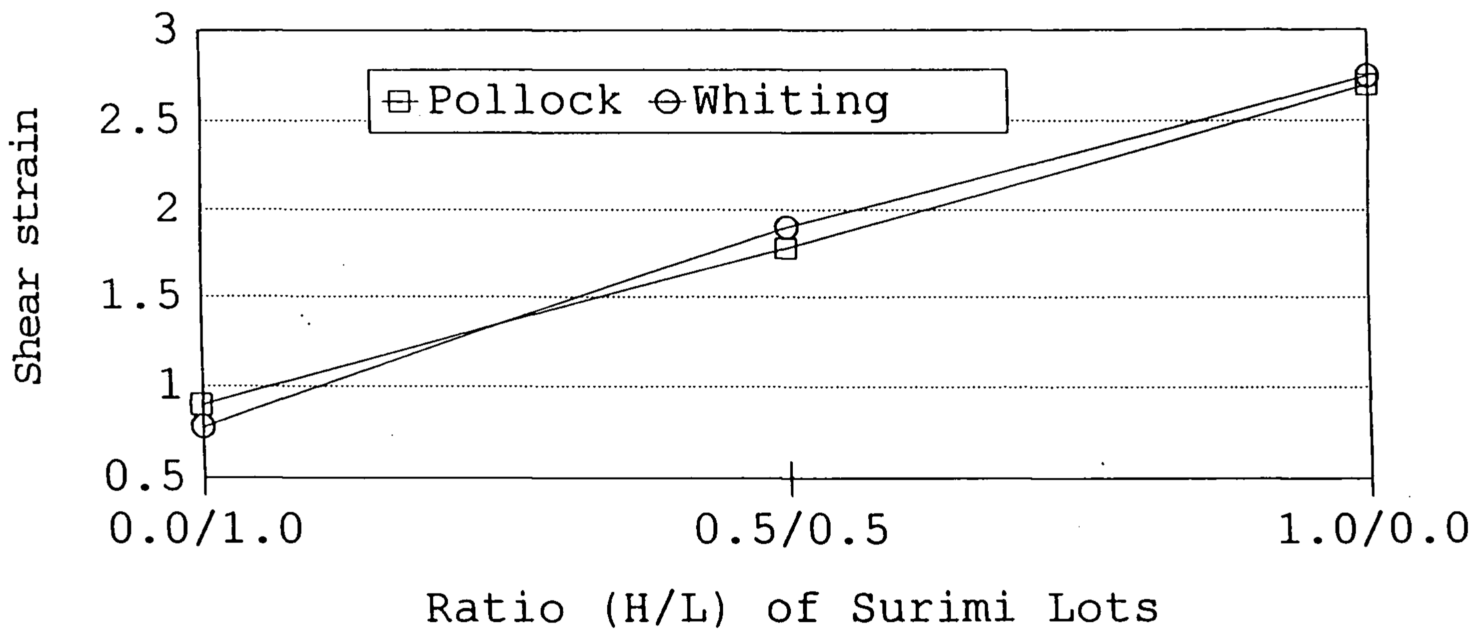

Fig. 3.3. Effect of blending surimi lots on the failure shear strain. The linearity of blending various gades of surimi lots was proved by their $r^2 > 0.99$ and $p < 0.0001$ (H: high grade, L: low grade of surimi)

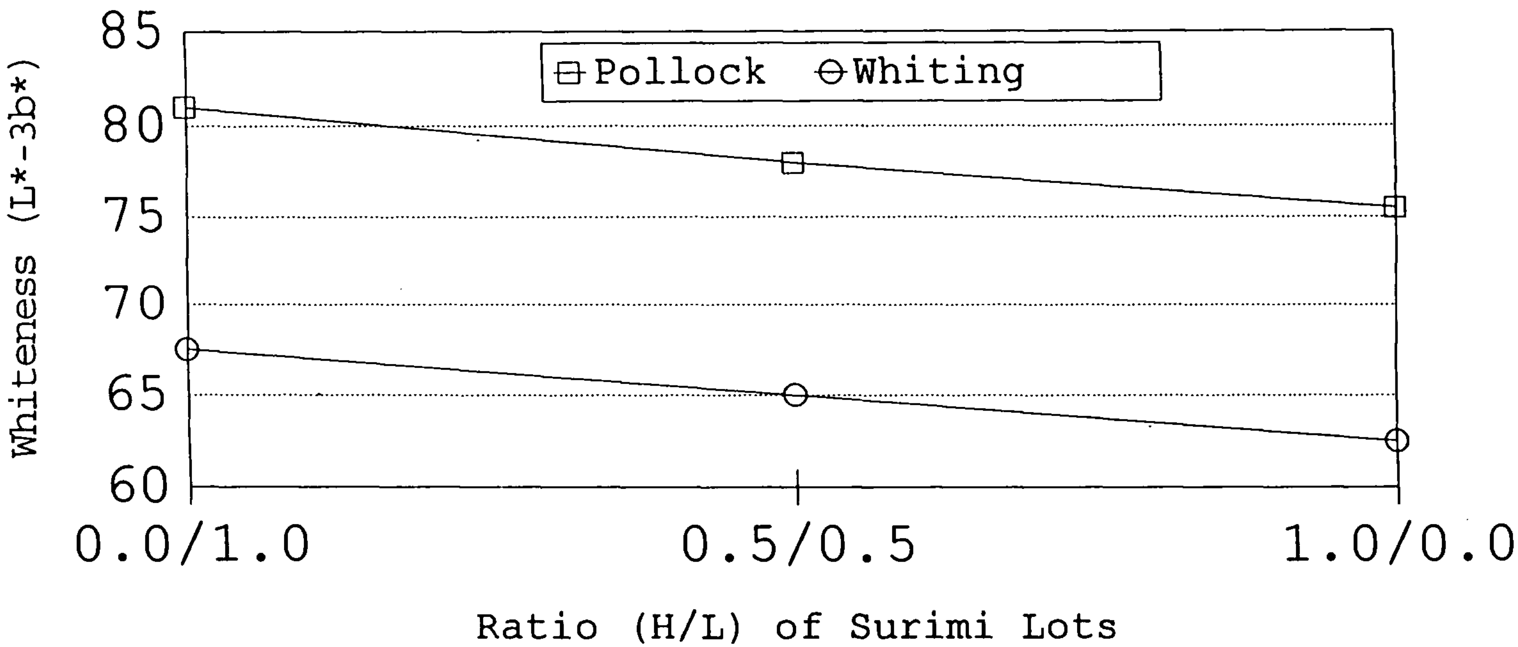

Fig. 3.4. Effect of blending surimi lots on the whiteness. The linearity of blending various grades of surimi lots was proved by their $r^2 > 0.99$ and $p < 0.0001$ (H: high grade, L: low grade of surimi)

Table 3.2. Coefficient of each component in the canonical form of linear regression model.

Response	Pollock		Whiting	
	High	Low	High	Low
Shear stress (kPa)	64.50	28.20	52.50	23.50
Shear strain	2.65	0.93	2.75	0.85
Whiteness	75.50	81.00	63.00	67.00

Table 3.3. Computer output of optimum surimi blending using LCLP

Surimi Code	A	B	C	D		
Surimi	Pollock	Pollock	whiting	Whiting		
Lot/Grade	High	Low	High	Low		
Price ($/lb)	1.25	0.8	1.05	0.75		
						Target
Shear stress	64.5	28.2	52.5	23.5	≥	38
Shear strain	2.65	0.93	2.75	0.85	≥	2.50
Whiteness	75.5	81	63	67	≥	70
Weight	1	1	1	1	=	1
Objective Value ($/lb)		1.10	**<Least Cost>**			
Surimi Code	A	B	C	D		
Fraction	0.39	0.12	0.49	0.00		
Lower limit	0	0	0	0		
Upper limit	1	1	1	1		
Constraints of Blended Surimi						
Shear stress	54.41					
Shear Strain	2.50					
Whiteness	70.00					
Weight	1					
Total fraction	1					

constraints in functionality but also provided the least cost ($1.10/lb). This surimi blending experiment was carried out withconstant moisture content (75%). Although blending various grades appeared to be a good method to obtain consistent quality and least cost for surimi only, it is logical to investigate the feasibility of controlling moisture content and adding other ingredients to determine a least cost formulation of surimi seafood.

Effect of moisture content on gel functionality

The addition of water to surimi seafood is indispensable to maintain acceptable texture as well as to minimize the cost of raw materials. Shear stress of both H and L grade pollock linearly decreased from ~65 to ~3 kPa (r^2=0.97) and ~48-~3 kPa (r^2=0.94), respectively, as moisture content increased from 75 to 85.5% (Fig. 3.5). Pacific whiting showed the same trends as pollock. Shear stress of both H and L grade of Pacific whiting decreased linearly from ~53 to ~3 kPa (r^2=0.97) and ~45-~3 kPa (r^2=0.99), respectively. Shear strain, commonly referred to as an indicator of protein quality (Hamann and MacDonald, 1992), was not affected within a certain range of moisture content (Fig. 3.6). Shear strain values of both H and L grade pollock surimi were not affected by the moisture contents between 75-81%. However, their values decreased linearly from ~2.6 to ~1.9 (r^2=0.94) and ~2.1-~1.5 (r^2=0.99), respectively, as higher moisture content changed from 81-

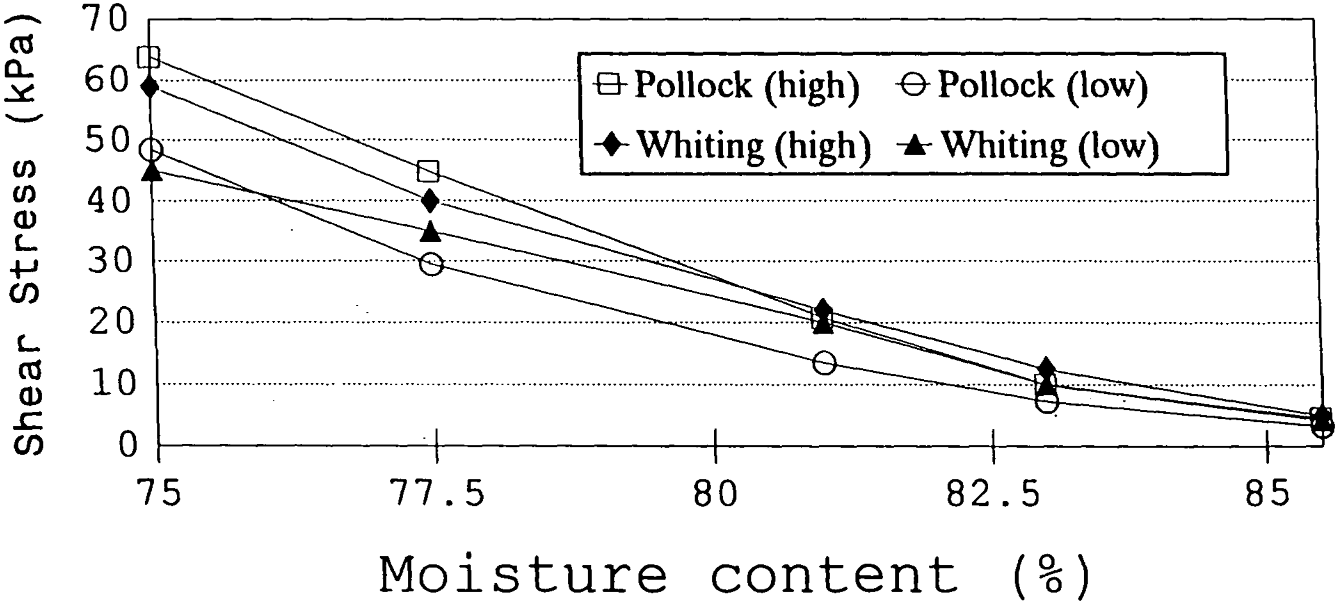

Fig. 3.5. Effect of moisture on failure shear stress of Alaska pollock and Pacific whiting surimi gels.

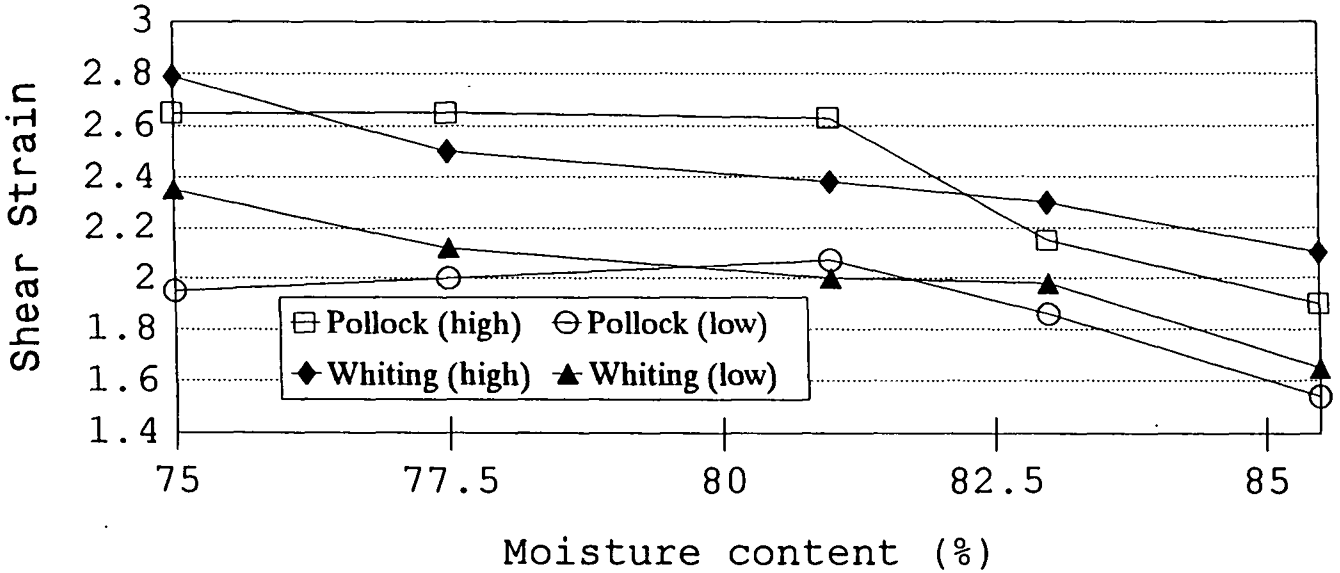

Fig. 3.6. Effect of moisture on failure shear strain of Alaska pollock and Pacific whiting surimi gels.

85.5%. Unlike pollock, shear strain of Pacific whiting gel behaved differently with varied moisture contents. Their values decreased linearly from ~2.75--~2.1 (r^2=0.94) for H grade and from ~2.35--~1.65 (r^2=0.91) for L grade as the moisture contents increased from 75-85.5% (Fig. 3.6).

A significant effect of water on shear stress of pollock surimi while an insignificant effect of water on shear strain has been reported previously by other researchers (Lanier et al., 1985; Hamann and MacDonald, 1992). Lanier et al. (1985) reported shear stress of Alaska pollock gel dropped from 80-27 kPa as moisture content increased from 75-79%, while strain dropped only slightly, 2.9-2.7, indicating that shear strain was influenced much less by moisture content (or protein content inversely) than shear stress. At a constant temperature condition, shear stress values are proportional to the concentration of crosslinked polymers and shear strains are proportional to the mean molecular weight of the chains adjoining adjacent crosslinks (Treloar, 1975; Hamann and MacDonald, 1992). These observations coincided with our results that shear stress values decrease with reduced concentration of fish protein. Hamann and MacDonald (1992) and Amato et al. (1989) reported that higher strain values were associated with lower free moisture in surimi gels depending on species. Our observation appears to result from the difference in amount of free water in surimi gels. As the amount of moisture content increased over 75% for whiting and

81% for pollock, in our study the strain values decreased dramatically in both surimis.

Modeling and optimization for surimi and water combination

Based on the above results (Fig. 3.4,5,&6), a canonical model including the fraction of components was applied to linear programming with lower and upper limits of moisture content. However the canonical model contained linear terms, such as surimi (S) and water (W), as well as a non-linear (interaction) term (S*W). The result of r^2 values, as an index of linearity calculated from linear regression analysis in surimi and water combinations, is shown in Table 3.4. Shear stress showed greater r^2 values (0.94-0.99), whereas shear strain showed lower r^2 values (0.47-0.95). The addition of water to surimi is less effectively applicable to the LP due to its poor linearity.

The addition of water apparently affected the textural property of surimi gels (Fig. 3.3). However, the highest textural properties, such as shear stress and strain, were obtained at 75% moisture content. No optimum solution for least cost may exist when the constraint values are higher than the highest textural properties of surimi gels containing moisture >75%. Thus, it has a limitation to develop an optimization model for a practical purpose. It is desired to investigate the possible addition of other ingredients for a least cost formulation of surimi seafood.

Table 3.4. r^2 values from linear regression analysis for surimi and water combination.

Component	Pollock		Whiting	
	High	Low	High	Low
Shear stress	0.98	0.94	0.98	0.99
Shear strain	0.76	0.47	0.95	0.91

Table 3.5. r^2 values of linear regression analysis for starch and surimi combination.

Response	MP	P	MW	W	MWC	C
Pollock, High						
Shear stress	0.19	0.29	0.61	0.81	0.07	0.39
Shear strain	0.66	0.50	0.44	0.21	0.73	0.81
Whiting, High						
Shear stress	0.00	0.00	0.35	0.50	0.00	0.37
Shear strain	0.13	0.47	0.51	0.11	0.00	0.30

(MP: modified potato starch, P: potato starch, MW: modified wheat starch, MWC: modified waxy corn starch, W: wheat starch, and C: corn starch)

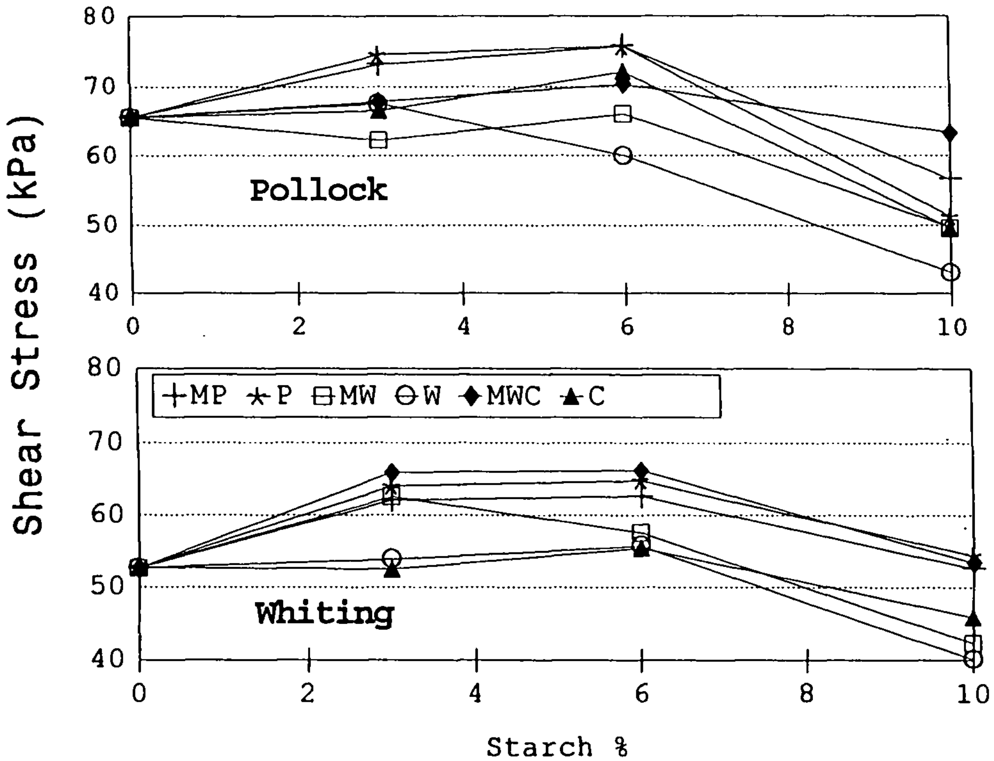

Fig. 3.7. Effect of starch on failure shear stress of pollock and whiting surimi gels. MP:modified potato starch, P:potato starch, MW:modified wheat starch, W:wheat starch, MWC:modified waxy corn starch, and C:corn starch.

Effects of starch on gel functionality

The overall effects of added starch on shear stress of both pollock and whiting surimi were highlighted when the starch content increased from 0-6% (Fig. 3.7). The texture-reinforcing ability of starch in surimi gels was explained by its swelling and water uptake during gelatinization upon heating (Lee et al., 1992). When 10% starch was added, failure shear stress values reduced significantly for all starches indicating that starch inhibits gelation of fish proteins by competing for available water (Park et al., 1996). Shear strain of surimi gels with added starch responded differently from shear stress. Shear strain values of pollock-starch gels, except MWC, slightly increased with starch content from 0-3%. However strain values remains constant with starch up to 10%, except starch and MWC (Fig. 3.8). Whiting-starch gels (except MWC) did not exhibit any significant difference in shear strain as the starch content increased up to 10%. In general, at the higher level of starch (6-10%), shear stress decreased while shear strain maintained constantly indicating the presence of interaction between surimi and starch.

Modeling and optimization for surimi and starch combination

The addition of starch improved textural properties of surimi gels as well as decreased the cost. However, the r^2 values in every combination of starch and surimi were less

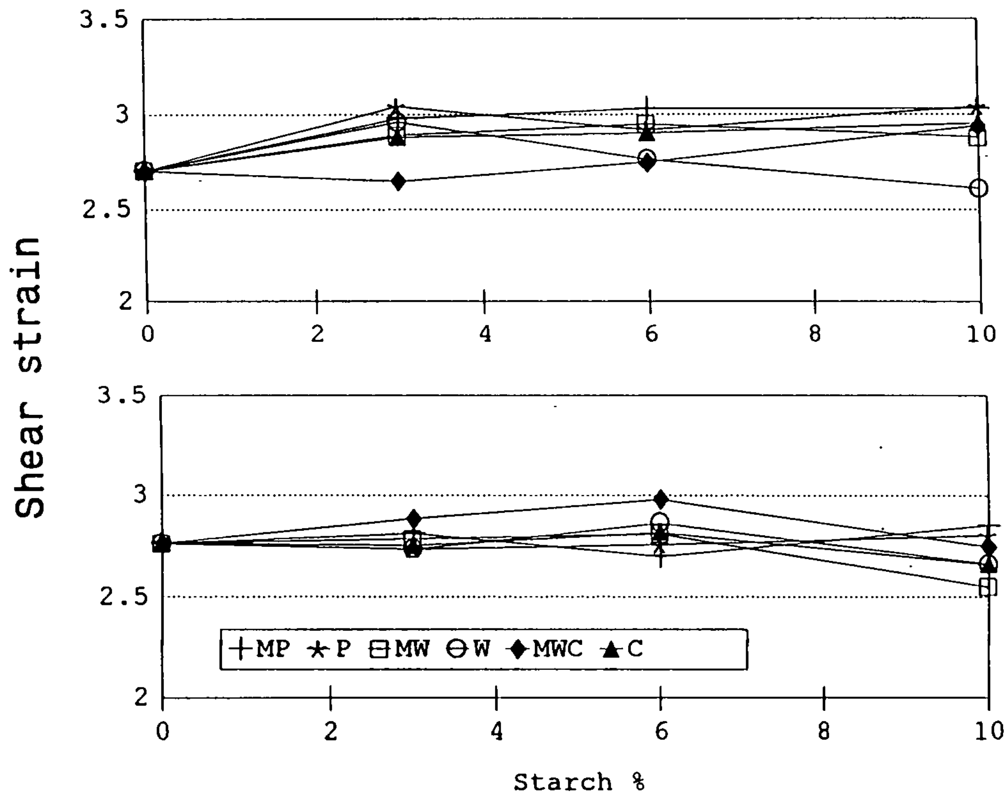

Fig. 3.8. Effect of starch on failure shear strain of pollock and whiting surimi gels. MP:modified potato starch, P:potato starch, MW:modified wheat starch, W:wheat starch, MWC:modified waxy corn starch, and C:corn starch.

than 0.81 (Table 3.5). The effects of starch (St) on surimi (S) gels are represented by both the linear (S and St) and nonlinear term (S*St) in the formulation. The results also revealed that changes of response were dependent on the different species (pollock and whiting) of surimi. Pollock surimi showed higher r^2 value (0.19-0.81) than whiting (0-0.51). Lee et al. (1992) reported that texture-reinforcing effects of starch on surimi gels were greater with low grade surimi than with high grade surimi. Thus, it is recommended to standardize surimi lots by blending different grades of surimi before investigating effects of starch on surimi gel and developing an optimization model. For surimi seafood containing surimi, water, and starch, it was necessary to investigate the interactions between mixture before being applied to linear programming. Therefore, another experimental design needs to be introduced to determine the interaction effect of each component on the final product (Yoon et al., 1996a).

CONCLUSIONS

Linear programming was successfully applied to determine the least cost blending of various surimi lots due to their strong linearities and no interaction between different grades of surimi. Effect of moisture content on gel functionality showed a linear and nonlinear pattern depending on the species of surimi and a specific range of moisture content. The use of starch for various surimi seafood was a possible solution for least cost. However, starch addition did not fit to linear programming due to the interaction term between starch and surimi (St*S) or starch and water (St*W).

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Chapter 4.

Study of Surimi-Starch Interactions using Mixture Design and Regression Models

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Submitted to Journal of Food Science,
Institute of Food Technologist, Chicago, Illinois
1996.

III. Study of Surimi-Starch Interactions using Mixture Design and Regression Models

ABSTRACT

Interaction effects of starch mixtures within surimi gel were investigated by modified distance-based design and analyzed by linear and nonlinear backward regression model. The addition of starch into surimi enhanced gel texture, but decreased the whiteness of surimi gels. Nonlinear regression models showed highly significant interaction terms of starch-surimi, starch-water, and starch-starch. The response trace plot revealed that shear stress and shear strain were quite sensitive to changes in the amount of various starch components, whereas whiteness was positively affected by water, but negatively affected by starch. Linear programming showed the addition of corn and modified waxy maize starch strongly improved the functional properties and reduced the cost of surimi seafood.

Keyword: surimi, starch, mixture design, trace plot, linear/nonlinear programming.

INTRODUCTION

Surimi is the stabilized fish myofibrillar protein that is used as a raw material for surimi seafood. The consumption of surimi seafood has reached nearly 160 million pounds a year in the U.S. seafood market (Park, 1995). Starch is the second most important ingredient used to control the functionalities and cost of surimi seafood (Okada, 1963; Kim and Lee, 1987; Yoon et al., 1996b). Starch granules fill the interstitial spaces of the fish protein network, swell in water surrounding the protein matrix, and expand themselves until the granules are confined by the matrix resulting in a cohesive and firm gel structure (Lee and Kim, 1986; Park et al., 1996).

Several optimization methods were studied to solve engineering problems in the food industry, such as evaporator systems (Beesley and Rhinesmith, 1980), dehydration systems (Mishikin et al., 1982), heat processing (Lund, 1982), and management policies to minimize cost. Linear programming has also been used as an optimization technique for surimi seafood (Chen et al., 1983; Lanier 1988; Hsu 1995; Yoon et al., 1996b). Yoon et al. (1996b) demonstrated a good feasibility of linear programming for least cost blending of various surimi grades. Since compositional variables, quality parameters, and constraints in linear programming are expressed in the form of linear equations, linear programming dose not provide an adequate solution for multi-ingredient mixtures due to their interactions (Arteaga et al., 1993; Yoon et al., 1996b).

With respect to finding optimum formulations, response surface methodology (RSM) and simplex methods are commonly applied to determine the interaction effect (Johnson and Zabic., 1981; Gondar et al., 1992; Mouquet et al., 1992; Gillou and Floros., 1993; Chen et al., 1993; Hsu, 1995). However, RSM cannot be efficiently automated due to its graphical approach which involves superimposing the different responses for an optimum solution (Arteaga et al., 1994). Derringer and Suich (1980) suggested a method to determine the best combination of responses within constraints. It requires a new objective function, the desirability function, D(x), which reflects the desirable ranges. It is considered a nonlinear programming method for an optimum solution since the models have simultaneous constraints (Box and Drapper, 1987). A Contour map is also used to explain the results from RSM (Guillou and Floros, 1993; Hsu, 1995). However, it can not show the effects of all components on the responses when the number of components is > 3. Therefore, the trace plot was introduced to illustrate the effect of > 3 ingredients in the mixture (Cornell, 1990). As the amount of one component increases, the amounts of the other remaining components decrease in the trace plot, but their ratios remain constant. Therefore, the components that most affect the response and the trends of response can be determined in the trace plot.

When a large number of factors are used in an experiment, fractional factorial design (Taguchi's orthogonal arrays) is often used as a screening technique to select key factors affecting responses (Charteris, 1992; Arteaga et al., 1994). However, mixture design methods are used to develop an empirical model for the optimum formulation (Hare, 1974; Cornell, 1990). Simplex-lattice designs, simplex-centroid designs, and augmented simplex-centroid designs are commonly used when the experimental range of each variable covers the entire simplex area (Arteaga et al., 1994). An extreme-vertices design is also used in the food formulations if there are the minimum (or maximum) proportions of some (or all) components composing the mixture (Hare, 1974).

In contrast to a large number of studies dealing with individual ingredients on the functional properties of surimi gels (Lee et al., 1992; Park, 1994; Yoon et al., 1996b), relatively few studies have focused on the interaction effects of starch at the desirable experimental design in mixture. Thus, the overall objective of our study was to investigate the interaction effects of each starch component in mixture formulations through experimental design and modeling.

MATERIALS & METHODS

Materials

Optimum surimi blend was prepared by mixing high and low grades of surimi lots (Yoon et al., 1996b). The surimi was stored at -25 °C during the study. Six different commercial starches [wheat starch (W), corn starch (C), potato starch

(P), modified potato starch (MP), modified waxy corn starch (MWC), and modified wheat starch (MW)] were used for the study.

Functional properties of surimi gels

Preparation of surimi gels and measurement of functional properties, such as failure shear stress, failure shear strain, and whiteness, were conducted according to Yoon et al. (1996b).

Experimental design

Optimization to determine a least cost formulation was conducted based on Fig. 4.1. Experimental design, data analysis, and optimization were accomplished by the software, Design Expert (Stat-Easy Co., Minneapolis, MN).

Each starch, in addition to surimi, was considered as a key factor because its price and functionality played an important role in determining an optimum solution. The minimum and maximum proportions of surimi, individual starch, and water for extreme vertices design were set at 35-50%, 0-10%, and 33-48%, respectively, according to typical commercial products (Park, 1995a). Fixed levels of salt (2%) and sorbitol (5%) were equally applied to all treatments. Upper and lower limits of total starch and moisture content in surimi-starch mixture were set at 4-12% and 70-80%,

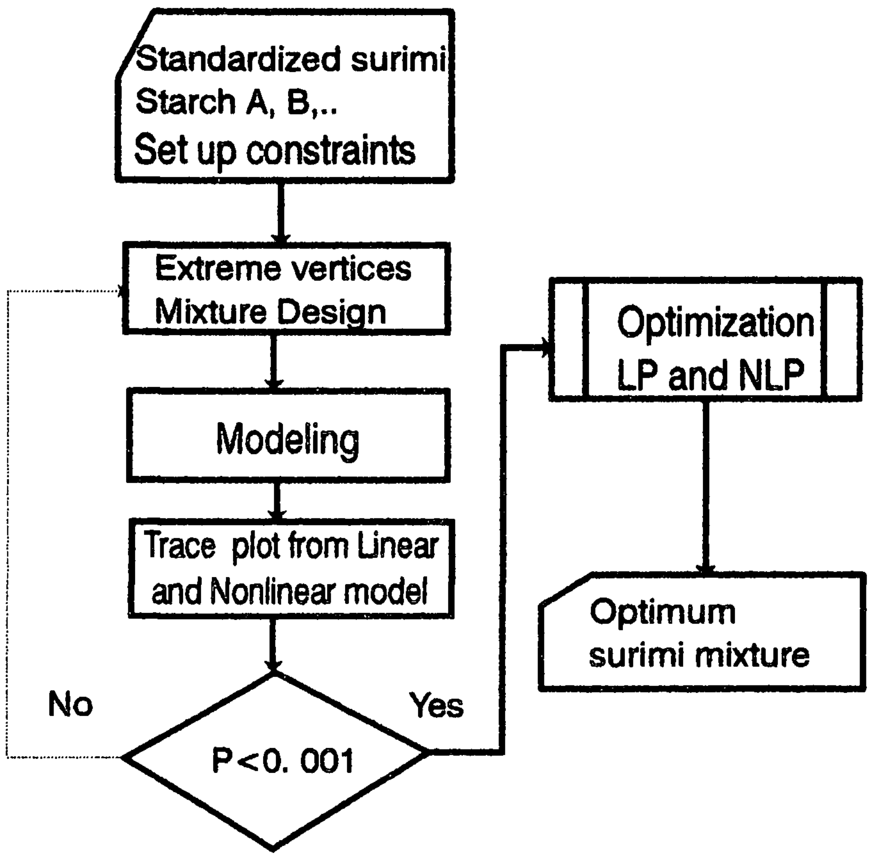

Fig. 4.1. Optimization outline for surimi-based seafood product.

respectively. The moisture content of blended surimi was ~75% (Yoon et al., 1996b) and that of starch was 10%. The weight constraint (sum of all variables) was 93% while fixed ingredients remained constant at 7%, such as sorbitol (5%) and salt (2%). Modified distance-based design (Snee, 1979) was selected to allocate different ratios of mixture within the feasible design region. Quadratic experimental design was selected to determine experimental points and to investigate interactions between surimi and starch, as well as starch and starch.

The pseudo components of each experimental point were calculated by the following equation:

$$X_i' = \frac{X_i - a_i}{1-L} \qquad \text{(Eq. 4.1)}$$

where X_i' is the pseudo component, X_i the actual value of each component, a_i the lowest level of individual component, and $L = \Sigma\, a_i < 1$. Coefficients were used to develop a regression model based on Scheffe's polynomial form (Cornell, 1990).

Statistical analysis, modeling, and trace plot

Linear (1st order) and quadratic (2nd order) models with a canonical form were obtained by modified least square regression (Cornell, 1990). The full quadratic model was reduced in order to select effective terms using a backward elimination method (at $\alpha = 0.05$). The model was evaluated in terms of 1) F-test for model ($p < 0.001$) and 2) t-test for each coefficient. Trace plots of each model were drawn in order to see all components in mixture using Piepel's direction (Cornell, 1990).

Optimization

Linear and nonlinear programming methods were used as an optimization technique. The 1st order canonical model was applied to linear programming in order to show the activity of each component. As an objective function to minimize the cost, the optimum solution was determined (Yoon et al., 1996b).

For the nonlinear functions, Derringer and Suich's method (DSM) (1980) was used to determine the optimum solutions. Each estimated response variable, denoted Y_i, was transformed to a desirability value, d_i, where $0 \leq d_i \leq 1$. The value of d_i increased from 0 (minimum) to 1 (maximum) as the desirability of the associated response increased. Two methods were used to transform Y_i to d_i: one-sided and two-sided.

1) One-sided transformation:

$$d_i = \left[\frac{Y_i - Y_{i\,min}}{Y_{i\,max} - Y_{i\,min}} \right]^r \qquad Y_{i\,min} < Y_i < Y_{i\,max} \qquad \text{(Eq. 4.2)}$$

If Y_i is $< Y_{i\,min}$, d_i is the minimum desirability, 0, and if Y_i is $> Y_{i\,max}$, d_i is the maximum desirability, 1. $Y_{i\,min}$ and $Y_{i\,max}$

indicate a minimum and a maximum acceptable value of Y_i, respectively. The value of r denotes a weight of response variable.

2) Two-sided methods:

$$d_i = \left[\frac{Y_i - Y_{i\,min}}{C_i - Y_{i\,min}} \right]^s \qquad Y_{i\,min} < Y_i < C_i \qquad \text{(Eq.4.3)}$$

$$= \left[\frac{Y_i - Y_{i\,max}}{C_i - Y_{i\,max}} \right]^t$$

When Y_i is not in the range between minimum and maximum value, such as $Y_i < Y_{i\,min}$ or $Y_i > Y_{i\,max}$, d_i is equal to 0. C_i indicates a target value, and s and t play the same role as r in the one-sided transformation. The overall assessment of the desirability, D, was calculated by the geometric mean of the individual desirabilities, $D = (d_1 \times d_2 \times \ldots \times d_k)^{1/k}$, where k represents the number of individual desirability.

The higher the D value, the more desirable the method. The constraint values for linear and nonlinear programming were set according to typical commercial products (Park, 1995a) (Table 4.1). In the linear programming, the constraints of shear stress, shear strain, and whiteness were set at ≥38 kPa, ≥2.5, and ≥70, respectively. For the one-sided transformation in DSM, the target constraints of shear stress, shear strain, and whiteness were 38-44 kPa,

Table 4.1. Target constraint for linear and nonlinear programming for a least cost formulation of surimi-based seafood product.

	Linear	Nonlinear				
		One-sided		Two-sided		
Response		Low	High	Target	Low	High
Stress	> = 38 kPa	38.0	44.0	38.0	38.0	44.0
Strain	> = 2.50	2.20	2.60	2.50	2.20	2.60
Whiteness	> = 70	70.0	80.0	70.0	70.0	80.0

Cost ($/lb) : *Surimi = 1.10, MP = 0.40, MW = 0.35, P = 0.30, MWC= 0.55, W= 0.15, C = 0.15, Water 0.00 * The price of optimum blended surimi using LP was obtained by Yoon et al. 1996, while others through an industry survey (Park, 1995a)

2.2-2.6, and 70-80, respectively. In the case of two-sided transformations, the target values of shear stress, shear strain, and whiteness were ≥38 kPa, ≥2.5, and ≥70, respectively.

RESULTS AND DISCUSSION

Experimental design

The experimental points in terms of actual values and responses are shown in Table 4.2. Each mixture ratio of surimi-starch was obtained from the modified distance-based design. From the calculation, total 46 experimental points were determined with including 5 for replicates. Shear stress values ranged from 5.53 to 62.45 kPa, depending on the ratio of mixture and type of starches. Shear strain value and whiteness were distributed in the range of 2.12-3.08 and 71.38-82.01, respectively. Experimental points in terms of pseudo components transformed from actual values were obtained according to Eq. 4.1 (Table 4.3). The concept of pseudo components was employed to simplify the construction of our experimental design (Cornell, 1990). When each coefficient of the regression models was calculated in terms of pseudo component, the coefficients represented the effect of each component, such as starch, surimi and water. It was noted

Table 4.2. Experimental points in actual value and responses.

Observation	Surimi	MP	MW	P	MWC	W	C	Water	Stress	Strain	Whiteness
1	0.35	0	0	0	0	0.05	0	0.53	5.53	2.12	80.63
2	0.48	0	0.1	0	0	0	0.02	0.33	41.44	2.98	74.79
3	0.35	0.1	0.02	0	0	0	0	0.46	25.17	2.95	72.99
4	0.35	0.1	0.02	0	0	0	0	0.46	25.16	2.87	72.98
5	0.5	0.1	0	0	0	0	0	0.33	51.27	2.98	76.15
6	0.5	0.1	0	0	0	0	0	0.33	49.78	2.89	76.14
7	0.35	0	0.1	0.02	0	0	0	0.46	21.85	2.92	76.15
8	0.35	0	0	0	0	0.1	0.02	0.46	23.27	2.83	82.01
9	0.48	0	0	0.02	0	0.1	0	0.33	45.92	2.97	79.23
10	0.5	0	0	0.1	0	0	0	0.33	54.35	3.08	77.66
11	0.5	0	0	0	0.1	0	0	0.33	50.99	2.9	74.36
12	0.35	0	0	0	0	0	0.1	0.48	24.42	2.4	78.86
13	0.5	0	0	0	0	0	0.1	0.33	55.69	2.8	75.44
14	0.48	0.06	0	0	0	0	0.06	0.33	55.38	2.84	75.36
15	0.415	0.1	0	0	0	0	0.02	0.395	37	2.9	73.38
16	0.415	0	0.02	0	0	0	0.1	0.395	37.53	2.64	73.75
17	0.415	0	0.1	0	0	0.02	0	0.395	29.99	2.9	77.62
18	0.415	0	0.02	0	0	0.1	0	0.395	32.55	2.81	79.66
19	0.48	0.06	0	0	0	0.06	0	0.33	48.54	2.6	73.78
20	0.48	0	0	0.06	0	0	0.06	0.33	55.21	2.69	75.8
21	0.48	0	0.06	0	0.06	0	0	0.33	54.39	3.02	71.48
22	0.48	0	0.06	0	0.06	0	0	0.33	54.32	3	71.38
23	0.415	0	0	0.1	0	0.02	0	0.395	36.9	2.94	75.08
24	0.35	0.06	0	0.06	0	0	0	0.46	21.89	2.8	76.25
25	0.48	0.06	0	0	0.06	0	0	0.33	62.7	2.89	73.53
26	0.415	0.02	0	0	0.1	0	0	0.395	40.78	2.74	72.97
27	0.48	0	0	0	0.06	0	0.06	0.33	62.45	2.81	73.11
28	0.35	0	0	0	0.06	0.06	0	0.46	61	2.88	73.15
29	0.35	0	0	0	0.06	0.06	0	0.46	24.14	2.76	74.36
30	0.48	0.06	0	0.06	0	0	0	0.33	36.87	2.6	73.01
31	0.5	0	0.05	0	0	0.05	0	0.33	37.33	2.64	76.75
32	0.35	0	0	0.06	0.06	0	0	0.46	25.21	2.74	75.58
33	0.35	0	0	0.06	0.06	0	0	0.46	24.48	2.74	74.58
34	0.35	0	0	0.075	0	0	0	0.505	14.02	2.83	80.32
35	0.48	0	0	0	0	0.06	0.06	0.33	61.12	2.96	80.17
36	0.48	0	0.06	0.06	0	0	0	0.33	50.71	2.94	73.9
37	0.35	0.06	0	0	0.06	0	0	0.46	26.14	2.64	72.37
38	0.35	0	0	0	0.06	0	0.06	0.46	30.36	2.63	70.81
39	0.35	0.06	0	0	0	0	0.06	0.46	26.92	2.87	75.17
40	0.35	0	0	0.06	0	0.06	0	0.46	27.01	2.96	74.67
41	0.35	0	0	0.06	0	0	0.06	0.46	21.57	2.51	72.95
42	0.35	0.06	0	0	0	0.06	0	0.46	14	2.61	74.99
43	0.35	0	0	0	0.075	0	0	0.505	13.81	2.68	72.69
44	0.5	0	0	0	0.02	0	0.02	0.39	22.04	2.94	75.07
45	0.438	0	0	0	0	0.04	0	0.452	12.88	2.63	78.36
46	0.3806	0.0082	0.033	0.008	0.008	0.01	0.008	0.4751	14.55	2.68	76.38

MP: modified starch, MW: modified wheat starch, P: potato starch, MWC: modified waxy corn, W:wheat, C:corn.

Table 4.3. Experimental points for starch mixture in pseudo value,

Observation	Surimi	MP	MW	P	MWC	W	C	Water
1	0	0	0	0	0	0.2	0	0.8
2	0.52	0	0.4	0	0	0	0.08	0
3	0	0.4	0.08	0	0	0	0	0.52
4	0	0.4	0.08	0	0	0	0	0.52
5	0.6	0.4	0	0	0	0	0	0
6	0.6	0.4	0	0	0	0	0	0
7	0	0	0.4	0.08	0	0	0	0.52
8	0	0	0	0	0	0.4	0.08	0.52
9	0.52	0	0	0.08	0	0.4	0	0
10	0.6	0	0	0.4	0	0	0	0
11	0.6	0	0	0	0.4	0	0	0
12	0	0	0	0	0	0	0.4	0.6
13	0.6	0	0	0	0	0	0.4	0
14	0.52	0.24	0	0	0	0	0.24	0
15	0.26	0.4	0	0	0	0	0.08	0.26
16	0.26	0	0.08	0	0	0	0.4	0.26
17	0.26	0	0.4	0	0	0.08	0	0.26
18	0.26	0	0.08	0	0	0.4	0	0.26
19	0.52	0.24	0	0	0	0.24	0	0
20	0.52	0	0	0.24	0	0	0.24	0
21	0.52	0	0.24	0	0.24	0	0	0
22	0.52	0	0.24	0	0.24	0	0	0
23	0.26	0	0	0.4	0	0.08	0	0.26
24	0	0.24	0	0.24	0	0	0	0.52
25	0.52	0.24	0	0	0.24	0	0	0
26	0.26	0.08	0	0	0.4	0	0	0.26
27	0.52	0	0	0	0.24	0	0.24	0
28	0	0	0	0	0.24	0.24	0	0.52
29	0	0	0	0	0.24	0.24	0	0.52
30	0.52	0.24	0	0.24	0	0	0	0
31	0.6	0	0.2	0	0	0.2	0	0
32	0	0	0	0.24	0.24	0	0	0.52
33	0	0	0	0.24	0.24	0	0	0.52
34	0	0	0	0.3	0	0	0	0.7
35	0.52	0	0	0	0	0.24	0.24	0
36	0.52	0	0.24	0.24	0	0	0	0
37	0	0.24	0	0	0.24	0	0	0.52
38	0	0	0	0	0.24	0	0.24	0.52
39	0	0.24	0	0	0	0	0.24	0.52
40	0	0	0	0.24	0	0.24	0	0.52
41	0	0	0	0.24	0	0	0.24	0.52
42	0	0.24	0	0	0	0.24	0	0.52
43	0	0	0	0	0.3	0	0	0.7
44	0.6	0	0	0	0.08	0	0.08	0.24
45	0.352	0	0	0	0	0.16	0	0.488
46	0.1225	0.0328	0.1328	0.0328	0.0328	0.0328	0.0328	0.5805

Each fraction represents pseudo value.

MP: modified starch, MW: modified wheat starch, P: potato starch, MWC: modified waxy corn, W:wheat, C:corn.

that a specific starch component had a maximum proportion while the other starches had a minimum proportion in constraint vertices.

Linear and nonlinear canonical models

Linear and nonlinear models in a canonical form built by modified least square regression were evaluated statistically as shown in Table 4.4. Both linear and nonlinear models showed low p-values (<0.001) for all responses, such as, shear stress, shear strain, and whiteness. Due to the low p-value of each model, both linear and nonlinear models were used as an empirical model to describe the effects of components in the mixture and to apply for optimization techniques.

The linear canonical model was composed of all components, such as, surimi, six kinds of starches, and water (Table 4.5). The coefficient value of starch components was in the range of 54.4-92.8, while that of surimi and water was 32.2 and -17.1, respectively. The addition of starch in surimi products was recommended because the effect of starch on the gel functionality of surimi was higher than that of surimi alone. Compared to the effects of individual starches without interaction on gel functionality (Yoon et al., 1996b), modified waxy corn starch (MWC) showed the highest effect on shear stress. Individual starch showed different effects on the functionality when mixed with other starches. It might be due to the interactions between components in the mixture, such as starch and starch (St*St) and starch and various

Table 4.4. ANOVA tables for linear and nonlinear (reduced quadratic) model built by Modified least square linear regression.

a. Shear stress

Model	Source	SS	DF	MS	F-value	Prob > F
Linear	Model	28434.9	7	4062.1	81.11	< 0.001
	Residual	6510.7	130	50.1		
NonLinear	Model	31476.3	24	1311.5	42.73	< 0.001
	Residual	3468.6	113	30.7		

b. Shear strain

Model	Source	SS	DF	MS	F-value	Prob > F
Linear	Model	1.656	7	0.237	8.04	< 0.001
	Residual	3.824	130	0.029		
NonLinear	Model	4.146	27	0.154	12.66	< 0.001
	Residual	1.334	110	0.012		

c. Whiteness

Model	Source	SS	DF	MS	F-value	Prob > F
Linear	Model	562.2	7	80.31	21.44	< 0.001
	Residual	486.9	130	3.75		
NonLinear	Model	947.5	28	33.84	36.3	< 0.001
	Residual	101.6	109	0.93		

Table 4.5. Coefficients of constraints of linear model based on pseudo values.

Response	Coefficients							
	Surimi	MP	MW	P	MWC	W	C	Water
Shear stress	32.2	67.5	54.4	67.8	92.8	70.9	83.8	-17.1
Shear strain	2.70	3.16	3.34	3.24	3.13	3.01	2.77	2.43
Whiteness	79.4	67.3	69.5	71.8	61.7	79.6	71.4	79.6

* Developed using a general form of linear model (Yoon et al., 1996)

ranges (70-80%) of water (St*Wa) (Yoon et al., 1996b). The coefficients of starches for the shear strain and whiteness were in the range of 2.77-3.34 and 61.73-79.61, respectively (Table 4.5). Generally, the addition of starches highly enhanced shear stress and shear strain values whereas they slightly reduced the whiteness.

The interaction term was considered as a nonlinear function in this study. All interaction terms are selected with significant levels at $t < 0.05$ and $t < 0.01$ (Table 4.6). Each interaction term showed synergistic effects on the shear stress and shear strain. However, there were some significant interaction terms with antagonistic effects, having negative coefficients in interaction terms, on the shear strain and whiteness. Coefficient terms in strain and whiteness showed more significant interaction effects ($t<0.01$) than those of stress ($t<0.05$).

Analysis of each component in the trace plot

On the basis of the linear model, a trace plot was generated to show the trends of each component in mixture (Fig. 4.2). The center of the plot, indicating a reference blend, was set at a centroid of vertices of mixture. The composition of a reference blend in terms of pseudo value was surimi (S) = 0.245, water (Wa) = 0.361, and each starch (MP, MW, MWC, P, W, and C) = 0.066. The slope of each starch was steeper than that of surimi (Fig. 4.2). It showed that shear stress values were more affected by contents of starches

Table 4.6. Coefficients of constraints of nonlinear model based on pseudo value.

Component	Coefficient Estimate					
		Stress		Strain		Whiteness
A - Surimi		-11.4		2.043		75.71
B - MP		-204		-6.68		-9.43
C - MW		93.8		5.39		86.09
D - P		-39.1		-1.75		79.56
E - MWC		-80.9		-4.27		102.7
F - W		-135		-0.36		136.4
G - C		-107		-3.21		114.2
H - Water		-46.2		0.634		90.52
	*AB	578.5	*AB	18.25	*AB	143.4
	*AD	309.3	AC	-2.33	AE	-50.7
	AE	383.2	*AD	10.46	*AF	-86
	*AF	469.1	*AE	14.23	AG	-61
	AG	445.6	AF	8.183	BC	-53.3
	BC	361.9	*AG	11.87	*BH	125.1
	*BE	234.5	*AH	2.048	*BF	-56.2
	BG	173.4	*BC	10.92	*CE	-121
	*BH	536.6	*BE	4.788	*CF	-81.2
	CE	161.5	*BG	8.08	*CG	172
	DH	383.3	*BH	21.55	*CH	-37.7
	*EF	404.3	*CD	-88.4	*DF	-95.7
	EG	171.7	*CF	-7.03	DE	27.21
	EH	330.4	*DH	13.96	DG	-63.6
	FG	174.5	EF	3.575	*DH	-33.9
	FH	431.6	*EG	5.124	*EF	-52
	GH	390.1	*EH	16.6	*EG	-72.5
			*FG	4.26	*EH	-102
			FH	10.57	*FH	-120
			*GH	13.76	*GH	-92.4

(all interaction terms were selected significant levels (t<0.05) and * indicates significant

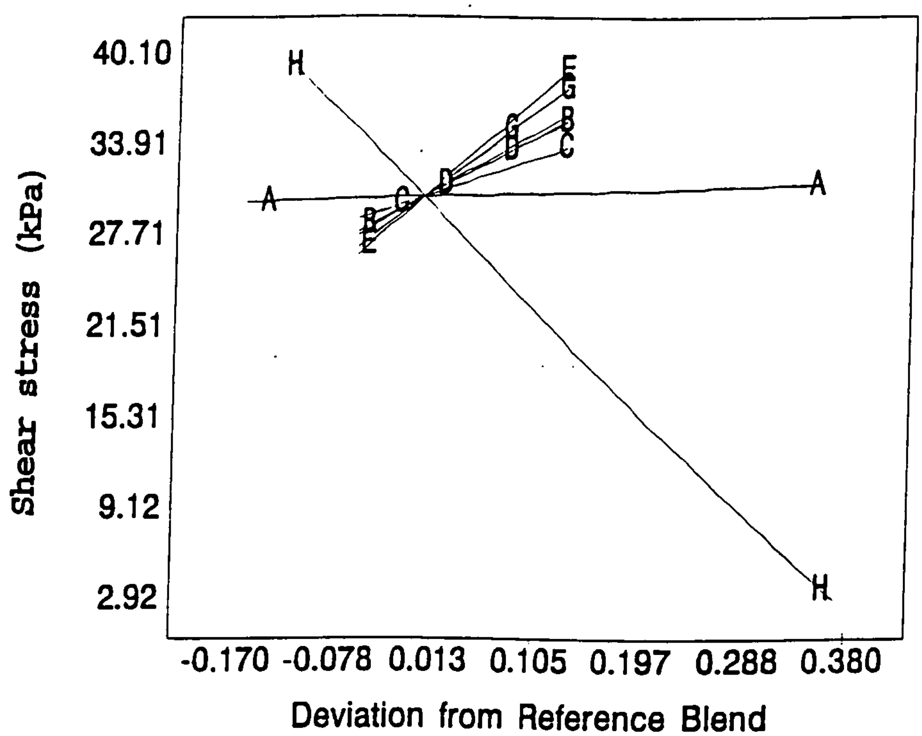

Fig. 4.2. Trace plot of linear model to describe effect of starch mixture on failure shear stress. A:surimi, B:modified potato starch, C:modified wheat starch, D:potato starch, E:modified waxy corn starch, F:wheat starch, G:corn starch, H:water.

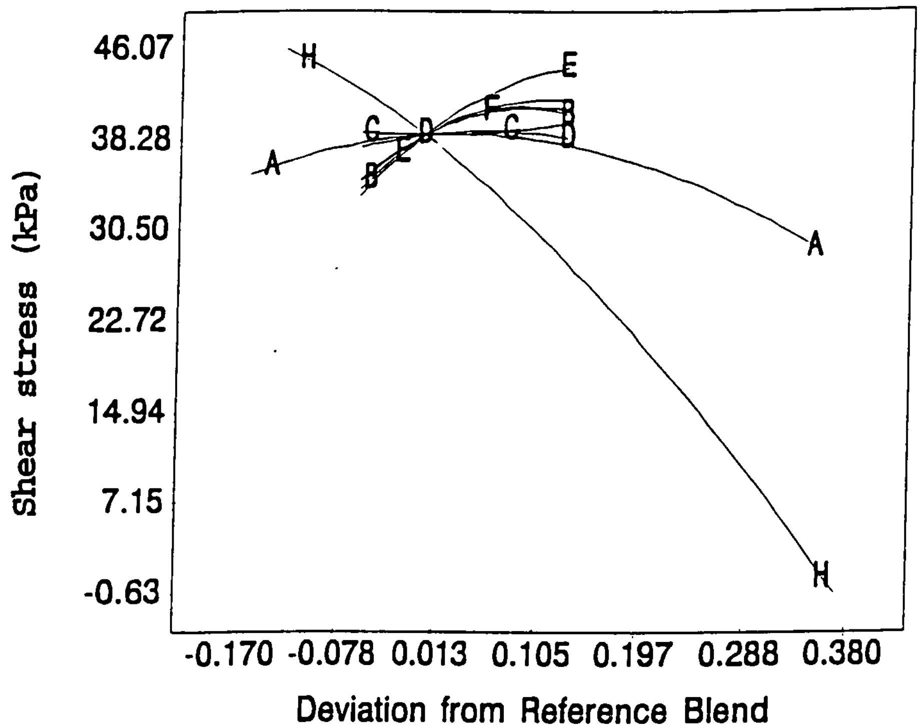

Fig. 4.3. Trace plot of nonlinear model to describe effect of starch mixture on failure shear stress. A:surimi, B:modified potato starch, C:modified wheat starch, D:potato starch, E:modified waxy corn starch, F:wheat starch, G:corn starch, H:water.

than by surimi. The addition of water could negatively affect the shear stress. The Trace plot of each component in the nonlinear model showed similar trends to the linear model (Fig. 4.3). According to the nonlinear model, the effect of added surimi on shear stress in the presence of starch was maximized, but decreased beyond a certain level of surimi.

A linear trace plot of shear strain showed slightly different trends from that of shear stress (Fig. 4.4). Shear strain values decreased with an increased content of surimi and corn starch. Starches (except corn starch) showed an extremely positive impact on strain. Negative impacts were made slightly by surimi and corn starch and extremely by water. Compared to the effect of individual starches on shear strain (Yoon et al., 1996b), the negative impacts of surimi might be due to the ignorance of interaction effects between starch and surimi (St*S), and between water and surimi (Wa*S). The interaction terms in the nonlinear model implied that the shear strain in mixture was affected not only by the interactions between surimi and water (S*Wa) but also by interactions of each component, such as St*St, St*S, and St*Wa. The effects of water and surimi on shear strain exhibited strong nonlinearity due to their interactions with other components in the mixture (Fig. 4.5). Unlike the linear model, the nonlinear model showed a descending trend of shear strain beyond a reference blend. It should be noted that the nonlinear model produced an exact curve fitting for each response, whereas linear model could not make an exact curve

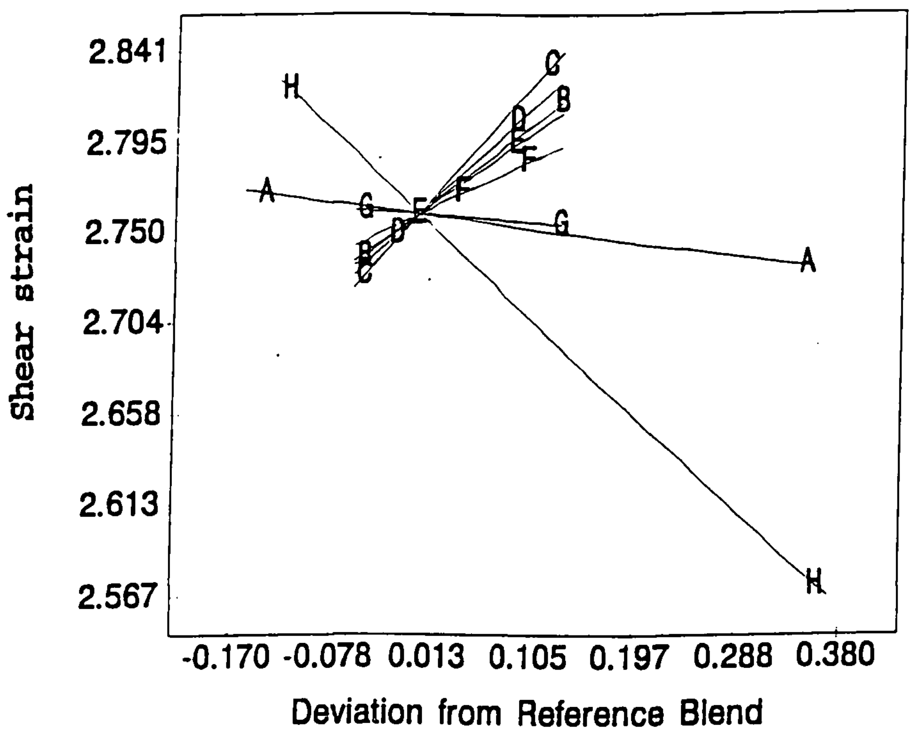

Fig. 4.4. Trace plot of linear model to describe effect of starch mixture on failure shear strain. A:surimi, B:modified potato starch, C:modified wheat starch, :potato starch, E:modified waxy corn starch, F:wheat starch, G:corn starch, H:water.

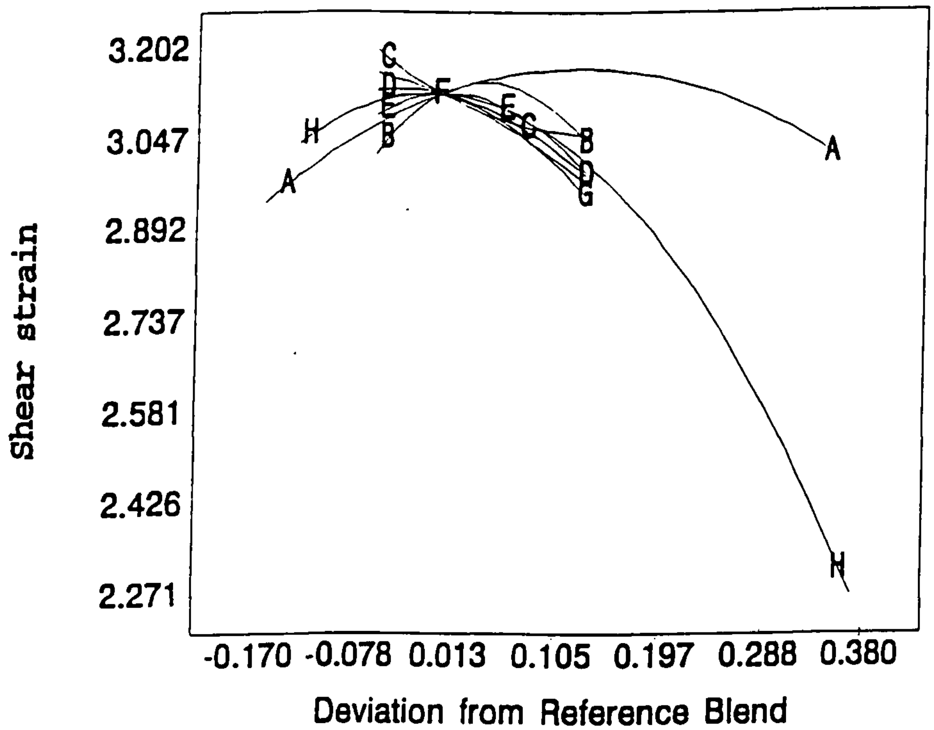

Fig. 4.5. Trace plot of nonlinear model to describe effect of starch mixture on failure shear strain. A:surimi, B:modified potato starch, C:modified wheat starch, D:potato starch, E:modified waxy corn starch, F:wheat starch, G:corn starch, H:water.

due to the lack of fitness. The nonlinear model showed a decreased shear strain with an increased starch content. As a result of these two different curve fitting methods (Fig. 4.2,3,4,&5), absolute values of each response (stress values of 26-38 kPa and 32-45 kPa, strain 2.7-2.84 and 2.9-3.2) can not be compared to each other. Only their trends should be evaluated. The addition of water and surimi significantly increased the whiteness, while the increase of starch showed negative impacts (except wheat starch) (Fig. 4.6&7). Water was the most effective parameter to increase the whiteness in both models. This is probably due to increased lightness (L*) and decreased yellowness (b*) caused by higher moisture concentration (Park, 1995b). This suggests that the amount of added water plays an important role to control the optimum whiteness as well as the cost of product.

Optimization.

On the basis of p-value of the model (Table 4.4a,b,c), the optimum solutions were determined using linear and nonlinear programming (Table 4.5&6). In the one-sided transformation, the value of the cost response was minimized while the value of the other responses were kept within acceptable values. In the two-sided transformation, the value of the cost response was also minimized as the value of the other responses approached to the target value (Table 4.1). During 99 iterations, the highest response values from both methods were selected as optimum solutions.

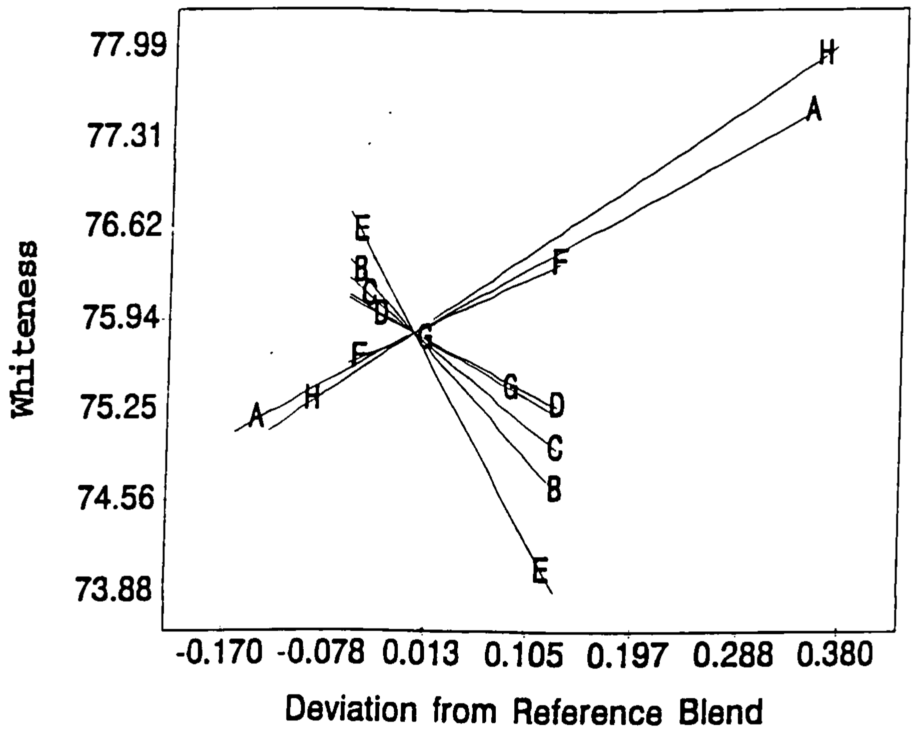

Fig. 4.6. Trace plot of linear model to describe effect of starch mixture on whiteness. A:surimi, B:modified potato starch, C:modified wheat starch, D:potato starch, E:modified waxy corn starch, F:wheat starch, G:corn starch, H:water.

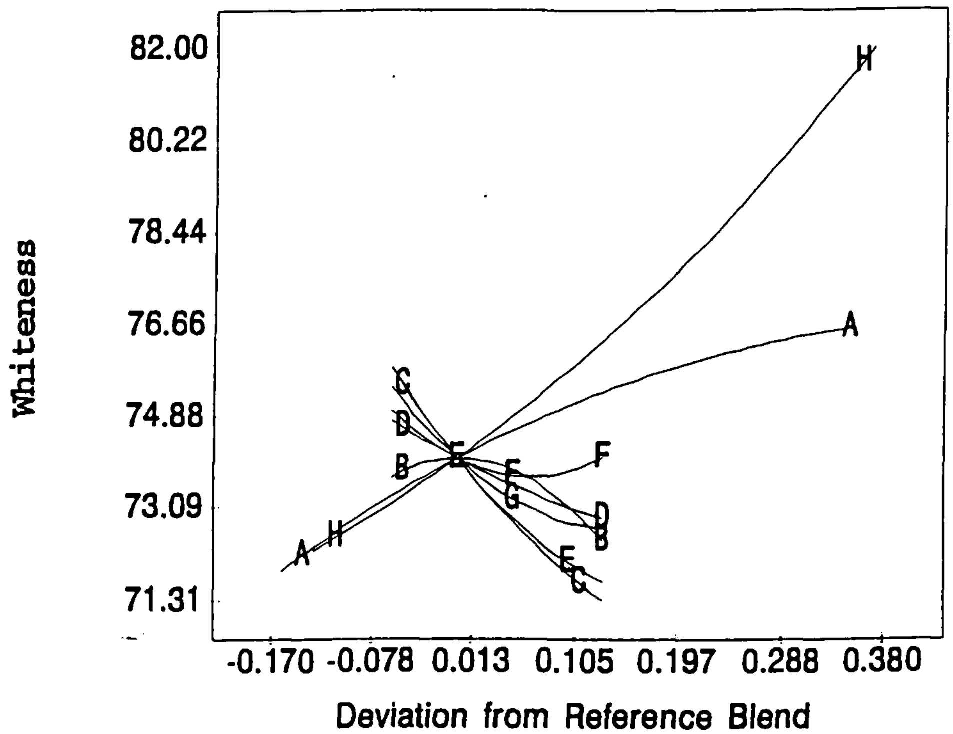

Fig. 4.7. Trace plot of nonlinear model to describe effect of starch mixture on whiteness. A:surimi, B:modified potato starch, C:modified wheat starch, D:potato starch, E:modified waxy corn starch, F:wheat starch, G:corn starch, H:water.

The objective value of linear programming was \$0.441/lb with the optimum formulation being surimi 38%, MWC 2%, C 10%, and water 43% (Table 4.7). It is obvious that the addition of starch could reduce the cost, from \$1.100/lb (Yoon et al., 1996b) to \$0.441/lb, while maintaining the same constraints. From the DSM, using a one-sided transformation, the minimum cost was \$0.413/lb and the optimum formulation was surimi 35%, MWC 3%, W 6%, C 3% and water 46%. In the two-sided transformation analysis, the minimum cost was \$0.422/lb with the desirability of 0.971 and the optimum formulation was surimi 35%, MW 1%, MWC 4%, W 5%, C 2%, and water 46%. Nonlinear programming generated a lower objective value than linear programming from both one-sided and two-sided transformations. It appears that the objective value is a function of the interaction effects regardless of the model.

However, it is known that DSM can generate an impractical answer although high values of desirability are obtained. This is due to the overall desirability depending on the individual desirability which is a function of upper and lower limit constraints, target, and weight as described in Eq. 4.2&3. When each response had different weight values, they generated more impractical answers. Perfect understanding of the system is required in order to avoid impractical solutions from DSM (Box and Drapper, 1987)

Table. 4.7. Optimum solution of two methods.

Variable	Linear	Nonlinear	
		One-sided	Two-sided
Surimi	0.38	0.35	0.35
MP	0	0	0
MW	0	0	0.01
P	0	0	0
MWC	0.02	0.03	0.04
W	0	0.06	0.05
C	0.1	0.03	0.02
Water	0.43	0.46	0.46
Objective Value ($/lb)	0.441	0.413	0.422
Desirability	N/A	0.902	0.971

CONCLUSIONS

Shear stress, and shear strain of surimi seafood was significantly enhanced by the addition of various types of starches due to the interaction terms. However, whiteness is reduced with increased starch contents, but increased with the amount of water content. Compared to the linear regression model, the nonlinear regression model exhibited interaction terms of each component and coefficient value, representing the effect of each component accurately in mixture formulation. Trace plots, obtained as a result of the regression model analysis, gave graphical information on the response trends of each starch component as well as surimi and water to the gel functionality.

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IV. SUMMARY

In formula optimization, the main goal is to find the best level for each key ingredient or component. With the growing trend of surimi seafood production in the U.S.A. (160 million lbs a year), there is a need to develop a simple and efficient optimization method for this industry. The main objective of this study was to determine a least cost formulation for surimi seafood using a least coast linear/nonlinear programming. Moreover, linear/nonlinear relationships between independent and dependent variables as well as the interaction effect of ingredients were investigated.

Shear stress, shear strain, and whiteness of surimi gels made with high and low grades of Alaska pollock and Pacific whiting were investigated to determine a linearity with a mixture design. Interaction effects of starch mixtures within surimi gel were investigated by modified distance-based design and analyzed by linear and nonlinear backward regression model. A canonical form of least square linear model in mixture design showed a greater linearity (r^2=0.99) for blending high and low grade surimi lots. Due to their linearities without any interaction ($p<0.001$), a least cost linear program provided optimum blending for surimi lots based on a cost, constraints, and decision variables. The addition of starch into surimi enhanced gel texture, but decreased the whiteness of surimi gels. Nonlinear regression model showed highly significant interaction terms of starch-surimi, starch-water, and starch-starch. The response trace plot revealed that shear stress and shear strain were quite sensitive to changes in the amount of various starch components, whereas whiteness was positively affected by water, but negatively affected starch. Linear (LP) and nonlinear programming (NLP) showed the addition of corn and modified waxy maize starch strongly improved the functional properties and reduced the cost of surimi seafood. Our results suggested that there is a strong feasibility of the application of LP and NLP in order to determine systematically a least cost formulation of surimi seafood with use of suitable experimental designs.

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