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Optimization programming techniques were applied to develop the least cost formulations for Pacific whiting surimi-based seafood (PWSBS). To develop the quality constraint functions, texture and color of whiting surimi gels were determined by torsion test and colorimeter, respectively. Whiting surimi gels were produced by heating at 90°C for 15 min. with 2% NaCl, five final moisture contents (74, 76, 78, 80, 82%), and various combinations of beef plasma protein (0-2%), potato starch (0-8%), and two whey protein concentrates (0-8%). Due to the non-linear constraint functions describing texture and color, a non-linear programming search technique was required to solve the least cost model for PWSBS. Results for target quality constraints are reported in this study and show that whey protein concentrate increases the texture properties and can remain economically competitive with other ingredients which similarly influence functionality in PWSBS. Water holding capacity indicated by thermal

transition was also studied as a measure of gel quality. The water evaporization process was quantified using differential scanning calorimetry (DSC) for surimi gels with added potato starch or whey protein concentrate. Pacific whiting surimi gels were produced by heating in a sealed DSC pan from 30 to 90°C at a rate of 5°C/min.; gelled samples were then re-heated from 30 to 180°C at 2°C/min. in an open pan using an equivalent water mass as a reference. The DSC thermogram showed one exothermic peak followed by one endothermic peak, the former indicating a relative energy flow from the protein gels due to the delayed water evaporation. DSC parameters derived in this study showed good correlation with the texture properties of protein gels. The addition of whey protein concentrate and the increase of heating rate increased the water holding capacity of whiting surimi gels.

Evaluation of Physical and Thermal Methods to Support Nonlinear Cost Optimization Models of Surimi Seafood

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CONTRIBUTION OF AUTHORS

Dr. Edward Kolbe was involved in the design, analysis, and writing of each manuscript. Dr. Marshall English assisted in the design, analysis and writing of the optimization/modeling study.

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Chapter 1

INTRODUCTION

Pacific whiting (Merluccius productus) was long underutilized by the U.S. fishing industry due to its inherently soft texture. A further heat softening caused by protease enzymes that may be related to parasites is another, and more important limitation (Erickson et al., 1983). The allowable catch of Pacific whiting is about 200,000 metric tons/year, the largest trawl fishery off the west coast of the United States (not including Alaska). Whiting is commonly processed into surimi, a washed mince to which is added cryoprotectants such as sorbitol and sucrose, which maintain protein quality during frozen storage. Surimi is then further processed into various surimi-based gelled products such as artificial crab legs and meats. However, during the processing of Pacific whiting surimi-based seafood (PWSBS), the addition of protease inhibitors and/or gel strength enhancers such as starch and hydrolyzed beef plasma protein, is generally required to maintain good texture characteristecs (Morrissey et al., 1993).

Whey protein concentrate (WPC), a by-product from cheese or casein manufacture, is another potential functional ingredient currently under consideration due to its abilities to improve texture properties and water-holding capacity of surimi-based seafoods (Burgarella et al., 1985; Lee et al., 1992; Chung and Morrissey, 1993). The dairy industry annually produces thousands of tons of WPC, which is now available as a steady source of functional protein for the food industry due to the improvement of processing techniques. The application of an ultrafiltration process, a pressure-driven filtration process in which porous membranes are used to recover proteins from liquid whey, allows the dairy industry to produce WPC in a quite efficient way (Matthews, 1979; Maubois, 1980; Hobman, 1992). With protein content in the range of 30-80%, WPC not only serves as an excellent nutritional source (Delaney, 1976; Forsum, 1979; Kunachowicz et al. 1976), but also provides the food industry with a product possessing diverse functional properties, such as gelation, whippability, foaming, solubility, and emulsifying capacity (Morr, 1984; Morr and Foegeding, 1990; Mangino, 1992).

The use of WPC has been found to improve the texture properties of PWSBS (Chung and Morrissey, 1993). Piyachomkwan and Penner (1995) suggested that WPC may protect the myofibrillar proteins of surimi by acting as a true protease inhibitor or by serving as an alternative substrate. The use of WPC in PWSBS has therefore been found to be technically effective, however, its economic feasibility is subject to further study. To determine whether WPC is economically competitive to other ingredients used in PWSBS, the development of least cost formulations of PWSBS is needed. The application of least cost formulation techniques not only allows us to estimate the potential use of WPC in the formulation but also allows us to reduce the cost of PWSBS.

Optimization techniques such as linear or nonlinear programming allow us to find a minimum cost while maintaining desired levels of product quality. This process, which includes experiments and application of quantitative models, additionally describes interrelationships among the costs of ingredients, the amount of each ingredient in the formulation, and the quality of final products. The decision concerning a linear or nonlinear programming approach to the least cost formulations depends on whether the relationships between quality parameters, such as texture and color, and ingredient levels are linear or nonlinear functions. The application of linear programming has been more common than nonlinear programming not only due to the simplicity in mathematical and computer skills but also to the ease of building the models. On the other hand, nonlinear programming requires complicated mathematical and computer skills. The characteristics and relative strengths of several approaches for unconstrained and constrained nonlinear programming are described in Appendix A. In fact, linear programming has often been used to approximate phenomena that were actually nonlinear in the real world. Therefore, the linear assumption needs to be checked out seriously before it can be applied to least cost food formulations, otherwise inaccurate result can lead to erroneous management decisions.

The application of least cost formulation using linear programming has been found to improve the market profit and/or quality control for various food products and to provide management with more detailed and precise decision-making information (IBM, 1966; Kramlich et al., 1973; Lanier and Park, 1989). In food industries, linear programming was first applied to formulate the blended meat products, such as frankfurthers, bologna, sausage, etc. (IBM, 1966). Linear programming has also been used to maintain minimum cost of surimi-based seafoods while blending different grades of surimi lots to reach a desired level of texture and color. Lanier and Park (1989) showed that the texture and color properties in blended surimi products are an approximate linear function of the mass of each surimi lot added to the formulation. However, questions arise concerning whether such linear relationships would still hold when protease inhibitors and/or gel strength enhancers are added to surimi products. In a study to optimize the texture properties of Alaska pollock surimi with the addition of starch and egg white, Chen et al. (1993) showed that a response surface methodology (which accounts for non-linear relationships) provided a more accurate prediction of texture behavior than did a linear programming approach. Daley et al. (1978), optimizing a sausage product from minced fish using response surface methodology, showed that the relationships between texture properties and ingredient levels were non-linear. Hastings and Currall (1989) also found significant interactions (both synergistic and antagonistic nonlinearities) between ingredients and the texture of cod surimi gels. As mentioned, understanding the relationships between quality parameters and ingredient levels is necessary to allow selection of proper optimization techniques to develop least cost formulations of food products. This is particularly important in whiting surimi due to its intrinsic autoproteolytic activity. To control the protease activity in whiting surimi, a number of inhibitors or gel enhancers can be used. These include hydrolyzed beef plasma protein, starches, and whey protein concentrates. Chapter 2 describes the development of an experimental and analytical procedure to general least cost formulation models of PWSBS with the ingredients just mentioned. Chapter 3 details the application of these models to evaluate the economical feasibility of using WPC as a functional ingredient in surimi seafoods.

The accuracy of least cost formulations depends strongly on the precision of instrumental measurements for building the relationships (or models) relating quality parameters and ingredient levels. The unique texture properties are the most important sensory factors affecting the consumer's acceptance of surimi-based seafood. Thus, the continuous development of reliable measurements for the texture properties is very important in the application of least cost formulation techniques for surimi-based seafood.

The torsion test was originally developed to measure the texture of vegetables and fruits and was subsequently used to test the gel-forming ability of surimi. Hamann and Lanier (1988) showed that the torsion test produced results which were superior to those of the punch test, a traditional method of measuring the gel strength of protein gels, since changes in specimen shape and size were minor considerations in torsion testing. Montejano et al. (1985) found a good correlation between torsion parameters and most sensory characteristics. A torsion test was set up in our laboratory to evaluate its ability to measure the texture properties of fish muscle proteins. We found that the results obtained from torsion tests have high correlations with conventional biochemical methods, and therefore torsion test can be considered as a useful tool in determining the quality of surimi-based seafoods (Hsu et al., 1993).

Another concern regarding the quality of surimi-based seafood is its water holding capacity (WHC), which is closely related to the texture and flavor quality (Lee and Kim, 1986a; Lee et al., 1992). For example, WHC has been used as a indictor of the freeze-thaw stability of surimi-based seafood which are intended to be distributed frozen (Lee and Kim, 1986a). In surimi-based seafood with low WHC, the texture can become hard and rubbery; flavoring can be lost as a result of excessive thaw drip caused by intense temperature fluctuation and/or freeze-thaw cycles (Lee et al., 1992).

Conventional methods for determining WHC of surimi gels are based on measuring the amount of lose water liberated by applying pressure on sliced gels. The pressure can be produced in different ways: centrifugal force or pressing between two plates (Suzuki, 1981). WHC in surimi gel systems has been correlated with gel strength at failure commonly measured by either the punch or torsion tests (Akahane et al., 1981; Lee and Kim, 1986b; Chung and Lee, 1990). Lee and Kim (1986b) reported that a decrease in gel strength of surimi gels prepared with egg albumin is accompanied by a decrease in WHC. Chung and Lee (1990) noted a strong correlation between the WHC and the compressive force of surimi gels with the addition of various nonfish proteins. Thus, WHC has been commonly used as an indirect measurement of texture properties of surimi-based seafoods (Lee and Kim, 1986b; 1986a; Chung and Lee, 1990; Yoon and Lee, 1990).

Differential scanning calorimetry (DSC) is a technique in which difference in energy inputs into a substance and a reference material are measured as a function of temperature, while the substance and the reference material are subjected to a controlled temperature program (Wright, 1984). DSC has been commonly used to determine the thermal stability of various food proteins by measuring their heat transition temperature and enthalpy (Wright et al., 1977; Stabursvik and Martens, 1980; Hastings et al., 1985). DSC has also been applied in determining the WHC of fish protein gels. Akahane et al. (1981) observed a good correlation between DSC parameter and texture measurement of fish protein gels and suggested that DSC can be used to determine the quality of fish protein gels.

It is well-known that intermediate holding (setting) temperatures and heating rates are critical to the final textural quality of protein gels. In general, a slow heating rate allows formation of a more uniform and rigid gel structure. However, with some species like whiting, the opposite result (a gel softening) may occur, because the maximum protease activity is around 60°C (Morrissey et al., 1993). In this study, DSC was used not only to determine the WHC of whiting surimi gels but also to control the accuracy of temperature setting and heating rate. DSC offers a excellent control of heating rate, and thus allows us to study the effects of heating rates on the WHC in surimi gels. To determine the effect of heating rates on WHC of whiting surimi gels, the surimi paste was sealed in a DSC sampling pan and gelled by applying different heating rates. The gelled sample was then rescan in an open sampling pan to evaporize the water in surimi gels. The thermal transition of water evaporization process of surimi gels was recorded and compared. Appendix B describes the potential of using DSC to determine the WHC of whiting surimi gels.

The objectives of this study were: 1) to identify effective optimization approaches that will give least cost formulations of protease inhibitors and gel enhancement ingredients in PWSBS; 2) to evaluate the potential of using WPC as an economically viable gel enhancer in PWSBS; 3) to evaluate the potential of using DSC to measure the quality of surimi gels by correlating WHC measured by DSC to the gel strength.

Chapter 2

A Nonlinear Programming Technique to Develop Least Cost Formulations of Surimi Products

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A Nonlinear Programming Technique to Develop Least Cost Formulations of Surimi Products

ABSTRACT

Optimization programming techniques were applied to develop the least cost formulations for Pacific whiting surimi-based seafood (PWSBS). To develop the quality constraint functions, texture and color of whiting surimi gels were determined by torsion test and colorimeter, respectively. Whiting surimi gels were produced by heating at 90°C for 15 min. with 2% NaCl, five final moisture contents (74, 76, 78, 80, 82%), and various combinations of beef plasma protein (0-2%), potato starch (0-8%), and two whey protein concentrates (0-8%). Due to the non-linear constraint functions describing texture and color, a non-linear programming search technique was required to solve the least cost model for PWSBS. Results for representative target quality constraints are reported in this study and show that whey protein concentrate both increases the texture properties and remains economically competitive with other ingredients which similarly influence functionality in PWSBS.

Key Words: formulation, surimi gel, non-linear programming

INTRODUCTION

Pacific whiting (Merluccius productus) was an underutilized species due to its soft texture caused by protease enzymes that may be related to parasites (Erickson et al., 1983). Whiting is commonly processed into surimi, a washed mince to which is added cryoprotectants, such as sorbitol and sucrose, which maintain protein quality during frozen storage. Surimi is then further processed into various surimi-based gelled products such as artificial crab legs and meats. It is well known that texture and color are the most important sensory factors affecting the consumer's acceptance of surimi-based seafood. During the processing of Pacific whiting surimi-based seafood (PWSBS), the addition of protease inhibitors and/or gel strength enhancers is generally required to maintain good texture characteristics (Morrissey et al., 1993). However, the addition of these food grade additives to enhance texture may increase the total cost of ingredients and/or change the color properties of final products, thereby reducing the market acceptance. Thus, it is necessary to determine the optimal formulation that leads to minimum cost of PWSBS while maintaining good texture and color.

Optimization techniques such as linear or non-linear programming allow us to find a minimum cost while maintaining desired levels of product quality. This process, which includes experiments and application of quantitaive models, additionally describes relationships among the costs of ingredients, the amount of ingredients in the formulation, and the quality of final products. The use of least cost formulation techniques has been found to improve the profitability and/or quality control for various food products (IBM, 1966; Kramlich et al., 1973; Lanier and Park, 1989; Park, 1992).

Linear programming has been used to maintain minimum cost of surimi-based seafoods while blending different grades of surimi lots to reach a desired level of texture and color. Lanier and Park (1989) showed that the texture and color properties in blended surimi products are an approximate linear function of the mass of each surimi lot added to the formulation. However, questions arise concerning whether such linear relationships would still hold when protease inhibitors and/or gel strength enhancers are added to surimi products. In a study to optimize the texture properties of Alaska pollock surimi with the addition of starch and egg white, Chen et al. (1993) showed that a response surface methodology (which accounts for non-linear relationships) provided a more accurate prediction of texture behavior than did a linear programming approach (which accounts only for linear relationships). Daley et al. (1978), optimizing a sausage product from minced fish using response surface methodology, showed that the relationships between texture properties and ingredient levels were non-linear. Hastings and Currall (1989) also found significant interactions (both synergistic and antagonistic nonlinearities) between ingredients and the texture of cod surimi gels. Understanding the relationships between quality parameters and ingredient levels is necessary to allow selection of proper optimization techniques to develop least cost formulations of food products. This is particularly important in whiting surimi due to its intrinsic autoproteolytic activity. To control the protease activity in whiting surimi, a number of inhibitors or gel enhancers can be used. These include hydrolyzed beef plasma protein, potato starch, and whey protein concentrates.

The dairy industry annually produces thousands of tons of whey protein concentrate (WPC) world-wide, and this is available as a steady source of functional protein for the food industry. The use of WPC has been found to improve the texture properties of PWSBS (Chung and Morrissey, 1993). Piyachomkwan and Penner (1995) suggested that WPC may protect the myofibrillar proteins of surimi by acting as a true protease inhibitor or by serving as an alternative substrate. The use of WPC in PWSBS has therefore been found to be technically effective, however, its economic feasibility is subject to further study. The objectives of this study were to identify effective optimization approaches that will give least cost formulations of protease inhibitors and gel enhancement ingredients in PWSBS, and to evaluate the potential of using WPC as an economically viable gel enhancer in PWSBS.

MATERIALS & METHODS

Washed and dewatered mince was made from Pacific whiting within 24 hrs. of harvest at Point Adams Seafood Inc. in Hammond, Oregon. This mince was immediately transported, on ice, to the OSU Seafood Laboratory in Astoria, 30 min away by car. After mixing with cryoprotectants (4% sucrose, 4% sorbitol, and 0.3% sodium tripolyphosphate) in a cool room, the mince weighing about 650 g was vacuum-packaged in plastic bags. The packages were then frozen to a core temperature of -25°C and stored in insulated boxes inside a blast freezer at -34°C. Two packages of frozen surimi were removed from storage and used as one surimi sample.

Surimi Gel Preparation

Frozen surimi was thawed at room temperature for 2 hr. A Stephan vacuum mixer (Model UM5 Universal, Stephan Machinery Corporation, Columbus, OH) was used to mix approximately 1 kg of whiting surimi with 2% NaCl and various combinations of beef plasma protein (BPP, American Meat Protein Corp. Inc., IA) (0-2%), potato starch (PS, Avebe America, Inc., NJ) (0-8%), and two kinds of whey protein concentrate: WPC33 (with 33% protein content, Avonmore West, Inc., ID) and WPC72 (with 72% protein content, New Zealand Milk Products, Inc., CA) (0-8%). The mixture was chopped for 4 min. with the addition of ice (vs. water) to adjust the final moisture content to five different levels (74, 76, 78, 80, and 82%) while maintaining a low temperature (below 10°C). A 5-lb-capacity sausage stuffer (The Sausage Maker, Buffalo, NY) was used to extrude the mixture into stainless steel cooking tubes (inside diameter 1.9 cm, length 17.8 cm). Surimi gels were produced by heating in a 90°C water bath for 15 min., followed by cooling in ice water for 10 min. They were then stored in ziplock bags at a refrigerated temperature of about 5°C. Gels were removed from a refrigerated storage within 48 hrs., and allowed to set at room temperature for 1 hr. before slicing into small sections (diameter 1.9 cm, length 2.9 cm). These served as samples for color and texture measurement.

Color Measurement

The color of surimi gels was measured using a Minolta CR-200 colorimeter (El Monte, CA) calibrated with a standard hitch tile (Hunter Associates Laboratory, Inc., Reston, Virginia) specified for testing the color of surimi gels (NFI, 1991). The L^*, a^*, and b^* values were recorded, with L^* denoting lightness on a 0 to 100 scale from black to white; a^*, red (+) or green (-); and b^*, yellow (+) or blue (-). A "whiteness" index for overall color evaluation of surimi is also used and calculated as: $L^* - 3*b^*$ (Park, 1994). Each experimental point had eight replicates.

Torsion Test

The gels were cut into hourglass shapes, then subjected to twisting in a torsion gelometer (Gel Consultants, Raleigh, NC) to the point of failure, following the procedures described in NFI (1991). The results of the torsion test for our experiments were defined as shear stress and shear strain at failure, calculated from the equations provided by Hamann (1983). Eight replicate samples were tested for each experimental point.

Composition Analysis

The analysis of protein and moisture contents of whiting surimi and of each ingredient was performed according to standard AOAC methods (1984).

Experimental Design

To develop the mathematical functions giving texture and color as a function of five ingredient variables, an appropriate experimental design was needed to limit the number of experimental points. Response surface methodology is the approach most commonly used for seeking optimal responses from experiments involving multiple variables (Box et al, 1978; Cochran and Cox, 1957). In this study, a second-order central composite design for five variables was adopted (Cochran and Cox, 1957) with some modifications. According to Chung and Morrissey (1993) and Morrissey et al. (1993), the maximum concentrations of BPP, PS, WPC33, and

WPC72 that improve the texture properties of PWSBS are 2, 4, 4, and 4%, respectively, while not much improvement was observed beyond these concentrations. Therefore in this study the levels for each ingredient were initially selected as 0, 0.5, 1, 1.5, and 2% for BPP; 0, 1, 2, 3, and 4% for PS, WPC33, and WPC72; and 74, 76, 78, 80, and 82% for moisture content. As shown in Tab. 2.1, the experimental points No.1 - 27 included these combinations of ingredients based on the second order central composite design (Cochran and Cox, 1957) for five variables at the five different levels given above. In central composite design, it is assumed that the optimum is located at the center level of each variable. So additional experimental points are selected about this center level, allowing us to accurately pinpoint the optimum while taking only a few experimental points at the end-levels of each variable. Since a major objective of this study was to investigate methods to minimize the cost of PWSBS rather than simply to optimize the quality of texture and color, it was desired to derive mathematical functions of texture and color having the same level of accuracy over the expected experimental range of each variable. Thus, adding extra experimental points, No.28 - 45 (Tab. 2.1), to increase accuracy of prediction at the end-levels of each variable was found to be necessary. All experimental runs were performed in a random order. After initial analysis, it was learned that a broader range of ingredient levels was needed to reach the optimum

No.	BPP (%)	PS (%)	WPC33 (%)	WPC72 (%)	Moisture (%)	Color L*	Color a*	Color b*	Texture Stress (kPa)	Texture Strain
1	0.5	1	1	1	76	78.2	-4.4	4.1	42.7	2.23
2	1.5	1	1	1	80	79.9	-4.1	5.2	24.5	2.49
3	0.5	3	1	1	80	75.6	-4.6	1.9	24.7	2.38
4	1.5	3	1	1	76	78.8	-4.0	6.2	44.9	2.45
5	0.5	1	3	1	80	83.5	-3.8	5.4	17.6	2.15
6	1.5	1	3	1	76	78.1	-4.7	5.8	47.3	2.35
7	0.5	3	3	1	76	80.4	-4.0	5.3	37.9	2.18
8	1.5	3	3	1	80	77.5	-5.0	4.9	19.9	2.43
9	0.5	1	1	3	80	82.7	-3.8	5.2	19.9	2.20
10	1.5	1	1	3	76	79.6	-4.2	7.2	44.9	2.11
11	0.5	3	1	3	76	79.7	-4.0	5.3	45.5	2.18
12	1.5	3	1	3	80	75.7	-4.7	4.9	26.4	2.17
13	0.5	1	3	3	76	79.3	-4.7	5.3	41.6	2.29
14	1.5	1	3	3	80	84.9	-3.8	7.9	14.8	2.07
15	0.5	3	3	3	80	81.6	-4.1	5.2	18.3	2.17
16	1.5	3	3	3	76	77.5	-4.8	6.3	45.5	2.24
17	0	2	2	2	78	77.9	-4.6	3.2	29.5	2.25
18	2	2	2	2	78	82.8	-3.7	8.3	27.6	2.20
19	1	0	2	2	78	79.4	-4.4	5.1	27.4	2.15
20	1	4	2	2	78	81.5	-3.5	6.6	30.8	2.25
21	1	2	0	2	78	78.1	-4.4	4.6	40.2	2.62
22	1	2	4	2	78	80.0	-4.6	6.2	27.5	2.27
23	1	2	2	0	78	78.8	-4.2	4.5	34.1	2.51
24	1	2	2	4	78	82.2	-4.2	6.9	31.9	2.04
25	1	2	2	2	82	85.1	-3.2	6.3	11.8	2.23
26	1	2	2	2	74	76.3	-4.8	5.2	62.3	2.36
27	1	2	2	2	78	80.6	-3.9	6.0	27.1	2.34
	1	2	2	2	78	81.1	-3.9	6.2	32.5	2.27
28	0	0	0	0	74	80.5	-3.5	4.1	22.0	1.07
	0	0	0	0	74	78.6	-3.6	2.9	21.3	1.03
29	2	0	0	0	82	81.0	-3.8	6.1	14.6	2.44
	2	0	0	0	82	80.0	-3.6	6.7	20.8	2.23
30	0	4	0	0	82	80.4	-3.2	1.0	7.1	1.68
	0	4	0	0	82	79.0	-3.5	1.5	9.5	1.50
31	2	4	0	0	74	79.3	-3.4	7.9	62.3	2.36
32	0	0	4	0	82	82.5	-3.9	3.2	7.1	1.69
	0	0	4	0	82	82.9	-3.7	3.6	6.2	1.45
33	2	0	4	0	74	79.6	-4.2	7.9	35.4	2.11
34	0	4	4	0	74	80.4	-3.7	5.0	31.7	1.87
35	2	4	4	0	82	85.6	-3.3	7.0	7.8	1.98
36	0	0	0	4	82	83.2	-3.7	4.9	10.0	1.97
	0	0	0	4	82	82.0	-3.4	4.5	13.0	1.91
37	2	0	0	4	74	79.8	-4.1	8.5	54.6	1.99
38	0	4	0	4	74	75.0	-4.7	3.2	75.6	2.41
39	2	4	0	4	82	84.4	-3.2	7.8	14.9	2.01

Tab. 2.1 The experimental design and experimental data

40	0	0	4	4	74	81.3	-4.5	6.6	39.8	1.95
41	2	0	4	4	82	88.4	-3.5	9.3	3.6	1.31
	2	0	4	4	82	87.7	-3.5	9.5	3.7	1.33
42	0	4	4	4	82	85.4	-3.7	5.6	8.4	1.74
43	2	4	4	4	74	78.8	-4.2	8.1	56.7	2.01
	2	4	4	4	74	78.8	-4.4	8.7	48.8	2.05
44	0	0	0	0	78	80.2	-3.4	3.5	19.5	1.12
	0	0	0	0	78	79.8	-3.2	3.3	16.9	0.98
45	0	0	0	0	82	80.6	-3.7	1.3	6.0	1.17
	0	0	0	0	82	82.3	-3.3	2.2	6.2	1.38
46	0	0	0	8	78	81.1	-4.7	5.5	37.3	1.80
	0	0	0	8	78	80.0	-4.3	6.0	43.6	1.59
47	0	0	8	0	78	81.9	-4.4	8.4	8.2	1.57
	0	0	8	0	78	82.9	-4.7	8.9	9.5	1.65
48	0	8	0	0	78	75.2	-3.8	0.6	19.0	1.53
	0	8	0	0	78	77.0	-3.4	1.3	16.1	1.39
49	1	2	2	6	78	81.3	-4.5	7.9	24.0	1.64
50	1	2	6	2	78	82.2	-4.1	9.5	13.9	1.73
51	1	6	2	2	78	75.4	-5.0	4.6	32.9	2.20
52	1	2	6	6	74	83.8	-4.1	11.7	19.8	1.35
53	1	6	2	6	74	78.5	-4.6	8.6	53.1	1.67
54	1	6	6	2	74	78.5	-4.6	10.0	36.5	1.81
55	2	0	4	8	74	83.5	-4.0	11.6	27.7	1.27
56	0	4	0	8	76	78.2	-4.9	5.6	66.0	1.77
57	2	0	8	4	74	82.9	-4.0	12.4	14.9	1.30
58	0	4	8	0	76	79.5	-4.6	8.6	18.9	1.65
59	2	8	4	0	74	73.2	-4.8	7.2	75.8	2.42
60	0	8	0	4	76	74.2	-4.4	3.0	62.7	2.29
61	1	2	2	8	76	81.7	-4.4	9.2	37.8	1.37
	1	2	2	8	76	83.6	-4.1	10.1	32.3	1.44
62	1	2	8	2	76	82.9	-4.1	11.1	13.3	1.49
	1	2	8	2	76	83.2	-3.5	11.4	12.8	1.50
63	1	8	2	2	76	73.0	-4.9	4.8	57.4	2.35
	1	8	2	2	76	74.1	-4.0	6.1	39.2	2.31

Table 2.1 (continued)

solution because the use of PS and WPC33 higher than 4% appears to further lower the formulation cost of PWSBS. Thus, the upper levels of PS, WPC33, and WPC72 were further increased from 4% to 8% (experimental points No. 46-63).

Model and Validation

A stepwise regression procedure in the SAS package (SAS Institute, Inc., Cary, NC) was used to fit the texture and color data into second order polynomial equations with interaction terms:

$$Z=A_o+\sum_{i=1}^{5} A_i Y_i+\sum_{i=1}^{5} A_i Y_i^2+\sum_{i=1}^{5}\sum_{j=1}^{5} A_{ij} Y_i Y_j \quad (i \neq j)$$

where Z is the dependent variable, A_o, A_i, A_{ij} are regression coefficients of the model, and Y_i are concentrations (in weight percent) of each ingredient (subscripts i, j = 1..5 represent BPP, PS, WPC33, WPC72, and the final moisture content, respectively). An F test for lack of fit was used to determine whether the regression models adequately fit the experimental data. Once the regression models were developed, 14 new experimental points determined randomly in separate experiments were then used to test the models.

Least Cost Model of PWSBS

The objective function to be minimized in the least cost model of PWSBS, was the total cost of ingredients. The cost of each ingredient was collected from the commercial suppliers. Cost of ingredients and the experimental values of ingredient protein and moisture contents are reported in Tab. 2.2. Using results of Tab. 2.2, the final moisture content of PWSBS (Y_5) in the regression models of texture and color can be substituted by the summation of moisture contents of each ingredient as the following equation:

$$(Y_5) = 0.076X_1 + 0.17X_2 + 0.064X_3 + 0.052X_4 + X_5 + 0.751X_6$$

where X_1, X_2, X_3, X_4, X_5, and X_6 are the weight percent of BPP, PS, WPC33, WPC72, water, and surimi, respectively.

Upper and lower boundaries of the parameter which defines each constraint function (i.e. texture, color, and ingredients) were used to define the quality of PWSBS. According to Lanier (1988) and Park (1993), one example of a set of constraints depicting high quality PWSBS are listed in Tab. 2.3. Hamann and MacDonald (1992) and Park (1992) define a texture mapping procedure that might be used to identify boundaries of constraints which would simulate certain textural characteristics (One example might characterize properties of given frankfurther product). The example constraints given in Tab. 2.3 simulate a good quality surimi seafood and were used in this study to develop the least cost formulations for PWSBS.

Ingredient	Protein (%)	Moisture (%)	Cost (per lb.)
BPP	68.7	7.6	$2.50
PS	0.0	17.0	$0.39
WPC33	33.0	6.4	$0.60
WPC72	72.3	5.2	$2.05
Water	0.0	100.0	$0.00
Surimi	15.7	75.1	$1.00
NaCl	0.0	0.0	$0.22

Tab. 2.2 The protein content, moisture content, and the cost (in 1993) of each ingredient in PWSBS

Qualty Index	Low- and/or High-boundary Values
Protein content	$\geq$ 10%
Moisture content	$\geq$ 74% and $\leq$ 77%
Surimi content	$\geq$ 40%
Salt	= 2%
Texture	
Shear stress	$\geq$ 36 and $\leq$ 44 kPa
Shear strain	$\geq$ 2.0 and $\leq$ 2.6
Color	
Yellowness	$\leq$ 7
Whiteness	$\geq$ 60

Tab. 2.3 General constraints depicting high quality surimi-based seafoods

Nonlinear and Linear Programming

A primal simplex method (Dantzig, 1963) was used to solve the linear programming problem. In the case of solving a nonlinear constrained nonlinear programming problem, it was transformed, with the augmented Lagrangian procedures described by Robinson (1972) and Murtagh and Saunders (1982), into a sequence of linearly constrained nonlinear subproblems which could be solved by using a reduced gradient algorithm (Wolfe, 1967). In solving nonlinear programming problems, 20 different starting quests were randomly used to avoid getting local minima instead of a global minimum. The random number function in the commercial spreadsheet, Quattro Pro (Borland International, Inc., Scotts Valley, CA), was used to generate these starting quests. A commercial linear and nonlinear programming package "AMPL" (The Scientific Press, San Francisco, CA) (Murtagh and Saunders, 1978; 1982) was used to search least cost formulations of PWSBS with varied composition, texture, color, and constraints.

RESULTS AND DISCUSSION

Texture of Whiting Surimi Gels

The effects of ingredient levels on the texture properties of whiting surimi gels are presented in Tab. 2.1. The regression coefficients (R^2) of the models for shear stress and shear strain were 0.92 and 0.85, respectively

(Tab. 2.4). To show the results graphically, the response surface plots of shear stress and shear strain (Fig. 2.1 and 2.2) were derived from the regression models in Tab. 2.4. It was found that adding BPP, WPC72, and PS while maintaining constant moisture content increased the shear stress values, however a reverse effect was found with the addition of WPC33 (Fig. 2.1). As shown in Fig. 2.2, the addition of all the ingredients increased the shear strain values. The addition of WPC72 in quantities to 5% has been found to improve the texture properties of whiting surimi gels (Chung and Morrissey, 1993). The results of this study showed, however, that as WPC72 concentrations exceeded 6%, shear strain values began to decrease. The regression models of shear stress and shear strain were clearly nonlinear (Tab. 2.4) with interactions between ingredients being statistically significant. As shown in Fig. 2.1, for example, the addition of WPC72 increased shear stress at low BPP levels but not at high BPP levels, indicating an antagonistic interaction between BPP and WPC72.

The ability of WPC to improve the texture properties in surimi gels has been related to its ability to inhibit the protease activity in surimi (Chang-Lee et al., 1990; Akazawa et al., 1993). In this study, WPC72 had more influence on texture properties of PWSBS than did WPC33. The study of Piyachomkwan and Penner (1995) also suggests that the extent of inhibition by the WPC on the protease activity in whiting surimi is dependant upon the protein content of WPC. Thus,

	L*	a*	b*	whiteness	stress	strain
Intercept	601.3994	92.2516	10.4949	18.4010	202.1753	- 1.4390
BPP	----------	----------	2.1424	- 9.7260	58.5442	0.6923
PS	- 5.9840	----------	- 0.2027	- 4.9118	33.3563	0.1264
WPC33	0.5669	- 0.2235	0.0878	0.5107	1.2762	1.3320
WPC72	0.3995	- 1.8800	0.4964	- 1.1134	42.2810	1.4146
Moisture	- 13.8035	- 2.4921	- 0.1021	0.6831	- 2.3675	0.0339
BPP^2	----------	----------	----------	1.8087	----------	- 0.1175
PS^2	----------	----------	----------	- 0.0842	----------	- 0.0086
$WPC33^2$	----------	0.0171	0.0849	- 0.2911	- 0.3481	- 0.0223
$WPC72^2$	----------	0.0152	----------	----------	- 0.5245	- 0.0301
$Moisture^2$	0.0911	0.0162	----------	----------	----------	---------
BPP x PS	----------	----------	----------	----------	----------	---------
BPP x WPC33	----------	----------	- 0.1576	0.5018	----------	- 0.0538
BPP x WPC72	----------	----------	----------	----------	- 1.9289	- 0.0941
BPP x Moisture	----------	----------	----------	----------	- 0.6565	----------
PS x WPC33	----------	----------	0.0448	- 0.1223	----------	- 0.0158
PS x WPC72	----------	----------	----------	----------	----------	- 0.0137
PS x Moisture	0.0705	----------	----------	0.0719	- 0.4186	----------
WPC33 x WPC72	----------	0.0441	----------	----------	- 1.0516	- 0.0298
WPC33 x Moisture	----------	----------	----------	----------	----------	- 0.0143
WPC72 x Moisture	----------	0.0215	----------	----------	- 0.4477	- 0.0142
R^2	0.69	0.53	0.93	0.97	0.92	0.85
F test for lack of fit						
F statistic[1]			2.99	1.31	1.65	4.56
F critical value[1]			~2.99	~3.01	~3.01	~3.04
Test result			adequate	adequate	adequate	inadequate

---------- the coefficient is not significant ($p > 0.05$)

[1] with significance level, $\alpha = 0.01$

Tab. 2.4 Regression coefficients of the second order polynamials for texture and color of PWSBS

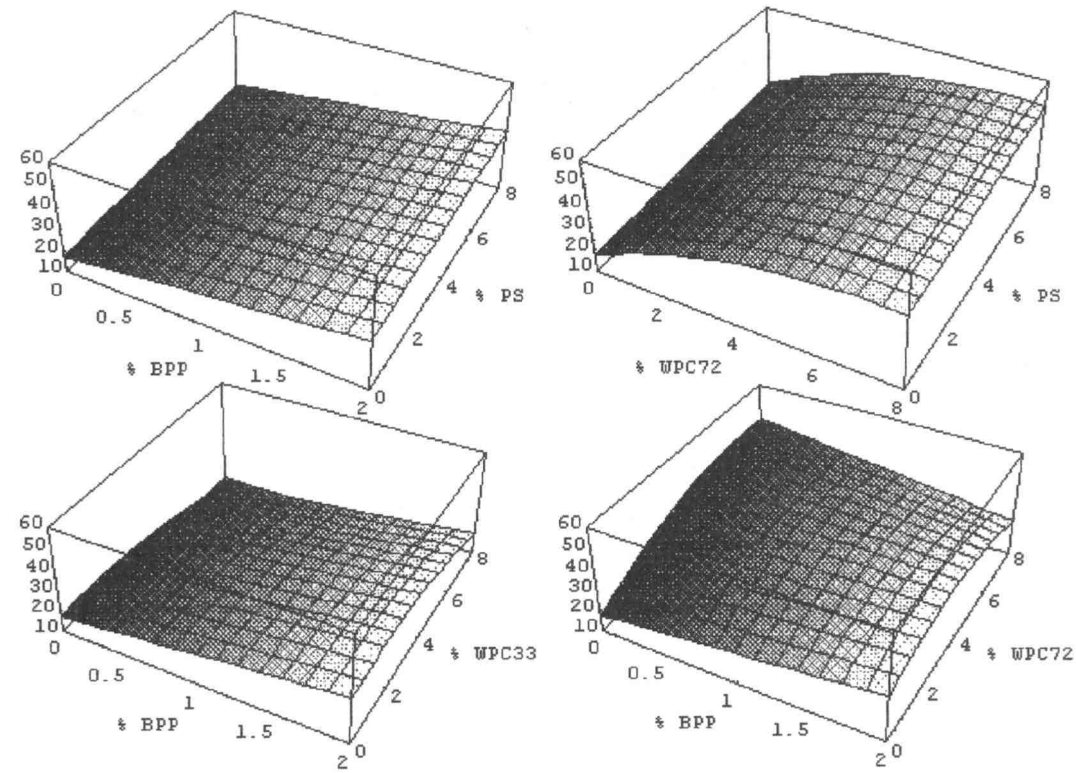

Fig. 2.1 The response surfaces of the shear stress (kPa) of whiting surimi gels with 78% moisture content

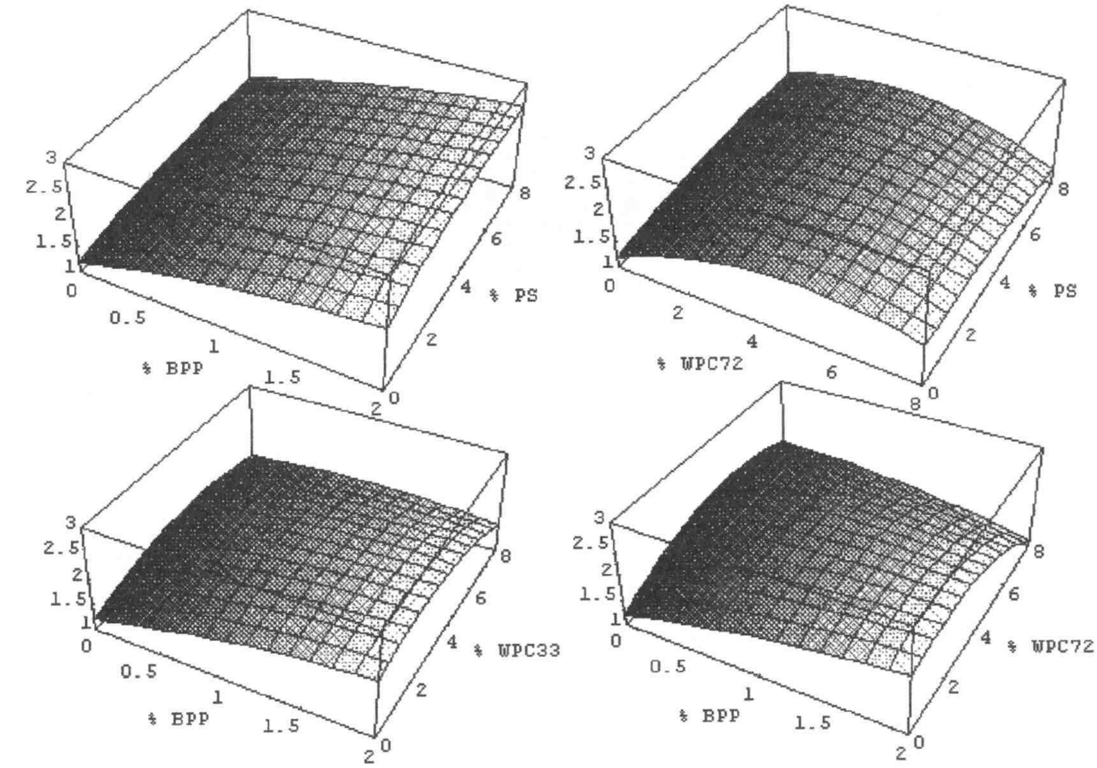

Fig. 2.2 The response surfaces of the shear strain of whiting surimi gels with 78% moisture content

the protein content of WPC is shown not only to influence its cost (Tab. 2.2) but also its ability to improve the texture properties of whiting surimi gels.

Color of Whiting Surimi Gels

The effects of ingredient levels on the color properties of whiting surimi gels are presented in Tab. 2.1. The regression coefficients (R^2) of the regression models for L^*, a^*, b^* and whiteness ($L^* - 3b^*$) were 0.69, 0.53, 0.93 and 0.97, respectively as shown in Table 2.4. This indicates that b^* (an indictor of yellowness or blueness) and whiteness are parameters capable of describing significant color changes of PWSBS, with the ingredients used in this study. Adding BPP, WPC72, and WPC33 was found to decrease the whiteness and increase the yellowness of surimi gels. However, the addition of PS decreased the yellowness and showed little effect on the whiteness of surimi gels. The low R^2 value for the regression models of a^* (an indictor of redness or greenness), indicated that a^* was little affected by the addition of ingredients used in this study. Park (1994; 1995) also reported the independence of a^* values of surimi gels upon protein addition and changing processing variables.

Nonlinear vs. Linear Model

An F test for lack of fit (with significance level 0.01) indicated that the second order regression models of

b^*, whiteness, and shear stress adequately fit the experimental data. However, the F test indicated that the model of shear strain did not adequately fit its experimental data (Tab. 2.4). This suggests that still higher order terms in the model might be required or that some transformation of the shear strain data set is needed (Box and Draper, 1987). Various transformations (logarithmic, square, square root) on the data of shear strain were applied and showed no significant improvement.

Table 2.4 (and Figures 2.1-2) indicates that the relationships between either texture or color of PWSBS and its ingredient levels are clearly nonlinear. When the experimental data of texture and color were fitted into linear models, an F test for lack of fit showed that the linear models of b^*, whiteness, shear stress, and shear strain did not adequately fit their experimental data (Tab. 2.5). To examine the predictive capability of both nonlinear and linear regression models of texture and color, 14 separate experiments using randomly selected variables were run, and results appear in Tab. 2.6-7. The nonlinear models of shear strain, whiteness, and b^* provided quite reasonable estimates, but the nonlinear model for shear stress slightly underestimated the experimental results. As shown in Tab. 2.6-7, the mean errors between experimental data and estimated values from linear models of b^*, whiteness, shear stress, and shear strain were all significantly higher than that of nonlinear models. Thus,

	b^*	whiteness	stress	strain
Intercept	11.6618	2.3186	362.3784	1.8584
BPP	1.5908	-4.3733	3.1203	0.2115
PS	-0.1563	-0.1183	1.7157	0.0444
WPC33	0.6568	-1.4308	-3.0265	-0.0412
WPC72	0.4366	-0.9325	0.9875	-0.0296
Moisture	-0.1178	0.8913	-4.3100	-0.0008
R^2	0.88	0.89	0.72	0.25
F test for lack of fit				
F statistic*	4.88	5.61	5.44	20.19
F critical value*	~2.98	~2.98	~2.98	~2.98
Test result	inadequate	inadequate	inadequate	inadequate

* with significance level, $\alpha = 0.01$

Tab. 2.5 Regression coefficients of the linear equation for texture and color of PWSBS

Independent variables					Texture					
					stress (kPa)			strain		
BPP	PS	WPC33	WPC72	Moisture		Nonlinear	Linear		Nonlinear	Linear
(%)	(%)	(%)	(%)	(%)	Exp.[1]	Esti.[2]	Esti.[3]	Exp.[1]	Esti.[2]	Esti.[3]
0	0	4	2	74	47.9	34.3	33.3	2.15	2.18	1.58
0	0	7	3	75	20.0	15.8	20.9	1.65	1.98	1.42
0	1	1	4	76	53.9	45.1	37.5	2.16	2.14	1.69
0	4	1	0	80	14.9	13.2	21.4	1.85	1.74	1.93
0	5	6	2	74	45.0	37.6	35.8	1.79	1.97	1.72
0.5	2	4	2	82	10.0	6.7	3.8	2.03	1.91	1.77
0.5	2	4	8	78	8.4	6.1	27.0	1.26	0.98	1.59
1	5	3	3	75	54.0	50.6	44.7	2.30	2.29	2.02
1.5	3	2	3	78	41.2	34.2	32.9	2.25	2.29	2.08
2	0	3	1	76	44.1	41.0	33.0	2.06	2.29	2.07
2	1	6	6	75	14.0	12.7	34.8	1.20	0.87	1.84
2	2	3	4	74	68.8	52.5	48.0	2.08	2.15	2.07
2	3	3	3	82	9.2	6.2	14.2	1.80	1.89	2.14
2	7	1	1	76	49.0	54.1	51.0	2.38	2.51	2.46

	stress Nonlinear Esti.	stress Linear Esti.	strain Nonlinear Esti.	strain Linear Esti.
Mean error between estimate and experimental values	18.6%	50.9%	8.6%	14.8%

[1]experimental values
[2]estimated values from the nonlinear regression model (Table 2.4)
[3]estimated values from the linear regression model (Table 2.5)

Tab. 2.6 Validation of regression models for the texture of PWSBS

Independent variables					Color					
					b*			whiteness		
BPP	PS	WPC33	WPC72	Moisture		Nonlinear	Linear		Nonlinear	Linear
(%)	(%)	(%)	(%)	(%)	Exp.[1]	Esti.[2]	Esti.[3]	Exp.[1]	Esti.[2]	Esti.[3]
0	0	4	2	74	5.4	5.6	6.4	63.5	64.1	60.7
0	0	7	3	75	9.4	9.1	8.7	54.4	55.6	56.4
0	1	1	4	76	4.4	4.7	5.0	65.7	66.4	64.8
0	4	1	0	80	0.7	1.7	2.3	74.7	74.8	71.7
0	5	6	2	74	7.9	7.8	7.0	54.8	55.6	57.2
0.5	2	4	2	82	5.1	5.5	6.0	67.9	66.8	65.4
0.5	2	4	8	78	9.2	8.9	9.1	54.1	56.8	56.2
1	5	3	3	75	6.3	6.7	6.9	58.4	57.3	57.1
1.5	3	2	3	78	6.8	6.9	7.0	58.7	59.8	59.3
2	0	3	1	76	7.5	7.6	8.3	57.1	58.9	56.1
2	1	6	6	75	10.2	11.9	12.4	52.4	49.0	46.1
2	2	3	4	74	8.3	9.2	9.5	52.7	54.0	51.3
2	3	3	3	82	9.0	7.8	8.0	57.7	61.9	59.2
2	7	1	1	76	6.0	6.3	5.9	58.3	57.1	58.1

	b* Nonlinear Esti.	b* Linear Esti.	whiteness Nonlinear Esti.	whiteness Linear Esti.
Mean error between estimate and experimental values	17.7%	26.2%	2.7%	3.4%

[1]experimental values
[2]estimated values from the nonlinear regression model (Table 2.4)
[3]estimated values from the linear regression model (Table 2.5)

Tab. 2.7 Validation of regression models for the color of PWSBS the predictive capability of linear models of texture and color for the new data set was less than that of nonlinear models.

The least cost model of PWSBS is shown in Tab. 2.8. Due to the nonlinearity of the functions of texture and color, nonlinear programming techniques must be used to search the solution of the least cost model of PWSBS.
As shown in Tab 2.9, the levels of WPC33 and WPC72 in the least cost formulation which included BPP were 4.08 and 2.98%, respectively, with the total concentration of WPC reaching 7.06%. When BPP was not used in the formulation, the amount of WPC33 and WPC72 became 2.72 and 3.82%, respectively. This indicated that WPC is economically competitive with PS and BPP under the quality constraints listed in Tab. 2.3. A comparison between the least cost formulations using nonlinear and linear models is listed in Tab. 2.9. To determine whether it is possible to produce PWSBS without using BPP, the least cost fromulations with and without BPP were also reported in Tab. 2.9. It was found that the percentages of BPP and WPC33 in the formulation were quite different between nonlinear and linear models. It was also found that the least cost of PWSBS obtained from linear models was higher than that from nonlinear models and could not be treated as the true least cost in this case. The results of Tab. 2.9 further suggest that BPP may be excluded from the least cost formulation, with only a slight increase of the ingredient cost (0.5¢/lb.

Note that 2% NaCl was added to each formulation

Objective Function
Cost: $c_1 X_1+c_2 X_2+c_3 X_3+c_4 X_4+c_5 X_5+c_6 X_6+2c_7$
Where

X_1: BPP (%) X_2: PS (%) X_3: WPC33 (%)
X_4: WPC72 (%) X_5: Water (%) X_6: Surimi (%)
$c_1, c_2, c_3, c_4, c_5, c_6$ are costs of each ingredient; c_7 = cost of salt

Constraint Functions
Note: l, m, n, p, q, r, s are low- or high-boundary parameters defined by the quality target

Weight Constraint: $X_1+X_2+X_3+X_4+X_5+X_6+2 = 100$

Surimi Constraint: $X_6 \geq 1$

Protein Constraint: $0.687 X_1+0.33 X_3+0.723 X_4+0.157 X_6 \geq m$

Moisture Constraint: $0.076 X_1+0.17 X_2+0.064 X_3+0.052 X_4+X_5+0.751 X_6 \geq n_1$ and $\leq n_2$

Stress Constraint:

$$202.17532+58.36425 X_1+32.95384 X_2+1.12465 X_3+42.15790 X_4-2.36747 X_5 -1.77797 X_6-0.04989 X_1^2-0.07116 X_2^2-0.34813 X_3^2-0.54781 X_4^2-0.14341 X_1 X_2 -0.04201X_1 X_3-1.99703 X_1 X_4-0.65647 X_1 X_5-0.49301 X_1 X_6-0.02679 X_2 X_3 -0.09787 X_2 X_4-0.41861 X_2 X_5-0.31438 X_2 X_6-1.08021 X_3 X_4-0.44768 X_4 X_5 -0.33621 X_4 X_6 \geq p_1 \text{ and } \leq p_2$$

Strain Constraint:

$$-1.43904+0.69489 X_1+0.13215 X_2+1.33419 X_3+1.41631 X_4+0.03385 X_5+0.02542 X_6 -0.11746 X_1^2-0.00861 X_2^2-0.02325 X_3^2-0.03087 X_4^2-0.05489 X_1 X_3-0.0952 X_1 X_4 -0.01824 X_2 X_3-0.01611 X_2 X_4-0.03148 X_3 X_4-0.01428 X_3 X_5-0.01072 X_3 X_6 -0.01422 X_4 X_5-0.01068 X_4 X_6 \geq q_1 \text{ and } \leq q_2$$

b* Constraint:

$$10.49493+2.13462 X_1-0.22006 X_2+0.08131 X_3+0.49107 X_4-0.10214 X_5-0.07671 X_6 +0.08494 X_3^2-0.15758 X_1 X_3+0.04475 X_2 X_3 \leq r$$

Whiteness Constraint:

$$18.4010-9.67407 X_1-4.79570 X_2+0.55437 X_3-1.07783 X_4+0.68307 X_5+0.51298 X_6 +1.80867 X_1^2-0.07201 X_2^2-0.29106 X_3^2+0.00547 X_1 X_2+0.50178 X_1 X_3-0.11770 X_2X_3 +0.00374 X_2 X_4+0.07193 X_2 X_5+0.05402 X_2 X_6 \geq s$$

Tab. 2.8 The least cost model of PWSBS

Ingredient	Nonlinear Model With BPP	Nonlinear Model Without BPP	Linear Model With BPP	Linear Model Without BPP
BPP	0.32%	0.00%	0.75%	0.00%
PS	5.67%	5.76%	5.67%	6.74%
WPC33	4.08%	2.72%	2.85%	0.31%
WPC72	2.98%	3.82%	3.13%	2.91%
Water	44.95%	45.33%	45.59%	38.40%
Surimi	40.00%	40.37%	40.00%	49.64%
NaCl	2.00%	2.00%	2.00%	2.00%
Total Cost (per lb.)	$0.520	$0.525	$0.527	$0.589

Tab. 2.9 The least cost formulation of PWSBS

of PWSBS), particularly when the use of BPP presents some difficulty with product labeling and sensory requirements (Akazawa et al., 1993). However, the use of a linear model may require us erroniously to include BPP in the formulation to avoid a significant predicted increase in total ingredient cost. This indicates that the linear assumption needs to be checked out seriously before it can be applied to least cost food formulations, otherwise inaccuracies may result.

CONCLUSION

The relationships between the quality properties of texture and color for Pacific whiting surimi-based seafood (PWSBS) and its ingredient levels are non-linear. Non-linear programming techniques thus provided a better method than linear programming to solve the least cost model. The use of WPC was found to be promising in terms of improving texture properties of PWSBS while remaining economically competitive. It was found that WPC could be a potential replacement of BPP based on the quality constraints and 1993 prices. The use of the least cost formulation model allows us to obtain more insight regarding the relationships among ingredient costs, ingredient percentage, and the desired quality levels (Results are presented in a separate article).

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Chapter 3

The Market Potential of Using Whey Protein Concentrate as Functional Ingredient in Surimi Seafoods

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The Market Potential of Using Whey Protein Concentrate as Functional Ingredient in Surimi Seafoods

The dairy industry annually produces thousands of tons of whey protein concentrate (WPC), a by-product from cheese or casein manufacture, which is now available as a steady source of functional protein for the food industry due to the improvement of processing techniques. The application of ultrafiltration, a pressure-driven filtration process in which porous membranes are used to recover proteins from liquid whey, allows the dairy industry to produce WPC in a quite efficient way (Hobman, 1992). Research exploring the compositional and functional chacteristics of WPC, and identifying the processing factors that influence them, also supports new uses of WPC as a functional ingredient in foods. With protein content in the range of 30-80%, WPC not only serves as an excellent nutritional source (Delaney, 1976; Forsum, 1979; Kunachowicz et al. 1976), but also provides the food industry with diverse functional properties, such as gelation, whippability, foaming, solubility, and emulsifying capacity (Morr, 1984; Morr and Foegeding, 1990; Mangino, 1992). Even though WPC has been used as a functional ingredient in ice cream, frozen desserts, baked goods, beverages, and meat products, the continuous development of new product forms is still the key for promoting the utilization of WPC (Morr, 1984; 1992).

It is important to recognize that the utilization of WPC in the food industry depends not only on its technical feasibility but also on its economic feasibility. The application of least cost formulation using optimization techniques has been found to improve the market profit and/or quality control for various food products and to provide management with more detailed and precise decision-making information (IBM, 1966; Kramlich et al., 1973; Lanier and Park, 1989). This article explores the economic potential of using WPC as a functional ingredient in Pacific whiting surimi-based seafoods (PWSBS) by applying a least cost formulation technique.

Pacific whiting (Merluccius productus) was an underutilized species due to its soft texture caused by protease enzymes that may be related to parasites (Erickson et al., 1983). The allowable catch of Pacific whiting varies around 200,000 metric tons/year, the largest trawl fishery off the west coast of the United States (not including Alaska). Most of Pacific whiting is headed, gutted, deboned, minced, and then washed to produce "surimi". The addition of cyroprotectants (such as sucrose, sorbitol, and sodium tripolyphosphate) prevents its quality deterioration in subsequent frozen storage (Lee, 1984). The surimi is subsequently processed into various gelled products, such as artificial crab legs and meats, that are very popular in the U.S. and particularly in Japan and Korea due to their unique textural quality (Zalke, 1992; Kano, 1992).

During the processing of whiting surimi-based products, gel-strength enhancers and/or enzyme inhibitors such as beef plasma protein and starches are needed to overcome soft texture problems caused by the protease enzymes (Morrissey et al., 1993). To ensure a finished product with the desired target texture, Hamann and MacDonald (1992) and Park (1992) described a texture mapping procedure using a stress vs. strain diagram, as shown in Fig. 3.1.

The use of WPC has been found to increase the gel strength of whiting surimi seafood (Chung and Morrissey, 1993; Hsu et al. 1995). Piyachomkwan and Penner (1995) also suggested that WPC protects the myofibrillar proteins of surimi from the attack of protease enzymes. Thus, the use of WPC in PWSBS is technically feasible; its economic viability is further studied and reported in this article.

Potential Utilization of WPC

To estimate the potential utilization of WPC as a functional ingredient in PWSBS, approximate percentages of WPC in the least cost formulation are needed. Hsu et al (1995) have developed least cost models of PWSBS with four food additives. These are potato starch, beef plasma protein, and two varieties of whey protein concentrate: WPC72 (New Zealand Milk Products Inc., CA) and WPC33 (Avonmore West Inc., Idaho). The objective function to be minimized was simply the total ingredient cost of PWSBS. The mathematical constraint functions representing product

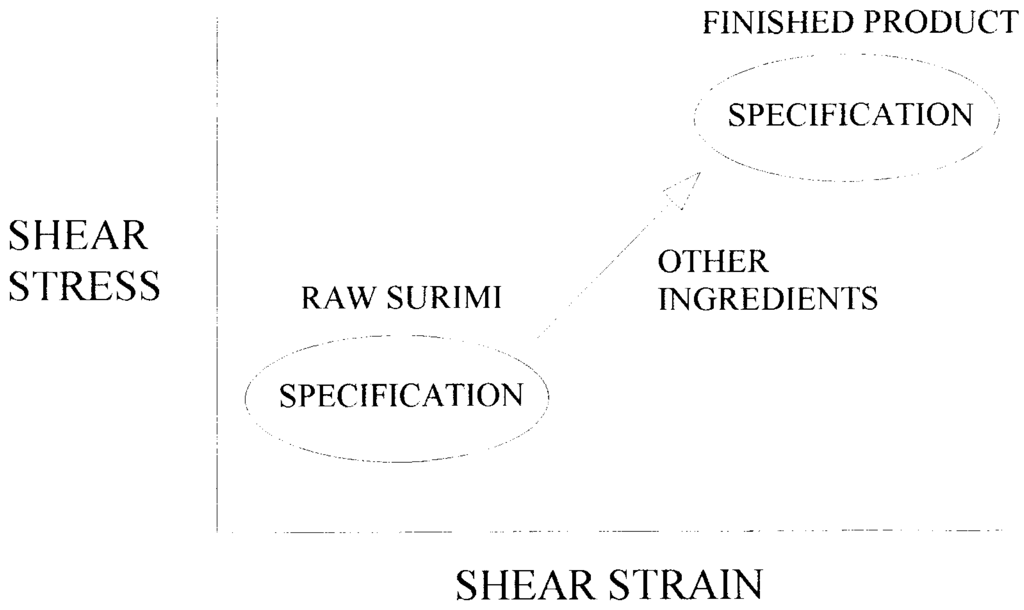


Fig. 3.1 Control of finished product specification

texture and color were nonlinear, thus nonlinear programming techniques are needed to search for the optimal solutions of the least cost model. Each constraint function contained low- and/or high-boundary values of parameters to define the quality of PWSBS. By changing these boundary values, various least cost formulations can be obtained to reflect the levels of quality requirements.

Here, we use these models to present example PWSBS formulations based on the following assumptions/conditions:

1. The relationships between product quality parameters (texture and color) and ingredient levels, are based on the models developed by Hsu et al. (1995).
2. The low- and/or high-boundary values for the constraint functions of texture, color, and composition are based on experience and recommendations of Lanier (1988) and Park (1993) and are listed below. Note that the texture properties of PWSBS are presented as shear stress and shear strain, indicating the gel strength and the cohesiveness, respectively (Hamann, 1988). The color parameter L^* represents lightness on a 0 to 100 scale from black to white; b^* indicates yellowness (+: positive value) or blueness (-: negative value). A "whiteness" index for overall color evaluation of PWSBS is also used and calculated as $L^* - 3*b^*$ (Park, 1994).

Protein content	≥ 10%
Moisture content	≥ 74% and ≤ 77%
Surimi content	≥ 40%
Salt	= 2%
Texture	
Shear stress	≥ 36 and ≤ 44 kPa
Shear strain	≥ 2.0 and ≤ 2.6
Color	
Yellowness	≤ 7
Whiteness	≥ 60

3. The cost of each ingredient is based on the manufacturer's listed cost in 1993 (Tab. 3.1).

As shown in Tab. 3.1, the percentage of WPC, including WPC72 and WPC33 (with 72% and 33% protein content, respectively), in the least cost formulation of PWSBS was 2.98% and 4.08%, respectively. This indicated that WPC is economically competative with potato starch (PS) and beef plasma protein (BPP) under the assumptions/conditions described above. In fact, since the difference between the least cost of PWSBS with and without BPP is only a half cent per pound, BPP may likely be excluded from the formulation when or if the use of BPP presents some difficulties with product labeling and/or sensory requirements (Akazawa et al., 1993).

Ingredient	Cost in 1993	Formulation with BPP	Formulation without BPP
BPP	$2.50/lb.	0.32%	0.00%
PS	$0.39/lb.	5.67%	5.76%
WPC33	$0.60/lb.	4.08%	2.72%
WPC72	$2.05/lb.	2.98%	3.82%
Water	$0.00/lb.	44.95%	45.33%
Surimi	$1.00/lb.	40.00%	40.37%
NaCl	$0.22/lb.	2.00%	2.00%
	Total Cost:	$0.520 per lb.	$0.525 per lb.

Tab. 3.1 The least cost formulation of PWSBS with and without BPP

Factors Affecting Amounts of WPC Used in the Formulations

Factors that affect least cost food formulations include the cost of each ingredient, the required levels of functional and compositional properties, and the relationships between ingredients and properties of the final food products. Among these factors, ingredient costs are most subject to change, due to variable market conditions. Our example application of least cost formulation shows how the costs of WPC72 and WPC33 will affect the amount that can be used, subject to the assumed constraint boundary values given in the previous section. Figure 3.2 shows that the amount of WPC72 in the least cost formulation remained unchanged even if its cost increased from $2.05 (its cost in 1993) to $3.80/lb. (This assumes costs of other ingredients are held constant). However, as cost of WPC72 exceeds $3.80/lb., the allowable level falls rapidly to zero because of the need to increase the relative amounts of BPP and surimi in the formulation. Similarly, the allowed amount of WPC33 in the formulation first decreased, then remained constant with increase of its cost (Fig. 3.3). However, WPC33 was excluded from the formulation only when its cost reached $4.80/lb, 8 times the cost in 1993.

It was found that in the range of $0.10-$1.00/lb., the cost of potato starch ($0.39/lb. in 1993) showed no influence on the percentages of WPC72 and WPC33 used in the formulation. It was also found that even if the cost of

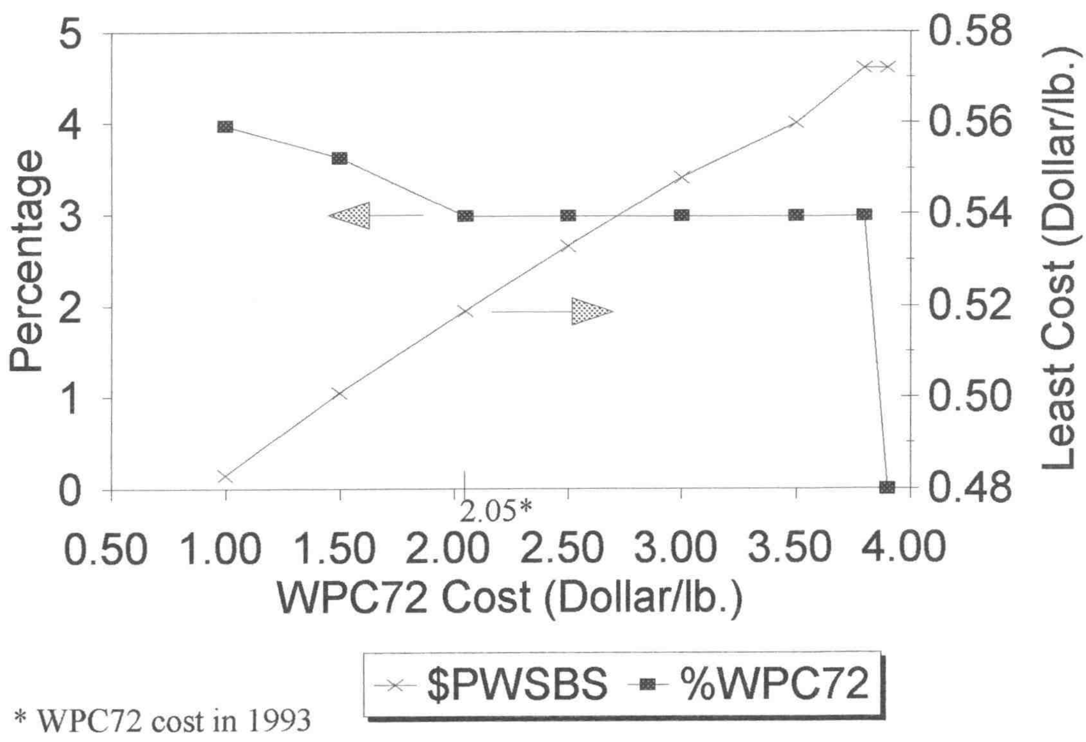
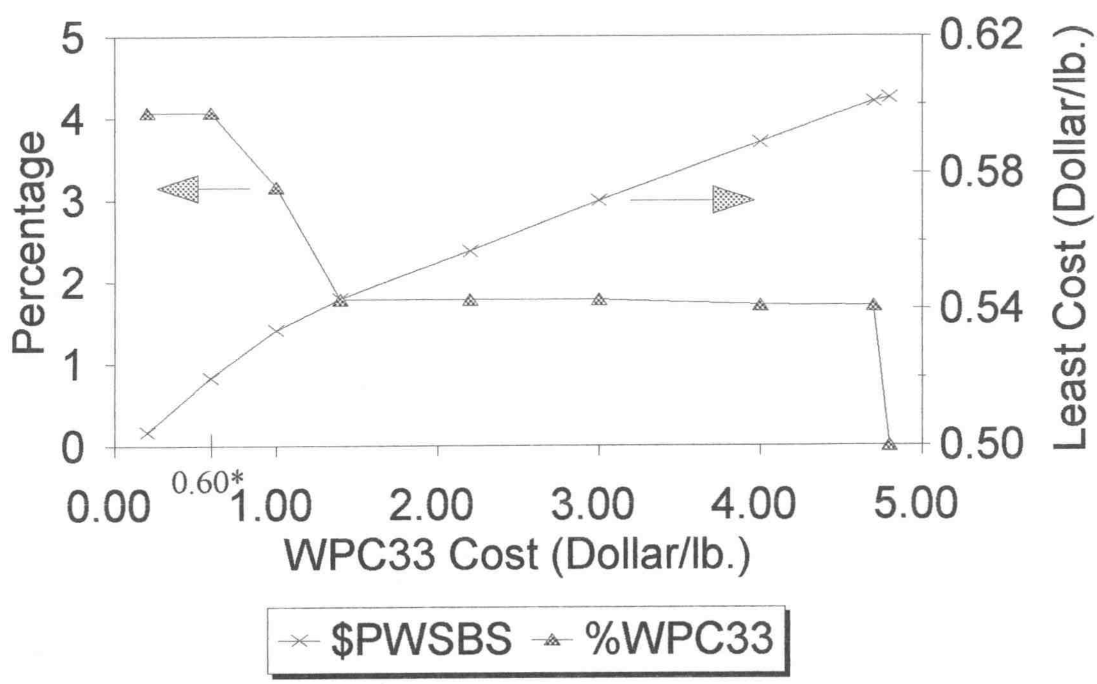


Fig. 3.2 How cost of WPC72 affects its use in least cost formulation of PWSBS



* WPC33 Cost in 1993

Fig. 3.3 How cost of WPC33 affects its use in least cost formulation of PWSBS beef plasma protein (BPP) decreased from \$2.50/lb. (its cost in 1993) to \$0.50/lb., the percentage of total WPC in the formulation still remained at 6.3%. This results further indicate that under the quality constraint levels listed previously, both WPC72 and WPC33 are economically competitive with PS and BPP, ingredients which are commonly used in PWSBS to modify its texture properties.

Figure 3.4 shows how a variation in the quality boundaries of texture and color of PWSBS affects the amount of ingredients in the least cost formulation. In this example, the authors assumed the base quality level to be defined by the boundary values for texture and color listed previously. As the low- and high-boundary values for the constraint functions of texture and color increase simultaneously, the allowed percentage of WPC33 in the formulation decreases; however, the percentage of WPC72 used in the formulation increases with this quality increase. As the required quality level increases above 10%, it is impossible to find a formulation using these ingredients. Note that the least cost of PWSBS increases with the increase of the texture and color quality levels.

The least cost formulation and the total ingredient cost of PWSBS depend strongly upon the cost of whiting surimi and its minimal percentage needed in the formulation (assumed to be 40% in all previous cases). Fig. 3.5 shows that while surimi cost remains above \$0.50/lb., the percentages of all other ingredients remained the same.

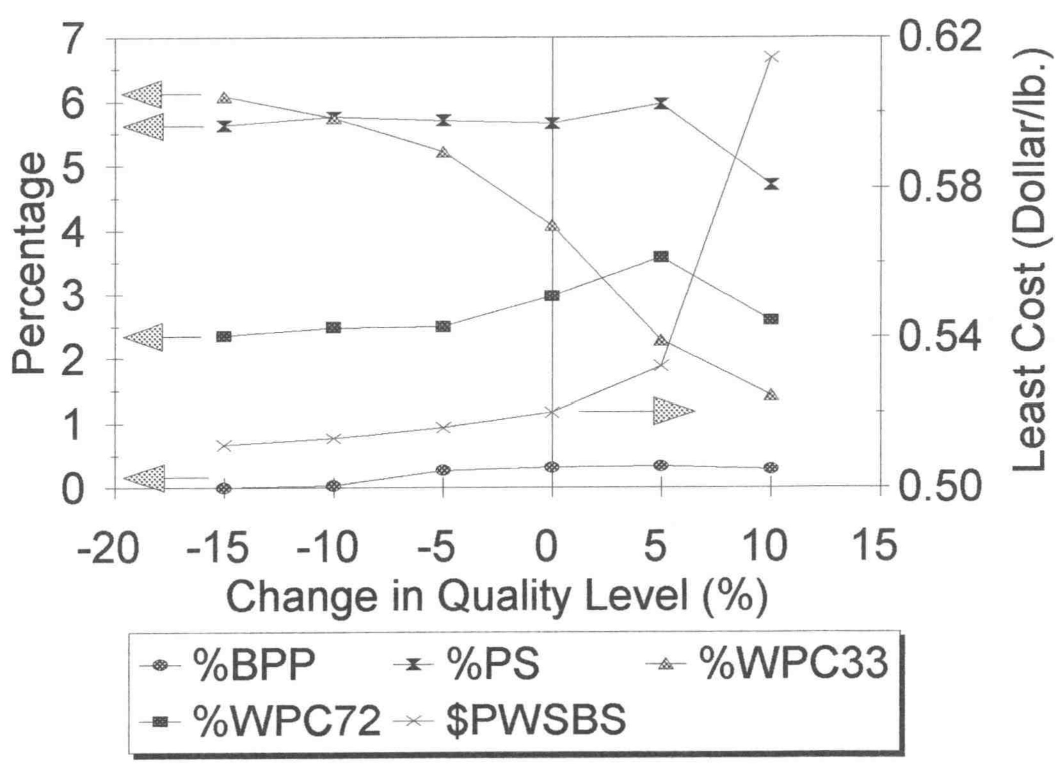
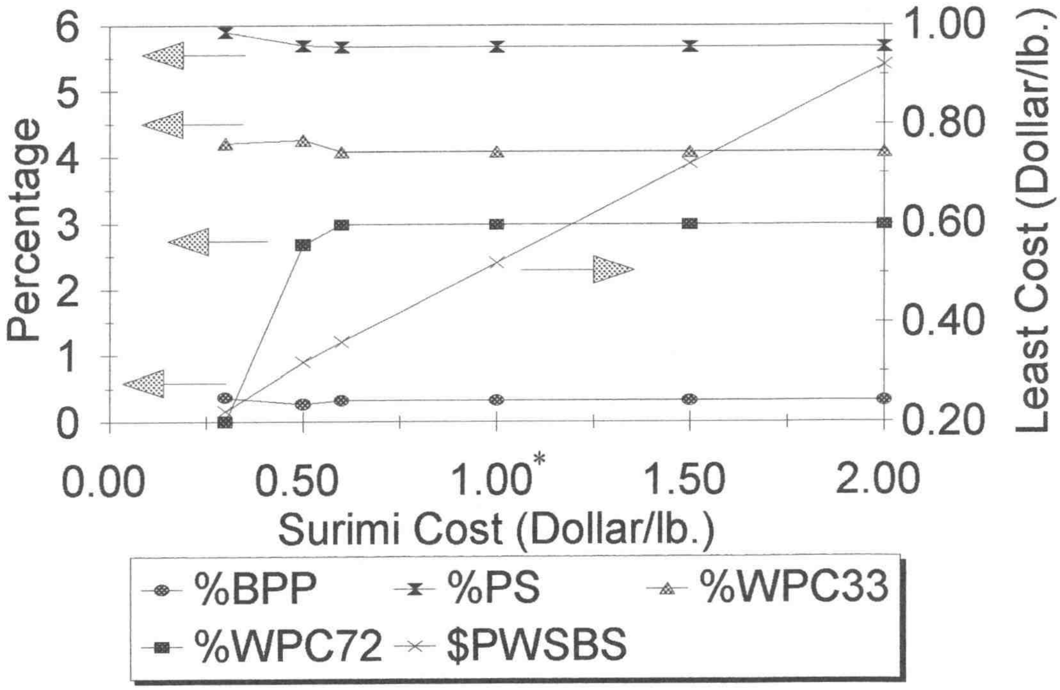


Fig. 3.4 How levels of quality (texture and color) affect ingredients and least cost of PWSBS



* Surimi Cost in 1993

Fig. 3.5 How surimi cost affects the levels of other ingredients and the least cost of PWSBS

However, if the cost of whiting surimi were to fall below $0.50/lb. (quite unlikely), the least cost formulation would then begin to change since it would be then affordable to increase the percentage of whiting surimi in the formulation. If the minimum required percentage of whiting surimi were to increase without changing the assumed target quality levels of PWSBS, the use of WPC would decrease (Fig. 3.6). However, this would also mean an increase in the total cost of ingredients, a factor which may reduce the product's market acceptance. Nevertheless, if the consumers are willing to pay a higher price for a higher surimi content, then it is clear that the opportunities to use WPC become limited.

Maximum Selling Prices for WPC

The use of our least cost formulation model also allows WPC manufacturers to estimate the maximum selling price for WPC as an ingredient in PWSBS. Based on the quality constraints and 1993 costs, the authors further assumed the existence of a maximum allowable total ingredient cost of PWSBS subject of course to variation. Once the total ingredient cost of PWSBS approaches its allowable limit, manufacturers would seek less costly ingredients. For this example, the authors arbitrarily selected $0.52/lb, the value previously determined and indicated in Tab. 3.1; Figs. 3.7-10 indicate the maximum selling prices of WPC72, WPC33, potato starch, and beef plasma protein, respectively.

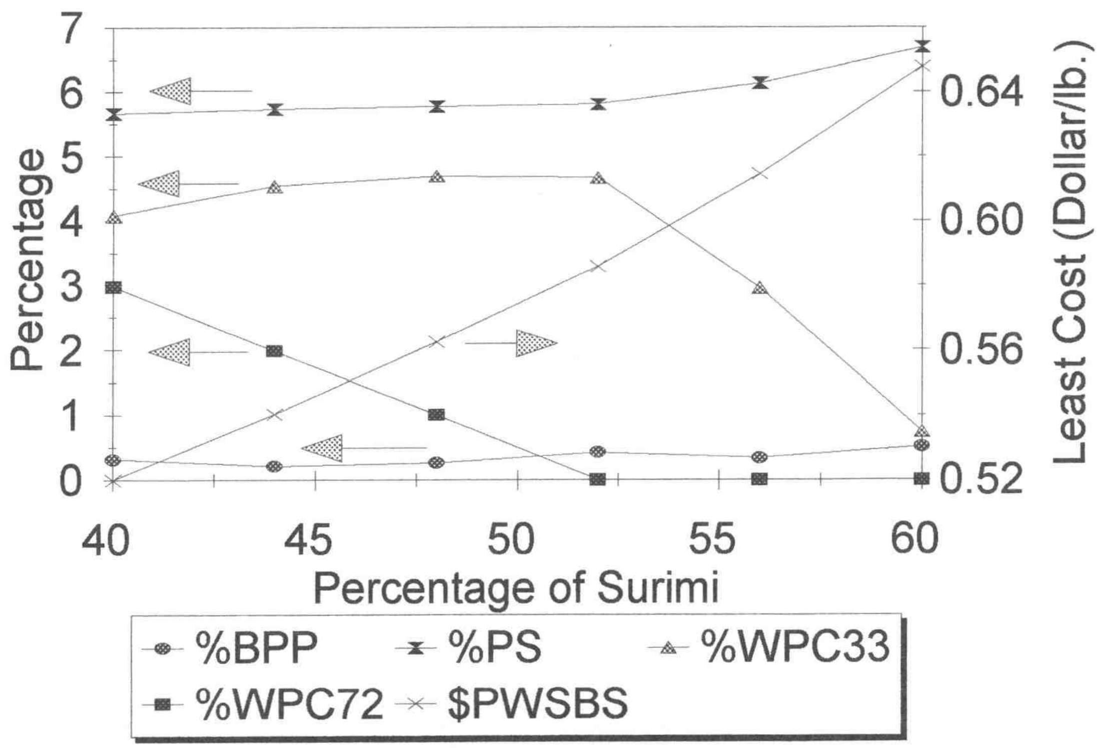
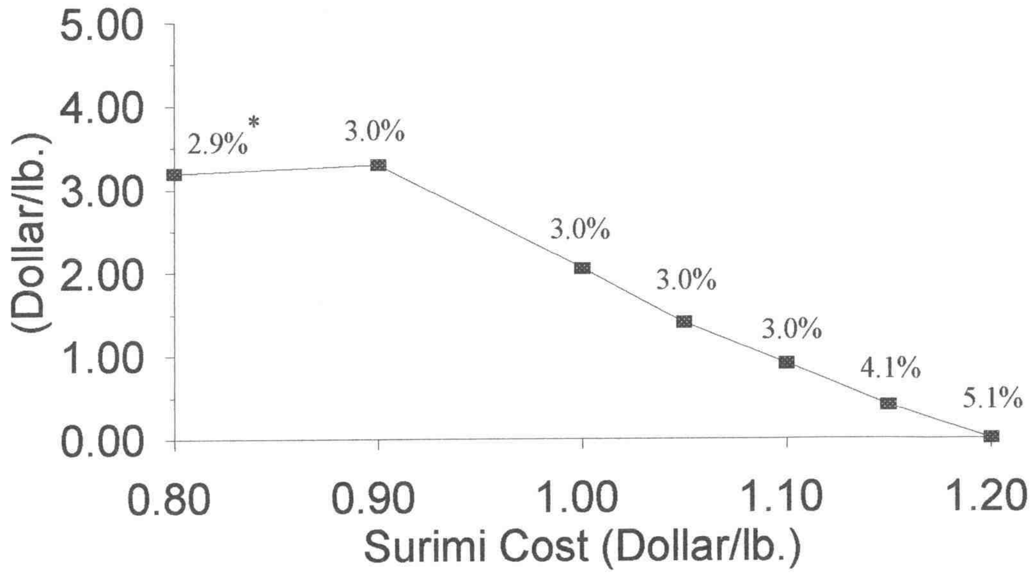
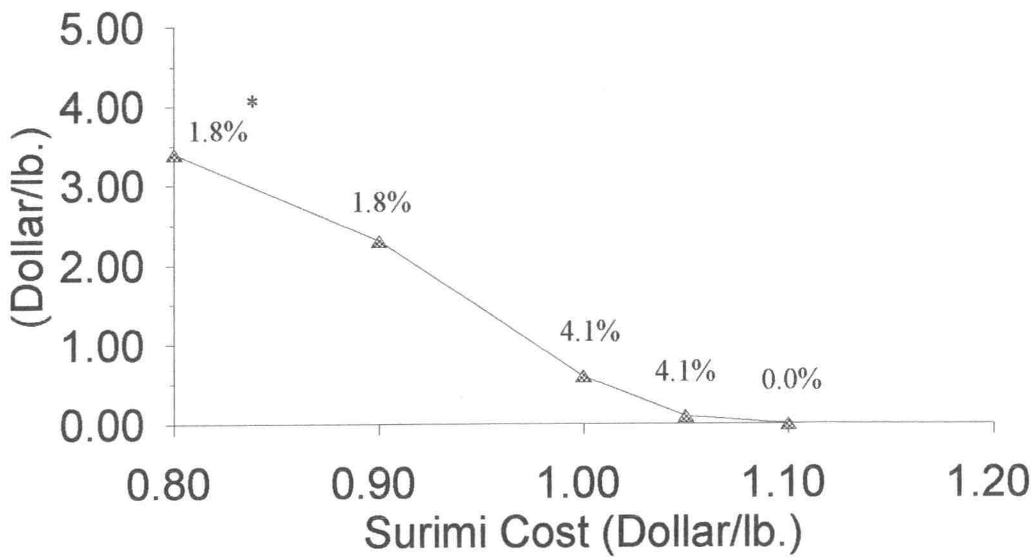


Fig. 3.6 How the required minimum level of surimi affects the level of other ingredients and the least cost of PWSBS



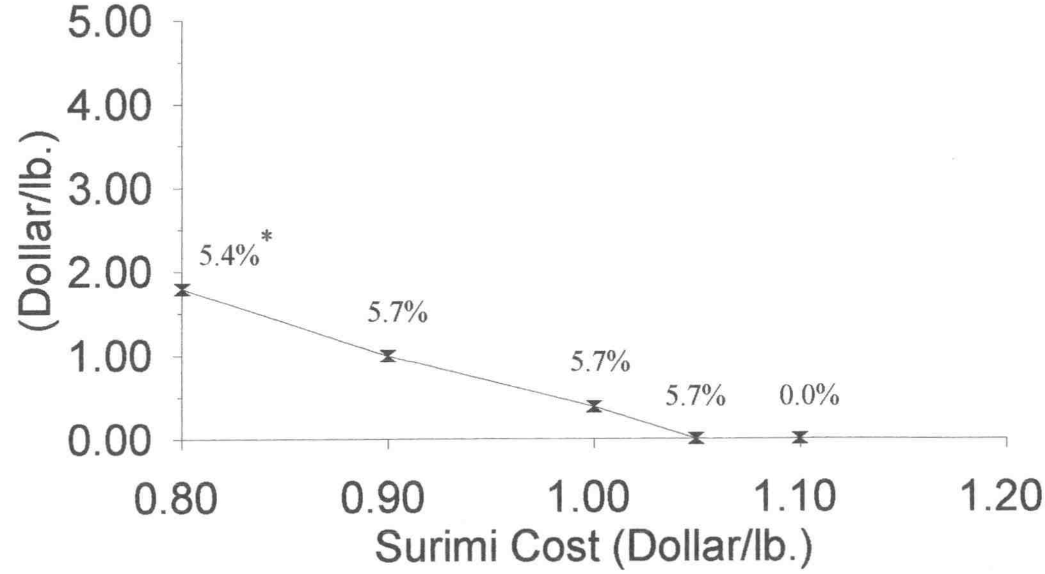
* Numbers represent the percentage of WPC72 in the formulations

Fig. 3.7 The effect of surimi cost on the maximum selling prices of WPC72



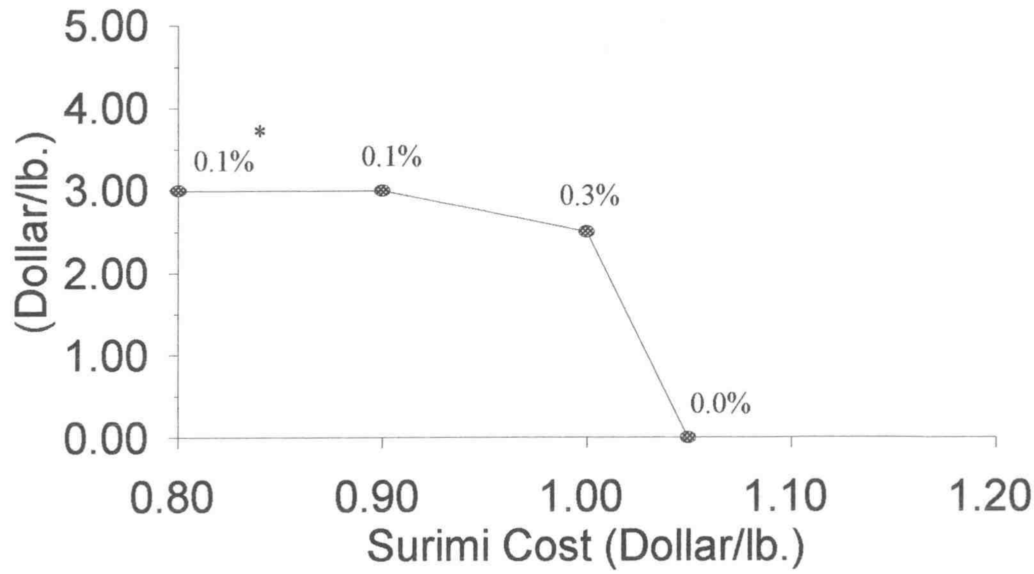
* Numbers represent the percentage of WPC33 in the formulations

Fig. 3.8 The effect of surimi cost on the maximum selling prices of WPC33



* Numbers represent the percentage of PS in the formulations

Fig. 3.9 The effect of surimi cost on the maximum selling prices of PS



* Numbers represent the percentage of BPP in the formulations

Fig. 3.10 The effect of surimi cost on the maximum selling prices of BPP

As surimi cost increases, the rate of decrease of the maximum selling prices for other ingredients followed the order: BPP > PS > WPC33 > WPC72 -- further indicating the competitive role of WPC in the formulation. (Note that these results differ from those shown in Fig. 3.5, in which no maximum ingredient cost was assumed).

Thus, the estimation of maximum selling price for each ingredient under an assumed maximum allowable total ingredient cost, allows us to obtain additional insight regarding the relationships among ingredient cost, ingredient percentage, and the desired quality levels.

Summary

The use of WPC72 and WPC33 was found to be promising, because they remained economically competitive with potato starch and beef plasma protein, ingredients which are commonly used in PWSBS to modify its texture properties. It was found that WPC could serve as a potential replacement for BPP, based on representative quality constraints and 1993 costs. Significant percentages of WPC72 and WPC33 were found to be feasible in the least cost formulations regardless of a wide variation of their costs and/or the costs of other ingredients. However, the requirements of high quality level and/or high required surimi content could limit the opportunities to use WPC.

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APPENDICES

Appendix A

The Characteristics and Relative Strengths of Numerical Approaches for Unconstrained and Constrained Nonlinear Optimization

The methods for solving unconstrained and constrained nonlinear optimization problems are described in this appendix. Unconstrained optimization deals with the problem of minimizing or maximizing a function in the absence of any restrictions. The methods for the minimization of a nonlinear function of one variable and a function of several variables are discussed. These methods can be further characterized into two categories depending on whether they use the information regarding to function derivatives or simply function evaluations.

Constrained optimization deals with the problem of optimizing an objective function in the presence of equality and/or inequality constraints. The term "nonlinear programming (NLP)" is referred to the techniques for solving constrained optimization problems with at least one of the objective function or constraint functions is nonlinear. Nonlinear programming problems are often solved by converting them into unconstrained problems using penalty function or barrier function. Another type of methods solving nonlinear programming problems by using methods of improving feasible directions. This class of methods solves a nonlinear programming problem by moving from a feasible point to an improved feasible point by funding an improving feasible directions. After such a direction is determined, a one-dimensional optimization problem is solved to determine how far to proceed along the direction. The purpose of this appendix is only a review of some background on the methods for solving nonlinear optimization; an exhaustive discussion of these methods can be the subject matter of an entire book.

METHODS FOR UNCONSTRAINED NONLINEAR OPTIMIZATION

Univariable Problems

Solving univariable optimization problems is the backbone of many algorithms for solving a unconstrained and constrained nonlinear problems. Some of the methods for optimizing mutlivariable nonlinear functions simply repeat the procedure of one dimensional linear search used in univariable problems. Many nonlinear programming algorithms proceed from a chosen initial point to find an improving direction vector and then a suitable step size yielding a new point; the process is then repeated until the criterion for termination is reached (Wolfe, 1963, 1967). Finding the step size is a one-dimensional line search problem and its efficiency greatly affects the overall performance of the solution technique.

Line Search without Using Derivatives

The Dichotomous search, golden section search (Wilde, 1964; Wilde and Beightler, 1967) and Fibonacci search (Kiefer, 1953; Box et al., 1969) are sequential line search methods that are based on function evaluations but not function derivatives. When minimizing a mathematical function over a closed bounded interval, these methods exclude portions of the interval that do not contain minimum and thus gradually reduce the interval including minimum solution. Among these methods, Fibonacci and golden section search method can be considered as efficient methods (Wilde, 1964; Wilde and Beightler, 1967).

Another type of line search uses quadratic curve fitting techniques (Davidon, 1959; Fletcher and Powell, 1963). These methods are based on fitting a polynomial equation (quadratic or cubic function) through a number of points in the neighborhood of the minimum. The minimum of the derived polynomial equation is determined and this point replaces one of the initial points. The quadratic curve fitting technique can be considered even more efficient than Fibonacci and golden section methods (Himmelblau, 1972; Murtagh and Sargent, 1970).

Line Search Using Derivatives

The bisection and Newton's method are line search techniques that require the information of function derivatives. At any iteration of bisection search, the function derivative is evaluated at the midpoint of the interval containing minimum. Based on the value of function derivative, the interval is reduced to half that at the previous iteration. The bisection method is one that always works, however, the convergence rate is quite slow.

Newton's method uses quadratic approximation to the function being minimized and its use is not restricted to one-dimension problem. At each iteration, the search procedure leads to a new point by setting the derivative of quadratic approximation function equal to zero. Even though Newton's method has the benefit of quadratic convergence rate, however, convergence is guaranteed only if the initial starting point is close to the solution point (Saguy, 1983).

Multivariable Problem

As the number of independent variables increases, the search techniques tend to be more complicated and have to be capable of handling multidimensional searches. Nevertheless, many methods are based on one-dimensional line search techniques applied at different levels of sophistication (Saguy, 1983).

Multidimensional Search without Using Derivatives

The alternating variable method, Hooke and Jeeves method (1961), and Rosenbrock methods (1960) handle multidimensional optimization problems without using the information of function derivatives. Alternating variable method searches only a single independent variable at a time, along the coordinate axes using line search methods, while the other independent variables are held constant. After searching all the variables, the entire procedure is then repeated with each successive variable until a suitable termination criterion is satisfied (Swann, 1972). The procedure tends to be quite slow and may have the difficulty in locating the extremum (Swann, 1972).

To overcome some drawbacks of the alternating variable search methods, improved procedures were suggested by Hooke and Jeeves (1961). The method of Hooke and Jeeves performs two types of search--exploratory search and pattern search. Given an initial point, a line search along the coordinate directions as alternating variable method products a new point. Then a line search, called pattern search, in the direction passing through these two points lead to another new point. The additional pattern search in Hooke and Jeeves method avoids the difficulty of stalling at sharp ridges. A quite efficient method searching along a set of linearly independent and orthogonal directions was also developed by Rosenbrock (1960).

The method proposed by Spendley et al. (1962) and modified by Nelder and Mead (1965), a sequential simplex search method, is distinctively different with the methods mentioned. The method essentially looks at the functional values at three points. The worst point is rejected and replaced by a new point along the line joining this point and the centroid of the remaining points. The process is repeated until no further function improvement is observed. The simplex method seems to be less effective as the dimensionality of the problem increases (Bazaraa et al., 1993).

Multidimensional Search Using Derivatives

Multidimensional search using the information of function derivatives includes steepest descent, Newton's method, and the methods using conjugate directions, such as quasi-Newton's method and conjugate gradient methods. The method of steepest descent uses a linear (first-order) approximation of a differentiable function being minimized, thus the search direction is the negative gredient vector of the function [$d_i = - \nabla f(x_i)$] (Murray, 1972; Fletcher, 1969). The method works quite well during early stages of the optimization process, however, as a stationary point is approached, the method usually behaves poorly, taking very small steps (Fletcher, 1969). The general use of the steepest descent method is not recommended due to its poor behavior near a minimum (Saguy, 1983; Murray, 1972).

Newton's methods originated from the quadratic approximation of the function being minimized provides a better estimation of the direction of the minima then steepest descent method (Gill and Murray, 1974). The method of Newton can be seen as a procedure that deflects the steepest descent direction by premultiplying it by the inverse of the Hessian matrix [$d_i = -H(x_i)^{-1}\nabla f(x_i)$]. As mentioned earlier, its efficiency is usually greatly reduced if the initial point is not in the neighborhood of the extremum. The reason for this is that the Hessian matrix may be singular when the initial point is far away from the extremum, so that the inverse of Hessian matrix is not defined. Even if the inverse of Hessian matrix exists, the search direction may not be a decent direction (Gill and Murray, 1974). A modification of Newton's method that guarantees convergence regardless of the starting point was introduced by Levenberg (1944) and Marquardt (1963). They used $\epsilon I + H(x)$ instead of $H(x)$ to maintain the positive definiteness of Hessian matrix, where $\epsilon \geq 0$ is the smallest scalar that would make all the eigenvalues of $\epsilon I + H(x)$ becoming positive and I is the identity matrix (Fletcher, 1987).

Quasi-Newton method was originally proposed by Davidon (1959) and later developed by Flectcher and Powell (1963). In stead of using the inverse of the Hessian matrix of the function being minimized, the quasi-Newton method use an n x n positive definite symmetric matrix that approximates the inverse of the Hessian matrix. The search procedure generates a sequence of conjugated directions ($d_i H(x) d_j = 0$, for i not equal to j). The mathematical complexity of the quasi-Newton method can be found in Fletcher (1981), Gill and Murray (1972), and Gill et al. (1981). Generally, the quasi-Newton method has now become the standard method for finding an unconstrained minimum of a differentiable function (Saguy, 1983). More (1981) also stated that quasi-Newton is an excellent method for small and medium scale unconstrained minimization problems.

Conjugate gradient methods also use the concept of conjugated directions. Hestenes and Stiefel (1952) proposed a conjugate gradient method for solving systems of linear equations. The extension of conjugate gradient methods to solve general unconstrained minimization problems was first done by Fletcher and Reeves (1964). The conjugate gradient methods can be viewed as a gradient deflection methods that deflects the negative gradient direction (steepest descent direction) using the previous direction [$d_{i+1} = -\nabla f(x_{i+1}) + \alpha d_i$, where α is a suitable deflection parameter]. Different α values has been introduced by Hesenes and Stiefel (1952) and Flecher and Reeves (1964). Although these methods are typically less efficient than quasi-Newton methods, they require very modest storage space and are quite indispensable for large-sized problems (the number of variable exceeding about 200) when quasi-Newton methods become impractical because of the size of the Hessian matrix (Bazaraa et al., 1993).

METHODS FOR CONSTRAINED NONLINEAR OPTIMIZATION

In general, the methods for solving constrained NLP can be placed into two categories. A successful and frequently used approach, such as the methods of penalty and barrier functions, is to define an auxiliary unconstrained problem such that the solution of the unconstrained problem yields the solution of the constrained problem (Fiacco and McCormick, 1964; 1967). Once the constraints are removed from model, the previous mentioned search procedures for unconstrained optimization problems can be applied. A second approach such as successive linear programming (SLP), successive quadratic programming (SQP), gradient projection method, and reduced gradient method is to solve NLP by moving from a feasible point along a feasible improving direction to a new improved feasible point.

Penalty Functions

A constrained problem may be transformed into an unconstrained one by placing the constraints into the objective function via a penalty parameter in a way that penalizes any violation of the constraints. Then, the methods for unconstrained nonlinear optimization can be used to obtain the optimal solution. Consider the following problem with one equality constraint:

Minimize $f(x)$

subject to the constraint $h(x)= 0$ ....(1)

(note: an inequality constraint $g(x) \leq 0$ can be written as $g(x) + s^2 = 0$, where s is a slack variable)

This problem is replaced by the following unconstrained problem, where u is a penalty parameter having a large positive value:

Minimize $f(x) + u\ h^2(x)$ ....(2)

With a large u value, it can be seen intuitively that an optimal solution to the above problem must have $h^2(x)$ close to zero, because otherwise a large penalty $u\ h^2(x)$ will be incurred. Thus, by choosing the penalty parameter sufficiently large, the solution to the penalty problem (2) will satisfy the constraint in original problem (1) (Fiacco and McCormick 1964; 1967, 1968). However, to avoid large penalty associated with large u value, especially in the presence of nonlinear equality constraints, a very small step size is needed and may result in slow convergence and premature termination (Zangwill 1967a; 1969; Fiacco and McCormick 1967; 1968).

Several approaches have been developed to overcome the difficulties associated with large penalty parameter. Fiacco and McCormick (1967; 1968) employed a sequence of increasing penalty parameters, such an approach is referred to as a sequential unconstrained minimization technique (SUMT). Another type of penalty function can recover an optimal solution by using a reasonable finite value of penalty parameter (Pietrzykowski, 1969; Fletcher, 1970; Hestenes, 1969; Powell, 1969). Fletcher (1970) introduced L_1, or absolute value, penalty function by using $u\ |h(x)|$ as a penalty term instead of $u\ h^2(x)$. Hestenes (1969) and Powell (1969) developed an augmented Lagrangian penalty function (ALAG) in which the Lagrangian function, $f(x) + \mu\ h(x)$ where μ is the Lagrangian parameter, instead of simply f(x), is augmented with a penalty term $u\ h^2(x)$.

The concept of penalty function is often coupled with other methods, such as successive linear programming (Palacios-Gomez et al., 1982; Zhang et al., 1985) and successive quadratic programming (Han and Magasarian, 1979; Powell, 1978; Fletcher, 1981), to yield even more robust and effective search procedures.

Barrier Functions

Similar to penalty functions, barrier functions are also used to transform a constrained problem into an unconstrained problem. The barrier function approach was first proposed by Carroll (1961) and was used to solve nonlinear inequality constrained problems by Box et al. (1966) and Kowalik (1968). Consider the following problem with one inequality constraint:

$$\text{Minimize} \quad f(x)$$
$$\text{subject to} \quad g(x) < 0 \qquad \ldots\ldots\ldots(3)$$

This problem is replaced by the following unconstrained problem, where v is a barrier parameter with small positive value:

$$\text{Minimize} \quad f(x) - v/g(x) \quad \ldots\ldots\ldots(4)$$

The solution to the problem (4) can be made extremely close to the optimal solution of the original problem (3) by choosing the barrier parameter, v, to approach zero. The use of barrier functions for solving constrained NLP also faces several computational difficulties with illconditioning and round-off errors as the boundary of feasible region is approached (Kowalik, 1968; Ryan, 1974). To handle equality constraints problem, Fiacco and McCormick (1968) introduced the mixed penalty-barrier auxiliary functions which equality and inequality constraints are handled, respectively, by a penalty term and a barrier term.

Successive Linear Programming (SLP)

The SLP method, also know as an approximation programming method, was proposed by Griffith and Stewart (1961) to solve NLP via a sequence of linear programming (LP). They used linear approximations to the nonlinear objective and constraint functions and solved the resulting LP problem successively. SLP procedures are attractive because they are fairly easy to implement due to the availability of the efficient and stable LP solvers and can be applied to large-sized problem (often thousands of constraints and variables). Palacios-Gomez et al. (1982) introduced a SLP approach with the L_1 penalty function.

However, the SLP methods are not guaranteed to converge (Zhang et al., 1985). Zhang et al. (1985) presented a penalty successive linear programming (PSLP) method which significantly strengthened and refined the SLP procedure described in Palacios-Gomez et al. (1982); it also guaranteed to convergence. In PSLP, the search direction is determined by solving a LP simplification which results from a linear approximation to the L_1 penalty function associated with original NLP, and the distance moved along that direction is determined by the size of a trust region following the idea of Fletcher (1981). Fletcher (1981) defined R_k as the ratio of actual to predicted descent. If R_k is too small relative to unity, then the trust region needs to be reduced; but if it is close to unity, the trust region can actually be expanded. A simplified version of this algorithm has been used by Baker and Lasdon (1985) to solve nonlinear oil refinery models having up to 1000 rows. However, since SLP is a steepest descent procedure, sometime it may suffer a slow convergence rate (Waren et al., 1987).

Successive Quadratic Programming (SQP)

The SQP method concept or the projected Lagrangian method was introduced by Wilson (1963). At each iteration, the minimization of a quadratic approximation to the Lagrangian function is optimized over a linear approximation to the constraints. The use of quasi-Newton approximations to the Hessian matrix of the Lagrangian function was suggested by Han (1976) and Powell (1978b). A major disadvantage of the SQP is that convergence is guaranteed only when the algorithem is initialized sufficiently close to a desirable solution (Han, 1975). Han and Magasarian (1979) and Powell (1978) showed that the L_1 penalty function can be used to derive global convergence. Fletcher (1981) proposed a L_1SQP algorithm by modifying the algorithm described by Powell (1978) with trust region methods to yield a very effective procedure.

Gradient Projection Method of Rosen

In the presence of constraints, moving along the steepest descent direction (the negative gradient), may lead to infeasible points. The gradient projection method of Rosen (1960) projects the negative gradient onto the nullspace of the binding constraints and thus improves the objective function and meanwhile maintains feasibility. Rosen (1961) also extended the gradient projection method to solve nonlinear constrained NLP. When deals with nonlinear constrained problem, the projected gradient will usually not lead to feasible points, since it is only tangential to the feasible region. Therefore, a movement along the projected gradient must be coupled with a correction move to the feasible region.

Reduced Gradient Method

The reduced gradient method was first developed by Wolfe (1963) to solve linear constrained NLP. The method depends upon reducing the dimensionality of the problem by representing all the variables in terms of an independent subset of the variables (nonbasic variables), and then projecting the problem onto the subset of the variables. The reduced gradient method move along the negative reduced gradient, then a line search procedure is followed to find a new feasible point. Zangwill (1967b) proposed the convex-simplex method which is identical to the reduced gradient method except that only one nonbasic variable is modified while all other nonbasic variables are fixed at their current levels. The reduced gradient method of Wolfe was later generalized to handle nonlinear constraints by using linear approximation to nonlinear constraints (Abadie and Carpentier, 1969).

The direction-finding procedures in the reduce gradient methods of Wolfe adopt a linear approximation to objective function and may result a slow zigzagging convergence behavior. Murtagh and Saunders (1978) and Gill et al. (1981) described a efficient direction-finding procedures using second-order function approximation. The algorithm was included in the code MINOS 5.0 (Murtagh and Saunders, 1982; 1983) for solving linearly constrained NLP. In MINOS 5.0 nonlinearly constrained NLP is transformed, with the augmented Lagrangian procedures described by Robinson (1972) and Murtagh and Saunders (1982), into a sequence of linearly constrained NLP subproblems which can be solved by using reduced gradient algorithm. According to Waren et al. (1987), MINOS 5.0 has become the most widely used of all large scale NLP code.

Appendix B

Thermal Techniques to Determine the Quality of Protein Gels

Cheng-Kuang Hsu and Edward Kolbe

Appendix B

Thermal Techniques to Determine the Quality of Protein Gels

ABSTRACT

Differential scanning calorimetry (DSC) was used to determine the water-holding capacity of protein gels by recording the water evaporization process. Pacific whiting surimi gels were produced by heating in a sealed DSC pan from 30 to 90°C at a rate of 5°C/min.; gelled samples were then re-heated from 30 to 180°C at 2°C/min. in an open pan while an equivalent water mass served as a reference. The DSC thermogram showed one exothermic peak followed by one endothermic peak, the former indicating a relative energy flow from the protein gels due to the delayed water evaporization. DSC parameters derived in this study showed good correlation with the texture properties of protein gels. The addition of whey protein concentrate and the increase of heating rate increased the water holding capacity of whiting surimi gels.

INTRODUCTION

Pacific whiting (<u>Merluccius productus</u>) was an underutilized species due to its soft texture caused by protease enzymes (Erickson et al., 1983). Whiting is commonly processed into surimi, a washed fish mince having added cryoprotectant such as sorbitol and sucrose, which maintains protein quality during frozen storage. Surimi is then further processed into various surimi-based gelled products such as artificial crab legs and meat. Use of whiting also requires the addition of protease inhibitors and/or gel strength enhancers because its inherent enzyme system (Morrissey et al., 1993).

One of the most important concerns regarding the quality of surimi-based seafood is its water holding capacity (WHC), which is closely related to texture and flavor quality (Lee and Kim, 1986a; Lee et al., 1992). For example, WHC has been used as an indictor of the freeze-thaw stability of surimi-based seafoods which are intended to be distributed frozen (Lee and Kim, 1986a). In surimi-based seafood with low WHC, the texture can become hard and rubbery and flavors can be lost as a result of excessive thaw drip caused by excessive temperature fluctuation and/or freeze-thaw cycles (Lee et al., 1992).

Conventional methods for determining WHC of surimi gels are based on measuring the amount of lose water liberated by applying pressure on a sliced gel. The pressure can be produced in different ways: centrifugal force or pressing between two plates (Suzuki, 1981). WHC in surimi gel systems has been correlated with gel strength at failure commonly measured by either the punch or torsion modes (Akahane et al., 1981; Lee and Kim, 1986b; Chung and Lee, 1990). Lee and Kim (1986b) reported that a decrease in gel strength of surimi gels with egg albumin is accompanied by a decrease in WHC. Chung and Lee (1990) noted a strong correlation between the WHC and the compressive force of surimi gels with the addition of various nonfish proteins. Thus, WHC has been commonly used as an indirect measurement of texture properties of surimi-based seafoods (Lee and Kim, 1986b; 1986a; Chung and Lee, 1990; Yoon and Lee, 1990).

Differential scanning calorimetry (DSC) is a technique in which difference in energy inputs into a substance and a reference material are measured as a function of temperature, while the substance and the reference material are subjected to a controlled temperature program (Wright, 1984). DSC has been commonly used to determine the thermal stability of various food proteins by measuring their heat transition temperature and enthalpy (Wright et al., 1977; Stabursvik and Martens, 1980; Hastings et al., 1985). DSC has also been applied in determining the WHC of fish protein gels. Akahane et al. (1981) observed a good correlation between DSC and texture measurement of fish protein gels and concluded that DSC can be used to determine the quality of fish protein gels.

It is well-known that intermediate holding (setting) temperatures and heating rates are critical to the final textural quality of protein gels. In general, a slow heating rate allows formation of a more uniform and rigid gel structure. However, with some species like whiting, the opposite result, a gel softening, may occur, because the maximum protease activity is around 60°C (Morrissey et al., 1993). In this study, DSC was used not only to determine the WHC of whiting surimi gels but also to control the accuracy of temperature setting and heating rate. The advantages of using DSC to investigate the water retainability in protein gels include: 1) more accurate control of heating rate for making protein gels; 2) offering very flexible temperature setting and heating schemes; 3) record the thermal transition of water evaporization process in protein gels. The overall objective of this study was to evaluate the potential of using DSC to measure the quality of whiting surimi gels and to identify and correlate useful DSC parameters to the gel strength. The effects of heating rates and protease inhibitors and/or gel strength enhancers on the WHC of whiting surimi gels were also investigated.

MATERIALS & METHODS

Washed and dewatered mince was made from Pacific whiting within 24 hrs. of harvest at Point Adams Seafood Inc. in Hammond, Oregon. This mince was immediately transported, on ice, to the OSU Seafood Laboratory in

Astoria, 30 min. away by car. After mixing with cryoprotectant, 4% sucrose, 4% sorbitol, and 0.3% sodium tripolyphosphate, the minces weighing a total of about 650 g were placed in a plastic box and packaged with vacuum. The packages were then frozen in a blast freezer in which the core temperature reached -20°C. Frozen whiting surimi were placed in insulated boxes and stored at -23°C. Two packages of frozen surimi were removed from the freezer and served as a sample for making surimi gels.

Sample Preparation

Frozen surimi was thawed at room temperature for 2 hr. A Stephan vacuum mixer (Model UM5 Universal, Stephan Machinery Corporation, Columbus, OH) was used to mix approximate 600 g of whiting surimi with 2% NaCl and whey protein concentrate (WPC72, with 72% protein content, New Zealand Milk Products, Inc., CA) or potato starch (PS, Avebe America, Inc., NJ) at 0, 1, 4, and 11% levels. Ice was added during mixing to adjust the final moisture content to 75%. The mixture was chopped for 4 min. while maintaining a temperature below 10°C, to produce a paste.

DSC Measurement

The protein/salt paste samples (about 55 mg) were sealed in high pressure capsules (No. 0319-0218, The Perkin Elmer Co.), then heated from 30 to 90°C at 5°C/min using a DuPont 910 DSC (DuPont Instruments, Wilmington, DE). For experiments intended to test the effect of heating rate on the WHC of whiting gels, the heating rates were adjusted to 0.5, 2, 10, 30, 50, and 80°C/min. After cooling, the high pressure capsules were opened and the sample gels were reheated in the opened pan from 30 to 180°C at 2°C/min. with water served as a reference (having the same weight as the amount of water in sample gels). Slow heating rate, 2°C/min., was used because high heating rate reduces the water evaporization process before boiling temperature is obtained. A cap was inserted (No. 0219-0062, The Perkin Elmer Co.) in the high pressure capsules to ensure a smooth exposed concave surface of the gel after opening. At least four replicates were run for each sample.

A representative DSC thermogram of whiting surimi gel is shown in Fig. 1. The DSC thermogram showed one exothermic peak followed by one endothermic peak. The exotherm indicates a difference in energy flow from the protein gels (compared to the reference) due to the delayed water evaporization process. The endotherm indicates the continuation of the water evaporization process from protein gels after water in the reference pan is completely evaporized. The temperature that separates these two peaks is about 100°C. As shown in Fig. 1, it was clear that the DSC cruves with and without the addition of WPC are quite different, indicating distinct differences in the water evaporization process of these gels.

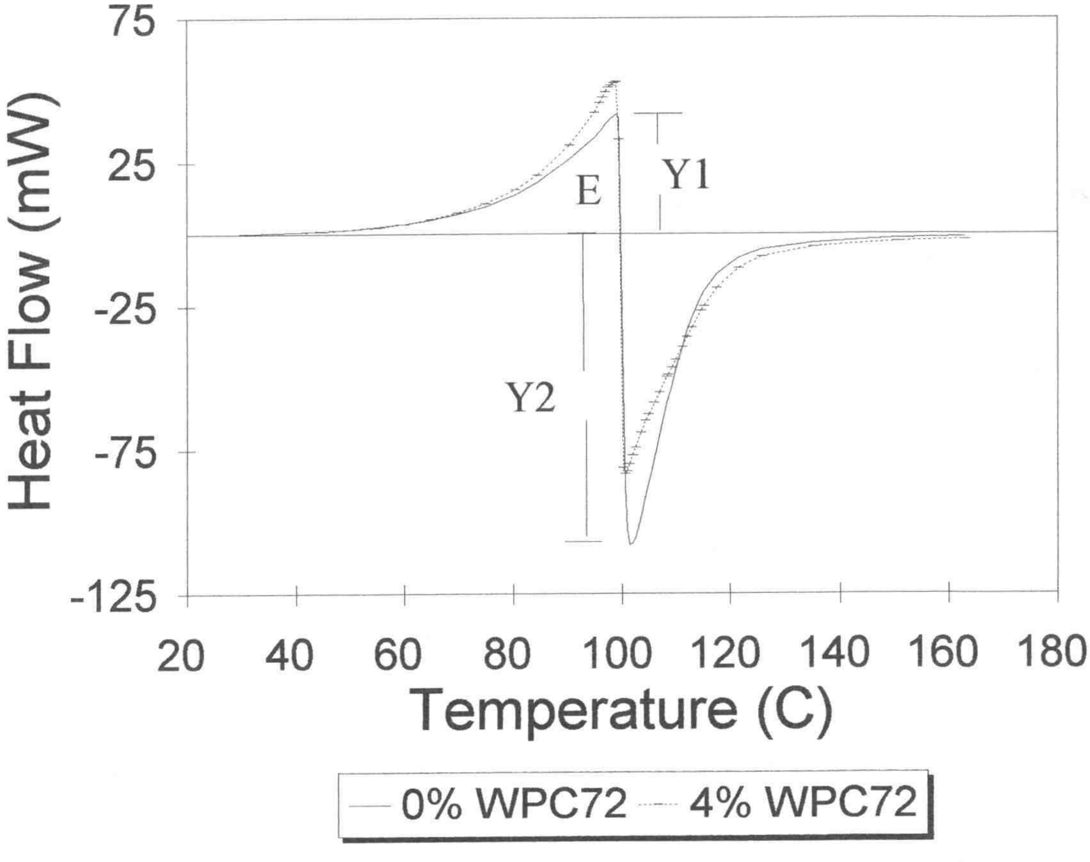

Fig. 1 DSC thermogram of whiting gels

Torsion Test

A sausage stuffer (5-lbs capacity, The Sausage maker, Buffalo, NY) was used to extrude the paste into stainless steel cooking tubes (inside diameter 2.2 cm, length 17.8 cm). Protein gels were produced by heating in a 90°C water bath for 15 min., followed by cooling in ice water for 10 min. The torsion test system involved cutting the protein gels into hourglass shapes, and twisting them to the point of failure in a torsion gelometer (Gel Consultants, Raleigh, NC) following the procedures described in NFI (1991). The results of the torsion test were presented as shear stress and shear strain at failure, calculated from the equations described by Hamann (1983).

Ohmic Heating

For experiments intended to test the effect of heating rate on the texture properties of whiting gels, the heating rates were adjusted to 0.5, 2, 10, 30, 50, and 80°C/min. using ohmic heater. PVC sample tubes (inside diameter 1.9 cm, length 20 cm) containing surimi paste were placed between two electrodes and heated from 30 to 90°C at desired heating rates in an ohmic heater described by Yongsawatdigul et al. (1995). The voltage gradents for these heating rates were (7, 7.7, 12, 14.7, 17.3 V/cm) respectively. Temperature, voltage, and current changes during heating were recorded at 1 sec intervals on a datalogger (Model 21X, Campbell Scientific, Inc., Logan, UT). To avoid damage of the protein gels due to a sudden release of pressure inside the sample tubes, the electrodes were removed after the temperature of protein gels had cooled to about 65°C. Further cooling of the protein gels was achieved by putting them in ice water for 10 min. The texture properties of ohmically heated gels were determined by using torsion test.

RESULTS & DISCUSSION

Three parameters E, Y1, and Y2, which are the enthalpy value of the first (exothermic) peak, the height of the first peak, and the height of the second (endothermic) peaks, respectively, were selected and evaluated their ability to indicate the quality of protein gels (Fig. 1). The effects of adding WPC and PS on the quality of whiting gels are shown in Tab. 1 and 2. The addition of WPC reaching 4% was found to increase E and Y1 but decrease Y2. However, at extreme high WPC content, 10% for example, a decrease of E and Y1 values was observed. The addition of PS was also found to increase E while showing little influence on Y1 and Y2 values. Compared to WPC, PS was found to be less effective in changing DSC parameters. Torsion test results are presented as shear stress and shear strain indicating the gel strength and the cohesiveness of surimi gels respectively. Adding WPC increases both shear stress and shear strain, while PS increases shear stress but not shear strain (Tab. 1 and 2). As shown in Tab. 3, good correlations were found between shear strain and both Y1 and

Percent of WPC72	E	DSC Y1	Y2	Torsion Test Stress(kPa)	Strain
0	660(59*)^{a}	38(4)^{a}	108(2)^{a}	9.9(1.5)^{a}	0.96(0.12)^{a}
1	722(58)^{ab}	50(3)^{b}	90(5)^{b}	12.7(0.8)^{a}	1.22(0.09)^{b}
4	833(59)^{c}	55(2)^{c}	82(4)^{c}	38.8(2.4)^{b}	1.85(0.10)^{c}
10	753(57)^{bc}	49(4)^{d}	83(4)^{c}	41.2(2.3)^{c}	1.57(0.05)^{d}

^{a,b,c,d} Mean Values in the same column followed by different letters are significantly ($p<0.05$) diferent

* Numbers inside parentheses are the standard deviation

Tab. 1 The effect of WPC72 on DSC and texture parameters of whiting gels

Percent of PS	E	DSC Y1	Y2	Torsion Test Stress(kPa)	Strain
0	660(59*)^{a}	38(4)^{a}	108(2)^{a}	9.9(1.5)^{a}	0.96(0.12)^{a}
1	687(67)^{ab}	44(2)^{b}	101(4)^{bc}	15.6(2.3)^{b}	1.19(0.12)^{b}
4	748(40)^{b}	42(3)^{ab}	104(4)^{ab}	14.0(0.6)^{b}	0.96(0.09)^{a}
10	627(63)^{a}	43(6)^{ab}	96(8)^{c}	18.6(1.8)^{c}	1.09(0.05)^{b}

^{a,b,c,d} Mean Values in the same column followed by different letters are significantly ($p<0.05$) diferent

* Numbers inside parentheses are the standard deviation

Tab. 2 The effect of PS on DSC and texture parameters of whiting gels

	E	Y1	Y2	EY1	E/Y2	Y1/Y2	EY1/Y2
Stress	0.67	0.72	-0.86	0.75	0.86	0.82	0.83
Strain	0.77	0.90	-0.91	0.91	0.94	0.94	0.95

Tab. 3 Correlation coefficients for DSC and texture parameters of whiting gels with the addition of WPC or PS

Y2 for whiting surimi gels with the addition of both gel enhencers. Combinations of DSC parameters, E*Y1, Y1/Y2 and E*Y1/Y2, haves even higher correlations with shear strain. The correlations between these DSC parameters and shear stress were found to be lower than that of shear strain. Hamann (1988) suggested that shear strain at failure is a fairly stable measure of protein functional quality whereas shear stress is strongly influenced by protein concentration, processing conditions, and ingredient variables.

The effect of heating rate on the quality of whiting surimi gels is reported in Tab. 4. In general, high heating rate increased E and Y1, but decreased Y2 values. High heating rate was also found to increase both shear stress and shear strain values of whiting surimi gels. The correlations between DSC and torsion testing for whiting surimi gels made at different heating rate are shown in Tab. 5. Among the three DSC parameters, it was found that E value had highest correlation coefficient with both shear stress and shear strain. The combination of E*Y1 had even higher correlation coefficient value with both shear stress and shear strain.

Based on their correlations with texture parameters, it was found that Y1 and Y2 are significant parameters to describe the qulity of whiting gels with the addition of gel enhancers, while E value was found to be more useful to differentiate the quality of whiting gels made at different

Heating Rate °C/min.	DSC E	Y1	Y2	Torsion Test Stress(kPa)	Strain
0.5	682(86*)^{a}	45(8)^{ab}	102(12)^{ab}		
2	741(39)^{abc}	43(3)^{a}	110(6)^{a}	2.7(0.7)^{a}	0.30(0.06)^{a}
10	726(21)^{ab}	54(3)^{c}	85(2)^{cd}	11.7(4.1)^{b}	0.93(0.21)^{b}
30	805(63)^{bcd}	54(1)^{c}	82(1)^{c}	18.8(1.8)^{c}	1.63(0.25)^{c}
50	823(58)^{d}	50(5)^{bc}	95(7)^{b}	22.9(1.6)^{d}	1.82(0.15)^{cd}
80	809(60)^{cd}	54(5)^{c}	93(7)^{bd}	24.4(2.8)^{d}	1.99(0.13)^{d}

^{a,b,c,d} Mean Values in the same column followed by different letters are significantly ($p<0.05$) diferent

* Numbers inside parentheses are the standard deviation

Tab. 4 The effect of heating rates on DSC and texture parameters of whiting gels

	E	Y1	Y2	EY1	E/Y2	Y1/Y2	EY1/Y2
Stress	0.86	0.69	-0.52	0.92	0.75	0.55	0.76
Strain	0.88	0.69	-0.53	0.93	0.77	0.56	0.78

Tab. 5 Correlation coefficients for DSC and texture parameters of whiting gels made with different heating rates

heating rates. It is important to aware that in fact Y value (including Y1 and Y2) and E value represent different aspects of water evaporization process of protein gels. Y value indicate the maximum differential heat flow between sample gels and reference, while E value is the enthalpy of the first peak. As shown in Tab. 5, there were low correlations between E and both Y1 and Y2 (r = 0.31 and -0.2, respectively), while the correlation between Y1 and Y2 was quite significant (r = -0.93). This indicated that E and Y values obtained from DSC thermogram may be used independently to describe the water retainability in protein gels made at different processing factors, such as with the addition of other ingredients or different heating rates. In fact, it is also interested for us to point out that E*Y1 appears to be the only parameter having reasonably good capability to represent the quality of protein gels made either with the addition of other ingredients or with different heating rates.

CONCLUSION

The use of DSC to determine the quality of protein gels by recording the water evaporization process looks promising. DSC provided very flexible and accurate control on the heating schemes which are crucial to the quality of heat gelated protein gels. Based on their correlations with texture measurement, two DSC parameters, E and Y1 values, were found to be useful to describe the quality of protein gels. The addition of whey protein concentrate and the increase of heating rate increased the water holding capacity of whiting surimi gels.

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