Monitoring and Optimization of the Effects of the Blending Ratio of Corn, Sesame, and Perilla Oils on the Oxidation and Sensory Quality of Seasoned Laver *Pyropia* spp.

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Abstract

Seasoned laver *Pyropia* spp. is one of the most well-known Korean traditional seafoods, and is becoming more popular worldwide. Various mixed oils are used in the preparation of seasoned laver; however, there is no information available regarding the effects of the blending ratio of oils on the quality of seasoned laver. In this study, the effects of the blending ratio of corn, sesame, and perilla oils on the oxidation and sensory quality of seasoned laver were monitored and optimized using a response surface methodology. An increase in the proportion of corn and sesame oils resulted in an excellent oxidation induction time, whereas a high ratio of perilla oil reduced the thermal oxidative stability of the mixed oil. In the sensory test, the seasoned laver with the highest proportion of sesame oil was preferred. The optimal blending ratio (v/v) of corn, sesame, and perilla oils for both oxidation induction time (Y_1) and sensory score (Y_2) was 92.3, 6.0, and 1.7%. Under optimal conditions, the experimental values of Y_1 and Y_2 were 4.41 \pm 0.3 h and 5.58 \pm 0.8 points, and were similar to the predicted values (4.34 h and 5.13 points). Our results for the monitoring and optimization of the blending ratio provide useful information for seasoned laver processing companies.

Key words: Pyropia spp., Seasoned laver, Corn oil, Sesame oil, Perilla oil

Introduction

Seasoned laver is a unique seaweed product that is prepared by roasting a sheet of dried laver *Pyropia* spp., to which various vegetable oils have been applied, at an ultra-high-temperature (UHT) of 300°C for about 10 s (Hwang, 2013; Jo et al., 1995). It is one of the most well-known Korean traditional seafoods, and has become popular worldwide because of its special taste, compactness, texture, and health benefits (Park et al., 2001; Cho et al., 2009). The value of seasoned laver products exported in 2013 was USD 180 million (Korea Customs Service, 2014). In the preparation of seasoned laver, vegetable oils are used as the major ingredient (usually 30–40%, w/w) (Lee, 1999; Jo et al., 1995). Our previous study, thermal oxidative stability of six vegetable oils (sesame, perilla, sunflower, rice bran, canola, and olive) was investigated (Kim et al., 2015). In commercial seasoned laver products, a mixture of corn, sesame, and perilla oils is most frequently used. In particular, because it is inexpensive, the corn oil content of seasoned laver oils generally exceeds 80% (w/w).

The blending ratio of seasoned laver oils is usually decided

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on the basis of economical and sensory considerations. However, the effects of the blending ratio on the oxidative stability of seasoned laver oils have not yet been studied. During the processing of seasoned laver, UHT treatment at 300°C induces the thermal oxidation of the oils (Jo et al., 1995). In addition, due to the high oil content of the seasoned laver, the thermal oxidative stability of the oil is the most important factor in determining the product's shelf life (Wang et al., 2010; Hasenhuettl and Wan, 1992).

In this study, the effects of the blending ratio of corn, sesame, and perilla oils on the oxidation and sensory quality of seasoned laver were monitored and optimized using a response surface methodology (RSM). In addition, the variations in price with different blending ratios of seasoned laver oils were also monitored. The thermal oxidative stability of the oils was evaluated by determination of the oxidation induction time using a Rancimat instrument.

Table	 Blending ratio of corn, sesame, and perilla o 	ils at the center point
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Oil	Blending ratio (%, v/v)	
Corn oil	86.3	
Sesame oil	10.7	
Perilla oil	3.0	
Total	100	

 Table 2. Experimental range and values of the independent variables in the central composite rotatable design for the optimization of blending ratio of corn oil, sesame oil, and perilla oil

6h - l		Ra	nge and le	vels	
Symbol	-1.414	-1	0	+1	+1.414
X_1	0.66	2.32	6.33	10.34	12.00
X_2	0.20	1.20	3.60	6.00	7.00

 $X_1 = \text{corn oil} / (\text{sesame oil} + \text{perilla oil}); X_2 = \text{sesame oil} / \text{perilla oil}.$

Materials and Methods

Materials

Corn (CJ Cheiljedang Co., Ltd., Seoul, Korea), sesame (Chamgoeul Co. Ltd., Seoul, Korea), and perilla (Chamgoeul Co., Ltd.) oils were purchased from a local market and stored in a refrigerator until their use in the experiment. Sheet-type dried laver (*Pyropia* spp.) was purchased from Korea Fishery Co., Ltd (Pyeongtaek, Korea). All reagents used were analytical grade.

Experimental design

A central composite rotatable design (CCRD; Montgomery, 1996) was used to monitor the effects of the blending ratio of corn, sesame, and perilla oils on the oxidation and sensory quality of the seasoned laver. The oil blending ratio (v/v) at the center point was: corn 86.3 %, sesame 10.7 %, and perilla 3.0%. The center point was based on the average blending ratio of the commercial seasoned laver in Korean market (Table 1). Two independent variables (X_1 and X_2) were defined using the following equations, and their range and levels are shown in Table 2.

 $X_1 = \text{corn oil} / (\text{sesame oil} + \text{perilla oil}) = 6.33$ $X_2 = \text{sesame oil} / \text{perilla oil} = 3.60$

The oxidation induction time (Y_1 , h), sensory score (Y_2 , point), and unit cost (Y_3 , won/L) were selected as the dependent variables. This CCRD matrix consisted of 2² factorial points, 4 axial points ($\alpha = 1.414$), and 3 replicates of the center point (Table 3).

Table 3. Central composite rotatable design matrix and values of dependent variables for the optimization of blending ratio of corn oil, sesame oil, and perilla oil

	Independent variables			Blending ratio (%, v/v)			Dependent variables			
Run No.	Coded Uncoded									
	X_1	X_2	X_1	X_2	Corn oil	Sesame oil	Perilla oil	Y_1	Y_2	<i>Y</i> ₃
1	-1	-1	2.32	1.20	69.9	16.4	13.7	3.15	4.41	3,238
2	+1	-1	10.34	1.20	91.2	4.8	4.0	4.25	4.05	2,716
3	-1	+1	2.32	6.00	69.9	25.8	4.3	4.13	5.85	3,133
4	+1	+1	10.34	6.00	91.2	7.6	1.3	4.37	4.38	2,690
5	-1.414	0	0.66	3.60	39.8	47.1	13.1	3.71	6.20	3,816
6	+1.414	0	12.00	3.60	92.3	6.0	1.7	4.05	5.15	2,669
7	0	-1.414	6.33	0.20	86.4	2.3	11.4	3.07	3.13	2,896
8	0	+1.414	6.33	7.00	86.4	11.9	1.7	4.00	3.92	2,783
9	0	0	6.33	3.60	86.4	10.7	3.0	3.98	3.62	2,802
10	0	0	6.33	3.60	86.4	10.7	3.0	3.79	3.74	2,802
11	0	0	6.33	3.60	86.4	10.7	3.0	3.87	3.50	2,802

 $X_1 = \text{corn oil} / (\text{sesame oil} + \text{perilla oil}); X_2 = \text{sesame oil} / \text{perilla oil}.$

Y₁, oxidation induction time (h); Y₂, sensory score (point); Y₃, unit cost (won/L).

Analysis of data

For the response surface regression procedure, the MINIT-AB software (Ver. 14, Minitab Inc., Harrisburg, PA, USA) was used to fit the following quadratic polynomial equation:

$$Y = \beta_0 + \sum_{i=1}^2 \beta_i X_i + \sum_{i=1}^2 \beta_{ii} X_i^2 + \sum_{i=1}^1 \sum_{j=i+1}^2 \beta_{ij} X_i X_j$$

where *Y* is the dependent variable (induction time, sensory score, and unit cost), β_0 is constant, β_i , β_{ii} , and β_{ij} are regression coefficients, and X_i and X_j are the levels of the independent variables. The adequacy of the model was predicted through regression analysis (R^2) and an analysis of variance (ANO-VA). Three dimensional response surface plots were produced using the Maple software (Ver. 7, Waterloo Maple Inc., Ontario, Canada), and represented a function of two independent variables.

Optimization procedure

The blending ratio of corn, sesame, and perilla oils was individually optimized for the oxidation induction time (Y_1) , sensory score (Y_2) , and unit cost (Y_3) , respectively. The optimization targets of the dependent variables Y_1 , Y_2 , and Y_3 were set as the maximum, maximum, and minimum, respectively. Response optimization was calculated by the response optimizer of the MINITAB software. In addition, multiple response optimization was performed to search for the condition that simultaneously satisfied the oxidation induction time (Y_1) and sensory score (Y_2) .

Preparation of seasoned laver

Seasoned laver was prepared using an automatic roasting machine (G-400, Woojeong machine Co., Ltd., Seoul, Korea). A sheet of dried laver (2.5 g) was roasted at 150°C for 10 s. It was the roasted again at 300°C for 10 s, after the application of salt (0.08 g) and the mixed oil (1.6 g) containing corn, sesame, and perilla oils.

Oxidative stability using a Rancimat method

For the measurement of the oxidative stability of seasoned laver oil, the oil samples were isolated from the seasoned laver product using a press machine. The oxidative stability of the seasoned laver oils was evaluated by measuring the oxidation induction time using a Rancimat instrument (Metrohm CH series 743, MetrohmAG, Herisau, Switzerland). The oxidation process was monitored for a 3 g sample of oil using an air velocity of 20 L/h at 120°C. During the Rancimat test, volatile compounds, such as formic acid, were rapidly produced and carried by the stream of air to be collected in deionized water. The vapors were continually monitored by measuring the conductivity of the deionized water. The end point was determined in hours.

Sensory evaluation

The sensory evaluation of the seasoned laver samples was performed with a panel consisting of 10 members (3 male, 7 female, aged 25-40 years). All 11 samples were evaluated simultaneously in a randomized order. The quality attributes selected for sensory evaluation were flavor, taste, and crispiness (Liang et al., 2008; Gkatzionis et al., 2013; Sinija and Mishra, 2011). Panel members were asked to take two or three samples to taste and provide a score for each. Between tastings each panel member rinsed their mouth with lukewarm water. The sensory factors assigned to each of the quality attributes were: dislike very much (1), dislike moderately (2), dislike slightly (3), neither like or dislike (4), like slightly (5), like moderately (6), and like very much (7).

Results and Discussion

Diagnostic checking of the fitted models

It was necessary to fit a quadratic polynomial equation to describe the behavior of the dependent variables on the independent variables (Bezerra et al., 2008). The response surface regression procedure was used to fit the quadratic polynomial

D	Y_1		Y_2		Y ₃	
Parameter	Coefficient	<i>P</i> -value	Coefficient	<i>P</i> -value	Coefficient	P-value
Constant	3.880	0.001	3.620	0.001	2802.00	0.001
X_1	0.228	0.037	-0.414	0.001	-323.39	0.001
X_2	0.302	0.013	0.361	0.001	-36.35	0.433
X_1X_1	0.067	0.516	1.046	0.001	196.06	0.012
X_2X_2	-0.106	0.321	-0.029	0.654	-5.44	0.919
X_1X_2	-0.215	0.118	-0.278	0.013	19.75	0.757

Y₁, oxidation induction time (h); Y₂, sensory score (point); Y₃, unit cost (won/L).

equation to the experimental data. The significance of all the coefficients of the constant, linear (X_1, X_2) , quadratic (X_1X_1, X_2X_2) , and interaction (X_1X_2) terms were calculated for their significance using a *t*-test (Table 4). The constant coefficients of all dependent variables were highly significant (P < 0.01). The linear coefficients, except for the X_2 term of Y_3 (unit cost), were also significant (P < 0.05 and P < 0.01). The fitted response surface model equations are shown in Table 5. The determination coefficient (R^2) value indicated that the model equations adequately described the experimental design (Cho et al., 2005). The R^2 values of Y_1, Y_2 , and Y_3 were 0.848, 0.989, and 0.937, respectively, and were significant at the 95% probability level. This confirmed that the experimental design was adequate.

 Table 5. Response surface model equations for the optimization of blending ratio of corn oil, sesame oil, and perilla oil

Quadratic polynomial model equations	R^2	<i>P</i> -value
$Y_1 = 3.880 + 0.228X_1 + 0.302X_2 + 0.067X_1^2 - 0.106X_2^2 - 0.215X_1X_2$	0.848	0.041
$Y_2 = 3.620 - 0.414X_1 + 0.361X_2 + 1.046X_1^2 - 0.029X_2^2 - 0.278X_1X_2$	0.989	0.001
$Y_3 = 2802.00 - 323.39X_1 - 36.35X_2 + 196.06X_1^2 - 5.44X_2^2 + 19.75X_1X_2$	0.937	0.005

 Y_1 , oxidation induction time (h); Y_2 , sensory score (point); Y_3 , unit cost (won/L).

Table 6. Analysis of variance for response of dependent variables

Analysis of variance

The statistical significance of the quadratic polynomial model equation was evaluated by an analysis of variance (ANOVA). Table 6 shows the ANOVA results for the models that explain the response of the three dependent variables. The linear terms (X_1 , X_2) of Y_1 , Y_2 , and Y_3 were significant (P = 0.015, P = 0.001, and P = 0.002, respectively), whereas their interaction terms (X_1X_2), except for Y_2 , were not significant at the 95% probability level (P > 0.05). The results of the lack-of-fit test, which indicates the fitness of the model (Isa et al., 2011), showed that the *P*-values of Y_1 (oxidation induction time) and Y_2 (sensory score) were not significant (0.103 and 0.374, respectively) at the 95% probability level. The *P*-value of Y_3 (unit cost) was not calculated because the pure error value of Y_3 mean square was zero (Santos and Boaventura, 2008).

Effects of factors and response surface plots

RSM is a useful statistical technique for the evaluation of the relationships between independent (factor) and dependent (response) variables (Dorta et al., 2013). Fig. 1. shows the estimated response function and the effect of the independent variables (X_1 and X_2) on the dependent variables (Y_1 , Y_2 , and Y_3). The oxidation induction time of the mixed oil increased with an increase in the proportion of corn and sesame oils. In

Responses	Sources	Degrees of freedom	Sum of square	Mean square	<i>F</i> -value	P-value
Y_1	Regression					
	Linear	2	1.144	0.572	11.02	0.015
	Square	2	0.122	0.061	1.18	0.381
	Interaction	1	0.185	0.185	3.56	0.118
	Residual					
	Lack of fit	3	0.241	0.080	8.83	0.103
	Pure error	2	0.018	0.009		
	Total	10	1.710			
Y_2	Regression					
	Linear	2	2.416	1.208	56.20	0.000
	Square	2	6.876	3.438	159.96	0.000
	Interaction	1	0.308	0.308	14.33	0.013
	Residual					
	Lack of fit	3	0.079	0.026	1.82	0.374
	Pure error	2	0.029	0.014		
	Total	10	9.707			
Y_3	Regression					
	Linear	2	847209	423604	29.09	0.002
	Square	2	241692	120846	8.30	0.026
	Interaction	1	1560	1560	0.11	0.757
	Residual					
	Lack of fit	3	72798	24266	-	-
	Pure error	2	0	0		
	Total	10	1163259			

Y₁, oxidation induction time (h); Y₂, sensory score (point); Y₃, unit cost (won/L).

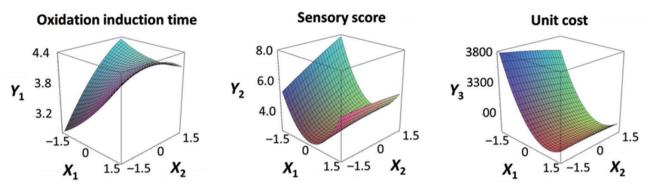


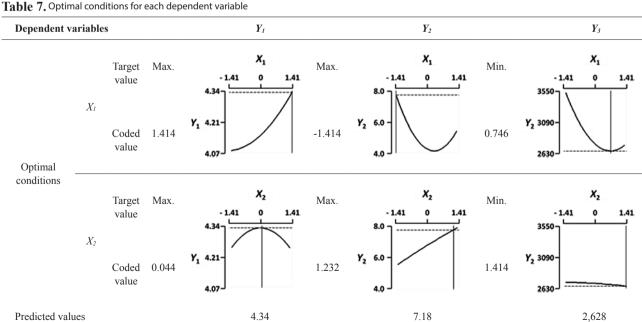
Fig. 1. Three dimensional response surface plots for oxidation induction time (Y1), sensory score (Y2), and unit cost (Y3).

contrast, perilla oil accelerated the thermal oxidation of the mixed oil. Sesame oil contains natural antioxidants such as sesamin, sesamol, and sesamolin, and a high content of oleic and linoleic acids, which promote the stability of oxidation (Bayder et al., 1999; Lee et al., 2008). However, perilla oil contains a high content (59%) of oxidation-susceptible linolenic acid, which can induce rapid oxidation during UHT treatment (Wang, 2010; Zhao, 2012). These results indicate that the blending ratio of corn, sesame, and perilla oils significantly influences the thermal oxidation stability of the UHT processed seasoned laver. In Korea, sesame and perilla oils are most frequently used for seasoned laver preparation because of their excellent savory taste (Yang et al., 2012). In this sensory test, the seasoned laver with a high proportion of sesame oil (Nos. 3 and 5 in Table 3) was the most preferred product.

When considering the overall results of this study, perilla oil was found to be ineffective in terms of oxidation stability, sensory properties, and the cost of the seasoned laver.

Optimization of the oil blending ratio

The blending ratio of corn, sesame, and perilla oils was individually optimized for the oxidation induction time (Y_1) , sensory score (Y_2) , and unit cost (Y_3) . In addition, multiple response optimization was performed to search for the condition that simultaneously satisfied the oxidation induction time (Y_1) and sensory score (Y_2) . The optimal conditions of the independent variables X_1 and X_2 on each dependent variable were 1.414 and 0.044 for Y_1 , -1.414 and 1.232 for Y_2 , and 0.746 and 1.414 for Y_3 , respectively (Table 7). The multiple optimal con-



 Y_{1} , oxidation induction time (h); Y_{2} , sensory score (point); Y_{3} , unit cost (won/L).

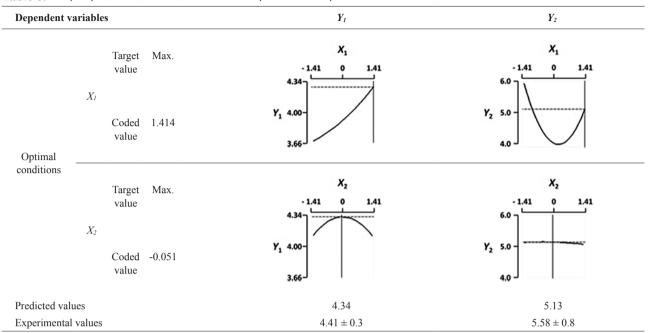


Table 8. Multiple optimal conditions and verification of the predicted and experimental values

 Y_1 , oxidation induction time (h); Y_2 , sensory score (point).

Value of Y₃ (unit cost) at the multiple optimal conditions was 2,669 won/L.

 Table 9. Optimal blending ratios of corn oil, sesame oil, and perilla oil at the each optimal condition

Response	Corn oil (%, v/v)	Sesame oil (%, v/v)
Y_I	92.3	6.7
Y_2	39.8	52.3
Y_3	90.3	8.5
Y_1 and Y_2	92.3	6.0

Y₁, oxidation induction time (h); Y₂, sensory score (point); Y₃, unit cost (won/L).

ditions for the oxidation induction time (Y_1) and sensory score (Y_2) were X_1 : +1.414 and X_2 : -0.051 (Table 8). The blending ratios of corn, sesame, and perilla oils at each optimal condition are shown in Table 9. The optimal blending ratio of corn, sesame, and perilla oils for both oxidation induction time (Y_1) and sensory score (Y_2) were 92.3, 6.0, and 1.7%.

Experimental verification of the predicted values at the optimal condition

The predicted values of the oxidation induction time (Y_1) and sensory score (Y_2) at the optimal condition were 4.34 h and 5.13 points, respectively (Table 8). To verify the accuracy of the predicted values of the dependent variables at the optimal condition $(Y_1 \text{ and } Y_2)$, seasoned laver was prepared using a mixture of corn (92.3%, v/v), sesame (6.0%), and perilla (1.7%) oils. Under multiple optimal conditions, the ex-

perimental values of Y_1 and Y_2 were 4.41 ± 0.3 h and 5.58 ± 0.8 points, and were similar to the predicted values calculated in the RSM design.

In conclusion, our results show the effects of the blending ratio of corn, sesame, and perilla oils on the oxidation and sensory quality of seasoned laver. The price of the blended oil was also monitored. In addition, this study was designed and analyzed using an RSM. Therefore, the optimal conditions and values of the dependent variables in the RSM design matrix may be useful information for seasoned laver processing companies.

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