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Application of Response Surface Analysis for Predicting Moisture Content of Binary Mixture

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다중 회귀분석에 의한 二相混合物의 수분함량 예측

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Abstract

The water sorption isotherms of binary mixtures, prepared by corn starch and isolated soybean protein (ISP) or casein, were measured and analyzed. Simple equations to predict moisture content from knowledge of composition and water activity of the mixture were derived by applying Response Surface Analysis. Comparison between predicted and experimental moisture content for 13 combinations of corn starch-ISP mixture at the range of a_w 0.25-0.87 resulted in a maximum error of only 6.06% and an absolute mean error of 2.60%, and for the mixture of corn starch-casein the error was −4.39% and 2.12%, respectively. The agreement between experimental and predicted water sorption isotherms was shown to be "highly acceptable" for the binary mixtures of 50% corn starch-50% ISP and 50% corn starch −50% casein.

Introduction

Corn starch, ISP, and casein are often used as sourses of carbohydrate and protein for fabricated foods, in which each component has shown a different water sorption isotherm. Therefore, water sorption isotherms of fabricated foods would be affected according to the composition of components. Labuza[1] suggested that the amount of water sorbed at any water activity may be derived by the weight percentage of each component times the amount it would sorb alone. This hypothesis gave satisfactory results in various binary mixtures while in gelatin-starch gel the predicted values were significantluy higher than the experimental values[2].

Lang and Steinberg[3] developed an equation which calculates the water activity (a_w) of a mixture of known composition at a given moisture content and is shown to give and excellent accuracy with noncrystalline materials such as starch and casein. Studies on the equations for prediction of the water sorption isotherm for a multicomponent products of known composition have been investigated by other several workers[4-7]. Each equation appears to be accurate only under a narrow a_w range or for specific ingredients and particularly the equations derived by Norrish[5] and Ross[6] have shown good accuracy when applied to the solutions of sugars and sdalts.

Response Surface Analysis was often used as a useful statistical tool for analyzing experimental data from the food products to optimize the physical properties of the food products.[8]

The objective of this work was to apply the Response Surface Analysis as a simple equation to predict moisture content from a composition of binary mixture at a given water activity and to compare the agreement between experimental and predicted moisture sorption isotherms of the binary mixtures.

Materials and Methods

Materials

Ingredients were as follows: (1) corn starch, Sun-il brand Sun-il Glucose Co., Inchon, Kyonggi-do, Korea) at 12.3% moisture, wet bais (w.b.); (2) isolated soybean protein (ISP), Golden Cal brand (Golden Califonia Co., Sepulveda, CA) at 6.1% moisture, w.b.; (3) casein, purified (Junsei Chemical Co., Tokyo, Japan) at 4.2% moisture, w.b.. Sulfuric acid and various salts used were extra pure and reagent grade, respectively.

Binary mixtures of the model system corn starch-ISP studied, expressed on a wet basis, were; (A) 0:100 starch: ISP; (B) 14.65:85.35 starch: ISP; (C) 50:50 starch: ISP; (D) 85.35:14.65 starch:ISP; (E) 100:0 starch: ISP and those of the model system corn starch-casein were; (A) 0:100 starch: casein; (B) 14.65:85.35 starch:casein; (C) 50:5C starch:casein; (D) 85.35:14.65 starch:casein; (E) 100:0 starch: casein.

The mixtures were mixed in a 4.5*l* Hobart mixer for 60 min. The bowl was covered with aluminum foil to prevent the loss of small airborne particles[3].

Moisture determination

Moisture content was determined gravimetrically ±0.0003g by the vacuum oven method[9] using 60°C and 29.8 in. Hg vacuum for 36hr. Samples of 1-2g were used for determination. All analyses were made in triplicate.

Water sorption isotherms

Sorption isotherms (moisture content vs. water activity) were determined by exposing 1-2*g* of each sample over various aqueous sulfuric acid solutions or saturated salt solutions of known water activity. Sulfuric acid solutions were made up volumetrically, and their composition, from which water activity was determined[10], was measured by titration before and after each solution isotherm measurement. The a_w values for the saturated salt solutions were those accepted by the National Bureau of Standards[11] or those reported by Rockland[12]. The values were: $MgCl_2$, 0.33; K_2CO_3, 0.43; NaBr, 0.57; $CuCl_2$, 0.67; NaCl, 0.75 and K_2CrO_4, 0.87 at 25°C.

Modified proximity equilibration cells (MPEC) were used for each mixture as referred by McCune *et al.*[13]. The inner diameter and height of MPEC were 51*mm* and 67*mm*, respectively. All samples were stored at 25°C until moisture determined in 21 days. The isotherm curves were established by graphical interpolation of the experimental data points.

Experimental design

Appropriate combinations of two independent variables (X_1 and X_2 or X and X_2), each at five different levels, were studied (Table 1). Response surface analysis described by Cochran and Cox[14] was used to estimate regression coefficients according to the second order model equation. Regression coefficients were calculated by a numerical method from the experimental data.

Results and Discussion

Table 2 shows the design and results of the trials for the second order model. Thirteen trials were conducted to obtain response surface model equation for moisture content of binary mixture of the two model systems. Coded levels of independent variables are defined by the following relation:

$$X_1 = \frac{\text{\% corn starch of a mixture} - 50.00}{35.35}$$

$$X_1' = \frac{50.00 - \text{\% ISP of a mixture}}{35.35} \text{ or } \frac{50.00 - \text{\% casein of a mixture}}{35.35}$$

$$X_2 = \frac{\text{water activity} - 0.56}{2.2192}$$

The range of corn starch, ISP, and casein for the factorial design was based on the entire percentage by weight (0-100%) of a component and the range of water activity was decided according to the experimental results of water sorption isotherms of the model systems. The final second order response models for Y (moisture content of binary mixture, % dry basis) in the system of starch-ISP as a function of X_1 and X_2 or of X_1' and X_2, are shown below:

Table 1. Composition of mixture studied

Independent variables	Symbols	Levels				
		-1.4142	-1	0	1	1.4142
Corn starch (%)	X_1	0	14.65	50	85.35	100
ISP or Casein (%)	X_1'	100	85.35	50	14.65	9
Water activity	X_2	0.25	0.34	0.56	0.78	0.87

$$Y = 13.458 + 1.276X_1 + 4.348X_2 - 0.673X_1X_2 - 0.264X_1^2 + 0.816X_2^2$$

By definition and levels of independent variables, the sum of % corn starch and % ISP in a mixture is 100% by weight.

$X_1 - X_1 = 0$ and $X_1 = X_1'$. Therefore,

$$Y = 13.458 + 1.276X_1' + 4.348X_2 - 0.673X_1'X_2 - 0.264X_1^2 + 0.816X_2^2$$

Similarly the model equations for Y in the system starch-casein could be easily derived and are defined as:

$$Y = 12.300 + 1.696X_1 + 3.561X_2 - 0.148X_1X_2 \quad 0.052X_1^2 + 1.083X_2^2$$

$$Y = 12.300 + 1.696X_1' + 3.561X_2 - 0.148X_1'X_2 - 0.052X_1'^2 + 1.083X_2^2$$

The analyses of variance of response surface models for moisture content of the model systems are shown in Table 3 and Table 4 and evaluate how well the models account for variation in the actually observed data of moisture content. The model for moisture content (Y) in the system starch-ISP accounted for 98.75% of variation in the observed values and for 99.09% in the system

Table 2. Effects of independent variable combination upon moisture content of corn starch-ISP and corn starch-casein binary mixtures

Model system	Trial no.	Independent variables		Dependent variables		
				Y (moisture content, % dry basis)		
		X_1	X_2	Experi-mental	Predicted	Error (%)
Corn starch - ISP	1	−1 (B)*	−1	8.16	7.713	−5.48
	2	1 (D)	−1	11.81	11.611	−1.69
	3	−1 (B)	1	17.29	17.755	2.69
	4	1 (D)	1	18.25	18.961	3.90
	5	−1.4142 (A)	0	11.08	11.125	0.41
	6	1.4142 (E)	0	15.04	14.735	−2.03
	7	0 (C)	−1.4142	8.43	8.941	6.06
	8	0 (C)	1.4142	22.01	21.239	−3.50
	9	0 (C)	0	13.05	13.458	3.13
	10	0 (C)	0	13.32	13.458	1.04
	11	0 (C)	0	13.98	13.458	−3.73
	12	0 (C)	0	13.47	13.458	−0.09
	13	0 (C)	0	13.47	13.458	−0.09
Corn starch – CaseIn	1	−1 (B)	−1	8.29	7.926	−4.39
	2	1 (D)	−1	11.58	11.614	0.29
	3	−1 (B)	1	15.05	15.344	1.95
	4	1 (D)	1	17.75	18.440	3.89
	5	−1.4142 (A)	0	9.68	9.798	1.22.
	6	1.4142 (E)	0	15.04	14.594	−2.97
	7	0 (C)	−1.4142	9.13	9.430	3.29
	8	0 (C)	1.4142	20.13	19.502	−3.12
	9	0 (C)	0	12.35	12.300	−0.40
	10	0 (C)	0	12.34	12.300	−0.32
	11	0 (C)	0	12.61	12.300	−2.46
	12	0 (C)	0	12.16	12.300	1.15
	13	0 (C)	0	12.04	12.400	2.16

* Code for binary mixture is shown in Materials.

starch-casein. All the models were found to be significant at the 1% level.

Thirteen combinations between predicted and experimental moisture content for the system starch-ISP over a_w 0.25-0.87 resulted in a maximum error of 6.06% and an absolute mean error of 2.60%, and for the system starch-casein the error was −4.39% and 2.12%, respectively (Table 2). Lang and Steinberg[3] reported that from the equation derived by them, twenty-one comparisons between calculated and experimental a_w over 0.30-0.95 resulted in a maximum error of 1.86% and a mean error of −0.25%. This result means that although the response surface model is less accurate than the Lang and Steinberg equation, the model could be used as a tool to predict the moisture content of binary mixture at a given water activity and under a given composition.

Table 5 shows the second order equation of each binary mixture in the systems starch-ISP and starch-casein, obtained by replacing X_1 or X_1' values corresponded to the % corn starch or % ISP and % casein into the response surface model equation. The results in Table 5 indicated that the moisture content is increased as water activity and the mixing ratios of corn starch increased.

The comparison of experimental and predicted isotherms will be simply made by evaluating the maximum observed percentage difference between measured and predicted equilibrium moisture contents[2], and comparing this differnce with the maximum error in the experimental design of response surface analysis. Thirteen combinations in Table 2 resulted in a maximum error of 6.06% for the model system starch-ISP and of −4.39% for the model system starch-casein. With this maximum errors in mind we found that the maximum observed percentage difference between experimental and predicted equilibrium moisture contents was about 6.0% at a_w 0.25 in the binary mixture of 50% starch- 50% ISP, and about 3.2% at a_w 0.25 in the binary mixture of 50% starch- 50% casein (Fig. 1 & 2). In none of these mixtures is the percentage difference in moisture content at a_w 0.25-0.87 higher than the maximum error of each model

Table 3. Analysis of variance of response surface analysis for moisture content of the system corn starch-ISP

Souce of variance	d.f	Sums of squares	Mean square	F	Model SS / Total SS
Model	5	171.80	34.36	110.84*	98.75%
Residual	7	2.17	0.31		
Lack of fit	3	1.71	0.57	4.96	
Real error	4	0.46	0.115		
Total	12	173.97			

* Significant at the 1% level

Table 4. Analysis of variance of response surface analysis for moisture content of the system corn starch-casein

Souce of variance	d.f	Sums of squares	Mean square	F	Model SS / Total SS
Model	5	133.31	26.66	110.84*	99.09%
Residual	7	1.23	0.18		
Lack of fit	3	1.04	0.35	7.29**	
Real error	4	0.19	0.048		
Total	12	134.54			

* Significant at the 1% level
** Significant at the 5% level

Table 5. Prediction equation of moisture content (%, drybasis) for the binary mixtures

Model system	Binary mixture	Prediction equation*
Corn starch	A**	$Y = 11.125 + 5.300X_2 + 0.816X_2^2$
- ISP	B	$Y = 11.918 + 5.021X_2 + 0.816X_2^2$
	C	$Y = 13.458 + 4.348X_2 + 0.816X_2^2$
	D	$Y = 14.470 + 3.675X_2 + 0.816X_2^2$
	E	$Y = 14.735 + 3.396X_2 + 0.816X_2^2$
Corn starch	A	$Y = 9.798 + 3.770X_2 + 1.083X_2^2$
- Casein	B	$Y = 10.552 + 3.709X_2 + 1.083X_2^2$
	C	$Y = 12.300 + 3.561X_2 + 1.083X_2^2$
	D	$Y = 13.944 + 3.413X_2 + 1.083X_2^2$
	E	$Y = 14.594 + 3.352X_2 + 1.083X_2^2$

* X_2 is coded variable of water activity in Table 1.
** Code for binary mixture is shown in Materials.

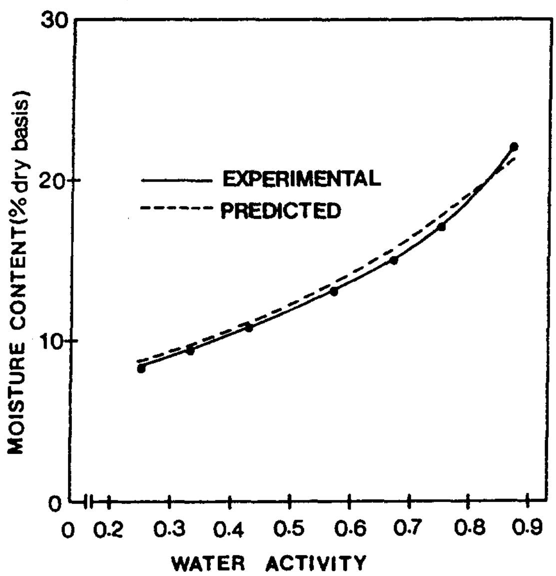

Fig. 1. Comparison of predicted water sorption isotherm for 50% corn starch-50% ISP with experimental isotherm at 25.0°C

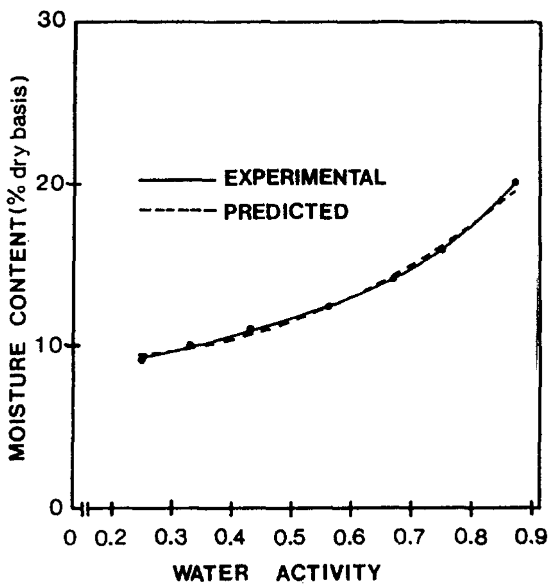

Fig. 2. Comparison of predicted water sorption isotherm for 50% corn starch-50% casein with experimental isotherm at 25.0°C

system. Therefore, it may be concluded that in many observed cases the agreement between predicted and experimental isotherms may be considered "acceptable", and that response surface analysis can be used as a useful tool to predict moisture content in a binary mixture with a_w 0.25-0.87.

The extent of disagreement in the sorption isotherm of a binary mixure appeared to be related to the components of the model system, to the composition ratio of the components, and to the experimental a_w range. Consequently, it would seem reasonable that the components involved in a model system would be very important factor in giving accuracy to the response surface model equation. Therefore, more research would be needed to increase the accuracy of predicting moisture content of the binary mixture from a know composition and a given water activity in applying the response surface analysis to a model equation.

요 약

옥수수전분과 분리대두단백 혹은 옥수수전분과 카제인으로 제조된 二相混合物의 수분흡습을 측정분석하였으며, 다중회귀분석법을 利用 混合物의 구성비와 수분활성도의 數値로부터 混合物의 수분함량을 예측가능케 하는 다중회귀방정식을 구하였다. 옥수수전분과 분리대두단백으로 구성된 13개의 실험구에서 수분함량 측정値와 예측値를 비교했을때 최대오차는 6.06%이었고, 오차의 절대値 평균은 2.60%로 나타났다. 그리고 옥수수전분과 카제인으로 구성된 二相混合物은 최대오차 −4.39%, 오차의 절대치 평균은 단지 2.12%로 측정値와 예측値 間의 거의 일치함을 보여 주었다. 또한 중량比 50 : 50인 二相混合物의 수분흡습곡선을 비교 분석하였을 때도 측정한 흡습곡선과 예측한 흡습곡선 間에는 거의 일치하는 것으로 나타났다.

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