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# Combination of the Simple Additive (SAW) Approach and Mixture Design to Determine Optimum Cocoa Combination of the Hot Chocolate Beverage

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Physicochemical (pH, brix, and color), sensory (color, taste, odor, mouthfeeling, consistency, bitter flavor, and general acceptability), and rheological properties of the hot chocolate beverages including different cocoa combinations were investigated in the present study. Cocoa type significantly affected all of the properties. Simple additive weighting approach was applied to obtain one score from seven different sensory parameters and simple additive weighting score was used in mixture design to determine optimum cocoa type or cocoa combination. Ostwald de Waele model described the flow behavior of the hot chocolate beverage samples with  $R^2$  values ranged between 0.818 and 0.999. The consistency coefficient ( $K$ ) and apparent viscosity at shear rate  $50 \text{ s}^{-1}$  ( $\eta_{50}$ ) were significantly affected by cocoa type found in the formulation of the beverage. The mixture design approach was performed in order to determine variation of the responses (physicochemical, sensory, and rheological parameters) as a function of cocoa concentration. Simple additive weighting scores were satisfactorily described by established equation as a function of cocoa concentration to be used in the formulation of the hot chocolate beverage ( $R^2 = 0.8645$ ).

*Keywords:* Hot chocolate, SAW, Mixture design, Cocoa, Sensory, Rheology.

## INTRODUCTION

Hot chocolate beverage is widely consumed throughout the world by people of all ages. Sugar, cocoa powder, skimmed milk powder, whey powder, starch, salt, and hydrocolloids are ingredients found in the formulation of the beverage.<sup>[1]</sup> The hot chocolate beverage is prepared by adding these powder ingredients to water or milk.<sup>[2]</sup> The sensory properties of the beverage including taste, odor, color, and appearance are important for desirableness of the beverage. Among the ingredients of the hot chocolate beverage, the cocoa type found in the formula plays an important role in determination

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of the sensory properties of the product. Therefore, chemical composition, especially fat concentration, of the cocoa butter concentration is very important since soft texture, plasticity, viscosity, easy diffusion of taste and flavor, gloss, and unusual melting characteristics of the product are significantly affected by fat concentration.<sup>[3]</sup> Cocoa bean polyphenols are also associated with the flavor and color of the chocolate.<sup>[4]</sup> Fermentation and drying are important processes applied during curing of the cocoa beans and volatile compounds formed during fermentation are responsible for sensory characteristics of the cocoa.<sup>[5]</sup> In addition to the color and flavor, pH, fineness, alkalinity, wettability, solubility, density, and microbiological quality determine quality of the cocoa powder,<sup>[6]</sup> which is important for acceptability of the product. In this aspect, the selection of optimum cocoa is very important for the quality of the hot chocolate beverage which might be determined by sensory analyses.

Sensory analyses of the product are important to determine acceptance or rejection of a product which might have understood from the responses of the panelists. Generally, sensory properties are composed of appearance, color, taste, odor, mouthfeel, and overall preference parameters. Therefore, the interpretation of the sensory results, combination of the sensory parameters which are independent from each other such as taste and odor, is very difficult.<sup>[7]</sup> While one sample might be preferred considering the color, another sample might be preferred in terms of taste parameter. This problem can be prevented by using multi-criteria techniques since they provide only one result, resulting in ease of interpretation of the results and selection of the best sample.<sup>[7]</sup> The weighting factor of the criteria, relative importance of the criteria, directly affects the results of the multi-criteria decision techniques. There are several methods which are analytic hierarchy process (AHP), technique for order preference by similarity to ideal solution (TOPSIS), elimination et choix traduisant la realite-elimination and choice translating reality (ELECTRE) and simple additive weighting (SAW). Gurmeric et al. satisfactorily performed different multi-criteria decision techniques to determine optimum prebiotic pudding flavor based on sensory properties.<sup>[7]</sup> However, we have not encountered any other study about the use of these techniques in the food industry. The present study aims at combination of the SAW technique and mixture design approach to determine optimum cocoa type or different cocoa blend to be used in the formulation of the hot chocolate beverage. In addition to sensory properties, rheological characteristics of the hot chocolate beverages might be affected by cocoa type found in the formulation.

Rheological properties are an important quality indicator of the products<sup>[8]</sup> such as hot chocolate, salep drink, or dairy based foods.<sup>[9]</sup> Rheological properties play an important role in the efficiency of processes like mixing and pumping, and chocolate applications involving enrobing, shell formation, and moulding processes.<sup>[10]</sup> Rheological properties of the hot chocolate beverages were affected by several factors like hydrocolloids type and concentration, starch type.<sup>[11,12]</sup> In addition, cocoa type may be another factor which might affect rheological properties of the hot chocolate beverage as well as sensory properties. Therefore, use of different cocoa types could improve both properties, and optimization of the cocoa combination to be used in the formulation is important for quality of the product. Mixture design is widely used for optimization purposes and it provides the relationship between mixture factors and responses by means of mathematical representation.<sup>[13]</sup> The effects of the ingredients on the responses and the importance of the ingredient interactions might be determined using mixture design approach.<sup>[14,15]</sup> Optimization of the ingredients of different products, mixture design was satisfactorily performed.<sup>[15–21]</sup> However we have not encountered any study about the optimization of the cocoa formulation based on sensory parameters and combination of the SAW method and mixture design to determine optimum cocoa blend.

The aims of the present study were (1) to determine physicochemical, sensory, and rheological properties of the hot chocolate beverage including different cocoa type or blends, (2) to perform SAW technique to combine sensory scores of the samples, and (3) to combine SAW method and mixture design approach to determine optimum cocoa combination to be used in the formulation of the hot chocolate beverage.

## MATERIALS AND METHODS

### Materials

All cocoa samples were obtained from the companies of the national market and they are named as Usta Cocoa, Gerkens Cocoa, and Ulker Gold Cocoa. Sugar, skimmed milk powder (Pinar Food Co., Turkey), whey powder (Ova Food Co., Turkey), modified corn starch (Bayrak Food Co., Turkey), chocolate powder and flavor of chocolate (Aromsa Food Co., Turkey), salt, and xanthan gum (XG) were obtained from a firm manufacturing instant beverage in Kayseri, Turkey.

### Preparation of Hot Chocolate Beverage Samples

Ten g sucrose, 3 g skimmed milk powder, 1.4 g whey powder, 4 g cocoa, 0.6 g modified corn starch, 0.2 g powdered chocolate, 0.06 g chocolate flavor, 0.01 g salt, and 0.16 g gum were mixed. As seen from Table 1, nine powder mixtures including different cocoa type or combination were prepared. To prepare hot chocolate beverage, 160 mL of distilled water was heated to 80°C on a hot plate (Yellowline, Germany) and homogenized powder mixture was added into water slowly to prevent agglomeration and stirred constantly with a magnetic stirrer at 80°C for 15 min. Then the hot chocolate drink was cooled to 60°C in a water bath temperature of which was 60°C. During analyses temperature of sample is kept at 60°C by means of water bath temperature.

### Measurement of the Brix and pH Value and Color Properties

Soluble solid (brix) content of the samples were determined using an automatic refractometer (Reichert AR 700, USA) at room temperature and the results were expressed as degrees Brix at 25°C. The pH values were determined by a pH meter (WTW-Inolab Level 3 Terminal, Weilheim, Germany) at room temperature. Both measurements were done in triplicate in two replications. Color of samples was measured by a colorimeter (Lovinbond Reflectance Tintometer 962, Canada). The illuminant type and observer angle was D50 and 2°, respectively.  $L^*$ ,  $a^*$ , and  $b^*$  values of each samples were obtained ( $L^*$ : brightness,  $a^*$ : redness,  $b^*$ : yellowness). Each measurement was done in triplicate on each of two repetitions.

TABLE 1  
Cocoa compositions of the hot chocolate beverage samples

Samples	Ingredient proportions			X <sub>1</sub> (%)	X <sub>2</sub> (%)	X <sub>3</sub> (%)
	X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>			
S1	1.000	0.000	0.000	100	0	0
S2	0.000	1.000	0.000	0	100	0
S3	0.000	0.000	1.000	0	0	100
S4	0.167	0.167	0.667	16.7	16.7	66.7
S5	0.667	0.167	0.167	66.7	16.7	16.7
S6	0.167	0.667	0.167	16.7	66.7	66.7
S7	0.500	0.000	0.500	50	0	50
S8	0.000	0.500	0.500	0	50	50
S9	0.500	0.500	0.000	50	50	0

X<sub>1</sub>: cocoa 1; X<sub>2</sub>: cocoa 2; X<sub>3</sub>: cocoa 3.

## Rheological Measurements

A strain/stress controlled rheometer (Thermo-Haake, Rheostress 1, Germany) equipped with a temperature-control unit (Haake, Karlsruhe K15, Germany) and with a cone-plate configuration (cone radius of 35 mm and a gap of 1.00 mm between the cone and plate) was used for determination of the rheological properties of the hot chocolate samples. Measurements were carried out in the shear rate range of 1-300 s<sup>-1</sup> at constant temperature (60°C). Approximately 0.85 mL of the hot chocolate sample was placed with micropipette between the cone and plate and after that the measurement was started immediately. A total of 25 data points were recorded at 10 s intervals during the shearing. Each measurement was replicated five times on the same sample with two repetitions. The apparent viscosity was determined as a function of shear rate. The flow curve, shear rate versus shear stress was plotted. According to obtained data, Ostwald de Waele model was best model which described flow behavior of the sample. By using the following equation, the parameters of the model were determined.<sup>[22]</sup>

$$\tau = K(\dot{\gamma})^n \quad (1)$$

where,  $\tau$  is the shear stress (Pa),  $K$  is the consistency index (Pa s<sup>n</sup>),  $\dot{\gamma}$  is the shear rate (s<sup>-1</sup>), and  $n$  is the flow behavior index (dimensionless).

## Sensory Analysis

The hot chocolate samples were prepared at 80°C for sensory analyzes. For sensory evaluation, hot chocolate samples (15 mL) were presented at 80°C to panelists at certain intervals in odorless, randomly coded glass beakers. The sensory evaluations were carried out by 15 selected staffs and post graduate students of the food engineering department of Erciyes University, Kayseri, Turkey. Also, before the analyses the sensory panelists were trained about the sensory evaluation techniques. The panelists drank tap water to cleanse their palates before analyzing the next sample. The sensory attributes evaluated were color, taste, odor, mouthfeeling, consistency, bitter flavor, and general acceptability. The scale of the sensory evaluation was evaluated between 1–9 points where 1 reflected a very low and 9 very high score. Panelists evaluated all samples in two sessions (five at first and four at second session).

## Application of SAW Approach on Sensory Properties of the Samples

After determination of the sensory properties of the hot chocolate samples including different cocoa combinations, the SAW method was used to determine which sample is better based on the sensory properties of the products. In the present method, weighting factor of the criteria was determined by using opinion of the different academicians in the food engineering department of Erciyes University, Kayseri, Turkey. The weighting factor reflects the relative importance of the criteria in terms of describing sensory property of the product. The weighting factor of the criteria is shown in Fig. 1. SAW has the following steps:

1. Construction of the decision matrix ( $m \times n$ ) that includes  $m$  alternative (hot chocolate beverage samples including different cocoa combination [S1-9]) and  $n$  criteria (sensory parameters which are taste and odor, bitter flavor, mouthfeel, color, consistency, general acceptability). As can be seen from Fig. 1, there are nine alternatives and six criteria in the present study.
2. Normalization of the  $X_{ij}$  (sensory score of the  $i^{\text{th}}$  sample regarding  $j$  parameter any of the sensory parameter mentioned above) matrix. Normalization is equal to the ratio of magnitude of the relevant parameter to the magnitude of the sum of the its row.

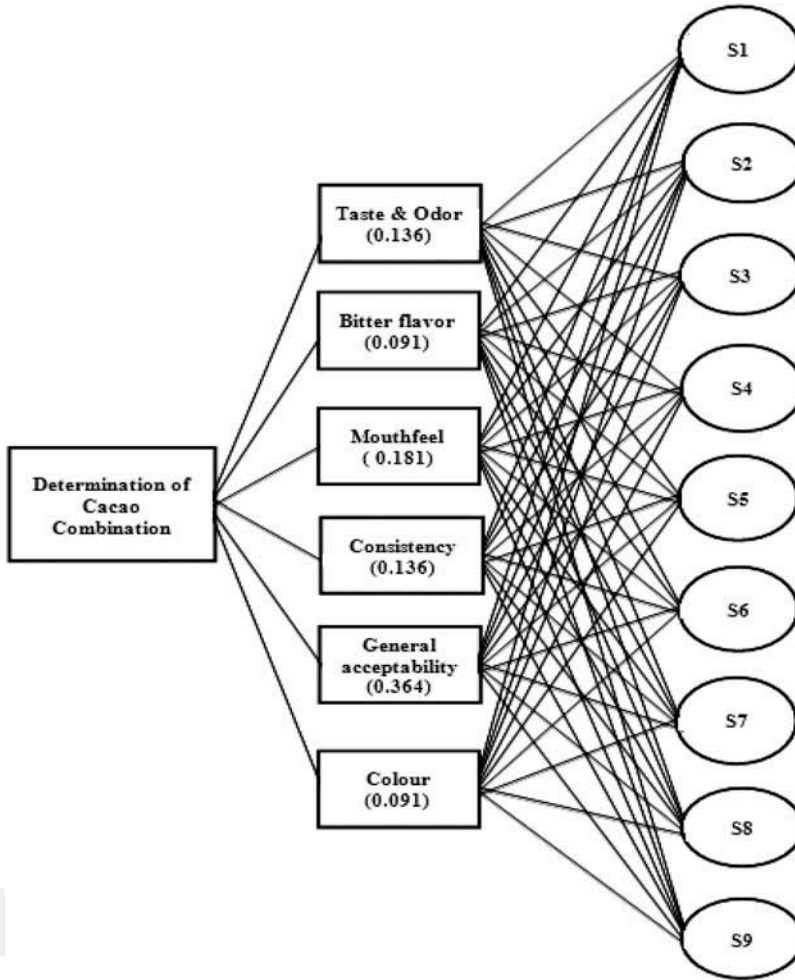


FIGURE 1 Scheme of the decision hierarchy of cocoa combination selection to be used in formulation of the hot chocolate beverage (values in parentheses represent weighting factor of the criteria).

3. Formation of the weighted normalized matrix by using the following equation:

$$A_i = \sum w_j x_{ij} \tag{2}$$

where,  $x_{ij}$  is the normalization score of the  $i^{th}$  alternative with respect to the  $j^{th}$  criteria, and  $w_j$  is the weight of the criteria.<sup>[23]</sup>

4. Ranking of the alternatives by calculating the sum of the rows of the weighted normalized vectors.

### Experimental Design and Statistical Analysis

In this study, the mixture design was used to observe the effect of Ulker Gold Cocoa ( $X_1$ ), Usta Cocoa ( $X_2$ ), and Gerkens Cocoa ( $X_3$ ) on the rheological, physicochemical, and sensory properties

of the hot chocolate beverage samples. In a mixture experimental design, the total cocoa amount is held constant and the concentrations of the cocoa types are changed in the formulation. Therefore, the aim of this methodology is to verify how the interested properties are affected from the variation of the mixture components. The proportional levels of the cocoas were set at 0–1 (0–100%). Nine combinations of the three cocoas are given in Table 1. The following equation was fitted to data obtained from experimental points.

$$Y = \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 \quad (3)$$

where,  $Y$  is the predicted response (Brix, pH,  $L^*$ ,  $a^*$ ,  $b^*$ ,  $K$ ,  $n$ ,  $\eta_{50}$ , color, taste, odor, mouthfeeling, consistency, bitter flavor, and general acceptability);  $\beta_1$ ,  $\beta_2$ ,  $\beta_3$ ,  $\beta_{12}$ ,  $\beta_{13}$ , and  $\beta_{23}$  are the linear and non-linear constants for each term.  $X$  is the cocoa concentration used in the hot chocolate beverage samples ( $X_1$ : cocoa 1;  $X_2$ : cocoa 2,  $X_3$ : cocoa 3). The predicted equation of each response was obtained by Design Expert package software (Version 8.0.5 Stat-Easy Co., Minneapolis, MN, USA). Backward elimination method was used to remove the insignificant parameters of the models in order to improve accuracy of the models.

## RESULTS AND DISCUSSION

### Physicochemical Properties of the Samples

The pH, brix (soluble solids content) and color values ( $L^*$ ,  $a^*$ , and  $b^*$ ) of the hot chocolate samples including different cocoa compositions are shown in Table 2. The pH values of the samples were in the range of 7.83–9.79. As can be seen from Table 2, the cocoa composition significantly affected the pH values of the samples ( $P < 0.05$ ). As the S4 sample had the highest pH value, the S2 sample had the lowest pH value. The variation of the pH value of the samples might be resulted from the pH of the cocoa ingredients. The pH of the cocoa 1, 2, and 3 were approximately 6.0, 7.8, and 8.5, respectively, which were obtained from a producer company. The pH values of the hot chocolate beverage including different starch gum combinations and gum combinations changed between 8.06–8.33 and 8.29–8.57, respectively.<sup>[1,11]</sup> Table 3 shows the established equations obtained from mixture design in order to determine the variation of the pH value of the hot chocolate beverage based on cocoa concentration. The  $R^2$  value was found as 0.3370 indicating that established models

TABLE 2  
Physicochemical properties of the hot chocolate beverages including different cocoa composition

Sample	pH	Brix	Color properties		
			$L^*$	$a^*$	$b^*$
S1	8.17 ± 0.00 <sup>h</sup>	10.17 ± 0.07 <sup>b</sup>	13.13 ± 0.22 <sup>b</sup>	10.78 ± 0.20 <sup>a</sup>	12.83 ± 0.41 <sup>a</sup>
S2	7.83 ± 0.01 <sup>i</sup>	10.79 ± 0.08 <sup>a</sup>	15.67 ± 0.44 <sup>a</sup>	9.78 ± 0.25 <sup>cd</sup>	12.13 ± 0.35 <sup>b</sup>
S3	9.17 ± 0.01 <sup>d</sup>	9.79 ± 0.19 <sup>c</sup>	8.88 ± 0.09 <sup>f</sup>	7.81 ± 0.06 <sup>f</sup>	6.55 ± 0.09 <sup>e</sup>
S4	9.79 ± 0.01 <sup>a</sup>	9.45 ± 0.09 <sup>d</sup>	11.80 ± 0.08 <sup>cd</sup>	9.37 ± 0.07 <sup>e</sup>	10.35 ± 0.08 <sup>c</sup>
S5	9.42 ± 0.01 <sup>c</sup>	9.65 ± 0.10 <sup>cd</sup>	11.39 ± 0.19 <sup>d</sup>	10.35 ± 0.15 <sup>b</sup>	11.90 ± 0.28 <sup>b</sup>
S6	9.46 ± 0.01 <sup>b</sup>	9.55 ± 0.06 <sup>cd</sup>	11.96 ± 0.15 <sup>c</sup>	9.99 ± 0.10 <sup>c</sup>	11.58 ± 0.15 <sup>b</sup>
S7	8.85 ± 0.01 <sup>e</sup>	9.75 ± 0.09 <sup>c</sup>	10.38 ± 0.21 <sup>e</sup>	9.66 ± 0.17 <sup>cde</sup>	9.15 ± 0.25 <sup>d</sup>
S8	8.76 ± 0.01 <sup>f</sup>	9.66 ± 0.09 <sup>cd</sup>	11.57 ± 0.29 <sup>cd</sup>	9.62 ± 0.22 <sup>de</sup>	10.18 ± 0.45 <sup>c</sup>
S9	8.31 ± 0.01 <sup>g</sup>	10.08 ± 0.20 <sup>b</sup>	11.45 ± 0.26 <sup>d</sup>	9.31 ± 0.19 <sup>e</sup>	9.94 ± 0.32 <sup>c</sup>

\*Different superscript lowercase letters show differences between the samples ( $\alpha = 0.05$ ).

TABLE 3  
Established equations and  $R^2$  values of the parameter based on cocoa concentration

	Parameter	Established equation	$R^2$
Physicochemical properties	pH	$8.63 X_1 + 8.38 X_2 + 9.57 X_3$	0.3370
	Brix	$9.86 X_1 + 10.53 X_2 + 9.72 X_3 - 2.88 X_2 X_3^{***}$	0.6529
	$L^*$	$12.97 X_1^* + 15.25 X_2^* + 9.06 X_3^* - 11.25 X_1 X_2^{**}$	0.8811
	$a^*$	$11.00 X_1^{**} + 9.77 X_2^{**} + 8.01 X_3^{**} - 3.24 X_1 X_2^{***} + 3.87 X_2 X_3^{***}$	0.9200
	$b^*$	$12.13 X_1^{**} + 11.90 X_2^{**} + 7.51 X_3^{**}$	0.6995
Rheological properties	$K$	$0.10 X_1^{**} + 0.046 X_2^{**} + 0.082 X_3^{**}$	0.8204
	$n$	$0.55 X_1^{***} + 0.63 X_2^{***} + 0.56 X_3^{***}$	0.6175
	$\eta_{50}$	$0.017 X_1^* + 0.011 X_2^* + 0.014 X_3^*$	0.8355
Sensory properties	Taste & odor	$8.06 X_1^{**} + 6.39 X_2^{**} + 5.89 X_3^{**}$	0.7685
	Bitter flavor	$7.78 X_1^{**} + 7.03 X_2^{**} + 6.73 X_3^{**}$	0.7553
	Mouthfeel	$6.65 X_1^{**} + 6.14 X_2^{**} + 5.45 X_3^{**} + 3.40 X_1 X_3^{***}$	0.7626
	Consistency	$6.68 X_1^{**} + 5.64 X_2^{**} + 5.39 X_3^{**}$	0.6595
	Color	$7.70 X_1 + 6.99 X_2 + 6.37 X_3 - 3.37 X_1 X_2^{***}$	0.6674
	G. acceptability	$7.16 X_1^* + 5.91 X_2^* + 5.36 X_3^* - 2.44 X_1 X_2^{***}$	0.9025
	SAW score	$0.13 X_1^* + 0.11 X_2^* + 0.10 X_3^* - 0.041 X_1 X_2^{***}$	0.8649

\* $P < 0.01$ , \*\* $P < 0.05$ , \*\*\* $P < 0.1$ ;

$X_1$ ,  $X_2$ ,  $X_3$ : Concentrations of the cocoa 1, cocoa 2, and cocoa 3 found in the hot chocolate beverage formulation, respectively.

can not accurately predict the pH value based on cocoa concentration used in the formula since it was lower than 0.75.<sup>[24]</sup> Brix values of the samples changed between 9.45 and 10.79, which was convenient with the previous study.<sup>[11]</sup> However the result of the present study was different from the other studies,<sup>[1,12]</sup> which might be resulted from the different formulations of the hot chocolate beverage. The model established for the prediction of the brix value was not satisfactorily used due to  $R^2$  value of 0.6529. As seen from Table 2, the color properties of the samples were generally significantly affected by the cocoa combination used in the hot chocolate formulation.  $L^*$ ,  $a^*$ , and  $b^*$  values varied between 8.88–15.67, 7.81–10.78, and 6.55–12.83, respectively. The differences between the color values might have resulted from the chemical composition of the cocoa used in the formula. Cocoa beans are rich in polyphenols,<sup>[25]</sup> which are associated with the color of the chocolate.<sup>[4]</sup> The  $R^2$  values of the established models of  $L^*$ ,  $a^*$ , and  $b^*$  were found as 0.8811, 0.9200, and 0.6995, respectively (Table 3), indicating that  $L^*$  and  $a^*$  values were accurately predicted by the established models. As can be seen from Table 3, all of the linear terms were significantly affected the  $L^*$  and  $a^*$  values. The quadratic effect of the  $X_1$  and  $X_2$  was found as significant ( $P < 0.05$  for  $L^*$  and  $P < 0.1$  for  $a^*$ ). The effects of the cocoa concentration on the physicochemical properties were shown in Fig. 2 as a ternary contour plots. As seen from the figure, magnitudes of all physicochemical parameters increased with increasing all of the cocoa concentration. As cocoa 3 and 2 was found as predominant for pH and Brix,  $L^*$  values, cocoa 1 was found as predominant for  $a^*$  and  $b^*$  values.

### Sensory Properties of the Hot Chocolate Beverages

In addition to the physicochemical properties, sensory parameters (color, taste, odor, mouthfeeling, consistency, bitter flavor, and general acceptability) of the hot chocolate beverage including different cocoa combinations as shown in Table 1 are presented in Table 4. As can be seen from Table 3, the

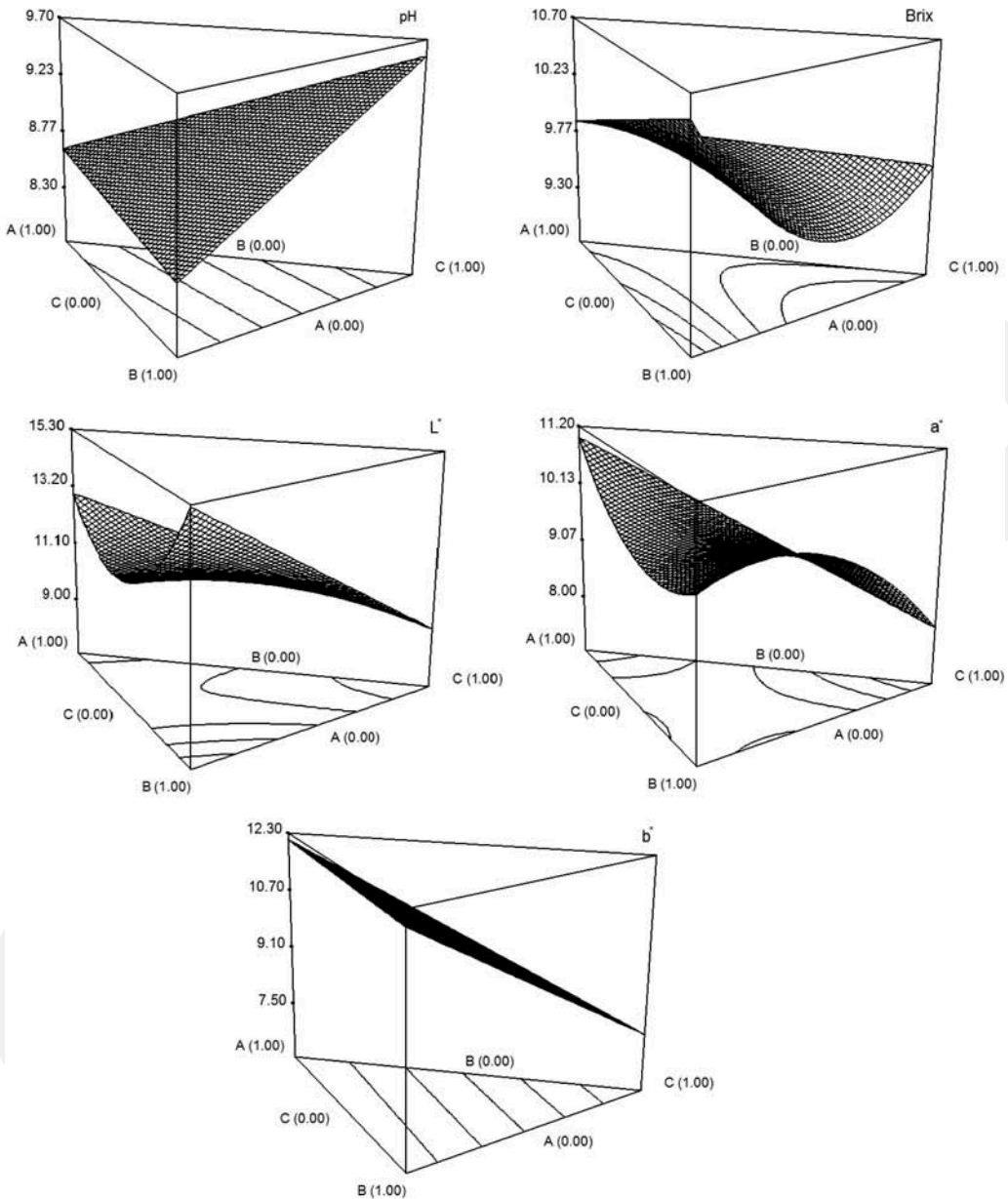


FIGURE 2 Ternary contour plots of the effects of the cocoa combinations on the physicochemical properties (Brix, pH,  $L^*$ ,  $a^*$  and  $b^*$ ) of the hot chocolate beverage (A: cocoa 1, B: cocoa 2, C: cocoa 3).

cocoa combination to be used in formulation of the hot chocolate beverage significantly affected the sensory scores of the sample, which was expected since cocoa is very important ingredient determining the sensory properties of the chocolate beverages. Therefore, variation in the chemical composition of the cocoa caused to differences between sensory properties. Polyphenols found in cocoa affected the flavor of the chocolate.<sup>[4]</sup> Astringency and bitter flavor of the cocoa reduced by

TABLE 4  
Normalized, weighted normalized matrices of the hot chocolate beverages including different cocoa combinations

<i>Samples</i>	<i>Taste and odor</i>	<i>Bitter flavor</i>	<i>Mouthfeel</i>	<i>Color</i>	<i>Consistency</i>	<i>General accept.</i>	<i>Result</i>
Analysis results							
S1	8.38	7.88	6.63	7.63	6.80	7.00	—
S2	6.63	7.13	6.13	6.88	5.75	5.88	—
S3	5.88	6.63	5.60	6.38	5.40	5.25	—
S4	6.50	7.14	5.75	6.63	5.30	5.75	—
S5	7.75	7.67	6.80	7.38	6.25	6.63	—
S6	6.75	7.17	6.75	7.13	6.13	6.00	—
S7	6.63	7.13	7.00	6.88	6.40	6.38	—
S8	6.13	6.88	5.75	6.50	5.50	5.50	—
S9	6.38	7.00	6.00	6.10	5.60	5.70	—
Normalized matrix							
S1	0.1373	0.1219	0.1175	0.1240	0.1280	0.1294	—
S2	0.1086	0.1103	0.1086	0.1118	0.1082	0.1086	—
S3	0.0963	0.1026	0.0993	0.1037	0.1016	0.0971	—
S4	0.1066	0.1106	0.1020	0.1078	0.0998	0.1063	—
S5	0.1270	0.1187	0.1206	0.1200	0.1176	0.1225	—
S6	0.1107	0.1109	0.1197	0.1159	0.1153	0.1110	—
S7	0.1086	0.1103	0.1241	0.1118	0.1205	0.1179	—
S8	0.1004	0.1064	0.1020	0.1057	0.1035	0.1017	—
S9	0.1045	0.1084	0.1064	0.0992	0.1054	0.1054	—
Weighted normalized matrix							
S1	0.01872	0.01108	0.02136	0.01128	0.01745	0.04707	<b>0.12697</b>
S2	0.01481	0.01003	0.01975	0.01017	0.01476	0.03951	0.10902
S3	0.01313	0.00932	0.01805	0.00943	0.01386	0.03530	0.09910
S4	0.01453	0.01005	0.01854	0.00980	0.01360	0.03867	0.10519
S5	0.01732	0.01079	0.02192	0.01091	0.01604	0.04455	0.12154
S6	0.01509	0.01009	0.02176	0.01054	0.01572	0.04035	0.11354
S7	0.01481	0.01003	0.02257	0.01017	0.01643	0.04287	0.11687
S8	0.01369	0.00967	0.01854	0.00961	0.01412	0.03699	0.10262
S9	0.01425	0.00985	0.01934	0.00902	0.01437	0.03833	0.10517

condensation of the proteins and polyphenols.<sup>[4]</sup> As can be seen from the table S6 sample had the highest sensory scores in terms of the color, taste and odor, consistency, bitter flavor, and general acceptability scores. However, when considering mouthfeeling score, it was seen that S4 sample was better than S6 sample.

In order to ease determination of which sample is better based on sensory properties, multi criteria decision techniques might be used since there are many factors affecting decision. In the present study, the SAW technique was performed for this aim. Table 4 also shows the normalized and weighted normalized matrix of the results. According to the result of the SAW technique, it was seen that the S6 sample had the highest score. The rank of the samples was determined as S6, S2, S5, S4, S3, S1, S9, S7, and S8, respectively (Table 4). The differences between the SAW scores of the samples might be resulted from the butter content of the cocoa since it plays an important role for soft texture, plasticity, viscosity, easy diffusion of taste and flavor, gloss, and unusual melting characteristics of the chocolate.<sup>[24]</sup> The characteristics of the cocoa butter depend on the proportions of the fatty acids associated with the growing conditions,<sup>[26]</sup> type and position of fatty acids on the glycerol molecule.<sup>[27]</sup> The weighting factor of the criteria is very important factor affecting the

scores obtained from the SAW technique. We have encountered only two studies about application of the multi-criteria decision technique in the food industry. In that study, different multi-criteria decision techniques AHP, TOPSIS, ELECTRE, and SAW were satisfactorily performed to determine optimum aroma of the prebiotic pudding samples.<sup>[7]</sup> In the other study, persimmon concentration added to ice cream was determined using TOPSIS model with respect to sensory and functional properties of the samples.<sup>[28]</sup> Mixture design was also performed to determine effects of the cocoa concentration on the sensory properties of the samples. The significant factors and  $R^2$  values of the established models are also shown in Table 3. The  $R^2$  values of the models established for the taste and odor, bitter flavor, mouthfeel, and general acceptability were determined as the 0.7685, 0.7553, 0.7626, and 0.9025, respectively. As can be understood from the  $R^2$  values, it was seen that the sensory parameters of the hot chocolate beverage sample might be determined as a function of cocoa concentrations to be used in the formulation. All the linear terms significantly affected those parameters and  $X_1$  type cocoa had the highest effect, which can be understood from the constants of this factor which was the highest value. However the other two parameters, consistency and color, were not satisfactorily predicted based on cocoa concentration since their  $R^2$  values were lower than 0.75. As known desirability function is used to optimize several responses simultaneously. When considering all of the sensory parameters and maximizing them it was seen that the use of the only  $X_1$  cocoa type in the formulation of the hot chocolate beverage maximize all of the sensory scores (desirability function was equal to 0.906). As mentioned above the aim of the present study was to combine SAW technique and mixture design in order to determine optimum cocoa composition to be used in the formulation of the hot chocolate beverage sample. Mixture design was applied to SAW scores for this aim. As can be seen from Table 3, established models for the SAW scores might be used for prediction purpose since  $R^2$  value of this model was 0.8649. All of the linear terms significantly affected the SAW score of the samples. The ternary contour plots of the variation of the sensory parameters and SAW score are presented in Figs. 3 and 4. The  $R^2$  value of the established model showed that the SAW technique and mixture design might be satisfactorily combined to determine optimum cocoa combination to be used in the formula. The highest score of the sample indicates that this sample was mostly preferred based on sensory parameters. The optimum cocoa formulations obtained from mixture design results were found as cocoa combinations which are (1): 100%  $X_1$ , (2): 96.5%  $X_1$  and 3.5%  $X_3$ , and (3): 92.1%  $X_1$  and 7.9%  $X_3$ . The optimum combination obtained from using desirability function and from combination of SAW and mixture design was equal, indicating that this combination might have satisfactorily used in the food industry to optimize ingredients based on the sensory analyses.

### Rheological Properties of the Hot Chocolate Beverages

The variation of the shear stress values as a function of shear rate is shown in Fig. 5. As can be understood from this figure, the apparent viscosity of the hot chocolate beverage samples including different cocoa combinations decreased with increase in shear rate, indicating that the samples showed shear thinning behavior. The shear thinning behavior of the samples might have explained by several reasons. One of them is the hydrodynamic forces generated during shear break structural units in solutions.<sup>[29]</sup> In addition, disruption of polysaccharide entanglements and the orientation of the biopolymer strands during shearing might be also another reason resulting in shear thinning behavior. Shear thinning behavior of the hot chocolate beverages was also reported in several studies.<sup>[1,11,30,31]</sup> Obtained data of the shear stress ( $\sigma$ ) and shear rate for the hot chocolate beverages were well fitted to the Ostwald de Waele model with  $R^2$  value ranged between 0.818 and 0.999 as shown in Table 5. Table 5 also presents the parameters of the Ostwald de Waele model (consistency coefficient ( $K$ ) and flow behavior index ( $n$ ) values) and  $\eta_{50}$ , considered as shear rate in the mouth,<sup>[32]</sup> values of the hot chocolate beverage samples. As can be seen from Table 5,  $K$  and  $\eta_{50}$  values of the samples changed between 0.0457–0.1025 Pa s<sup>n</sup> and 0.0112–0.0176 Pa.s, respectively. Dogan et al.

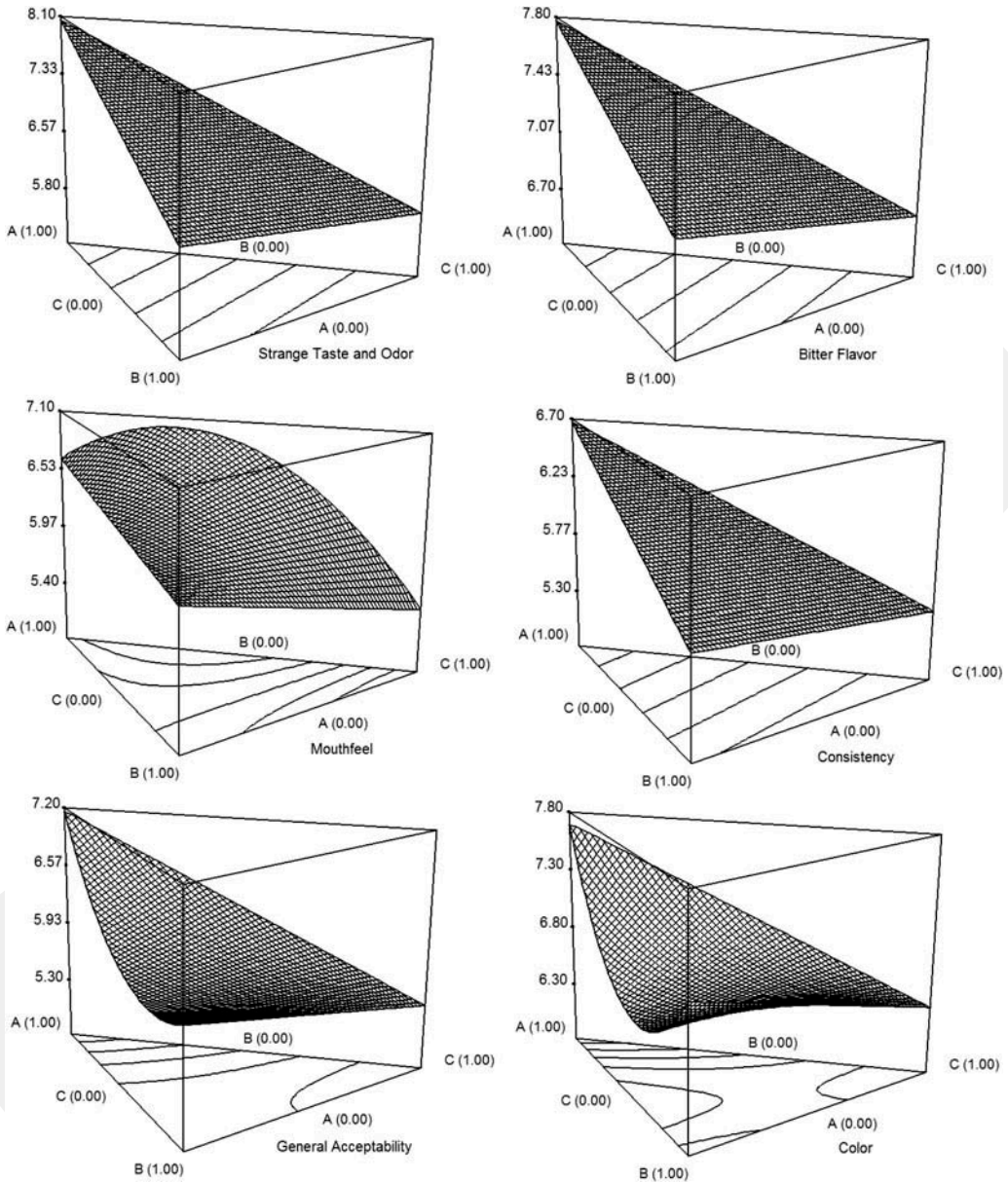


FIGURE 3 Ternary contour plots of the effects of the cocoa combinations on the sensory properties of the hot chocolate beverage (A: cocoa 1, B: cocoa 2, C: cocoa 3).

reported that  $K$  values of the hot chocolate beverage including different gum combinations changed between 0.81 and 32.97 Pa sn,<sup>[11]</sup> which are very high when compared with the  $K$  values of the hot chocolate beverage found in the present study. The reason is gum concentration used in the formula of the product. In the previous study, in order to determine effects of the gum on the rheological parameters of the hot chocolate beverage, the amount of the gum in the formulations were two times that of the present study. Different results were also observed in the studies,<sup>[12,31]</sup> which might have

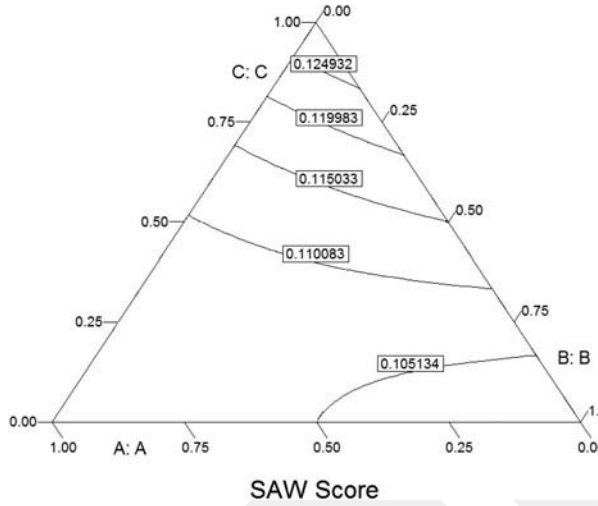


FIGURE 4 Ternary contour plots of the effects of the cocoa combinations on the SAW score of the hot chocolate beverage (A: cocoa 1, B: cocoa 2, C: cocoa 3).

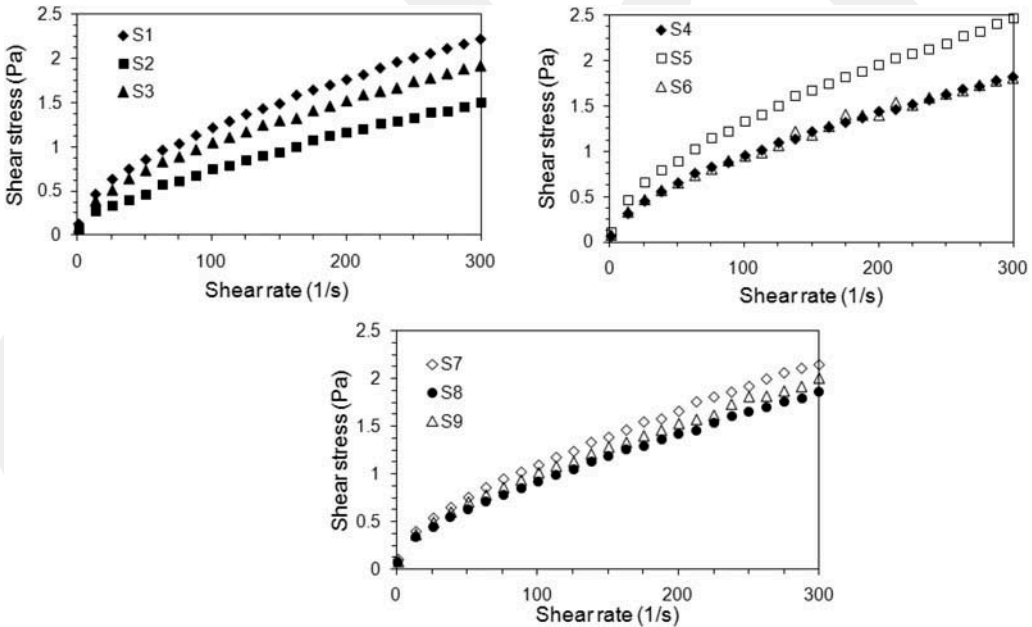


FIGURE 5 Flow curves of the hot chocolate beverages including different cocoa combinations.

resulted from several factors including analyzing conditions (temperature) and formulation of the beverages especially type and amount of the gum in the formulation since gum type and concentration significantly affected the rheological properties of the beverage.<sup>[1,11]</sup> Flow behavior index value of the hot chocolate beverages varied between 0.5373 and 0.6481 as seen from Table 5, also indicating that shear thinning and non-Newtonian behavior of the hot chocolate beverages. The positive correlation between  $K$  and  $\eta_{50}$  ( $R = 0.926$ ) and negative correlation between  $K$  and  $n$  value ( $R$

TABLE 5  
Ostwald de Waele parameters and  $\eta_{50}$  values of the hot chocolate samples including different cocoa combination

Samples	Ostwald de Waele parameters			$\eta_{50}$ (Pa s)
	K (Pa s <sup>n</sup> )	n	R <sup>2</sup>	
S1	0.1025 ± 0.0072 <sup>b</sup>	0.5373 ± 0.0154 <sup>e</sup>	0.999	0.0167 ± 0.0005 <sup>a</sup>
S2	0.0457 ± 0.0007 <sup>f</sup>	0.6481 ± 0.0380 <sup>a</sup>	0.999	0.0112 ± 0.0015 <sup>f</sup>
S3	0.0872 ± 0.0095 <sup>b</sup>	0.5408 ± 0.0251 <sup>de</sup>	0.998	0.0145 ± 0.0013 <sup>c</sup>
S4	0.0879 ± 0.0045 <sup>b</sup>	0.5602 ± 0.0328 <sup>de</sup>	0.919	0.0150 ± 0.0006 <sup>bc</sup>
S5	0.1035 ± 0.0011 <sup>a</sup>	0.5546 ± 0.0093 <sup>de</sup>	0.999	0.0176 ± 0.0014 <sup>a</sup>
S6	0.0682 ± 0.0083 <sup>cd</sup>	0.5757 ± 0.0223 <sup>cd</sup>	0.991	0.0128 ± 0.0003 <sup>e</sup>
S7	0.0713 ± 0.0047 <sup>c</sup>	0.5982 ± 0.0290 <sup>bc</sup>	0.998	0.0148 ± 0.0015 <sup>bc</sup>
S8	0.0560 ± 0.0033 <sup>e</sup>	0.6122 ± 0.0279 <sup>b</sup>	0.999	0.0123 ± 0.0009 <sup>e</sup>
S9	0.0661 ± 0.0021 <sup>d</sup>	0.5957 ± 0.0234 <sup>bc</sup>	0.818	0.0139 ± 0.0008 <sup>d</sup>

\*Different superscript lowercase letters show differences between the samples ( $\alpha = 0.05$ ).

= -0.851) were observed in the present study. The similar relationship between  $K$  and  $\eta_{50}$  values was reported in previous studies.<sup>[17,33,34]</sup> As can be seen from Table 5, the cocoa type significantly affected the rheological parameters of the hot chocolate beverages, which might have resulted from the chemical composition of the cocoa ingredients. It is known that fat plays an important role in appearance, texture, and mouthfeel of the products.<sup>[35,36]</sup> Fat found in the formulation also affects the interactions among the ingredients, resulting in the variation in color, flavor, and texture of the product.<sup>[37]</sup> In addition moisture content and particle size of the cocoa also another factors affecting rheological properties of the beverage. After determination of the rheological parameters of the hot chocolate beverages including different cocoa combinations, mixture design was also performed to determine change in the parameters based on cocoa concentration to be used in the formulation of the beverage. Table 3 also shows the established models of the rheological parameters and their  $R^2$  values. As can be seen from Table 3, magnitude of the  $n$  cannot be predicted based on cocoa concentration since  $R^2$  value was found as 0.6175 lower than 0.75. The  $R^2$  values of established models of  $K$  and  $\eta_{50}$  parameters were 0.8204 and 0.8355, respectively, indicating that these models describe the variation of the  $K$  and  $\eta_{50}$  values as a function of cocoa concentration. All the linear terms were found as significant as seen from Table 3. The most effective cocoa was found as cocoa 1 for both of two parameters, which was understood from the constants of the terms and from the ternary contour plots as shown in Fig. 6. One unit increase in cocoa 1, 2, and 3 concentration resulted in 0.10, 0.046, and 0.082 unit increase in  $K$  value. According to the results of the mixture design, the sample including only cocoa 1 in the formula had the highest  $K$  and  $\eta_{50}$  value with the desirability function value of 0.957 and 0.954, respectively.

## CONCLUSIONS

The improvement of the sensory properties of the product is very important for increasing desirability of the product. Optimization of the ingredients of the hot chocolate beverage in terms of sensory properties is important for this aim. The cocoa type found in the formulation is one of the most important factors affecting physicochemical, sensory, and rheological properties of the beverage. In order to ease interpretation of the sensory results, SAW technique was performed since the sensory characteristics of the product are composed of different criteria involving appearance,

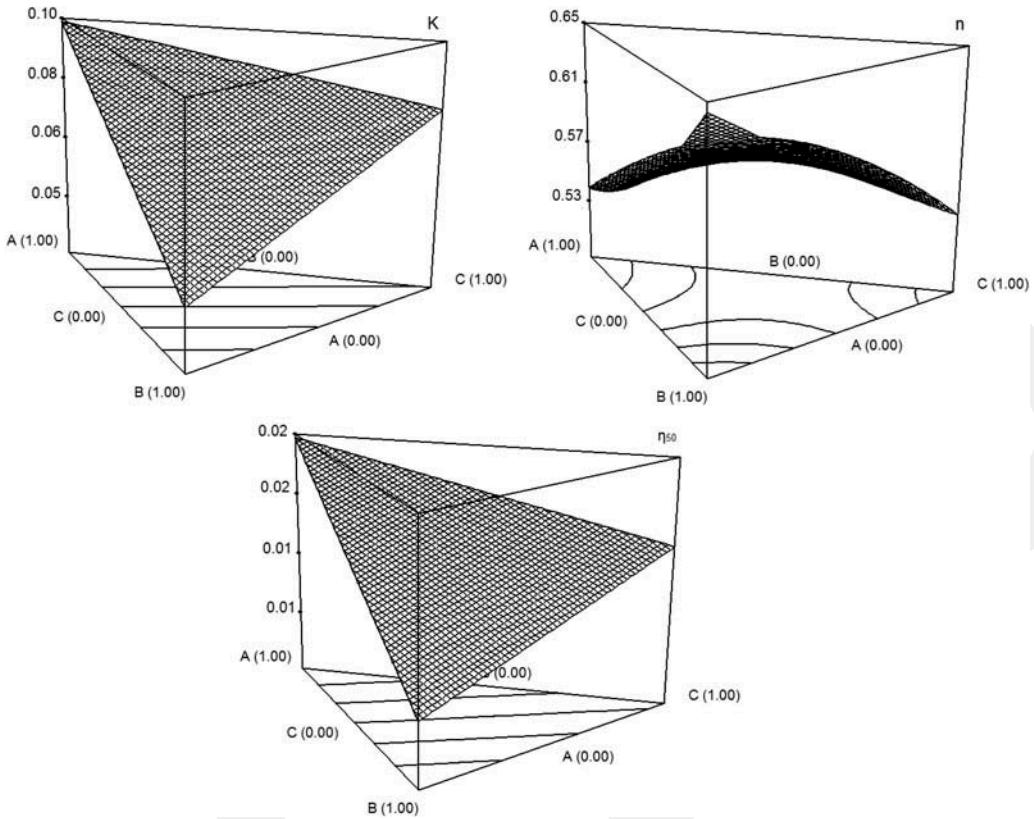


FIGURE 6 Ternary contour plots of the effects of the cocoa combinations on the rheological parameters of the hot chocolate beverage (A: cocoa 1, B: cocoa 2, C: cocoa 3,  $K$ : Consistency coefficient,  $n$ : Flow behavior index,  $\eta_{50}$ : apparent viscosity at shear rate  $50 \text{ s}^{-1}$ ).

color, taste, odor, overall preference. Instead of optimization of the sensory parameters simultaneously, SAW score of the hot chocolate beverage samples was satisfactorily optimized using mixture design approach. According to the results of the present study, it was concluded that the combination of mixture design and SAW technique might be performed in the food industry for optimization purposes especially research and development areas.

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