Effects of Process Conditions on Citrus Beverage Emulsions' Creaming Index: RSM Approach

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***Abstract*—Beverage emulsions are oil-in-water (O/W) emulsions prepared in concentrated form. emulsion stability is of great importance in various industrial processes. Creaming index is a key parameter to investigate stability of beverage emulsions. In this study, the stability properties of beverage emulsions obtained by using different citrus peel oils (lemon, orange, mandarin) ratios, gum Arabic levels, homogenization pressures were determined by examining the response surface method (RSM) approach and creaming index values. For each citrus beverage emulsions, optimum creaming index values (1.35-2.82). For mandarin emulsions, the optimum mandarin peel oil level, gum Arabic level and homogenization pressures for creaming index were estimated as 15.65 g, 16.34 g and 242.43 bar, respectively. These values were determined as 15.65 g, 16.84 g and 166.84 bar for lemon emulsions. For orange emulsions, the optimum gum Arabic level and homogenization pressures for creaming index were estimated as 15.31 g and 253.13 bar, respectively. This study shows that more stable beverage emulsions can be obtained by optimization of homogenization pressure, aromatic oil and emulsifier levels.**

***Index Terms*—beverage; citrus oil; emulsion; RSM**

I. Introduction

Emulsions are heterogeneous systems in which at least two liquids that do not mix with each other are dispersed in droplets. Flavor emulsions are lipophilic compounds (such as lemon, mandarin, lime or orange oils) that primarily have the functions of providing flavor and aroma to the beverages. Clouding emulsions are used in certain beverages to regulate visual properties. These emulsions are prepared using a highly water-insoluble oil phase which is also resistant to chemical degradation,

The constituents of the droplet composition show differences in properties (molecular weight, molecular conformation and functional group) which cause the physicochemical properties (such as polarity, water solubility, density, viscosity, refractive index, melting point) to vary. These molecular and physicochemical properties have a major impact on the formation, stability and functionality of emulsions [1].

In general, the droplet concentration in the emulsion affects the texture, stability, appearance, sensory properties and nutritional quality of the emulsion [2]. Control of droplet concentration in beverage emulsions is of importance for several reasons. Beverage emulsions are often prepared in concentrated form (>10% aromatic oil) because they facilitate production and transport. However, they are present at low levels with high dilution in the final product (<0.1% aromatic oil). The concentration of the emulsion affects the appearance of the final product. Because the emulsion turbidity and/or cloudiness increases with the oil droplet concentration. In addition, dilution also affects the total amount of aroma molecules in the final product and the distribution between the oil and water phases [3].

Beverage emulsions are generally prepared by a two-step process; (i) preparing the beverage emulsion concentrate (3-30% oil, w/w), (ii) diluting the final product (<0.1%, oil). When the beverage emulsion concentrate is prepared using high energy homogenization techniques (such as high pressure valve homogenizers, microfluidizers, ultrasonic homogenizers), all of the components primarily forming water and oil phase are mixed with each other separately.

Beverage emulsions are oil-in-water (O / W) emulsions [5] prepared in concentrated form diluted in hundreds of fold sugar/acid solution before consumption, consumed as carbonated and non-carbonated beverages. The physical stability and rheological properties of beverage emulsions have been investigated in various studies [6]-[12] Emulsion-based products are key parameters because they are related to turbidity, particle size, polydispersity index (PDI) and density, physical stability, rheological properties of end products and also creaming index [11]. As is the case in some beverage types, the

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quality characteristics expected in emulsion-based products are strongly influenced by their stability rheology and appearance. In addition, emulsion stability is of great importance in various industrial processes. Oil globules have a large effect on the particle size and distribution of this size, the stability of the emulsion and the products obtained by using this emulsion [13].

Orange, lemon, mandarin peel oils are aroma agents commonly used in the food and beverage industry [14], because they carry volatile compounds that form characteristic aroma profiles. The composition of these oils depends on their biological origins, the extraction processes used for their isolation, and the processes that they later (if any) perform. Differences in the chemical composition of aromatic oils can cause differences in their ability to form beverage emulsions and their physicochemical properties (such as water solubility, viscosity, refractive indices and optical properties) that affect their stability [15].

In this study, the stability properties of beverage emulsions obtained by using different citrus peel oils (lemon, orange, mandarin) ratios, gum arabic levels, homogenization pressures were determined by examining the response surface method (RSM) approach and creaming index values.

II. Materials and Methods

A. Materials

Citrus (mandarin, lemon and orange) peel oils, gum Arabic, clouding agent (resin gum), antioxidant (Origanox®), coloring agent (β-carotene) citric acid and sodium benzoate were provided by Etol-Frutarom (Gebze, Kocaeli, Turkey).

B. Preparation of Citrus Beverage Emulsion

Citrus beverage emulsions were prepared by using the method as described in Fig.1. Compositions of sample were given in Table I

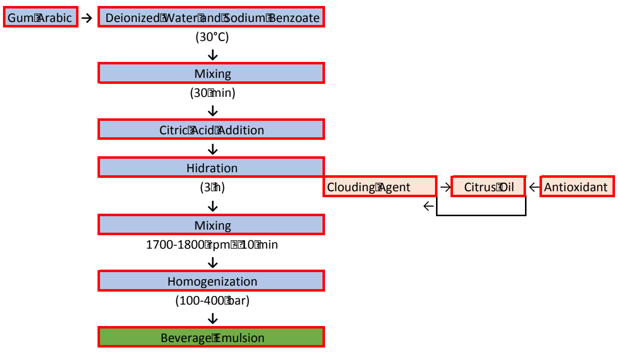

Figure 1. Preparation of citrus beverage emulsions

C. Creaimg Index

The physical stability of beverage emulsions was investigated by determining the size of the gravitational phase separation [16]. The creaming index values were determined by examining the ratio of the volume of the cream and sediment to the volume of the total emulsion sample. A 10 mL emulsion sample was taken in a 15 mL test tube and monitored for 2 months at 25 ± 3 ℃. The emulsions will be visually monitored and the stability index calculated using the following equation.

ES (%)= (SEY/BEY) x 100

SEY = BEY – (KTY + SFY)

ES: Emulsion stability as creaming index, SEY: Last emulsion height, BEY: Initial emulsion height, KTY: Cream layer height, SFY: Sedimentation phase height

TABLE I. Compositions of Citrus Beverage Emulsions

Ingredient	(g/100g)
Citrus oil[a]	10, 15 and 20
Gum Arabic	10, 15 ve 20
Deionized water	40-60[b]
Clouding agent	19,3
Antioxidant	0.10
Coloring agent (β-carotene)	0.10
Citric acid	0.40
Sodium benzoate	0.10

[a]as mandarin, orange or lemon peel oil, [b]formulations were completed to 100 g by using deoinized water

D. Experimental Desing and Statistical Analysis

Mixture design experiments were designed and analysed using Design Expert (v. 7.6.1, Stat-Ease Inc., Minneapolis, MN, USA). The effect of ingredient proportions on creaming index of beverage emulsions were studied using D-optimal design for the 3-component mixture systems with constraints, which comprised citrus oil (X_1), gum arabic content (X_2) and homogenization pressure (X_3). A total of 16 experimental sample preparation for each citrus oil type were performed within this study (Table I), each representing a different process conditions to prepare beverage emulsion, each corresponding to a vertex, edge or surface point of the design surface. In order to create a robust model, extremes/maxima were replicated. Creaming index were assessed. After data collection linear, quadratic or Scheffe's special cubic models (depending on the degree of fit, predictive power and robustness of the model) for three components were used to model the responses:

TABLE II. Central Composite Design of Experiments

Run		Citrus oil	Gum arabic	Homogenization pressure (bar)
1	+++	20	20	400
2	−+−	10	20	100
3	000	15	15	250
4	00a	15	15	100
5	0A0	15	20	250
6	+−−	20	10	100
7	−−−	10	10	100
8	A00	20	15	250
9	000	15	15	250
10	+−+	20	10	400
11	a00	10	15	250
12	0a0	15	10	250
13	00A	15	15	400

14	−−+	10	10	400
15	−++	10	20	400
16	++−	20	20	100

The actual values of the levels of aromatic oil (10.0-20.0%), gum arabic (10.0-20.0%) and homogenization pressures (100-400 bar) are indicated in the experimental points created by the central composite design..

III. Results and Discussion

The equation for the polynomial model describing the effect of orange aromatic oil level, gum arabic level and homogenization pressure on the creaming index of the emulsions as a result of the response surface analysis according to the experiment based on the experimental two central composite design was found as follows. The variance analysis results of the effects of the factors on the intensity of the emulsion beverages are given in Table III.

TABLE III. Variance Analysis Results of Effects of Orange Emulsions Creaming Index Values

Source	DF	SS	F	p value	R^2
Model	9	28,76	0,59	0,77	0,47
X_1 citrus peel oil	1	0,73	1,00	0,35	
X_2 gum Arabic level	1	0,16	0,22	0,83	
X_3 Homogenization pressure	1	0,06	0,09	0,93	
$X_1 * X_2$	1	0,13	0,17	0,87	
$X_1 * X_3$	1	0,02	0,03	0,97	
$X_2 * X_3$	1	0,05	0,06	0,95	
$X_1 * X_1$	1	2,26	1,58	0,16	
$X_2 * X_2$	1	1,49	1,04	0,33	
$X_3 * X_3$	1	1,78	1,43	0,25	
Lack of fit	5	32,42	212,74		
Pure Error	6	32,45			
Total	15	61,22	0,77		

***p <0.01 **p<0.05 * p<0.1 S.S: Sum of squares

As shown in Table III, the reliability of the equation for the orange emulsion samples was found to be 0.47 (R^2) according to the ANOVA test. The multiple coefficient of determination accounts for 56% of the variance of the orange aromatic oil level, gum arabic level and homogenization pressure. Mathematical models that define the independent variables are obtained. The polynomial equation for the creaming index (Y) is as follows.

$$Y_{Kİ} = 2{,}882 - 0{,}733X_1 - 0{,}163X_2 + 0{,}066X_3 + 0{,}137X_1X_2 + 0{,}028X_1X_3 + 0{,}050X_2X_3 + 2{,}263X_1X_1 - 1{,}490X_2X_2 - 1{,}787X_3X_3$$

The quadratic effect of the level of orange peel oil was found to be significant and the increase in this effect was found to be linearly increased in creaming index. The linear effect of the level of aromatic oil was effected in the negative direction and caused the crema index to decrease. Gum arabic quadratic effect was found to be significant and it was determined that creaming index decreased with increasing of this effect. The quadratic effect of the homogenization pressure was found to be significant and it was determined that the creaming index decreased with increasing this effect (Fig. 2).

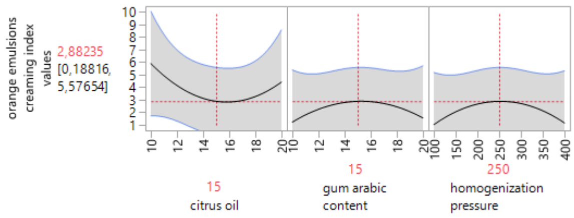

Figure 2. Optimum conditions for orange emulsion

For orange emulsions, the optimum gum arabic level and homogenization pressures for creaming index were estimated as 15.31 g and 253.13 bar, respectively. The estimated creaming index is 2.82 (Fig. 3, 4, and 5).

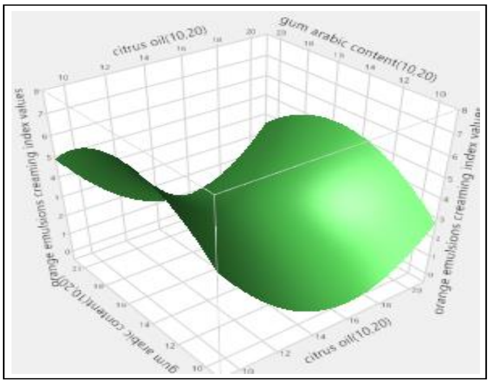

Figure 3. Orange peel oil level x gum Arabic level interactions on creaming index of orange emulsions

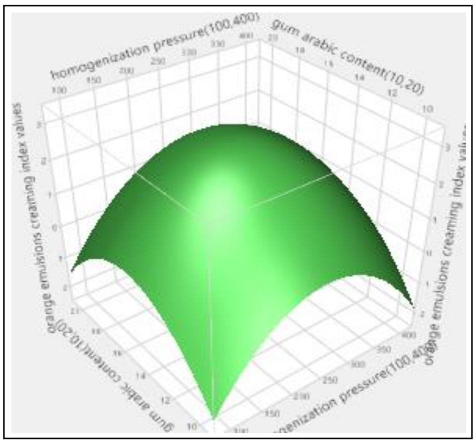

Figure 4. Homogenization pressure x gum Arabic level interactions on creaming index of orange emulsions

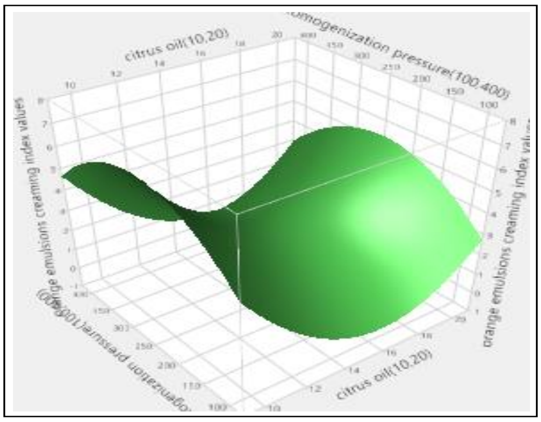

Figure 5. Homogenization pressure x orange peel oil level interactions on creaming index of orange emulsions

The equilibrium of the polynomial model describing the effect of the lemon peel oil level, the gum arabic level and the homogenization pressure on the creaming index of the emulsions as a result of the response surface analysis made according to the two-central composite design was found as follows. The variance analysis results of the effects of the factors on the density of the emulsion beverages are given in Table IV.

TABLE IV. VARIANCE ANALYSIS RESULTS OF EFFECTS OF LEMON EMULSIONS CREAMING INDEX VALUES

3	DF	SS	F	p value	R^2
Model	9	4,38	3,50	0,07	0,84
X_1 citrus peel oil	1	0,33	2,43	0,16	
X_2 gum Arabic level	1	0,47	0,41	0,11	
X_3 Homogenization pressure	1	0,54	3,93	0,09	
$X_1 * X_2$	1	1,53	11,07	0,01**	
$X_1 * X_3$	1	076	5,52	0,05	
$X_2 * X_3$	1	0,48	3,51	0,10	
$X_1 * X_1$	1	0,14	1,07	0,34	
$X_2 * X_2$	1	0,07	0,55	0,48	
$X_3 * X_3$	1	0,00	0,02	0,87	
Lack of fit	5	0,81	8,16		
Pure Error	6	0,83			
Total	15	5,22	0,07		

***p <0.01 **p<0.05 * p<0.1   S.S: Sum of squares

As can be seen from Table IV, the reliability of the equation for lemon emulsion samples was found to be 0.84 (R^2) according to the ANOVA test. The multiple coefficient of determination accounts for 84% of the variance of the lemon oil level, gum Arabic level and homogenization pressure. Mathematical models describing the independent variables are obtained. The polynomial equation for the creaming index (Y) is as follows.

$$Y_{Kİ} = 1{,}738 - 0{,}183X_1 + 0{,}218X_2 - 0{,}233X_3 - 0{,}438X_1X_2 + 0{,}309X_1X_3 - 0{,}247X_2X_3 + 0{,}287X_1X_1 - 0{,}149X_2X_2 - 0{,}039X_3X_3$$

The interaction effect between the lemon peel oil level and the gum Arabic level was statistically significant. This interaction effect is positive and has been found to increase the creaming index. However, the interaction effect between the lemon peel oil level and the homogenization pressure was found to be negatively affected and the creaming index to be decreased. The quadratic effect of the level of lemon peel oil was found to be significant and the increase in this effect was found to be linearly increased in creaming index. The linear effect of the level of lemon peel oil was effective in the positive direction and caused the crema index to increase (Fig. 6).

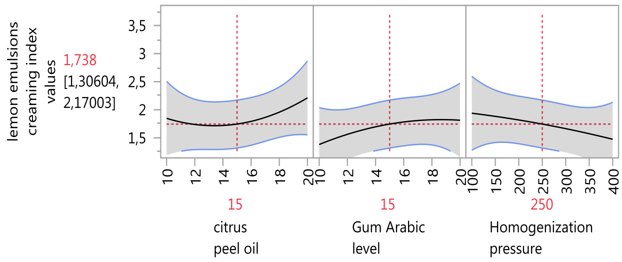

Figure 6. Optimum conditions for lemon emulsion

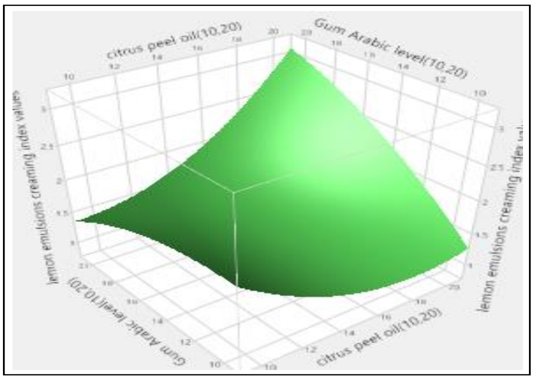

Figure 7. Lemon peel oil level x gum Arabic level interactions on creaming index of lemon emulsions

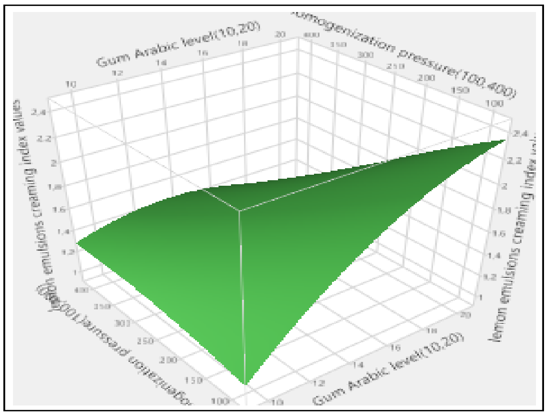

Figure 8. Homogenization pressure x gum Arabic level interactions on creaming index of lemon emulsions

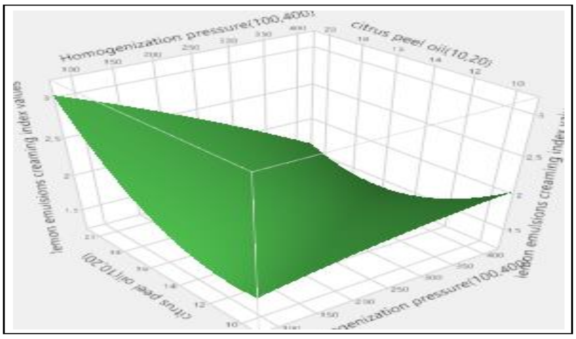

Figure 9. Homogenization pressure x lemon peel oil level interactions on creaming index of lemon emulsions

For lemon emulsions, the optimum lemon peel oil level, gum Arabic level and homogenization pressures for creaming index were estimated as 15.65 g, 16.84 g and 166.84 bar, respectively. The estimated cremation index is 1.75 (Fig. 7, 8 and 9).

In the present study, the equilibrium of the polynomial model describing the effect of mandarin peel oil level, gum Arabic level and homogenization pressure on the creaming index of emulsions as a result of response surface analysis based on the experimental 2-centered central mixed design was found as follows (Table V).

TABLE V. VARIANCE ANALYSIS RESULTS OF EFFECTS OF MANDARIN EMULSIONS CREAMING INDEX VALUES

Source	DF	SS	F	p value	R^2
Model	9	0,03	2,22	0,17	0,77
X_1 citrus peel oil	1	0,00	0,60	0,57	
X_2 gum Arabic level	1	0,01	0,95	0,37	
X_3Homogenization pressure	1	0,01	1,07	0,32	
$X_1 * X_2$	1	0,01	0,86	0,42	
$X_1 * X_3$	1	0,05	3,51	0,01**	
$X_2 * X_3$	1	0,02	1,56	0,16	
$X_1 * X_1$	1	0,02	1,15	0,29	
$X_2 * X_2$	1	0,02	0,94	0,38	
$X_3 * X_3$	1	0,01	0,64	0,54	
Lack of fit	5	0,00	0,15		
Pure Error	6	0,01			
Total	15	0,04	0,17		

***p <0.01 **p<0.05 * p<0.1 S.S: Sum of squares

As shown in Table V, the reliability of the equation for tangerine emulsion samples was determined to be 0.77 (R^2) according to the ANOVA test. The multiple coefficient of determination accounts for 77% of the variance of orange aromatic oil level, gum arabic level and homogenization pressure. Mathematical models describing the independent variables are obtained. The polynomial equation for the creaming index (Y) was as follows.

$$Y_{Ki} = 1{,}351-0{,}007X_1 +0{,}012X_2 -0{,}014X_3 -0{,}012X_1X_2 +0{,}0521X_1X_3 +0{,}0232X_2X_3 +0{,}0297X_1X_1 -0{,}024X_2X_2 - 0{,}016X_3X_3$$

The interaction effect between the mandarin peel oil level and the homogenization pressure was statistically significant. This interaction effect is positive and has been found to increase the creaming index. The interaction effect of the homogenization pressure with gum arabic level was found to be positive in the positive direction and cause the creaming index to increase. The quadratic effect of the level of mandarin peel oil was found to be significant and the increase in this effect was found to be linearly increased in creaming index. The linear effect of the homogenization pressure was determined to be negative and to reduce the creaming index. The linear effect of the level of mandarin peel oil was effected in the negative direction and caused the creaming index to decrease (Fig. 10).

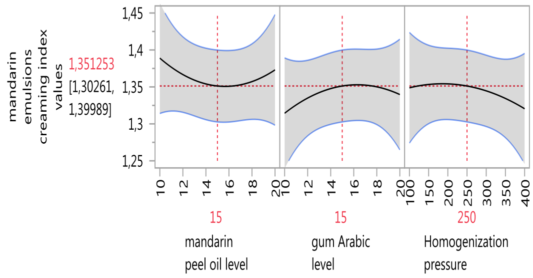

Figure 10. Optimum conditions for mandarin emulsion

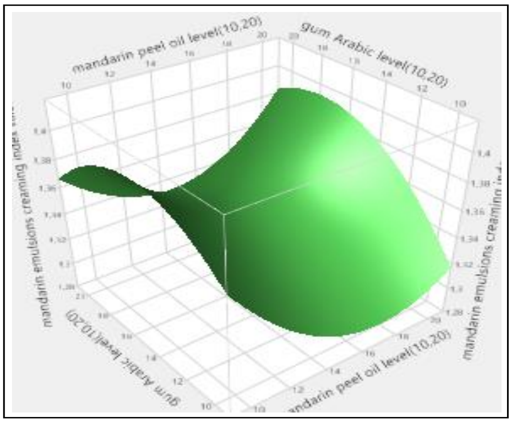

Figure 11. Mandarin peel oil level x gum Arabic level interactions on creaming index of mandarin emulsions

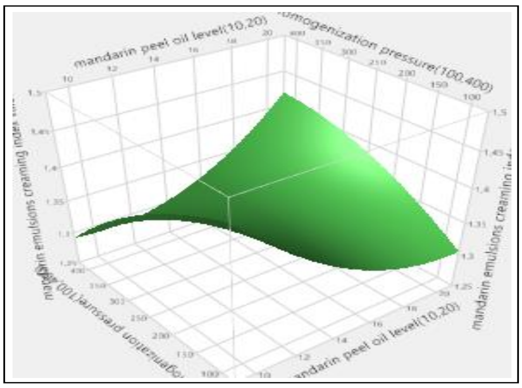

Figure 12. Homogenization pressure x mandarin peel oil level interactions on creaming index of mandarin emulsions

For mandarin emulsions, the optimum lemon peel oil level, gum Arabic level and homogenization pressures for creaming index were estimated as 15.65 g, 16.34 g and 242.43 bar, respectively. The estimated cremation index is 1.35 (Fig. 11, 12 and 13).

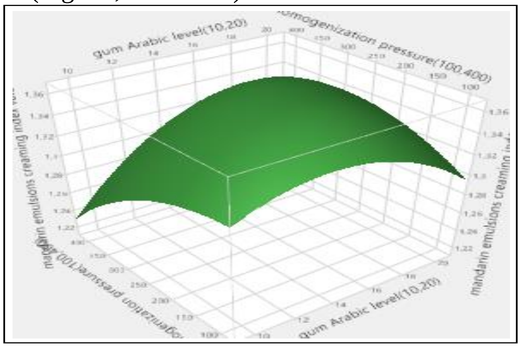

Figure 13. Homogenization pressure x gum Arabic level interactions on creaming index of mandarin emulsions

IV. Conclusion

Physical stability is of great importance in beverage emulsions. It may be possible to improve the quality level by specifying the parameters and components that are effective on these stability characteristics. The results obtained from this study show that process conditions have to be changed in beverage emulsions depending on the emulsifier and homogenization pressure as well as the origin of aromatic oil. With further studies, it is important to examine some parameters other than creaminess index. These studies may address process conditions and parameters as well as other quality parameters. Especially working with model beverages including emulsion prepared under various conditions may be helpful to investigate emulsions characteristics and to optimization of composition.

Acknowledgment

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