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Ice cream properties affected by lambda-carrageenan or iota-carrageenan interactions with locust bean gum/carboxymethylcellulose mixtures

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Abstract

The effect of the interaction of iota-carrageenan (ICG) or lambda-carrageenan (LCG) with locust bean gum and carboxymethylcellulose on the properties of ice cream was studied employing a mixture design approach. A model formulation was employed with of 5% (w / w) of hydrocolloids like stabilizers. Hydrocolloids mixture effect on ice cream properties (base viscosity, ice-cream overrun, hardness, first drop and melting rate) was determined. The mixtures with LCG presented higher viscosity values than ICG at the same proportion. However, mixtures with higher ICG proportion resulted in a softer texture enhancing melting properties (longer first drop time and lower melting rate). The interaction between ICG with locust bean gum and carboxymethylcellulose modified the formation of ice crystals during ice cream manufacture, improving the texture and characteristics of melting of the formulated ice cream.

Introduction

Ice cream are complex systems consisting of air cells, ice crystals, fat globules partially coalesced or aggregated, surrounded by a sugar, protein, salts and water matrix. Each one of the ingredients in formulation influence ice cream properties (Goff, 2002; Clarke, 2004; Robijn, 2006; Rincón *et al*., 2008; Soukoulis *et al*., 2008; William and Harpell, 2010). Hydrocolloids in ice cream are important due their effect on ice crystals structure formation and their stability during freezing and shelf life, characteristics reflected on ice cream texture. Hydrocolloids enhance emulsion stability binding free water (Hagiwara and Hartel, 1996; Akesowan, 2008; Hernández *et al*., 2011), increase viscosity and overrun improving air incorporation (Hagiwara and Hartel, 1996; Akesowan, 2008; Hernández *et al*., 2011).

Carrageenans are the most employed hydrocolloid in milk industry due to their specific interaction with milk proteins (Piculell, 1995). The strength of the interactions between the different types of carrageenan (lambda, kappa and iota) and milk proteins depends on carrageenan negative charge due to the number of sulphate groups, and environmental conditions (Imeson, 2000; Ye, 2008). Nonetheless, at same environmental conditions the carrageenan type affects system functionality (Langerdorff *et al*., 1999, 2000). Combination of 2 or 3 hydrocolloids as stabilizers (in concentrations of 0.2-0.5%) are applied in ice cream production to create a positive effect on the viscosity of the ice cream base, in order to overcome ice crystals formation during processing and storage and preserve the structure by slowing down melting at the consumption stage (Crichett and Flack 1977; Clarke, 2004). Main hydrocolloids employed in ice cream manufacture are mixtures of locust bean gum, kappa-carrageenan and/or carboxymethylcellulose (Wang *et al*., 1998; Flores and Goff, 1999; Akesowan, 2008; Philip and Laaman, 2011). Also locust bean gum and lambda carrageenan has been employed to decrease ice cream hardness during freezing (Camacho *et al*., 2001).

The aim of this work was to determinate the effect of iota-carrageenan or lambda-carrageenan interaction on locust bean gum-carboxymethylcellulose mixtures as ice cream stabilizers by a mixture design approach.

Materials and Methods

Ice cream manufacture

For ice cream base manufacture, a standard formulation was employed dispersing dry ingredients

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as: sugar (15.0%), non-fat dry milk and whey protein concentrate (8.0% and 4.0% respectively, provided by DILAC S.A de C.V., Cuautitlan Izcalli, Mexico), hydrocolloids mixture (0.5%), emulsifiers (sorbitan monoestereate and diglycerides (0.25%, ARCY S.A de C.V, Ecatepec, Mexico) in water (ca. 58%) at 60°C, in order to disperse butyric (10.0%, ARCY S.A de C.V, Ecatepec, Mexico) and vegetal (4.0%, La Mixteca, Ecatepec, Mexico) fats. Two different ice cream were formulated, one with Viscarin SD 389 iota-carrageenan (ICG), and the other one with Viscarin GP 209 lambda-carrageenan (KCG); both mixed Avicel carboxymethylcellulose (CMC) (FMC Biopolymers) and Viscogum locust bean gum (LBG) (Texturant Systems) to conform the hydrocolloid mixture. The ice cream bases were pasteurized at 70°C during 30 min, ice-cooled and stored at 4°C overnight. Viscosity of the base was determined after cold storage with a Brookfield RVT viscosimeter (Brookfield Laboratories, Middleboro) at 50 rpm with spin # 07 after 30 s, reporting viscosity in Centipoises.

Ice cream base was frozen in a 2 quarters Frozen Ice Cream CIM-50RSA machine (Cuisinart, East Windsor), mixing during 25 min until obtain a uniform frozen paste. Ice cream was immediately distributed in 250 mL containers and kept in frozen storage at -23°C until further analysis after at least 24 h.

Overrun was determined adapting the methodology reported by Marshall *et al*. (2003), determining the weight gained during ice cream manufacture (freezing).

Ice cream hardness was measured according to the methodology reported by Soukoulis *et al*. (2008). Ice cream samples were settle at room temperature during 10 min. Samples were penetrated 8 mm from surface with an acrylic probe at a constant speed of 1 mm/s in a Brookfield LFRA 4500 texturometer (Brookfield Engineering Lab, Meddleboro), reporting the maximum force in grams registered during the test.

Ice cream melting properties were determined removing the ice cream samples from the containers and put them on in stainless steel mesh (size 14, 1.41 mm) at room temperature (25±2°C) in order to register the time (min) elapsed for the first drop of melting ice cream. Weight of the melting ice cream was recorded each 5 min during one h to obtain the melting rate (calculated as the change of weight versus time, in g/min) (Soukoulis *et al*., 2008).

Experimental design and data analysis

A three component constrained simplex lattice mixture design was used. Components of the mixture

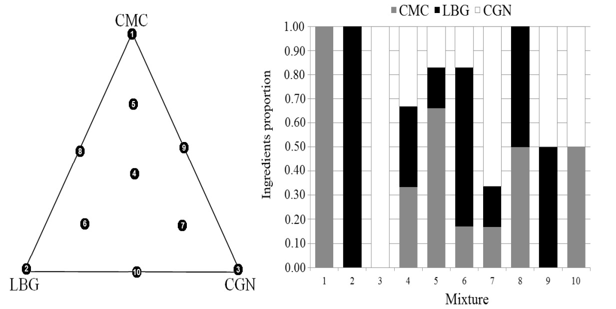

Figure 1. Simplex centroid design for three components and ingredients proportions

was carboxymethylcellulose (CMC, X_1), locust bean gum (LBG, X_2), and lambda-carrageenan (LCG, X_3) or iota-carrageenan (ICG, X_3). Components were expressed as fractions of the mixture and the sum ($X_1 + X_2 + X_3$) of the proportions was one. The ten points consisted of three single ingredients systems, three two-ingredients mixtures and four thee-ingredient mixtures (Figure 1).

Scheffe's canonical special cubic equation for 3 components was fitted to data collected at each experimental point using backward stepwise multiple regression analysis as described by Cornell (1980). Variables in the regression models, which represent two-ingredient or three-ingredient interaction terms, were referred to as "non-linear" terms. Canonical special cubic equation postulated was:

$$\eta = \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \beta_{123} x_1 x_2 x_3$$

Where η is the dependent variable (viscosity, overrun, hardness, first drop and melting rate); β_1, β_2, β_3, β_{12}, β_{13}, β_{23} and β_{123} are the corresponding parameters estimates for each linear and cross-product term produced for the prediction models for CMC (X_1), LBG (X_2), and carrageenans (X_3). Data were analyzed with SAS Statistical Software (SAS Institute, Cary).

Results and Discussions

Table 1 shows the experimental results for the ice cream base mixtures. Hydrocolloids mixtures containing LCG was had a highly significantly effect ($P<0.01$) on the ice cream base viscosity, as compared to mixtures containing ICG. In ICG mixtures, CMC and LBG had a highly significantly effect ($P<0.01$), with a significantly ($P<0.05$) effect of ICG on this parameter (Table 2). In Figure 2 can be observed that LCG proportions above 0.28 provoked a decrease in ice cream base viscosity. For ICG, the decrease in viscosity occurred at higher concentrations, where ICG proportions above 0.58 resulted in lower viscosity values. The higher viscosity values were

Table 1. Experimental results for viscosity, overrun, hardness, first drop and meting rate of ice cream formulated with CMC (carboxylmethylcellulose)/LBG (locust bean gum) and LCG (lambda carrageenan) or ICG (iota carrageenan)

Mixture	Viscosity (Cp)		Overrun (%)		Hardness (g)		First drop (min)		Melting rate (g/min)	
	LCG	ICG	LCG	ICG	LCG	ICG	LGB	ICG	LCG	ICG
1	6600	4880	1.72	1.17	3053	1064	34	30	1.058	0.08
2	6200	5720	2.67	0.64	4013	2388	20	42	1.648	0.28
3	8920	6320	5.8	0.19	1780	1770	10	10	0.528	0.48
4	5520	6000	10.9	10.8	292	271	22	27	0.407	0.37
5	8400	8040	3.7	25.9	684	916	25	50	1.09	1.74
6	7640	9520	0.65	26.7	493	857	32	50	1.407	0.04
7	7080	8080	4.6	1.09	2012	2321	17	31	0.351	0.39
8	9800	9480	11.7	1.08	701	733	37	60	0.115	1.43
9	9240	9200	9.8	6	1082	1140	30	35	0.206	0.21
10	8200	8480	4.08	5.7	2142	1382	17	20	0.173	0.39

Table 2. Regression coefficients and correlation coefficient for the ice cream base viscosity of ice cream base formulated with CMC (carboxylmethylcellulose)/LBG (locust bean gum) and LCG (lambda carrageenan) or ICG (iota carrageenan)

Mixture	Carrageenan	Linear terms			Non linear terms				R^2
		β_1	β_2	β_3	β_{12}	β_{13}	β_{23}	β_{123}	
CMC+LBG	LCG	8,333**	5,835**	6,482**	10,500	-1,260	966	19,671	0.9949
CMC+ICG	ICG	8,531**	5,726**	4,938*	7,354	5,839	669	28,930	0.9958

**Highly significantly effect (P <0.01)
*Significantly effect (P <0.05).
β_1: CMC, β_2: LBG, β_3: LCG or ICG

Table 3. Regression coefficients and correlation coefficient for the ice cream overrun and hardness of ice cream base formulated with CMC (carboxylmethylcellulose)/LBG (locust bean gum) and LCG (lambda carrageenan) or ICG (iota carrageenan)

Mixture		Linear terms			Non linear terms				R^2
		β_1	β_2	β_3	β_{12}	β_{13}	β_{23}	β_{123}	
Overrun (%)									
CMC+LBG	LCG	5.76*	10.06	1.49	11.07	9.87	-16.83	-94.10	0.8874
CMC+LBG	ICG	3.14	10.71	1.86	-14.75	-13.25	-20.00	553.6	0.6876
Hardness (g)									
CMC+LBG	LCG	2,084**	398.2*	3,041**	-465.5	-2,524	9,559	-54,047*	0.9814
CMC+LBG	ICG	1,160*	289.4	1,116*	814.2	4,042	7,038	-9,577	0.9433

**Highly significantly effect (P <0.01)
*Significantly effect (P <0.05).
β_1: CMC, β_2: LBG, β_3: LCG or ICG

observed when LCG interacted with LBG in LCG formulations. Increase in ice cream base viscosity was provoked by the different interaction between carrageenans, lambda and iota, and LBG mainly. Carrageenans area linear polysaccharides with the capacity to extend their configuration interacting with other polysaccharides, provoking a polymer volume increase that results in more water junction zones, due to negative charges sulphate groups interactions. LCG with more charged sulphate groups that ICG generate more junction zones. On the other hand, LBG is a hydrocolloid with the capacity to interact mainly with carrageenans and celluloses, due to positive charge galactomannans in its structure (BeMiller and Huber, 2012). These interactions between negative charged sulphate groups in carrageenans with positive charges in locust bean gum resulted in the increase of ice cream base viscosity, more markedly for the LBG-LCG mixtures. It has been reported that in mixed systems of LBG with CMC and LCG, LCG had a major influence on mixture viscosity, increasing when low concentrations were employed (Hernández *et al*., 2001). Main objective of hydrocolloids in ice cream formulation is to increase viscosity to improve ice cream viscosity during mixing and storage (Hagiwara and Hartel, 1996).

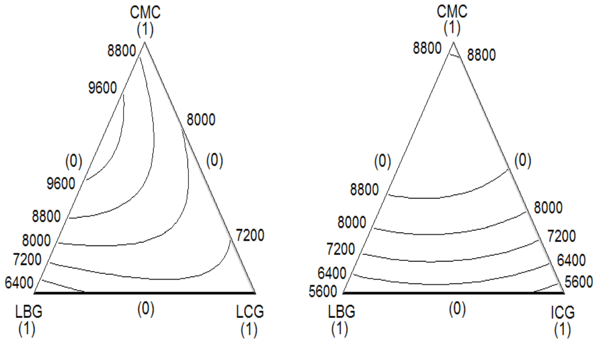

Figure 2. Isoresponse curve for the viscosity (Centipoise) of the ice cream base formulated with CMC (carboxylmethylcellulose), LBG (locust bean gum) and LCG (lambda carrageenan) or ICG (iota carrageenan)

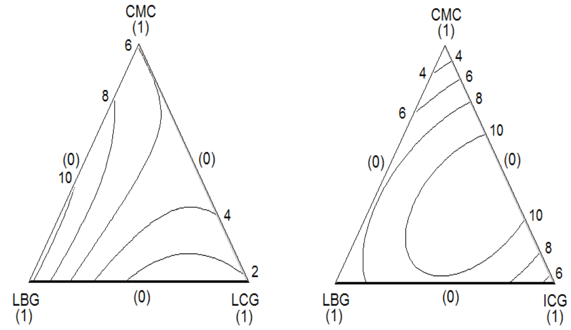

Figure 3. Isoresponse curve for the overrun (%) of ice cream formulated with CMC (carboxylmethylcellulose), LBG (locust bean gum) and LCG (lambda carrageenan) or ICG (iota carrageenan)

Table 1 shows the experimental results for the ice cream properties. In mixtures with LCG, only CMC had a significantly effect (P<0.05) on ice cream overrun (Table 3). In the isoresponse curve can be observed that at same proportions of the three hydrocolloids, mixtures with ICG resulted in higher overrun values (Figure 3). This effect could be associated to the ICG effect on ice cream base viscosity. The use of LBG with CMC and sodium alginate improved air incorporation reflected in higher overrun values (Guven and col., 2003). The relatively lower viscosity allowed the incorporation of more air avoiding ice cream collapsing during freezing (Clarke, 2004; Muse and Hartel, 2004).

For ice cream hardness, in hydrocolloids mixtures containing LCG, both CMC and LCG resulted in a highly significantly effect (P<0.01) on this parameter. LBG and the triple interaction (CMC-LBG-LCG) had a significantly (P<0.05) effect on ice cream texture. The negative sign of the β_{123} coefficient (central point of the design, i.e., same ingredients proportions) indicate a marked decrease in ice cream hardness at this point for formulations with LCG. For ice cream

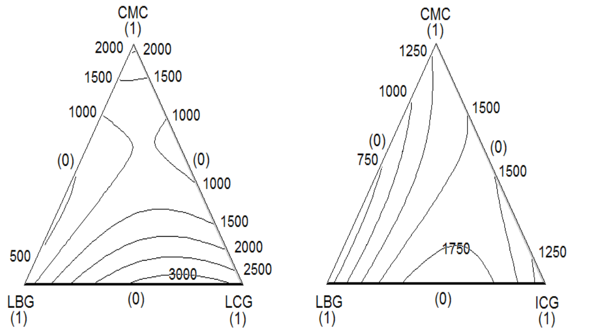

Figure 4. Isoresponse curve for the hardness (g) of ice cream formulated with CMC (carboxylmethylcellulose), LBG (locust bean gum) and LCG (lambda carrageenan) or ICG (iota carrageenan)

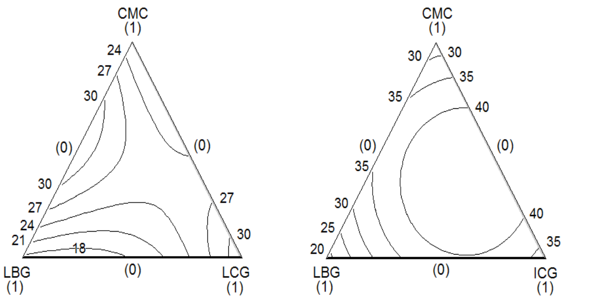

Figure 5. Isoresponse curve for first drop (min) of ice cream formulated with CMC (carboxylmethylcellulose), LBG (locust bean gum) and LCG (lambda carrageenan) or ICG (iota carrageenan)

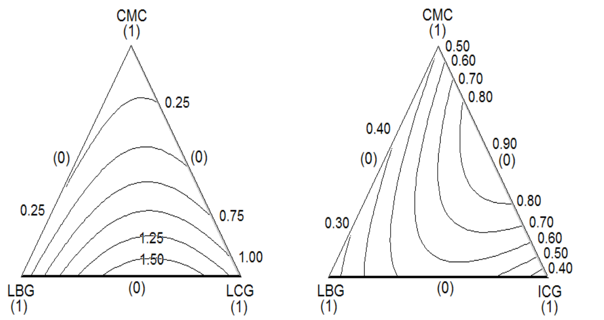

Figure 6. Isoresponse curve for melting rate (g/min) of ice cream formulated with CMC (carboxylmethylcellulose), LBG (locust bean gum) and LCG (lambda carrageenan) or ICG (iota carrageenan)

formulated with ICG, only CMC and ICG had a significantly ($P<0.05$) effect on ice cream hardness at the central point (Table 3). In the isoresponse curve can be observed that hardness of ice cream with hydrocolloids mixture containing LCG were lower than formulation with ICG at same proportions. De diminution of ICG proportion resulted in a softer texture (Figure 4). Ice cream hardness is determined by the number and size of ice crystal formed during freezing and subsequent storage. Free water availability influences the ice crystals formation. Hydrocolloids or stabilizers had an effect on free water, preventing the growth of ice crystals (Goff, 1997; Akesowan, 2008). Flores and Goff (1999) reported a cryo-protector effect of locust bean gum, avoiding free water re-crystallization provoked by the ice crystals nucleation due to temperature fluctuations during ice cream manufacture and storage. Interaction between locust bean gum and lambda carrageenan resulted in less free water decreasing ice cream hardness, acting like stabilizer during freezing-melting process (Camacho *et al*., 2001). Less free water can be related to ice crystals size, affecting ice cream texture. Sakurai *et al*. (1996) showed that ice cream containing higher amount of larger ice crystals was harder than ice cream with fewer large ice crystals. Hydrocolloids retaining free water avoid the nucleation of ice, provoking the formation of large size crystals. On other hand, overrun as the air incorporation in ice cream affect ice cream texture, since the larger volume of a compressible dispersed phase led to less resistance to an applied force (Flores and Goff, 1999; Muse and Hartel, 2004; Sofjan *et al*., 2004).

Table 4. Regression coefficient and correlation for the ice cream melting properties, first drop and melting rate, of ice cream base formulated with CMC (carboxylmethylcellulose)/LBG (locust bean gum) and LCG (lambda carrageenan) or ICG (iota carrageenan)

Mixture		Linear terms			Non linear terms				R^2
		β_1	β_2	β_3	β_{12}	β_{13}	β_{23}	β_{123}	
First drop (min)									
CMC+LBG	LCG	20.41*	17.64*	34.24	39.96	-26.19	-40.68	235.27	0.9429
CMC+LBG	ICG	26.91*	23.02	29.23	52.41	36.93	43.84	-84.72	0.8784
Melting rate (g/min)									
CMC+LBG	LCG	0.103	0.356*	1.092*	-0.585	-1.131	3.615	10.291*	0.9487
CMC+LBG	ICG	0.519	0.513	0.008	-0.086	0.735	0.363	15.826	0.6774

**Highly significantly effect ($P<0.01$)
*Significantly effect ($P<0.05$).
β_1: CMC, β_2: LBG, β_3: LCG or ICG

For the ice cream melting properties, in ice cream formulated with LCG, CMC and LBG had a significantly effect ($P<0.05$) on first drop time. For ICG formulations, only CMC had a significantly effect ($P<0.05$) (Table 4). In the isoresponse curve can be observed that the hydrocolloids mixtures containing ICG resulted in higher first drop times, i.e., ice cream formulated with ICG take longer times to melt (Figure 5). The melting rate of LCG mixtures presented a significantly effect ($P<0.05$) for LBG, LCG and the triple interaction CMC-LBG-LCG (Table 4). In the isoresponse curve can be observed that the mixtures with higher LCG proportions resulted in higher melting rates. When ICG was in the hydrocolloids mixture, proportions higher to 0.80 or lower to 0.20 resulted in lower melting rates. At same carrageenan proportion, ICG showed lower melting rate (Figure 6).

Non gelling hydrocolloids, like carboxymethylcellulose, produced minor water crystallization and hence longer melting rates, due to their capacity to absorb water and the steric impediment resulted of hydrocolloids interaction (Regand and Goff, 2003; Akesowan, 2008). Although both lambda and iota carrageenans are non-gelling hydrocolloids, mixtures with ICG required longer times to detect the first melt drop and presented longer melting rates. These melting properties are expensed of gradual heat penetration from environment to ice cream interior, provoking ice crystals fusion making that the water contained in ice cream flowed through out the foamy structure and finally drop. Hydrocolloids retain water improving the ice fusion or melt rate (Muse and Hartel, 2004). A stable ice cream resists or delay structural changes in a dynamic environment (Goff, 1997). In this way, the less marked interaction between CMC and LBG with ICG (with less charges groups) resulted in a more stable structure with better melting properties, as compared to LCG formulations, letting less free water.

Conclusions

The use of hydrocolloids mixtures of CMC-LBG containing ICG resulted in lower ice cream base viscosity, probably associated to a better handling during manufacture. Ice cream with ICG obtained higher overrun and a softer texture; maybe the increase air incorporation provoked a low resistance to ice cream penetration. Mixes with ICG improved melting characteristics due to less hard of ice cream during the storage, provoking longer melting time. The use of non gelling hydrocolloids in ice cream formulation improved ice cream properties, moreover when ICG with lower negative charged sulphate groups, was employed.

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