DEVELOPMENT OF ICE LOLLIES FROM FRESH OR FREEZE-CONCENTRATED SUGAR-CANE (*SACCHARUM OFFINARUM*) JUICE AND HYDROCOLLOIDS

Mok Kar Wei, Kooid Pooi Yein, Tan Yin Kuan and Azhar Mat Easa*

Food Technology Division, School of Industrial Technology

11800, Universiti Sains Malaysia

Minden, Penang,

Malaysia

Fax: 6 04 657 3678

Tel: 604 653 3888 ext 2260

Email: azhar@usm.my

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Abstract

Six formulations of ice lollies were developed using fresh sugar-cane juice (total soluble solid , TSS ~ 15 °brix) or freeze-concentrated sugar-cane juice (TSS ~ 30 °brix) with the incorporation of 0.3 % w/v of sodium alginate or carrageenan. The samples were designated as fresh juice lollies (FJ lollies), fresh juice + sodium alginate lollies (FJ-SA lollies), fresh juice + carrageenan lollies (FJ-Car lollies), freeze-concentrated juice lollies (FCJ lollies), freeze-concentrated juice + sodium alginate lollies (FCJ-SA lollies) and freeze-concentrated juice + carrageenan lollies (FCJ-Car lollies). Lollies were tested for hardness, meltdown time and sensory evaluation. The hardness was in the order; FJ lollies > FJ-SA lollies > FJ-Car lollies > FCJ lollies > FCJ-SA lollies > FCJ-Car lollies. The different level of hardness between lollies made from fresh juice and lollies made from freeze-concentrated juice were attributed to differences in the TSS of the solutions used. The use of carragenan helped to reduce the hardness of FJ-Car lollies, even though the TSS of FJ-Car was half that of lollies made from freeze-concentrated juice. Other than affecting texture, incorporation of hydrocolloids also helped delay meltdown time of the lollies. The order of meltdown time was; FJ-Car lollies > FJ-SA lollies > FCJ-Car lollies >FCJ –SA lollies > FJ lollies > FCJ lollies. The result of hardness and meltdown suggest the critical importance of TSS and hydrocolloids choice in lollies production. Even though lollies made from freeze-concentrated juice were sweeter in taste and softer in texture than those made from fresh juice, the overall acceptability of the lollies were not significantly different ($P < 0.05$).. It is possible for formulators to use fresh or freeze-concentrated juice with hydrocolloids combinations to produce good quality ice lollies from sugar-cane juice.

Keywords: *Freeze-concentrated juice; fresh sugar-cane juice; ice lollies; hydrocolloids; sodium alginate; carrageenan*

Introduction

Sugar-cane juice is a popular thirst-quenching drink in many South East Asia countries. Due to its high sugar content it is also a potential ingredient for a natural energy product. Alternatively, the sugar composition of the juice can be modified in order to obtain the so called "functional sugar-cane juice"; a juice that is high in fructose-oligosaccharides and low in sucrose (Easa, 2000). In addition, the content of chlorophyll in the juice is also quite substantial (~ 1 mg/100 ml) (Yusof *et al*, 2000) and may be an important component of the juice since this has been suggested as one of the promising anticancer ingredients (Lin, 1999). However, the preservation of sugar-cane juice is far from straightforward. Being of a non-fruit origin, the pH of the juice is above 5.0 (Yusof *et al*, 2000), thus making the juice a low acid product. Therefore, the shelf life of fresh sugar-cane juice cannot be satisfactorily extended using pasteurization alone as the treatment is insufficient to destroy spore forming microorganism in the juice. A more elevated heating treatment on the other hand is considered detrimental to product's quality since the high sugar content of the juice is vulnerable to sugar degradation if processed at high temperatures such as the processes of sterilization, evaporation and drying. Several attempts to preserve the sugar-cane juice include the use of chilling, heat treatment and the incorporation of chemical preservatives (Bhupinder *et al* 1991; Yusof *et al*, 2000). The use of low temperature storage has been the most effective in maintaining the quality of sugar-cane juice (Yusof *et al*, 2000; Bhupinder *et al*, 1991) without altering sensory appeals. Extending from this idea, it is thought commercially feasible that sugar-cane juice be preserved in the form of ice lollies.

Ice lolly or water ice, is a simple product that contains frozen sugar solution or juice on a stick that would typically consist of water, sugar, color, flavorings, fruit acid and stabilizers (Marshall and Goff, 2003). Sugar is the only source of solid in the mix and ranges typically from 16 – 19 %. During freezing, the ice lolly solution freezes at a lower temperature due to depression of the freezing point and the solution that remains becomes more concentrated as water is removed in the form of ice crystals. The remaining solution will freeze at even lower temperature. Thus the consequence is that an ice lolly made from sugar solution or juice high in sugar (such as sugar-cane juice) will contain both ice crystals and unfrozen, concentrated sugar solution at normal frozen storage temperatures. A difference in the total solid due to sugar can thus be expected to affect the final texture of ice lolly products. As the sugar content of sugar-cane juice ranges between 15 - 18 % (Tee *et al* 1997; Yusof *et al* 2000) that is similar to the typical sugar content of commercial ice lollies, it is thought possible to preserve sugar-cane juice in the form of ice lollies. The product developed can be considered a natural product since no sugar is added in the formulation. The texture of the product such as hardness can be controlled by modifying the solid content (TSS) of the juice, thus making the lollies more acceptable in term of sensory appeals. The use of stabilizers may further enhance quality of the lollies as they can affect melt-down time, texture or flavor retention. The hydrocolloids contribute to these properties by absorbing water and limiting its migration, increasing viscosity and in some instances forming a gel-like structure.

The objective of this study is to develop and evaluate ice lollies made from fresh sugar-cane (~ 15 °Brix) and freeze-concentrated sugar-cane juice (~ 30 °Brix). Freeze-concentration process was applied to protect the heat sensitive natural flavor of the sugar-cane juice while increasing the TSS of the juice with the intention of affecting the final texture of the lollies. The freeze-concentration process has been reported in products or conditions where heat is damaging to product quality (Despande *et al*, 1982; Braddock and Marcy, 1985).

Materials and methods

Materials

Sugar-canes (*Saccharum officinarum*) of 'yellow variety' obtained from a plantation in Selangor (a state in Peninsular Malaysia) were used in this study. All canes were stored at 4 °C prior to extraction that was performed within 2-3 days of storage. Sodium alginate and carrageenan were obtained from BDH Laboratory supplies Poole, England and Sigma Chemical Company, USA respectively. All other chemicals used for the project were of reagent grades.

Extraction of sugar-cane juice

Canes were cut into uniform lengths about 0.4 m long (after removing the nodes and outer skin from the cane). They were then washed with plain water to remove any dirt or foreign particles from the cane surfaces. Canes were then blanched at 80 °C for 15 min using a steaming cabinet (MSM-2001, Malaysia). After rinsing, a three-roller power crusher (Mindong Electric, model CH-316, Taiwan) was used to extract the juice. The juice was filtered by passing through a layer of muslin cloth. The extracted juice was collected in a chilled container and chilled immediately before being analyzed or further processed.

Production of freeze-concentrated sugar cane juice

Extracted juice was filled into polypropylene plastic casings (30.5 cm x 21 cm) that was then sealed and subjected to a rapid chilling treatment to -18 °C using an air blast freezer (Irinox, Italy). The process of rapid chilling from the ambience to -18 °C took between 30 to 35 min to complete. The juice was then transferred into a domestic freezer (Sharp, Malaysia) and stored for 24 hrs after which the hardening and completion of ice formation occurred. At this stage separation of ice and unfrozen phase consisted mainly of concentrated sugar-cane juice were evidenced. A small opening was made at one end of the plastic casing to allow the flow of the concentrated juice into a volumetric flask. This process of thawing was performed at room temperature and stopped once the total solid content of the juice reached ~ 30° Brix. The thawing process took between 50 to 70 min to complete.

Production of ice lollies

0.3 % (w/v) sodium alginate or carrageenan was incorporated into fresh or freeze-concentrated sugar-cane juice. Six formulation of ice lollies were prepared; fresh juice lollies (FJ lollies), fresh juice + sodium alginate lollies (FJ-SA lollies), fresh juice + carrageenan lollies (FJ-Car lollies), freeze-concentrated juice lollies (FCJ lollies), freeze-concentrated juice + sodium alginate lollies (FCJ-SA lollies) and freeze-concentrated juice + carrageenan lollies (FCJ-Car lollies). Maximum temperature and heating time used during incorporation of hydrocolloids was 85 ± 5 °C and 20 min respectively. The juice was then cooled to ~ 50 °C and either transferred into 14 x 4 cm polypropylene casings containing wooden ice lollies sticks or Universal bottles and stored in a domestic freezer (Sharp, Malaysia) for 24 hrs for lollies formation and hardening.

Texture analysis and melt-down time

Texture analysis was carried out on the ice lollies formed inside Universal bottles immediately after removals of samples from the freezer. The analysis was performed in an air-conditioned room (22 ± 2 °C) using a TA-XT2 Texture Analyzer Version 1.05 (Stable Micro System) with a load cell of 25 kg. The probe used was P/2, 2 mm diameter aluminum cylinder with a test speed of 0.5 mm/s. The instrument was set to measure force at compression and the maximum force required to penetrate the lollies into 15 mm depth was taken as the break force or hardness.

To measure melt-down time, ice lollies were hung from clips and a stopwatch started immediately. The time taken for the first drop of melted lollies to fall from each lolly was taken as the melt-down time.

Color, pH and total soluble solid (TSS) analysis

The color of sugar-cane juice was determined by using the Minolta colorimeter (model CM-3500d, Japan) with spectra magic software and CIELAB color system. Color values expressed as lightness 'L*' (100 %, white; 0 %, black), redness 'a*' (+, red; -, green) and yellowness 'b*' (+, yellow; -, blue) were obtained. The color of juice was expressed as; Chroma/Saturation = $(a^{*2} + b^{*2})^{1/2}$

The total soluble solids was measured using an Otago refractometer (model HSR-500, Japan; 0-42° Brix) and pH was measured using a Horiba F series pH meter (model F 21).

Sensory evaluation

Samples of lollies prepared in polypropylene casings were taken out of freezer and served immediately. Sensory evaluation of the lollies was carried out by 10 panelists. The panelists rated the samples for hardness, color, sweetness, flavor and overall acceptability using a hedonic scale of 1-9 (1=dislike very much, 9=like very much).

Statistical analysis

Data were analyzed by the analysis of variance and Duncan multiple range test using a Statistical Analysis System (SAS) program.

Results and discussion

The yield of fresh and concentrated juice can be estimated from the weight of canes used and the amount of juice obtained after extraction and freeze-concentration process respectively. 4 kg of canes yielded approximately 2 L of fresh juice and this was later processed to produce approximately 500 ml of freeze-concentrated juice. The exact yield of the freeze-concentrated juice could not be established since the TSS of freeze-concentrated juice was controlled at ~30 °Brix. The TSS of the unthawed ice was ~ 2 °Brix. Despite differing in TSS the freeze- concentrated juice was similar in appearance to that of the fresh juice.

The physical data of the two types of juice are displayed in Table 1. It can be seen that the freeze-concentration process employed in this project had doubled the TSS of sugar-cane juice. The separation of concentrated juice from the frozen ice phase was performed manually by allowing the gravitational flow of concentrated juice into a beaker. This process was stopped when the level of TSS had reached ~ 30 °Brix (typically the range of TSS obtained was between 28 – 32 °Brix) and this took between 50 to 70 min. Slight changes in pH and color were apparent after the freeze-concentration process. Freeze-concentrated juice had a lower pH and higher chroma/saturation value thus suggesting that freeze-concentrated juice was slightly higher in organic acids content, more saturated in color and may have had a higher level of water soluble compounds. The differing chroma or saturation of the concentrated juice could have been attributed to some level of non-enzymic browning (Butchelli and Robinson,1994) occurring during cane stalk blanching. It is also possible that chlorophyll, the main pigment responsible for the color of sugar-cane juice (Yusof *et al*, 2000) may have had accumulated in the concentrated juice and contributed to the color difference.

All formulations yielded self-standing, green colored ice lollies. Acid, flavor and color were not added into the formulation in order to preserve the authentic natural flavor and color of sugar-cane juice. The texture of ice lollies was assessed using a texture analyzer and sensory evaluation (Fig. 1). The FJ and FJ-SA lollies had the highest values of break-force as compared to other lollies. It is evident that all lollies made from freeze-concentrated juice were significantly lower in break-force values ($P < 0.05$) as compared to those made from fresh sugar-cane juice. Other than imparting sweetness to the lollies, higher sugar in lollies made from freeze-concentrated juice had contributed to the lowering of freezing point of the mix. 15 % sucrose by weight can potentially lower the freezing point of pure solution by nearly 1.2 °C (Marshall and Goff, 2003). Of interest are the FJ-Car lollies that exhibited lower break-force value ($P < 0.05$) as compared to those of FJ and FJ-SA lollies. Even though the TSS of the lollies made from fresh juice was similar, lollies incorporated with carrageenan exhibited lower value of break-force and sensory hardness. It is established that carrageenan does not contribute to freezing point depression (Budiaman and Fennema, 1987), however it could contribute to the retardation of growth of ice crystal (Marshall and Goff, 2003) and this may affect product's texture.

The results of instrumental assessment of texture of lollies compared favorably to that using the hedonic scores. When the break-force values of each lollies was regressed against the hedonic scores of hardness, the correlation coefficient obtained was 0.954 (Fig. 2) indicating the suitability of the two assessment methods for texture evaluation. Nevertheless, since ice lollies is a frozen product that changes with time and temperatures, a more reliable instrumental method of texture evaluation that considers dynamic meltdown of products during consumption needs to be developed.

Hydrocolloids, either singly or in combinations have been commercially applied in ice lollies to impart rheological properties that could further enhance product quality. The stabilizing ingredients most used in frozen products are guar gums, locust bean gum, CMC, sodium and propylene glycol alginates, xanthan gum, gelatine and carrageenan (Marshall and Goff, 2003). In this project sodium alginate and carrageenan were selected to perform these functions. The results of meltdown time of ice lollies as a function of lollies types are shown in Fig. 3. As could have been expected the meltdown time for FJ and FCJ lollies were the fastest among all lollies tested. During consumption, this is not desirable as it may reflect the ease of sucking the liquid phase out of the lollies and leaving the crystalline ice on the sticks. The incorporation of hydrocolloids however, had slowed down the meltdown time of the lollies. The meltdown times obtained were in the order; FCJ < FJ < FCJ-SA < FJ-SA < FCJ-Car < FJ-Car. This suggests that TSS of the juice used for lollies production was not an important factor for the meltdown time of the lollies. Even though the viscosity of the solutions was not assessed, it is possible to suggest that the incorporation of carrageenan or sodium alginate into the juice had an impact on viscosity of the unfrozen, concentrated sugar solution formed during frozen storage. Hydrocolloids are known to increase the viscosity of solutions or even form a gel as solutions become more concentrated during freezing (Marshall and Goff, 2003). As evidenced, carrageenan would better suit the application of sugar-cane based lollies as compared to sodium alginate, even though various hydrocolloids combination may also exhibit similar effects.

The sensory evaluation of the ice lollies was conducted using samples prepared in the polypropylene casings (Table 2). Despite differing in texture, no significant difference ($P < 0.05$) was observed for the attributes of flavor and overall acceptability of the lollies. The lollies with the highest hardness score were those prepared using fresh sugar-cane juice (FJ and FJ-SA lollies), except for those incorporated with carrageenan (FJ-Car lollies). The hardness of the latter was similar to the hardness level of FCJ lollies prepared singly or with incorporation of hydrocolloids. Even though TSS has been an important parameter that affects the final texture of ice lollies, carrageenan may contribute to textural attributes by preventing formation of large ice crystals (Marshall and Goff, 2003) on storage. The improvement in texture upon incorporation of carragenan into FJ lollies further supports the suitability of this hydrocolloid as an additive for sugar-cane based lollies. This hydrocolloid may have had increased the viscosity of the mix during freezing, or form a gel as the solution becomes more concentrated during freezing. The roles of hydrocolloids however were less apparent in the sweetness and color attributes of the lollies. All lollies prepared using freeze-concentrated juice were significantly sweeter ($P< 0.05$) than those made using fresh sugar-cane juice. This was expected since the FCJ lollies had higher TSS, they also had higher sugar content. There are also indications of a stronger and more acceptable color of the lollies made from freeze-concentrated juice.

Conclusion

Ice lollies were developed from fresh or freeze-concentrated juice of sugar-cane. Lollies that were made from freeze-concentrated sugar-cane juice were softer in texture and sweeter in taste as compared to those made from fresh sugar-cane juice. Incorporation of hydrocolloids particularly carrageenan, improved the quality of ice lollies. Since the overall acceptability of the lollies were similar, various combinations of sugar-cane juice with different TSS and hydrocolloids are possible.

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References

Bhupinder, K., Sharma, K.P. and Harinder, K. (1991) Studies on the development and storage stability of ready to serve bottled sugar-cane juice. International Journal of Tropical Agricultural, 9(2), 128-134.

Braddock, R.J. and Marcy, J.E. (1985) Freeze concentration of pineapple juice. J. Food Sc. 50, 1636-1639.

Bucheli, C.S. and Robinson, S.P. (1994) Contribution of enzymic browning to color in sugar cane juice. J. Agric. and Food Chem., 42, 257-261.

Budiaman, E.R. and Fennema, O.R. (1987) Linear rate of water crystallization as influenced by viscosity of hydrocolloid suspensions. J. Dairy Sci., 70: 547-554.

Despande, S.S., Bolin, H.R. and Salunkhe, D.K. (1982) Freeze concentration of fruit juices. Food Technol., 36(5): 68.

Easa, A.M. (2000) A method to produce functional sugar cane juice, "Shaping the future" Forum at the Global Dialogue 6 "Health – the key to Human Development, Hannover, Germany.

Lin, R.I-S. (1999) Phytochemicals and antioxidants, in "Functional Foods; Designer foods, Pharmafoods, Nuraceuticals" (ed. Goldberg, I.), Chapman and Hall, 406.

Marshall, R.T. and Goff, D. (2003) Formulating and manufacturing ice cream and other frozen desserts. Food Tech. 57(5), 33.

Rangana, S. (1977) Manual of analysis of fruit and vegetable products, New Delhi: Tata: McGraw-Hill.

Tee, E.S., Noor, M.I. and Idris, K. (1997) Nutrient composition of Malaysian foods, Kuala Lumpur. Institute of Medical Research, Malaysia.

Yusof, S., Shian, L.S. and Osman, A. (2000) Changes in quality of sugar-cane juice upon delayed extraction and storage. Food Chemistry 68, 395-401.

Table 1 Physicochemical properties of sugar-cane juices used for the manufacture of ice lollies. For TSS and chroma/saturation values, means in the same column with the same subscript are not significantly different ($P < 0.05$).

Types of juice	Physicochemical data		
	pH	TSS (°Brix)	Chroma/ saturation
Fresh Juice	5.3	15.0_a	9.0_a
Fresh Juice + sodium alginate	5.1	15.0_a	9.1_a
Fresh Juice + carrageenan	5.1	17.0_b	9.3_a
Freeze-concentrated Juice	5.1	30.0_c	16.2_b
Freeze-concentrated Juice + sodium alginate	5.0	30.0_c	16.7_b
Freeze-concentrated Juice + carrageenan	5.0	31.0_c	14.8_c

Table 2 Sensory attributes (mean Hedonic scores) of ice lollies produced from various sugar-cane juice and hydrocolloid types. Means in the same column with the same subscript are not significantly different ($p < 0.05$).

Types of ice lollies	Sensory Attributes (Hedonic scores)				
	Hardness	Flavor	Sweetness	Color	Overall acceptability
Fresh Juice	7.5_b	4.5_a	4.9_a	$4.6_{a,b}$	4.6_a
Fresh Juice + sodium alginate	7.3_b	4.3_a	5.0_a	$5.1_{a,b}$	5.1_a
Fresh Juice + carrageenan	4.9_a	3.9_a	5.1_a	5.0_a	4.2_a
Freeze-concentrated Juice	4.3_a	5.5_a	8.1_b	6.8_b	4.7_a
Freeze-concentrated Juice + sodium alginate	4.4_a	5.5_a	8.8_b	6.7_b	4.2_a
Freeze-concentrated Juice + carrageenan	3.5_a	5.0_a	8.7_b	6.8_b	3.6_a

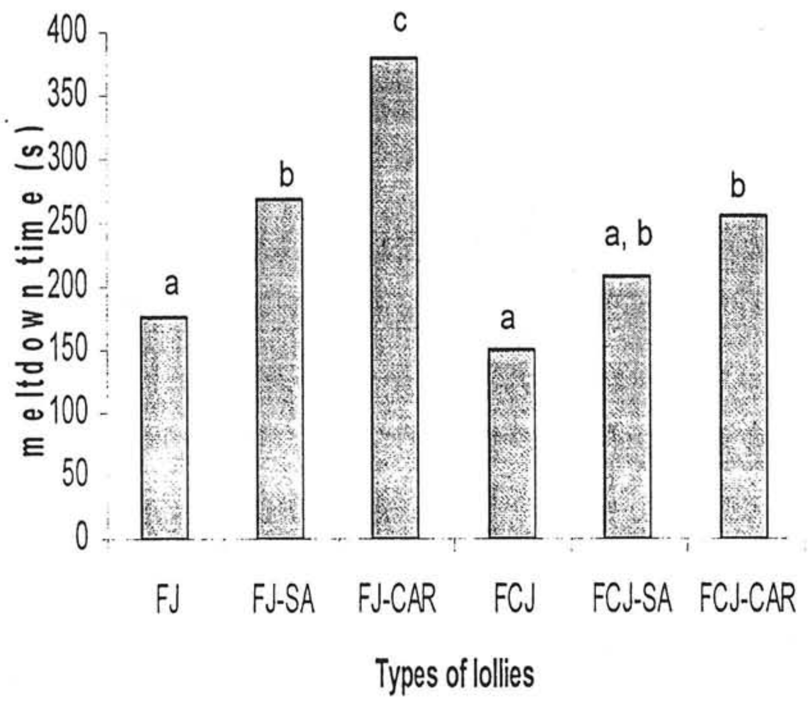
meltdown time (s)
400
350
300
250
200
150
100
50
0
c
b
b
a, b
a
a
FJ
FJ-SA
FJ-CAR
FCJ
FCJ-SA
FCJ-CAR
Types of lollies

Fig. 3