Carbon Dioxide Flash-Freezing Process Applied to Ice Cream Production

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ABSTRACT

Ice cream can be flash-frozen using carbon dioxide as a direct-contact refrigerant. An emulsion of ice cream mix and liquid carbon dioxide is throttled to the saturated carbon dioxide pressure associated with the desired temperature of the frozen ice cream. A carbon dioxide to ice cream mix mass ratio of approximately 1:1 is sufficient. A proof-of-principle apparatus using atomizing fuel nozzles to form and throttle the emulsion was built to test the process. A powdery, carbonated ice cream product with a mean ice crystal size of approximately 17 microns is obtained. The process and resulting product are described and compared to ice cream frozen by conventional methods. Potential advantages of the flash-freezing process include energy savings, novel texture and consistency, and opportunities to produce ice cream in new venues.

INTRODUCTION

Conventional ice cream freezing processes involve a combination of dynamic and static freezing steps. During dynamic freezing, liquid ice cream mix is pumped into one end of an annular chamber where the walls are actively cooled. Compressed air is also injected into the chamber. The mix begins to freeze onto the walls of the chamber where it is scraped off by a rotating scraper, the beater-dasher. The beater-dasher assembly also mixes the injected air as small bubbles into the forming ice cream. The scraper blades of the dasher operate with small clearances against large forces in order to shear ice off the wall in small crystals. As the cream mixture progresses down this scraped wall heat exchanger, the ice content of the mixture increases where ultimately the ice cream exits at approximately –5°C, with 30-55% of the water content frozen[1] (Clarke, 2004). Any dry or soft ingredients, such as nuts, cookie dough or caramel, are added at this point in the process. The mix is poured into cups, cones, or containers as desired.

Since high quality ice cream is associated with a small crystal structure, the ice cream must be rapidly cooled to arrest further ice crystal growth. The ice cream containers are passed through a hardening tunnel where the ice cream is frozen to temperatures below -20°C. In this process no new ice crystals are nucleated and the remaining water freezes out of solution onto existing ice crystals in the mix.

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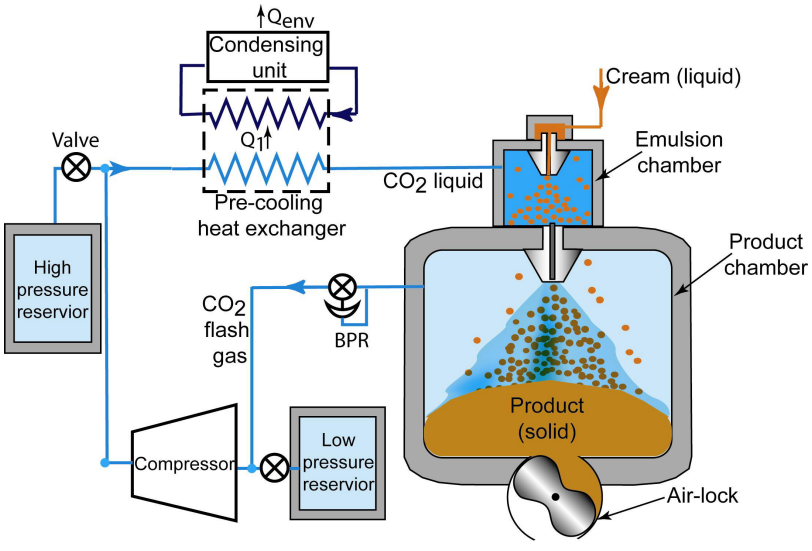

Figure 1. Basic implementation of the carbon-dioxide flash-freezing process. BPR-back pressure regulator, Q-heat transfer. In this schematic it is assumed that the ice cream mix enters at 4°C from typical mix preparation processes.

In the new process discussed here, liquid carbon dioxide is used as a direct refrigerant to freeze ice cream mix. Figure 1 shows a basic implementation of the process. The ice cream mix and liquid carbon dioxide are pre-cooled to near the freezing temperature of water. The ice cream mix is then sprayed into the liquid carbon dioxide in the emulsion chamber as a fine mist, creating an emulsion of ice cream mix and liquid carbon dioxide. This emulsion is then passed through a second nozzle into a thermally-insulated product chamber that is maintained at a low pressure. The second nozzle atomizes the emulsion and, because of the low pressure in the product chamber, the carbon dioxide component vaporizes. The vaporizing carbon dioxide flash freezes the ice cream component of the mixture. The very fine ice cream crystals collect in the bottom of the product chamber. The gaseous carbon dioxide in the product chamber is collected, filtered and recompressed. The recompressed carbon dioxide is then passed back through the pre-cooling heat exchanger to be used again. An additional supply of carbon dioxide gas is used to make-up for the carbon dioxide incorporated into the product as well as gas lost due to leakage in the system. In this continuous cycle, the product is extracted from the product chamber through some sort of air-lock system.

The pressures in the cycle are dictated by the properties of carbon dioxide. The pre-cooling heat exchanger and the emulsion chamber are maintained at pressures above 3.97×10^6 Pa (576 psi), the saturation pressure of pure carbon dioxide at 5°C, to ensure the CO_2 is in the liquid phase. The pressure in the product chamber limits the temperature achievable in the product chamber, a typical operating pressure for the product chamber is 1.965×10^6 Pa (285 psi) which corresponds to a saturation temperature of -20°C for pure carbon dioxide.

The flash-freezing process offers several benefits for frozen desserts. The product formed is unique with a powdery texture that flows easily and, in addition, the product can be carbonated. The process can also be used to produce conventional ice cream by allowing the carbon dioxide to diffuse out and compressing the uncarbonated powder. The flash-freezing apparatus can replace both the continuous freezer and the hardening tunnel since the liquid cream is directly cooled to temperatures below –20°C. The hardening tunnel energy consumption is large due to the low-temperature and large separation between packages required to achieve fast freezing. In

addition, the large number of parts involved in the conveyer belts in the tunnel requires significant maintenance. Models suggest energy savings on the order of 50% for the freezing stage of ice cream production.

THEORY

The minimum ratio of carbon dioxide to ice cream mix for successful freezing is found by balancing the enthalpy of each fluid entering the emulsion chamber and exiting the product chamber. Carbon dioxide enters the emulsion chamber as a sub-cooled liquid and is vented from the product chamber as a saturated vapor. Ice cream mix enters the emulsion chamber as a pressurized solution and leaves the product chamber as a frozen powder.

The change in the specific enthalpy of the carbon dioxide from the emulsion chamber entrance and to the product chamber exit can be found using saturation tables for a pure substance. Carbon dioxide enters the emulsion chamber at 5°C and 4 x10^6 N/m^2 (580 psi) and leaves the product chamber as a saturated vapor at -20°C. The change in the specific enthalpy of the ice cream mix during the process is found by considering the sum of the enthalpy decreases due to the sensible heat that is removed to cool the unfrozen and partially frozen mix and the latent heat of fusion released in formation of the ice content (334.2 kJ/kg). The heat capacity of unfrozen mix is approximately 3.35 kJ/kgK.[2] The heat capacity of ice cream decreases as the volume of ice in the mix increases because ice has a lower heat capacity than water. The heat capacity of partially frozen ice cream is about 2.72 kJ/kgK (Marshall, 2003). The water content of a typical ice cream mix is 65% by mass, but only 80% of the water content is frozen in the final product. For the typical heat capacities and ice fraction stated above, the enthalpy change is

$$\Delta h_{icm} = (5-^{-}3)°\mathrm{C} \times 3.35\frac{kJ}{kg°\mathrm{C}} + 0.85 \times 0.60 \times 334.2\frac{kJ}{kg} + (^{-}3 - T_{exit})°\mathrm{C} \times 2.72\frac{kJ}{kg°\mathrm{C}}. \quad (1a)$$

If pure water is frozen instead of cream mix, the change in specific enthalpy can be found using pure substance tables for liquid water at 5°C and solid water at the appropriate exit temperature,

$$\Delta h_{icm} = h_{H_2O,l,5C} - h_{H_2O,s,-20C} \quad (1b)$$

The mass flow ratio of carbon dioxide to mix or water is calculated according to,

$$R = \frac{\Delta h_{icm}}{h_{CO_2,sat,v} - h_{CO_2,l}}, \quad (2)$$

where $h_{CO2,sat,v}$ is the specific enthalpy of the saturated carbon dioxide vapor exiting the product chamber and $h_{CO2,l}$ is the specific enthalpy of the liquid carbon dioxide entering the emulsion chamber. To form ice at -20°C from pure water, the carbon dioxide mass flow rate must be 1.76 times the water mass flow rate. To freeze ice cream mix to -20°C, the carbon dioxide mass flow rate only needs to be 1.1 times the mass flow rate of ice cream mix. This mass flow ratio calculation assumes that the product chamber is already at a steady state temperature close to the desired product temperature.

PROOF-OF-PRINCIPLE APPARATUS

The expansion process has been tested and demonstrated using a proof-of-principle apparatus shown in Figure 2. The continuous cycle is modified in several ways to implement the small-scale batch process. A 2.28 kg (5 lb) carbon dioxide cylinder is mounted upside down to supply liquid carbon dioxide. The carbon dioxide is used both to pressurize the ice cream mix and in the emulsion. Carbon dioxide that will pressurize the cream mix is passed through a heat exchanger coil in a warm-water bucket. This ensures that the pressurizing carbon dioxide is a vapor upon reaching the ice cream mix. Ice cream mix is pre-loaded into an ingredient chamber and pressurized by vapor phase carbon dioxide. Before entering the emulsion chamber, the ice cream mix and the liquid carbon dioxide are pre-cooled by passing through separate coils of 6.35 x 10^{-3}m (0.25”) tubing in an ice bucket heat exchanger. The ice bucket heat exchanger is a

substitute for the condensing unit described for the basic implementation of the flash-freezing process.

The ice cream product is not continuously extracted from the product chamber. Instead, at the end of a test, the product chamber is opened by removing six bolts that secure the bottom plate of the chamber. The ice cream powder falls into a collection bowl. The batch process apparatus can hold approximately three liters of ice cream in the product chamber. The exhaust carbon dioxide is not captured and recompressed. It is instead vented to the atmosphere through a back pressure regulator[3] (BPR). Because the proof-of-principle apparatus is used to freeze a small batch of ice cream mix, the product chamber walls are pre-cooled before each test.

Fuel nozzles[4] are used to form and throttle the emulsion of ice cream mix and carbon dioxide. The cream mix is metered into the emulsion chamber by a 1.0 GPH nozzle and the emulsion is throttled into the product chamber by a 2.0 GPH nozzle. The nozzle sizes were chosen after experimentation with a variety of nozzles. While larger nozzles allow a larger flow rate, the texture of the frozen product is coarser. Instead, the flow rate through a nozzle is increased by increasing the pressure drop across it. Significant increases in flow rate would be achieved by operating multiple nozzles in parallel.

The operating pressures for the process are set by the desired exit temperature of the saturated carbon dioxide vapor, the pressure required to ensure that the carbon dioxide is a liquid in the emulsion chamber, and the pressure in the ingredient mix that will give the desired flow ratio. The pressure in the product chamber is the pressure of saturated carbon dioxide vapor at -20°C, 1.97×10^6 Pa (285 psi). The pressure in the emulsion chamber must be greater than 3.96×10^6 Pa (575 psi). To find the necessary ice cream mix pressure, the flow rates of ice cream mix and liquid carbon dioxide through the 1.0 and 2.0 GPH fuel nozzles were calibrated separately. The effect of pressure drop on the flow rate of the emulsion through the 2.0 GPH nozzle was estimated based on the calibrations for the individual flows. For a carbon dioxide to ice cream mix ratio of 1.1 at a cream flow rate of approximately 1 g/s, the required pressure drop across the 1.0 GPH nozzle is 1.29×10^6 Pa (187 psi) with a 2.03×10^6 Pa (295 psi) pressure drop across the 2.0 GPH nozzle. Therefore the ice cream mix must be pressurized to 5.29×10^6 Pa (767 psi).

Before a batch of ice cream is produced the ice bucket heat exchanger is prepared and the product vessel walls are pre-cooled. The ice bucket is filled with ice and water is added to improve the thermal contact between the ice and the heat exchanger coils. The temperature in the bucket is less than 3°C at the start of each test. The temperature of the bucket increases less than 1°C during the test. Based on a simple uniform wall temperature model of the heat transfer between the ice-bucket heat reservoir and the water or carbon dioxide flowing at 1 g/s in 6.35×10^{-3} m (0.25 ") tubing, the approach temperature of the flow is better than 0.04°C for 3.66 m (12 ft) of tube. Water is approximately an order of magnitude more viscous than liquid carbon dioxide, so the Reynolds number for the water flow in the coil is 275, laminar, while the Reynolds number for the liquid carbon dioxide flow is 4356, turbulent. Liquid carbon dioxide has a lower heat capacity and thermal conductivity than water so the thermal resistances are similar. The warming experienced by the fluids during the transit from the ice bucket to the emulsion chamber is negligible due to the small average heat transfer coefficient of natural convection from a 0°C surface to a room temperature environment and the small perimeter of the 6.35×10^{-3} m (0.25") tubing.

The product chamber must be pre-cooled to ensure that the frozen product is not melted by the high heat capacity chamber walls. The product chamber is formed by a 0.10m (4 in) diameter stainless steel pipe bolted between two 0.01 m (0.5 in) thick stainless steel plates. To reduce the consumption of carbon dioxide, liquid nitrogen is used for pre-cooling. Because there are no thermocouples in the product chamber the saturation properties of carbon dioxide are used to estimate the internal temperature. To pre-cool the product chamber it is filled with carbon dioxide vapor at 1.38×10^6 Pa (200 psi) and then sealed. Liquid nitrogen is poured into the foam-insulated container that fully surrounds the length of the chamber. The liquid nitrogen is removed when the pressure in the product chamber begins to fall, signifying that the carbon dioxide has begun to condense. The insulation is replaced on the product chamber when the

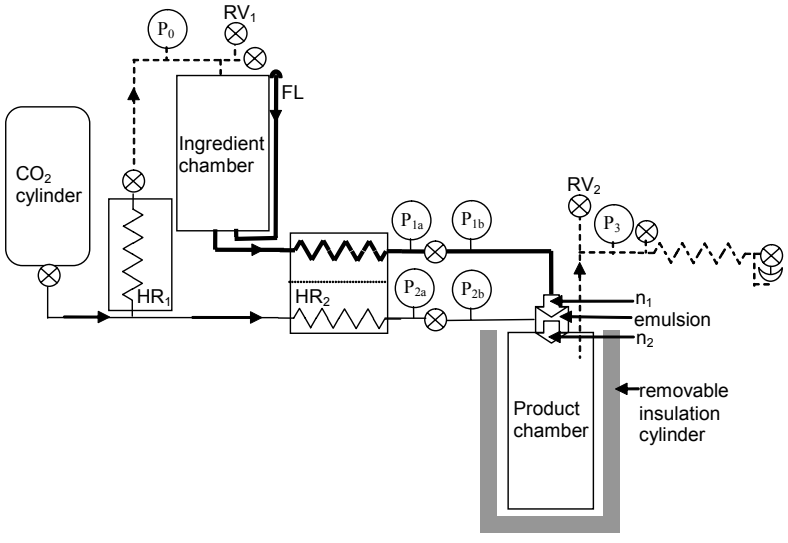

Figure 2a. Schematic of the proof-of-principle apparatus. FL-fill line, RV-relief valve, BPR-back pressure regulatior, HR_1-heat reservoir (~30°C), HR_2-heat reservoir (2°C), n_1-ingredient nozzle, n_2-combined fluid nozzle, $P_{2b} = P_{CO2,l}$, $P_3 = P_{sat,v}$.

Figure 2b. Proof-of-principle apparatus.

pressure in the chamber reaches 10^6 Pa (145 psi), the saturation pressure corresponding to –40 °C for carbon dioxide. The BPR is set to maintain the product chamber at this pressure. Using this pre-cooling method there is a gradient in temperature between the top and bottom of the product chamber. Some carbon dioxide condenses on the coldest surface, the bottom plate of the product chamber. The condensed phase fixes the pressure in the chamber, but the vapor near the top of the chamber can be warmer. The change in temperature along the length of the chamber varies with the mass of nitrogen used for pre-cooling and the delay between pre-cooling and

running the flash-freezing process. When the chamber is pre-cooled poorly the temperature of the top plate has been measured as much as 40°C warmer than the temperature of the bottom plate.

RESULTS AND DISCUSSION

The proof-of-principle apparatus has been used to freeze water, ice cream, frozen yogurt, and sorbet mixes. The first successful tests of the apparatus used water and a 3.0 GPH nozzle. After pre-cooling the product chamber the ingredient chamber was filled with tap water and sealed. The warm-water bath was filled with warm tap water (~30°C). The water in the ingredient chamber was then slowly pressurized to 5.516×10^6 Pa (800 psi) by partially opening a valve to allow the carbon dioxide vapor to flow into the top of the ingredient chamber. At room temperature the pressure of the saturated carbon dioxide in the cylinder is 6.07×10^6 Pa (880 psi). Heat was applied to the carbon dioxide cylinder to increase the available pressure as necessary. The valve controlling the pre-cooled carbon dioxide flow was opened to allow flow at 4.137×10^6 Pa (600 psi). The valve controlling the pre-cooled water flow was opened to allow flow at 5.516×10^6 Pa (800 psi). The valves were left open for approximately ten minutes. The second nozzle was frequently blocked by prematurely formed solids. This condition was indicated by the pressure in the emulsion chamber increasing to the pressure of the water flow before the first nozzle. A heat gun was directed at the bottom of the emulsion chamber until the flow through the nozzle was restored. In some cases the pressure in the emulsion chamber increased to 6.2×10^6 Pa (900 psi) before dropping to the pressure of the incoming pre-cooled carbon dioxide. Even after heating, the flow through the second nozzle started and stopped in spurts identified by listening near the top of the product vessel. This behavior may be due to clathrates. Clathrates are solid water structures with an interstitial carbon dioxide molecule that form at high pressure and temperatures up to 10°C.[5]

After the test run the product chamber was vented. The six bolts were removed and the cup of carbonated snow-ice dropped out of the chamber. The snow was white and powdery with a large gas volume fraction and some tendency to clump. The amount of water frozen during a run cannot be determined until the product chamber is opened because the flow is unsteady. In some cases the product chamber walls were coated with snow and the cup was only partially filled. The product chamber can be over-cooled, which exacerbates the nozzle blockage problems. If the water does not freeze when it is emitted from the nozzle, it can freeze to the bottom wall of the chamber, making it difficult to extract the sample.

The flash freezing process was used to freeze homemade ice cream mixes of 8.5 – 13.8 % fat content. The ingredients included light cream, whole milk, granulated sugar and vanilla extract purchased from a local grocery store. The ingredients were mixed by shaking the contents in a bottle, but no homogenization process was performed. The pre-cooling and pressure regulation were carried out identically to the tests with water. To make ice cream, the valves were opened to allow flow at the appropriate pressures for 2-3 minutes. Nozzle blockage was not typically a problem when freezing ice cream mix. Clathrate formation may be inhibited by the other ingredients in addition to water that are present in the mix. The valves were closed when small amounts of ice cream mix began to come out of the carbon dioxide vent system. After venting and opening the product chamber the collection cup was removed by lightly tapping on the base. Additional ice cream powder was removed from the upper half of the product chamber by a long handled spoon. Both the 3.0 GPH and the 2.0 GPH nozzles were tested successfully.

Fresh ice cream mix produced at Bliss Brothers Dairy Farm in Attleboro, Massachusetts was also tested. The 14% fat mix included additional stabilizers and surfactants which would improve the texture of the frozen product if frozen in a conventional freezing process. The proof-of-principle apparatus again worked successfully. Possibly due to the mix recipe, the flakes were more dense and cohesive; the ice cream collection container as well as the upper section of powder slid coherently out of the product vessel.

In some cases the frozen ice cream consistency was stratified in the product vessel, with a highly carbonated, very dry powder at the bottom and a warmer, moister consistency in the upper layer. The lower layer may have additionally contained solid carbon dioxide micro-flakes. This product variation is probably due to temperature gradients in the product vessel walls caused by the pre-cooling method and the insulation system. In extreme cases, the uppermost layer in the product vessel had bubbles covered with ice cream mix film. This may be due to some distortion of the spray cone. If there is a leak between the nozzle and the emulsion chamber some ice cream mix flows through the opening with the consistency of whipped cream.

The frozen dessert produced by the expansion process is different from conventional ice cream. The ice cream product has a free-flowing, powdered form, very high gas volume fraction, and some level of carbonation. The powder micro-flakes have a mean diameter of approximately 30 microns. A group with access to a sample of the ice cream powder reported a mean ice crystal size of 17 microns. Such fine grains melt easily due to the large surface area and the open structure of the flakes. Tasters have commented on the sensation that the ice cream powder dissolves on the tongue. The high gas volume fraction of the product makes it susceptible to collapse during storage. The presence of carbon dioxide as vapor or in solution in the powder gives the product a tangy fizz if it is eaten immediately after freezing. In portions with solid carbon dioxide flakes, due to excessive cooling of the product chamber with liquid nitrogen and or a low pressure in the product chamber, there is a 'whoosh' of cold vapor out of the mouth when the ice cream product is eaten. The solid flakes do not cause a burning sensation (or frostbite) in the mouth, possibly due to the insulation of the ice cream mix ingredients.

Low fat content mixes produce a highly carbonated product that tingles in the mouth. The product frozen using a 3.0 GPH combined fluid nozzle had a carbonation level that was qualitatively similar to product frozen using a 2.0 GPH nozzle despite the increased carbon dioxide to ice cream mix flow ratio. The Bliss Brothers Dairy mix produced a powder with a noticeably warmer mouth feel. This is expected where water is displaced by fats.[2]

CONCLUSIONS

The flash-freezing process has been successfully demonstrated using a proof-of-principle, batch-process apparatus. The ratio of carbon dioxide to ice cream mix mass flows is typically 1.1. Further tests are required to understand and control the state of the carbon dioxide in the ice cream product.

ACKNOWLEDGMENT

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REFERENCES

[1] Clarke, C., *The Science of Ice Cream*, Royal Society of Chemistry, Cambridge, UK (2004).
[2] Marshall, R., Goff, H., and Hartel, R., *Ice Cream, 6th ed.*, Kluwer Academic/Plenum Publishers, New York (2003).
[3] Tescom Corporation <http://www.tescom.com/icd/icd04.php>.
[4] Goodrich Delavan Spray Technologies http://www.delavaninc.com/oilburner.htm
[5] Wendland, M., Hass, H., and Maurer, G., "Experimental Pressure-Temperature Data on Three- and Four-Phase Equilibria of Fluid, Hydrate, and Ice Phases in the System Carbon Dioxide-Water", *Journal of Chemical Engineering Data*, vol. 44, (1999), pp. 901-906.