Carbon Dioxide Flash-Freezing Applied to Ice Cream Production

by

Teresa Susan Baker

B.S. Mechanical Engineering
B.S. Earth, Atmospheric, and Planetary Sciences
Massachusetts Institute of Technology, 2003

SUBMITTED TO THE DEPARTMENT OF MECHANICAL ENGINEERING IN
PARTIAL FULLFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE IN MECHANICAL ENGINEERING

AT THE

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

FEBRUARY 2006

Signature of Author:_____
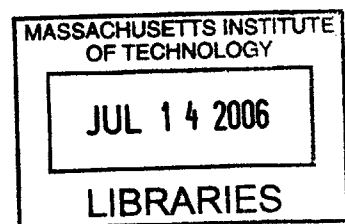
Department of Mechanical Engineering
January 20, 2006

Certified by:____

John G. Brisson II
Associate Professor of Mechanical Engineering
Thesis Supervisor

Accepted by:_____

Lallit Anand
Chairman, Department Committee on Graduate Students

Carbon Dioxide Flash-Freezing Applied to Ice Cream Production

by

Teresa Susan Baker

Submitted to the Department of Mechanical Engineering
on January 20, 2006 in Partial Fulfillment of the
Requirements for the Degree of Master of Science in
Mechanical Engineering

ABSTRACT

Ice cream mix and other liquids are frozen by direct contact with carbon dioxide while carbon dioxide is throttled from a liquid phase to a saturated vapor phase. The process is demonstrated with a proof-of-principle apparatus that freezes discrete batches of mix. The fluid consumption, power consumption and space requirement of a continuous cycle implementation are modeled. In the proof-of-principle apparatus and the continuous cycle model, the ice cream mix is sprayed into the liquid carbon dioxide using 1.0 GPH Delavan fuel nozzles; the combined fluid is throttled by 2.0 GPH Delavan fuel nozzles, forming a fine mist during flash-freezing. The pressure at the outlet of the throttle determines the temperature of the saturated carbon dioxide vapor after the flashing process. The resulting product is a frozen carbonated ice cream powder. Depending on the implementation, 50-99% of the carbon dioxide flow is vented and can be compressed and recycled with additional make-up carbon dioxide flow.

The required ratio of carbon dioxide to ice cream mix is found by balancing the change in enthalpy of each liquid from the inlet to the outlet state. For ice cream mix frozen from 5°C to -20°C, the ratio is shown to be about 1.1. Carbon dioxide is recompressed from 1.97×10^6 Pa (285 psi) to 3.96×10^6 Pa (575 psi). The process is scaled by increasing the number of nozzles to accommodate the desired flow rate. Only 165 nozzles are required to flash freeze the ice cream mix at a 2000 L/hr ice cream production rate. The power consumption of a continuous cycle implementation is modeled including single or double stage carbon dioxide recovery and compression, pre-cooling of the carbon dioxide by a standard condensing unit, pumping of the ice cream mix at high pressure and extrusion of the ice cream powder by a piston or screw extruder. The power consumption of an implementation recovering 95% of the carbon dioxide is approximately 37.3% of the power consumption of a conventional process. The cost of the make-up carbon dioxide is $0.002 per liter of ice cream. A cart implementation is also possible.

Thesis Supervisor: John G Brisson II
Title: Associate Professor of Mechanical Engineering

Table of Contents

List of Figures

List of Tables

List of Symbols

A-area
b-distance between flights (for screw extruder)
D-barrel diameter (for screw extruder)
e-flight wall thickness (for screw extruder)
F-volume flow rate
f-frequency
h-specific enthalpy (except in screw extruder geometry)
L-length
$\dot{m}$-mass flow rate
N-rotation rate of screw extruder
n-number of nozzles
$\overline{O}$-overrun
P-pressure
Q-heat
$\dot{Q}$-volume flow rate (for screw extruder)
R-ratio of carbon dioxide and water or mix mass flow rates
R-radius of hexagonal nozzle arrangement
r-number of hexagonal rings
T-temperature
U-velocity
V-volume
$\dot{V}$-volume flow rate
w-volume fraction in flow (except in screw extruder geometry)
x-distance piston has traveled
δ-clearance between flight and barrel wall (for screw extruder)
γ-percent of carbon dioxide flow recycled
μ-viscosity
η-compressor efficiency
ρ-density
φ-helix angle (for screw extruder)

List of Subscripts

CO_2-carbon dioxide
$CO_{2,\ makeup}$-carbon dioxide supplied from reservoir, not recycled
$CO_{2,\ l}$-carbon dioxide liquid entering emulsion chamber
H_2O-water
NH_3-ammonia
0-initial (i.e. density of powder)
a,b-used to differentiate measurement at different conditions
atm-at atmospheric condition
c-cross-sectional
comp-compression, compressor
container-container holding ice cream
exit-value for CO_2 established in the product chamber
f-final
i-initial
icm-ice cream mix
in-before pre-cooling
l-liquid
main-compression of CO_2 from $P_{sat,v}$ to $P_{CO2,l}$
max-maximum density of solid particulates
new- value for combined fluid
partial-mixed liquid and vapor phase
pc-pre-cooling
pg-pressurizing gas
piston-piston extruder for ice cream powder
pump-ice cream mix pump
rev-reversible
s-solid
sat-saturated state
sat,v-condition at product chamber exit
stage1-compression of CO_2 from atmospheric pressure to $P_{sat,v}$
stroke-portion of piston cycle in one direction
tot-value for combined fluid (emulsion)
total-ice cream and container
v-vapor

CHAPTER 1 - INTRODUCTION

A new process for freezing ice cream and similar desserts has been developed. Liquid carbon dioxide is used as a direct refrigerant to freeze ice cream mix as these emulsified fluids are throttled through a nozzle to form a fine mist. This chapter describes the flash-freezing process. In Chapter 2 basic information about ice cream, conventional freezing and factors important to ice cream quality are presented. Chapter 3 discusses the design parameters for implementing the process. This includes the thermodynamics of the fluid interaction and additional refrigeration and processing required. Chapter 3 includes consideration of continuous, large scale implementations of the process and cart implementation without carbon dioxide recovery. Chapter 4 presents the proof-of-principle apparatus that was developed to test the flash-freezing concept. In Chapter 5 a comparison of the novel and conventional freezing processes is presented, with consideration of food grade equipment requirements. Preliminary sizing of a cart implementation and a home implementation are discussed. Chapter 6 identifies aspects of the process that should be studied in further work.

1.1 Flash-Freezing Process

For the flash-freezing process, ice cream mix and liquid carbon dioxide are pre-cooled to near the freezing temperature of water. The carbon dioxide is maintained above its 5°C saturation pressure, 3.97×10^6 Pa (576 psi). Figure 1-1 shows a basic implementation of the process. The ice cream mix is sprayed as a fine mist into the liquid carbon dioxide, creating a temporary emulsion of the fluids. This emulsion is sprayed through a second nozzle into a product chamber at the saturation conditions of carbon dioxide at –20°C. The carbon dioxide vaporizes upon entering the lower pressure chamber. The ice cream mix is flash-frozen, rapidly losing enthalpy because it is in intimate contact with the carbon dioxide. The ice cream micro-crystals fall to the bottom of the chamber, trapping some carbon dioxide. The remaining vaporized carbon dioxide escapes through an exhaust vent.

In a continuous implementation, the vented carbon dioxide is filtered and recompressed as shown in Figure 1-1. This carbon dioxide is supplemented by additional make-up carbon dioxide and re-used in a partially closed cycle. The ice cream micro-crystals are extracted from the chamber through a pressure lock and compressed to the desired gas volume fraction.
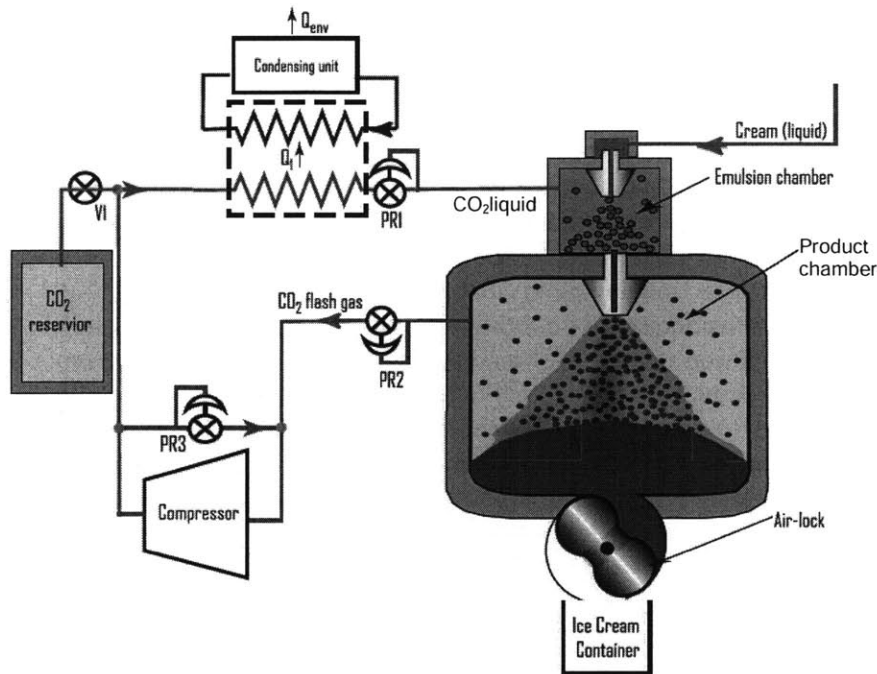
Figure 1-1 Novel freezing process, basic implementation. PR-pressure regulator, V-valve, Q-heat transfer

The use of carbon dioxide in food and even in dairy products is not new. Carbon dioxide is generally regarded as safe (GRAS) and is commonly found in beverages such as soda pop, champagne and beer. In addition, carbon dioxide is commonly added to dairy foods to extend the shelf life of the food (Hotchkiss, 1996). Carbon dioxide is a natural antimicrobial agent present in raw milk. Carbon dioxide is also more soluble in water than oxygen, so it replaces oxygen and may limit rancidity which is caused by oxidation. With the addition of carbon dioxide, the shelf life of ice cream mix can be increased from 18 days to 60 days (Hotchkiss, 1996). Studies of ice cream produced with a gas such as nitrogen or carbon dioxide replacing air found some reduction in oxidation, particularly for mixes with milkfat substitutes such as canola and soybean oil (Marshall, 2003).

Industrial carbon dioxide for beverage service is available through most gas distributors. Other cryogenic gases are not practical for this process because either the critical point is much lower than the desired temperature of ice cream (i.e. Nitrogen), the gas is not consumable (i.e. Ammonia), or the gas is prohibitively expensive (i.e. Krypton).

CHAPTER 2 - BACKGROUND

2.1 Ice Cream

Ice cream is made from a mixture of dairy ingredients, sweeteners and flavoring. In commercial processing the mix also includes emulsifiers and stabilizers to improve the whipping properties of the mix and the body of the product. Air is incorporated into the ice cream during the freezing process.

Various related frozen desserts are available on the market and many are standardized by federal regulations. In the United States, for a product to be called ice cream it must be at least 10% milkfat by weight. Sweeteners are generally 12-16% of the composition by weight. Custards or French ice cream must additionally be 1.4% egg yolk solids. Sherbets have 1-2% milkfat content, and sorbet and ices are generally defined as containing no dairy ingredients. Regulations vary from country to country.

Ice cream is an emulsion of milkfat in a solution of water, ice crystals, milk proteins, and carbohydrates. Approximately 85% of the water content is frozen at –20°C (Marshall, 2003). The remaining water is a highly concentrated solution of sugars. As the water freezes out of solution the freezing temperature of the solution progressively lowers. Figure 2-1 shows a schematic of the texture of ice cream. The milkfat exists in tiny globules that are formed by the homogenizer before the mix is frozen. The fat globules agglomerate on the surface of the air cells, helping to stabilize the foam structure of ice cream. Nonfat milk solids (NMS) are the proteins, lactose and mineral salts derived from milk products. NMS are important to the texture of ice cream, improving the distribution of air cells and surrounding the fat globules to prevent too large an agglomeration (Tetrapak, 2004). Fat globules in ice cream have an average diameter of 1 micron, leading to an extremely large total surface area of fat in ice cream. One study found that it is the surface of the fat globules that contributes to the flavor and consistency, while the interior of a molecule merely adds calories (Freedman, 2004).
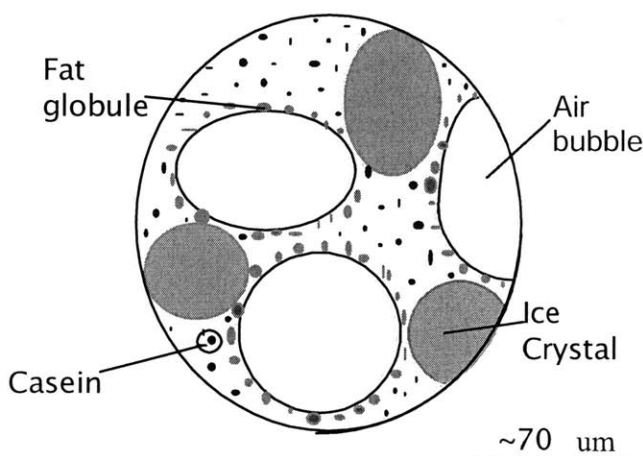
Figure 2-1 Ice cream structure schematic.

2.2 Ice Cream Quality

High quality ice cream is recognized largely based on mouth feel. The mouth feel is affected most strongly by the size of the ice crystals and also the density of the frozen ice cream. Smaller crystals give a creamier texture. Ice crystals in ice cream are of average diameter 50 microns and air bubbles are of average diameter 70 microns. In premium ice creams the ice crystal diameter may be less than 30 microns. If the ice crystals become larger, due to recrystallization after melting and re-freezing or due to incomplete processing, the ice cream can incur a grainy texture. The fat content of the ice cream additionally improves the creamy texture and the smoothness of the mouth feel. Premium ice creams can be more than 20% milkfat.

The density of frozen ice cream is indicated by percent overrun. With too much air the ice cream will seem to lack substance. Overrun is ratio of the volume of gas to the volume of ice cream mix in ice cream. The overrun, $\overline{O}$, can be calculated for any full collection container according to

$$\overline{O} = \left(\frac{V_{container}}{V_{icm}} - 1 \right)$$

$$V_{icm} = \frac{m_{total} - m_{container}}{\rho_{icm}}, \tag{1}$$

where $V_{container}$ is the volume of the container of ice cream, V_{icm} is the volume of ice cream mix in the container, m_{total} is the mass of the full container of ice cream, and $m_{container}$ is the mass of the container. This calculation neglects additions to the ice cream such as nuts that do not incorporate air. Typically, the production rate of an ice cream machine is quoted at 100% overrun; the volume of air in the frozen structure is equal to the volume of ice cream mix in the frozen structure. The legal maximum in the United States is around 120%. Super premium ice creams may have as low as 60% overrun. Homemade ice cream and small batch machines often have lower air content due to reduced whipping.

The quantity of each ingredient in a mix can affect the freezing properties of the ice cream, and therefore the ice crystallization. Mix calculations are typically based on the percent mass of each constituent in the mix. Particular constituents in the mix, including NMS, fat, sucrose and water often come from multiple sources, such as cream, milk, sweetened condensed milk and nonfat dry milk. The contribution of NMS from each source (i.e. milk and cream) is summed. Whole milk is typically 3.25% fat and 8.25% NMS; light cream is typically 20% fat and 7.2% NMS. Appendix A gives an example calculation of the milkfat, sucrose and NMS content of a mix used to test the flash-freezing proof-of-principle apparatus described in Chapter 4. The mix has a 2:1:0.5 mass ratio of light cream to whole milk to sugar, resulting in 12.4% fat, 6.5% NMS and 14.3% sucrose, with the remaining 66.8% being nominally water. The water content and density of a typical ice cream mix are ~60% and 1054-1087 kg/m^3 respectively. The NMS content of the 2:1:0.5 mix is low compared to commercial mixes. Whole milk is slightly denser than light cream, and both fluids are denser than sugar; however the mass ratio can be used as a volume ratio with negligible change to the mix calculation.

2.3 Conventional Ice Cream Freezing Process

Conventional freezing processes involve both a dynamic and a static freezing step. During dynamic freezing, ice cream mix is pumped through an annular chamber with a refrigerant such as ammonia or R-22 surrounding and actively cooling the walls. Compressed air is concurrently metered and injected into the chamber. The mix is churned and aerated by a beater-dasher assembly, shearing and dispersing small air bubbles in the ice cream. The mix freezes on the cylinder walls and is continuously scraped off by rotating blades on the dasher. These blades operate with small clearances in order to shear small ice crystals off the wall. Crystals that have been scraped off the wall can grow in the volume of the cylinder, so an additional pump is sometimes used to push the ice cream quickly through the freezer. A schematic of the basic barrel freezer assembly is shown in Figure 2-2. The mix exits the continuous freezer at approximately –5 °C, with 30-55% of the water content frozen. 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. Continuous freezers are available with capacities from 50-4000 L/hr.

A second step is required to arrest the crystal growth process and maintain the fine structure achieved in the barrel freezer. The ice cream containers are passed through a hardening tunnel where the ice cream is frozen below -20°C. No new ice crystals are nucleated, water freezes out of solution onto existing ice in the mix. Blast freezers and cold-plate freezers are operated at temperatures of -40°C to facilitate rapid freezing and maintain the quality of the ice cream. The hardening time is defined as the time required for the temperature in the middle of a package to decrease to -18°C. A hardening time of 6-8 hours for an 18.9 L (5 gal) package is typical of a conventional hardening room operating at optimal conditions. Large commercial manufacturing plants may freeze 5,000 -10,000 L/hr (Tetrapak, 2004). Figure 2-3 is an example of a hardening tunnel.

The ice cream freezing process achieves three important features in the frozen dessert. At least 80% of the water content is frozen, air is incorporated into the mix and dispersed in small bubbles, and fat globules partially coalesce helping to stabilize the dessert structure. To improve the quality of the ice cream some processes incorporate an additional dynamic freezing step with a double screw apparatus. In small plants batch freezers sometimes replace the continuous freezer. These tend to incorporate less air and require an increased ice cream residence time. Small plants may place the partially frozen mix directly into the cold storage facility to avoid the cost of a hardening tunnel. Until the ice cream has been hardened, extra space between packages must be maintained to allow for cooling. Larger ice crystals typically result from the slower hardening.

13
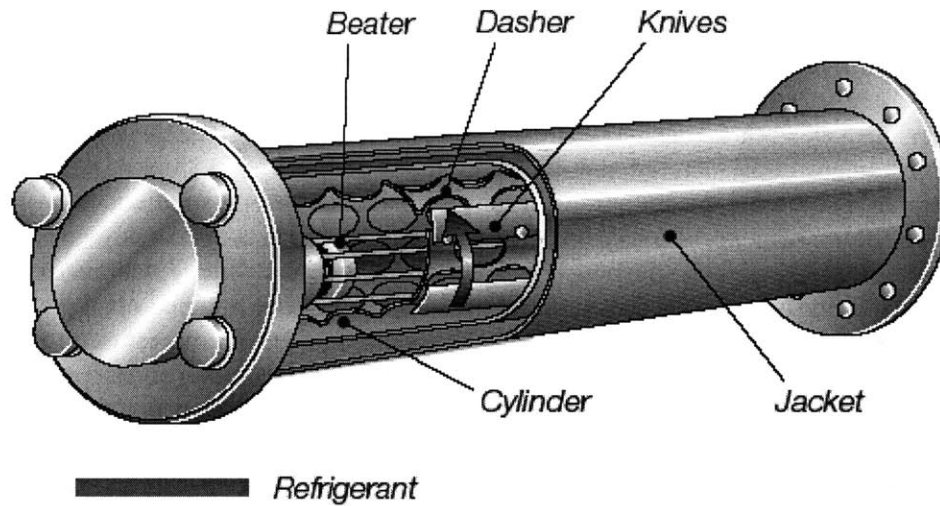
Figure 2-2 Continuous freezer assembly. [Source: Tetrapak]
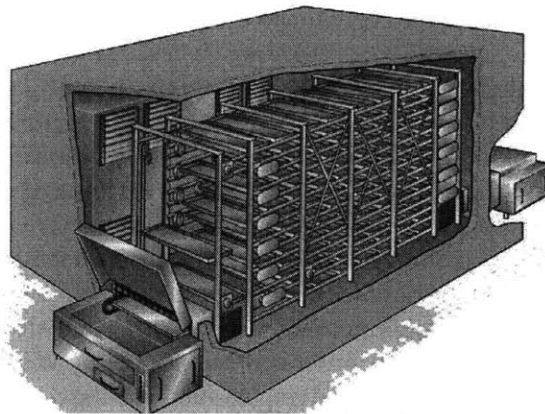
Figure 2-3. Ice cream plant hardening tunnel. [Source: Tetrapak]

2.4 Industry Interests

Ice cream is a $20 billion market in the US alone, but the market is highly competitive. Industry players are particularly interested in opportunities to differentiate their product, such as novel molded forms or unique flavors. In addition, the conventional ice cream freezing process is expensive. The continuous freezers and a hardening tunnel require capital investments of greater than $100,000 each. The beater-dasher assembly in the continuous freezer operates with small clearances against a high viscosity mix; the blades must be carefully maintained. The hardening tunnels involve intricate conveying mechanisms. The equipment has a large footprint on the plant floor. The conventional ice cream freezing process is a significant energy consumer. The largest energy consumer is the hardening tunnel, where rapid freezing requires low

14

temperatures and plenty of space between packages for effective heat transfer. Energy is also consumed in the continuous freezer to shear the ice crystals and move the high viscosity mix. The re-introduction of sheared crystals into the bulk of the mix allows the crystals to grow. Additional cooling is required to remove the heat generated in the shearing process.

Low temperature continuous freezers were introduced by Tetra Pak in June 2003, based on ice cream plant manufacturers' interests (Tetra Pak Hoyer, 2003). These freezers draw ice cream at -12°C, in many cases obviating the need for a hardening tunnel and shortening the production line. These low temperature freezers can produce fine ice crystals, leading to a smooth creamy ice cream texture with a lower fat content. In addition, the ice cream has improved melting resistance. Drawing the ice cream at -12°C is not advantageous for adding inclusions like nuts or chips because the ice cream viscosity is significantly increased at the colder temperature.

A method to produce lightly carbonated yogurt was developed at Brigham Young University. Streams of yogurt and carbon dioxide gas pass through a pressurized shear-field to incorporate the carbon dioxide in the yogurt. Preliminary market tests were carried out for sales of the yogurt in an on-campus convenience store. Additional market tests were carried out by Ipsos-Insight in Brussels in 2000. The yogurt received high acceptance rates, particularly by teenagers and young adults. There is typically also a small segment, ~10%, which do not like carbonated yogurt at all (BYU, 2000). Various fruit flavors were tested. Carbon dioxide was also injected into a pressurized freezing chamber with non-fat soft-serve yogurt mix. In a 160 kg mix with 60% overrun, the frozen yogurt contained 156 g of dissolved CO_2 (975 ppm) and 208 g of CO_2 gas bubbles (1300 ppm) (Ogden, 2002). This is on the order of the concentration of carbon dioxide in soda, ~1800 ppm, based on the solubility of CO_2 in water, 1.8g/L at 20°C.

CHAPTER 3 - THEORY

3.1 Design Parameters

Implementation of the novel ice cream freezing process involves several design parameters, including choice of nozzle size and the pressure and temperature states in each chamber. The expansion process requires liquid phase initial fluid states, emulsion of the fluids, an effective refrigerant/mix balance and exit conditions that will induce flash freezing of the ice cream mix.

To implement the flash-freezing process the desired exit state of the ice cream and the required production rate should be chosen. Table 3.1 shows the design parameters for three exit conditions referred to in the following sections. Ice cream exiting at -20°C can be directly compared to the conventional process, ice cream exiting at -40°C corresponds to the existing proof-of-principle apparatus, and ice cream frozen directly to atmospheric pressure is applicable for a cart implementation. Note that for the first two cases, the temperature of the ice cream product corresponds to the temperature of the saturated carbon dioxide exiting the product chamber at $P_{sat,v}$. In the third case, the carbon dioxide is throttled to a pressure and temperature below its triple point; carbon dioxide sublimates at -78.5°C and atmospheric pressure. In this case the mix is frozen to -20°C rather than -78.5°C by maintaining an appropriate fluid ratio. Cooling ice cream to -78.5°C would require a very large ratio of carbon dioxide to mix and would not provide any advantages for the microstructure of the ice cream or the ice cream distribution chain.

For standard implementations of the flash freezing process, the following parameters should be assumed: initial ice cream mix and liquid carbon dioxide temperature of 5°C, initial carbon dioxide pressure of 4.0×10^6 Pa (580 psi), and Delavan fuel nozzles rated at 1.00 GPH for the mix and 2.00 GPH for the combined flow. The initial carbon dioxide temperature and pressure ensure liquid phase carbon dioxide in the emulsion. The nozzle sizes are based on tests with the proof-of-principle apparatus that led to a desirable powder consistency. The choice of nozzle is discussed in detail in Chapter 4. Larger nozzles would make the texture of the frozen product coarser. The required production rate should be met by increasing the number of nozzles rather than increasing the size of the nozzles or the pressure drop across the nozzles. Although increasing the pressure drop across a nozzle would increase the total flow rate, the power required to pump and compress the fluids would be increased.

In addition to the size of the nozzles and the pressure drop across each nozzle, the composition of the ice cream mix affects the flow rate of the fluids and the product overrun. The values in Table 3.1 are for a 10% fat mix. The effects of alternate recipes are described in the discussion of the proof-of-principle apparatus in Chapter 4.

Ice cream mix can include many ingredients, which alter the freezing properties of the mix. Typically 60% of the mass of ice cream mix is contributed by the water content (TetraPak, 2004). The sweeteners, cane and beet sugar or corn syrup, depress the initial freezing temperature of the mix. The freezing point of common mixes is depressed by approximately 3°C. During freezing the water solidifies in fine crystals, leaving an increasingly concentrated serum solution of carbohydrates, fats and NMS. In a conventional process the concentration of sweeteners in the solution will increase as

some of the water is frozen out, further depressing the freezing point. Below approximately -30°C a sucrose solution undergoes a transition to a glass phase and no more water can be frozen out of the highly concentrated serum (Clarke, 2004); only ~85% of the water content is frozen.

Table 3.1 Design parameters for three exit states. 1.0 GPH ingredients nozzle, 2.0 GPH combined fluid nozzle. Carbon dioxide entrance pressure is 4×10^6 Pa (580 psi).

Exit State	Mix flow rate [g/s]	CO_2:H_2O ratio*	CO_2:Ice Cream Mix ratio	ΔP_1 [psi]	ΔP_2 [psi]	Pre-Cooling Refrigeration [kJ/s]**
-20°C, 285 psi	1.72	1.76	1.085	187	295	0.4882
-40°C, 146 psi	1.79	1.94	1.336	201	434	0.6257
-40°C, 14.7 psi	1.93	2.07	1.424	236	565	0.2165

*CO_2:H_2O mass flow ratio included for reference, all other values refer to mix. Flow rate and ΔP_1 would be reduced for water fluid properties.
**Pre-cooling calculation for first two exit states assumes all CO_2 must be condensed from vapor, calculation for third exit state assumes CO_2 enters as a liquid from a CO_2 cylinder, as in a cart implementation. The third calculation also includes pre-cooling of ice cream mix.

3.2 Carbon Dioxide-Mix Mass Flow Ratio

The mass flow ratio of liquid carbon dioxide to ice cream mix must be balanced so that the enthalpy carried away by the vaporized carbon dioxide matches the enthalpy released by the freezing of the ice cream mix. Before calculating the required ratio, the enthalpy change of each fluid for the expected entry and exit states must be determined. The appropriate carbon dioxide enthalpies are found in the saturation tables for a pure substance. Carbon dioxide is expanded from saturated liquid at 5°C to saturated vapor at the exit condition chosen for the process implementation. The values for the relevant conditions are provided in Appendix B.

The water content of the ice cream mix freezes out of solution while the rest of the mix is cooled to the freezer temperature. The specific enthalpy of the ice cream mix is decreased by the sum of the latent heat of fusion of the ice content (334.2 kJ/kg) and the sensible heat that is removed to cool the unfrozen mix and the partially frozen mix. The heat capacity of unfrozen mix is approximately 3.35 kJ/kgK (Marshall, 2003). This is less than the heat capacity of pure water due to the presence of the fats, sugars and other ingredients. The heat capacity of the 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, while the heat capacity of ice cream near -20°C is typically 1.88 kJ/kgK. For the typical ice cream heat capacities stated above, the enthalpy change is

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

The heat capacity of semi-frozen ice cream was used for the sensible heat that must be removed from the partially frozen mix. This leads to a small over-estimate of the carbon dioxide required because the heat capacity of the ice cream decreases as it freezes. If the mix is replaced by pure water, the enthalpy change 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 enthalpy of the solid can be found in a solid-vapor equilibrium table.

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 carbon dioxide exiting the product chamber and $h_{CO2,l}$ is the specific enthalpy of the liquid carbon dioxide entering the emulsion chamber. For the implementation conditions presented in Table 3.1, the carbon dioxide flow must be greater than the ice cream mix flow rate. To freeze pure water, the carbon dioxide flow rate must be approximately double the water mass flow rate. This mass flow ratio calculation assumes that the product chamber is already at a steady state temperature close to the desired product temperature. In the proof-of-principle tests the product chamber is pre-cooled using liquid nitrogen. In a continuous process, a start-up period during which carbon dioxide is expanded in the absence of ice cream flow can be used to cool the process equipment.

The specific enthalpy that the carbon dioxide vapor can carry away decreases as the temperature of the exit state decreases. In addition, the specific enthalpy that must be removed from the ice cream mix increases for colder product temperatures. Therefore, the carbon dioxide to mix ratio must be increased to produce a colder product. The flow ratio increases by 21% for the 20 degree decrease in the product exit temperatures provided in Table 3.1.

The mass flow ratio calculation can also be applied if only the carbon dioxide or if both fluids enter the emulsion chamber near room temperature. The specific enthalpy of the incoming flow is increased when the flow enters at the temperature of the environment, reducing the change in enthalpy of the carbon dioxide and or increasing the change in enthalpy of the mix. The mass flow ratio required to freeze ice cream mix is increased by approximately 15% if both fluids enter at room temperature. In addition, the incoming fluid pressures must be increased to maintain liquid phase carbon dioxide before the combined fluid nozzle. The power required for a cycle without pre-cooling refrigeration is slightly larger than for a cycle with pre-cooling, however, omitting the pre-cooling condensing unit could be preferable for environmental reasons. This is discussed in Section 5.1.3.

18

3.3 Pre-cooling Refrigeration Requirement

For a standard implementation of the flash-freezing process, the ice cream mix and the liquid carbon dioxide enter the emulsion chamber at 5°C. An evaporating refrigerant can be used to separately pre-cool the mix and the carbon dioxide. A standard condensing unit can be used for the refrigeration cycle.

Carbon dioxide for the freezing process comes from two sources. The majority of the flow is the carbon dioxide vented from the product chamber. This recycled flow is a vapor slightly warmer than the temperature of the environment after passing through the compressor and the after-cooler. The additional make-up CO_2 enters as a vapor at the temperature of the environment. The recycled flow has been compressed to the pressure required in the emulsion chamber. The pressure of the make-up CO_2 is regulated to match the pressure of the recycled flow. The percent of the carbon dioxide flow that is recycled is calculated based on the difference between the mass of carbon dioxide required for flash-freezing the mix and the mass of carbon dioxide removed from the cycle with the product. The mass of carbon dioxide removed with the product is estimated as the mass of carbon dioxide required to fill the void space in the product,

$$\gamma_{sat} = 1 - \frac{\overline{O} \times \rho_{CO_2, sat, v}}{R \times \rho_{H_2O}}. \tag{3a}$$

The mass of carbon dioxide recovered varies with the density of the carbon dioxide gas contained in the frozen powder and the overrun. This calculation neglects carbon dioxide in solution in the product and solid carbon dioxide present with the product. Carbon dioxide has low solubility in water and ice, so the mass of carbon dioxide dissolved in the product is much less than the mass of carbon dioxide filling the void volume. Formation of solid carbon dioxide is not expected for the general case; formation of dry ice powder would require product temperatures less than -78.5°C or flashing to atmospheric pressure with excess carbon dioxide. More than 99% of the carbon dioxide flow can be recovered from ice cream product exiting at -20°C, atmospheric pressure and 100% overrun. Approximately 95% of the carbon dioxide flow can be recovered as saturated vapor if the powder is compacted to 100% overrun before it is removed from the product chamber. Additional carbon dioxide can be recovered from the gas volume in the ice cream powder after it passes through the airlock. The tests with the proof-of-principle apparatus described in Chapter 4 suggest high overrun at the saturated vapor carbon dioxide exit conditions. As little as 52% of the total carbon dioxide flow may be recovered from the product while it is at the saturated vapor pressure.

Additional carbon dioxide can be recovered when the product is brought from saturated to atmospheric pressure. This carbon dioxide must be compressed in at least two stages. First it is compressed from atmospheric pressure to the saturated vapor pressure and then it is mixed with the recovered saturated vapor and compressed to the pressure required for flash-freezing. The percent of the carbon dioxide recompressed from atmospheric pressure is the difference between Eq. 3a evaluated for the overrun and density at saturated conditions and Eq. 3a evaluated for overrun and density at atmospheric pressure,

$$\gamma_{atm} = \frac{R \times m_{H_2O} - (\overline{O} \times \frac{m_{H_2O}}{\rho_{H_2O}} \times \rho_{CO_2,atm})}{R \times m_{H_2O}} - \gamma_{sat}. \tag{3b}$$

The make-up carbon dioxide flow rate is then

$$\frac{m_{CO_2,makeup}}{m_{H_2O}} = (1 - \gamma_{sat} - \gamma_{atm}) \times R. \tag{4}$$

If carbon dioxide is only recovered from the saturated vapor, γ_{atm} can be omitted from Eq. 4 and the make-up carbon dioxide mass flow must be increased. The carbon dioxide remaining in the interstitial space in 100% overrun powder at atmospheric pressure is less than 0.25% of the total carbon dioxide flow.

The heat that must be removed from the carbon dioxide flow, per mass ice cream mix flow, can be calculated as

$$\frac{Q_{CO_2}}{m_{H_2O}} = R \times \left(\gamma \times (h_{CO_2,35^\circ C,v} - h_{CO_2,5^\circ C,l}) + (1 - \gamma) \times (h_{CO_2,20^\circ C,v} - h_{CO_2,5^\circ C,l}) \right), \tag{5}$$

where γ is the sum of γ_{atm} and γ_{sat} or just γ_{sat} if only one compression stage is used. For this model, 20°C is the assumed environmental temperature and 35°C is the assumed temperature of the vapor CO_2 that has been recompressed and air-cooled.

The heat that must be removed to pre-cool the ice cream mix is

$$\frac{Q_{pc}}{m_{H_2O}} = (T_{in} - 5)^\circ C \times 3.35 \frac{kJ}{kg^\circ C}. \tag{6}$$

The heat that must be removed to pre-cool the ice cream mix is significantly less than the heat that must be removed to condense the carbon dioxide. The ice cream mix does not need to be pre-cooled in an ice cream manufacturing plant because the mix is stored in aging tanks for 4-24 hours after it is pasteurized and homogenized (Marshall, 2003). To allow the fat to crystallize, the aging tanks are cooler than 4°C. Pre-cooling should be incorporated for a laboratory continuous cycle or cart implementation if the ice cream mix source is warm.

3.4 Power Consumption

The flash-freezing cycle has four main power consuming elements. Power is required for the carbon dioxide compressor, the condensing unit, extraction and compression of the ice cream powder from the product chamber, and for pumping the ice cream mix at the appropriate entrance pressure, typically greater than 4.83×10^6 Pa (700 psi). Figure 3-1 shows a flow diagram with these power inputs.
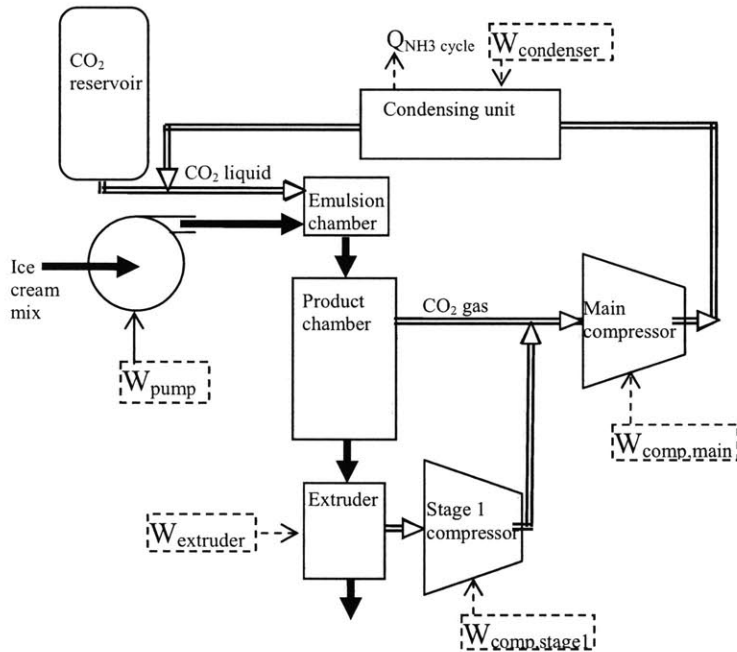
Figure 3-1. Flow diagram with power inputs. The carbon dioxide content of the ice cream mix exiting the product chamber and the carbon dioxide content of the ice cream mix exiting the extruder vary with process implementation.

3.4.1 Compressor Power Consumption

The flash freezing cycle includes one to two compressors to recycle the carbon dioxide. The main compressor compresses carbon dioxide from the saturated vapor exit pressure, $P_{sat,v}$, to the pressure of the liquid CO_2 in the emulsion chamber, $P_{CO2,l}$. In Figure 3-1, this power input is labeled $W_{comp,main}$. If incorporated, a second compressor compresses carbon dioxide recovered from the product at atmospheric pressure, P_{atm}, to the pressure at the entrance to the main compressor, $P_{sat,v}$. In Figure 3-1, this power is labeled $W_{comp,stage1}$.

Figure 3-2 shows a simplified model of the main carbon dioxide refrigeration cycle on a pressure-enthalpy diagram. Line segment A represents the heat removed by the air-cooled after-cooler. Line B represents the cooling provided by the condensing unit. Line C corresponds to the constant enthalpy throttling of the carbon dioxide flow

and line D corresponds to the expansion during flash freezing. The compression work is shown by line segment E. Both an isentropic compressor and a 70% efficient compressor are represented. The model shows constant carbon dioxide enthalpy through the throttle (segment C). It is actually the net enthalpy of the carbon dioxide and ice cream mix emulsion that remains constant through the throttle. Interaction between the carbon dioxide and the ice cream mix could be significant despite the short time scale of the throttle due to the large interfacial surface area of the emulsion. If the carbon dioxide exits the product chamber as a saturated vapor at the pressure set by the BPR, the compression work is not changed by the assumption that the throttle process is isenthalpic for carbon dioxide.
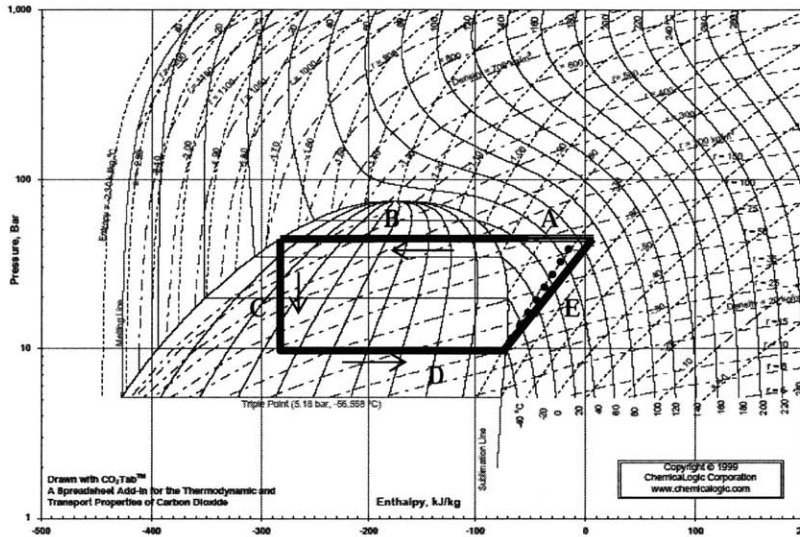
Figure 3-2 Carbon dioxide pressure-enthalpy diagram with cycle for main compressor. Dotted line represents isentropic compression.

The carbon dioxide compression work for the simple cycle shown in Figure 3-2, per unit mass flow of ice cream mix is

$$\frac{W_{comp}}{m_{H_2O}} = \frac{\gamma_{sat} \times R \times (h_{rev,P_{CO2,l}} - h_{sat,v})}{\eta},$$ (7)

where η represents the compressor efficiency and $h_{rev,PCO2,l}$ is the specific enthalpy of the carbon dioxide for an ideal compression to the pressure, $P_{CO2,l}$, that the carbon dioxide must have in the emulsion chamber. The specific enthalpy for an ideal, adiabatic compression is equal to the enthalpy of carbon dioxide at 3.96×10^6 Pa (575 psi) and the same specific entropy as the saturated vapor exiting the flash freezing. The enthalpy and hence temperature of the carbon dioxide after a real compression can be found by adding the compressor work to the enthalpy of the saturated vapor. The first two terms on the right-hand side of Eq. 7 represent the mass of carbon dioxide that is recompressed per unit mass of water or mix.

22

The power consumption of a flash freezing cycle that recovers carbon dioxide in two stages is larger than for the process described above. The work to compress part of the flow from atmospheric pressure to the saturated pressure of the vapor carbon dioxide exiting the product chamber is calculated by,

$$\frac{W_{comp,stage1}}{m_{CO_2}} = \frac{h_{rev,P_{sat,v}} - h_{v,P_{atm}}}{\eta}. \tag{8}$$

This portion of the carbon dioxide flow is then cooled to room temperature by an after-cooler and mixed with the recovered saturated vapor. The new specific enthalpy and entropy of the carbon dioxide flow entering the main carbon dioxide compressor are greater than the enthalpy and entropy of the saturated vapor alone. The work done by the main compressor is calculated as in Eq. 8, substituting a mass averaged value for the enthalpy of the incoming carbon dioxide and using the mass averaged entropy of the incoming flow to the compressor to determine the final enthalpy for a reversible process. The work per unit mass of water or ice cream mix can be found as

$$\frac{W}{m_{H_2O}} = R * \left(\gamma_{atm} \times \frac{W_{comp,stage1}}{m_{CO_2}} + (\gamma_{atm} + \gamma_{sat}) \times \frac{W_{comp,main}}{m_{CO_2}} \right). \tag{9}$$

3.4.2 Condensing Unit Power Consumption

The compression work and refrigerant flow rate for the condensing unit are calculated based on a refrigerant evaporating at -5°C in a heat exchanger. The pre-cooling refrigeration cycle could be represented similarly to the carbon dioxide cycle on a pressure-enthalpy diagram for ammonia or another refrigerant. The throttling process for the refrigerant is again assumed to be isenthalpic. The refrigerant to ice cream mix mass flow ratio is calculated according to

$$R_{NH_3} = \frac{\dfrac{Q_{CO_2}}{m_{H_2O}} + \dfrac{Q_{pc}}{m_{H_2O}}}{h_{NH_3,-5°C,v} - h_{NH_3,-5C,l_{partial}}}. \tag{10}$$

The enthalpy of the refrigerant before the heat exchanger, $h_{NH3,-5C,lpartial}$, is determined by the enthalpy of the condensed refrigerant before it is throttled to the -5 °C saturation pressure. The refrigerant is two-phase after the isenthalpic throttle. In this model, it is assumed that the refrigerant in the condensing unit is air-cooled to 35°C before throttling. Water-cooling would reduce the compression work required as well as the ratio of refrigerant to ice cream mix flow. When the ice cream mix comes directly from the aging tanks, the term corresponding to pre-cooling the ice cream mix, Q_{pc}, can be omitted from the numerator of Eq. 10. The work required for the refrigeration cycle is calculated

as in Eq. 7, replacing the first two terms on the right-hand side with R_{NH3}; γ is omitted because refrigerant leak from the pre-cooling refrigeration cycle is neglected.

The thermal energy that must be removed from the carbon dioxide flow by the condensing unit is increased slightly when carbon dioxide is recovered in two stages. The specific enthalpy of the carbon dioxide vapor entering the condensing unit is not changed assuming the increased flow is still air-cooled to 35°C. The mass of the carbon dioxide flow that must be condensed from a superheated vapor is increased by γ_{atm} x R x m_{H2O}. The power consumption of the condensing unit is correspondingly increased. The calculation is the same as in Eq. 7 with R_{NH3} replacing γ x R as described above.

3.4.3 Ice Cream Pump and Extruder Power Consumption

Power is also required to move the ice cream mix and frozen powder through the flash freezing process. The ice cream mix must be pumped to the first nozzle under high pressure and the powder must be extracted from the pressurized flash chamber and compressed to a desired overrun. The pressure of the incoming mix must be at least 6.89×10^5 Pa (100 psi) greater than the pressure in the emulsion chamber, approximately 4.83×10^6 Pa (700 psi). The power required to pump the ice cream mix is

$$\frac{W_{pump}}{m_{H_2O}} = \frac{\Delta P}{\rho_{H_2O} \times \eta},$$ (11)

where ΔP is the difference between the pressure at the first nozzle and the pressure of the mix leaving the aging tank, typically atmospheric pressure. Ice cream mix is one to two orders of magnitude more viscous than water at standard temperature and pressure. Ice cream mix is shear-thinning. The pump must be designed to accommodate these fluid properties. Typically pumps for ice cream mix do not achieve pressures greater than $\sim 1.38 \times 10^6$ Pa (200 psi), except where the mix is pumped through a homogenizer, at pressures greater than 5.5×10^6 Pa (800 psi).

The ice cream product can be extracted by a piston-cylinder system, a screw extruder or another positive displacement pump. Figure 3-3 shows a simple piston-cylinder geometry. In this model the cylinder length is shorter than the piston stroke so that the powder is compressed against the end of the cylinder. The model includes a valve in the cylinder to allow carbon dioxide flow and a removable bottom plate to allow the powder "block" to fall out of the extruder. With each stroke, a fixed volume of powder is moved out of the collection area and compressed against the cylinder end. During the forward stroke carbon dioxide at $P_{sat,v}$ flows into the carbon dioxide exhaust stream from the product chamber through the open valve. When the piston reaches the end of its stroke, L_s, the valve is closed and the bottom plate is opened slightly to allow carbon dioxide to escape until the compressed product reaches atmospheric pressure. The escaping carbon dioxide could be captured and recompressed using an additional CO_2 compressor stage as described in Section 3.4.1. The bottom plate is removed and the powder block drops out of the cylinder. The bottom plate is then replaced and the valve is reopened. Carbon dioxide vapor at $P_{sat,v}$ refills the compressed product volume. The piston retracts to its starting position.
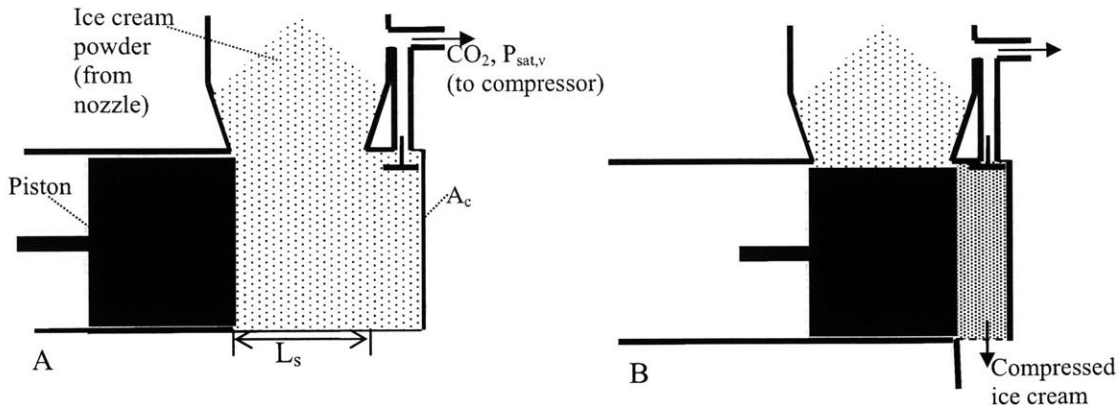
Figure 3-3. Piston extruder geometry. A: initial piston position. B: compressed powder exiting extruder. (Schematic for 100% overrun product.)

For this simplified model the piston is assumed to be massless and frictionless. Air at atmospheric pressure is present in the volume of the cylinder after the product is removed, but it is neglected for this model. This model does not include filtering of the carbon dioxide passing through the valve, but an actual implementation may require filtering to remove ice cream powder entrained in the carbon dioxide flow.

In this model the piston only does work against the carbon dioxide vapor and the ice cream powder. By assuming that the powder remains permeable to carbon dioxide vapor during the compression and recognizing that the valve is open during the entire piston stroke, the carbon dioxide pressure can be modeled as uniform throughout the volume and constant during the entire stroke. The work done by the piston on the gas is equal to the product of the pressure at the piston face and the change in volume during the piston stroke. The work done by the piston on the gas during the forward stroke is exactly equal to the work done by the gas on the piston when the piston is retracted. This could be implemented using a fly-wheel. Thus, the net power consumption of the piston is solely due to moving and compressing the powder. If the inertia of the powder and the friction between the powder and the cylinder walls are neglected, power is mainly required to compress the powder. The power required to simply move the powder out of the product chamber is neglected based on these assumptions.

The bulk mechanical properties of the ice cream powder are not understood at this time. Tests with the proof-of-principle apparatus suggest an initial overrun of at least 400%. It may be necessary to compress the powder to a typical density for ice cream, 100% overrun. Snow compaction has been studied for several applications including tire traction and forming ice blocks for stored cooling; Shapiro et al present an overview (Shapiro, 1997). The microstructure of snow has a significant impact on the particle deformation and stresses during compression. The force required to compress snow varies with the age and temperature of the snow and the strain rate applied due to changes in the bonding between particles, particle contact area and fracture and recrystallization of particles. Fresh snow is typically not well-bonded. In addition, in the ice cream

powder, bonding between particles may be reduced by the presence of ingredients other than water.

For simplicity, the ice cream powder is modeled here as incompressible particulate solids with interstitial gas. Because the ice cream powder is only compressed to 100% overrun it is assumed that the bulk density of the powder is increased mainly by particle realignments rather than deformation of the particles. A commonly used relationship based on experiments with various powders is given by Osswald and Stradinis (Osswald, 1995). The density of the solids is an exponential function of pressure,

$$\rho(P_f) = \rho_{max} + (\rho_0 - \rho_{max})e^{-\beta \times P_f}, \tag{12}$$

where ρ_0 is the initial density of the powder, ρ_{max} is the maximum density of the particulates, and β is an empirical compressibility coefficient; Osswald and Stradinis give an average value of 2.38 MPa^{-1} for wax-coated RDX. An appropriate value of β for ice cream powder is not known. The maximum density of the ice cream mix is similar to that of water, 1000 kg/m^3. Assuming 400% overrun, the initial density of the powder is 200 kg/m^3. The density of a 100% overrun product is 500 kg/m^3. Using Eq. 12 and 2.38 MPa^{-1} for β, the additional pressure required to achieve this compression ratio (5:2) is 1.97 x 10^5 Pa (28.64 psi). This is the same order of magnitude as was applied to an ice cream powder sample in a test described in Chapter 4.

A rough estimate of the power required to compress the powder can be made by assuming that the piston applies a force equal to P_f times the cross-sectional area, A_c, for its entire forward stroke. The force transmitted through the particles along the length of the cylinder decays exponentially (Rosenzweig, 1995), so the powder closest to the piston is compacted first, until it reaches the maximum density for the applied force. The force is then transmitted through the compacted portion of the powder to the uncompressed portion. Eventually the powder at the end of the cylinder is influenced by the force applied by the piston. This model does not account for the possibility that particles could form interconnected chains along the cylinder length and no longer behave as a fine powder. The compression work can be estimated as the product of the applied force and the distance traveled by the piston. The frequency of the piston motion determines the power required. The frequency, f, of the piston cycle is determined by the uncompressed volume flow rate of the ice cream powder,

$$f = \frac{(\bar{O}+1) \times \dfrac{m_{H_2O}}{\rho_{H_2O}}}{A_c \times L_s}. \tag{13}$$

This frequency calculation neglects pauses of the piston stroke to vent carbon dioxide and allow the compacted "block" to drop out. The power for the compression is then

$$\dot{W}_{extruder} = P_f \times A_c \times L_s \times f. \tag{14}$$

Because A_c and L_s are also in the denominator of the expression for frequency, these terms drop out, leading to an expression independent of the piston-cylinder geometry.

$$\frac{\dot{W}_{extruder}}{m_{H_2O}} = P_f \frac{\bar{O}+1}{\rho_{H_2O}}. \tag{15}$$

This model should be revisited after the properties of the ice cream powder are investigated.

26

3.4.4 Sample Power Consumption of Four Components

Table 3.2 shows the power requirement for the three exit conditions modeled using the methods presented in the previous sections. The carbon dioxide compressor and pre-cooling refrigeration cycle compressor are the main power consumers. In the cart model, carbon dioxide is not recycled or condensed, so the power consumption of the compressor and the condensing unit are zero. The power required to compress the powder is small relative to the other process components; however compressing the powder has a very strong effect on the power required for the carbon dioxide compression. More carbon dioxide is recovered at $P_{sat,v}$ when the compression is carried out, reducing the load on the first stage carbon dioxide compressor.

Table 3.2. Energy consumed per kilogram ice cream mix.

Exit State	Carbon Dioxide Compression[1]	Condensing Unit	Ice cream Mix Pump	Piston Extrusion
-20°C, 285 psi	58.16 kJ/kg[2]	71.28 kJ/kg	7.03 kJ/kg	3.19 kJ/kg[2]
-20°C, 285 psi	98.98 kJ/kg	71.28 kJ/kg	7.03 kJ/kg	~0 kJ/kg
-40°C, 146 psi	118.32 kJ/kg	87.97 kJ/kg	7.16 kJ/kg	~0 kJ/kg
-40°C, 14.7 psi	0 kJ/kg	0 kJ/kg	7.49 kJ/kg	~0 kJ/kg

[1]assumes 400% overrun powder, carbon dioxide recovered and compressed in two stages
[2]assumes powder compression from 400% to 100% overrun, carbon dioxide recovered at $P_{sat,v}$ during powder compression

3.4.5 Screw Extrusion

Screw extrusion is an alternate method to extract the ice cream powder. The incompressible solids flow can be modeled according to (Bernhardt, 1959). In the screw size required to accommodate the flow rate of the ice cream, the fine powder will undergo internal shear, so the flow can be modeled as a fluid with an appropriate viscosity. The flow is moved down the channel by viscous drag and impeded by the pressure gradient imposed by the die at the end of the screw. If there is no die the flow is moved forward by the pressure gradient from $P_{sat,v}$ at the entrance to the screw to P_{atm} at the end of the screw. Figure 3-4 shows the screw geometry. For a simple model, the screw channel is "unwound" into a straight channel of width w and height h, with the walls corresponding to the flight(s) in the screw. Assuming h<<w, the Boussinesq approximation is valid.
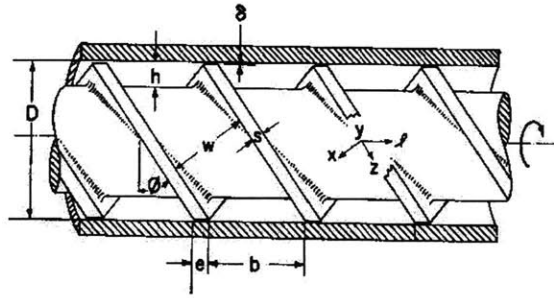
Figure 3-4 Screw extruder geometry. [Modified from (Bernhardt,1959).]

Using the variables shown in Figure 3-4, Bernhardt gives the volumetric drag flow rate, Q_d, as

$$\dot{Q}_d = \frac{U_z * w * h * F_d}{2},\tag{19}$$

where F_d is a shape factor for drag flow based on the channel depth-to-width ratio and U_z is the velocity of the barrel in the down the channel direction, given by

$$U_z = N * \pi * D * \cos(\varphi).\tag{20}$$

N is the rotation rate of the screw, D is the diameter of the barrel around the screw and φ is the helix angle. Typically in a single flight screw, the channel width is similar to the diameter of the screw, giving $\varphi \sim 17.6$ degrees. The shape factor, F_d varies from 1.0 for a depth-to-width ratio approaching zero to a value of 0.5 for a depth-to-width ratio of 1.0.

The volumetric pressure flow, Q_p, again following Bernhardt, is

$$\dot{Q}_p = \frac{-w * h^3 * F_p * \dfrac{dp}{dz}}{12\mu},\tag{21}$$

where F_p is a shape factor for pressure-flow, $\dfrac{dp}{dz}$ is the pressure gradient along the channel and μ is the viscosity of the powder. F_p varies from 1.0 for a depth-to-width ratio approaching zero to a value of 0.42 for a depth-to-width ratio of 1.0. The powder viscosity should be high due to the large solids content and the cohesion of the particles as any melting occurs. For these models, the viscosity of cookie cream premix at 65°C was used, 29.6 Pa-s. The pressure gradient is determined by the required pressure gain for compression or the pressure drop to atmospheric conditions along the length of the screw channel. The sum of the drag and pressure flows gives the total volume flow of the ice cream product. The small volume of back flow through the clearance between the channel flights and the barrel is neglected. The channel length, rotation rate and screw

28

diameter can be varied to design an extruder that meets the flow requirements. The rotation rate should not typically exceed 180 rpm, and smaller values will reduce the shearing and heating of the powder.

In the screw extrusion model by Bernhardt there are three causes of power dissipation: shear in the channel, the pressure gradient down the channel and shear in the clearance between the flight and the barrel wall. Bernhardt gives the power dissipation by shear in the channel as

$$P_s = \pi^3 D^3 N^2 \mu * \left(1 - \frac{e}{e+b}\right) * \left(\left(1 + 3\left(\frac{Q_p}{Q_d}\right)^2\right)\cos^2(\varphi) + 4\sin^2(\varphi)\right) * \frac{L}{h}, \quad (22)$$

where e is the flight thickness, b is the screw flight width in the axial direction, and L is the length of the screw. Power dissipation due to pressure is

$$P_p = (Q_p + Q_d) * \Delta P, \quad (23)$$

where ΔP is the change in pressure from the beginning to the end of the screw. Power dissipation due to the clearance between the flights and the barrel is

$$P_c = \frac{\pi^2 D^2 N^2 \mu_\delta e L}{\delta * \tan(\varphi)}, \quad (24)$$

where δ is the clearance between the flight and the barrel. The viscosity in the clearance, μ_δ, is the viscosity of a highly sheared layer of the ice cream. For these models, the viscosity of light cream was used, 0.004 Pa-s.

Table 3.3 shows the resulting geometry and power requirement for a screw to extrude 400% overrun ice cream powder at a mix flow rate of approximately 1000 L/hr. The depth-to-width ratio is 0.39, giving F_d equal to 0.78 and F_p equal to 0.74. The power required for screw extrusion can be compared to the power required for the piston-cylinder apparatus by multiplying the result in Table 3.2 by the mix flow rate and the density of ice cream mix. The power required to extract and compress ~1000 L/hr of ice cream mix by screw extrusion, 1.51 kW, is slightly larger than the power required to compress the powder with the piston-cylinder apparatus, 0.93 kW; however the screw extrusion model accounts for shearing of the powder along the extruder walls. If the powder does not need to be compressed, the screw extruder simply meters the product continuously and reduces the pressure in the product from $P_{sat,v}$ to P_{atm} in a controlled manner. The pressure in the product chamber provides most of the motive power.

Table 3.3 Screw extruder geometry and power consumption (~1000 L/hr ice cream mix).

Exit state	D [m]	H [m]	L [m]	N [rpm]	Power [kW]
Uncompressed, -20°C, 1.965 x 10⁶Pa (285psi)	0.05	0.017	0.2	60	0.52
100% overrun, -20°C, 1.965 x 10⁶Pa (285psi)	0.16	0.047	1	180	1.51

3.5 Clathrate Hydrates

Clathrate hydrates are solid formations of water with a small non-polar molecule, such as a light hydrocarbon or carbon dioxide, trapped in the lattice. The hydrogen-bonded water molecules trap the guest gas molecule by geometrical constraints, not by chemical bonding. The water-carbon dioxide clathrate phase is thermodynamically stable in two of the pressure and temperature ranges that occur in the flash freezing process. A viable thermodynamic state for clathrates occurs in the emulsion chamber if the fluids are cooler than 284 K and in the product chamber at $P_{sat,v}$ before the powder is brought to atmospheric pressure. A phase diagram for carbon dioxide and water is shown in Figure 3-5.
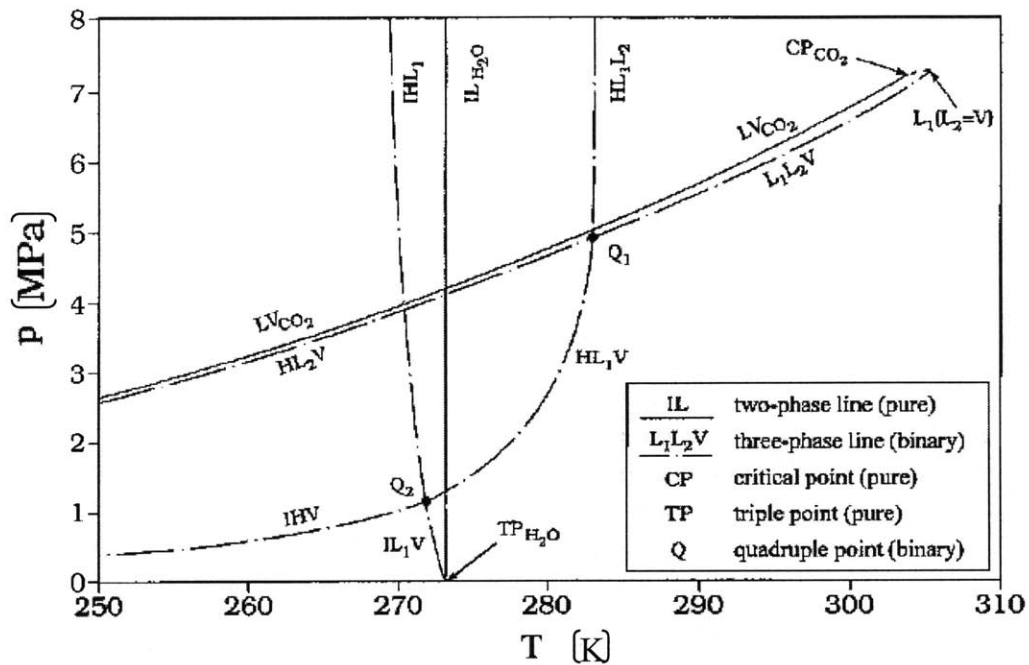
Figure 3-5 Carbon dioxide-water phase diagram. H-hydrate, L1-water, L2-liquid carbon dioxide, V-carbon dioxide vapor, I-water ice [Source: Wendland]

Clathrates form upon contact at the interface between liquid carbon dioxide and water (Irvin et al, 2000), particularly with increasing pressure and decreasing temperature from the phase boundary. A hydrate skin forms, limiting the rate of formation to the CO_2-water diffusion rate, less than 1.95×10^{-9} m^2/s (Mills, 1995). The hydrate skin is likely to collapse when it is disturbed, exposing new surface area for further clathrate formation (Irvin et al, 2000). In the flash freezing process conditions for clathrate formation are favorable. The atomized spray from the first nozzle ensures a very large water or ice cream mix surface area in the liquid carbon dioxide. In addition, the fluid in the chamber is moving turbulently, possibly increasing the collapse of hydrate skins. The

30

rapid mixing and short residence time of the fluids prevent the emulsion chamber from freezing solid.

The clathrate particle diameter is typically close to 6×10^{-6} m, but can be as large as 2.7×10^{-5} m (Clarke, 2005). In the proof-of-principle apparatus, the nozzle channels are approximately 1.27×10^{-4} m wide, but several particles could form a clump across the gap. Nozzle blockage is more likely when freezing pure water than when freezing ice cream mix because the additional ingredients in ice cream mix reduce the water-carbon dioxide contact and may moderate clumping of clathrates. Heat can be applied to dissociate the clathrates and reopen the nozzle. The hydration number, or ratio of water to carbon dioxide molecules, in a clathrate is approximately six, giving a carbon dioxide to water mass ratio of 0.407 in a clathrate. The mass flow ratio of carbon dioxide to water in the flash freezing process is greater than one, ensuring that even if all of the water were converted to clathrates, a \carbon dioxide solution would remain.

In ice cream mix, clathrate formation is reduced because the water volume is only ~60% of the mix volume and some of the ingredients are inhibitors to clathrate formation. Clathrate formation is inhibited by the presence of electrolytes, alcohol or sucrose dissolved in the water solution (Chun, 1999). Ice cream contains about 10% sucrose by mass and 20-30% fats and NMS.

Carbon dioxide-water clathrates are not thermodynamically stable at atmospheric pressure; however, particularly at temperatures below 0°C, the dissociation rate is extremely slow (Gudmundsson, 2000). In a test by Kang et al (Kang, 2001), significant clathrate dissociation in a solid block of carbon dioxide clathrates did not occur for at least 92 minutes after the sample was exposed to atmospheric pressure. The enthalpy of dissociation of the carbon dioxide clathrate (~560 kJ/kg) (Anderson, 2003) is larger than the enthalpy of fusion of water (334.2 kJ/kg), causing the water molecules to go directly to conventional ice when the clathrate collapses, as well as providing additional cooling. Clathrates may exist with the ice in the flash frozen product. The density of clathrates is approximately 1120 kg/m^3 (Anderson, 2003), which is larger than the density of ice. If a volume of product contains a high concentration of clathrates, the amount of water or ice cream mix in the product will be over-estimated. In addition, a high concentration of clathrates will reduce the amount of carbon dioxide recovered from the product.

3.6 Emulsion

The emulsion of carbon dioxide and ice cream mix is important for the direct freezing of the mix. The solubility of carbon dioxide in water in the emulsion chamber is less than 8.8×10^{-4} kg CO_2/kg H_2O (0.02 moles CO_2/L H_2O) (Chapoy, 2004). Under quiescent conditions in the absence of clathrate formation, the non-polar, less dense carbon dioxide droplets rise from a mixture of the fluids and coalesce to form a continuous phase above the water. Gentle stirring of the fluids can easily redisperse the carbon dioxide in the water (Lee, 1999). The fluids do not form a thermodynamically stable emulsion, but addition of surfactants may stabilize the emulsion for a long period of time. Emulsions with high molecular weight surfactants that are nevertheless unstable are maintained for less than a couple seconds (Lee, 1999). The highly turbulent emulsion chamber and short residence time found in the flash-freezing process are necessary to

mechanically mix the fluids to ensure intimate direct contact as the mix and carbon dioxide are pumped through the nozzle.

The emulsion direction, carbon dioxide in water or water in carbon dioxide, could have implications for the volume flow rate of the combined fluids through the second nozzle because water has a higher volume flow rate than carbon dioxide in the atomizing nozzles. The water or ice cream mix is broken up into micro-droplets by the first nozzle and sprayed into the liquid carbon dioxide. The volume ratio of carbon dioxide to mix in the emulsion chamber is greater than one. While the favorable emulsion direction is carbon dioxide in a continuous water phase (Lee, 1999), it is unlikely that the emulsion inverts in the chamber. In tests with the proof-of-principle apparatus the volume flow rate for the combined fluids is between the flow rate of pure water and the flow rate of pure carbon dioxide. The flow properties of both fluids may have an effect because the estimated diameter of the water or ice cream mix droplets is on the order of the dimension of the channels in the nozzle ($\sim 10^{-4}$ m).

The ingredients found in ice cream mix in addition to water should not significantly change the state of mixing in the emulsion chamber. Milk fat is mostly solid up to 38 °C. Vapor carbon dioxide would favor dissolving in liquid phase fat due to the low polarity of both species; however at refrigerator temperatures, pH and freezing point measurements indicate that the carbon dioxide dissolves in the aqueous skim portion of milk (Ma, 2003). The triglycerides in ice cream have varying freezing temperatures (Marshall, 2003), but the majority of the fat content should be solid after the pre-cooling step and therefore insoluble with carbon dioxide.

CHAPTER 4 – PROOF OF PRINCIPLE APPARATUS

4.1 Overview of Apparatus

The expansion process has been demonstrated and explored using a proof-of-principle apparatus, initially freezing water, then freezing ice cream, frozen yogurt, and sorbet mixes. Figure 4-1 shows the proof-of-principle apparatus. The batch process apparatus can hold approximately three liters of ice cream in the product chamber. This apparatus allows investigation of nozzle sizes and initial correlation of product characteristics with process parameters and ingredients.

The continuous cycle is modified in several ways to implement the small-scale batch process. Ice cream mix is pre-loaded into the ingredients chamber. Vapor phase carbon dioxide is used to pressurize the ice cream mix and drive it through the system. A warm-water bucket ensures that the carbon dioxide is in the vapor phase. In place of a condensing unit, both liquids are pre-cooled in an ice bucket heat exchanger. Before each test the product chamber is pre-cooled by liquid nitrogen in a removable insulated container. The product chamber can be opened at the bottom to extract product at the end of a test. The exhaust carbon dioxide is vented to the atmosphere.
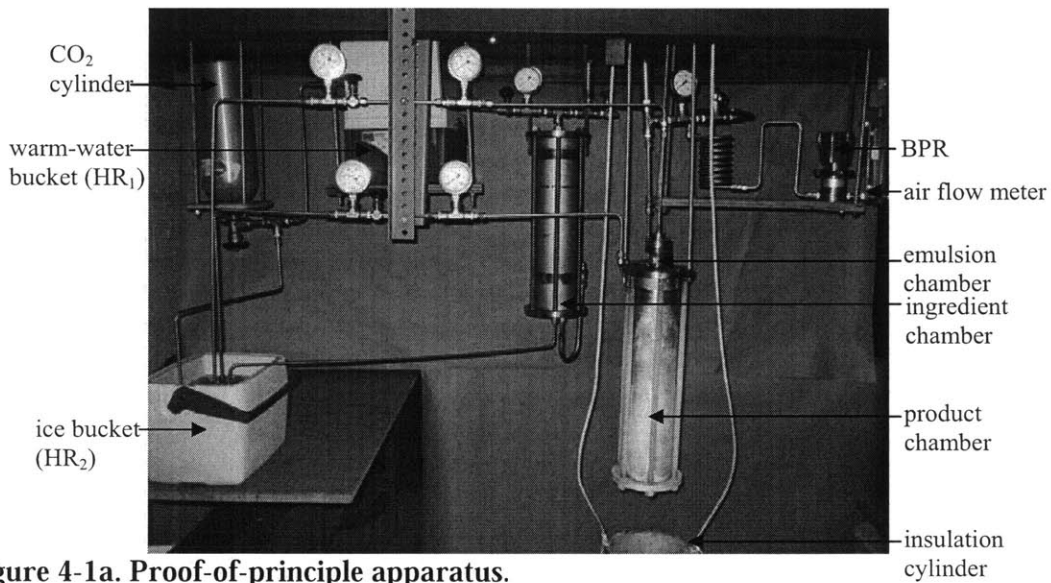
Figure 4-1a. Proof-of-principle apparatus.
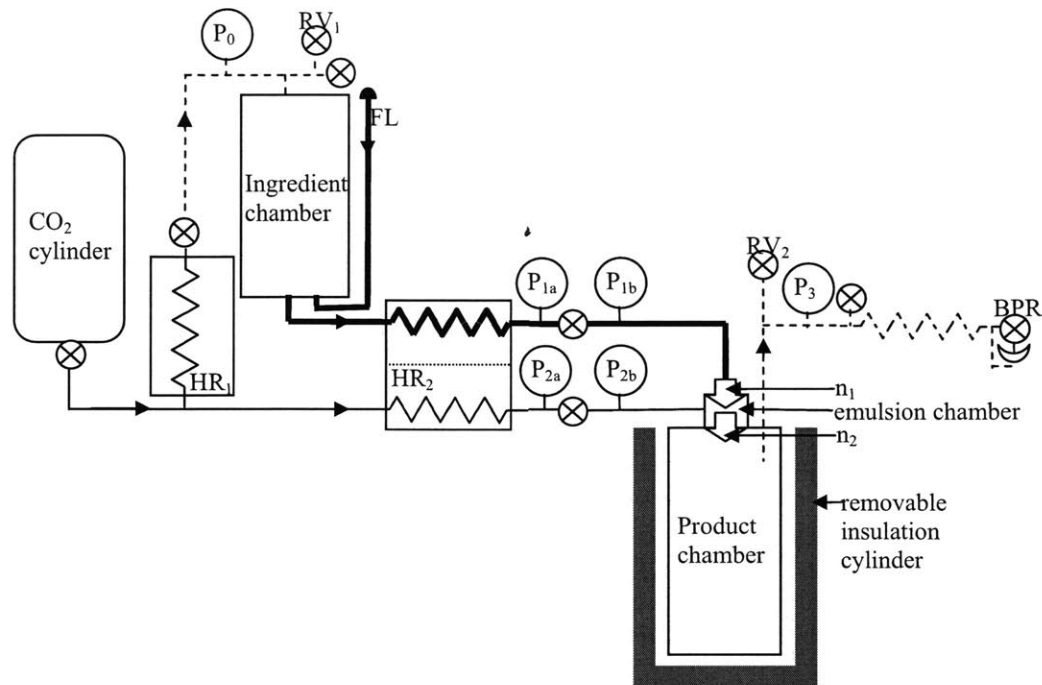
Figure 4-1b. Schematic of proof-of-principle apparatus. FL-fill line, RV- relief valve, HR_1-heat reservoir (~30°C), HR_2-heat reservoir (2°C), n_1-ingredient nozzle, n_2-combined fluid nozzle, $P_{2b} = P_{CO2,l}$, $P_3 = P_{sat,v}$

Stainless steel is preferred for dairy processing equipment because it is corrosion resistant. In addition, milk in contact with copper or iron can take on a metallic flavor. The proof-of-principle apparatus uses parts made of steel with the exception of the nozzles and the relief valves. The ingredient chamber is formed from 0.4064 m (16") of 0.1016 m (4") ANSI Schedule 40 steel pipe and 0.0127 m (0.5") thick steel end plates held together by six 0.0127 m (0.5") steel bolts. A pressure seal is formed by compressing rubber o-rings between a groove in each end plate and the matching pipe lip. The size of the ingredient chamber affects the amount of carbon dioxide used in the batch process because the ingredient chamber volume must be filled with high pressure carbon dioxide vapor when all of the ice cream mix has been driven out of the ingredient chamber. Standard swagelok pipe fittings are threaded into holes in the end plates for inlet and outlet ports. A Bertram Controls 5100 Series relief valve[1] rated for 9.79×10^6 Pa (1420 psi) is in-line with the inlet to the ingredient chamber. A 0.0127 m (0.5") tube with a capped end above the top of the ingredient chamber is also threaded into the bottom end plate to allow for filling.

The product chamber is formed from 0.453 m (18") of ANSI Schedule 40 pipe. The size of the product chamber constrains the volume of product produced in one batch. The volume of mix used is less than one fourth the volume of the product chamber due to the low density of the product powder. A pressure seal is formed by steel end plates and rubber o-rings as in the ingredient chamber, and a relief valve is installed in-line with the

---

[1] Available from Circle Seal Controls, Inc. (http://www.circle-seal.com/prod/relief/relief_valves.html)

carbon dioxide vent. The vent for carbon dioxide vapor exiting the product chamber is 6.35×10^{-3} m (¼") tubing welded into the top end plate 0.030 m (1.2") from the nozzle, extending 0.054 m (2.125") down. Because this places the vent opening within the nozzle spray cone a 0.0254 m (1") diameter simple plastic shield is attached to the vent to prevent frozen solids from blocking the vent. A 2.0 GPH Delavan oil burner spray nozzle[2] is threaded into a hole in the top end plate.

The emulsion chamber is formed by a 0.0254 m (1") outer diameter steel cylinder welded to the top end plate of the product chamber. The emulsion chamber is 0.0381m (1.5") tall. This volume (1.93×10^{-5} m^3) is five to ten times the total volume of fluid that passes through the chamber each second. A length of 6.35×10^{-3} m (0.25") tube is welded into the emulsion chamber wall for the carbon dioxide inlet. The top of the emulsion chamber is bolted to a 0.0508 m (2") diameter, 0.0127 m (0.5") thick steel end plate with a matching lip and groove compressing a rubber o-ring to form a pressure seal. A Delavan 1.0GPH oil burner spray nozzle is threaded into the bottom of the steel end plate and a length of 6.35×10^{-3} m (0.25") tube is welded to the top end of the plate for the ice cream mix inlet.

The product and emulsion chamber are mounted at shoulder height below a platform. This allows the bottom of the product chamber to be opened to remove the frozen product without disturbing the nozzle and vent at the top end of the chamber. Two tabs are welded to the side of the product vessel so that it does not fall when the bolts are removed to take off the bottom plate. For insulation, two nested cylinders longer than the length of the product chamber are filled with FOAM-IT Series 3 two-component rigid polyurethane foam[3]. The insulation is hung from the platform by rope so that it can be dropped down and raised quickly.

The pressure in the product vessel is controlled by a 26-1700 Series TESCOM Back Pressure Regulator (BPR)[4] with a range of 6.89×10^4 to 1.03×10^7Pa (10-1500 psi) and 1.03×10^5 (14.9 psi) accuracy. The flow of ice cream mix is controlled by the valve next to pressure gage P_{1b} in the figure. The flow of carbon dioxide into the emulsion chamber is controlled by the valve next to pressure gage P_{2b}. An additional valve placed before the BPR makes it possible to bypass the BPR when the product vessel is vented. Pressure gages P_0 and P_{1a} follow the pressure driving the ice cream mix. Pressure gage P_{2a} follows the pressure available from the carbon dioxide. Pressure gage P_{2b} follows the pressure in the emulsion chamber and is used to determine the appropriate valve opening for the flow of carbon dioxide into the emulsion chamber.

The heat exchanger coils and connecting piping are made from 6.35×10^{-3} m (¼") tubing, attached by standard swagelok fittings. The coils are made by winding 3.66 m (12 ft) of tubing for each flow. The carbon dioxide is vaporized by two full coil lengths placed in heat reservoir one, a Coleman 8 Qt. Personal Cooler that is filled with hot tap water (~30°C). The ice cream mix and liquid carbon dioxide are pre-cooled by two full coil lengths placed in heat reservoir two, a Coleman 6 Personal Cooler that is filled with ice and water. An additional coil length is inserted between the carbon dioxide vent in the product chamber and the BPR. This was intended to warm the vented carbon dioxide to a temperature appropriate for the BPR.

---

[2] Available from Goodrich Delavan Spray Technologies (http://www.delavaninc.com/oilburner.htm)
[3] Available from Smooth-On Liquid Rubbers and Plastics (http://www.smooth-on.com/foams).
[4] Available from Tescom Corporation (http://www.tescom.com/icd/icd04.php)

The carbon dioxide source for the proof-of-principle apparatus is a 22.24 N (5 lbf) CO_2 cylinder. The cylinder is inverted so that gravity causes liquid phase carbon dioxide to enter the system. The cylinder is filled with food grade carbon dioxide, which has a minimum purity of 99.95% (Toromont Process Systems). Carbon dioxide for beverage service is available from Airgas in 222.4 N (50 lbf) cylinders[5]. Fifty pound cylinders are also available with a siphon, which would allow the cylinder to be mounted upright.

4.2 Nozzles

4.2.1 Types

The proof-of-principle apparatus uses two Delavan fuel nozzles typically found in oil burners. These high pressure "atomizing" nozzles break the fluid up into a uniform spray of micro-droplets, which is important in the novel freezing process to create the emulsion of carbon dioxide and ice cream mix as well as form the powdery texture of the frozen ice cream. The nozzles use a swirl chamber to induce rotation in the flow before ejecting the liquid through a small orifice. The Delavan nozzles are rated for standard flow capacities in gallons per hour (GPH), standard spray angles in degrees, and solid (B) or hollow (A) cone spray geometries. In this apparatus the ingredient nozzle is a 1.0 GPH 70°B and the combined fluid nozzle is a 2.0 GPH 70°B. With No. 2 fuel oil, the 1.0 GPH nozzle, operating at 6.9×10^5 Pa (100 psi), sprays oil droplets with an average diameter of 50 microns (Olson, 2003). Droplet size decreases with increasing pressure drop, decreasing nozzle flow rating, wider spray angles or decreasing fluid viscosity.

Alternate standard nozzle flow rates, spray angles and geometries are available. Smaller angle nozzles may be desirable to increase the distance that frozen micro-droplets fall before hitting the walls of the product chamber. This is particularly pertinent for expansions to atmospheric pressure to reduce the surrounding insulation requirements. Hollow cone geometries may be useful to avoid blocking the nozzle in a batch process. The fluid that is ejected from the center of the nozzle is dispersed over a smaller area than the fluid at the edges of the spray. A cone-shaped snow pile forms because the snow adheres loosely to itself due to small amounts of remaining moisture and or the structure of the fat. The tip of the cone pile can obstruct the nozzle orifice before a collection container is full.

4.2.2 Flow rates

The fluid flow rate through the Delavan nozzles is determined by the nozzle size, the pressure drop across the nozzle and the fluid properties, in particular viscosity and density. According to the information provided with the oil burner nozzles (Olson, 2003), the flow rate scales with pressure according to the approximate relation

$$F_b = F_a * \left(\frac{P_b}{P_a}\right)^{0.5}, \tag{1}$$

[5] Item number FG50

where P_a is the pressure at which the nozzle is calibrated and F_a is the corresponding flow rate. For a nozzle of a different size, the calibrated flow rate can be multiplied by the ratio of the GPH ratings for the two nozzles.

The 1.0 GPH nozzle was calibrated by driving water from the ingredient chamber through the ice bath heat exchanger and then through the nozzle with a pressure drop across the nozzle of 6.89×10^5 to 13.79×10^5 Pa (100-200 psi) and measuring the time required to collect 50 mL in a beaker. The predicted flow rate at 6.89×10^5 Pa (100 psi) was calculated for each measurement according to Eq. 1. Figure 4-3a shows the measured flow rates and the curve given by Eq. 1 with the average flow rate calculated for a pressure drop of 6.89×10^5 Pa (100 psi).
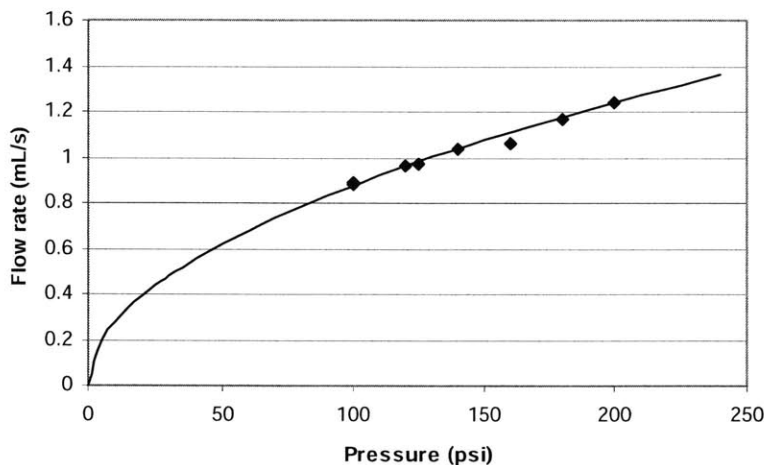
Figure 4-2a. Water flow rate, 1.0 GPH nozzle. The solid line is the predicted flow rate for the calculated calibration at 6.98×10^5 Pa (100 psi).

A flow rate calibration for carbon dioxide was calculated similarly using a 2.0 GPH nozzle. The fluid was passed through the ice bath heat exchanger and the pressure before the nozzle was maintained at greater than 4.137×10^6 Pa (600 psi) to ensure liquid phase upstream of the nozzle. The pressure drop across the nozzle was maintained by controlling the pressure in the product chamber with the back pressure regulator. The volume flow rate of the vented carbon dioxide vapor was measured at atmospheric pressure using a Dwyer Rate-Master air flow meter. The vapor volume flow rate was converted to a mass flow rate based on the density of carbon dioxide at standard temperature and pressure. The volume flow rate of liquid carbon dioxide through the nozzle was calculated from the vented mass flow rate and an average calibration value for 6.89×10^5 Pa (100 psi) was calculated as for water. The assumption of standard temperature and pressure carbon dioxide vapor in the flow meter is made because the flow meter is connected after the BPR and the product chamber remained at room temperature during the test due to its large heat capacity. Figure 4-2b shows the measured flow rates and the curve given by Eq. 1 and the average calibration for 6.89×10^5 Pa (100 psi). Two points, indicated by triangles, are not near the predicted curve. These points correspond to tests where the pressure before the nozzle dropped below 4.137×10^6 Pa (600 psi) and at least some vapor phase carbon dioxide passed through the

nozzle. The calibration tests may indicate that the carbon dioxide flow rate does not follow Eq. 1 due to flashing at or near the exit of the nozzle.
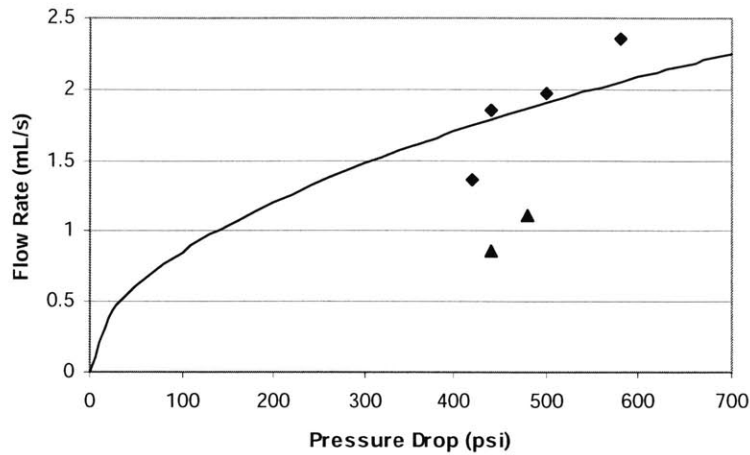
Figure 4-2b. Carbon dioxide flow rate, 2.0 GPH nozzle. The solid line is the predicted flow rate for the calculated calibration at 6.98×10^5 Pa (100 psi). The two triangle points correspond to cases where the pressure before the nozzle dropped below 4.137×10^6 Pa (600 psi).

In addition to pressure drop, the flow rate through the nozzle is affected by viscosity. Higher viscosity fluids produce a larger volumetric flow rate in the Delavan oil burner spray nozzles. This is indicated both by laboratory data collected by Delavan (Olson, 2003) and in the calibration data presented here. Table 4.1 shows the calibrated volume flow rates of water, 10% fat ice cream mix and liquid phase carbon dioxide through the relevant nozzle at 6.89×10^5 Pa (100 psi). The flow rate of ice cream mix is larger than that of water. The flow rate of carbon dioxide through a 1.0 GPH nozzle would be approximately half that of water. Water at 5 °C is 15 times more viscous than liquid carbon dioxide. A standard ice cream mix at 5 °C is 50 to 80 times more viscous than water, with a viscosity of approximately 0.080-0.120 Pa-s (Bohn, 2005). It should be noted that ice cream mix is a non-Newtonian, shear-thinning fluid (Clarke, 2004) and fluid undergoes high shear in the swirl chamber of the nozzle. Olson suggests in the literature accompanying the nozzles (Olson, 2003) that the increased flow rate with viscosity is due to an increase in the thickness of the flow in the nozzle swirl chamber, accommodated by a decrease in the volume of the air column through the swirl chamber and the nozzle orifice.

Table 4.1 Nozzle flow rate calibration.

Fluid	Nozzle	Pressure Drop [Pa]	Flow rate [m^3/s]
Carbon dioxide	2.0 GPH 70°B	6.89×10^5	9.085×10^{-7}
Water	1.0 GPH 70°B	6.89×10^5	8.779×10^{-7}
Ice cream mix (10% fat)	1.0 GPH 70°B	6.89×10^5	11.95×10^{-7}

For the freezing process, the pressure drop across each nozzle is used to meter the fluids in the appropriate ratio. The minimum pressure drop across the ingredient nozzle is 6.89×10^5 Pa (100 psi) in order to ensure a well formed spray, based on literature from Delavan about the nozzle performance (Olson, 2003). The pressure drop across the combined fluid nozzle is constrained on the upstream side by the minimum pressure to maintain the carbon dioxide in the liquid phase and on the downstream side by the pressure of saturated carbon dioxide at the chosen exit temperature.

The flow rate and the ratio of fluids in the combined fluid nozzle has not been calibrated and can be affected by the formation of clathrates, the quality of the emulsion, separation of the fluids due to centrifugal forces in the swirl chamber and the extent of carbon dioxide flashing before the nozzle exit. Based on tests with the proof-of-principle apparatus, the average flow rate through the combined fluid nozzle is much less than the flow rate expected for pure water or ice cream mix and much greater than the flow rate expected for flashing liquid carbon dioxide. The mass of carbon dioxide used during a test was calculated by subtracting the mass of carbon dioxide required to pressurize the ingredient chamber from the change in mass of the carbon dioxide cylinder from the beginning to the end of a test. This value may be over-estimated by 5-10% due to the mass required to initially fill the tubing before the emulsion chamber. The mass of water or ice cream mix used during a test was found by weighing the amount of product formed. This measurement may be underestimated by 1-2% due to product frozen to the product chamber walls or lost in the opening of the product chamber.

The flow rate and ratio of fluids in the combined fluid nozzle was measured for water and carbon dioxide at ~2°C, water and carbon dioxide at room temperature and ice cream mix and carbon dioxide at ~2°C. Under clathrate forming conditions (tests performed at less than 11°C), the total flow rate of water and carbon dioxide through the combined fluid nozzle is dominated by the water flow rate. In tests with the fluids at approximately 2°C, the water-carbon dioxide flow ratio is approximately three, even after reducing the incoming water flow rate by 30% by decreasing the pressure drop across the ingredient nozzle from 1.38×10^6 Pa (200 psi) to 6.89×10^5 Pa (100 psi). Under this condition the water is not successfully frozen; instead the product is cold, carbonated liquid. The large volume of water passing through the nozzle may indicate that the clathrate formation occurs immediately at the entrance to the emulsion chamber. The water tests were repeated without placing ice in the ice-bucket heat exchanger, so that the fluids enter the emulsion chamber at approximately room temperature, and clathrate formation is not possible. The pressure in the emulsion chamber was increased to ensure that the room temperature carbon dioxide did not flash before entering the nozzle and the pressure drop across the ingredient nozzle was maintained at 6.89×10^5Pa (100 psi) to ensure a well developed spray cone. The water-carbon dioxide flow ratio measured was approximately 0.5. The product was again unfrozen, this time due to the higher enthalpy of the incoming flows rather than the low ratio of carbon dioxide to water. The test was finally repeated with ice cream mix, which indicated an ice cream mix-carbon dioxide ratio of 0.73. Frozen powdered ice cream product was obtained. These tests indicate that the flow rate of the combined fluids must be calibrated separately for water and ice cream mix, and the water flow rate is affected by the formation of clathrates.

To make a more general estimate of the volume flow rate of the emulsion through the combined fluid nozzle a new calibration value based on the volume fraction of water

or ice cream mix in the flow was calculated. The calculation is presented for the case of ice cream mix. Assuming that frozen product is formed, the flow ratio of carbon dioxide to ice cream mix can be estimated as the ratio required to freeze the ice cream for the chosen inlet and outlet states. The total volume flow rate of the emulsion is the volume flow rate of ice cream mix plus the volume flow rate of carbon dioxide,

$$\dot{V}_{tot} = \frac{\dot{m}_{icm}}{\rho_{icm}} + R \frac{\dot{m}_{icm}}{\rho_{CO_2,l}},$$ (2a)

where R is the mass ratio of carbon dioxide to ice cream mix required to freeze the ice cream as described in Chapter 3. All of the calculations for the combined fluid volume flow rate through the nozzle are based on the liquid properties of CO_2 in the emulsion chamber; $\rho_{CO2,l}$ is the density of liquid carbon dioxide. The volume fraction of ice cream mix in the flow is then

$$W_{icm} = \frac{m_{icm}}{\rho_{icm} * V_{tot}}$$ (2b)

and the estimated volume flow rate of the combined fluids through a 1.0 GPH nozzle with a 6.89 x 10^5 Pa (100 psi) pressure drop is

$$F_{new} = W_{icm} * F_{icm} + (1 - W_{icm}) * \frac{F_{CO_2}}{2},$$ (2c)

where F_{icm} and F_{CO2} are the calibrated flow rates found in Table 4.1 for the pure fluids in 1.0 GPH and 2.0 GPH nozzles respectively. This flow model predicts pressure drops similar to the pressure drops used for tests with the proof-of-principle apparatus that resulted in frozen product. According to the nozzle literature (Olson, 2003), the flow rate through a nozzle increases with the square root of the density of the fluid and the effect of viscosity is more important than the effect of density. A linear relation between the flow rate of the emulsion through the nozzle and the volume ratio of the fluids is unlikely to be generally correct, but satisfies the data for the small range applicable for this process.

In designing an ice cream process, the required pressure drop across the combined fluid nozzle can be estimated according to Eq. 1, substituting F_{new} for the term F_a, V_{tot} for the term F_b and solving for P_b. The gauge pressure before the combined fluids nozzle (P_{2b} in figure 4-1b) should be equal to the sum of the exit condition pressure (P_3 in figure 4-1b) and P_b calculated according to Eq. 1. The gauge pressure before the first nozzle (P_{1b} in figure 4-1b) is equal to the sum of the pressure before the combined fluids nozzle and the pressure required for the desired ice cream mix flow rate.

In the proof-of-principle apparatus, the maximum pressure available to drive the flows is the pressure of the room temperature carbon dioxide supply, approximately 5.5 x 10^6 Pa (800 psi). This pressure can be increased temporarily by heating the carbon dioxide cylinder. In typical tests pressure P_{1b} is 55.16±2.068 x 10^5Pa (800±30 psi), pressure P_{2b} is 41.37±1.38 x 10^5Pa (600±20 psi) and pressure P_3 is 9.997± 1.034 x 10^5Pa (145±15psi).

4.2.3 Cleaning

The Delavan nozzles come with sintered filters upstream of the nozzle swirl chamber and orifice. In typical applications, the Delavan nozzles are not cleaned because new replacements are cheaper than the labor required for cleaning. During a run on the proof-of-principle apparatus some milk solids build up on the nozzle filters, particularly on the first nozzle. This has not caused a problem for multiple consecutive productions of ice cream batches; a continuous run for longer than 10 minutes has not been tested.

After a run, the nozzles are rinsed by high pressure water and blown out with compressed air. The nozzles are sanitized in boiling water. The nozzles can be taken apart with a screwdriver and the four small slits that make up the swirl chamber can be cleared with a thin piece of brass foil. The nozzles have been taken apart or replaced approximately every 10 tests with the proof-of-principle apparatus. Partially blocked nozzles are indicated by decreased flow rates, stopped flow at low pressure drops and asymmetrical spray cones. In addition, the sintered filter may appear clogged. Proper cleaning and sanitation of the nozzles is essential for health reasons.

4.3 Tests with Water

The proof-of-principle apparatus was initially tested with water to reduce the variables affecting the process and minimize the cleaning requirements. Before a test can be performed, the product chamber must be pre-cooled to ensure that the frozen product is not melted by the high heat capacity chamber walls. 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 a 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 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 volume of nitrogen used for pre-cooling and the delay between pre-cooling and making a batch of product. When the chamber is pre-cooled poorly the temperature of the top plate has been measured as 40°C warmer than the temperature of the bottom plate.

The ice bucket is prepared before pre-cooling the product chamber to allow the water in the ice bucket to equilibrate near the temperature of the ice. 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 0.001 kg/s in 6.35×10^{-3} m (¼") tubing, the approach temperature of the flow is better than 0.04°C for 3.6576 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, marginally 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 based on the small average heat transfer coefficient for natural convection from a 0°C surface to a room temperature environment and the small perimeter of the 6.35×10^{-3} m (¼") tubing.

For short tests using water, the amount of carbon dioxide required to drive the flow was reduced by filling the ingredient chamber. After the test the unused water was drained. Multiple batches of product can be produced without opening the ingredient chamber, but long periods of pressurization with carbon dioxide vapor allow time for the carbon dioxide to dissolve in the unfrozen water or ice cream mix, which could enhance clathrate formation and cause blockage in the nozzle.

The first successful tests with water used a 3.0 GPH nozzle. After pre-cooling the product chamber the ingredient chamber was filled with cold water from the tap and sealed. The warm-water bath was filled with warm tap water (~30°C). The water was then slowly pressurized to 5.516×10^6 Pa (800 psi) by partially opening the valve to allow the carbon dioxide vapor to flow slowly into the top of the ingredient chamber. 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 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.

After the 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 high overrun and some tendency to clump. The amount of water frozen during a run can not 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. A temperature gradient along the length of the product chamber is present because the upper end is exposed to room temperature air and the liquid nitrogen cools from the bottom of the chamber. If the water does not freeze when it is emitted from the nozzle, it can freeze to the bottom wall of the cylinder, making it difficult to extract the sample.

An additional run was carried out using a 2.0 GPH nozzle for the combined flow to reduce the mass flow rate of the carbon dioxide. P_{2b} was increased to 4.41×10^6 Pa (640 psi) and P_{1b} was reduced to 5.378×10^6 Pa (780 psi). The frozen product had 700 % overrun.

In all of the tests, the combined fluid nozzle blocked when the valves were closed at the end of a run. The blockage in the nozzle could hold a 4.137×10^6 Pa (600 psi) pressure difference until it warmed sufficiently to release the small amount of fluids trapped in the intervening piping. In some unsuccessful first attempts the pressure drop from P_{1b} to P_{2b} was restricted to less than 2.76×10^5 Pa (40 psi). It is likely that a well-formed spray of water was not established so the water was not emulsified in the liquid carbon dioxide. Under flow conditions where there was not enough carbon dioxide, the water froze into solid ice due to the cooling capacity of the product vessel base. Carbon dioxide trapped in the ice blocks caused the ice to "pop" as it warmed to atmospheric conditions.

4.4 Tests with Ice Cream Mix

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 the 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. The valves were closed when small amounts of ice cream mix began to come out of the carbon dioxide vent system. The presence of ice cream mix in the vented carbon dioxide indicates that the high overrun frozen product in the vessel has reached the level of the vent opening. In some cases, ice cream mix that had been taken up into the vent was ejected from the bypass valve as whipped foam during venting. 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 was somewhat stratified in the product vessel, with a highly carbonated, very dry powder at the bottom and a warmer, more moist 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 as well as the carbon dioxide-rich environment at the start of a run. The process

was operated one time without replacing the insulation after pre-cooling the product vessel. The frozen powder at the bottom of the vessel was slightly moister and the product at the top approached soft serve consistency. 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.

## 4.5 Carbon Dioxide Flow Observations

The batch process proof-of-principle system typically fills the product vessel in less than four minutes if the nozzles are not blocked by premature formation of solids. In this short period, it is difficult to investigate steady-state behavior, but several inferences can be made from overrun measurements, product vessel fill time and the carbon dioxide vent flow meter readings. The overrun measurement gives the density of the product at atmospheric pressure and can be used to estimate the amount of gas held between the product powder particles while the product is in a carbon dioxide atmosphere. Overrun was measured by weighing an empty collection container of known volume, placing the container in the bottom of the product chamber, making product with the proof-of-principle apparatus and then weighing the container filled with powder. The change in mass divided by the density of the ice cream mix gives the volume of mix in the container. The overrun is the volume of the container minus the volume of the mix divided by the volume of the mix, as described in Chapter 2.

The product chamber fill time can be used to estimate the overrun of the product at saturated carbon dioxide conditions. The fill time corresponds to the first appearance of ice cream mix in the vent system. This is the time required for product to build up to a high enough level in the product chamber that ice cream mix droplets or powder can be entrained in the vented carbon dioxide. The volume of mix in the chamber is estimated as the fill time times the flow rate through the ingredient nozzle calculated according to Eq. 1. The volume of product in the product chamber is estimated based on the interior dimensions of the product vessel below the vent opening. Overrun is calculated as described for the overrun measurement of product at atmospheric pressure.

The vent flow meter reading indicates the amount of carbon dioxide that can be recaptured from the process as a saturated vapor without any special separation work. The carbon dioxide vapor flow rate is measured using the air flow meter that was used for the carbon dioxide flow rate calibration. As before, a correction factor based on the ratio of the specific gravities of carbon dioxide and air is applied to the flow meter reading. The carbon dioxide vapor volume flow rate is converted to a mass flow of carbon dioxide gas at standard temperature and pressure. The flow meter typically settles from a high value near the start of a run to a lower value in the last two minutes of the run. The high initial value may be due to the carbon dioxide initially in the product chamber for the pre-cooling process.

The mix ingredients have a strong effect on the measurements described above. Figure 4-3 shows the trends in the observed overrun, fill time, and vent flow rate for several different fat content mixes. The fat content of mixes made from whole milk and

light cream from the grocery store is varied by changing the milk-cream ratio. The mass of sugar and vanilla are kept constant. The nonfat milk solids (NMS) content of the mix increases slightly as the portion of light cream decreases, but the total solids content of the mix decreases. These mixes have a total solids content close to 30%, whereas mixes from an ice cream manufacturer, such as the Bliss Brothers Dairy mix, typically have 40% total solids.
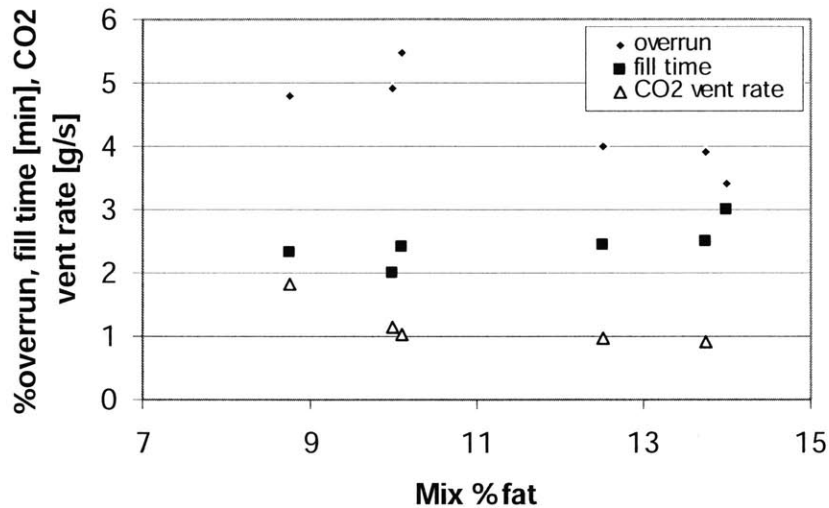
Figure 4-3. Overrun, product vessel fill time and CO_2 vent flow rate versus fat content of ice cream mix. Each test used 1.0 GPH ingredient nozzle, 2.0 GPH combined fluid nozzle, and pressures P_{1b}, P_{2b}, and P_3 equal to 5.5 x 10^6, 4.1 x 10^6, and 1.03 x 10^6 Pa (800, 600, and 150 psi) respectively.

For a fixed pressure drop across the ingredient nozzle and the combined fluid nozzle, lower fat content mixes produce higher overrun product. The product chamber fill time decreases with decreasing fat content. The increased overrun and decreased fill time of lower fat mixes may be because nonfat mixes have better whipability, or ability to incorporate air, than high fat mixes (Marshall, 2003). Additionally, when the collection container is removed from the product chamber, the increased presence of fat could increase the flake cohesion, reducing the gas volume between flakes and thus the overrun of higher fat mixes.

Both the vent rate and the product chamber fill time suggest that the product has a higher overrun in the saturated carbon dioxide environment than at atmospheric pressure. The fill time for 10% fat mix suggests that the ice cream powder has an overrun of up to 1500% before the pressure vessel is vented to atmospheric pressure. This may be an over-estimate of the overrun in the saturated pressure environment because the length scale for uptake of mix into the vent system by convection is unknown and the dimensions of the powder cone in the product chamber are unknown. The estimated powder overrun based on the vent rates is 1050%. This may also be an over-estimate because this estimate assumes that carbon dioxide is only held as a vapor in the

45

interstitial space between the powder particles and does not account for reduced carbon dioxide venting due to solid carbon dioxide flakes or carbon dioxide in solution with the ice cream product. The vent rate is only ~50% of the estimated total carbon dioxide flow rate for the freezing process. The flash-freezing process may require additional power in order to remove more carbon dioxide at saturated pressure or compress a large portion of the flow from atmospheric pressure. Alternatively, the make-up carbon dioxide flow may be significantly increased. The vent rate measurements are only a rough estimate because the vent rate is affected by the pressure drop from the emulsion chamber to the product chamber. This pressure drop varies during a test due to changes in the BPR setting, the actual pressure in the product chamber and the emulsion chamber pressure. To thoroughly investigate this behavior a well instrumented, controlled apparatus is required.

The decrease in vent rate with increased fat content seems to contradict the observation of lower overrun in the product; however, it is possible that the overall carbon dioxide flow rate is reduced with high fat mixes because high fat mixes accommodate less carbon dioxide flow through the combined fluid nozzle. A high fat mix has greater solids content and increased viscosity. This will cause an increase in the volume of mix that flows through the mix nozzle. The increased volume of mix may displace an equivalent volume of carbon dioxide liquid passing through the combined fluid nozzle. The mix is frozen despite the low carbon dioxide to mix ratio because the mix has reduced water content and thus a lower cooling requirement.

4.6 Expansion to Atmospheric Pressure

Ice cream mix was also frozen directly to atmospheric pressure. This mode of operation could be beneficial in a cart-style implementation of the freezing process, obviating the need for a compressor to recycle the carbon dioxide as well as a pressurized product chamber. This reduces the start-up transients as well as simplifying access to the product. The ice cream cannot be sprayed into a completely open environment, however, because the ice cream micro-droplets melt when they are entrained in the warm surrounding air.

Several ice cream product collection methods have been tested, including a 0.15m tall polyethylene terephthalate peanut butter container with a 0.001 m thick wall pressed directly against the top product chamber end plate and a 240 mL (~1 cup) plastic cup held at the bottom end of the open product chamber (about 0.46m below the nozzle). Figure 4-4 is a schematic of these set ups. The peanut butter container significantly reduced air entrainment, allowing frozen product to pile up in a cone shape at the base of the container. The container did not require pre-cooling, but a metal block with a large heat capacity was used to hold the container in place to avoid heat transfer from the operator's hand. The open product chamber has an air-tight o-ring seal near the nozzle. The chamber walls were already cool, due to a prior closed chamber run. The frozen product collected along the length of the chamber walls and then fell as small clumps into the collection container below.

46
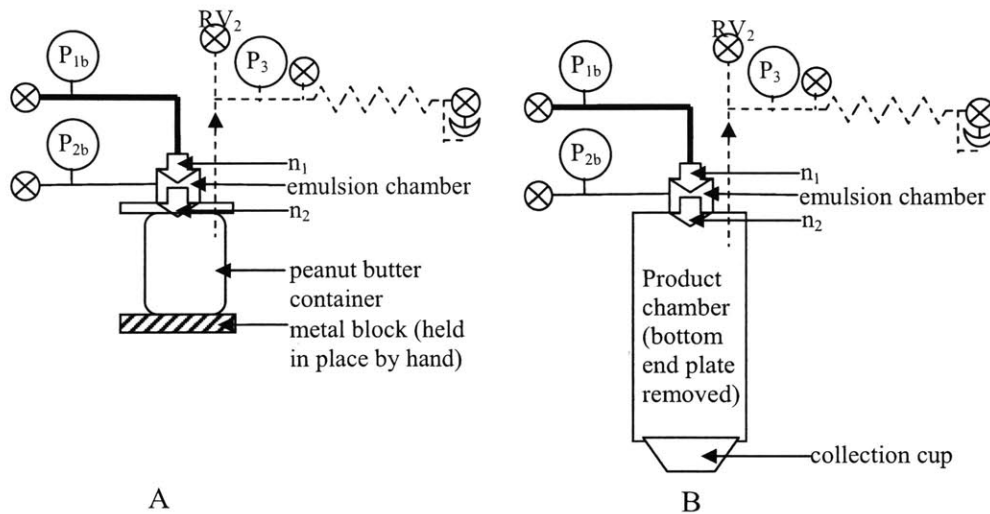
Figure 4-4. Sample atmospheric expansion set-ups. A-plastic peanut butter container held against chamber end plate by hand with metal block, B-collection cup held at bottom of product chamber.

For both collection mechanisms, the ice cream that formed had a moister, creamier, more continuous consistency than the powder formed in a controlled environment. The ice cream was less dense than conventional ice cream, similar to the consistency of whipped topping from a can. The ice cream product melted similarly to soft-serve ice cream when allowed to stand at room temperature. Even increasing the carbon dioxide mass flow ratio by changing the combined flow nozzle to a 3.0 GPH nozzle did not produce the colder, light, dry powder of the product removed from the closed product chamber tests, probably due to the reduced control of the environment in which the expansion occurs.

4.7 Product Details

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 overrun, and some level of carbonation. The powder micro-flakes are approximately 30 microns in diameter. A group with access to a sample of the ice cream powder reported 17 micron ice crystals. Such fine grains melt easily individually due to the large surface area for heat transfer and the open structure of the flakes. Tasters have commented on the sensation that the ice cream powder dissolves on the tongue. The high overrun 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 frostbite in the mouth, possibly due to the insulation of the ice cream mix ingredients.

Packaging and compression tests were carried out on the product. The ice cream was stored in a 1 L plastic peanut butter container with a rubber gasket in an ice chest containing dry ice for three days. At this storage temperature, the free flowing powdered consistency was maintained, though the powder bulk density increased. A light "pfff" upon opening indicated that the carbon dioxide was held in as well. If no attempt to contain the carbonation is made, the carbon dioxide diffuses out of the product, similar the way a soda goes flat as it warms.

The compressibility of the powder was tested using a pre-cooled can and piston. The powder was compressed by a factor of two from an initial 400% overrun with approximately 1.27×10^5 Pa (18.4 psi) pressure. Using an arbor press the ice cream powder was further compressed until some product was extruded through the small gap between the piston and the can. The final volume was approximately one fourth of the initial volume. The ice cream powder was packed densely similar to tightly packed sand. The powder did not melt or recrystallize.

4.8 Effect of Ingredients

Further demonstrations of the process included attempts with sorbet, beer and frozen yogurt mixes. Pectin, an ingredient in commercial sorbet mix, forms a gel that clogs the nozzle channel slits, but a recipe made from store-purchased cranberry juice worked successfully. It was necessary to use the heat gun to unblock the nozzle during the cranberry juice test. Corn syrup, which is present in cranberry juice and some ice cream mixes, depresses the freezing temperature more than cane or beet sugar (Marshall, 2003) and requires increased freezing capacity, which can be achieved by adjusting the pressure drops across the nozzle to cause increased carbon dioxide flow. The beer produced a similar powder to the snow from other mixes; however it is likely that the water froze out of solution with the alcohol. Both frozen yogurt and chocolate flavored ice cream were successful.

The carbonated texture of the ice cream product seems to be affected by the fat content of the mix. The ice cream powder must be observed under a microscope to see the size of the fat globules and whether the fat is partially destabilizing. It is possible that in the emulsion chamber the fat goes into solution in the liquid carbon dioxide because the fat is non-polar and the liquid carbon dioxide is only weakly polar. This could aid in placing the fat on the outside of ice cream micro-flakes, improving the creamy texture. Some tasters have commented on the creamy texture of the product as well as the cohesive behavior of the micro-flakes, possibly caused by the fat structure.

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 to reduce the carbon dioxide flow. Some tasters found that the powder texture was finer for the smaller combined fluids nozzle and the carbon dioxide seemed more finely distributed. The Bliss Brothers Dairy mix produced a powder with a noticeably warmer mouth feel. This is expected where water is displaced by fats (Marshall, 2003).

Ice cream made with high fat content mix has hardly detectable levels of carbonation. The minimum sensory detection of carbonation in yogurt is between 227

and 305 ppm (Ogden, 2002). The carbon dioxide content and state in the product are not known. One limit can be calculated based on the solubility of carbon dioxide in water near ice temperatures, 8.8×10^{-4} kg CO_2/kg H_2O, and the typical water content of ice cream mix, 60%. If the maximum mass of carbon dioxide is dissolved in the water content of the product, the product would be 528 ppm CO_2. If the carbon dioxide content of the product is instead in clathrates, the carbon dioxide concentration could be much larger. Assuming an average composition of six water molecules to one carbon dioxide molecule for the entire water content of the mix, the carbon dioxide concentration in the product would be 245000 ppm. This is much greater than the concentration of carbon dioxide in soda, ~1800 ppm. Product with easily detectable carbon dioxide levels may contain a combination of carbon dioxide in solution with the ingredients and carbon dioxide in clathrates. The concentration of carbon dioxide in the space between the powder particles drops rapidly to the levels in the local atmosphere when the product is removed from the product chamber. The gas phase of the product can diffuse easily because it is continuous around the powder particles. The mass diffusion rate depends on the surface area of the product, but is on the order of seconds. The diffusion constant for carbon dioxide in air is $1.55 \times 10^{-4} m^2$/s. Using 0.1 m as a characteristic length for a product sample, the time constant for diffusion of CO_2 out of the product is 64 seconds.

CHAPTER 5 - DISCUSSION

5.1 Comparison to Conventional Process

To compare the ice cream flash freezing process to a conventional freezing process, standard temperatures and flow rates must be established. The flash freezing process replaces the continuous freezer as well as the hardening tunnel in a conventional ice cream plant. Properties of ice cream freezing systems are typically stated for 100% overrun ice cream frozen to -20°C. Tetra Pak, a manufacturer of ice cream freezers and other equipment, produces continuous freezers with outlet capacities from 10 to 4000 L/hr and hardening tunnels with capacities ranging from 500 L/hr to 15000 L/hr. In a large manufacturing plant a hardening tunnel is typically supplied by several continuous freezers. The following comparisons are made for a 2000 L/hr production rate.

5.1.1 Equipment and Expenses

The equipment for the flash freezing process includes nozzles, an oil-free gas compressor, a high pressure pump for the ice cream mix, a standard cooling unit and an extruder to remove and compress the final product. The number of ingredient nozzles required for this flow rate is calculated using the calibration for 10% fat ice cream mix given in Table 4.1. A 5.56×10^{-4} m³/s (2000 L/hr) freezer making 100% overrun ice cream freezes 2.78×10^{-4} m³/s (1000 L/hr) of mix. With a 6.89×10^{5} Pa (100 psi) pressure drop, 233 1.0 GPH nozzles are needed. The number of nozzles can be reduced to 165 nozzles if the pressure drop is increased from 6.89×10^{5} Pa (100 psi) to 1.38×10^{6} Pa (200 psi), increasing the mix flow rate through one nozzle from 11.95×10^{-7} m³/s to 16.90×10^{-7} m³/s. An equivalent number of 2.0 GPH nozzles are required for the combined fluid. The total cost of these nozzles is on the order of $1000, based on Delavan nozzles purchased from a distributor at $3.20 each.

The minimum area for the required number of nozzles can be calculated for the geometry in Figure 5-1. The Delavan nozzles fit a 5/8" hex wrench (0.016 m). Figure 5-1 shows an arrangement of 18 nozzles in two hexagonal rings around a center nozzle. The number of nozzles in each ring increases by six moving out from the center so that there are 6 nozzles in the first ring, 12 in the second, and so on. The total number of nozzles for an arrangement with one ring is then 1+6=7, for two rings it is 1+6+12=19, and so on. This pattern can be generalized as

$$n = 1 + 6 * \sum_{1}^{r_{tot}} r, \tag{1}$$

where r_{tot} is the number of rings and n is the number of nozzles. The radius R of a circle approximately encompassing these nozzles is given by the distance from the center of the hexagonal rings to outer edge of the arrangement.

$$R = (r_{tot} + 0.5) * d, \tag{2}$$

where d is the characteristic dimension of a nozzle, 0.016m. One hundred sixty nine nozzles can be arranged in seven hexagonal rings around a center nozzle, approximately filling a circle with a radius of 0.119 m (4.7 in). The area of a circle of this radius is 0.0445 m^2.
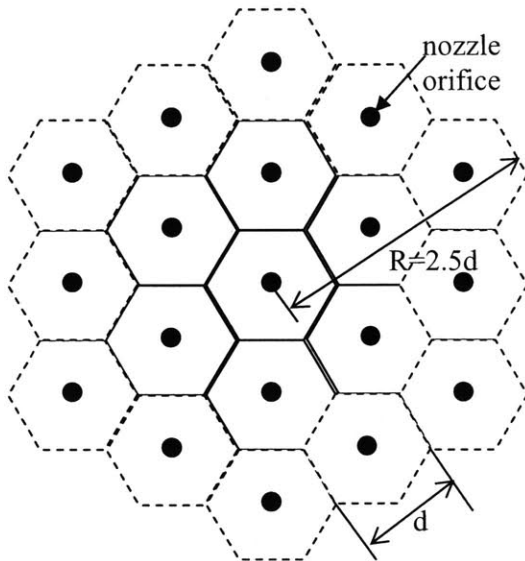
Figure 5-1. Nozzle packing. Two rings, 19 nozzles, d=0.016m (5/8").

A 2000 L/hr continuous freezer typically takes up ~3.1 m^2 (33 ft^2) (Bohn, 2005) of floor space. The floor space required for flash freezing could be significantly smaller than the floor space required for conventional freezing. In addition to the small foot print of the nozzles, the single-step flash freezing process does not require a hardening tunnel, which typically takes up 88 m^2 (Bohn, 2005), or ~29.4 m^2 per continuous freezer.

There are additional costs involved in the time required to freeze the ice cream mix and the maintenance needs of equipment. Both the ice cream mix and the frozen ice cream must be stored to meet distribution demands, but the frozen product requires cooler temperatures and 50% more storage volume than ice cream mix. The flash freezing of the mix occurs within seconds as the carbon dioxide vaporizes. In contrast, the time the mix spends in a scraped heat-exchanger freezer is on the order of minutes and full hardening of a five gallon package takes 6-8 hours in a good hardening tunnel (Marshall,2003).

The actual freezing process does not require any moving parts, whereas the conventional continuous freezer relies on shearing of the ice crystals by the dasher-beater assembly. The conventional hardening tunnel additionally involves several layers of trays conveyed back and forth within the tunnel. These moving parts are likely to require more maintenance than the flash freezing cycle components.

5.1.2 Power

The minimum power consumption for the conventional process is estimated based on the electric draw of a Tetra Pak continuous freezer, the cooling required in the continuous freezer and a typical value for the hardening step. The total electric draw on a 2000 L/hr continuous freezer is approximately 25 kW, the majority of that being for the main dasher drive (Bohn, 2005). The cooling in the continuous freezer is the sum of the cooling to reduce the temperature of the mix from 2°C to -5°C and the cooling required to freeze 50% of the water content in the ice cream mix. For a 2000 L/hr continuous freezer, the cooling rate is 34.9 kJ/s. In an ice cream manufacturing plant, a single ammonia refrigeration cycle typically provides the refrigeration for all of the processes involved in production of the dessert. An ammonia refrigeration cycle operating between -6°C and 22°C with a 70% efficient compressor requires 5.85 kW for the continuous freezer portion of a 2000 L/hr production facility. Conventional continuous freezers typically use ammonia evaporating at -30.6°C (Marshall, 2003) and reject entropy to the environment at a temperature warmer than 22°C, resulting in an underestimate on the order of 50%. For the hardening step the industry rule of thumb is 118.5 kJ/L (425 Btu/gallon) of 100% overrun ice cream (Bohn, 2005), or 65.8 kW for an ice cream production rate of 2000 L/hr. The net power consumption for producing 2000 L/hr of ice cream by the conventional method is estimated as 96.7 kW.

The total power required for the flash-freezing process is the sum of the power to compress the carbon dioxide, pre-cool the fluids, pump the ice cream mix at high pressure and compress the product to 100% overrun. As described in Chapter 3, the power required for the carbon dioxide compression varies depending on the amount of carbon dioxide recovered and the state of the vapor when it is recovered. Using the specific energy consumptions given in Table 3.2 for ice cream at -20°C and 100% overrun the 2000 L/hr system consumes 40.9 kW. This is 42.3% of the estimated power consumption of the conventional continuous freezer and hardening tunnel. This comparison is based on two stages of carbon dioxide recovery assuming carbon dioxide is recovered at $P_{sat,v}$ during the compaction from 400% overrun to 100% overrun powder. 99.8% of the carbon dioxide mass flow is recycled.

Alternatively, if the powder is compressed from 400% to 100% overrun\and the remaining carbon dioxide in the product that passes through the airlock is simply vented, the power consumption is approximately 37.3% of the conventional consumption. The make-up flow of carbon dioxide must be increased to 4.5% of the total carbon dioxide flow, or ~52 kg/hr carbon dioxide for a 2000 L/hr ice cream freezer. In the US the cost of carbon dioxide is on the order of $0.10/kg ($100/ton) (Royal, 2005). For the flash-freezing process, the cost of carbon dioxide per liter of ice cream is $0.0026. The carbon dioxide compression work is 42.6 kJ/kg, about 25% less than the compression work for two stage recovery. Only one compressor is required, reducing equipment and maintenance costs. The pre-cooling cycle requirement is not changed significantly (70.5 kJ/kg).

5.1.3 Pre-Cooling Alternatives

The energy consumption of the condensing unit per kilogram of ice cream mix, 70.5 kJ/kg, is greater than the energy consumption of the single-stage carbon dioxide compressor per kilogram of ice cream mix, 42.6 kJ/kg. The energy consumption rate of the condensing unit could be decreased if the compressed carbon dioxide enters the condensing unit at a temperature cooler than 35°C, which was assumed in the previous calculations based on an air-cooled after-cooler. A lower temperature could be achieved using a water-cooled after-cooler. Assuming water is available at 20°C and the after-cooler heat exchanger achieves an approach of 5°C, the recompressed carbon dioxide would enter the condensing unit at 25°C. The power requirement of the condensing unit would be decreased by almost 30%, making its energy consumption rate comparable to the single-stage carbon dioxide compressor energy consumption rate. Some additional power would be required to pump the water. Water is typically readily available in ice cream manufacturing plants for cleaning purposes.

The flash-freezing process can be implemented without a condensing unit if the carbon dioxide to mix flow ratio and the pressure in the emulsion chamber are increased appropriately for warmer saturated carbon dioxide. This leads to a simpler system with carbon dioxide as the only refrigerant. Figure 5-2 shows the adjusted carbon dioxide refrigeration cycle. Water cooling of the compressed carbon dioxide flow is assumed to condense the carbon dioxide at 25 °C, with a corresponding saturated pressure of 6.43 x 10^6 Pa (933 psi). The new carbon dioxide to mix flow ratio is 0.67. To maintain well-formed spray cones from the ingredient nozzles, ice cream mix must be pumped at a minimum pressure of 7.12 x 10^6 Pa (1033 psi). The power requirement, assuming the ice cream is compressed to 100% overrun while in the product chamber and carbon dioxide is recovered in one stage, is approximately 36.3% of the power estimated for a conventional cycle. This estimate does not include power for pumping the cooling water. Without a condensing unit, the flash freezing process requires a larger carbon dioxide flow, but this may be a minor consideration when a large percent of the flow is recovered.
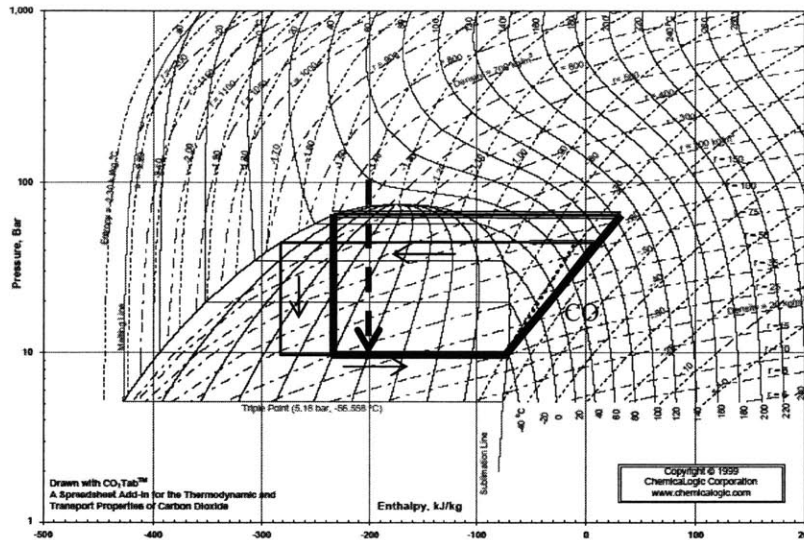
Figure 5-2 Carbon dioxide P-h diagram with main compressor cycle assuming no condensing unit. Bold lines represent water-cooled cycle. Thin lines show original cycle for reference. Dashed arrow indicates path for throttling supercritical carbon dioxide from 40°C and 10 x 10⁶ Pa.

As the temperature of the carbon dioxide entering the emulsion chamber increases, the carbon dioxide to mix flow ratio must be increased as well as the inlet pressure, so the power consumption of the compressor increases. The critical point of carbon dioxide is 31°C. Above this temperature, carbon dioxide is supercritical. Neglecting the presence of ice cream mix, the super critical carbon dioxide will become a mixture of saturated liquid and vapor when it is throttled isenthalpically to the pressure in the product chamber. The quality of the saturated carbon dioxide is determined by the initial carbon dioxide pressure. The dashed arrow in Figure 5-2 shows the path for carbon dioxide at an initial pressure and temperature of 10 x 10⁶ Pa and 40°C respectively. Pure carbon dioxide vapor would exit the product chamber as a saturated vapor at the pressure set by the BPR. The net change in enthalpy of the carbon dioxide during the flash-freezing process depends on the initial pressure and temperature of the carbon dioxide, but for most combinations, the flow ratio of carbon dioxide to ice cream mix must be increased. In the emulsion chamber, ice cream mix may interact differently with supercritical carbon dioxide than liquid carbon dioxide. If more carbon dioxide dissolves in the mix, the cooling due to flashing carbon dioxide and the mass of carbon dioxide recovered may be reduced.

5.2 Food Grade Design

All of the equipment used in the flash-freezing process must be designed to meet food grade standards. Any new food processing technology would require FDA approval. High pressure pumps and screw extruders have been used previously in ice cream mix homogenization and ice cream production. Atomizing nozzles have been used in spray-drying of milk powder. Gas compressors have been used to provide pure gases

54

for breathing and other medical applications. The International Dairy Foods Association (IDFA) provides outlines of basic sanitation, good manufacturing processes and preventive practices. These practices guide consideration of the requirements for sanitary flash-freezing. As stated previously, stainless steel is commonly used in dairy processing equipment. Surfaces are typically polished to reduce the presence of cracks and crevices in which microorganisms can reside.

The elements of the system in contact with the ice cream mix or frozen product should be designed to use standard cleaning-in-place (CIP) processes typically found in dairy manufacturing facilities. These elements include the nozzles, emulsion chamber, product vessel and extrusion mechanism, and the ice cream mix pre-cooling heat exchanger if included. All internal surfaces should be as smooth as possible because any aberration is a location for residue build up. Internal surfaces should also be sloped and free from other depressions to allow draining. CIP normally uses several rinse cycles with water, acidic and alkaline chemicals at up to 5.5×10^5 Pa (80 psi) (Marshall, 2003). The flash-freezing process uses pressures much greater than this, so no special adjustments to accommodate the CIP pressures should be necessary. To clean large chambers, special nozzles with multi-directional spray are typically used. These nozzles feature retractable heads so the manufacturing process is not disturbed. Some auxiliary piping for the CIP process or access inside the pressure vessel to change the nozzles between atomizers for the flash freezing process and cleaning heads may be required. Following the cleaning cycles a chemical sanitizer, such as sodium hypochlorite is typically used. Hot water is not typically used by frozen dessert manufacturers because of the potential for damage to equipment due to large temperature changes.

The sintered filters on the flash freezing nozzles must be removed and cleaned out of place because the cap-shaped filters are designed to catch any material too large to pass through the nozzle spiral chamber. The sintered filters could be replaced by flat in-line filters with an appropriate mesh size, allowing CIP by cross-flow. Related experience with dairy powders and spray atomization can be found in the milk powder processing industry. The Niro Group specializes in milk powder technology, including pressure nozzles and rotary atomizers to atomize the spray into approximately 50 micron droplets and flow separators to remove the fine powder from the recovered airflow. A milk powder facility is typically designed for cleaning-in-place (CIP), but the nozzles are routinely removed, disassembled and cleaned by hand. The nozzles typically operate at $150\text{-}400 \times 10^5$ Pa (>2175 psi) (Westergaard, 2004), at least double the mix pressure required in the continuous flash-freezing cycle models.

The carbon dioxide flow also comes in direct contact with the ice cream mix, so it must be free from contaminants such as oil or metal chips. Ideally the components in contact with the carbon dioxide will be stainless steel. An oil-free compressor and carefully sealed heat exchanger for the after-cooling and pre-cooling are necessary. The CIP circulation should not pass through the compressor and heat exchanger because any ice cream mix in the recovered flow should be removed before the carbon dioxide passes through these components. Carbon dioxide additionally provides a slightly acidic environment, which is a good microbial inhibitor. The carbon dioxide compressor must be "food grade" because the carbon dioxide comes in direct contact with the ice cream mix. Blackmer makes a series of oil-free compressor models, such as HDL322[6], for

---

[6] Available from: HD Industrial Gas Compressors. http://www.blackmer.com. 2005.

chemical and industrial processes. These compressors use special seals to prevent contamination of the fluid chambers. A compressor purchased new and sanitized should be acceptable.

Food grade carbon dioxide is sometimes recovered from the exhaust of ammonia and ethanol processing facilities. Typically a screw compressor with a lubricant separation system is used, resulting in ~5 ppb lubricant in the compressed carbon dioxide (Toromont, 2005). Activated carbon bed filters are used to increase the product purity. Several synthetic food grade lubricants have been developed (i.e. Summit Industrial Products - FG Series), which could be used with an additional filter. Any section of the carbon dioxide recovery line that is before the separator to remove liquid contaminants should be included in the fluid loop for CIP and sanitization. If the carbon dioxide is not recycled, the vent system should still be easily rinsable so that the exhaust does not take on a rancid smell due to milk residue.

5.3 Considerations for Cart Implementation

The flash freezing process produces a powdery carbonated dessert rapidly. This product could lend itself to point-of-sale production, such as a cart or small ice cream stand. A cart implementation can provide advantages in packaging and distribution. The carbonation and low density of the product do not need to be maintained during storage and shipment. A cart system can be autonomous from a power source for short periods of time. Particularly in Europe there is an emphasis on getting the ice cream product to the consumer, in a variety of locations. A cart implementation would ideally be low in weight and space requirements for mobility and simple to operate to accommodate unskilled workers. To this end, the carbon dioxide recompression can be omitted; the ice cream mix and liquid carbon dioxide can be pre-cooled in an ice bucket; and the mix can be pressurized by a pure gas such as carbon dioxide or nitrogen. In the cart implementation it is important to pre-cool the ice cream mix and the carbon dioxide so that a minimum flow ratio can be used because none of the carbon dioxide is recycled.

The cart must be designed for easy access to the ice cream. The ice cream can either be expanded to atmospheric pressure with appropriate reduction of air entrainment, as described in Chapter 4, or the ice cream can be expanded to the desired carbon dioxide saturation pressure by using an insulated product chamber. The product chamber should be as light as possible while meeting the pressure requirements for the process. If a pressurized product chamber is used it must have an air lock to allow extraction of the product. Continuous runs are desirable for two reasons: the heat capacity of the piping will cause start-up transients and in the proof-of-principle batch process the nozzles commonly became blocked when the flow was shut off, requiring heating to restart the flow.

Additionally, the cart must be easily cleanable to maintain sanitary conditions. Clean-in-place standards can be applied as for the continuous cycle implementation. Cleaning could be carried out at a "base station" by connecting to a flow of pressurized cleaning fluids.

5.3.1 Example Cart Sizing

The fluid weight and volume requirements for a mobile cart can be considered according to the time period that a cart should be able to run without returning to a base station and the intended number of servings. The following calculations are for a run time of 2 hours, assuming 150 30 gram servings per hour. This corresponds to freezing approximately 1.25 grams of mix per second, which could be accomplished using one 1.0 GPH nozzle and one 2.0 GPH nozzle. Figure 5-3 shows a schematic of the cart. Ice cream mix and carbon dioxide are pre-cooled in an ice bucket. A model of the fluid requirements is developed for a product collection container that is attached around the nozzle orifice to reduce entrainment of air in the product spray. A vent maintains atmospheric pressure in the product collection container. The model is additionally developed for a separate pressurizing unit for the ice cream mix.

A separate pressurizing unit for the ice cream mix is recommended because the saturated carbon dioxide in the CO_2 cylinder cools as it expands to fill the vacated volume of the ice cream mix cylinder, leading to a decrease in the pressure of the saturated fluid. More carbon dioxide must be contained in the cylinder than can be used for flash freezing. The excess mass of carbon dioxide required depends on the lowest cylinder pressure at which the flash-freezing can still be carried out for the particular cart implementation and the rate of heat transfer into the cylinder from the surroundings. If carbon dioxide is used to pressurize the ice cream mix, as in the proof-of-principle apparatus, the flash-freezing process must stop when the pressure in the cylinder falls below the pressure at which the ice cream mix enters the ingredient nozzle. With a separate pressurizing unit for the mix, the flash-freezing process can continue until the pressure in the cylinder reaches the pressure of saturated carbon dioxide at the temperature of the ice bucket, $P_{CO2,I}$. If the cylinder walls are adiabatic, the specific entropy of the saturated carbon dioxide in the cylinder can be modeled as constant during the expansion. Under this assumption, the mass of carbon dioxide initially in the cylinder must be approximately double the mass of carbon dioxide that is consumed for flash freezing. If instead a high heat transfer rate into the cylinder maintains the carbon dioxide cylinder at the temperature of the environment, the mass of carbon dioxide initially in the cylinder should be approximately 1.2 times the mass of carbon dioxide consumed for flash freezing.

The ice cream mix could be pressurized mechanically or by a separate pressurizing gas. A back-of-the-envelope calculation of the volume and pressure required to use an ideal gas to pressurize the ice cream mix can be made by modeling an isentropic expansion of the ideal gas. Assuming that the ideal gas is always in equilibrium with the ice cream mix and does not go into solution with the ice cream mix, the pressurizing gas will fill the ice cream mix container slowly as mix is metered out of the container through the ingredient nozzle.

The pressure of the gas when it fills the ice cream mix cylinder must be the minimum pressure required to drive the ice cream mix, $P_{CO2,I}+\Delta P_{nozzle1}$, $\sim 5.34 \times 10^6$ Pa (775 psi). The initial gas pressure, P_i, can be calculated from the relation for isentropic expansion of an ideal gas,

$$\frac{P_i}{P_{CO_2,1} + \Delta P_{nozzle1}} = \left(\frac{V_{icm} + V_{pg}}{V_{pg}}\right)^{1.4}. \tag{3}$$

where V_{icm} is the volume of ice cream mix that must be displaced, and V_{pg} is the initial volume of the pressurizing gas. Assuming a volume of pressurizing gas that is twice the volume of mix it must displace, the initial pressure must be 1.76 times the required mix pressure, 9.4×10^6 Pa (1550 psi). A cylinder of nitrogen gas could meet this requirement. This model assumes that the initial pressure in the full ice cream mix cylinder is equal to the initial pressure of the ideal gas.
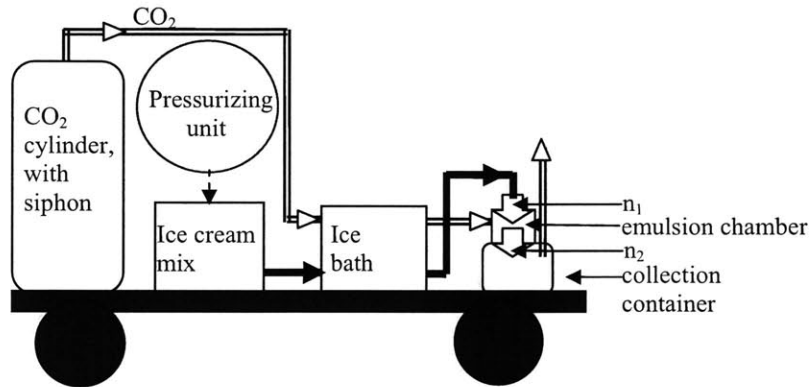
Figure 5-3. Flow diagram for cart implementation. n_1-ingredient nozzle, n_2-combined fluid nozzle. Ice cream mix is pressurized unspecified separate unit.

Table 5.1 shows the volume and mass of carbon dioxide, ice cream mix and ice required for the flashing process. The carbon dioxide to ice cream mix ratio is calculated assuming powder exiting at -20°C and carbon dioxide flashing to atmospheric pressure (solid phase) and then sublimating. The minimum carbon dioxide ratio is 1.18, but excess carbon dioxide flow may be necessary to compensate for exposure of the flashing fluids to air at the temperature of the environment. The mass of ice required is based on the heat of fusion of ice balancing the enthalpy that must be removed from the ice cream mix and carbon dioxide when the fluids are cooled from room temperature to 5°C, the pre-cooled state. This back of the envelope estimate neglects any heat leaks and assumes good insulation. The piping lengths between the heat exchanger and the emulsion chamber should be kept to a minimum to reduce warming of the ice cream mix and liquid carbon dioxide.

Table 5.1 Fluid requirements for 300-serving cart

Fluid	Volume [L]	Mass [kg]	Heat Transfer in Ice-Bath Heat Exchanger [kJ]
Ice cream mix	8.60	9.06	-515.96
Carbon dioxide	14.30	10.66	-587.62
Ice	3.30	3.30	1003.58

(T_{env} = 22 °C)

In a cart setup with no carbon dioxide recompression, the vented carbon dioxide has some cooling capacity, which could be recuperated to provide some of the necessary pre-cooling. The enthalpy of carbon dioxide increases by 53.41 kJ/kg from saturated vapor at -40 °C to vapor at 5 °C and atmospheric pressure, or by 36.51 kJ/kg at atmospheric pressure going from -40 °C to 5 °C. To use the carbon dioxide in recuperation there must be an enclosed product vessel with a vent and heat exchanger for the recovered carbon dioxide. The enthalpy that must be removed to pre-cool the ice cream mix from 22 to 5 °C is 56.95 kJ/kg. The mass flow of carbon dioxide is approximately 1.2 times that of mix, but some portion of the carbon dioxide will be removed with the frozen ice cream. Tests with the proof of principle apparatus indicate that only about 50% of the carbon dioxide flow could be recovered during the flash-freezing process. Even neglecting fouling and considering a 100% effective heat exchanger, recuperation of the vented carbon dioxide cooling capacity would provide less than half of the cooling needed to pre-cool the ice cream mix. The mass of ice required for pre-cooling is much less than the mass of the ingredients, so the additional complications of recuperation are not worth it.

5.4 Comments on Home Implementation

Discussions of the flash freezing process have also brought out interest in a simple home implementation. There are several challenges associated with a home version. The system will inherently be a batch process due to the discrete ice cream consumption in a typical home setting. The batch process must run quickly, for a short period of time; the container in contact with the ice cream product should have low heat capacity or be pre-cooled. The ice cream mix must be pressurized to the appropriate pressure for the emulsion.

One possible implementation would involve using superheated carbon dioxide vapor to pressurize the ice cream mix in a sealed cylinder. Assuming access to electricity, the amount of carbon dioxide required to pump all of the ice cream mix at high pressure can be reduced by continuously heating the saturated fluid to maintain the desired pressure and passing the carbon dioxide through a warming coil to ensure vapor phase carbon dioxide pressurizing the ice cream mix. A small mass of low density, high pressure carbon dioxide would fill the volume vacated as the ice cream mix is consumed, as in the proof-of-principle apparatus. The ice cream mix and liquid carbon dioxide used for flash freezing can be stored separately in a refrigerator to obviate the need for a pre-cooling heat exchanger. Cylinders of ice cream mix, saturated carbon dioxide and pressurizing carbon dioxide, as well as a pre-cooled collection cup, could be inserted in a counter-top apparatus that would provide the heating and regulate the fluid flow rates to run the process. The user would be alerted after the product vessel is vented that the ice cream is ready. Safety precautions must be incorporated for working with the high pressure fluids. In addition, a procedure for retrieval of the used-but-not-empty carbon dioxide cylinders should also be developed, or the excess carbon dioxide can simply be vented to the atmosphere.

59

CHAPTER 6 - CONCLUSION

The flash-freezing process involves emulsifying ice cream mix in liquid carbon dioxide and throttling the combined fluid through an atomizing nozzle. In a batch process, the carbon dioxide is vented. In a continuous process more than 95% of the carbon dioxide flow is captured and recompressed in one or two stages. The carbon dioxide and ice cream mix are condensed and or cooled before the fluids are emulsified. The process has been investigated using a proof-of-principle apparatus and theoretical models. In the proof-of-principle apparatus, Delavan fuel nozzles are used to emulsify the ice cream mix and atomize the emulsified fluid. Ice cream has been successfully produced with characteristics varying from soft-serve consistency and minimal carbonation to dry powdered consistency and prominent carbonation. The thermodynamic model of the power consumption of the continuous cycle is based on carbon dioxide and ammonia refrigeration cycles operating with 70% efficient compressors and 5-10°C approach temperatures in the heat exchangers. Simple models are also made for the power consumption of the ice cream mix pump and screw or piston extrusion mechanisms. The total power consumption estimate is strongly dependent on the carbon dioxide vent rate; the vent rate is affected by the overrun of the final product and the carbon dioxide remaining in the final product. The initial model of the continuous cycle suggests reasonable scaling for larger flow rates, an acceptable low cost for the make-up carbon dioxide per liter of ice cream and energy savings better than 50% relative to conventional processes.

Tests with the proof-of-principle apparatus indicate that the product and the carbon dioxide consumption are affected by the mix ingredients, the pressure and temperature of the fluids in the emulsion chamber, the flow ratio, and the conditions in the product chamber. The flash-freezing process must be studied in a continuous or semi-continuous cycle before it can be implemented in an ice cream manufacturing plant. Here, semi-continuous refers to a system that recycles carbon dioxide but uses a batch of ice cream mix large enough to attain steady state conditions. A continuous cycle demonstration will address the behavior of the process in steady state, which is important both for understanding carbon dioxide recovery and for relating the product properties to the process states and ingredients. Ultimately, it is important to understand how to control the carbonation of the powder, adjust for a change in ingredients and minimize process costs.

In a continuous or semi-continuous demonstration, instrumentation will be important to improve understanding of the process. The inlet temperature of the fluids, the temperature in the emulsion chamber, the temperature distribution in the product chamber and the temperature of the carbon dioxide exiting the product chamber should be monitored by thermocouples. Because the carbon dioxide will be captured and recycled, the product chamber can be pre-cooled uniformly by flashing CO_2 without ice cream mix present. The mass flow rate of ice cream mix and carbon dioxide at the inlet to the emulsion chamber should be monitored, giving an accurate measurement of the flow ratio. Additionally, a mass flow meter should monitor the carbon dioxide vent rate. Cameras or view windows could be installed to observe the emulsion and the state of overrun in the product chamber. Pressure regulators could be used for the inlet ice cream

mix and carbon dioxide flows to improve control of the process. Pressure gauges should be included as in the proof-of-principle apparatus.

In addition to process monitoring, the properties of the product should be studied to guide the development of extrusion mechanisms and product packaging. The product overrun can be measured as in the proof-of-principle tests. The carbon dioxide content can be measured by allowing the product to melt in a sealed environment. The micro-structure of the ice cream powder should be investigated to understand the state of fat in the powder and how carbon dioxide is trapped in the product. Additionally, the effect of compression, meltdown and heat shock on the micro-structure should be observed.

Other aspects of the flash-freezing process that could be addressed in a future demonstration include the emulsion chamber size, nozzle arrangement and vent placement. This would allow investigation of the maximum emulsion chamber size, the effect of closely packed nozzles operating in parallel and the optimum placement of the vent in the product vessel. It is possible that the fluids will separate in a large emulsion chamber with a long residence time. It is possible that interference between spray cones of adjacent nozzles will cause clumping or other changes in the product characteristics. The vent placement affects both carbon dioxide recovery and blocking potential as well as filtering requirements for the recovered gas flow.

Investigation of the continuous cycle can be expedited by using off-the-shelf components when possible. This will not provide a demonstration of energy efficiency, but it will help in understanding the factors affecting power consumption, including the rate of carbon dioxide recovery and the extrusion mechanism. An oil-free compressor, such as the Blackmer HDL322, is likely to be larger than the size desired for the demonstration cycle, but excess flow could be cycled through an auxiliary loop. Alternatively, compression of carbon dioxide gas has be demonstrated in multiple applications, so in place of a compressor, the saturated carbon dioxide vapor could be collected and condensed by a refrigerant evaporating at a temperature cooler than the saturated carbon dioxide vapor. A liquid pump could then be used to increase the pressure of the liquid to the pressure in the emulsion chamber. The Niro NS1001 homogenizer pump could meet the demonstration continuous cycle requirements, with 9.8 L/hr capacity and 1.034×10^7 Pa (1500 psi) maximum pressure.

With improved understanding of the flash-freezing process, the process can be implemented in a large ice cream plant setting or in a cart for mobile distribution.

Acknowledgements

REFERENCES

Anderson, G. "Enthalpy of dissociation and hydration number of carbon dioxide hydrate from the Clapeyron equation." *Journal of Chemical Thermodynamics.* 35 (2003):1171-1181.

Bernhardt, E.C. *Processing of thermoplastic materials.* New York:Reinhold, 1959.

Blackmer Spec Sheet 901-001. HD Industrial Gas Compressors.
http://www.blackmer.com. March 2005.

Bohn, Robert. Sales Manager, Tetra Pak Processing Systems. Personal communication.
May 24, 2005.

BYU Technology Transfer Office, Brigham Young University. "Sparkling Yogurt."
http://techtransfer.byu.edu/techabstracts/yogurt.htm. 2000.

Chapoy, A., Mohammadi, A., Chareton, A., Tohidi, B., and Richon, D., "Measurement and Modeling of Gas Solubility and Literature Review of the Properties for the Carbon Dioide-Water System." *Ind. Eng. Chem. Res.* 43 (2004):1794-1802.

Chun, M., Lee, H. "Phase Equilibria of Carbon Dioxide Hydrate System in the Presence of Sucrose, Glucose, and Fructose." *Journal of Chemical Engineering Data* 44 (1999):1081-1084.

Clarke, C. *The Science of Ice Cream.* Cornwall, UK:Royal Society of Chemistry, 2004.

Clarke, M., Bishnoi, P. "Determination of the intrinsic kinetics of CO2 gas hydrate formation using in situ particle size analysis." *Chemical Engineering Science* 60 (2005): 695-709.

Freedman, M. "Pressure Cooker." *Forbes Magazine.* 1 November 2004.

Goff, H. "Structure of Ice Cream."
http://www.foodsci.uoguelph.ca/dairyedu/icstructure.htm. January, 2006.

Gudmundsson, J., Parlaktuna, M., Levik, O., Andersson, V. "Laboratory for Continuous Production of Natural Gas Hydrates." *Annals of New York Academy of Sciences.* 912 (2000):851-858.

Hotchkiss, J, Chen, J. "Microbiological effects of the direct addition of CO_2 to pasteurized milk." *Journal of Dairy Science.* 79(Supplement 1) (1996):87.

Irvin, G., Sichu, L. Simmons, B., John, V., McPherson, G., Max, M., Pellenbarg, R. "Control of Gas Hydrate Formation." *Annals of New York Academy of Sciences.* 912 (2000):515-526.

Kang, S, Lee, H. "Enthalpies of dissociation of clathrate hydrates of carbon dioxide, nitrogen, (carbon dioxide+nitrogen), and (carbon dioxide+nitrogen+tetrahyrofuran)." *J. Chemical Thermodynamics*. 33. (2001):513-521.

Lee, C., Psathas, P., Johnston, K., deGrazia, J., Randolph, T. "Water-in-Carbon Dioxide Emulsions: Formation and Stability." *Langmuir* 15. (1999):6781-6791.

Ma, Y., Barbano, D. "Effect of Temperature of CO_2 Injection on the pH and Freezing Point of Milks and Creams." *Journal of Dairy Science*. 86. (2003):1578-1589.

Marshall, R., Goff, H., and Hartel, R., *Ice Cream*, 6th ed. New York: Kluwer Academic/Plenum Publishers, 2003.

Murray, C.N., Visintini, L., Bidoglio, G. and B. Henry. "Permanent storage of carbon dioxide in the marine environment: the solid CO_2 penetrator." *Energy Convers. Mgmt*. 37 (1996):1067-1072.

Ogden, LV., Jefferies, LK, and Ellsworth, A., "Carbonation of frozen soft-serve confections." (Abstr.) Journal of Dairy Science. 85(Suppl. 1). (2002):1530.

Olson, E. "Fuel Nozzles for Oil Burners-Technical Aspects of Applications." *Delavan Fuel Metering Products Operation*. South Carolina. 2003.

Osswald, T. and Stradinis, L. "Compression Molding of Granulated Materials." In *Polymer Powder Technology* edited by M. Narkis and N. Rosenzweig. Chichester, England: John Wiley & Sons Ltd., 1995. pgs. 349-385.

Rosenzweig, N. "Ram Extrusion of Particulate Polymers." In *Polymer Powder Technology* edited by M. Narkis and N. Rosenzweig. Chichester, England: John Wiley & Sons Ltd., 1995. pgs. 388-425.

Royal, John. Associate Director of Cryogenic Equipment R&D, Praxair. Personal communication, February 2003.

Shapiro, L, Johnson, J, Sturm, M, Blaisdell, G. "Snow Mechanics: Review of the State of Knowledge and Applications." CRREL Report 97-3. U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH. 1997.

Tetra Pak. *Dairy Processing Handbook*. Denmark:International Dairy Books, 2004.

Tetra Pak Hoyer. "Presenting Hoyer Frigus LF1000 F1 Low Temperature Freezer." Ice Cream Alert. No. 21. June 2003.

Toromont Process Systems. "Typical liquid carbon dioxide specification for food and beverage grade." In *All About Carbon Dioxide.* http://www.toromontsystems.com/library/All%20About%20CO2.pdf.

Westergaard, V., *Milk Powder Technology.* Niro A/S. Copenhagen, Denmark. 2004. http://www.niro.com/ndk_website/niro/cmsdoc.nsf/webdoc/ndkw5y4brlLibrary.

Wright, A., Ogden, L., Eggett, D., "Determination of carbonation threshold in yogurt." *Journal of Food Science.* 68(1). (2003):378-381.

XtraordinaryDairy. Technology Fact Sheet. "Carbon Dioxide Can Extend Shelf Life of Dairy Foods." Dairy Management Inc. 1999.

Appendix A Milkfat and NMS Properties of Common Ingredients for Mix Calculation

Ingredient	NMS	Milkfat
whole milk	8.25-8.71%	3.25-4.0%
light cream	7.2%	~20%
heavy cream	5.4%	~40%
skim milk	8.9%	0.02%
half and half	7.7%	11%
nonfat dry milk	97%	~0%

(Data based on *Ice Cream, 6th ed*, Chapter 5, Marshall, 2003.)
(NMS is typically ~9% of the non-fat portion (serum) of a dairy ingredient.)

Example Mix Calculation

Ingredients: 2 kg light cream, 1 kg whole milk, 0.5 kg sugar, ~0.012 kg vanilla
12.4% fat = (2 kg light cream x 0.2 + 1 kg whole milk x 0.0325)/3.51 kg mix
6.5% NMS = (2 kg light cream x 0.072 + 1 kg whole milk x 0.0825)/3.51 kg mix
14.3% sucrose = 0.5 kg sugar/3.51 kg mix.

Appendix B Relevant Fluid Properties

Fluid	Pressure [MPa]	Temp [K]	Enthalpy [kJ/kg]	Entropy [kJ/kgK]	Density [kg/m^3]
CO_2(l)	3.9695	278	212.50	1.0434	896.03
CO_2(v)	1.9711	253	436.92	1.9506	51.74
CO_2(v)	1.0045	233	435.32	2.0485	26.12
H_2O(l)	3.9695	278	24.961	0.0762	1001.9
H_2O(s)	--	253	-374.03	-1.377	919.62

(Data from NIST Standard Reference Database 69, June 2005 Release: *NIST Chemistry WebBook*)

Appendix C Ice Cream and Ice Cream Mix Properties

Density	1054-1123 kg/m^3
Heat capacity	3.35 kJ/kgK (at 0 C)
	1.88 kJ/kgK (at -30 C)
Freezing point depression	~3.3 C
Overrun	60-120%
Ice crystal size	30-60 microns
Air cells	110-185 microns
Individual fat globules	0.5-2.0 microns
Agglomerated fat	~25 microns

* these properties are typical for conventional processing
(Data based on *Ice Cream, 6th ed*, Marshall, 2003.)

Typical Composition [%] of Commercial Ice Cream

Product	Milkfat	NMS	Sweeteners	Stabilizers and emulsifiers
Nonfat	<0.7	12-14	18-22	1.0
Reduced fat	7-9	10-11	18-19	0.4
Regular	11-12	10-11	14-17	0.3
Superpremium	17-20	6-8	16-17	0.2

(Source: *Ice Cream, 6th ed*, Table 2.1, Marshall, 2003.)

C.1 Recipes Used with Proof-of-Principle Apparatus

Label	Whole Milk	Light Cream	Sugar	Vanilla
First test	2 cups	-	0.5 cups	1 tsp
First test w/ cream	1 cup	2 cups	0.5 cups	1.33 tsp
8.74%	6 cups	4 cups	1.5 cups	6 tsp
10.1%	4 cups	4 cups	1.5 cups	3 tsp
Half'n'half	8 cups half-n-half	-	1.3 cups	3 tsp
Chocolate	8 cups half-n-half	-	1.5 cups	8 oz semi-sweet chocolate chips (melted)
13.76%	1.5 cups	4 cups	0.75 cups	3 tsp