

DESIGN AND TESTING OF AN APPARATUS TO MEASURE CARBON DIOXIDE  
SOLUBILITY IN LIQUID FOODS

By

THELMA FRANCISCA CALIX LARA

A THESIS PRESENTED TO THE GRADUATE SCHOOL  
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT  
OF THE REQUIREMENTS FOR THE DEGREE OF  
MASTER OF SCIENCE

UNIVERSITY OF FLORIDA

2008

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To those that have guided and inspired me

## ACKNOWLEDGMENTS

I wish to express my special gratitude to my major advisor, Dr. Murat O. Balaban, for his valuable support, guidance and for being an example of motivation and hard work to us. I also like to thank my advising committee, Dr. Charles A. Sims and Dr. Allen F. Wysocki, for their guidance, assistance and time for my research.

I am very grateful for my lab partners and friends, Luis, Jose, Max, Milena, Alberto, Zareena, Mutlu, Diana, Wendy, Yavuz, Maria and Giovanna for their assistance and for making the work in the lab such an enjoyable experience.

I thank infinitely to my parents, Winston and Sagrario, my sister and my brother, Lourdes and Winston, for their unconditional love and support during my entire life. They have been my primary inspiration to pursue my goal.

Finally, my dearest thanks to Jorge, for all the support and happiness he brought to my life.

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Abstract of Thesis Presented to the Graduate School  
of the University of Florida in Partial Fulfillment of the  
Requirements for the Degree of Master of Science

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Thelma Francisca Calix Lara

May 2008

Chair: Murat O. Balaban  
Major: Food Science and Human Nutrition

Carbon dioxide (CO<sub>2</sub>) is a non-toxic, inexpensive, chemically inert, non-flammable fluid and a safe solvent. It has multiple applications in the beverage industry, such as carbonation and dense phase carbon dioxide (DPCD) technology, a cold pasteurization process.

The solubility of CO<sub>2</sub> in water depends on pressure and temperature (Dodds and others 1956). Increasing pressure increases solubility of CO<sub>2</sub> and increasing temperature decreases it. In addition, the presence of other dissolved substances could have a positive or negative effect in CO<sub>2</sub> solubility (Meysami and others 1991). DPCD is a continuous cold pasteurization method that affects microorganisms and enzymes under pressures below 50 MPa (7,250 psi) without the use of high temperature treatments. Currently, the use of CO<sub>2</sub> in DPCD treatments is not optimized, since solubility of CO<sub>2</sub> in liquid foods at different temperatures, pressures, and compositions is not known. Therefore, excess CO<sub>2</sub> is used to assure saturation. If CO<sub>2</sub> solubility could be predicted at any temperature, pressure and composition for a liquid food, then the amount of CO<sub>2</sub> used would be slightly above this theoretical value, and the process would be more economical. The first step towards this type of prediction is the experimental measurement of CO<sub>2</sub> solubility in model liquid food systems and its correlation with pressure, temperature and composition. Therefore, the objectives of this study were: 1) to design, build and test a high-

pressure carbon dioxide solubility apparatus, 2) to compare the volume of CO<sub>2</sub> that dissolves in pure water with the current literature; and finally 3) to determine the maximum amount of CO<sub>2</sub> in solution with model liquid foods of known composition (binary solutions of fructose and malic acid).

An experimental system to measure the CO<sub>2</sub> solubility was designed and tested. The pressure and temperature were controlled in the system, and the design assured an accurate measurement of solubility. Experimental results of CO<sub>2</sub> in solution in pure water were compared with the literature, and there was no significant difference at pressures of 7.56 MPa (1100 psi) and 10.3 MPa (1500 psi), at a constant temperature of 40°C. At pressures of 7.58 and 10.34 MPa, solubilities of CO<sub>2</sub> in water were  $4.77 \pm 0.15$  and  $5.51 \pm 0.20$  g/100 g of distilled water, respectively.

By increasing the concentration of malic acid or fructose, solubility of CO<sub>2</sub> decreased significantly. At 7.58 MPa of pressure, the amount of CO<sub>2</sub> dissolved in the solutions of 0.5 and 5% of malic acid concentration was  $4.47 \pm 0.03$  and  $4.47 \pm 0.02$  g/100 g of solution. When the concentrations of fructose in the solution were 5 and 10%, solubilities of CO<sub>2</sub> in the solutions were  $4.55 \pm 0.11$  and  $4.12 \pm 0.07$ , respectively (at 7.58 MPa). At 10.34 MPa of pressure, solubilities of CO<sub>2</sub> in solution with 0.5 and 5% of malic acid concentration were  $4.90 \pm 0.08$  and  $4.79 \pm 0.07$  g/100 g of solution. When the amount of fructose in the solution increased to 5 and 10 g/100 g of solution, solubilities of CO<sub>2</sub> at 10.34 MPa were  $4.78 \pm 0.14$  and  $4.19 \pm 0.17$ , respectively.

This equipment design and method can experimentally measure CO<sub>2</sub> solubility in real liquid foods, and therefore is a significant contribution to the DPCD field. This is the first step in the generation of experimental data for the thermodynamic modeling of CO<sub>2</sub> solubility in liquid

foods. The experimental apparatus could offer an advantage to the food industry, primarily to soft drink industry, and to the DPCD users, by eliminating the need to use excess CO<sub>2</sub> and therefore reducing the production cost.

## CHAPTER 1 INTRODUCTION

Carbon dioxide (CO<sub>2</sub>) has numerous food applications and many others are being developed, providing simple and economic process alternatives to the beverage industry. CO<sub>2</sub> gas is used in the carbonation of soft drinks, beers and wines because many studies have demonstrated that CO<sub>2</sub> prevents fungal and bacterial growth (Eastoe and others 1996; Del Pozo-Insfran and others 2006<sup>b</sup>; Gunes and others. 2005). In addition, CO<sub>2</sub> enhances the physical properties and sensory attributes of carbonated beverages (Kappes and others 2007; Del Pozo-Insfran and others 2006<sup>a</sup>).

In 1998 and 2003, the global beverage consumption volume reached an estimated 1.2 trillion liters and 1.4 trillion liters, respectively. Carbonated soft drinks represented 14% of the total in both years, increasing by 3.0 million liters during that period (Roethenbaugh 2005). In 2003, the United States was the biggest consumer, with 30% of the total volume of carbonated soft drinks, followed by Mexico with 9%. However, the overall compound annual growth forecasts a growing concern for health and wellness. That forecast will drive the growth of bottled water and still drinks consumption in the coming years; save for soft drinks, which have increased in importance in recent years against other beverage categories (Roethenbaugh 2005).

Carbon dioxide is a non-toxic, chemically inert, non-flammable fluid and a safe solvent for process applications (Eastoe and others 1996). Carbon dioxide has a specific gravity of 1.53 (based on air), and its molecular weight is 44.01 grams per mol and/or 22.4 liters per mol (Steen 2005; Subramaniam and Busch 2002). In food applications, CO<sub>2</sub> can be present as a gas, liquid or solid, depending on temperature and pressure. According to the phase diagram, CO<sub>2</sub> has a triple point (-56.6 °C at 0.52 MPa=5.11 atm), a sublimation range and a critical point (temperature 31 °C and pressure 7.4 MPa=73 atm). The triple point is the condition that CO<sub>2</sub>

simultaneously exist as a solid, liquid and gas. The sublimation range is when CO<sub>2</sub> gas can become solid CO<sub>2</sub> (dry ice), without passing through the liquid phase (and vice-versa). The critical point is the temperature above which it is impossible to liquefy the gas (Steen 2005).

Most of the studies about supercritical CO<sub>2</sub> have been mainly focused on supercritical extractions. However, the purpose of this project was focused on the area of dense phase carbon dioxide (DPCD) pasteurization, to design and build an experimental apparatus to measure solubility of CO<sub>2</sub> in liquid foods. DPCD is a cold pasteurization method that kills microorganisms, inactivates certain enzymes and viruses at pressures below 50 MPa without applying high temperature treatments (Damar and Balaban 2006). The microbial inactivation effect of DPCD is partly based on gas dissolution under pressure in a microbial cell that, when decompressed to atmospheric pressure, causes fatal damage (Balaban and others 1991; Park and others 2002). Furthermore, there is the theory that high pressure carbon dioxide dissolves in water to produce carbonic acid, thus the pH will be temporarily lowered and therefore inactivates enzymes (Damar and Balaban 2006).

Kincal and others (2005) tested a continuous high-pressure carbon dioxide system for microbial reduction in orange juice, and Arreola and others (1991) studied the effects of CO<sub>2</sub> on some quality attributes. Results showed that the treatment was able to cause a 5-log reduction of the natural flora in spoiled juice and could achieve a 5-log reduction of pathogenic *Escherichia coli* O157:H7, *Salmonella typhimurium* and *Listeria monocytogenes*. Balaban and others (1991) stated that pectinesterase was inactivated under supercritical conditions, suggesting that its inactivation was due to the combination effects of pressure, temperature, pH reduction and process time. Dagan and Balaban (2006) measured the effect of DPCD pasteurization on beer quality using a continuous system, and the process was able to produce a clear, consistently

fresh-tasting beer with extended shelf life.

In DPCD, the use of carbon dioxide is not optimized, since solubility is not known, and not predicted. Thus, excess carbon dioxide is used to assure saturation. In addition, Ji and others (2007) mentioned that the reduction of greenhouse gases emissions has become an issue of worldwide concern ( $\text{CO}_2$  represents about 64% of the enhanced greenhouse effect). If  $\text{CO}_2$  solubility could be measured at any temperature, pressure and composition of food, the amount of  $\text{CO}_2$  used would be slightly above this theoretical value, and the process would be more economical. Therefore, the objectives of this study were:

- To design and build a high-pressure apparatus to measure  $\text{CO}_2$  solubility in liquid foods.
- To test the accuracy and precision of the high-pressure  $\text{CO}_2$  solubility apparatus, and compare with the literature the amount (v/v) of  $\text{CO}_2$  dissolved in pure water.
- To determine the maximum amount (v/v) of  $\text{CO}_2$  in solution with a model liquid food of known composition (solution of sugar or acid).

CHAPTER 2  
LITERATURE REVIEW

**2.1 Carbonated Soft Drinks**

According to Roethenbaugh (2005), soft drinks are sweetened water-based beverages, usually balanced by acidity, and their primary function is hydration. Soft drinks are divided into two large groups, the ready-to-drink (RTD), and the concentrated or diluted-to-taste products. RTD products are subdivided into carbonated products. Figure 2.1 shows the beverage sectors and segments.

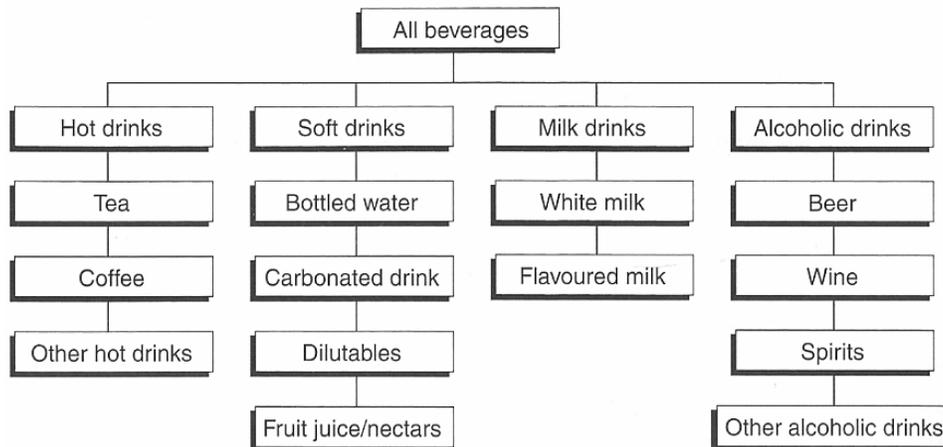


Figure 2-1. Beverage sectors and segments (Roethenbaugh 2005).

The dominant world players in the carbonated RTD soft drink industry are Coca Cola, Pepsi and Cadbury-Schweppes. Together with their associated brand names, they constitute over half the world's consumption of such products. In 2003, carbonated soft drinks became the world's second most popular beverage after tea. In 1998 and 2003, the global beverage consumption volume reached an estimated 1.2 trillion liters and 1.4 trillion liters, respectively, and approximately fourteen percent (14%) of the total were carbonated soft drinks (Figure 2-2) (Roethenbaugh 2005).

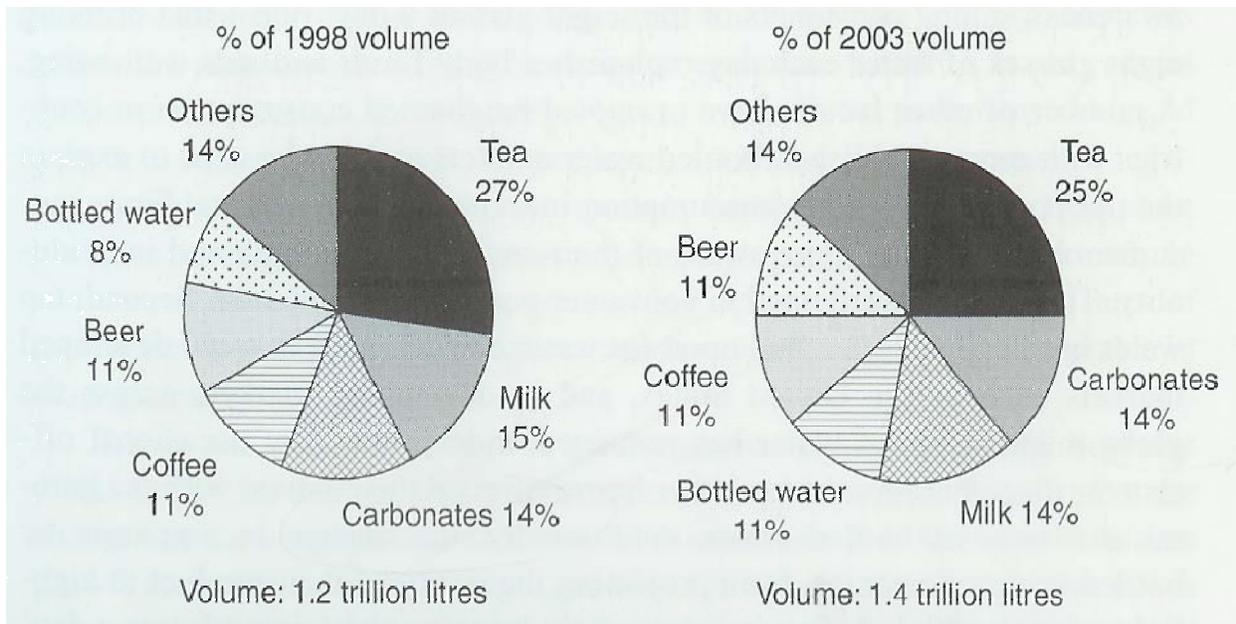


Figure 2-2. Global beverage consumption by category, 1998-2003 (Roethenbaugh 2005).

Over the period 1998-2003, the global consumption of beverages was dominated by the United States (15%), followed by India (10%) and China (9%) (Figure 2-3). In carbonated soft drinks the United States represented thirty percent (30%) of global consumption, followed by Mexico (9%). The fastest growing consuming countries between 1998-2003 were Bosnia-Herzegovina (160% increase), Serbia (86%) and China (86%).

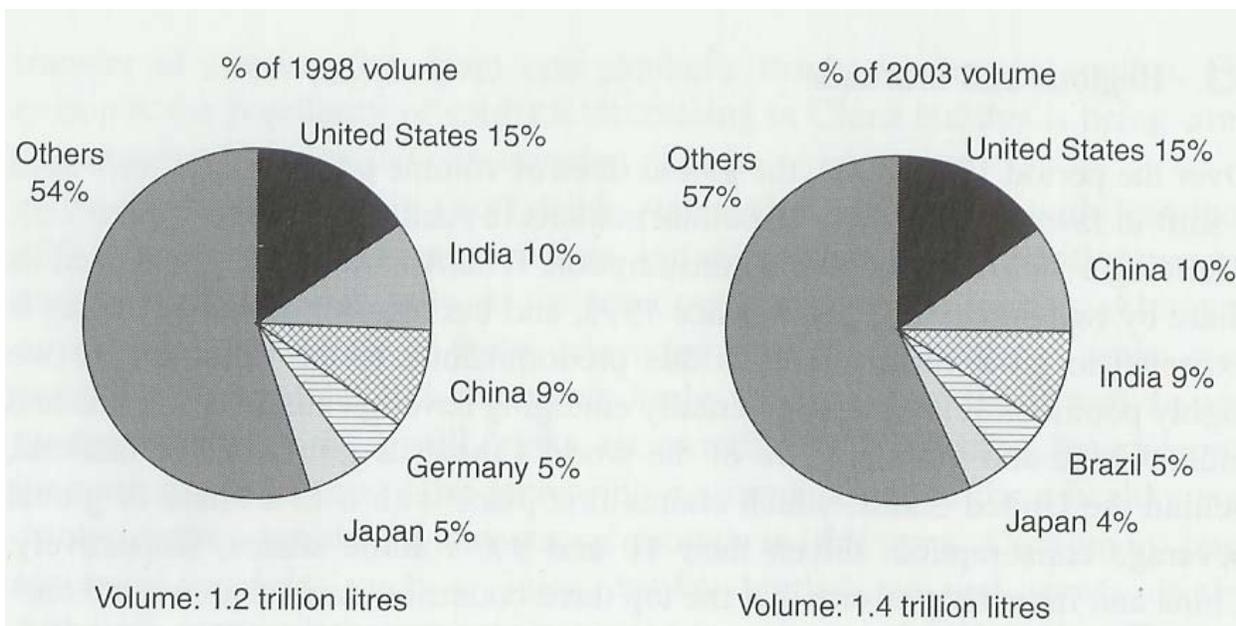


Figure 2-3. Beverage consumption by countries (1998-2003).

## 2.2 Carbon Dioxide

### 2.2.1 General Information

Carbon dioxide (CO<sub>2</sub>) is a non-toxic, inexpensive (approximately 4.85 cents/kg in 2007), chemically inert, non-flammable fluid and a safe solvent for process applications (Eastoe and others 1996, Steen 2005). It has a specific gravity of 1.53 (based on air) under conditions of room temperature and atmospheric pressure, and its molecular weight or molar mass is 44.0098 ± 0.0016 grams and/or 22.4 liters per mol (Steen 2005; Subramaniam and Busch 2002; Span and Wagner 1996). The molecule of CO<sub>2</sub> is linear with a double bond between the carbon and oxygen atoms (O=C=O) (Song 2002).

The effects of temperature and pressure on the state of CO<sub>2</sub> (physical properties) are shown in Figure 2-4. The triple point (-56.6 °C at 0.52 MPa=5.11 atm) is the condition in which CO<sub>2</sub> can be present as a solid, liquid or gas (the three phases coexist). The sublimation range is when CO<sub>2</sub> solid (dry ice) directly becomes gas (and vice-versa), for example at -78.8 °C and 1 atm (Song 2002; Steen 2005, Levelt 2000).

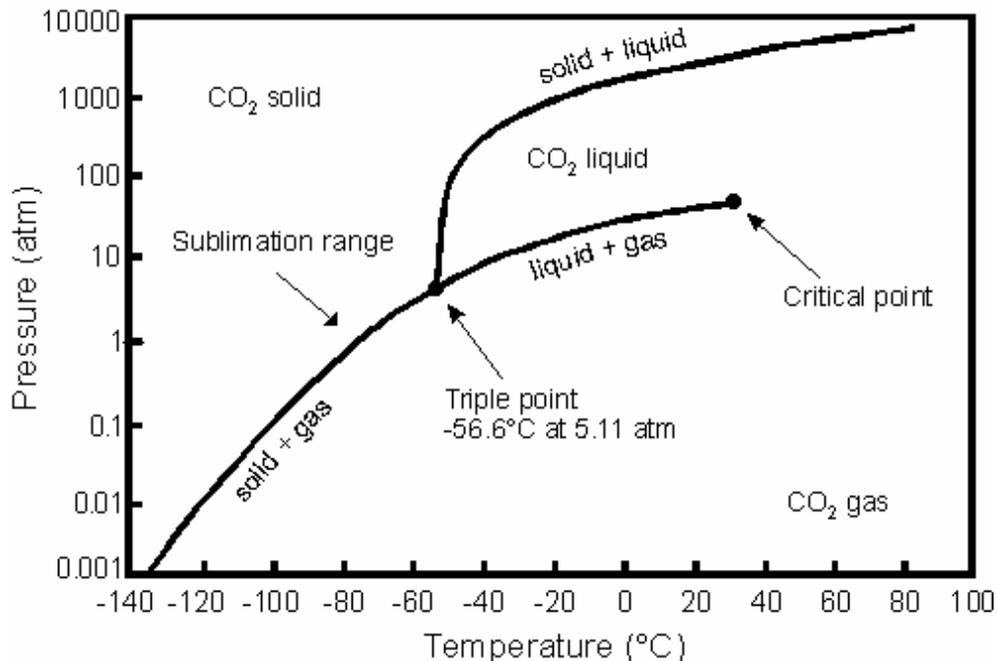


Figure 2-4. Carbon dioxide phase diagram (Steen 2005).

Above the critical point (temperature 31 °C and pressure 7.4 MPa=73 atm) it is impossible to liquefy the gas, and CO<sub>2</sub> exists as a fluid or dense gas (Song 2002). At atmospheric pressure and room temperature (25 °C), CO<sub>2</sub> cannot be present as liquid. To liquefy CO<sub>2</sub> it is necessary to compress and cool between the triple point and the critical point conditions (Steen 2005). The density, viscosity and diffusion coefficient associated with different phases of CO<sub>2</sub> are shown in Table 2-1.

Table 2-1. Physical properties associated with the phase diagram of CO<sub>2</sub> (Koutchma and Murakami 2005; Buhler and others 1998).

States	Density (g/ cm <sup>3</sup> )	Viscosity (cP)	Diffusion coefficient (cm <sup>2</sup> /s)
Gas	0.002	0.014	0.01
Super Critical	0.467	0.02-0.12	0.0001
Liquid	1.0	1.0	0.00001

In CO<sub>2</sub>, the density ( $\rho$ ) increases rapidly around the critical pressure ( $p_c$ ). When the temperature decreases, the change in  $\rho$  is more remarkable and it does not move to higher pressures as fast as at high temperatures; thus,  $\rho$  becomes difficult to control around the critical temperature (Clifford and Williams 2000). Figure 2-5 shows four density-pressure isotherms.

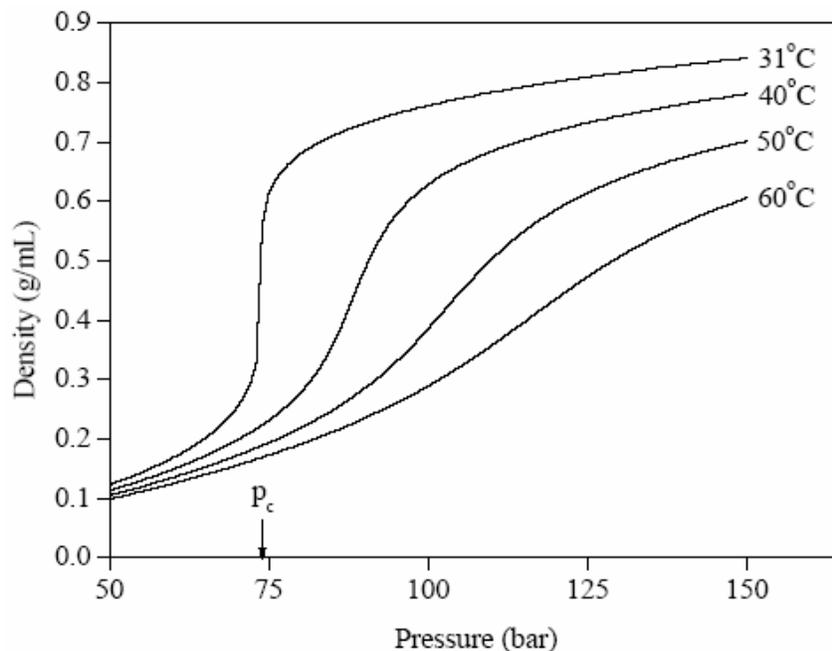


Figure 2-5. Density-pressure isotherms for carbon dioxide (Clifford and Williams 2000).

According to Steen (2005), the European Industrial Gases Association, the Compressed Gases Association of America and the International Association of Beverage Technologists have described the standard quality of CO<sub>2</sub> for use in foods and beverages. Table 2-2 shows the specifications for commercial liquid CO<sub>2</sub>.

Table 2-2. Quality standard of carbon dioxide (Steen 2005).

<b>Component</b>	<b>Specification</b>
Assay	99.9% v/v min.
Moisture	50 ppm v/v max. (20 ppm w/w max)
Acidity	To pass JECFA* test
Ammonia	2.5 ppm v/v max.
Oxygen	30 ppm v/v max.
Oxides of nitrogen (NO/NO <sub>2</sub> )	2/5 ppm v/v max. each
Non-volatile residue (particulates)	10 ppm w/w max.
Non-volatiles organic residue (oil and grease)	5 ppm w/w max.
Phosphene	≤0.3 ppm v/v
Total volatile hydrocarbons (calculated as methane)	50 ppm v/v max. of which 20 ppm v/v max. non-methane hydrocarbons
Acetaldehyde	0.2 ppm v/v max.
Benzene	0.02 ppm v/v max.
Carbon monoxide	10 ppm v/v max.
Methanol	10 ppm v/v max.
Hydrogen cyanide	<0.5 ppm v/v
Total sulphur	0.1 ppm v/v max
Taste and odor in water	No foreign taste or odor

\* JECFA: Joint FAO/WHO Expert Committee on Food Additives.

In commercial use, there are several methods of CO<sub>2</sub> production. Fermentation and direct combustion are two typical processes. Fermentation consists of mixing a carbohydrate-based solution with yeast and oxygen in a fermenter; CO<sub>2</sub> and alcohol are obtained. The CO<sub>2</sub> is passed through a separator to eliminate the foam; then CO<sub>2</sub> is compressed. Finally, CO<sub>2</sub> is washed with water to remove water-soluble impurities. Direct combustion consists of burning a hydrocarbon fuel, such as light oil or natural gas, to produce a gas containing less than 0.5% oxygen by volume. The gas is cooled, scrubbed (to remove impurities) and passed through an absorbent tower that gets in contact with a CO<sub>2</sub> absorbing solution. This solution is then pumped to a stripping tower, used to release the CO<sub>2</sub> in vapor form (Steen 2005).

Carbon dioxide is delivered as a liquid to the customer, often by road tanker, and then it is transferred to pressurized vessels (20.5 bars) of 5-50 tons capacity at  $-17^{\circ}\text{C}$ ; temperature is controlled by a small refrigeration unit. To change  $\text{CO}_2$  liquid to  $\text{CO}_2$  gas is necessary to use a carbon dioxide vaporizer. Every batch supplied must have a certificate of conformance to ensure that there are no dangerous residues in  $\text{CO}_2$ , such as benzene, and to assure the safety of the user. A hazard analysis and critical control points (HACCP) survey of the installed system is required (Steen 2005). Figure 2-6 shows how  $\text{CO}_2$  is delivered: A liquid and gas phases are connected in both tanks (Steen 2005).

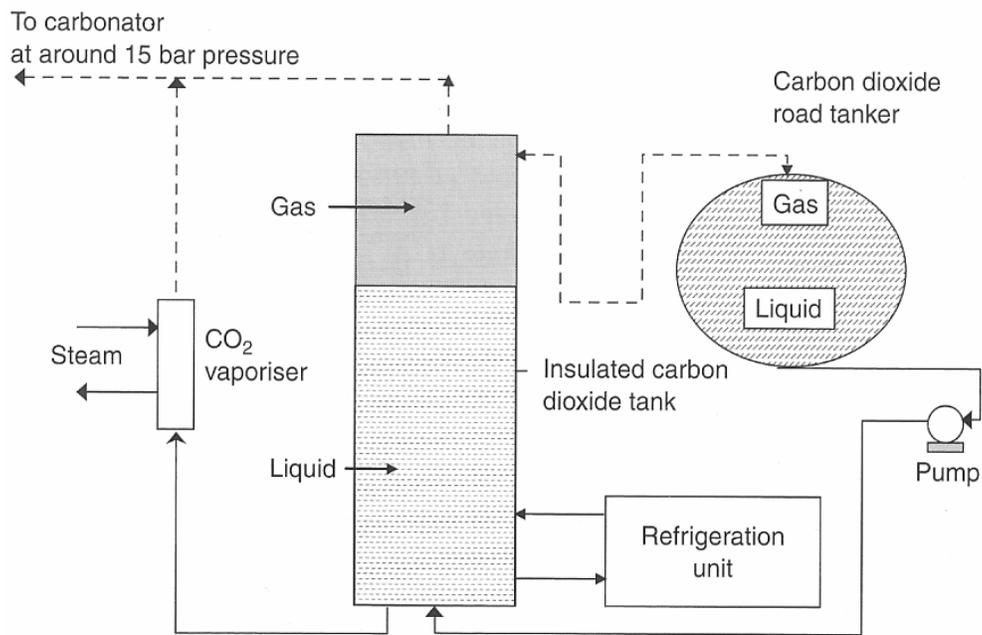


Figure 2-6. Carbon dioxide delivery process (Steen 2005).

### 2.2.2 Applications

Carbon dioxide has numerous applications in the food and beverage industries.  $\text{CO}_2$  liquid or solid is used for quick freezing, surface freezing, chilling and refrigeration in the transportation of foods. Cold sterilization can be obtained with a mixture of 90%  $\text{CO}_2$  and 10% ethylene oxide;  $\text{CO}_2$  has a stabilizing effect on the ethylene oxide and diminishes the hazard of explosion.  $\text{CO}_2$  gas is used in the processing of carbonated soft drinks, beers and wines.  $\text{CO}_2$

provides sensory characteristics. For consumers, CO<sub>2</sub> can be a pleasurable and sought-after sensation; while, for some people, CO<sub>2</sub> can be an irritating or even painful sensation (Dessirier and others 2000). CO<sub>2</sub> bubbles are responsible for several sensations because they stimulate the mechanoreceptors on the tongue and because of chemogenic origin by formation of carbonic acid (Descoins and others 2004). In addition, dense phase CO<sub>2</sub> is used in beverages due to its effective antimicrobial effects (Eastoe and others 1996).

During the last 20 to 30 years, considerable interest has centered on supercritical fluid extraction (SFE) using CO<sub>2</sub> (Bamberger and others 1999; Harris and Yung 1995). Isolation of flavors, decaffeination of coffee beans, removal of hexane from soybean oil, extraction of triglycerides, cedarwood oil, cedarleaf oil, carotenoids, and anthocyanins (a type of flavonoid or a group of phenolic compounds (Netzel and others (2006)) are some examples of SFE applications (Bamberger and others 1999). Identification of acetylated soybean lecithin components was also performed to test the surfactant potential of supercritical CO<sub>2</sub> (Nasir and others 2007).

## **2.3 Carbonation**

### **2.3.1 Definition**

Carbonation is the impregnation of a liquid with CO<sub>2</sub> gas (Steen 2005) and its effectiveness depends on the quantity of gas in solution with the soft drink (Mitchell 1978). Solubility of gases in liquids has been studied by many investigators since the early nineteenth century (Battino and Clever 1965; King and others 1992). Solubility of a solute (solid, liquid or gas) is the analytical composition of a saturated solution, expressed in terms of the proportion of the designated solute in a designated solvent (Karukstis and Van Hecke 2000). Dodds and others (1956) state that solubility of CO<sub>2</sub> in water depends on its pressure and temperature in equilibrium with the solution. Pressure has a direct effect on the solubility of CO<sub>2</sub> (pressure

increases the solubility of CO<sub>2</sub>). On the other hand, with increasing temperature, solubility of CO<sub>2</sub> decreases. The presence of other substances could have a positive or negative effect in solubility (Descoins and others 2006; Meyssami and others 1991). In addition, solubility of CO<sub>2</sub> has an opposite behavior than solubility of solids (e.g. sugar or salt) in water. Most solids dissolve more readily in hot water than in cold. Figure 2-7 shows how the relationship between pressure and temperature affect the volume of CO<sub>2</sub> in solution with pure water at relatively low pressures. Figure 2-8 shows the effect of temperature and pressure on the solubility of CO<sub>2</sub> in pure water.

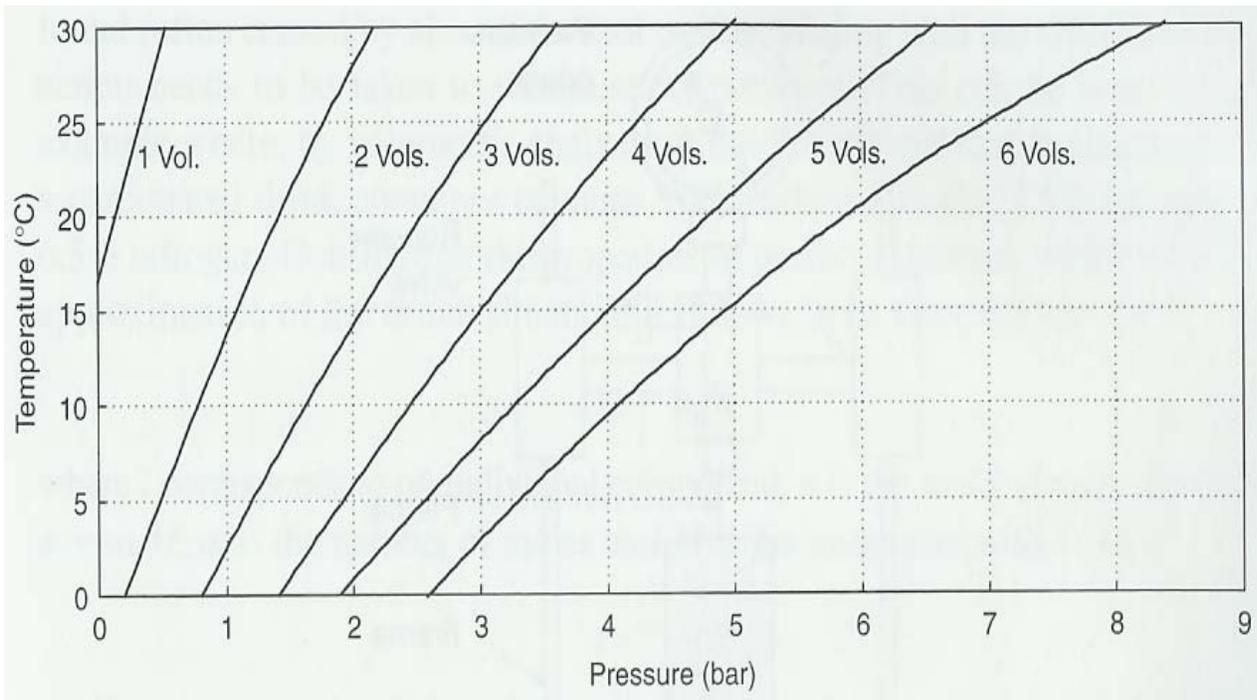


Figure 2-7. Carbonation: CO<sub>2</sub> chart in solution with pure water (Steen 2005).

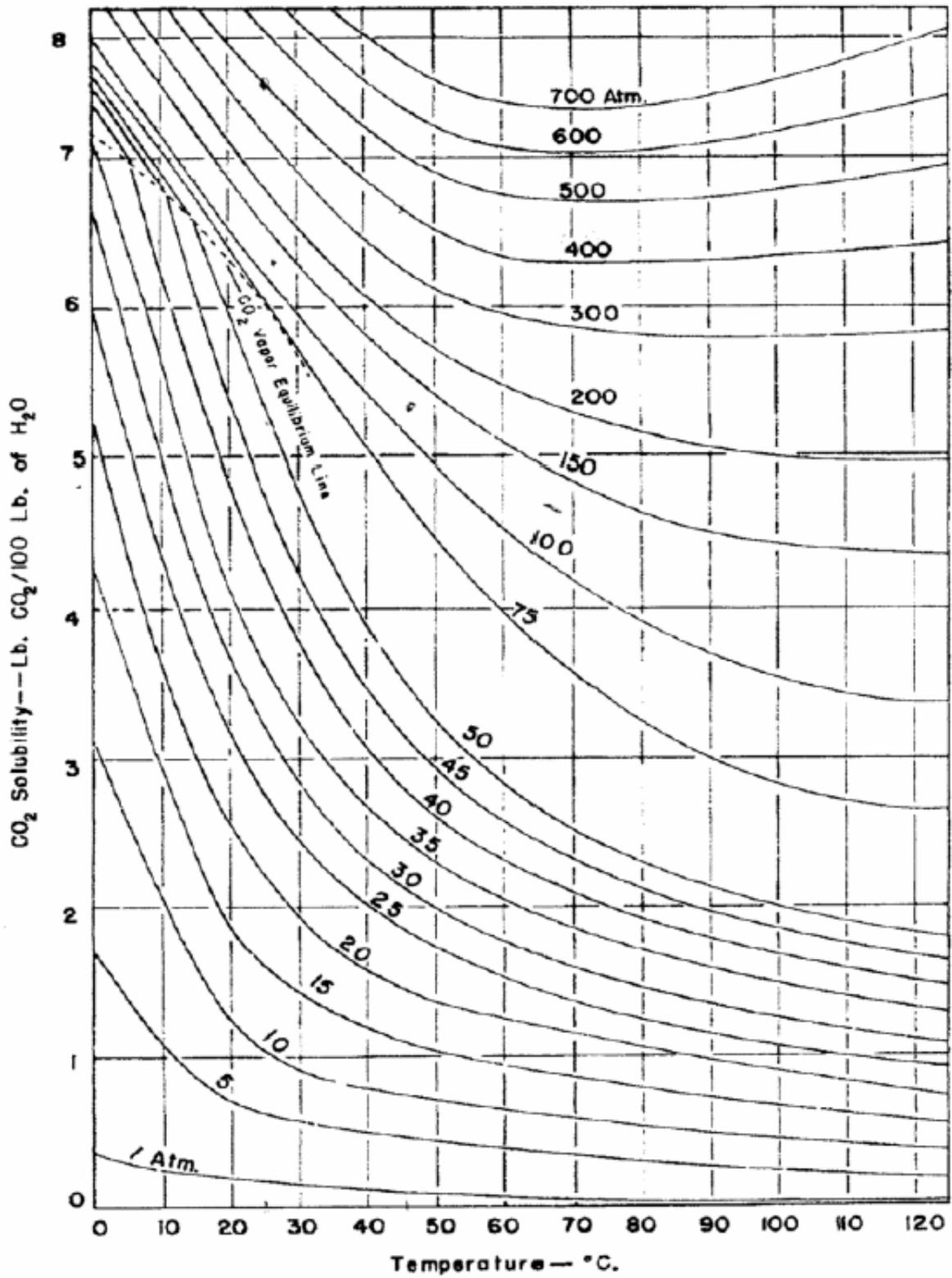
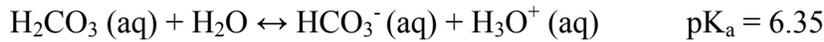


Figure 2-8. Solubility of carbon dioxide in water as a function of pressure and temperature (Dodds and others 1956).

When CO<sub>2</sub> is dissolved in water, it forms carbonic acid (Equation 2-1). Carbonic acid, in combination with the product, produces the acidic and biting taste in carbonated beverages, making the beverage more palatable and visually attractive (Steen 2005; Descoins and others 2006).



According to Steen (2005), Henry's law postulated by William Henry (1774-1836) states that "the amount of gas dissolved in a given volume of solvent is proportional to the pressure of the gas with which the solvent is in equilibrium". The universal ideal gas law is:

$$pV = mRT \quad (2-2)$$

$p$  is the absolute pressure in atmospheres (atm),  $V$  is the volume of the gas (m<sup>3</sup>),  $m$  is the number of moles of gas,  $R$  is the specific gas constant (J kg mol<sup>-1</sup> K<sup>-1</sup>) and  $T$  is absolute temperature (in Kelvins). CO<sub>2</sub> molar mass ( $M$ ) is 44.0098 ± 0.0016 g mol<sup>-1</sup> and its molar gas constant ( $R_m$ ) is 8.314510 ± 0.000210 J kg mol<sup>-1</sup>K<sup>-1</sup>. The specific gas constant for CO<sub>2</sub> ( $R = R_m/M$ ) is 0.1889241 ± 0.0000116 kJ kg<sup>-1</sup> K<sup>-1</sup> (Span and Wagner 1996).

Diamond and Akinfiev (2003) state that solubility of CO<sub>2</sub> in terms of the Henry's law can be expressed as follows:

$$x\text{CO}_2(\text{aq}) = \frac{f_{\text{CO}_2(P,T)}^0 y \gamma_y}{k_{H(P,T)} \gamma_{\text{CO}_2(\text{aq})}} \quad (2-3)$$

$\chi_{\text{CO}_2(\text{aq})}$  and  $y$  are the mole fractions of carbon dioxide in the aqueous and non-aqueous phase respectively,  $k_{H(P,T)}$  in MPa is the Henry's constant of carbon dioxide in pure water on a mole fraction basis at specified pressure and temperature conditions,  $f^0_{\text{CO}_2(P,T)}$  is the fugacity of pure

carbon dioxide (in MPa) at specified pressure and temperature conditions,  $\gamma_{\text{CO}_2(\text{aq})}$  is the asymmetric activity coefficient carbon dioxide in Henry's law ( $\gamma_{\text{CO}_2(\text{aq})} \rightarrow 1$  as  $\chi_{\text{CO}_2(\text{aq})} \rightarrow 0$ ) and  $\gamma_y$  is symmetric (Raoult's law) activity coefficient of carbon dioxide in the non-aqueous phase ( $\gamma_y \rightarrow 1$  as  $y \rightarrow 1$ ).

To calculate solubilities using Eq. (3), it is necessary to assume that  $\gamma_{\text{CO}_2(\text{aq})}$  and  $\gamma_y$  are equal to unity and  $f^0_{\text{CO}_2(\text{P,T})}$  for the  $\text{CO}_2$ -rich vapor and for the  $\text{CO}_2$ -rich liquid are calculated from the fundamental equation of state, expressed in form of the Helmholtz energy (Span and Wagner 1996):

$$\frac{A(\rho, T)}{RT} = \phi(\delta, \tau) = \phi^\circ(\delta, \tau) + \phi^r(\delta, \tau), \quad (2-4)$$

where  $A$  is the specific Helmholtz energy,  $\rho$  is mass density,  $T$  is temperature,  $R$  is the gas constant,  $\phi$  is the dimensionless Helmholtz energy ( $\phi = A/RT$ ),  $\delta$  is the reduced density ( $\delta = \rho/\rho_c$ ) and  $\tau$  is the inverse reduced temperature ( $\tau = T_c/T$ ). The dimensionless Helmholtz energy ( $\phi$ ) is split into a part depending on the ideal gas behavior ( $\phi^\circ$ ) and a part which takes into account the residual fluid behavior ( $\phi^r$ ). The critical density of carbon dioxide ( $\rho_c$ ) is  $467.6 \text{ kg/m}^3$  and critical temperature ( $T_c$ ) is  $304.1282 \text{ K}$  (Span and Wagner 1996).

The vapor pressure ( $p_s$ ) and the densities of saturated liquid (') and saturated vapor (") can be determined from an equation explicit in  $\phi$  by simultaneous solution of the equations:

$$\frac{p_s}{RT\rho'} = 1 + \delta' \phi^r_{\delta}(\delta', \tau), \quad (2-5)$$

$$\frac{p_s}{RT\rho''} = 1 + \delta'' \phi^r_{\delta}(\delta'', \tau),$$

$$\frac{p_s}{RT} \left( \frac{1}{\rho'} - \frac{1}{\rho''} \right) - \ln \left( \frac{\rho'}{\rho''} \right) = \phi^r(\delta', \tau) - \phi^r(\delta'', \tau),$$

which correspond to the equality of pressure, temperature and specific Gibbs energy in the coexisting phases (Span and Wagner 1996). The Gibbs energy ( $G^E$ ) is used to describe the non-ideality of the H<sub>2</sub>O-rich phase in the equation of state (Costa-Gomez 2007; Jödecke and others 2007; Krichevsky and Kasarnosky 1935). The Helmholtz energy of the ideal gas is given by:

$$A^o(\rho, T) = h^o(T) - RT - Ts^o(\rho, T), \quad (2-6)$$

where the enthalpy  $h^o$  of the ideal gas is a function of the temperature only, and the entropy  $s^o$  of the ideal gas depends on temperature and density (Span and Wagner 1996).

Also,  $y$  (mole fraction of CO<sub>2</sub> in the non-aqueous phase) is estimated according to the Lewis-Randall rule (at low pressures):

$$y = 1 - \frac{P_{watersat}}{P_{total}}, \quad (2-7)$$

where  $P_{watersat}$  is the pressure of liquid-vapor equilibrium of pure H<sub>2</sub>O (in MPa) and  $P_{total}$  is the total pressure (in MPa), at a specified temperature. At high pressures,  $y$  is determined from the following empirical equation:

$$y = 1 - (0.1256t - 0.0212) \times 10^{-3} - P(0.065t + 1.121) \times 10^{-5}, \quad (2-8)$$

where  $t$  is temperature in °C and  $P$  in MPa.

Henry's constant ( $k_H$ ) is calculated from the equation of state (Akinfiev and Diamond 2003):

$$\ln(k_H) = (1 - \xi) \ln f_{H_2O}^0 + \xi \ln \left( \frac{RT}{M_W} \rho_{H_2O}^0 \right) + 2\rho_{H_2O}^0 \left[ a + b \left( \frac{1000}{T} \right)^{0.5} \right], \quad (2-9)$$

where  $f^0_{H_2O}$  is the fugacity (in MPa) and  $\rho^0_{H_2O}$  is the density (in g cm<sup>-3</sup>) of pure water at determined  $P$  and  $T$  (in Kelvins),  $R$  is the gas constant (8.31441 cm<sup>3</sup> MPa K<sup>-1</sup> mol<sup>-1</sup>),  $M_W$  is the molar mass of H<sub>2</sub>O (18.0153 g mol<sup>-1</sup>), and  $\xi$  (dimensionless),  $a$  (in cm<sup>3</sup> g<sup>-1</sup>) and  $b$  (in cm<sup>3</sup> K<sup>0.5</sup> g<sup>-1</sup>) are empirical parameters (Diamond and Akinfiev 2003; Akinfiev and Diamond 2003).

Many of the parameters and thermodynamic coefficients require experimental data for accurate calculation. Such CO<sub>2</sub> solubility data for real liquid foods is rare or non-existent.

### 2.3.2 Methods and Apparatus for Carbonation

The complexity and cost of the equipments used to carbonate and to measure solubility of CO<sub>2</sub> in liquids are extended from mass spectrometer to the simple manometric van Slyke apparatus, used to measure gas quantities released from blood (Battino and Clever 1965). Figure 2-9 shows different schemes of carbonation methods. The most common method is the ‘bubbler’ that consists of sparging CO<sub>2</sub> into the liquid under pressure, to form small bubbles of gas which can be easily absorbed by the liquid (Steen 2005). The waterfall method represents the early carbonators which used to operate at around 4°C.

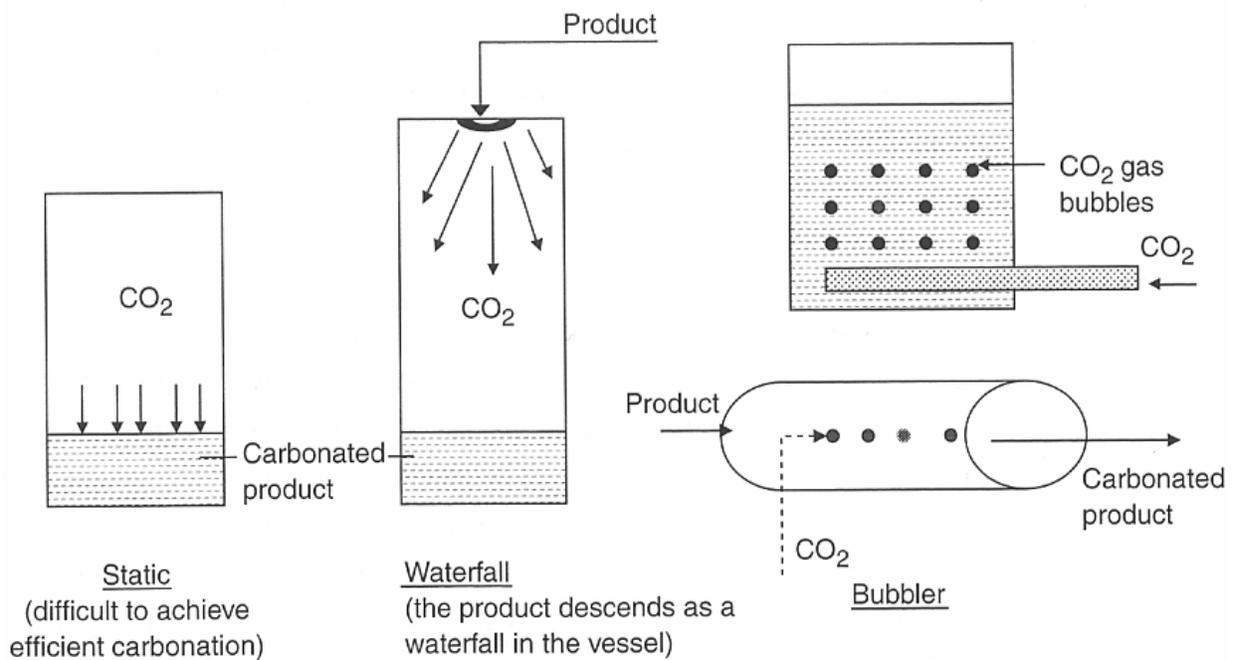


Figure 2-9. Carbonation methods (Steen 2005).

According to Steen (2005), the rate of flow and the pressure of CO<sub>2</sub> are critical to ensure the correct carbonation level. When the pressure increases, the gas bubbles formed at the sparger will be smaller and the gas bubbles' surface area will facilitate the gas absorption by the liquid.

In addition, the greater surface area of liquid exposed to CO<sub>2</sub> will increase the rate of absorption of CO<sub>2</sub> by the liquid.

Figure 2-10 shows an example of a typical apparatus to measure carbonation which consists of a jig to restrain the container, and a piercer connected to a pressure gauge. The container is shaken before the pressure is measured and the release valve is opened until the pressure gauge reads zero. For a second time, the container is shaken and the pressure is retaken and the temperature measured. The volume of carbonation is then obtained from a carbonation chart by finding the point that relates the conditions of temperature and pressure previously measured (Steen 2005).

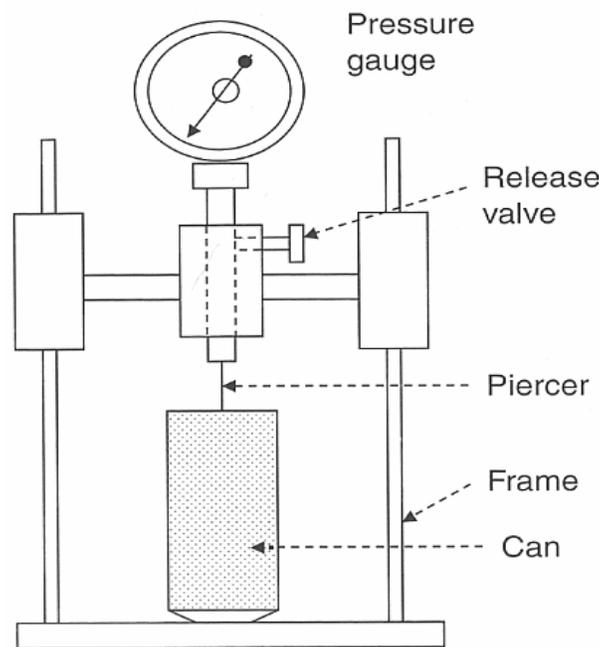


Figure 2-10. Measurement of carbonation (Steen 2005).

The purpose of releasing the pressure for the first time is to exclude other gases from the head space of the can (container) or from the beverage. Air has approximately one fiftieth the solubility of CO<sub>2</sub> in a liquid. Air constituents are approximately 79% nitrogen and 21% oxygen. Due to the differing solubility and proportion of oxygen and nitrogen, the dissolved air actually

contains 35% oxygen and 65% nitrogen (low solubility). The presence of oxygen could create spoilage problems (Steen 2005). This method is not practical or safe under pressures used by the DPCD method.

## 2.4 Supercritical Carbon Dioxide

### 2.4.1 Definition

According to Subramaniam and others (2002), supercritical phase reactors are gaining acceptance in industry. DuPont has announced a US\$ 40 million demonstration plant for supercritical polymerization. Turner (2006) states that supercritical gas or liquid occurs when the temperature increases over the critical point. In the CO<sub>2</sub> phase diagram (Figure 2-4), the curves represent coexistence between the phases. When the curve representing the liquid + gas phase ends at the critical point, the distinction between vapor and liquid disappears (Levelt 2000) and the densities of the two phases become identical (Clifford and Williams 2000).

In supercritical fluid mixtures, it is important to predict the phase equilibria to successfully develop and operate the physical separation processes and solubility models (Stratmann and Schwiger 2004). The fundamental equation of phase equilibria establishes that, at a given temperature and pressure, the fugacity of a component  $i$  in the gas phase,  $f_i^g$  must be equal to the fugacity of the same component in the solid phase  $f_i^s$  (Valderrama and others 2006). Binary fluid mixture phase diagrams are usually represented as two-dimensional projection of P-T (pressure-temperature) (Levelt 2000). Phase equilibria diagram between the binary mixture of water and CO<sub>2</sub> system is represented in Figure 2-11.

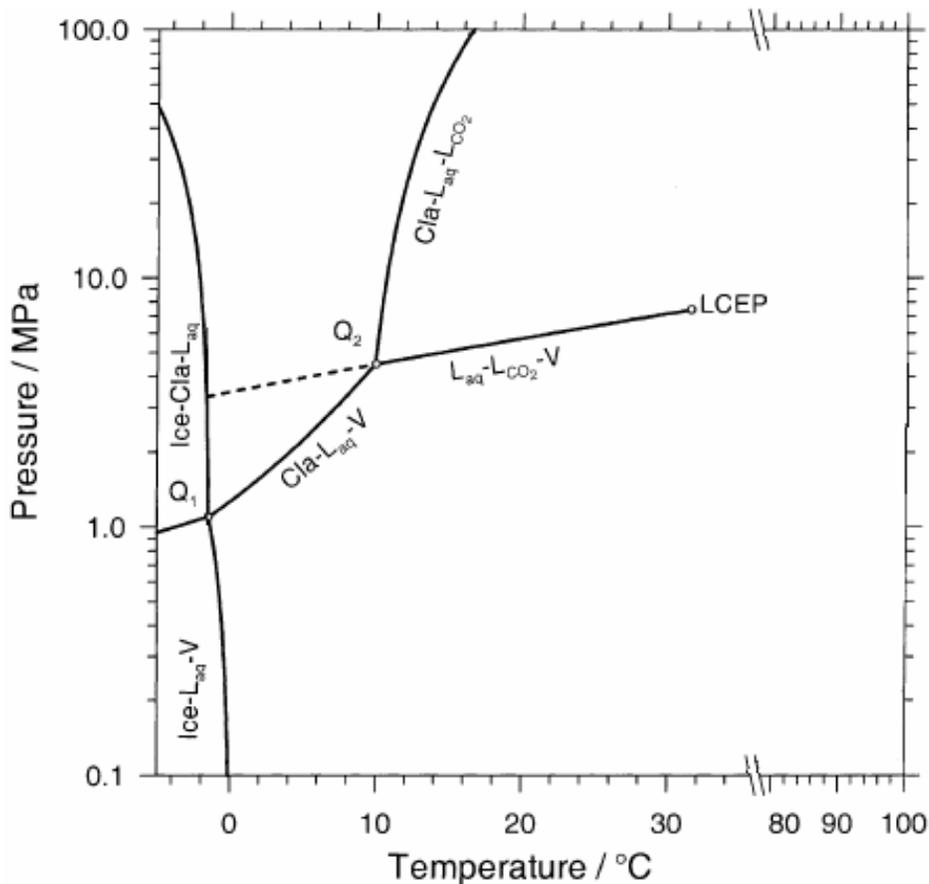


Figure 2-11. Phase equilibrium in the H<sub>2</sub>O and CO<sub>2</sub> system (Diamond and Akinfiev 2003).

LCEP denotes the lower critical end-point of the system. Quadruple point Q<sub>1</sub> indicates the equilibrium between H<sub>2</sub>O-ice, CO<sub>2</sub>-clathrate-hydrate, CO<sub>2</sub>-bearing water and CO<sub>2</sub>-vapor (Ice-Cla-L<sub>aq</sub>-V). The quadruple point Q<sub>2</sub> shows the equilibrium between CO<sub>2</sub>-clathrate-hydrate, CO<sub>2</sub>-bearing water, CO<sub>2</sub>-liquid and CO<sub>2</sub>-vapor (Cla-L<sub>aq</sub>-L<sub>CO2</sub>-V) (Diamond and Akinfiev 2003; Longhi 2004). At LCEP, liquid and gas phases critically merge to form a single fluid phase in the presence of a non-critical solid phase (McHugh and Krukoniš 1994).

Carbon dioxide clathrate hydrate is formed at temperatures below approximately 10 °C (Someya and others 2005; Anderson 2002). The clathrate hydrate is a non-stoichiometric crystalline compound, suggested as a natural gas storage medium, formed by a modification of the crystal structure of ice (Someya and others 2005; Ferdows and Ota 2005; Anderson 2002).

The CO<sub>2</sub> hydrate is a structure -I hydrate. Structure-I hydrate consists of 46 water molecules and 8 guest molecules at most per unit cell and forms two smaller cages of pentagonal dodecahedron (5<sup>12</sup>) and six larger cages of tetrakaidodecahedron (5<sup>12</sup>6<sup>12</sup>). CO<sub>2</sub> hydrates consist of three parts: interaction between water-water molecules, interaction between water-CO<sub>2</sub> molecules and interaction between CO<sub>2</sub>-CO<sub>2</sub> molecules. According to Anderson (2002), once carbon dioxide clathrate begins to form, it becomes nearly impossible to assess the partitioning of CO<sub>2</sub> between the liquid and solid phase. Regarding solubility of CO<sub>2</sub>, several studies state that solubility with the hydrate would decrease with decreasing temperature and pressure (Ferdows and Ota 2005).

#### **2.4.2 Dense Phase Carbon Dioxide**

Dense phase carbon dioxide (DPCD) processing, which includes liquid and supercritical CO<sub>2</sub>, is a continuous cold pasteurization method that affects microorganisms and enzymes under pressures below 50 MPa (7,252 psi) without applying high temperature treatments, based on the hypothesis that high pressure CO<sub>2</sub> dissolves in water to produce carbonic acid, thus the pH value will be temporarily lowered and able to inactivate enzymes (Damar and Balaban 2006; Del Pozo-Insfran and others 2006b; Ishikawa and others 1995; Shimoda and others 2001). Moreover, DPCD system removes dissolved oxygen, preventing degradation of several compounds, such as antioxidant phytochemicals; thus, DPCD process decreases phytochemical and antioxidant losses that occur during storage of juices (Del Pozo-Insfran 2006a; Subramaniam and others 2001). Fraser (1951) was the first to prove that DPCD technology can disrupt bacterial cells and some years later, Taniguchi and others (1987) showed the effect that supercritical CO<sub>2</sub> (20 MPa, 35 C, 2 hr) has on the enzyme activity. Furthermore, supercritical CO<sub>2</sub> has been recognized for sterilizing and inactivating viruses. Usually, supercritical reaction media have the potential to increase reaction rates, selectivity of chemical reactions, and facilitate separation of reactants, products and catalysts after reaction. In addition, principles for gas or liquid phase reactions may

be applied to supercritical phase reactions (Figure 2-12) (Subramaniam and Busch 2002; Subramaniam and others 2002).

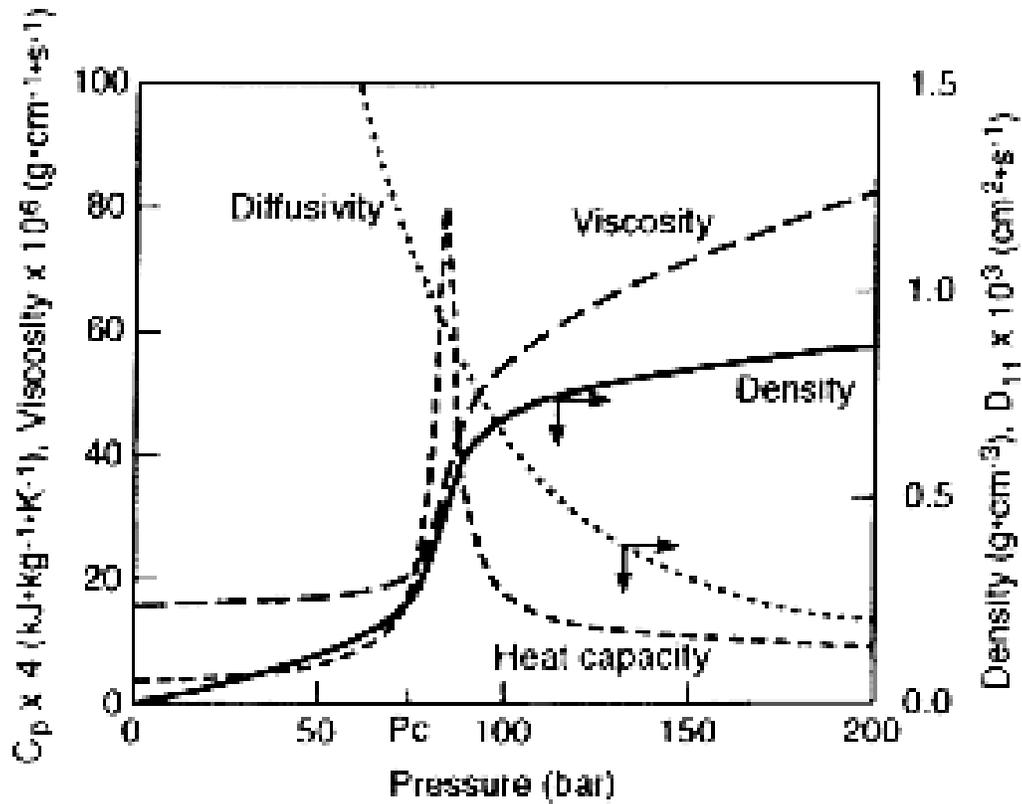


Figure 2-12. Variation of physico-chemical properties of CO<sub>2</sub> at near-critical conditions (Subramaniam and others 2002).

### 2.4.3 Supercritical Fluid Extraction (SFE)

Extraction is an important method to isolate natural odor/flavor components and other natural products such as essential oils. The product obtained from distillation/extraction, vacuum distillation, extraction with liquid solvents and adsorption has solvent residues (Bamberger and others 1999). However, supercritical CO<sub>2</sub> extraction results in a product without solvent residues and with a better taste/aroma, because it is a non-thermal process (Marteau and others 1995; Palazoğlu and Balaban 1998). According to Subramaniam and Busch (2002), CO<sub>2</sub> has limited reactivity; thus, supercritical CO<sub>2</sub> has many chemical applications to replace conventional organic solvents. To perform supercritical fluid extractions it is necessary to pump CO<sub>2</sub> through

a vessel previously filled with sample. After extraction, the supercritical fluid is depressurized for collection of extracted compounds (Schneider and others 2000). According to Clifford (1999), the factors that control supercritical fluid extraction are: the solute must be sufficiently soluble in the supercritical fluid to be removed by solution in the fluid flow; the solute must be transported sufficiently rapidly from the interior of the matrix in which it is contained and; the solute must be released by the matrix. A supercritical fluid instrument includes a high-pressure pump (one or two) to carry the supercritical fluid, a high pressure vessel to contain the sample, a polar cosolvent (ethanol) if necessary, a restrictor and a collection vial (Turner 2006). Figure 2-13 shows a schematic of SFE equipment.

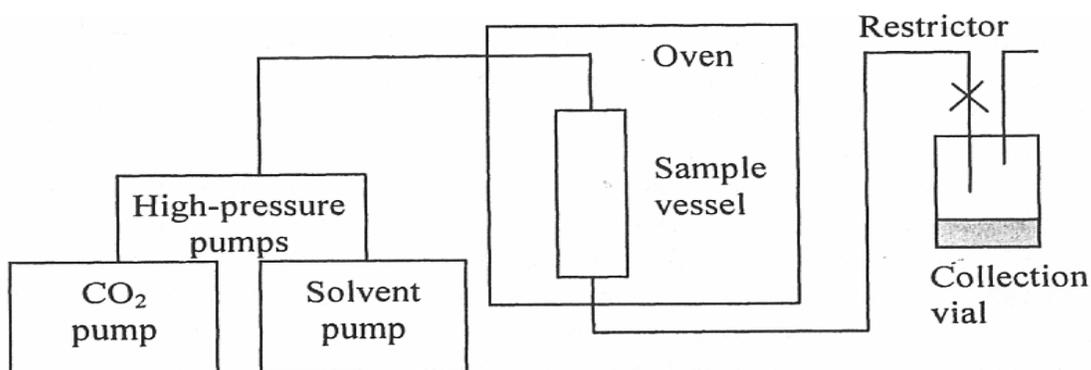


Figure 2-13. Diagram of supercritical fluid extraction equipment (Turner 2006).

## 2.6 Constituents that Affect Carbon Dioxide Solubility in Beverages

### 2.6.1 Carbonated Soft Drinks

Carbon dioxide solubility can be affected positively or negatively by different constituents present in the formulation of different soft drinks. The term soft drink applies to beverages containing flavors and/or fruit juices together with other constituents of technological or nutritional value designed to enhance the appearance and stability of the product and to ensure that its sensory properties remain intact during a reasonable shelf life (Taylor 2005). Some categories of ingredients are discussed in more detail in the following sections, in terms of CO<sub>2</sub>

solubility. The functional constituents of soft drinks and their typical usage levels are listed in Table 2-3.

Table 2-3. Soft drink components and their typical use level (Taylor 2005).

Component	Typical use level
Water	Up to 98% v/v when high-intensity sweeteners in use
Sugars	7-12% m/v when sole source of sweetener
Fruit juice	Widely variable usage
High-intensity sweeteners	Use based upon sucrose equivalent (e.g. aspartame might be employed at 0.40-6% m/v as sole sweetener)
Carbon dioxide	0.30-6% m/v
Acids (e.g. citric)	0.05-0.03% m/v
Flavours	Nature-identical and artificial: 0.10%-28% m/m. Natural: up to 0.5% m/m
Emulsifier	0.1% m/v
Colours (naturals or synthetic)	0-70 ppm
Preservatives	Statutory limits apply (e.g. sorbic acid up to 250 ppm in EU)
Antioxidants (e.g. BHA)	Less than 100 ppm, subject to user-country legislation
Quillaia extract (saponins)	Up to 200 mg/l (EU), up to 95 mg/l (USA)
Hydrocolloids (mucilaginous gums)	0.1-0.2% per GMP, minimum amount required to create desired effect
Vitamins/Minerals	ADI <sup>a</sup> applies

<sup>a</sup>ADI: acceptable daily intake.

### 2.6.1.1 Carbohydrate sweetener

According to Bessley (1990), the first association between sugars and carbonated soft drinks occurred in the seventeenth century when lemon juices containing natural sugars were added to spring water. Since Captain Cook, the use of carbohydrate sweeteners in juices and drinks has increased, in order to preserve the juice for long periods (O'Donnell 2005; Bessley 1990). In the past 10-15 years, the profile of bulk and intense sweetener use in soft drinks has changed (technical improvements in the manufacture of bulk sweetener with different carbohydrate profiles that deliver equivalent sweetness and mouthfeel properties to sugar at lower cost). In addition, due to an increasing consumer awareness of healthy eating and concern about the growing incidence of obesity and Type 2 diabetes, interest in low calorie carbonated soft drinks has increased considerably (O'Donnell 2005). An extensive number of carbohydrate sweeteners are used in soft drink industry, providing sweetness, mouthfeel, stability and color (in

some cases). Table 2-4 illustrates the properties of some carbohydrate sweeteners used in soft drinks.

Table 2-4. Properties of bulk sweeteners (O'Donnell 2005).

Sweetener/ carbohydrate	Relative sweetness (sucrose=1)	Solubility (g/100g water at 20°C)	Insulin- dependent metabolism	Caloric value (kcal/g)	Approval for use in soft drinks	
					EU	USA
Sucrose	1	200	Yes	4	N/A	N/A
Glucose syrup	0.6	High <sup>a</sup>	Yes	4	N/A	N/A
HFGS	0.9-1.0	High <sup>a</sup>	Yes	4	N/A	N/A
Fructose	1.2-1.8	374.83	No	4	N/A	N/A
FOS <sup>b</sup>	0.3-0.6	75	No	2	N/A	N/A
Inulin	0	10	No	1	N/A	N/A
Polydextrose	0	80	No	1	Yes	Yes
Trehalose	0.45	40.8	Yes <sup>c</sup>	4	Yes	Yes
Tagatose	0.92	62.0	No	1.5	No	Yes

<sup>a</sup> Solubility good, but varies with products of different specifications. <sup>b</sup>Fructo-oligosaccharides. <sup>c</sup>Glucose and insulin responses lower than glucose.

In general, sugars diminish the average level of CO<sub>2</sub> solubility, at pressures from 1 to 6 bars and pH set at 3.1 (Descoins and others 2006). In addition, sugars contribute sweetness and body to the drink, act as synergist and give balance to flavor (Steen 2005). Carbohydrate sugars used in carbonated soft drinks can be divided into those in a dry, granular form (e.g. granulated sucrose) and those in a liquid or syrup form (e.g. liquid sugar (sucrose in solution with water and glucose-type syrup produced from maize or wheat, e.g. glucose syrup or high-fructose glucose syrup)). Granulated sugar is a dry, crystallized disaccharide extracted from sugar beet and sugar cane called sucrose and liquid sugar consists of an aqueous solution of sucrose at a saturated concentration of 67 °Brix at 20 °C (Bessley 1990).

In United States, high-fructose corn syrups dominate the carbohydrate-sweetened soft drinks sector; however, in Europe the use of high-fructose glucose syrup (HFGS) is restricted by production quotas. Fructose (levulose) is a sugar in crystalline or syrup form. It is produced by hydrolyzing sucrose to a glucose-fructose mixture; the resulting monosaccharides (glucose and fructose) are separated using chromatography and the fructose is crystallized. Its sweetener

capacity is higher than sucrose (Table 2-4); thus, it can be used at lower concentrations to decrease the level of energy content in the formulations. The absorption and metabolic process of fructose by the body is very slow and does not depend of insulin production, being appropriate for diabetics (O'Donnell 2005).

### 2.6.1.2 Acidulants

The use of acidulants is an essential part of beverage formulation. Acidulants contribute to sharpness, sourness, background to flavor and increase thirst-quenching effects in soft drinks (Steen 2005). In addition, acidulants can indirectly prevent discoloration and rancidity, by acting as a synergist to antioxidants (Taylor 2005). Table 2-5 shows the list of the most common acidulants used in soft drinks.

Table 2-5. Acidulants used in beverage formulation (Taylor 2005).

Acidulants	Molecular weight	Melting point (°C)
Citric acid : 2-hydroxy-1,2,3-propane tricarboxylic acid	192.1	152-154
Tartaric acid (D-tartaric): 2,3-dihydroxy butanedioic acid	150.1	171-174
Phosphoric acid: orthophosphoric acid	98.0	42.35
Lactic acid (DL-lactic): 2-hydroxy propanoic acid	90.1	18
Malic acid (D-malic): 2-hydroxy butanedioic acid	134.1	98-102
Fumaric acid: <i>trans</i> -butenedioic acid	116.1	299-300
Acetic acid: ethanoic acid	60.0	16-18

Citric acid is the most widely used acid in fruit-flavored beverages. It used to be commercially produced from lemons, limes or bergamots by concentrating and precipitating the juice. Recently, it is produced using enzymes starting from glucose and other sugars. Tartaric acid is naturally present in grapes, currants, blackberries and cranberries. Tartaric acid has a sharper flavor than citric acid; thus, it is used in lower concentration to provide equivalent palate acidity. However, tartaric acid has lower solubility than citric acid. Phosphoric acid is used in soft drinks for its astringency to complement the dry and balsamic characteristic of cola drinks. It has a drier and sharper flavor than citric and tartaric acid. Malic acid is closely associated with

apples and it is a preferred acidulants in low-calorie drinks. It is also used to mask the off-taste of some sugar substitutes (Taylor 2005).

### **2.6.2 Milk**

Skim milk contains about 9% total solid, casein (2.5%), whey proteins (0.5%) and lactose. Solubility of CO<sub>2</sub> in milk has had the same behavior as in water, at different conditions of pressure and temperature. However at 25°C, solubility of CO<sub>2</sub> in milk was less. At 5.5 MPa and at 38 and 50 °C, solubility of CO<sub>2</sub> in milk was very similar to the solubility of water because casein was completely precipitated. This proved that casein was competing with CO<sub>2</sub> to get in solution (Tomasula and Boswell 1998).

## CHAPTER 3 MATERIALS AND METHODS

### 3.1 Design of the High Pressure Carbon Dioxide Solubility Apparatus

The concept of the solubility of a gas in a liquid at high pressures is simple. After the gas is saturated in the liquid, isolate a known amount of liquid at high pressure, reduce its pressure and measure the amount of gas that comes out of the liquid. The ratio of the mass of gas to that of liquid gives solubility. However, there are many design-related and practical challenges. Designing, building and testing the high pressure CO<sub>2</sub> solubility apparatus took one year and a half. The idea started from previous attempts to build an apparatus to measure CO<sub>2</sub> solubility, under high pressures, without success. The principle of the machine was to assure that the CO<sub>2</sub> measured was previously in solution in a liquid of known mass. Several versions of the machine were tested with water. The main dilemma was compressed gas (CO<sub>2</sub>) trapped in the system, during processing under high pressures, giving the impression that solubility of CO<sub>2</sub> was three or even four times higher than literature values. The solution was to generate a system able to recirculate the liquid during processing; based on the hypothesis that the density of CO<sub>2</sub> is lower than the density of water (or liquid food), at experimental conditions.

The experimental apparatus was designed to accurately measure the amount (v/v) of CO<sub>2</sub> in solution with water or any other liquid. There are two vessels: vessel 2 is above vessel 1. Vessel 1 has a capacity of approximately 200 ml and can be operated at temperatures between 0 to 45°C and pressure up to 24 MPa. Figure 3-1 shows the schematic drawing of the apparatus. Figure 3-1 shows the CO<sub>2</sub> tank, high pressure pump (HPP), heat exchanger (HE), pressure gauge (PG), back pressure regulator (BPR), thermocouple (T), metering valve (MV), gas meter (GM), water bath, bottle, stopper, fume hood (FH), two way valves (V), three way valves (TV), vessels and quick connects (QC). Figure A-1 shows some pictures of the equipment. From the CO<sub>2</sub>

tank until QC3, the apparatus is fixed, and between QC3 and BPR the apparatus is mobile (Figure A-2).

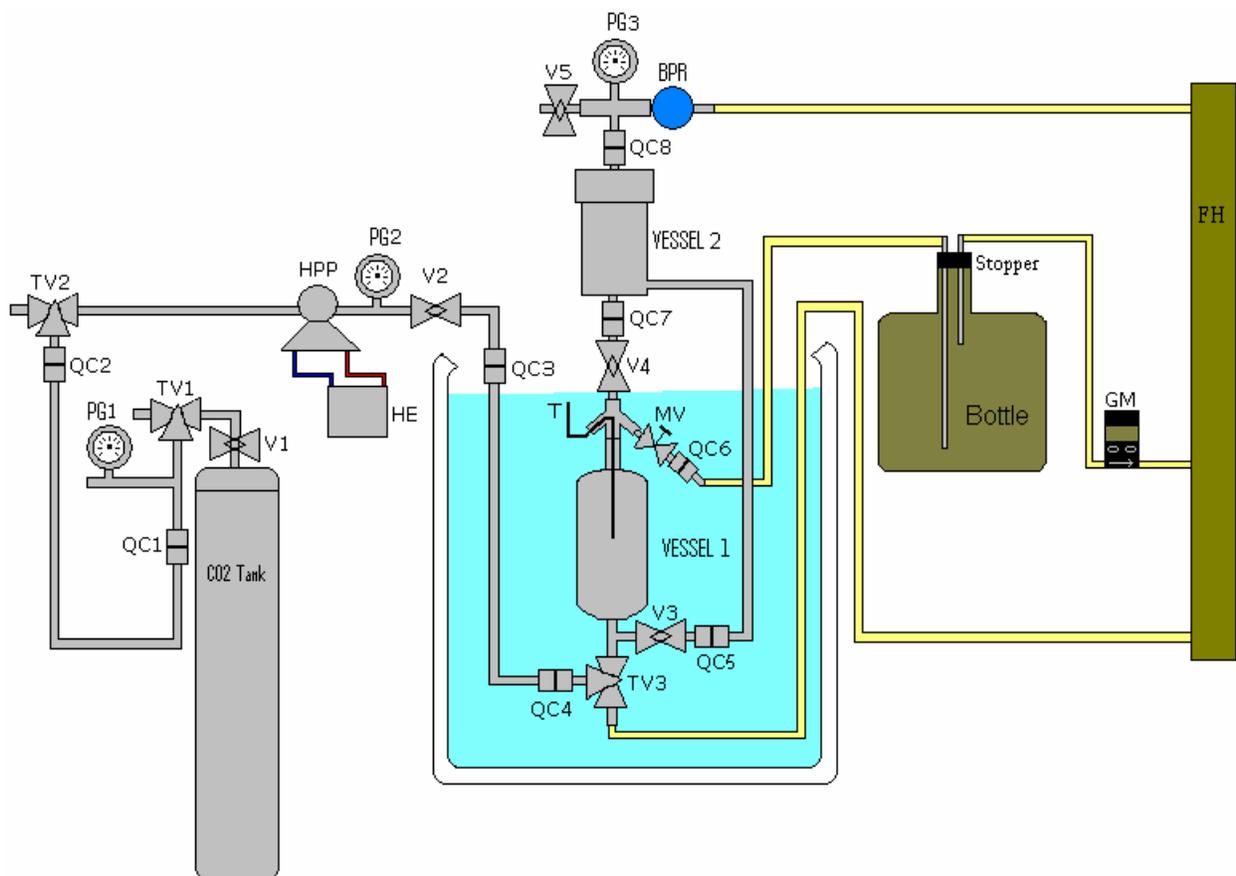


Figure 3-1. Schematics of the high pressure CO<sub>2</sub> solubility apparatus.

To connect various pieces of the apparatus together, it was necessary to use Teflon tape in the threads. The Teflon tape avoids leaks at high pressures. The Teflon tape has to be applied clockwise to every male connection (Figure A-3). Leaks were detected using a soap solution, from ACE Hardware Corp (Oak Brook, IL).

The CO<sub>2</sub> tank was ordered from Airgas South, Inc (in Gainesville, FL). It had a siphon tube, and contained 34 kg of liquid CO<sub>2</sub> (99.91% of purity). The tank valve was labeled as V1 in Figure 3-1. It was connected to TV1, a three-way valve to purge the line, followed by a pressure gauge PG1 (Figure A-4), to control and regulate the flow of CO<sub>2</sub> from the tank. TV1, TV2 and

TV3 were ordered from Swagelok Company (Jacksonville, FL, model SS-83XKF4). They were made of stainless steel, and can hold 41.2 MPa of pressure at temperature of 38 °C. TV2 was used to depressurize the line from the tank, in case of emergency. TV3 was also used to depressurize the line from the tank, during processing.

The high pressure pump (HPP) is from Milton Roy Company in Ivyland, PA (model X-10, serial N° M229150-1). It was used to pump liquid CO<sub>2</sub> through the system, to increase the pressure up to 27.5 MPa (Figure A-5). To liquefy CO<sub>2</sub>, it was necessary to use a heat exchanger (HE), containing a solution of water (50%) and antifreeze (50%), to reach very low temperatures (approximately -15 °C). The heat exchanger (HE) was from Fisher Scientific, model 900 and serial N° 870075 (Figure A-6).

The back pressure regulator (BPR) was used to regulate the pressure in the system. It was purchased from TESCO Industrial Controls, Elk River (part number is 26-1762-24). Its body and trim are made of stainless steel, the back-up ring is made of Teflon, the O-rings are made of buna-N, the seal is made of CTFE and remaining parts are made of stainless steel. Its controlled pressure range is from 0.34 to 41.37 MPa. Its inlet and outlet port type is NPT and the size is ¼". Its weight is 5 lbs (2.2 kg) and the BPR ambient operating and fluid media temperature is -40 °C to 73.8 °C. Figure A-7 shows the schematics of the high pressure/back pressure regulator and Figure A-8 shows the BPR used in the machine.

To control the pressure, the back pressure regulator is turned clockwise (to increase pressure) or counter-clockwise (to decrease it). When the system is depressurized using the BPR, the exiting CO<sub>2</sub> expands, cools and may turn to solid (dry ice), and the BPR may be obstructed. To prevent this, it was necessary to use an electrical heating tape around the BPR, and a variable autotransformer (Staco Energy Products, Dayton, OH) used to control the voltage

supplied to the belt. The percent used for the experiment varied between thirty and forty percent (30-40%) of 110 V. This setup is shown in Figure A-9.

The “water bath” was a cooler with a capacity of about 60 L water. The water in the cooler was recirculating through plastic tubes to a small high precision water bath (Hart Scientific, Utah; model 6035) that was set at 46-50 °C to increase and/or maintain a constant temperature in the system. To recirculate the water, it was necessary to use a Masterflex peristaltic pump (Cole Parmer, Chicago; model 7553-50), set around 3.5 in the speed control dial (Figure A-10).

To control the temperature in the cooler and inside the system, it was necessary to use thermocouples. The thermocouple used in the cooler was ordered from Omega® Engineering, part # JMQSS-125G-12. The thermocouple was made of stainless steel, 12” of length and 0.125” of diameter. The thermocouple inside the system was also ordered from Omega® Engineering (part # TQSS-116G-12 and QC# PL040052). The thermocouple was made of stainless steel, 1/16” of diameter, and 12” of length. It was designed to withstand vibration, high temperature and high pressure (Figure A-11). To connect this thermocouple to the system, a Swagelok tube fitting (part # SS-100-1-4) was used. It is a male connector 1/16” and male NPT 1/4”.

The metering valve (MV) was ordered from Swagelok Company (Jacksonville, FL, model # SS-31RF4). It is a medium-flow high pressure (34.47 MPa) metering valve. It was used to control the flow of the CO<sub>2</sub> coming out of the system (Figure A-12), to be measured using the gas meter (GM). The GM was obtained from Alicat Scientific (Tucson, AZ), model number M-1SLPM-D (CO<sub>2</sub>). It is calibrated to measure CO<sub>2</sub> specifically, at a maximum flow of 1 standard liter per minute (Figure A-13). The GM is based on the accurate measurement of volumetric flow at a standard temperature and pressure (0.1 MPa and 25 °C). The volumetric flow rate is

determined by creating a pressure drop across a unique internal restriction, name as Laminar Flow Element (LFE), and measuring the difference on pressure across it. Its operating principle is known as the Poiseuille Equation:

$$Q = \frac{(P_1 - P_2)\pi \cdot r^4}{8\eta L}, \quad (3-1)$$

where Q is the volumetric flow rate,  $P_1$  is the static pressure at the inlet,  $P_2$  is the static pressure at the outlet, r is the radius of the restriction,  $\eta$  is the (eta) absolute viscosity of the fluid, and L is the length of the restriction. Since  $\pi$ , r (radius) and L (length) are constant; Equation 3-1 is rewritten as:

$$Q = K \left( \frac{\Delta P}{\eta} \right), \quad (3-2)$$

where K is a constant factor calculated from the restriction geometry,  $\Delta P$  is the differential pressure and  $\eta$  the absolute viscosity. Viscosity of carbon dioxide at 0.1 MPa and 25 ° C is  $149.33 \text{ g}\cdot\text{cm}^{-1}\cdot\text{sec}^{-1}$ . The volumetric flow rate units are SLPM (standard liters per minute).

The cross-angled connector between the MV, V4, T and Vessel 1 was designed and made of stainless steel to withstand high pressures. Based on the buoyancy principle, the angle connections allow any possible bubble in the system to move to the top of the equipment. This reduces / eliminates the error of excess  $\text{CO}_2$  reading in the gas meter (GM) when the system is depressurized (Figure A-14).

The two way valves (V), and quick connects (QC) were ordered from Swagelok Company (Jacksonville, FL), and are made of stainless steel. The two way valves (straight ball valves) are model SS-83KF4, 1/4" end connections size and female NPT end connection type. Their pressure rating is 41.37 MPa at 38 °C (Figure A-15). The QC are also made of stainless steel, their pressure rating is 41.37 MPa at 21.11 °C. The quick connect stems are model SS-QF4-S-

4PF (female NPT) and SS-QF4-S-4PM (male NPT). The quick connects bodies are model SS-QF4-B-4PF (female NPT) and SS-QF4-B-4PM (male NPT) (Figure A-16).

Vessel 1 has a maximum allowable working pressure of 34.4 MPa at 121 °C. It was made of stainless steel, its capacity is 150 ml, and its end size connections are 1/4" NPT (Figure A-17). Vessel 2 has a maximum allowable working pressure of 68.95 MPa at 22 °C. Its body and cover were made of stainless steel; the o-ring of Buna N; and the cap of alloy steel. Its capacity is 55 ml, and its end size connections are 1/4" NPT (Figure A-18 and Figure A-19). The main difficulty was that the gas that remained in vessel 1 at the end of the saturation period had to "bubble up" to vessel 2 through valve V4, and at the same time some liquid from vessel 2 had to flow down to vessel 1 by gravity. Because of the small inner diameter of the valve V4, this did not happen, and some gas was left trapped in vessel 1. Since this gas was under pressure, upon de-pressurization its volume expanded greatly, and gave false readings about solubility. Valve V4 was replaced with a larger diameter gate valve (a forged stainless steel gate valve, Figure A-20, class 1500, 0.38" of opening diameter, 1/2" NPT connection, model number 15GT-6L-U-G, from NEWCO/OIC Valves, Jacksonville, FL) with the expectation of easier CO<sub>2</sub>-liquid exchange between vessels 1 and 2. However, this valve leaked. Another solution had to be found. To recirculate the liquid from the top vessel 2 to the bottom vessel 1, it was necessary to drill an opening (1/4" NPT) in the bottom of vessel 2 (Figure A-19) and connect it to the bottom of vessel 1. This assured that the liquid pressure at the top would force the liquid to flow from vessel 2 to vessel 1 by gravity by the side arm, and therefore "push" any gas remaining in vessel 1 to bubble up to vessel 2 through valve V4. Therefore, it was assured that after the flow of CO<sub>2</sub> from the bottom of vessel 1 (to reach saturation) was stopped, all gas remaining in vessel 1 would bubble up to vessel 2. The accuracy of the experimental solubility measurement depended

on no un-dissolved gas remaining in vessel 1. Please note that at pressures where the density of CO<sub>2</sub> becomes higher than that of the liquid, this system will not work properly.

The plastic bottle has a capacity of 5 gallons and it was made of high density polyethylene (HDPE). The opening of the bottle was restricted by a stopper (number 11) with two holes. One opening was for the incoming CO<sub>2</sub> (with possible entrained liquid), and the other was for the CO<sub>2</sub> to go out to the gas meter. The tube attached in the outgoing opening was shorter, to allow just the CO<sub>2</sub> to exit, and be measured at the GM (Figure A-21)

### **3.2 Preparation of the Samples**

#### **3.2.1 Distilled Water**

To verify that the high-pressure CO<sub>2</sub> apparatus worked properly, it was necessary to compare its results with the literature values (v/v) of CO<sub>2</sub> dissolved in pure water. The distilled water used was obtained from the building source (triple filtration). The volume of distilled water used was approximately 500 ml per run.

#### **3.2.2 Fructose**

The D-Fructose (reagent grade) was ordered from Fisher Scientific (Fair Lawn, New Jersey; lot number 068019). The sample with 10% fructose and 90% water (200 grams of fructose in a total solution of 2000 ml with distilled water) corresponds to 9.7 °Brix, and the sample with 5% fructose and 95% water (100 grams of fructose in a total solution of 2000 ml with distilled water) corresponds to 4.8 °Brix. The fructose was measured using an analytical balance (model PG603-S), Mettler Toledo. The °Brix data was measured with a portable refractometer, model 13-946-20, from Fisher.

#### **3.2.3 Malic Acid**

The malic acid (food grade, C<sub>4</sub>H<sub>2</sub>O<sub>5</sub>) in powder was ordered from Presque Isle Wine Cellars (Philadelphia, PA). The sample with 0.5% malic acid and 99.5% water (10 grams of

malic acid in a total solution of 2000 ml with distilled water) had a pH of 2.35. The sample with 5% malic acid and 95% water (100 grams of malic acid in a total solution of 2000 ml with distilled water) had a pH of 1.79. The pH values were measured using an expandable ion analyzer (EA 920, model Q027A), from Orion Research Incorporated (Cambridge, MA).

### **3.3 Experimental Procedure**

#### **3.3.1 Preliminary Procedure**

First, the HE was turned on for about 20 minutes before starting the HPP (HE had to reach approximately -15 °C). During that period, the cooling jacket of the HPP was getting covered with a thin layer of ice. At the same time, the high precision water bath was turned on, to start warming up the water inside of the cooler. Since the warming process could take about 1.5 to 2 hours, batches with water (approximately 2 liters per batch) were heated in the microwave and added to the cooler, to speed up the process.

In the stationary part of the apparatus, it was important to verify that V1 (that corresponds to the tank) and V2 were closed, TV1 was turned to the right and TV2 was turned to the left. The previous procedure was performed to prevent CO<sub>2</sub> to escape out of the apparatus, at the time to open V1; therefore, to avoid gas inhalation. Then, before submerging the mobile part in the cooler, it was important to confirm that V5 and MV were closed, and that V3 and V4 were opened. TV3 should be turned to the left or facing up and the BPR should be slightly open (clockwise), to hold a back-pressure of approximately 2.76 MPa. Also, QC4, QC5, QC6 and QC7 should be already connected (Figure B-1).

When the complete apparatus was connected (stationary and mobile parts), and the plastic tubes coming from TV3, BPR and GM were placed inside of the fume hood (FH), it was necessary to ensure that between QC6 and GM there was only CO<sub>2</sub>. For that reason, V1 was slightly opened until approximately 2.76 MPa was reached (pressure was confirmed in PG2).

Next, V2 was slowly opened and the BPR was regulated to increase the pressure up to 1.38 MPa (pressure was confirmed in PG3); then, V2 was closed. The GM was zeroed and cleared (Alicat Scientific 2007), and the stopper was verified to be in place. Then, the MV was opened slowly and the CO<sub>2</sub> coming out of the system was measured until read about 0.250 standard liters /min, MV was closed. The system was depressurized, and when the pressure was 0 psig (pressure read at PG3), QC3 was disconnected.

### **3.3.2 Pumping the Liquid Sample into the System**

Before starting, QC8 should be disconnected and a plastic tube should be connected to QC8 stem. The sample was held in a small container of approximately 2 liters. By using the peristaltic pump, the sample was pumped through a plastic tube to the stem connection of QC3. The liquid was pumped until both vessel 1 and 2 were filled. When the system was full, water started coming from the plastic tube connected to the QC8 stem (Figure B-2). The peristaltic pump was turned off. The plastic tube in the QC3 stem was removed, and the QC3 stem was quickly connected to its QC3 body. The plastic tube in the QC8 stem was also removed, and QC8 body was connected to its corresponding stem.

### **3.3.3 Carbonating the Sample**

Before starting the carbonation process, it was necessary to verify that the temperature inside of the system was the desired temperature. Then, V1 was opened until reaching approximately 2.76 MPa (pressure was confirmed in PG2); then, it was closed. Next, V2 was opened very slowly and the BPR was turned to increase the pressure, at the same time. The flow rate of the CO<sub>2</sub> with water coming from the BPR should be very slow. The previous step was performed to ensure that the system was filled with CO<sub>2</sub>, and that there were no other gases. The V2 was closed, the BPR was regulated to hold approximately 6.89 MPa and the HPP was set to about 77% of flow rate using the micrometers (Figure A-5).

V1 was opened again and the HPP was turned on. The variable autotransformer was also turned on. V2 was opened very slowly and, if some gas with water was coming out of the system, the BPR was opened to increase the pressure, until around 1.03-1.38 MPa above the desired pressure was reached. At that point, the CO<sub>2</sub> flow rate of the HPP was reduced to about 37%, by turning clockwise the micrometers. The HPP remained on during 1 hour and 10 minutes to reach saturation of CO<sub>2</sub> in the liquid. During this time, CO<sub>2</sub> continuously bubbled through the liquid (entering from the bottom of vessel 1, and exiting off the top of vessel 2 through BPR), and saturated the liquid with CO<sub>2</sub>.

### **3.3.4 Measuring Solubility**

After the saturation time, with CO<sub>2</sub> passing through the system, V2 was closed. Immediately after this, the HPP was turned off; and V1 was closed. Next, TV3 was very slowly turned to the right (clockwise); and V2 was opened very slowly, while it was warmed up with some hot water from the cooler. The variable transformer was turned off. When the pressure was 0 MPa (pressure was confirmed in PG2), QC3 and QC4 were disconnected. Then, the mobile part of the equipment was shaken from side to side, while still immersed in water (around 1 minute per side) and up/down (20 times). The purpose of this was to loosen any CO<sub>2</sub> bubbles attached to the inner surfaces of vessel 1, and allow them to bubble up to vessel 2. This procedure took around 3-5 minutes. If the pressure (read in PG3) was just at the desired level, first V3 and then V4 were closed. However, if the pressure was still higher than desired, it was necessary to adjust it to the desired level.

The variable transformer was turned on and the BPR was turned very slowly, to depressurize the top part of V4. The GM was again zeroed and cleared.

At this point, it was certain that there was only liquid phase in vessel 1, and the dissolved CO<sub>2</sub> in that liquid. The MV was slightly opened to start depressurization, and this continued

until all the dissolved gas came out of the system and the pressure read in PG3 was 0 MPa. The maximum flow rate allowed in the GM was 0.350 slpm (standard liters per minute), to prevent that the system cooled by expansion of CO<sub>2</sub>. To expand and read all the CO<sub>2</sub> that was in solution took around 20-25 minutes. When the volumetric flow rate in the GM was 0 slpm, QC8 was disconnected and the rest of the mobile part was removed from the ice cooler. As soon as the equipment was removed, QC5 was disconnected under a small container of 2 liters of volume, to allow the liquid coming out of vessel 2 to be collected. Then QC7 was disconnected.

All the end connections were dried. QC6 was disconnected and all the liquid in the plastic tube and in the bottle was collected in a container of 5 liters (Figure B-3). V4 was opened inside of the same container of 5 liters (Figure B-4), subsequently TV3 was turned to the left and all the liquid from vessel 1 was collected. At the end, the liquid collected was measured using a graduated cylinder (Figure B-5). This amount was the basis of the solubility calculations.

To convert the volumetric flow (standard liters) to mass flow of CO<sub>2</sub>, it was necessary to divide it by 22.4 slt·mol<sup>-1</sup>, and then, multiply it by 44.01 g mol<sup>-1</sup>. Solubility was calculated as the rate of grams of CO<sub>2</sub> in 100 grams of liquid.

### **3.3.5 Cleaning the Apparatus**

The mobile part of the apparatus was separated by disconnecting the QC's. The various parts were washed in a solution of water with soap. Then, the parts were rinsed with abundant water, and consequently, they were rinsed with distilled water.

## **3.4 Experimental Design**

The carbonation process variables were pressure, temperature and composition. The pH and °Brix of the model liquid samples were also measured. Experimental conditions were decided with the goal of measuring the solubility of CO<sub>2</sub> above its critical point (temperature 31°C and pressure 7.4 MPa) and below high CO<sub>2</sub> density levels at high pressures. The first

phase of the experiment consisted of testing the high pressure CO<sub>2</sub> solubility apparatus, and comparing the experimental solubility values of CO<sub>2</sub> in pure water with literature data. Two levels of pressure were used: 7.58 MPa (74.85 atm) and 10.34 MPa (102.07 atm) at 40 °C. Carbon dioxide density at those pressures and temperature was approximately 0.2 g/ml and 0.65 g/ml, respectively (Clifford and Williams 2000).

The second phase of the experiment consisted in determining the solubility of CO<sub>2</sub> in a model liquid food of known composition (different concentrations of fructose and malic acid). Two levels of fructose concentration (5% and 10% w/v), and two levels of malic acid concentration (0.5% and 5% w/v) were used. The two concentrations of fructose and malic acid were selected according to the typical usage levels of functional constituents in soft drinks (Taylor 2005). Every solubility measurement was performed in duplicate. Table 3-1 shows the different levels of each carbonation variable.

Table 3-1. Different levels of each variable in the two phases of the experiment.

Treatment	First Phase		
	Temperature	Pressure	Model Liquid
1	40 °C	7.58 MPa	Distilled water
2	40 °C	10.34 MPa	Distilled water
Second Phase			
	Temperature	Pressure	Model Liquid
3	40 °C	7.58 MPa	Fructose 5 % m/v
4	40 °C	7.58 MPa	Fructose 10 %m/v
5	40 °C	10.34 MPa	Fructose 5 % m/v
6	40 °C	10.34 MPa	Fructose 10 % m/v
7	40 °C	7.58 MPa	Malic Acid 0.5 % m/v
8	40 °C	7.58 MPa	Malic Acid 5 % m/v
9	40 °C	10.34 MPa	Malic Acid 0.5 % m/v
10	40 °C	10.34 MPa	Malic Acid 5 % m/v

### 3.5 Data Analysis

Statistical analysis consisted of performing an analysis of variance (ANOVA) and mean separation to evaluate the difference between solubilities at the different conditions of pressure and composition, at 40 °C. The analysis was divided into two phases. In the first phase

significant differences between the experimental and literature values were evaluated. The null hypothesis ( $H_0$ ) was: At least one of the experimental mean results is different from literature results. The alternative hypothesis ( $H_1$ ) was: Means of the experimental results are equal to literature results. The second phase consisted in determining if the reduction in the solubility of  $CO_2$  in solution with pure water was significant, by increasing the solute (fructose or malic acid) concentration in the liquid. The null hypothesis ( $H_0$ ) was: Means of the solute experimental results are equal to the experimental mean reference. The alternative hypothesis ( $H_1$ ) was: There was significant difference between solute experimental results and the mean of experimental reference. The statistical data analysis was conducted by performing a Least Square Mean (LS-Mean) analysis and the Least Significant Differences (LSD) test, with  $P < 0.05$ . The software programs used were STATISTICA 97 and SAS 9.1.

CHAPTER 4  
RESULTS AND DISCUSSION

**4.1 Solubility of Carbon Dioxide in Distilled Water**

To demonstrate the accuracy and precision of the high-pressure CO<sub>2</sub> solubility apparatus, it was necessary to compare the experimental results of CO<sub>2</sub> solubility in pure water with the literature values. The CO<sub>2</sub> solubility chart developed by Dodds and others (1956) was used as reference. Also the chemical/thermodynamic simulation program Aspen Plus<sup>TM</sup> 12.1 (Schweiss 1997) was used as a simulation reference. The CO<sub>2</sub> solubility chart (Figure 2-8) shows the solubility of CO<sub>2</sub> in pure water (kg/100 kg of water), at pressures from 1 to 70.93 MPa, and at temperatures from 0 to 120 °C. According to this chart, solubility of CO<sub>2</sub> at 110.34 MPa and 40 °C is 5.68 kg/100 kg of pure water. At conditions of 7.58 MPa and 40 °C, solubility of CO<sub>2</sub> is 5.00 kg/100 kg of water. The Aspen Plus<sup>TM</sup> 12.1 was designed to predict the behavior of chemical systems (Schweiss 1997). According to this program, at a constant temperature of 40 °C, solubilities of CO<sub>2</sub> in pure water at 7.58 MPa and 10.34 MPa of pressures are 4.6 and 5.7 kg/100 kg of liquid, respectively.

The experimental results of solubility of CO<sub>2</sub> in pure water obtained from the apparatus, at a constant temperature of 40 °C, are displayed in Table 4-1.

Table 4-1. Experimental results of solubility of CO<sub>2</sub> in pure water.

Pressure (MPa)	Distilled water (g)	CO <sub>2</sub> (slt <sup>1</sup> )	CO <sub>2</sub> (g)	Solubility (g/100g <sup>2</sup> )	Mean (g/100g <sup>2</sup> )	St. Dev.	Literature (g/100g <sup>2</sup> )	Difference (g/100g <sup>2</sup> )
7.58	171	4.063	7.98	4.67				
7.58	168	4.176	8.20	4.88	4.77	0.15	5.00	0.23
10.34	169	4.625	9.08	5.38				
10.34	169	4.863	9.55	5.65	5.51	0.20	5.68	0.17

<sup>1</sup>Standard liters. <sup>2</sup>Grams of CO<sub>2</sub> per 100 g of pure water. <sup>3</sup>Standard Deviation in g of CO<sub>2</sub> per 100 g of pure water.

According to Table 4-1, the mean solubility of CO<sub>2</sub> in water at pressure of 7.58 MPa is 0.23 g/100 g lower than the literature. Also, at pressure of 10.34 MPa, the mean of solubility of

CO<sub>2</sub> is 0.17 g/100g below the reference. Those differences could be attributed to the time of saturation with CO<sub>2</sub>. If the time of passing CO<sub>2</sub> through the system increases, solubility of CO<sub>2</sub> in liquids would increase until it reaches saturation. This has been demonstrated in preliminary experiments (data not shown). According to statistical analysis using Statistica 97 and SAS 9.1 programs, those differences were not significantly different. Tables 4-2, 4-3 and 4-4 show the summary of the analysis of variance (ANOVA), summary of least square mean (LS Mean) analysis and the least significant difference (LSD) tests, respectively.

Table 4-2. Summary of the analysis of variance (ANOVA) of the solubility of CO<sub>2</sub> in pure water.

Source	DF	Sum of squares	Mean square	F value	Pr > F	Multiple R	Multiple R <sup>2</sup>	Adjusted R <sup>2</sup>
Model	1	0.5462	0.5462	17.77	0.0519	0.9480	0.8988	0.8482
Error	2	0.0614	0.0307					
Corrected Total	3	0.6076						

Table 4-3. Summary of the least square mean (LS Mean) analysis of the solubility of CO<sub>2</sub> in pure water.

Pressure (MPa)	Solubility Mean (g/100g*)	Solubility Standard Error	Solubility -95.00%	Solubility +95.00%	Standard deviation	Coefficient of variation
7.58	4.77	0.1239	4.24	5.30	0.15	0.03
10.34	5.51	0.1239	4.98	6.05	0.20	0.03

\*Grams of CO<sub>2</sub> per 100 g of pure water.

Table 4-4. P-values from the least significant difference (LSD) test between experimental mean data and literature data of solubility of CO<sub>2</sub> in pure water.

Treatments	Experimental data		Literature data	
	7.58 MPa	10.34 MPa	7.58 MPa	10.34 MPa
Experimental data	7.58 MPa	-	0.0519	0.4045
	10.34 MPa	0.0519	-	0.1390
Literature data	7.58 MPa	0.4045	0.1390	-
	10.34 MPa	0.0499	0.4776	0.1059

Note: P-values in italic font are lower than  $\alpha = 0.05$ ; thus, the correspondent groups are significantly different.

Table 4-2 shows that the null hypothesis ( $H_0$ ) was not rejected, due to a P-value higher than  $\alpha = 0.05$  ( $Pr > F = 0.0519$ ); therefore, at least on the experimental mean results is different from the literature. Table 4-4 shows significant difference between the pressure of 7.58 MPa,

from experimental mean data, and the pressure of 10.34 MPa, from literature results. However, within the same conditions of pressure, there was no significant difference between the experimental mean results and the literature data; differential values were higher than  $\alpha = 0.05$ , and the average coefficient of variation level was 0.03. In addition, the confidence interval for pressures of 7.58 and 10.34 MPa were  $5.51 \pm 1.76$  and  $4.77 \pm 1.37$  g of CO<sub>2</sub>/100g of liquid, respectively. The corresponding literature values for each pressure fits within the confidence interval. Therefore, the experimental results, obtained from the high-pressure carbon dioxide solubility apparatus are statistically acceptable and the apparatus is a functional instrument to measure CO<sub>2</sub> solubility in liquids at the conditions of pressure and temperature tested in this study.

#### 4.2 Solubility of Carbon Dioxide in Fructose Solutions

Solubility of CO<sub>2</sub> in fructose solutions was measured at a constant temperature of 40 °C and at two levels of pressures (7.58 and 10.34 MPa). Table 4-5 shows the experimental results of CO<sub>2</sub> solubility in the different fructose solution concentrations (5% and 10%).

Table 4-5. Experimental results of CO<sub>2</sub> solubility in solutions with different concentration of fructose.

Pressure (MPa)	Fructose solution (g)	CO <sub>2</sub> (slt <sup>1</sup> )	CO <sub>2</sub> (g)	Solubility (g/100g <sup>2</sup> )	Mean (g/100g <sup>2</sup> )	St. dev <sup>3</sup>	DW <sup>4</sup> (g/100g <sup>2</sup> )	Difference <sup>5</sup> (g/100g <sup>2</sup> )
5% Fructose Concentration								
7.58	169	3.983	7.82	4.63				
7.58	172	3.913	7.69	4.47	4.55	0.11	4.77	0.23
10.34	172	4.102	8.06	4.68				
10.34	170	4.228	8.31	4.89	4.78	0.14	5.51	0.73
10 % Fructose Concentration								
7.58	170	3.608	7.09	4.17				
7.58	172	3.563	7.00	4.07	4.12	0.07	4.77	0.66
10.34	170	3.523	6.92	4.07				
10.34	172	3.774	7.41	4.31	4.19	0.17	5.51	1.32

<sup>1</sup>Standard liters. <sup>2</sup>Grams of CO<sub>2</sub> per 100 grams of solution. <sup>3</sup>Standard Deviation in grams of CO<sub>2</sub> per 100 grams of solution. <sup>4</sup>Mean solubility of CO<sub>2</sub> in distilled water. <sup>5</sup>Differences between DW and Mean.

According to Table 4-5, by increasing the fructose concentration in a liquid, solubility of carbon dioxide decreases. Descoins and others (2004) stated that at conditions of 6 atm of pressure and at pH of 3.1 an increment of the concentration of sugar (0, 10 and 40 g/l of sugar) yields a decrease of the average level of dissolved CO<sub>2</sub> due to different orientation of the water molecules around the solute particles; therefore, water is less free to interact with other compounds, in this case CO<sub>2</sub>. Figure 4-1 shows the change in solubility of CO<sub>2</sub> in different concentrations of fructose in the solution. The 0% of fructose concentration is represented by solubility of CO<sub>2</sub> in pure water.

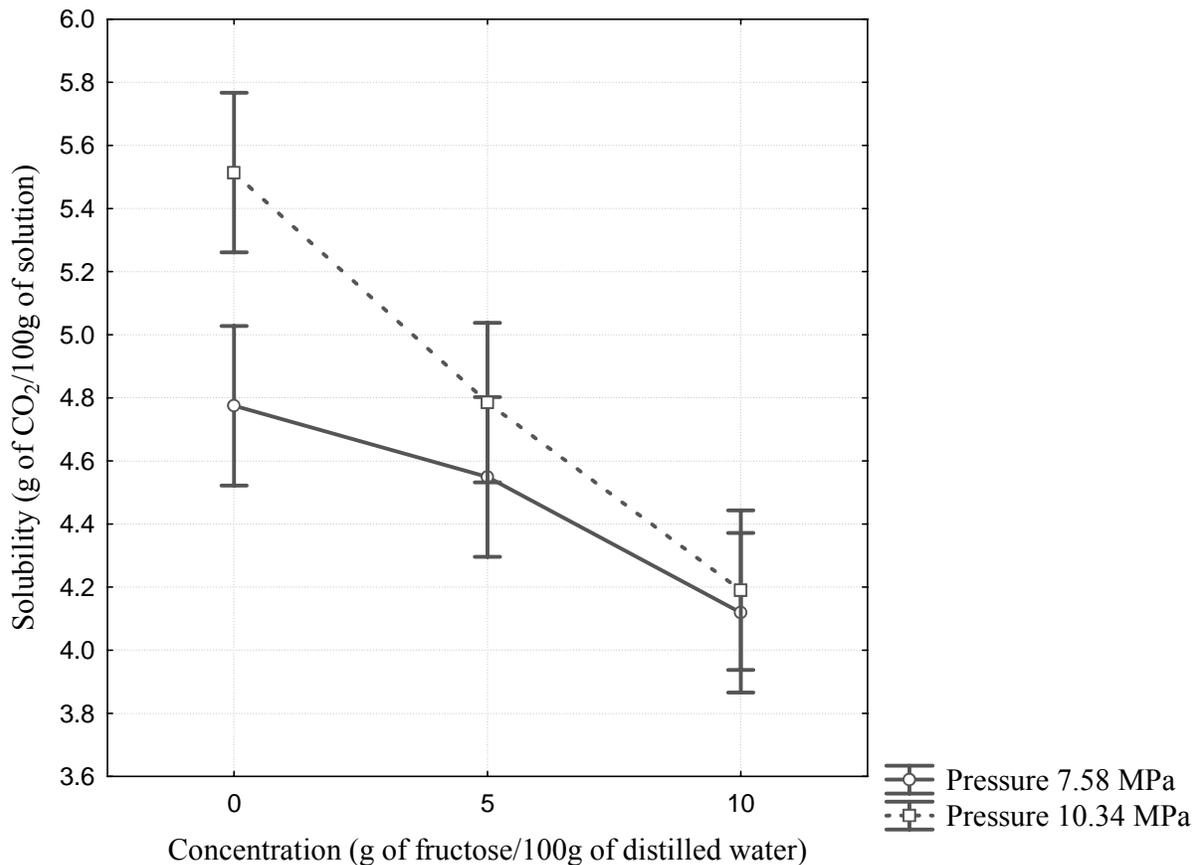


Figure 4-1. Solubility of CO<sub>2</sub> versus concentration of fructose solutions, at 7.58 and 10.34 MPa, and at a constant temperature: 40 °C. Vertical bars denote 0.95 confidence intervals.

Figure 4-1 shows the solubility of CO<sub>2</sub> at 7.58 MPa (blue line), and at 10.34 MPa (no continue red line). At 7.58 MPa, the mean solubility of CO<sub>2</sub> in pure water (0% of fructose) did

not decrease significantly at 5% of fructose; nevertheless, at 10% the difference is noticeable. At 10.34 MPa, the mean solubility of CO<sub>2</sub> in pure water decreased significantly while concentration of fructose in the solution increased to 5% and to 10%. Tables 4-6, 4-7 and 4-8 display the analysis of variance (ANOVA), the LS mean analysis and the LSD test, respectively.

Table 4-6. Analysis of variance (ANOVA) of solubility of CO<sub>2</sub> in fructose solutions of different concentrations.

Source	DF	Sum of squares	Mean square	F value	Pr > F	Multiple R	Multiple R <sup>2</sup>	Adjusted R <sup>2</sup>
Model	5	2.5671	0.5134	24.05	0.0007	0.9759	0.9524	0.9128
Error	6	0.1281	0.0213					
Corrected Total	11	2.6952						

Table 4-7. Least Square (LS) Mean analysis of solubility of CO<sub>2</sub> in fructose solutions of different concentrations.

Pressure (MPa)	Fructose (%)	Solubility mean (g/100g <sup>1</sup> )	Solubility standard error	Solubility -95.00%	Solubility +95.00%	Standard deviation	Coefficient of variation
7.58	5	4.77	0.1158	4.15	4.80	0.11	0.02
10.34	5	5.47	0.1158	5.15	5.80	0.14	0.03
7.58	10	4.47	0.1158	4.14	4.79	0.07	0.02
10.34	10	4.68	0.1158	4.36	5.00	0.17	0.04

<sup>1</sup>Grams of CO<sub>2</sub> per 100 g of fructose solution.

Table 4-8. P-values from the least Significant Difference (LSD) test of solubility of CO<sub>2</sub> in fructose solutions of different concentrations.

Treatments		7.58 MPa			10.34 MPa		
		0 %	5 %	10 %	0 %	5 %	10 %
7.58 MPa	0 %	-	0.1732	<i>0.0042</i>	<i>0.0023</i>	0.9476	<i>0.0071</i>
	5 %	0.1732	-	<i>0.0258</i>	<i>0.0006</i>	0.1577	<i>0.0495</i>
	10 %	<i>0.0042</i>	<i>0.0258</i>	-	<i>0.0001</i>	<i>0.0039</i>	0.6426
10.34 MPa	0 %	<i>0.0023</i>	<i>0.0006</i>	<i>0.0001</i>	-	<i>0.0025</i>	<i>0.0001</i>
	5 %	0.9476	0.1577	<i>0.0039</i>	<i>0.0025</i>	-	<i>0.0066</i>
	10 %	<i>0.0071</i>	<i>0.0495</i>	0.6426	<i>0.0001</i>	<i>0.0066</i>	-

Note: Values in italic font are less than  $\alpha = 0.05$ ; thus, the correspondent groups are significantly different.

In the ANOVA (Table 4-6), the p-value denotes (0.0007) that at least one of the treatments was significant difference between one or more treatments (0, 5 and 10 % of fructose concentration). In the LS mean analysis (Table 4-7), the maximum coefficient of variation (0.04) reveals that the experimental procedure has an acceptable error, below 5%. The LSD test

showed the mean solubilities that were statistically different. According to Table 4-8, the fructose concentration of 5% (4.8 °Brix) decreased significantly the solubility of CO<sub>2</sub> at pressure of 10.34 MPa; however, at 7.58 MPa solubility did not change considerably. The 10% (9.7 °Brix) concentration of fructose reduced considerably the solubility of CO<sub>2</sub> in the solution, at both pressures (7.58 and 10.34 MPa).

### 4.3 Solubility of Carbon Dioxide in Malic Acid Solutions

Solubility of CO<sub>2</sub> in malic acid solutions was measured at a constant temperature of 40 °C and at pressures of 7.58 and 10.34 MPa. Figure 4-2 shows the effect of increasing the malic acid concentration of a solution on the solubility of CO<sub>2</sub>.

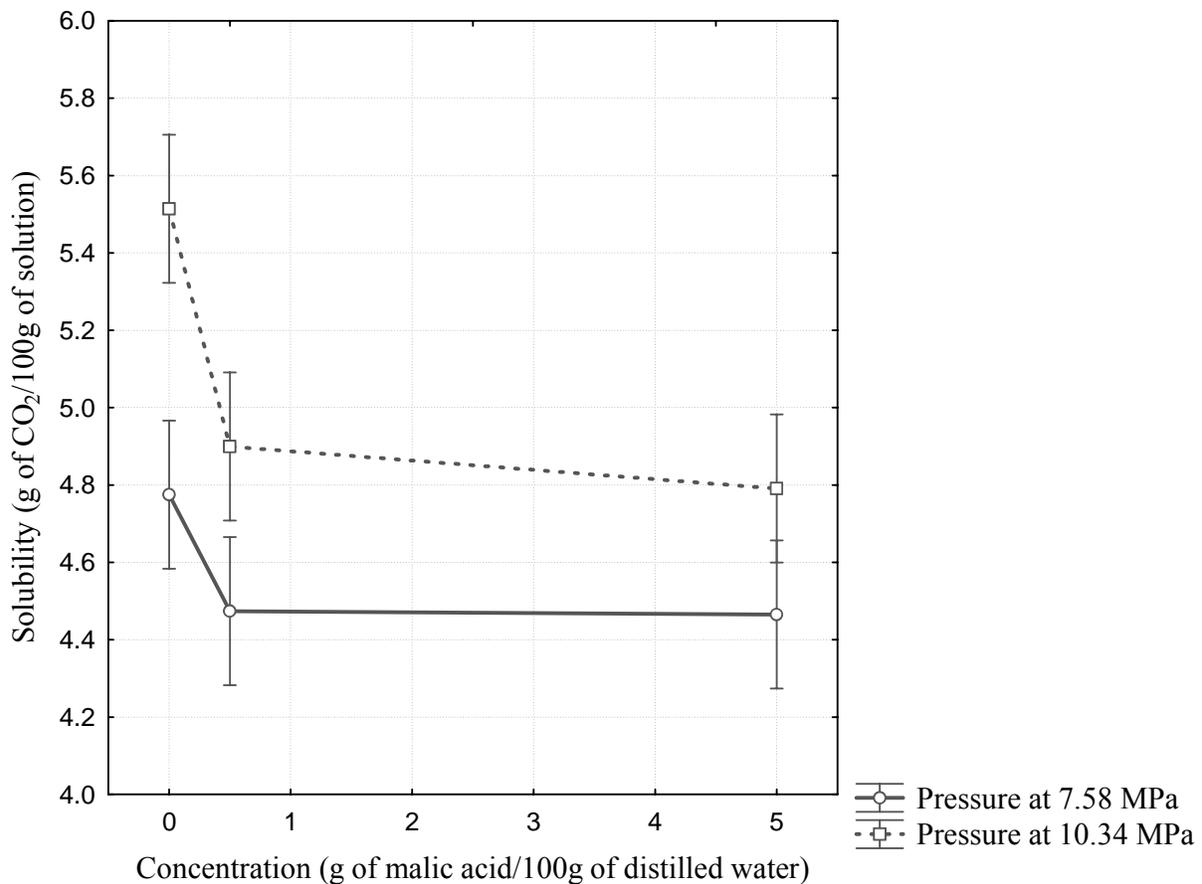


Figure 4-2. Graph of solubility of carbon dioxide versus concentration of malic acid solutions, at two different pressures: 7.58 and 10.34 MPa, and at a constant temperature: 40 °C. Vertical bars denote 0.95 confidence intervals.

Table 4.-9 shows the experimental data. The results of the ANOVA and LS mean analysis, and LSD test are shown in Tables 4-10, 4-11 and 4-12. According to Table 4-10, at least one of the treatments (0, 0.5 and 5 % malic acid concentration, at both pressures) is significantly different because the p-value ( $Pr > F = 0.0007$ ) is lower than  $\alpha = 0.05$ . In addition, the maximum coefficient of variation was 0.02 that shows a good experimental performance (Table 4-11).

Table 4-9. Experimental data of CO<sub>2</sub> solubility in solutions with different concentration of malic acid.

Pressure (MPa)	Malic acid solution (g)	CO <sub>2</sub> (slt <sup>1</sup> )	CO <sub>2</sub> (g)	Solubility (g/100g <sup>2</sup> )	Mean (g/100g <sup>2</sup> )	St Dev <sup>3</sup>	DW <sup>4</sup> (g/100g <sup>2</sup> )	Difference <sup>5</sup> (g/100g <sup>2</sup> )
0.5% Malic Acid Concentration								
7.58	172	3.933	7.73	4.49				
7.58	172	3.902	7.66	4.46	4.47	0.03	4.77	0.30
10.34	169	4.191	8.23	4.84				
10.34	169	4.315	8.48	4.96	4.90	0.08	5.51	0.02
5% Malic Acid Concentration								
7.58	172	3.900	7.66	4.45				
7.58	172	3.902	7.70	4.48	4.47	0.02	4.77	0.31
10.34	171	4.129	8.11	4.69				
10.34	172	4.237	8.32	4.84	4.79	0.07	5.51	0.77

<sup>1</sup>Standard liters. <sup>2</sup>Grams of CO<sub>2</sub> per 100 grams of solution. <sup>3</sup>Standard Deviation in grams of CO<sub>2</sub> per 100 grams of solution. <sup>4</sup>Mean solubility of CO<sub>2</sub> in distilled water. <sup>5</sup>Differences between DW and Mean.

Table 4-10. Analysis of variance (ANOVA) of solubility of carbon dioxide in malic acid solutions of different concentrations.

Source	DF	Sum of squares	Mean Square	F Value	Pr > F	Multiple R	Multiple R <sup>2</sup>	Adjusted R <sup>2</sup>
Model	5	1.4727	0.2945	24.06	0.0007	0.9760	0.9525	0.9129
Error	6	0.0734	0.0122					
Corrected Total	11	1.5461						

Table 4-11. Least Square (LS) Mean analysis of solubility of carbon dioxide in malic acid solutions of different concentrations.

Pressure (MPa)	Malic Acid (%)	Solubility Mean (g/100g <sup>1</sup> )	Solubility Standard Error	Solubility -95.00%	Solubility +95.00%	Standard deviation	Coefficient of variation
7.58	0.5	4.47	0.0387	4.36	4.58	0.03	0.01
10.34	0.5	4.90	0.0387	4.79	5.00	0.08	0.02
7.58	5	4.47	0.0387	4.35	4.57	0.02	0.00
10.34	5	4.68	0.0387	4.68	4.90	0.07	0.01

<sup>1</sup>Grams of CO<sub>2</sub> per 100 g of malic acid solution.

Table 4-12. P-values from the least Significant Difference (LSD) test of solubility of carbon dioxide in malic acid solutions of different concentrations.

Treatments		7.58 MPa			10.34 MPa		
		0 %	0.5 %	5 %	0 %	0.5 %	5 %
7.58 MPa	0 %	-	<i>0.0346</i>	<i>0.0312</i>	<i>0.0005</i>	<i>0.3028</i>	0.8900
	0.5 %	<i>0.0346</i>	-	0.9408	<i>0.0001</i>	<i>0.0085</i>	<i>0.0286</i>
	5 %	<i>0.0312</i>	0.9408	-	<i>0.0001</i>	<i>0.0078</i>	<i>0.0259</i>
10.34 MPa	0 %	<i>0.0005</i>	<i>0.0001</i>	<i>0.0001</i>	-	<i>0.0014</i>	<i>0.0006</i>
	0.5 %	0.3028	<i>0.0085</i>	<i>0.0078</i>	<i>0.0014</i>	-	0.3638
	5 %	0.8900	<i>0.0286</i>	<i>0.0259</i>	<i>0.0006</i>	0.3638	-

Note: Values in italic font are less than  $\alpha = 0.05$ ; thus, the correspondent groups are significantly different.

Table 4-12 shows the difference between treatments. At pressure of 7.58 MPa, there was significant difference between solubility in water (0% malic acid concentration) and solubility in 5 % of malic acid concentration; however there was no significant difference between 0.5% and 5% of malic acid concentration. At pressure of 10.34 MPa, solubility in water was significantly different than 0.5% and 5% of malic acid concentrations; however there was no significant difference between 0.5% and 5% of malic acid concentrations, as in 7.58 MPa of pressure.

According to Meysami and others (1991), the presence of acids (e.g. ascorbic acid, citric acid, etc.) contributes to the reduction of solubility of CO<sub>2</sub> in the solution. They reported a decrease in pH at pressures of 0 and 5.5 MPa and temperature of 32, 37 and 42 °C, in comparison with pH of pure water. At those conditions of pressure and temperature, the pH dropped in the binary water- CO<sub>2</sub> system from about 5.68 to 3.19 (difference was approximately 2.5 units), while at the ternary system (water-acid- CO<sub>2</sub>), the pH dropped from about 3.74 to 3.13 (difference was around 0.61 units).

Due to lack of experimental studies in the area of measurement of CO<sub>2</sub> solubility in model and in real liquid foods, no more references are cited to compare with current experimental results.

CHAPTER 5  
SUMMARY, CONCLUSIONS AND SUGGESTIONS FOR FUTURE STUDY

**5.1 Summary**

The use of CO<sub>2</sub> in Dense Phase Carbon Dioxide (DPCD) technology is not optimized; excess of CO<sub>2</sub> is used to reach saturation, due to unknown solubility of CO<sub>2</sub> in the liquid foods. The high pressure CO<sub>2</sub> solubility apparatus was designed and built to measure CO<sub>2</sub> solubility in liquid foods at high pressures and different temperatures. The apparatus was tested at a constant temperature of 40 °C, and at pressures of 7.58 and 10.34 MPa. Solubility values were reported in grams of CO<sub>2</sub> per 100 grams of liquid. The average experimental error (coefficient of variation) was 0.02%.

Adding fructose to a liquid solubility of CO<sub>2</sub> decreased significantly. At pressure of 7.58 MPa of, solubility of CO<sub>2</sub> in water was  $4.77 \pm 0.15$  g/100 g of distilled water. When the concentrations of fructose in the solution were 5 and 10%, solubilities of CO<sub>2</sub> in the solutions were  $4.55 \pm 0.11$  and  $4.12 \pm 0.07$ , respectively. At pressure of 10.34 MPa, the CO<sub>2</sub> in solution with water was  $5.51 \pm 0.20$  g/100 g of distilled water, and when the amount of fructose in the solution increase to 5 and 10 g/100 g of solution, solubilities of CO<sub>2</sub> were  $4.78 \pm 0.14$  and  $4.19 \pm 0.17$ , respectively.

Adding malic acid to a solution also decreased solubility of CO<sub>2</sub>. The reference used to compare was the experimental solubility of CO<sub>2</sub> in water. At 7.58 MPa of pressure, the amount of CO<sub>2</sub> dissolved in the solutions of 0.5 and 5% of malic acid concentration was  $4.47 \pm 0.03$  and  $4.47 \pm 0.02$  g/100 g of solution. At 10.34 MPa of pressure, solubilities of CO<sub>2</sub> in solution with 0.5 and 5% of malic acid concentration were  $4.90 \pm 0.08$  and  $4.79 \pm 0.07$  g/100 g of solution.

## 5.2 Conclusions

It is possible to conclude that the apparatus is a functional, accurate and precise instrument to measure solubility of CO<sub>2</sub> in model liquid foods. The significance of this study is that the experimental apparatus could offer an advantage to the food industry, primarily to soft drink industry, and to the DPCD users, by eliminating the need to use excess CO<sub>2</sub> and therefore reducing the production cost.

This apparatus could be used for the measurement of CO<sub>2</sub> in real liquid foods. Versatility of the apparatus allows carbonation of various samples, at conditions above critical temperature and pressure, and below density of 0.9 g·ml<sup>-1</sup>. In addition, the side connection between Vessel 1 and Vessel 2 ensures a correct liquid circulation and an appropriate measurement of solubility.

## 5.3 Suggestions for Future Study

Future works in the area of DPCD technology should focus on first experimentally determining and then thermodynamically predicting the “theoretical” level of CO<sub>2</sub> to use, at any given pressure and temperature, and for any liquid food of known composition. More studies on the effect of temperature on the solubility of CO<sub>2</sub> in solutions with different concentrations of fructose and malic acid should be performed.

This experimental apparatus is a valuable instrument to measure CO<sub>2</sub> solubility in liquid food to reduce the need to use excess CO<sub>2</sub> to reach saturation, at the conditions tested. Moreover, experiments under pressures higher than 10.34 MPa could be performed to determine the effect on density changes of CO<sub>2</sub> on the accuracy of the apparatus.

APPENDIX A  
DESIGN OF THE HIGH PRESSURE CARBON DIOXIDE SOLUBILITY APPARATUS



Figure A-1. Pictures of the high pressure carbon dioxide solubility apparatus.

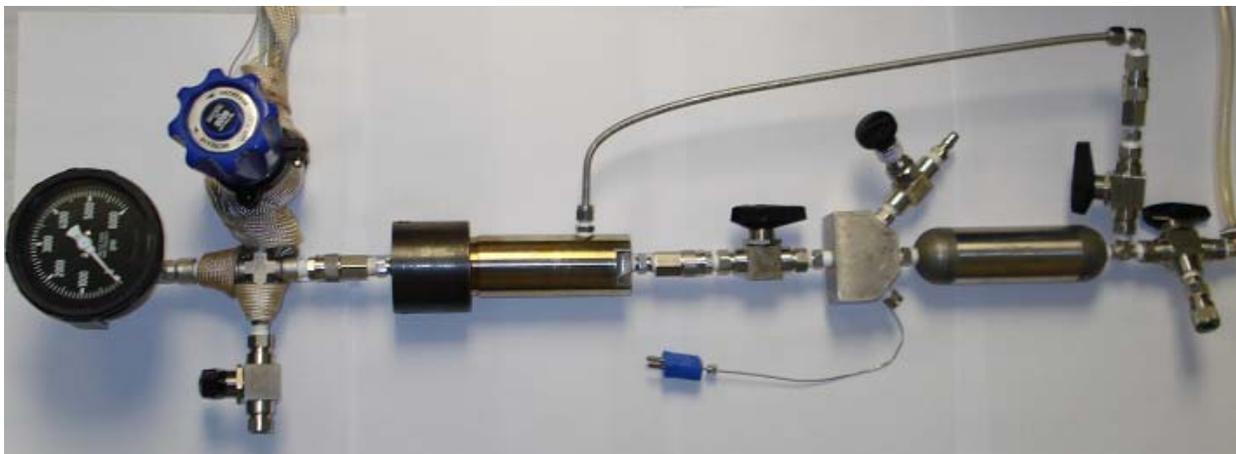


Figure A-2. Picture of the mobile part of the apparatus.



Figure A-3. Picture of the teflon tape used in every male connection.

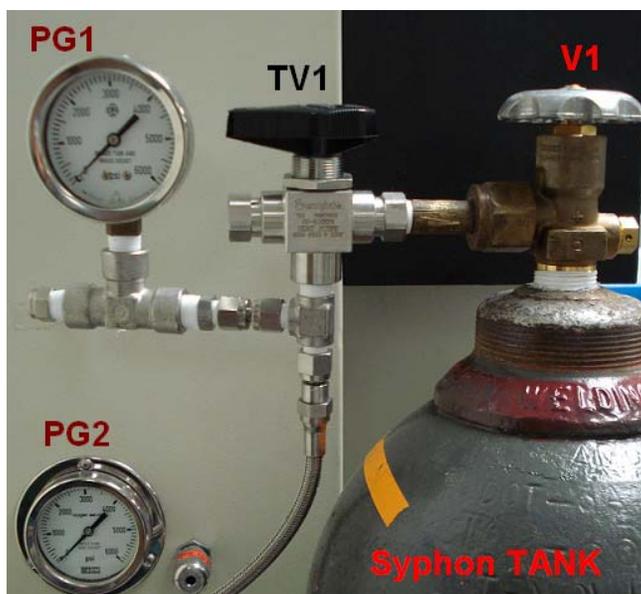
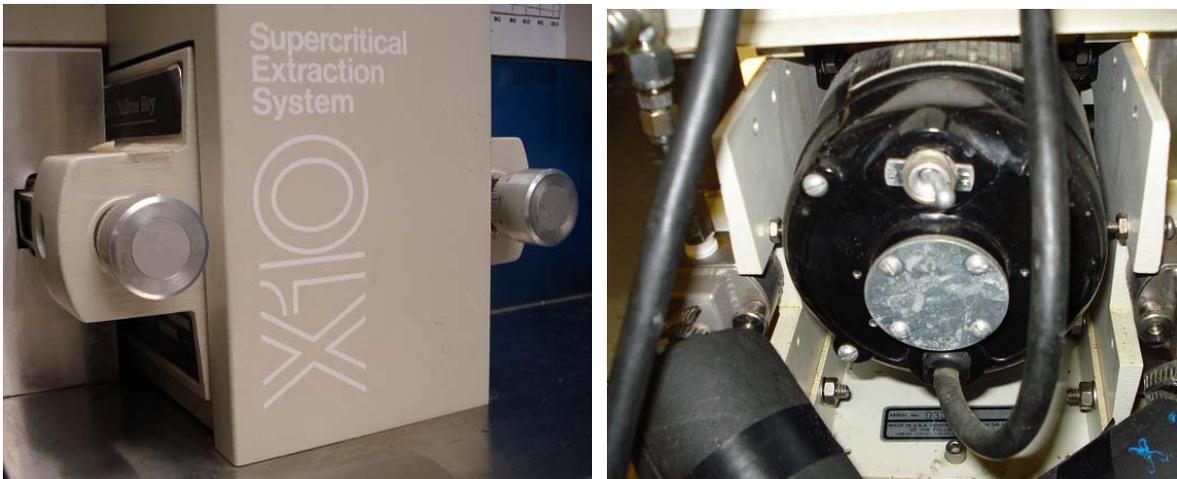


Figure A-4. Picture of the CO<sub>2</sub> tank connections. The carbon dioxide tank, the three-way valve 1 (TV1), and the pressure gauge 1 (PG1).



A  
Figure A-5. Pictures of the high pressure pump (HHP). A) From the front, micrometers. B)  
From the back, cooling jacket. B



Figure A-6. Picture of the heat exchanger (HE).

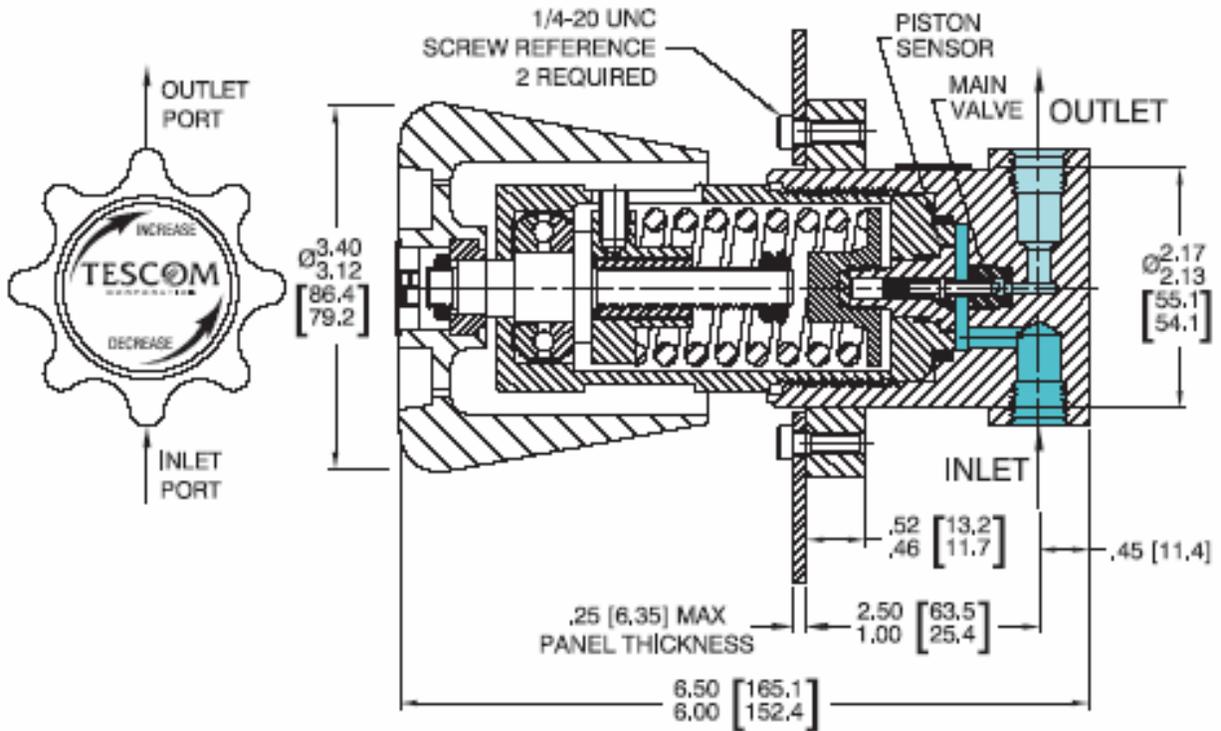


Figure A-7. Back Pressure Regulator (BPR) diagram (Tescom Industrial Controls 2006).



A



B

Figure A-8. Pictures of the back pressure regulator (BPR) used in the machine. A) From the side. B) From the top.

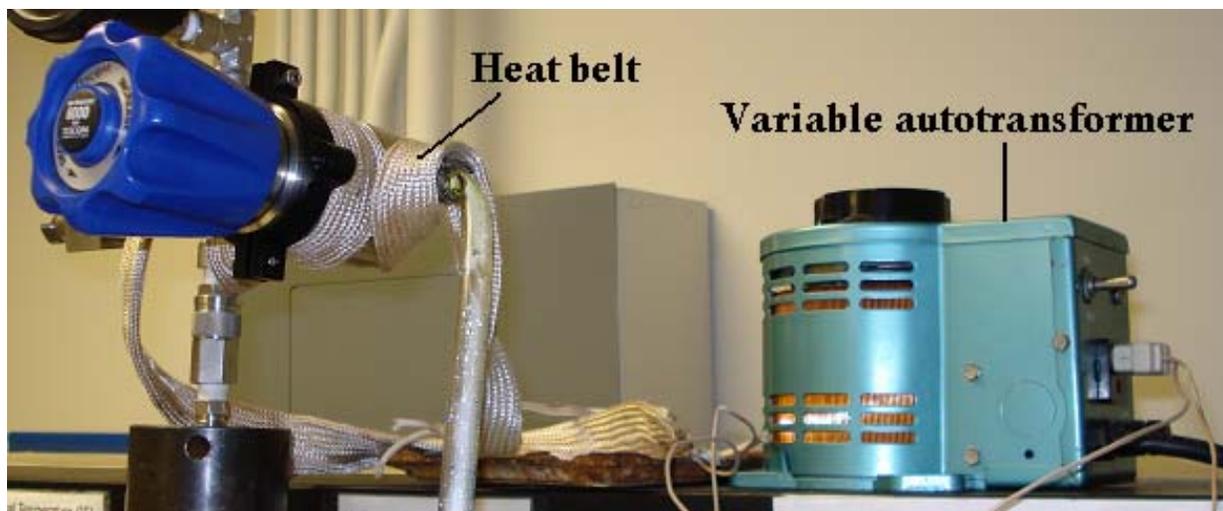


Figure A-9. Picture of the heating tape (around the BPR) and the variable autotransformer.



Figure A-10. Picture of the Hart Scientific high precision water bath and the Masterflex peristaltic pump.

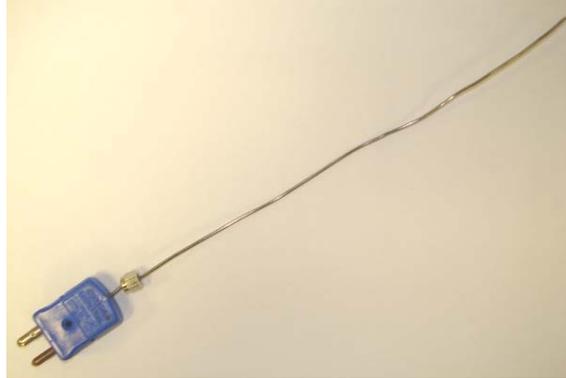


Figure A-11. Picture of the thermocouple used inside the vessel 1.



Figure A-12. Picture of the metering valve (MV).



Figure A-13. Picture of the gas meter (GM).

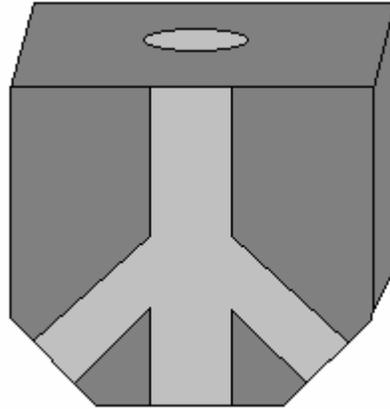
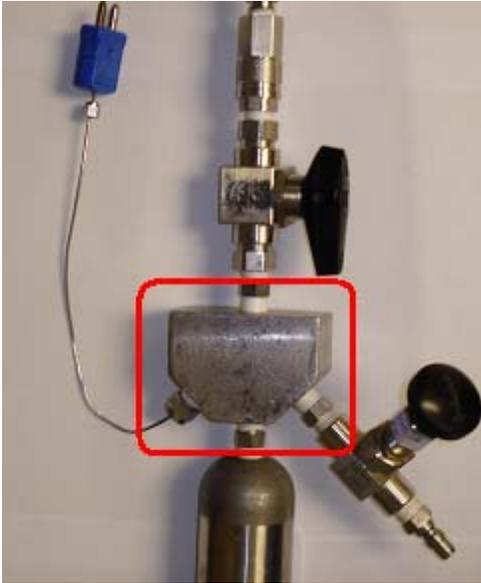


Figure A-14. Picture and diagram of the cross angles connector.



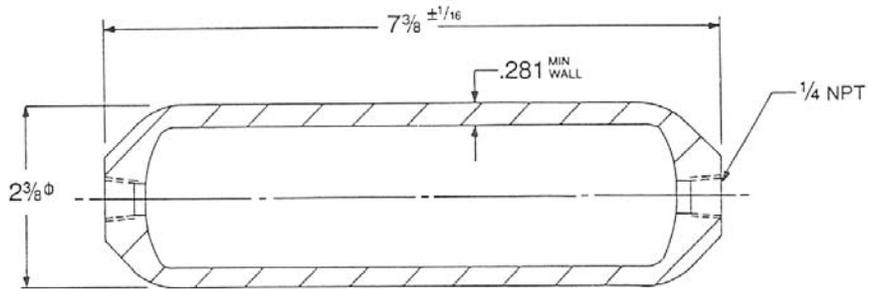
Figure A-15. Picture of the two way valve (V).



Figure A-16. Picture of the quick connect stem (female NPT) and body (male NPT).



A



B

Figure A-17. Vessel 1. A) Picture of vessel 1. B) Diagram of vessel 1 (Milton Roy 1986).

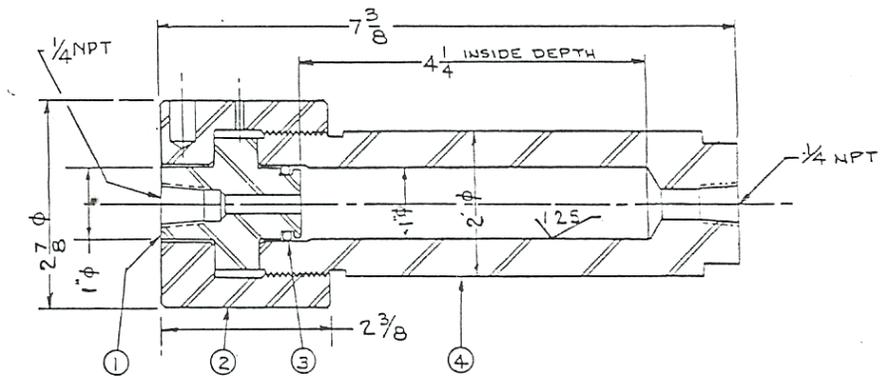


Figure A-18. Diagram of vessel 2 (Milton Roy 1986).



Figure A-19. Picture of vessel 2 with the hole at the bottom.



Figure A-20. Picture of the forged stainless steel gate valve.



A B  
Figure A-21. Picture of the bottle and the stopper. A) Picture of the 5 gallons bottle. B) Picture of the stopper in the opening of the bottle.

APPENDIX B  
THE HIGH PRESSURE CARBON DIOXIDE SOLUBILITY APPARATUS PROCEDURES

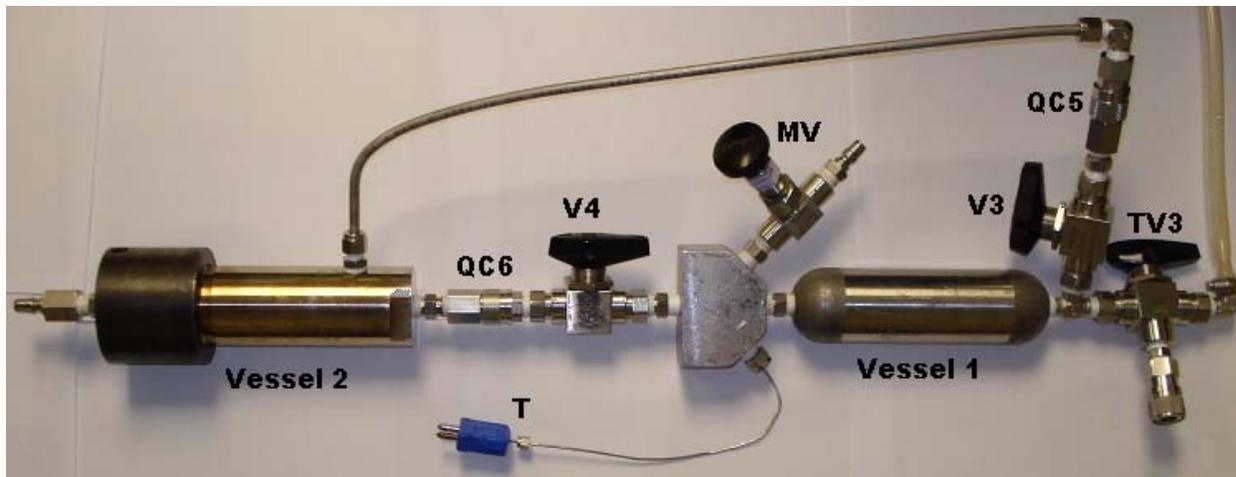


Figure B-1. Picture of the mobile part of the equipment, before immersion into the cooler.



Figure B-2. Pictures showing the sample being pumped.



Figure B-3. Picture of disconnecting QC6.



Figure B-4. Picture showing when V4 was opened to collect the liquid sample.



Figure B-5. Picture showing the measurement of the liquid sample collected.

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## BIOGRAPHICAL SKETCH

Thelma Francisca Calix Lara was born on 1984, in Tegucigalpa, Honduras, Central America. After graduating from high school in December 2001, she entered the Escuela Agrícola Panamericana (University of Zamorano), earning her Bachelor of Science in Agroindustry in December 2005. During spring 2005, she performed an internship at the Food Technology of Fruits and Vegetables Department at the Center of Investigation in Food and Development (CIAD) in Mexico. During fall of the same year, she was offered an assistantship to pursue her graduate studies, advised by Dr. Murat O. Balaban. In December 2007, she earned a Master of Science in Food Science and will continue her studies towards a doctoral degree.