

## Milk pH as a Function of CO<sub>2</sub> Concentration, Temperature, and Pressure in a Heat Exchanger<sup>1</sup>

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### ABSTRACT

Raw skim milk, with or without added CO<sub>2</sub>, was heated, held, and cooled in a small pilot-scale tubular heat exchanger (372 ml/min). The experiment was replicated twice, and, for each replication, milk was first carbonated at 0 to 1°C to contain 0 (control), 600, 1200, 1800, and 2400 ppm added CO<sub>2</sub> using a continuous carbonation unit. After storage at 0 to 1°C, portions of milk at each CO<sub>2</sub> concentration were heated to 40, 56, 72, and 80°C, held at the desired temperature for 30 s (except 80°C, holding 20 s) and cooled to 0 to 1°C. At each temperature, five pressures were applied: 69, 138, 207, 276, and 345 kPa. Pressure was controlled with a needle valve at the heat exchanger exit. Both the pressure gauge and pH probe were inline at the end of the holding section. Milk pH during heating depended on CO<sub>2</sub> concentration, temperature, and pressure. During heating of milk without added CO<sub>2</sub>, pH decreased linearly as a function of increasing temperature but was independent of pressure. In general, the pH of milk with added CO<sub>2</sub> decreased with increasing CO<sub>2</sub> concentration and pressure. For milk with added CO<sub>2</sub>, at a fixed CO<sub>2</sub> concentration, the effect of pressure on pH decrease was greater at a higher temperature. At a fixed temperature, the effect of pressure on pH decrease was greater for milk with a higher CO<sub>2</sub> concentration. Thermal death of bacteria during pasteurization of milk without added CO<sub>2</sub> is probably due not only to temperature but also to the decrease in pH that occurs during the process. Increasing milk CO<sub>2</sub> concentration and pressure decreases the milk pH even further during heating and may further enhance the microbial killing power of pasteurization.

(**Key words:** carbon dioxide concentration, pH in heat exchanger, temperature, pressure)

### INTRODUCTION

To achieve a long shelf life of pasteurized milk, the fluid milk industry typically applies a heat treatment with a time and temperature combination substantially higher than the legal minimum (72°C for 15 s) specified by the Pasteurized Milk Ordinance (PMO, 1999). For example, in New York State, the typical temperature and time combinations used by fluid milk processors are 76.7 to 77.2°C for 30 to 35 s (Ma et al., 2000). Recently, Loss and Hotchkiss (2000) reported that the addition of CO<sub>2</sub> at concentration of about 1500 ppm decreased the thermal resistance of *Pseudomonas fluorescens* and suggested that dissolved CO<sub>2</sub> could be used as a processing aid to enhance microbial kill during pasteurization and thus reduce the extent of heating needed to achieve longer shelf life of milk. Using CO<sub>2</sub> as a processing aid is promising because, if CO<sub>2</sub> is undesirable in the final product, CO<sub>2</sub> can be removed by applying a vacuum after its desirable impact has been achieved. More importantly, CO<sub>2</sub> is a GRAS (generally recognized as safe) food additive (Code of Federal Regulations, 2001).

Only a few studies were focused on the chemical changes in milk with added CO<sub>2</sub> during pasteurization (Calvo and de Rafael, 1995; Ruas-Madiedo et al., 1998). An important change that occurs in milk upon carbonation at low CO<sub>2</sub> levels and pressures is a decrease of milk pH (Ma et al., 2003). Although the antimicrobial effect of CO<sub>2</sub> is not pH dependent (King and Mabbitt, 1982; Ma et al., 2003), many dairy processing steps are pH dependent (Corredig and Dalgleish, 1996; Singh et al., 1996; Oldfield et al., 2000). This is particularly true when heating is involved. The effect of heating on the quality and functional properties of dairy foods is highly pH dependent (Corredig and Dalgleish, 1996; Oldfield et al., 2000).

During heating of milk without added CO<sub>2</sub>, milk pH decreased linearly with increasing temperature, and the decrease was related to shifts in degree of associa-

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tion of calcium phosphate (Dixon, 1963; Chaplin and Lyster, 1988; Fox and McSweeney, 1998). Using the linear coefficients of  $-0.0073$  pH unit/ $^{\circ}\text{C}$  reported by Chaplin and Lyster (1988), the pH of a milk without added  $\text{CO}_2$  at  $80^{\circ}\text{C}$  would be about 0.58 pH units lower than the pH of the same milk at  $0^{\circ}\text{C}$ . This is a very dramatic decrease in milk pH caused simply by heating. The change in milk pH with temperature is usually reversible if the heating does not exceed  $100^{\circ}\text{C}$  and there is no degradation of milk protein or lactose during heating (Fox and McSweeney, 1998). The measurement of pH in previous studies (Chaplin and Lyster, 1988) was conducted while milk was mixed and heated under a nitrogen atmosphere in a water bath. No data are available on the pH of milk under the conditions of heating and pumping in a heat exchanger, but the effect of temperature on milk pH would be expected to be the same. In addition, no information is available on the extent of pH reduction in milk with added  $\text{CO}_2$  during heating in a heat exchanger.

The objective of this study was to measure the pH of raw skim milk, without and with added  $\text{CO}_2$ , directly inline as milk was heated in a tubular heat exchanger at temperatures of 40, 56, 72, and  $80^{\circ}\text{C}$  and under pressures of 69, 138, 207, 276, and 345 kPa (i.e., 10, 20, 30, 40, and 50 psi). The unique feature of this study is the measurement of milk pH directly inline as milk was being heated in a heat exchanger at 72 and  $80^{\circ}\text{C}$ . The measured pH represented the pH values that a milk without and with added  $\text{CO}_2$  would experience in an HTST pasteurizer at various pressures.

## MATERIALS AND METHODS

### Experimental Design and Statistical Analysis

The experiment was replicated two times using different batches of fresh raw skim milk. Each replication was completed in 3 d. On the first day, milk was carbonated at 0 to  $1^{\circ}\text{C}$  to contain 0 (control), 600, 1200, 1800, and 2400 ppm added  $\text{CO}_2$  using a continuous tubular carbonation unit (230 ml/min). After overnight storage at 0 to  $1^{\circ}\text{C}$ , subportions of milk at each  $\text{CO}_2$  concentration were heated to 40, 56, 72, and  $80^{\circ}\text{C}$ , held at the desired temperature, and cooled to 0 to  $1^{\circ}\text{C}$  in a tubular heat exchanger at a flow rate of 372 ml/min. The 40 and  $56^{\circ}\text{C}$  processing was done on the second day, and the 72 and  $80^{\circ}\text{C}$  processing was done on the third day. At each temperature five pressures were applied: 69 (control without added pressure), 138, 207, 276, and 345 kPa. The pH of skim milk at each carbonation level, each temperature, and each pressure was measured directly inline at the end of the holding sec-

**Table 1.** ANOVA model used for analysis of the effect of  $\text{CO}_2$  concentration and pressure on milk pH at the end of the holding section of a tubular heat exchanger at a fixed temperature (i.e., 40, 56, 72, or  $80^{\circ}\text{C}$ ).

	df	Analyzed as	Error term
Replicate	1	Block	
$\text{CO}_2$	4	Fixed effect	Replicate $\times$ $\text{CO}_2$
Replicate $\times$ $\text{CO}_2$	4	Interaction	
Pressure	4	Fixed effect	E
$\text{CO}_2 \times$ pressure	16	Interaction	E
Error (E)	20		

tion as milk was being pumped through the heat exchanger.

Because it is known that milk pH decreases with increasing temperature (Chaplin and Lyster, 1988), data from the experiment would be best presented by focusing on how milk pH changed during heating as a function of  $\text{CO}_2$  concentration and system pressure. The entire dataset was analyzed as four independent split-plot designs by setting temperature at a fixed level (i.e., at 40, 56, 72, or  $80^{\circ}\text{C}$ ). The whole plot factor was  $\text{CO}_2$  concentration (five levels) and the subplot factor was pressure (five levels). The ANOVA model is listed in Table 1. Analyses were done using SAS (Version 8.02, 1999-2001).

### Carbonation

Carbonation was conducted at 0 to  $1^{\circ}\text{C}$  in a laboratory-scale continuous inline  $\text{CO}_2$  injection system at a milk flow rate of 230 ml/min. The injection system was a countercurrent stainless steel tubular heat exchanger (i.d. = 0.5 cm) cooled by circulating ice water. Milk was pumped through the system with a peristaltic pump (Amicon LP-1 pump, Beverly, MA, with Cole-Palmer Masterflex 7015-81 pump head, Vernon Hills, IL) and  $\text{CO}_2$  (beverage grade, Empire Air Gas, Radnor, PA) was injected (60 psi input pressure) through a stainless steel tube (i.d. = 0.08 cm) inserted through a Tee-fitting perpendicular to the milk flow immediately after the feed pump. The residence time of milk in the heat exchanger was approximately 60 s. Desired carbonation levels were achieved by adjusting the flow rate of  $\text{CO}_2$  while keeping the flow rate of milk constant. Milk with added  $\text{CO}_2$  was collected in plastic 2-L screw-cap jugs and stored overnight at 0 to  $1^{\circ}\text{C}$  in a walk-in cooler prior to processing. Preliminary work indicated that very little loss of  $\text{CO}_2$  from milk occurred under this storage condition.

### Inline pH Measurement and Pressure Control

Milk pH was measured inline as milk was heated to 40, 56, 72, and  $80^{\circ}\text{C}$  in a laboratory-scale counter-

current stainless steel tubular heat exchanger (i.d. = 0.5 cm). The system consisted of 19 straight pieces of tube that were each 105 cm long, interrupted by eighteen 13-cm diameter U-turns with flow entering at the lowest point in the system and having an upward pitch on successive loops of tubes until reaching the system exit. This was done to promote turbulent flow. The heat exchanger consisted of eight sections, they were sequentially from inlet to exit: 1) a milk feed reservoir; 2) a peristaltic pump, which fed the milk (0 to 1°C) into the heat exchanger at a flow rate of 372 ml/min; 3) a heating section, which heated the milk to the target temperature; 4) a holding section, which kept the milk at the target temperature for a fixed time period; 5) a sanitary pressure gauge (Anderson Instrument Company, Inc., Fultonville, NY) that registered the system pressure at the end of the holding section; 6) pH probes (model HA 405 DXK-58/120 combination pH probe; Mettler Toledo, Columbus, OH) that were inserted perpendicular to the milk flow through Tee-fittings to measure milk pH continuously inline at the end of the holding section; 7) a cooling section, circulated with ice water that cooled the milk to 0 to 1°C for collection at the exit; and 8) a needle valve that was opened and closed for decreasing and increasing of system pressure. Throughout the system, several temperature probes were inserted inline to monitor the inlet, heating, holding, and exit temperature of the milk.

The heating and holding sections were circulated with hot water to achieve the desired temperature targets. For both replications, each of the four target temperatures was achieved and well maintained in the holding section for each of the five CO<sub>2</sub> concentrations and the five pressures. For the first replication, the average temperatures ( $n = 25$ ) were  $40.2 \pm 0.2^\circ\text{C}$ ,  $56.0 \pm 0.2^\circ\text{C}$ ,  $72.2 \pm 0.1^\circ\text{C}$ , and  $80.4 \pm 0.2^\circ\text{C}$  and for the second replications, temperatures were  $40.5 \pm 0.2^\circ\text{C}$ ,  $56.5 \pm 0.4^\circ\text{C}$ ,  $72.1 \pm 0.2^\circ\text{C}$ , and  $80.3 \pm 0.2^\circ\text{C}$ . For the 40, 56, and 72°C treatments, it took the milk 19.5 s (heating time) to reach the target temperature, and the milk was maintained at the target temperature for 31.2 s (holding time) before being cooled. For the 80°C treatment, the heating time and holding time were 29.6 and 20.9 s, respectively. The 72°C for 31.2 s and 80°C for 20.9 s heating conditions produced a comparable degree of heat denaturation of whey proteins as the conditions used for milk pasteurization in the fluid milk industry in New York (Ma et al., 2000).

Both a pressure gauge and pH probe were inline next to each other and were both at the end of the holding section, just before the cooling section. Pressures were set at 69 (control, without added pressure and with the needle valve completely open), 138, 207,

276, and 345 kPa. Increasing pressure up to 345 kPa did not change the flow rate of milk (i.e., 372 ml/min).

The pH probe was calibrated first with buffers (Fisher Scientific, Fair Lawn, NJ) before being inserted inline. To obtain accurate pH measurement, the pH probe and the calibration buffers were tempered to the temperature at which the pH of the milk was measured. This tempering procedure ensured more rapid response and more stable readings of the pH probe. In addition, the appropriate reference pH for each calibration buffer at each temperature was used. The pH of the buffers were 6.97 and 4.03 at 40°C, 6.98 and 4.08 at 56°C, 6.98 and 4.14 at 72°C, and 6.98 and 4.16 at 80°C.

### Sample Analysis

Raw milk was tested for percentage fat (Mojonnier method, AOAC, method number 989.05; 33.2.26), TS (AOAC, method number 990.20; 33.2.44), total nitrogen (AOAC, method number 991.20; 33.2.11), and NPN (AOAC, method number 991.21; 33.2.12). Percentage true protein was calculated as (total nitrogen-NPN)  $\times$  6.38. The CO<sub>2</sub> concentration in milk before heating on each of the processing days (i.e., second and third day) was measured (Ma et al., 2001). To verify that no loss of CO<sub>2</sub> occurred in the heat exchanger, the CO<sub>2</sub> concentration of milk collected at the exit of the heat exchanger after heating and cooling was also determined at the four temperatures (i.e., 40, 56, 72, and 80°C) and three selected pressures (69, 207, and 345 kPa).

## RESULTS

### Milk Composition, Carbonation Level, and Initial Pressure

Mean ( $n = 2$ ) TS, fat, and true protein for the two batches of raw skim milk were 8.85, 0.07, and 3.16% respectively. Before heating, calculated mean ( $n = 5$ ) CO<sub>2</sub> concentrations and standard deviations of the control and carbonated milks were  $121 \pm 12$ ,  $648 \pm 35$ ,  $1187 \pm 12$ ,  $1761 \pm 18$ , and  $2352 \pm 48$  ppm. After heating and cooling, no significant change in milk CO<sub>2</sub> concentration was observed at each of the heating temperatures at 69, 207, and 345 kPa [Table 2, only data for the lowest (40°C) and highest (80°C) temperatures are shown]. Similar values were obtained at the intermediate temperatures and pressures (data not shown). There was no loss of CO<sub>2</sub> in the heat exchanger as milk was being pumped, heated, and cooled.

The control level pressures registered by the pressure gauge at the end of the holding section when the needle valve was completely open were between 41

**Table 2.** CO<sub>2</sub> concentration of the heated and cooled milk that had been processed at 69 (control, without added pressure), 207, and 345 kPa at 40 and 80°C in a tubular heat exchanger.

Temperature	Target carbonation level	CO <sub>2</sub> concentration in heated and cooled milk, ppm		
		69 kPa	207 kPa	345 kPa
40°C	Control	121	119	121
	600 ppm	630	634	650
	1200 ppm	1180	1185	1185
	1800 ppm	1790	1789	1795
	2400 ppm	2394	2370	2379
80°C	Control	121	121	121
	600 ppm	636	636	645
	1200 ppm	1170	1194	1170
	1800 ppm	1729	1748	1762
	2400 ppm	2335	2340	2359

and 76 kPa. In general, the control pressure increased with increasing CO<sub>2</sub> concentration of the milk being heated in the heat exchanger and with increasing heating temperature (data not shown). For example, at 40, 56, 72, and 80°C, mean (n = 2) pressures with the needle valve fully open were 41, 43, 48, and 46 kPa, respectively, for milk without added CO<sub>2</sub>, and were 62, 69, 76, and 76 kPa, respectively, and for milk with 2400 ppm of CO<sub>2</sub>. In the ANOVA analysis, pressure was treated as a category variable and the control pressure level was designated as “69 kPa”.

### pH as a Function of CO<sub>2</sub> Concentration and Pressure

At each temperature level, the ANOVA found a significant effect for CO<sub>2</sub>, pressure, and CO<sub>2</sub> × pressure (Tables 3 and 4). The effect of CO<sub>2</sub> was expected because it has been shown in many previous studies (Ma et al., 2001; Ma and Barbano, 2003a, 2003b) that increasing CO<sub>2</sub> decreases milk pH (Figures 1 to 4). The effects of pressure and CO<sub>2</sub> × pressure are reflected as the differences in the pressure dependence of milk pH at various carbonation levels (Figures 1 to 4).

**pH at 40°C.** For both the milk without added CO<sub>2</sub> and milk with 600 ppm of CO<sub>2</sub>, milk pH did not change with increasing pressure and averaged at 6.58 and 6.27, respectively (Figure 1). At 1200 ppm of CO<sub>2</sub>, without added pressure (69 kPa), milk pH was 6.07. Increasing pressure decreased milk pH and a significant ( $P < 0.05$ ) decrease was observed at 276 kPa (pH = 6.05). However, the overall change of pH in the range of pressure from 69 to 345 kPa was small for milk with 1200 ppm of CO<sub>2</sub> at 40°C. Similar pH reduction pattern was observed for milk with 1800 ppm of CO<sub>2</sub>: pH was 5.91 at 69 kPa, decreased to 5.89 at 138 kPa, and did not change upon further increase in pressure up to 345 kPa (Figure 1). At 2400 ppm of CO<sub>2</sub>, milk pH continued to decrease with increasing pressure from 5.88 (69 kPa) to 5.82 (138 kPa), and to 5.78 (207 kPa), but increasing pressure above 207 kPa did not further decrease milk pH (Figure 1).

**pH at 56°C.** In general, the pH of milk at each carbonation level, without or with added CO<sub>2</sub>, was lower at 56°C (Figure 2) than at 40°C (Figure 1). Similar to the observations at 40°C, the pH of milk without added CO<sub>2</sub> (6.47) and milk with 600 pm (6.17) did not change with increasing pressure up to 345 kPa. At

**Table 3.** Sum of squares (SS) and probabilities ( $P$ ) from the ANOVA of pH data for milk with various levels of carbonation and processed at various pressures at 40°C and 56°C in a tubular heat exchanger.

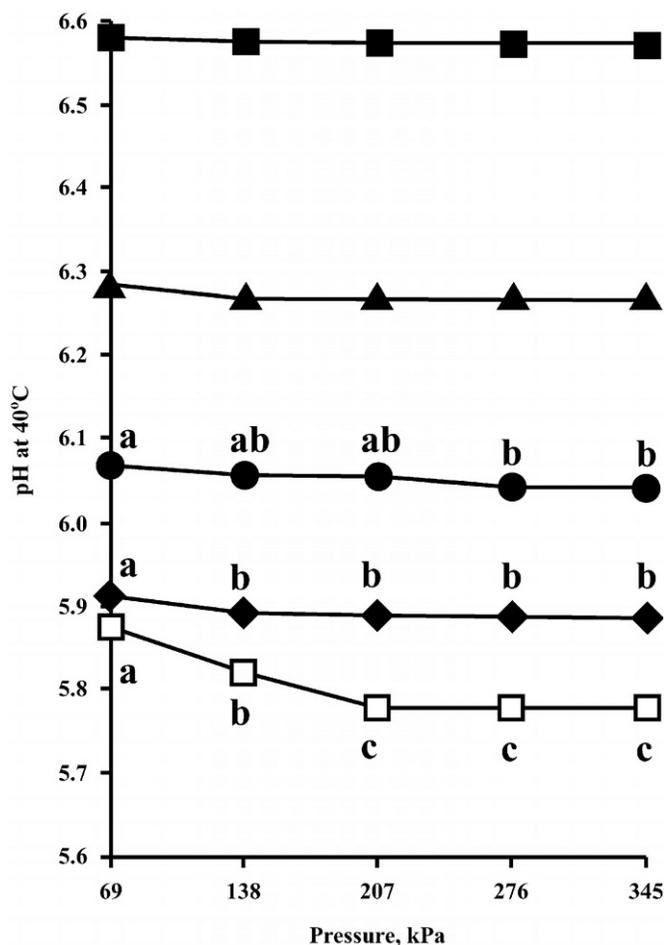
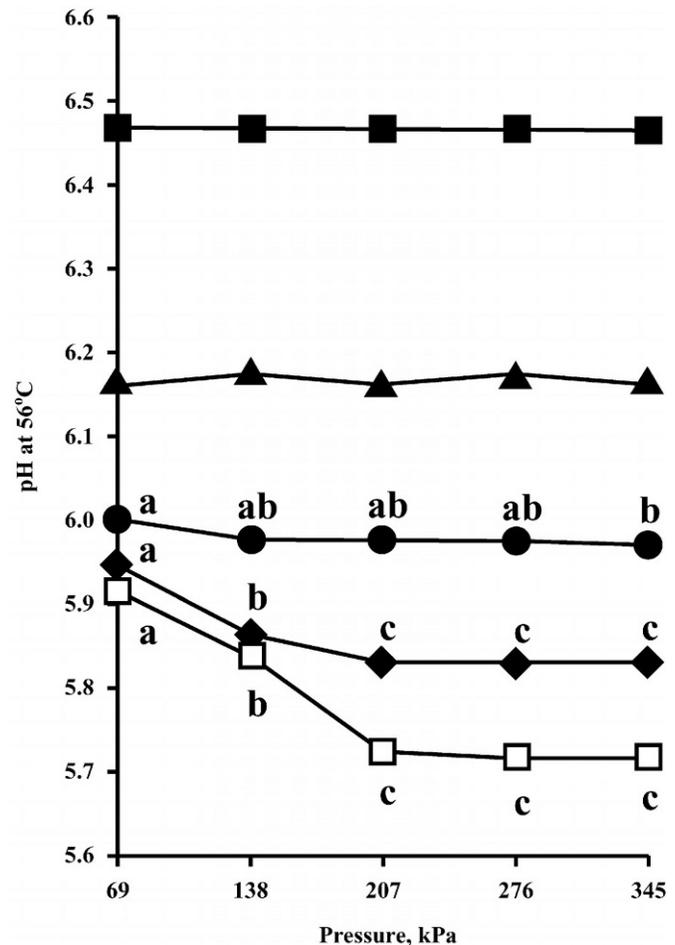
Independent variable	pH at 40°C SSM <sup>1</sup> = 3.870 Model R <sup>2</sup> = 0.999		pH at 56°C SSM = 3.070 Model R <sup>2</sup> = 0.999	
	SS <sup>2</sup>	$P$	SS	$P$
Replicate	0.0014		0.0001	
CO <sub>2</sub>	3.8518	<0.01	2.9827	<0.01
Replicate × CO <sub>2</sub>	0.0005		0.0016	
Pressure	0.0074	<0.01	0.0350	<0.01
CO <sub>2</sub> × pressure	0.0084	<0.01	0.0502	<0.01
Error (E)	0.0014		0.0035	

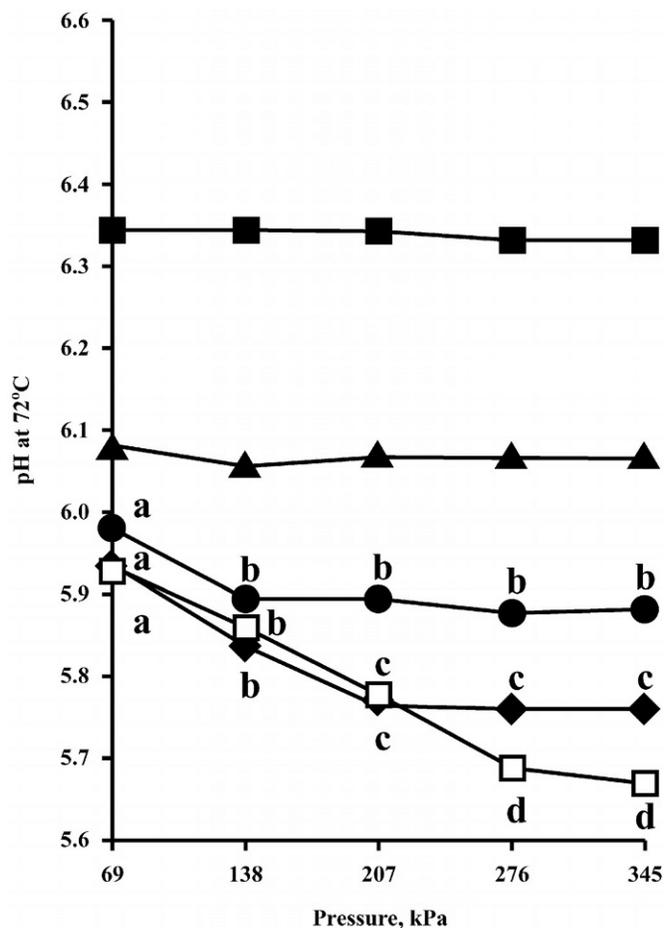
<sup>1</sup>SSM = Sum squares of model.

<sup>2</sup>SS = Sum squares of individual factors.

**Table 4.** Sum of squares (SS) and probabilities (*P*) from the ANOVA of pH data for milk with various levels of carbonation and processed at various pressures at 72°C and 80°C in a tubular heat exchanger.

Independent variable	pH at 72°C SSM <sup>1</sup> = 2.273 Model R <sup>2</sup> = 0.998		pH at 80°C SSM = 1.913 Model R <sup>2</sup> = 0.998	
	SS <sup>2</sup>	<i>P</i>	SS	<i>P</i>
Replicate	0.0141		0.0093	
CO <sub>2</sub>	2.0956	<0.01	1.6552	<0.01
Replicate × CO <sub>2</sub>	0.0019		0.0041	
Pressure	0.0840	<0.01	0.1516	<0.01
CO <sub>2</sub> × pressure	0.0772	<0.01	0.0925	<0.01
Error (E)	0.0042		0.0029	

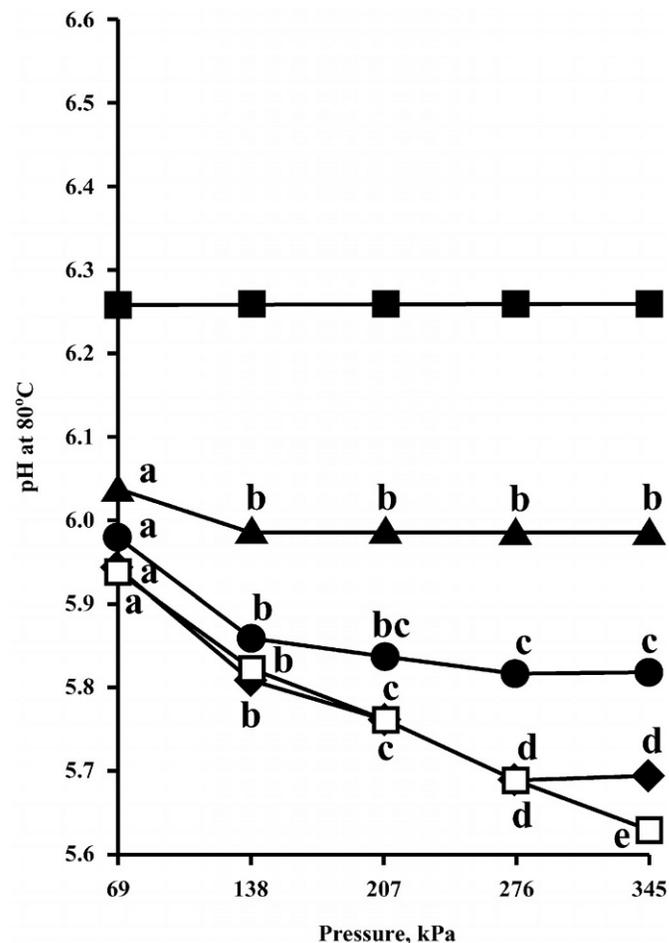
<sup>1</sup>SSM = Sum squares of model.<sup>2</sup>SS = Sum squares of individual factors.**Figure 1.** Mean (*n* = 2) milk pH at the end of the holding section of a tubular heat exchanger as a function of CO<sub>2</sub> concentration and pressure during heating at 40°C. The five CO<sub>2</sub> concentrations are control (■), 600 ppm (▲), 1200 ppm (●), 1800 ppm (◆), and 2400 ppm (□). At the same CO<sub>2</sub> concentration, values with no common letter are significantly different (*P* < 0.05, lsd = 0.017).**Figure 2.** Mean (*n* = 2) milk pH at the end of the holding section of a tubular heat exchanger as a function of CO<sub>2</sub> concentration and pressure during heating at 56°C. The five CO<sub>2</sub> concentrations are control (■), 600 ppm (▲), 1200 ppm (●), 1800 ppm (◆), and 2400 ppm (□). At the same CO<sub>2</sub> concentration, values with no common letter are significantly different (*P* < 0.05, lsd = 0.027).



**Figure 3.** Mean ( $n = 2$ ) milk pH at the end of the holding section of a tubular heat exchanger as a function of CO<sub>2</sub> concentration and pressure during heating at 72°C. The five CO<sub>2</sub> concentrations are control (■), 600 ppm (▲), 1200 ppm (●), 1800 ppm (◆), and 2400 ppm (□). At the same CO<sub>2</sub> concentration, values with no common letter are significantly different ( $P < 0.05$ , lsd = 0.030).

1200 ppm of CO<sub>2</sub>, increasing pressure from 69 to 138 kPa decreased milk pH from 6.00 to 5.98 and further increase in pressure up to 345 kPa did not affect milk pH in the heat exchanger. At both 1800 ppm and 2400 ppm of CO<sub>2</sub>, milk pH decreased with increasing pressure up to 207 kPa and a further increase in pressure up to 345 kPa did not further decrease milk pH (Figure 2). At pressures of 69 and 138 kPa, even though their CO<sub>2</sub> concentrations in the starting milk were different, milks with 1800 and 2400 ppm of CO<sub>2</sub> had similar pH ( $P > 0.05$ ). Difference in their pH was only observed between 207 and 345 kPa.

**pH at 72°C.** Similar to observations at 40 and 56°C, the pH of milk without added CO<sub>2</sub> (6.34) and milk with 600 ppm (6.07) did not change with increasing pressure (Figure 3). For milk with 1200, 1800, and 2400 ppm of CO<sub>2</sub>, pH decreased with increasing pressure up to



**Figure 4.** Mean ( $n = 2$ ) milk pH at the end of the holding section of a tubular heat exchanger as a function of CO<sub>2</sub> concentration and pressure during heating at 80°C. The five CO<sub>2</sub> concentrations are control (■), 600 ppm (▲), 1200 ppm (●), 1800 ppm (◆), and 2400 ppm (□). At the same CO<sub>2</sub> concentration, values with no common letter are significantly different ( $P < 0.05$ , lsd = 0.025).

138, 207, and 276 kPa, respectively (Figure 3). As observed at 56°C, even though their CO<sub>2</sub> concentrations in the starting milk were different for milks with 1800 and 2400 ppm of CO<sub>2</sub>; their pH in the heat exchanger was similar ( $P > 0.05$ ) at 69, 138, and 207 kPa; and difference in their pH was only observed at pressures of 276 and 345 kPa.

**pH at 80°C.** The pH of milk without added CO<sub>2</sub> (6.26) did not change with increasing pressure at 80°C (Figure 4). For milk with 600 ppm of CO<sub>2</sub>, unlike observations at 40, 56, and 72°C, milk pH was decreased with increasing pressure from 6.04 at 69 kPa to 5.99 at 138 kPa, and further increase in pressure did not further decrease milk pH. The pH of milks with 1200 and 1800 ppm of CO<sub>2</sub> continued to decrease until pressure in the heat exchanger reached 276 kPa. The pH

of milk with 2400 ppm of CO<sub>2</sub> decreased almost linearly with increasing pressure from 69 to 345 kPa and reached 5.63 at 345 kPa. It is likely that the pH of milk containing 2400 ppm of CO<sub>2</sub> would have decreased further at pressure greater than 345 kPa. At 80°C, for milk with 1800 and 2400 ppm of CO<sub>2</sub>, regardless of their carbonation level, no difference ( $P > 0.05$ ) in their pH in the heat exchanger at the end of the holding section was observed between 69 and 276 kPa (Figure 4).

## DISCUSSION

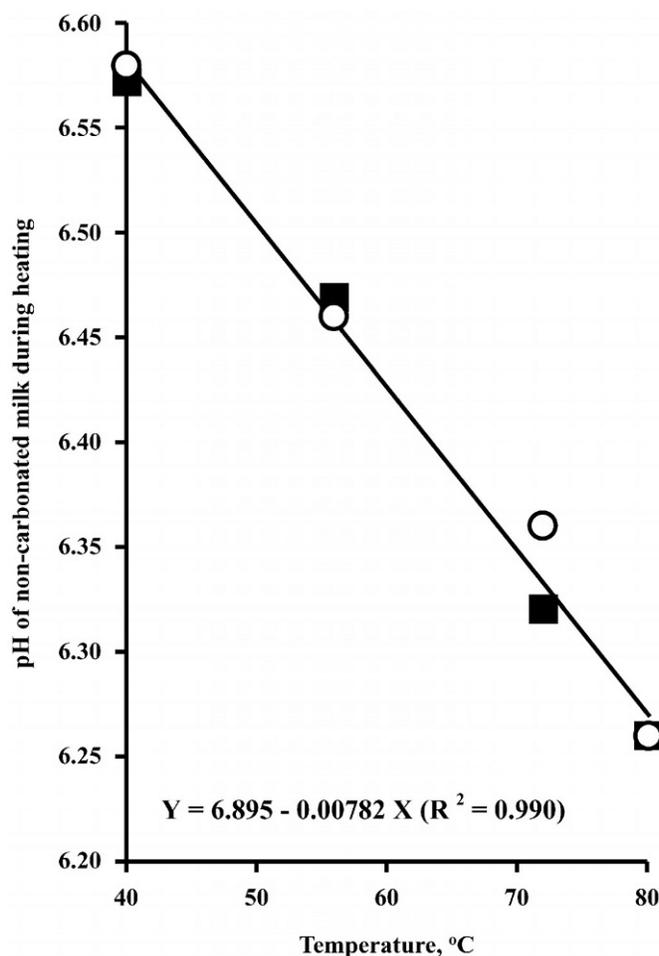
### pH of Milk Without Added CO<sub>2</sub>

Because at 40, 56, 72, and 80°C, the pH of milk without added CO<sub>2</sub> was independent of pressure (Figures 1 to 4), its mean ( $n = 5$ ) pH at 40, 56, 72, and 80°C averaging over the five pressure levels for each replication were calculated (Figure 5). The pH of milk without added CO<sub>2</sub> decreased linearly with increasing temperature, and the least square linear regression line is  $Y = 6.90 - 0.0078X$  ( $R^2 = 0.99$ ), where  $Y$  is pH and  $X$  is the temperature in °C. The linear coefficient ( $-0.0078$  pH unit/°C) obtained in the current study for milk without CO<sub>2</sub> in a tubular heat exchanger was consistent with the coefficient ( $-0.0073$  pH unit/°C) reported by Chaplin and Lyster for milk stirred with a nitrogen atmosphere in a water bath (1988). During heating in a heat exchanger, we found that the pH of milk without added CO<sub>2</sub> decreased linearly with increasing temperature in the temperature range from 40 to 80°C.

### pH of Milk with Added CO<sub>2</sub>

During heating in the tubular heat exchanger, the pH of milk with added CO<sub>2</sub> was dependant on CO<sub>2</sub> concentration, heating temperature, and pressure in the heat exchanger. In general, the pH of milk with added CO<sub>2</sub> in the heat exchanger decreased with increasing CO<sub>2</sub> concentration and increasing pressure. For milk with added CO<sub>2</sub>, at a fixed CO<sub>2</sub> concentration, the effect of pressure on pH was greater at a higher temperature (Figures 1 to 4).

Regardless of pressure and temperature, the CO<sub>2</sub> concentration of milk remained the same before and after the milk was processed in the heat exchanger (Table 2); therefore, the change in pH with pressure must be related to the degree of interaction of CO<sub>2</sub> with milk during heating at the various pressures. The solubility of CO<sub>2</sub> decreases with increasing temperature (Fogg and Gerrard, 1991). In the pasteurizer, without added pressure, the originally dissolved CO<sub>2</sub> might not stay dissolved in milk especially when the



**Figure 5.** pH of milk without added CO<sub>2</sub> at the end of the holding section of a tubular heat exchanger during heating from 40 to 80°C. The solid squares (■) and open circles (○) represent data from replication 1 and 2, respectively. The line is the least square linear regression line.

initial carbonation level and heating temperature were high. Increasing pressure in the pasteurizer increased the amount of dissolved CO<sub>2</sub> and resulted in a decrease in milk pH. Increasing the applied pressure decreased the pH to a minimum value that was a function of the total CO<sub>2</sub> in the milk. Once the minimum pH was reached for a constant CO<sub>2</sub> concentration, a further increase in pressure did not decrease milk pH further. The stabilization of milk pH probably indicated that at a fixed CO<sub>2</sub> concentration and temperature, the CO<sub>2</sub> interaction with milk had reached equilibrium condition at that temperature and pressure.

For milk without added CO<sub>2</sub>, milk pH decreased with increasing temperature in the heat exchanger (Figure 5). However, for milk with added CO<sub>2</sub>, especially at high CO<sub>2</sub> concentration, an increase in temperature does not necessarily mean a decrease in milk pH in

the heat exchanger as one would expect for the milk without added CO<sub>2</sub>. For example, when the heating temperature was increased from 72 to 80°C (Figures 3 and 4), there was very little difference in the pH of milk with 1800 or 2400 ppm of CO<sub>2</sub> at 69, 138, and 207 kPa.

Increasing CO<sub>2</sub> concentration from 0 to 2400 ppm at atmospheric pressure has been shown to decrease milk pH, but that pH change was influenced by both milk composition and temperature (0 to 40°C) at which the CO<sub>2</sub> was injected (Ma et al., 2001; Ma and Barbano, 2003a, 2003b). However, when milk with added CO<sub>2</sub> was heated in a heat exchanger, increasing CO<sub>2</sub> concentration does not necessarily mean a decrease in milk pH either. For example, at 80°C and pressures from 69 to 276 kPa, increasing CO<sub>2</sub> concentration from 1800 to 2400 ppm did not decrease milk pH significantly (Figure 4). It was only when pressure was increased to 345 kPa that a difference in pH of milks with 1800 and 2400 ppm of CO<sub>2</sub> became apparent.

### Implication of the Current Study

Under HTST pasteurization conditions in the current study, even for the milk without added CO<sub>2</sub>, there was a substantial decrease in milk pH as it was being pasteurized at 72 to 80°C in the heat exchanger. The change in milk pH with temperature is typically reversible if the heating does not exceed 100°C and there is no degradation of milk protein or lactose during heating (Fox and McSweeney, 1998). Therefore, the decrease in milk pH during pasteurization is usually “invisible” because milk pH at the exit of the pasteurizer after cooling to 0 to 1°C is the same as milk pH at 0 to 1°C at the inlet of the pasteurizer. Therefore, thermal death of bacteria during pasteurization of milk without added CO<sub>2</sub> is probably due not only to temperature but also to this “invisible” decrease in pH in the pasteurizer. By adding CO<sub>2</sub> to milk and increasing pressure, the pH of milk can be decreased even further during pasteurization. At 80°C and a pressure of 345 kPa, the pH of milk with 2400 ppm of CO<sub>2</sub> can be decreased to as low as 5.63 versus 6.26 for milk without added CO<sub>2</sub>. This decrease in pH may further enhance the microbial killing power of pasteurization.

As CO<sub>2</sub> continues to find applications other than its antimicrobial effect (Hotchkiss and Lee, 1996; Hotchkiss et al., 1999) in the dairy industry, knowing the pH of milk with added CO<sub>2</sub> during heating, a common dairy processing step, may be important. The extent of pH reduction during heating will affect the properties of milk after heating. If a decrease in milk pH is needed to achieve a certain change in a dairy food

system, then the conditions during heating, such as pressure, need to be defined and properly set so that the effect of added CO<sub>2</sub> on milk component interactions can be optimized.

### CONCLUSIONS

The pH of milk in a heat exchanger depended on CO<sub>2</sub> concentration, temperature, and pressure. During heating of milk without added CO<sub>2</sub>, pH decreased linearly as a function of increasing temperature but was independent of pressure. A linear coefficient of  $-0.0078$  pH unit/°C in the temperature range from 40 to 80°C was obtained. Thermal death of bacteria during pasteurization of milk without added CO<sub>2</sub> is probably due not only to temperature but also to this “invisible” decrease in pH in the pasteurizer. In general, the pH of milk with added CO<sub>2</sub> decreased with increasing CO<sub>2</sub> concentration and pressure. For milk with added CO<sub>2</sub>, at a fixed CO<sub>2</sub> concentration, the effect of pressure on pH decrease was greater at a higher temperature. At a fixed temperature, the effect of pressure on pH decrease was greater for milk with a higher CO<sub>2</sub> concentration. Decreased milk pH at high CO<sub>2</sub> concentration and high pressure may further enhance the microbial killing power of pasteurization.

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