INITIAL FREEZING TEMPERATURE RISES WITH RISE IN MEAT pH: THE IMPLICATIONS

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***Abstract*— this study tested the hypothesis that there is a link between initial freezing temperature and pH in meat. *M. longissimus thoracis et lumborum* from both sides of 9 lambs (n =18) and one side of 64 beef (n = 64) carcasses of varying pH were used in two experiments to determine the freezing behaviour of normal (< 5.8) and high (> 6.2) pH meat. Lamb samples were cooled to -1.5°C or frozen to -10°C and beef were frozen slowly in an insulated chamber at -80°C and the cooling and freezing temperatures of the samples were recorded every 30 sec and analysed. The temperature profiles of both lamb and beef showed minimal evidence of supercooling. High pH meat from both species froze at higher temperature relative to low pH meat. The range of initial freezing temperatures measured for beef were -0.9 to -1.5 °C (Δ = 0.6°C) with the highest initial freezing temperature associated with high- and the lowest temperature with low pH meat. There was a significant correlation (r = +0.73, P < 0.01) between beef pH and freezing point temperature in the present study supporting our hypothesis that meat pH has an effect on the likelihood of product freezing during chilled storage at -1.5°C. With the increasing proportion of beef and lamb being exported chilled rather than frozen due to the higher premium the former commands, the outcome of this study has a strong implication for the meat industry suggesting that accurate temperature control is very important and that even small variations in storage temperature can have disastrous effects on meat quality.**

***Index Terms*—pH, freezing point, beef, lamb.**

I. INTRODUCTION

Chilled meats generally command a premium over frozen meats, for this reason, meat processors, particularly in export oriented countries like New Zealand, continually looked to increase the proportion of chilled products that they export. Technologies for chilled exports are now well established, these primarily include hygienic processing, vacuum/controlled atmosphere packaging and strict chiller temperature control (Bell, 1993). New Zealand meat processors typically keep the temperature of their chilled meat shipping containers at -1.5°C, in order for the vacuum packaged meat to maintain the desired temperature of -1.5°C on receipt in markets all over the world. There has been anecdotal evidence that on rare occasions some chilled products have become partially frozen or hard to the touch upon receipt in some markets. This partial surface freezing appears to have happened in cuts located in various parts of cartons and the shipping container and therefore, cannot be attributed to difference in temperature gradients. The anecdotal evidence also suggests darker meat cuts were likely to freeze at higher temperatures.

Water-based biological products such as meat generally have an initial freezing temperature below the 0°C freezing point of pure water (0°C) depending on the type and concentration of solutes within the water phase of the product. According to Pham (1996), the initial freezing temperature of meat can be estimated using the equation: $\Theta_F = -4.66x_0/x_w - 46.4x_a/x_w$ (where Θ_F = initial freezing temperature, x = mass fraction, a = ash, o = other components, and w = water) underscoring the importance of the composition of the water phase of meat in determining its freezing point. Because pH has a strong relation to meat colour and darker meats generally indicate higher pH, the present study was designed to test the hypothesis that there is a link between higher freezing point and elevated pH in meat.

II. MATERIALS AND METHODS

The present study was conducted in two stages using 9 lambs in the initial stage to serve as a preliminary study and then followed by a more involved study using 64 bulls.

A. Lamb sample preparation

M. longissimus thoracis et lumborum from 9 lambs (5-6 months old) were obtained from a New Zealand meat processor. The 18 loins varied in ultimate pH levels, ranging from 5.4 to 6.6 (i.e. normal to high ultimate pH) determined at the abattoir. Each loin was cut in half to give a total of 36 samples, and each sample was randomly

assigned to one of two cooling treatments: Cooled in air at -10°C or -1.5 °C. All the samples were equilibrated to a temperature of approximately +10°C before the freezing point determination commenced.

Temperature measurement and recording was carried out using Grant Squirrel data loggers and a set of 40 fine gauge (0.2 mm wire diameter, Class 1 Tolerance) thermocouples that had been calibrated against an RT200 reference thermometer. Two thermocouples were inserted into the samples (positioned at the surface and centre of each sample) and 4 thermocouples were used to monitor the air temperature. The loggers were set to continuously measure the meat and air temperature at 30 second intervals. The individual samples were packed into un-sealed plastic bags once the thermocouples were inserted and placed into open-topped cartons for cooling.

The two cooling treatments (-10°C or -1.5 °C) were carried out separately using an Environmental Test Chamber with programmable air temperature and velocity control. The set point temperature in the chamber was adjusted to provide the required temperature and an air velocity of approximately 2.5 m/s.

B. Beef sample preparation

M. longissimus thoracis et lumborum from 64 bull beef carcasses were selected based on their pH values. The meat pH was measured 48 hours post slaughter as described for lamb. The samples were then vacuum packed and stored in a -1.5°C chiller until they were all analysed over a period of 8 weeks.

An insulated box was designed and built to control the rate of temperature decline in the samples during freezing. The box could hold six meat samples, with each sample filling a plastic specimen bottle (no lid) 42 mm diameter and 55 mm high. A T-type thermocouple probe (using the same wire used for the lamb trials) was then inserted into the centre of each of the meat samples. The assembled insulated box was then placed in a -80°C freezer until the samples were frozen to below -10°C. A high precision (12 floating point) Agilent Data Acquisition Unit (DAU) was used to record the temperature every 30 seconds from the six thermocouples as well as a thermocouple monitoring the air temperature inside the freezer.

The thermocouples were calibrated using the same insulated test rig and procedures used for the experimental samples, except high purity (Milli-Q) water was placed into the sample pots instead of meat. The difference between the measured initial freezing temperature of the pure water and its actual 0°C freezing point was used to correct the thermocouples.

Each run (set of six samples) was set up by first selecting a random set of 6 samples that were likely to provide a range of pH values. The samples were cut and fitted into the sample pots with the muscle fibres running vertical. The pH of each sample was re-measured and then the insulated box was closed carefully to ensure the thermocouple probes were centralised in the sample pots. Once the box was closed and sealed with tape, the thermocouple lead was plugged in and the data logger was started. The sample rig was then carefully placed in a -80°C freezer, ensuring that it was always oriented the same way.

C. Statistical analyses

The lamb and beef samples were classified into two groups based on their pH: low (<5.8) and high pH (>6.2). Data were analysed using the statistic directive of Microsoft Office Excel 2007.

III. RESULTS AND DISCUSSION

A. pH and the initial freezingtemperature of lamb

The temperature profiles and data analysis of the lamb samples frozen at -10 ºC showed no supercooling occurred in the samples during the freezing process contrary to what was expected of typical cooling curves (Cleland, 1990). Rahman, Guizani, Al-Kaseibi, Al-Hinai, Al-Maskri & Al-Hamhami (2002) also did not observe a zone of supercooling in the cooling curves of starch gels. Rahman et al. (2002) used the slope of the cooling curve to determine the initial and the end points of freezing of the gels. Similarly in the present study due to the lack of clear zone of supercooling, the average temperature profiles from the low and high pH samples in the -10°C experiment were plotted together (Figure 1) and the plateau points on the curve were used to determine the ice nucleation or equilibrium freezing point of the samples. The average temperature profiles indicated significant differences in the freezing rate of low and high pH samples. The high pH samples spent a shorter length of time near the freezing temperature (in the latent heat phase) than the low pH samples, as indicated by the shorter plateau time of the higher pH lambs (Figure 1). The observed temperature plateau indicates the period most of the water in the product converted to ice. Therefore, the data indicate that high pH lambs took a shorter time to freeze than normal pH lambs when subjected to a similar cooling process. These results show that high pH samples would more rapidly form ice crystals than low pH samples.

Due to the fast rate of freezing in the -10°C experiment there was no clear indication of the initial freezing temperature for the samples (i.e. there was no clear or flat plateau). Interestingly, the results from the -1.5°C experiment showed that, while the low pH samples reached -1.5°C, the high pH samples only cooled to an average temperature of -1.4°C (Figure 2). This finding indicates that the high pH samples had probably reached their freezing temperature and they were unable to cool down to -1.5°C because the heat being removed from the samples during this period was latent heat of freezing. By contrast the low pH samples, which cooled to -1.5°C, had either reached their freezing

temperature at -1.5°C or, more likely, had not reached their freezing temperature yet. Regardless, these results indicate that the low pH samples probably have a freezing temperature at least 0.1°C lower than high pH samples.

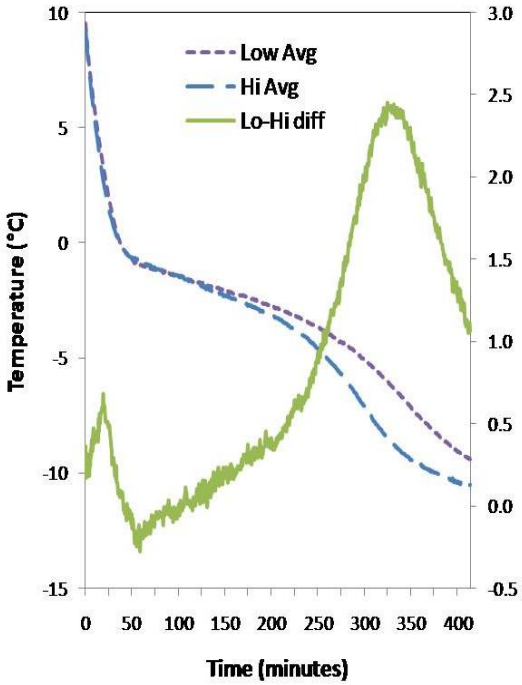

Figure 1. Temperature profile of lamb surface at -10°C.

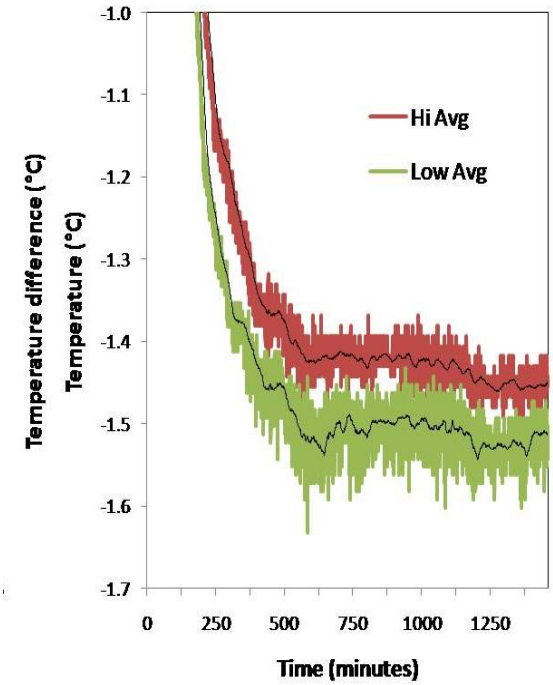

Figure 2. Temperature profile of lamb surface at -1.5°C

B. pH and the initial freezingtemperature of beef

Similarly to the lamb samples, the temperature profile of the beef samples did not show a region of supercooling despite the significant reduction in the chilling rate of the beef samples relative to lamb (Fig 3). There was a significant positive correlation ($r = 0.73$, $P < 0.01$) between beef pH and freezing point temperature (Fig 4). The reason for the rise in freezing point temperature with meat pH is unclear. We speculate that because meat pH has an effect on the water mobility and a higher pH reduces water mobility (Bertram *et al*., 2007) that it is easier to align, nucleate and crystallise water molecules in high pH meat. Other reasons may include that normal pH meats have a higher amount of dissolved solutes, considering that muscles with lower ultimate pH have a higher concentration of lactic acid and are more likely to contain residual glycogen than high pH muscles (Young, Thomson, Merhtens & Loeffen, 2004).

IV. DISCUSSION

The range of initial freezing temperatures measured in this work for beef was -0.9°C to -1.5°C ($\Delta = 0.6$°C) with the highest of the recorded temperature associated with high and the lowest with low pH beef (Fig 4). The range observed in this study was within the range of initial freezing point temperatures reported for various muscles and meat cuts (Rahman, 1995). Unfortunately there was no indication of the effect of pH or the status of pH of the samples reported in Rahman (1995) and as far as we know this may be the first time a link is being established between the pH and freezing point of meat.

The average initial freezing temperatures were -1.24 and -1.05 °C for low and high pH beef respectively. It is not easy to extend the results from this study, which were obtained using a -80°C freezer, to what happens in chilled meat storage where the product is held vacuum packed in an environment of approximately -1.5°C for many weeks. However, with the range of initial freezing temperatures measured in this study, one might expect the incidence of ice crystal formation in vacuum packed chilled meat held at -1.5°C to be higher than being currently reported. However, the result suggest that for ice crystals to form in the product, the storage temperature needs to be lower than the initial freezing temperature (probably by 0.5-1.0°C) in order to overcome the supercooling phase and to cause nucleation of ice crystals. The implication of this is that any attempt to lower the storage temperature of meat to below the current -1.5°C could result in an increased number of cases of chilled meat product freezing.

Ice crystal formation in vacuum packed chilled meat can be reduced or avoided by: (1) raising the average storage temperature above -1.5°C, which could lead to shorter shelf-life and would run contrary to the current drive by the meat industry to extend the chilled storage life of meat even further by lowering the storage temperature to (e.g. -1.7°C); (2) by segregating high value meat cuts on the basis of pH to determine an appropriate shipping storage regime for the cuts; or (3) ideally to develop better packaging technologies, which would allow for a similar or longer storage life at a temperature higher than -1.5°C.

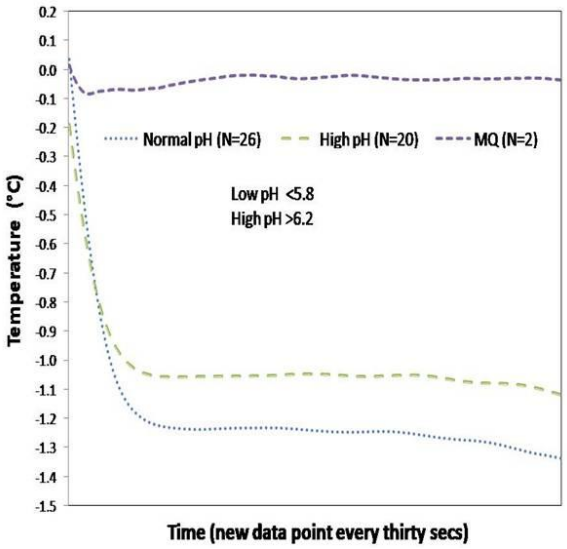

Figure 3. Internal centre temperature profile of beef

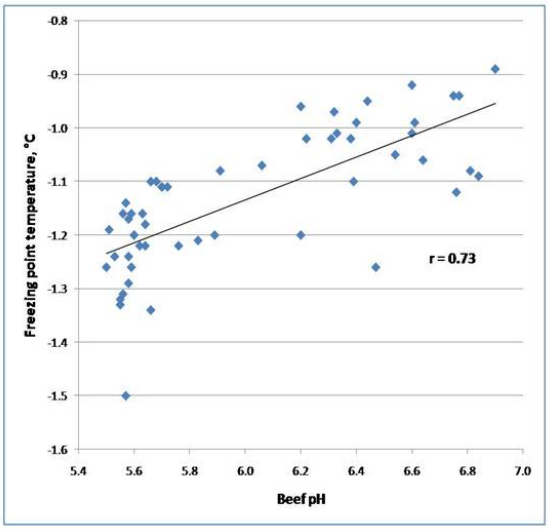

Figure 4. Correlation between beef pH and freezing point temperature

V. CONCLUSION

The results of this study support the hypothesis that meat pH has a strong influence on initial freezing point of red meat. The evidence suggests that high pH meat is more likely to have a higher freezing temperature and a more rapid rate of ice crystallisation than normal pH meat. The results can be used in the development of strategies to avoid the problem of ice crystal formation in chilled meat products during active chilling and during storage and transport. The findings may also be useful to the refrigeration industry by providing a more thorough understanding of the impact that natural product variation and storage temperature variation can have on the quality of chilled products.

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