Heat stability of goat’s milk

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My Background

• Educated at Birmingham Univ. Chem. Eng.
• 38 years at Reading University
• Physical properties of foods
• Food processing operations
• Pilot plant activities (UHT pilot plant)
• Supervised over 30 PhD students and 150 BSc and MSc students
• Fascinated by milk, biological fluid, naturally occurring variations
Summary

• Ionic calcium, pH and ethanol stability
• Measurement of heat stability
• Factors affecting heat stability
• Fouling of heat exchangers
• Centrifugation of milk and sediment formation
• Measuring properties at high temperature
• Is ethanol stability a good predictor of heat stability (practical work)
## Chemical composition (g / 100g) of milk different species of mammals

<table>
<thead>
<tr>
<th>Species</th>
<th>Water</th>
<th>Fat</th>
<th>Protein</th>
<th>Lactose</th>
<th>Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ass</td>
<td>89.0</td>
<td>2.5</td>
<td>2.0</td>
<td>6.0</td>
<td>0.5</td>
</tr>
<tr>
<td>Buffalo</td>
<td>82.1</td>
<td>8.0</td>
<td>4.2</td>
<td>4.9</td>
<td>0.8</td>
</tr>
<tr>
<td>Camel</td>
<td>87.1</td>
<td>4.2</td>
<td>3.7</td>
<td>4.1</td>
<td>0.9</td>
</tr>
<tr>
<td>Cow</td>
<td>87.4</td>
<td>3.9</td>
<td>3.3</td>
<td>4.7</td>
<td>0.7</td>
</tr>
<tr>
<td>Goat</td>
<td>87.0</td>
<td>4.5</td>
<td>3.3</td>
<td>4.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Horse</td>
<td>88.8</td>
<td>1.9</td>
<td>2.6</td>
<td>6.2</td>
<td>0.5</td>
</tr>
<tr>
<td>Reindeer</td>
<td>63.3</td>
<td>22.5</td>
<td>10.3</td>
<td>2.5</td>
<td>1.4</td>
</tr>
<tr>
<td>Sheep</td>
<td>81.6</td>
<td>7.5</td>
<td>5.6</td>
<td>4.4</td>
<td>0.9</td>
</tr>
<tr>
<td>Yak</td>
<td>82.7</td>
<td>6.5</td>
<td>5.3</td>
<td>4.6</td>
<td>0.9</td>
</tr>
<tr>
<td>Zebu</td>
<td>86.5</td>
<td>4.8</td>
<td>3.3</td>
<td>4.7</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Adapted from Lenter (1981), Jenness (1988) and Holland et al.
<table>
<thead>
<tr>
<th>Species</th>
<th>Total Calcium (mM)</th>
<th>Ionic Calcium (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Human</td>
<td>7.5</td>
<td>3.0</td>
</tr>
<tr>
<td>Cow</td>
<td>30</td>
<td>1.80</td>
</tr>
<tr>
<td>Goat</td>
<td>34</td>
<td>2.67</td>
</tr>
<tr>
<td>Sheep</td>
<td>55</td>
<td>2.01</td>
</tr>
<tr>
<td>Mouse</td>
<td>71</td>
<td>?</td>
</tr>
<tr>
<td>Human Blood</td>
<td>2.05-2.5</td>
<td>1.1 – 1.32</td>
</tr>
</tbody>
</table>
Distribution of ionic calcium in cow’s and goat’s milk
Distribution of ethanol stability in cow’s and goat’s milk

![Graph showing the distribution of ethanol stability in cow’s and goat’s milk. The x-axis represents ethanol stability (%) ranging from 35-39 to 95-99, and the y-axis represents samples (%). The graph compares cow’s milk (black bars) and goat’s milk (gray bars).]
One model for the casein micelle

Acidification
pH < 6.7
> 20°C

Heating
> 80°C-min
pH = 6.7

Soluble Ca phosphate

Limited dissociation of (β-)casein

Denatured β-Lg/α-La

Calcium phosphate

Some κ-casein

Hydrodynamic radius

Hairy layer

50 nm
The soluble phase of milk
Methods for assessing heat stability

• Heat coagulation temperature
• Heat coagulation time
• Viscosity measurement
• Heat exchanger fouling
• Sediment formation
• Coagulation
• Casein micelle size
• others
Figure 2.8 Heat coagulation time-pH profile of unconcentrated type A milk.

Some observation on this method

• Why does heat stability go through a maximum and minimum.

• As pH is increased, Ca2+ decreases, micelles less susceptible to coagulation.

• At pH maximum, K-casein dissociation occurs, this has a destabilising effect

• However at minimum, Ca2+ is further reduced and this becomes the dominating influence
Noteworthy Observations

• However, despite all the research work, problems related to poor heat stability of milk are still encountered in commercial processes.

• Singh (2004) stated that the heat coagulation time (heat stability) often correlates very poorly with the stability of milk on commercial sterilization.

• He also pointed out that from an industry point of view, the use of a pilot scale or laboratory scale sterilizer which simulates sterilization conditions used in practice provides more reliable results and prediction of behaviour of milk in commercial plants, although this is not possible without access to pilot plant facilities.
Miniature UHT plant

- Pump
- Overflow valve
- Flow meter
- Hot water in
- Preheater
- Main heater
- Steam in
- Out
- Steam out
- Cooler
- Cold water in
- Filter
- Backpressure valve
- Water tank
- Product tank
- Overflow valve
- 3-way valve
- Product tank
- Pump
Monitoring Fouling

• Monitoring temperature, pressure and flow rate and overall heat transfer coefficient.

• \[ \text{OHTC} = \frac{GCp\Delta\theta}{A\Delta T_{lm}} \]

  Where \( U \) = overall heat transfer coefficient in kcal/hr-m2
  \( G \) = mass flow rate in kg/h
  \( Cp \) = specific heat of milk in kcal/kg -°C
  \( \Delta\theta \) = Temperature difference in °C
  \( A \) = surface area of the tubings in m²
  \( \Delta T_{lm} \) = log mean temperature difference in °C =
  \[ [(\text{steam in} – \text{milk out})-(\text{steam out} – \text{milk in})]/ \log [(\text{steam in} –\text{milk out})/(\text{steam out} – \text{milk in})] \]
Comparison of cows’ and goats’ milk

Cow VS Goat

OHTC, W/m² K

Time, S

Cow
Goat
Table showing the effect of additives on pH, ethanol stability and ionic calcium for goat’s milk

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>Ionic Calcium (mMol)</th>
<th>Ethanol stability (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh goat milk</td>
<td>6.63</td>
<td>2.55</td>
<td>54</td>
</tr>
<tr>
<td>Fresh goat milk with 0.2% tri-sodium citrate</td>
<td>6.76</td>
<td>1.24</td>
<td>76</td>
</tr>
<tr>
<td>Fresh goat milk with 0.2% sodium hexa metaphosphate</td>
<td>6.73</td>
<td>0.83</td>
<td>98</td>
</tr>
<tr>
<td>Fresh goat milk with resins (0.3%)</td>
<td>6.62</td>
<td>1.72</td>
<td>68</td>
</tr>
</tbody>
</table>
Comparison of ionic calcium reduced milk with raw goats’ milk

![Graph showing comparison of OHTC, W/m²K over time for different treatments: Phosphate, Citrate, Resins, and Raw.](image-url)
Table showing the effect of CaCl$_2$ on pH, ethanol stability and ionic calcium in cows’ milk

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>Ionic Calcium (mMol)</th>
<th>Ethanol stability (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh cow milk</td>
<td>6.76</td>
<td>1.75</td>
<td>86</td>
</tr>
<tr>
<td>Fresh cow milk with 0.01% CaCl$_2$</td>
<td>6.73</td>
<td>1.99</td>
<td>80</td>
</tr>
<tr>
<td>Fresh cow milk with 0.03% CaCl$_2$</td>
<td>6.70</td>
<td>2.36</td>
<td>78</td>
</tr>
<tr>
<td>Fresh cow milk with 0.05% CaCl$_2$</td>
<td>6.64</td>
<td>2.97</td>
<td>58</td>
</tr>
</tbody>
</table>
Effect of increased ionic calcium level in Cows’ milk

![Graph showing the effect of increased ionic calcium level in Cows’ milk. The x-axis represents time in seconds (S) ranging from 60 to 3180. The y-axis represents OHTC, W/m²K. The graph includes three lines for different calcium levels: 0.01%, 0.03%, and 0.05%, each marked with different symbols and colors. The graph shows a decrease in OHTC over time for all calcium levels, with the 0.01% line starting higher and maintaining a steady decrease, the 0.03% line showing a sharper decline, and the 0.05% line starting lower and showing a gradual decrease.](image-url)
Measuring Sediment in milk

- Centrifuge milk at ~ 3000 G for 30 min to 1 h
- Useful for assessing heat stability
- Emulsion stability during storage
- All milk contains sediment
- One important question is how much sediment is required before it can be detected by taste?
Sedimentation in UHT goat’s milk

- Goat’s milk has a higher ionic calcium than cow’s milk and a lower alcohol stability.

- Two batches of goats milk were subject to UHT treatment.

- Four different stabilisers were evaluated (DSHP, SDHP, TSC SHMP)
## Effects of stabilisers on properties of UHT goat’s milk

<table>
<thead>
<tr>
<th>Stabiliser</th>
<th>Ethanol stability (%)</th>
<th>Ionic Calcium (mM)</th>
<th>pH</th>
<th>Sediment Dry weight (g/100 ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No stabiliser</td>
<td>&lt;50</td>
<td>2.43</td>
<td>6.56</td>
<td>5.44</td>
</tr>
<tr>
<td>SDHP (0.2%)</td>
<td>&lt;50</td>
<td>2.45</td>
<td>6.29</td>
<td>4.94</td>
</tr>
<tr>
<td>DSHP (0.2%)</td>
<td>68</td>
<td>1.42</td>
<td>6.69</td>
<td>2.28</td>
</tr>
<tr>
<td>TSC (0.2%)</td>
<td>74</td>
<td>1.22</td>
<td>6.82</td>
<td>0.15</td>
</tr>
<tr>
<td>SHMP (0.2%)</td>
<td>80</td>
<td>0.85</td>
<td>6.49</td>
<td>0.13</td>
</tr>
</tbody>
</table>
Sediment formed in direct and indirect UHT treatment

<table>
<thead>
<tr>
<th>Stabilizer</th>
<th>SEDIMENT Direct</th>
<th>SEDIMENT Indirect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>2.31</td>
<td>4.44</td>
</tr>
<tr>
<td>0.15 TSC</td>
<td>0.58</td>
<td>0.60</td>
</tr>
<tr>
<td>0.20 TSC</td>
<td>0.56</td>
<td>0.55</td>
</tr>
<tr>
<td>0.25 TSC</td>
<td>0.56</td>
<td>0.55</td>
</tr>
<tr>
<td>0.15 DSHP</td>
<td>0.75</td>
<td>4.02</td>
</tr>
<tr>
<td>0.20 DSHP</td>
<td>1.46</td>
<td>5.44</td>
</tr>
<tr>
<td>0.25 DSHP</td>
<td>1.76</td>
<td>5.89</td>
</tr>
</tbody>
</table>
Caprine milk:

**Figure 3.** The effect of added DSHP, TSC and CaCl$_2$ on the sediment following UHT and in-container sterilisation for three fully replicated trials.
Can we measure pH and ionic calcium at high temperatures?

What is the pH and ionic calcium of milk at 140°C?

Separate milk permeate or dialysate at various temperatures and measure it at room temperature.

Comparison of UF and dialysis between 20 and 80°C.

Use of dialysis and UF at 90 to 120°C.
Ionic calcium at high temperatures measured by dialysis
Experimental Set-Up
Range of pH and Ionic calcium in goat milk samples prior to sterilisation

![Graph showing the range of pH and Ionic calcium in goat milk samples prior to sterilisation. The graph includes data points for three trials: trial 1, trial 3, and trial 4.]
Milk sterilised at 120°C for 15 min

Different phosphates, citrate, EDTA and calcium chloride additions
Discussion of Alcohol Stability

• It has some potential for UHT processing
• If alcohol stability is below 75%, show some caution
• If alcohol stability is above 75% but fouling or sediment is encountered, perhaps too much stabilisier has been added
• It is useful for formulating products for pilot plant trials
Concluding remarks

• Ionic calcium is worth measuring because:
  ionic calcium and pH are useful indicators of heat stability
  (together with buffering capacity)

• However for a better understanding of factors affecting heat
  stability

• pH and ionic calcium should be measured at high
  temperatures.

• Goat milk can be made to behave like cow’s milk and vice
  versa

• In addition: pH and ionic calcium serve as useful indicators for
  best use of milk.