دانشگاه صنعتی اصفهان

صنایع لبنی تکمیلی

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1391

صنایع لبنی تکمیلی

تعداد واحد: ۲

نوع واحد:نظری

پیشنیاز:ندارد

سرفصل درس:

اثرعملیات حرارتی - اصول اساسی، سنتیک واکنشها طی عملیات حرارتی - اثر حرارت برمیکروارگانیسمها و آنزیمها، اثر حرارت بر نمکها و pH شیر، واکنش میلارد، عوامل موثربر قهوه‌ای شدن- تشخیص آزمایشگاهی شیرهای استریل در ظروف و روشهای UHT ـ اثر حرارت بر پروتئینهای شیر- پروتئینهای سرمی - پیامدهای دناتوراسیون پروتئینهای سرمی - واکنشهای گوگرد موجود در پروتئینها- پایداری محلولهای کلوئیدی پروتئین در حین عملیات حرارتی - عوامل موثر بر پایداری حرارتی - تغییرات فیزیکو شیمیایی تغییر طعم - تغییر خاصیت اکسیداتیو- تغییر رنگ - رویه بستن شیر- تغییر ارزش تغذیه‌ای - شیر به عنوان محیط کشت برای پرورش استارترها- خاصیت کلوئیدی و پدیده سطحی - شیمی سطحی - پایداری کلوئیدی - تغییرات انتشار- پراکندگی (اندازه) میسل کازئین - خصوصیات پایداری کلوئیدی - اثر آنزیم رنیتین - بسته شدن پیری - مقاومت حرارتی گویچه‌های چربی - خصوصیات پایداری امولسیون - عکس العمل درمقابل سرما- (اگلوتیناسیون سرما)- هموژنیزاسیون - خامه‌ای شدن - اثر متقابل ترکیبات شیر با هوا- تئوریهای کف کردن - کف کردن فرآورده‌های لبنی - چرنینگ (زدن)، خصوصیات رئولوژیکی - رفتار نیوتنی - محلولهای غیرنیوتنی - ژل و چربی شیر. خصوصیات ترکیبات تغلیظ شده شیر - عکس العمل آب - اثر تغلیظ / تبخیر - انجماد - خشک کردن - فرایند ممبران - تغلیظ پروتئین - بازسازی / طعم و آروما- خصوصیات کلی - آرومای شیر / آرومای مختلف لبنی - تغییرات آروما در شیر و فراورده‌های لبنی .

Refrences:

1- Dairy processing handbook. 1995-2005. Tetrapak.
2- Dairy science qnd technology. 2006. Walstra et al
3- Dairy Science and Technology Handbook. 1993. YH HUI
4- Dairy Chemistry. 1997. Fox
5- Dairy Chemistry and Biochemistry. 1998. Fox and McSWEENEY.
6- Dairy processing Improving quality. 2000. Gerrit Smit. CRC Press.

هدف از فرایند حرارتی:

1- تضمین سلامت مصرف کننده:

Coxiella burnetii
Mycobacyerium tuberculosis
Staphylociccus aureus
Listeria monocytogenes,
Salmonella species
Campylobacter jejuni

پاتوژن های مقاوم به حرارت ممکن است:

- در شیر وجود نداشته باشند (*Bacillus anthracis*)،
- یا به دلیل رشد سایر گونه ها فرصت رشد نمی یابند (*Clostridium perfringens*)،
- یا در شیر رشد نمی کنند (*Clostridium botulinum*)،
- یا در تعداد زیاد ایجاد مسمومیت یا بیماری می نمایند (*Bacillus cereus*)

2- افزایش عمر نگهداری
3- ایجاد خصوصیات ویژه در برخی محصولات

CHANGES CAUSED BY HEATING:

- **Reversible or irreversible**

Reversible: mutarotation equilibrium of lactose and changes in ionic equilibriums, including pH

Chemical and Physical Changes:

- Gases, including CO_2, are partly removed
- The amount of colloidal phosphate increases and the $[Ca^{2+}]$ decreases
- Lactose isomerizes and partly degrades to yield, for instance, lactulose and organic acids
- milk pH decreases
- Most of the serum proteins are denatured
- Part of the serum protein (especially of β-lactoglobulin) becomes covalently bound to κ-casein and to some proteins of the fat globule membrane.
- Enzymes are inactivated
- Reactions between protein and lactose occur, Maillard reactions in particular
- Casein micelles become aggregated. Aggregation may eventually lead to coagulation

- Several changes occur in the fat globule membrane, e.g., in its Cu content
- Some vitamins are degraded

Consequences:

- Bacterial growth rate of the organisms surviving, or added after heat treatment, can be greatly affected, generally increased:

  IgM (agglutinin) Bacillus cereus

  lactoperoxidase system lactic acid bacteria

  Lactoferrin Bacillus stearothermophilus

  Bacteriophages can be inactivated, depending on the heating intensity
- Nutritive value decreases
- The flavor changes appreciably
- Color may change
- Viscosity may increase slightly
- Heat coagulation in evaporated milk serum protein is denatured before concentrating
- Age gelation in sweetened condensed milk is also reduced when the milk is intensely heated before concentrating.

- The *rennetability of milk and the rate of syneresis of the rennet gel* decrease (serum proteins bound to k-casein)
- *Creaming tendency of the milk decreases*

Possible Reactions of Side Chain Groups of Amino Acid Residues Linked in the Peptide Chain (|) of Proteins at High Temperature

With serum denaturation (reactions 4, 5, 6)

Cross-linking in or between petides (reactions 5, 6, 9, 10, 11, 12)

1. $\vdash CH_2{-}CONH_2 + H_2O \longrightarrow \vdash CH_2{-}COO^- + NH_4^+$
   Asparagine → Aspartic acid
2. $\vdash (CH_2)_2{-}CONH_2 + H_2O \longrightarrow \vdash (CH_2)_2{-}COO^- + NH_4^+$
   Glutamine → Glutamic acid
3. $\vdash CH_2{-}O{-}PO_3^{2-} + H_2O \longrightarrow \vdash CH_2{-}OH + HPO_4^{2-}$
   Phosphoserine → Serine
4. $\vdash CH_2{-}SH + OH^- \rightleftharpoons \vdash CH_2{-}S^- + H_2O$
   Cysteine
5. $\vdash CH_2{-}S{-}S{-}CH_2{-}\dashv \; + \; \vdash CH_2{-}S^- \rightleftharpoons \vdash CH_2{-}S^- \; + \; \vdash CH_2{-}S{-}S{-}CH_2{-}\dashv$
6. $\vdash CH_2{-}S^- + {}^-S{-}CH_2{-}\dashv \longrightarrow \vdash CH_2{-}S{-}S{-}CH_2{-}\dashv + 2\ominus$
   Cysteine → Cystine
7. $\vdash CH_2{-}S^- \longrightarrow \Vdash CH_2 + HS^-$
   Cysteine → Dehydroalanine
8. $\vdash CH_2{-}O{-}PO_3^{2-} \longrightarrow \Vdash CH_2 + HPO_4^{2-}$
   Phosphoserine → Dehydroalanine
9. $\Vdash CH_2 + HS{-}CH_2{-}\dashv \longrightarrow \vdash CH_2{-}S{-}CH_2{-}\dashv$
   Dehydroalanine + Cysteine → Lanthionine
10. $\vdash (CH_2)_4{-}NH_3^+ + H_2C{=}\dashv + OH^- \longrightarrow \vdash (CH_2)_4{-}NH{-}CH_2{-}\dashv + H_2O$
    Lysine + Dehydroalanine → Lysinoalanine
11. $\vdash CH_2{-}(C_3H_3N){-}NH^+ + H_2C{=}\dashv + OH^- \longrightarrow \vdash CH_2{-}(C_3H_3N){-}N{-}CH_2{-}\dashv + H_2O$
    Histidine + Dehydroalanine → Histidinoalanine
12.[a] $\vdash CH_2{-}COOH + H_2N{-}(CH_2)_4{-}\dashv \longrightarrow \vdash CH_2{-}CO{-}NH{-}(CH_2)_4{-}\dashv + H_2O$
    Aspartic acid + Lysine → Isopeptide
13.[b] $\vdash (CH_2)_4{-}NH_2 + C_6H_{12}O_6 \longrightarrow \vdash (CH_2)_4{-}NH{-}C_6H_{11}O_5 + H_2O$
    Lysine + Glucose → Amadori product

[a] Reaction also occurs with glutaminic acid residues.

[b] First step in the Maillard reaction with glucose or another reducing sugar. See Figure 7.4.

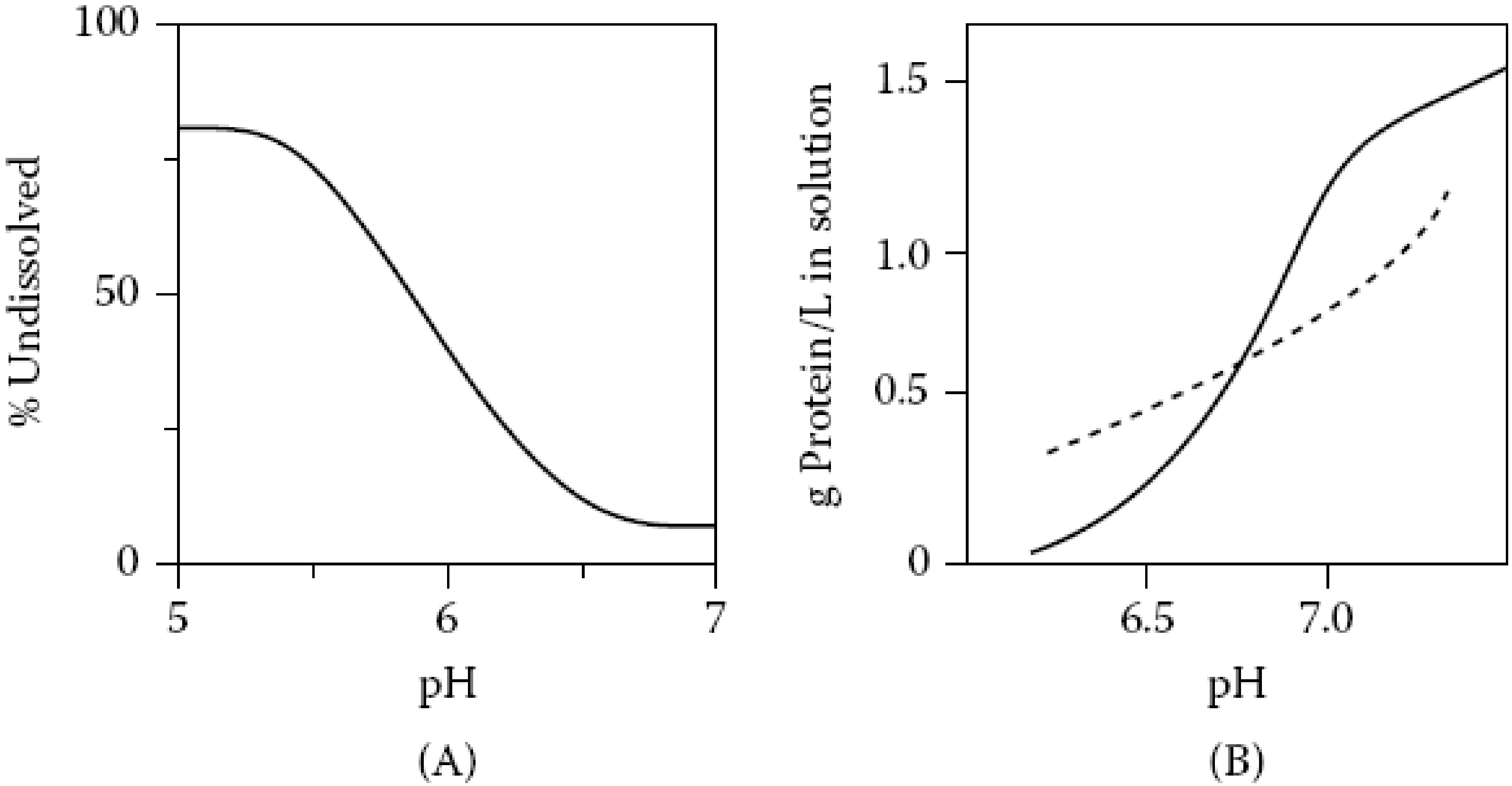
Denatuation of serum proteins

Unfolding in peptide chains (temperature 80 °C): reaction in or between side groups chains → preventing refolding

These changes happen for serum proteins specially BLG, ALA, serum albumin, Immunoglubolins.
Proteose peptones do not denatured (caseins)
At high temperature, thiol group react with –s-s- groups → Dimer, trimer, tetramer, ….

In milk during heating: BLG react with k-casein → casein micells cover with BLG (depending on pH)

Whey proteins show different thermal stabilities: alpha-lactalbumin > betalactoglobulin> bovine serum albumin > immunoglobulins.



Influence of pH on the effects of heating on proteins. (A) Percentage of the proteins that become precipitated after heating whey for 10 min at 80°C. (B) Amount of protein that remains in solution, i.e., not associated with the casein micelles, after heating milk (—) or serum protein free milk (----) at 140°C.

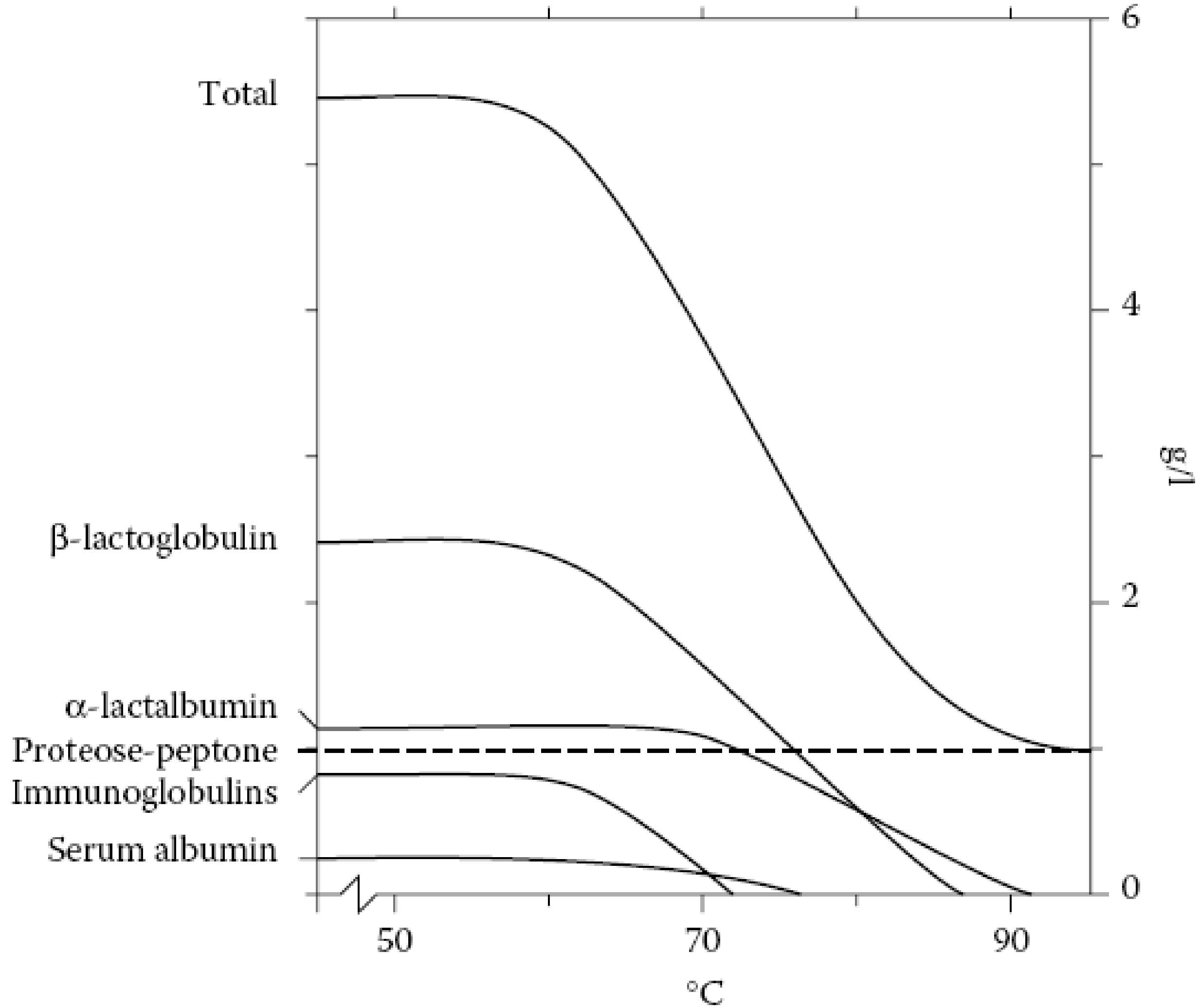
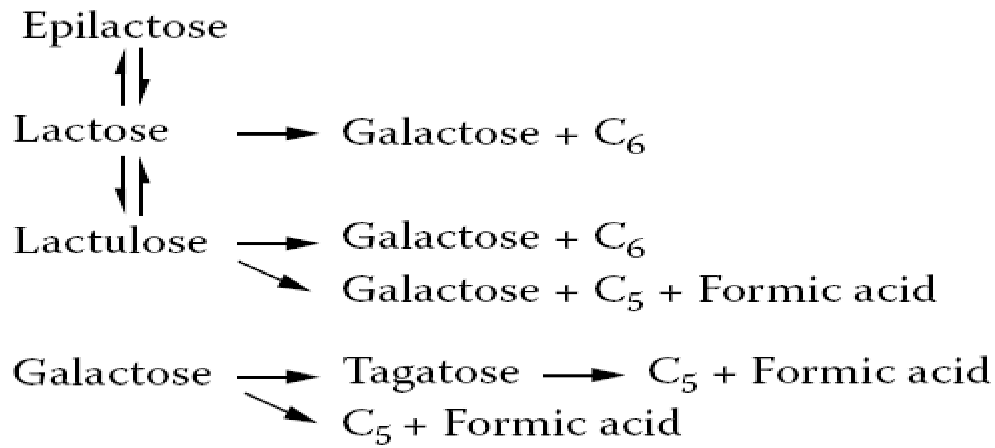


FIGURE 7.3 Effect of heating milk for 30 min at various temperatures on quantity of serum proteins that remain dissolved after cooling and acidification to pH 4.6. (Mainly adapted from B.L. Larson and G.D. Rolleri, *J. Dairy Sci.*, **38**, 351, 1955.)

ISOMERIZATION AND SUGAR DEGRADATION REACTIONS



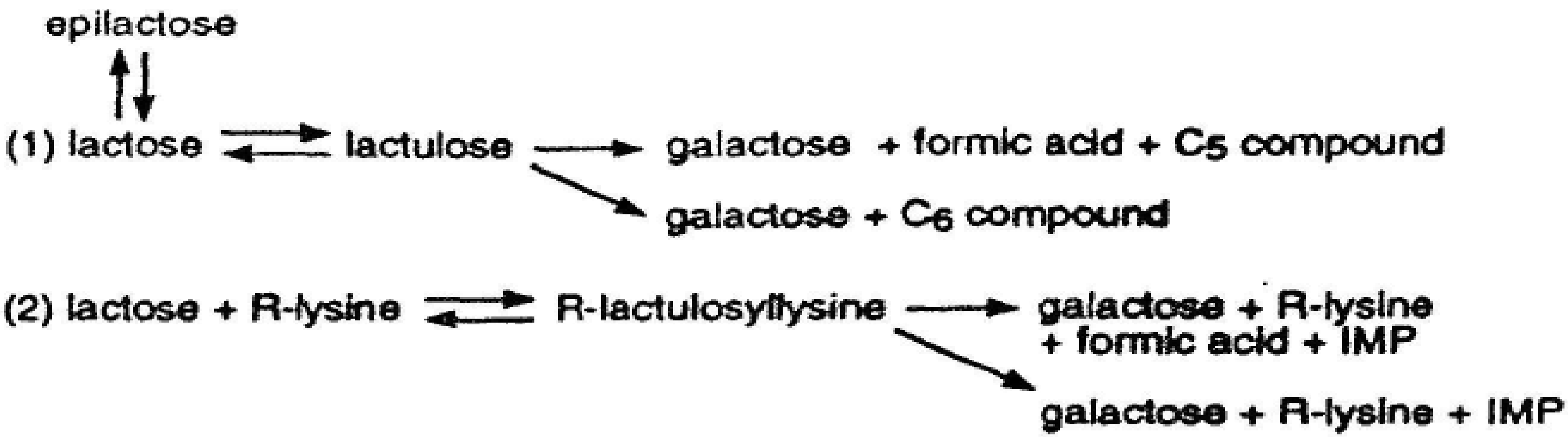


FIGURE 6.5 Simplified scheme of reactions occurring in the initial stage of the breakdown of lactose during the heating of milk (sterilization temperatures). IMP, intermediate Maillard products.

MAILLARD REACTIONS

Initial

Lactose + lysine–R → Lactulosyl-lysine–R

Galactose + lysine–R → Tagatosyl-lysine–R

Intermediate

Lactulosyl-lysine–R → Lysine–R + Galactose + C_6

↘ Lysine–R + Galactose + C_5 + Formic acid

Tagatosyl-lysine–R → Lysine–R + C_n ($n = 1–6$)

Advanced

C_n + Lysine–R → Melanoidins

C_n + Arginine–R → Melanoidins

FIGURE 7.4 Simplified scheme of reactions occurring with lactose during the heating of milk at sterilization temperature. R stands for a peptide chain, Cn for an organic compound containing n carbon atoms.

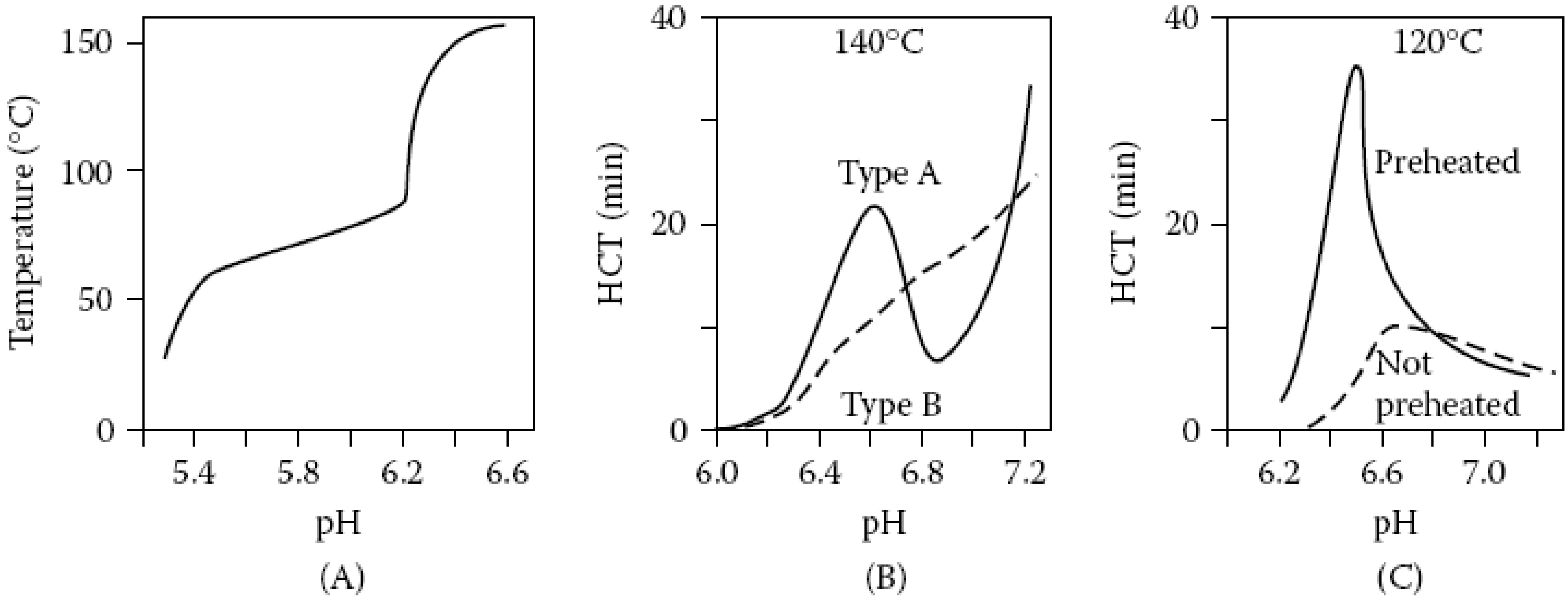


FIGURE 7.6 Heat coagulation of milk as a function of the initial pH. (A) Temperatures at which coagulation starts at fairly rapid warming of the milk (approximate results). (B) Heat coagulation time at 140°C of two different samples of fresh milk. (C) HCT at 120°C of evaporated skim milk, with or without preheating of the milk before concentration.

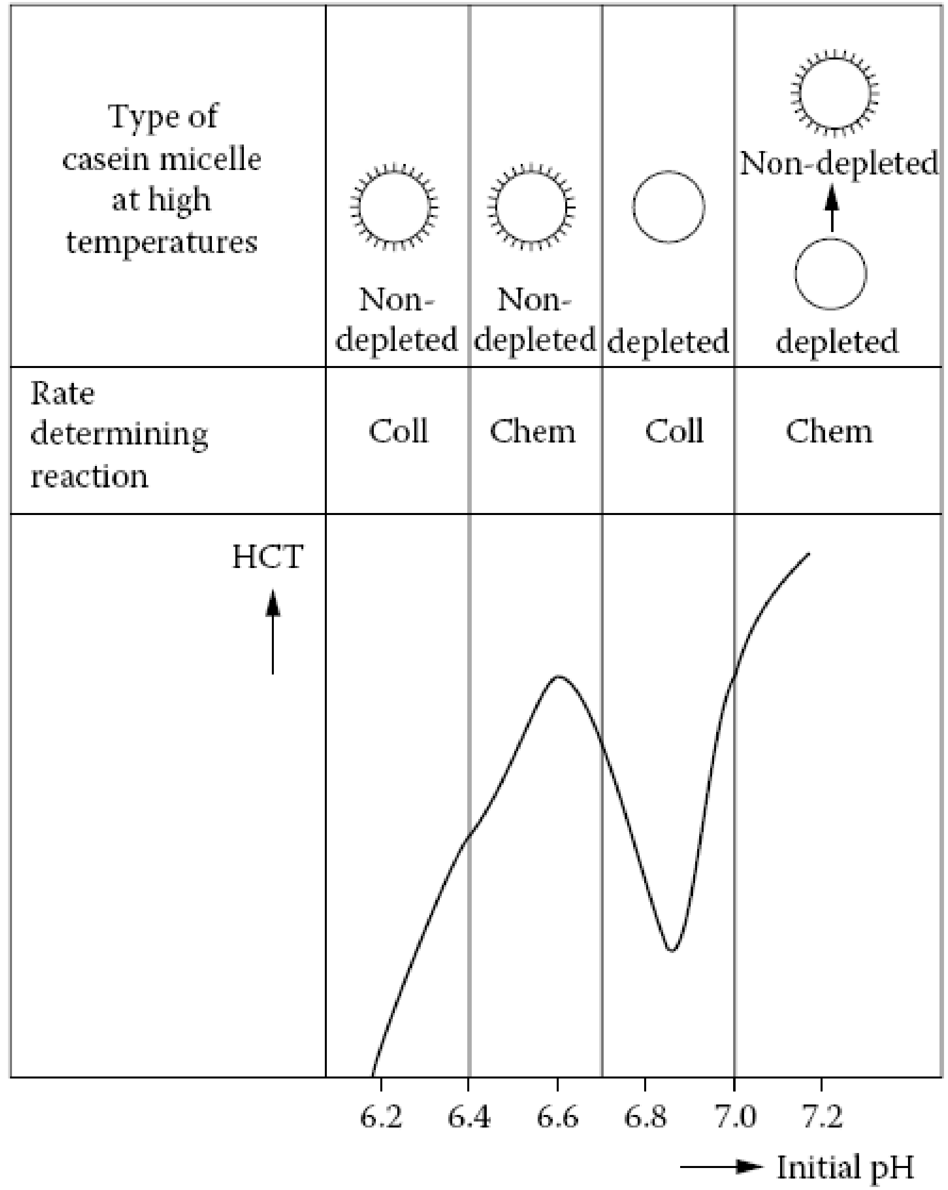


FIGURE 7.7 Model for the effect of initial pH on the type of casein micelle emerging at high temperature and thereby on the heat coagulation time (HCT) of milk. coll = colloidal aggregation, chem = chemical reaction

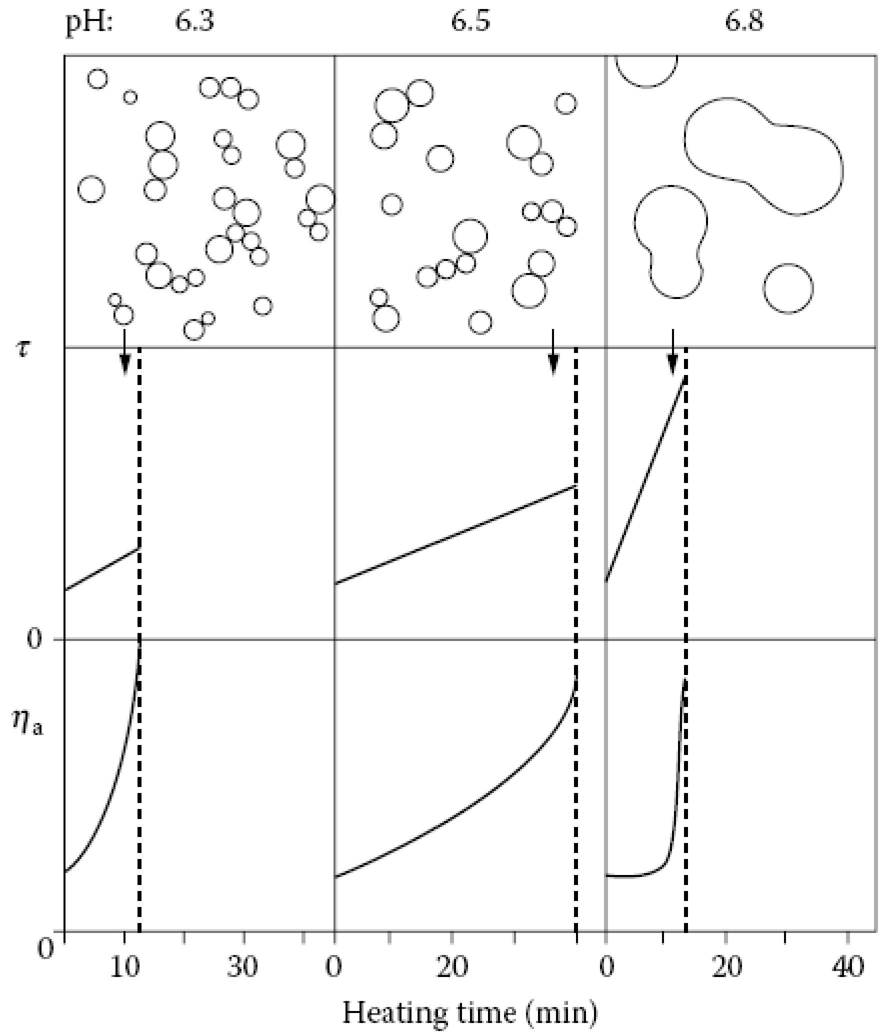


FIGURE 7.8 Heat coagulation at 120°C of concentrated skim milk at various initial pH. The upper row shows the appearance of the casein micelles (derived from electron micrographs) at the moments indicated by arrows, i.e., shortly before heat coagulation. The HCT is indicated by a vertical broken line. The second row gives the turbidity (*t) as a* function of heating time, the lowest row the apparent viscosity (*ha). t and ha were* determined in situ, i.e., at 120°C. Approximate results.

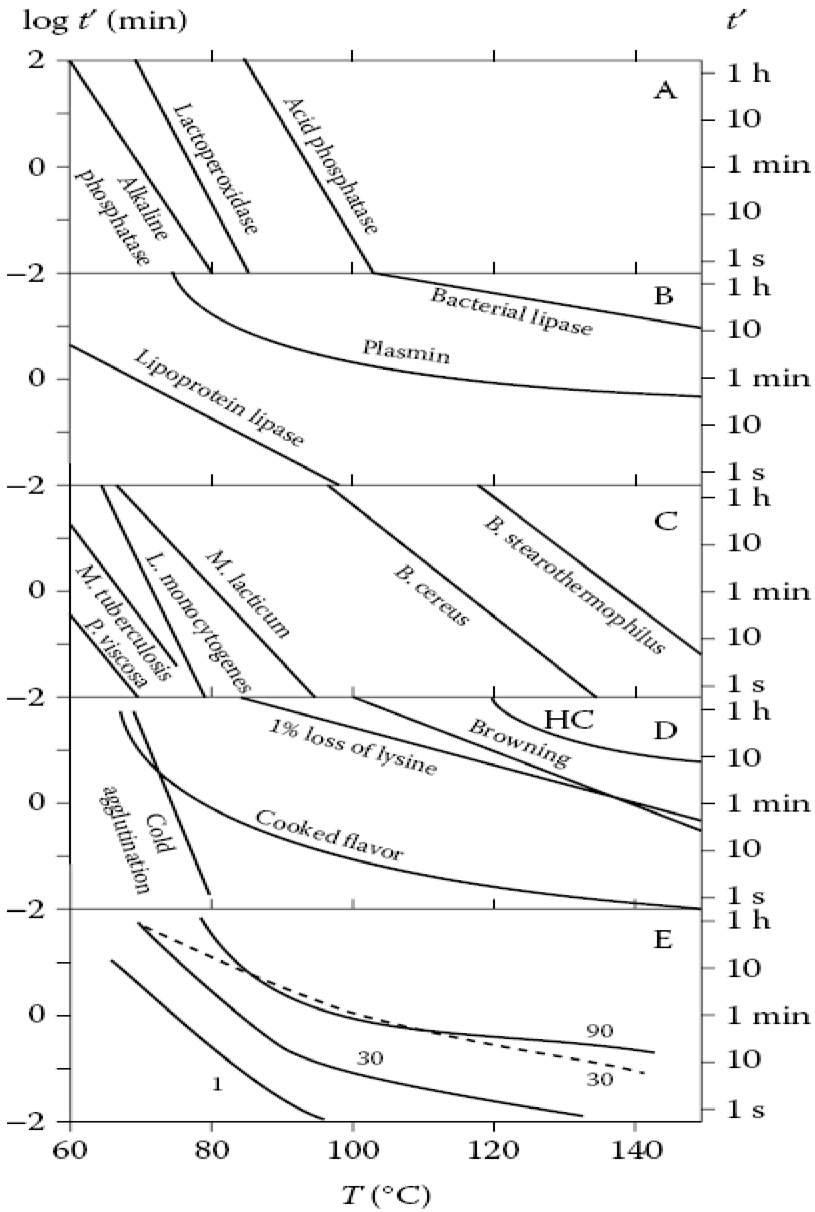


FIGURE 7.9 Combinations of temperature (*T) and time (t') of heat treatment of milk that* cause (A, B) inactivation (reduction of activity to about 1%) of some milk enzymes and a bacterial lipase; (C) the killing (reduction of the count to 10−6) of strains of the bacteria *Pseudomonas viscosa, Mycobacterium tuberculosis, Listeria monocytogenes, and Microbacterium lacticum, and of spores (10−4) of Bacillus cereus and B. stearothermophilus;* (D) visible heat coagulation (HC), a certain degree of browning, decrease in available lysine by 1%, a distinct cooked flavor and inactivation of cold agglutination; (E) insolubilization of 1%, 30%, and 90% of the β-lactoglobulin, and of 30% of the α-lactalbumin (----). Approximate results.

Kinetic aspects of milk heat treatment

$$-\mathrm{d}c/\mathrm{d}t = Kc$$

$$\ln (c_0/c) = Kt$$

$$c = c_0\, e^{-Kt}$$

$$t' = \ln (c_0/c')/K$$

$$D = (\ln\ 10)/K \approx 2.3/K$$

$$\mathrm{d}c/\mathrm{d}t = K$$

$$c = Kt + c_0$$

$$K(T) = K_0 \exp\left(-E_a/RT\right)$$

$$Q_{10} \equiv K(T + 10)/K(T)$$

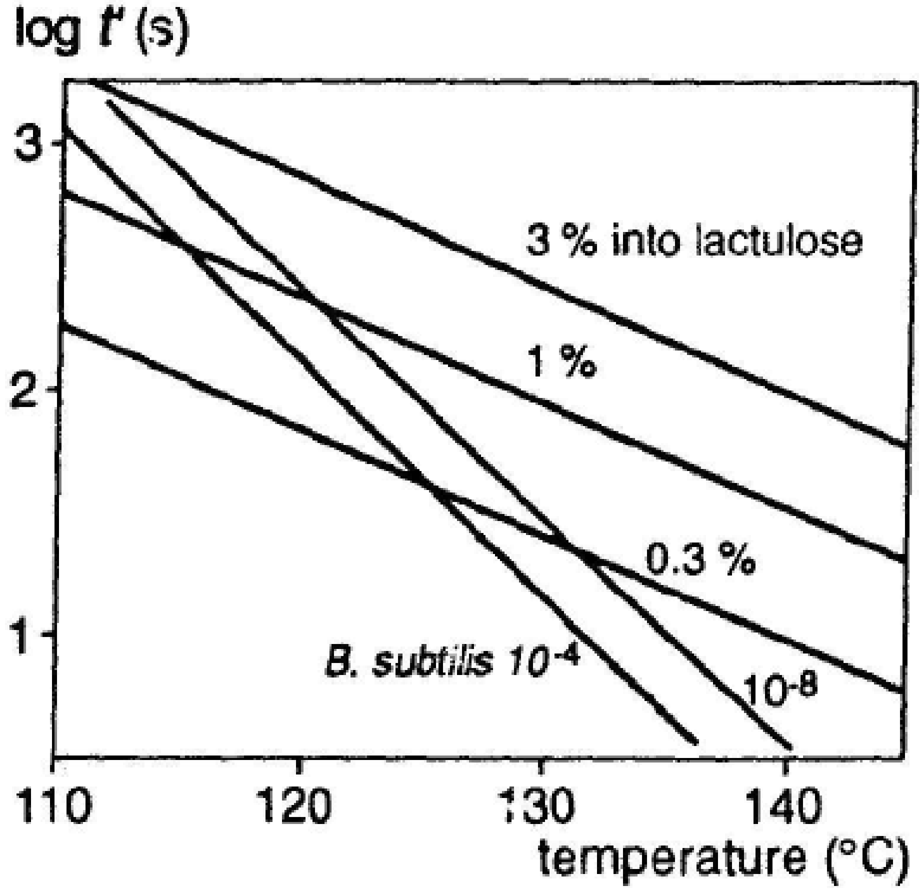


FIGURE 6.10 The time needed (t') at various temperatures to convert certain percentages of lactose to lactulose, and to obtain a certain extent of killing of *Bacillus subtilis* spores.

TABLE 6.3 Typical Examples of the Temperature Dependence of Some Reactions

Type of reaction	Activation energy* ($kJ \cdot mol^{-1}$)	Q_{10} at 100°C
Many chemical reactions	80–125	2–3
Many enzyme-catalyzed reactions	40–60	1.4–1.7
Autoxidation of lipids	40–100	1.4–2.4
Maillard reactions	100–180	2.4–5
Heat denaturation of proteins	200–600	6–175
Enzyme inactivation, e.g.,	450	50
Killing of vegetative bacteria	200–600	6–175
Killing of spores	250–330	9–17

* Often an apparent or average activation energy because it mostly concerns a number of different ensuing reactions.

Table 6.4 Killing of Some Bacteria Due to Heating

	Heating medium	Temp. (°C)	*D* (min)	Z (K)
Psychrotrophs				
Pseudomonas fragi	Milk	49	7–9	10–12
Pseudomonas fragi	Skim milk	49	8–10	10–12
Pseudomonas fragi	Whey, pH 6.6	49	32	
Pseudomonas fragi	Whey, pH 4.6	49	4–6	10.9
Pseudomonas viscosa	Milk	49	1.5–2.5	4.9–7.9
Pseudomonas viscosa	Whey, pH 6,6	49	3.9	
Pseudomonas viscosa	Whey, pH 4.6	49	0.5	
Pseudomonas fluorescens	Buffer	60	3.2	7.5
Microbacterium thermosphactum	Skim milk	50	2.5	
Listeria monocytogenes	Milk	65	0.1	6.6
Listeria monocytogenes	Skim milk	72	0.07	6.5
Yersinia enterocolitica	Milk	62.8	0.01–0.3	
Other non-spore-forming bacteria				
Salmonella (6 spp.)	Milk	62.8	1.5–4.5	4.0–5.2
Salmonella (2 spp.)	Milk chocolate	62.8	1100–1950	18–19
Staphylococcus aureus	Milk	62.8	7–30	5.0–5.2
Campylobacter jejuni	Milk	50	3.5–5.5	6–8
Escherichia coli	Skim milk	62.8	0.13	4.6
Escherichia coli	Whey, pH 4.6	62.8	0.26	6.7
Streptococcus sp., group D	Skim milk	62.8	2.6	
Streptococcus faecalis	Skim milk	62.8	3.5	
Streptococcus faecium	Skim milk	62.8	10.3	
Streptococcus durans	Skim milk	62.8	7.5	
Streptococcus bovis	Skim milk	62.8	2.6	

Lactococcus lactis ssp. *lactis*	Whey, pH 4.6	62.8	0.32	7.3
Lactococcus lactis ssp. *cremoris*	Whey, pH 4.6	62.8	0.036	6.7
Lactobacillus spp.	Milk	65	0.5–2.0	
Microbacterium flavum	Skim milk	65	2.0	
Microbacterium lacticum	Skim milk	70	4.0	
Spore-forming bacteria				
Bacillus cereus, spores	Milk	121	0.04	9.4–9.7
Bacillus cereus, vegetative	Water or 2 M sucrose	70	0.013–0.016	
Bacillus cereus, germinating spore	Water	70	0.35	
Bacillus cereus, germinating spore	2 M sucrose	70	39	
Bacillus licheniformis	Skim milk, pH 6.7	111	0.48	8
Bacillus licheniformis	Skim milk, pH 6.3	111	0.35	8
Bacillus subtilis, spore	Milk	121	0.03–0.5	10.7
Bacillus subtilis, vegetative	Water	55	1.0–5.6	
Bacillus subtilis, vegetative	2 M sucrose	55	0.8–62	
Bacillus coagulans, spore	Milk	121	0.6–4	
Bacillus pumilus, spore	Milk	95	1.4	9.7
Bacillus stearothermophilus, spore	Milk	121	4–7	8–11
Clostridium sporogenes, spore	Milk, pH 7.0	121	1.7	
Clostridium botulinum, spore	Milk, pH 7.0	121	0.2	
Clostridium botulinum, type A, spore	Phosphate buffer, pH 7.0	110	0.6–0.7	7–12
Clostridium botulinum, type B, spore	Phosphate buffer, pH 7.0	110	0.4–1.1	7–8
Other microorganisms				
Aspergillus sp., conidia	Buffer, pH 4.5 [illegible]	55	2	3.5–4
Aspergillus sp., ascospores	Buffer, pH 4.5	75	2	6–8
Saccharomyces cerevisiae, vegetative	Buffer	60	1	5.0
		60	10	5.0