STELLINGEN

behorend bij het proefschrift
Modelling and Optimization of Thermal Processes in the Dairy Industry
P. de Jong

1. Het eiwit β-lactoglobuline in gedenatureerde en nog niet geaggregeerde toestand speelt de sleutelrol bij de chemische vervuiling van apparatuur ten behoeve van de warmtebehandeling van melkprodukten.

   dit proefschrift

2. Omdat de genetische varianten van β-lactoglobuline in melk met elkaar kunnen aggregeren, heeft het weinig zin om de denaturatiekinetiek van deze varianten afzonderlijk te bepalen.

   H.G. Beyer, Thesis Technical University Munich (1990)

3. Uit het oogpunt van produktbeschadiging is het injecteren van melk in hogedrukstoom te prefereren boven het injecteren van hogedrukstoom in melk.

   C. Esnouf & E.A. Mansour, *Lait* 70 (1990) 233-254 en dit proefschrift

4. Een belangrijk gemis bij de optimalisatie van produktieprocessen in de voedingsmiddelenindustrie is een goede mathematische beschrijving van de acceptatie door de consument.

5. De communicatie over chemische en biochemische reacties tussen chemisch-technologen en levensmiddelentechnologen zal vergemakkelijkt worden wanneer de laatsten de grote verscheidenheid aan gehanteerde kinetische constanten beperken tot de reactieorde, de activeringsenergie en de pre-exponentiële factor.

6. De wetenschap probeert slechts een vaste grond te vinden der dingen die men ziet.

   Hebr. 11:1

7. Wanneer modellen te ver worden geëxtrapoleerd, verandert wetenschap in een wankel geloof. Dit staat in contrast met de stelligheid waarmee de hypotheses van prehistorici worden verdedigd.

8. Wanneer een tak van industrie in enig land de resultaten van zijn, op basis van de landelijk verwerkte hoeveelheid grondstof gefinancierde, centrale onderzoeksinstelling in toenemende mate gaat gebruiken ten behoeve van buitenlandse vestigingen, verdient het aanbeveling om bij de financiering van de onderzoeksinstelling ook de verwerkte grondstof in de buitenlandse vestigingen in rekening te brengen.

9. Door de regeringsnota "Kennis in Beweging" dreigt de kennis te bewegen van het als voorbeeld gestelde vraaggestuurde onderzoek bij NIZO naar TNO dat nog "de markt op moet" en een lagere kennisintensiteit op zuivelgebied bezit.

N. van Grieken, *Zuivelzicht* 87 (1995) (21) 9

10. In onze westerse maatschappij wil men zelfs de wetenschappelijke onderzoeker doen geloven dat geld gelukkig maakt.

11. De relatie tussen de ontwikkeling van de muziek en de ontwikkeling van de letterkunde is het meest treffend bij *minimal music* welke geïnspireerd lijkt te worden door telefoonboeken.

12. Als de stelling juist is dat het veelvuldig gelijktijdig gebruik van beide handen en voeten de intelligentie verhoogt, heeft dit een belangrijke bijdrage gehad aan de totstandkoming van dit proefschrift.

D. Grunwald, De muziek van de speler. Haarlem, De Toorts (1992)

Delft, 29 januari 1996

Modelling and optimization
of thermal processes
in the dairy industry

MODELLING AND OPTIMIZATION OF THERMAL PROCESSES IN THE DAIRY INDUSTRY

PROEFSCHRIFT

ter verkrijging van de graad van doctor
aan de Technische Universiteit Delft,
op gezag van de Rector Magnificus, Prof. ir. K.F. Wakker,
in het openbaar te verdedigen ten overstaan van een commissie,
door het College van Dekanen aangewezen,
op maandag 29 januari 1996 te 16 uur,

door Pieter DE JONG,

HTS ingenieur chemische technologie,

geboren te Utrecht.

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Soli Deo gloria
I TIM. 1:17

Voor Anja

Aan mijn ouders

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CHAPTER 1

General introduction

Abstract

In the dairy industry, physical, chemical and biochemical phenomena are the basis for the strong relation between the product quality and the process operation and design. This is particularly valid for heat treatment, where a number of heat-induced transformations of milk components determine the functional properties of the final product. Not only the product quality is affected by the heat-induced reactions, also fouling of equipment by deposit formation on walls is governed by specific reactions of milk components. These typical undesired reactions reduce the heat transfer coefficient, increase the pressure drop over heat treatment equipment and increase product losses, resulting in higher operating costs.

With respect to the design and operation of heat treatment equipment in the dairy industry the following objectives were defined by the Netherlands Institute for Dairy Research: (i) development of a methodology for optimization of heat treatment equipment with respect to product quality and fouling of equipment walls; (ii) introduction of the knowledge obtained into the dairy industry by the development of versatile computer programs. It is assumed that the heat treatment equipment can be considered as a cascade of model reactors.

1.1 Introduction

Chemical reactor engineering is not counted as one of the classical disciplines in dairy science. Nevertheless, in the dairy industry, physical, chemical and biochemical phenomena are the basis for the strong relation between the product quality and the process operation and design. This is particularly valid for heat treatment, where a number of heat-induced transformations of milk components determine the functional properties of the final product, e.g., biological safety, shelf-life, flavour, taste and texture. Fresh milk, cheese, milk powder, fermentation products such as yoghurt, etc., all require a different heat treatment, i.e., a specific temperature-time history.

The heat treatment or pasteurization of milk derives its principles from the work of Louis Pasteur (1822-1895). In 1864 he developed a method to prevent abnormal fermentation in wine by destroying the organisms reponsible by heating to 60 °C. Since 1880, milk for babies has been heated to reduce the risk of infection by heating milk in a continuous flow to temperatures of about 60 - 75 °C. A hundred years later the International Dairy Federation gives the following definition of pasteurization: 'Pasteurization is a process applied to a product with the objective of minimizing possible health hazards arising from pathogenic micro-organisms associated with milk by heat treatment which is consistent with minimal chemical, physical and organoleptic changes in the product.' Today the basic heat treatments in the dairy industry can be summarized by five types: *thermization* (e.g., 20 s, 65 °C) for inactivation of psychrotrophic micro-organisms, *low pasteurization* (e.g., 20 s, 72 °C) for inactivation of pathogenic micro-organisms, *high pasteurization* (e.g., 20 s, 85 °C) for inactivation of all micro-organisms but not spores and finally *sterilization* and *UHT (ultra-high-temperature) treatment* (e.g., 30 min, 110 °C; 5 s, 140 °C) to destroy spores. The effect of the heat treatment on the final product quality depends on the combination of temperature and time applied; this determines the equipment selection.

Not only the product quality is affected by the heat-induced reactions, also fouling of equipment by deposit formation on walls is governed by specific reactions of milk components. These typical undesired reactions reduce the heat transfer coefficient, increase the pressure drop over heat treatment equipment and increase product losses, resulting in higher operating costs.

As a result of the complexity of the milk reaction system the design and operation of equipment for thermal treatment of milk have been based mainly on simplifying assumptions and empirical experience. However, now that kinetic data of relevant transformations are becoming available, a reaction engineering approach appears to be applicable to the optimal design and operation of dairy heat treatment equipment [1].

1.2 Design of heat treatment equipment

In the dairy industry two major types of heat treatment equipment can be distinguished according to the heat-exchange system which is applied. These are the so-called *direct* and *indirect* heating systems with respectively steam and hot water as the heating medium. Which type of heating system is selected mainly depends on the desired heating rate; the direct system is used for high heating rate (10 - 100 K/s), the indirect system for lower rates (0.01 - 10 K/s).

With both direct and indirect systems, a part of the heat transfer is achieved in the form of heat recovery, i.e., heat is extracted from the product to cool it from the heating temperature and is transferred to the incoming product. Heat recovery results in considerable energy savings and is therefore an important factor in operation costs [2].

1.2.1 Indirect heating systems

The indirect heating systems can be subdivided according to the shape chosen for the heat transfer surface. The heat exchanger can consist of an assembly of plates, or of a tubular heat exchange system.

Figure 1.1 shows schematically the operation principle of a *plate heat exchanger*. The specific surface texture of the plates increases the degree of turbulence and thus

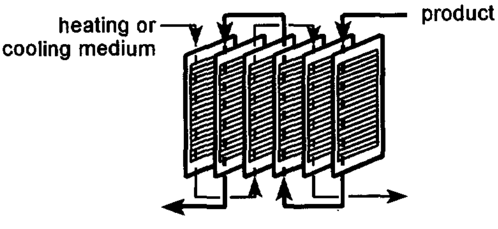


Figure 1.1 Operation principle of a plate heat exchanger

stimulates the heat transfer. The plates are assembled in packs and clamped in a frame, each adjacent pair of plates forming a flow channel with the two media flowing in alternate channels. Different channel grouping can be chosen to give the desired pressure drop characteristics and flow pattern [3].

The tubular heat exchangers used are mainly of two types: *concentric tube exchangers* and *shell-and-tube heat exchangers*. Tubular systems are more robust than plate heat exchangers, but the specific heat exchange area (area per m^3) is smaller than that of plate exchangers, and mainly natural turbulence as a result of a high Reynolds number can be used to improve the heat transfer coefficient.

1.2.2 Direct heating systems

With direct heating systems the heating is performed by mixing the product with steam under pressure. The steam condenses, transferring its latent heat of vaporization to the product and giving a much more rapid heating rate than is available with indirect systems. After the required time at the heating temperature, the product is expanded through a restrictor into an expansion cooling vessel to realize similar rapid rate of cooling.

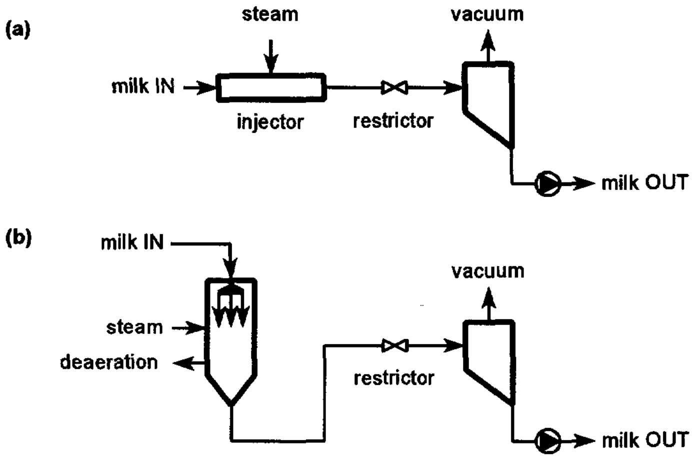


Figure 1.2 Schematic representation of injection (a) and infusion (b) heating systems

There are two types of system, depending on the method used for mixing the product with steam. Figure 1.2 gives a schematic representation of the two systems. In one type (Figure 1.2a), steam, at a pressure higher than that of the product, is injected into the product stream through a suitable nozzle and condenses to give the required temperature. This system is called the *injection* or *steam-into-product* type. Alternatively (Figure 1.2b), a vessel is pressurized with steam. The product is sprayed into the top of the vessel and while it falls, steam condenses on the product. This system is called the *infusion* or *product-into-steam* type.

1.3 Heat-induced reactions in milk

During the heat treatment milk behaves like a complex reaction system; Table 1.1 gives an outline of the components in milk. A large number of chemical, physical and biochemical reactions take place. Some of these transformations are important because they change those characteristics of milk that are easily recognized by a potential consumer. Others may change the nutritional value and increase the biological safety of the milk, or may be of use as an indicator to assess the severity of the process applied.

Table 1.1 Approximate composition of milk [13]

Component	Average percentage (w/w)
Water	87.3
Fat *(triglyderides)*	3.9
Carbohydrates *(lactose)*	4.6
Proteins *(caseins, β-lactoglobulin, α-lactalbumin, bovine serum albumin, immunoglobulins)*	3.3
Minerals *(sodium, potassium, calcium, phosphate, citrate)*	0.7
Miscellaneous *(enzymes, vitamins, trace elements)*	0.14

1.3.1 Bulk reactions

The heat-induced reactions in the bulk of the milk can be subdivided into five groups: destruction of micro-organisms, inactivation of enzymes, denaturation of proteins, loss of nutrients and formation of new components. Most of the reactions can be described by a single irreversible reaction step

$$A \rightarrow B$$

with the rates of disappearance and formation given by a standard reaction rate equation

$$r_A = -kC_A^n, \quad r_B = -r_A \tag{1.1}$$

The way in which the reaction rate constant k is affected by temperature is important in determining the extent of the overall conversion after heat treatment. Although in the dairy industry several relations are used, particularly with the destruction of micro-organisms [2, 4, 5], the most appropriate description of the temperature dependence is given by the Arrhenius relationship [6].

$$k = k_0 \exp(-E_a/RT) \tag{1.2}$$

The kinetic parameters k_0 and E_a are dependent on the reaction involved and the composition of the product. Table 1.2 gives an overview of the available kinetic constants of the heat-induced reaction, partly calculated from experimental data reported in literature.

Destruction of micro-organisms

According to the high activation energies (> 300 kJ/mol) of most of the reactions, the required destruction of micro-organisms is strongly dependent on temperature. A slight increase in temperature causes a relatively much higher reaction rate constant, i.e. destruction rate. Since destruction is assumed to be a first order reaction, the degree of destruction is generally expressed as the number of decimal reductions ($\log N_0/N$) of active micro-organisms, independent of the initial concentration.

Inactivation of enzymes

In general the inactivation of enzymes is a desired reaction because of their negative effect on the flavour and shelf-life of the dairy product. However, some enzymes stimulate the development of flavours. An example is xanthine-oxidase, which has

Table 1.2 Overview of kinetic constants for reactions in milk available in literature

Component	System	Concentration in milk (g/l)	Temperature range (°C)	ln k_0	E_a (kJ/mol)	Reaction order	Ref.
Destruction of micro-organisms							
Bacillus cereus Vc1 spores	milk	-	90-105	56.47	179.4	1	7[a]
Bacillus cereus Vb1 spores	milk	-	95-110	91.92	294.5	1	7[a]
Bacillus coagulans spores	milk	-	116-123	151.29	509	1	8
Bacillus stearothermophilus spores	milk	-	100-140	101.15	345.4	1	9
Clostridium botulinum spores	1.5% fat milk	-	104-113	107.50	351	1	10
Escherichia coli	milk	-	62-82	132.22	378	1	11
	40% fat cream	-	52-80	132.42	375	1	12
Micrococcus luteus	milk	-	60-90	112.71	330	1	9
Inactivation of enzymes							
Catalase	milk	-[b]	60-80	180.72	529	1	13[a]
Chymosin	milk	-	50-70	134.10	372	1	14[a]
Phosphatase	milk	-	60-82	95.17	275	1	15
Lipase	milk	-	60-90	53.70	160	1	13[a]
Lipase *Pseudonomas*	milk	-	150	22.60	91	1	16
Lipase *Pseudonomas fluorescens*	milk	-	150	21.16	83	1	17
Peroxidase	milk	-	70-90	225.26	663	1	13[a]

[a] Calculated from published experimental data.

[b] Enzyme activity in raw milk is defined as 100 %

Table 1.2 Overview of kinetic constants for reactions in milk available in literature *(continued)*

Component	System	Concentration in milk (g/l)	Temperature range (°C)	ln k_0	E_a (kJ/mol)	Reaction order	Ref.
Inactivation of enzymes *(continued)*							
Protease	milk	-[b]	70-150	15.19	64	1	9
Protease *Pseudomonas fluorescens*	milk	-	70-130	24.64	101	1	18
Xanthine-oxidase	milk	-	60-80	127.29	380	1	13
Denaturation of proteins							
Bovin serum albumin	skimmilk	0.4	60-82	23.68	80	1	15
			82-150	13.18	49	1	15,19[a]
Immunoglobulin	milk	0.7	60-76	90.38	275	1	15
			76-82	54.21	170	1	15
α-Lactalbumin	skimmilk	1.2	70-85	84.92	269	1	20
			85-150	16.95	69	1	20
β-Lactoglobulin	skimmilk	3.2	70-90	89.43	280	1.5	20
			90-150	12.66	48	1.5	20
	milk	3.2	75-85	120.64	374	1.8	21
Lysine (amino acid)	milk	2.88	130-160	8.77	109	2	22

[a] Calculated from published experimental data
[b] Enzyme activity in raw milk is defined as 100 %

Table 1.2 Overview of kinetic constants for reactions in milk available in literature *(continued)*

Component	System	Concentration in milk (g/l)	Temperature range (°C)	ln k_0	E_a (kJ/mol)	Reaction order	Ref.
Loss of nutrients							
Thiamin	milk	$4\cdot10^{-4}$	120-150	29.78	100.8	2	22
Formation of new components							
Colour	milk	0^c	50-160	29.09	116	0	22
Furosin	milk	0	120-150	16.01	81.6	0	9
5-Hydroxymethylfurfural (HMF)	milk	0	75-130	30.31	135.1	0	9
			130-160	30.72	139	0	22
Lactulose	milk	0	60-145	30.52	120.2	0	9
Lysinoalanine	milk	0	110-130	18.39	101.4	0	9

[c] 1 = no change in colour (perception threshold), 2 = light ivory, 4 = saffron-yellow, 10 = brown-yellow.

a positive effect on the quality of cheese during ripening [23]. The degree of inactivation is expressed as a percentage of the initial enzyme activity.

Denaturation of proteins

The most reactive proteins in milk are the whey-proteins: serum albumin, immunoglobulin, α-lactalbumin and β-lactoglobulin. Especially the denaturation of β-lactoglobulin is strongly related to many functional properties of dairy products [21]. For example, the texture of yoghurt is improved [24] and the solubility of milk powder is decreased with the denaturation degree of β-lactoglobulin [21]. Although the denaturation is recognized as a complex reaction with many reaction steps [25], it can still be quantitatively described with one overall reaction. This explains the broken orders in Table 1.2.

A special case of protein denaturation is the flocculation of casein micelles as a result of dephosphorization, partial hydrolysis and several cross-linking reactions at high temperatures [13]. Up till now there are no quantitative models available with reasonable accuracy.

Loss of nutrients

The major nutrient which is lost due to heating is thiamin (vitamin B_1). For example, in the case of UHT-milk the loss of thiamin should be less than 3% [5].

Formation of new components

In general the formation of new components is undesired and is governed by the Maillard reaction. The Maillard reaction is a complex series of steps [26] in which reactions occur between lactose and proteins. Various pathways lead to the production of brown pigments which are responsible for the brown colour of heated milk. In some cases, e.g. for coffee-creamers, this colour formation is a desired phenomenon. Hydroxymethylfurfural (HMF) appears in the early stages of the Maillard reaction and it has been suggested as a measure of the severity of the heat treatment to which milk has been subjected [2].

1.3.2 Surface reactions

The transformations of some milk components in the bulk have an additional undesired effect: deposition of milk components on heat treatment equipment walls. The exact mechanism of deposition is presently unknown and there are no mathematical models with sufficient physical background which can be applied for process optimization. However, the correlation between protein denaturation and fouling of heat exchangers has been confirmed by several investigators [27, 28, 29]. It appears that particularly the denaturation of β-lactoglobulin plays an important role in the fouling process of heat exchangers.

1.4 Reaction engineering approach

In general terms the heat treatment of dairy products can be described by a cascade of non-isothermal reactors (see Figure 1.3). They are non-isothermal because of the temperature changes in the product during the process. The quality of the final product depends on the conversion of the so-called key-components; in Figure 1.3 these are indicated by A, B, D and E. For example, the texture of yoghurt is related to the degree of denaturation of the protein β-lactoglobulin and the consumer desires a fresh product without pathogens: objectives that make different demands of the heat treatment.

On the one hand the conversion of key-components like β-lactoglobulin and pathogens is determined by intrinsic factors like kinetic constants which describe the temperature dependence of the reaction rate. Concerning the control of func-

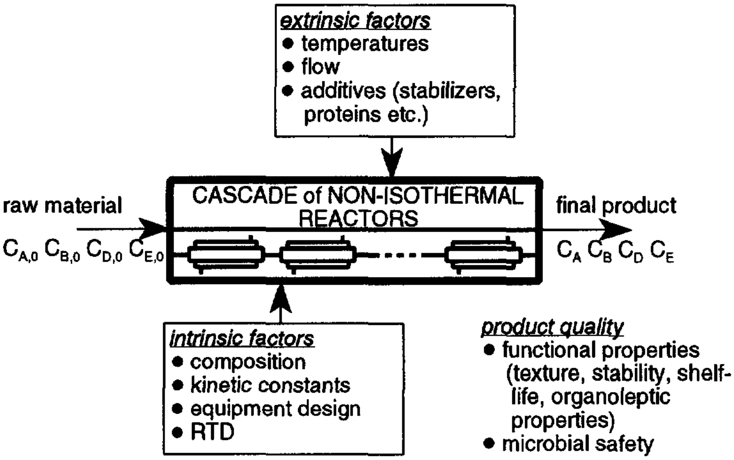


Figure 1.3 General reaction engineering approach to the heat treatment process in the dairy industry

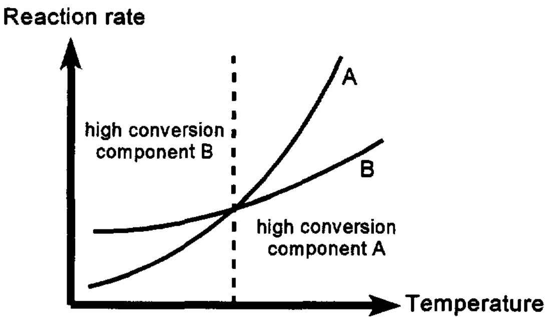


Figure 1.4 Principle of selectivity

tional properties of the final product it is important to minimize the effect of a residence time distribution (RTD) of liquid volume elements on product composition and quality. On the other hand there are the extrinsic factors like temperature, flow and additives (stabilizers, proteins, etc.). Most of these factors are easy to change during the operation time and are therefore used for process control.

In general the reaction rate increases with temperature. Since the temperature dependence differs for each reaction it is possible to find the optimal temperature profile in the equipment with the aid of numerical optimization routines. This means a high conversion of the desired reactions and a low conversion for the undesired ones. For example, when in Figure 1.4 component A represents a pathogenic micro-organism and component B a nutrient, a short heat treatment at high temperature will result in a better final product. The UHT-procedure is based on this principle. By integration of a quantitative fouling model in the optimization procedure it becomes possible to obtain the desired conversion of the key-components and simultaneously to reduce energy, cleaning, depreciation and emission costs.

1.5 Objectives

With respect to the design and operation of reactors in the dairy industry the following objectives are defined: (i) development of a methodology for optimization of heat treatment equipment with respect to product quality and fouling of equipment walls; (ii) introduction of the knowledge obtained into the dairy industry by the development of versatile computer programs. It is assumed that the heat treatment equipment can be considered as a cascade of model reactors.

1.6 Structure of this thesis

In *Chapter 2* a quantitative two-stage reaction model for the denaturation of β-lactoglobulin is described. The kinetic constants are based on experimental work. Results are given from exploratory experiments which were carried out to survey the effect of the denaturation of β-lactoglobulin on the fouling of heat treatment equipment. Referring to these first results, in *Chapter 3* a reaction model is introduced which describes the deposition of milk components on equipment walls. The deposition rate is correlated with the concentration of unfolded β-lactoglobulin, an intermediate component of the denaturation reaction.

Chapter 4 gives a description of HeatCARD: a computer program for simulation of concentration profiles and deposit distributions in heat treatment equipment as a function of the operating time. In *Chapter 5* a mathematical optimization method with respect to operating costs and product quality is introduced. The application of this method is demonstrated by a case-study in which a standard UHT plant is optimized.

In *Chapter 6* the operation of a steam infuser is evaluated with respect to protein denaturation and deposit formation. A mathematical model is given which describes the heat and mass transfer to milk. Finally in *Chapter 7* the significance of the results is discussed and demonstrated by some research projects in the dairy industry.

Notation

Symbols

C	Concentration ($g{\cdot}l^{-1}$, actual unit depends on the unit of the initial concentration)
E_a	Activation energy ($J{\cdot}mol^{-1}$)
k	Reaction rate constant ($l^{(n-1)}{\cdot}g^{(1-n)}{\cdot}s^{-1}$, actual unit depends on the unit of the initial concentration)
k_0	Pre-exponential factor ($l^{(n-1)}{\cdot}g^{(1-n)}{\cdot}s^{-1}$, actual unit depends on the unit of the initial concentration)
n	Reaction order

N	Number of micro-organisms
r	Reaction rate ($g \cdot l^{-1} \cdot s^{-1}$)
R	Gas constant, 8.314 ($J \cdot mol^{-1} \cdot K^{-1}$)
T	Temperature (K)

Subscripts

A, B	Components
0	Initial value

References

1. P. de Jong & H.J.L.J. van der Linden. Design and operation of reactors in the dairy industry. *Chem. Eng. Sci.* 47 (1992) 3761-3768.
2. H. Burton. Ultra-high-temperature processing of milk and milk products. Elsevier Appl. Sci., London (1988).
3. Heat exchanger guide. Alfa-laval, VM 60122 E4 (1987).
4. S.D. Holdsworth. Aseptic processing and packaging of food products. Elsevier Appl. Sci., London (1992).
5. H.G. Kessler. Lebensmittel- und Bioverfahrenstechnik, Molkereitechnologie. Verlag A. Kessler, Freising (1988).
6. B. Hallström, C. Skjöldebrand & C. Trägårdh. Heat transfer and food products. Elsevier Appl. Sci., London (1988).
7. J. Stadhouders, G. Hup & L.P.M. Langeveld. Some observations on the germination, heat resistance and outgrowth of fast-germinating and slow-germinating spores of *Bacillus cereus* in pasteurized milk. *Neth. Milk Dairy J.* 34 (1980) 215-228.
8. J. Hermier, P. Begue & O. Cerf. *J. Dairy Res.* 42 (1975) 437.
9. C. Peri, E. Pagliarini & S. Pierucci. A study of optimizing heat treatment of milk I. Pasteurization. *Milchwissenschaft* 43 (1988) 636-639.
10. C.B. Denny, B. Shafer & K. Ito. Inactivation of bacterial spores in products and on container surfaces. In: Proc. Int. Conf. on UHT processing. Raleigh, North Carolina (1980).
11. D.A. Evans, D.G. Hankinson & W. Litsky. Heat resistance of certain pathogenic bacteria in milk using a commercial plate heat exchanger. *J. Dairy Sci.* 53 (1970) 1659-1665.
12. R.B. Read, C. Schwartz & W. Lisky. Studies on the thermal destruction of *Escherichia coli* in milk and milk products. *Appl. Microbiology* 9 (1961) 415-418.
13. P. Walstra & R. Jennes. Dairy chemistry and physics. J. Wiley, New York (1984).

14. W. Luf. Erhitzungsbedingte chemische Veränderungen in Milch und deren Nachweis. *Milchwirtschaftliche Berichte* 101 (1989) 217-223.
15. P. de Jong & G. van den Berg. Unpublished results. NIZO Ede (1993).
16. D.M. Adams & T.G. Brawley. *J. Dairy Sci.* 64 (1981) 1951.
17. P.F. Fox & L. Stepaniak. *J. Dairy Res.* 50 (1983) 77.
18. F.M. Driessen. Lipases and proteinases in milk. Thesis, Agricultural University Wageningen (1983).
19. R.M. Hillier & R.L.J. Lyster. Whey protein denaturation in heated milk and cheese whey. *J. Dairy Res.* 46 (1979) 95-102.
20. F. Dannenberg & H.G. Kessler. Reaction kinetics and functional aspects of whey proteins in milk. *J. Food Sci.* 53 (1988) 258-263.
21. J.N. de Wit & G. Klarenbeek. Technological and functional aspects of milk proteins. In: Milk proteins in human nutrition, Proc. Int. Symp. Steinkopff, Kiel (1988).
22. H.G. Kessler & R. Fink. Changes in heated and stored milk with interpretation by reaction kinetics. *J. Food Sci.* 51 (1986) 1105-1111.
23. T.E. Galesloot & F. Hassing. Effect of nitrate and chlorate and mixtures of these salts on the growth of coliform bacteria: results of model experiments related to gas defects in cheese. *Neth. Milk Dairy J.* 37 (1983) 1-10.
24. F. Dannenberg & H.G. Kessler. Effect of denaturation of β-lactoglobulin on texture properties of set-style non-fat yoghurt II. Firmness and flow properties. *Milchwissenschaft* 43 (1988a) 700-704.
25. H. Singh. Heat-induced interactions of proteins in milk. In: Protein and fat globule modifications by heat treatment and homogenization, Int. Dairy Federation special issue nr. 9303 (1993).
26. J. Adrian. World review of nutrition and dietetics. Vol. 19. Karger, Basel (1974) p.71.
27. M. Lalande, J.P. Tissier & G. Corrieu. Fouling of heat transfer surfaces related to β-lactoglobulin denaturation during heat processing of milk. *Biotechnol. Progress* 1 (1985) 131-139.
28. F. Dannenberg. Zur Reaktionskinetik der Molkenproteindenaturierung und deren technologischer Bedeutung. Thesis, Technical University Munich (1986).
29. P.J. Fryer. The uses of fouling models in the design of food process plant. *J. Soc. Dairy Technol.* 42 (1989) 23-29.

CHAPTER 2

Two-stage reaction model for the denaturation of β-lactoglobulin in milk

Abstract

A quantitative model is developed which describes the denaturation of β-lactoglobulin (β-lg) as two consecutive reactions: unfolding and aggregation. The kinetic constants are obtained by a reinterpretation of experimental results in the literature. The aggregation is described by a second order reaction with an activation energy of 288.5±5.7 kJ/mol for temperatures below 90 °C and 54.7±0.5 kJ/mol for temperatures up to 150 °C. It turns out that the two-stage model gives a good description of the reported experimental data.

Results of fouling experiments show the importance of quantifying the concentration of unfolded β-lg and support the hypothesis that the local fouling rate in heat treatment equipment is related to the local concentration of unfolded β-lg.

2.1 Introduction

During the processing of milk, milk concentrate and whey, heat treatment changes characteristics such as stability and texture of the product. The major driving force of this phenomenon is the heat-induced denaturation of the whey proteins: bovine serum albumin, immunoglobulins, β-lactoglobulin and α-lactalbumin [1, 2], with β-lactoglobulin (β-lg) as the dominant representative. The importance of the denaturation of β-lg is evident from the numerous relations between its degree of denaturation and specific physical properties of the product found in the literature. Examples of these properties are: the viscosity of milk concentrate [3, 4], the texture of yoghurt [5, 6, 7], the stability of fat globules after homogenization [8, 9] and the formation and stability of foams [10]. The denaturation of β-lg can also induce deposit formation on walls of the heat treatment equipment [11]. This undesired effect causes increased operating costs due to a decreased running time of the heating plants, product losses, etc. Knowledge of the denaturation behaviour of β-lg is a key requirement for setting up operating conditions to minimize undesired effects and to optimize desired effects. A study of the kinetics of the reactions of protein denaturation should allow the development of a quantitative relationship between denaturation behaviour and technological consequences.

In this chapter a quantitative model is developed which describes the denaturation of β-lg as two consecutive reactions. The kinetic constants are obtained by a reinterpretation of experimental results in the literature. To demonstrate the usefulness of this model, the results of some preliminary fouling experiments with heat treatment equipment using skim milk are related to the denaturation model.

2.2 Theory

2.2.1 Denaturation mechanism

Bovine β-lg exists in nature in milk as a dimer of two monomeric subunits non-covalently linked; it is the main constituent (more than 50%) of the whey proteins [2]. Each monomer contains two disulphide bridges and one single thiol group which in the native state is buried in the interior of the molecule. In milk two genetic variants are found. When both genetic variants A and B are present, hybrid dimers can be formed [2].

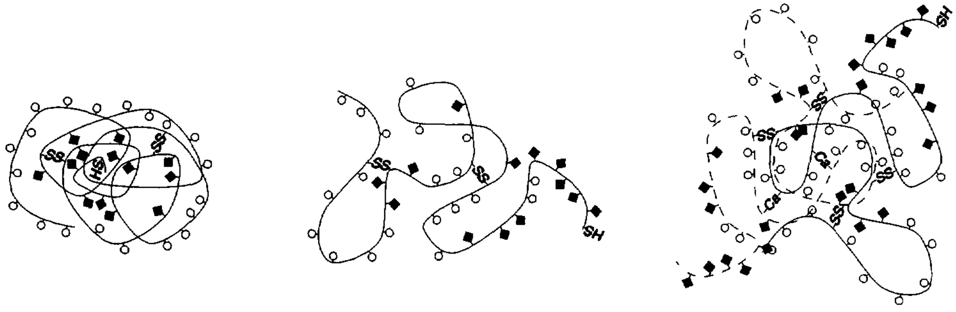


Figure 2.1 Schematic representation of the native, unfolded and aggregated state of β-lactoglobulin [13]; (◆) hydrophobic groups, (o) hydrophilic groups

The heat-induced denaturation of β-lg is generally assumed to be a process consisting of at least two steps: a transformation of the native state into an unfolded state, and a subsequent aggregation of the unfolded molecules [12]. Figure 2.1 gives a schematic representation of the native, unfolded and aggregated state of β-lg. At a temperature of 55 °C β-lg is dissociated into two monomers [14]. A further increase of temperature (>65 °C) results in an unfolding of the molecule: breakdown of hydrogen and hydrophobic bonds and exposure of the thiol group, which is able to react with other proteins, notably β-lg, α-lactalbumin and κ-casein. Although under mild denaturation conditions the unfolding is supposed to be a reversible reaction [12], it is likely that due to isomerization at higher temperatures (>70 °C) the unfolding becomes more or less irreversible [2, 15, 16, 17]. The second reaction step, irreversible aggregation, is a result of intra- and intermolecular disulphide formation, the latter constituting a polymerization. It is also reported that calcium is incorporated into the aggregates of protein [13]. Since due to termination of propagated molecules the number of thiol groups diminishes, the reactivity of β-lg also becomes less.

2.2.2 Two-stage reaction model

A model description in accordance with the denaturation process is given by a two-stage reaction model [18].

$$
\begin{aligned}
&\mathrm{N} \rightarrow \mathrm{U}\\
&n\mathrm{U} \rightarrow \mathrm{A}
\end{aligned}
$$

The rates of disappearance and formation are given by the corresponding reaction rate equations:

$$-r_N = k_U C_N \tag{2.1}$$

$$r_U = k_U C_N - k_A C_U^2 \tag{2.2}$$

$$r_A = k_A C_U^2 \tag{2.3}$$

Since unfolded β-lg not only aggregates with other unfolded β-lg molecules but also with other proteins and salts, the actual reaction order of the aggregation step is unknown. However, for reasons of perception and the unknown exact order, the aggregation is assumed to be a pseudo second order reaction. Typical concentration-time curves, calculated by numerical solution of equations (2.1), (2.2) and (2.3), are shown in Figure 2.2.

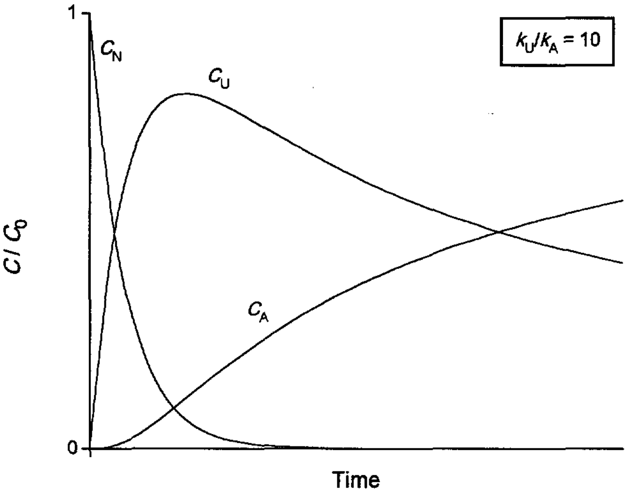


Figure 2.2 Typical concentration-time curves of native, unfolded and aggregated β-lg according to the two-stage model

2.2.3 Quantitative reaction models in the literature

In contrast with Figure 2.1, in the literature [1, 20, 21, 22] the kinetic constants of unfolding and aggregation of β-lg are based on a kinetic model which describes the denaturation by two single reaction steps in parallel

$$\begin{aligned} &\mathrm{N} \rightarrow \mathrm{U} \\ &n\mathrm{N}' \rightarrow \mathrm{A} \end{aligned}$$

where N, U and A are the native, the unfolded and the aggregated β-lg respectively. The use of N′ in the second reaction step is confusing because the authors explain this indication as non-denatured β-lg. However, according to Figure 2.1, N′ consists of native (N) and unfolded, i.e. denatured β-lg (U):

$$n(\mathrm{N} + \mathrm{U}) \rightarrow \mathrm{A}$$

The rate of formation of aggregated β-lg is given by the corresponding reaction rate equation:

$$\frac{\mathrm{d}C_\mathrm{A}}{\mathrm{d}t} = k_\mathrm{A}'(C_\mathrm{N} + C_\mathrm{U})^n \tag{2.4}$$

Disadvantages of this approach are that the model gives no exact description of the consecutive denaturation process and the concentration of unfolded β-lg does not follow directly from the reaction rate equations. Many authors have used different model systems to obtain the kinetic constants of these reactions. However, the applicability of these data for complex biological media such as milk is doubtful. They also use different analytical methods to investigate the amount of unfolded or aggregated β-lg [19].

De Wit [1] found first-order kinetics for the unfolding, with an activation energy of 261 kJ/mol and a ln k_0 of 86.41, using differential scanning calorimetry. Table 2.1 gives an overview of the kinetic constants determined for the denaturation, i.e. aggregation, of β-lg in milk. The kinetic data show a break in the Arrhenius plot at a temperature of about 90 °C. The exact reason for this phenomenon is unclear. Some authors [23] suggest that the break is due to the presence of different rate determining reaction steps.

Table 2.1 Overview of the determined kinetic constants in the literature for the denaturation, i.e., aggregation of β-lg in (skim) milk.

Ref.	Method of analysis	Genetic variant	T (°C)	Reaction order	E_a (kJ/mol)	ln k_0[a]
[20]	Solubility at pH 4.6 and UDIEF[b]	A	70-90	1.5	265.21	84.16
			95-150		54.07	14.41
		B	70-90	1.5	279.96	89.43
			95-150		47.75	12.66
[21]	Ultracentrifuge and FPLC[c]	A	70-90	2.0	276.5	87.31
			90-140		46.1	11.08
		B	70-90	2.0	259.8	81.10
			90-140		46.1	11.63
[22]	Solubility at pH 4.6 and RP-HPLC[d]	A	70-85	1.0	277.70	88.27
			85-90		102.98	29.67
		B	70-85	1.0	343.81	110.74
			85-95		83.54	23.31

[a] Here the *apparent* pre-exponential factor, defined as: $k_0 c_0^{n-1}$.
[b] Ultra-thin-layer isoelectric focusing.
[c] Fast-protein liquid chromatography.
[d] Reverse-phase high-performance liquid chromatography.

2.3 Material and methods

2.3.1 Calculation method of the reaction rate constants

To determine the kinetic constants of the two-stage reaction model, the concentrations of denatured β-lg measured by De Wit [24] and Dannenberg [20], presented in Figure 2.3 and Figure 2.4, were used. They both used skim milk as medium. De Wit standardized the samples at a total β-lg concentration of 4.8 g/l and heated the samples at 77.5, 80.0, 82.5, 85.0 and 87.5 °C. Dannenberg measured only conversions; however, he used normal milk and the total β-lg concentration was estimated at 3.2 g/l. The samples were heated between 70 and 150 °C. To determine the rates of protein aggregation De Wit [1] centrifuged the heated samples for 60 min at 90 000 g and analyzed the supernatant, consisting of non-aggregated material at pH 6.7, by high performance gel permeation chromatography SEC (Size Exclusion). Dannenberg acidified the heated samples to pH 4.6 to precipitate the denatured (i.e. aggregated) whey proteins by ultrathin-layer isoelectric focusing after Radola [25] and analyzed the precipitate by densitometry [20].

The kinetic constants of the aggregation of β-lg were calculated by evaluating the two-stage reaction model under the experimental conditions of De Wit and

Dannenberg. For the unfolding of β-lg the kinetic constants of De Wit were used. The temperature dependent reaction rate constants of the aggregation were obtained by parameter estimation with the SimuSolv® computer program [26], assuming second order kinetics. In this program the fitting is done through the statistical method of Maximum Likelihood [27]. The activation energy and pre-exponential factor were not estimated by linear regression of the Arrhenius plot but directly from the measured concentrations and temperatures, taking into account the standard deviation of the estimated reaction rate constants.

2.3.2 Fouling experiments

Preliminary experiments were carried out with preheated skim milk (10 s at 65 °C) during an operating time of 20 h with a tubular heat exchanger. The tubular heat exchanger consists of 24 pairs of two concentric tubes of 6.35 m, the inner and outer tube having an internal diameter of respectively 35.1 and 60.5 mm. The mass flow rate of the milk and the heating water was respectively 2700 and 8000 kg/h. The milk was heated in two experiments from 69 °C to about 80 °C and 89 °C, respectively. During the experiments the temperature of the milk and the water was measured at seven positions along the tube. At the end of an experiment the heat exchanger was rinsed with water, dismantled and the fouling distribution was investigated.

2.4 Results and discussion

2.4.1 The kinetic constants of the reaction model

The calculated reaction rate constants for the aggregation of β-lg according to the method described in 2.3.1 are given in Table 2.2 and represented graphically in Figure 2.3 and Figure 2.4. It turns out that the experimental data of De Wit and Dannenberg can be explained by the two-stage reaction model. In general the data of De Wit give a better fit of the model. This may be partly due to the longer heating times which decrease the disturbing effect on the investigated concentration of aggregated β-lg of the time necessary for reaching the heating temperature.

To quantify the effect of temperature, in Figure 2.5 the rate constants are plotted against the reciprocal of the absolute temperature according to the Arrhenius equation. It is evident that the relationship is reasonably linear in the given

Table 2.2 Results of the parameter estimation by SimuSolv for the two-stage reaction model: reaction rate constants

T (°C)	i	k_U[a] (l/g·s)	$k_A \cdot 10^3$ (l/g·s)	$s \cdot 10^3$ (l/g·s)	R_d^2
De Wit:					
77.5	10	0.0386	0.405	0.0062	0.9933
80.0	10	0.0728	0.981	0.0196	0.9932
82.5	10	0.136	1.93	0.055	0.9917
85.0	10	0.252	3.92	0.147	0.9923
87.5	10	0.464	5.14	0.995	0.9997
Dannenberg:					
75.0	7	0.0203	0.303	0.0142	0.9934
80.0	7	0.0728	1.74	0.201	0.9745
85.0	7	0.252	6.57	0.533	0.9905
90.0	9	0.845	17.7	1.10	0.9896
100.0	9	8.60	27.9	2.44	0.9733
110.0	9	$\geqslant 10$	40.1	1.92	0.9825
120.0	9	$\geqslant 10$	64.6	2.04	0.9933
130.0	9	$\geqslant 10$	88.9	4.52	0.9884
140.0	7	$\geqslant 10$	133	4.61	0.9981
150.0	4	$\geqslant 10$	217	12.5	0.9986

[a] Calculated according to De Wit [1]

temperature ranges from 90 to 150 °C and 70 to 90 °C. There are two temperature ranges in which the activation energies are markedly different. This manifests itself by differences in the slopes of the straight lines. The break in the line is at a temperature of about 90 °C. Table 2.3 gives the activation energies and the logarithm of the pre-exponential factors obtained by parameter estimation with SimuSolv®. The high values of the coefficient of multiple determination R_d^2 and the low standard deviations demonstrate that the experimental results could be described very well by the Arrhenius equation. Concerning the kinetic constants reported in the literature as shown in Table 2.1, the determined activation energies of the aggregation reaction step are in the same order of magnitude. Also the break in the Arrhenius plot at a temperature of 90 °C agrees with earlier investigations.

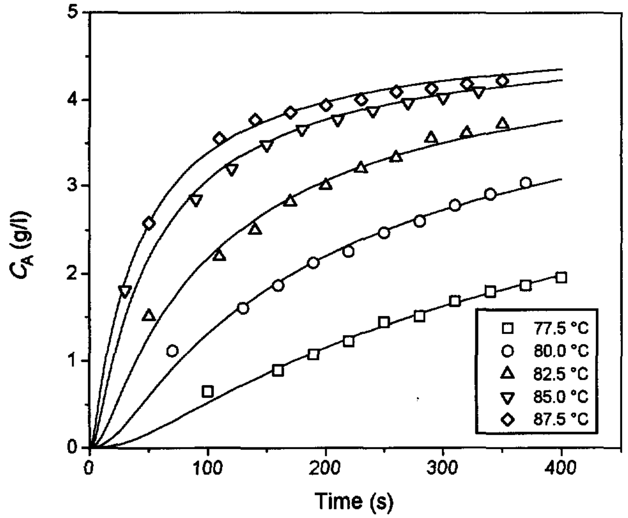


Figure 2.3 Evaluation of the reaction model for the concentration of aggregated β-lg (data of De Wit)

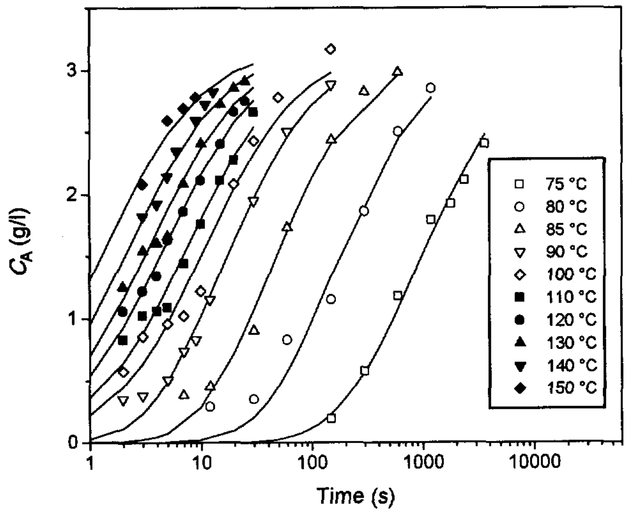


Figure 2.4 Evaluation of the reaction model for the concentration of aggregated β-lg (data of Dannenberg)

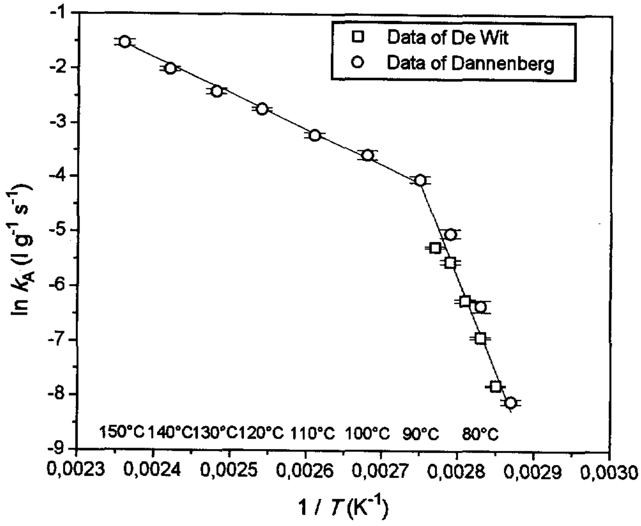


Figure 2.5 Effect of temperature on the reaction rate constant of the aggregation of β-lg

The agreement of the results with Table 2.1 can be explained by comparing the two-stage model and the conventional single-stage model. At the data points in Figure 2.3 and Figure 2.4, above 90 °C the concentration of native β-lg was zero. This means that dependent on the value of the reaction order n, equations (2.4) and (2.3) become almost the same, resulting in a more or less similar temperature dependence of the reaction rate constant for denaturation i.e., aggregation. It should be noted that at the beginning of the denaturation process when the concentration of native β-lg is relatively high and the concentration of aggregated β-lg → 0, the conventional model gives an over-estimate of the aggregation rate (native β-lg is directly transformed into aggregated β-lg) in comparison with the two-stage model. This phenomenon is demonstrated by Figure 2.6, where experimental data of

Table 2.3 Results of the parameter estimation by SimuSolv for the two-stage reaction model: activation energies and pre-exponentional factors

Reaction	n	T (°C)	E_a (kJ/mol)	ln k_0	i	R_d^2
Unfolding [24]	1	70-90	261.4	86.41	8	0.970
Aggregation	2	70-90	288.5±5.7	91.32±1.92	80	0.979
		90-150	54.7±0.5	13.99±0.15	56	0.987

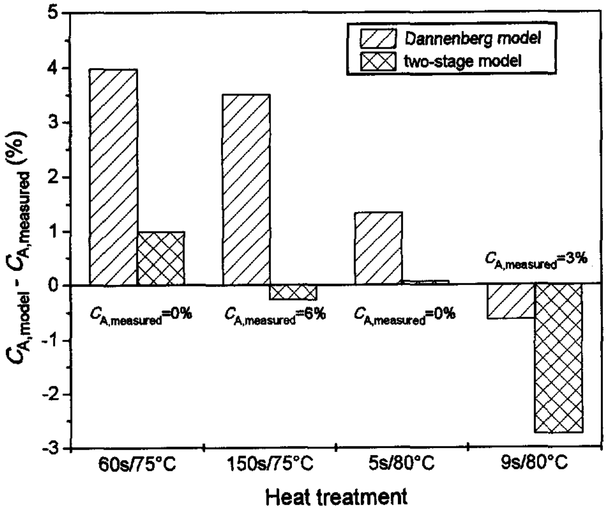


Figure 2.6 Experimental data of Dannenberg [20] at low conversions into aggregated β-lg compared with the model of Dannenberg and the two-stage model

Dannenberg are compared with the model of Dannenberg and the two-stage model according to the kinetic constants from Table 2.1 and Table 2.3, respectively. Although at low conversions (< 10 %) the determination methods of aggregated β-g are not very accurate, in general the conventional model shows a considerable over-estimation. In the case of the Dannenberg model the standard error was 3.9 % and for the two-stage model the standard error was 2.1 %.

2.4.2 The denaturation of β-lactoglobulin and the fouling of heat exchangers

The measured temperature profiles in the tubular heat exchanger are shown in Figure 2.7. As a result of fouling of the heat transfer surface, the local temperatures changed during the experiment. Concerning the local temperature drop in the tubes after 20 h it can be concluded that the fouling rate during experiment 2 was much higher than during the first experiment. Figure 2.8 and Figure 2.9 show the determined fouling distribution and the calculated concentration profile of unfolded β-lg based on the mean bulk temperature profile and the reaction kinetics from Table 2.3 belonging to the two-stage reaction model. It is obvious that the local fouling rate parallels the local bulk concentration of unfolded β-lg. These results support the hypotheses [28] that the unfolded β-lg plays an important role in the fouling process. The higher fouling level of experiment 2 may be due to the higher

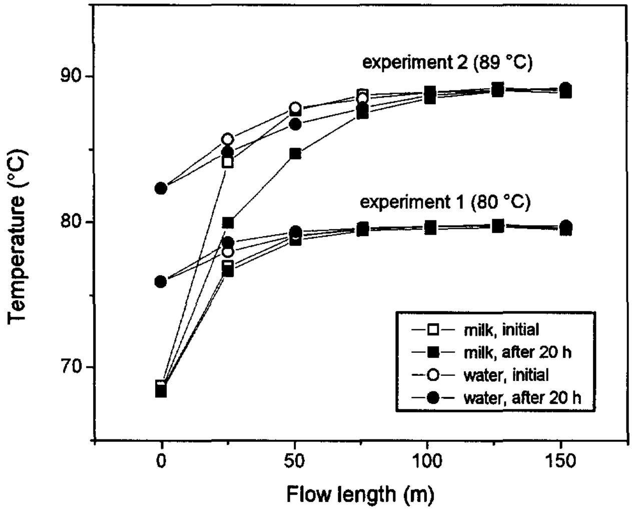


Figure 2.7 Measured temperature profiles in the tubular heat exchanger after 0 and 20 h operating time

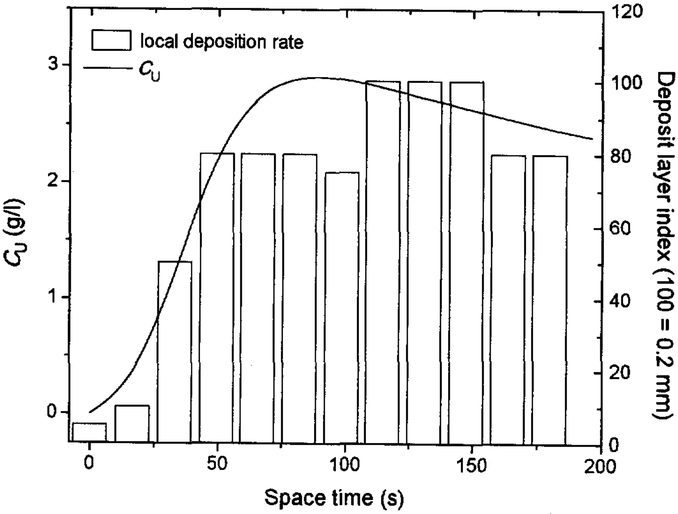


Figure 2.8 Relation between the local concentration of unfolded β-lg (—) and the local thickness of deposit layer (bar); experiment 1 (80 °C)

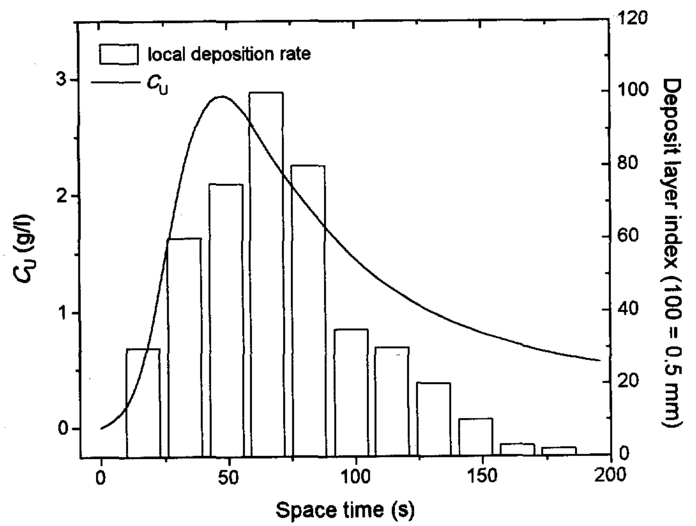


Figure 2.9 Relation between the local concentration of unfolded β-lg (—) and the local thickness of deposit layer (bar); experiment 2 (89 °C)

wall temperature and indicates a surface reaction with unfolded β-lg.

2.5 Conclusions

A reinterpretation of results from denaturation experiments of β-lg makes it possible to obtain the kinetic constants of a two-stage reaction model. This model describes the denaturation of β-lg in milk by unfolding and aggregation reaction steps in series. The two-stage model gives a good description of the reported experimental data. Results of fouling experiments show the importance of quantifying the concentration of unfolded β-lg and support the hypothesis that the local fouling rate in heat treatment equipment is related to the local concentration of unfolded β-lg.

Notation

C_A, C_N, C_U	Concentration of aggregated, native and unfolded components ($g \cdot l^{-1}$)
C_0	Initial concentration ($g \cdot l^{-1}$)
E_a	Activation energy ($J \cdot mol^{-1}$)

g	Acceleration by gravity ($\mathrm{m \cdot s^{-2}}$)
i	Number of experimental data (used for parameter estimation)
k_A, k_U	Reaction rate constant of the aggregation and unfolding reaction step ($\mathrm{l}^{(n-1)} \cdot \mathrm{g}^{(1-n)} \cdot \mathrm{s}^{-1}$)
k'_A	Reaction rate constant of the denaturation i.e., aggregation reaction according to the conventional single-stage model ($\mathrm{l}^{(n-1)} \cdot \mathrm{g}^{(1-n)} \cdot \mathrm{s}^{-1}$)
k_0	Pre-exponential factor ($\mathrm{l}^{(n-1)} \cdot \mathrm{g}^{(1-n)} \cdot \mathrm{s}^{-1}$)
n	Reaction order
R	Gas constant, 8.314 ($\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$)
$\mathrm{R_d}$	Coefficient of multiple determination; correlation coefficient for multiple and non-linear regression
s	Standard deviation
t	Time (s)
T	Temperature (K)

References

1. J.N. de Wit. Thermal stability and functionality of whey proteins. *J. Dairy Sci.* 73 (1990) 3602-3612.
2. P. Walstra & R. Jennes. Dairy chemistry and physics. J. Wiley, New York (1984).
3. T.H.M. Snoeren, A.J. Damman & H.J. Klok. The viscosity of skim milk concentrates. *Neth. Milk Dairy J.* 36 (1982) 305-316.
4. T.H.M. Snoeren, A.J. Damman & H.J. Klok. The viscosity of whole milk concentrate and its effect on the properties of whole milk powder. *Zuivelzicht* 75 (1983) 847-849.
5. A.Y. Tamine & R.K. Robinson. Yoghurt: Science and technology. Pergamon Press (1985) p47-60.
6. F. Dannenberg & H.G. Kessler. Effect of denaturation of β-lactoglobulin on texture properties of set-style non-fat yoghurt. 1. Syneresis. *Milchwissenschaft* 43 (1988) 632-634.
7. F. Dannenberg & H.G. Kessler. Effect of denaturation of β-lactoglobulin on texture properties of set-style non-fat yoghurt. 2. Firmness and flowproperties. *Milchwissenschaft* 43 (1988) 700-704.
8. H. Oortwijn & P. Walstra. The membranes of recombined fat globules. 2. Composition. *Neth. Milk Dairy J.* 33 (1979) 134-154.
9. M. Britten, H.J. Giroux & N. Rodrigue. Emulsifying properties of heat-denatured/undenatured whey protein composite blends. In: Protein and fat

globule modifications by heat treatment and homogenization, Int. Dairy Federation special issue nr. 9303 (1993).

10. J.N. de Wit, E. Hontelez-Backx & M. Adamse. Evaluation of functional properties of whey protein isolates. 3. Functional properties in aqueous solution. *Neth. Milk Dairy J.* 42 (1988) 155-172.
11. H.G. Kessler. Lebensmittel- und Bioverfahrenstechnik, Molkereitechnologie. Verlag A. Kessler, Freising (1988).
12. D.M. Mulvihill & M. Donovan. Whey proteins and their thermal denaturation, a review. *Irish J. Food Sci. Technol.* 11 (1987) 43-75.
13. C.V. Morr. Functionality of heated milk proteins in dairy and related foods. *J. Dairy Sci.* 68 (1985) 2773-2781.
14. C. Georges, S. Guinand & J. Tonnelat. Etude thermodynamique de la dissociation réversible de la β-lactoglobuline B pour des pH supérieurs a 5.5. *Biochim. Biophys. Acta* 59 (1962) 737.
15. V.R. Halwalker. Kinetics of thermal denaturation of β-lactoglobulin at pH 2.5. *J. Dairy Sci.* 63 (1980) 1052-1057.
16. T. Arnebrant. Proteins at the metal/water interface, adsorption in relation to interfacial structure. Thesis, University Lund (1987).
17. S.M. Gotham, P.J. Fryer & A.M. Pritchard. β-Lactoglobulin denaturation and aggregation reactions and fouling deposit formation: a DSC study. *Int. J. Food Sci. Technol.* 27 (1992) 313-327.
18. P. de Jong, S. Bouman & H.J.L.J. van der Linden. Fouling of heat treatment equipment in relation to the denaturation of β-lactoglobulin. *J. Soc. Dairy Technol.* 45 (1992) 3-8.
19. H.G. Beyer. Zum Einfluss der Proteinkonzentration auf das Denaturierungsverhalten der Molkenproteine sowie die damit verbundenen rheologischen Veränderungen. Thesis, Technical University Munich (1990).
20. F. Dannenberg. Zur Reaktionskinetik der Molkendenaturierung und deren technologischer Bedeutung. Thesis, Technical University Munich (1986).
21. B. Manij & Y. Kakuda. Thermal denaturation of whey proteins in skim milk. *Can. Food Sci. Technol. J.* 19 (1986) 163-166.
22. W. Luf. Zur Kinetik der Thermodenaturierung von α-lactalbumin un β-lactoglobulin A und B in Magermilch im Temperaturbereich zwischen 70°C und 95°C. Anwendung der Hochleistungs-Flüssigkeits-Chromatographie. *Österr. Milchwissenschaft* 43 (1988) 7-12.
23. F. Dannenberg & H.G. Kessler. Reaction kinetics of the denaturation of whey proteins in milk. *J. Food Sci.* 53 (1988) 258-263.
24. J.N. de Wit. Unpublished results, available at NIZO and shown in Figure 2.3 and Figure 2.4. (1990).

25. B.J. Radola. Ultrathin-layer isoelectric focusing in 50-100 μmpolyacrylamide gels on silanized glass plates or polyester films. *Electrophoresis* 1 (1980) 43-56.
26. SimuSolv®, modeling and simulation software. European representative: Rapid Data Ltd. West Sussex BN11 5RW, UK (1989).
27. Y. Bard. Nonlinear parameter estimation. Academic Press, New York (1974).
28. T. Nylander. Proteins at the metal/water interface, adsorption and solution behaviour. Thesis, University Lund (1987).

Chapter 3

Reaction model for fouling of heat treatment equipment

Abstract

The relationship between the denaturation of β-lactoglobulin (β-lg) and the deposition of milk constituents in a heat exchanger was investigated. Experiments were carried out on a plate heat exchanger with skim milk by applying different temperature-time combinations in the temperature range from 45 to 122 °C.

Based on the results of the experiments, a fouling model for heat exchangers related to the denaturation kinetics of the key component β-lg has been developed for surface temperatures of equipment walls up to 115 °C. The main mechanism is controlled by the adsorption rate of unfolded β-lg at an external heat transfer surface. This model gives good agreement with the experimental data. By application of an interstage holding section in the heating zone, the amount of deposits in the regenerative section can be reduced substantially, by over 50 %.

It was shown that the fouling model for skim milk can also be used for predicting the deposit distribution in heat treatment equipment due to fouling by whole milk, which supports the chemical and physical basis of the model. In addition it was found that the absolute fouling level is not only related to heat-induced protein transformations but also strongly influenced by the age of milk.

3.1 Introduction

Deposit formation on the heating surface of heat-treatment equipment for milk is an undesired reaction resulting in a reduced heat transfer coefficient and an increased pressure drop. There are two distinct types of deposit [1]. The first type is a relatively soft, voluminous material which is formed at temperatures between 75 °C and 115°C. Due to the high protein content (50-70%) this is called protein fouling. A second type of deposit forms at higher temperatures and is hard and of a granular structure with increasing mineral content. This type is called mineral fouling. Because of the voluminosity of the first type of deposit, it is protein fouling that restricts the area of flow passages and the heat transfer in the heat exchanger and therefore may reduce the operating time.

The exact mechanism of protein fouling is presently unknown. It turns out that the absolute fouling level is not only related to process design and conditions but also affected by age of milk [2] and seasonal influences [3]. However, the correlation between protein denaturation and fouling of heat exchangers has been confirmed by many investigators [4, 5, 6]. Results obtained by Tissier et al. [7] showed that β-lactoglobulin (β-lg) plays a dominant role in the fouling process of heat exchangers; it appeared that the denaturation of β-lg and the formation of deposits evolved simultaneously in the flow passage through the heat exchanger. Even for whipping cream the correlation between the denaturation of whey proteins and the fouling rate has been demonstrated [8]. Some investigators assumed an interaction between casein and β-lg, resulting in the deposition of casein micelles and β-lg together on the stainless steel wall [2].

In this chapter a reaction model for fouling of heat treatment equipment is developed in which denaturation of β-lg and deposition are described as consecutive reactions. It is assumed that the participation of casein micelles in the fouling process plays a passive role. The reaction order and the kinetic data of the adsorption reaction are determined from fouling experiments with skim milk. To evaluate the suitability of the model, results of fouling experiments with whole milk are discussed as well.

3.2 Model development

3.2.1 Theory

According to the conclusions of Chapter 2, where the concentration of unfolded β-lg appears to be an important factor in the fouling process, the following schematic fouling mechanism is proposed:

$$N \rightarrow U$$

$$nU \rightarrow A$$

$$U \xrightarrow{+M} F \rightarrow F*$$

where N, U, A, M, F and F* are the native β-lg, the unfolded β-lg, the aggregated β-lg, milk constituents, aggregates of milk constituents and deposited milk constituents, respectively. The local fouling process is considered as a heterogeneous adsorption reaction of milk constituents at the surface with mass transfer and reaction in series: transport in the boundary layer and the reaction process at the interface [9]. Since only the amount of adsorbed milk constituents (F*) and the bulk concentration of unfolded β-lg (U) can be measured properly, it is assumed that the amount of aggregated and adsorbed milk constituents is proportional to the local concentration of unfolded β-lg and is defined by a constant ratio r_U:

$$r_U = \frac{C_U}{C_F} = \frac{C_{U*}}{C_{F*}} \qquad (3.1)$$

where C_{U*} is the concentration of deposited β-lg. For protein fouling, r_U is about 0.3 [4].

The fouling process can be described by the concentration profile shown in Figure 3.1. Aggregates of milk constituents are transported to the interface by diffusion and next adsorb at the surface of the deposit layer. The actual model to describe the fouling rate is given by the following equations:

Mass transfer equation:

$$J_F = \frac{D_F}{\delta}\left[\frac{\overline{C_U}}{r_U} - \frac{C_{Ui}}{r_U}\right] \qquad (3.2)$$

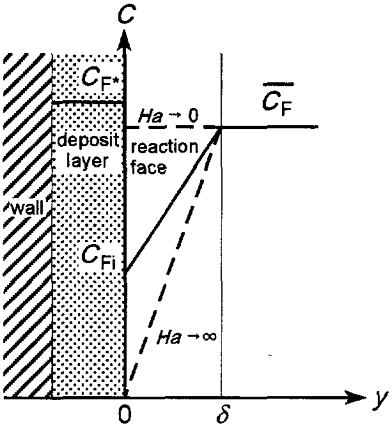


Figure 3.1 Proposed concentration profile for deposit formation

where r_U is the fraction of β-lg in the deposit and C_{Ui} the local concentration of U at the interface.

Reaction rate equation:

$$R_F^{//} = k^{//} C_{Ui}^n \tag{3.3}$$

where

$$k^{//} = k_0^{//} \exp(-E_a/RT_{\text{surface}}) \tag{3.4}$$

Since it is assumed that the local heat flux to the milk is constant, the surface temperature of the deposit layer is equal to the initial temperature of the heat transfer surface [6].

Mass balance:

$$J_F = R_F^{//} \tag{3.5}$$

Elimination of the unknown concentration of U at the interface with equations (3.2), (3.3) and (3.5) results in:

$$J_F = \frac{D_F}{r_U\delta}\left[\overline{C_U} - \left[\frac{J_F}{k^{//}}\right]^{\frac{1}{n}}\right] \tag{3.6}$$

The equation for J_F can be simplified by use of its asymptotic solutions. When the mass transfer rate is slow compared to the reaction rate, the fouling is controlled by mass transfer and so equation (3.2) with $C_{Ui} = 0$ can be used. In the case of a relatively slow reaction rate, J_F is described by equation (3.3). Whether fouling is controlled by chemical reaction or mass transfer follows from the Hatta number. The square of the Hatta number is defined as the ratio of the maximum reaction rate of the adsorption and the maximum diffusional transport:

$$Ha^2 = \frac{k^{//}\,\overline{C_U}^{n}}{\dfrac{D_F}{r_U\delta}\overline{C_U}} \tag{3.7}$$

When $Ha < 0.3$, the kinetic reaction rate completely limits the adsorption rate and when $Ha > 2$, the rate of mass transfer limits the adsorption rate [9].

The diffusion coefficient of the adsorbed milk constituents and the film thickness δ is unknown and should be estimated. When the diameter of the particles is known, the diffusion coefficient could be estimated by the Wilke-Chang relation [10]:

$$D_F = 1.3 \cdot 10^{-17}\frac{T_L}{\eta_L V_F^{0.6}} \tag{3.8}$$

and with V_F as molar volume of the adsorbed particles:

$$V_F = N_{Av}\frac{1}{6}\pi d_F^3 \tag{3.9}$$

The thickness of the boundary layer δ can be estimated from the Sherwood number:

$$\left.\begin{aligned} Sh &= \frac{k_L d}{D_F} \\ k_L &= \frac{D_F}{\delta} \end{aligned}\right\} \quad \delta = \frac{d}{Sh} \tag{3.10}$$

In the range $2000 < Re < 10^5$ and $Sc > 0.7$ a relation for mass transfer between a wall and a turbulent flow is given by [11]:

$$Sh = 0.027 Re^{0.8} Sc^{0.33} \tag{3.11}$$

The reaction order and the temperature dependence according to the Arrhenius equation of k'' of the deposition rate can be derived by fitting experimental data with equation (3.6).

3.2.2 Material and methods

Experimental set-up

The experiments with preheated skim milk (10 s at 65 °C) were carried out during operating times of 6 h with a plate heat exchanger (Alfa-Laval, type H7-RC). The mass flow rate of the milk was 2300 kg/h ($Re \approx 8000$).

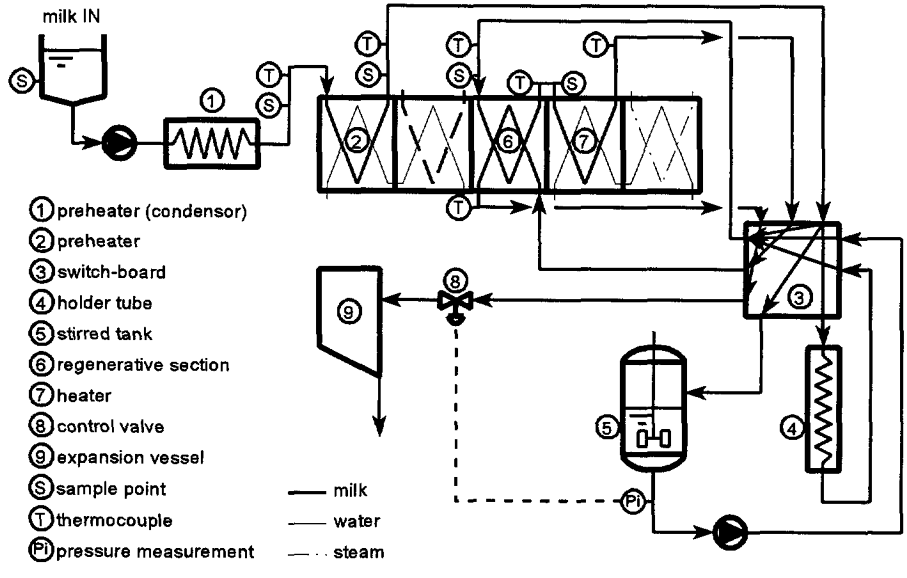


Figure 3.2 Arrangement of the experimental heat exchanger plant

The plate heat exchanger consists of four sections: preheater, holder (optional), regenerative section and heater. The arrangement of the sections of the experimental set-up is given in Figure 3.2. From the storage tank the milk was heated to 45 °C in a preheater (i.e., condenser of a falling-film evaporator plant). In the preheater of the plate heat exchanger the milk was heated to 85 °C. With the switch-board it was possible to select no holder, a stirred tank holder (d_{inner} = 0.39 m, height = 0.83 m) or a tube holder (d_{inner} = 0.035 m, length = 75.0 m). The liquid level in the tank was controlled by the flow out. After holding at 85 °C the milk was heated in the regenerative section and the heater to 117 and 122 °C, respectively. Table 3.1 gives the dimensions and the residence time of each section of the plate heat exchanger. Before the milk entered the first stage of the evaporator it was cooled down in the regenerative section and the expansion vessel, respectively.

Table 3.1 Dimensions of the plate heat exchanger and the residence time of each section at a flow of 2300 kg/h (plate distance = 5 mm)

Section	Number of plates	Heat transfer surface (m^2)	Plate configuration	Residence time (s)
Preheater	11	3.6	5 x 1	14.3
Regenerative section	21	7.6	10 x 1	28.2
Heater	11	3.6	5 x 1	13.9

Measurements, analyses and calculation methods

During the experiments the following data were collected:

- The temperature of the milk was measured by thermocouples at six positions (see Figure 3.2) twice an hour. The intermediate temperatures in the bulk and at the plate surface were calculated with a computer program [12] based on algorithms given by René and Lalande [13].
- The aggregation of β-lg was determined at four sample points (see Figure 3.2), twice in each experiment. As a result of sampling, the milk samples were at high temperatures for at least 10 seconds before they could be cooled with ice water. The degree of aggregation was measured by HP-GPC (High Performance Gel Permeation Chromatography) at pH 6.7 as described by De Wit & Klarenbeek [14]. The pH of the samples taken was measured.

At the end of an experiment the heat exchanger was rinsed with water and dismantled. Each plate of the preheater and regenerative section was cleaned with 16 litres of a 1 vol% sodium hydroxide solution. To determine the quantity of organic material on each plate, a sample was taken from the cleaning agent. The amount of deposits at the downstream side of the regenerative section was negligible (< 5% of total).

The fouling rate of organic material was related to the COD (Chemical Oxygen Demand, [15]) of the samples according to the following equation:

$$J_F = \frac{V_{NaOH}}{A_{plate} \cdot t_r} C_{F*} \tag{3.12}$$

with

$$C_{F*} = \frac{C_{O_2,COD}}{1.27} \tag{3.13}$$

It was assumed that the induction time (time during which no fouling occurs) was negligible in comparison with the run time [6]. The value of 1.27 gives the measured oxygen demand of 1 concentration unit of protein [16].

Summarizing, the local fouling rate (J_F) followed from the measured amount of deposited milk constituents (C_{F*}). The local concentration of unfolded β-lg ($\overline{C}_U$) was calculated according to the two-stage denaturation model developed in Chapter 2. The outcomes of the denaturation model were tested by measuring the concentration of aggregated β-lg (C_A).

3.2.3 Results and discussion

Denaturation of β-lactoglobulin

The mean temperature-time curves measured at three different holding times corresponding with the different holders are given in Figure 3.3(a-c). The effect of time and temperature of the heat treatment on the rates of denaturation of β-lg is shown in Figure 3.4, which compares the degree of aggregation measured at the sample points after the preheater and holder, and the degree of aggregation calculated according to the kinetic data determined in Chapter 2. The accuracy of the HP-GPC method was not sufficient to measure aggregation levels above 90%. Consequently the aggregation of β-lg for the sample point after the regenerative section could not be determined accurately. The points plotted on the graph are the mean of the values from each experiment. The calculated degrees take into account a sampling time of 10 seconds. The total concentration of β-lg in the milk was 3.8 g/l. The pH of the samples varied between 6.64 and 6.71.

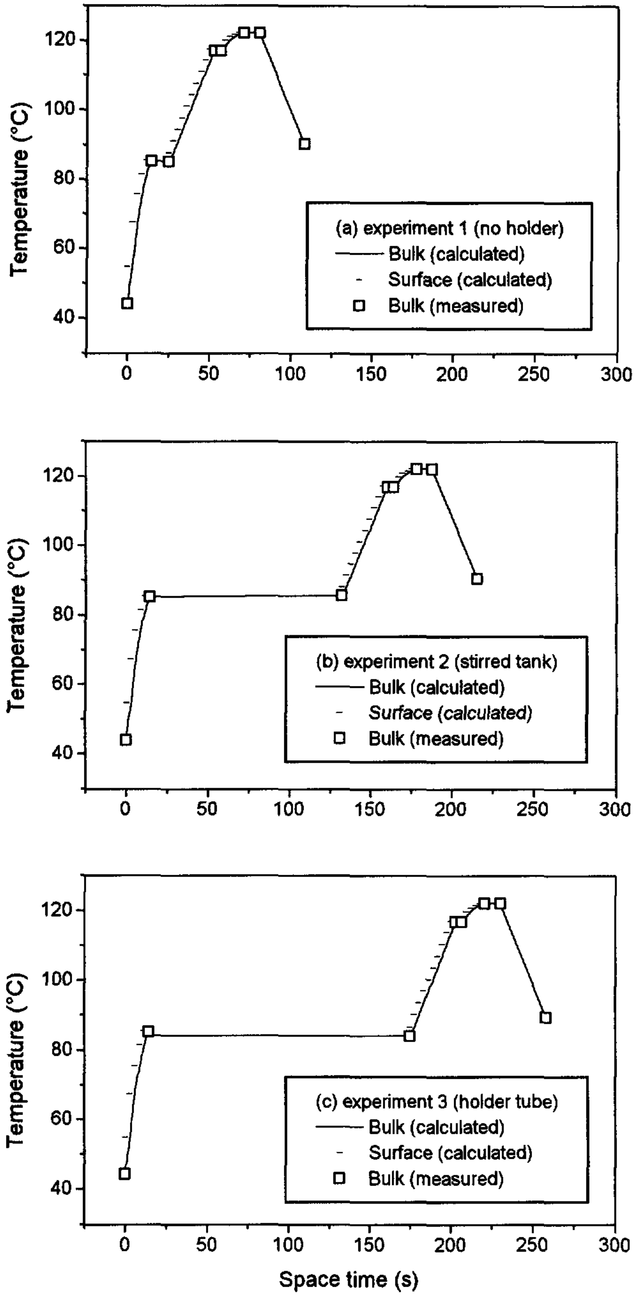


Figure 3.3 Temperature-time curves during the experiments; symbols = mean measured value, — = calculated bulk temperature, -- = calculated mean surface temperature

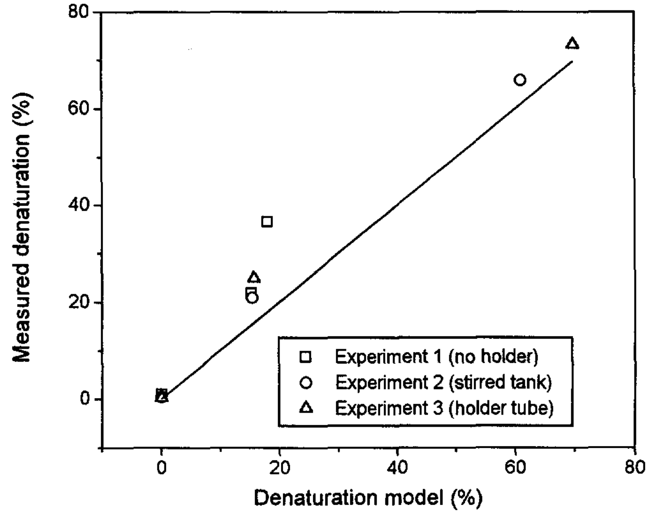


Figure 3.4 Comparison between measured and calculated (according to the denaturation model) degree of aggregation of β-lg, after preheater and holder

In general there is a reasonable agreement between the measured and calculated degree of aggregation. In all cases the calculated values are lower than the measured ones. This might be due to the fact that during cooling of the samples, the product sample is held at temperatures above 70 °C for several seconds, resulting in a continuing denaturation.

Distribution of fouling

Figure 3.5 represents the fouling rate distribution in the preheater and regenerative section after an operating time of 6 hours. The measured values of each experiment show a maximum of the fouling rate at the end of the preheater and of the

Table 3.2 Total amount of deposits in the preheater, holder and regenerative section

Experiment	τ_{holder} (s)	Total amount of organic material (g)		
		Preheater	Holder	Regenerative
1 (no holder)	-	36.4	-	160.6
2 (stirred tank)	91	34.5	2.7	73.9
3 (holder tube)	160	36.8	nd	48.5

nd = not determined

regenerative section (the reverse sides of the plates in the regenerative section were almost clean).

The first maximum can be explained by a higher local concentration of unfolded β-lg. According to equations (3.2) and (3.3) this causes a higher deposition rate of milk constituents. At surface temperatures above 115 °C, at the end of the regenerative section, the fouling process is probably not governed by the denaturation of β-lg only [1]. It is remarkable that in the regenerative section at temperatures below 115 °C the deposition rate stays nearly unchanged while the surface temperature increases substantially. This phenomenon can be explained by the proposed fouling model. Apparently the decreasing concentration of unfolded β-lg and the increasing surface temperature along the flow length results in a more or less constant adsorption rate (see equation (3.3)).

The results of the application of a holder section at 85 °C are shown in Table 3.2. It appears that the mean fouling rate in the regenerative section is reduced by over 50 percent. This can be explained by the denaturation kinetics of β-lg. In the holder reactive, unfolded β-lg is transformed into aggregated β-lg which behaves as a more or less inert component. So the concentration of reactive β-lg downstream from the holder is decreased, resulting in less deposits in the regenerative section.

Fouling model

The experimental data were used to determine the model parameters. In general the fouling model is given by equation (3.6) and the Arrhenius equation of k''. Substitution of the Arrhenius equation in (3.6) gives:

$$\ln J_F = \ln k_0'' - \frac{E_a}{R}\frac{1}{T_{surface}} + n \ln\left[\overline{C_U} - \frac{r_U \delta J_F}{D_F}\right] \tag{3.14}$$

The constants n, k_0'' and E_a were determined by multiple regression analyses from the experimental results. The values of J_F and $T_{surface}$ were obtained from the experimental data (Figure 3.3(a-c) and Figure 3.5). The concentration of unfolded β-lg at any point in the heat exchanger was calculated with the determined kinetic data in Chapter 2. The coefficient of mass transfer D_F/δ was estimated with equations (3.8) to (3.11).

To determine whether the protein fouling is reaction or mass transfer controlled, the experimental data were fitted to equation (3.14) and the mean Hatta

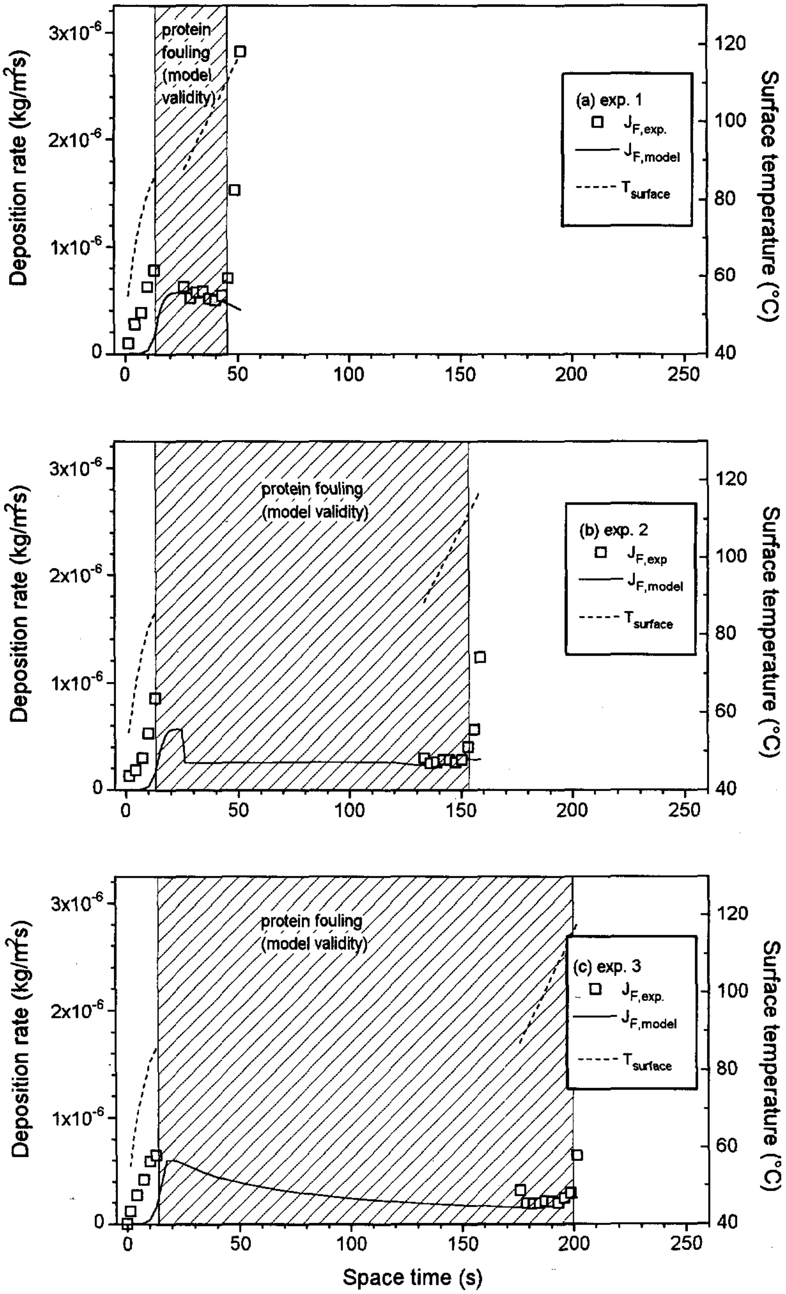


Figure 3.5 Fouling distribution in the preheater and regenerative section after a run time of 6 hours

number was calculated. Since the actual diameter of the adsorbed particles was unknown, the regression analyses were done with several supposed particle diameters of the adsorbing milk components (C_F). The results of these considerations are shown in Figure 3.6. The highest correlation coefficients were obtained with particle diameters smaller than 50 nm and small Hatta numbers (Ha < 0.3). This means that the most accurate model is achieved by the assumption of a reaction-controlled fouling process ($C_{Ui} \approx \overline{C}_U$). In this case the results, including the standard deviations of the regression analysis are:

n = 1.2±0.07
$\ln k_0''$ = -0.82±1.45
E_a = 45.1±4.5 kJ/mol
R_d^2 = 0.944

In Figure 3.5 the continuous lines represent the adsorption rate of milk constituents calculated by the model. The experimental data and the model show good agreement for surface temperatures between 85 and 115 °C.

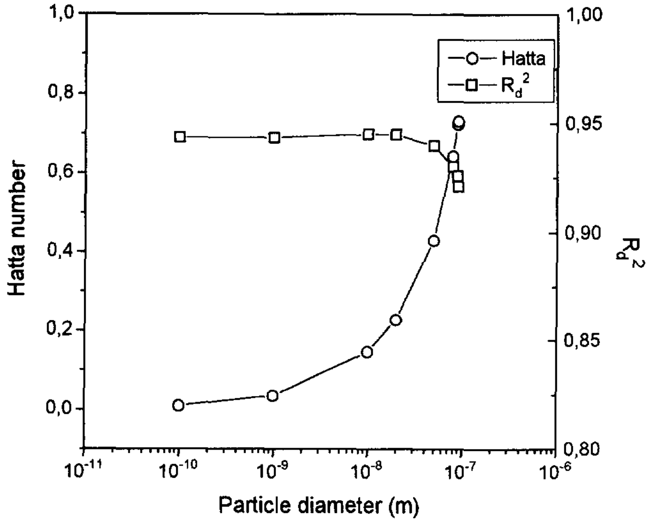


Figure 3.6 Correlation coefficient and Hatta number in relation to the supposed particle diameter

Fouling mechanism

From Figure 3.6 it follows that a mean diameter of the adsorbed milk components above 50 nm does not give good agreement with the experimental results. When casein micelles participate in the fouling process, the mean diameter of the micelles should be smaller than 50 nm. According to the size distribution of the number of casein micelles in milk [17] the mean diameter of the casein micelles is about 30 nm. This means that the participation of casein can be included in the established fouling model. Especially when the higher diffusion coefficients of the smaller casein micelles are taken into account, it is obvious that small casein/whey protein complexes are involved in the fouling process.

The model describes the key role of β-lg in the fouling process. The transport of micelles is not rate determining in fouling kinetics although there is a substantial proportion of these relatively large particles in the deposit [7, 18].

3.3 Model evaluation

3.3.1 Material and methods

Experimental set-up

Two series of experiments with preheated whole milk (10 s at 65 °C, 3.7 % fat) were carried out during operating times of 6 h with the experimental installation, described in paragraph 3.2.2. To avoid errors in the determination of protein denaturation the milk was not homogenized (homogenized whole milk causes a turbid supernatant). The milk used in the first experiment of a series had been stored at 5 °C for 4 days in the case of the first series, and 3 days in the case of the second series. The next experiment of a series was carried out with the same milk, one day later. The second series of experiments (4-6) was carried out 2 months later than the first series (1-3).

Table 3.3 summarizes the process conditions during the experiments. The mass flow rate of the milk was 2300 kg/h. With different holder sections and temperature settings, 6 combinations of temperature and time were realized.

Measurements, analyses and calculation methods

The temperature of the milk, the aggregation of β-lg, the aggregation of α-lactalbumin (α-la) and the fouling of the plate heat exchanger were determined in the same way as during the experiments with skim milk (see paragraph 3.2.2). The fouling rate in the heater was estimated by comparing visually the amount of deposits in the heater with the final plate of the regenerative section.

The samples of the cleaning agent were analyzed by the following determinations: calcium, chemical oxygen demand (COD) [15] and the nitrogen quantity according to Kjeldahl [20]. The concentrations of protein and fat are given by:

$$C_{\mathrm{protein}} = C_{\mathrm{N,Kjeldahl}} \cdot 6.38 \tag{3.15}$$

$$C_{\mathrm{fat}} = \frac{C_{\mathrm{O_2,COD}} - 1.27 \cdot C_{\mathrm{protein}}}{2.96} \tag{3.16}$$

The deposition rate of protein and milk fat (j) follows from:

$$J_{\mathrm{j}} = \frac{V_{\mathrm{NaOH}}}{A_{\mathrm{plate}} \cdot t_{\mathrm{r}}} C_{\mathrm{j}} \tag{3.17}$$

It was assumed that the induction time (time during which no fouling occurs) was negligible in comparison with the run time [6] and that the organic deposits consist mainly of protein and milk fat [21]. The value 6.38 gives the measured ratio

Table 3.3 Process conditions of the whole milk experiments

	Experiment					
	1	2	3	4	5	6
Preheater						
T_{inlet} (°C)	44.8	44.9	41.4	44.4	44.8	44.6
T_{outlet} (°C)	85.2	85.2	85.1	85.1	85.1	85.2
Holder	*tube*	*tube*	-	-	*tank*	*tube*
T_{inlet} (°C)	85.2	85.2	-	-	85.1	85.2
T_{outlet} (°C)	83.8	83.9	-	-	85.1	84.0
Reg. section						
T_{inlet} (°C)	83.8	83.9	84.9	84.9	86.8[a]	84.0
T_{outlet} (°C)	116.7	107.8	124.1	116.5	116.9	116.6
Heater						
T_{inlet} (°C)	116.7	107.8	124.1	116.5	116.9	116.6
T_{outlet} (°C)	122.0	111.7	132.1	121.7	121.9	122.0

[a] Temperature increase due to pump energy.

between the concentration of protein and Kjeldahl nitrogen. The value of 1.27 and 2.96 gives the measured oxygen demand of 1 concentration unit of protein and milk fat, respectively [16].

3.3.2 Results and discussion

Denaturation of β-lactoglobulin and α-lactalbumin

The effect of the combination of temperature and time on the denaturation of β-lg and α-la is shown in Table 3.4. The accuracy of the HP-GPC method was not sufficient to measure aggregation levels above 90%. Consequently the aggregation of β-lg for the sample point after the regenerative section could not be determined accurately.

The literature on the denaturation kinetics of β-lg and α-la has been focused mostly on the kinetics of skim milk rather than on the kinetics in whole milk. De Wit and Klarenbeek [14] established the overall aggregation kinetics for a small temperature range and demonstrated that the kinetic data of β-lg in whole milk

Table 3.4 Measured aggregation degrees of β-lg and α-la

Exp.	Total concentration (g/l)	Degree of aggregation (%)		
		Outlet preheater	Inlet regener.	Outlet regener.
β-lactoglobulin				
1	4.06	12.9	75.9	> 90
2	4.06	14.5	76.0	> 90
3	4.06	15.7	32.4	> 90
4	3.75	26.7	38.9	> 90
5	3.61	19.5	72.6	> 90
6	3.65	19.0	75.9	> 90
α-lactalbumin				
1	1.30	0.4	24.4	43.6
2	1.29	1.1	25.4	44.3
3	1.27	2.3	6.1	37.3
4	1.23	6.2	10.2	33.6
5	1.19	3.6	26.0	38.3
6	1.20	4.0	28.3	41.6

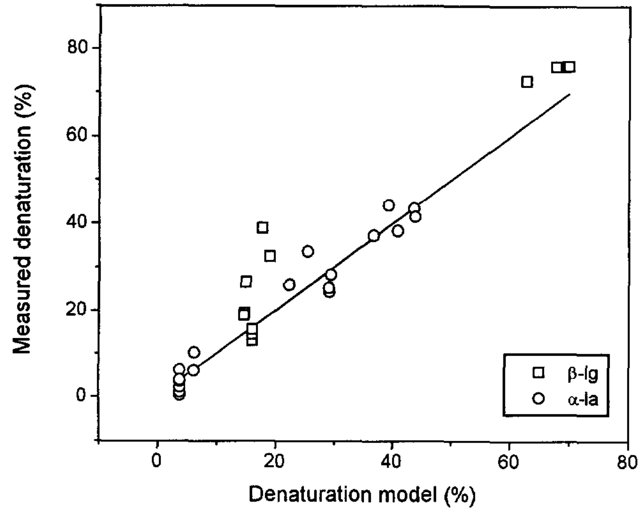


Figure 3.7 Comparison between measured and calculated degree of aggregation of β-lg (two-stage model) and α-la [19], after preheater and holder

differ from those in skim milk (see Chapter 1, Table 1.2). Since the necessary kinetic data of the two-stage model to determine the concentration of unfolded β-lg in whole milk are not available, the specific fouling model parameters for whole milk cannot be established. To evaluate the fouling model for whole milk, in Figure 3.7 the measured aggregation degrees are compared with the calculated values according to the two-stage reaction model for the denaturation of β-lg in skim milk, as described in Chapter 2. The aggregation degrees of α-la are calculated according to the kinetics reported by Dannenberg [19], which are given in Table 3.5. The calculated degrees take into account a sampling time of 10 seconds.

Although the reaction kinetics were obtained for skim milk, there is a fair agreement between the measured and the calculated aggregation degree of β-lg. As in the case of skim milk, in general the calculated values are lower than the

Table 3.5 Kinetic data of the denaturation (i.e., aggregation) of α-la in skim milk [19]

Temperature range (°C)	Reaction order	E_a (kJ/mol)	ln k_0
70-80	1	269	84.92
80-150	1	69	16.95

measured ones. Since the errors with whole milk are in the same order of magnitude as with skim milk, it can be concluded that within the given temperature range the higher fat content of whole milk has no significant effect on the proposed denaturation kinetics of β-lg. The calculations based on the kinetics of α-la in skim milk are in good agreement with the measured values in whole milk.

Composition of the deposit layer

The determined compositions of the deposit layer are summarized in Table 3.6. From each experiment the mean percentage of protein, calcium and fat is spread over 3 temperature ranges. In accordance with the results of Lalande *et al.* [4], the deposits at temperatures between 80 and 110 °C turn out to be largely protein fouling, consisting of more than 50 % protein. This confirms the key role of whey proteins in the fouling process, especially in this temperature range. Both at temperatures lower than 80 °C and higher than 110 °C, the protein content decreases and the calcium content increases, which indicates a growing role of calcium phosphate precipitation [1].

Table 3.6 Composition of the deposit layer

Temperature range (°C)	Component	Experiment					
		1	2	3	4	5	6
60-80	Protein (%)	36.7	42.1	41.3	39.1	34.9	40.0
	$Ca_3(PO_4)_2$ (%)[a]	60.2	53.7	50.9	55.4	60.7	57.5
	Fat (%)	3.0	4.2	7.8	5.5	4.4	2.5
80-110	Protein (%)	52.7	58.4	67.3	50.8	50.7	54.6
	$Ca_3(PO_4)_2$ (%)[a]	37.5	31.8	14.2	41.4	38.9	31.1
	Fat (%)	9.8	9.8	18.6	7.8	10.4	14.3
110-120	Protein (%)	40.1	-	59.0	47.9	48.7	42.0
	$Ca_3(PO_4)_2$ (%)[a]	45.3	-	29.6	43.5	40.2	46.2
	Fat (%)	14.6	-	11.4	8.6	11.1	11.8

[a] Assuming that calcium precipitates as $Ca_3(PO_4)_2$ [2].

Effect of whole milk ageing

As shown in Figure 3.8 the amount of deposits in the preheater, under the same process conditions (see Table 3.3) and milk charge, increased with the age of milk. Based on the experimental points in this figure an ageing factor can be defined. When the milk is older than 3 days, the adsorption rate according to equation (3.14) has to be multiplied by this correction factor giving a first approximation of the

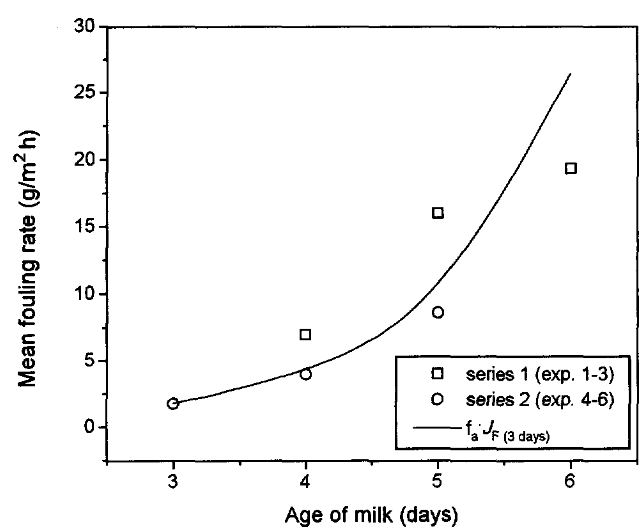


Figure 3.8 Effect of whole milk ageing on the mean deposition rate in the preheater

effect of milk ageing on the fouling level. Regression analysis ($r^2 = 0.938$) resulted in:

$$J_{F(t)} = f_a \cdot J_{F(3\ \text{days})} \tag{3.18}$$

with

$$f_a = \exp\left[0.9 \cdot (t - 3)\right] \quad (3 \leq t \leq 6\ \text{days}) \tag{3.19}$$

The increase of the fouling level after a series of experiments by a factor 3 can probably be explained by the action of proteolytic enzymes in milk which results in a decreasing heat stability of the casein micelles and additional protein deposition [2]. It is obvious that these results confirm the proposition that the absolute fouling level cannot be predicted by a fouling model based on heat-induced transformations of milk components alone.

Model evaluations

Figure 3.9 shows the measured and calculated deposition rates in the preheater and regenerative section for the six experiments. Table 3.7 gives the estimated rates in the heater. To evaluate the fouling model developed for skim milk, the calculated deposition rates are shown by two different curves: one dotted curve based on the kinetic constants for skim milk and another curve for which the kinetic parameter k_0'' has been fitted to eliminate the effect of the varying absolute fouling level.

As with skim milk, the deposition rate in the preheater increases with the flow length. In the heater the deposition rate did not increase further, excluding experiment 3 where the surface temperature was above 125 °C. Up to surface temperatures of 115 °C the profile of the local deposition rate is similar to that of skim milk and can be largely explained by the presented fouling model for skim milk. From equations (3.2) and (3.3) it follows that the deposition rate increases with both the concentration of unfolded β-lg and the surface temperature. In the preheater the temperature rises and native β-lg transforms into unfolded β-lg, resulting in an increase of the deposition rate. In the additional tube holder or stirred tank the concentration of unfolded β-lg is reduced by aggregation (see Chapter 2). In this way the deposition rate in the regenerative section will be reduced. At the beginning of the regenerative section the aggregation rate dominates and consequently, the concentration of unfolded β-lg decreases. The rise in temperature however, results apparently in a nearly constant deposition rate. When the temperature effect becomes predominant, the deposition rate will rise again.

The relatively strong increase of the deposition rate at the end of the regenerative section cannot be explained by the fouling model. The local concentration of unfolded β-lg is too low to cause the determined deposition rate. However, it is remarkable that the protein content of the deposit layer is still substantial (see Table 3.6). Considering the relatively high local concentration of non-aggregated α-la and the known interaction between β-lg and α-la aggregation resulting in additional reactive SH-groups [17, 22], it is reasonable to propose that the deposition rate above 115 °C is also governed by the denaturation of α-la.

The applicability of the fouling model developed for skim milk for predicting deposit distributions caused by whole milk is demonstrated in Figure 3.10. This

Table 3.7 Determined local deposition rates ($\cdot 10^7$ kg/m^{2}s) in the heater

Passage	Experiment					
	1	2	3	4	5	6
first	8.1	5.6	33.9	22.5	9.4	5.6
last	7.2	4.2	40.8	3.3	7.8	4.7

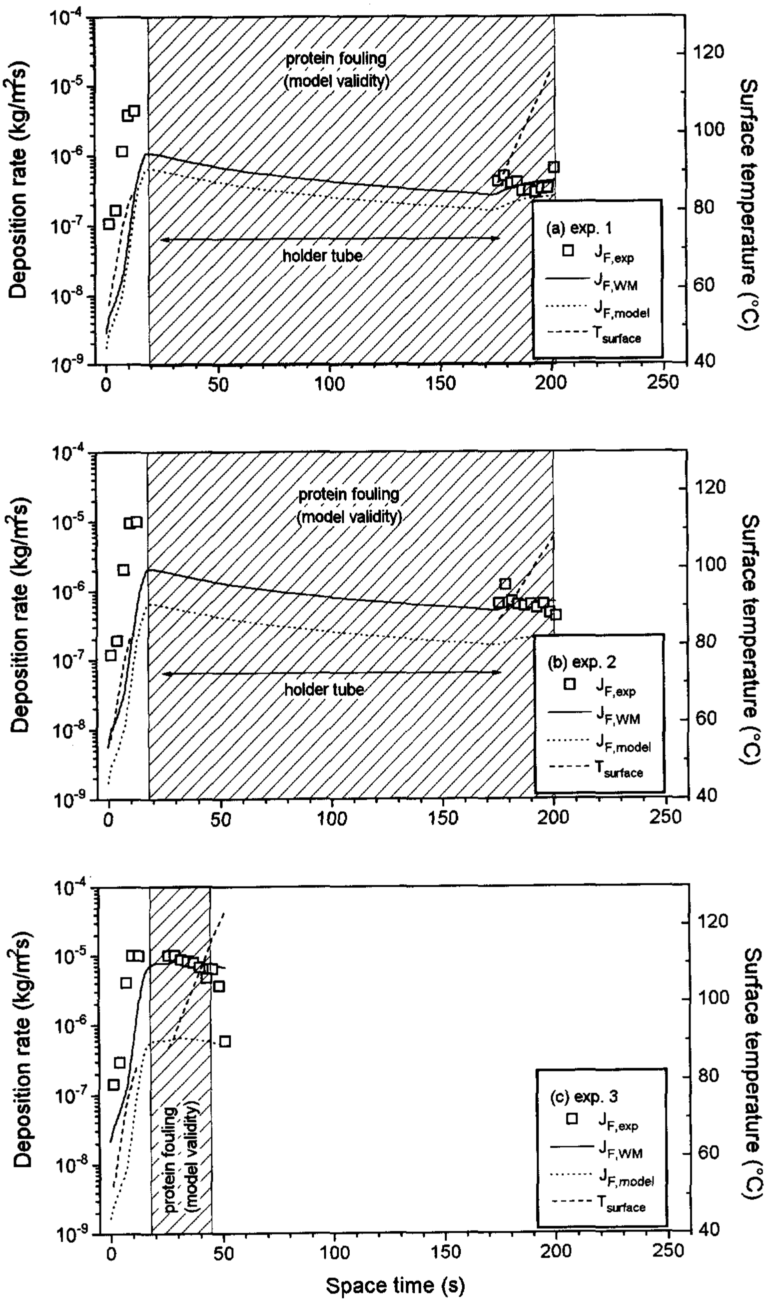


Figure 3.9(a-c) Fouling distribution in the preheater and regenerative section; ln $k_0''_{,WM}$: (a) -0.30±0.11, (b) 0.35±0.12, (c) 1.73±0.11

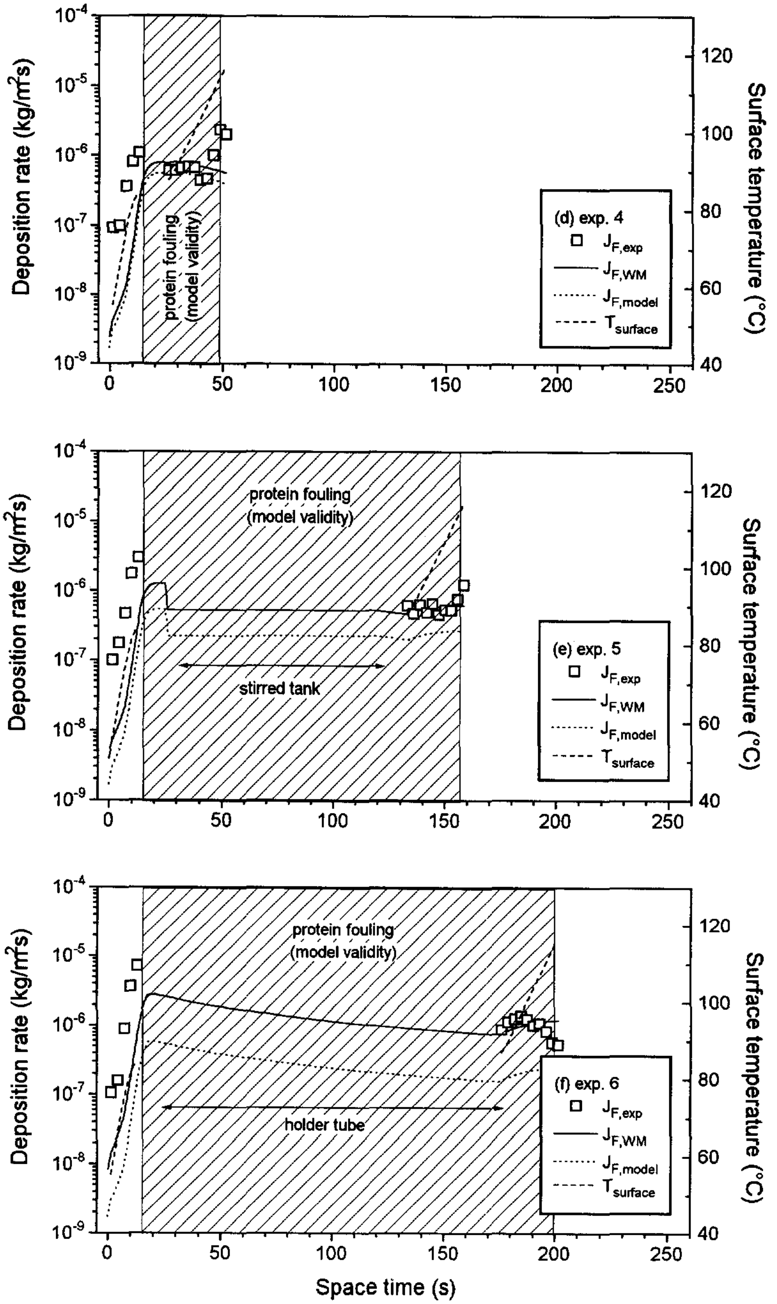


Figure 3.9(d-f) Fouling distribution in the preheater and regenerative section; ln $k_0{}''_{,WM}$: (d) -0.47±0.21, (e) 0.04±0.07, (f) 0.76±0.13

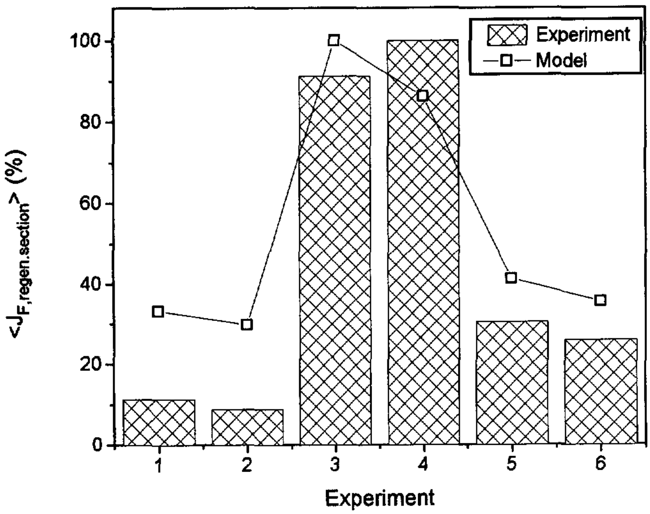


Figure 3.10 The mean fouling rate related to the maximum mean fouling rate (= 100 %) in the regenerative section corrected for the fouling level in the preheater

figure shows the amount of deposits in the regenerative section corrected for the change in absolute fouling level, caused by ageing of milk. It appears that the effect of the combination of temperature and time on the amount of deposits in the regenerative section can be estimated very well. This makes the fouling model in the given temperature range useful for process optimization, in the case of both skim milk and whole milk.

3.4 Conclusions

A fouling model for heat exchangers based on the kinetics of the key component β-lg has been developed for surface temperatures of equipment walls up to 115 °C. The main mechanism is controlled by the adsorption rate of unfolded β-lg at an external heat transfer surface. This model gives good agreement with the experimental data. By application of an interstage holding section in the heating zone, the amount of deposits in the regenerative section can be reduced substantially, by over 50 %.

The developed reaction model for skim milk can also be used for predicting the deposit distribution in heat treatment equipment due to fouling by whole milk. Consequently, the model can be applied for design of heat treatment equipment and the determination of the optimal combination of temperature and time resulting in minimal fouling of equipment. Besides the effect of heat-induced protein transformations, the absolute fouling level is strongly influenced by the age of milk. When the milk is older than 3 days, the results of the model have to be corrected by an ageing factor.

Notation

A_{plate}	Plate area (m^2)
C	Concentration ($kg \cdot m^{-3}$)
$\overline{C}$	Bulk concentration ($kg \cdot m^{-3}$)
COD	Chemical oxygen demand ($kg \cdot m^{-3}$)
d	Characteristic diameter (m)
d_F	Particle diameter of adsorbing milk constituents (m)
D_F	Effective diffusion coefficient of adsorbing milk constituents ($m^2 \cdot s^{-1}$)
E_a	Activation energy ($J \cdot mol^{-1}$)
f_a	Aging factor (-)
Ha	Hatta number, form depends on kinetics (-)
J_F	Mass flux of adsorbing milk constituents ($kg \cdot m^{-2} \cdot s^{-1}$)
k	Reaction rate constant ($m^{3(n-1)} \cdot kg^{(1-n)} \cdot s^{-1}$)
k''	Reaction rate constant of surface reactions ($m^{3(n-1)+1} \cdot kg^{(1-n)} \cdot s^{-1}$)
k_0	Pre-exponential factor ($m^{3(n-1)} \cdot kg^{(1-n)} \cdot s^{-1}$)
k_0''	Pre-exponential factor of surface reactions ($m^{3(n-1)+1} \cdot kg^{(1-n)} \cdot s^{-1}$)
k_L	Mass transfer coefficient ($m \cdot s^{-1}$)
n	Reaction order (-)
N_{Av}	Avogadro constant, $6.022 \cdot 10^{23}$ (mol^{-1})
r^2	Correlation coefficient for linear regression (-)
r_U	Fraction of β-lg in the deposit ($kg \cdot kg^{-1}$)
R	Gas constant, 8.314 ($J \cdot mol^{-1} \cdot K^{-1}$)
R_d	Coefficient of multiple determination; correlation coefficient for multiple and non-linear regression
R_F''	Production rate of adsorbed milk constituents ($kg \cdot m^{-2} \cdot s^{-1}$)
Re	Reynolds number, $\rho v d/\eta$ (-)
Sc	Schmidt number, $\eta/\rho D_F$ (-)
Sh	Sherwood number, $k_L d/D_F$ (-)
t	Time (s)

t_r	Run, operating time (s)
T	Absolute temperature (K)
V_F	Molar volume of adsorbed particles ($m^3 \cdot mol^{-1}$)
V_{NaOH}	Volume of the sodium hydroxide solution (m^3)
y	Distance (m)
δ	Thickness of the boundary layer (m)
η_L	Viscosity of the liquid phase ($kg \cdot m^{-1} \cdot s^{-1}$)
ρ	Specific mass ($kg \cdot m^{-3}$)
τ	Space time (s)

Subscripts

A	Aggregated β-lg
F	Aggregates of milk constituents
F*	Adsorbed aggregates of milk constituents
i	Interface
L	Liquid phase
M	Milk constituents
N	Native β-lg
U	Unfolded β-lg

References

1. H. Burton. Ultra-high-temperature processing of milk and milk products. Elsevier Appl. Sci., London (1988).
2. T.J.M. Jeurnink. Effects of proteolysis in milk on fouling in heat exchangers. *Neth. Milk Dairy J.* 45 (1991) 23-32.
3. A.S. Grandison. UHT-processing of milk: seasonal variation in deposit formation in heat exchangers. *J. Soc. Dairy Technol.* 41 (1988) 43-49.
4. M. Lalande, J.P. Tissier & G. Corrieu. Fouling of heat transfer surfaces related to β-lactoglobulin denaturation during heat processing of milk. *Biotechnol. Progress* 1 (1985) 131-139.
5. F. Dannenberg. Zur Reaktionskinetik der Molkendenaturierung und deren technologischer Bedeutung. Thesis, Technical University Munich (1986).
6. P.J. Fryer. The uses of fouling models in the design of food process plant. *J. Soc. Dairy Technol.* 42 (1989) 23-29.
7. J.P. Tissier, M. Lalande & G. Corrieu. A study of milk deposit on heat exchange surface during UHT treatment. In: Engineering and Food, ed. B.M. McKenna, Elsevier Applied Science, London (1984).

8. J. Hiddink, M. Lalande, A.J.R. Maas & A. Streuper. Heat treatment of whipping cream. I. Fouling of the pasteurization equipment. Milchwissenschaft 41 (1986) 542-546.
9. K.R. Westerterp, W.P.M. van Swaaij & A.A.C.M. Beenackers. Chemical reactor design and operation. Wiley, New York (1987).
10. R.H. Perry & D. Green. Perry's chemical engineers' handbook. 6th ed., p3.286, McGraw-Hill, New York (1985).
11. W.J. Beek & K.M.K. Muttzall. Transport Phenomena. Wiley, Chichester, p247 (1980).
12. Plate heat exchanger simulation program. NIZO, Ede (1993).
13. F. René & M. Lalande. Échangeur de chaleur à plaques et joints, Résolution numérique des équations d'échange thermique entre les différent canaux. *Rev. Gén. Therm.* 311 (1987) 577-584.
14. J.N de Wit & G. Klarenbeek. Technological and functional aspects of milk proteins. In: Milk proteins. Steinkopff, Darmstadt, p211-222 (1989).
15. Dutch Standard NEN 6633. Determination of chemical oxygen demand. (1990).
16. Measurements by NIZO Milieudienst, Ede (1990).
17. P. Walstra & R. Jennes. Dairy chemistry and physics. Wiley, New York (1984).
18. J. Yoon & D.B. Lund. Effect of operating conditions, surface coatings and pretreatment on milk fouling in a plate heat exchanger. In: Proceedings ICFC III, Ed. H.G. Kessler & D.B. Lund, p59-80 (1989).
19. F. Dannenberg & H.G. Kessler. Reaction kinetics and functional aspects of whey proteins in milk. *J. Food Sci.* 53 (1988) 258-263.
20. Dutch Standard NEN 3198. Determination of the nitrogen amount according to Kjeldahl. (1984).
21. M. Lalande & F. René. Fouling by milk and dairy products and cleaning of heat exchange surfaces. In: Fouling Science and Technology, Ed. L. Melo, T.R. Bott & C. Bernado, Kluwer Nato Asi. Ser. E 145, Amsterdam (1989).
22. P.J.J.M. van Mil & S.P.F.M. Roefs. Denaturation of whey proteins studied by thermal analysis and chromatography. In: Food Colloids and Polymers: Stability and Mechanical Properties, Ed. E. Dickinson & P. Walstra, Royal society of chemistry, p45-54 (1993).

Chapter 4

HeatCARD: a simulation program for heat-treatment equipment

Abstract

A computer program has been developed for the Netherlands dairy industry, called HeatCARD (Heat exchanger Computer Aided Reactor Design). The program is capable of evaluating the product transformations and the deposit distribution in the equipment simultaneously, and of quantifying the interaction between them. The core of the program is formed by the reaction models described in the previous chapters. The availability of this program means that the use of empirical kinetic constants with an intrinsically small range of validity is no longer necessary. The proposed computational approach may contribute to a better understanding, a more functional design and an improved operation of heat treatment equipment in the dairy industry.

4.1 Introduction

In the past in the dairy industry relatively little attention was given to a mathematical approach towards the heat-induced transformations in the product. Graphs were used which give the conversion of a milk component at a constant temperature and time [1, 2]. However, these graphs ignore the temperature dependence of the rate processes in the heating and cooling trajectories of the process and it is therefore impossible to evaluate more than one heat treatment in series. In spite of the restrictions of this rough approximation, the constant temperature-time graphs are still widely used in the industry. To include the heating and cooling trajectories, the integral of the reaction rate over a certain time range has been applied [3, 4]. This so-called F-value is used to compare different temperature profiles; however, this approach is only valid for conversions lower than 10% and small changes in temperature with regard to the reference temperature. Appendix 4.I gives the fundamentals of some kinetic constants generally used in the food industry.

A more accurate and versatile method to evaluate the effect of heat treatment on heat-induced product transformations would be to calculate the conversions directly from the reaction rate equations with the aid of a user-friendly computer program. For that purpose a computer program has been developed for the Netherlands dairy industry, called HeatCARD (Heat exchanger Computer Aided Reactor Design). Specifications of the program are given in Appendix 4.II. The main power of this program is the possibility to evaluate the product transformations and the deposit distribution in the equipment simultaneously and to quantify the interaction between them. To date about twenty copies of HeatCARD have been distributed to the Netherlands dairy companies.

In this chapter the basics of the HeatCARD program are described and some potential industrial applications are given. The core of the program is formed by the reaction models described in the previous chapters. More details of the results obtained by application of HeatCARD in the Netherlands dairy industry will be given in Chapter 7.

4.2 Simulation method

4.2.1 Equipment description

Generally, heat treatment of dairy products is part of a larger production unit and may consist of several sections like heaters, coolers, connection tubes and holding sections in which the product is held at a constant temperature. To simulate a heat treatment trajectory in HeatCARD, the equipment has to be translated into a series of model reactors. Table 4.1 gives an overview of the reactor types available in HeatCARD.

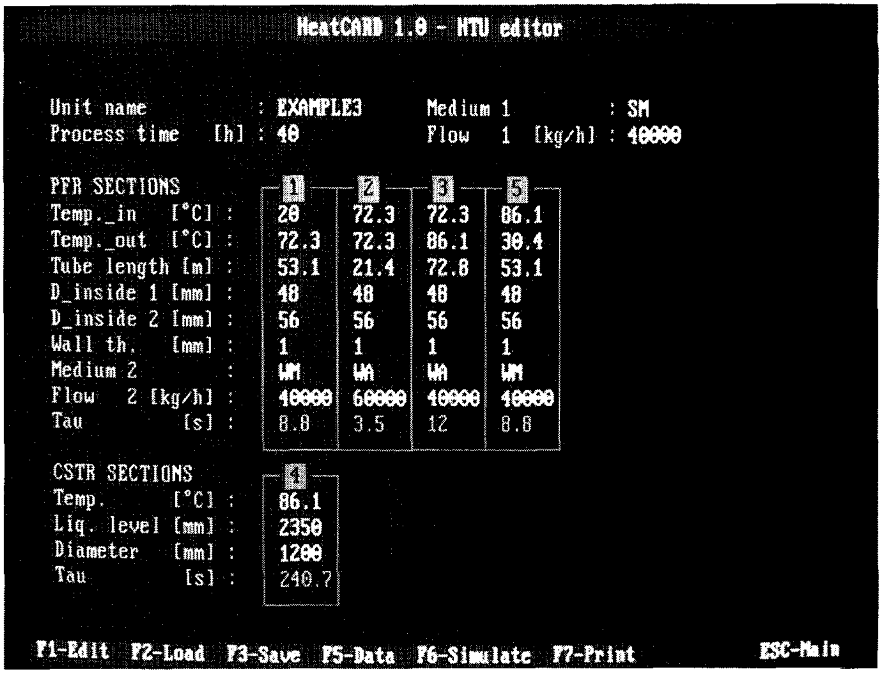
The heat exchangers are described by non-isothermal plug flow reactors (PFR I) operating as counter-current tubular heat exchangers. The advantages of a tubular heat exchanger are its simple configuration and well-defined heat transfer coefficients. Most of the heat exchangers used in the dairy industry are tubular or plate heat exchangers. The translation from, for example, a plate heat exchanger into a non-isothermal plug-flow reactor should be based on the liquid volume and specific area to approximate the actual residence time and amount of deposits:

$$L_{\mathrm{PFR}} = \frac{V}{\frac{1}{4}\pi D_{\mathrm{PFR}}^2}, \quad D_{\mathrm{PFR}} = \frac{4V}{A_{\mathrm{plates}}} \tag{4.1}$$

where D_{PFR} is equal to the hydraulic diameter of the channels in a plate heat exchanger. Figure 4.1 shows the heat-transfer-unit (HTU) editor where the equipment design and process conditions can be entered. In this editor the reactor

Table 4.1 Reactor types available in HeatCARD

Reactor type	Appearance	Characteristic dimensions	Example
non-isothermal plug flow reactor (PFR I)	countercurrent tubular heat exchanger	length, inner-diameters, wall thickness	tubular and plate-heat exchangers
isothermal plug flow reactor (PFR II)	tube	length, inner-diameter	holding sections, connection tubes
isothermal continuously stirred tank reactor (CSTR)	tank	innerdiameter, liquid level	holding sections, storage tanks



```
                  HeatCARD 1.0 - HTU editor

Unit name          : EXAMPLE3     Medium 1          : SM
Process time   [h] : 40           Flow    1  [kg/h] : 40000

PFR SECTIONS         1      2      3      5
Temp._in    [°C] :  20     72.3   72.3   86.1
Temp._out   [°C] :  72.3   72.3   86.1   30.4
Tube length [m]  :  53.1   21.4   72.8   53.1
D_inside 1 [mm]  :  48     48     48     48
D_inside 2 [mm]  :  56     56     56     56
Wall th.   [mm]  :  1      1      1      1
Medium 2         :  WM     WA     WA     WM
Flow   2 [kg/h]  :  40000  60000  40000  40000
Tau          [s] :  8.8    3.5    12     8.8

CSTR SECTIONS        4
Temp.       [°C] :  86.1
Liq. level [mm]  :  2350
Diameter   [mm]  :  1200
Tau          [s] :  240.7

F1-Edit  F2-Load  F3-Save  F5-Data  F6-Simulate  F7-Print          ESC-Main
```

Figure 4.1 The heat-transfer-unit editor of HeatCARD

types can be connected in any desired sequence. All the data shown in the HTU-editor can be edited, saved to file or loaded from a file.

4.2.2 Calculation algorithm

An important feature of HeatCARD is the possibility to quantify the interaction between the local reaction rates and deposit formation or, more precisely, between the local temperatures and the adsorption rate of milk constituents according to the reaction model for fouling (see Chapter 3). In Figure 4.2 the algorithm of the calculation sequence is given.

At time t, first the local heat transfer coefficients and the temperature profile of section i with length Δx are calculated according to

$$T_{1_{\mathrm{i},t}} = T_{1_{\mathrm{i}-1,t}} + U_{\mathrm{i},t}\pi D \frac{T_{2_{\mathrm{i}-1,t}} - T_{1_{\mathrm{i}-1,t}}}{\phi_1 C_p}\Delta x \tag{4.2}$$

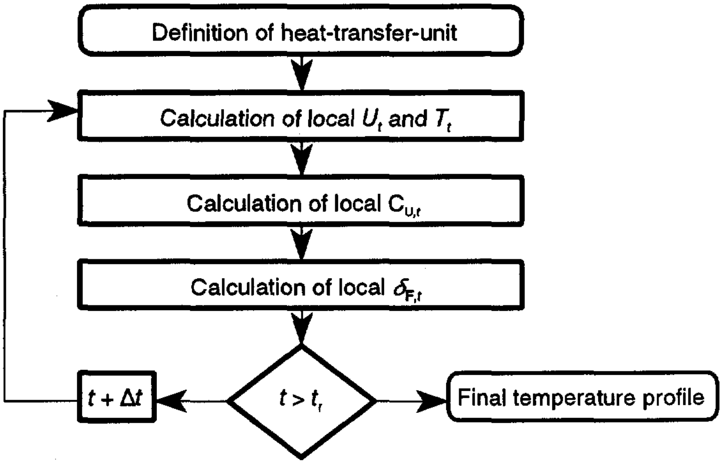


Figure 4.2 Schematic representation of the calculation algorithm to calculate the temperature profile in the equipment as a function of operating time

for non-isothermal plug flow reactors and

$$T_{1_{i,t}} = T_{1_{i-1,t}} \tag{4.3}$$

for isothermal reactors, where

$$\frac{1}{U_{i,t}} = \frac{1}{\alpha_1} + \frac{1}{\alpha_2} + \frac{\delta_{\text{wall}}}{\lambda_{\text{wall}}} + \frac{\delta_{F_{i,t}}}{\lambda_F} \tag{4.4}$$

In the case of non-isothermal plug flow reactors the inlet and outlet temperatures of the heating or cooling medium are unknown and have to be calculated by iteration.

Before the local deposition rate can be calculated, the correlated local concentration of unfolded β-lactoglobulin (β-lg) has to be known (see Chapter 3). The concentration profile follows from the reaction rate equations in the discrete form

$$C_{N_{i,t}} = C_{N_{i-1,t}} - \frac{k_U\left(T_{1_{i-1,t}}\right) C_{N_{i-1,t}} \Delta x}{v_1} \tag{4.5}$$

$$C_{A_{i,t}} = C_{A_{i-1,t}} + \frac{k_A\left(T_{1_{i-1,t}}\right) C^2_{A_{i-1,t}} \Delta x}{v_1} \tag{4.6}$$

$$C_{U_{i,t}} = C_0 - C_{N_{i,t}} - C_{A_{i,t}} \tag{4.7}$$

The growth of the local deposit layer is given by

$$\delta_{F_{i,t}} = \delta_{F_{i,t-\Delta t}} + \frac{k^{//}\left(T_{\text{surface}_{i,t-\Delta t}}\right)}{\rho_F} C^{1.2}_{U_{i,t-\Delta t}} \Delta t \tag{4.8}$$

where Δt means a time step of the operating time. The new thickness of the deposit layer results again in changed local heat transfer coefficients at time $t+\Delta t$ and consequently in changed temperature and concentration profiles, et cetera.

4.2.3 Variables

Table 4.2 gives an overview of the variables of a simulation. Some variable types are specific for the type of reactor selected, PFR or CSTR, others are global program variables. Since in the non-isothermal plug flow reactor the product is heated or cooled, a second medium has to be entered. This might be water or, in case of a heat recovery section, the product itself. All the variables are used with the calculation of the temperature profiles in the equipment. The type of medium only

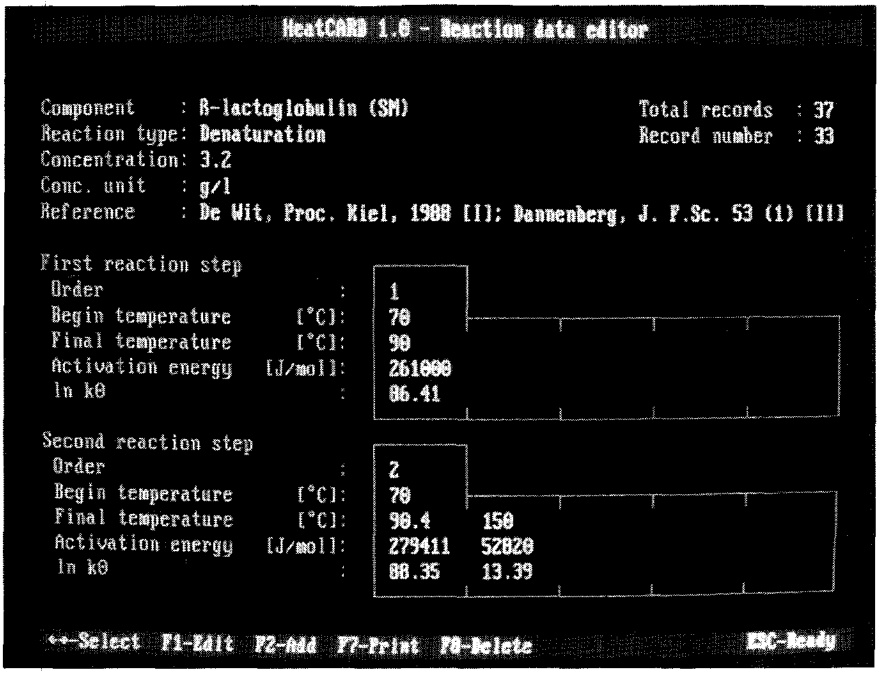
Table 4.2 Variables in HeatCARD

Symbol	Name	Type
$D_{1,\text{inner}}$	Inner diameter (mm) of product tube, tank	PFR, CSTR
$D_{2,\text{inner}}$	Inner diameter (mm) of tube with heating or cooling medium	PFR
H_L	Liquid level (mm)	CSTR
L	Tube length (m)	PFR
t_r	Operating or process time (h)	global
$T_{1,\text{in}}$	Inlet temperature of a section (°C)	PFR
$T_{1,\text{out}}$	Outlet temperature of a section (°C)	PFR, CSTR
δ_{wall}	Wall thickness (mm)	PFR
Δt	Step length related to operating time (s)	global
Δx	Step length related to flow length (m)	global
Φ_1	Mass flow medium 1 (kg·h^{-1})	global
Φ_2	Mass flow medium 2 (kg·h^{-1})	PFR
-	Medium 1	global
-	Medium 2 (WA = water, SM = skim milk, WM = whole milk)	PFR

affects the physical properties of the medium like specific mass and viscosity and not the reaction kinetic data. The operating time (t_r) affects the change in the local temperatures as a result of fouling (see section 4.2.2). The step lengths related to operating time (Δt) and flow length (Δx) are parameters of the numerical integration of the local temperature change and reaction rates, respectively.

4.2.4 Reaction data editor

HeatCARD is linked to a data base consisting of the kinetic data of more than 30 milk components. Figure 4.3 shows the screen of the reaction data editor in which data records can be changed, added and deleted. HeatCARD recognizes five reaction types: denaturation (proteins), inactivation (enzymes), loss (nutrients), formation (reaction products) and destruction (micro-organisms). These reactions can be described by one reaction step



```
Component    : ß-lactoglobulin (SM)                          Total records  : 37
Reaction type: Denaturation                                  Record number  : 33
Concentration: 3.2
Conc. unit   : g/l
Reference    : De Wit, Proc. Kiel, 1988 [I]; Dannenberg, J. F.Sc. 53 (1) [II]

First reaction step
 Order                       :   1
 Begin temperature      [°C]:   70
 Final temperature      [°C]:   90
 Activation energy  [J/mol]:   261000
 ln k0                       :   86.41

Second reaction step
 Order                       :   2
 Begin temperature      [°C]:   70
 Final temperature      [°C]:   90.4     150
 Activation energy  [J/mol]:   279411   52820
 ln k0                       :   88.35    13.39
```

Figure 4.3 The reaction (kinetic) data editor of HeatCARD

$A \rightarrow B$

or two reaction steps in series

$A \rightarrow B \rightarrow D$

with arbitrary reaction orders.

It turns out (see Chapter 1) that for some reactions the activation energy and pre-exponential factor are not constant but dependent on temperature. Therefore it is possible to enter kinetic constants for up to five temperature ranges.

4.3 Results

After calculation of the deposit distribution and the temperature profiles, HeatCARD enters a graphical environment. In this mode the local temperatures, the concentrations of milk components and the deposit distribution can be shown. Figure 4.4 shows the graphics screen of the program. The graphics screen contains two graphs: a temperature graph and a concentration or deposit layer graph. All the available components in the reaction data base can be evaluated for the actual temperature profile. Since the temperature profiles changed during the operating time, the graphs show the concentration profiles at the start and at the end of operation. The calculation results can be saved as ASCII-files.

4.4 Applications

The first application of HeatCARD is that a given heat treatment can easily be evaluated for every milk component and the effect of a change in the process conditions and design on the conversion of the component can be quantified. Empirical parameters like F- and z-values (see Appendix 4.I) based on simplifying assumptions with a relatively small range of validity are no longer necessary. When the key components which determine the functional properties of a product are known, it is possible to estimate the best process conditions for a certain product and to determine the critical points in the process.

Another important application is the possibility to predict the deposit distribution in relation to the process conditions and design. As a consequence it is also possible to affect the deposit distribution and total amount of deposits by

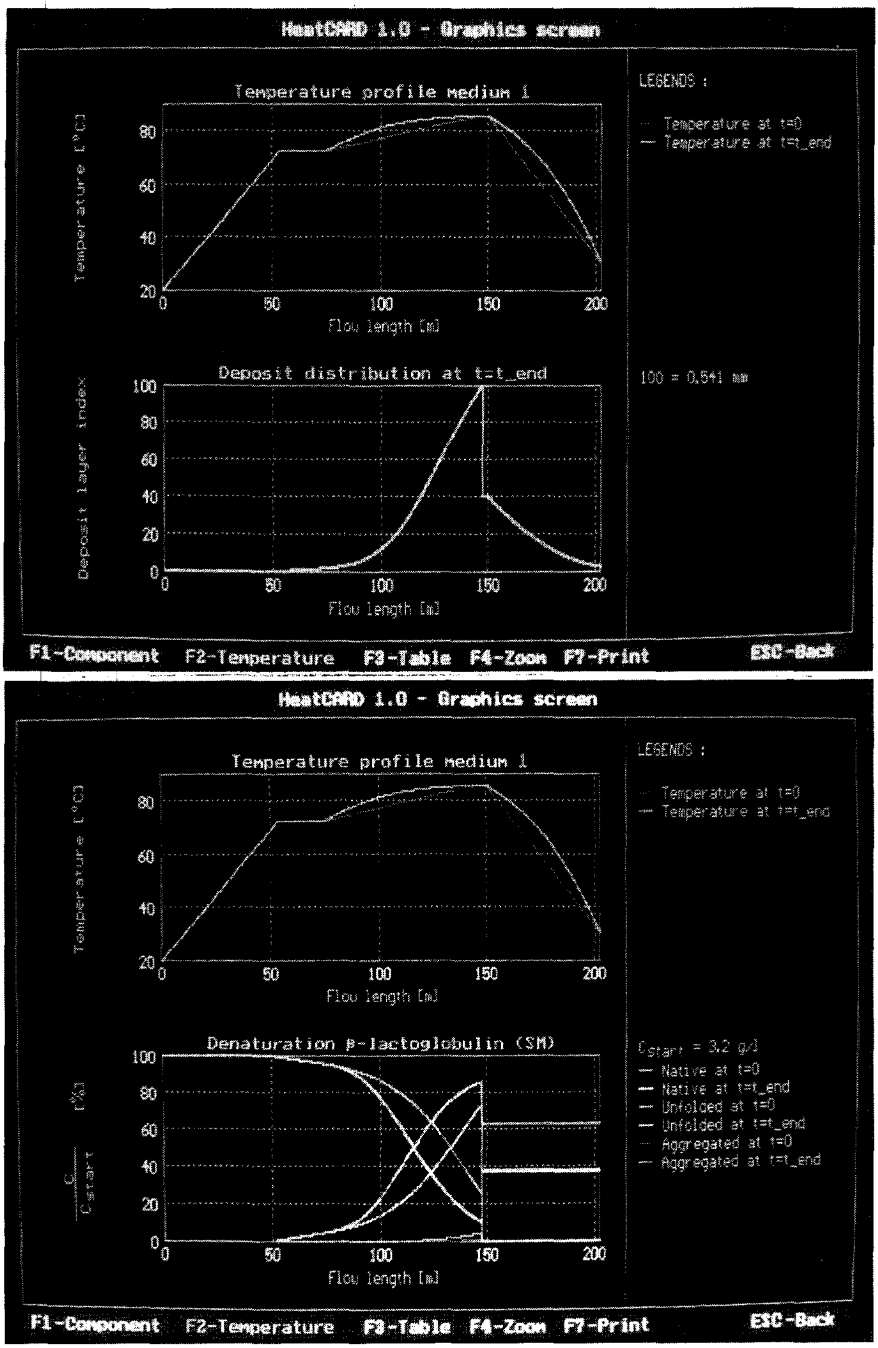


Figure 4.4 The graphical environment of HeatCARD: deposit distribution (top) and concentration profile of native, unfolded and aggregated β-lg (bottom)

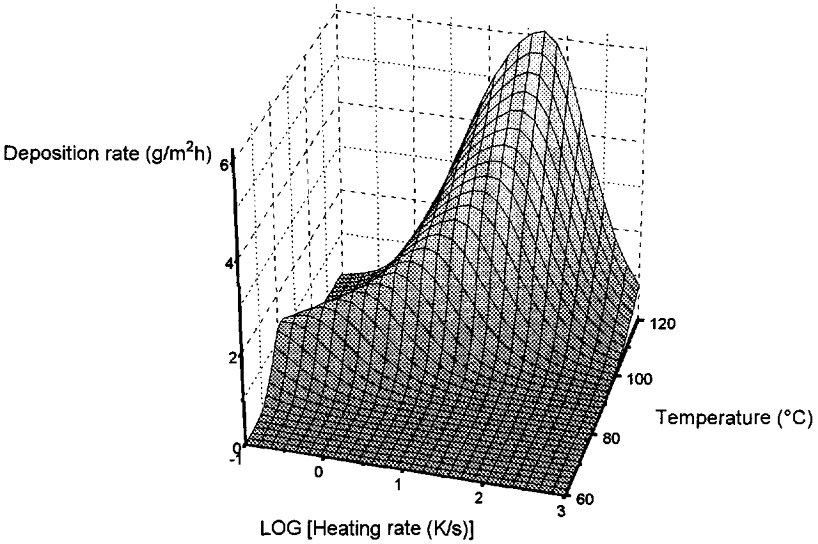


Figure 4.5 The local deposition rate in a heater as a function of the heating rate; linear temperature increase, milk heated from 60 to 120 °C

changing the related process parameters. For example, it is known that the amount of deposits in heat exchangers is reduced by installing an additional holder section in the heating trajectory [2]. In this holder unfolded β-lg is transformed into the aggregated state which plays no key role in the fouling process, resulting in less deposit downstream from the holder. In other words, the region with the maximum deposition rate is positioned in a holder without heat transfer surfaces and a low specific surface area.

Figure 4.5 shows the relation between the heating rate and the deposition rate in the heater. On the y-axis the local temperature in the heat exchanger is shown. The milk is heated from 60 to 120 °C with a heating rate between 0.1 and 1000 K/s. It is assumed that the temperature profiles are linear (i.e. constant heating rate) and that the wall temperature is equal to the temperature of the bulk. It is obvious that the optimal holding temperature to reduce fouling lies below the temperature at which the deposition rate reaches its maximum. The volume of the holder is fixed by the holding time which is given by the admitted conversion of unfolded into aggregated β-lg in the appropriate situation.

In order to minimize the amount of deposits in heat treatment equipment there may be two trivial solutions. The first is that the product should not be heated at all and the second is a complete denaturation of β-lg in the holder section (i.e.,

$C_U \approx 0$). However, both solutions result in inferior products: a product with pathogens and a product with a undesired degree of denaturation, respectively. With HeatCARD it is possible to evaluate the deposit distribution and the conversion of key components simultaneously. This may result in minimal fouling of the equipment without concessions to the product quality.

4.5 Conclusions

The HeatCARD computer program is developed for evaluation of heat treatments in the dairy industry with respect to heat-induced product transformations and fouling of equipment. With the program it is possible to calculate the local conversion of milk components and deposition rate at heat transfer surfaces in heat treatment equipment. Details of the results obtained by application of HeatCARD in the Netherlands dairy industry will be given in Chapter 7.

HeatCARD may be used for simulating of existing and new processes to control and improve product quality and for screening potential microbiological problems, hence reducing the need for unfocused challenge testing. The program can also help design optimal heat treatments for a range of food formulations with respect to functional properties and fouling of equipment.

Notation

A	Area (m^2)
C	Concentration ($kg \cdot m^{-3}$)
C_p	Specific heat ($J \cdot kg^{-1} \cdot K^{-1}$)
D	Diameter (m)
k_A	Reaction rate constant aggregation ($m^3 \cdot kg^{-1} \cdot s^{-1}$)
k_U	Reaction rate constant unfolding (s^{-1})
k''	Reaction rate constant for surface reactions ($m^{1.6} \cdot kg^{-0.2} \cdot s^{-1}$)
L	Length (m)
F	Process value
n	Reaction order
N	Number of microorganisms
R	Gas constant (8.314 $J \cdot mol^{-1} \cdot K^{-1}$)
t	Time (s)
T	Temperature (K)

U	Overall heat transfer coefficient ($W \cdot m^{-2} \cdot K^{-1}$)
v	Velocity ($m \cdot s^{-1}$)
V	Volume (m^3)
x	Coordinate (m)
z	Measure for temperature dependence (K)
α	Heat transfer coefficient ($W \cdot m^{-2} \cdot K^{-1}$)
δ	Thickness (m)
λ	Heat conductivity ($W \cdot m^{-1} \cdot K^{-1}$)
ρ	Specific mass ($kg \cdot m^{-3}$)
ϕ	Mass flow ($kg \cdot s^{-1}$)

Subscripts, indices

A,B,D	Components
F	Fouling, deposit
i	Index
N,U,A	Native, unfolded and aggregated β-lactoglobulin, respectively
PFR	Plug Flow Reactor
ref	Reference value
t	Time
0	Initial
1	Product
2	Heating or cooling medium

References

1. P. Walstra & R. Jennes. Dairy chemistry and physics. J. Wiley, New York (1984).
2. H.G. Kessler. Lebensmittel- und Bioverfahrenstechnik, Molkereitechnologie. Verlag A. Kessler, Freising (1988).
3. C.O. Ball & F.W. Olson. Sterilization in food technology. Mc Graw-Hill, New York (1957).
4. H. Burton. Ultra-high-temperature processing of milk and milk products. Elsevier Appl. Sci., London (1988).

Appendix 4.I: Kinetic constants used in the dairy industry

Q_{10}-value

Definition

Ratio between the reaction rate constants at a temperature difference of 10 K.

Relation with activation energy

$$Q_{10} = \frac{k_0 \cdot \exp\left[\frac{-E_a}{R(T+10)}\right]}{k_0 \cdot \exp\left[\frac{-E_a}{RT}\right]} = \exp\left[10\frac{E_a}{RT(T+10)}\right] \tag{1A.1}$$

D-value

Definition

Reaction time necessary for 1 decimal reduction (90 % conversion) at a constant temperature, restricted to first order kinetics.

Relation with Arrhenius reaction rate constant

$$\left.\begin{array}{l} \frac{N}{N_0} = 0.1 \\ \frac{N}{N_0} = \exp(-kD) \quad (n=1) \end{array}\right\} D = \frac{\ln(10)}{k} \tag{1A.2}$$

z-value

Definition

Increase in reaction temperature necessary for a 10-fold increase of the reaction rate constant.

Relation with activation energy

$$\frac{k_0 \cdot \exp\left[\frac{-E_a}{R(T+z)}\right]}{k_0 \cdot \exp\left[\frac{-E_a}{RT}\right]} = 10 \Leftrightarrow \exp\left[\frac{E_a z}{RT(T+z)}\right] = 10 \Leftrightarrow \tag{1A.3}$$

$$z = \frac{\ln(10) R T^2}{E_a - \ln(10) R T} \qquad (1A.4)$$

It should be noticed that a high activation energy results in a small z-value.

F-value

Definition

Quantity to compare different heat treatments.

For conversions smaller than 0.1 it is assumed that the reaction order has no influence on the conversion. Assuming zero-order kinetics the conversion can be calculated by

$$\left.\begin{aligned} kt &= XC_0 \\ t_{0.1} &= \frac{0.1 \cdot C_0}{k} \end{aligned}\right\} \quad X = 0.1 \frac{t}{t_{0.1}} \qquad (1A.5)$$

where X is the conversion of a component and $t_{0.1}$ the time necessary for a conversion of 0.1. The value of $1/t_{0.1}$ is temperature dependent and proportional to k. In terms of z

$$t_{0.1} = 10^{\frac{T_{t=1} - T}{z}} \qquad (1A.6)$$

Substitution in (1A.5)

$$X = \frac{1}{10} \cdot 10^{\frac{T - T_{t=1}}{z}} \cdot t \qquad (1A.7)$$

F is defined as proportional to X

$$F = 10^{\frac{T - T_{t=1}}{z}} \cdot t \quad \text{or} \quad F = \int_0^t 10^{\frac{T - T_{t=1}}{z}} \, dt \qquad (1A.8)$$

Appendix 4.II: Specifications of the HeatCARD computer program

System requirements
MS-DOS 4.00 or later, hard disk with 1 MB or more of free space, video graphics adapter (VGA) monitor, 400 kB or more of RAM, DOS-compatible printer
Number of files
11
Sub-directories:
HTU (data of heat-transfer-units), OUTPUT (simulation results), TPR (ASCII-files with temperatures and times)

More detailed information is given in the HeatCARD manual (P. de Jong & P.F.J. l'Amie, NIZO-report 1692v, 1992).

Chapter 5

Process optimization with respect to product transformations, fouling and operating costs

Abstract

A comprehensive optimization method has been developed based on minimizing an objective function which comprises the costs of deviating from the ideal product quality and the processing costs. The method is integrated in a computer program, called HCOPT. The main advantages of the method are the incorporation of deposit formation at heat transfer surfaces and the versatility of defining the process and equipment design, supporting non-isothermal sections like heaters and coolers. The method also accounts for the relative importance of the individual heat-induced product transformations determining the product characteristics.

To illustrate the potential of this approach a given industrial UHT (Ultra High Temperature) plant is optimized. The optimization results demonstrate that with regard to conventional industrial plants this approach may result in a substantial (more than 50 %) reduction of the operating costs, without concessions to the product quality. In the plant described the milk should be heated to 145 °C with a heating rate of 4 K/s and minimum holding time at this temperature. An additional holder should be applied in the heating trajectory at an operating temperature of 90.5 °C and a residence time of about 15 minutes.

5.1 Introduction

The increasing availability of kinetic data of relevant transformations has stimulated a reaction engineering approach to obtain optimal product quality. Some papers have been published on this topic over the last ten years [1, 2]. However, these authors based their investigations on a constant temperature and have not considered the complete time-temperature profiles during the heat treatment of milk. The dynamic optimization method recently used by Arteaga et al. [3] was a first attempt to incorporate heating and cooling zones. They divided the time-temperature profile into a limited number of sections operating at a constant temperature.

Besides the product transformations, the fouling of heat treatment equipment is an important aspect of process operation. The major part of the variable production costs is related to this phenomenon. Therefore, optimization of heat treatment processes requires appropriate mathematical models for both heat-induced product transformations and fouling. In principle the quantitative fouling model of Chapter 3 clears the way for process optimization with respect to product transformations and operating costs; the latter in terms of investment, energy costs, environmental load and product losses.

In this chapter a comprehensive optimization method is developed based on minimizing a formulated objective function, which comprises the costs of deviating from the ideal product quality and the processing costs. The method is integrated in a computer program, called HCOPT. To illustrate the potentiality of this approach a given industrial UHT (Ultra High Temperature) plant is optimized.

5.2 Optimization method

5.2.1 Objective function

The functional properties of the final product and the fouling rate of the equipment are determined by the conversion of so-called key-components, which is influenced by a number of factors. For heat-induced conversions the main factors are temperatures and residence times in the equipment. For fouling the dimensions of the equipment are also important factors. All these factors may be considered as control variables of the process optimization.

In order to determine the optimal values of the control variables, a general objective function is formulated:

$$F'_{obj}(\mathbf{u},\mathbf{x}) = \alpha c_{quality}(\mathbf{u},\mathbf{x}) + \beta c_{process}(\mathbf{u}) \tag{5.1}$$

where **u** is a vector of control variables such as temperature and flow, and **x** a vector of process variables such as desired properties of the product. The value of F'_{obj} represents the distance to the objective defined by the two terms. These terms are: (1) costs due to a deviation from the desired functional properties, the quality of the product and as a consequence the consumer acceptance, and (2) costs due to operation of the process, e.g. fouling of the equipment. The absolute minimum of the function corresponds with the optimal process conditions and design. To avoid trivial and undesired solutions, the weight factors α and β are introduced. These weight factors give the relative importance of each term of the objective function. For example: too high a value of β may result in a clean apparatus but an inferior product quality.

In fact the objectives of process operations in terms of product characteristics are often difficult to measure in an objective manner, since the only direct sensors are the consumer's eyes, hands, mouth and health [4]. Such measurement methods are long, costly and may even be dangerous. This introduces a human factor or, more precisely, a management decision, indicating that the choice of weight factors will always be a matter of weighing up the product quality and operating costs against each other. Since it is almost impossible to fit the consumer's behaviour into a mathematical model, the objective function has to be reduced to terms which are indirectly related to costs. In that case the costs related to the product characteristics might be represented by the deviation from the desired conversion of milk components, and the process operating costs might be related to the fouling of the equipment. So the objective function is given by:

$$F_{obj}(\mathbf{u},\mathbf{x}) = \sum_{i=1}^{n_x} \alpha_i \left[\frac{x_{i,des} - x_i(\mathbf{u})}{x_{i,des}} \right]^2 + \beta \int_0^{A_{tot}} \frac{J_F(\mathbf{u})}{A_{tot} J_{F,ref}(\mathbf{u})} \, dA \tag{5.2}$$

where α_i is the weight factor relating to the desired conversion ($x_{i,des}$) of milk component i. The first term is the sum of deviations from the desired conversions

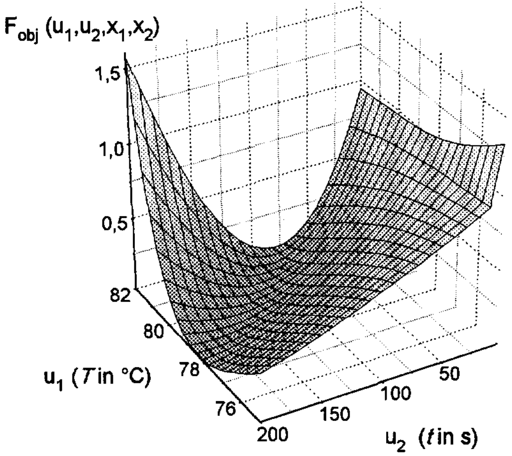


Figure 5.1 Example of evaluation of F_{obj} with 2 control variables; $x_{1,des}=0.15$ (α-lactalbumin), $x_{2,des}=0.999$ (*M.luteus*)

of milk components. The second term gives the total fouling rate of the equipment divided by a reference value, for example, the maximum fouling rate in a given situation.

An example of the shape of the objective function is shown in Figure 5.1. There are two control variables: the temperature and the time of a heat treatment. The minimum of the three-dimensional surface corresponds with the optimal temperature and time with respect to the desired conversion of component 1 and 2 (x_1 and x_2). It is obvious that the smoothness of the surface and the number of local minima depend largely on the number of process values, i.e. the number of (sub)terms of the objective function.

5.2.2 Numerical methods

To find the minimum of the objective function a modified search method is used, based on the constrained Hooke & Jeeves method [5, 6]. Figure 5.2 shows a flow chart of the search method. First the objective function is defined by selection of the control variables, the process variables and the weight factors. There are defined four types of process variables: the absolute, maximum, minimum and range type. The contribution to the objective function of each type of process variable is given

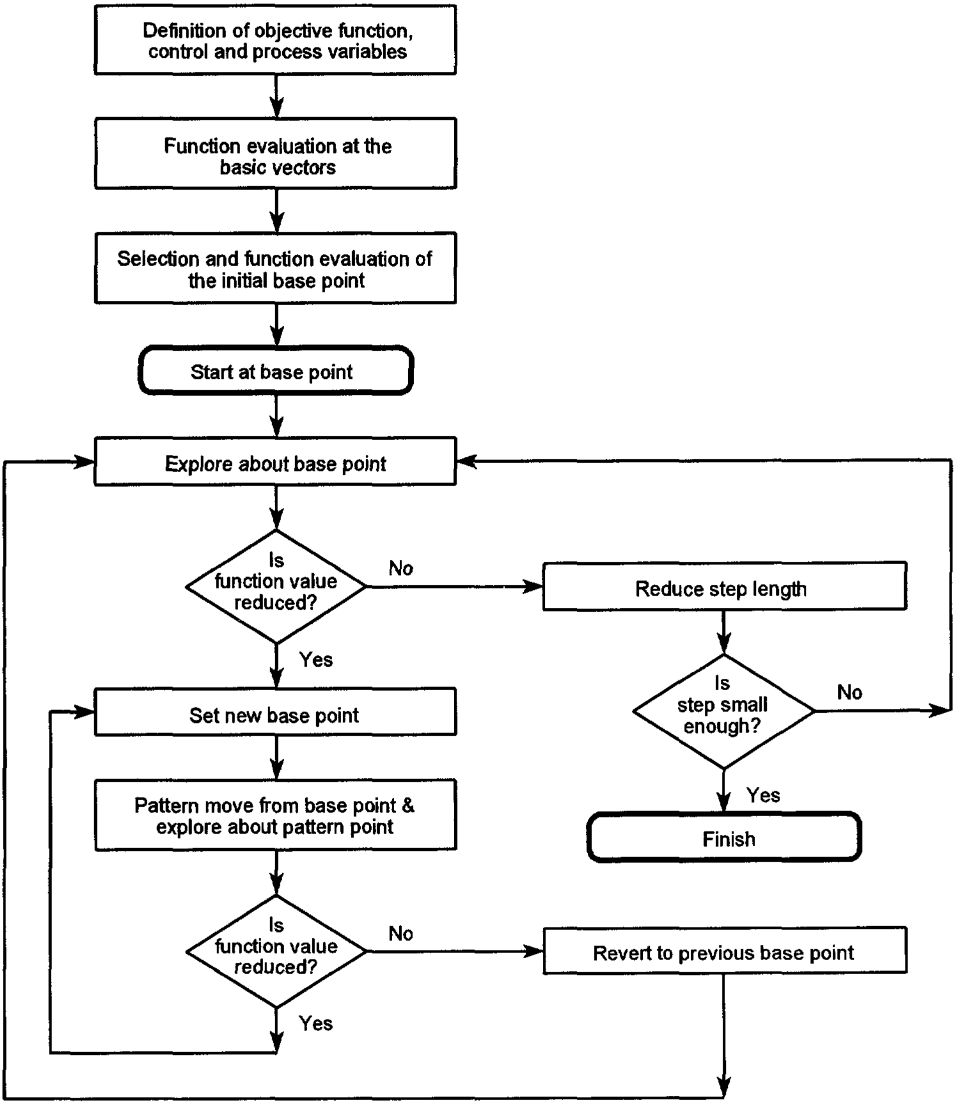


Figure 5.2 Flow chart of the constrained search method [5, 6]

Table 5.1 Types of process variables

Type	Condition	Contribution to F_{obj}	Example
absolute		$(x_{des}- x)^2$	protein denaturation (x_{des}=..% denatured β-lactoglobulin)
minimum	$x \le x_{des} \rightarrow$ $x > x_{des} \rightarrow$	$(x_{des}- x)^2$ 0	destruction of micro-organisms (x_{des}= 8 decimal reductions)
maximum	$x \le x_{des} \rightarrow$ $x > x_{des} \rightarrow$	0 $(x_{des}- x)^2$	fouling (x_{des}= 0)
range	$x_{des,min} < x < x_{des,max} \rightarrow$ $x < x_{des,min} \vee x > x_{des,max} \rightarrow$	0 $(x_{des}- x)^2$	protein denaturation

in Table 5.1. For example: milk used for production of yoghurt should have an *absolute* denaturation degree of β-lactoglobulin of about 90 % [7, 8]. In the case of sterile dairy products, no active spores should be present [7]; generally expressed as a *minimum* number of decimal reductions (-log C/C_0). In principle the conversion of each milk component, as listed in Chapter 1, might be a process variable. However, it turned out that each dairy product has its own desired conversion of key-components [7]. In Appendix 5.I an example is given of the definition of an objective function and its evaluation in the constrained search method.

After definition of the objective function, the function is evaluated for the basic vectors of the search region. The search region can be imagined by a full N-dimensional space of vectors containing N control variables (xy-plane in Figure 5.1). Since the control variables have an upper and lower limit, the vector space is limited by boundary walls and spanned by 2^N so-called basic vectors [9]. Each basic vector contains a combination of upper and lower limits of the control variables. For example, in Figure 5.1 the search region can be imagined by a rectangle with four basic vectors, i.e. the angular points of the xy-plane.

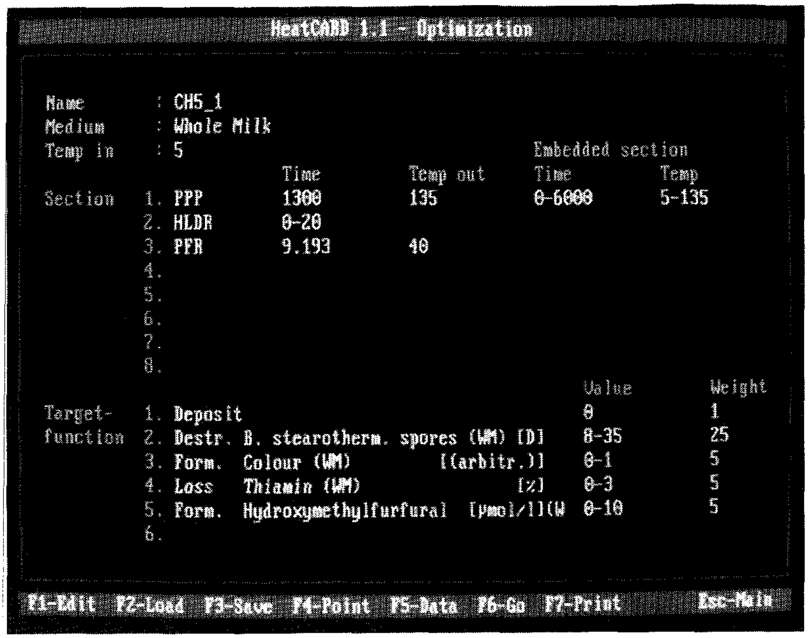
The next step is the selection of the initial base point from which the search starts. The purpose of the succeeding exploration about the base point is to acquire knowledge about the local behaviour of the function. If the function is reduced by adding a step length, the length is increased. If not, the step length is decreased. The knowledge of the exploration is used to find a likely direction for the pattern move (new base point) to obtain a larger reduction in the value of the function. The optimization is terminated when the step length has been reduced to a predetermined small value.

To escape from local minimum points, several initial base points can be selected. There are three types: (i) the best basic vector, (ii) the weighted centre vector of the space or (iii) a vector with selected values of the control variables, e.g. the optimal values of a preceding optimization.

5.2.3 Program description

To apply the described optimization method, the computer program HCOPT (HeatCard-OPTimization) is developed. HCOPT is programmed in Pascal and runs on an MS-DOS PC. The user interface of the program and the calculation procedures are similar to HeatCARD (see Chapter 4). Figure 5.3 shows the input window of the program.

The heat treatment equipment which has to be optimized is defined by a cascade of up to 8 model reactors (sections) in series. The residence time and the inlet and outlet temperatures of each reactor can be defined as control variables. In Figure 5.3 the control variables are defined by a lower and upper limit. For example: the residence time of the holder (HLDR) is varied between 0 and 20



```
                     HeatCARD 1.1 - Optimization

Name        : CH5_1
Medium      : Whole Milk
Temp in     : 5                                Embedded section
                         Time         Temp out    Time          Temp
Section     1. PPP       1300         135         0-6000        5-135
            2. HLDR      0-20
            3. PFR       9.193        40
            4.
            5.
            6.
            7.
            8.
                                                        Value        Weight
Target-     1. Deposit                                  0            1
function    2. Destr. B. stearotherm. spores (WM) [D]   0-35         25
            3. Form.  Colour (WM)        [(arbitr.)]    0-1          5
            4. Loss   Thiamin (WM)               [%]    0-3          5
            5. Form.  Hydroxymethylfurfural  [µmol/l](W 0-10         5
            6.
```

Figure 5.3 Input window of the optimization program HCOPT (PPP is equal to PHP)

Table 5.2 Available reactor types in HCOPT

Reactor type	Control variables					
	T_{outlet}[a] (°C)	τ (s)	A_{spec}[b] (m^2/m^3)	Embedded section		
				T (°C)	τ (s)	A_{spec}[b] (m^2/m^3)
PFR: Non-isothermal plug flow reactor	●	●	●			
CSTR: Continuous stirred tank reactor		●	●			
HLDR: Isothermal holder tube		●	●			
PHP: PFR with embedded HLDR section	●	●[c]	●	●	●	●
PCP: PFR with embedded CSTR section	●	●[c]	●	●	●	●

[a] T_{inlet} only at the first reactor of the cascade
[b] Kept constant during one optimization
[c] Residence time of the embedded section excluded

seconds; the inlet and outlet temperature of the heater section (PPP = PHP) are taken as constant. Table 5.2 gives a review of the available reactor types. The reactors PHP and PCP were introduced to evaluate the effect of an interstage holding section in the heating zone on the amount of deposits (see Chapter 3). The temperature of this "embedded" section determines its location in the heating zone. For example, in Figure 5.3 an optimal holding temperature of 70 °C means that the embedded section should be positioned exactly in the middle of the heater.

With HCOPT it is possible to construct an objective (or target) function based on the reaction data editor of HeatCARD (see Chapter 4). In total 6 process variables with regard to fouling or conversion of key-components can be defined. The desired (or target) value of the process variable can be entered as a range or as an absolute value. In the case of minimum and maximum values as mentioned in Table 5.1, the upper and lower limit has to be set to a high value or zero, respectively. For example, a minimal decimal reduction of 8 spores is entered as a range between 8 and, e.g. 40. The unit of the target value corresponds to the unit of the initial concentration of the key-component given in the reaction data editor.

HCOPT has some features to avoid the trouble of finding a local minimum. It is possible to select several initial base points. Besides, when an optimum is found the program explores about other points away from the actual optimum, e.g. the best basic vector of the vector space.

5.3 Case-study

5.3.1 Equipment definition

Figure 5.4 shows a schematic representation of an arbitrary plate-type indirect UHT plant as described by Burton [10] which has been used to illustrate the optimization method. Whole milk with a temperature of 5 °C is heated to a variable UHT temperature, held at this temperature for a certain time and cooled again to 40 °C. Heat recovery is obtained by circulating water. During the optimization the milk inlet and outlet temperature were kept constant and the UHT temperature was

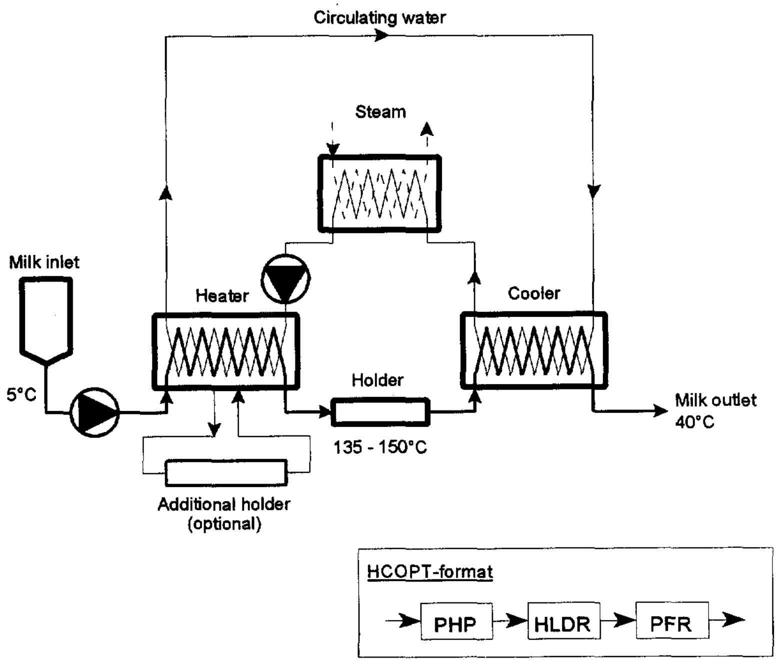


Figure 5.4 Arrangement of the optimized UHT plant with its HCOPT-format

varied between 135 and 150°C. The heating rate was varied between 0.1 and 10 K/s. As a result of the chosen temperatures, the heat recovery of the plant lies between about 73 and 75%.

At the prescribed constant temperatures and heating rates, the necessary heat transfer area in the heater and the cooler follows from the heat balance and the heat transfer equation as given in Appendix 5.II. Figure 5.5 shows the calculated size of the heat transfer area as a function of the heating rate and the UHT temperature. It is obvious that a high heating rate results in a high temperature difference in the heater. Consequently due to the increasing water outlet temperature, the temperature difference in the cooler will be lower and thus the heat transfer area in the cooler will have to be increased. At low heating rates the temperature difference in the cooler will reach the maximum value of 35 degrees. The maximum heating rate lies at about 10 K/s. In that case the temperature difference in the cooler is zero, resulting in an infinite heat transfer area.

The amount of deposits in heat treatment equipment can be reduced by an additional holder in the heating trajectory (see Chapter 3). In this holder section the unfolded β-lactoglobulin (β-lg) is transformed into aggregated β-lg, which is unable

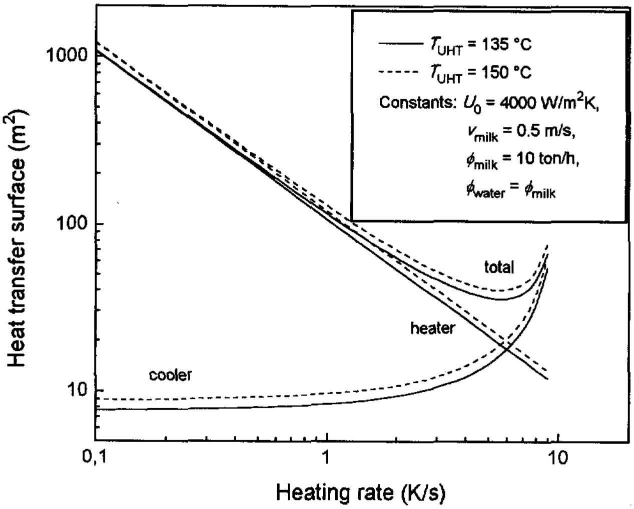


Figure 5.5 The calculated heat transfer area in the given UHT plant related to the heating rate and UHT temperature

to play an active role in the fouling process downstream of the holder section. To quantify the advantage of this additional holder, the optimization runs were carried out both with and without the additional holder.

5.3.2 Process and control variables

According to Kessler [7] the quality of UHT milk is controlled by destruction of spores on the one hand and the loss of thiamin (vitamin B_1) and formation of hydroxymethylfurfural (HMF) on the other hand. The concentration of HMF is considered as an important parameter for controlling the progress of the Maillard reactions (see Chapter 1), resulting in a cooked flavour and browning [10, 7].

Table 5.3 gives the desired values of the process variables used during the case-study. It is obvious that these are target values. Particularly with respect to deposit formation the target value will never be reached. The ratio between the weight factors for the conversion of the key-components and the deposition is based on the boundary condition that product quality is considered as a more important topic than fouling of the equipment and that the destruction of *B. stearothermophilus* spores should be more than 8 decimal reductions ($C/C_0 < 10^{-8}$) in any case [2]. The selected ratios in Table 5.3 turned out to give satisfactory results. Lower ratios between the weight factors resulted in less than 7.5 decimal reductions of spores in some cases. Higher ratios had almost no effect on the product characteristics but increased the fouling rate of the equipment. The weight factors belonging to the loss of thiamin and the formation of colour had a minor effect on the value of the objective function.

Table 5.3 Process values and their weight factors

Reaction[a]	Desired value of process variable	Weight factor α,β
Destruction of *B. stearothermophilus* spores	> 8 decimal reductions	25
Loss of thiamin	< 3 %	5
Formation of hydroxymethylfurfural (HMF)	< 10 μmol/l	5
Formation of colour (browning)[b]	< 1	5
Deposit formation	0	1

[a] Kinetic data given in Chapter 1 (key-components) and Chapter 3 (deposit formation).
[b] 1 = no change in colour (perception threshold), 2 = light ivory, 4 = saffron-yellow, 10 = brown-yellow.

Table 5.4 Constraints on the control variables

Control variable	Constraints	
	Lower limit	Upper limit
UHT temperature (°C)	135	150
Temperature of additional holder (°C)	5	UHT temperature
Heating rate (K/s)	0.1	10
Residence time of holder at UHT temperature (s)	0	2000
Residence time of additional holder[a] (s)	0	2500

[a] A_{spec} = 30 m^2/m^3.

Table 5.4 gives an overview of the control variables and their constraints. These are the UHT temperature, the heating rate and the use of an additional holder section. A number of control variables affect not only the selected process variables, but also the operating costs of the plant.

5.3.3 Results of minimizing the objective function

Control variables

Figure 5.6a-c show the optimal values of the control variables as a function of the UHT temperature and the heating rate, with and without an additional holder. The operating temperature of this second holder increases with the heating rate and turns out to be independent of the UHT temperature. This can be explained by the denaturation kinetics of β-lg (see Chapter 2). In the holder "sticking", unfolded β-lg is transformed into aggregated β-lg, which behaves as a more or less inert component. So the concentration of unfolded β-lg downstream of the holder is decreased, resulting in less deposits in the heat exchanger. It is obvious that the holder should be positioned in the heating trajectory before the maximum concentration of unfolded β-lg has been reached. At a low heating rate the concentration peak of unfolded β-lg and the related deposition rate of milk constituents is obtained at a relatively low temperature (see Chapter 3). Therefore the optimal holder temperature increases with heating rate. The plateau at 90.5 °C between a heating rate of 1 and 8 K/s has relation to the changing kinetics of β-lg at this temperature (see Chapter 2).

The optimal residence time of the additional holder is related to the total heat transfer surface, i.e. residence time of the UHT plant (see Figure 5.5). Too long

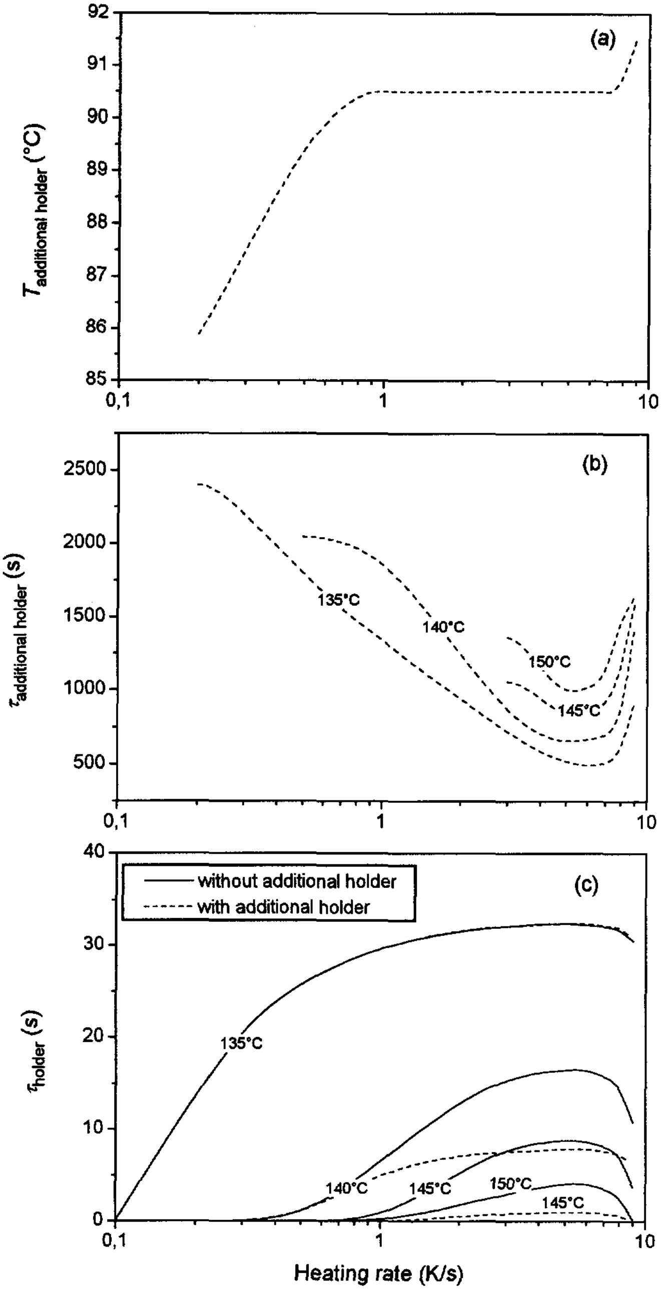


Figure 5.6a-c Optimization results: optimal values of the *control variables*, with and without additional holder

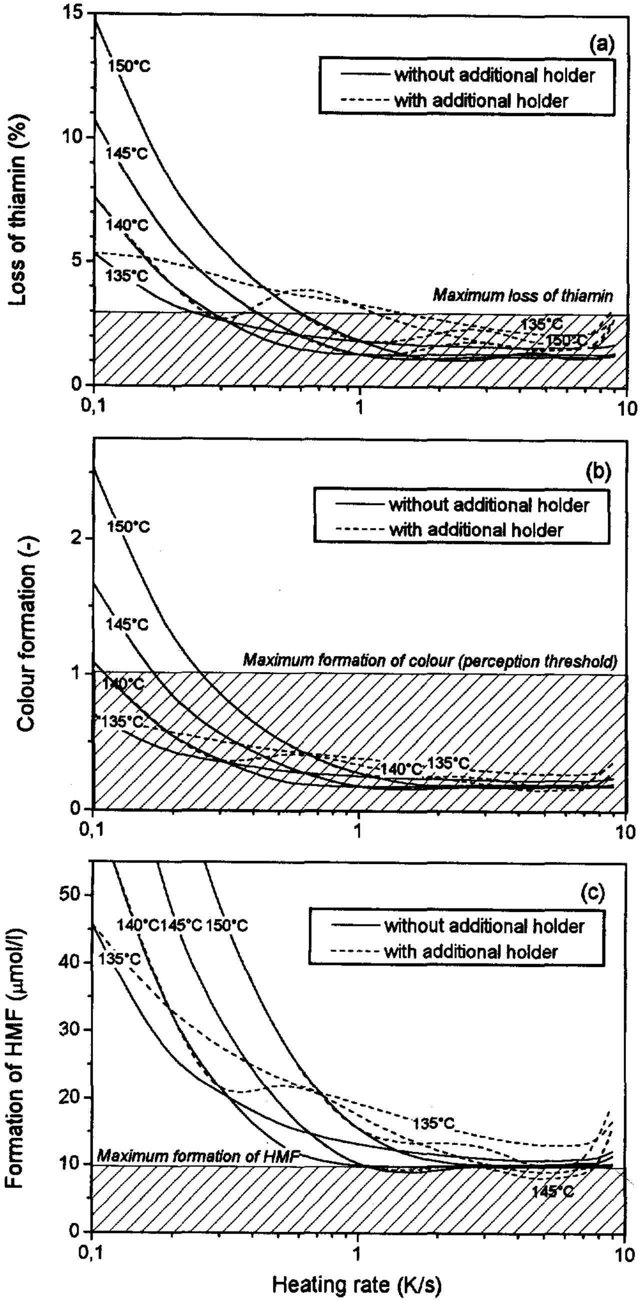


Figure 5.7a-c Optimization results: values of the *process variables*, with and without additional holder

residence times will result in an over-processed product. At relatively high UHT temperatures and low heating rates, no additional holders can be used because of exceeding the upper limits of the process variables, particularly the formation of HMF.

The required residence time at UHT temperature is governed by the desired destruction of spores. Figure 5.6c shows the required residence times to achieve at least 8 decimal reductions. At low heating rates, i.e. large residence times in the heater, a part of the destruction takes place in the heater, resulting in a shorter necessary residence time at UHT temperature. With an additional holder and a UHT temperature of 150 °C all the spores are destroyed in the heater and the first part of the cooler at any heating rate.

Process variables

Figure 5.7a-c show the transformation of the key-components at the optimal values of the control variables as a function of the UHT temperature and the heating rate, with and without an additional holder. The destruction of *B. stearothermophilus* spores was more than 8 decimal reductions in all cases.

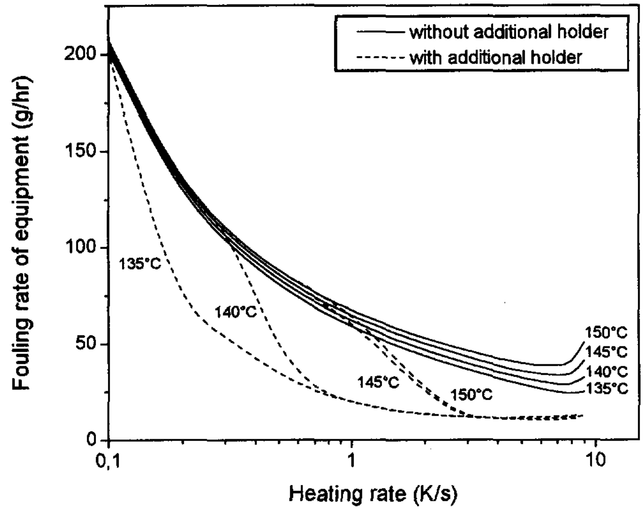


Figure 5.8 Optimization results: total fouling rate of the UHT plant (*process variable*), with and without additional holder

In general the transformations decrease with increasing heating rate as a result of the shorter residence times in the plant. Regarding the desired values of the process variables in Table 5.3, it can be concluded that the applicable heating rate is limited by the formation of HMF. Depending on the UHT temperature and the use of an additional holder, the heating rate should be higher than about 1 K/s. With an additional holder the lowest HMF concentration is obtained at a heating rate between 4 and 7 K/s and a UHT temperature of 145 °C. Under certain conditions the use of an additional holder increases the heat-induced transformations in the product. Particularly in the case of loss of thiamin the dashed lines lie above the continuous lines. However, between a heating of 4 and 7 K/s the maximum loss of 3 % is not exceeded.

The calculated fouling rate of the equipment is shown in Figure 5.8. Since the total heat transfer area is reduced by an increasing heating rate, the total fouling rate in the UHT plant also decreases with increasing heating rate. The total fouling is substantially reduced by the additional holder section. In the range of a heating rate of 4 to 7 K/s and a UHT temperature of 145 °C, fouling is reduced by more than 65 %.

5.3.4 Effect on operating costs

Figure 5.9 shows the operating costs of the UHT plant, expressed in Dutch guilders per (metric) ton of treated milk, as a function of the cost-related control variables. Taken into account are: depreciation of the plant, interest, energy costs, product losses, cleaning costs and costs of pollution. An extensive description of the method for calculation of the operating costs and the assumed charges are given in Appendix 5.III.

Considering the shape of the curves it is clear that the operating costs are most affected by the fouling rate and the size of the heat transfer area. Including the preceding optimization results it is possible to estimate the optimal process conditions of the UHT plant with respect to product quality and operating costs. From the point of view of operating costs an additional holder should be used and the heating rate in the heater should be about 4 K/s with an arbitrary UHT temperature. Combining this with the conclusions of the values of the process variables, especially the formation of HMF, the optimal heating rate is 4 K/s with a UHT temperature of 145 °C. From Figure 5.6a-c it follows that under these conditions the additional holder should have an operating temperature of 90.5 °C

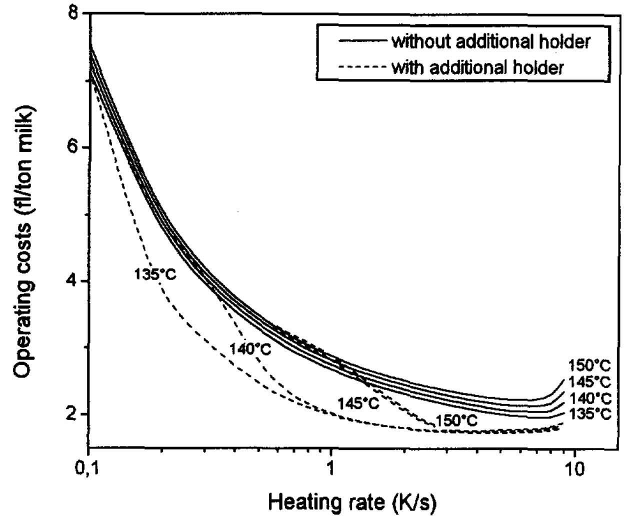


Figure 5.9 Optimization results: total operating costs of the UHT plant expressed in Dutch guilders per treated ton of milk, with and without additional holder

and a residence time of about 15 minutes. When the optimized UHT plant is compared to a number of conventional UHT plants without an additional holder [11], it is found that the operating costs are reduced by more than 50 %.

Regarding the relatively large volume of the additional holder (2500 litres), the use of a continuously stirred tank instead of a tubular holder may be recommended. The disadvantage of an increased residence time distribution by the tank has no effect on the microbial quality of the product, since the spores are destroyed downstream the additional holder.

5.4 Conclusions

The complex relation between process design and operation, operating costs and the product characteristics recognized by the consumer requires a systematic optimization approach. The described optimization method for heat treatment of milk and milk products turns out to be a useful method for defining the optimal design and operation of heat treatment equipment in the dairy industry. The main advantages of the method are the incorporation of deposit formation at heat transfer surfaces and the versatility with respect to the equipment design, supporting non-isothermal sections like heaters and coolers. The method also accounts for the relative importance of the individual heat-induced product transformations determining the product characteristics.

The optimization of a given industrial UHT plant demonstrates that this approach may result in a substantial (more than 50 %) reduction of the operating costs, without concessions to the product quality. In the plant described the milk should be heated to 145 °C with a heating rate of 4 K/s and minimum holding time at this temperature. An additional holder should be applied in the heater at an operating temperature of 90.5 °C and a residence time of about 15 minutes.

Notation

A	Area (m^2)
A_{spec}	Specific area (m^2·m^{-3})
c	Costs (fl·(unit of material)$^{-1}$)
C	Concentration (kg·m^{-3})
C_p	Heat capacity (J·kg^{-1}·K)
$\mathrm{F_{obj}}$	Objective function
$\mathrm{F'_{obj}}$	General objective function (fl·h^{-1})
i	Interest (%)
j	Costs (fl·h^{-1})
J	Operating costs (fl·yr^{-1})
J_{F}	Mass flux of adsorbing milk constituents (kg·m^{-2}·s)
L	Length (m)
n	Number
s	Plate distance (m)
t	Time (s)
T	Temperature (K)
$\mathbf{u}$	Vector of control variables
U	Heat transfer coefficient (W·m^{-2}·K)
v	Velocity (m·s^{-1})
w	Width (m)
x	Conversion (kg·kg^{-1})
x	Mass fraction (kg·kg^{-1})
$\mathbf{x}$	Vector of process variables, i.e. conversions
α	Vector of weight factors with respect to conversion of key-components
β	Weight factor with respect to deposition

ρ	Density ($kg \cdot m^{-3}$)
τ	Residence time of a reactor (s)
ϕ	Mass flow ($kg \cdot s^{-1}$)

Subscripts, indices and abbreviations

ch	Change-over (rinsing losses)
cl	Cleaning
CSTR	Continuous Stirred Tank Reactor
depr	Depreciation
des	Desired
emb	Embedded (section)
en	Energy
F	Aggregates of milk constituents
HLDR	Holder
IE	Inhabitant Equivalent
int	Interest
loss	Product losses
max	Maximum
min	Minimum
op	Operator
PFR	Plug Flow Reactor
PCP	Pfr - Cstr - Pfr
PHP	Pfr - Hldr - Pfr
pol	Pollution
prot	Protein
ref	Reference
run	Run (time), operating (time)
tot	Total
UHT	Ultra High Temperature
x	Process variable
0	Initial

References

1. C. Peri, E. Pagliarini & S. Pierucci. A study on optimizing heat treatment of milk, I. Pasteurization. *Milchwissenschaft* 43 (1988) 636-639.
2. E. Pagliarini, C. Peri & S. Pierucci. A study on optimizing heat treatment of milk, II. Sterilization. *Milchwissenschaft* 43 (1988) 720-722.

3. G.E. Arteaga, M.C. Vazquez-Arteaga & S. Nakai. Dynamic optimization of the heat treatment of milk. *Food Res. Int.* 27 (1994) 77-82.
4. J.J. Bimbenet. Food technology in relation to chemical engineering. In: Strategies 2000, Proceedings of the fourth world congress of chemical engineering, Ed. D. Behrens, Dechema, Frankfurt am Main (1992).
5. R. Hooke & T.A. Jeeves. Direct search solution of numerical and statistical problems. *J. Assn. Comp. Mach.* 8 (1961) 212-229.
6. B.D. Bunday & G.R. Garside. Optimization methods in Pascal. Edward Arnhold, London (1987).
7. H.G. Kessler. Lebensmittel- und Bioverfahrenstechnik; Molkereitechnologie. Kessler Verlag, Weihenstephan (1988).
8. T.E. Galesloot & F. Hassing, Continued investigations concerning the consistence of yoghurt. NIZO-report M7 (1973) p15-33.
9. W.H. Press, B.P. Flannery, S.A. Teukolsky & W.T. Vetterling. Numerical recipes in Pascal. Cambridge University Press, Cambridge (1990) p352.
10. H. Burton. Ultra-high-temperature processing of milk and milk products. Elsevier Applied Science, London (1988).
11. H. Reuter, H.G. Biewendt & M. Konietzko. Bewertung der thermischen Wirksamkeit von UHT-Anlagen. *Deutsche Molkereizeitung* 48 (1980) 1793-1798.

Appendix 5.I: The definition and evaluation of the objective function in the constrained search method

In this appendix an example of the definition of an objective function is given, based on the input window shown in Figure 5.3. The vectors $\mathbf{u}$ and $\mathbf{x}_{des}$ of equation (5.2) are then given by:

$$\mathbf{u} = \begin{bmatrix} \tau_{\mathrm{PHP,emb}} \\ T_{\mathrm{PHP,emb}} \\ T_{\mathrm{HLDR}} \end{bmatrix} \qquad \mathbf{x}_{des} = \begin{bmatrix} >8 \text{ dec.red.} \\ <1 \\ <3\ \% \\ <10\ \mu\text{mol/l} \end{bmatrix} \tag{5A.1}$$

with

$$\alpha = \begin{bmatrix} 25 \\ 5 \\ 5 \\ 5 \end{bmatrix} \ ; \quad \beta = 1 \tag{5A.2}$$

Since there are 3 control variables, the objective function has to be evaluated for $2^3 = 8$ basic vectors (see Figure 5.2):

$$\begin{array}{llll} \mathbf{u}_1 = \begin{bmatrix} 0 \\ 5 \\ 0 \end{bmatrix} & \mathbf{u}_2 = \begin{bmatrix} 0 \\ 5 \\ 20 \end{bmatrix} & \mathbf{u}_3 = \begin{bmatrix} 0 \\ 135 \\ 0 \end{bmatrix} & \mathbf{u}_4 = \begin{bmatrix} 0 \\ 135 \\ 20 \end{bmatrix} \\ \mathbf{u}_5 = \begin{bmatrix} 6000 \\ 5 \\ 0 \end{bmatrix} & \mathbf{u}_6 = \begin{bmatrix} 6000 \\ 5 \\ 20 \end{bmatrix} & \mathbf{u}_7 = \begin{bmatrix} 6000 \\ 135 \\ 0 \end{bmatrix} & \mathbf{u}_8 = \begin{bmatrix} 6000 \\ 135 \\ 20 \end{bmatrix} \end{array} \tag{5A.3}$$

where each basic vector contains a combination of upper and lower limits of the control variables.

Next the initial base point of the optimization can be calculated from the weighted centre of the basic vectors:

$$\mathbf{u}_{base} = \begin{bmatrix} 0 + \dfrac{F_{obj}(\mathbf{u}_{1,2,3,4},\mathbf{x})}{F_{obj}(\mathbf{u}_{1..8},\mathbf{x})} \cdot (6000 - 0) \\ 5 + \dfrac{F_{obj}(\mathbf{u}_{1,2,5,6},\mathbf{x})}{F_{obj}(\mathbf{u}_{1..8},\mathbf{x})} \cdot (135 - 5) \\ 0 + \dfrac{F_{obj}(\mathbf{u}_{1,3,5,7},\mathbf{x})}{F_{obj}(\mathbf{u}_{1..8},\mathbf{x})} \cdot (20 - 0) \end{bmatrix} \tag{5A.4}$$

Another possibility is to select the basic vector with the lowest value of the objective function as the initial base point.

Appendix 5.II: Calculation of the heat transfer area of the UHT plant

The size of the heat transfer area of the heater is determined by the heating rate and the UHT temperature (see also the legend of Figure 5.5). The residence time of the heater follows from:

$$\tau_{\text{heater}} = \frac{T_{\text{UHT}} - 5°C}{\dot{T}} \tag{5A.5}$$

with $\dot{T}$ the heating rate.
The heat transfer area of the heater is given by:

$$A_{\text{heater}} = 2\,n_{\text{plates}} L_{\text{plate}} w_{\text{plate}} \tag{5A.6}$$

with

$$n_{\text{plates}} L_{\text{plate}} = \tau_{\text{heater}} v_{\text{milk}} \tag{5A.7}$$

and

$$w_{\text{plate}} = \frac{\phi_{\text{milk}}}{\rho_{\text{milk}} v_{\text{milk}} s_{\text{plate}}} \tag{5A.8}$$

Substitution of (5A.7) and (5A.8) in (5A.6) results in

$$A_{\text{heater}} = 2 \cdot \frac{\tau_{\text{heater}} \phi_{\text{milk}}}{\rho_{\text{milk}} s_{\text{plate}}} \tag{5A.9}$$

with s_{plate} the plate distance (= 0.008 m).
With $\phi_{\text{milk}} = \phi_{\text{water}}$, the water temperatures follow from the heat balances:

$$(\phi C_p)_{\text{milk}} (T_{\text{UHT}} - 5°C) = (\phi C_p)_{\text{water}} (T_{\text{water},0} - T_{\text{water},1}) \tag{5A.10}$$

$$(\phi C_p)_{\text{milk}} (40°C - T_{\text{UHT}}) = (\phi C_p)_{\text{water}} (T_{\text{water},1} - T_{\text{water},2}) \tag{5A.11}$$

$$UA_{\text{heater}} \frac{1}{2} \left[(T_{\text{water},0} - T_{\text{UHT}}) + (T_{\text{water},1} - 5°C) \right] = (\phi C_p)_{\text{milk}} (T_{\text{UHT}} - 5°C) \tag{5A.12}$$

where $T_{\text{water},0}$, $T_{\text{water},1}$ and $T_{\text{water},2}$ are the water temperatures at the inlet of the heater, the outlet of the heater and the outlet of the cooler, respectively (see Figure 5.4). The heat transfer surface of the cooler is given by the heat balance of the cooler:

$$UA_{\text{cooler}}\frac{1}{2}\left[\left(T_{\text{water},2} - T_{\text{UHT}}\right) + \left(40°\text{C} - T_{\text{water},1}\right)\right] = \left(\phi C_p\right)_{\text{milk}}\left(T_{\text{UHT}} - 40°\text{C}\right) \tag{5A.13}$$

Appendix 5.III: Method for calculation of the operating costs

Table 5.5 Assumed constants and charges with respect to operating costs of a UHT plant

Description	Value		Symbol
Charges			
I.E. (Inhabitant Equivalent)	60	$fl \cdot year^{-1}$	j_{IE}
Steam	22.50	$fl \cdot ton^{-1}$	c_{steam}
Overall equipment costs	1000	$fl \cdot m^{-2}$	c_A
Milk	0.80	$fl \cdot kg^{-1}$	c_{milk}
Energy, water, cleaning agent during cleaning			
Product change over (rinsing losses)	2.10	$fl \cdot h^{-1}$	$j_{cl,en}$
Operator costs during cleaning	2.30	$fl \cdot h^{-1}$	$j_{cl,ch}$
Depreciation of cleaning equipment	6	$fl \cdot h^{-1}$	$j_{cl,op}$
Interest	6	$fl \cdot h^{-1}$	$j_{cl,depr}$
	8	$\% \cdot year^{-1}$	i
Process conditions			
Milk flow	10	$ton \cdot h^{-1}$	-
Annual operation time	5000	$h \cdot year^{-1}$	t_{year}
Cleaning time per run	2.5	h	t_{cl}
Overall heat transfer coefficient	4000	$W \cdot m^{-2} \cdot K^{-1}$	-
Reference fouling rate of equipment (t_{run} = 10 h)	80	$g \cdot h^{-1}$	$\phi_{F,ref}$
Others			
Protein fraction in deposits	0.6	-	$x_{prot,F}$
Protein fraction in milk	0.033	-	$x_{prot,milk}$
Number of I.E.'s per kg of deposits	18	$(kg\ deposit)^{-1}$	n_{IE}
Depreciation of UHT plant	10	year	t_{depr}

The assumed constants, charges and their notation with respect to the operating costs are given in Table 5.5. The total operating costs per year of a UHT plant are divided into six parts: costs of depreciation of the UHT equipment, interest, costs of product losses, costs of cleaning, costs of pollution and costs of steam, respectively:

$$J_{total} = J_{depr} + J_{int} + J_{loss} + J_{cl} + J_{pol} + J_{steam} \tag{5A.14}$$

where

$$J_{depr} = (A_{heater} + A_{cooler}) \cdot \frac{c_A}{t_{depr}} \tag{5A.15}$$

$$J_{int} = (A_{heater} + A_{cooler}) \cdot \frac{0.5 \cdot i}{100} \cdot c_A \tag{5A.16}$$

$$J_{loss} = \phi_F \cdot t_{year} \cdot \frac{x_{prot,F}}{x_{prot,milk}} \cdot c_{milk} \tag{5A.17}$$

$$J_{cl} = \frac{t_{year}}{t_{run}} \cdot t_{cl} \cdot (j_{cl,en} + j_{cl,ch} + j_{cl,op} + j_{cl,depr}) \quad (t_{run} \leq 25 \text{ h}) \tag{5A.18}$$

$$J_{pol} = \phi_F \cdot t_{year} \cdot \frac{n_{IE} \cdot j_{IE}}{365} \tag{5A.19}$$

$$J_{steam} = \phi_{steam} \cdot t_{year} \cdot c_{steam} \tag{5A.20}$$

with

$$t_{run} = \frac{\phi_{F,ref}}{\phi_F} \cdot t_{ref} \tag{5A.21}$$

where t_{ref} is taken as 10 h. The deposition rate of the UHT plant, ϕ_F, includes the deposition rate of the holder sections. To avoid unrealistically long calculated operating times the maximum of the operating time was set to 25 hours. Longer operating times are not applied in the dairy industry because of possible bacterial growth in the equipment.

The operating costs can be expressed in costs per (metric) ton of treated milk by dividing the total costs by the annual production.

Chapter 6

Performance of a direct heating system

Abstract

This chapter presents the results of experiments with a commercial infuser in which jets of milk were heated. A mathematical model is developed to describe the heat and mass transfer from steam to milk in the presence of air. The model showed reasonable agreement with the experimental results and is used for quantitative interpretation of the experimental results.

With the infuser it was possible to increase and decrease successively the temperature of the milk by more than 90 K within one second. Air accumulation within the bundle of jets turned out to be related to the number of jets and had a negative effect on the heating rate. Comparing the denaturation measurements of whey proteins with recent results of other authors indicated that the heat treatment of the infuser investigated is more gentle and gives less damage to the product than a steam injection plant. Fouling of the distribution device could be avoided if the initial Reynolds number of the milk jets was over 10 000.

6.1 Introduction

In general, high heating and cooling rates and short residence times of holder sections in pasteurization and sterilization equipment result in a high quality and a long shelf-life of the dairy product [1, 2]. In other words, an optimal selectivity of desired conversions (e.g., destruction of bacteria) over undesired conversions (e.g., loss of vitamins) is then obtained. Theoretically it is possible to inactivate a certain micro-organism without other chemical or physical conversions like for instance protein denaturation. The well-known UHT (Ultra-High-Temperature) procedure is based on this principle (see Chapters 1 and 5).

The highest heating rates can be reached by direct heating systems: injection of steam into the product or distribution of milk in a steam vessel, i.e. steam infusion. Other advantages of direct heating systems are their ability to process more viscous products, particularly those that cannot satisfactorily be handled in plate heat exchangers, and their comparative freedom of fouling. Burton [3] suggests that the heating process is gentler with steam infusers than with steam injectors, since steam infusion does not involve condensation of vapour bubbles and associated implosion of cavities. Besides, energy can be recovered by coupling of two or more infusers in series.

Esnouf & Mansour [4] used the steam injection process to obtain a temperature rise from 80 °C to 160 °C in 0.15 s. The milk they treated had organoleptic properties close to those of pasteurized milk. The whey protein denaturation was, however, higher than expected.

This chapter presents the results of experiments with a commercial infuser in which jets of milk were heated. A mathematical model is developed to describe the heat and mass transfer from steam to milk. The model is used for quantitative interpretation of the experimental results. The results of the protein denaturation measurements are compared with those of Esnouf & Mansour [4].

6.2 Mathematical model for heat and mass transfer

6.2.1 Problem definition and assumptions

Figure 6.1 shows a schematic representation of the infuser system. In most cases there is a steam pressure vessel with a conical base in which the heated product is collected. Depending on the distribution method used, the product passes

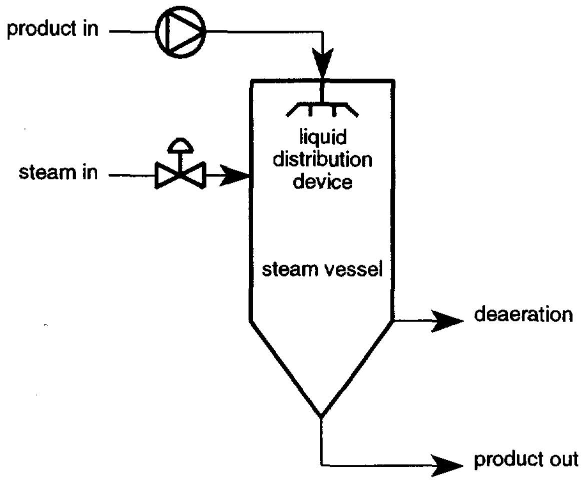


Figure 6.1 Scheme of the infuser system

downwards as a film, as a jet or as droplets through the steam atmosphere. Most of the research in this area has focused on the condensation of steam from steam-air mixtures on single water droplets, resulting in very complex models [5, 6, 7]. The temperature responses were best described by a model in which it is assumed that the liquid in the droplets is partially mixed [6].

In this study the rate of heat transfer is predicted for a bundle of free-falling jets in a mixture of steam and air as schematically shown in Figure 6.2. In case of an effective deaeration of the vessel, the concentration of air outside the bundle of jets is assumed to be negligible. However, within the bundle air might be accumulated as a result of restricted deaeration of the liquid due to the configuration of jets and the steam flux towards the bundle.

Heat transfer to one jet

The rate of heat transfer to a jet is equal to the increase of enthalpy of the jet:

$$q_t A_j = \frac{d(v_j V_j \rho_L C_{pL} T_L)}{dx} \tag{6.1}$$

It has been proved that in this type of heat transfer problems the internal resistance to heat transfer is so low that it can be ignored [5]. This assumption implies that

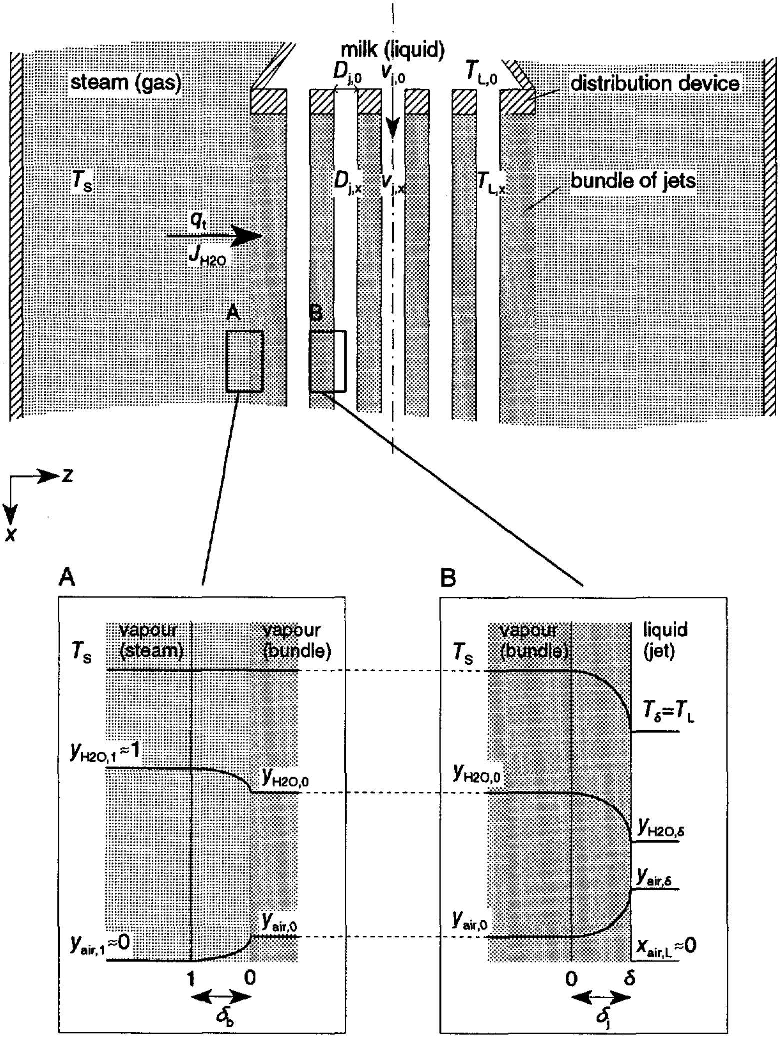


Figure 6.2 Scheme of the proposed model for simultaneous heat and mass transfer by steam condensation on a bundle of free-falling jets

there is no temperature gradient within the jet.

The total heat release at the interface, q_t, is equal to the sum of q_s and the latent heat of condensation at the interface:

$$q_t = q_s + h_v J_{H_2O} \tag{6.2}$$

Mass transfer occurs simultaneously with the transfer of heat as a result of the imposed temperature difference and the absorption of heat by condensation of steam. Assuming that no absorption of air occurs, the local total mass transfer through a boundary layer with thickness δ_j (see Figure 6.2) is given by the following equation [8]:

$$J_{H_2O} = Ck_j \int_{y_{H_2O,\delta}}^{y_{H_2O,0}} \frac{dy_{H_2O}}{y_{air}} = Ck_j \ln\left[\frac{1 - y_{H_2O,\delta}}{1 - y_{H_2O,0}}\right] \tag{6.3}$$

By approximation, for small gradients equation (6.3) can be simplified to [9]:

$$J_{H_2O} = \frac{Ck_j}{\overline{y}_{air}}\left(y_{H_2O,0} - y_{H_2O,\delta}\right) \tag{6.4}$$

where $\overline{y}_{air}$ is the average air fraction in the boundary layer.

As a result of the temperature difference, there is a heat flux described by the ordinary heat transfer coefficient α in the absence of mass transfer. In terms of the film theory this heat flux is $\lambda(-dT/dz)$, with $\lambda = \alpha\delta_j$. The local sensible heat flux q_s to the interface includes the sensible heat as a result of the decrease in temperature of the water vapour passing the film:

$$q_s = \lambda\left[-\frac{dT}{dz}\right] + J_{H_2O} C_{p,H_2O}(T_0 - T_\delta) \tag{6.5}$$

Rearranging with $\lambda = \alpha\delta_j$:

$$-\frac{1}{\alpha\delta_j}\int_{\delta}^{0}\mathrm{d}z = \int_{T_\delta}^{T_0}\frac{\mathrm{d}T}{q_s - J_{H_2O}C_{p,H_2O}(T - T_\delta)} \tag{6.6}$$

and integrating [8]:

$$q_s = \frac{J_{H_2O}C_{p,H_2O}}{1 - \exp\left[\dfrac{-J_{H_2O}C_{p,H_2O}}{\alpha}\right]}(T_0 - T_\delta) \tag{6.7}$$

The first term after the equal sign in equation (6.7) may be considered as a heat transfer coefficient corrected for mass transfer.

Substitution of equations (6.7) and (6.2) into equation (6.1) with $A_j/V_j = 4/d_j$ and $T_L = T_\delta$ gives:

$$\frac{\mathrm{d}T_L}{\mathrm{d}x} = \frac{4}{\rho_L C_{pL} v_j d_j}\left[\frac{J_{H_2O}C_{p,H_2O}}{1 - \exp\left(-J_{H_2O}C_{p,H_2O}/\alpha\right)}(T_0 - T_L) + h_v J_{H_2O}\right] \tag{6.8}$$

where

$$v_j = \sqrt{v_0^2 + 2gx} \tag{6.9}$$

At a given increase of the liquid temperature the air fraction between the jets $(1 - y_{H_2O,0})$ can be calculated. Appendix 6.1 gives a more detailed description of the calculation method.

Heat transfer to the bundle of jets

Assuming that the air fraction outside the bundle of jets is negligible, the steam flux towards the bundle jets can be described by

$$J_{H_2O,b} = k_b C\left(1 - y_{H_2O,0}\right) \tag{6.10}$$

where the reciprocal of k_b represents the resistance of the bundle of jets to mass transfer.

6.2.2 Heat and mass transfer coefficients

Heat transfer to one jet

The heat transfer coefficient α and the mass transfer coefficient k_j of the gas phase are described by experimental correlations, expressed in the dimensionless groups of Nusselt and Sherwood. The analogy expressed in terms of the Nusselt and Sherwood numbers is reported as [8]:

$$Nu \text{ or } Sh = 0.023 Re^{0.8} (Pr \text{ or } Sc)^{0.33} \tag{6.11}$$

where

$$Nu = \frac{\alpha d_j}{\lambda_{H_2O}} \tag{6.12}$$

$$Sh = \frac{k_j d_j}{D_{AB}} \tag{6.13}$$

To estimate the diffusion coefficient D_{AB} the Fuller, Schettler and Giddings relation is used [10]:

$$D_{AB} = \frac{0.01\, T^{\frac{7}{4}} \left[\dfrac{M_{H_2O} + M_{air}}{M_{H_2O} M_{air}} \right]^{\frac{1}{2}}}{p_t \left[v_{H_2O}^{\frac{1}{3}} + v_{air}^{\frac{1}{3}} \right]^2} \tag{6.14}$$

where p_t is the total pressure of the gas mixture.

Heat transfer to the bundle of jets

To quantify the mass transfer coefficient for the transport of steam to the bundle of jets (k_b) a modified Sherwood relationship is used:

$$Sh_b = a \cdot Re_b^{\,b} \cdot n_j^{\,c} \tag{6.15}$$

where

$$Sh_\mathrm{b} = \frac{k_\mathrm{b}\overline{d}_\mathrm{j}n_\mathrm{j,outer}}{\overline{D_\mathrm{AB}}} \tag{6.16}$$

and

$$Re_\mathrm{b} = \frac{\overline{\rho_\mathrm{s} v_\mathrm{s} d_\mathrm{j}}\, n_\mathrm{j,outer}}{\overline{\eta}_\mathrm{s}} \tag{6.17}$$

averaged over the length of the jets. The coefficients *a*, *b* and *c* are unknown and have to estimated from experimental results. It is known that for gas flow perpendicular to a cylinder, *b* is about 0.6 [8]. Besides it is expected that the number of jets will affect the resistance to mass transfer and deaeration of accumulated air within the bundle of jets.

6.3 Materials and methods

6.3.1 Experimental set-up

The experiments were carried out with preheated skim milk (10 s at 65 °C) on a commercial infuser system. The nominal capacity was 2500 l/h and the maximum pressure in the vessel was 8.5 bar. The arrangement of the experimental set-up is shown in Figure 6.3. The milk was heated in two preheaters from 5 °C to the desired inlet temperature of the infuser, which was varied between 45 and 70 °C. In the infuser the product is split into a number of jets and passes downwards through the steam atmosphere within 0.4 to 0.6 s, depending on the flow rate of the milk and the liquid level in the cone. To reduce the degree of protein denaturation, during the experiments the holding time after infusion was minimized to less than 0.5 s by maintaining a low level in the cone of the infuser and reduction of the length of the connection tube to the expansion vessel. The cone of the infuser vessel, where milk contacts the wall, could be cooled with water. The cooling time of milk during instantaneous flashing to about 70 °C in the expansion vessel was assumed to be negligible.

Table 6.1 gives a survey of the process conditions of the experiments. During one experiment the temperatures were measured continuously by PT-100 elements. The thermal efficiency was defined as:

$$\vartheta = \frac{T_L - T_{L,0}}{T_s - T_{L,0}} \tag{6.18}$$

Samples were taken from two local sampling devices and cooled immediately. Each process condition was held for at least 45 minutes. After a series of experiments the infuser system was rinsed with water, dismantled, visually inspected for fouling and cleaned by a CIP-installation (Cleaning-In-Place).

6.3.2 Analyses

From each sample the following data were collected:

- Degree of denaturation of the whey proteins immunoglobulin, bovine serum albumin, β-lactoglobulin and α-lactalbumin separated by high performance gel

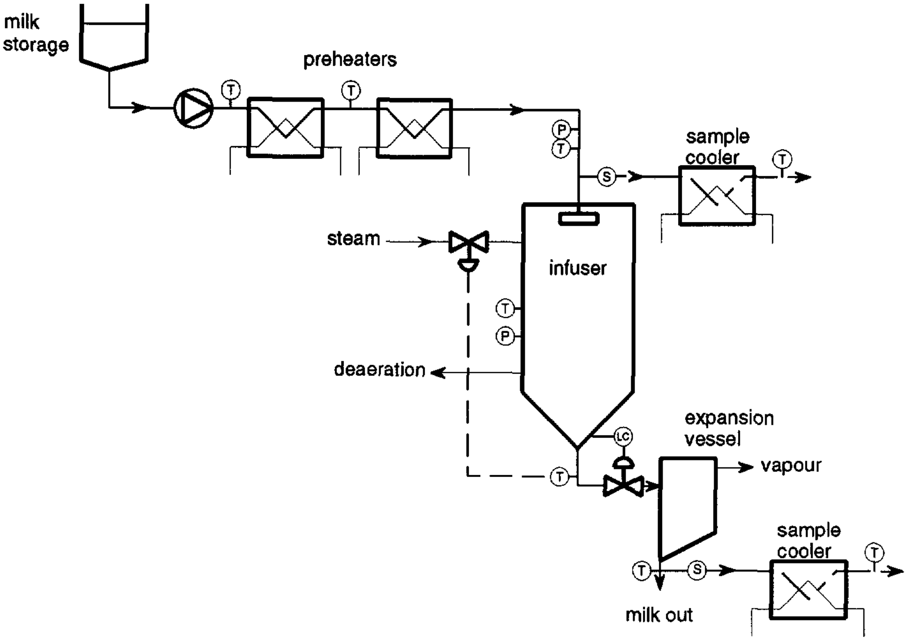


Figure 6.3 Arrangement of the experimental infuser plant; P = pressure transmitter, S = sampling device, T = temperature transmitter (PT 100)

Table 6.1 Process conditions of the infuser during the experiments (for explanation of symbols, see Notation)

Exp.	ϕ (m^3/h)	n_j	$d_{j,0}$ (mm)	t_{inf} (s)	t_{hold} (s)	$T_{L,0}$ (°C)	$T_{L,out}$ (°C)	T_s (°C)	ϑ
1	1.5	65	3.9	0.66^a	1.74	65.8	100.5	103.0	0.93
2	1.5	26	3.9	0.58	1.56	66.0	140.0	141.0	0.99
3	1.5	26	3.9	0.58	1.66	66.0	119.6	121.1	0.97
4^b	1.5	26	3.9	0.52	23.31	66.0	100.4	108.8	0.80
5	2.5	26	3.9	0.52	1.02	65.9	136.8	140.4	0.95
6	2.5	26	3.9	0.50	2.66	65.9	131.4	139.0	0.90
7	2.5	26	3.9	0.48	4.75	65.9	128.6	135.2	0.90
8	2.5	26	3.9	0.48	6.21	66.2	119.3	126.4	0.88
9	2.5	26	3.9	0.49	4.45	65.8	109.0	116.3	0.85
10^b	2.5	26	3.9	0.52	1.13	65.9	98.8	107.9	0.78
11	1.5	26	3.9	0.56^a	6.94	48.6	78.9	85.1	0.83
12	1.5	26	3.9	0.59^a	2.42	48.1	83.3	87.1	0.90
13	1.5	26	3.9	0.59^a	2.39	48.6	89.3	91.3	0.95
14	1.5	26	3.9	0.59^a	2.35	48.1	94.3	95.1	0.98
15	1.5	26	3.9	0.58^a	2.37	51.5	94.4	96.6	0.95
16	1.5	26	3.9	0.59^a	2.19	48.4	120.6	120.8	1.00
17^b	1.5	26	3.9	0.59^a	2.06	48.4	139.8	140.9	0.99
18	2.5	26	3.9	0.52	1.43	65.1	119.1	126.2	0.88
19	2.5	26	3.9	0.52	1.43	65.2	118.8	124.8	0.90
20^b	2.5	26	3.9	0.49	3.95	65.2	118.9	126.6	0.88
21	2.5	26	3.9	0.52	1.37	65.3	134.6	138.0	0.95
22	2.5	26	3.9	0.52	1.40	65.3	128.3	135.9	0.89
23^b	2.5	26	3.9	0.52	1.40	65.2	129.4	136.5	0.90
24	2.5	72	2.5	0.54	1.01	46.6	99.0	106.6	0.87
25^b	2.5	72	2.5	0.54	1.02	46.9	99.2	105.3	0.90
26	2.5	72	2.5	0.54	1.00	65.5	118.0	123.2	0.91
27^b	2.5	72	2.5	0.53	1.06	65.6	118.8	123.5	0.92
28	2.5	26	3.9	0.52	0.50	70.5	129.3	131.4	0.97
29	2.5	26	3.9	0.52	0.49	70.2	138.6	145.0	0.92
30	2.5	26	3.9	0.52	0.48	70.5	149.5	156.0	0.92
31	2.5	26	3.9	0.52	0.50	70.3	158.4	163.8	0.94
32^b	2.5	26	3.9	0.51	0.69	70.3	168.5	173.7	0.95
33	2.5	13	3.9	0.39	0.51	70.6	128.1	135.1	0.89
34	2.5	13	3.9	0.39	0.50	70.7	138.6	143.8	0.93
35	2.5	13	3.9	0.39	0.48	70.5	147.9	153.7	0.93
36	2.5	13	3.9	0.39	0.47	70.3	159.1	161.1	0.98
37^b	2.5	13	3.9	0.39	0.46	70.8	168.4	171.1	0.97

[a] The actual time would be higher than calculated because of fouling of the distribution device resulting in diverging jets.

[b] Last experiment of a series.

permeation chromatography (HP-GPC) at pH 6.7 as described by De Wit and Klarenbeek [11]. The determined degrees of denaturation were adjusted for the normal concentration of total solids in skim milk (9 %).

- Amount of total solids in the samples.

After some experiments, deposits from the infuser system were analysed for the amount of calcium, phosphorus and proteins.

6.4 Results and discussion

6.4.1 Heat and mass transfer

Effect of flow characteristics

During the experiments it was observed that after about 0.2 m the jet surface became irregular but the jets did not break up into droplets. Therefore the milk flow is considered as a number of jets, as mentioned above. It is assumed that due to turbulence induced in the distribution device, the jets are ideally mixed (5 000 < $Re_{L,0}$ < 35 000) with a negligible internal heat resistance. This statement is supported by Figure 6.4. Although there is an external resistance due to simulta-

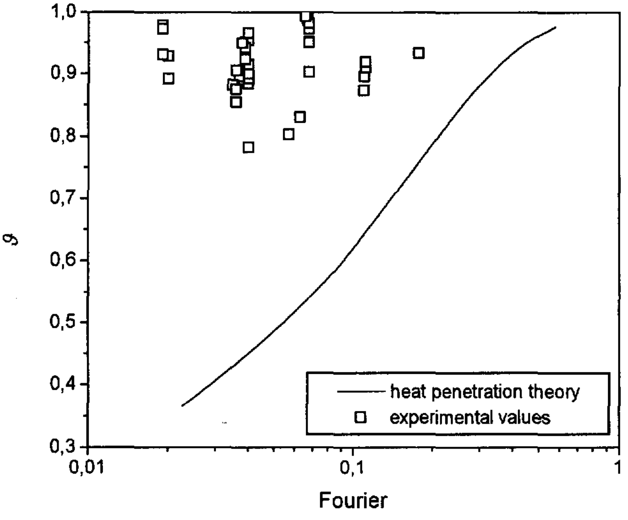


Figure 6.4 Thermal efficiency (ϑ) as a function of Fourier number; theoretical heat penetration considering the jets as an infinite cylinder

neous heat and mass transfer, the heating rate in the infuser turns out to be much higher than according to the conventional heat penetration theory in a stagnant cylinder [12] under ideal conditions, i.e. no external heat resistance. This confirms the internal mixing in the jet.

The high degree of internal mixing of the jets has two important consequences. Firstly the heating rate in the infuser will be high in comparison with the heating rate in droplets with less turbulence and partial internal mixing [6]. Secondly there is no radial conversion gradient of heat-sensitive milk components. Each volume element of milk has the same temperature-time history, which is important for adequate destruction of micro-organisms [13].

Effect of air (inert) accumulation

Under operating conditions the infuser vessel was continuously deaerated and the initial air concentration of milk ($x_{\mathrm{air,L}}$) was less than $5 \cdot 10^{-5}$; the desorption of air out of the heated milk was less than 1 percent of the steam flux to the interface. This means that the air fraction in the infuser vessel was very small and not detectable by pressure measurements. However, within a bundle of jets the air fraction of the gas phase might be substantially higher due to the accumulation of

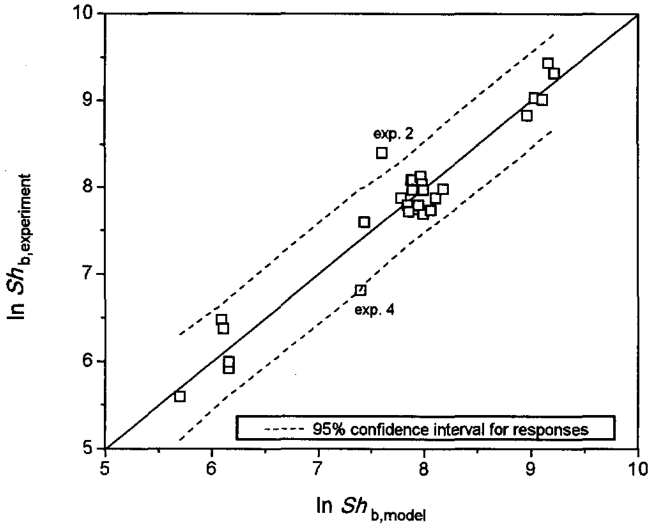


Figure 6.5 Correlation between Sh_b according to the experimental results and to the model; experiments with fouled distribution device were rejected

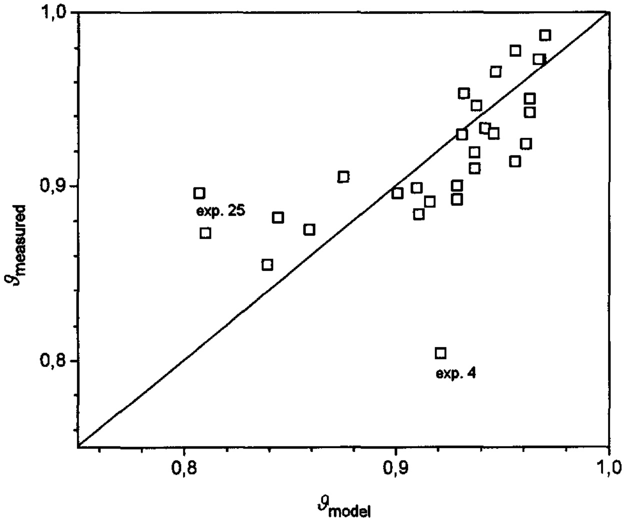


Figure 6.6 Comparison between the thermal efficiency (ϑ) measured and calculated with the model

air between the jets, i.e. air is trapped by the steam flow to the jet surface. In addition, the flow of steam together with traces of air may cause a local higher concentration of air within the bundle of jets due to steam condensation (see also Figure 6.2).

To quantify the air fraction in the boundary layer around the jets, the unknown value of $y_{H_2O,0}$ in equation (6.3) was calculated from the measured heat pick-up during the experiments. With this value of $y_{H_2O,0}$ the mass transfer coefficient of the bundle of jets (k_b), given by equation (6.10), could be calculated and fitted to the Sherwood relation given by equation (6.15):

$$Sh_b = 1280.5 n_j^{-0.83} Re_b^{0.58} \tag{6.19}$$

As shown in Figure 6.5 there was a good correlation (R_d^2 = 0.937) between the Reynolds number the number of jets and the Sherwood number calculated from the experiments. Obviously accumulation of air increases with the number of jets. This indicates that a more effective deaeration, e.g. positioned within the centre of the bundle of jets, would considerably increase the combined heat and mass transfer rate. As a result of the process conditions during the experiments, the variation of the Schmidt number was too small (0.6-0.9) to establish a correlation with the

Sherwood number. The power of the Reynolds number (0.58) is very close to data reported in literature [8].

Figure 6.6 shows a comparison between the thermal efficiencies measured and calculated with the heat and mass transfer model developed. Especially at values above 0.9, the thermal efficiency is properly estimated by the model.

6.4.2 Denaturation of whey proteins

In Table 6.2 the results of the analyses by HP-GPC are summarized. The degree of denaturation of the whey protein fractions in milk at the infuser inlet and after the expansion vessel is shown. The measured values were adjusted to content of total solids in skim milk (9 %). The measured initial concentrations of the whey proteins fractions were:

- Immunoglobulin (Ig) 0.58 - 0.66 g/l;
- Bovine Serum Albumin (BSA) 0.26 - 0.29 g/l;
- β-Lactoglobulin (β-lg) 3.62 - 3.86 g/l;
- α-Lactalbumin (α-la) 1.20 - 1.23 g/l.

The concentration of proteose-peptone was taken as 0.6 g/l [4].

To evaluate the results, the measured degrees of denaturation were compared with the calculated degrees of denaturation based on the kinetic data given in Chapter 1 (Ig, BSA, α-la) and 2 (β-lg). The low denaturation level at the inlet of the infuser was confirmed by the calculated values, which did not exceed 1 percent. In Figure 6.7 determined degrees of denaturation of the whey protein fractions after the expansion vessel are plotted against the calculated values. Figure 6.7d shows a substantial underestimation of the denaturation of α-la by the kinetic models. Better agreement was obtained with β-lg and BSA, although the points were scattered. This suggests that the underestimation in case of the α-la is not only due to experimental inaccuracies but also to incorrect kinetic data.

Although the scatter of estimates of denaturation of the whey proteins may be due to invalidity of the relative kinetic data, especially at high temperatures, other facts may also play a role. At high temperatures a slight increase in residence time may occur by diverging jets or deposit formation at the cone of the infuser vessel. This would cause a considerably higher extent of denaturation with the high denaturation rates at those high temperatures. For example, an increase in residence time in the infuser by 0.5 s at a temperature of 160 °C would result in about 25 % more denaturation of β-lg.

Table 6.2 Measured denaturation of whey proteins (-, protein not present, more than 90 % denatured)

Exp.	Infuser inlet					Expansion vessel outlet				
	Ig (%)	BSA (%)	β-lg (%)	α-la (%)	total (%)	Ig (%)	BSA (%)	β-lg (%)	α-la (%)	total (%)
1	8.0	11.6	3.4	0.5	3.3	-	39.1	29.7	0.2	27.2
2	0.0	1.9	2.9	0.0	1.8	-	39.1	31.8	0.0	28.4
3	0.0	0.1	2.1	0.0	1.2	-	32.7	26.1	0.0	24.8
4	0.0	6.0	3.8	0.5	2.5	-	54.2	51.8	9.5	42.4
5	0.0	1.8	5.6	3.5	4.0	-	40.5	29.9	3.9	28.1
6	0.0	0.0	3.4	3.2	2.6	-	29.8	32.0	4.3	28.9
7	0.5	6.3	4.0	0.9	2.8	-	54.3	58.8	12.4	47.1
8	0.0	0.0	4.4	1.1	2.8	-	54.6	58.5	13.6	47.1
9	0.0	0.0	4.4	1.6	2.9	-	45.5	54.7	8.2	43.6
10	0.0	0.0	4.3	1.2	2.7	-	-	-	-	-
11	1.9	1.4	0.3	0.0	0.4	17.8	11.3	7.0	0.0	6.3
12	2.5	1.8	1.3	0.0	1.1	39.2	16.6	11.4	0.0	11.2
13	2.2	1.5	1.0	0.0	0.8	41.2	18.3	10.0	0.0	10.6
14	0.4	0.0	0.0	0.0	0.0	-	20.5	12.5	0.0	16.8
15	0.0	0.0	0.0	0.0	0.0	-	23.8	16.2	0.0	19.2
16	2.7	1.5	0.5	0.0	0.6	-	28.9	32.1	0.0	28.7
17	0.8	0.0	0.8	0.0	0.5	-	37.9	42.6	15.3	38.0
18	5.9	8.4	2.3	0.0	2.3	-	58.6	37.5	2.6	33.3
19	5.6	7.1	1.1	0.8	1.7	-	48.8	28.6	1.4	27.4
20	6.6	8.6	1.6	0.7	2.1	-	60.5	52.5	7.6	43.0
21	5.4	8.6	1.4	0.6	1.8	-	56.8	43.8	4.8	37.2
22	5.6	7.2	0.7	0.0	1.2	-	53.9	36.8	3.3	32.8
23	6.8	8.6	1.7	1.2	2.2	-	52.6	36.6	1.4	32.2
24	0.9	0.0	0.4	0.1	0.3	-	44.4	25.4	0.7	25.1
25	2.0	0.0	0.1	0.0	0.2	-	43.6	21.0	1.7	22.7
26	7.1	9.4	3.6	1.1	3.4	-	43.6	24.1	1.3	24.4
27	6.0	8.5	3.6	1.0	3.2	-	59.1	53.0	9.7	43.5
28	15.6	7.9	4.6	0.0	4.5	83.7	35.2	19.6	2.6	21.8
29	16.4	8.8	4.8	0.8	5.0	81.0	64.9	69.9	27.1	56.0
30	18.0	8.5	4.2	0.0	4.6	85.8	68.5	73.2	40.9	61.2
31	16.1	8.7	3.8	0.0	4.2	-	-	-	-	-
32	18.3	11.7	4.6	2.1	5.4	78.6	-	73.7	39.9	60.4
33	17.9	12.0	5.0	1.7	5.5	-	-	-	-	-
34	16.6	9.9	4.8	1.5	5.1	81.5	-	53.5	11.3	43.1
35	19.5	10.9	6.3	2.5	6.5	-	-	33.7	3.8	30.8
36	17.3	8.2	3.3	0.2	4.0	80.5	-	43.9	7.9	36.6
37	18.8	8.3	3.7	0.0	4.4	-	-	76.3	43.6	63.7

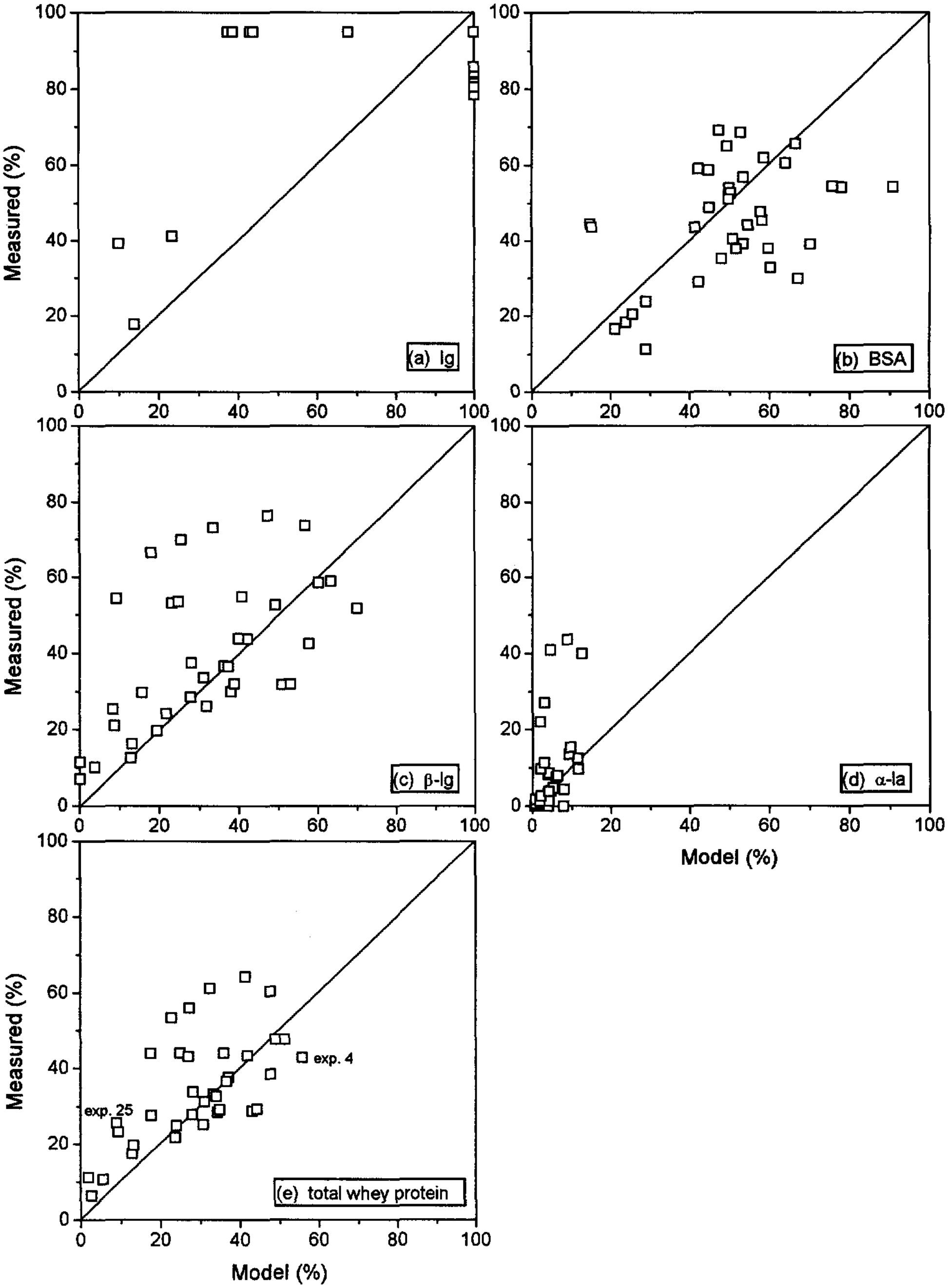


Figure 6.7 Measured extents of denaturation plotted against those calculated from the kinetic data given in Chapter 1 and 2

Table 6.3 Results for denaturation of total whey proteins in two direct heating systems

Steam infusion[a]						Steam injection[b]					
Exp.	Process conditions[c]			Measured and calculated denaturation resp. (%)		Exp.	Process conditions[c]			Measured and calculated denaturation resp. (%)	
	pre-heating (°C/s)	heating (°C/s)	cooling (°C/s)				pre-heating (°C/s)	heating (°C/s)	cooling (°C/s)		
30	71/34	150/0.48	69/8	61	33	6.1	75/30	160/0.35	65/30	67	30
32	70/34	169/0.69	69/8	60	48	7.1	75/30	160/0.35	65/30	52	30
35	71/34	148/0.48	69/8	31	31	8.1	73/30	160/0.35	65/30	56	29
36	70/34	159/0.47	69/8	37	37	9.1	69/30	159/0.35	65/30	53	28
37	71/34	168/0.46	69/8	64	42	10.1	75/30	160/0.20	65/30	46	25
						11.1	75/30	160/0.20	65/30	45	25
						13.1	73/30	159/0.45	65/30	48	31

[a] This thesis
[b] Esnouf and Mansour (1990)
[c] Combination of temperature and holding time

The statement that steam injection damages a product more than steam infusion [3] can be supported by a comparison with the results of Esnouf and Mansour [4]. They described a steam injection process, heating milk from 80 to 160 °C in 0.15 s with a holding time of 0.2 - 0.4 s. In spite of an extremely high heating rate, they found degrees of denaturation of total whey protein between 30 and 70 %. In Table 6.3 the measured and calculated degrees of denaturation of the infuser and the steam injection plant of Esnouf and Mansour are compared. For both steam infusion and injection the same kinetic data are used. In the case of the steam injection plant the difference between measured and calculated values is (at the 0.05 level of significance) larger than in the case of steam infusion: 85 % and 34 %, respectively. Besides it should be noted that Esnouf and Mansour found quite normal calculated denaturation degrees when the milk was treated in a regular indirect heat exchanger. So at temperatures above 150 °C, steam injection may indeed give more damage to the product by cavitation or local superheating.

6.4.3 Fouling

The infuser plant becomes fouled by formation of deposit at two places: the distribution device and at the cone of the infuser vessel. The latter has little effect on plant operation, but may be difficult to clean off [3]. Fouling of the distribution device, however, causes severe problems like fouling of the infuser wall and an increase of the residence time as a result of diverging jets. In Table 6.4 the degree, the location and the composition of fouling in the infuser are summarized. In general the cone of the infuser was slightly fouled and the remaining surface was visually clean. Only at high temperatures, from 130 to 160 °C, the cone of the infuser was substantial fouled, and at temperatures up to 170 °C the deposit had brown color.

Table 6.4 Formation of deposit in the infuser

Temp. range[a] (°C)	Cooling of infuser cone	$Re_{L,0}$	Degree of fouling[b]		Composition of deposits (cone of infuser)	
			Distribution device	Cone of infuser	mass ratio of protein to $Ca_3(PO_4)_2$	molar ratio of Ca to P
100 - 140	no	[c]3 800/9 500	+ + + +/-	nd[d]	nd	
100 - 140	no	15 800	-	nd	nd	
80 - 140	no	7 000	+ + +	nd	nd	
120	yes	15 700	-	+	3.5	1.47
130	yes	15 700	-	+ + +	14.1	1.49
100	yes	6 400	-	+	1.4	1.58
120	no	8 900	-	+	1.4	1.65
130 - 170	no	16 900	-	+ + + + +	6.5	1.47
130 - 170	yes	33 900	-	+ + + + + +	nd	

[a] Global temperature range during a series of experiments
[b] Degree of fouling is equivalent to the number of +
[c] Number of jets changed during one sequence
[d] nd = not determined

To minimize the contact area between heated milk and the infuser wall, all the jets should be directed to the centre of the cone. The formation of deposits on the distribution device turned out to be prevented by an initial jet Reynolds number over 10 000. Cooling of the cone of the infuser vessel seemed to have no effect on the extent of deposits. Since fouling already started at a temperature of 70 °C as a result of the denaturation of β-lactoglobulin (see Chapter 3), cooling would only have an effect when the wall surface could be cooled down to at least below 80 °C, which could not be realized in practice. Fouling might be reduced by giving the milk an extra pre-treatment (e.g. 30 s/85 °C) but that would increase denaturation.

The deposits consist of proteins and calcium phosphate as indicated by the molar ratio of Ca and P [14]. At high degrees of fouling of the infuser, the mass ratio of protein and calcium phosphate was high. Apparently protein plays a prominent role in deposit formation, even at high temperatures, because the high heating rate (i.e. short residence time) in the infuser would result in a lower concentration of aggregated and a higher concentration of unfolded β-lactoglobulin in the milk when it contacts the wall of the cone (see Chapter 2). So proteins would still make a substantial contribution to fouling, because of the active role of unfolded β-lactoglobulin in the fouling process (see Chapter 3).

6.4.4 Energy utilization and predesign

To save energy, thermal efficiency in the infuser must be high, i.e. the final temperature difference between steam and milk must be small. Figure 6.8 shows that considerable energy is saved by regenerative use of energy by coupling infusers in series. The effect of a high thermal efficiency on the specific steam consumption of two infusers in series is also demonstrated. An increase of the thermal efficiency from 0.90 to 0.99 results in an additional decrease of the energy costs by 8 %.

The heat and mass transfer model allows prediction of the effect of infuser geometry on thermal efficiency. A result of model simulations based on the heat and mass transfer model described is given in Figure 6.9. In general, the thermal efficiency decreases strongly with the number of jets and increases with infuser height. Decreasing the number of jets at a given diameter and flow has two important consequences: firstly it increases the jet velocity and thus the Reynolds number of the bundle of jets; and secondly it decreases the residence time of milk in the infuser. The first will decrease the resistance to mass transfer (see equation (6.19)) and will affect the efficiency positively. A decrease in residence time, however,

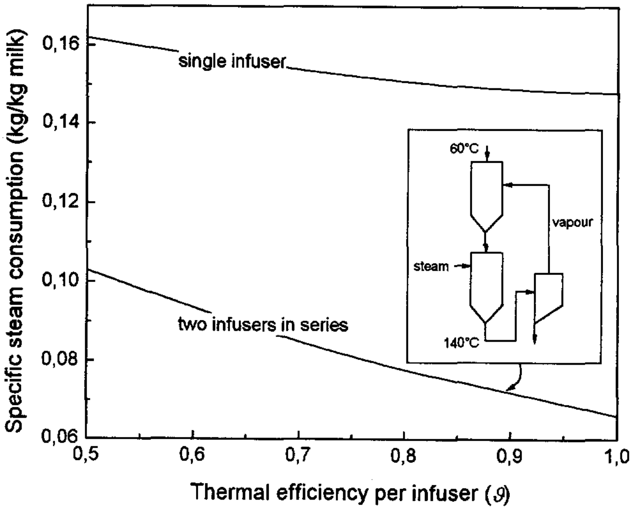


Figure 6.8 Calculated effect of thermal efficiency of a single infuser and two infusers in series on specific steam consumption

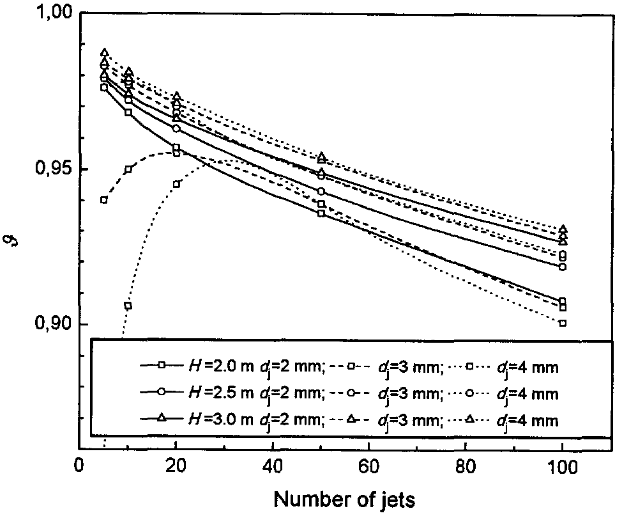


Figure 6.9 Thermal efficiency of an infuser related to its geometry with deaeration at the bottom of the infuser vessel for 2 ton/h skimmilk heated from 80 to 140 °C

decreases efficiency, as happened with relatively small infuser height and large jet diameters. It should be noticed that a better position of the deaeration device in the infuser (e.g. within the bundle of jets) may result in a substantial reduction of air accumulation between the jets. Consequently the relation between the accumulated air fraction and the number of jets will then change too.

6.5 Conclusions

A general heat and mass transfer model for heating of milk jets by steam infusion has been developed which showed reasonable agreement with the experiments. As a result of jet turbulence high heating rates can be realized. With the infuser it was possible to increase and decrease successively the temperature of the milk by more than 90 K within one second. Air accumulation within the bundle of jets turns out to be related to the number of jets and has a negative effect on the heating rate. The resistance to mass transfer of the bundle of jets could be described by a Sherwood correlation.

Denaturation measurements of whey proteins indicate that the heat treatment of the presented infuser is more gentle and gives less damage to the product than a steam injection plant. Fouling of the distribution device can be avoided if the initial Reynolds number of the milk jets is over 10 000.

Notation

A	Heat transfer area (m^2)
C	Concentration ($kg \cdot m^{-3}$)
C_p	Heat capacity at constant pressure ($J \cdot kg^{-1} \cdot K^{-1}$)
d_j	Diameter of jet (m)
D_{AB}	Molecular diffusivity ($m^2 \cdot s^{-1}$)
Fo	Fourier number: $4\lambda_L t/(\rho_L C_{p,L} d_j^2)$
g	Acceleration due to gravity ($m \cdot s^{-2}$)
h_v	Enthalpy of vaporization ($J \cdot kg^{-1}$)
H	Infuser height (m)
J	Mass flux ($kg \cdot m^{-2} \cdot s^{-1}$)
k_b, k_j	Mass transfer coefficient of the bundle of jets and the jet interface, resp. ($m \cdot s^{-1}$)
M	Molecular mass ($kg \cdot mol^{-1}$)

n_j	Number of jets
Nu	Nusselt number
p, p_t	Partial and total pressure, resp. ($N \cdot m^{-2}$)
Pr	Prandtl number: $C_p\eta/\lambda$
q_s, q_t	Sensible heat flux, total heat flux ($J \cdot s^{-1} \cdot m^{-2}$)
R_d	Coefficient of multiple determination; correlation coefficient for multiple regression
R	Gas constant: 8.314 ($J \cdot kg^{-1} \cdot K^{-1}$)
Re	Reynolds number: $\rho_z v_L d_j/\eta_z$ (gas phase), $\rho_L v_L d_j/\eta_L$ (milk)
Sc	Schmidt number: $\eta/\rho D_{AB}$
Sh	Sherwood number: $k_j d_j/D_{AB}$ (milk jet)
t	Time (s)
T	Temperature (K)
v	Velocity ($m \cdot s^{-1}$)
V	Volume (m^3)
x	Coordinate (m)
x,y	Molar fraction
z	Coordinate (m)
α	Heat transfer coefficient ($J \cdot s^{-1} \cdot m^{-2} \cdot K^{-1}$)
δ	Film thickness (m)
η	Dynamic viscosity ($kg \cdot m^{-1} \cdot s^{-1}$)
ϑ	Thermal efficiency: $(T_L - T_{L,0})/(T_s - T_{L,0})$
λ	Thermal conductivity ($J \cdot s^{-1} \cdot m^{-1} \cdot K^{-1}$)
ρ	Density ($kg \cdot m^{-3}$)
ϕ	Flow ($m^3 \cdot s^{-1}$)
υ	Atomic diffusion volume: 20.1 and 12.7, air and H_2O respectively

Subscripts, indices

hold	holding (time) at constant temperature
H_2O	water vapour
inf	infuser
j	jet
L	liquid (milk)
out	out of infuser(s)
outer	outer ring of the bundle of jets
s	steam

z	boundary layer (average quantity)
δ	jet interface
0	initial condition, bulk within the bundle of jets
1	bulk outside the bundle of jets

References

1. C. Peri, E. Pagliarini & S. Pierucci. A study on optimizing heat treatment of milk, I. Pasteurization. *Milchwissenschaft* 43 (1988) 636-639.
2. E. Pagliarini, C. Peri & S. Pierucci. A study on optimizing heat treatment of milk, II. Sterilization. *Milchwissenschaft* 43 (1988) 720-722.
3. H. Burton. Ultra-high-temperature processing of milk and milk products. Elsevier Applied Science, London (1988).
4. C. Esnouf & E.A. Mansour. Un nouveau procédé d'injection de vapeur: application à la mise au point d'un nouveau traitement thermique du lait. *Lait* 70 (1990) 233-254.
5. E. Kulic, E. Rhodes & G. Sullivan. Heat transfer rate predictions in condensation on droplets from air-steam mixtures. *Can. J. Chem. Eng.* 53 (1975) 252-258.
6. E. Kulic & E. Rhodes. Direct contact condensation from air-steam mixtures on a single droplet. *Can. J. Chem. Eng.* 55 (1977) 131-137.
7. T. Sundararajan & P.S. Ayyaswamy. Hydrodynamics and heat transfer associated with condensation on a moving drop: solutions for intermediate Reynolds number. *J. Fluid Mech.* 149 (1984) 33-58.
8. R.E. Treybal. Mass transfer operations. McGraw-Hil, New York (1968).
9. J.A. Wesselingh & R. Krishna. Mass transfer. Ellis Horwoord Series in Chemical Engineering, New York (1991).
10. E.N. Fuller & J.C. Schettler. *J. Gas Chrom.* 3 (1965) 222.
11. J.N. de Wit & G. Klarenbeek. Technological and functional aspects of milk proteins. Proceedings of the Int. Symp. Milk Proteins in Human Nutrition. Steinkopff, Darmstadt (1988).
12. W.J. Beek & K.M.K. Muttzall Transport Phenomena. John Wiley and Sons, New York (1988).
13. P. de Jong & H.J.L.J. van der Linden. Design and operation of reactors in the dairy industry. *Chem. Eng. Sci.* 47 (1992) 3761-3768.
14. T.J.M. Jeurnink, D.W. Brinkman & A.D. Stemerdink, Distribution and composition of deposit in heat exchangers. Proceedings of the Third Int. Conf. on Fouling and Cleaning in Food Processing. Ed. H.G. Kessler and D.B. Lund, Munich (1989).

Appendix 6.I: Calculation of the air fraction within the bundle of jets

The total heat pick-up in the infuser can be derived from equation (6.8). Rearranging this equation and assuming that ϱ and C_p are constant gives:

$$T_{\mathrm{L,out}} = \frac{4}{(\rho C_p)_{\mathrm{L}}} \cdot \int_0^{t_{\mathrm{out}}} \frac{1}{d_{\mathrm{j}}} \left[\frac{J_{\mathrm{H_2O}} C_{p,\mathrm{H_2O}}}{1 - \exp\left(-J_{\mathrm{H_2O}} C_{p,\mathrm{H_2O}} / \alpha\right)} (T_0 - T_{\mathrm{L}}) + h_{\mathrm{v}} J_{\mathrm{H_2O}} \right] \mathrm{d}t \tag{6A.1}$$

where T_0 is the steam temperature and t_{out} is the residence time in the infuser.

Boundary conditions:

at $t = 0 \rightarrow T_{\mathrm{L}} = T_{\mathrm{L,0}}$
at $t = t_{\mathrm{out}} \rightarrow T_{\mathrm{L}} = T_{\mathrm{L,out}}$

Equation (6A.1) can be solved by numerical integration, dividing the jet into a n_{k} segments with a residence time of Δt. The temperature change of one segment is given by:

$$\Delta T_{\mathrm{L,k-1}} = \frac{4}{(\rho C_p)_{\mathrm{L}} d_{\mathrm{j,k-1}}} \cdot \left[\frac{J_{\mathrm{H_2O,k-1}} C_{p,\mathrm{H_2O}}}{1 - \exp\left(-J_{\mathrm{H_2O,k-1}} C_{p,\mathrm{H_2O}} / \alpha_{\mathrm{k-1}}\right)} (T_0 - T_{\mathrm{L,k-1}}) + h_{\mathrm{v}} J_{\mathrm{H_2O,k-1}} \right] \Delta t \tag{6A.2}$$

and

$$T_{\mathrm{L,k}} = T_{\mathrm{L,k-1}} + \Delta T_{\mathrm{L,k-1}} \tag{6A.3}$$

Taking into account that due to steam condensation the flow increases, the local jet diameter $d_{\mathrm{j,k-1}}$ follows from:

$$d_{\mathrm{j,k-1}} = \left[\frac{\phi_{\mathrm{L,k-1}}}{\frac{1}{4}\pi\left(v_{\mathrm{L,0}} + g t_{\mathrm{k-1}}\right)} \right]^{\frac{1}{2}} \tag{6A.4}$$

The local steam flux $J_{H_2O,k-1}$ to the jet interface is given by equation (6.3):

$$J_{H_2O,k-1} = C_{k-1} k_{j,k-1} \ln \left[\frac{1 - y_{H_2O,\delta,k-1}}{1 - y_{H_2O,0}} \right] \tag{6A.5}$$

with

$$C_{k-1} = \frac{p_{z,k-1}}{R\,T_{z,k-1}} \tag{6A.6}$$

where $p_{z,k-1}$ and $T_{z,k-1}$ are respectively the local average pressure and temperature of the boundary layer.

Under saturated conditions, the local molar fraction of steam at the jet interface $y_{H_2O,\delta,k-1}$ is related to the local interface temperature $T_{\delta,k-1}$ (= $T_{L,k-1}$):

$$y_{H_2O,\delta,k-1} = \frac{p_{H_2O,\delta,k-1}}{p_t} \tag{6A.7}$$

where $p_{H_2O,\delta,k-1}$ is in equilibrium with $T_{\delta,k-1}$, according to the steam table.

The local heat transfer coefficient α_{k-1} and local mass transfer coefficient $k_{j,k-1}$ can be obtained from equation (6.11) to (6.13).

The only unknown quantity is the molar fraction of steam within the bundle of jets, $y_{H_2O,0}$, which is assumed to be the same for each segment. Since the total temperature change was measured during the experiments, $y_{H_2O,0}$ can be calculated by an iteration procedure: searching of the value of $y_{H_2O,0}$ at which the calculated temperature change is in agreement with the measured one.

Finally the air fraction within the bundle of jets can be calculated by:

$$y_{air,0} = 1 - y_{H_2O,0} \tag{6A.8}$$

Chapter 7

Industrial applications

Abstract

As a follow-up of the development of mathematical models and optimization procedures for heat-induced product transformations and fouling of equipment, some case-studies have been done, focused on the Netherlands dairy industry. These studies showed that a reactor engineering approach to heat treatment of milk and milk products offers a powerful tool for relating process conditions to product quality and production costs. The integration of this knowledge in computer software such as HeatCARD has increased the accessibility of this approach and therefore encourages its industrial implementation.

For example, in the case of the pasteurization of cheese milk it is possible to reduce the annual production costs of cheese in the Netherlands by 12 Mfl. Besides, the approach demonstrated may be used for future process certification by a better and more direct control of the destruction of bacteria. The fouling model can be used for extension of the operating time of heat treatment equipment and for the examination of innovative heat exchangers. Even for other products than milk the fouling model may give appropriate results. For example, in the case of heating whey-protein-concentrate the parameters of the fouling model can be adjusted by only a limited number of experiments.

7.1 Introduction

The proposed methodology for optimization of the heat treatment, described in the previous chapters, may result in considerable benefits for the dairy industry. From a related study by the Netherlands Agency for Energy and the Environment (NOVEM) and the Netherlands Institute for Dairy Research (NIZO) it was calculated that the total potential of cost-savings for the Netherlands dairy industry, as a result of minimizing the fouling of heat treatment equipment, amounts up to 5.2 Mfl. per year [1]. About 75 % of the total benefits are in the form of energy-savings ($1.5 \cdot 10^7$ normal m^3 natural gas per year). Besides, it was recognized that implementation of versatile and user-friendly computer programs such as HeatCARD encourages the industry in achieving better control of functional properties of the product and in screening of potential microbiological problems.

The major problem of a reaction engineering approach to the heat treatment of dairy products is the lack of kinetic data. The majority of the data have been determined with whole milk or skim milk. However, these are not the only products which are heat treated. Industrial problems particularly occur with more complex and new products such as evaporated milk (coffee creamer), whey protein concentrates, cream, desserts, etc. The determination of the kinetic parameters such as activation energies, pre-exponential factors and reaction orders on a laboratory scale is time-consuming and expensive. Moreover, application of kinetics determined in small test-tubes does not necessarily give the expected results on an industrial scale [2]. So, a more practical and effective method would be a determination method based on samples taken from a selected number of points along the flow length of the industrial process.

Figure 7.1 gives an example of the proposed determination method. The figure represents an arbitrary heat treatment consisting of three sections: a heater, a holder tube and a cooler. Since the heat treatment equipment in the dairy industry is designed for plug flow it is a valid assumption to ignore the residence time distribution in most cases. The temperature profile is shown in Figure 7.1a. At four points samples are taken and analyzed for the conversion of a certain milk component Z, in this example the activity of an enzyme. The activation energy (E_a), the pre-exponential factor (k_0) and the reaction order (n) can be obtained by fitting these data with the reaction rate equation and the Arrhenius relationship by non-linear regression:

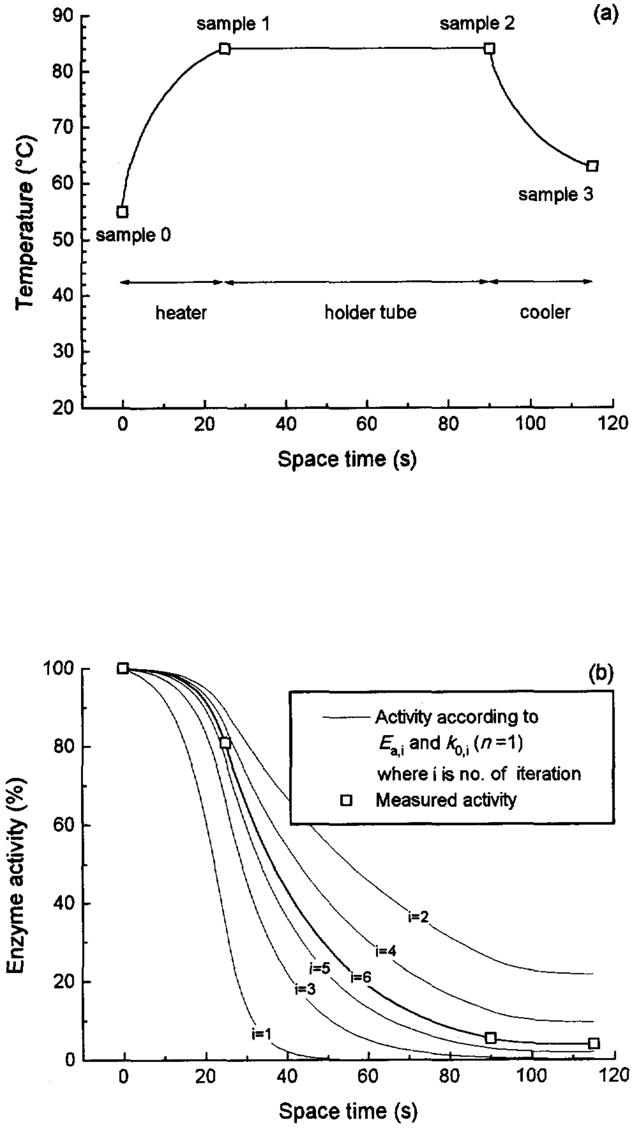


Figure 7.1 Demonstration of the proposed determination method for kinetic data of heat-induced product transformations

$$r_Z(x) = k(x)\left(C_Z(x)\right)^n \tag{7.1}$$

$$k(x) = k_0 \exp\left[-\frac{E_a}{R\,T(x)}\right] \tag{7.2}$$

where

$$x = f(\tau) \tag{7.3}$$

In principle this approach is similar to the optimization method described in Chapter 5. In that case the process conditions instead of the kinetic constants were the parameters which had to be optimized.

The final result of the determination method is illustrated in Figure 7.1b. After six iterations the best values of E_a and k_0 are determined. In this special case of enzyme inactivation the reaction order is assumed to be 1 (see Table 1.2). For other reactions such as the denaturation of proteins, the reaction order might be also a variable. Summarizing, the advantages of the proposed on-line determination of kinetic data are (i) the relatively few number of necessary analyses; often good results can be obtained from old analyses and (ii) the kinetic data are based on a practical situation.

As a follow-up of the development of mathematical models and optimization procedures for heat-induced product transformations and fouling of equipment, some case-studies have been done, focused on the dairy industry in the Netherlands. In this chapter the results of some industrial applications are reported.

7.2 Case-studies

7.2.1 Quality control of cheese milk

Problem definition

In the Netherlands yearly about $5.8 \cdot 10^9$ kg of milk (1993) is used for cheese-making. An important unit-operation in cheese-making is the pasteurization of the cheese milk, generally operated at a temperature of about 72 °C during 15 seconds [3]. Figure 7.2 shows an example of a pasteurization plant. For reasons of efficiency, raw milk may be mixed with milk powder or whey cream which are by-products of cheese manufacture. In general the amount of additives is depending on the

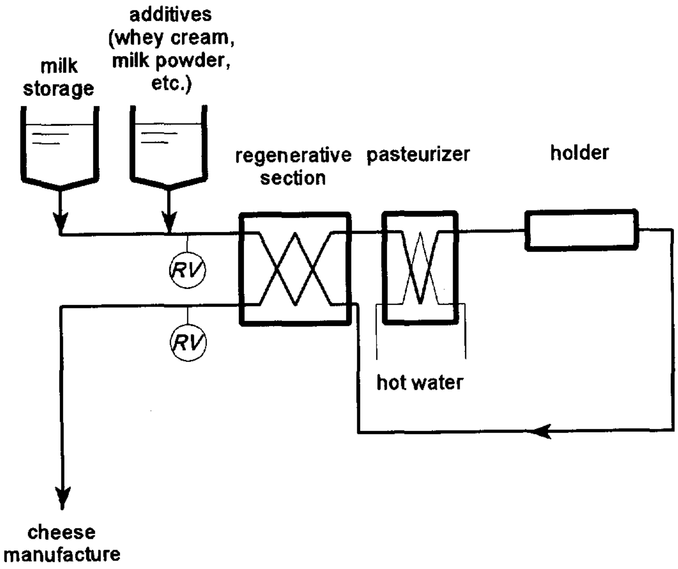


Figure 7.2 Example of a pasteurization plant for cheese milk (*RV* = sample point for determination of the *RV*-value)

season. The plate heat exchanger consists of two sections: a regenerative section for heat recovery and a pasteurizer. After cooling of the milk in the regenerative section the milk is stored in the cheese vat where the coagulant is added and the curd is formed.

The main objective of the heat treatment is to destroy the pathogenic bacteria and to denature a part of the proteins in the serum of the milk, the so-called whey proteins. This denaturation of whey proteins increases the yield of cheese, since the denatured whey proteins form a complex with the caseins and are thus incorporated into the curd instead of staying in solution in the whey [4]. However, denatured whey proteins may decrease the quality of cheese, resulting in typical flavour and texture defects. For that purpose the Netherlands central dairy organization (COKZ) has initiated legislation to control the amount of denatured whey proteins in cheese milk [5]. They introduced the so-called *RV*-value which represents the ratio between the non-denatured whey proteins immunoglobulin (Ig), bovine serum albumin (BSA) and β-lactoglobulin (β-lg). The *RV*-value is defined as:

$$RV = \frac{C_{\mathrm{Ig}} + C_{\mathrm{BSA}}}{C_{\beta\text{-lg}}} \cdot 100\% \qquad (7.4)$$

The concentration of non-denatured β-lg is assumed to be almost constant. To control the effect of cheese milk pasteurization on the denaturation of whey proteins, the RV-values before and after the heat treatment are compared (see Figure 7.2). The ratio of these RV-values is called the "residual value" and is defined as:

$$Y_{\text{res}} = \frac{RV_{\text{after past.}}}{RV_{\text{before past.}}} \cdot 100\% \tag{7.5}$$

Thus, a low value of Y_{res} corresponds to a high degree of denaturation of the whey proteins Ig and BSA. Depending on the season, the value of Y_{res} has to be at least 78 or 80 %. Operating the pasteurization at lower values is discouraged by penalties.

An estimation of the standard deviation of the residual values in the Netherlands cheese industry is about 3.5 %. This means that to avoid penalties and offspec products, the setpoint of the residual value has to be increased from, for example, 80 to 87 % (80 plus two times the standard deviation). However, as a consequence, the yield of cheese decreases since less denatured whey protein is incorporated in the cheese. For example, in the case of decreasing the standard deviation from 3.5 to 1.0 % by a better control of the the process operation, the production costs are reduced by 12 Mfl. per year (see Appendix 7.I). Therefore the objective of the industry is to minimize the standard deviation of Y_{res}.

Another source of problems might be that the configuration of the heat treatment equipment is often changed. For example, to increase the heat recovery of the pasteurization plant, the regenerative sections in the industry were extended resulting in larger volumes of the heat exchanger. As a consequence in some cases the standard for denaturation of whey proteins was exceeded.

Summarizing, to meet the requirements of the COKZ, the selection and control of the process conditions play an essential role. Changes in equipment configuration, in milk composition and the addition of other materials such as milk powder require continuously adjusted process conditions.

Results

A useful method for better control of the residual value (Y_{res}) is to incorporate the process of cheese milk pasteurization into the HeatCARD computer program (see Chapter 4). Simulations with HeatCARD may help the process operator to select the optimal process conditions, e.g. temperatures and flow, with respect to the desired conversions of the whey proteins and the bacteria. However, it turned out that the available kinetic data for denaturation of whey proteins as given in Table 1.2 are not appropriate for those low operating temperatures (< 75 °C) and relatively low denaturation rates. Besides, the determination method of COKZ may be different from the method used by the authors reporting the data of Table 1.2.

In order to "adjust" HeatCARD to the results of the analyses of COKZ, new kinetic data were determined with the method described in section 7.1. Samples were taken from cheese milk pasteurized at NIZO at temperatures between 67 and 82 °C. The samples were analyzed by COKZ. Figure 7.3 shows a comparison between the measured and calculated denaturation of whey proteins and the related Y_{res}. It is obvious that the kinetic data available in the literature [6, 7, 8] cannot be used for modelling the cheese milk pasteurization. Much better results were obtained with the new kinetic data based on measurements of COKZ. The determined kinetic data are given in Table 7.1.

An example of applying HeatCARD in a Process Management System (PMS) for pasteurization of cheese milk is shown in Figure 7.4. The milk is standardized on the fat and protein content and treated in a pasteurization plant as shown in Figure 7.2. During the heat treatment the cheese vat is filled. When the cheese vat is completely filled the coagulant is added for curdling of the milk. The most important process variables of the cheese milk pasteurization are Y_{res} and the activity of the enzyme phosphatase which is a measure of the activity of pathogenic bacteria [9]. Before the milk is pasteurized the enzyme phosphatase has a certain activity (+) and the *RV*-value follows from the milk composition. With the actual process conditions and the on-line determined kinetic data, the computer can predict Y_{res} and the phosphatase activity and optimize the process conditions. With this information the process operator is able to take the right measures when the process circumstances change. For example, when a change in the flow or milk

Table 7.1 Kinetic constants of the denaturation based on samples taken from cheese milk pasteurized at different temperatures (67 - 82 °C) analyzed by COKZ

Protein	T (°C)	n	E_a (kJ/mol)	ln k_0	No. of points	R_d^2
Ig	67-78 78-82	1	275.8 101.6	90.63 30.94	6	0.995
BSA	67-82	1	79.9	23.22	6	0.997
β-lg	67-82	1.5	149.5	45.51	6	0.997

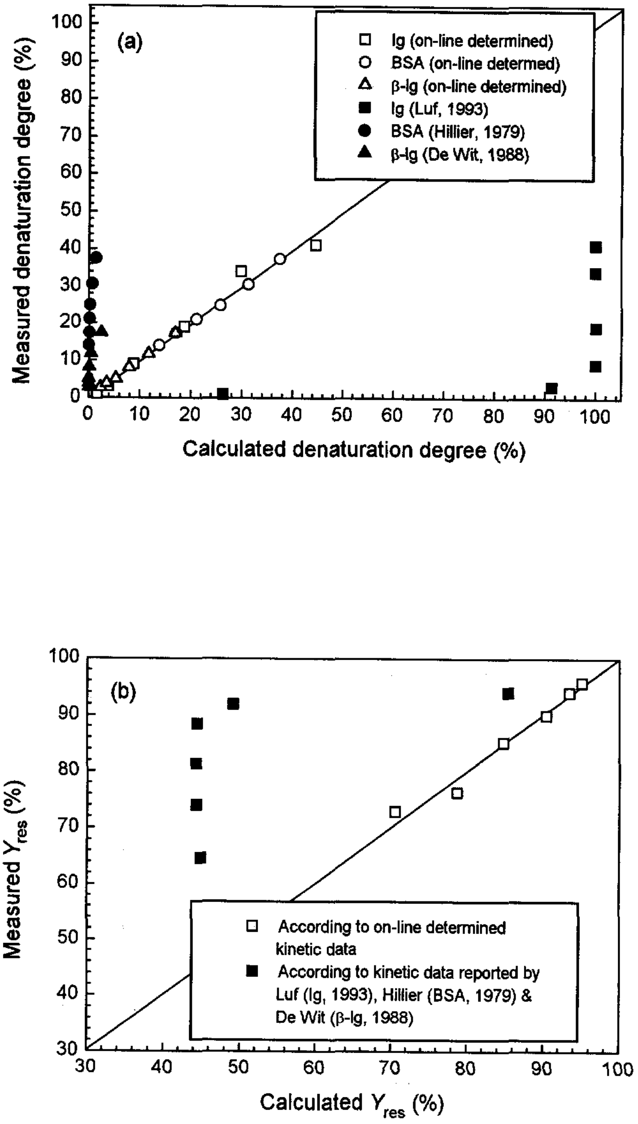


Figure 7.3 Comparison between measured and calculated denaturation of whey proteins according to kinetic data in the literature and obtained by on-line determination

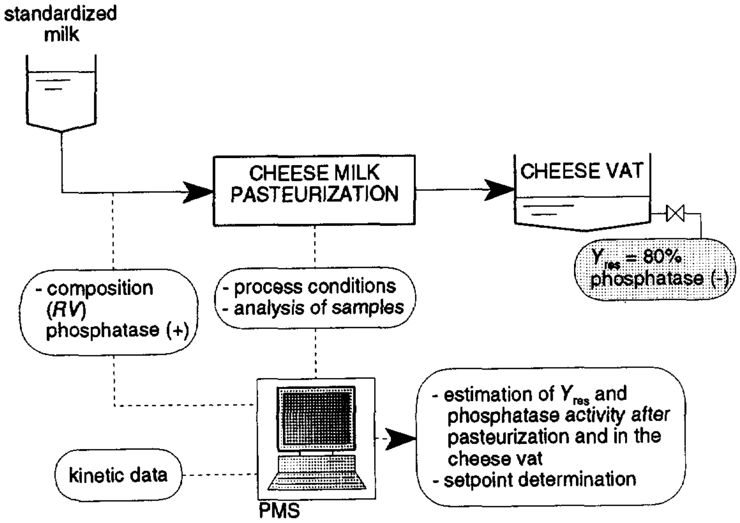


Figure 7.4 Process management system (PMS) for the pasteurization of cheese milk

composition occurs, the computer can indicate how the pasteurization temperature setpoint has to be changed so as not to endanger the phosphatase inactivation (−) while maintaining the desired level of Y_{res} in the cheese vat.

In principle, when the computer is integrated in the process control system it is even possible to control the process on product quality directly instead of temperature or flow. The setpoints such as the pasteurization temperature are then controlled by a computer which continuously estimates one or more functional properties like Y_{res} and phosphatase activity based on the actual process conditions. The dairy industry already has good experience with this so-called model-based process control for the manufacture of milk powder [10, 11].

The latest developments in legislation show that the dairy industry will be encouraged to minimize the fluctuations of the residual values. It is proposed to relate the minimum of the residual value at which a factory is allowed to operate, to the standard deviation of the residual values measured by COKZ: the lower the standard deviation, the lower the minimum residual value and thus, the higher the cheese yield.

7.2.2 Operating time extension in the case of highly depositing products

Problem definition

In the dairy industry not only the heat treatment of milk causes fouling problems. A number of important products such as whey protein concentrates and milk containing starches result in substantially different and mostly higher fouling rates under comparable process conditions. Figure 7.5a-b shows some photographs of deposited material found in heat treatment equipment after an operating time of about two hours. The main problem in reduction of fouling by mathematical optimization of the process is the lack of kinetic data for both the denaturation of β-lactoglobulin and deposit formation. In Chapter 3 a fouling model has been developed which predicts the deposit distribution in the equipment in the case of skim milk and whole milk. However, it is known that for milk products the kinetic constants are relatively strongly dependent on the composition, pH, ionic strength, etc. [9, 12]. Particularly the heat-induced denaturation behaviour of milk proteins is different in every product. The major reason is that the exact mechanism of the denaturation is unknown and the number of reaction steps involved is probably much higher than one.

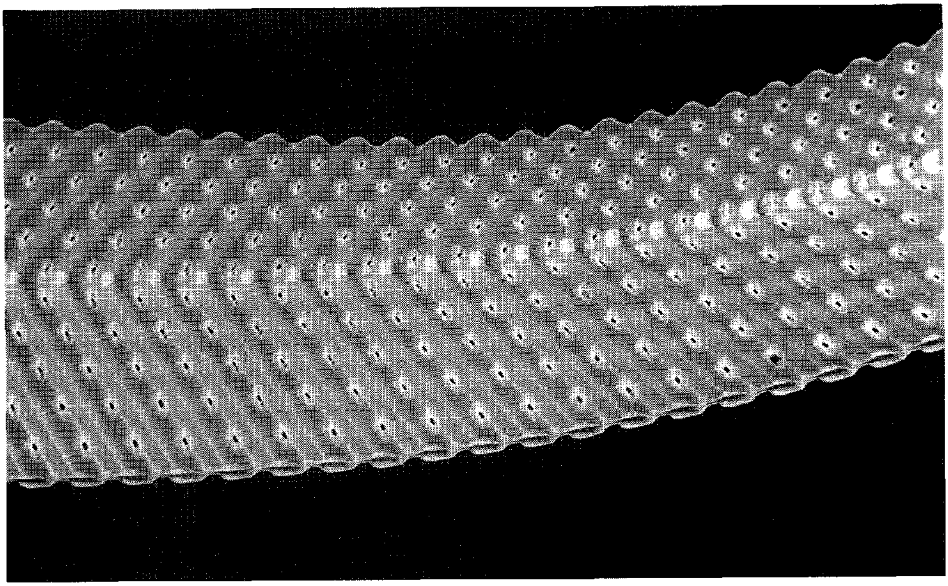


Figure 7.5a Protein-"tie", formed between two plates of a plate heat exchanger after 2 h heating of whey-protein-concentrate

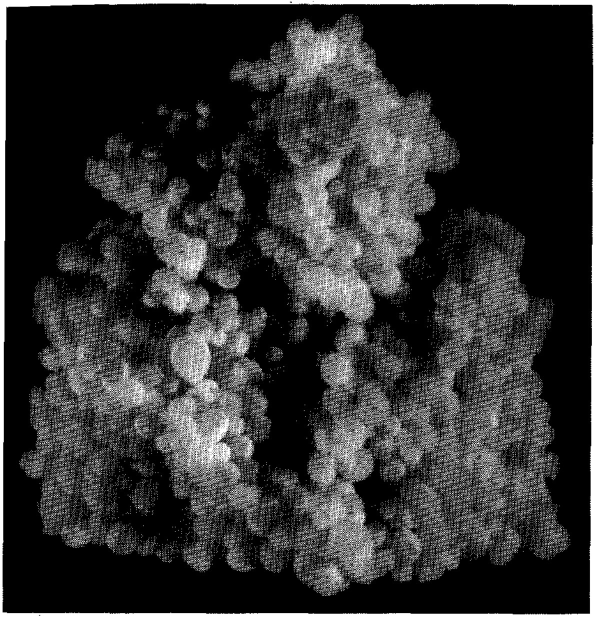


Figure 7.5b Aggregates of spherical deposits found in a tubular holding section (T = 80 °C) after 2 h heating of whey-protein-concentrate

Results

From research in the dairy industry it was learned that in the case of milk-based products and temperatures lower than 115 °C (protein fouling) the determined kinetic constants of the adsorption reaction of milk components are still valid. The reaction rate of the adsorption is described by:

$$R_F^{\prime\prime} = k^{\prime\prime}\, C_U^{1.2} \tag{7.6}$$

where the activation energy and the ln k_0 of the reaction rate constant are equal to 45.1 kJ/mol and -0.82, respectively (see also Chapter 3). The concentration of unfolded β-lactoglobulin (C_U) follows from the two-stage reaction model for the denaturation of β-lactoglobulin (β-lg) as described in Chapter 2:

$$-r_N = k_U C_N \tag{7.7}$$

$$r_U = k_U C_N - k_A C_U^2 \tag{7.8}$$

$$r_A = k_A C_U^2 \tag{7.9}$$

Table 7.2 Comparison between kinetics of skim milk and whey protein concentrate ($c_{\beta\text{-lg}}$ = 20 g/l); 70<T<90 °C

Reaction	n	Skim milk		Whey protein concentrate	
		E_a (kJ/mol)	ln k_0	E_a (kJ/mol)	ln k_0
Unfolding	1	261.4	86.41	[a]346	118.00
Aggregation	2	288.5	91.32	330	104.95

[a] According to De Wit [8], determined for whey protein concentrate

For example, in the case of heating whey protein concentrate with about 20 g/l of β-lg (in milk 3.2 g/l) in a heat exchanger similar to that of Figure 7.2, the measured fouling distributions and degrees of denaturation of the product could be quantified properly by changing the pre-exponential factor of the unfolding of β-lg and the pre-exponential factor and activation energy of the aggregation of β-lg. The values of the changed parameters are given in Table 7.2. The kinetic parameters were determined by the method described in section 7.1 and integrated in the computer program HeatCARD (see Chapter 4). It should be noted that, according to equation (7.6), in the given example due to the high concentration of β-lg in the whey

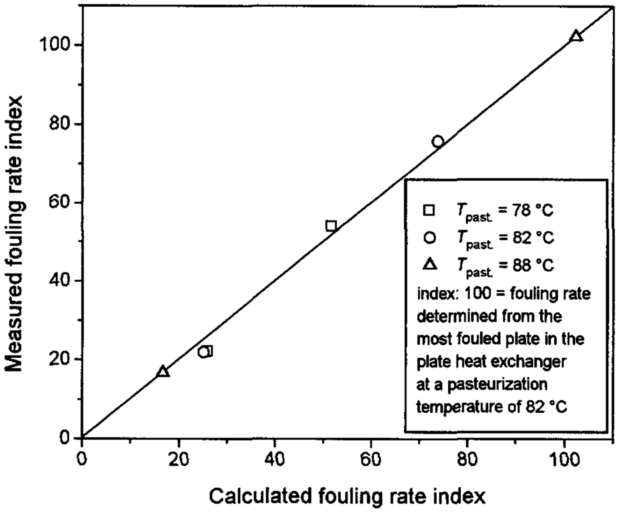


Figure 7.6 Comparison of the measured and calculated (HeatCARD) fouling rates with heating of whey protein concentrate at three different pasteurization temperatures

protein concentrate, the mean fouling rate was approximately 9 ($[20/3.2]^{1.2}$) times higher than in the case of milk. Figure 7.6 shows a comparison between the measured and calculated fouling rate in the regenerative and pasteurization section of the plate heat exchanger concerned, at three different pasteurization temperatures. It is remarkable that the calculated fouling rates agree very well with the measured ones.

To meet the required properties of the final product it was desired that a certain amount of the proteins was denatured and all pathogenic bacteria were destroyed. With the computer program HeatCARD it was possible to find the optimal process conditions at which the fouling of the heat exchanger was minimized, taking into account the desired denaturation of proteins and destruction of bacteria. The residence time at the pasteurization temperature in the holder after the pasteurization is determined by the desired properties of the product, i.e. the lower the pasteurization temperature the larger the necessary volume of the holder has to be to get the same conversion.

7.2.3 Examination of innovative heat exchangers

Problem definition

In the dairy industry there is a continuous need for innovative heat treatment equipment for reasons of reduction of costs and the introduction of new products. An example is the development of indirect heat exchangers with very high heat transfer coefficients (up to 10 000 W/m^2K) obtained by a high mixing intensity of the fluid. Figure 7.7 gives a schematic representation of their operation. This type of heat exchanger may reach high heating rates (up to 50 K/s) and may be an alternative to direct heating systems. The main advantage of indirect heat exchangers is that no water, i.e. condensed steam, is added to the product, having to be removed by expansion or evaporating afterwards. However, due to their small cross-sections and high heat transfer coefficients, these advanced heat exchangers are very sensitive to fouling of the heat transfer surface. A thin layer of deposits will result in a relatively strong decrease of the heat transfer coefficient, resulting in increasing temperature differences and, as a consequence, higher wall temperatures and fouling rates, etc.

In Figure 7.8 an example is given of an industrial plant in which a direct heating system is applied. Before the product is concentrated in a falling-film evaporator it is heated to inactivate the enzymes and bacteria. The objective of the case-study was to replace the steam injector by an advanced indirect heat exchanger.

In order to avoid high costs for experimental work with new innovative heat exchangers, it may be very useful to do a preliminary study with the HeatCARD computer program, eventually completing the investigation with one or two experiments. With HeatCARD it is possible to get a first estimation of the maximum operating time of the new apparatus.

Results

In one experiment the steam injector was replaced by the advanced heat exchanger and the milk was heated from 85 to 130 °C within 1.5 s. The initial steam temperature was 190 °C and the overall heat transfer coefficient was 6450 W/m^{2}K. The performance of the heat exchanger was strongly related to the formation of deposits. A mean deposit layer of 10 μm already decreased the heat transfer coefficient by 10 %:

$$\frac{1}{U_t} = \frac{1}{U_0} + \frac{\delta_F *}{\lambda_F *} = \frac{1}{6450} + \frac{10^{-5}}{0.6} \quad \rightarrow \quad U_t = 5824 \text{ W/m}^2\text{K} \qquad (7.10)$$

Since the outlet temperature was controlled by the steam temperature, the process was terminated when the maximum steam temperature (200 °C) was exceeded. In the case of the experiment this maximum temperature was reached after 1 h of operation. The heat transfer coefficient (U_t) had decreased to 5650 W/m^{2}K. The mean thickness of the deposit layer was calculated then as 13 μm.

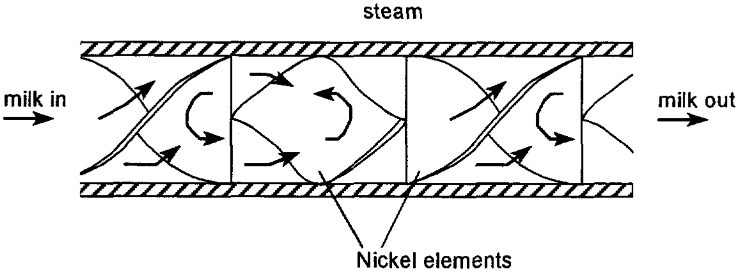


Figure 7.7 Schematic representation of an advanced heat exchanger with a high mixing intensity of the fluid

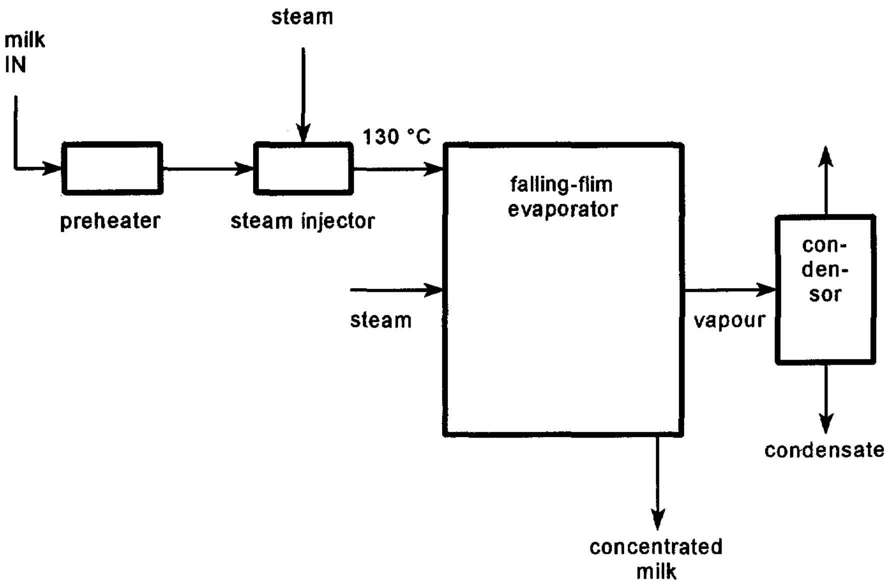


Figure 7.8 Example of an industrial evaporator plant with a direct heating system

The operating time can be increased in two ways: (i) by decreasing the mean fouling rate by, for example, installation of a holder section upstream from the heat exchanger in which the reactive and depositing, unfolded β-lg is transformed into the inert aggregated state (see Chapter 3) or (ii) by decreasing the temperature difference, resulting in a lower initial steam temperature, so that the maximum temperature is reached at a higher thickness of the deposit layer. Assuming that the thickness of the deposit layer is proportional to the operating time [13], the maximum operating time can be estimated by the following equation:

$$t = \frac{\delta_{\max}}{\delta_{\max,\mathrm{ref}}} \cdot \frac{J_{\mathrm{F,ref}}}{J_{\mathrm{F}}} \cdot t_{\mathrm{ref}} \qquad (7.11)$$

where $\delta_{\max}$ is the thickness of the deposit layer at which the maximum temperature of the heating medium is reached at a constant product temperature and J_F is the mean fouling rate of the heat exchanger calculated with HeatCARD. The subscript "ref" indicates the calculated values with respect to the experiment with operating time t_{ref}. For the experiment the mean fouling rate was calculated as $8.2 \cdot 10^{-7}$

kg/m^{2}s. When an extra holder operating at a temperature of 80 °C with a residence time of 98 s is installed and the outlet temperature of the heat exchanger is decreased from 130 to 110 °C, HeatCARD calculated that $J_F = 5.9 \cdot 10^{-7}$ kg/m^{2}s. The initial steam temperature is decreased to 150 °C. Since the temperature difference between steam and product is decreased, the minimum heat transfer coefficient becomes:

$$U_t = U_0 \frac{\Delta T_{\log,0}}{\Delta T_{\log,t}} = 6450 \cdot \frac{\dfrac{(150-80)-(150-110)}{\ln\left(\dfrac{150-80}{150-110}\right)}}{\dfrac{(200-80)-(200-110)}{\ln\left(\dfrac{200-80}{200-110}\right)}} = 3315\ \mathrm{W/m^2K} \tag{7.12}$$

With equation (7.10) the maximum thickness of the deposit layer (δ_{max}) was calculated as 88 μm and thus the operating time was predicted as:

$$t = \frac{88}{13} \cdot \frac{8.2 \cdot 10^{-7}}{5.9 \cdot 10^{-7}} \cdot 1\ \mathrm{h} = 9.4\ \mathrm{h} \tag{7.13}$$

which means a ninefold increase of the operating time.

Summarizing, when an operating time of at least 8 h is required, the milk should not be heated to temperatures above 110 °C. To heat the milk to 130 °C a direct heating system, e.g. steam injection, has to be installed downstream of the advanced heat exchanger. In comparison with direct heating from 85 to 130 °C by steam injection alone, the proposed partial use of an advanced heat exchanger may reduce the addition of water by more than 65 %. Whether the advanced heat exchanger should be installed or not depends on the costs of investment and installation. In the given situation the benefits were recognized by the company as too small. However, in the case of a new plant the proposed application may be much more attractive.

7.3 Conclusions

With the results of some industrial case-studies it is demonstrated that a reactor engineering approach to heat treatment of milk and milk products offers a powerful tool for adjusting process conditions to product quality and production costs. The integration of this knowledge in computer software such as HeatCARD has increased the accessibility of this approach and therefore encourages its industrial implementation.

For example, in the case of the pasteurization of cheese milk it is possible to reduce the annual production costs of cheese in the Netherlands by 12 Mfl. Besides, the approach demonstrated may be used for future process certification by a better and more direct control of the destruction of bacteria. The fouling model can be used for extension of the operating time of heat treatment equipment and for examination of innovative heat exchangers. Even for other products than milk the fouling model may give appropriate results. For example, in the case of heating whey-protein-concentrate the parameters of the fouling model can adjusted by only a limited number of experiments.

Notation

C	Concentration ($\mathrm{kg \cdot m^{-3}}$)
E_a	Activation energy ($\mathrm{J \cdot mol^{-1}}$)
J_F	Mean deposition rate ($\mathrm{kg \cdot m^{-2} \cdot s^{-1}}$)
k	Reaction rate constant ($\mathrm{m}^{3(n-1)} \cdot \mathrm{kg}^{(1-n)} \cdot \mathrm{s}^{-1}$)
k_0	Preexponential ($\mathrm{m}^{3(n-1)} \cdot \mathrm{kg}^{(1-n)} \cdot \mathrm{s}^{-1}$)
k''	Reaction rate constant of surface reactions ($\mathrm{m^{1.6} \cdot kg^{-0.2} \cdot s^{-1}}$)
n	Reaction order
r	Reaction rate ($\mathrm{kg \cdot m^{-3} \cdot s^{-1}}$)
r_Z	Reaction rate of component Z ($\mathrm{kg \cdot m^{-3} \cdot s^{-1}}$)
R	Gas constant, 8.314 ($\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$)
$\mathrm{R_d}$	Correlation coefficient for multiple regression
R_F''	Production rate of adsorbed milk constituents ($\mathrm{kg \cdot m^{-2} \cdot s^{-1}}$)
RV	Measure for the concentration of native protein (%)
t	Time (s)
T	Temperature (K)
U	Overall heat transfer coefficient ($\mathrm{W \cdot m^{-2} \cdot K^{-1}}$)
x	Flow length coordinate (m)
Y_{res}	Residual value, measure of protein denaturation (%)
δ	Thickness of deposit layer (m)
λ	Thermal conductivity ($\mathrm{W \cdot m^{-1} \cdot K^{-1}}$)

Subscripts, indices and abbreviations

A	Aggregation, aggregated (β-lg)

F^*	Adsorbed milk components
max	Maximum
N	Native (β-lg)
ref	Reference
t	Operating time, value at time t
U	Unfolding, unfolded (β-lg)
0	Initial state

References

1. T.J.M. Jeurnink & P. de Jong. Energiebesparing door verbetering van warmtebehandelingsprocessen [Energy-savings by improving of heat treatment processes]. Nizo/Novem report NOV-1879 (1994).
2. H. Burton, A.G. Perkin, F.L. Davies & H.M. Underwood. Thermal death kinetics of *Bacillus stearothermophilus* spores at ultra high temperatures. III. Relationship between data from capillary tube experiments and from UHT sterilizers. *J. Food Technol.* 12 (1977) 149-161.
3. H. Lolkema & J. Blaauw. Kaasbereiding [Cheese-making]. Beroepsopleiding Levensmiddelenindustrie, Apeldoorn (1974).
4. R.C. Lawrence. Incorporation of whey proteins in cheese. In: Factors affecting the yield of cheese. IDF Special Issue 9301, Brussels (1991).
5. Department of Agriculture. Ontheffing inzake de analysemethode voor de controle op de kaasmelkpasteurisatie [Dispensation concerning the analyzing method for control of the pasteurization of cheese milk]. VZ 922071, The Hague (1992).
6. W. Luf, G. Feiersinger & E. Brandl. On kinetics of thermal denaturation of immunoglobulins in milk: application as a heat treatment indicator. In: Protein & fat globule modifications by heat treatment and homogenization, IDF Special Issue 9303, Brussels (1993).
7. R.M. Hillier & R.L.J. Lyster. Whey protein denaturation in heated milk and cheese whey. *J. Dairy Res.* 46 (1979) 95-102.
8. J.N. de Wit & G. Klarenbeek. Technological and functional aspects of milk proteins. In: Milk proteins in human nutrition, Proc. Int. Symp., Steinkoppf, Kiel (1988).
9. P. Walstra & R. Jennes. Dairy chemistry and physics. J. Wiley, New York (1984).
10. J. Straatsma, P.J. Alderlieste & G. van Houwelingen. Implementatie van de DrySPEC-Process-Manager op een industriële tweetrapsdroger [Implementation of the DrySPEC-Process-Manager on an industrial two-stage dryer]. NIZO-report 1711 (1993).

11. V. Delemarre. Nieuwe regeling drooginstallatie verdient zich zeer snel terug [New control system of spray dryer results in a considerable reduction of operating costs]. *Voedingsmiddelentechnologie* 27(3) (1994) 20-21.

12. H.G. Kessler. Lebensmittel- und Bioverfahrenstechnik, Molkereitechnologie. Verlag A. Kessler, Freising (1988).

13. P.J. Fryer. The uses of fouling models in the design of food process plant. *J. Soc. Dairy Technol.* 42 (1989) 23-29.

Appendix 7.I: Estimation of the costs due to variation of the residual value

Assumptions

1. Milk consists of 26.0 g/l casein and 6.3 g/l whey protein [9].
2. Denatured whey protein has more or less the same effect on the yield of cheese as casein [4].
3. About 5 % of the whey protein is denatured after a standard pasteurization (Y_{res} = 80 %).
4. 100 kg milk gives 10.45 kg cheese [4].
5. 1 kg of cheese yields fl. 6.

Calculation

Milk used for cheese manufacture (1993): $5.8 \cdot 10^9$ kg per year.
The standard concentration of denatured whey protein is 0.05 × 6.3 = 0.31 g/l.
This gives an additional yield of 0.31/26.0 × 100 % = 1.2 %.
In fl.: 0.012 × 6 = 0.072 fl. per kg of cheese.
So a residual value of 100 %, i.e. no denaturation, would result in a loss of about 7 cents per kg of cheese.
Expressed in fl. per % of Y_{res}: 0.072/(100-80) ≈ <u>0.004 fl. per % and kg of cheese</u>.

In the case that the mean Y_{res} is reduced from 80 + 2 × 3.5 % = 87 % to 80 + 2 × 1.0 % = 82 % the loss of yield for the Dutch cheese industry amounts to:

Annual cheese production = $5.8 \cdot 10^9 \times 10.45/100 = 6.06 \cdot 10^8$ kg
Loss of yield = $(87-82) \times 0.004 \times 6.06 \cdot 10^8$ = <u>12 Mfl. per year</u>.

Summary

Modelling and optimization of thermal processes in the dairy industry

P. de Jong

In the dairy industry, physical, chemical and biochemical phenomena are the basis for the strong relation between the product quality and the process operation and design. This is particularly valid for heat treatment, where a number of heat-induced transformations of milk components determine the functional properties of the final product. Not only the product quality is affected by the heat-induced reactions, also fouling of equipment by deposit formation on walls is governed by specific reactions of milk components. These typical undesired reactions reduce the heat transfer coefficient, increase the pressure drop over heat treatment equipment and increase product losses, resulting in higher operating costs.

With respect to the design and operation of heat treatment equipment in the dairy industry the following objectives were defined by the Netherlands Institute for Dairy Research: (i) development of a methodology for optimization of heat treatment equipment with respect to product quality and fouling of equipment walls; (ii) introduction of the knowledge obtained into the dairy industry by the development of versatile computer programs. This project had the financial support of the Netherlands Agency for Energy and the Environment (NOVEM).

One of the most important heat-induced reactions is the denaturation of β-lactoglobulin (β-lg). A quantitative model was developed which describes the denaturation of β-lg as two consecutive reactions: unfolding and aggregation. The kinetic constants were obtained by a reinterpretation of experimental results in the literature. The aggregation is described by a second order reaction with an activation energy of 288.5 ± 5.7 kJ/mol for temperatures below 90 °C and 54.7 ± 0.5 kJ/mol for temperatures up to 150 °C. It turned out that the two-stage model gives a good description of the reported experimental data. Results of fouling experiments showed the importance of quantifying the concentration of unfolded

β-lg and supported the hypothesis that the local fouling rate in heat treatment equipment is related to the local concentration of unfolded β-lg.

The relationship between the denaturation of β-lg and the deposition of milk constituents in a heat exchanger was investigated. Experiments were carried out on a plate heat exchanger with skim milk by applying different temperature-time combinations in the temperature range from 45 to 122 °C. Based on the results of the experiments, a fouling model for heat exchangers related to the denaturation kinetics of the key component β-lg has been developed for surface temperatures of equipment walls up to 115 °C. The main mechanism was controlled by the adsorption rate of unfolded β-lg at an external heat transfer surface. This model gave good agreement with the experimental data. By application of an interstage holding section in the heating zone, the amount of deposits in the regenerative section could be reduced substantially, by over 50 %. It was shown that the fouling model for skim milk can also be used for predicting the deposit distribution in heat treatment equipment due to fouling by whole milk, which supported the chemical and physical basis of the model. In addition it was found that the absolute fouling level is not only related to heat-induced protein transformations but also strongly influenced by the age of milk.

To stimulate the industrial implementation of the models generated, a computer program has been developed for the Netherlands dairy industry, called HeatCARD (Heat exchanger Computer Aided Reactor Design). The program is capable of evaluating the product transformations and the deposit distribution in the equipment simultaneously, and of quantifying the interaction between them. The core of the program is formed by the reaction models for the heat-induced product transformations such as the denaturation of β-lg, and the fouling of equipment walls. The availability of this program means that the use of simplifying kinetic constants with an intrinsically small range of validity is no longer necessary. The proposed computational approach may contribute to a better understanding, a more functional design and an improved operation of heat treatment equipment in the dairy industry.

In order to apply the models for process optimization, a comprehensive optimization method has been developed based on minimizing an objective function which comprises the costs of deviating from the ideal product quality and the processing costs. The method was integrated in a computer program, called HCOPT. The main advantages of the method are the incorporation of deposit formation at heat transfer surfaces and the versatility of defining the process and equipment design, supporting non-isothermal sections like heaters and coolers. The method also accounts for the relative importance of the individual heat-induced product transformations determining the product characteristics. To illustrate the potential of this approach a given industrial UHT (Ultra High Temperature) plant was optimized. The optimization results demonstrated that with regard to conventional industrial plants this approach may result in a substantial (more than 50 %) reduction of the operating costs, without concessions to the product quality. In the plant described the milk should be heated to 145 °C with a heating rate of 4 K/s and minimum holding time at this temperature. An additional holder should be applied in the heating trajectory at an operating temperature of 90.5 °C and a residence time of about 15 minutes.

The performance of a direct heating system was investigated with a commercial infuser in which jets of milk were heated. A mathematical model was developed to describe the heat and mass transfer from steam to milk in the presence of air. The model showed reasonable agreement with the experimental results and was used for quantitative interpretation of the experimental results. With the infuser it was possible to increase and decrease successively the temperature of the milk by more than 90 K within one second. Air accumulation within the bundle of jets turned out to be related to the number of jets and had a negative effect on the heating rate. Comparing the denaturation measurements of whey proteins with recent results of other authors indicated that the heat treatment of the infuser investigated is more gentle and gives less damage to the product than a steam injection plant. Fouling of the distribution device could be avoided if the initial Reynolds number of the milk jets was over 10 000.

As a follow-up of the development of mathematical models and optimization procedures for heat-induced product transformations and fouling of equipment, some case-studies have been done, focused on the Netherlands dairy industry. These studies showed that a reactor engineering approach to heat treatment of milk and milk products offers a powerful tool for relating process conditions to product quality and production costs. The integration of this knowledge in computer software such as HeatCARD has increased the accessibility of this approach and therefore encourages its industrial implementation. For example, in the case of the pasteurization of cheese milk it is possible to reduce the annual production costs of cheese in the Netherlands by 12 Mfl. Besides, the approach demonstrated may be used for future process certification by a better and more direct control of the destruction of bacteria. The fouling model can be used for extension of the operating time of heat treatment equipment and for the examination of innovative heat exchangers. Even for other products than milk the fouling model may give appropriate results. For example, in the case of heating whey-protein-concentrate the parameters of the fouling model could be adjusted by only a limited number of experiments.

Samenvatting

Het modelleren en optimaliseren van warmtebehandelingsprocessen in de zuivelindustrie

P. de Jong

In de zuivelindustrie bestaat een sterke relatie tussen de fysische, de chemische en de biochemische verschijnselen enerzijds en de produktkwaliteit en procesvoering anderzijds. Dit geldt met name voor de warmtebehandeling waar een groot aantal transformaties van melkcomponenten de functionele eigenschappen van het eindprodukt bepalen. Niet alleen de produktkwaliteit maar ook de vervuiling van warmtebehandelingsapparatuur wordt beheerst door specifieke reacties in melkprodukten. Door een verminderde warmteoverdracht, een toename in de drukval en de produktverliezen resulteert deze vervuiling in verhoogde produktiekosten.

In het kader van het terugdringen van de vervuiling en het beheersen van de produktkwaliteit zijn door het Nederlands Instituut voor Zuivelonderzoek (NIZO) de volgende doelstellingen geformuleerd: (i) de ontwikkeling van een methode waarmee de warmtebehandeling kan worden geoptimaliseerd met betrekking tot produktkwaliteit én produktiekosten; (ii) implementatie van deze kennis in de zuivelindustrie middels computerprogramma's. Voor het onderzoek is een financiële bijdrage ontvangen van de Nederlandse Ontwikkelingsmaatschappij voor Energie en Milieu (NOVEM).

Eén van de belangrijkste reacties die tijdens de warmtebehandeling van melk optreden, is de denaturatie van het eiwit β-lactoglobuline (β-lg). Een kwantitatief model is ontwikkeld dat de denaturatie van β-lg beschrijft met twee volgreacties: ontvouwing en aggregatie. De kinetische constanten als activeringsenergie, pre-exponentiële factor en reactieorde zijn bepaald door een herinterpretatie van de experimentele resultaten. De aggregatie van ontvouwen β-lg met andere melkbestanddelen is beschreven met een tweede-orde reactie met een activeringsenergie van 288.5±5.7 kJ/mol bij temperaturen lager dan 90 °C en 54.7±0.5 kJ/mol bij temperaturen hoger dan 90 °C. Het is gebleken dat de experimentele resultaten met dit model nauwkeurig kunnen worden gereproduceerd. Daarnaast bleek uit experimenten gericht op de vervuiling van de warmtebehandelingsapparatuur dat er een verband bestaat tussen de lokale concentratie aan ontvouwen β-lg en de lokale adsorptiesnelheid van melkcomponenten.

Met het doel de relatie tussen de denaturatie van β-lg en de vervuiling van apparatuur te kwantificeren, zijn experimenten uitgevoerd met een platenwarmtewisselaar waarin magere melk werd verhit binnen een temperatuurbereik van 45 tot 122 °C. Met de experimentele resultaten is een vervuilingsmodel ontwikkeld, gerelateerd aan het denaturatiemodel voor β-lg en geldig voor wandtemperaturen tot 115 °C. De lokale vervuilingssnelheid bleek bepaald te worden door de adsorptiesnelheid van ontvouwen β-lg aan het wandoppervlak. Zoals op basis van het vervuilingsmodel kon worden verwacht, verminderde door de toepassing van een extra warmhouder in het verwarmingstraject van de warmtewisselaar, de vervuiling van het regeneratief met meer dan 50 %. Het is aangetoond dat het vervuilingsmodel ook kan worden gebruikt voor het voorspellen van de vuilverdeling in warmtewisselaars bij de warmtebehandeling van volle melk. Het absolute niveau van de vervuilingssnelheid werd beheerst door de ouderdom van de melk.

Met het doel de gegenereerde modellen te implementeren in de Nederlandse zuivelindustrie is het computerprogramma HeatCARD (Heat exchanger Computer Aided Reactor Design) ontwikkeld. Met dit programma is het mogelijk de vuilverdeling, de produkttransformaties en de interactie tussen die beiden te evalueren. De kern van het programma wordt gevormd door het vervuilingsmodel en de reactiemodellen voor de transformaties van melkcomponenten als microorganismen, enzymen en eiwitten. De beschikbaarheid van HeatCARD betekent dat het gebruik van grootheden met een relatief beperkte geldigheid voor het vaststellen van de warmtebelasting van het produkt niet langer noodzakelijk is. De conversies van belangrijke melkcomponenten in warmtebehandelingsapparatuur kunnen nu eenvoudig afzonderlijk worden gekwantificeerd.

Naast het simulatieprogramma HeatCARD is een optimalisatiemethode ontwikkeld waarbij een doelfunctie, samengesteld uit de produktiekosten en de kosten ten gevolge van een afwijking in de gewenste produktkwaliteit, wordt geminimaliseerd. De methode is geïntegreerd in een computerprogramma met de naam HCOPT (HeatCard OPTimization). De belangrijkste voordelen ten opzichte van andere beschreven optimalisatiemethoden zijn dat (i) een aaneenschakeling van warmtebehandelingen, inclusief verhitters en koelers, in de optimalisatie kan worden betrokken en (ii) het effect van de vervuiling is gekwantificeerd. Voor de afweging tussen de mate van vervuiling en de gewenste transformaties zijn gewichtsfactoren toegepast. Ter illustratie is een gegeven UHT (Ultra Hoge Temperatuur) installatie geoptimaliseerd. Uit de resultaten bleek dat de toepassing van de beschreven optimalisatiemethode kan resulteren in een halvering van de produktiekosten, zonder concessies te doen aan de gewenste produktkwaliteit. In de beschreven installatie is de optimale UHT-temperatuur 145 °C met een verhittingssnelheid van 4 K/s en minimale verblijftijd op deze temperatuur. Om de vervuiling in de warmtewisselaars te verminderen moet in het verhittingsgedeelte een extra warmhouder worden geïnstalleerd op een temperatuur van 90.5 °C en met een verblijftijd van circa 15 minuten.

De werking van een direct verhittingssysteem is onderzocht met een industriële stoom infusor waarbij straaltjes melk worden verhit in een stoomruimte. Voor de beschrijving van het massa- en warmtetransport in de aanwezigheid van lucht is een mathematisch model ontwikkeld. Met het model konden de experimentele resultaten redelijk tot goed worden gereproduceerd. Met de infusor bleek het mogelijk om de melk binnen een seconde 90 K op te warmen en weer terug te koelen tot de begintemperatuur. De luchtophoping in de stralenbundel was gerelateerd aan het aantal straaltjes en verminderde de thermische efficiency. Een vergelijking tussen eigen denaturatiemetingen en metingen beschreven in de literatuur gaf aan dat verhitting middels stoominjectie meer beschadiging aan het produkt veroorzaakt dan stoominfusie. Vervuiling van de vloeistofverdeelkop kon worden voorkomen door een hoge intreesnelheid van de melk (Reynolds > 10 000).

Als een vervolg op de ontwikkeling van de mathematische modellen en de optimalisatieprocedures zijn een aantal case-studies uitgevoerd, gericht op de Nederlandse zuivelindustrie. De resultaten tonen aan dat een reactorkundige beschrijving van de warmtebehandeling van melk en melkprodukten een goede methode is voor het relateren van de procesvoering aan de produktkwaliteit en de produktiekosten. Het beschikbaar stellen van computer software als HeatCARD bevordert de acceptatie en de toepassing van deze aanpak in de industrie. Bijvoorbeeld bij de pasteurisatie van melk voor de kaasbereiding blijkt een jaarlijkse besparing van 12 miljoen gulden mogelijk. Daarnaast kan HeatCARD een aandeel leveren in procescertificering door een meer directe controle van de gewenste bacteriële afdoding. Het vervuilingsmodel kan worden gebruikt voor het bereiken van langere produktietijden, zelfs bij het verhitten van andere produkten dan melk zoals wei-eiwitconcentraat.

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List of publications

P. de Jong, S. Bouman & H.J.L.J. van der Linden. Fouling of heat treatment equipment in relation to the denaturation of β-lactoglobulin. *J. Soc. Dairy Technol.* 45 (1992) 3-8.

P. de Jong & H.J.L.J. van der Linden. Design and operation of reactors in the dairy industry. *Chem. Eng. Sci.* 47 (1992) 3761-3768.

P. de Jong, R. Waalewijn & H.J.L.J. van der Linden. Validity of a kinetic fouling model for heat treatment of whole milk. *Le Lait* 73 (1993) 293-302.

P. de Jong & H.J.L.J. van der Linden. Process design based on heat-induced transformations of milk components. In: *Proc. of the IDF-Seminar Protein- and Fat globule Modifications by Heat Treatment, Homogenization and other Technological Means for High Quality Dairy Products* (ed. H.G. Kessler), IDF Special Issue 9303, Brussels (1993) 277-284.

P. de Jong, R. Waalewijn & H.J.L.J van der Linden. Performance of a steam infusion plant for heating milk. *Neth. Milk Dairy J.* 48 (1994) 177-195.

P. de Jong. Performance of a direct heating system with steam infusion. In: *Proc. of the Symposium on Heat Treatment and Alternative Methods*, IDF Special Issue, Brussels (1996) Submitted.

P. de Jong, P.F.J. l'Amie & H.J.L.J. van der Linden. Mathematical optimization of heat treatment equipment with respect to fouling and product quality. In: *Proc. of the Conference on Fouling and Cleaning in Food Processing (ed. P.J. Fryer),* Jesus College, Cambridge (1996) In press.

P. de Jong. Reactorkundig ontwerp van warmtebehandelingsapparatuur. In: Procesmodellen: nieuwe mogelijkheden voor de zuivelindustrie. NIZO Mededeling M22 (1990) 14-21.

P. de Jong. Modellering van warmtebehandelingsprocessen in de zuivelindustrie. *Voedingsmiddelentechnologie* 26 (1993) 9-12.

P. de Jong. Optimaliseren van verhittingsprocessen in de zuivelindustrie. *Procestechnologie* 3 (1993) 29-32.

P. de Jong. Heat treatment from a chemical reactor engineering point of view. *NIZO annual report 1993* (1994) 15-19.

P. de Jong. Modelleren van warmtegeïnduceerde transformaties van melkcomponenten. In: Modelleren en modelsystemen, KNCV Symposia-reeks 10, (1994) 33-42.

P. de Jong. Process optimization with respect to product safety and operating costs. In: New shelf-life technologies and safety assessments, VTT Symposium 148, Espoo, Finland (1995) 203.

Curriculum vitae

Pieter de Jong was born on July 19, 1965 in Utrecht, the Netherlands. In 1982, he finished the secondary school at the Driestar college in Gouda. From September 1982 to June 1986 he studied Chemical Technology at the Hague College of Technology. In addition he worked at the Research and Development department of Melkunie B.V. in Woerden for a period of 5 months. In April 1987 he joined the group of Process Engineering at the Netherlands Institute for Dairy Research in Ede. About 3 years later he studied the fouling of heat treatment equipment in the dairy industry in a project sponsored by the Dutch government (Netherlands Agency for Energy and the Environment) resulting in a Ph.D. study at the Technical University of Delft which he finished in 1995.

Pieter is married to Anja de Jong-Assink and has two sons. He has been the organist of the Grote of St. Jans Kerk in Montfoort since 1983.