

Confectionery and Chocolate Engineering

PRINCIPLES AND APPLICATIONS

Ferenc Á. Mohos

WILEY Blackwell

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Principles and Applications

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SECOND EDITION

WILEY Blackwell

This edition first published 2017 © 2017 by John Wiley & Sons Ltd

Registered office: John Wiley & Sons, Ltd, The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, UK

Editorial offices: 9600 Garsington Road, Oxford, OX4 2DQ, UK The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, UK 111 River Street, Hoboken, NJ 07030-5774, USA

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Library of Congress Cataloging-in-Publication Data

Names: Mohos, Ferenc Á., author.
Title: Confectionery and chocolate engineering: principles and applications / Ferenc Á. Mohos.
Description: Chichester, West Sussex, United Kingdom ; Hoboken, New Jersey : John Wiley & Sons Inc., 2017. | Includes bibliographical references and index.
Identifiers: LCCN 2016035917 | ISBN 9781118939772 (cloth) | ISBN 9781118939765 (Adobe PDF) | ISBN 9781118939758 (ePub)
Subjects: LCSH: Confectionery. | Chocolate. | Chemistry, Technical. | Food–Analysis.

Classification: LCC TX783 .M58 2017 | DDC 641.86–dc 3 LC record available at https://lccn.loc.gov/2016035917

A catalogue record for this book is available from the British Library.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic books.

Cover image: SerAlexVi/Gettyimages

Set in 9.5/13pt, MeridienLTStd by SPi Global, Chennai, India.

 $10 \quad 9 \quad 8 \quad 7 \quad 6 \quad 5 \quad 4 \quad 3 \quad 2 \quad 1$

To the memory of my parents Ferenc Mohos and Viktória Tevesz

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Preface

The purpose of this book is to describe the features of the unit operations in confectionery manufacturing. The approach adopted here might be considered as a novelty in the confectionery literature. The choice of the subject might perhaps seem surprising, owing to the fact that the word *confectionery* is usually associated with handicraft instead of engineering. It must be acknowledged that the attractiveness of confectionery can be partly attributed to the coexistence of handicraft and engineering in this field. Nevertheless, large-scale industry has also had a dominant presence in this field for about a century.

The traditional confectionery literature focuses on technology. The present work is based on a different approach, where, by building on the scientific background of chemical engineering, it is intended to offer a theoretical approach to practical aspects of the confectionery and chocolate industry. However, one of the main aims is to demonstrate that the structural description of materials used in chemical engineering must be complemented by taking account of the hierarchical structure of the cellular materials that are the typical objects of food engineering. By characterizing the unit operations of confectionery manufacture, without daring to overestimate the eventual future exploitation of the possibilities offered by this book, I intend to inspire the development of new solutions in both technology and machinery, including the intensification of operations, the application of new materials and new and modern applications of traditional raw materials.

I have studied unit operations in the confectionery industry since the 1960s. During my university years, I began dealing with the rheological properties of molten chocolate (the Casson equation, rheopexy, etc.). This was an attractive and fruitful experience for me. Later on, I worked for the Research Laboratory of the Confectionery Industry for 3 years. Altogether I spent – on and off – half a century in this field, working on product development, production, quality control/assurance, purchasing and trading. These tasks, related mainly to sugar confectionery and chocolate, convinced me that a uniform attitude is essential for understanding the wide-ranging topics of confectionery and chocolate manufacture. As a young chemical engineer, I also started lecturing undergraduate and graduate students. Having gathered experience in education (compiling lectures, etc.), I found that this conviction was further confirmed.

In the late 1960s, my attention was firmly focused on the unit operations in this industry, and I tried to utilize and build on the results produced by the Hungarian school of chemical engineering (M. Korach (Maurizio Cora), P. Benedek, A. László and T. Blickle). Benedek and László discussed the topics of chemical engineering, placing the Damköhler equations in the centre of the theory, similarly to the way in which electricity is based on the Maxwell equations. Blickle and the mathematician Seitz developed structure theory and applied it to chemical engineering. Structure theory exploits the tools of abstract algebra to analyse the structures of system properties, materials, machinery, technological changes, etc. It is a useful method for defining concepts and studying their relations. The outcome of these studies is well reflected in several books and university lectures published by me and serves as the theoretical background for the present book as well.

Chapter 1 introduces the Damköhler equations as a framework for chemical engineering. This chapter outlines the reasons why this framework is suitable for studying the unit operations of the confectionery industry in spite of the cellular structure of the materials. In Chapter 2, the structural characterization of raw materials and products is discussed by means of structure theory. This chapter also demonstrates in detail the methods for preparing confectionery recipes taking compositional requirements into account.

Chapter 3 and Appendices 1 and 2 all deal with the engineering properties of the materials used in confectionery. Heat transfer and mass transfer are not discussed individually but are included in other chapters.

Rheology is essential to confectionery engineering. Therefore, a relatively large part of the book (Chapter 4) discusses the rheological properties of both Newtonian and non-Newtonian fluids, along with elasticity, plasticity, extensional viscosity, etc. Non-Newtonian flow, especially that of Casson fluids, is discussed in Chapter 12 and Appendix 3.

Some relevant topics in colloid chemistry are discussed in Chapters 5 and 11. In this context, the basics of fractal geometry cannot be ignored; thus, Appendix 4 offers an outline thereof. Comminution plays an important role in this field, as new procedures and machines related to comminution enable new chocolate technologies to be developed.

Chapters 7–9 discuss the operations of mixing, as well as the topics of solutions of carbohydrates in water and the evaporation of these solutions. These chapters provide confirmation that the Dühring rule, the Ramsay–Young rule, etc. are also valid for these operations.

Crystallization (Chapter 10) from aqueous solutions (candies) and fat melts (chocolate and compounds) is a typical operation in confectionery practice, and thus I highlight its dominant characteristics. In Chapter 13, pressing is briefly discussed. Extrusion (Chapter 14) and agglomeration (Chapter 15) are typical operations that manifest the wide-ranging nature of the confectionery industry.

Chapter 16 deals with inversion, the Maillard reaction and such complex operations as conching and also new trends in chocolate manufacture and (tangentially) baking.

Chapter 17 deals with the issues of water activity and shelf life. A separate chapter (Chapter 18) is devoted to food stability. The real meaning of such an approach is that from the start of production to the consumer's table, the kinetics

of the changes in the raw materials and products must be taken into consideration. Furthermore, in the light of this attitude, the concept of *food stability* must be defined more exactly by using the concepts of stability theory.

For the sake of completeness, Appendix 6 contains some technological outlines.

I intended to avoid the mistake of *he who grasps much holds little* (successfully? who knows?); therefore, I have not been so bold as to discuss such operations – however essential – as fermentation, baking and panning, about which I have very little or no practical knowledge. Similarly, I did not want to provide a review of the entire circle of relevant references.

Thus the substance that I grasped turned out to be great but rather difficult, and I wish I could say that I have coped with it. Here the gentle reader is requested to send me their remarks and comments for a new edition hopefully to be published in the future.

My most pleasant obligation is to express my warmest thanks to all the colleagues who helped my work. First of all, I have to mention the names of my professors, R. Lásztity (Technical University of Budapest) and T. Blickle (University of Chemical Engineering, Veszprém), who were my mentors in my PhD work, and Professor J. Varga (Technical University of Budapest), my first instructor in *chocolate science*. I am grateful to Professor S. Szántó and Professor L. Maczelka (Research Laboratory of the Confectionery Industry), who consulted me very much as a young colleague on the topics of this field. I highly appreciate the encouragement obtained from Mr M. Halbritter, the former president of the Association of Hungarian Confectionery Manufacturers; Professor Gy. Karlovics (Corvinus University of Budapest and Bunge Laboratories, Poland); Professor A. Fekete (Corvinus University of Budapest); Professor A. Salgó (Technical University of Budapest); Professor G. Szabo (Rector, Szeged University of Sciences); Professor A. Véha (Dean, Szeged University of Sciences); and Professor E. Gyimes (Szeged University of Sciences).

I am also indebted to Professor C. Alamprese (Università degli Studi di Milano, Italy); Ms P. Alexandre, a senior expert at CAOBISCO, Brussels, Belgium; Professor R. Scherer (Fachhochschule Fulda, Germany); and Professor H.-D. Tscheuschner and Professor K. Franke (Dresden University of Technology, Germany), as well as to D. Meekison for his valuable help provided in copyediting.

Last but not least, I wish to express my deep and cordial thanks to my family: to my daughter Viktória for correcting my poor English and to my wife Irén, who with infinite patience has tolerated my whimsicality and the permanent and sometimes shocking disorder around me and (despite all this) assured me a normal way of life.

> Ferenc Á. Mohos Budapest, Hungary

Preface to the second edition

Since the appearance of the first edition in 2010, important developments have emerged in the food engineering that called for a certain revision of the original version of the work completed 5 years ago. Therefore, the objectives of the current edition are twofold: on the one hand, it seeks to reflect main relevant research results, and on the other hand, it also intends to incorporate the discussion of such operations as drying, baking and roasting which are important topics in the confectionary practice. My hope is that new additions will not only enrich the content of the first edition but also shed light on fresh trends in the industry.

Individual chapters have been completed by the following themes: In Chapter 1 (and Appendix 5), the Blickle–Seitz system theory and SAFES methodology are presented in connection with the principles of food engineering. An easy matrix method of dimensional analysis is outlined. Relevant new issues in relation to food safety and quality assurance are also discussed in this chapter. Chapter 2 now also includes recipes of chocolate of high cocoa content and confectioneries for special dietetic purpose. Further in Chapter 4, new results concerning yield stress, microrheology and food oral processing are discussed. Chapter 10 highlights an important new initiative of the European Union, the so-called the ProPraline project. As a result of the new edition, Chapter 16 includes the topic of acrylamide formation in confectioneries of high current relevance. Also the operations of drying, baking and roasting are discussed here. A completely new chapter was added (Chapter 19) in order to reflect on the topics of manufacturing artisan chocolate and confectioneries. Important modifications also concern Appendix 3 in relation to linear flow models, whereby the Bingham, the Casson and the Ostwald-de Waele flow curves and the corresponding volume rates are presented. Furthermore, the constitutive equations of rheology in tensorial and in fractional calculus are briefly presented. Finally, topics of ultrasonic and photoacoustic testing are also highlighted as new emerging topics.

Acknowledgements

The author gratefully acknowledges the permission granted to reproduce the copyright material in this book: AarhusKarlshamn, Denmark (Figs 10.8–10.10 and 10.21); Akadémiai Kiadó, Budapest (Fig. 14.1); AVI Publishing Co. Inc., Westport, USA (Figs 3.1–3.3; Tables 3.1, 3.2, 3.19 and 3.20); Archer Daniels Midland Co. (ADM), IL, USA (Fig. 17.5); Carle & Montanari SpA, Milan (Figs 6.3, 6.5 and 6.6; Table 6.4); Elsevier Science Ltd, The Netherlands (Figs 5.10, 9.1, 9.2, 10.5(a)–(d), 10.6, 10.24–10.30 and 11.6; Tables 3.8 and 3.9); Professor K. Kerti, Budapest (Table 10.3); Professor R. Lásztity, Budapest (Figs 4.26 and 4.27); Professor J. Nyvlt, Prague, Czech Republic (Figs 10.1 and 10.7); Springer Science and Business Media, The Netherlands (Tables 17.2, 17.3 and 17.8; Section 17.1.6); Professor J.F. Steffe, Michigan, USA (Figs 4.5, 4.11, 4.13, 4.15–4.18 and 4.23; Table 4.1); P. Székely, Budapest (Figs 16.1 and 16.2; Tables 16.3 and 16.4); Wiley-VCH Verlag GmbH & Co KGaA, Germany; and Mrs Liselotte Rumpf, Karlsruhe, Germany (Figs 15.1–15.4; Table 15.1).

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PART I Theoretical introduction

CHAPTER 1 Principles of food engineering

1.1 Introduction

1.1.1 The Peculiarities of food engineering

Food engineering is based to a great extent on the results of chemical engineering. However, the differences in overall structure between chemicals and foods, that is, the fact that the majority of foods are of cellular structure, result in at least three important differences in the operations of food engineering – the same is valid for biochemical engineering.

- 1 Chemical engineering applies the Gibbs theory of multicomponent chemical systems, the principal relationships of which are based on chemical equilibrium, for example, the Gibbs phase rule. Although the supposition of equilibrium is only an approximation, it frequently works and provides good results. In the case of cellular substances, however, the *conditions of equilibrium do not apply in general*, because the cell walls function as semipermeable membranes, which make equilibrium practically possible only in aqueous media and for long-lasting processes. Consequently, the Gibbs phase rule cannot be a basis for determining the degrees of freedom of food engineering systems in general. For further details, see Section 1.3.2.
- **2** Another problem is that cellular substances prove to be chemically very complex after their cellular structure has been destroyed. In the Gibbs theory, the number of components in a multicomponent system is limited and well defined, not infinite. *The number of components in a food system can be practically infinite or hard to define; in addition, this number depends on the operational conditions*. Certainly, we can choose a limited set of components for the purpose of a study and this is the usual way but this choice will not guarantee that exclusively those components will participate in the operation considered.

Therefore, interpretation of the degrees of freedom in food engineering systems causes difficulties and is often impossible, because the number and types of participants (chemical compounds, cell fragments, crystalline substances, etc.) in food operations are hard to estimate: many chemical and physical changes may take place simultaneously, and a small change in the conditions (temperature, pH, etc.) may generate other types of chemical or physical changes. If we compare this situation with a complicated heterogeneous catalytic chemical process with many components, it is evident that

Confectionery and Chocolate Engineering: Principles and Applications, Second Edition. Ferenc Á. Mohos. © 2017 John Wiley & Sons Ltd. Published 2017 by John Wiley & Sons Ltd.

in food engineering we struggle with complex tasks that are not easier, only different.

Evidently, comminution plays a decisive role in connection with these peculiarities. However, in the absence of comminution, these two peculiarities – the existence of *intact cell wall* as barriers to equilibrium and the very high number of operational participants – may appear together as well; for example, in the roasting of cocoa beans, the development of flavours takes place inside *unbroken* cells. In such cases, cytological aspects (depot fat, mitochondria, etc.) become dominant because the cell itself works as a small chemical plant, the heat and mass transfer of which cannot be influenced by traditional (e.g. fluid-mechanical) means. This problem is characteristic of biochemical engineering.

3 The third peculiarity, which is a consequence of the cellular structure, is that the operational *participants* in food engineering may be not only chemical compounds, chemical radicals and other molecular groups but also *fragments of comminuted cells*.

In the case of chemical compounds/radicals, although the set of these participants can be infinitely diverse, the blocks from which they are built are well defined (atoms), the set of atoms is limited and the rules according to the participants are built are clear and well defined.

In the case of cellular fragments, none of this can be said. They can, admittedly, be classified; however, any such classification must be fitted to a given task without any possibility of application to a broader range of technological problems. This is a natural consequence of the fact that the fragments generated by comminution, in their infinite diversity, do not manifest such conspicuous qualitative characteristics as chemicals; nevertheless, they can be distinguished because slight differences in their properties, which occur by accident because of their microstructure, may become important.

This situation may be understood as the difference between discrete and continuous properties of substances: while chemical systems consist of atoms and combinations of them, to which stoichiometry can be applied, the systems of food engineering cannot be built up from such well-defined elements. This stoichiometry means that well-defined amounts by mass (atomic masses or molecular masses) may be multiplied by integers in order to get the mass fluxes in a reaction. However, in the recipes that are used for describing the compositions of foods, the mass fluxes are treated as continuous variables, contrary to the idea of stoichiometry.

1.1.2 The hierarchical and semi-hierarchical structure of materials

Although foods also consist of atoms in the final analysis, it is characteristic of food engineering that it does not go to an elementary decomposition of the entire raw material; however, a certain part of the raw material will be chemically
modified, and another part will be modified at the level of cells (by comminution). The structures of materials are hierarchical, where the levels of the hierarchy are joined by the *containing relation*, which is reflexive, associative and transitive (but not commutative): $A \rightarrow B$ means that B contains A, that is, \rightarrow is the symbol for the containing relation. The meaning of the reflexive, associative and transitive properties is:

- Reflexive: A contains itself.
- Associative: if $A \rightarrow (B \rightarrow C)$, then $(A \rightarrow B) \rightarrow C$.
- Transitive: if $A \rightarrow B \rightarrow C$, then $A \rightarrow C$ (the property is inheritable).

The transitive property is particularly important: if A = atom, B = organelle and C = cell (considered as levels), then the transitive relation means that if an organelle (at level B) contains an atom (at level A) and if a cell (at level C) contains this organelle (at level B), then that cell (at level C) contains the atom in question (at level A) as well.

The hierarchical structure of materials is illustrated in Figure 1.1. For the sake of completeness, Figure 1.1 includes the hierarchical levels of tissue, organs and organisms, which are of interest when one is choosing ripened fruit, meat from a carcass and so on. In a sense, the level of the organism is the boundary of the field of food (and biochemical) engineering.

This hierarchical structure is characteristic of cellular materials only when they are in an intact, unbroken state. Comminution may disrupt this structure; for example, if cellular fragments are dispersed in an aqueous solution and these fragments may themselves contain aqueous solutions as natural ingredients,



Figure 1.1 Hierarchical structure of materials.

then these relations can be represented by

$$A_1 \rightarrow C \rightarrow A_2$$

where A_1 represents the natural ingredients of a cell (an aqueous solution), C represents the cellular material and A_2 represents the aqueous solution in which the cellular material is dispersed. Evidently, in this case, the hierarchical levels are mixed, although they still exist to some extent. Therefore, for such cases of bulk materials, the term *semi-hierarchical structure* seems more appropriate.

If we allow that the degrees of freedom cannot be regarded as the primary point of view, a more important, in fact crucial, question is whether the set of chemical and/or physical changes that occur in an operation can be defined at all. The answer is difficult, and one must take into consideration the fact that an exact determination of this set is not possible in the majority of cases. Instead, an approximate procedure must be followed that defines the decisive changes and, moreover, the number and types of participants. In the most favourable cases, this procedure provides the result (i.e. product) needed.

1.2 The Damköhler equations

1.2.1 The application of the Damköhler equations in food engineering: conservative substantial fragments

In spite of the differences discussed earlier, the Damköhler equations, which describe the conservation of the fluxes of mass, component, heat and momentum, can provide a mathematical framework from the field of chemical engineering that can be applied to the tasks in food engineering (and biochemical engineering), with a limitation referring to the flux of component.

The essence of this limitation is that the entire set of components cannot be defined in any given cases. This limitation has to be taken into account by defining both the chemical components studied and their important reactions. The conservation law of component fluxes does hold *approximately* for this partial system. The correctness of the approximation may be improved if this partial set approaches the entire set of components. For example, if we consider the backing of biscuit dough, it is impossible to define all the chemical reactions taking place and all the components cannot be exact, because of the disturbing effect of by-reactions. However, what counts as a by-reaction? This uncertainty is the source of inaccuracy.

The conservation equations for mass, heat and momentum flux can be used without any restriction for studying the physical (and mechanical) operations since their concern is bulk materials. In Appendix 5, the concepts *conservative elements* and *conservative substantial fragments* are discussed in detail. In food

engineering, the concept conservative substantial fragment can substitute the concept of conservative elements (Mohos, 1982) which latter are essential in the chemistry. The epithet *conservative* practically means here that the Damköhler conservation equations hold also for these fragments. For example, diffusion of humidity (water) in cellular substances can be regarded if the other fraction of the substances were unchanged, that is, for the water content the Fick equation [see the Damköhler equation (1.4)] were exactly hold. However, it has to be mentioned that the conservation of these fragments are determined by the technological (physical and chemical) conditions. The situation is the same as in the case of atoms: in certain conditions also the atoms are splitting.

1.2.2 The Damköhler equations in chemical engineering

This chapter principally follows the ideas of Benedek and László (1964). Some further important publications (although not a comprehensive list) that are relevant are Charm (1971), Pawlowski (1971), Schümmer (1972), Meenakshi Sundaram and Nath (1974), Loncin and Merson (1979), Stephan and Mitrovic (1984), Zlokarnik (1985), Mahiout and Vogelpohl (1986), Hallström *et al.* (1988), Stichlmair (1991), VDI-Wärmeatlas (1991), Zogg (1993), Chopey (1994), Stiess (1995), Perry (1998), Hall (1999), Sandler (1999), McCabe *et al.* (2001), Zlokarnik (2006) and Dobre and Marcano (2007).

According to Damköhler, chemical–technological systems can be described by equations of the following type:

$$convection + conduction + transfer + source = local change$$
(1.1)

In detail,

$$\operatorname{div}[\Gamma \mathbf{v}] - \operatorname{div}[\delta \operatorname{grad} \Gamma] + \omega \varepsilon \ \Delta \Gamma + G = -\frac{\partial \Gamma}{\partial t}$$
(1.2)

where **v** is the linear velocity (in units of m/s); Γ is a symbol for mass, a component, heat or momentum; δ is the generalized coefficient of convection (m²/s); ω is the transfer surface area per unit volume (m²/m³); ϵ is the generalized coefficient of transfer; *G* is the flux of source and *t* is the time (s). Such equations can be set up for fluxes of mass, components, heat and momentum.

The Damköhler equations play a role in chemical and food engineering similar to that of the Maxwell equations in electrodynamics. The application of the Damköhler equations to food-technological systems is presented in Chapter 2. Let us consider these equations one by one.

Flux of mass:

$$\operatorname{div}[\rho \mathbf{v}] - [D\operatorname{grad}\rho] + \omega\beta'\Delta\rho + G = -\frac{\partial\rho}{\partial t}$$
(1.3)

where **v** is the linear velocity (m/s), ρ is the density (kg/m³), β' is the mass transfer coefficient (m/s), *D* is the self-diffusion coefficient (m²/s) and *G* is the source of mass flux (kg/m³ s).

Flux of a component:

where c_i is the concentration of the *i*th component (mol/m³), *D* is the diffusion coefficient (m²/s), β is the component transfer coefficient (m/s), v_i is the degree of reaction for the *i*th component and *r* is the velocity of reaction [(mol/(m³ s)].

Flux of heat:

div
$$[\rho c_p T v]$$
 – div $[\lambda \text{ grad } T]$ + $\omega \alpha \Delta T + v_i r \Delta H = -\partial(\rho c_p T) / \partial t$
Fourier's 2nd law Newton's law of cooling (1.5)

where c_p is the specific heat (*p* is constant) [J/(kgK)], *T* is the temperature (K), λ is the thermal conductivity (W/mK), ΔH is the heat of reaction (J/mol) and α is the heat transfer coefficient [J/(m² s K)].

The flux of momentum is described by the Navier-Stokes law,

$$\operatorname{Div}\{\rho \mathbf{v} \cdot \mathbf{v}\} - \operatorname{Div}\{\eta \text{ Grad } \mathbf{v}\} + \omega \gamma \ \Delta \mathbf{v} + \operatorname{grad } p = -\frac{\partial[\rho \mathbf{v}]}{\partial t}$$
(1.6)

where Div is tensor divergence, Grad is tensor gradient, \cdot is the symbol for a dyadic product, η is dynamic viscosity [kg/(m s)], $\gamma = (f' \rho \mathbf{v}/2)$ is coefficient of momentum transfer [kg/(m² s)], f' is frictional (or Darcy -) coefficient [dimensionless], and p is pressure [kg/(m s²)].

Equations (1.3)–(1.6) are called the *Damköhler equation system*.

In general, the Damköhler equations cannot be solved by analytical means. In some simpler cases, described later, however, there are analytical solutions. For further details, see Grassmann (1967), Charm (1971), Loncin and Merson (1979), Hallström *et al.* (1988) and Banks (1994).

1.3 Investigation of the Damköhler equations by means of similarity theory

1.3.1 Dimensionless numbers

Let us suppose that a set of Damköhler equations called *Form 1* are valid for a technological system called *System 1*, and a set of equations *Form 2* are valid for *System 2*. It is known from experience that if similar phenomena take place in the two systems, then this similarity of phenomena can be expressed by a relationship denoted by \sim , as in *Form 1* \sim *Form 2*. Similarity theory deals with the description of this relationship.

The simplest characteristics of this similarity are the ratios of two geometric sizes, two concentrations and so on. These are called *simplex values*.

1.3.1.1 Complex values

The first perception of such a relationship is probably connected with the name of Reynolds, who made the observation, in relation to the flow of fluids, that System 1 and System 2 are similar if *the ratios of momentum convection to momentum conduction in these systems are equal to each other*.

Let us consider Eqn (1.1),

$$convection + conduction + transfer + source = local change$$
(1.1)

for *momentum flux*. Since the terms for convection, conduction and so forth on the left-hand side evidently have the same dimensions in the equation, their ratios are dimensionless. One of the most important dimensionless quantities is the ratio of momentum convection to momentum conduction, which is called the *Reynolds number*, denoted by *Re*. $Re = Dv\rho/\eta$, where *D* is a geometric quantity characteristic of the system and *v* is a linear velocity,

$$v = \frac{Q}{R^2 \pi} \tag{1.7}$$

where *Q* is volumetric flow rate (m^3/s) and *R* is radius of tube (m).

For conduits of non-circular cross section, the definition of the *equivalent diam*eter D_e is

$$D_{\rm e} = \frac{\text{area of stream cross section}}{\text{wetted perimeter}}$$
 (1.8)

The value of D_e for a tube is $4D^2\pi/4D\pi = D$ (the inner diameter of the tube), and for a conduit of square section, it is $4a^2/4a = a$ (the side of the square). For heat transfer, the total length of the heat-transferring perimeter is calculated instead of the wetted perimeter (e.g. in the case of part of a tube).

It has been shown that several different types of flow can be characterized by their Reynolds numbers:

Re < about 2300: laminar flow

Re > 2300 to *Re* < 10 000: transient flow

 $Re > 10\,000$: turbulent flow

This means, for example, that if for System 1 the Reynolds number Re(1) is 1000 and for System 2 the Reynolds number Re(2) is 1000, then the flow shows the same (laminar) properties in both systems. Moreover, *all systems in which the Reynolds numbers are the same show the same flow properties*.

In order to understand the role of the Reynolds number, let us interpret the form of Eqn (1.6) as

momentum convection + momentum conduction = local change of momentum

If Re = 1, this means for the momentum part that convection = 50% and conduction = 50%; if Re = 3, then convection = 75% and conduction = 25%; and if Re = 99, then convection = 99% and conduction = 1%.

It is difficult to overestimate the importance of Reynolds' idea of similarity, because this has become the basis of modelling. One can investigate the

phenomena first with a small model, which is relatively cheap and can be made quickly, and then the size of the model can be increased on the basis of the results. Modelling and increasing the size (scaling-up) are everyday practice in shipbuilding, in the design of chemical and food machinery, and so on.

If, for a given system, *D*, ρ and η are constant, the type of flow depends on the linear velocity (*v*) if only convection and conduction take place.

Using similar considerations, many other dimensionless numbers can be derived from the Damköhler equations; some of these are presented in Tables 1.1 and 1.2. From Table 1.1, we have the following, for example:

• In Eqn (1.4), the ratio of convection to conduction is the Peclet number for component transfer (*Pe'*),

$$Pe' = \frac{\operatorname{div}[c_i \mathbf{v}]}{\operatorname{div}[D \operatorname{grad} c_i]} = \frac{\mathbf{v}d}{D}$$

• In Eqn (1.6), the ratio of the momentum source to the momentum convection is the Euler number (*Eu*),

$$Eu = \frac{\operatorname{grad} p}{\operatorname{Div}\{\rho \mathbf{v} \cdot \mathbf{v}\}} = \frac{\Delta p}{\rho v^2}$$

Another way of deriving dimensionless numbers is illustrated in Table 1.2. In the third column of this table, the ratio of transfer to conduction is represented instead of the ratio of transfer to convection, and in this way another system of dimensionless numbers (i.e. variables) is derived.

Note that:

- If the source is a force due to a stress, equal to $\Delta p d^2$, then the *Euler number* is obtained.
- If the source is a gravitational force, equal to $\rho g d^3$, then the *Fanning number* is obtained.

| Flux | Convection/conduction | Transfer/convection | Source/convection |
|---------------------|-----------------------|---------------------|-------------------|
| Component (Eqn 1.4) | Pe' | Sť′ | Da(I) |
| Heat (Eqn 1.5) | Pe | St | Da(III) |
| Momentum (Eqn 1.6) | Re | f'/2 | Eu or Fa |

 Table 1.1 Derivation of dimensionless numbers.

Table 1.2 Another way of deriving dimensionless numbers.

| Flux | Convection/conduction | Transfer/conduction | Source/convection |
|---------------------|-----------------------|---------------------|-------------------|
| Component (Eqn 1.4) | Pe' | Nu' | Da(I) |
| Heat (Eqn 1.5) | Pe | Nu | Da(III) |
| Momentum (Eqn 1.6) | Re | A (no name) | Eu or Fa |

The dimensionless numbers in Tables 1.1 and 1.2 are as follows:

Pe' = vd/D, the Peclet number for component transfer.

- Pe = vd/a, the *Peclet number for heat transfer* (*a* = temperature conduction coefficient or heat diffusion coefficient).
- $St' = \beta/\nu$, the *Stanton number for component transfer* (β = component transfer coefficient).

 $St = \alpha / \rho c_p v$, the Stanton number for heat transfer (α = heat transfer coefficient).

 $\gamma = f' \rho v/2$, the momentum transfer coefficient $(f'/2 = \gamma / \rho v)$.

 $Da(I) = v_i r d/c_i v$, the *first Damköhler number*; this is the component flux produced by chemical reaction divided by the convective component flux.

 $Da(III) = v_i \Delta H r d \rho c_p v \Delta T$, the *third Damköhler number*; this is the heat flux produced by chemical reaction divided by the convective heat flux.

 $Eu = \Delta p / \rho v^2$, the *Euler number*; this is the stress force divided by the inertial force. Fa = gd/v², the *Fanning number*; this is the gravitational force divided by the inertial force.

 $Nu' = \beta \beta d/D$, the Nusselt number for component transfer (D = diffusion coefficient). $Nu = \alpha d/\lambda$, the Nusselt number for heat transfer ($\lambda =$ thermal conductivity).

Following van Krevelen's treatment (1956), $3 \times 3 = 9$ independent dimensionless numbers can be derived in this way from three equations (*rows*) and four types of phenomena (*columns*, namely, convection, conduction, transfer and sources), and three rates can be produced from these numbers. With the help of such matrices of nine elements (see Tables 1.1 and 1.2), other dimensionless numbers can also be obtained, which play an important role in chemical and food engineering. For example, values of *efficiency* can be derived in this way:

Pr = Pe/Re = v/a, the *Prandtl number* Sc = Pe'/Re = v/D, the *Schmidt number*

Le = Sc/Pr = a/D, the Lewis number

1.3.2 Degrees of freedom of an operational unit

The number of degrees of freedom of an operational unit is a generalization of corresponding concept in the Gibbs phase rule. The question of how to determine the number of degrees of freedom of an operational unit was first put by Gilliland and Reed (1942); further references are Morse (1951), Benedek (1960) and Szolcsányi (1960).

For multiphase systems, the Gibbs classical theory, as is well known, prescribes the equality of the chemical potentials for each component in each phase in equilibrium. If μ_k^{f} (where k = 1, 2, ..., K, and f = 1, 2, ..., F) denotes the chemical potential of the *k*th component in the *f*th phase, then the following holds in equilibrium:

• For the *f*th phase, when there are *K* components,

$$\mu_1^f = \mu_2^f = \dots = \mu_K^f$$

that is, F(K-1) equations.

• For the *k*th component, when there are *F* phases,

$$\mu_k^1 = \mu_k^2 = \dots = \mu_k^F$$

that is, K(F-1) equations.

In equilibrium, the additional variables which are to be fixed are *T* and *p*. Consequently, in equilibrium, the number of variables (φ) which can be freely chosen is

$$\varphi = F(K-1) - K(F-1) + 2 = K - F + 2 \tag{1.9}$$

This is the Gibbs phase rule, which is essential for studying multiphase systems.

Even in the extreme case where the solubility of a component in a solvent is practically zero, the phase rule can nevertheless be applied by considering the fact that the chemical potential of this component is sufficient for equilibrium in spite of its very small concentration.

The generalization that we need in order to obtain φ for an operational unit is given by

$$\varphi = L - M \tag{1.10}$$

where φ is the number of degrees of freedom, *L* is the total number of variables describing the system and *M* is the number of independent relations between variables.

In the simplest case, that of a simple stationary operational unit with an isolated wall, if the number of input phases is F and the number of output phases is F', then the total number of variables is

$$L = (F + F')(K + 2)$$

where *K* is the number of components. (To describe a homogeneous phase, (K+2) data points are needed.)

Let us now consider the constraints. There are constraints derived from the conservation laws for every component and also for energy and momentum, which means (K+2) constraints for every phase.

The number of constraints for equilibrium between two phases is (K+2), which means (F'-1)(K+2) constraints for the output phases. Consequently, the total number of constraints is

M = (K+2) + (F'-1)(K+2)

and, finally,

$$\varphi = F(K+2) \tag{1.11}$$

However, in the case of *cellular substances*, the conditions of equilibrium typically do not apply; moreover, the number of components can usually not be determined. Therefore, the Gibbs phase rule cannot be used for food-technological systems except in special cases where exclusively chemical changes are taking place in the system studied. This uncertainty relating to the degrees of freedom is an essential characteristic of food engineering.

1.3.3 Polynomials as solutions of the Damköhler equations

The solution of the Damköhler equation system can be approximated by the product:

 Π_1^{a} can be obtained in the form

$$\prod_{2}^{b} \times \prod_{3}^{c} \times \dots \times \prod_{i}^{d} \times \dots$$
 (1.12)

where Π_i is dimensionless numbers created from the terms of the Damköhler equations and *a*, *b*, *c*, *d*, ... are exponents which can be positive/negative integers or fractions.

First of all, it is to be remarked that Eqn (1.12) supposes that the solution is provided by the so-called *monom* (not by *binom* as, e.g. Π_1^a can be obtained in the form $\Pi_2^b \times \Pi_3^c \times \cdots \times \Pi_i^d \times \cdots$, i.e. monom does not contain addition but multiplication operation only) – this supposition is not fulfilled in each case!

While derivation of dimensionless numbers from the Damköhler equations refers to a special circle of phenomena of transfer, which is crucial from our point of view, dimensional analysis is a general method that is not limited to chemical engineering. The principle of dimensional analysis has been first expressed likely by Buckingham, therefore, it is known as Buckingham's Π -theorem. This theorem is the base of Eqn (1.12) as well. According to the formulation of Loncin and Merson (1979), 'if *n* independent variables occur in a phenomenon and if *n*' fundamental units are necessary to express these variables, every relation between these *n* variables can be reduced to a relation between *n*–*n*' dimensionless variables.'

The principal idea represented by Eqn (1.12) is that convergent polynomial series, for example, a Taylor series, can approximate well almost any algebraic expression and thus also a solution of the Damköhler equations. But it is not unimportant how many terms are taken into account. There are algebraic expressions that cannot be approximated by a monomial, because they are not a product of terms but a sum of terms.

However, the general idea is correct, and formulae created from the dimensionless numbers Π_i according to Eqn (1.12) provide good approximations of monomial or binomial form. (Trinomials are practically never used.)

How can this practical tool be used? Let us consider a simple example. A warm fluid flows in a tube, which heats the environment; for example, this might be the heating system of a house. If heat radiation is negligible, the Nusselt, Reynolds and Peclet numbers for the simultaneous transfer of momentum and heat should be taken into account (see Table 1.2). Since the appropriate dimensionless numbers created from the terms of the Damköhler equations are:

Nu for heat (convection/conduction)

Re for momentum (convection/conduction)

Pe for heat (convection/conduction) or Pr = Pe/Re, therefore, neglecting the gravitational force We obtain the following function *f*:

$$Nu = f(Re, Pr) \tag{1.13}$$

which is an expression of Eqn (1.12) for the aforementioned case.

Equation (1.12) is one of the most often applied relationships in chemical and food engineering. Its usual form is

$$Nu = CRe^a \times Pr^b \tag{1.14}$$

which has the same monomial form as Eqn (1.12).

Many handbooks give instructions for determining the values of the exponents *a* and *b* and the constant *C*, depending upon the boundary conditions. Let us consider the physical ideas on which this approach is based.

1.4 Analogies

1.4.1 The Reynolds analogy

An analogy can be set up between mechanisms as follows:

Momentum transfer ↔ heat transfer

Momentum transfer ↔ component transfer

Component transfer ↔ heat transfer

This analogy can be translated into the mathematical formalism of the transfer processes.

From physical considerations, Reynolds expected that the momentum flux (J_p) and the heat flux (J_a) would be related to each other, that is, if

$$J_q = \frac{\alpha}{c_p \rho} \times A \Delta(\rho c_p T)$$
(1.15)

then

$$J_q = \frac{\gamma}{\rho} \times A\Delta(\rho \mathbf{v}) \tag{1.16}$$

In other words, *the moving particles transport their heat content also*. Then he supposed that

$$\frac{\alpha}{c_p \rho} = \frac{\gamma}{\rho} \tag{1.17}$$

or, in another form,

$$\frac{f'}{2} = \frac{\alpha}{c_p \rho} = St \tag{1.18}$$

If the flux of a component is

$$J_i = \beta F \Delta c_i \tag{1.19}$$

then Reynolds' supposition can be extended to this third kind of flux as follows:

$$St = St' = \frac{f'}{2} \tag{1.20}$$

where *St* is the Stanton number for heat transfer $(St = \alpha/c_p \rho)$, *St'* is the Stanton number for component transfer $(St' = \beta/\mathbf{v})$, $f'/2 = \gamma/\rho \mathbf{v}$ and γ is the momentum transfer coefficient.

If the Reynolds analogy formulated in Eqn (1.20) is valid, then if we know one of the three coefficients α , β or γ , the other two can be calculated from this equation. This fact would very much facilitate practical work, since much experimental work would be unnecessary.

But proof of the validity of the Reynolds analogy is limited to the case of strong turbulence. In contrast to the Reynolds analogy,

$$a \neq v \neq D \tag{1.21}$$

that is,

$$Pr \neq Sc \neq Le \tag{1.22}$$

Equation (1.17) is valid only for turbulent flow of gases. In the case of gases,

$$Pr \approx 0.7 - 1 \tag{1.23}$$

is always valid.

1.4.2 The Colburn analogy

Colburn introduced a new complex dimensionless number, and this made it possible to maintain the form of the Reynolds analogy:

$$J_q = St P r^{2/3}$$
(1.24)

$$J_i = St' \, Sc^{2/3} \tag{1.25}$$

and

$$J_p = \frac{f'}{2} \tag{1.26}$$

Finally, formally similarly to the Reynolds analogy,

$$St Pr^{2/3} = St' Sc^{2/3} = \frac{f'}{2}$$
 (1.27)

The Colburn analogy formulated in Eqn (1.27) essentially keeps Reynolds' principal idea about the coupling of the momentum (mass) and thermal flows and gives an expression that describes the processes better. *Equation* (1.27) *is the basis of the majority of calculations in chemical engineering.*

In view of the essential role of Eqn (1.27), it is worth looking at its structure:

$$St = \frac{Nu}{RePr} = \frac{\alpha}{\rho c_p v}$$
$$St' = \frac{Nu'}{ReSc} = \frac{\beta}{v}$$
$$\frac{f'}{2} = \frac{\gamma}{\rho v}$$

The numbers *Pr* and *Sc* are parameters of the fluid:

$$Pr = \frac{v}{a}$$
$$Sc = \frac{v}{D}$$

Additional material parameters are needed for calculations, namely, α , ρ and c_p . If **v** is known, f and β can be calculated.

This theoretical framework (see Eqns 1.13, 1.14 and 1.27) can be modified if, for example, a buoyancy force plays an important role – in such a case, the *Grashof number*, which is the ratio of the buoyancy force to the viscous force, appears in the calculation. A detailed discussion of such cases would, however, be beyond the scope of this book. A similar limitation applies to cases where the source term is related to a chemical reaction: chemical operations in general are not the subject of this book.

A more detailed discussion of these topics can be found in the references given in Section 1.2.

1.4.3 Similarity and analogy

Similarity and analogy are quite different concepts in chemical and food engineering, although they are more or less synonyms in common usage. Therefore, it is necessary to give definitions of these concepts, which emphasize the differences in our understanding of them in the present context.

Similarity refers to the properties of machines or media. Similarity means that the geometric and/or mechanical properties of two machines or streaming media can be described by the same mathematical formulae (i.e. by the same dimensionless numbers) that our picture of the flux (e.g. laminar or turbulent) is similar in two media. Similarity is the basis of scaling-up.

Analogy refers to transfer mechanisms. Analogy means that the mechanisms of momentum, heat and component transfer are related to each other by the way that components are transferred by momentum and, moreover, components transfer heat energy (except in the case of heat radiation). This fact explains the important role of the Reynolds number, which refers to momentum transfer.

1.5 Dimensional analysis

This is a simple mathematical tool for creating relationship between physical variables, keeping the rule that *the physical expressions shall be homogeneous from the viewpoint of dimension:* both sides of the equations must have the same dimension. Homogeneity also means that the equation remains unchanged if the system of the fundamental units changes (e.g. SI \leftrightarrow Anglo-Saxon system). Dimensional analysis can be very fruitful for solving complicated problems easily in various fields of physics, biology, economics and others.

Dimensional analysis contracts physical variables into dimensionless groups, which will be the new variables; by so doing, the number of variables will be decreased. The lesser the number of variables, the greater the advantage: for example, if instead of 6 variables only 3 variables are to be studied experimentally, supposed that 5 points of every variable are to be measured, then instead of $5^6 = 15\,625$ only $5^3 = 125$ points are to be measured in the labour experiments.

There is a developed theory of dimensional analysis which abundantly applies the results of linear algebra and computerization (see Barenblatt, 1987; Huntley, 1952; Zlokarnik, 1991). Instead of discussing these classical methods based on solutions of linear equation system, we represent here the Szirtes method (Szirtes, 1998; 2006) by examples in a rather simplified and slightly modified form, which is very easy and can be generally used.

Szirtes exhaustively details the cases as well for which the approaches of dimensional analysis must be cautiously used. Two considerations of him are mentioned here:

- **1** The Buckingham Π -theorem relates to *products* of dimensionless π -numbers, that is, monoms, which do not contain the algebraic operation addition (+). If a formula contains addition (i.e. it is binom, trinom, etc.), its transformation into a dimensionless formula by dimensional analysis either needs some special considerations or impossible.
- **2** The obtained dimensionless formula needs *experimental checking* in every case, since the dimensional correctness is only a necessary but not a sufficient condition.

Example 1.1 Heat transfer by fluid in tube

The choice of variables is done according to physical considerations:

- α : heat transfer coefficient (kg s⁻³)
- w: velocity of fluid (m s⁻¹)
- q: heat capacity (kg m⁻¹ s⁻²)
- v : kinematic viscosity of fluid (m² s⁻¹)
- *d*: diameter of tube (m)
- λ : coefficient of thermal conductivity (kg m s⁻³)

 Δt : temperature different between the fluid and the tube wall (K)

| | Variables | | | | | | | |
|--------------|-----------|----|----|----|---|----|------------|--|
| Units | α | w | q | v | d | λ | Δt | |
| M (kg) | 1 | 0 | 1 | 0 | 0 | 1 | 0 | |
| <i>L</i> (m) | 0 | 1 | -1 | 2 | 1 | 1 | 0 | |
| T (s) | -3 | -1 | -2 | -1 | 0 | -3 | 0 | |
| t (K) | -1 | 0 | -1 | 0 | 0 | -1 | 1 | |

We obtained the so-called *dimension matrix* of (4×7) size. In dimension matrix, a non-singular quadratic matrix has to be chosen (i.e. its determinant is not zero),

which is shown by bold numbers here, denoted by **A**. The sequence of variables has to be written in such a way that this quadratic matrix should be on the right side. The residue of the dimension matrix on the left side is denoted by **B**. That is, the dimension matrix has \boxed{B} \boxed{A} the following form:

In the next step, this dimension matrix of (4×7) size has to be completed to a quadratic matrix as follows.

| 1 | 0 | 0 | 0 | 0 | 0 | 0 |
|----|----|----|----|---|----|---|
| 0 | 1 | 0 | 0 | 0 | 0 | 0 |
| 0 | 0 | 1 | 0 | 0 | 0 | 0 |
| 1 | 0 | 1 | 0 | 0 | 1 | 0 |
| 0 | 1 | -1 | -2 | 1 | 1 | 0 |
| -3 | -1 | -2 | -1 | 0 | -3 | 0 |
| -1 | 0 | -1 | 0 | 0 | -1 | 1 |

The completed quadratic matrix has the following form (I: unit matrix; 0: zero matrix):

The next step is to calculate $\begin{bmatrix} I & 0 \\ B & A \end{bmatrix}$ the inverse of the completed quadratic matrix.

| Variables | π_1 | π_2 | π_3 | | | | |
|------------|---------|---------|---------|----|---|----|---|
| α | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| W | 0 | 1 | 0 | 0 | 0 | 0 | 0 |
| 9 | 0 | 0 | 1 | 0 | 0 | 0 | 0 |
| ν | 0 | -1 | 1 | -3 | 0 | -1 | 0 |
| d | 1 | 1 | 0 | 5 | 1 | 2 | 0 |
| λ | -1 | 0 | -1 | 1 | 0 | 0 | 0 |
| Δt | 0 | 0 | 0 | 1 | 0 | 0 | 1 |

The structure of the inversed matrix is as follows:

From the inverse matrix $\begin{array}{|c|c|c|} I & 0 \\ \hline -A^{-1} \times B & A^{-1} \end{array}$, the values of the dimensionless numbers can be directly obtained:

 $\pi_1 = \alpha d\lambda^{-1} =$ Nusselt number

 $\pi_2 = wdv^{-1} = \text{Reynolds number}$

 $\pi_3 = q v \lambda^{-1} =$ Prandtl number

That is, the classical formula is obtained: $Nu = \text{constant} \times Re^a Pr^b$

Evidently, the choice of variables is contingent: in this case, the temperature difference (Δt) turned out to be a surplus! This uncertainty can be, on the one hand, an inadequacy of dimensional analysis but sometimes also an advantage as the aforementioned example shows, since it can be seen from the calculation – before any experiment! – that Δt can be neglected. The lesson of this example is that only six variables have to be accounted instead of seven; in addition, the experiments need only three variables (*No*, *Re*, *Pr*), and the constants can be determined by linearization.

Example 1.2 By the Szirtes method, let us calculate the flow rate (*V*) in a tube of *D* diameter if the pressure difference is Δp and the viscosity of fluid is η (the solution is the well-known Hagen–Poiseuille equation). This example is derived from Szirtes (1998, 2006).

| | V | Δp | η | | D |
|--------------|---------|------------|----|----|---|
| | 1 | 0 | 0 | | 0 |
| M(kg) | 0 | 1 | 1 | | 0 |
| <i>L</i> (m) | 3 | -2 | -1 | | 1 |
| <i>T</i> (s) | -1 | -2 | -1 | | 0 |
| | π_1 | | | | |
| V | 1 | 0 | 0 | 0 | |
| Δp | -1 | -1 | 0 | -1 | |
| η | 1 | 2 | 0 | 1 | |
| D | -4 | 0 | 1 | -1 | |

The completed dimension matrix and its inverse.

Solution: $\pi_1 = (V\eta/\Delta p D^4)$, that is, $V = \text{constants} \times \Delta p D^4/\eta$

Remark: In case of more or other variables (e.g. the length or/and cross section of tube), the solution is too complicated. Also this example demonstrates that albeit dimensional analysis is very many-sided but not omnipotent.

1.6 System theoretical approaches to food engineering

A strong tendency in food process engineering is the growing attention paid to the relations between processes, products, emerging technologies, heat treatments and food safety. Research tools like mathematical modelling, especially computer fluid dynamics, and sophisticated methods of product characterization are the most intensively developing fields (see Bimbenet *et al.*, 2007).

The models currently used in food process engineering simplify too much both the food system description and the mechanisms and rate equations of changes: The food system is supposed to be homogeneous and continuous. In this way, thermodynamic and kinetic equations deduced for ideal gas or liquids, in conditions close to equilibrium are applied to cellular solid foods, in conditions far away from the equilibrium. However, it is necessary to develop advanced concepts and methodologies in food process engineering. The new models for food and processes development must incorporate information about all these aspects (thermodynamic, structural, chemist and biochemist and even mechanics). Only in this way, they would be able to calculate and predict the real changes in the whole quality of food product in line with the process progression.

In the spirit of such ideas the system theory of chemical engineering developed by Blickle and Seitz (1975), Blickle (1978) was adapted to food engineering by Mohos (1982). For the mathematical details and examples, see Appendix 5.

Fito *et al.* (2007) present a comprehensive model of food engineering called systematic approach to food process engineering (*SAFES*) in the sense of food process engineering for product quality. The SAFES methodology (Fito *et al.*, 2007) recognizes the complexity of food system and allows coordinating the information about food structure, composition, quality, thermodynamic and so on in adequate tools to develop real food and processes models. This brief review is not capable of replacing the original article, which can be found in the Internet; therefore, it is limited to itemize the main ideas of it.

- *Food product engineering*: modelling of food and biological systems by studying the structure of food system as the structure–properties ensemble (e.g. levels of complexity in matter condensation).
- The SAFES defines a *simplified space of the structured phases and components*, moreover, of *aggregation states* in order to describe the material structure.
- It defines the descriptive matrix, a *mathematical tool to describe the food system* by the help of:
 - The state variables: the share-out of matter among components and structured phases
 - Mass and volume balances inside the product
 - The energy inside the system: the Gibbs free energy
 - Equilibrium and driving forces
 - Transport mechanisms and rate equations
- Food process engineering consists of modelling of food operations and processes:
 - Definition of unit operation and stage of change
 - Mass balances and transformed matrices: matrix of changes
 - To construct the process matrix

1.7 Food safety and quality assurance

When studying the principles of food engineering, the concepts food safety and quality assurance (QA) must not be omitted although a detailed discussion of them exceeds the possibilities of this work. Therefore, this presentation is limited to a sketch and provides the appropriate essential references, which can be found in the Internet.

In the food industry, QA systems such as the Hygiene Code (FAO/WHO, 2009; Codex Alimentarius Committee, 1969), the Hazard Analysis Critical Control Points (HACCP) and the International Organization for Standardization (ISO) 9000 series are applied to ensure food safety and food quality to prevent liability claims and to build and maintain the trust of consumers.

Quality is defined by the ISO as 'the totality of features and characteristics of a product that bear on its ability to satisfy stated or implied needs.' Safety differs from many other quality attributes since it is a quality attribute that is difficult to observe. A product can appear to be of high quality, that is, well coloured, appetizing, flavourful and so on, and yet be unsafe because it is contaminated with undetected pathogenic organisms, toxic chemicals or physical hazards. On the other hand, a product that seems to lack many of the visible quality attributes can be safe.

Safety or QA program should focus on the prevention of problems, not simply curing them. Safety and QA should be ongoing processes incorporating activities beginning with selecting and preparing the soil and proceeding through to consumption of the product. Both safety and QA should focus on the prevention of problems, not simply curing them since, once safety or quality is reduced, it is virtually impossible to go back and improve it for that item. It is possible, however, to assure that the same problem does not affect future products (Silva *et al.*, 2002).

HACCP aims to assure the production of safe food products by using a systematic approach (i.e. a plan of steps) to the identification, evaluation and control of the steps in food manufacturing that are critical to food safety (Leaper, 1997). HACCP focuses on technological aspects of the primary process.

CAOBISCO (2011) provides a Guide of Good Hygiene Practices that can be regarded a competent document in this field.

The ISO 9000 series aims to achieve uniformity in products and/or services, preventing technical barriers to free trade throughout the world. ISO consists of a checklist to assure managerial aspects. It requires the establishment of procedures for all activities and handling, which must be followed by ensuring clear assignment of responsibilities and authority (Hoogland *et al.*, 1998). See further ISO (1984, 1990, 1994) documents.

For studying further references concerning food safety, QA and food quality, see Lásztity (2008), Carpenter *et al.* (2000), Defence Fuel & Food Services (2013), Food Safety Authority of Ireland (2011) and Martin (1997). References to the

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CHAPTER 2

Characterization of substances used in the confectionery industry

2.1 Qualitative characterization of substances

2.1.1 Principle of characterization

The characterization of the substances used in the confectionery industry is based on two suppositions:

- 1 The substances are partly of colloidal and partly of cellular nature.
- **2** From a technological point of view, their properties are essentially determined by the hydrophilic/hydrophobic characteristics of their ingredients.

These substances are complex colloidal systems, that is, organic substances of mostly natural origin which consist of various simple colloidal systems with a hierarchical or quasi-hierarchical structure. Let us consider the example of the hierarchical structure of a food represented in Figure 2.1.

Figure 2.1 (a) shows, in outline, the structure of a substance: a solution containing solids and oil droplets. Figure 2.1 (b) shows a structural formula using an oriented graph consisting of vertices and arrows. The vertices of the graph are symbols representing the components from which the substance is theoretically constructed. The arrows relate to the *containing relation* and are directed from the contained symbol to the containing symbol; for example, dissolved substances are contained by water. Such a diagram can be regarded as a primitive formula of the given substance which, to some extent, imitates the structural formulae of the simplest chemical compounds.

A *quasi-hierarchical* attribute is more expressive, since there can be cross relations as well; see the position of *emulsifier*. The structure shown in Figure 2.1 is less complex than this, however. Although this way of representing structural relations is very simple, it can express the hydrophilic/hydrophobic behaviour of a system. Evidently, from an external viewpoint, this system behaves like a hydrophilic system, as does, for example, milk cream (as opposed to milk butter); that is, it is an oil-in-water (O/W) system.

The materials studied often have a *cellular* structure. The cell walls hinder the free transport of material to a great extent, and therefore the actual material flows are determined by the particle size, since comminution more or less destroys the cell walls. This effect can be important in the case of cocoa mass because the

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Figure 2.1 Hierarchical structure of foods. Example: an aqueous solution contains solid particles and oil droplets coupled by an emulsifier to the aqueous phase.

amount of free cocoa butter equals the total cocoa butter content only if all the cocoa cells are cut up.

This characterization of substances is not capable of reflecting those properties which need to be explored by microstructural studies, for example, the polymorphism of lactose in milk powder and the fine structure of proteins.

2.1.2 Structural formulae of confectionery products

Structural formulae of various confectionery products obtained by the application of structure theory (see Appendix 5) are shown in Figures 2.2–2.16. The







Figure 2.9 Structural formula of marzipan (or of persipan, with apricot stones). d = dispersion.

Cut

almonds



Figure 2.10 Structural formula of confectionery foams. s = solution; sw = swelling; f = foaming.

Figure 2.11 Structural formula of granules, tablets and lozenges. s = solution; d = dispersion; sw = swelling.

Figure 2.12 Structural formula of dragées.



Figure 2.13 Structural formula of dough. s = solution; e = emulsion; g = gelling; sw = swelling.









Figure 2.16 Structural formula of ice cream. s = solution; e = emulsion; sw = swelling; f = foaming; cry = crystallization

substances named in these figures may be considered as *conserved substantial fragments* (referred to from now on simply as *fragments*). The set of fragments is tailored to the technological system studied.

Let us consider chocolate (Fig. 2.2). Although the usual ingredients of milk chocolate are sugar powder, cocoa mass, cocoa butter, milk powder and lecithin, it is expedient to use the following fragments to describe the manufacture of milk chocolate: sugar (powder), cocoa butter, fat-free cocoa, water and lecithin. This is because these fragments determine such essential properties of chocolate as viscosity and taste. The recipe for a chocolate product must obey some restrictions on the ratios of these fragments because, on the one hand, there are definitive prescriptions laid down by authorities (see e.g. European Union, 2000) and, on the other hand, there are certain practical rules of thumb concerning the fragments that provide a starting point for preparing recipes:

- Content of cocoa butter, 30–38 m/m%
- Content of sugar, 30–50 m/m% (depending on the kind of chocolate, i.e. dark or milk)
- Content of milk dry matter (milk fat + fat-free milk solids), 15–25 m/m%
- content of milk fat, minimum 3.5 m/m%
- Content of lecithin, 0.3–0.5 m/m%

Example 2.1

Let us consider a milk chocolate with the following parameters (in m/m%):

- Sugar content, ca. 40–44
- Total fat content, 31–33
- Cocoa mass content, 12–16 (cocoa butter 50% of this)
- Lecithin content, 0.4
- Whole milk powder, 20–24 (milk fat 26% of this) The calculation of the recipe is an iterative task. The procedure for the calculation is:
- Calculate Total 1, which contains all the ingredients without cocoa butter (e.g. 79.2 in Version 1).

- Calculate the amount of cocoa butter required to make up the total to 100 (20.8 in Version 1).
- Calculate the fat content of the ingredients (Total 1) without cocoa butter (12.72 in Version 1).
- Add the amount of cocoa butter calculated previously (in Version 1, 20.8 + 12.72 = 33.52 the value is too high).

Note that the milk fat content is higher than 3.5 m/m% in every case. Moreover, no chemical reactions are taken into consideration. Consequently, the elements of set A (see Appendix 5) are sufficient for preparing the recipe. However, when the Maillard reaction that takes place during conching is to be studied, a *deeper* analysis of the participant substances is necessary; that is, the elements of set B must be determined, for example, the lysine content of the milk protein, the reducing sugar content of the sugar powder and water (Table 2.1).

2.1.3 Classification of confectionery products according to their characteristic phase conditions

In colloids and coarse dispersions, various phases are present (see Chapter 5). Since the gaseous phase is of minor importance in the majority of confectionery products, the basis of classification is the hydrophilic/hydrophobic character, which applies to both the liquid and the solid phases.

Table 2.2 (Mohos, 1982) represents a classification of confectionery products with the help of a 3×3 Cartesian product, which represents a combination of hydrophobic solutions (1), hydrophilic solutions (2) and (hydrophilic) solids (3). The gaseous phase is not represented but can be taken into account as a possible combination in particular cases. The first factor in an element of this Cartesian product represents the dominant or continuous phase, and the second factor represents the contained phase; for example, 1×2 means a water-in-oil (W/O) emulsion (e.g. milk butter or margarine) and 2×1 means an O/W emulsion (e.g. toffee, fudge or ice cream).

| Raw materials | Version 1 | Fat, Version 1 | Version 2 | Fat, Version 2 | Version 3 | Fat, Version 3 |
|----------------------|-----------|----------------|-----------|----------------|-----------|----------------|
| Lecithin | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 |
| Sugar | 42 | 0 | 43 | 0 | 43 | 0 |
| Whole milk powder | 22 | 5.72 | 23 | 5.98 | 23 | 5.98 |
| Cocoa mass | 14 | 7 | 14 | 7 | 15 | 7.5 |
| Water content | 0.8 | 0 | 0.8 | 0 | 0.8 | 0 |
| Total 1 | 79.2 | 12.72 | 81.2 | 12.98 | 82.2 | 13.38 |
| Cocoa butter | 20.8 | 20.8 | 18.8 | 18.8 | 17.8 | 17.8 |
| Total 2 | 100 | 33.52 | 100 | 31.78 | 100 | 31.18 |
| Comments | | Too high | | Fair | | Good |

 Table 2.1 Calculation of a milk chocolate recipe (all values in m/m%).

| 1×1 | 1×2 | 1×3 |
|---|----------------------------|------------------------|
| Fat melts | (W/O) | Chocolate, compounds |
| | Emulsions | |
| 2×1 | 2×2 | 2×3 |
| (O/W) | Hard-/soft-boiled candies | Jellies, foams, wafers |
| Toffee, fudge, ice cream | | |
| 3×1 | 3×2 | 3×3 |
| Cocoa/chocolate powders, pudding powders | Dragées, tablets, lozenges | Biscuits, crackers |

 Table 2.2
 Cartesian product of phases.^a

^a**1** = hydrophobic phase; **2** = hydrophilic phase; **3** = solids (hydrophilic).

It should be emphasized that this classification is a simplification in the following senses:

- There is not one single classification that is appropriate in all cases, and other classifications which take the phase conditions into account in more detail may give a more differentiated picture of the important properties.
- Table 2.2 contains only some large groups of finished confectionery products that are characteristic of each element $(i \times j)$ of the product; however, all materials used or made in the confectionery industry can be classified into one or other of these elements.
- The classification of products containing flour (biscuits, wafers, crackers, etc.) is very haphazard because of the complexity of their structure.
- The elements (3×1) , (3×2) and (3×3) can hardly be regarded as different; the only difference is that the hydrophobicity decreases from cocoa/chocolate powders to biscuits and crackers containing flour. However, cases showing the opposite trend in the hydrophobicity are very frequent (e.g. cocoa powder with 8% cocoa butter content compared with cakes with 30% fat content).
- Chocolate and compounds are actually W/O emulsions [see element (1 × 2)], but the water content is in practice less than 1 m/m%.
- There are likely to be other appropriate classifications that are not based on combinations of hydrophilic/hydrophobic/solid/liquid phases.

Despite these objections and contradictions, this classification correctly expresses the hydrophobic/hydrophilic properties of the materials used and/or made in the confectionery industry because these properties play an essential role in the technologies used and in the shelf life of the substances (i.e. raw materials, semi-finished products and finished products).

2.1.4 Phase inversion: a bridge between sugar sweets and chocolate

To study the phase conditions of chocolate, Mohos, 1982 produced the so-called *crystal chocolate* in the Budapest Chocolate Factory (former Stühmer). The method

| Experiment 1 | | Exper | Experiment 2 | | Experiment 3 | | Experiment 4 | |
|-------------------------|--------------|---------------|--------------|---------------|--------------|---------------|--------------|--|
| Time (min) | Water (%) | Time (min) | Water (%) | Time (min) | Water (%) | Time (min) | Water (%) | |
| 0 | 17.4 | 0 | 17.4 | 0 | 17.4 | 0 | 17.4 | |
| 30 | 3.85 | 30 | 3.73 | 25 | 7.31 | 20 | 10.7 | |
| 45 | 1.57 | 45 | 1.46 | 60 | 1.54 | 50 | 9.74 | |
| 90 | 0.52 | 90 | 0.33 | 120 | 0.35 | 70 | 9.2 | |
| 165 | 0.43 | 165 | 0.22 | 180 | 0.34 | 100 | 5.2 | |
| | | | | | | 120 | 6.21 | |
| | | | | | | 140 | 4.67 | |
| | | | | | | 160 | 3.53 | |
| | | | | | | 190 | 2.68 | |
| | | | | | | 235 | 1.75 | |
| | | | | | | 265 | 1.38 | |
| | | | | | | 295 | 0.88 | |
| | | | | | | 325 | 0.72 | |
| Air temperature (°C) | 43 | | 43 | | 34 | | 72 (input) | |
| Air RH (%) ^a | 35 | | 35 | | 38 | | 20 (input) | |
| Air velocity (m/s) | 2 | | 2 | | 2 | | 22.3–25.1 | |

 Table 2.3
 Manufacture of crystal chocolate: experimental results.

^aRH = relative humidity.

starts from an O/W emulsion which is typical to the sugar confectioneries (e.g. fudge), and then this O/W emulsion reverts – on the effect of evaporation and kneading – to a W/O emulsion, the texture of which corresponds to that of chocolate. The brief technology is as follows:

Recipe for Experiments 1–3 (laboratory scale) (in g): sugar, 58.5; water, 19.5; cocoa mass, 18.0; cocoa butter, 16 (sum = 112.0)

Recipe for Experiment 4 (plant scale) (in kg): sugar, 50.0; water, 16.7; cocoa mass, 15.5; cocoa butter, 13.7 (sum = 95.9)

The results are presented in Table 2.3.

Three steps may be distinguished in the experiments:

- *Step 1:* At a water content of about 10%, the cocoa butter phase separates. (The consistency of the mass is similar to that of sugar sweets.)
- Step 2: At about 100 min (water content $\approx 5.2\%$), a *phase inversion* (O/W \rightarrow W/O) starts, and this lasts up to a water content of about 1.38% (235 min). In the final period, the crystallization of sugar and the comminution of sugar crystals by the rubbing effects of conching start.

Step 3: The consistency of crystal chocolate is developed.

A plot of water percentage versus time can be approximated by the function

$$w_t = (w_0 - w_\infty) \exp(-k_i t) + w_\infty$$
 (2.1)

where *t* = time of conching/drying (min), w_0 = initial water content (%), w_{∞} = water content after long drying ($\approx 0.3\%$), k_i = velocity constant of drying (min⁻¹) and *i* = the number of the experiment. For the aforementioned experiments, $k_1 = 9.83 \times 10^{-3}$, $k_2 = 8.4 \times 10^{-3}$, $k_3 = 7.78 \times 10^{-3}$ and $k_4 = 2.17 \times 10^{-3}$.

At the end of production, the size of the sugar crystals is similar to that in a fondant mass (*ca*. $5-30 \mu$ m); however, after a short time, the larger crystals are in the majority because of Ostwald ripening, similar to the changes that occur in fondant.

A noteworthy phenomenon: The two methods of (1) comminution by mill and (2) solution + crystallization provide similar results. However, while comminution is not followed by Ostwald ripening, the operations of solution + crystallization are. Just the same phenomenon can be observed when a ripened fondant is re-kneaded and then shaped. While the structure of the centres of ripened fondant hardly changes in storage, the centres of unripened fondant are easily dried; that is, their structure is more changeable and less stable. All of this emphasizes the importance of Ostwald ripening (see Sections 5.9.5, 10.6.1 and 16.4).

2.2 Quantitative characterization of confectionery products

2.2.1 Composition of chocolates and compounds

Quantitative relations can be given which characterize the composition of chocolates and compounds [see the (1×3) element of the Cartesian product in Table 2.2]; the latter contain special fats instead of cocoa butter as the dispersing phase. *Dark chocolate* and *milk chocolate* are typical examples of these product groups.

2.2.1.1 Composition of dark chocolate

If the proportions of the ingredients (in %) are *S*, sugar; *B*, cocoa butter; *M*, cocoa mass; and *L*, lecithin, then

$$S + M + B + L = 100 \tag{2.2}$$

The cocoa content (C) is

$$C = M + B \tag{2.3}$$

Taking into account the consistency requirements, the total fat content (F) must be between 30% and 40%, that is,

$$F = L + c_{\rm M}M + B = 30 - 40 \tag{2.4}$$

where $c_{\rm M}$ is the cocoa butter content (mass concentration) of the cocoa mass (*ca.* 0.50–0.56). The usual value of *S* for dark chocolate is 30–50%, and the usual value of *L* is 0.3–0.5%.

| Raw materials | Version 1 | Fat, Version 1 | Version 2 | Fat, Version 2 | Version 3 | Fat, Version 3 |
|------------------|-----------|----------------|-----------|----------------|-----------|----------------|
| Sugar | 36 | 0 | 30 | 0 | 39.6 | 0 |
| Cocoa mass (50%) | 60 | 30 | 70 | 35 | 46 | 23 |
| Cocoa butter | 3.7 | 3.7 | 0 | 0 | 14 | 14 |
| Lecithin | 0.3 | 0.3 | 0 | 0 | 0.4 | 0.4 |
| Total | 100 | 34 | 100 | 35 | 100 | 37.4 |
| Cocoa content | 63.7 | | 70 | | 60 | |

| Table 2.4 | Recipes | for dark | chocolate. |
|-----------|---------|----------|------------|
|-----------|---------|----------|------------|

On the basis of these relations, many chocolate recipes can be prepared, as shown in Table 2.4. Because of price considerations, the total fat content is chosen to be nearer to 30% than to 40% (usually, F = 30-33).

A more detailed picture of the fragments is not needed in general for preparing a recipe for chocolate; for example, the water content does not usually play any role, since only the cocoa mass has a relatively high water content (1-2 m/m%), which is decreased during conching. The water content of sugar, cocoa butter (particularly if it is deodorized) and lecithin can be neglected. Also, the water content of cocoa mass can be made low if it is refined by a special film evaporator (e.g. the Petzomat, from Petzholdt), which can be regarded as a pre-conching machine.

2.2.1.2 Composition of milk chocolate

The following equation (in %) is valid for a milk chocolate:

$$S + M + B + L + W + b = 100 \tag{2.5}$$

where *S*, *M*, *B* and *L* have meanings similar to those mentioned earlier, *W* is the percentage of whole milk powder and *b* is the percentage of (dry) milk fat (about 1 m/m% of the water content). The use of dry milk fat is optional.

Equation (2.3) is valid for the cocoa content. The usual value of *S* for milk chocolate is 40–45%, and the usual value of *L* is 0.3-0.5%.

Taking into account the consistency requirements, the total fat content must be between 30% and 40%; that is,

$$F = L + c_{\rm M}M + B + Wc_{\rm W} + b = 30 - 40 \tag{2.6}$$

where c_W is the milk fat content (mass concentration) of whole milk powder (*ca*. 0.26–0.27).

An additional requirement related to the consistency is the ratio R = cocoa butter/non-cocoa butter fats (mass/mass) because non-cocoa butter fats soften the consistency and, in extreme cases, make it too soft for correct shaping of the chocolate.

One principal requirement for milk chocolate, which is laid down by authority (European Union, 2000), is that the milk fat content should be at least 3.5 m/m%. (In tropical countries, a value of 2.5 m/m% is accepted because of the hot climate.) The usual values of milk fat content are in the range 3.5-6%, and the usual values of total fat content are in the range 30-40%; consequently, the value of *R* + 1 can theoretically vary as follows:

$$\frac{40}{3.5} \approx 11.4 \ge R+1 \ge \frac{30}{6} = 5$$

that is,

$$10.4 \ge R \ge 4$$

However, a ratio R = 4 is not available, since the consistency would be very soft. Instead, the practical minimum value is given by R + 1 = 30/3.5 = 8.57, that is about R = 7.6.

On the other hand, an intense milky taste is an important quality requirement too, and therefore increasing the dry milk content is an understandable ambition of producers. Another way to produce milk chocolate with an intensely milky taste is to use special milk preparations, for example, condensed sugared milk (milk crumb) or chococrumb (see Chapter 16), where the Maillard reaction is used.

An essential quality requirement is a suitably high value of the fat-free cocoa content, which gives the product its cocoa taste. The practical value is at least 3-4 m/m% for compounds and at least 5-6 m/m% for milk chocolate. However, for compounds, cocoa powder of low cocoa butter content (10-12 m/m%) has to be used because the fats used in compounds are not compatible with cocoa butter or are only partly compatible. For a milk chocolate, this minimum value of fat-free cocoa content means that the percentage of cocoa mass must be at least 10-12 m/m% (assuming that the cocoa butter content of cocoa mass is about 50 m/m%).

Example 2.2

| Ingredients | Total fat | |
|--------------------------------|-----------|------|
| Sugar (S) | 40.0 | 0.0 |
| Lecithin (L) | 0.4 | 0.4 |
| Whole milk powder (<i>W</i>) | 20.0 | 5.2 |
| Cocoa mass (M) | 12.0 | 6.0 |
| Total | 72.4 | 11.6 |

Let us calculate the recipe of a milk chocolate, supposing that the initial values of the ingredients are as follows:

If the balance of these ingredients is made up by cocoa butter (100 - 72.4 = 27.6), then the total fat content will be 27.6 + 11.6 = 39.2% – too high!

| Ingredients | Total fat | |
|-------------------|-----------|------|
| Sugar | 43.0 | 0.0 |
| Lecithin | 0.4 | 0.4 |
| Whole milk powder | 20.0 | 5.2 |
| Cocoa mass | 14.0 | 7.0 |
| Total | 77.4 | 12.6 |

If M = 14 and S = 43, then we do the following calculation.

If the balance of these ingredients is made up by cocoa butter (100 - 77.4 = 22.6), then the total fat content will be 22.6 + 12.6 = 35.2% – this is acceptable. Taking the price of cocoa butter into account, this is an important alteration.

In the aforementioned recipe, R + 1 = 35.2/(5.2 + 0.4) = 6.28, that is, R = 5.28. The usual way of reducing the proportion of non-cocoa butter fat is to use whole and skimmed milk powder together as follows. The amount of whole milk powder is calculated according to the minimum requirement of 3.5% milk fat, that is, $3.5\%/0.26 \approx 13.5\%$. This amount is then made up to 20%; that is, the amount of skimmed milk powder is 6.5%.

The calculation is modified as follows.

| Ingredients | | Total fat |
|---------------------|-------------------|-----------|
| Sugar | 43.0 | 0.0 |
| Lecithin | 0.4 | 0.4 |
| Whole milk powder | 13.5 | 3.5 |
| Skimmed milk powder | 6.5 | 0.0 |
| Cocoa mass | 14.0 | 7.0 |
| Total | 77.4 | 10.9 |
| Cocoa butter | 100 - 77.4 = 22.6 | 22.6 |
| Total | 100 | 33.5 |

In this recipe, $R + 1 = 33.5/(3.5 + 0.4) \approx 8.6$, that is, $R \approx 7.6$.

Note that in this example, a blend of two kinds of milk powder has been used; the average milk fat content of this blend is 3.5/20 = 17.5% (instead of 26%).

2.2.1.3 Preparation of gianduja recipes

The relevant European Union directive (European Union, 2000) defines Gianduja chocolate as a blend of dark or milk chocolate and hazelnut paste (and pieces); both dark and milk Gianduja chocolate are defined in detail. The minimum and maximum amounts of hazelnut are 20% and 40%, respectively, for dark Gianduja and 15% and 40% for milk Gianduja. The recipes for both types of Gianduja chocolate are actually very simple.

Example 2.3

Seventy-five percent dark chocolate is mixed with 25% hazelnut paste, or 70% milk chocolate is mixed with 30% hazelnut paste.

Since shelled hazelnuts have an oil content of about 40-60% and hazelnut oil has a very low cold point (-18 °C), the hazelnut paste softens the consistency of the product to a great extent. If milk chocolate of the composition calculated earlier is used in a proportion of 70% and the assumed oil content of the hazelnuts is 50%, then the distribution of the various oils/fats will be:

70% milk chocolate: $0.7 \times (22.6 + 7)$ % cocoa butter + 0.7×3.9 % (lecithin + milk fat)

30% hazelnut paste: 0.5 × 30% hazelnut oil

In summary, this Gianduja product contains 20.72% cocoa butter + 2.73% (lecithin + milk fat) + 15% hazelnut oil (total fat content 38.45%), and therefore

$$R + 1 = \frac{38.45}{38.45 - 20.72} = \frac{38.45}{17.73} \approx 2.17$$
, i.e. $R \approx 1.17$

In order to avoid a consistency that is too soft, the hazelnuts are used partly as paste and partly as tiny pieces. The hazelnut oil remains in the cells in the latter, and therefore this portion of hazelnut oil does not soften the consistency of the chocolate.

For example, the aforementioned composition can be modified so that 70% milk chocolate is mixed with 15% hazelnut paste and 15% chopped hazelnuts. The milk Gianduja mass will have the following composition and fat/oil distribution:

70 kg milk chocolate: 20.72 kg cocoa butter + 2.73 kg (lecithin + milk fat) 15 kg hazelnut paste: 7.5 kg hazelnut oil

The distribution of the various fats in this milk Gianduja mass will be (in %): 20.72/0.85 = 24.38% cocoa butter

2.73/0.85 = 3.21% lecithin + milk fat

7.5/0.85 = 8.82% hazelnut oil

Total: 36.41% oils/fats

For this solution, $R + 1 = 36.41/(36.41 - 24.38) = 36.41/12.03 \approx 3.03$, that is, $R \approx 2.03$. Evidently, the softness of the consistency has been moderated.

For the sake of completeness, let us calculate a recipe for a compound that is similar to milk chocolate. The corresponding formula (in %) is

$$S + P + V + L + m = 100 \tag{2.7}$$

where *S* refers to sugar, *P* to cocoa powder, *V* to special vegetable fat, *L* to lecithin and *m* to whole or skimmed milk powder.

Taking the consistency requirements into account, the total fat content (F) must be between 30% and 40%, that is,

$$F = L + c_m m + V + P c_P = 30 - 40 \tag{2.8}$$

where c_m is the milk fat content of whole or skimmed milk powder (m/m) and c_p is the cocoa butter content of cocoa powder (m/m).

The further requirements concerning compounds are similar to those for chocolate.

Example 2.4

Let us take an example in which a blend of milk powder of 15% milk fat content and cocoa powder of 10% cocoa butter content is used. *Comment*: From the point of view of cocoa taste, 6% cocoa powder (10% cocoa butter content) is equivalent to $2 \times 6\% \times 0.9 = 10.8\%$ cocoa mass (50% cocoa butter content) since the fat-free cocoa content of both is $6\% \times 0.9 = 5.4\%$. (This would be acceptable for milk chocolate as well.) If the cocoa powder content is less than 3%, the taste of the product is not characteristic of cocoa.

| Ingredients | | Total fat |
|-----------------------|-------------------|-----------|
| Sugar | 43.0 | 0.0 |
| Lecithin | 0.4 | 0.4 |
| Milk powder blend | 20.0 | 3.0 |
| Cocoa powder | 6.0 | 0.6 |
| Total | 69.4 | 4.0 |
| Special vegetable fat | 100 - 69.4 = 30.6 | 30.6 |
| Total | 100 | 34.6 |

2.2.1.4 Composition of dark chocolates of high cocoa content

Using the designations S = sugar, B = cocoa butter, M = cocoa mass, L = lecithin, C = total cocoa content and F = total fat content and, moreover, taking into consideration that exclusively dark chocolate are made with high cocoa content, the following two relationships are valid:

$$S = 100 - B - M - L \approx 99.6 - C \tag{2.4a}$$

where L = 0.4 (mostly used value) and C = B + M.

$$F \ge B + 0.5 \times M + L \tag{2.4b}$$

The taste of chocolate of high cocoa content, namely, the (sweet: bitter) balance is strongly influenced by the {sugar (S): cocoa mass (M)} ratio.

The cocoa butter (*B*) does not directly influence the development of taste. However, the strong bitterness of cocoa mass can be reduced also by increasing the ratio of the cocoa butter; consequently, an indirect effect can be attributed to the cocoa butter content as well.

But cocoa butter is the far most expensive ingredient; therefore, its portion is typically low or zero.

Regarding these points of view, some compositions $[kg \approx \%]$ can be found in the following:

| | Version 1 | Version 2 | Version 3 | Version 4 | Version 5 |
|----------|-----------|-----------|-----------|-------------|-----------|
| S | 36 | 27.6 | 27.6 | 27.6 | 20 |
| М | 60 | 72 | 70 | 80 | 80 |
| В | 3.6 | 0 | 2 | 0 | 0 |
| L | 0.4 | 0.4 | 0.4 | 0.4 | 0 |
| С | 63.9 | 72 | 72 | 80 | 80 |
| <u>F</u> | <u>34</u> | 36.4 | 37.2 | <u>40.4</u> | <u>40</u> |

2.2.2 Composition of sugar confectionery

The composition of the various types of sugar confectionery is principally determined by the water content and the syrup ratio (*SR*) in the product (see Chapters 8 and 9 for further details). The *SR* is the ratio of the starch syrup dry content to the sugar content, expressed in the form 100 : X or 100/X, where for each 100 kgof sugar, there is *X* kg of starch syrup dry content.

Example 2.5

If SR = 100:50, this means that in the prepared solution there are dissolved 100 kg of sugar and 50 kg of starch syrup dry content. Assuming the usual dry content of starch syrup of 80 m/m%, 100 kg of sugar and 50 kg/0.8 = 62.5 kg of (wet) starch syrup should be blended.

In addition to the water content, the reducing sugar content plays an important role in determining the properties of sugar confectionery.

The reducing content of a sugar/starch syrup solution, *derived from the dextrose content of the syrup,* can be calculated using the formula

$$R = (1 - W) \times \frac{DE}{SR + 1} \tag{2.9}$$

where *R* is the reducing sugar content of the solution (%), *W* is the concentration of water in the solution, *DE* is the dextrose equivalent of the starch syrup (%) and *SR* is the syrup ratio.

The other important source of the reducing content of carbohydrate solutions is *inversion*, which produces the reducing sugar glucose (also known as dextrose)

by hydrolysis of sucrose (also known as saccharose) under the action of catalysts (acids or the enzyme invertase):

 $sucrose + H_2O = glucose + fructose$

(Water is chemically built into the dry content during inversion: 342 g sucrose + 18 g water = 180 g glucose + 180 g fructose, i.e. a 5% increase in dry content.)

The reducing sugar content of carbohydrate solutions and sugar confectionery can easily be determined. Titrimetric or iodometric methods are the methods mostly used for the determination of reducing sugar content and do not require sophisticated, expensive laboratory equipment. However, what is measured by these iodometric methods?

According to Erdey (1958), iodometric methods (the Fehling/Bertrand and Fehling/Schoorl–Regenbogen methods) may be used for the quantitative determination of glucose, fructose, invert sugar, sucrose (after inversion), maltose, galactose, mannose, arabinose, xylose and mannose by use of a table containing the corresponding data for reduced Cooper measuring solution (0.1 N) versus the kind of sugar measured (in mg). (The determination is not strictly stoichiometric.) Aldoses may be oxidized easily; the oxidation of ketoses (e.g. fructose) takes place only in more strongly oxidizing media, but the alkaline medium that is typically used in these methods of sugar determination is favourable for oxidation of all the various sugars; for further details, see Bruckner (1961).

Colorimetric methods are also widely used for determining reducing sugar content (e.g. in investigations of human blood; see Section 16.1.1).

Why does the reducing sugar content of carbohydrate solutions play such an important role in confectionery practice? The reducing sugar content, together with the water content, determines the following:

- The crystallization of sucrose
- Water adsorption on the surface of the product, that is, the hygroscopic properties of the surface
- The consistency of the product

The *ability of sucrose to crystallize* is an important property from two contradictory points of view:

- Certain products are of crystalline structure (e.g. crystalline drops, fondant and fudge).
- There are types of sugar confectionery (e.g. drops, toffees, jellies and marshmallows) which must not be of crystalline structure. During their production, the crystallization of sucrose must be hindered by glucose syrup, invert sugar, etc.

The *hygroscopic properties of the surface* of sugar confectionery may have unintended consequences. Packaging materials can defend sugar confectionery against water adsorption, which would make the surface sticky. The water permeability of packaging materials can be adjusted to the given task. However, if the product is left unpacked for some time, stickiness becomes a serious problem. Experience shows that when the reducing sugar content of a sugar
mass is more than 16 m/m%, the mass becomes stickier and stickier. The *SR* for a reducing sugar content of 16% (and a water concentration *W* of 0.02 and DE = 40%) can be obtained from Eqn (2.9):

$$16 = (1 - W) \times DE/(SR + 1) = 0.98 \times 40/(SR + 1)$$

From this equation, SR = 1.45, hat is, 100 kg of sugar and 100/1.45 \approx 69 kg of glucose syrup dry content (*ca*. 69/0.8 \approx 86.25 kg *wet* glucose syrup) should be mixed to produce a solution of 16% reducing sugar content. This ratio is economic, since the dry content of glucose syrup is always a little cheaper than sugar.

However, Eqn (2.9) does not take into account the *inversion* of sucrose, which is caused by the acid content (sulphuric and hydrochloric acid) of glucose syrup derived from the acidic conversion of starch. Although the acid content of glucose syrup remaining after the conversion of starch is neutralized and the pH of glucose syrups is about 4.5–5.5, hydrolysis caused by the residual acid must not be ignored.

An additional reason for increasing the reducing sugar content is the presence of other acidic agents in candies, above all the various flavouring acids (citric, malic, lactic and tartaric acids).

The inversion abilities of various acids are rather different and cannot be exactly characterized by a single parameter, because inversion is catalysed by hydrogen ions: that is, the process of inversion is strongly dependent on the conditions in the acidic medium (the kind of acid, the concentration, etc.) (for more details, see Section 16.1 and Chapter 17).

Sokolovsky (1958) discussed in detail the hygroscopicity of sugar masses and their ingredients under various conditions of production and storage. In confectionery practice, the typical hygroscopic substances are fructose, invert sugar, sorbitol and glycerol. The orders of hygroscopicity and of solubility are the same:

glucose < sucrose < invert sugar < fructose

On the basis of the aforementioned considerations, the conclusion is that the reducing sugar content itself cannot characterize the hygroscopicity of sugar masses. Instead, the kinds of sugar (monosaccharides and disaccharides) that the reducing sugar content is composed of are decisive: the value of 16% is a rough threshold only, and reducing sugar contents of 16% derived exclusively from glucose and derived partly from glucose and partly from fructose have entirely different effects.

An increase in the reducing sugar content makes the consistency of *candies* softer, although an exact description of the circumstances that influence the consistency has to be limited to individual cases.

Taking into account the effects of water content and reducing sugar content, Figure 2.17 shows the approximate intervals which can be regarded as optimal for various sugar confectioneries; see Mohos (1975). Naturally, these intervals are experimentally determined and are not derived from any scientific law. Moreover, their boundaries are not strictly fixed, and this statement relates to the



Figure 2.17 Reducing sugar versus water content in sugar confectionery.

dividing line between the amorphous and crystalline regions too. Nevertheless, Figure 2.17 should be informative for the preparation of recipes for sugar confectionery.

A typical instance of the crucial role of reducing sugar content is provided by the technology for *crystalline drops* (or *grained drops*), the characteristic region for which is denoted by *II* in Figure 2.17. Two kinds of technology are possible: inversion of sucrose by cream of tartar (also known as cremor tartari or potassium hydrogen tartrate) and the use of sucrose + glucose syrup. Before flavouring, colouring and pulling, a sugar mass made by either of these technologies has to have the following composition:

4% water,

3% glycerol,

6% reducing sugar

The recipe for the cream of tartar technology is:

92–93 kg sugar

3 kg glycerol

ca. 0.2 kg cream of tartar

25-30 kg water for dissolution

Yield: ca. 100 kg sugar mass

In the case of the recipe for the glucose syrup technology, we assume that the parameters of the glucose syrup are DE = 40% and dry content = 80%, that is, 100 kg of glucose syrup contains $40 \text{ kg} \times 0.8 = 32 \text{ kg}$ of reducing sugar. Therefore, 6 kg of reducing sugar is contained in 6 kg/0.23 = 18.75 kg of (wet) glucose syrup, the dry content of which is $18.74 \text{ kg} \times 0.8 = 15 \text{ kg}$. Compared with the cream of tartar technology, the amount of sugar is decreased by 15 kg, and the amount is water is decreased by 3-4 kg (= 18.75 - 15). The recipe is:

77–78 kg sugar

18.75 kg (wet) glucose syrup

3 kg glycerol

23-27 kg water for dissolution

Yield: c. 100 kg sugar mass

In both technologies, first atmospheric and then vacuum evaporation are necessary, and there must be strictly no mixing or moving of the solution. Moreover, an essential requirement is that the dissolution of the sugar must be perfect, that is, no sugar crystals must remain undissolved, otherwise crystallization of sucrose will start during the evaporation. To avoid such a mistake, sufficient water must be used for dissolution.

But these two technologies are very different. The cream of tartar technology is based on the inversion effect of cream of tartar, a process which is strongly time dependent; consequently, the durations of the two evaporation steps have definite limits imposed on them. A slow evaporation results in more reducing sugar than necessary, and the crystallization in the end product will occur late or be impossible. The other *sensitive point* of this technology is that sugar always contains Ca^{2+} and Mg^{2+} ions, which form salts with cream of tartar, and the Ca salt is insoluble.

Example 2.6

A simple calculation shows that this consumption of cream of tartar by calcium and magnesium ions may be considerable.

The molecular mass of cream of tartar ($KHC_4H_4O_6$) is 188; that is, 188 g of cream of tartar reacts with 40 g of calcium or 24.3 g of magnesium. The average calcium content of sugar per kilogram is *c*. 0.15 g, and the corresponding value for magnesium is *c*. 0.025 g. This means that 90 kg sugar contains *c*. 13.5 g Ca and 2.25 g Mg, which react with

 $13.5 \text{ g} \times (188/40) + 2.25 \text{ g} \times (188/24.3) = 80.87 \text{ g cream of tartar}$

If *ca*. 200 g of cream of tartar is used in the batch, the decrease in the amount of it because of the effect of Ca^{2+} and Mg^{2+} is *ca*. 40%. (Naturally, these data are indicative only.) This consumption is the reason why we give only an approximate amount of cream of tartar (*ca*. 0.2 kg) in the recipe. This means that the amount of cream of tartar has to be adjusted to the sugar used.

However, the quality of the product made by the cream of tartar technology is much better: the sucrose crystals are of small $(5-9\,\mu\text{m})$ and very homogeneous size, whereas the product made by the glucose syrup technology has a consistency somewhat similar to that of starch sugar made from potatoes. (If potato starch is converted by acid in aqueous solution, the evaporated reaction mixture, containing *ca*. 80 m/m% dextrose, can be sold as a cheap product. In former years, this process was done in the kitchen at home as well.) But the glucose syrup technology is practically insensitive to the duration of the evaporation steps.

An improved variation of the glucose syrup technology which eliminates the consistency properties of the end product that remind consumers of starch sugar



Figure 2.18 Pulling of sugar mass. Source: Data from Sokolovsky (1951).

uses liquid sugar instead of glucose syrup as follows: 18.75 kg of wet glucose syrup (dry content = 80%, DE = 40%) contains about 15 kg of dry content and 6 kg of reducing sugar, and 9 kg sugar + 6 kg liquid sugar dry content is equivalent to 15 kg syrup dry content. Taking into account the usual parameters of liquid sugars (dry content = 75% and fructose : glucose = 55:45), this means a blend of 9 kg sugar + 6 kg/0.75 = 8 kg liquid sugar.

The acid residues in both glucose syrup and liquid sugar cause unwanted inversion, and therefore the acid content has to be rather low.

(In both technologies, glycerol is added because its hygroscopic effect accelerates the crystallization of the product.)

Both technologies are very sensitive to the reducing sugar and water content parameters from the point of view of both pulling and crystallization of sucrose in the product – these latter operations are very closely connected with each other.

Sokolovsky (1951) studied the effect of pulling on the density and water content of sugar masses made for the production of grained drops; Figure 2.18 has been compiled from this study.

It can be seen that in the pulling operation, the density of the sugar mass first decreases, and later – after about $7 \min$ – the density starts to increase again, which shows that its tubular structure is becoming more and more broken. In the pulling operation, the water content increases linearly up to about the seventh minute, then a drying process starts, and after about 10 min of pulling, the initial water content is restored. Both of these phenomena show that there is an optimum pulling time (*ca*. 6–7 min); after this, pulling will be disadvantageous. In fact, Sokolovsky measured a value of about 2.6 m/m% for the water content of the sugar mass, whereas this parameter had a minimum of 4 m/m% in the

present author's studies in the Research Laboratory of the Hungarian Confectionery Industry in 1969 (unpublished).

However, the present author also found that if the reducing sugar content is lower than 6 m/m%, crystallization of the sugar mass is liable to start dramatically during the pulling operation. This may have the result that the entire amount of sucrose is crystallized in only a few minutes, and the latent heat of crystallization is liberated. Meanwhile, the sugar mass transforms into large crystalline pieces and falls from the pulling arms. Because of the huge amount of liberated latent heat, the bulk sugar mass gets very hot, almost *glowing*. (This may happen in both technologies.)

Example 2.7

In order to estimate the warming effect of this crystallization, let us do a calculation. First, as an approximation, the effect of the size of the batch (mass, surface area, etc.) can be neglected. The specific heat capacity of sucrose is about 1.42 kJ/kg, and its latent heat of solution (positive) or of crystallization (negative) is about 18.7 kJ/kg (see Chapter 3). For a unit weight of sugar mass, the following equation is valid when the temperature *t* is close to 40 °C:

$$(t-40) \times 1.42 - 18.7 = 0 \rightarrow t = 53.16$$
 °C

(The liberation of latent heat – negative enthalpy – means that the system loses heat, i.e. it is warmed; this is a thermodynamic convention.)

The temperature *t* increases to a value of 53.16 °C because of the latent heat of crystallization. This calculation supposes a homogeneous distribution of heat during crystallization; however, thermal inhomogeneities cause strong overheating, which can easily be observed as mentioned earlier.

On the other hand, as the reducing sugar content approaches 10 m/m%, the crystallization of sucrose in the product becomes slower and slower, and at about a value of 12%, crystallization becomes impossible. Since it is rather difficult to obtain exactly 6 m/m% of reducing sugar, a range of 6-8 m/m% is recommended. Before packaging, storage of the end product for 1 or 2 days in a hot (*ca.* 40 °C), wet (*ca.* 80% RH) room is desirable because crystallization is to a certain extent stimulated by humidity and heat.

The phenomenon discussed earlier raises the question of stability; for more details, see Chapter 18.

It is important to discuss the technology for grained drops because this product represents an extreme case in sugar confectionery. Of all of the grained products (e.g. fondant), grained drops have the lowest water content and reducing sugar content.

Some other examples of the effect of reducing sugar content are:

• If the reducing sugar content of a jelly is 12–14 m/m%, graining is very probable (this is unambiguously a fault).

• If filled hard-boiled sugar confectionery is being produced and the sugar mass used is *dry* enough (reducing sugar content *ca*. 12–13 m/m%), the filling, if it is an aqueous solution (e.g. a fruit filling), can induce crystallization of the sugar mass cover. The final product will be soft and crisp. This may be the aim in some cases, but otherwise it qualifies as a fault.

It should be emphasized that the reducing sugar content and the water content cannot on their own characterize completely the production conditions and the properties of the products; nevertheless, the relations presented in Figure 2.17 should provide a useful orientation for preparing recipes and for making judgements about how a product will behave if its composition is known.

Let us consider some recipes in order to show how Figure 2.17 can be applied for preparing recipes. In these recipes, the glucose syrup has the parameters

dry content = 80%; DE = 40%

2.2.2.1 Drops

The parameters of the end product are water content, 2 m/m% and reducing sugar content, 15%. One hundred kilograms of *wet* glucose syrup has 32 kg of reducing sugar and 80 kg of dry content. Therefore, 15% of reducing sugar is contained in $100 \text{ kg} \times (15/32) = 46.9 \text{ kg}$ of glucose syrup, which contains 37.5 kg dry content (+11.4 kg water). The recipe is:

46.9 kg glucose syrup

60.5 kg sugar (=98 – 37.5)

ca. 30 kg water (for dissolution, which will be evaporated)

Yield: 100 kg sugar mass (2 m/m% water content)

2.2.2.2 Agar jelly

The parameters of an agar jelly are water content, 23 m/m; reducing sugar content, 12 m/m; and agar-agar content, 1.25 kg. The amount of glucose syrup is 12 kg/0.32 = 37.5 kg, which has a dry content (obtained by multiplying by 0.8) of 30 kg. The dry content of the jelly (100 kg - 23 kg = 77 kg) consists of 30 kg dry glucose syrup + 1.25 kg agar-agar + 45.75 kg sugar. The recipe is 1.25 kg agar-agar mixed with 10 kg sugar is added to 35.75 kg sugar +20 kg water for dissolution.

The solution is cooked to *ca*. 106 °C. At this temperature, 37.5 kg of glucose syrup is added to the solution, which is then boiled again. Finally, the agar solution may be flavoured, coloured, dosed with starch powder, etc.

2.2.2.3 Fudge

The parameters are: Water content (*W*), 10 m/m% Reducing sugar content (*R*), 10 m/m% Milk dry content (*M*), 10 m/m%

The fondant content is to be 20 m/m%, which has the following parameters: Water content, 9 m/m% Reducing sugar content, 7 m/m% The task is to prepare a mass I, which does not contain fondant, and to prepare a mass II of fondant; these are then to be mixed in the proportion 4:1.

Recipe for mass I: Because the parameters of the fudge relate to the end product, the parameters of mass I are calculated as follows:

$$W \times 0.8 + 9\% \times 0.2 = 10\%$$
, i.e. $W = 10.25\%$
 $R \times 0.8 + 7 \times 0.2 = 10\%$, i.e. $R = 10.75\%$
 $M \times 0.8 = 10\%$, i.e. $M = 12.5\%$

Because the dry content of the condensed milk used is 70%, the amount of condensed milk for mass I must be

$$12.5 \text{ kg}/0.7 = 17.9 \text{ kg}$$

The amount of glucose syrup for mass I must be 10.75 kg/0.32 = 33.6 kg, which has a dry content of $33.6 \text{ kg} \times 0.8 = 26.9 \text{ kg}$. The dry content of mass I (100 kg - 10.25 kg = 89.75 kg) consists of:

12.5 kg condensed milk dry content

26.9 kg glucose syrup dry content

50.35 kg sugar

17.9 kg condensed milk + 33.6 kg glucose syrup + 50.35 kg sugar are dissolved in *ca*. 30 kg water, and this solution is boiled to *ca*. 122 °C.

Recipe for mass II: If the reducing sugar content is 7%, then the amount of glucose syrup must be

$$7 \text{ kg}/0.32 = 21.9 \text{ kg}$$

The dry content of this is

$$21.9 \text{ kg} \times 0.8 = 17.5 \text{ kg}$$

Because the total dry content of the fondant mass II is 91%, the amount of sugar is

$$(91 - 17.5)$$
kg = 73.5 kg

Therefore, 73.5 kg sugar and 21.9 kg glucose syrup are dissolved in *ca*. 25 kg water and boiled to *ca*. 124 °C.

Finally, 80 kg of mass I and 20 kg of mass II are mixed.

Comment: The exact values of the water contents mentioned earlier can be established only by measuring the boiling points of the solutions.

These examples of agar jelly and fudge may also be informative for calculating recipes for sugar confectioneries (e.g. marshmallow) that contain ingredients other than sugar and glucose syrup.

2.2.3 Composition of biscuits, crackers and wafers

It is almost impossible to compile a comprehensive survey of the composition of the various biscuits, crackers, etc. that exist. Table 2.5 presents some typical composition values of various confectionery products containing flour. Table 2.6