Calorimetry in Food Processing: Analysis and Design of Food Systems

Part 1

Analysis of Food and Biological Materials by Calorimetry

Chapter 1

Calorimetric Methods as Applied to Food: An Overview

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Introduction

Several thermal and nonthermal methods are applied to process and preserve food materials and to manufacture value-added products. The goals of food processing are to inactivate spoilage and pathogenic microorganisms and to maintain this status in storage during the intended shelf life of the product. During processing, changes take place in food components, including vitamins, lipids, carbohydrates, and proteins. Such changes lead to structural and functional changes in foods at the micro- and macromolecular levels that affect the physical, organoleptic, and nutritional properties of the food.

Food materials are complex biological systems. Food products may have a broad range of structures spanning the three states of matter, including dilute to concentrated liquids, solids, and mixtures of multi-liquid, liquid-solid, liquid-gas, and solid-gas structures. The combination of complex structures making up complex biological compounds makes the characterization of food systems challenging. To address the wide variety of compositions and structures, many biophysical techniques are uesd to characterize the structure and properties of food materials before and after processing to develop a fundamental

understanding of the impact of processing and storage conditions. The data resulting from such studies can be used to predict the physical properties of foods so that food processing and storage conditions are optimized.

Calorimetry

Among biophysical techniques, calorimetry presents itself as particularly well suited for analysis of food materials. Among many reasons, the first is the relevance of the experimental protocols of calorimetry to the majority of processes employed in food preservation. Specifically, because many food-processing methods involve thermal treatment (heating, cooling, freezing) of the materials, thermal characterization of food systems and their components leads to data that can be related directly to the processing protocols. Determination of thermal properties of food materials, such as specific heat as a function of temperature, is essential for heat transfer and energy balance calculations (Kaletunç 2007). Generation of a reliable database to develop equations predicting thermal properties of food materials for optimization of food processes can be accomplished by using calorimetry. Moreover, food materials and their components go through conformational and phase transitions during processing. Calorimetry data can be analyzed to evaluate the thermal and thermodynamic stability of various phases for a rational design of food product formulations and process conditions.

Differential scanning calorimetry, which measures heat capacity as a function of temperature, is a well-established thermal analysis technique that detects and monitors thermally induced conformational transitions and phase transitions as a function of temperature. During temperature scanning, depending on the complexity of the material, many peaks or inflection points (one to several) reflecting the thermally induced transitions can be observed. The direction of the peak corresponds to the nature of the transition, being heat absorbing (endotherms) or heat releasing (exotherms). While melting of solids and denaturation of proteins display endotherms, crystallization of carbohydrates and aggregation of proteins manifest themselves as exotherms. The temperatures for the endothermic and exothermic transitions and

the heat involved in such transitions are measured using a calorimeter. Inflection points are indicative of glass transitions; that is, transitions from a glassy to rubbery state. The transition temperatures (T_{peak} or T_g) reflect the thermal stability of the phase or state going through the transition. One can extract from calorimetry data values for the thermal and thermodynamic changes in free energy (ΔG), enthalpy (ΔH), entropy (ΔS), and heat capacity (ΔC_p) of the various transitions in addition to determination of the bulk heat capacity of the material.

The basis for thermodynamic study of food materials is that the relevant initial and final states (preprocessing and postprocessing states) can be defined and the energetic and structural differences between these states can be measured using calorimetric instrumentation. To this end, calorimetry can be used to evaluate the effect of other physical and chemical variables by comparing the thermograms of the materials before and after exposure to the variable outside the calorimetry.

The basics of application of calorimetry to food materials are discussed in detail in this book. However, it is important to start the discussion with a summary of the advantages of using calorimetry for study of biological materials. These advantages can be outlined as follows:

- Direct measurement of the energetics of the transition is obtained (ΔH and ΔC_p). The experimental results are not model dependent.
- Calorimetry can be applied to a range of materials, pure or complex. Materials do not have to be optically transparent or have chromophores as required by spectroscopic methods.
- Materials do not have to be uniform or have to be a homogeneous mixture. In fact, in addition to pure materials, the technique can be used to evaluate the interactions among the components in a complex system and how the interactions are altered by the processing.
- Calorimetry does not require elaborate or destructive sample preparation.
- Calorimetry is an established technique which has been around since the 16th century (Haines 1995). Today, the instruments are highly developed for accurate measurement of thermal events. The theory behind the technique is well developed, which facilitates interpretation of the data (Höhne et al. 2003).

While the technique is powerful, the validity and utility of the data depend strongly on the careful use of the equipment and correct interpretation of data. Some analytical methods provide results specific to materials; however, calorimetry data depends on the conditions used during the experiment (Haines 1995). One must be careful in choosing the calorimetry parameters:

1. Time scale: Especially in dynamic measurement systems, for events to be detected the experimental time scale should match the time scale of the observed event.
2. Magnitude of the heat flow: If the energy associated with the transition is small, it can lead to ambiguities in its detection. Increasing the scanning rate enhances the signal; however, it may cause deviation from equilibrium conditions, which requires models beyond the standard equilibrium thermodynamics treatment of calorimetry data.
3. Moisture loss during experiment: Biological samples in general are high-moisture content materials. If the sample cell is not sealed well, the moisture content of the sample will change due to evaporation during the course of experiment. This may lead to overestimation of the transition temperature as well as the transition enthalpy change.
4. Interpretation of overlapping peaks: Biological samples may contain multiple components that undergo thermally induced transitions at similar temperatures. As a result, overlapping peaks may be observed on a differential scanning calorimetry (DSC) thermogram. Even if the origin of the event is known, because the peak temperatures may shift due to overlap, individual events may appear to happen at different temperatures. The individual peaks can be resolved experimentally (Barrett et al. 2002, 2005), or the complex thermograms can be deconvoluted by using special software (Fessas and Schiraldi 2000).

An Overview of the Book

This book focuses on the basics of calorimetry and specific applications for characterization of food systems. The material in this book is designed to provide food scientists, food technologists, and food engi-

neers with knowledge about the potential uses of calorimetry as a tool in process design and optimization as well as product development and improvement. The book consists of two sections. The first section includes eight chapters describing the principles of calorimetry alone and coupled with other techniques as well as the use of calorimetry to characterize biological systems ranging from pure single phase to multicomponent and multiphase systems of solids, dilute and concentrated solutions of macromolecules, emulsions, foams, and bacteria. The second section of the book is designed to illustrate the use of calorimetric data to guide engineers and processors in design and optimization of processes.

The multicomponent nature of the food materials presents a challenge in that the specific component undergoing a conformational or phase transition may be in small quantity relative to the whole, thus generating an insufficient heat signal to detect. As an alternative to increasing the heating rate, the heat signal can be enhanced by increasing the sample size. In Chapter 2, the challenges of increasing sample size and strategies to overcome these challenges by using microcalorimetry are discussed.

The increased interest of consumers in minimally processed foods pushed the food research community to explore novel technologies that present alternatives to thermal processing. High hydrostatic pressure (HHP) processing has become the most promising alternative technology. Currently, HHP processing is implemented for several foods and has a market value of more than $500 million. The optimization of HHP processing requires knowledge of physical properties under conditions relevant to the pressures attained during the process. The design of calorimeters operating under the pressures used in industry is very challenging. Chapter 3 focuses on the design of a high-pressure calorimeter and the protocols to be followed for calibration, data collection, and analysis.

Applications of ultrasensitive calorimetry to proteins and their interactions in dilute solution are examined in Chapter 4. Emphasis is placed on the practical aspects of collecting and analyzing differential scanning calorimetry (DSC) data to characterize the thermal and thermodynamic stability and the thermodynamic origins of that stability in a protein in solution. The thermodynamics of association between a protein and a small molecule or another macromolecule are quantifiable by application of isothermal titration calorimtery (ITC). The

design and execution of ITC experiments are described with emphasis on the information content of titration curves. Together or separately, DSC and ITC provide valuable tools for developing a predictive understanding of protein stability and interactions as a function of temperature and solution conditions.

Investigation of dilute systems is essential to elucidate the behavior of macromolecules thermodynamically. However, in biological systems and foods, dilute systems are rarely encountered. Commonly, macromolecules exist in foods at high concentration and in complexes with other macromolecules and low-molecular-weight compounds. Heat denaturation and aggregation of proteins are common during food processing and affect the quality attributes of food. Therefore, Chapter 5 uses calorimetry to study the effects of pH, salts, alcohols, and polysaccharides on thermal denaturation and aggregation of food proteins in order to elucidate the mechanisms of structure formation, structure-texture and structure-physical property relationships in foods.

Proteins also play an important role in development of emulsions and foams that are examples of multicomponent and multiphase food systems. Both the formation and the stability of such complex systems depends on the adsorption properties of proteins at oil-in-water or gas-in-water interfaces. Chapter 6 reviews the use of DSC in scanning and isothermal mode for monitoring effects of food composition and physicochemical environment on the conformation and structural modifications of proteins in emulsions under the time-temperature combinations relevant to processing. The results presented in this chapter illustrates that a combination of thermodynamic and kinetic data obtained by using DSC in scanning and isothermal modes provide a better understanding of emulsions and the ability to control structure-forming mechanisms in food systems.

The main goal of food processing is to manufacture foods that are stable and safe to consume, which requires the inactivation of bacteria to prevent spoilage and foodborne diseases. Thermal inactivation of microorganisms is associated with irreversible denaturation of membranes, ribosomes, proteins, and nucleic acids. DSC can be used to monitor the reversible and irreversible changes in the cellular components of bacteria. Chapter 7 describes using DSC to provide an insight into the mechanism of bacterial cell inactivation. Also illustrated is the utility of DSC data to quantitatively evaluate bacterial inactivation kinetics. Calorimetry can be used to evaluate the effect of food-

processing variables other than heat on bacteria. Chapter 7 describes the analysis by calorimetry of damage to bacterial cells due to chemical, nonthermal, or antibiotic treatments and the relationship between the calorimetric data and loss of cell viability.

The data collected by calorimetry are complementary to data collected by other biophysical methods. Thermal analysis is a valuable tool to observe phase transition, but especially for complex systems, such as lipids, the thermal observables can be due to a variety of structures forming during the heating or cooling process. Generally, another technique such as Fourier transform infrared spectroscopy or x-ray diffraction (XRD) is used in parallel to acquire structural information. Obtaining complementary data can be further improved by performing simultaneous DSC-FTIR (Yoshida 1999) or DSC-XRD (Yoshida et al. 1996; Ollivon et al. 2006) measurements on the same sample. Chapter 8 describes in detail the development of a new instrument, called MICROCALIX, combining XRD at both wide and small angles as a function of temperature (XRDT) or time (XRDt), and high-sensitivity DSC, in the same apparatus with scanning or isothermal modes over the temperature range −30 to +230 °C. This approach enables one to obtain complementary thermal and structural properties information on the same sample in one experiment.

Foods exhibit thermally induced transitions over a temperature range between −50 °C and 300 °C. The thermal behavior of a food is mainly a reflection of its major component, however, with some change due to interactions with other components. Chapter 9 focuses on the use of phase transition information in development of phase diagrams that can be used for efficient process design. Heat of a solution as a parameter of great importance for food powder dissolution is also emphasized. The relevance of calorimetric data to the food industry is illustrated by specific examples.

Biological samples undergo changes even when they are kept at constant temperature. Changes, physical or chemical in origin, may produce heat that can be studied with isothermal calorimetry. However, detection and monitoring of small quantities of heat, especially at the initial stage of the physical or chemical event, requires using a high-sensitivity calorimeter. Chapter 10 focuses on application of isothermal calorimetry, a relatively less-exploited application of calorimetry in comparison with DSC, for qualitative and quantitative analysis of food stability, shelf life, and isothermal cooking processes. Specific

examples are discussed, from simple ingredients to complex biological processes.

Cereal-based products are staple foods all around the world. Although the main component in such foods is starch, thermally induced transitions are highly affected by the presence of other compounds in cereals, including proteins, nonstarch carbohydrates, and lipids, either due to competition for available water or direct interactions. Chapter 11 provides a review of thermal analysis applications to cereal-based products and cereal processing. This chapter discusses in detail mathematical treatment of the complex thermograms to deconvolute the contributions from different components in the system.

Drying has been used as a method of food preservation since ancient times. In modern practice, water is removed by evaporation upon application of heat or by sublimation from a frozen product under vacuum. During the drying process, amorphous or partially crystalline states are formed. The thermal stability of the amorphous state is defined by the glass transition temperature, which depends strongly on the amount of water present in the food system. Chapter 12 reviews the use of calorimetric data for selection of dehydration parameters to produce products with improved storage stability. This chapter also discusses the relationship between the glass transition and collapse of structure in freeze-dried materials, flavor retention by encapsulation of volatiles in amorphous systems, solids crystallization, lipid oxidation, nonenzymatic browning, and enzymatic changes.

Chapter 13 describes the relatively new technique of scanning transitiometry developed by Randzio (1996) based on scanning of one of the three variables—pressure, volume, or temperature—and measurement of the other two, as well as the heat signal. This chapter also discusses the specific application of scanning transitiometry for gelatinization of wheat starch dispersions and for investigation of pressure shift freezing. In addition, the technique is applied to the study of water, water in pork muscle, solutions of gelatin in water, and lipids.

Chapter 14 focuses on the application of calorimetry to determine the effects of high hydrostatic pressure on starch gelatinization as well as to characterize the recrystallization of the gelatinized starch during subsequent storage for calculation of starch recrystallization kinetic parameters. These results are used in selection and optimization of HHP processing parameters and storage conditions for foods containing starch.

Foods show chemical reactivity leading to self-heating and self-ignition of hot spots. Especially handling of dry powders in bulk, such as in milling, drying, and packaging, can be dangerous due to potential dust explosions. Chapter 15 reviews the evaluation by calorimetry of the thermal consequences of exothermic decompositions in foods, describes the methodology for quantifying the risk in terms of its severity and its probability, and discusses methods for collecting the stability data correctly. Specific cases of formation of hot spots in dryers, storage and hot discharge, and transport safety are discussed. The importance of establishing safe conditions for handling of materials in prevention of accidents in the food industry is emphasized.

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