1 Introduction to Dense Phase Carbon Dioxide Technology

Giovanna Ferrentino and Murat O. Balaban

Abstract: The introduction aims to bring together accumulated knowledge in the areas of supercritical and dense phase CO_2 technology. A summary is given of the areas covered by the book's chapters. Recognized experts in their fields discuss the following topics: solubility of CO_2 in liquids; the effects of supercritical and dense phase CO_2 on microorganisms, including vegetative cells and spores; the application of supercritical and dense phase CO_2 on juices, beverages, and dairy products; progress in the use of pressurized CO_2 in pharmaceuticals. Finally an outlook regarding the future of the technology is presented.

Keywords: overview; dense phase; carbon dioxide; nonthermal processing.

Nonthermal technologies have gained increasing importance in recent years as potentially valuable processes to replace or complement the traditional technologies, currently used for preserving foods and other biological materials. Traditionally, many foods are thermally processed by subjecting them to a temperature range from 60°C to more than 100°C for few seconds to several minutes (Jay 1992). During thermal treatments, heat transferred to the food kills vegetative cells of microorganisms, yeast, and molds, and also inactivates spores depending on the severity of the applied conditions. This process also inactivates many undesirable enzymes in foods that cause quality loss. However, thermal treatment may cause unwanted reactions leading to undesirable changes or formation of by-products in the food.

Thermally processed foods can undergo organoleptic changes and a cooked flavor accompanied by a loss of vitamins, essential nutrients, and flavors.

Increased consumer demand for safe, nutritious, fresh-like food products with a high organoleptic quality and an extended shelf life resulted in the concept of preserving foods using nonthermal methods.

Dense Phase Carbon Dioxide: Food and Pharmaceutical Applications, First Edition. Edited by Murat O. Balaban and Giovanna Ferrentino.

During nonthermal processing, the temperature of the food is held below temperatures normally used in thermal processing. Therefore, the quality degradation expected from high temperatures is reduced and some vitamins, essential nutrients, and flavors are expected to undergo minimal or no changes (Barbosa-Cánovas 1998). High hydrostatic pressure (HHP), dense phase carbon dioxide (DPCD), oscillating magnetic fields, high-intensity pulsed electric fields, intense light pulses, irradiation, cold plasma, chemicals, biochemicals, and hurdle technology are some of the possibilities in the area of nonthermal technologies. Compared to traditional techniques, these avoid drawbacks such as loss of flavors and nutrients, production of undesirable side reactions, as well as changes in physical, mechanical, and optical properties of the food treated.

The use of dense phase carbon dioxide (DPCD) has been proposed as an alternative nonthermal pasteurization technique for foods (Spilimbergo *et al*. 2002), for the first time in the 1950s by Fraser (1951) and Foster *et al.* (1962) who reported the disruption of bacterial cells by the rapid decompression of carbon dioxide (CO_2) from a pressure of 500 lbf/in^2 (about 3.45 MPa) to ambient pressure. DPCD involves mostly the supercritical state of CO_2, but may also involve subcritical gases and sometimes liquids under pressure. In the DPCD technique, food is contacted with (pressurized) sub- or supercritical CO_2 for a certain amount of time in batch, semibatch, or continuous equipment. The DPCD technique presents some advantages over HHP due to its milder process conditions. The pressures applied are much lower (generally <30 MPa) compared to those used in HHP (300–1200 MPa). In addition, capital expenditure is considerably lower. In 1969 Swift & Co. (Chicago, IL) obtained the first US patent for food product pasteurization with CO_2 at "super atmospheric" pressure. Since 1980, others demonstrated the bacteriostatic action and inhibitory effect of CO_2 on the growth and metabolism of some microorganisms. *Pseudomonas* was found to be very sensitive while other types, such as *Lactobacillus* and *Clostridium*, were less sensitive. However, it was with the work published by Kamihira *et al.* (1987) that the inhibitory effect of CO_2 under pressure started to be addressed systematically. These authors tested the sterilizing effect of CO_2 in supercritical, liquid and gaseous phase on wet and dry *Escherichia coli, Staphilococcus aureus* and conidia of *Aspergillus niger* by using a supercritical fluid extraction apparatus. Since then, many studies investigated the effects of CO_2 on pathogenic and spoilage organisms, vegetative cells and spores, yeasts and molds, and enzymes. It has been proven that this technique can be considered a cold pasteurization method that affects microorganisms and enzymes, using CO_2 under pressures below 50 MPa without exposing foods to the adverse effects of heat. Thus foods retain their physical, nutritional and sensory qualities.

DPCD pasteurization of liquid foods is operational and almost ready to be employed on a commercial scale. Most of the commercialization efforts have been performed so far by Praxair Inc. (Burr Ridge, IL, US). Based on the technology, licensed from the University of Florida (Balaban *et al.* 1995; Balaban 2004a, b), Praxair developed a continuous process system which utilizes the DPCD as a nonthermal process alternative to thermal pasteurization (Connery *et al.* 2005). This system has been registered under the trademark "Better Than Fresh (BTF)." Praxair constructed four mobile BTF units for processing about 1.5 L/min of liquid foods for demonstration purposes. In addition, a commercial-scale unit of 150 L/min has also been constructed (Connery *et al.* 2005) and tested in an orange juice–processing plant in Florida. For the continuous treatment of liquid foods, pilot-scale equipment was also manufactured by Mitsubishi Kakoki Co. (Tokyo, Japan) on behalf of and according to the patents owned by Shimadzu Co. (Kyoto, Japan) (Osajima *et al.* 1997, 1999a, b). This equipment consisted of a vessel of 5.8 L through which CO_2 and liquid foodstuff were simultaneously pumped at maximum flow rates of 3.0 kg/h and 20 kg/h, respectively. In 2003, the apparatus was made available only to research laboratories in Japan (private communication, Shimadzu Belgium). At the moment, we have no information available on further commercialization efforts of Shimadzu in the field of DPCD processing for liquid foods. On the basis of their own patent (Sims 2000), PoroCrit LLC (Berkeley, CA, US) also developed a membrane contactor consisting of several hollow-fiber membrane modules for the continuous DPCD pasteurization of liquid foods, mainly beverages, juices, milk, and wine.

As for all non-thermal technologies, the most important issue involved in the commercialization of DPCD process is the regulatory approval. Foods processed thermally or nonthermally must comply with the safety regulations set forth by the US Food and Drug Administration prior to being marketed or consumed. For example, the regulations for thermally processed low-acid canned foods are contained in Title 21, Part 113 of the US Code of Federal Regulations, entitled "Thermally Processed Low-Acid Foods Packaged in Hermetically Sealed Containers." The regulations in Title 21 were established to evaluate (1) the adequacy of the equipment and procedures to perform safe processing operations, (2) the adequacy of record keeping proving safe operation, (3) justification of the adequacy of process time and temperature used, and (d) the qualifications of supervisory staff responsible for thermal-processing and container closure operations (Teixeira 1992). However, the validation of DPCD as a nonthermal method and the determination of compliance regulations necessary for commercialization are complex and challenging. The progress in the validation needs to be encouraged to address the regulatory needs in the near future.

This volume attempts to bring together the accumulated knowledge in the area of DPCD. Experts in many areas have contributed to this book regarding the following topics:

- Solubility of CO_2 in liquids, both from a thermodynamics–theoretical perspective, including models, and from an experimental approach. This is critical because the accumulated evidence points to the critical contribution of dissolved (and saturated) CO_2 to microbial inactivation.
- Effects of DPCD on microorganisms, including vegetative cells and spores; kinetics of microbial inactivation with DPCD; and inactivation of certain enzymes with DPCD. This area is very important because, first and foremost, a new technology must prove the safety of the foods that are processed using it.
- Application of DPCD on juices, beverages, and dairy products. There is a growing body of work in this area, reporting on effects on microorganisms, and especially on quality attributes and nutritional contents. If DPCD applications are to be successful, the organoleptic and nutritional quality of foods processed using DPCD must be known.
- Progress in the use of pressurized CO_2 in pharmaceuticals. This is a well-developed area, with many applications. It also opens up the exciting field of treatment of solids and powders with DPCD.
- An overview of the current technology. This chapter is written by experts in the industry, who have been involved with the design, development, and commercialization efforts of DPCD. Their hands-on views are very valuable.
- An outlook regarding the future of DPCD technology.

It is sincerely hoped that the reader will find the book valuable in bringing information, research results, and most importantly an extensive bibliography in the nonthermal field of DPCD.