# Sterilization of Quebec's duck *foie gras*: thermal resistance of *Clostridium sporogenes* PA3679, thermo-physical properties of the product, and mathematical modeling of the sterilization.

**Mémoire**

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# Résumé court

La résistance thermique de *Clostridium sporogenes* PA3679, ainsi que les propriétés thermo physiques comme la conductivité thermique, la chaleur spécifique, la densité et la diffusivité thermique ont été déterminées pour le *foie gras* produit au Québec et d'autres produits dérivées. Un modèle mathématique a été également développé pour simuler la température au centre (point froid) des conserves de *foie gras.* Les résultats obtenus pour la résistance thermique et les propriétés thermophysiques montrent, en général, un bon accord avec les données publiées. Ces valeurs ont été utilisées avec le modèle mathématique pour prédire la température à la zone la plus froide. Les températures prédites n'ont montré qu'une légère différence par rapport aux valeurs expérimentales. Avec ce modèle, la létalité totale de *C. sporogenes* a pu être aussi calculée, ce qui permet d'assurer la salubrité du produit et la sécurité des consommateurs.

# Short abstract

Thermal resistance of *Clostridium sporogenes* PA3679, and the thermophysical properties as thermal conductivity, specific heat, density and thermal diffusivity were determined for the *foie gras* produced in Québec and other derivative products. A mathematical model was also developed to simulate the temperature at the center (coldest point) of the *foie gras* preserves. The results for thermal resistance and thermal properties show in general a good agreement with the published data; these values were used with the model and to predict the temperature at the coldest zone. The predicted temperatures have low error when compared to the experimental temperatures. With this model, the total lethality of *C. sporogenes* can be also calculated, providing the necessary information to secure consumer safety.

# Résumé long

Une étude sur la stérilisation des produits de *foie gras* a été réalisée en collaboration avec l'Association des éleveurs de canards et d'oies du Québec (AECOQ). L'objectif principal de cette étude est de trouver un moyen de stériliser minimalement le produit, en évitant les éventuels défauts de qualité et ce, sans compromettre la sécurité des consommateurs. Pour cette étude, la résistance à la chaleur d'un microorganisme indicateur (*Clostridium sporogenes*) a été évaluée dans un tube d'inactivation thermique en acier inoxydable chauffé à différentes températures dans un bain d'huile, où le nombre de microorganismes ayant survécus aux traitements a été évalué en fonction du temps. Les valeurs *D* et *z* ont été ainsi déterminées. Ensuite, l'évaluation expérimentale des propriétés thermiques des produits de *foie gras* a été réalisée. La conductivité thermique a été déterminée avec un analyseur thermique KD2 Pro (Decagon Inc.). Le profil de fusion des graisses et la chaleur spécifique ont été analysés au moyen de la calorimétrie différentielle à balayage (Pyris1 PE). La masse volumique a été déterminée par pesée selon la méthode d'Archimède. Finalement, un modèle mathématique de transfert par conduction dans un cylindre fini (deux dimensions) a été développé pour représenter le traitement thermique dans les conserves de produits de *foie gras*. L'approximation discrétisée des dérivées a été réalisée par différences finies, puis résolue en utilisant Matlab R2012b. Des expériences de stérilisation de *foie gras* ont été réalisées en mesurant la température dans le point le plus froid de la conserve, dans un autoclave à la vapeur à différentes températures. Les résultats montrent un bon accord entre les valeurs théoriques et expérimentales. Les données obtenues dans cette étude aideront à la conception d'un processus amélioré pour préserver la qualité du *foie gras* en conserve.

# Long abstract

This sterilization study of *foie gras* products was carried out in collaboration with the Association of Ducks and Geese Producers in Quebec (AECOQ). The main objective of this study is to find a way to minimally sterilize the product, avoiding quality defects without compromising consumer safety. For this study, the thermal properties of *foie gras* products and heat resistance of an indicator organism (*Clostridium sporogenes*) were evaluated. The thermal conductivity was determined with a thermal analyzer KD2 Pro (Decagon Inc.). The melting profile of the fat and the specific heat were analyzed using differential scanning calorimetry (Pyris1 PE). The density was determined by using the Archimedes method. The thermal resistance of *C. sporogenes* was performed in a thermal inactivation stainless steel tube heated to different temperatures in an oil bath, where the number of surviving microorganisms was evaluated in function of time. The $D$ and $z$ values were thus determined. Then, a mathematical model of heat transfer by conduction in a finite cylinder (two dimensions) was developed to represent the thermal treatment in canned *foie gras* products. A discrete approximation of the derivative was performed by finite differences, and then solved with Matlab R2012b. Fatty liver sterilization experiments were performed by measuring the temperature in the coldest point of the product, in a steam autoclave at different temperatures. The results show good agreement between the theoretical and experimental values. The data obtained in this study will help to design an improved process to preserve the quality of canned *foie gras*.

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# Abbreviations List

| | |
|---|---|
| $A$ | Surface area of a cylinder |
| $a_0, a_1, a_2$ | Regression constants to satisfy equation 5.5 |
| $\alpha$ | Thermal diffusivity |
| $C_p$ | Specific heat |
| $C_{pi}$ | Specific heat of component i |
| $D$ | Decimal reduction time |
| $\rho$ | Density of the product |
| $\rho_0$ | Density of water |
| $\Delta t$ | time change |
| $F$ | Lethality value of a process |
| $F_0$ | Lethality value of a process with a z value of 10°C and a reference temperature of 121.1°C |
| $H$ | Total Height of a cylinder |
| $k$ | Thermal conductivity |
| $k_i$ | Thermal conductivity of component i |
| $L$ | Half height of a Cylinder |
| $LFF$ | Liquid Fat Fraction |
| $LFF_{df}$ | Liquid Fat Fraction of duck fat |
| $LFF_{fgf}$ | Liquid Fat Fraction of foie gras fat |
| $m$ | Mass |
| $N$ | Survival population at the end of a process |
| $N_0$ | Initial population |
| $q$ | Heat flux |
| $r$ | Radio of a cylinder in cylindrical coordinates |
| $R$ | Radio of a cylinder in cartesian coordinates |
| $SFF$ | Solid Fat Fraction |
| $t$ | Time |
| $T$ | Temperature |
| $T_{(c)}$ | Temperature at the coldest point of a product |
| $T_0$ | Initial temperature of a product |
| $T_\infty$ | Temperature of the heating fluid |
| $T_{ref}$ | Reference temperature for lethality calculation |
| $T_{ret}$ | Retort Temperature |
| $T_s$ | Temperature at the surface of a product |
| $w$ | Slope of equation 6.3 |
| $x$ | x direction in cartesian coordinates |
| $X_i^v$ | Volume fraction of component i |
| $X_i^w$ | Mass fraction of componen w |

| $X_t$ | Process time |
| --- | --- |
| $y$ | y direction of cylindrical coordinates |
| $z$ | Decimal reduction Temperature |

# Acknowledgements

First, I would like to thank Prof. Cristina Ratti, my supervisor for all her support as well as giving me the opportunity to study at Université Laval; I cannot thank her enough for all the help, patience, dedication and effort throughout the development of this project.

I would also like to thank my co-supervisor Prof. Linda Saucier for her constant support and work in the research and in the laboratory.

I gratefully acknowledge the Ministère de l'Agriculture, des Pêcheries et de l'Alimentation du Québec (MAPAQ) for the grant given to this project, with which I was benefitted and I could focus only in the studies. Also I am grateful to the Ministère de l'Edutation, Loisir et Sports du Québec (MELS) and the Secretaría de Relaciones Exteriores (SRE) of Mexico for granting me a scholarship to come and study in this province.

I am also grateful with all the people that was part of this project and helped me a lot, Khadidja Bualem and Monica Gil for their support in the microbiology aspects of the project, and the technicians in the Faculty who were always willing to help especially Jocelyne Giasson for her constant aid and availability to solve any presenting problems.

*To my family and close friends, for their daily support from afar; and to Gadea A. thanks for sharing this adventure with me.*

# 1 Introduction

*Foie gras* is a product made with the fatty liver of hand-fed fattened ducks or geese. In Québec, duck farms have existed for more than a century, but the consumption of duck derivative products, such as *foie gras*, has increased only in the last few years (AECOQ, 2015). The growth of the market pushes the duck producers to offer more products, maintaining the quality of the farm-made products. For preserving meat products, thermal treatments are the handiest methods, either for maintaining raw products in refrigerating conditions or applying heat to cook and killed all the bacteria that can cause spoilage to the product and harm to the consumer. Heat treated *foie gras* products are the most common in the market, normally commercialized in cylindrical glass or metal containers. The heat provided during the thermal treatment should be sufficient to assure that all the harmful or spoiling bacteria are inactivated, thus increasing the product shelf life. To guarantee that all heat treatments will achieve these goals, the government of Canada request a sterilization value ($F_o$) of at least three minutes for low acid canned foods; this is, the thermal process applied should be comparable to a process of 3 minutes at 121.1°C in the coldest point of the product (Canadian Food Inspection Agency, 2015). After this process, the product is microbiologically safe, but the quality of the product could be diminished since *foie gras* fatty matrix is very delicate. *Foie gras* being a relatively new product in Canada, general guidelines for canned low acid foods should be applied.

In France, where the product is quite popular and considered a cultural heritage, the quality of the product is important and the quantity of fat that melts and diffuses out from the meat matrix at the end of the heat treatment should be minimized for high quality products. An acceptable maximum of melted fat is 30% of the weight of the product (Goullieux, 2007). Reducing this factor is quite challenging, since *foie gras* fat is completely melted at 50°C, and the current sterilization temperatures are usually between 105 to 110°C. Several studies were conducted in research centers in France to optimize the heat transfer, while keeping the product safe for the

consumers. Their findings led to reduce the sterilization process to be equivalent to 1 minute at 121.1°C because of two main facts:

- The high composition of unsaturated fatty acids can inhibit the growth of spores (Tremoulet et al., 2002)
- Due to the high unsaturated free fatty acid content of the product, the initial contamination is never superior to $10^2$ spores/g, when GMP are followed (Tremoulet et al.,2002; André et al., 2010)

The main problem for producing good quality canned *foie gras* products in Quebec is that sterilization parameters are different in France and Canada, giving products with different organoleptic characteristics, mainly because of the differences in legislation that exist between both countries. For assuring that the Canadian product quality resembles the product made in France, studies on spores thermal resistance as well as determination of the thermal properties of *foie gras* produced in Québec are necessary, with the objective to optimize thermal treatments. A mathematical model may also serve to predict the temperature at the coldest zone of the preserves, in order to have a better control of the process.

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# 2  Literature Review

## 2.1  Foie gras

*Foie gras* is a delicacy, originally from France, declared "gastronomic and cultural heritage" (Code rural et de la pêche maritime, 2006) of the nation. According to this article, *foie gras* is made from the liver of ducks or geese that have been hand fed and fattened to create desired organoleptic attributes, such as obtaining the right amount of lipids in the product. France dominates the international *foie gras* market with 80% of the world production. In 2012 the production reached 19 500 tons, of which 19 000 (97.4%) was produced from duck liver. From this, 73.1% was transformed into ready to eat products, being 41.1% transformed in pasteurized products and 27.5% in sterilized preserves (Comité Palimipèdes à *Foie Gras*, 2013). Canadian production of *foie gras* is concentrated in the province of Québec, where it is prepared from the livers of ducks or geese. Production of geese and duck meat in 2014 represented a total of 11,304,078 kg of meat, obtained from 5,571,552 heads of ducks, only 0.2% higher than 2013, and 18% more than 10 years ago (2004) whereby representing a growth for this industry and the consumption of these products (Poultry Production Report, Agriculture and Agri-Food Canada).

In France and Québec, the mule duck is the preferred breed for the production of *foie gras* since it offers superior quality criteria, compared to other ducks, such as texture, flavor, and bigger weight of the liver, monounsaturated acids content, technological yield and the retention of lipids during cooking, it is used for more than 90% of the production of *foie gras* (Chartrin, 2006; AECOQ, 2015). The spectrum of *foie gras* products is quite wide and offers the consumer a variety of options from raw and mid raw (pasteurized) products, to fully cooked (sterilized) and complex formulations like emulsions and emulsions with pieces of whole *foie gras.* (Gouilleux, 2007). In Québec, a diversity of raw *foie gras* products can be found as  escalope, the whole product as well as nuggets and scraps; the

transformed or ready to eat *foie gras* goes from the whole sterilized product, and three types of emulsion depending on the minimum content of *foie gras*: "bloc" of *foie gras* that is composes of 90% of *foie gras,* "Parfait" of *foie gras* that is an emulsion of minimum 70% of *foie gras* with a delicate texture, and the "mousse" of *foie gras*, an emulsion composed of minimum 50% of *foie gras* distinguished for its creamy texture (AECOQ, 2015).

*Foie gras* is a product known for its high content in lipids, this compound alone can represent more than 50% of the total weight of the product. Rukke et al. (2008) studied the chemical composition of duck *foie gras* finding a concentration in lipids from 29.00 to 61.80%, the average being 51.06%. In this study, other components such as proteins (average 8.22%), ash (0.35%) and dry matter (68.64%) where also determined. Theron et al. (2012) found a composition for duck *foie gras* of 56.7 ± 3.7% for lipids, 7.49 ± 0.75% for proteins and 69.1 ± 2.8% for dry matter, values that resemble with those published by Rukke et al. (2008). Tremoulet et al. (2002) also found a value of more than 50% for lipids in duck's *foie gras* (55.3 ± 4.2%). This fat content is achieved by the duck natural ability to store fat in the liver for long migration (Gouilleux, 2007).

The microbiology of *foie gras,* as for all meat products is quite diversed, consisting of various strains mainly of psychotropic clostridia and lactic acid bacteria (Planchon et al., 2013). A study performed by Matamoros et al. (2010) with the objective to determine the spoilage flora present in *foie gras* after a thermal treatment, showed that the main species that survived and spoiled the product were various strains of *Lactobacillus*, mainly strains of *Lactobacillus sakei L. coryniformis* and *L. paraplantarum*. Another part of the study was performed on non-spoiled material and the main bacteria present were of the genera *Weissella*, the most abundant were *Weissella viridescens* and *W. minor*. Regarding the spores present in *foie gras* products, André et al. (2010) established that if good manufacturing practices are performed in the facilities, a concentration lower than

10 spores/g can be found in the product before thermal treatment, never higher than $10^2$ spores/g.

## 2.2 Thermal Processing

### 2.2.1 Sterilization

In the food industry, many processes exist in order to achieve food safety. Sterilization is a thermal process for preserving foodstuffs that permits to keep them at room or cold temperatures for months or years, while preserving the product safe for consumption (Simon, 2011; Smith, 2011). Preservation of foods by thermal processing started with the work of Nicholas Appert in 1810, when he was able to keep a variety of food products in glass jars by application of heat treatments (Stumbo, 1979; Ramaswamy and Singh, 1997). Canning history had three big breakthroughs; the first was the early works of Louis Pasteur, Prescott, and Underwood among others, during the last part of the XIX century. The main objective of these researches was in microbiology of heat-processed foods, introducing science into the preservation of foods by thermal processing. A second breakthrough was the commercial introduction of the "sanitary" can, in the 1900's. The use of this element revolutionized the industry of canning because high-speed mass production was achieved. The third event that marked the industry was the work developed by Ball, Bigelow and others around 1920; where they developed mathematical and graphical models for estimating the time and temperatures necessary to produce "commercially stable" and adequate sterilized foods. These findings lead to the improvement of calculations, evaluation and methods of measuring the temperature and the heat resistance of the bacteria that caused food spoilage, with the objective to minimize over processing of foods that could be translated in improvement of the organoleptic and nutritive properties of the processed foods (Stumbo, 1979).

### 2.2.2 Types of sterilization

Different methods for establishing thermal processes are available, which are designed to maintain quality of the product, without compromising the safety. Some of these processes are:

- **HTST.** High Temperature Short Time. After some research, it was concluded that treatments with high temperatures and short times could give a product the same level of safety as a process with shorter temperature and longer times, with the finding that nutritious and organolpetic characteristics in the HTST were better maintained or not at all affected (Stumbo, 1979). Conditions are generally 121°C for several minutes (Smith, 2011).
- **UHT.** Ultra High Temperature. This process was developed to submit the product to an ultra high temperature for a very short period of time, to reduce the severity of the heat treatment and assure product quality (Ramaswamy and Singh, 1997). Conditions for this process are generally temperatures above 135°C held just for a few seconds.
- **Aseptic treatment.** In this process, the product is treated separately from the package, in heat exchangers where it is heated and cooled quickly to minimize severity of heat treatment, and then packaged in a previously sterile container. This process generally used for liquid foods (Stumbo, 1979; Ramaswamy and Singh, 1997; Smith, 2011).

### 2.2.3 Autoclaves or Retorts

Sterilization is generally performed in closed containers called autoclaves or retorts, where the product is heated by hot water or saturated vapor. Vessels are designed to resist high pressure so the product could reach temperatures as high as 150°C, which can be only possible with high pressures of 475 kPa (Singh and Heldman, 2014). Sterilization process can be in batch operation, semi-continuous, continuous or in the aseptic treatment, which would be a form of continuous

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operation. Figure 2.1A shows the diagram of a typical retort used for batch sterilization. In this system, product is charged into the vessel, where vapor at high pressure is supplied until the temperature and pressure desired are achieved. After this, there is a holding phase in which the temperature is maintained constant for a desired period of time (Sharma et al., 2003; Singh and Heldman, 2014). Semi-continuous systems consist of an automated system for the charge and discharge of a batch retort. Figure 2.1B is an example of a completely continuous autoclave, in which a hydrostatic head of water is made to maintain the pressure and vapor inside the vessel; the product enters via a conveyor and the time of residence of the product in the internal chamber can be adjusted to reach the desired sterilization (Singh and Heldman, 2014).

Batch, semi-continuous and continuous sterilization is made on a packed product and it can be performed either for solid and liquid products. Aseptic sterilization can be performed only in products that can be pumped. For this type of sterilization, the procedure consists in two parts: a heat exchanger where the product flows and is heated and cooled rapidly; and a second part were the product is packed into previously sterilized containers in an aseptic ambiance. The fact that the product is unpacked eases the heat transfer making this system less severe compared with the sterilization where the product is packed. Various systems to optimize thermal treatments in batch and continuous systems have been developed, for instance, agitation of the product in the process is carried out to favor heat transfer inside the package (Stumbo, 1979; Smith, 2011; Singh and Heldman, 2014).
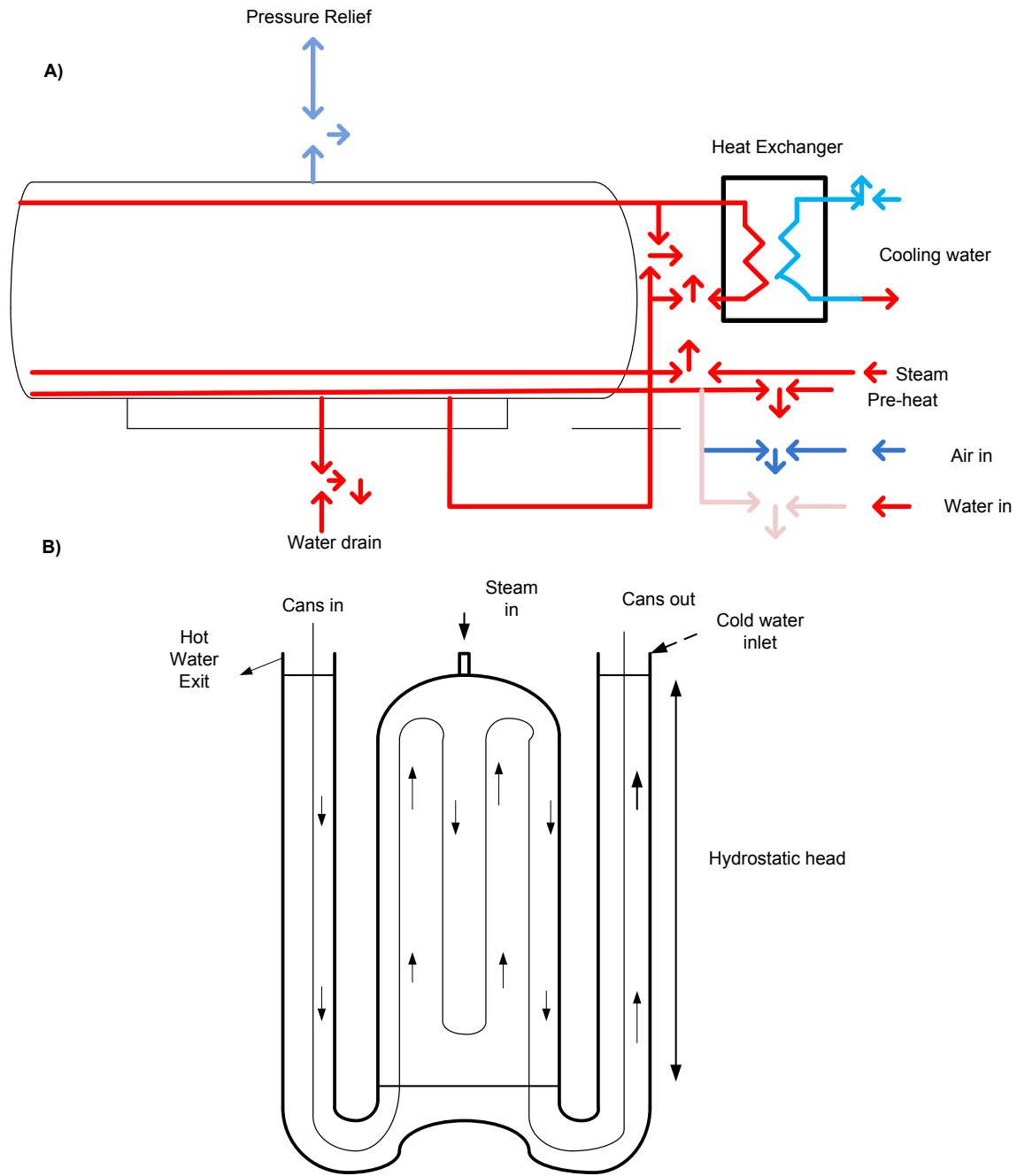
**Figure 2-1.** A) Example of a batch retort. B) Example of a hydrostatic autoclave for continuous sterilization (Adapted from Singh and Heldman, 2014)

### 2.2.4 Heat Penetration Curve

Regardless of the system chosen to perform the sterilization, the product always undergoes a thermal history similar to the one shown in Figure 2.2. At the first stage, the product enters the sterilization process at its initial temperature, it is crucial to consider this temperature in the process design since it will define how much heat is needed at the heating phase. After the product is charged into the retort, steam or hot water starts to fill the vessel, causing the product to heat, this process continues until the desired temperature of sterilization is reached. At this point, these conditions of temperature and pressure are hold for a determined period of time necessary to achieve the desired sterilization value. The end of the process comes with the cooling phase, in which the product is cooled, normally at ambient temperature, with air or water at temperatures smaller than the sterilizing temperature (Sharma et al., 2003). It is important to note that not only the holding phase is taken into account for the sterilization of the product; both the cooling and heating phase also contribute to the sterilization value since in these phases temperatures reached can also inactivate vegetative cells and spores. This is important when the process is being designed, to avoid over-processing of the product (Smith, 2011).

The temperature curve differs between the autoclave and the product on the coldest spot due to the thermal properties of the product, dictating how the heat will be transferred into the product, which normally takes longer times than pure compounds, like water or vapor.

### 2.2.5 Sterilization process design

For establishing the extent of a heat treatment, several factors must be taken into account; the most important are (Ramaswamy and Singh, 1997):

- Type and heat resistance of the target microorganism.
- pH of the food
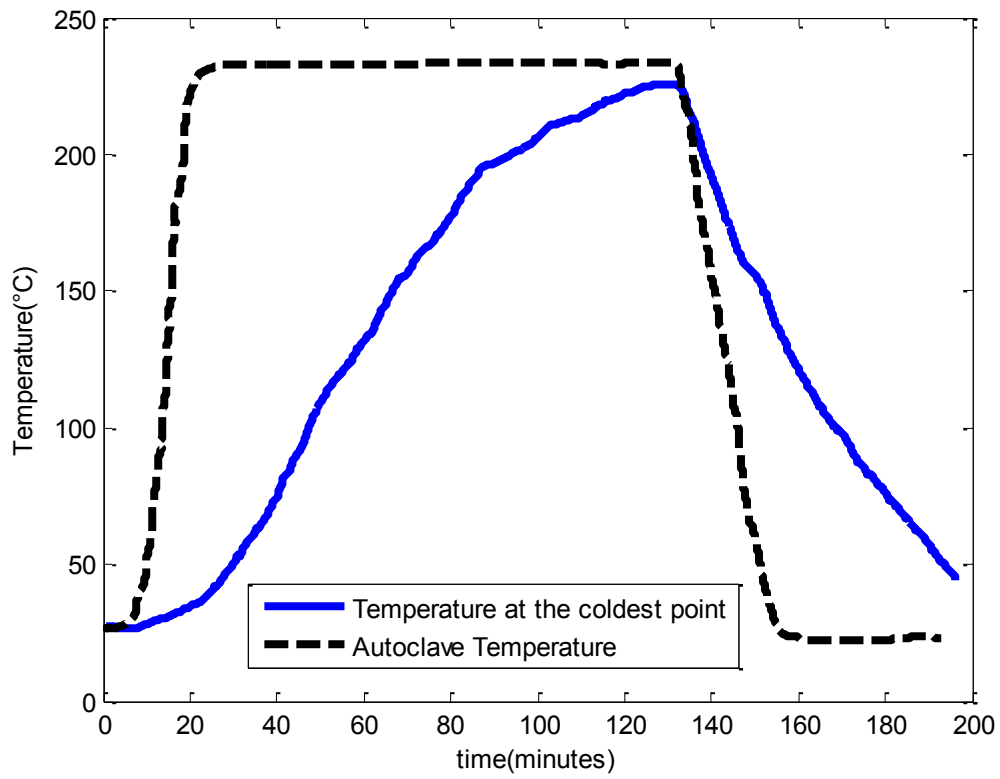
**Figure 2-2.** Heat Penetration Curve. (Adapted from Sharma, 2003)

- o High-acid foods: pH<3.7. Fruit juices, sour pickles, vinegar.
- o Acid foods: 3.7<pH<4.5. Fruit jams, tomato products, vegetable juice.
- o Low acid foods pH>4.5. All meats, vegetables, soups.
- Heating conditions.
- Thermo physical properties of the food.
- Container shape, size, and material.
- Storing temperature following the process (room or cool temperature).

From among the factors listed above, pH plays a crucial role into the process design, since the growth and survival of spore-forming bacteria highly depends on pH. Spores from spore-forming bacteria are known for their heat resistance. It has been noted that this type of bacteria does not grow at pH lower than 3.7. Hence, for high acid foods, the thermal processes do not need to be as severe compared to other ranges of higher pH. Low acid foods are of more concern in thermal processes since *Clostridium botulinum*, a bacterium of great importance with respect to health and safety concerns because the very potent toxin it produces could grow at this pH range and under anaerobic conditions such as those encountered in canned products. Therefore, designing processes is a hard task since the heat treatment should be severe enough to inactivate the spores and control their growth and yet not too severe to affect the quality of the product negatively (Stumbo 1979; Ramaswamy and Singh, 1997).

In sterilization, it is important to inactivate microorganisms or enzymes that can spoil the food during the storage life, and eliminate pathogenic bacteria that could cause foodborne illnesses to the consumers. is also important to take into account the quality of the product which depends of different factors, being the most important the security offered to the consumer, the final organoleptic factors of the preserve (flavor, smell, texture, etc.) its nutritional value and the "services" (functionality of the package; Ramaswamy and Singh, 1997; Smith, 2011). Thermal processes should not be designed to destroy all microorganisms present in food, because this will lead to high process times and temperatures, resulting in

low quality products; these processes should be designed to destroy target microorganisms such as pathogenic bacteria or other non pathogenic microorganisms that could spoil the food (Ramaswamy and Singh, 1997). The term "commercial sterility" is used for this, in which viable microorganisms are still present in the container, but the conditions for the growth are not optimal and the presence is not statistically significant (Stumbo 1979; Ramaswamy and Singh, 1997; Smith 2011).

The spore's ability to reproduce is used as a parameter to state if a thermal process has inactivated the population of microorganisms, this is because spores are more resistant than vegetative cells (Smith, 2011) and this is the basis for method MFHPB-1 used to validate commercial sterility (Health Canada, 2001). A lot of studies suggested that "the number of viable cells reduces exponentially with time of exposure to a lethal temperature" (Stumbo, 1979). If the logarithms of the viable cells are plotted against different process times at a determined temperature, a straight line should be obtained, provided that the treatment is deemed severe enough. Acording to several authors, thermal inactivation of microorganisms generally follows a first order (log-linear) kinetic reaction (Tandon and Bhowmick, 1986; Simpson et al., 1989; Silva et al., 1992; Hendrickx et al. 1993; Simpson et al., 1993; Juneja et al., 2001; Mah et at., 2008, Saucier and Plamondon, 2011; Santana et al., 2013). This is shown in Figure 2.3 and the mathematical relationship is represented in Eq. 2.1:

$$\log\left(\frac{N}{N_0}\right) = -\frac{1}{D} * t \qquad\qquad eq.\,2.1$$

where **N** is the survival population at the end of the heat treatment; **N₀** is the initial population of the microorganism; **t** is the time.

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The plot shown in Figure 2.3 allows determination of the decimal reduction time ($D$ value) defined as the required time to inactivate the initial cell population by 90% or 1 log unit. $D$ values differ with microorganism, product and even the packaging used (Stumbo, 1979; Jaczynski and Park, 2003; Saucier et al., 2011). The methods for measuring thermal resistance of the spores are generally performed in laboratory scale, for which a variety of methods exist depending on the nature of the matrix that will be tested. These methods include the thermal death time (TDT) in tubes or cans, the "tank" method, the flask method, the thermoresistometer method, unsealed TDT tube method and the capillary tube method; being the latter the most used method for testing thermoresistance of bacteria in liquid mediums such as buffer solutions (Stumbo, 1979).

The TDT tube method is one of the most versatile techniques, since it can be used to test bacteria in the actual food material of concern (Stumbo, 1979). In this method, the inoculated food sample is inserted in small diameter metal tubes (6-10 mm) (Odlaug et al., 1977; Stumbo, 1979). The tubes are heated using a temperature controlled water bath or oil bath (such as mineral or vegetable oils, propylene glycol) for temperatures higher than 100°C. The tubes are taken out from the heating media at different times and the survivors are enumerated, to construct the thermal death curves. The main advantage of this method is that it can be carried out in almost any laboratory, since the equipment needed is basic. The main disadvantage is that a lag in heating and cooling exists due to the tube and the material so the thermal resistance can be affected by this difference (Stumbo, 1979) and should be minimized.

An improvement to eliminate this heat lag is the use of capillary tubes where the small diameter glass capillary drastically reduces the heat transfer problems. This is a main advantage over the TDT tube method. The disadvantages of this method, however, are the laborious task of sealing and opening the tubes and the use of a solid food is almost impossible (Stumbo, 1979).
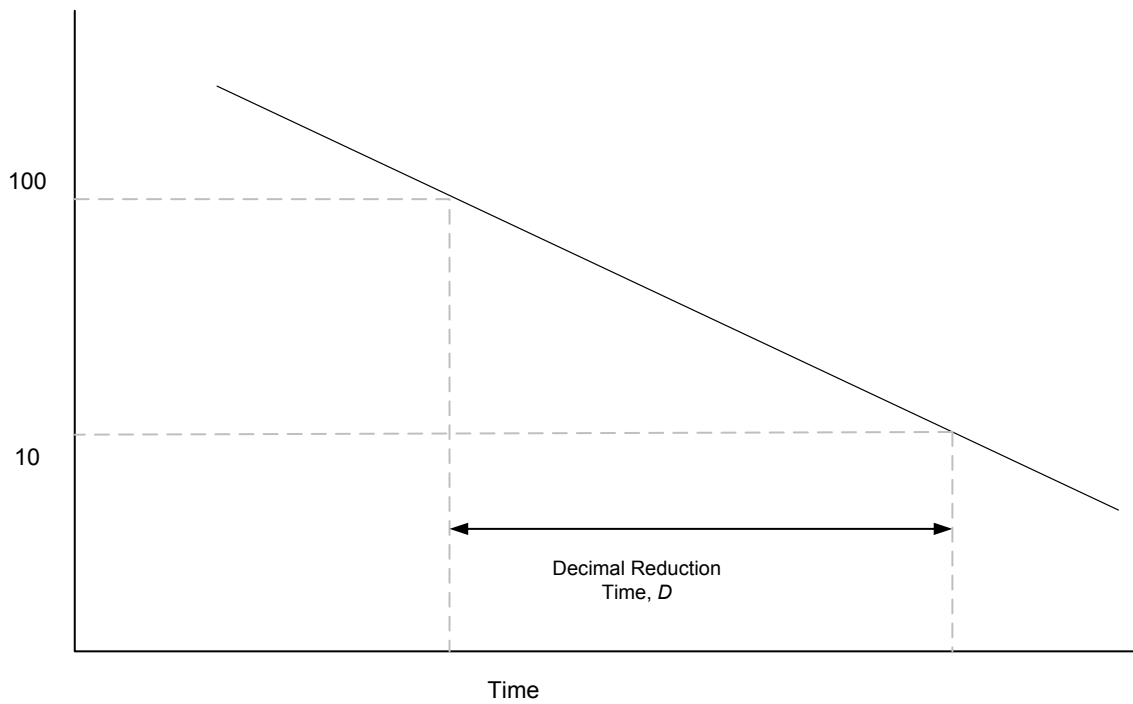
**Figure 2-3**. Example of thermal survivor curve (Adapted from Smith, 2011)

From the relationship between the *D* values and the temperatures at which they are determined, the *z* value can be obtained, which is defined as the temperature elevation in the process required to reduce the *D* value (by 90%) or 1 log unit of the microorganism *D* value (Figure 2.4) (Hendrickx et al., 1993).

As shown in eq. 2.1 for the in *D* value determination, the logarithm of *D* values also follows a linear relationship with temperature. The equation to calculate the *z* value of a microorganism is thus shown in eq. 2.2 (Jaczynski and Park, 2003; Saucier et al., 2011):

$$\log\left(\frac{D}{D_0}\right) = -\frac{1}{z} * T \qquad \text{eq. 2.2}$$

where **T** is the test temperature.

The inverse numerical value of the slope from the linear function shown in eq. 2.2, gives the *z* value for the specific microorganism and food matrix studied. Larger *z* values suggest that the spore is more tolerant to a heat treatment (Smith, 2011).

### 2.2.6  Sterilization value

The total lethality reached during a thermal process at a critical point of the product (geometrical center or the coldest temperature zone) can be calculated with the equation 2.3 (Manson et al., 1974; Tandon and Bhowmik, 1986, 1987; Banga et al., 1993; Hendrickx et al., 1993; Akterian and Fiikin, 1994; Simpson et al., 2003; Chen et al., 2011):

$$F = \int_0^t 10^{\frac{T_{(c)} - T_{ref}}{z}} dt \qquad \text{eq. 2.3}$$

where **F** is the total sterilization value; **T_{(c)}** is the product temperature at a given location (geometrical center or coldest point zone), which is a function of time; **T_{ref}** is the reference temperature, normally 121.1°C
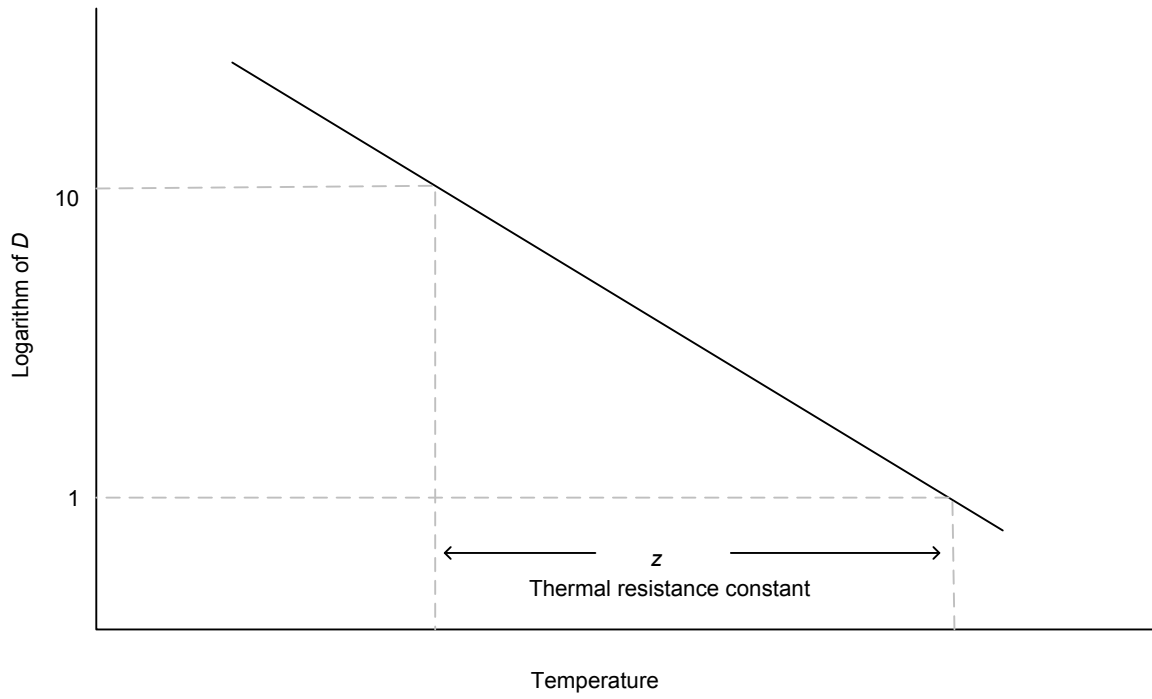
**Figure 2-4.** Exemple of thermal destruction curve (Adapted from Smith, 2011)

*z* is the *z* value of the target microorganism. If *z* is taken as the value corresponding to *C. botulinum* in buffer solution, which is *z*=10°C (Brown et al., 2011) then *F* is named $F_0$.

This value measures the severity of the heat treatment and allows the comparison of different sterilization processes. It uses a reference temperature, and it is equal to the time needed at this reference temperature, to inactivate an established population of microorganisms. For low-acid foods, such as meats, the processes are designed to reach a sterilization value of 3 min which is deemed sufficient to inactivate 12 log of *C. botulinum* (Stumbo, 1979; Singh and Heldman, 2014).

The function representing this equation is an integral because in order to achieve the desired lethality level, it is imperative to take into account all the lethality values accumulated at each set of time and temperature during the process at a selected location, generally the coldest point zone. The integral is calculated from the area under the curve (Smith, 2011) that this function generates as shown in Figure 2.5. Lethality is also important for mathematical modeling of thermal processes since it helps food technologist to have a comparison point between the experimental and the theoretical data. Although there exists an extensive debate about if this approach is correct or not because of the assumption that thermal death of microorganisms follows a log-linear behavior and not logarithmic one (due the deviations present in the heating and cooling time of the process) (Juneja et al., 2001; Chen et al., 2011), the first order kinetics model is the most extensively used in the food industry because its simplicity and also, since in most of the cases it leads to acceptable results (Hendrickx et al.,1993; Stumbo, 1979).
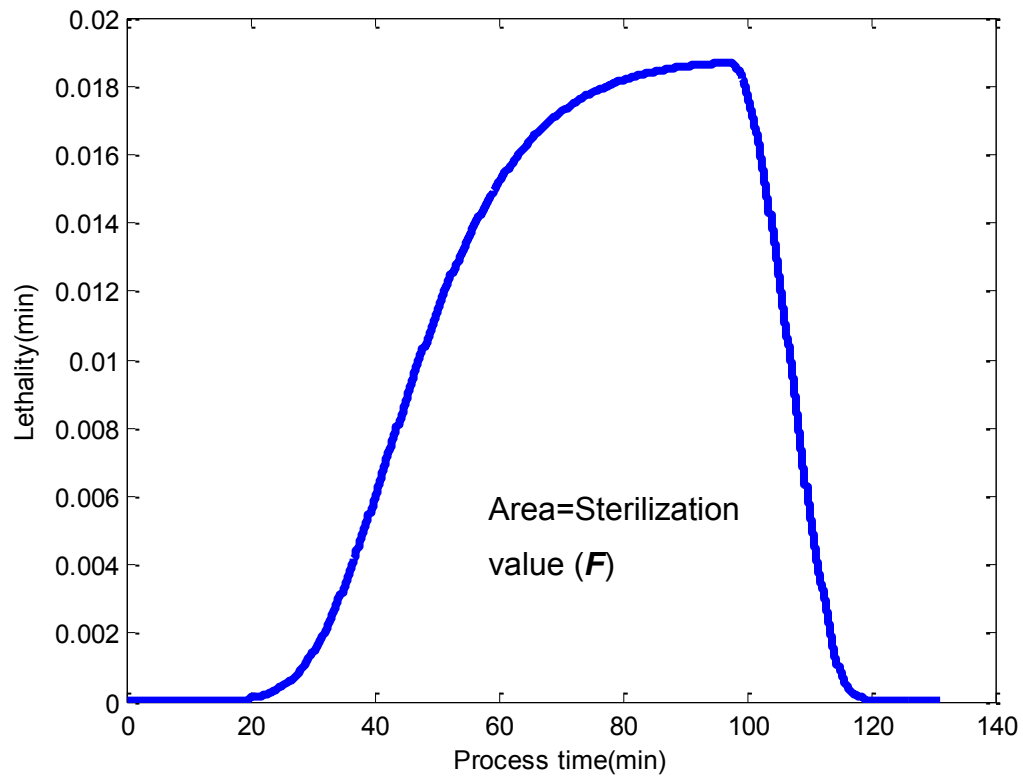
**Figure 2-5.** Curve of lethality values of a thermal process.

## 2.3  Heat Transfer

Heat propagates in a body with different temperatures at different locations, flowing from the hot parts to the colder ones, tending to attain equilibrium throughout the body (Fourier, 1955).  Several mechanisms of heat transfer exist, depending on the nature of the body:

- **Conduction**: where heat is transferred at a molecular level of the body within itself. In conduction, the molecules of a body gain more energy as temperature rises and energy is transferred to lower energy molecules, via rotational or vibrational motion of the molecules.  Conduction is normally present in solid materials, since there is no physical movement of the object (Carslaw and Jaeger, 1959; Bergman et al. 2011; Singh and Heldman, 2014).
- **Convection**: where heat is transferred by the motion of a fluid. This type of heat transfer is present normally in fluids; and it is because, in contact with a heating media, large amounts of molecules of the fluid will move collectively because of the temperature gradient, heating the colder parts of the fluid (Carslaw and Jaeger, 1959; Bergman et al. 2011; Singh and Heldman, 2014).
- **Radiation**: where the heat is transferred by electromagnetic waves. This form of heat transfer requires no physical media for its propagation (Byron et al., 1960; Singh and Heldman, 2014).

In sterilization processes first two mechanisms of heat transfer are involved. Convection represented by the heating fluid (water, vapor or air) that transports energy  to the surface of the package of the product and conduction being the heat transport form the surface of the package to the product. Depending on the nature of the product (solid or liquid) there could be internal heat transfer via conduction, convection or a combination of both.

### 2.3.1  Fourier´s Law of heat conduction

Heat transfer by conduction through a solid can be described by equation 2.4 (Fourier, 1955; Byron et al., 1960; Geankoplis, 1998):

$$q = -k\,\frac{dT}{dx} \qquad\qquad \text{eq 2.4}$$

where $q$ is the heat flow in the $x$ direction, $T$ is the temperature, $k$ is the thermal conductivity of the solid.

When eq. 2.4 is used to represent the non-steady state heat transfer in a cylindrical solid, the following equation is obtained (Özisik, 1994):

$$\frac{\partial T}{\partial t} = \alpha\left[\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial y^2}\right] \qquad\qquad \text{eq 2.5}$$

where $\alpha = (k/(Cp * \rho))$ is the relation between three properties, $\rho$ (density), $Cp$ (specific heat) and $k$, thermal conductivity. In this equation, temperature is a function of time and position in the solid, $T=f$ ($r,\ y,\ t$). The partial differential equation eq. 2.5 can be solved given the adequate boundary and initial condition of the solid of interest.

In a process like can sterilization, it is important to consider temperatures at all locations at all time during the process, since it will give valuable information on the process requirements.

### 2.3.2  Thermal properties

To satisfy the equation of propagation of heat in solids, several properties must be taken into account. The first and most important property is the thermal conductivity; expressed in W m$^{-1}$°C$^{-1}$ and defined as the ability of a material to conduct heat. Among several experimental methods available to measure thermal

conductivity, the probe method has been used extensively for foodstuffs (Sweat, 1995) due to its simplicity, low quantity of sample required, and precise results.

Another property present in equation 2.5 and important in heat transfer processes is the specific heat; defined as the amount of heat required by a material in order to increase their temperature by one degree per unit of mass (Sweat, 1995; Singh et al., 2009). Specific heat is directly affected by product composition and temperature, but is indirectly affected by mass density (Sweat, 1995). For measuring this property, the Differential Scanning Calorimeter (DSC) is the preferred technique because of its wide range of temperatures to be tested, the large amount of data obtained using just a small amount of sample and the accuracy of the results (Singh et al, 2009).

Density of the product is defined as the mass of a material per unit of volume (Michiadis et al., 2009). Foods are heterogeneous materials and sometimes different components can be present in different phases (solid, liquid or gaseous). The material may present certain porosity that could change the density value. This is why researchers have developed various ways of defining and measuring density. The apparent density includes all the pores or air voids present in the food product (Michiadis et al., 2009). The simplest way of measuring the apparent density of a food material is the buoyant force method that follows the Archimedes principle, in which the sample weight is determined in air and in a reference liquid, the relation between these weights and the reference liquid density calculates the food product apparent density. Density, as well as the other thermal properties, is directly affected by the composition of the food and in turn, the density of fats is directly affected by the fatty acid composition (Nichols, 2010).

Thermal diffusivity, defined by eq. 2.5, is the property relating the thermal conductivity with specific heat and density. Although methods for direct measurement of thermal diffusivity exist, i.e. the transient heating technique; the recommended method due to its simplicity and accuracy, to calculate it is from

independent experimental data of thermal conductivity, specific heat and density (Sweat, 1995).

Data on thermal properties of different products has been published. Poppendiek et al. (1966) reported the thermal conductivity for various muscles and organs of bovine and poultry. Values for the bovine muscle were found to be 0.527 W/m K, for bovine liver 0.488 W/m K, 0.356 W/ m K for chicken skin and a value of 0.230 W/m K for the bovine fat. A strong correlation was found in these products between thermal conductivity and moisture content, where higher water content give higher thermal conductivity. Santana et al. (2013) determined the values of density, thermal conductivity and diffusivity for moist pet food. The product had 55% of moisture, 8.8% of proteins and 19.7% of lipids. The value of thermal conductivity was 0.34 W/m K, density 1082 kg/m$^3$ and a thermal diffusivity of 1.08x10$^{-3}$ m$^2$/s. Hu et al. (2009) measured the apparent specific heat of milk at different fat contents (0.1, 3.5, 15, 25 and 35%). This value was strongly influenced by the fat content and varied considerably with skimmed milk (0.1%) ranging from 3.983 to 4.035 J/ kg K compared with those of higher fat content (35%) ranging from 3.378 to 3.409 J/kg K and thus showing that as the fat content increases, the specific heat decreases.

Density of a food product highly depends in the composition and temperature, but in porous materials, the size of the pores and structure also define this physical property. If all the data is known, precise predictions can be made of the density of solid food materials with predictive models (Michailidis et al., 2009).

### 2.3.3  Predicting temperature during sterilization

Mathematical models have a long standing use in industrial sterilization to predict the temperature of the product, integrating the relationship between physical properties, shape of container, kinetics, heat and mass balances in a mathematical language with the objective to describe and optimize a process. The mathematical modeling of a heat transfer problem during sterilization can be as simple as a

model based on empirical kinetics, or highly complex like fluid dynamics coupled with heat transfer. The first approach to mathematical modeling of processes involving sterilization of cans was presented by Bigelow (1920). In this method, the experimental data was collected and this was used to calculate the coldest point in the processed food; the temperature could be calculated by making the ideal assumptions of constant, uniform temperature and thermal properties of the food. This model was evaluated graphically because of the complexity of the equations involved, and some modifications were made in order to have an analytical solution. One of these was proposed by Ball (1923) and has been widely used in the industrial thermal treatment (Stoforos et al., 1997). In this method, several semi-empirical equations were developed to describe the temperature at the critical cold point of the product in order to calculate the sterilization value ($F_0$). Unlike Bigelow's method, Ball included experimental thermal parameters that were dependent on the food and the type of heat transfer involved in the process (conduction, convection or radiation) that could give a better fit of the model compared to the reality. Furthermore, it was also assumed a linear time-temperature relationship, both in the retort as in the product. This statement can result in over-processing of the product, because the initial heat period (lag time) and the cooling period follow a semi-logarithmic curve (Stoforos et al., 1997).

Another approach is solving the propagation equation of heat which is a partial differential equation with numerical methods. Several authors have used numerical methods to solve this equation and apply them to food materials (Tandon and Bhowmik, 1986; Simpson et al., 1989; Shin and Bhowmik, 1990; Silva et al., 1992; Hendrickx et al. 1993; Simpson et al., 1993; Akterian and Fiikin, 1994; Kim and Teixeira; 1997; Dincer, 1998; Erdogdu et al., 1998) These mathematical models integrate the lethality of the microorganisms (or nutrient retention) during thermal process, with the objective of making better quality foods and also because of the importance of their application to intelligent on-line computer control of retorts and computational aided decision support systems in the food canning industry.

In general, mathematical models involving heat transfer are non-linear, and the solution consists on a set of algebraic, partial and differential equations that can also include integral equations and logic (boundary/transition) conditions. When sterilization is occurring in a cylindrical can (common container for sterilization), Equation 2.5 could be used to represent the transfer of heat inside the product (Shin and Bhowmik, 1990; Banga et al., 1993; Simpson et. al. 1993; Chen et al. 2011). In this equation, the first term $(\frac{\partial^2 T}{\partial r^2})$ refers to the change in temperature through the diameter of the can, the second term $(\frac{1}{r}\frac{\partial T}{\partial r})$ is associated with the change in temperature that takes place in the radius of the can and the final term $(\frac{\partial^2 T}{\partial y^2})$ describes the temperature change in the height of the can. In order to solve this differential equation it is important to know the initial and boundary conditions which are displayed in Equations 2.6-2.10):

Initial conditions (temperatures at $t = 0$):

$$t = 0 \rightarrow \forall r T = T_0 \qquad\qquad eq.\,2.6$$

Boundary conditions for a two-dimensional cylinder ($t > 0$):

$$r = R \;\rightarrow\; -k\frac{\partial T}{\partial r} = h(T_\infty - T) \qquad\qquad eq.\,2.7$$

$$r = 0 \;\rightarrow\; \frac{\partial T}{\partial r} = 0 \qquad\qquad eq.\,2.8$$

$$y = H \;\rightarrow\; -k\frac{\partial T}{\partial y} = h(T_\infty - T) \qquad\qquad eq.\,2.9$$

$$y = 0 \quad \rightarrow \quad \frac{\partial T}{\partial y} = 0 \hspace{3cm} \text{eq. 2.10}$$

Equations 2.7 and 2.9 define the transfer of heat from the heating media (vapor, hot water) of the retort to the can. Equations 2.8 and 2.10 are the temperatures at the center of the can, which is taken as a boundary condition.

When the system of equations is defined (initial, boundary and propagation equations), a discretization is applied to transform the partial differential relations into differential equations; these methods may use finite difference, finite element, finite volume, lines method, among others (Banga et al., 2003). These boundary fitted methods have the advantage to create a well-behaved transformation of the product of interest into a set of grids (figure 2.6) adapted to specified boundary conditions. With the aid of this division, a numerical solution can be obtained for the internal temperature at the coldest point of the food since it takes into account thermal properties of the food and of packaging conditions. For example, the container's shape and the food to be of studied (Tandon and Bhowmik, 1986; Simpson et al., 1989; Kim and Teixeira, 1997), as well as heterogeneous thermos-physical properties of the food, and the coldest point of the food, among others (Califano and Zaritzky, 1993).

Once the conditions are defined and the model built, some experimental data is obtained with the objective of making an actual comparison between the model and the process, and how it is deviated or fitted with reality. Kim and Teixeira (1997) used polycarbonate to simulate a conduction-heated food with and odd shape (oval); the objective of this study was to extrapolate the developed model for cylindrical cans. They concluded that this extrapolation can be used with reasonable success as long as the model is used to predict the temperature at the same internal location that was used to produce the heat penetration factors entered in the model.
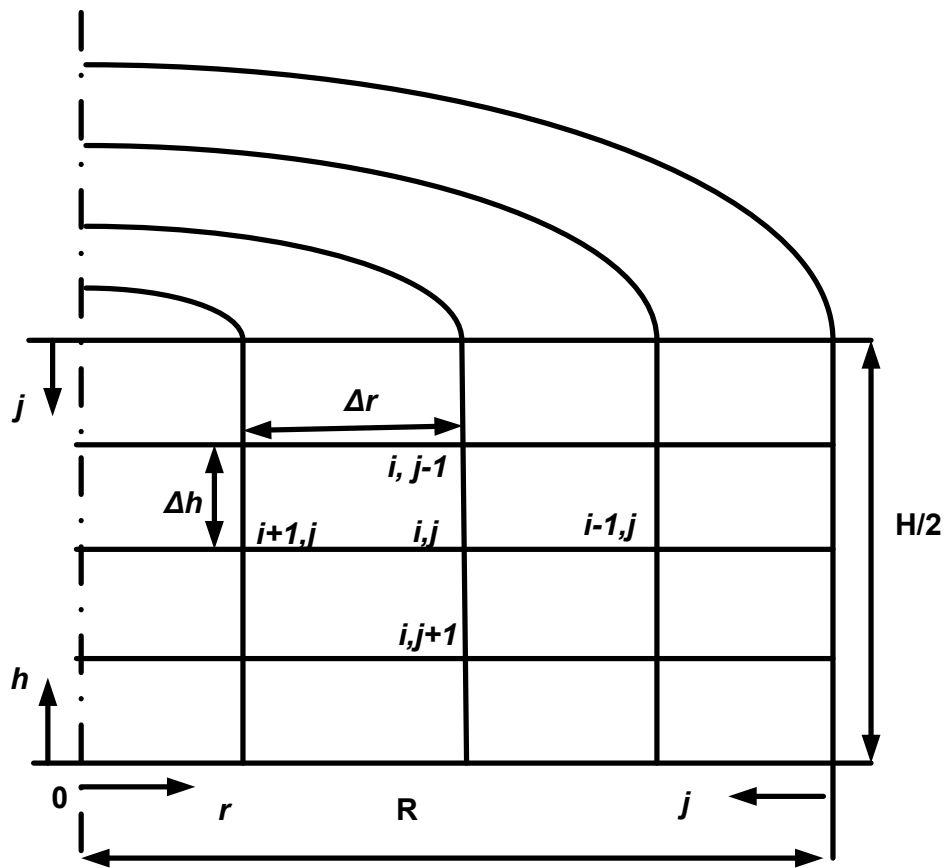
**Figure 2-6.** Grid points of a cylindrical container showing the coordinate system and the arrangement of the sequences for the finite difference model (Adapted from Chen et. al. 2011)

Figure 2.7 shows the comparison between the experimental data and the predicted ones using the mathematical model from results of Kim and Teixeira (1997). Even if the approach seems to be good enough to adjust it to a process, the graph shows a slight difference in the come up time (heating phase) and in the cooling phase. This model, if applied to an in-line process can cause over-heating of the product and a non-adequate cooling.

Cristianini and Rodrigues (2002) compared three different mathematical models to predict temperature profile of conduction-heated food packed in commercial size retort pouches during heat sterilization. They use a finite element in 2 and 3 dimensions and an analytical solution to predict the temperature of the coldest point. In Figure 2.8 the graphical comparison of the three methods and experimental data for the temperature profile in the coldest point can be seen. The authors concluded that a 3-dimensional grid model gives a better fit to the experimental data since it takes into account the actual shape of the retortable pouch and how the heat flows through the food. The temperatures calculated by this model are very similar as those in the experimental data. The disadvantage is, however, the long computation time required by this type of approach.

The discretization method most widely used for canned products is the finite difference method (Shin and Bhowmik, 1990; Banga et. al 1993; Mohammed, 2003; Chen et al., 2011) due to its simplicity and "short" computation times. Also, the boundary conditions have to be taken into account. Boundary conditions can be isotropic or anisotropic. In isotropic processes, the thermal properties of the product will remain constant at every time in every temperature, while in anisotropic processes, boundary conditions change since the heating is different in every direction (Bergman et al., 2011).
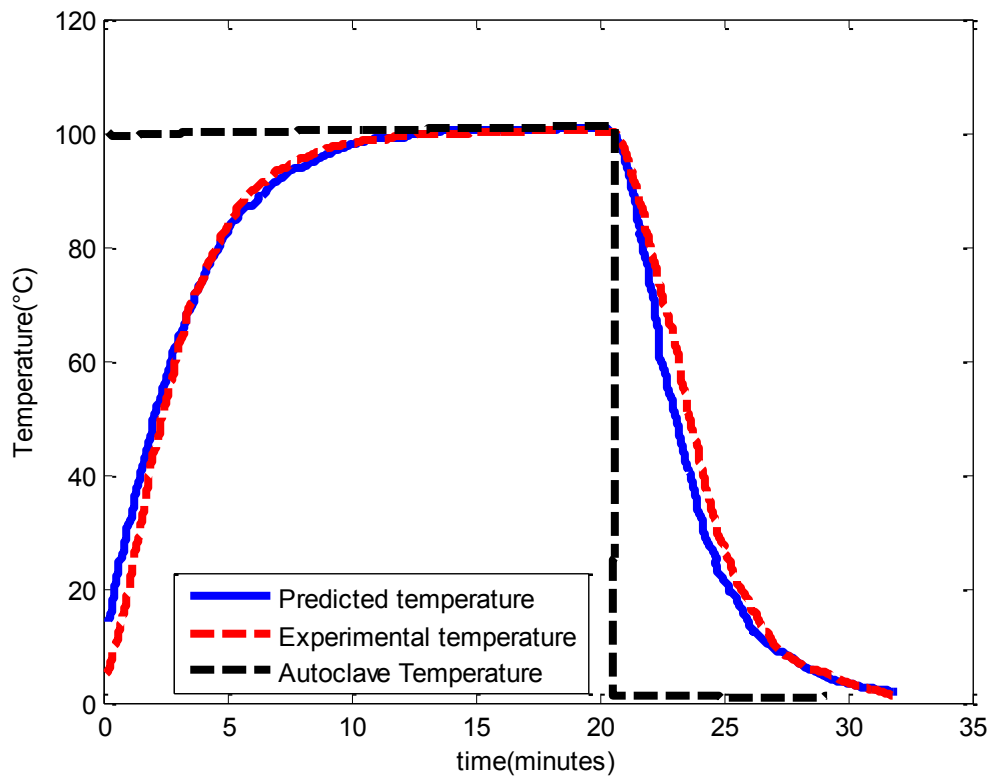
**Figure 2-7.** Experimentally measured and model predicted temperature profiles at the geometric centre of a cylinder shape poly-carbonate block heated under constant boundary temperature (Adapted from Kim and Teixeira, 1997)
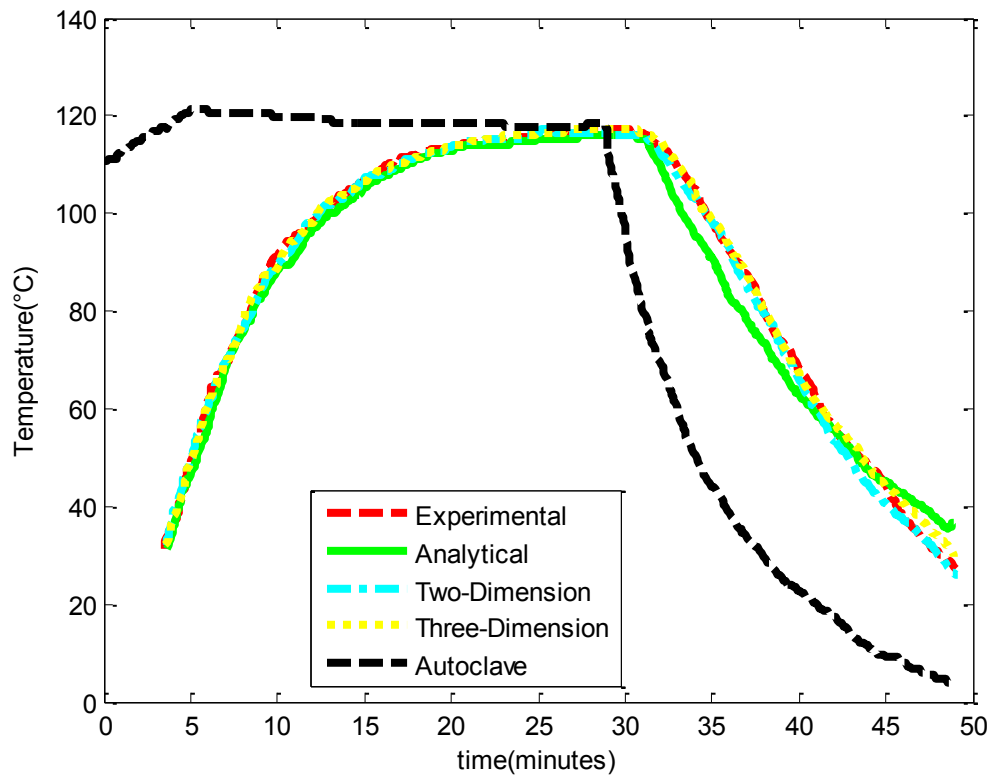
**Figure 2-8.** Retort pouch center temperature profiles using different models
(Adapted from Cristianini and Rodrigues, 2002)

Boundary isotropic conditions are described in equations 2.11 and 2.12 for initial and retort temperature, respectively (Banga et al. 1993):

$$T = T_0 \begin{Bmatrix} t = 0 \\ 0 \le r \le R \\ -L \le z \le +L \end{Bmatrix} \qquad \text{eq. 2.11}$$

$$T = T_{ret}(t) \begin{Bmatrix} 0 < t < X_T \\ r = R \\ z = \pm L \end{Bmatrix} \qquad \text{eq. 2.12}$$

Where $T_0$ is the initial temperature of the canned product, $t$ is the time, $r$ the radial coordinate in cylindrical system, $R$ the total radius of the can, $L$ the half of the height of the can, $T_{ret}$ the retort temperature and $X_t$ the process total time .

Another method to make and effective discretization of a food product is the finite element method, but this method is used more extensively when the container of the foodstuff represents and "odd-shape" and the computations times are larger compared to a finite difference method (Tandon and Bhowmik, 1986; Banga et al., 1993; Simpson et al. 2004; Santana et al., 2011).

In general, when equation 2.5 is submitted to a finite difference distcretization, it is converted in a vector of the difference equations (equation 2.13) (Özisik, 1994; Chen et al. 2011):

$$T_{i,j}^{t+\Delta t} = T_{i,j}^{t} + \frac{\alpha \Delta t}{\Delta r^2}\left[T_{i-1,j} - 2T_{i,j} + T_{i+1,j}\right]^{t} + \frac{\alpha \Delta t}{2r\Delta r}\left[T_{i-1,j} + T_{i+1,j}\right]^{t}$$
$$+ \frac{\alpha \Delta t}{\Delta y^2}\left[T_{i,j-1} - 2T_{i,j} + T_{i,j+1}\right]^{t} \qquad \text{eq. 2.13}$$

where $i$ and $j$ mark the location of the node on the grid shown in figure 2.6.

This equation indicates that the temperature at a given location and after a time interval $\Delta t$ can be calculated from the previous temperature and that of adjacent nodes, the solution to this equation can be calculated with the aid of a software so

that the values obtained can be used to calculate the temperature profiles at any chosen position of the product. Equation 2.13 is a general resolution of the heat transfer equation with the finite differences, but it can differ depending on the boundary conditions and the solution (discretization) method used by the author. Banga et al. (1993) developed finite difference models for predicting temperature in a sterilization process for canned tuna, using different boundary conditions (isotropic or anisotropic, homogeneous food) and compared it to a finite element model. They concluded that whereas the model they developed using finite element is the one that fits more precisely to the experimental data, they recommend using the finite difference with the anisotropic conditions because the computation time is less, and from the practical point of view it gives a good fit and the response time is lower.

The approximations for finite difference models are done from methods such as the forward time central space (FTCS), the alternate direction explicit procedure (ADEP), the alternate direction implicit procedure (ADIP) and also the modified variable grid (MVG; Banga et al., 1993, Özisik, 1994). The latter uses the ADEP method applied to a variable step grid. The nodal coordinates of this grid correspond to the roots of Legendre's polynomials of order equal to the number of nodes. This allows the evaluation of spatial integrals (overall nutrient retention, overall integrated lethality, energy absorbed by the product, etc.) by Gaussian quadrature, which provides a high accuracy and efficiency (Banga et al., 1993).

## 2.4 *Foie gras* sterilization

In the last 20 years, *foie gras* industry in France has evolved due to the research achieved, especially by the Centre technique de la conservation des produits agricoles (CTPCA) whose research lines focus in the improvement of the processing techniques, chemical and microbiological characterisation, organoleptic characteristics and quality control (Aurélie, 2008). Unfortunately, not much information is available in the scientific literature on the processing and quality of

French sterilized *foie gras* products. One of the first and few works that changed the processing conditions of the *foie gras* industry was conducted by Basset et al. (1997) where different heat treatments were established in order to obtain the desired sensory quality of the product. Also, a microbiological validation of the process was done using *Enterococcus feacalis* which unfortunately is not a sporeformer. The conclusion of the research was that *foie gras* can be pasteurised at temperatures from 77 to 83°C, these conditions assure food safety and desired organoleptic characteristics.

A study performed by André et al. (2010) in the same research center with the objective to determine the different factors that can influence the heat treatment, such as concentration of nitrite salts or the initial concentration of spores, comparing this with different sterilization values. The purpose was to propose recommendations for the industry to guarantee the safety and the organoleptic specifications of the product. It was found that for the *foie gras* emulsion ('bloc') and the whole *foie* gras, a sterilization value of 0.5 min and 0.6 min respectively, was sufficient to inactivate two levels of initial concentration ($10^3$ and $10^5$ spores/g) of *C.sporogenes* spores. Industrially, if the good manufacturing practices are followed, the contamination of the product before heat treatment should not be superior to $10^2$ spores/g. They also found that by adding nitrite salts to the *foie gras* emulsion, the sterilization value can be lowered form 0.5 min to 0.3 min.

Mathematical modeling of the heat transfer in *foie gras* and *foie gras* products for optimizing the sterilization process has been studied by Abidi et al. (2011). They developed a model by finite differences with variable retort temperature to process *foie gras* emulsion. The model was developed for predicting temperature of a 200 mL can fill with potato puree, in general, the simulated temperatures showed good agreements with the experimental results. Once the model was developed, the thermal properties were changed for that of the *foie gras* emulsion so the temperatures at the coldest point could be predicted; with the objective to find the exact combination of variable temperatures to assure a sterilization value of

minimum 0.6 min but also having an uniform cooking of the product (color, texture, flavor, melt). With the model and the optimization they could reduce the total sterilization time by 7%, and the "cooking value" by 8% comparing it with the normal processing conditions, this can be reflected in savings in processing times improved sensory characteristics, without compromising the safety of the product.

Other researches revealed that lipid composition of of *foie gras* plays a main role in the shelf life stability. Tremoulet et al. (2002) characterised the lipid content in *foie gras*, finding 5 main free fatty acids (FFA) and studied their inhibition capacity. They found that FFA content of linoleic, palmitoleic and oleic acids is higher than the threshold of inactivation. They conclude that this concentration is sufficient to inhibit the grow of sporulated bacteria, and that it can explain why a less "severe" heat treatment summed with the FFA can produce a shelf stable and safe product.

All this research has led to the conclusion that *foie gras* is a delicate product and because of its high fat content, the inhibitory effects of fatty acids (Tremoulet et al., 2002) and the low level of contamination (André et al., 2010), a thermal process equivalent to heating of 1 min at a reference temperature of 121.1°C should be sufficient to inactivate the microbiological load present in *foie gras.*

However, *foie gras* being a product increasing in popularity and demand in Canada, general guidelines for canned low acid foods ($F_0$ = 3) should be applied until it is demonstrated that a $F_0$ = 1 could lead to safe products.

Despite this, the research of new technologies for *foie gras* processing are in sight; for example the coupling of a microwave pre-treatment with a posterior autoclave process, can give almost the same sensory characteristics as a pasteurised product but with less processing time and prolonged shelf life. The high pressure technique is another option for the decontamination of *foie gras*. Test at high pressure and low temperatures (90°C) have been conducted to produce a whole *foie gras* stable at room temperature, but these technologies are not yet implemented to industrial processes (Aurélie, 2008).

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# 3 Hypothesis and objectives

**Hypothesis:** A mathematical model can accurately describe industrial processes of Quebec's *foie gras* sterilization. The optimization of this model can find the appropriate parameters (time and temperature) to inactivate the current initial microbiological contamination in commercial foie gras. This will also assure the resemblance of the sensory characteristics of Quebec's *foie gras* with that produced in France while maintaining food safety.

**Objectives:** The main objective of the present work is to develop a mathematical model in order to optimize the thermal processing of Québec *foie gras*. The goal is to make a safe product, yet sensory acceptable for the consumers. This is divided in 4 sub-objectives:

- Determine D and z vales for *C. sporogenes* in Quebec's duck *foie gras,* bloc of *foie gras* and fat obtained by melting from *foie gras*

- Study thermal properties (Cp, *k,* α) of Quebec's duck *foie gras,* bloc of *foie gras* and fat obtained by melting from *foie gras*

- Develop mathematical model of heat transfer in canned Quebec's *foie gras* products and compare it to experimental values

- Calculate total sterilization value ($F_0$)

# 4 Heat resistance of *Clostridium sporogenes* PA3679 in *foie gras* products from Québec

## 4.1 Résumé

La résistance thermique de *C. Sporogenes* PA3679 a été déterminée dans le *foie gras* entier, bloc de *foie gras* et le gras fondu du *foie gras*. Les échantillons ont été introduits dans des tubes de destruction thermique (TDT), puis inoculés avec des spores ($10^7$ spores/mL) et soumis à un traitement thermique. Les tubes ont été chauffés à des températures allant de 105 ° C à 120 ° C. Une courbe des survivants a été tracée en fonction du temps de traitement et les valeurs de *D* ont été calculées à partir de ces courbes. Le logarithme des valeurs *D* ont été tracées en fonction des valeurs de température correspondantes et les valeurs *z* ont été calculées à partir de la pente. Les valeurs *D* pour le *foie gras* entier, le bloc de *foie gras* et le gras provenant du *foie gras* allaient de 6,6 à 0,87 min, 12,90 à 0,83 min et 10,57 à 0,45 min, respectivement. Les valeurs *z* pour les produits de *foie gras* (entier, bloc et gras fondu) étaient 13,82 ± 1,4 °C, 13,13 ± 2,8 °C et 11,59 ± 2,3 °C, respectivement. En outre, un test de contrôle a été réalisé avec de l'eau peptonée et la valeur de *z* atteint 9,57 ± 0,55 ° C. Il n'y avait pas de différence significative (P<0.05) entre les valeurs *z* des différents produits évalués. Ces valeurs peuvent être utilisées pour la l'élaboration de traitements thermiques optimisés qui permettront d'améliorer la qualité du produit en réduisant les temps de traitement, sans compromettre l'innocuité des produits.

## 4.2  **Abstract**

Thermal resistance of *Clostridium sporogenes* PA3679 was determined in *foie gras, fat from foie gras* and emulsion. Samples were introduced into thermal death tubes (TDT), then inoculated with the spores ($10^7$ spores/mL) and submitted to a thermal treatment. The tubes were heated to temperatures ranging from 105°C to 120°C. The survivors were plotted against processing time and the *D* values were calculated from these curves. Obtained *D* Values were Log transformed and plotted against corresponding temperature and z values were calculated from the slope. D values for whole foie gras, foie gras emulsion and fat from foie gras ranged from 6.6 to 0.87 min, 12.90 to 0.83 min and 10.57 to 0.45 min, respectively. The z values for foie gras products (whole, emulsion and fat) were 13.82±1.4°C, 13.13±2.8°C and 11.59±2.3°C, respectively. Furthermore, a control test was performed with peptone water and the z value reached 9.57±0.55°C. There was no significant difference (P<0.05) between the *z* values of the different products evaluated. These values can be used to design optimized thermal treatments that will improve quality of the product by reducing processing times, without compromising consumer safety.

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## 4.3  Introduction

*Clostridium botulinum* is a pathogenic microorganism of public health concern in low acid canned foods due to the heat resistance of the spore-form, the anaerobic behavior and the production of the toxin that causes botulism. It has been proved that *C. botulinum* does not produce toxins at a pH lower than 4.5. However in meat products that normally present a pH > 4.5, the spore can develop and produce food borne illness (Ramaswamy and Singh, 1997; Brown et al., 2012). Proper knowledge of the thermal resistance of the spores is needed for the production of safe foods in order to avoid health problems.

*Clostridium sporogenes* PA 3679 is a non-pathogenic, spore-forming, putrefactive anaerobe widely used as surrogate of *C. botulinum* for validating thermal processes, due to its resemblance and slightly higher heat resistance (Mah et al., 2009; Byun et al., 2011; Brown et al., 2012). Although other bacteria are used for heat resistance studies, as some species of *Bacillus* (*stearmophillus, cereus;* Ababouch and Busta, 1987; Tremoulet et al., 2002), experts have chosen to validate thermal treatments using *C. botulinum*, or its surrogate (PA 3679), due to the health importance of this microorganism (Simon et al., 2009; Stumbo, 1979). Processes designed to inactivate PA 3679 with D values of 0.5 to 1.5 minutes at 121°C, will be adequate to eliminate *C. botulinum* (*D* values of 0.10 to 0.20 at 121°C; Stumbo, 1979).

Different studies on thermal resistance of *C. botulinum* and *C. sporogenes* PA 3679 have been performed in low acid meat products subjected to a sterilization process. In a test where a large number of samples were used, Gross, Vinton and Stumbo (1945) proved that thermal inactivation of PA 3679 followed a linear kinetics in meat products, but they also found out that the initial concentration of the spores played an important role in the thermal inactivation. Ababouch and Busta (1987) tested the thermal resistance of PA 3679, *C. botulinum* 62A and *Bacilus cereus* in olive and commercial oils. They found that spores were more resistant in the oils (*z* values of 28°C) compared to those of the spores suspended

in a buffer solution (10-12°C), the conclusion was that, due to the protective mechanisms that lipids exert over the spores as heat conduction is lower when compared to water, the thermo resistance was higher in these products.

*Foie gras* is a meat product having almost 50% of lipids (Rukke et al., 2008; Tremoulet et al., 2002). Little has been published about the resistance of *C. botulinum* or its surrogate in this product. Tremoulet et al. (2002) studied the minimum inhibitory concentration of *foie gras* fatty on the growth of spores from *Bacillus stearmophillus*. André et al. (2010) performed a stability study of *foie gras* and *foie gras* emulsion using different strains of *C. sporogenes.* They did not determine the thermo-resistance values of these strains but they found that a sterilization value of 0.8 min was sufficient to sterilize 100% of the samples that were inoculated with $10^5$ spores/g.

The aim of this study was to determine experimentally the *D* and *z* values for whole *foie gras*, *foie gras* emulsion and fat melted from *foie gras* as well as duck fat to determine if the different matrices affect the thermal resistance of the spores, with the aim of designing proper sterilisation parameters for these Quebec's products.

## 4.4    Materials and methods

### 4.4.1    Product Composition

*Foie gras*, *foie gras* emulsion, duck fat and fat melted from *foie gras* samples were obtained from a local producer and maintained at 4°C until arrival to the laboratory, where they were divided in smaller sample sizes, placed into sterile plastic bags (Whirl-pal, Nasco WI, USA) and stored at -20°C until used in experiments. The samples were thawed in the fridge at 4°C at least 24 hours before analysis; all the samples were analyzed in duplicate.

For water content determination, samples were weighed and transferred to freeze-resistant auto sealable bags, and then subjected to freeze-drying process (VirTis Virtual EL85, SP Scientific, Warminster, PA), where the samples were initially frozen to -40°C. Once frozen, the samples were placed in a chamber under vacuum at a pressure below 50 kPa, during 72 hours. Samples were weighed after the process; the difference in weight before and after freeze-drying divided by the freeze-dried mass was taken as the water content in dry basis.

Water activity was measured with an Aqualab apparatus (Decagon Devices, Pullman, WA). The apparatus was calibrated with deionized water. The sample was transferred to a plastic disk, which was not filled more than the half to avoid false results. Measures were made in duplicate.

Fat content was analyzed with a Soxtec 2050 (Foss Analytical, Denmark) fat extraction system under a chemical hood. Approximately 0.25 g of the freeze-dried sample was weighed into cellulose crucibles; the sample was then transferred to an oven at 100°C for at least two hours to eliminate any residual water that could interfere in the results. Aluminum cups (previously dried) were also weighed; these cups recuperated the fat after the process. The magnetized crucibles were inserted into the support of the Soxtec extractor, 90 mL of ether was poured into the aluminum cup previously dried. Ether was boiled in the apparatus for 30 min and

the sample was rinsed with the evaporated and condensed ether. Ether was then extracted from the sample, which was boiled for other 30 min, at the end all the ether has to be evaporated. The fat content is extracted from the boiling ether. At the end of the process, the fat should be in the aluminum glass, which is dried in an oven and cooled in a desiccator before taking the final weight. The fat content is calculated using equation 4.1:

$$Fat\ content = \frac{W_{G+F} - W_G}{W_S}$$  eq. 4.1

where $W_{G+F}$ is the weight of the glass plus the extracted fat; $W_G$ is the weight of the glass; and $W_s$, the weight of the sample.

The quantity of proteins was determined by the Dumas combustion method as reported in Theron et al. (2014) using a Tru Spec N apparatus (LECO, St. Joseph, MI, USA). For this analysis, a freeze dried, fat-free sample was used. The sample was totally combusted and the total nitrogen was determined, the protein content was then calculated by multiplying the nitrogen content in the sample by 6.25, conversion factor used in official methods (AOAC, 1968).

*Foie gras* and duck fat fatty acids profile was analyzed by a gas chromatography coupled to a flame ionization detector (GC-FID). Before the analysis, the sample was completely melted at 55°C and it was filtered through a no.1 Whatman filter paper to remove other component traces from the fat fraction. The filtered sample was placed in a freezer at -18°C until their preparation in the form of methyl esters of fatty acids. The sample profile was compared to a standard that was composed of a mix of different methylic fatty acids #GLC-607 (Nu-Check Prep., Elysian, MN). The peak areas of methylic fatty acids were corrected to express the contents in fatty acids. The analysis was made in duplicate and the average variation coefficient was 1.2% (±0.02g/100).

### 4.4.2 Preparation of the spores

The original spores were obtained through Cederlane Laboratoires (Ontario, Canada) and a frozen aliquot (100 µL) were spread on Brain Heart Infusion media (BHI, Becton, Dickinson and Company, NJ, USA) enriched with L-cystein (Sigma-Aldrich, MO, USA) and yeast extract (EMD Chemicals, NJ, USA) using a sterile glass rake. The 100 µL were poured on four Petri dishes (20 µL each) and kept for 4 days at 35°C in anaerobic jars, using an anaeroboise generator (AnaroGen anaerobic bags, Oxoid Limited, Hampshire, Enland). After incubation, the spores were recuperated with sterile peptone water (10 mL by each Petri dish inoculated) and a glass rake, scraping the entire surface to recuperate the cells. Spores were stored for 24h at 4°C to liberate the spores from the vegetative cells. Spore suspension was centrifuged at 5000 G for 10 minutes at 4°C and washed three times with 10 mL of sterile water between centrifugation. To avoid spores to form clumps in the solution, the spore suspension was subjectd to a sonication process for 5 minutes; this process was done after each washing. The final spore pellet was centrifugated in a 10 mL of a 50% sucrose solution for 20 minutes at 3200 x g and 4°C. The spores were submitted again to three washes at 5000 x g, 10 minutes and 4°C with 10 mL of sterile water, after the final centrifugation the spores were suspended in 10 mL peptone water (0.1%). The spore suspension sample was then placed in a 90°C water bath for 10 minutes to activate spores and inactivate vegetative cells (Byun et al., 2011). The finished spore suspension was stored at 4°C until further use in experiments (Mah et al., 2008).

### 4.4.3 *D* value measurement

The samples for measuring *D* value in *foie gras* and *foie gras* emulsion were thawed as stated before. The fat from *foie gras* was extracted by heating for 10 minutes the whole *foie gras* in a container placed in a water bath at 80°C, then the separated fat was recuperated in sterile screw-cap tubes (15 mL) and stored at 4°C until used in the experiments.

Thermal death tubes (TDT) were custom made in stainless steel with a length of 71.3 ± 0.14mm, inner diameter of 6.9 ± 0.05mm, and an outer diameter of 9.4 ± 0.04 mm, as shown in Figure 4.1. A threaded cap with an o-ring closed the tube. The emulsion of *foie gras,* duck fat and fat from *foie gras* were warmed in a water bath at 40°C for 5 minutes to obtain a viscous state prior to introducing aliquots (0.5 g) with a pipette into the TDT. Whole *foie gras* was kept cold in order to be able to cut it with the hollow tube of the same diameter as the TDT. The cylinder of *foie gras* was pushed into the TDT tube using a sterile metal rod of 6.7 mm diameter. Samples in the TDT tube were inoculated with 20 µL of the spore suspension (approx. $10^7$ CFU/g) using a Hamilton syringe.

In order to reduce the time to reach the experimental temperature, two oil baths were used. The first bath was set up at a temperature of 130°C and the tube was immersed until it reached the target temperature (105, 110, 113, 115, 117 and 120°C). Once the target temperature was reached, the tube was transferred to a high precision (±0.001°C) circulating programmable oil bath (Cole-Palmer Polystat Heated Circulating Bath, Cole-Palmer Canada Inc., Anjou, QC, Canada) at the experimental temperature for different times to determine the *D* value. The temperature of the different samples was followed using a datalogger equipped with a thin thermocouple (Food tracker Multipaq 21, Datapaq Inc, Wilmington, MA, USA) inserted in the tube through a small hole in the cap and the temperatures were displayed in a computer using Datapaq Insight software (Datapaq Inc).

TDT tubes were removed from the bath at different times during the process in which survivors were enumerated. Once the tube was taken from the oil bath, it was cooled in an ice-water bath for 30 seconds. The content of the tube was drained out into an empty stomacher bag and washed with 4.5 mL sterile peptone water (0.1%) to assure that all the content came out of the tube. The homogenization process took 2 minutes at 230 RPM with a Seward Stomacher 400 Circulator (Seward Company). After appropriate dilutions in peptone water (0.01%), 100 µL were added to 10 mL of BHI media with yeast extract, L-Cysteine

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molten agar, and poured into a Petri dish. After solidification of the agar, 5 mL of the same media were poured on top to favor anaerobic conditions. The agar plates were incubated at 37°C for 2 days in anaerobic jars as described above. After incubation, survivors were counted and the graph of the logarithm of survivors against time was plotted. A linear regression was obtained from the best fitted curve and the $D$ value was calculated from the slope. The process for the emulsion of *foie gras* is similar than for the fat except that the emulsion was warmed up at 25-30°C instead of 40°C. An experiment using the spore suspended in 0.1% sterile peptone water was carried out for control and comparison purposes between the results. This was done using the same method as described above.

$\varnothing_{in}=6.9\pm 0.05$ mm

$L=73.1\pm 0.14$ mm

$\varnothing_{out}=9.4\pm 0.04$ mm

**A)**

**B)**
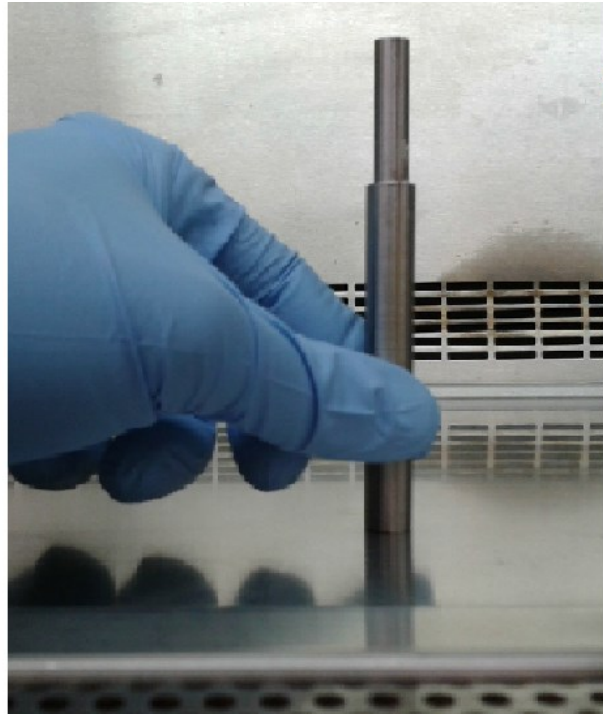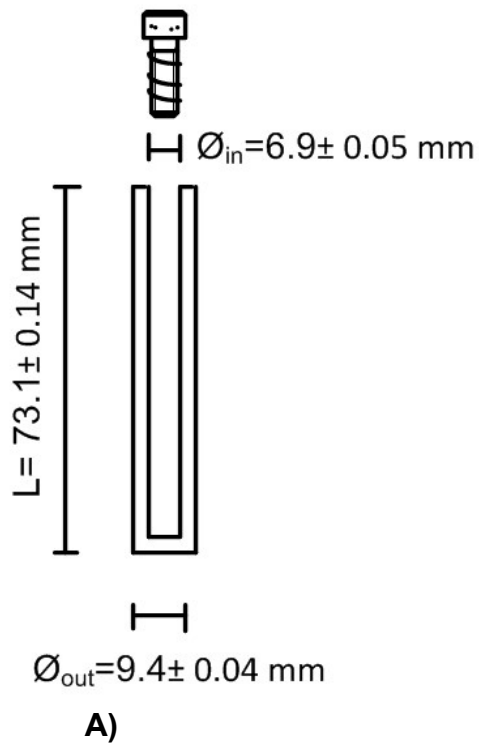
**Figure 4-1.** Thermal Deat Tube used in experimentation. A) Schema, B)Photo of the tube

### 4.4.4 *z* Value

A curve of the logarithm of the D values against temperature was plotted and the z value was calculated from the slope of the best fitted curve (equation I.2). This value was determined for each of the repetitions. A one-way ANOVA (StatGraphics Centurion XVI.I, Statpoint Technologies) was carried out to determine if there existed significant differences between the different matrices, with a confidence value of α=0.05.

## 4.5 Results and Discussion

## 4.6 Product Composition

Table 4.1 shows the composition of *foie gras*, *foie gras* emulsion, duck fat and fat melted from *foie gras*. The difference between the values of *foie gras* and *foie gras* emulsion is due to the formulation of the latter to which water is added. The values obtained for *foie gras* in this study are within the ranges presented in Rukke et al. (2008), which are 41.90-64.80% of lipids, 5.39-15.07% of proteins, and 61.41-74.52% of dry matter. Theron et al. (2014) found for duck *foie gras* a percentage of protein of 7.49±0.75 and values for lipids and water of 56.7±3.7 and 30.1±0.28, respectively, which are very close to the values in Table 4.1. Goullieux (2007) and Tremoulet et al. (2002) also reported similar values for the total lipids in *foie gras*.

**Table 4.1 Composition (w/w) of duck *foie gras* and sub-products**

| Product | Water | | | Lipids | | | Protein | | |
|---|---|---|---|---|---|---|---|---|---|
| *Foie gras* | 30.93 | ± | 1.69 | 57.11 | ± | 5.54 | 7.13 | ± | 0.55 |
| *Foie gras* emulsion | 40.45 | ± | 1.50 | 50.95 | ± | 5.25 | 5.36 | ± | 1.20 |
| Duck fat | 0.80 | ± | 0.34 | 99.27 | ± | 0 | ND | | |
| Fat of *foie gras* | 0.24 | ± | 0 | 99.89 | ± | 0 | ND | | |

The values of water activity measured at 23 to 24.5°C were found to be 0.975 to 0.982 and 0.971 to 0.987 for *foie gras* and *foie gras* emulsion, respectively. It can be noted that water activity of both products is similar. These high values for water activity may be due to the high fat content on the products, which interferes with water bonding; the range presented by the *foie gras* emulsion is higher compared to that of the whole *foie gras* and this may be due to the higher quantity of water present in the emulsion. The values found here are within the range proposed by Alzamora and Chirife (1983) for meat canned products going from 0.970 to 0.984. In their work, values for canned liver paste of different animals ranged from 0.975 to 0.980. Tapia et al. (2007) published approximate $a_w$ values for the *foie gras* emulsion, in a range of 0.95-0.96, which are slightly lower than the values in the present study.

Figure 4.2 shows an example of the fatty acid profiles obtained. A compilation of the fatty acid compounds of *foie gras* and duck fat is presented in Table 4.2. The main fatty acids present in *foie gras* and duck fats are unsaturated. As table 4.2 indecates, **oleic acid** is predominant in both profiles with more than 50% of the total fatty acids, followed by saturated **palmitic acid** at 28.1% for *foie gras* fat and 26.1% for duck fat. One of the biggest differences in these profiles is the percentage of **linoleic acid**, being present only 0.9% in the fat from *foie gras*  while 9%, ten times more, in the duck fat. Rukke et al. (2008) presents a similar profile for the fat from *foie gras* , while Pereira et al. (1976) obtained similar results for the fatty acids in the duck fat compared with the experimental results obtained in this study. Cobos et al. (2000) characterized the fatty acid profile of leg, breast and liver of wild ducks, finding more (45.1% w/w) saturated fatty acids in liver than in the breast (35.1% w/w) and leg (31.1% w/w).  The National Nutrient Database (USDA, 2011) reports for the duck fat a total value of saturated fats of 33.2 g/100g, 49.3 g/100g of monounsaturated fats and 12.9g/100g of polyunsaturated lipids. In the data for the fatty acid profiles of the fat from *foie gras*, a value of 39.6 g/100 g for saturated fats, 59.1 g/100 g of monounsaturated and 0.9 g/100g of polyunsaturated lipids were obtained (Table 4.2), being the value for polyunsaturated lipids the one

that differs the most with respect of that published by the USDA. The values for the saturated and monounsaturated lipids of duck fat are higher compared to those reported by the USDA and this difference may be because of the low content of polyunsaturated lipids. This information is not available for the liver of hand fed duck.

**Table 4.2. Fatty acid profile for fat of f*oie gras* and duck fat**

| Nomenclature | Denomination | Fatty acid content (g/100g fatty acids) | |
| --- | --- | --- | --- |
| | | Fat of *foie gras* | Duck fat |
| C14:0 | Myristic A. | 0.9 | 0.6 |
| C14:1 | Myristoleic A. | 0.1 | 0.1 |
| C16:0 | Palmitic A. | 28.1 | 26.1 |
| C16:1 | Palmitoleic A. | 2.9 | 3.2 |
| C18:0 | Stearic A. | 10.6 | 6.5 |
| C18:1 9t | Elaic A. | 0.2 | 0.2 |
| C18:1 9c | Oleic A. | 54.9 | 53 |
| C18:1 11c | Cis-Vaccenic A. | 1 | 1 |
| C18:2 | Linoleic A. | 0.9 | 9 |
| C18:3 | Linolenic A. | - | 0.3 |
| C20:1 | Gondoic A. | 0.1 | 0.2 |
| Unknown | | 0.5 | 0.4 |
| Total Saturated | | 39.6 | 33.2 |
| Total Monounsaturated | | 59.1 | 57.6 |
| Total Polyunsaturated | | 0.9 | 9.3 |

50
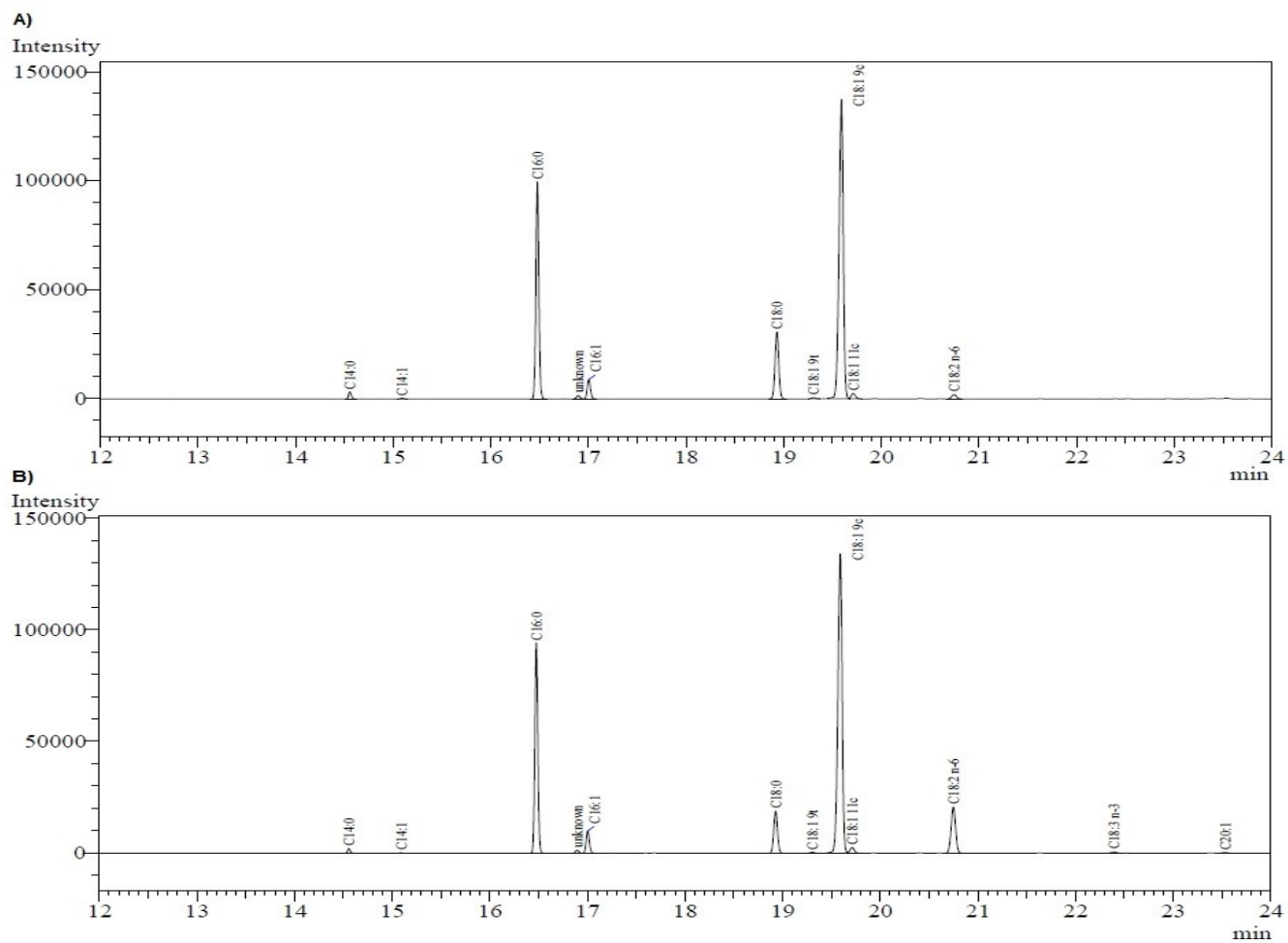
**Figure 4-2.** Fatty Acid profile of lipids. A)Fat obtained from *foie gras*. B) Duck fat

### 4.6.1  Heat resistance of spores

Figure 4.3 shows examples of thermal death curves obtained from plotting the logarithm of the survivors of a thermal process for the different matrix studied (whole *foie gras,* fat and emulsion of *foie gras* and the spores in 0.1% peptone water) at 110°C.

As it can be noted from Figure 4.3, the thermal death curves of *C. sporogenes* in *foie gras* and its derived products follows a log linear tendency, as described in Stumbo (1979) and Byun et al. (2011). *D* values were calculated from the linear regression of the curve. Table 4.3 shows the *D* and *z* values obtained for the four matrices tested. These values for the whole *foie gras*, *foie gras* emulsion and fat melted from *foie gras* ranged from 6.6 to 0.87 min, 12.90 to 0.83 min and 10.57 to 0.45 min, respectively; while the *D* values for the spore ranged from 6.66 to 0.21, temperatures ranged from 105 to 120°C.

Stumbo (1979) reported a range of *D* values for *C. sporogenes* at 121°C from 0.5 to 1.50 min*,* while in the compilation made by Brown et al. (2011), the range reported for the spore in phosphate buffer was from 0.189 to 3.5 min with a mean of 1.51 min. The $D_{121}$ values found for *C. sporogenes* in peptone water made in this study are within the ranges presented in literature; *D* values for the other matrices (whole *foie gras*, *foie gras* fat and emulsion) are also within these ranges, being similar to the published values of heat resistance of the spore in buffer solutions.

Byun et al. (2011) reported a *z* value for *C. sporogenes* of 10.16±0.90°C, and in the compilation of heat resistance of *C. sporogenes* presented in Brown et al. (2011), a range from 9.1 to 14.5°C was shown for buffer solutions. The method used in this study is comparable to those used in studies before, and the values of heat resistance of the strain obtained can be reliable. In literature presented before, *D* values that are different from table 4.3 are reported; however, the *z* value calculated in this study is similar than those published in the literature.
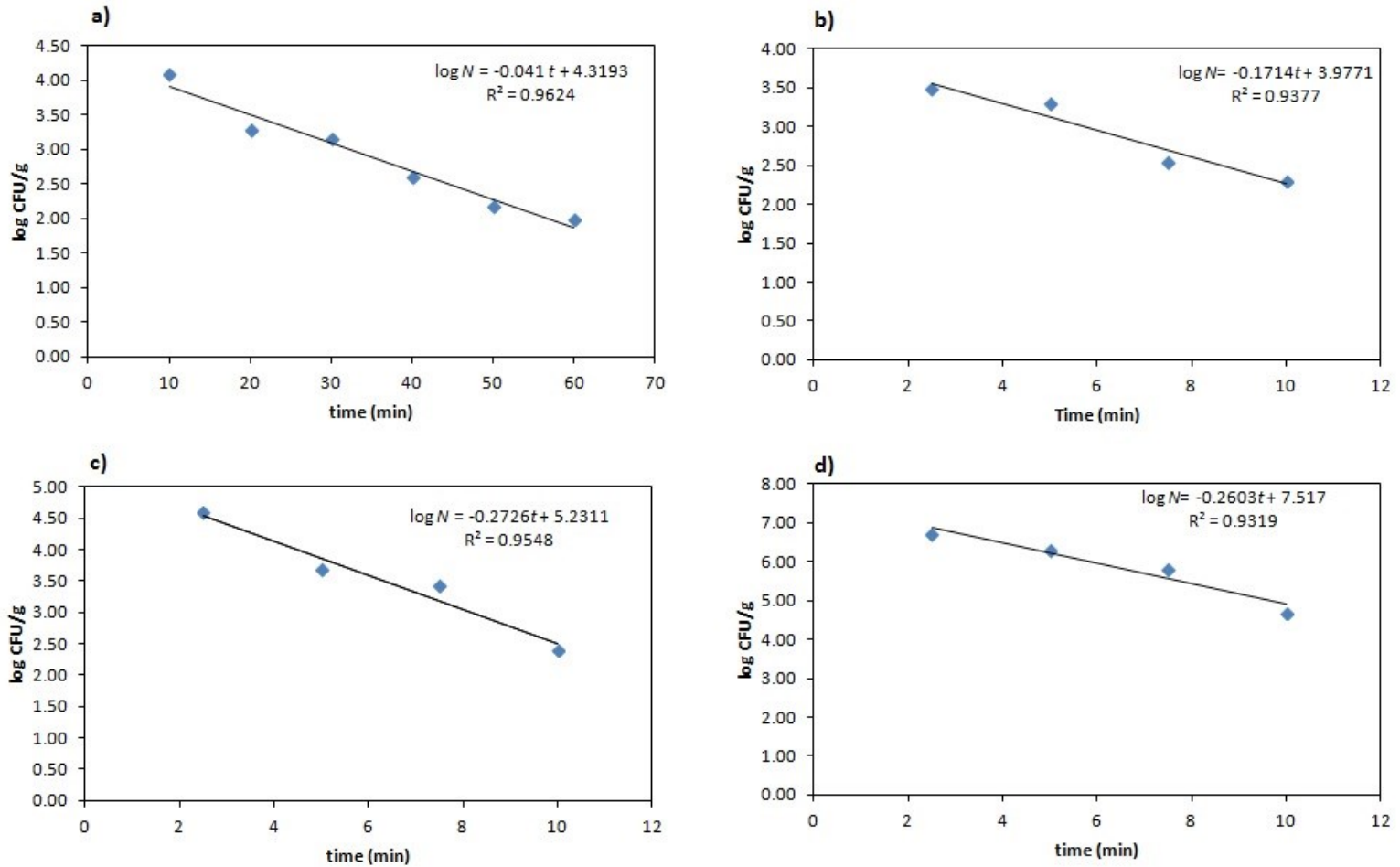
**Figure 4-3.** Thermal survivor curves for the different matrix at 110°C. a) whole *foie gras* b) *Foie gras* emulsion  c) Fat from *foie gras*  d) Spore in 0.1% peptone water

**Table 4.3. *D* and *z* values for *foie gras* and its products**

| *Foie gras* | | *Foie gras* emulsion | | Fat from *foie gras* | | Spore (in 0.1% peptone water) | |
|---|---|---|---|---|---|---|---|
| Temperature (°C) | *D* (min) | Temperature (°C) | *D* (min) | Temperature (°C) | *D* (min) | Temperature (°C) | *D* (min) |
| 105 | 6.61 ± 1.1 | 105 | 12.90 ± 2.7 | 105 | 10.57 ± 4.7 | 105 | 6.66 ± 0.57 |
| 110 | 4.3 ± 3.2 | 110 | 5.03 ± 1.8 | 110 | 4.60 ± 1.1 | 110 | 3.90 ± 1.38 |
| 113 | 1.98 ± 0.7 | 115 | 4.11 ± 2.4 | 115 | 3.78 ± 0.4 | 115 | 2.96 ± 0.55 |
| 117 | 0.87 ± 0.1 | 120 | 0.83 ± 0.3 | 120 | 0.45 ± 0.4 | 120 | 0.12 ± 0.04 |
| *z* (°C) | 13.82 ± 1.4 | *z* (°C) | 13.13 ± 1.8 | *z* (°C) | 11.59 ± 2.3 | *z* (°C) | 9.57 ± 0.55 |

Heat resistance of the spores present higher values in the the whole *foie gras,* the *foie gras* emulsion and fat from *foie gras* than the spores in peptone water for, showing a slight protective effect of the matrices. A one way ANOVA was performed to compare these values and reveal statistical differences. The test showed that there was no statistical difference between the *z* value of the different matrices ($p>0.05$) but, as it can be noted from figure 4.4, the *z* values of spores in whole *foie gras* and *foie gras* emulsion are not different from the *z* value of spores in peptone water. The heat resistance could be affected by the high fat content of the product, exerting a protective effect due to the thermal properties of the lipids from the lipid materials to the spores (Ababouch and Busta, 1987).

Fat from *foie gras* has is slightly lower *z* value than whole *foie gras* and *foie gras* emulsion, but not significantly different. One reason could be that unsaturated fatty acids in higher concentrations could exert an inhibitory action against the spore (Tremoulet, 2002). As shown in table 4.2, unsaturated acids represent the 60% of total fatty acids present in the fat of *foie gras*. The inhibitory effect of the unsaturated fatty acids is due to the unsaturated bonds that exert damage on the membrane of the cell, Gram positive bacteria are more susceptible to this inhibition than gram negative. Yet, this inhibitory effect could be affected by the presence of other components, such as saturated lipids or lipophilic proteins (Tremoulet, 2002).
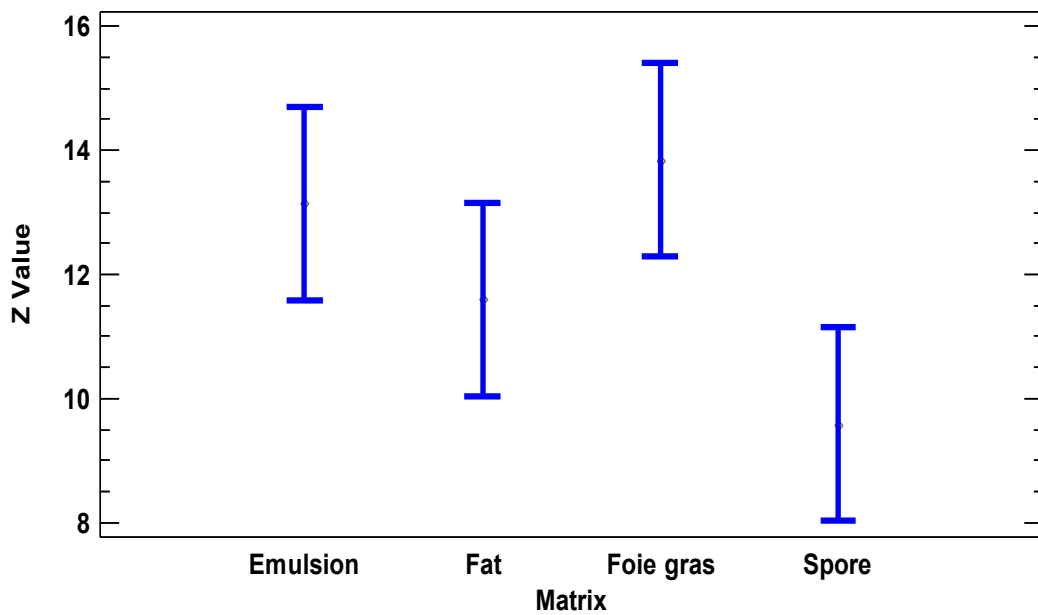
**Figure 4-4.** Means and 95% LSD intervals for the different matrices tested.

## 4.7    Conclusions

*D* and *z* values were evaluated in *foie gras* and products derived from it. The values were higher in the tested matrices (foie gras, foie gras emulsion and fat from foie gras) when compared to values of peptone water, making them more resistant to the heat treatment. These values can be used to design an optimal heat transfer process to ensure food safety while improving the quality of products to meet consumer standards and increase profitability for producers.

## 4.8   References

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# 5  Thermal properties of *foie gras* products

## 5.1  Résumé

Dans ce travail, les propriétés thermiques telles que la chaleur spécifique, le point de fusion, la densité et conductivité thermique ont été déterminées pour le *foie gras* entier, le bloc de *foie gras*, le gras fondu du *foie gras* et le gras de canard, en fonction de la température. La densité a été déterminée en utilisant le principe Archimède. Les mesures ont été effectuées sur une balance Metler Toledo AT couplé avec un kit de densité. Un calorimètre différentiel à balayage DSC Pyris 1 (Perkin Elmer) a été utilisé pour les déterminations de la chaleur spécifique et le point de fusion, dans un intervalle de température de -70 à 150° C et une vitesse de chauffage de 5°C/min. Pour la conductivité thermique, les différents produits de *foie gras* ont été placés dans un cylindre et chauffés à différentes températures allant de 5 à 80°C, puis la conductivité thermique a été déterminée avec un appareil qui chauffe le produit et mesures la température (KD2 Pro, Decagon Devices, Pullman, WA Les valeurs de densité du gras, du bloc et du *foie gras* entier s'élevaient à 836, 928 et 947 kg/m$^3$, respectivement.  DSC pour le gras fondu du *foie gras* conduit à des points de fusion variant de -20 à +40°C. Les valeurs de la chaleur spécifique à 65°C pour le *foie gras* entier, le bloc et le gras du *foie gras* et le gras de canard étaient de 1,79 ± 0,09, 2,38 ± 0,33, 1,71 ± 0,47 et 2,48 ± 0,31 J/g°C, respectivement. La conductivité thermique de *foie gras* entier et du bloc de *foie gras* à 40°C ont été déterminées s'élèvent à 0,33 et 0,43 428 W/m°C, respectivement. Ces valeurs étaient presque le double de celles du gras de canard et du gras fondu du foie gras. Une bonne connaissance des propriétés thermiques des produits de foie gras est importante à la compréhension des propriétés fonctionnelles, texturales et sensorielles de ce produit au cours d'un traitement thermique, et sont essentiels à la conception et à la modélisation mathématique des processus thermiques.

## 5.2  Abstract

In this work, thermal properties such as specific heat, melting points, density and thermal conductivity were determined for whole *foie gras*, *foie gras* emulsion, fat melted from *foie gras* and regular duck fat, as a function of temperature. Density was determined by using the Archimides principle; the measures were made in a Metler Toledo AT balance coupled with a density kit. A differential scanning calorimeter DSC Pyris 1 (Perkin Elmer) was used for specific heat and melting point determinations, at a temperature range from -70 to 150°C and a heating rate of 5°C/min. For thermal conductivity, the different *foie gras* products were placed in a cylinder and heated at different temperatures from 5 to 80°C, then thermal conductivity was determined with a probe that heated the product and measured the temperature increase (KD2 Pro, Decagon Devices, Pullman, WA). Density of fat, emulsion and whole *foie gras* was found to be 836, 928 and 947 kg/m$^3$ respectively. DSC scan for *foie gras* fat resulted in melting points in a range from -20 to +40°C. Values for the specific heat at 65°C for the whole, emulsion, fat of *foie gras* and duck fat were 1.79±0.09, 2.38±0.33, 1.71±0.47 and 2.48±0.31 J/g °C, respectively. Thermal conductivity of whole *foie gras* and the emulsion at 40°C were determined as 0.33 and 0.428 W/m°C, respectively. These values were almost double those of duck and *foie gras* fats. Proper knowledge of thermal properties of *foie gras* products can have a major impact in the understanding of functional, textural and sensorial properties of this product during processing, and are essential in the design and mathematical modelling of heat treatment processes.

## 5.3 Introduction

*Foie gras* is a product made from the fatty liver of ducks and geese that have been hand fed. This product can be consumed as a whole or in an emulsion form referred to as 'bloc' which is made of ground fatty liver, water and spices. One of the main problems of *foie gras* products during sterilization is the high amount of fat lost from the tissue during heating, which should be kept to a minimum to avoid changes in the quality of the product (Theron et al, 2012). Thermal properties of *foie gras* are thus of main importance in order to design a thermal process that keeps the quality of the product (e.g. to avoid overcooking) but at the same time ensures its safety when consumed.

Thermal properties play a major role in food process design, they are an important part in the modeling and evaluation of processes, especially those involving heat transfer such as heating or freezing. If more accurate heat transfer data are available, then more efficient processes can be developed, saving energetic, monetary resources and, at the same time, assuring a better quality and safety of the product (Marcotte et al. 2008; Sweat, 1995). During sterilization, convection heat from the retort penetrates the can and it transfers inside by conduction. The typical equation representing thermal transfer during sterilization is based in Fourier's law of heat conduction and includes three intrinsic properties: density, specific heat and thermal conductivity of the product (Fourier, 1955).

To our knowledge there is no published data on the thermal properties of *foie gras* or their products. However, information about meat properties was found. Sweat (1995) shows the dependence of thermal conductivity of meats with respect of the water content. Water content has a marked impact on thermal conductivity. This is also true for fats and oils whereas if the product is composed by pure lipids, with near zero water content, values reach only 0.2 W/m°C, while when having 90% of water in an emulsion, values can be as high as 0.6 W/m °C, almost 3 times the value or pure lipids. Pham and Willix (1989) studied the thermal conductivity of lamb fat, liver, meat and other organs; being the thermal conductivity of all the

products in the range of 0.390 to 0.497 W/m K for the muscles and a value of 0.219 W/m K for lamb fat. This study also related the thermal conductivity with the water content for the muscles studied, finding that as the water content rises in the muscles, thermal conductivity value also increases. Marcotte et al. (2008) find a correlation for the thermal properties of different processed poultry products with different moisture and fat contents. It was found that in these products the thermal conductivity increases with temperature, and showing a linear behavior above 60°C. For the specific heat, values also increase at higher temperatures; the product with the highest fat content (21.72%) showed fewer changes in the specific heat in comparison with the other products with less lipids.

No density values for duck *foie gras* or its derivative products were found in the literature, but some data is present for similar products. Marcotte et al. (2008) found that, for several cooked poultry emulsions with a fat content of above 20%, density ranged from 967 to 1067 $kg/m^3$. Michailidis et al. (2009) reported a review of several density values from different authors, the density of animal fat presents values of 920-957 $kg/m^3$ while the animal muscle presented a density in the range of 984-1080 $kg/m^3$.

Many mathematical models have been developed to predict the specific heat due to the fact that the prediction can be made based on one major component, water, with high accuracy ranges (Sweat, 1995). For prediction of thermal conductivity, there are some very simple models that just take into account a constant value of thermal conductivity at different water contents; or other much more complex matrices (Choi and Okos, 1986). Several research studies have been done in the area of model development to predict thermal properties of foods but, as these properties change not only with temperature but also with composition, generalizing one model for all food products is a hard task. Nevertheless, Choi and Okos (1986) were able to create models that precisely predict the most important thermal properties of foods involved in processing (Sweat, 1995; Santana et. al. 2011). On the principle that the sum of the thermal properties of individual

compounds present in the food multiplied by its mass fraction, this model can be used to predict the whole system thermal properties. Several models for the different thermal properties of main components in food (water, protein, fat, carbohydrates, and ashes) were developed as a function of temperature.

Several authors studied the mathematical representation of thermal properties of different food materials. For example Poppendiek et al. (1966) developed models for predicting the thermal conductivity of different animal tissues taking into account three major components (water, protein and fat), finding that their model differed ±3% from the experimental data. Miles et al. (1983) made an extended compilation of various models for predicting thermal properties of foods, selecting from those models the ones that better fit the experimental data and developed a computer program to predict the thermal properties of specific foods based in their composition, moisture, density and initial freezing point. They concluded that the program needed models to estimate the amount of bound water (unfreezable) for the property estimation below the freezing point, as well as other relationships like the temperature dependence of density and specific heat. Hu et al. (2009) did an important study in determining the specific heat of milk at temperatures from 1 to 59°C using a DSC, developing complex empirical equations for predicting *Cp* in milk with different fat contents. Santana et al. (2011) determined different thermal properties of pet food, comparing the prediction of different published models to their experimental data. They found that the tested models predicted with great accuracy the thermal properties.

The main objective of this work is to determine the thermal properties for *foie gras* (whole and derived products) such as density, specific heat and thermal conductivity, and to develop simple mathematical relationships to represent them from already published models.

## 5.4 Materials and methods

In this work, specific heat, melting points, density and thermal conductivity were determined for whole *foie gras*, *foie gras* emulsion, fat melted from *foie gras* and regular duck fat, as a function of temperature. Duck *foie gras*, *foie gras* emulsion and regular duck fat were bought from a local Quebec (Canada) producer. Also, fat was separated from whole *foie gras* by heating it in an oven at 80°C during 10 minutes.

### 5.4.1 Density (ρ)

A density determination kit was used with a balance AT 250 (Metler Toledo), this accessory follows the "Archimedes principle" (the value of weight for a body submerged in a liquid equals the weight of the displaced liquid). The sample was covered with a thin wax film to avoid water to go into the sample when the weight was taken in the reference liquid (water). Also, this avoided bubbles of air to get into the sample. The sample was first weighed in "air", and then it was transferred to the density kit that determined the weight in "water". The temperature of the distilled water was also measured. The density was calculated at 20°C with equation 5.1:

$$\rho = \frac{A}{A - B} * \rho_0 \qquad \text{eq. 5.1}$$

where *A* and *B* are the weights of the sample in "air" and "water", respectively, and $\rho_0$, the density of the auxiliary liquid at the measurement temperature.

### 5.4.2 Thermal conductivity (*k*)

Thermal conductivity measurements were performed with a probe KD2 Pro (Decagon Devices, Pullman, WA). The probe contains a heater and a temperature sensor was inserted into the sample. Temperature variation caused by the current

throught the heater was registered over time. Analysis of temperature change *vs* time data was used to determine thermal conductivity. The TR-1 probe (2.4 mm diameter x 100 mm long) was used for this particular measurement. The sample was transferred into a plastic tube (26 mm inner diameter x 115 mm long). Temperature of the sample was controlled by putting the sample in a recirculating bath (Fisher Scientific, Pittsburg, PA) at 5 to 70°C. Samples were left at least 10 minutes to reach equilibrium temperature. The water recirculation was turned off while the measurement was being taken to avoid losing sensibility in the test. Three measurements were done at each temperature. Measurements with 0.01% (or more) of error were discarded.

### 5.4.3 Differential Scanning Calorimetry (DSC)

The DSC was performed with a Pyris 1 calorimeter (Perkin Elmer, Waltham, MA). Calibration was made with indium. Samples (30 to 50 mg) were placed in high pressure stainless steel capsules and were tightly closed to avoid sample leakage during the test. The temperature range of the test was -50°C to 70°C so all the melting peaks of the fats could be determined. Samples were heated at 5°C/ min. An empty capsule was used as reference (air). Thermal curves were analyzed to obtain the *Cp* with equation 5.2:

$$Cp = \frac{H}{m \, * \, hr} \qquad\qquad \text{eq. 5.2}$$

where *H* is the height of the heat flow curve respect to the baseline at a determined (W) temperature, *m* is the mass of the sample(g) and *hr* is the heating rate (5°C/min).

Liquid fat fraction (*LFF*) is the amount of fat that has already melted at a certain temperature and thus, the solid fat fraction (*SLF*) is obtained by subtracting *LFF* to the total percentage of fat in the product. Miller et al. (1969) used the DSC technique to integrate the area under the DSC curves in order to obtain the solid

fat percentage. In the present work, the solid-liquid fat ratio was calculated integrating the melting region of the duck and *foie gras* fats thermograms. The total melting area is defined as the area under the curve of heat flow *vs.* temperature integrated from the starting melting point to the final melting temperature. This area was calculated with the trapezoid rule using MATLab R2012b. The different fractions were calculated as the areas integrated up to different temperatures inside the total melting area. Thus, the fraction at different temperatures was then calculated dividing each area by the total melting area. A third order polynomial was fitted into the graphs to predict *LFF* and *SLF* fractions as a function of temperature.

### 5.4.4 Modeling property

For the estimation of the thermal conductivity for the *foie gras* and *foie gras* emulsion, the model proposed by Choi and Okos (1986) for predicting this thermal property was used (equation 5.3):

$$k = \sum_i k_i X_i^V \qquad\qquad \text{eq. 5.3}$$

where $k_i$ is the specific heat of the component $i$, and $X_i^V$ is the volume fraction of component $i$. The models for **water**, **protein** and **lipids** prediction as a function of temperature were taken from Choi and Okos (1986).

For specific heat, the mathematical models from Choi and Okos (1986) were also applied:

$$C_p = \sum_i C_{pi} X_i^w \qquad\qquad \text{eq. 5.4}$$

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where $C_{pi}$ is the specific heat of the component $i$, and $X_i^w$ is the mass fraction of component $i$. Composition required for Eq. 5.3 and 5.4 was taken from results presented in Chapter 4 (Table 4.1).

In this case, only the models for **water** and **protein** were taken from Choi and Okos (1986); $C_p$ of **fat** was plotted against temperature and two graphs were obtained. One graph was done for solid fat (values before the melting peaks start) and the other, for liquid fat (at temperatures after the last melting peak). Then a second order polynomial regression of second order was applied in order to obtain the constants that satisfy the model:

$$C_{pf} = a_o + a_1 T + a_2 T^2$$  eq. 5.5

where $a_o$, $a_1$ and $a_2$ are the regression constants, and $T$ is the temperature ($^\circ$C).

## 5.5 Results and Discussion

### 5.5.1 Density

Density values for *foie gras*, emulsion of *foie gras* and the fats of duck and *foie gras*, calculated from experimental data by using eq. 5.1, are presented in Table 5.1.

**Table 5.1. Density of foie gras and derived products**

| Product | $\rho$ (kg/m$^3$) @ 20°C |
|---|---|
| *Foie gras* | 947 ± 73 |
| Emulsion of *foie gras* | 928 ± 47 |
| Fat of *foie gras* | 836 ± 37 |
| Duck fat | 843 ± 43 |
| *n=9* | |
| *P<0.05* | |

From Table 5.1 it can be seen that pure fats (duck or *foie gras*) have, as expected, lower density than whole *foie gras* or *foie gras* emulsion. The high content of fat in whole *foie gras* and *foie gras* emulsion makes their density lower than for other poultry products such as cooked poultry emulsions (density ranged from 967 to 1067 kg/m$^3$ and the animal muscle 984-1080 kg/m$^3$ (Michailidis et al., 2009). Duck fat density presents a slightly higher value than *foie gras* fat; this can be due to the fact that density is higher if the lipid is composed of unsaturated fatty acids (see Table 4.2). The complexity of the fatty acids (i.e. chain size of fatty acid) also plays a role in the density of the lipid (Nichols et al., 2010).

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### 5.5.2 Thermal conductivity

Thermal conductivity values from 5 to 70°C for *foie gras* and their products are presented in Figure 5.1. From this Figure, it can be concluded that thermal conductivity for the *foie gras* **emulsion** is slightly higher compared to that of the **whole** *foie gras*, this is because food's thermal conductivity increases proportionally as water content increases (Sweat, 1995). Poppendiek et al. (1966) reported values of thermal conductivity for different animal tissues, they found values of bovine and rabbit liver of 0.4879 $Wm^{-1}°C^{-1}$ and 0.3772 $Wm^{-1}°C^{-1}$, respectively, at 23°C. Bovine liver has a greater thermal conductivity compared to *foie gras* but for rabbit liver, $k$ is closer to the values presented in this study (0.287 to 0.323 $Wm^{-1}°C^{-1}$ at 18-20°C). Difference in values can be related to higher amount of fat in *foie gras* than in other types of liver products (Poppendiek et al. 1966).

Pham and Willix (1989) reported that thermal conductivity of lamb fat decreases at temperatures higher than ice melting point (0-40°C). The same tendency was observed in the *foie gras* and duck fats. Poppendiek et al. (1966) presented values for bovine fat and other fat (source not specified) and obtained 0.2301 and 0.1903 $Wm^{-1}°C^{-1}$ at 23°C, respectively. Measurements are comparable to those presented for the *foie gras* fat (0.172-0.195 $Wm^{-1}°C^{-1}$ for 19.5-20.7°C) and duck fat (0.162-0.185 $Wm^{-1}°C^{-1}$ at 20.5°C 21.8°C). Sweat (1995) proposed constant values for thermal conductivity for meats and fats, as 0.46 $Wm^{-1}°C^{-1}$ and 0.18 $Wm^{-1}°C^{-1,}$ respectively, which are close to the values obtained in this study.

For temperatures lower than 15°C (when almost 50% of the fat has not yet melted), a higher value of thermal conductivity is noted. This could be explained by the higher thermal conductivity of solids compared to liquids. It can also be noted that at temperatures of 50°C or higher, there is a linear tendency for this thermal property.
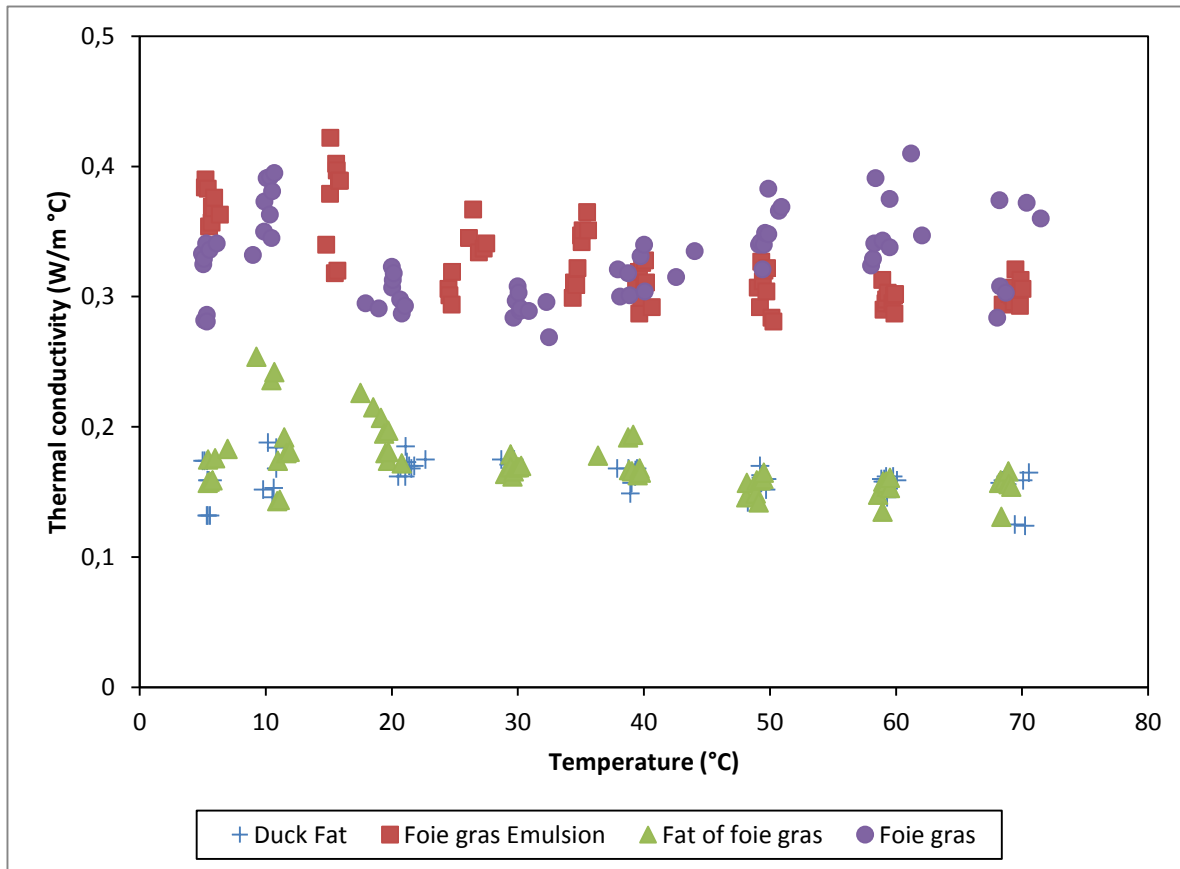
**Figure 5-1.** Thermal conductivity of foie gras and sub-products

As a first attempt to model thermal conductivity data, both quadratic and linear regression relationships were obtained as a function of temperature from the experimental data shown in Figure 5.1, which are presented in Table 5.2. The quadratic function for pure compounds (*foie gras* or duck fats) has been proposed to predict individual compound properties in the model given by Choi and Okos (1986).

**Table 5.2. Models adjusted for predicting thermal conductivity (W/ m °C) of foie gras and derived products**

| Product | Quadratic | Linear |
|---|---|---|
| *Foie gras* | $k_{fg} = 3E\text{-}05\ T^2 - 0.0017\ T + 0.3428$ | $k_{fg} = 0.0003\ T + 0.3197$ |
| *Foie gras* emulsion | $k_{fge} = 9E\text{-}06\ T^2 - 0.002\ T + 0.3866$ | $k_{fge} = -0.0013\ T + 0.3761$ |
| *Foie gras* fat | $k_{fgf} = -1E\text{-}06\ T^2 - 0.0005\ T + 0.1915$ | $k_{fgf} = -0.0006\ T + 0.1928$ |
| Duck fat | $k_{df} = -1E\text{-}05\ T^2 + 0.0007\ T + 0.156$ | $k_{df} = -0.0002\ T + 0.1667$ |

The complete model proposed by Choi and Okos (1986), equation 5.3, was then used to predict the values of thermal conductivity from individual compounds at different temperatures for whole *foie gras* and *foie gras* emulsion. For the individual fat from *foie gras* equation, the quadratic relationship developed in this work (shown in Table 5.2) was used. Results of this model are presented in Table 5.3 and 5.4 for whole *foie gras* and *foie gras* emulsion, respectively. A comparison between Choi and Okos (1986) model and the quadratic and linear models proposed in Table 5.2 is also presented in these Tables.

**Table 5.3. Experimental and predicted values of thermal conductivity for whole foie gras (W/ m °C)**

| Temperature (°C) | $k_{exp}$[1] | $k_{model1}$[2] | % Error[3] | $k_{model2}$[4] | % Error[3] | $k_{model3}$[5] | % Error[3] |
|---|---|---|---|---|---|---|---|
| 10 | 0.373 | 0.323 | 13.49 | 0.329 | 11.85 | 0.313 | 16.01 |
| 20 | 0.323 | 0.326 | -0.84 | 0.321 | 0.68 | 0.315 | 2.42 |
| 30 | 0.308 | 0.329 | -6.72 | 0.319 | -3.51 | 0.317 | -2.77 |
| 40 | 0.34 | 0.332 | 2.44 | 0.323 | 5.06 | 0.317 | 6.66 |
| 50 | 0.366 | 0.335 | 8.55 | 0.333 | 9.07 | 0.318 | 13.21 |
| 60 | 0.347 | 0.338 | 2.68 | 0.349 | -0.52 | 0.318 | 8.51 |

(1)   Experimental values

(2)   Linear regression from Table 4.2

(3)   %Error = (($k$exp-$k$model)/$k$exp)*100

(4)   Quadratic regression from Table 4.2

(5)    Model taken from Choi and Okos (1986)

**Table 5.4 Experimental and predicted values of thermal conductivity for *foie gras* emulsion (W/ m °C)**

| Temperature (°C) | $k_{exp}$[1] | $k_{model1}$[2] | % Error[3] | $k_{model2}$[4] | % Error[3] | $k_{model3}$[5] | % Error[3] |
|---|---|---|---|---|---|---|---|
| 5 | 0.384 | 0.37 | 3.75 | 0.377 | 1.87 | 0.348 | 9.47 |
| 15 | 0.379 | 0.357 | 5.91 | 0.359 | 5.38 | 0.351 | 7.28 |
| 25 | 0.319 | 0.344 | -7.71 | 0.342 | -7.28 | 0.355 | -11.15 |
| 35 | 0.347 | 0.331 | 4.73 | 0.328 | 5.58 | 0.357 | -2.9 |
| 40 | 0.31 | 0.324 | -4.55 | 0.321 | -3.55 | 0.358 | -15.43 |
| 50 | 0.284 | 0.311 | -9.54 | 0.309 | -8.84 | 0.36 | -26.55 |
| 60 | 0.302 | 0.298 | 1.29 | 0.299 | 0.99 | 0.363 | -20.22 |

(1)  Experimental values

(2)  Linear regression from Table 4.2

(3)  %Error = (($k$exp-$k$modeli)/$k$exp)*100

(4)  Quadratic regression from Table 4.2

(5)  Model taken from Choi and Okos (1986)

From Tables 5.3 and 5.4, it is shown that the model developed by Choi and Okos (1986) based on composition of individual compounds, does not predict thermal conductivity with great accuracy in *foie gras* and the emulsion type, probably since product structure has a marked impact on heat transfer by conduction, which is not taken into account in this model (Sweat, 1994). From Tables 5.3 and 5.4 it can also be seen that quadratic regression predicts better thermal conductivity of *foie gras* products than linear regression. Thus, it can be concluded that for both, whole *foie gras* and *foie gras* emulsion, the quadratic proposed model can be used to well predict the thermal conductivity of the product, having the lower error percentage when compared to experimental data.

### 5.5.3  Differential Scanning Calorimetry (DSC)

The results of the DSC for *foie gras* and their derivative products are shown in Figure 5.2. The temperature range of the study was from -50 to 70°C, this range was chosen so that changes like fat melting could be easily distinguished from the thermograms. It can be noted that thermograms from *foie gras* and *foie gras* emulsion present a similar thermal behavior. At 0°C, a big peak that is probably the melting point of ice can be observed. As can be seen, between the range of 10 to 20°C, the curves for whole *foie gras, foie gras emulsion* and fat from foie grasexibit a similar drop similar in the thermogram.

When comparing the thermal histories of both types of fat, it can be concluded that duck fat has a bigger melting range (the temperature when the fat starts melting until the temperature when heat flow stabilizes) than the *foie gras* fat. Melting starts at -30°C for both fats, while it finishes at 55°C and 45°C, for duck and fat from *foie gras*, respectively. To verify this, the liquid fat fraction was determined as a function of temperature for both products (Figure 4.2). Figure 4.3shows that melting of duck fat occurs in a larger spectrum of temperatures than the *foie gras* fat. A model of third order was fitted into the graphs to predict these fractions at

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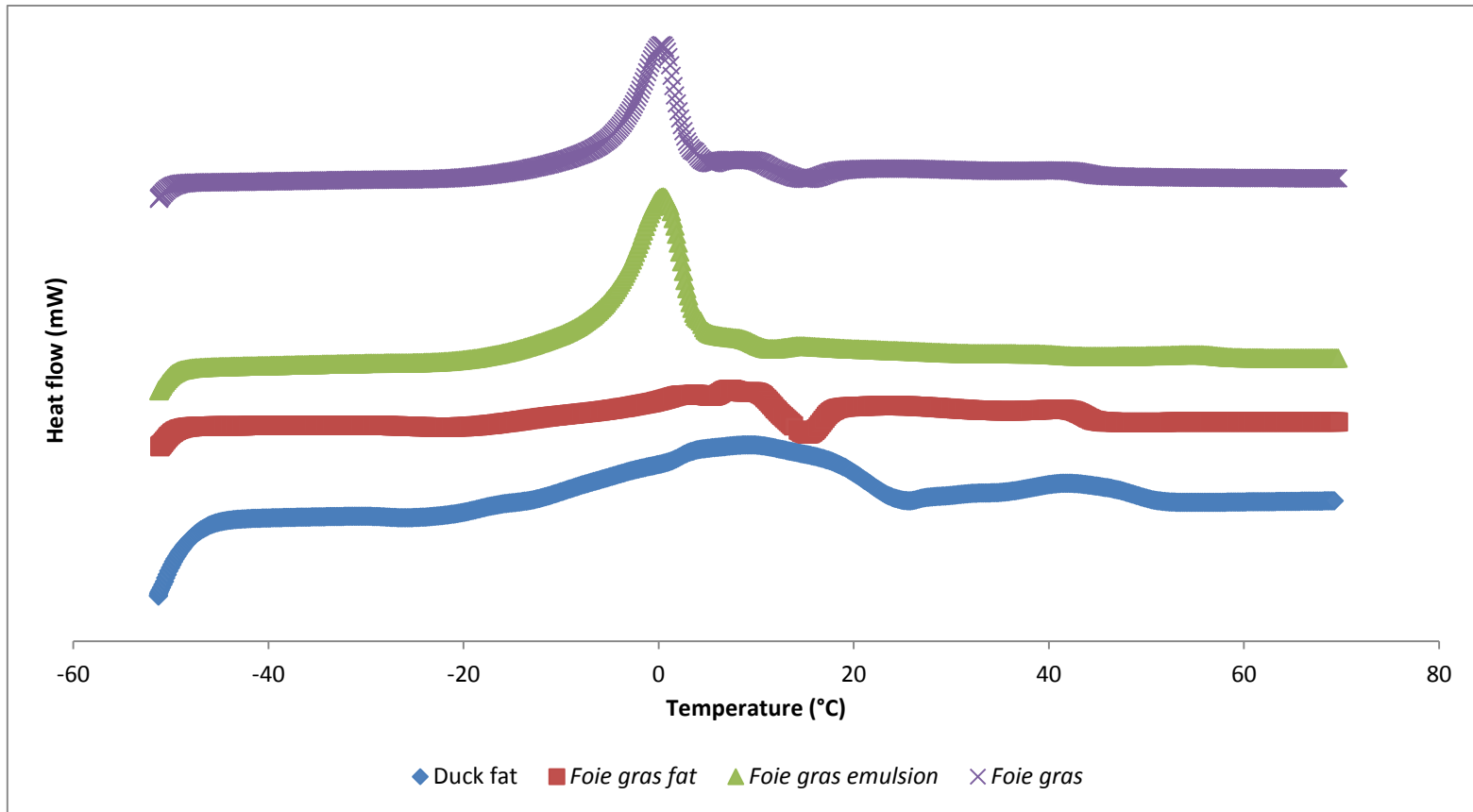
**Figure 5-2.** DSC for *foie gras* and sub-products in a range of -50 to 70°C
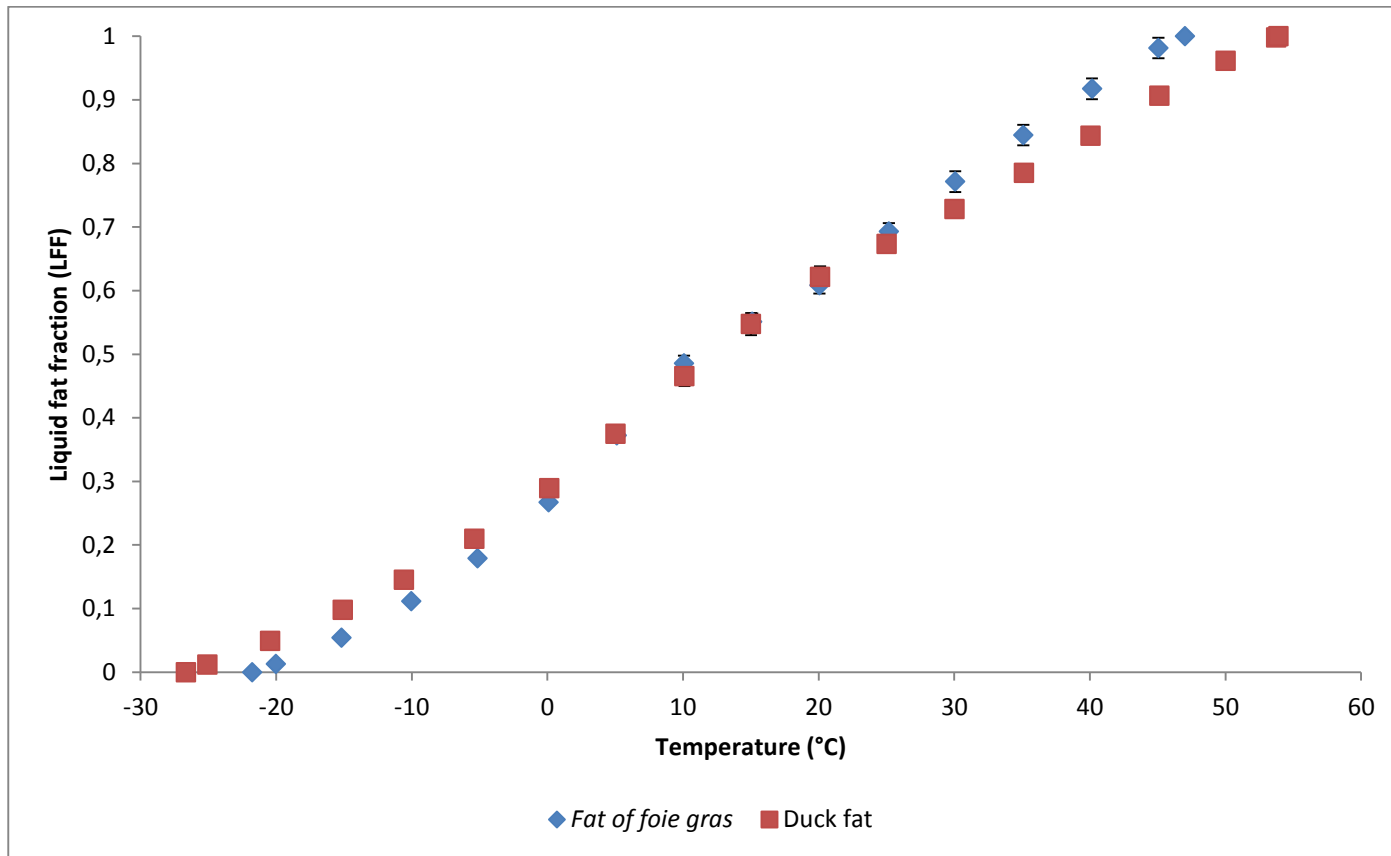
**Figure 5-3.** Liquid Fat Fraction at different temperatures for foie gras fat and duck fat

different temperatures; equations 5.6 and 5.7 represent these relationships with a linear regression (r²) of 0.9983 for the fat from *foie gras* and 0.9985 for the duck fat.

$$LFF_{fgf} = (-2.293 * 10^{-6})T^3 + (8.79 * 10^{-5})T^2 + 0.01618 * T + 0.2774 \quad \text{eq. 5.6}$$

$$LFF_{df} = (-1.585 * 10^{-6})T^3 + (5.87 * 10^{-5})T^2 + 0.01423 * T + 0.3007 \quad \text{eq. 5.7}$$

where $LFF_{fgf}$ the liquid fat fraction of fat from *foie gras*, $LFF_{df}$ the liquid fat fraction of duck fat and *T* is the temperature (°C).

From the thermograms shown in Figure 5.2, the specific heat of *foie gras* and derived products can be obtained by using eq.5.2. The $C_p$ was calculated before any sign of lipid melting appeared in the thermogram and when the heat flow was again constant, this happens after melting peaks disappeared from the graph. Figure 5.4 shows the $C_p$ values of *foie gras* and derived products at different temperatures.

As can be seen from Figure 5.4, $C_p$ values of *foie gras* emulsion (bloc) are higher than those for whole *foie gras*. For instance, at temperatures higher than the melting values, $C_p$ of whole *foie gras* was in the range of 1.9 – 2.0 J/gC, while for the emulsion, between 2 and 2.25 J/gC. This difference is likely due to the higher water content in the emulsion (Table 4.1). Hu et al. (2009) found that as the fat content in milk increased (i.e. water content decreased), the specific heat decreased, being the fat content related to this phenomena since lipids are known for its inability to conduct heat.
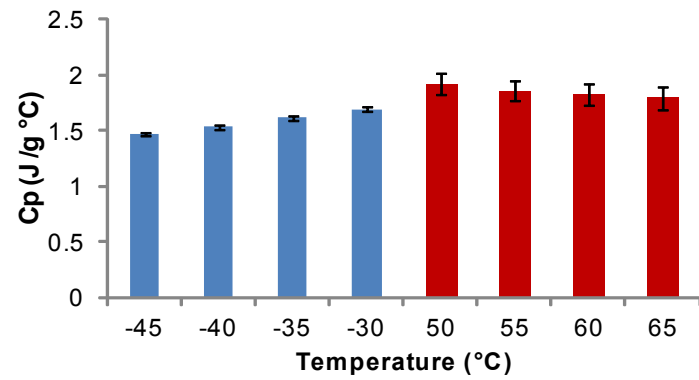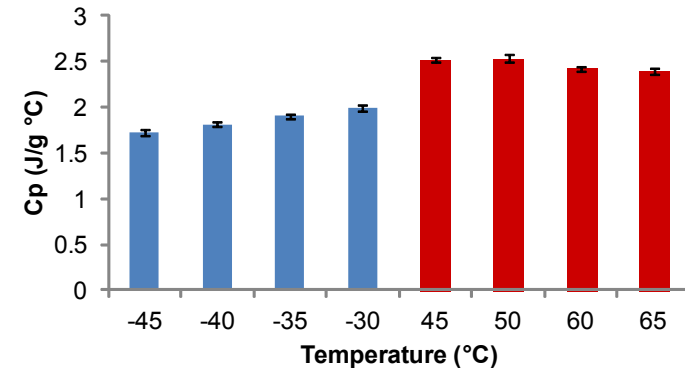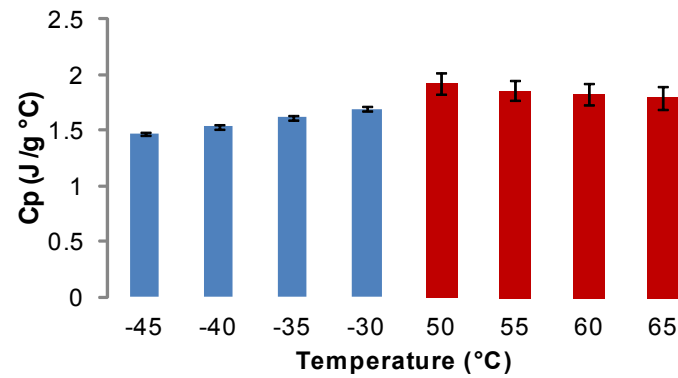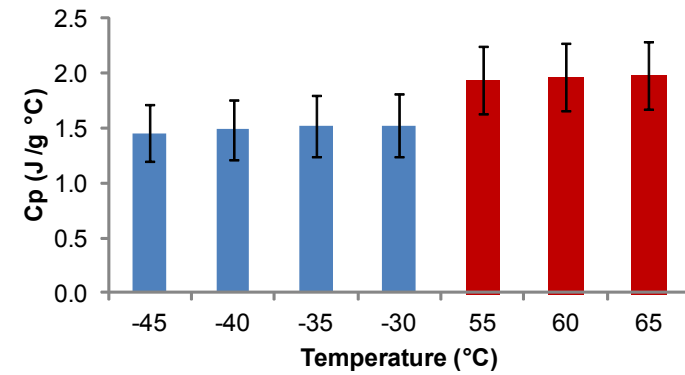
**Figure 5-4.** Specific heat (*Cp*) at different temperatures for *foie gras* and derived products. A) whole *foie gras*  B) *foie gras* emulsion C) fat from *foie gras* D) duck fat

$C_p$ for fat from *foie gras* ranged from 1.57 ± 0.02 to 1.71 ± 0.30 J/ g °C, while the values for duck fat covered a wider range going from 1.44 ± 0.26 to 1.98 ± 0.31 J/g °C. Kasprzycka-Guttman and Odzeniak (1991) reported values for several oils and fats. They found that the specific heat of olive oil (whose main constituent is oleic acid, the same as *foie gras* and duck fats) had a value of 2.08 J /g°C at 70°C, which is in agreement to values found in this work.

Specific heat for *foie gras* and *foie gras* emulsion was predicted at different temperatures (before and after melting of lipids), from the Choi and Okos (1986) model (equation 5.4), using regression constants for individual compounds or obtained in this work (compiled in Table 5.5) and the composition values presented in Chapter 4 (Table 4.2). The prediction values are presented in Tables 5.6 and 5.7.

**Table 5.5. Regression terms for the heat capacity of individual components, eqn. 5.5**

| Component | $a_2$ | $a_1$ | $a_o$ |
|---|---|---|---|
| Water* | 5.46E-06 | -9.09E-05 | 4.1762 |
| Protein* | -1.31E-06 | 1.21E-03 | 2.0082 |
| Liquid fat** | -0.00004 | 0.0032 | 1.6629 |
| Solid fat** | -0.0003 | -0.0201 | 1.2700 |

*Taken form Choi and Okos (1986)

**Obtained in this work by polynomial regression of eqn. 5.5 for fat from *foie gras*

As indicated in Table 5.6, values for $C_p$ of whole *foie gras* calculated from the model are higher than those obtained from experiments. When comparing both the predicted and experimental values, it can be seen that the predicted values show an estimated error higher than 20% when compared to experimental data. The

differences found between predicted and experimental values may be that whole *foie gras* is not a homogeneous product, and since a small sample size was used for the experimental determination, it may not be representative of the whole product.

For the *foie gras* emulsion, predicted and experimental values shown in Table 5.7 are in good agreement, with an experimental error less than 7%. It can be concluded that the model proposed by Choi and Okos (1986) can predict properly the values of specific heat for the *foie gras* emulsion. Unlike whole *foie gras*, *foie gras* emulsion is a more homogeneous product, for which a small sample is likely to be representative of the entire product.

### 5.5.4 Thermal diffusivity (α)

Thermal diffusivity was calculated with the following relation (equation 5.8) (Miles et. al., 1983; Sweat, 1995; Santana et. al., 2011):

$$\alpha = \frac{k}{\rho \, C_p} \qquad \text{eq. 5.8}$$

Results of these calculations at different temperatures and for the different *foie gras* products are shown in Table 5.8.

As shown with thermal conductivity results, thermal diffusivity of high fat foods is lower compared to the reference (water) having a value of $1.57*10^{-7}$ m$^2$/s at 54.4°C (Miles et al., 1983). The values of duck fat are the lowest presented, it be due to the composition of fatty acid presented in Table 4.2, which differs in the unsaturated acid content of fat from *foie gras*, having a higher thermal diffusivity value (Pereira et al. 1976; Rukke et al. 2008)

**Table 5.6. Predicted and experimental values of specific heat (*Cp*) for whole *foie gras* (J/g °C)**

| Temperature (°C) | Liquid Fat Fraction (LFF)[1] | $Cp_{LF}$[2] | $Cp_{SF}$[3] | $Cp_{exp}$[4] | $Cp_{pred}$[5] | % Error[6] |
|---|---|---|---|---|---|---|
| -45 | 0 | | 1.555 | 1.476 | 1.826 | 23.73 |
| -40 | 0 | | 1.585 | 1.535 | 1.844 | 20.08 |
| -35 | 0 | | 1.599 | 1.616 | 1.854 | 14.72 |
| -30 | 0 | | 1.599 | 1.696 | 1.855 | 9.36 |
| 50 | 1 | 1.525 | | 1.918 | 2.316 | 20.78 |
| 55 | 1 | 1.506 | | 1.857 | 2.307 | 24.24 |
| 60 | 1 | 1.484 | | 1.826 | 2.296 | 25.75 |
| 65 | 1 | 1.458 | | 1.793 | 2.283 | 27.31 |

(1)   Specific heat of liquid fat from equation 5.5

(2)   Specific heat of solid fat from equation 5.5

(3)   Experimental specific heat

(4)   Predicted specific heat from equation 5.2 (Choi and Okos, 1986)

(5)   %Error = ((*Cp*exp-*Cp*model)/*Cp*exp)*100

**Table 5.7. Predicted and experimental values of specific heat ($Cp$) for the *foie gras* emulsion (J/ g °C)**

| Temperature (°C) | Liquid Fat Fraction (LFF)[1] | $Cp_{LF}$[2] | $Cp_{SF}$[3] | $Cp_{exp}$[4] | $Cp_{pred}$[5] | % Error[6] |
|---|---|---|---|---|---|---|
| -45 | 0 | | 1.555 | 1.719 | 1.835 | 6.76 |
| -40 | 0 | | 1.585 | 1.816 | 1.855 | 2.19 |
| -35 | 0 | | 1.599 | 1.905 | 1.868 | 1.95 |
| -30 | 0 | | 1.599 | 1.991 | 1.873 | 5.91 |
| 45 | 0.97 | 1.542 | 0.209 | 2.519 | 2.575 | 2.19 |
| 50 | 1 | 1.526 | | 2.535 | 2.585 | 1.97 |
| 60 | 1 | 1.484 | | 2.423 | 2.567 | 5.95 |
| 65 | 1 | 1.458 | | 2.387 | 2.556 | 7.08 |

(1)  Specific heat of liquid fat from equation 5.5

(2)  Specific heat of solid fat from equation 5.5

(3)  Experimental specific heat

(4)  Predicted specific heat from equation 5.2 (Choi and Okos, 1986)

(5)  %Error = (($Cp$exp-$Cp$model)/$Cp$exp)*100

**Table 5.8. Thermal diffusivity at different temperatures for different products of _foie gras_**

| Temperature (°C) | Thermal diffusivity $\alpha$ (m$^2$/s$^2$) | | | |
|---|---|---|---|---|
| | _Foie gras_ | _Foie gras_ emulsion | Fat from _Foie gras_ | Duck fat |
| 50 | 1.48E-07 | 1.31E-07 | 1.13E-07 | - |
| 55 | 1.49E-07 | 1.29E-07 | 1.11E-07 | 9.57E-08 |
| 60 | 1.50E-07 | 1.27E-07 | 1.09E-07 | 9.40E-08 |
| 65 | 1.52E-07 | 1.25E-07 | 1.08E-07 | 9.26E-08 |
| 70 | 1.53E-07 | 1.23E-07 | - | 9.10E-08 |

## 5.6 Conclusions

Thermal properties for *foie gras* and its derived products were determined. Values for the specific heat at 65°C for the whole, emulsion, fat from *foie gras* and duck fat were 1.79±0.09, 2.38±0.33, 1.71±0.47 and 2.48±0.31 J/g °C, respectively. Thermal conductivity of whole *foie gras* and the emulsion at 40°C were determined as 0.33 and 0.428 W/m°C, respectively. These values were almost two times those of duck fat and fat from *foie gras*. The results generally show good agreement with published data for similar models or food. The knowledge of thermal properties of *foie gras* products will allow a more precise mathematical prediction of sterilisation times.The models developed in this study could be used to estimate the thermal properties of *foie gras* at different temperatures, and can therefore be used to design better thermal processes.

## 5.7 References

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# 6 Mathematical modeling of the heat transfer in canned *foie gras* products

## 6.1 Résumé

L'objectif de cette recherche était d'optimiser le processus de stérilisation de produits de *foie gras* en conserve par l'utilisation d'un modèle mathématique, afin de développer un outil pour améliorer les caractéristiques sensorielles finales sans compromettre l'innocuité du produit. Dans cette étude, un modèle numérique à deux dimensions a été développé pour étudier le transfert de chaleur dans un cylindre fini homogène afin de prédire la température locale et la valeur de stérilisation au cours de foie gras traitement thermique de l'émulsion de *foie gras*. Une méthode des différences finies a été utilisée dans la résolution de l'équation de transfert de chaleur de Fourier selon le schéma d'Euler. Le modèle a été validé par la comparaison des valeurs de prédiction du modèle avec des données expérimentales de températures réelles obtenues lors de la stérilisation de *foie gras* dans des bocaux en verre. L'emplacement de l'endroit le plus froid a été au centre géométrique. La comparaison entre les valeurs expérimentales et prédites a montré un bon accord dans la phase de stérilisation, mais pas pour la phase de refroidissement où la différence entre les deux courbes était plus significative. Les résultats indiquent que le modèle développé pourrait être appliquée avec succès pour prédire le traitement thermique de *foie gras* dans des bocaux en verre.

## 6.2 Abstract

The objective of this research was to optimize the sterilization process of canned *foie* gras products via a mathematical model and to develop a tool to improve the final sensory characteristics without compromising the safety of the product. In this study, a two-dimensional numerical model was developed to investigate heat transfer in a homogenous finite cylinder in order to predict the local temperature and the sterilizing value during the heat treatment of *foie gras* emulsion. A fixed grid finite difference method was used in the resolution of the Fourier's heat transfer equation according to Euler's scheme. The model was validated by the comparison of the model predicted values with actual experimental data on temperature obtained during canned *foie gras* sterilization in glass jars. The location of the coldest spot was at the radial center. The comparison between experimental and predicted values showed a good agreement except for the cooling phase where the difference between both curves were higher. The results indicated that the developed model could be successfully applied to simulate the *foie gras* thermal processing in glass jars.

## 6.3 Introduction

*Foie gras* is a delicacy, originally from France, made from the liver of ducks or geese that have been hand fed and fattened to create desired organoleptic attributes. Proper sterilization of such products must be sufficient to secure food safety and stable shelf life products but, thermal treatments should also be minimized to avoid quality defects such as overcooking and fat melting. In France, the required sterilization value ($F_0$) for *foie gras* is just 1 minute, because researchers have found a low concentration of spores in duck fatty liver in the industry, from $10^1$-$10^2$ CFU/g (André et al., 2010). This $F_0$ value is lower than the one recommended in the international and Canadian (CFIA) guidelines for low acid canned products established by the FAO (Huss et al., 2003), which is 3 minutes

Quebec's *foie gras* producers (Association des Éleveurs de canards et d'oies du Québec, AECOQ) are concerned with the fact that their product will not have the same sensory characteristics as the one produced in France, since the requirement in Canada is to heat 3 times or more at a reference temperature of 121°C, and the main problem that they face is the change in texture since longer exposure to high temperatures will melt the lipids, draining it to the surface and recrystallization on the interface between the product and the can once the product is cold, making the product much less attractive for the consumers. With a reduction of the heat treatment, similar organoleptic characteristics as the product from France could be achieved.

The total lethality achieved in the process at the critical point of the product (geometrical center or the coldest temperature zone) can be calculated with the equation 6.1 (Simpson et al., 2004; Chen et al., 2011):

$$F_0 = \int_0^t 10^{\frac{T_{(C)} - T_{ref}}{z}} dt \qquad \text{eq. 6.1}$$

where $F_o$ is the total sterilization value; $T_{(c)}$ is the product temperature history at a given location (geometrical center or coldest point zone)at a reference temperature ($T_{ref}$) of of 121.1°C. The z-value (temperature sensitivity) is the temperature change required for a one log reduction of the $D$-value of the target microorganism.

The temperature history of the product in the coldest point depends in the material characteristics, but also in the container size and the type of retort, and could be determined experimentally (unpractical and tedious method) or else predicted from a mathematical model.

Studies on mathematical modelling of sterilization of canned *foie gras* products are scarce in the literature. Abidi et al. (2011) developed a mathematical model to predict the temperature at the center of a can filled with potato puree (Figure 6.1). As can be seen from this figure, the agreement between prediction and experimental values are not particularly close. Once the model was developed and tested against experimental data on potato puree, the researchers changed the thermal properties to those of *foie gras* emulsion to simulate the temperature at the coldest point. These predictions were used to optimize the heating of the product in the autoclave. However, no actual comparison between experimental data and predictions of the model were done for *foie gras* emulsion.

Heat transfer characteristics of the container and the product are required in the design of an effective thermal process, which includes the chemical (composition, heterogeneity), physical and microbiological properties inherent to each food (Santana et al. 2013). The thermal properties that should take into account while modeling a thermal process are specific heat, thermal conductivity, density and thermal diffusivity (Sheen et al., 1993; Erdogdu et al., 1998; Santana et al. 2013).

In a thermal process of foods, heat is added or removed from the product most usually by convection. To describe this phenomenon, the convection heat transfer coefficient ($h$) needs to be known. It is defined from the Newton's law of heat transfer, in which $h$ represents the rate of heat transfer between a solid-liquid interface (Michailidis et al. 2009; Berman et al. 2011; eq. 6.2):

$$q = hA(T_s - T_\infty) \hspace{4cm} \text{eq. } 6.2$$

where $q$ is the heat flux, $A$ is the area of the surface of the solid, $T_s$ is the temperature at the surface of the solid and $T_\infty$ is the temperature of the heating fluid.

Convective heat transfer coefficient ($h$) depends on the heating fluid characteristics as its rheological and thermos-physical properties (Michailidis et al. 2009). This relationship is important since it describes how the surface of the product is heated, and is useful in determine process conditions. This coefficient is usually obtained experimentally or by empirical correlation for a specific process or equipment.

The objective of the present work is thus to develop a mathematical model that can accurately describe the heating at the coldest point in canned *foie gras* emulsion and whole *foie gras* during sterilization.
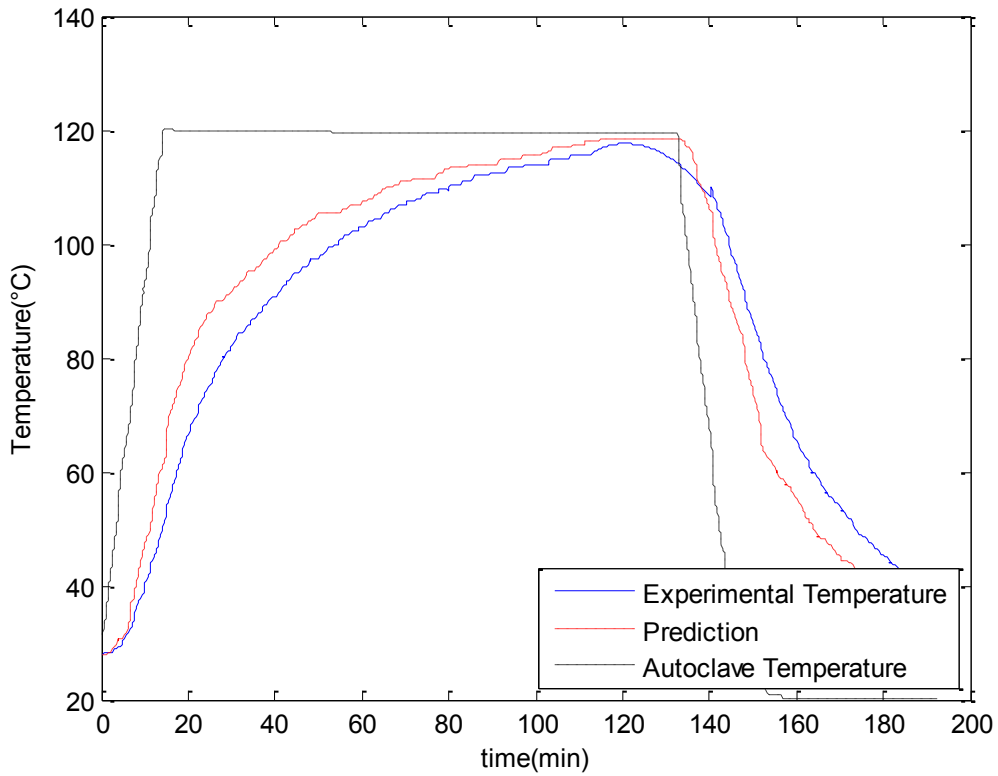
**Figure 6-1.** Experimental temperature vs simulated temperature. Adapted from Abidi et al. (2011)

## 6.4   Materials and Methods

### 6.4.1   Sterilization experiments

A glass jar (6.08±0.09 cm diameter, 4.78±0.03 cm height) fitted with a thermocouple (HiTemp 140, range from -20 to 140°C, ThermoWorks, Lindon, UT, USA) at the coldest point (center of the jar) was filled with 85 g of *foie gras* emulsion (Figure 6.2) or with similar mass of whole *foie gras* (both products were obtained from a local Quebec producer). The time-temperature profile was therefore measured at the coldest point of the jar during heat treatments. Heat treatment experiments were performed in a vapor/vacuum autoclave (Amsco Century Medium Sterilizer, Steris Corp., Mentor, OH, USA) at different set point temperatures from 105 to 120°C. The glass jar was positioned always at the same place inside the autoclave (Figure 6.3). Once the heating temperature reached the set point, it was kept constant for a predetermined time, after which the jar was cooled using the cooling system of the autoclave or accelerated by immersing the jars in a water bath at room temperature.

### 6.4.2   Mathematical model

Heating by conduction is defined by the Fourier's law. This law can be expressed in terms of one, two or three dimensions depending on the model requirements and its complexity. In the case of a cylindrical container of finite length containing a homogeneous solid that has a constant thermal diffusivity, $\alpha$, the heating by conduction can be described by the following partial differential equation (Chen et al. 2011):

$$\frac{\partial T}{\partial t} = \alpha \left[ \frac{\partial^2 T}{\partial r^2} + \frac{1}{2}\frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial y^2} \right] \qquad\qquad \text{eq. 6.3}$$

where $\alpha$ is the thermal diffusivity of the product; $r$ is the radius of the container; $y$ is the vertical coordinate of the container.

**Figure 6-2.**Glass jar filled up with *foie gras* emulsion having a thermocouple to measure the temperature at the center.

**Figure 6-3.** Position of the glass jar on the rack for the sterilization process.

This model used to represent heating inside the glass jar in a retort, is based on a work done by Richardson and Holdsworth (1989), where symmetry around the center axis could be considered since convection heating outside the container is uniform on all the surfaces. Inside the container, uniform conduction heating is also considered, so the analysis can be made just on the upper left part of the container (Figure 6.4). In the application of this model, the container is then separated in six different locations: a) internal nodes, b) center of the container, c) convection heating in the outer boundaries of the container and d) the locations along vertical and horizontal axis. For internal nodes and along horizontal axis (but not in the center), equation 6.3 applies. However, for other different nodes, the following equations were suggested (Richardson and Holdsworth, 1989).

Along the vertical axis (but not in the center):

$$\frac{1}{\alpha}\frac{\partial T}{\partial t} = 2\frac{\partial^2 T}{\partial r^2} + \frac{\partial^2 T}{\partial y^2} \qquad\qquad eq.\,6.4$$

In the center:

$$\frac{1}{\alpha}\frac{\partial T}{\partial t} = 2\frac{\partial^2 T}{\partial r^2} + \frac{\partial^2 T}{\partial z^2} \qquad\qquad eq.\,6.5$$

Convection heating over surfaces (vertical and horizontal):

$$k\frac{\partial T}{\partial r} = h(T_\infty - T) \qquad\qquad eq.\,6.6$$

where $k$ is the thermal conductivity of the product, $T_\infty$ is the retort temperature which is a function of time, and $h$ is the convection heat transfer coefficient.
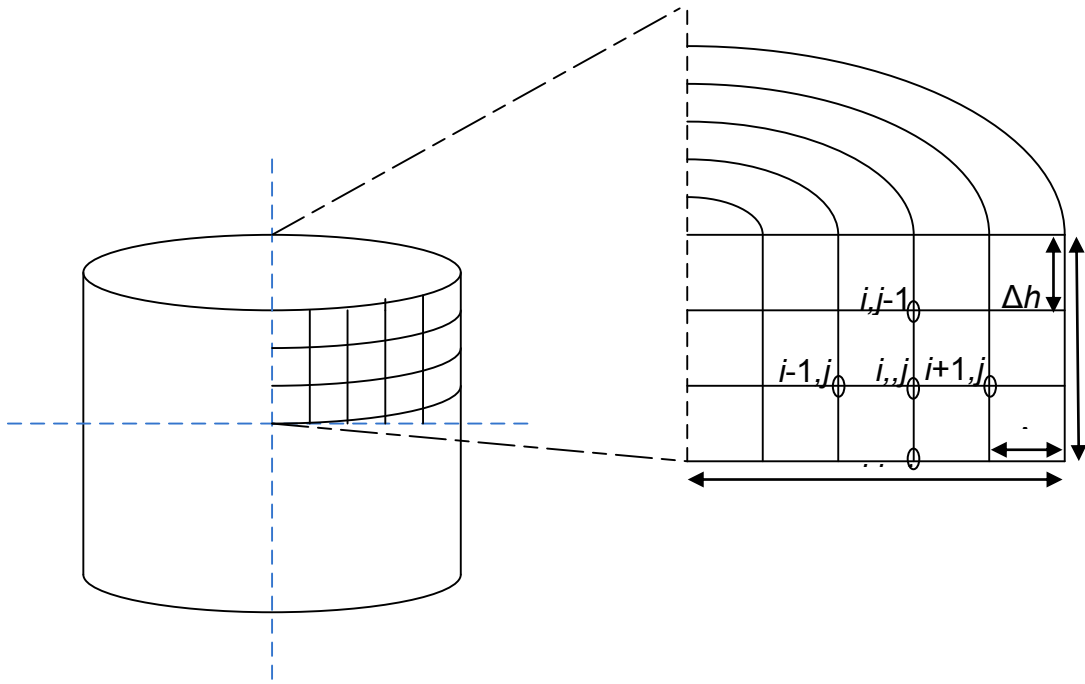
**Figure 6-4.** One quarter of the cylindrical container used for the discretization of the equations for different nodes

### 6.4.3  Convective heat transfer coefficient

In order to quantify how the heat is transferred from the vapor in the autoclave to the glass jars, the convective heat transfer coefficient *h* needs to be determined, which was calculated from experimental determinations in the vacuum/vapor autoclave at a set point temperature of 105°C. A solid cylinder having similar shape and dimensions as the glass jar was constructed out of steel (6.19 cm diameter, 4.52 cm height, and a total heat transfer area of 0.0148m$^2$). The cylinder was placed at the coldest spot of the vapor autoclave and the surface temperature was followed with a wireless thermocouple (HiTemp 140, range from -20 to 140°C, ThermoWorks, Lindon, UT) attached to the cylinder surface with tape (figure 6.5). Temperature of the autoclave was recorded using an iButton (22E, Alpha Mach, Ste-Julie, QC, Canada).

The convective heat transfer coefficient was determined from equation 6.3, where the differential of temperature with time was calculated for the heating lapse.

$$\frac{dT}{dt} = \frac{h\,A}{m\,C_p}\,(T_\infty - T) \qquad\qquad \text{eq. 6.7}$$

where $\frac{dT}{dt}$ is the differential of temperature and time, *h* is the convective heat transfer coefficient, *A* is the cylinder total heat transfer area, *m* is the cylinder's mass and *Cp* its specific heat (steel). $T_\infty$ is the temperature of the autoclave and *T*, the temperature at the cylinder surface.

Experimental values of the temperature-time derivative, which was calculated from the polynomial regression of the heating phase in the heating curve of the cylinder, and then applying the derivative to this function, were plotted against the difference between the autoclave and the cylinder's temperatures, and a linear regression from the origin was made to the data.

**Figure 6-5.** Steel cylinder and thermocouple.

As determined from equation 6.3, the convective heat transfer coefficient can be calculated from the value of the slope of this regression.

### 6.4.4 Equations discretization

The model represented by equations 6.3 to 6.6 cannot be solved without applying a "disctretization" method; this is, to approximate the derivatives of a function at a point in terms of its value at several neighbor points. The discretization method most widely used for canned products is the finite difference method (Shin and Bhowmik, 1990; Banga et al. 1993; Mohammed, 2003; Chen et al., 2011) due to its simplicity and limited computation times. Also, the boundary conditions as the surfaces temperature, the heating fluid temperature and the temperature at the center of the can, have to be taken into account.

The discretization of the differential equations was done applying the Euler's method (the so called "explicit" form). Thus, equations from 6.3 to 6.6 were discretized for each case as follows:

**Case 1**. Internal grid nodes:

$$T_{i.j}^{n+1} = T_{i,j}^n + \frac{\alpha \Delta t}{(\Delta r)^2}\left[T_{i-1,j}^n - 2T_{i,j}^n + T_{i+1,j}^n\right] + \frac{\alpha \Delta t}{(\Delta r)}\left[T_{i-1,j}^n - T_{i+1,j}^n\right]$$

$$+ \frac{\alpha \Delta t}{(\Delta y)^2}\left[T_{i,j-1}^n - 2T_{i,j}^n + T_{i,j-1}^n\right] \qquad\qquad \text{eq. 6.8}$$

**Case 2**. Along vertical axis (except center):

$$T_{i.j}^{n+1} = T_{i,j}^n + \frac{4\alpha \Delta t}{(\Delta r)^2}\left[T_{i-1,j}^n - T_{i,j}^n\right] + \frac{\alpha \Delta t}{(\Delta y)^2} \qquad\qquad \text{eq. 6.9}$$

**Case 3.** Along horizontal axis (except center):

$$T_{i,j}^{n+1} = T_{i,j}^n + \frac{\alpha \Delta t}{(\Delta r)^2} \left[ T_{i-1,j}^n - 2T_{i,j}^n + T_{i+1,j}^n \right] + \frac{\alpha \Delta t}{2r(\Delta r)} \left[ T_{i-1,j}^n - T_{i+1,j}^n \right]$$

$$+ \frac{\alpha \Delta t}{(\Delta y)^2} \left[ T_{i,j-1}^n - T_{i,j}^n \right] \qquad\qquad \text{eq. 6.10}$$

**Case 4.** At center:

$$T_{i,j}^{n+1} = T_{i,j}^n + \frac{4\alpha \Delta t}{(\Delta r)^2} \left[ T_{i-1,j}^n - T_{i,j}^n \right] + \frac{4\alpha \Delta t}{(\Delta z)^2} \left[ T_{i,j-1}^n - T_{i,j}^n \right] \qquad \text{eq 6.11}$$

**Case 5.** Convection heating in the horizontal axis:

$$T_{i,j}^{n+1} = \frac{2\alpha \Delta t}{(\Delta r)^2} \left[ T_{i+1,j}^n \right] + \left( 1 - \frac{2\alpha \Delta t}{(\Delta r)^2} \right) \left[ T_{i,j}^n \beta \right] + \frac{2\alpha \Delta t}{(\Delta r)^2} \gamma \qquad \text{eq. 6.12}$$

where

$$\beta = 1 + \left( 1 + \frac{1}{2} \right) \Delta r \frac{h}{k}$$

and

$$\gamma = \left( 1 + \frac{1}{2} \right) \frac{\Delta r}{k} h T_\infty$$

.

**Case 6.** Convection heating in the vertical axis:

$$T_{i,j}^{n+1} = \frac{2\alpha \Delta t}{(\Delta y)^2} \left[ T_{i+1,j}^n \right] + \left( 1 - \frac{2\alpha \Delta t}{(\Delta y)^2} \right) \left[ T_{i,j}^n \beta \right] + \frac{2\alpha \Delta t}{(\Delta y)^2} \gamma \qquad \text{eq 6.13}$$

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where

$$\beta = 1 + (1 + \frac{1}{2})\Delta y \frac{h}{k}$$

and

$$\gamma = (1 + \frac{1}{2})\frac{\Delta y}{k}hT_\infty$$

.

Once discretization was made, the container was divided in grids (figure 6.4) producing a matrix of $N$ equations which was then solved using MATLAB R2012b software (MathWorks, Natick, MA, USA). The written code is presented in the Annex. The input data of the model are values of retort temperature as a function of time, thermal conductivity, specific heat, density, initial temperature of the product, container dimensions and processing time. The output is the temperature at the center point.

### 6.4.5  $F_0$ calculation

The sterilization value ($F_0$) was determined using equation 6.1 for the experimental and simulated temperatures of whole *foie gras* and *foie gras* emulsion in the vapor autoclave at 105°C. This $F_0$ value was calculated with a $z$ value of 10°C and a reference temperature of 121.1°C (Stumbo, 1973; CFIA, 1995). Numerical integration in eq. (6.1) was done with the trapezoid method and solved using MATLAB R2012b software (MathWorks, Natick, MA, USA).

## 6.5 Results and discussion

### 6.5.1 Convective heat transfer coefficient (*h*)

Figure 6.6 shows the experimental surface temperature of the steel cylinder during the heating phase in an autoclave at 105°C, data from which the convective heat transfer coefficient was determined. Figure 6.7 shows the relationship between the temperature-time derivative and the temperature difference between the autoclave and the surface of the steel cylinder.

A linear regression that passes through the origin was then applied to the relationship shown in Figure 6.7. The obtained value for the slope *w* was used for the calculation of *h* from the following equation:

$$h = \frac{m \, w \, C_p}{A} \qquad \text{eq. 6.14}$$

In table 6.1, the values used to solve this equation (values for *Cp* of steel were used) are shown.

**Table 6.1. Values for calculating the convective heat transfer coefficient (*h*) of the vapor autoclave**

| Property | Value | |
|---|---|---|
| Area | 0.0148 | $m^2$ |
| $C_p$ [1] | 501.6 | J kg$^{-1}$ °C$^{-1}$ |
| Diameter | 0.0619 | m |
| Height | 0.0452 | m |
| Weight | 1.0615 | Kg |
| Slope, *w* [2] | 0.0207 | 1/s |
| r² | 0.4756 | |

[1]  Perry (1999)
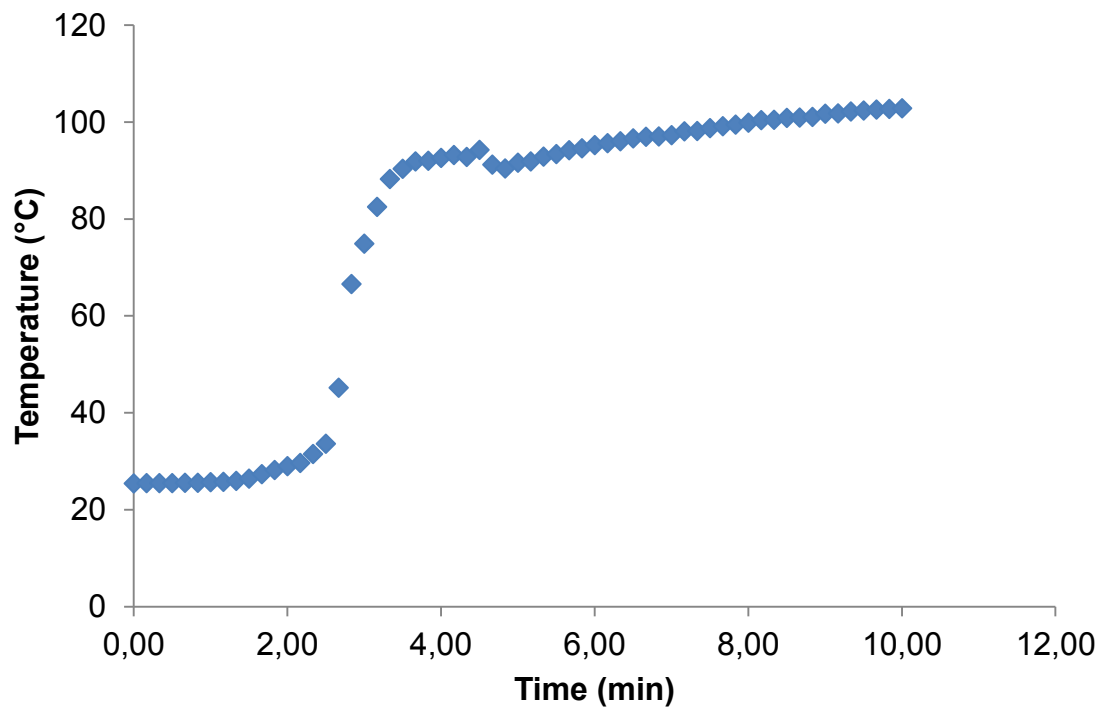
[2]  Determined slope from Figure 6.7

**Figure 6-6.** Temperatures during the heating phase of the solid cylinder.
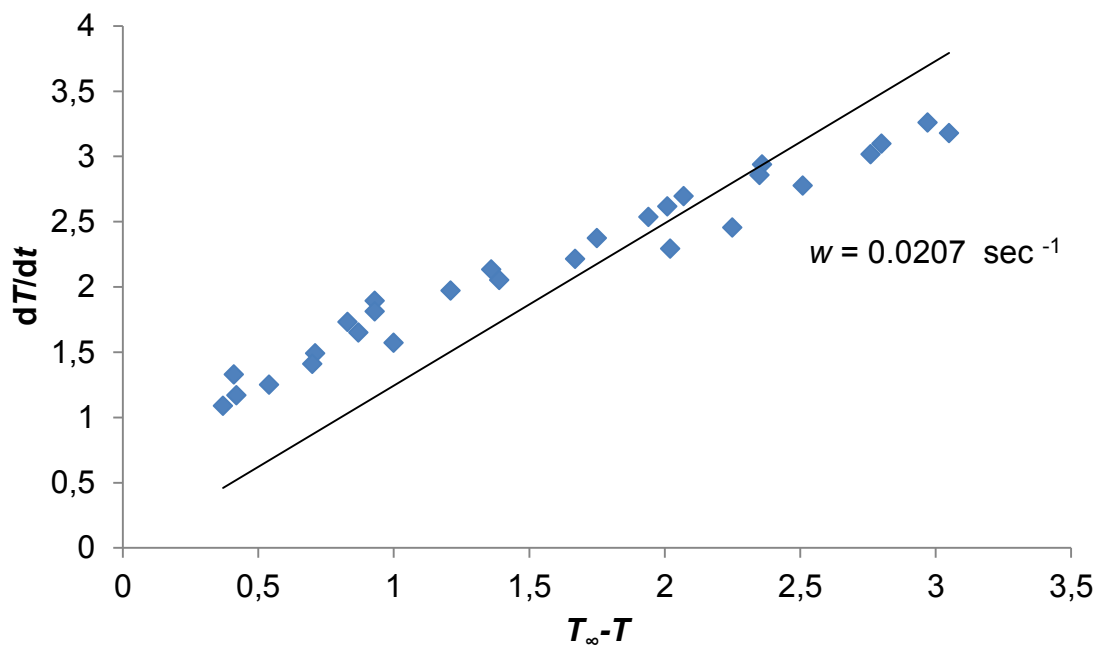
**Figure 6-7.** Graphical results of the change of temperature over the process time in comparison with the difference between the heating fluid temperature and the surface temperature.

From equation 6.14, the *h* coefficient was calculated, resulting in a value of 743.08 W m$^2$ $^{-1}$ °C$^{-1}$. This value is in the range of previously reported *h* values for heat treatments in retorts, although slightly lower than the minimum value of the range proposed by Bergman et al. (2011) (1000 to 20,000 W/ m$^2$ °C) and then the coefficient used by Abibi et al. (2011), which was 1200/ W/ m$^2$ °C for the heating of cylindrical cans. This coefficient may differ from other ones published because it may depend on the vapor used, and if the heating is by free convection or forced convection, etc. For the autoclave used in this work, the method of heat transfer was free convection and the heating was made with a mixture of air with vapor.

### 6.5.2 Sterilization data

Figure 6.8 and 6.9 show the experimental heating curves (temperature rise over time) in the center of a glass jar filled with *foie gras* emulsion during sterilization in a vapor retort having a set point of 105°C, 115°C and 120°C. Figures 6.8 A and 6.9 A and B show the heating curves of a process were the cooling was made by introducing air at lower temperatures than sterilization to avoid thermal shock. While in Figure 6.8 B, the cooling system was water at ambient temperature. As can be seen from Figure 6.8, the temperature increase measured at the center of the glass jar filled with *foie gras* emulsion, is similar to the heat penetration curve described in Figure 6.1 (Abidi et al. 2011). In the heating phase, a "shoulder" is observed in the four graphs shown in Figures 6.8 and 9 where the temperature stars to rise quickly and then it slows down, almost around 40°C (Figure 5.2). This is where the total fusion of the lipids contained in the *foie gras* emulsion happened. In figure 6.8 B, the process where the jar was cooled with water at ambient temperature until reaching 30°C is shown (done with the objective of having a rapid and more constant cooling of the product). It can be seen during this type of cooling that the product temperature decrease presents a smoother curve. At higher temperatures, as shown in figure 6.9 A (115°C) and B (120°C), the cooling phase was performed in the autoclave. Heating phase resembles to the curves shown in figure 6.8. However in the cooling phase, the temperatare in the

autoclave started to descend  and then it riso again, making the cooling phase of the product follow a similar tendency. If cooling with water would have been applied instead to these processes, the cooling phase could have been faster.

### 6.5.3   Simulation of the temperature at the center of the can

The model was solved with the finite difference method described previously; using the properties for *foie gras* (emulsion or whole; see chapter 5 for more details). The temperature at the center of the glass jar predicted with the model was compared to experimental temperature data as shown in Figure 6.8 and 6.9. As can be observed from these figures, simulation values from the mathematical model are in close agreement with experimental data exceptin the cooling part of the curves where the difference increased slightly. It should be pointed out, that no experimental data was used to 'fit' the mathematical model, all input properties were obtained from independent measurements or correlations, showing the strength of the present model to predict accurately heating temperatures during sterilization processes. The absolute error was calculated for each of the retort temperatures at different times, then an average was made for the total error, for each of the heating and cooling phases; these values are presented in table 6.2. For figure 6.8 A, the average percentage error was 4.71% showing that in general the values of simulated temperature resemble well those experimental. For the cooling phase, however, the percentage of error is higher with an average of 8.36%. This average error in the cooling phase increases as the retort temperature increase. This may be explained by the fact that  the model only uses one value for the convective heat transfer coefficient, the one determined for the heating phase, and this coefficient may change in the cooling phase of the product, especially if condensation is taking place on the surface of the can or the walls of the autoclave while cooling.
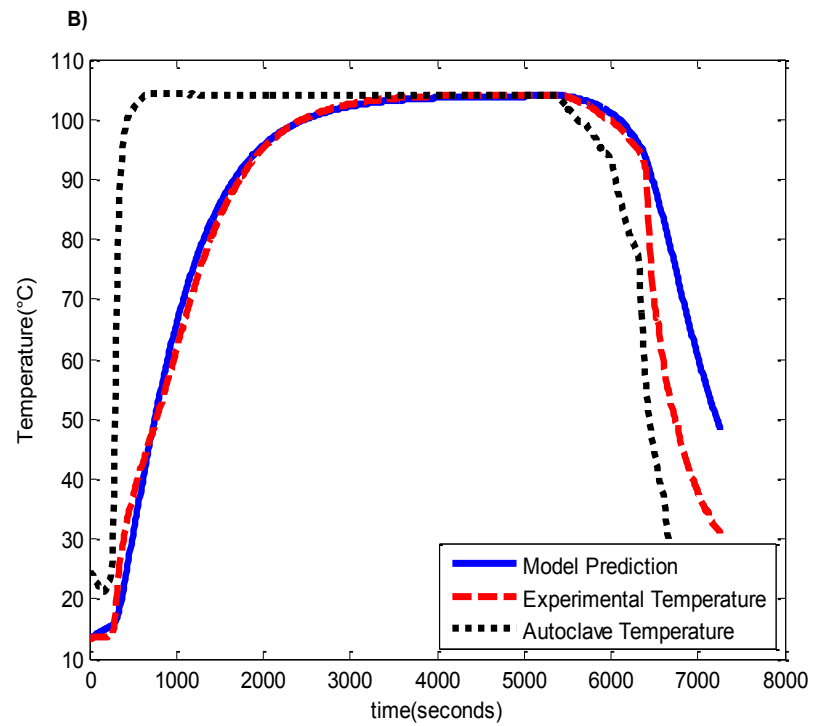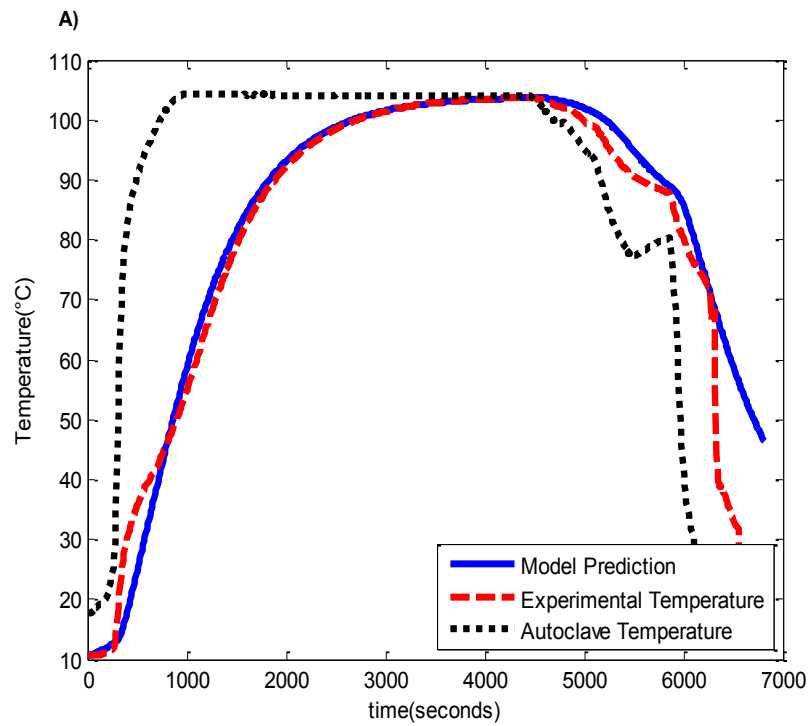
**Figure 6-8.** Simulated vs. experimental temperature for foie gras emulsion, A) 105°C and B) 105°C with water cooling
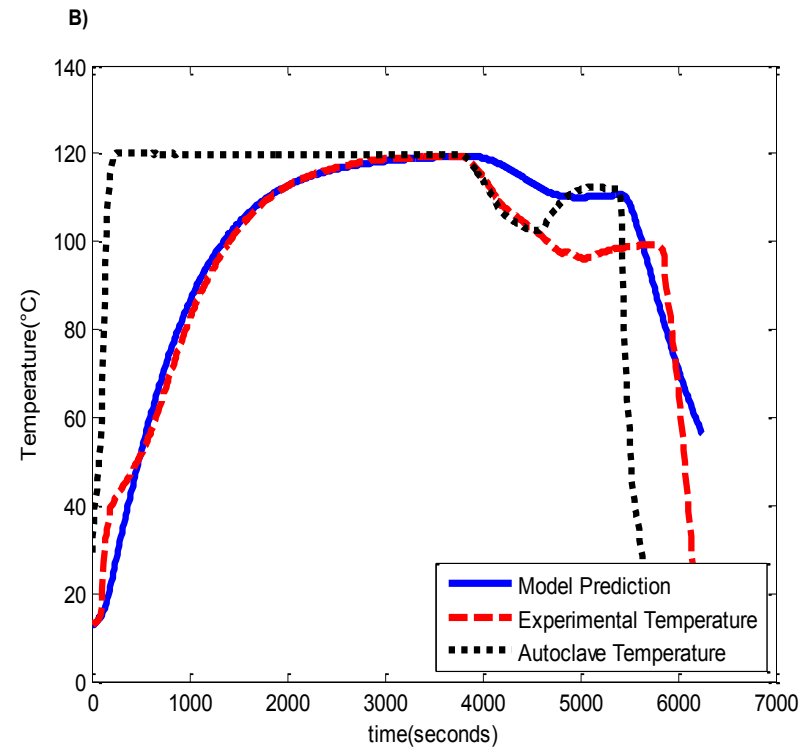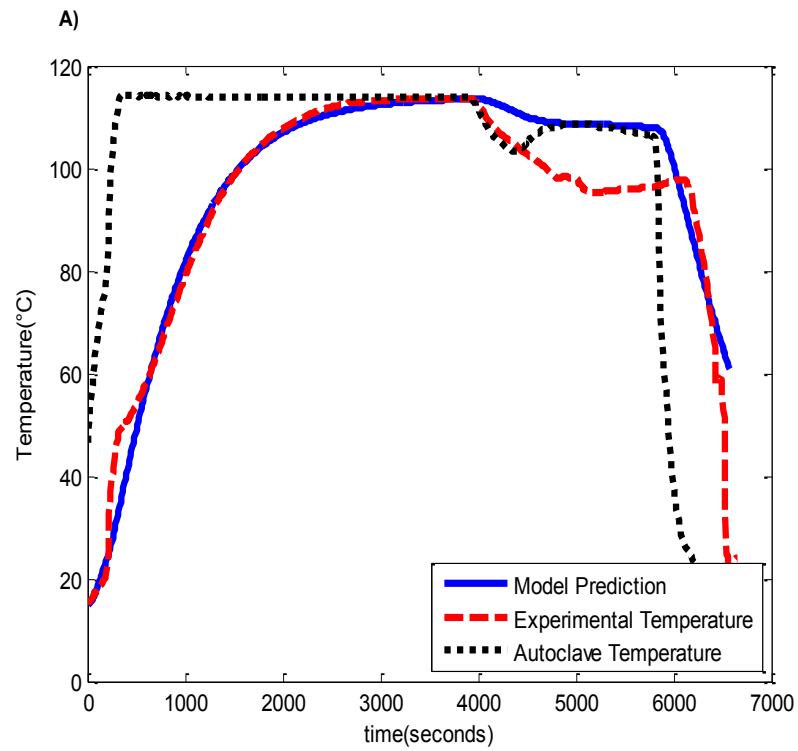
**Figure 6-9.**Simulated vs. experimental temperature for foie gras emulsion, A) 115°C and B) 120°C

**Table 6.2. Percentage of error between experimental and predicted temperature in different parts of the heating curve for foie gras emulsion**

| Temperature (°C) | Average error (%) | Heating phase error (%) | Cooling phase error (%) |
|---|---|---|---|
| 105 | 4.71 | 4.94 | 8.36 |
| 115 | 6.39 | 3.94 | 11.06 |
| 120 | 9.04 | 5.36 | 18.35 |

From values presented in table 6.2, the percentage of error in the heating phase is similar for each of the autoclave set point temperatures. In addition, the difference between experimental and predicted temperatures was higher when cooling was done with water (calculations not shown), this may be because the autoclave cooling temperature drops faster and with a different heat transfer system (water convection instead as vapor), but as the *h* and the thermal properties were kept the same in both simulations in the cooling phase, it was more difficult for the model to simulate accurate temperatures.

The model tested for the simulation of temperatures in *foie gras* emulsion was now used for prediction of the center temperature in whole *foie gras* canned in glass jars. This could provide information for the design of an optimal thermal process for whole *foie gras.* The same model was used, but the only modification was the change of thermal properties from *foie gras* emulsion to those for whole *foie gras*. Table 6.3 compiles the properties needed for the model, which were taken from results presented in the previous chapter.

**Table 6.3. Thermal properties used in the model for the different *foie gras* products**

| Product | Thermal Property | | | |
|---|---|---|---|---|
| | $k$ (W/ m °C) | $Cp$ (J/ kg °C) | $\rho$( kg/ m³) | $\alpha$ (m²/s²) |
| Whole *foie gras* | 0.38 | 1793 | 947 | 2.23E-07 |
| *Foie gras* emulsion | 0.35 | 2160 | 930 | 1.74E-07 |

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Figure 6.10 compares the experimental and simulated center temperatures for canned whole *foie gras* in glass jars. The fitting of the model for whole *foie gras* is better than for the emulsion (figure 6.8 and 6.9). The percentage of error between the simulated and experimental temperatures was also calculated for this product. For instance, the overall percentage of error was 3.28% for figure 6.10, instead of 4.71% for the emulsion at the same retort temperature. Unlike *foie gras* emulsion, whole *foie gras* simulated temperature starts with heating being very similar to that of the experimental, however, after the lipid melting point (around 50°C), the product starts heating faster. The percentage error between experimental and simulated temperatures for the cooling phase of canned whole *foie gras* was 0.89% (8.36% for the emulsion), which means that for this product the model could better predict the temperatures in the cooling stage of the product. A second experimental run was performed and the values of percentage of error for the difference between experimental and simulated temperature were similar than those of figure 5.9 (3.89% overall, 8.36% heating and 1.44% cooling).

Figure 6.11 shows a comparison of the predicted temperatures for the whole and emulsion of *foie gras.* As stated in the chapter 5, the properties of both products present different values, thermal conductivity and density are higher for the whole *foie gras*, but the specific heat in the *foie gras* emulsion presents a higher value than that of the whole *foie gras*. Thus, thermal diffusivity $\alpha$ (the property that points out how fast the heating will be from Equation 3.3.), indicates that whole *foie gras* should heat at a somewhat faster paste than the emulsion.
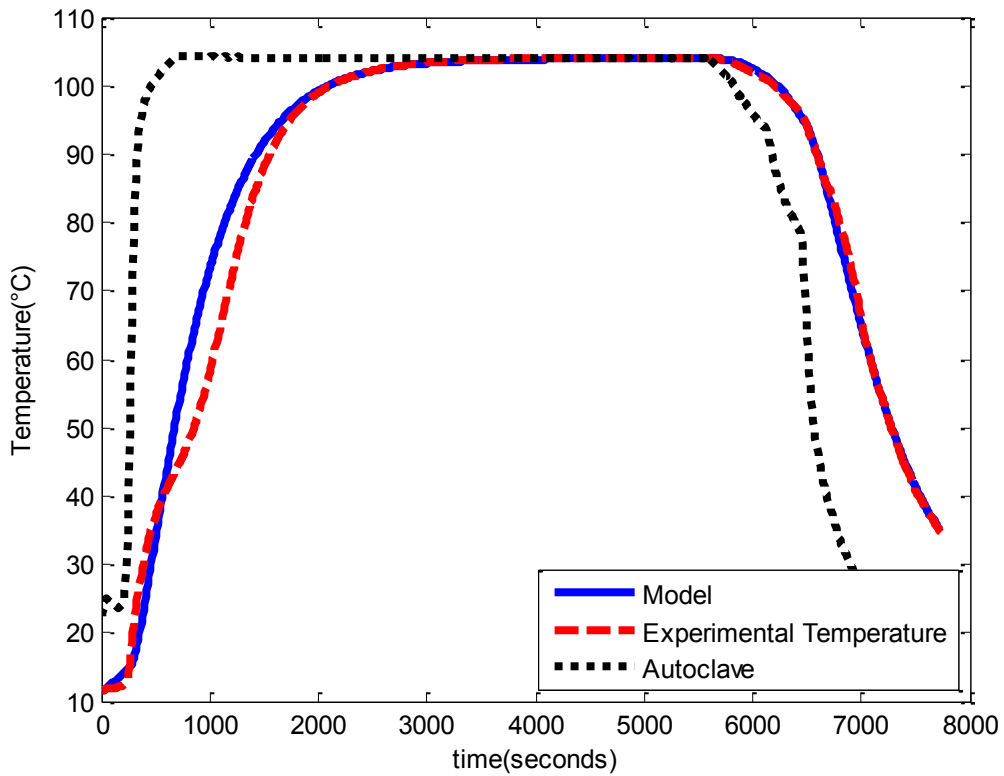
**Figure 6-10.** Graphical comparison of experimental and simulated temperature for the whole *foie gras* at 105°C
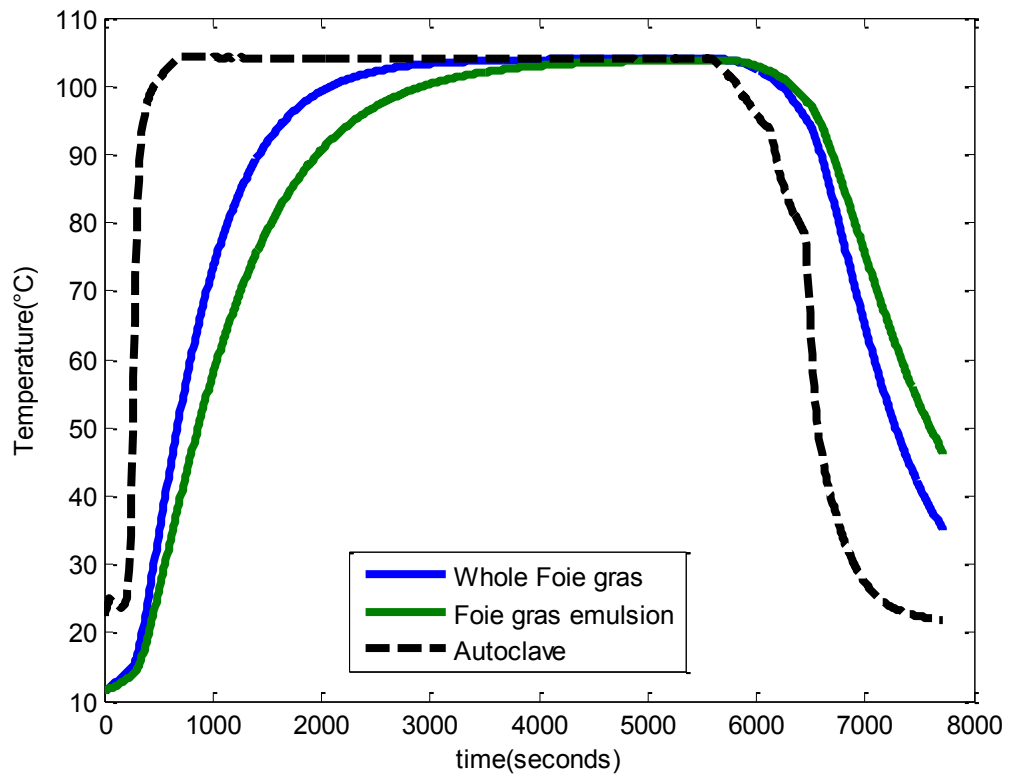
**Figure 6-11.** Comparison of simulated center temperatures of canned whole foie gras and foie gras emulsion

In Figure 5.11, it can be seen how the change in thermal properties affects the simulation of temperatures, especially in the heating phase. As whole *foie gras* needs less energy to rise its temperature (lower specific heat) than *foie gras* emulsion, the heating of this product should be faster.

## 6.6 $F_0$ calculation

The sterility or lethality value was calculated for the simulated and experimental temperatures of the *foie gras* emulsion and whole *foie gras* at 105°C (Figure 6.8 A and 6.10, respectively), this temperature was chosen because *foie gras* is a delicate product that will not stand higher temperatures (CTPCA, 1997). Figure 6.12 shows a comparison between the experimental and simulated temperatures with their corresponding $F_0$ value for *foie gras* emulsion sterilization. A red line at temperature of 90°C in the graph marks the "lethal zone" of the process (temperatures above 90°C). As it can be seen from the graph, the simulated and experimental lethality values are almost the same until 80 minutes. The lesser accurate prediction of the cooling phase temperatures makes the value of the predicted $F_o$ slightly higher than the experimental one at the end of the proces.

For whole *foie gras* (Figure 6.13) the predicted temperatures fit almost perfectly the experimental ones in the zone above 90°C, generating a low error when the lethality values of the simulated and experimental temperatures are compared. The model can determine appropriately the temperature at the center point of the jar as well as calculated lethality value when compared with the experimental temperatures.

In Table 6.4, a comparison of the $F_0$ values for the whole *foie gras* and *foie gras* emulsion calculated with the experimental and simulated temperatures at 96 and 109 minutes, respectively, is shown. Values from Table 6,4 show a good agreement between predicted and experimental $F_o$ values, having an error percentage of 10.8% for the *foie gras* emulsion and of just 0.49%, for the whole *foie gras*.

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**Table 6.4. Experimental and simulated $F_0$ values at 105°C**

| *Foie gras* emulsion | | | Whole *Foie gras* | | |
|---|---|---|---|---|---|
| $F_o$ (sim) | $F_o$ (exp) | %Error | $F_o$ (sim) | $F_o$ (exp) | %Error |
| 0.69 | 0.63 | 10.85 | 1.22 | 1.23 | 0.49 |

## 6.7 Conclusions

The two-dimension model developed in this work represents well the experimental data during heating and constant phases of the thermal history at the center of a glass jar filled with *foie gras* (whole and emulsion) to be sterilized. However, accuracy is not as strong in the decrease of temperature during cooling. Developing a three-dimension mathematical model could help in improving the predictions during cooling phase but increases enormously the computer time to obtain results, also the calculation of a convective heat transfer coefficient during cooling would have improved the model. The results of the calculation of $F_o$ showed an good agreement between experimental and predicted values since the lethal temperatures are in the range where the mathematical model predicts the best. Thus, it could be concluded that this simpler two-dimensional model is a good compromise for obtaining acceptable results and thus, it will be a great tool to optimize *foie* gras sterilization in order to improve the final sensory characteristics.
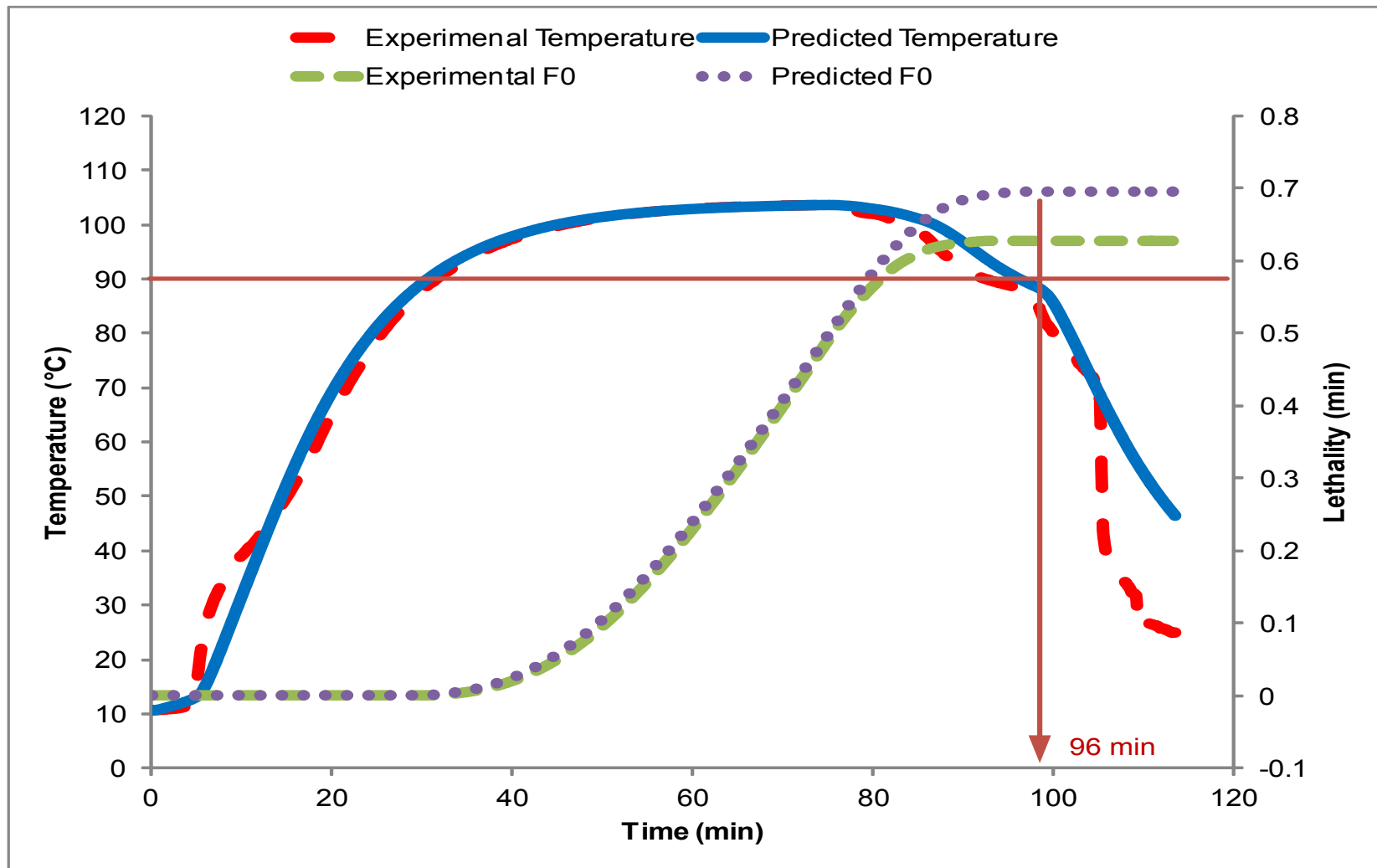
**Figure 6-12.** Simulated and experimental values for temperature and lethality value of *foie gras* emulsion at 105°C
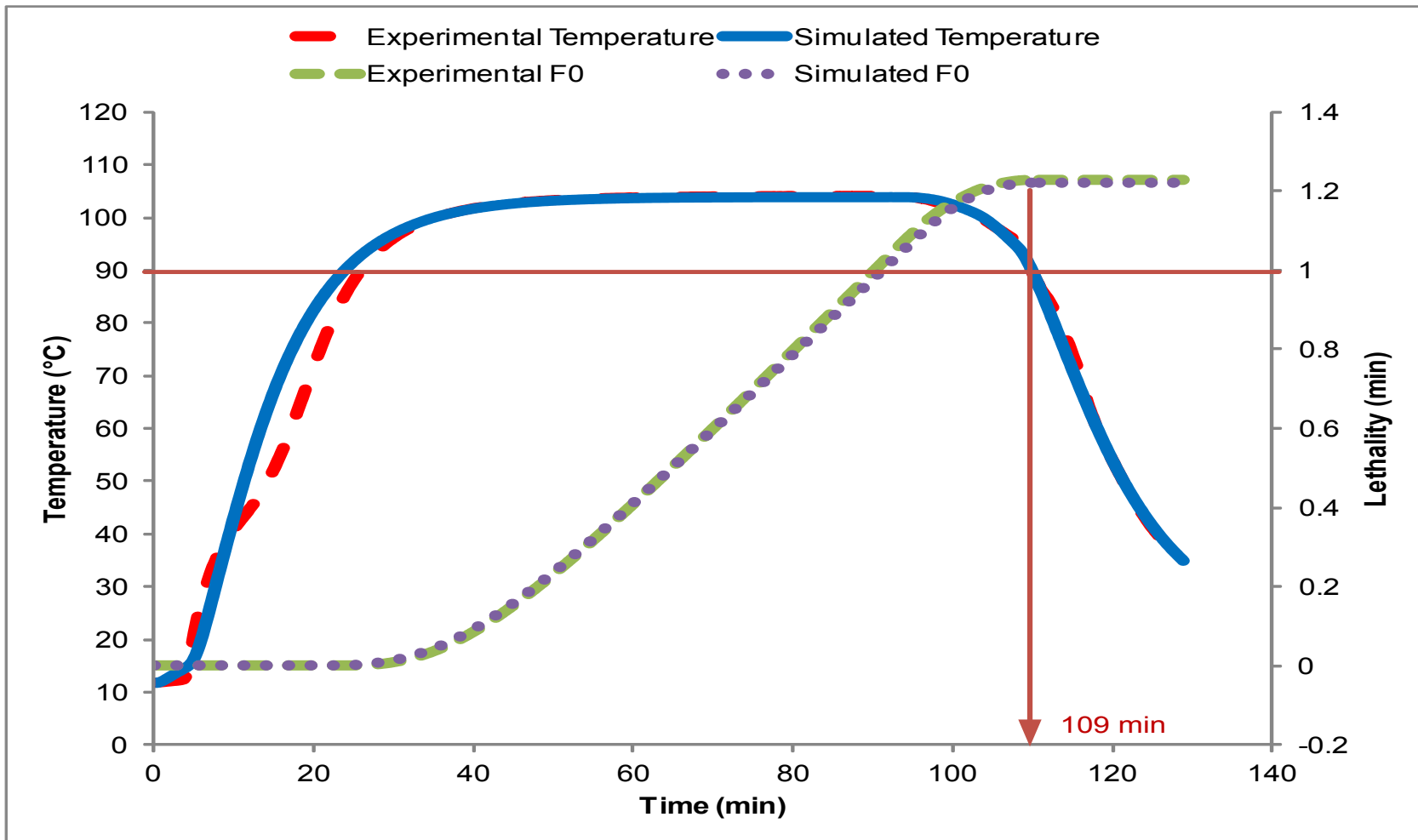
**Figure 6-13.** Simulated and experimental values for temperature and lethality value of whole *foie gras* at 105°C

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# 7 General Conclusions

Values of heat resistance of *Clostridium sporogenes* PA3679 was determined, as well as the thermal properties for *foie gras* produced in the province of Quebec and its derivative products. In general, the results show a good agreement with published results, and, in the case of thermal properties, a satisfactory correlation with predictive models. A two-dimension mathematical model was developed to predict the temperature at the center of the *foie gras* and *foie gras* emulsions in a glass jar. With the data obtained from the thermal properties, this model can simulate with great accuracy the temperature at the center point of the jar. These data, coupled with the calculation and determination of the lethality values ($F_0$), heat treatment for in Quebec's *foie gras* products can be optimized to improve product quality and thermal processes without compromising consumer safety and product quality.

As future work, a complete mathematical model including the heat transfer equation already developed in this work should be developed and should include a mass transfer equation to represent fat melting and draining in the *foie gras* matrix while sterilizing *foie gras* products in jars. Minimization of quality defects can be thus easily explored from simulations of this coupled model.

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# Annex. Code for solving the mathematical model

```
%Code:
clear all
close all
clc

%Can dimensions:
rad=0.0333;  %can radio
H=0.0239;    %can height

%Thermal properties of the material
k=0.38;    %Thermal conductivity foie gras (W/m K)
ro=947;      %density for foie gras (kg/m^3)
Cp=1793;     %Specific heat  of foie gras (J/kg °C)
alpha=k/(ro*Cp);  %Thermal diffusivity foie gras

%Grid division of the problem
m=;              %grid division in the radio direction
dr=rad/m;        %change of size in radio direction
r=(0:dr:rad);    %Radio vector(for the finite difference
formulation)
k=;              %grid division in the height direction
dy=H/k;          %change of grid size in the height direction
h=(0:dy:H);      %Radio vector(for the matrix generation)

%time
time=128.83*60;  %total time of the process
dt=10;         %The change of size in time (data collected
every 10 seconds)
t=(0:dt:time); %time vector

%boundary and Initial conditions
Tinf %Autoclave temperature

%Initial matrix dimensions
N=length(t);        %setting lenght of time
R=length(r);        %setting lenght of vector x
Z=length(h);        %setting lenght of vector z

T=zeros(Z,R,N);     %3 dimensional matrix

T(:,:,1)=11.67;    %first matrix equals initial conditions
(assuming equal temp at all points)

%convective heat transfer coefficient.
```

```
h=743.08;
betar=1+(1+(1/2))*dr*h/k;
gammar=(1+(1/2))*(dr/k)*h*Tinf;
betay=1+(1+(1/2))*dy*h/k;
gammay=(1+(1/2))*(dy/k)*h*Tinf;
rr=alpha*dt/(dr^2);
ry=alpha*dt/(dy^2);

%initializing method for calculating the temperature at the
center
for n=1:N-1

    %Case 1. Internal grid nodes.
    for i=2:m
        for j=2:k
            T(j,i,n+1)=T(j,i,n)+rr*(T(j,i-1,n)-
2*T(j,i,n)+T(j,i+1,n))+...
                ((alpha*dt)/(2*(i-1)*dr))*(T(j,i-1,n)-
T(j,i+1,n))+...
                ry*(T(j-1,i,n)-2*T(j,i,n)+T(j+1,i,n));
        end
    end

    %Case 2.Along vertical axis (r=0, Except centre). When
r=0, then i=m.
    for j=2:k
     T(j,m+1,n+1)=T(j,m+1,n)+((4*alpha*dt)/(dr^2))*(T(j,m,n)-
T(j,m+1,n))+...
        ry*(T(j-1,m+1,n)-2*T(j,m+1,n)+T(j+1,m+1,n));
    end

    %Case 3. Along horizontal axis (except centre). When y=0,
then j=k.

    for i=2:m
    T(k+1,i,n+1)=T(k,i,n)+rr*(T(k,i-1,n)-
2*T(k,i,n)+T(k,i+1,n))+...
        ((alpha*dt)/(2*(i-1)*dr))*(T(k,i-1,n)-
(T(k,i+1,n)))+...
        ((2*alpha*dt)/(dy^2))*(T(k-1,i,n)-T(k,i,n));
    End


    %Case 4.At centre.

T(k+1,m+1,n+1)=T(k+1,m+1,n)+((4*alpha*dt)/(dr^2))*(T(k+1,m,n)
-T(k+1,m+1,n))+...
```

```matlab
            ((2*alpha*dt)/(dy^2))*(T(k,m+1,n)-T(k+1,m+1,n));

    %Case 5. Change along vertical boundary (heating by
convection)

    for j=1:k+1
    T(j,1,n+1)=2*rr*T(j,2,n)+(1-
2*rr*betar)*T(j,1,n)+2*rr*gammar(n+1);
    end

    %Case 6. y=H, T=Tinf

    for i=2:m+1
        T(1,i,n+1)=2*rr*T(2,i,n)+(1-
2*rr*betay)*T(1,i,n)+2*rr*gammay(n+1);
    end
end

Tm=T(k+1,m+1,:);
Tm=reshape(Tm,[1 N]);

%Graphical results

te= %experimental time
Te= %experimental temperature

plot(t,Tm,'linewidth',3) %plot of predicted temperature
line(te,Te,'linestyle','--','color','r','linewidth',3); %line
of experimental temperature
line(te,Tinf,'linestyle',':','color','k','linewidth',3);
%line of autoclave temperature
xlabel('time(seconds)');ylabel('Temperature(°C)');
legend('Model','Experimental Temperature','Autoclave',4);
```