ON THE MODELLING AND SIMULATION OF HIGH PRESSURE PROCESSES AND INACTIVATION OF ENZYMES IN FOOD ENGINEERING

Juan Antonio Infante, Benjamin Ivorra, Angel Manuel Ramos and Jose Maria Rey

- Universidad Complutense de Madrid

Collaborations:
Outlines

- **Introduction**
  - Industrial context
  - Description of HP device
  - Interesting problems

- **Inactivation of enzymes**
  - Kinetic equation
  - Inactivation rate

- **Heat and Mass Transfer Modelling**
  - System of equations
  - Physical parameters

- **Coupled model**
  - Sensitivity analysis
  - Incomplete models

- **Numerical experiments**
  - Considered experiments
  - Numerical Results
Part I: Introduction
HP in Food industry

- **Industrial context:** Increase of the demand of **safe and minimally processed food (liquid or solid)** prepared for immediate consumption: restaurants, collective dining rooms, domestic consumption, etc.

- **Objective of the food treatments:** Increase the shelf life of the food by inactivating some **biological entities:** bacteria, fungus, **enzymes** ...

- **Most used treatments:** Pasteurization (using high temperature), Freezing (Using low temperature), Chemical (using additives), UV treatment, HP treatment (using high pressures)... **Hybrid** treatments can be considered.

- **Advantages of HP treatments:**
  - Not based on the incorporation of additives
  - **Avoid treatments with low/high temperatures** which affect **nutritional** and **organoleptic** properties of the food.
Evolution of the use of HP device:

- 72 equipments used by 50 companies
- Production 2004: 100,000 Tons?
HP in Food industry

Application of the HP-T treatments:

<table>
<thead>
<tr>
<th>PRODUCTO</th>
<th>PAÍS</th>
<th>COMPAÑÍA</th>
<th>TRATAMIENTO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zúmicos de mandarina</td>
<td>Japón</td>
<td>Wakayama Food Int.</td>
<td>300-400 MPa/2.3-20°C</td>
</tr>
<tr>
<td>Zúmicos de frutas</td>
<td>Japón</td>
<td>Takarans</td>
<td>?</td>
</tr>
<tr>
<td>Zúmicos de naranja</td>
<td>Japón</td>
<td>Orchard House Foods Ltd.</td>
<td>500 MPa/20°C</td>
</tr>
<tr>
<td>Frutas azucaradas</td>
<td>Japón</td>
<td>Nissin Fine Foods</td>
<td>50-200 MPa</td>
</tr>
<tr>
<td>Arroces</td>
<td>Japón</td>
<td>Echigo Saita</td>
<td>400-600 MPa/10/45-70°C</td>
</tr>
<tr>
<td>Salte</td>
<td>Japón</td>
<td>Chosensono</td>
<td>400 MPa/30/15°C</td>
</tr>
<tr>
<td>Guacamole y Salsa</td>
<td>USA</td>
<td>Avoclassic-Aromex</td>
<td>700 MPa/10/15-20°C</td>
</tr>
<tr>
<td>Hummus</td>
<td>USA</td>
<td>Hannah Internat. Foods</td>
<td>?</td>
</tr>
<tr>
<td>Jamón crudo</td>
<td>Japón</td>
<td>Fuji Chiku Mutterham</td>
<td>250 MPa/3 h/40°C</td>
</tr>
<tr>
<td>Productos cánicos</td>
<td>España</td>
<td>Esteban Espleña S.A.</td>
<td>400-500 MPa/20°C</td>
</tr>
<tr>
<td>Productos cánicos de cecídeos, filos de cebolletas, jamón, hamón, filetes de “Roast beef” loncheado</td>
<td>España</td>
<td>Campofrío Alimentación S.A.</td>
<td>500-600 MPa/10/7°C</td>
</tr>
<tr>
<td>Productos precocinados “listos para comer” de aves de corral</td>
<td>España</td>
<td>Vismara/Ferrini</td>
<td>600 MPa/10/7°C</td>
</tr>
<tr>
<td>Platos preparados de verdura “listos para comer”</td>
<td>Alemania</td>
<td>Gebr. Abraham GmbH</td>
<td>600 MPa/2/9°C</td>
</tr>
<tr>
<td>Productos precocinados de pescado reconstruido: salmón y merluza</td>
<td>Japón</td>
<td>Ito Ham Foods Inc.</td>
<td>600 MPa/6/9°C</td>
</tr>
<tr>
<td>Elaborados de pescado</td>
<td>Japón</td>
<td>Yaizu Fisheries</td>
<td>400 MPa</td>
</tr>
<tr>
<td>Ostras</td>
<td>USA</td>
<td>Midlif Seafoods, Inc.</td>
<td>200-350 MPa/1,2 MPa</td>
</tr>
<tr>
<td>Marisco</td>
<td>USA</td>
<td>Ocean Choice International</td>
<td>275 MPa/1°C</td>
</tr>
<tr>
<td>Margarina</td>
<td>Japón</td>
<td>Kanembe Corp.</td>
<td>?</td>
</tr>
</tbody>
</table>
General description of the HP device
General description of the HP device
Considered HP device

We consider: **ACB GEC Alstom – Instituto del Frío - CSIC.**
Interesting problems

We have studied two problems:

1- The control of the **food sample temperature** during a HP-T treatment: Increasing the pressure we also increase the temperature (can lead to **pasteurization**).


2- **Today we present:** The study of the **inactivation** of some enzymes in the food sample: useful in future works for **optimizing** a HP-T treatment.

Part II: Inactivation of enzymes

- Enzyme
- Kinetic equation
- Inactivation rate

Part III: Heat and Mass Transfer Modelling

Part IV: Coupled model

Part V: Numerical experiments

Conclusions and perspectives
What is an enzyme: Enzymes are molecules (essentially proteins) that **catalyze chemical reactions** essential for microorganisms.

Interest of inactivating enzymes: block **chemical reactions** in order to **reduce the activity** of non-desired microorganism in food (producing fermentation, toxic...).

Impact of the HP-T treatment on enzyme: Changing the pressure/temperature conditions, the enzyme progressively (in term of concentration) change form a **folded state** (active) to an **unfolded state** (inactive): thus the chemical reaction velocity decrease.
The activity $A$ of an enzyme inside a food ‘particle’ is defined by the considered experimental protocol of measurement. Mathematically, the time evolution of $A$ can be described by the following first–order kinetic equation:

\[
\frac{dA(t)}{dt} = -\kappa(P(t), T(t)) A(t),
\]

where $t$ is the time (min), $P(t)$ is the pressure (MPa) at time $t$, $T(t)$ is the temperature (K) at time $t$ and $\kappa(P, T)$ is the inactivation rate (min$^{-1}$).

The solution at time $t$ is obviously given by

\[
A(t) = A(0) \exp \left( - \int_0^t \kappa(P(\sigma), T(\sigma)) \, d\sigma \right).
\]

Here $\kappa(P, T)$ is chosen, depending on the considered enzyme.
Inactivation rate

1- As a combination of **Arrhenius equation** (modelling the temperature dependence) and **Eyring equation** (modelling the pressure dependence):

\[ \kappa(P,T) = \kappa_r \exp \left( -B \left( \frac{1}{T} - \frac{1}{T_r} \right) \right) \exp \left( -C(P - P_r) \right), \]

2- A model obtained by considering **Eyring’s transition state theory**:

\[
\kappa(P,T) = \kappa_r \exp \left[ \left( -\frac{\Delta V_r}{RT} (P - P_r) \right) + \left( \frac{\Delta S_r}{RT} (T - T_r) \right) + \left( \frac{\Delta \nu}{2RT} (P - P_r)^2 \right) \right.
\]
\[
+ \left( -\frac{2\Delta \zeta}{RT} (P - P_r)(T - T_r) \right) + \left( \frac{\Delta C_p}{RT} \left( T \ln \frac{T}{T_r} - 1 \right) + T_r \right) \] \]

The parameters of the selected equation are estimated using **regression techniques** on experimental data.
Part III: Heat and Mass Transfer Modelling
The pressure evolution of the device is given.

In order to determine the temperature evolution, we consider the following model:

In the **full device**:

- Energy conservation $\rightarrow$ **Conductive heat transfer Equation**.

In the **pressurized fluid and liquid food sample**:

- Momentum conservation $\rightarrow$ **Navier-Stokes Equations**. We assume: Fluids are **compressible and Newtonian** (like water) $\rightarrow$ **Stokes assumption**.

- Mass conservation $\rightarrow$ **Continuity equation**.

Note: Those both equations can be **neglected** in the solid food sample case when food sample **filling ratio is high enough**.
System of equations

\[
\begin{align*}
\rho C_p \frac{\partial T}{\partial t} - \nabla \cdot (k \nabla T) + \rho C_p \mathbf{u} \cdot \nabla T &= \alpha \frac{dP}{dt} \quad \text{en} \quad \Omega^* \times (0, t_f),
\\[4pt]
\rho \frac{\partial \mathbf{u}_F}{\partial t} - \nabla \cdot \eta (\nabla \mathbf{u}_F + \nabla \mathbf{u}_F^t) + \rho (\mathbf{u}_F \cdot \nabla) \mathbf{u}_F &= -\nabla P - \frac{2}{3} \nabla (\eta \nabla \cdot \mathbf{u}_F) - \rho g \quad \text{in} \quad \Omega_F^* \times (0, t_f),
\\[4pt]
\rho \frac{\partial \mathbf{u}_P}{\partial t} - \nabla \cdot \eta (\nabla \mathbf{u}_P + \nabla \mathbf{u}_P^t) + \rho (\mathbf{u}_P \cdot \nabla) \mathbf{u}_P &= -\nabla P - \frac{2}{3} \nabla (\eta \nabla \cdot \mathbf{u}_P) - \rho g \quad \text{in} \quad \Omega_P^* \times (0, t_f),
\\[4pt]
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}_F) &= 0 \quad \text{in} \quad \Omega_F^* \times (0, t_f),
\\[4pt]
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}_P) &= 0 \quad \text{in} \quad \Omega_P^* \times (0, t_f).
\end{align*}
\]

All physical parameters are assumed P-T dependent.
We consider the following **boundary conditions**:\\
\[
\begin{aligned}
    k \frac{\partial T}{\partial n} &= 0 \text{ in } \Gamma^* \setminus (\Gamma^*_r \cup \Gamma^*_up) \times (0, t_f), \\
    k \frac{\partial T}{\partial n} &= h(T_{amb} - T) \text{ in } \Gamma^*_{up} \times (0, t_f), \\
    T &= T_{ref} \text{ in } \Gamma^*_r \times (0, t_f), \\
    u_F &= 0 \text{ in } \Gamma^*_F \times (0, t_f), \\
    u_P &= 0 \text{ in } \Gamma^*_P \times (0, t_f), \\
    T &= T_0 \text{ in } \Omega^*, \\
    p &= 10^5 \text{ in } A_1 \times (0, t_f), \\
    p &= 10^5 \text{ in } A_2 \times (0, t_f).
\end{aligned}
\]
Numerical scheme

- Numerical tests computed in cylindrical coordinates using a **Finite Element Method**.

- Velocity and pressure spatial discretization is based on **P2–P1 Lagrange Finite Elements** satisfying the Ladyzhenskaya, Babuska and Brezzi (LBB) stability condition.

- The Time integration is performed using the Variable–Step–Variable–Order (VSVO) Backward Differentiation Formula (BDF)–based strategy.

- The nonlinear systems are solved with a **damped Newton method**.

- The algebraic linear systems are solved using Unsymmetric MultiFrontal Method for sparse linear systems (UMFPACK) combined with the stabilization technique Galerkin Least Squares (GLS).
Determination of physical parameters

- **Solid food sample (Tylose):** We have chosen tylose as an example of solid type food (*similar properties to meat*). The coefficients are obtained from literature for **atmospheric pressure**. A **rescaling procedure and a piecewise linear interpolation** have been applied for other values of pressure.

- **Liquid medium:** The physical parameters are supposed to be equal to those of water:
  - $\rho, C_p,$ and $k$ are computed through a **shifting approach** (using phase diagram) from **atmospheric pressure**.
  - $\alpha$ we use a **known expression**.
  - $\eta$ is computed by a **piecewise linear interpolation from given data**.
Part IV: Coupled model
Coupling models

In order to determine the **time and spatial** evolution of the activity in the food sample:

**Solid case:**

The particles of the food are **still**. The activity $A$ of a particle located at the point $x \in \Omega_F$ at time $t$:

$$A(x, t) = A(x, 0) \exp \left( - \int_0^t \kappa(P(\sigma), T(x, \sigma)) \, d\sigma \right).$$

**Liquid case:**

Due to mass transfer, the particles **move** in the food domain $\Omega_F$. In this case, for each point $x \in \Omega_F$ we consider the trajectory $X$ of a food particle that ends at point $x$.

$$A(x, t) = A(X(0), 0) \exp \left( - \int_0^t \kappa(P(\sigma), T(X(\sigma), \sigma)) \, d\sigma \right).$$
Sensitivity analysis

In practice:
- The model coefficients are usually approximated using experimental data with a standard deviation lower than $\pm 5\%$.
- Due to equipment limitations, some experimental discrepancies could occur during the process.

Objective: study the impact of these errors on the temperature and enzymatic activity evolutions.

We generate $N \in \mathbb{N}$ perturbed models from the original one, with coefficients perturbed randomly by $\pm 5\%$.

Then, we compute the mean error committed in the temperature and activity.
Incomplete models

Objective: reduce the computational complexity of the model.

We consider ‘simplified models’, cheaper to evaluate and with results close enough to the full models:

- **Solid food (SCC):** We consider constant coefficients, by setting $C_p$, $k$, $\alpha$, $\rho$ and $\eta$ to a mean value.

- **Liquid food (LCC):** As previously we consider constant coefficients except $\rho$.

- **Liquid food (LB):** Boussinesq approximation: considering the incompressible Navier-Stokes equations and constant coefficients except $\rho$ when combined with the gravitational force.

In all cases, we compute the error committed in the temperature and activity.
Part V: Numerical experiments
Considered enzymes

- **Bacillus Subtilis α—Amylase (BSAA):** It is an enzyme produced by a bacteria called Bacillus Subtilis. This bacteria, present in the ground, can contaminate food and in rare occasions cause **intoxications**. This enzyme catalyzes the hydrolysis of starch, generating sugars (as maltose) that can modify the taste of the aliment.

- **Lipoxygenase (LOX):** This enzyme is present in various plants and vegetables such as green beans and green peas. It is responsible of the appearance of **undesirable aromas** in those products.

- **Carrot Pectin Methyl–Esterase (CPE):** Common in most vegetables. It can be present in vegetable juices producing low–methoxyl pectin. This process **reduces juice viscosity and generates cloud loss** (affecting juice flavor, color, texture and aroma).
Considered treatments

We consider a **big solid and a small liquid** food sample submitted to one of the following treatment:

- **Process P1:** The initial temperature is $T_0 = 40^\circ C$ in the device and $22^\circ C$ in the food sample and the pressure is linearly increased during the first 305 seconds until reaching 600 MPa.

- **Process P2:** The initial temperature is $T_0 = 40^\circ C$ in the whole domain $\Omega$ and the pressure is linearly increased (with the same slope as before) during the first 183 seconds until reaching 360 MPa.
Temperature analysis

Final temperature distribution in the whole domain:
Temperature analysis

Final temperature distribution in the food sample:
Temperature analysis

Example of temperature distribution (liquid-P1):
Temperature analysis

Mean temperature evo:

![Graph 1](image1)

![Graph 2](image2)

![Graph 3](image3)

![Graph 4](image4)
Temperature analysis

Sensitivity analysis: **Mean Relative Temperature Error** (in %)

<table>
<thead>
<tr>
<th>Process</th>
<th>Food</th>
<th>Whole domain</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>Solid</td>
<td>2.74</td>
<td>3.34</td>
</tr>
<tr>
<td>P2</td>
<td>Solid</td>
<td>2.75</td>
<td>2.93</td>
</tr>
<tr>
<td>P1</td>
<td>Liquid</td>
<td>2.68</td>
<td>2.70</td>
</tr>
<tr>
<td>P2</td>
<td>Liquid</td>
<td>2.83</td>
<td>2.67</td>
</tr>
</tbody>
</table>
# Temperature analysis

Incomplete models: **Relative Temperature Error** (in %)

<table>
<thead>
<tr>
<th>Process</th>
<th>Model</th>
<th>Whole domain</th>
<th>Sample</th>
<th>Comp. Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>SFull</td>
<td>—</td>
<td>—</td>
<td>53</td>
</tr>
<tr>
<td>P2</td>
<td>SFull</td>
<td>—</td>
<td>—</td>
<td>51</td>
</tr>
<tr>
<td>P1</td>
<td>SCC</td>
<td>0.77</td>
<td>4.77</td>
<td>4</td>
</tr>
<tr>
<td>P2</td>
<td>SCC</td>
<td>0.10</td>
<td>0.52</td>
<td>4</td>
</tr>
<tr>
<td>P1</td>
<td>LFull</td>
<td>—</td>
<td>—</td>
<td>3135</td>
</tr>
<tr>
<td>P2</td>
<td>LFull</td>
<td>—</td>
<td>—</td>
<td>4141</td>
</tr>
<tr>
<td>P1</td>
<td>LCC</td>
<td>0.41</td>
<td>2.07</td>
<td>2459</td>
</tr>
<tr>
<td>P2</td>
<td>LCC</td>
<td>0.06</td>
<td>0.20</td>
<td>2877</td>
</tr>
<tr>
<td>P1</td>
<td>LB</td>
<td>0.37</td>
<td>1.96</td>
<td>2196</td>
</tr>
<tr>
<td>P2</td>
<td>LB</td>
<td>0.08</td>
<td>0.22</td>
<td>2475</td>
</tr>
</tbody>
</table>
Enzymatic analysis

Final temperature distribution in the food sample:
Enzymatic analysis

LOX final activity distribution in the food sample:
Enzymatic analysis

LOX Mean Activity evolution:

![Graph 1](image1.png)

![Graph 2](image2.png)

![Graph 3](image3.png)

![Graph 4](image4.png)
Enzymatic analysis

Example of temperature and LOX activity distribution (Solid-P1):
Enzymatic analysis

<table>
<thead>
<tr>
<th>Process</th>
<th>Food</th>
<th>BSAA</th>
<th>LOX</th>
<th>CPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>Solid</td>
<td>4.60</td>
<td>6.81</td>
<td>2.28</td>
</tr>
<tr>
<td>P2</td>
<td>Solid</td>
<td>5.01</td>
<td>6.43</td>
<td>0.52</td>
</tr>
<tr>
<td>P1</td>
<td>Liquid</td>
<td>4.02</td>
<td>7.45</td>
<td>2.40</td>
</tr>
<tr>
<td>P2</td>
<td>Liquid</td>
<td>3.97</td>
<td>2.51</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Sensitivity analysis: **Mean Activity Error** (in %)
## Enzymatic analysis

### Incomplete models: Activity Error (in %)

<table>
<thead>
<tr>
<th>Process</th>
<th>Model</th>
<th>BSAA</th>
<th>LOX</th>
<th>CPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>SCC</td>
<td>7.44</td>
<td>5.20</td>
<td>1.33</td>
</tr>
<tr>
<td>P2</td>
<td>SCC</td>
<td>0.96</td>
<td>1.11</td>
<td>0.10</td>
</tr>
<tr>
<td>P1</td>
<td>LCC</td>
<td>2.81</td>
<td>1.75</td>
<td>0.40</td>
</tr>
<tr>
<td>P2</td>
<td>LCC</td>
<td>1.14</td>
<td>0.65</td>
<td>0.06</td>
</tr>
<tr>
<td>P1</td>
<td>LB</td>
<td>3.04</td>
<td>2.00</td>
<td>0.45</td>
</tr>
<tr>
<td>P2</td>
<td>LB</td>
<td>2.23</td>
<td>1.31</td>
<td>0.12</td>
</tr>
</tbody>
</table>
Conclusions and perspectives
Conclusion and perspectives

- The mathematical models described in this paper provide a **useful design tool**.

- The model is **robust**.

- Several simplified versions of the full models are proposed and are **suitable** for optimization procedures.

Future work:

- **New model** for enzymatic inactivation.

- **Identify** the most important enzymes to be inactivated and the organoleptic properties to be preserved.

- Perform optimization techniques in order to **reduce the enzymatic activities and preserve organoleptic properties of the food**, without using high temperatures.
Conclusion and perspectives

!!! Thank You !!!