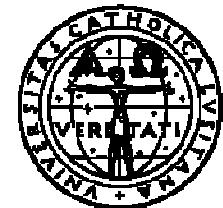


The Role of Mathematical Modelling in Chemical and Food Engineering Studies

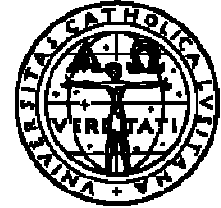
Teresa R. S. Brandão, Cristina L. M. Silva

Escola Superior de Biotecnologia - UCP, Portugal



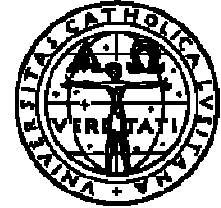
FEMo'03 - 2003 International Workshop on Finite Element Modelling in Chemical and Food Engineering
University of Salerno - Italy, October 9 - 10, 2003

OUTLINE



- General Introduction
- Mathematical Modelling
 - Processes
 - Safety and Quality
- Experimental Design and Data Analysis
- Case Studies

OUTLINE



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GENERAL INTRODUCTION



Model → mathematical expression

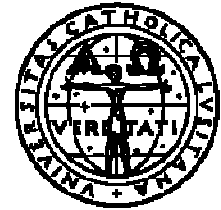
$$y_i = f(x_{ij}, \theta_k) + \varepsilon_i$$

$i=1,2,\dots,n$ (number of experimental runs/observations)

$j=1,2,\dots,v$

$k=1,2,\dots,p$

GENERAL INTRODUCTION

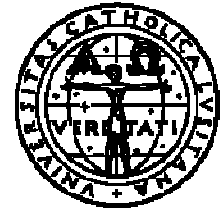


Modeling and Simulation

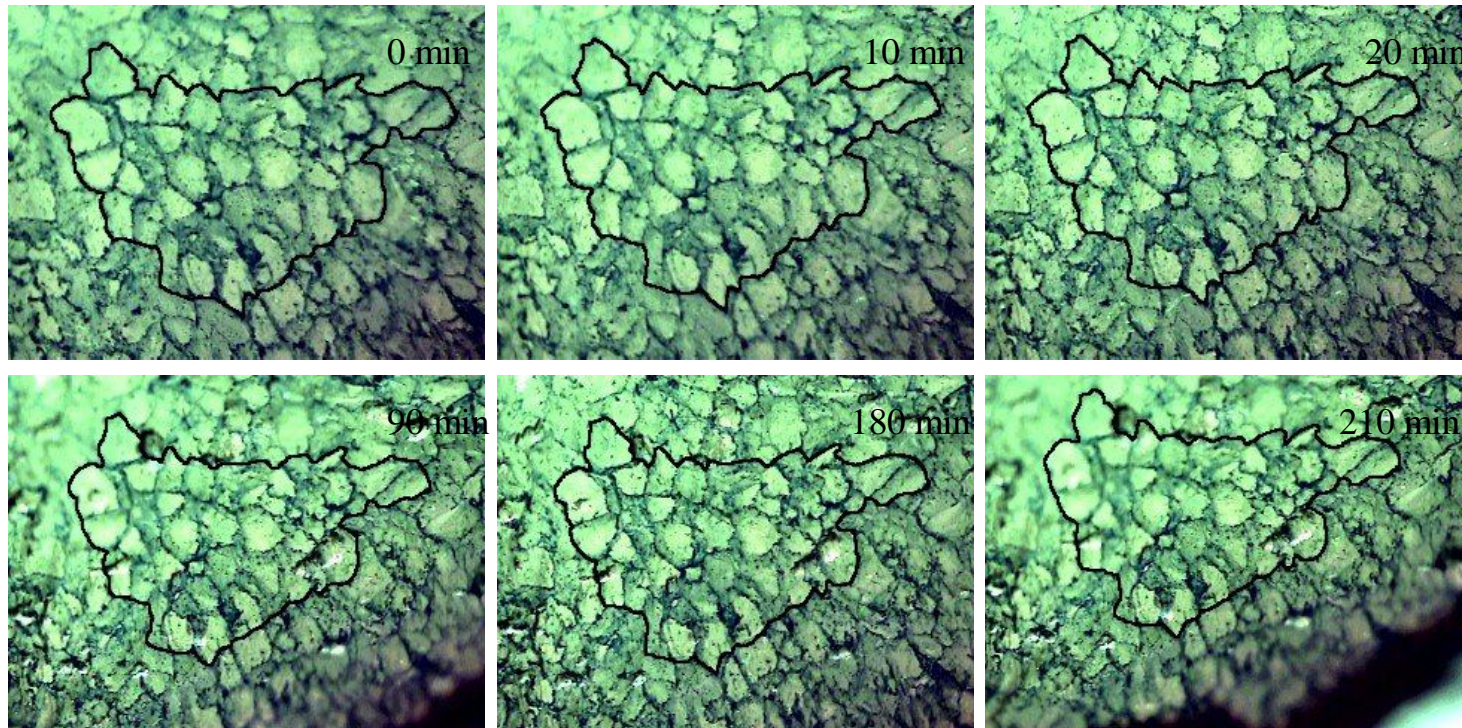
Makes it possible to:

- ▶ Gain more knowledge about the process and the effects on the product;

Microscopic Shrinkage

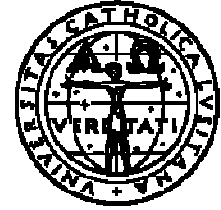


Cellular geometric features quantified by **image analysis**



Images of grape cells shrinkage at 40° C as a function of time.

GENERAL INTRODUCTION



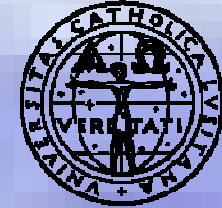
Modeling and Simulation

Makes it possible to:

Gain more knowledge about the process and the effects on the product;

▶ Reduce the number of experiments in the development stage;

Quality of Frozen Vegetables



Storage

• Storage
Time-Temperature

$T_1 > T_2 > T_3$

Accelerated Life Tests (ALT)

Product Tolerance

Product Shelf-Life

Quality Factor (A)

Vitamins degradation;
Pigments changes;
Colour changes;
Aroma;
Texture.

GENERAL INTRODUCTION

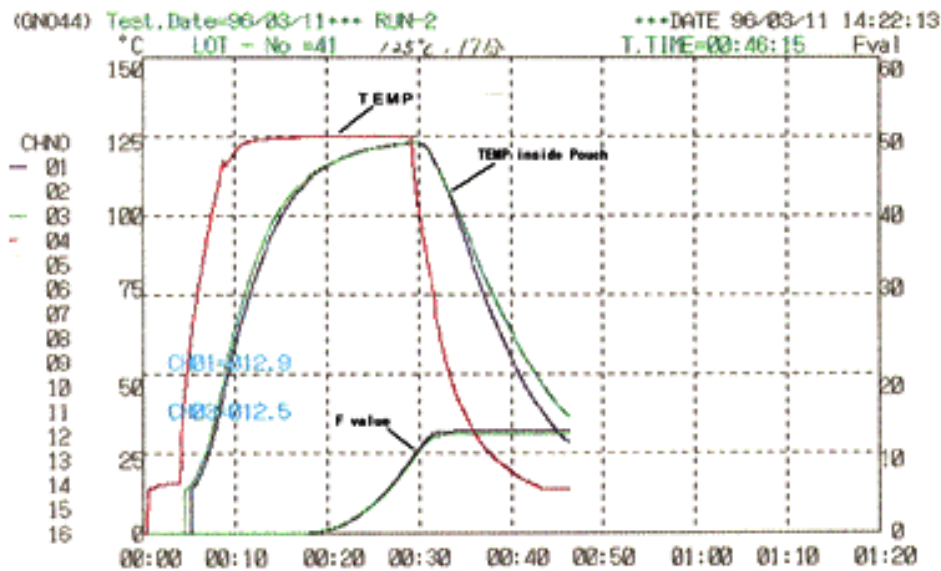
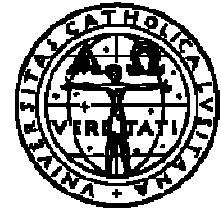


Modeling and Simulation

Makes it possible to:

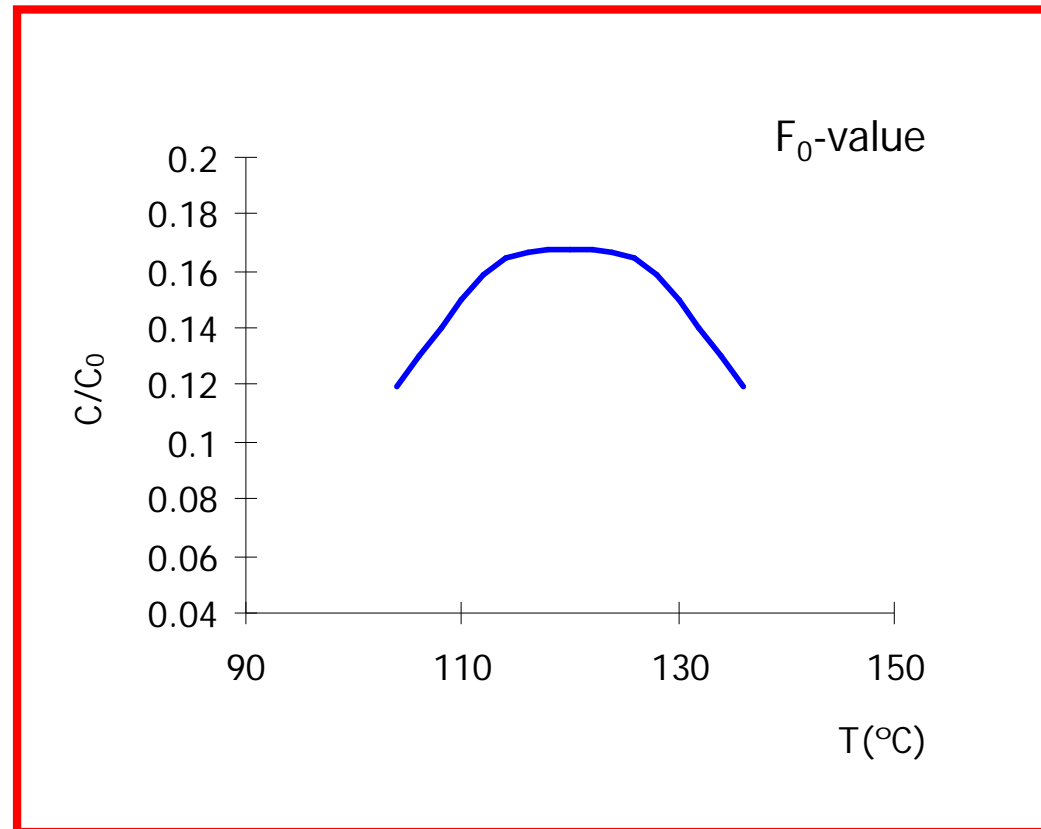
- ▶ Optimize the process with respect to different parameters, such as quality;

Pre-packaged (canned) foods





Calculation of optimal sterilisation conditions



GENERAL INTRODUCTION

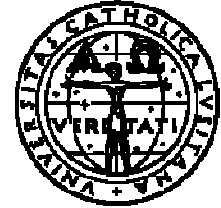


Modeling and Simulation

Makes it possible to:

Optimize the process with respect to different parameters, such as quality;

▶ Dimension and evaluate new process lines;

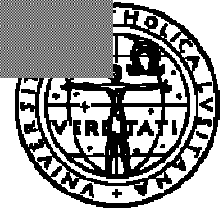


BUGDEATH – project (QLRT-2001-01415)

**Predicting the reduction in microbes on the
surface of foods during pasteurization**

<http://www.frperc.bris.ac.uk/bugdeath.htm>

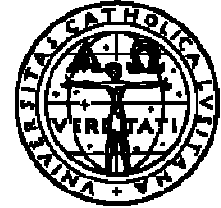
Bugdeath heat treatment apparatus



FEMo'03 - 2003 International Workshop on Finite Element Modelling in Chemical and Food Engineering
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GENERAL INTRODUCTION

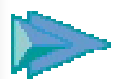


Modeling and Simulation

Makes it possible to:

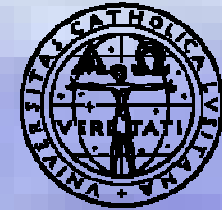
Optimize the process with respect to different parameters, such as quality;

Dimension and evaluate new process lines;



Study the influence on the product during process disturbances

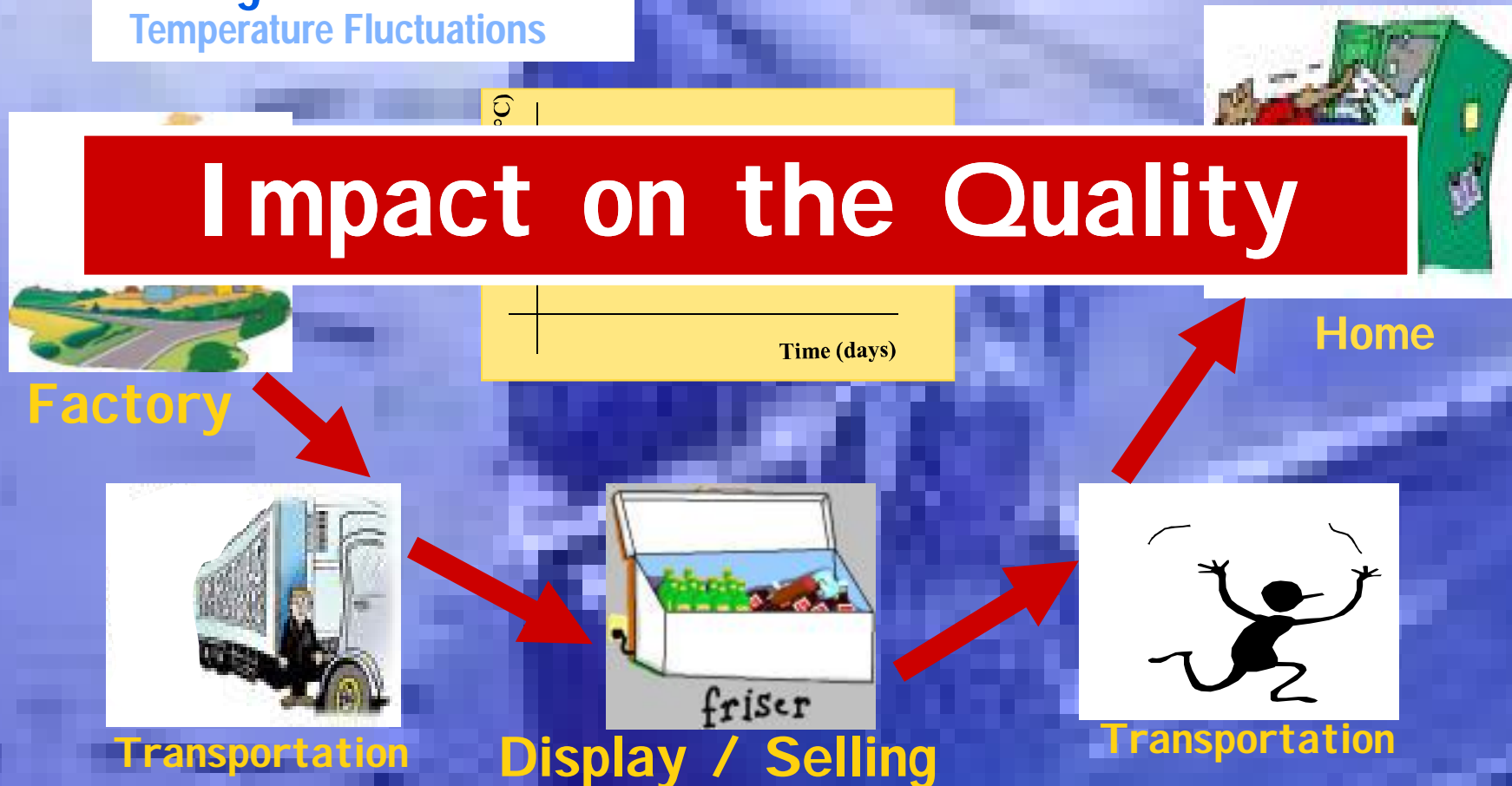
Quality of Frozen Vegetables



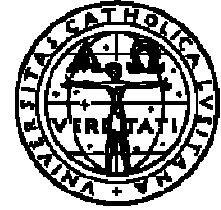
Storage

- Storage
Temperature Fluctuations

Impact on the Quality



GENERAL INTRODUCTION



■ Models should:

predict the response variable accurately

GENERAL INTRODUCTION



■ Models should:

predict the response variable accurately

adequacy of the model

GENERAL INTRODUCTION



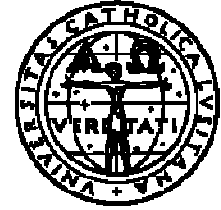
■ Models should:

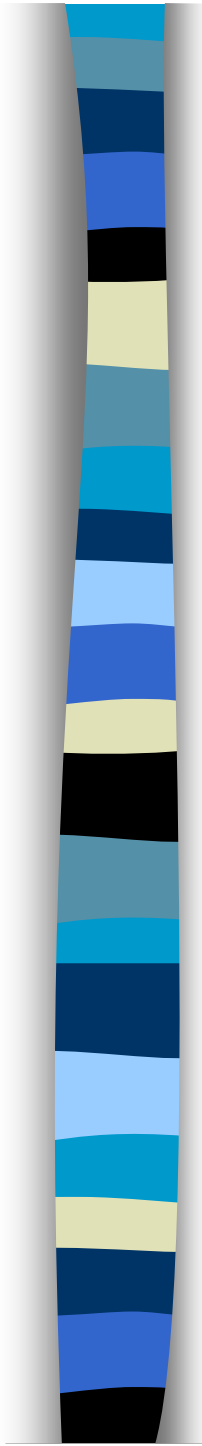
predict the response variable accurately

adequacy of the model

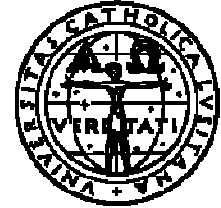
parameters quality

OUTLINE



- 
- General Introduction
 - **Mathematical Modelling**
 - Processes
 - Safety and Quality
 - Experimental Design and Data Analysis
 - Case Studies

MATHEMATICAL MODELLING

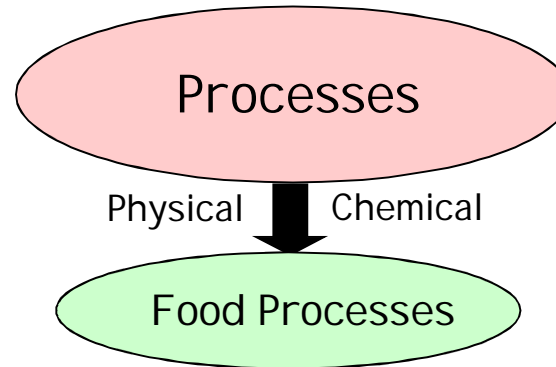


Transport phenomena

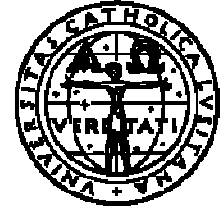
- heat transfer
- mass transfer
- momentum transfer

Reaction kinetics

Properties



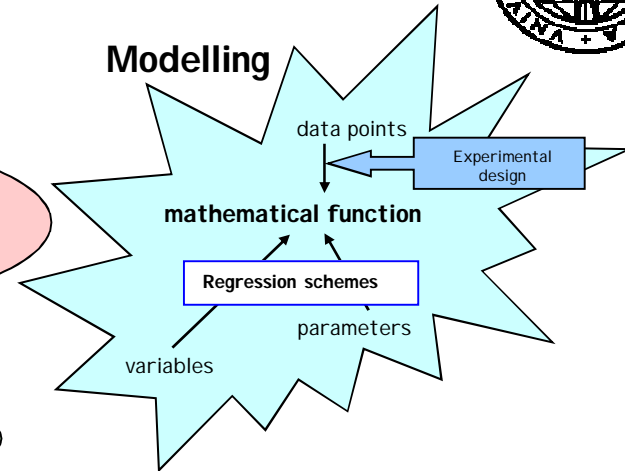
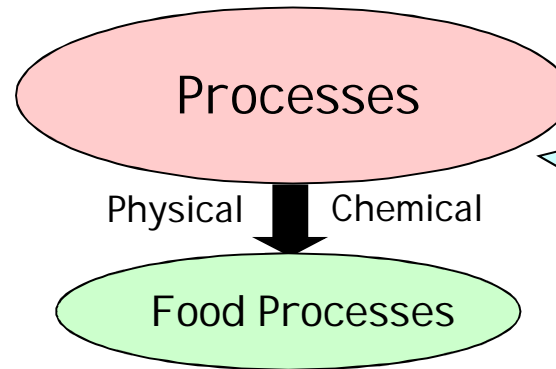
MATHEMATICAL MODELLING



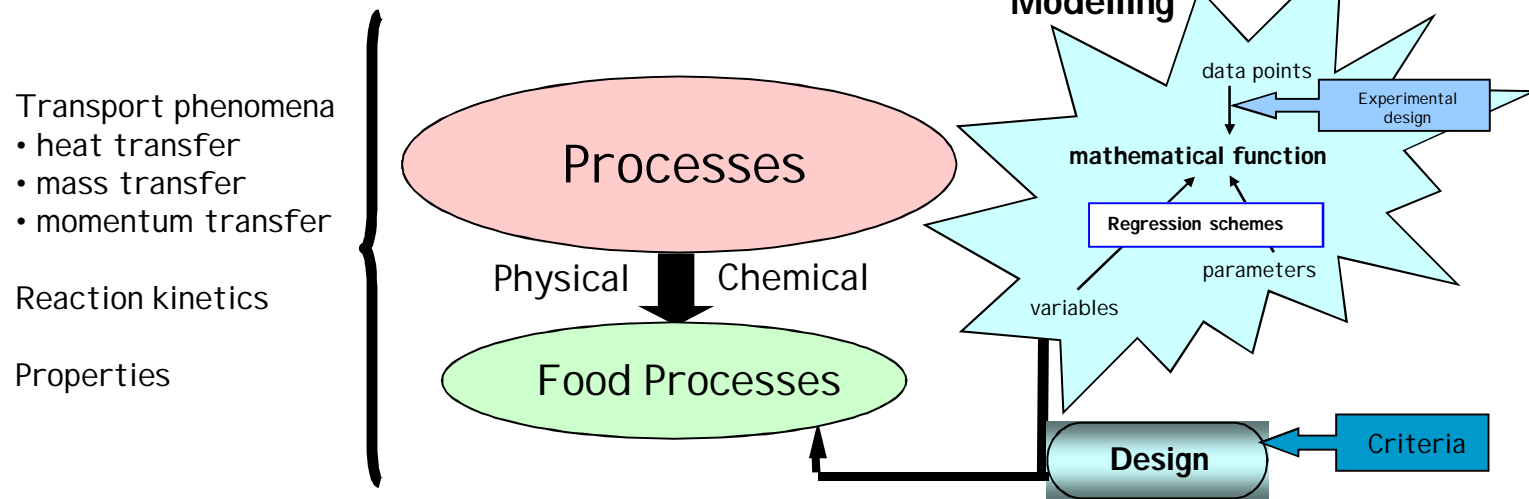
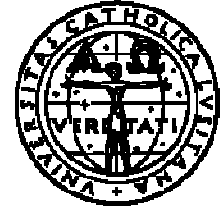
Transport phenomena
• heat transfer
• mass transfer
• momentum transfer

Reaction kinetics

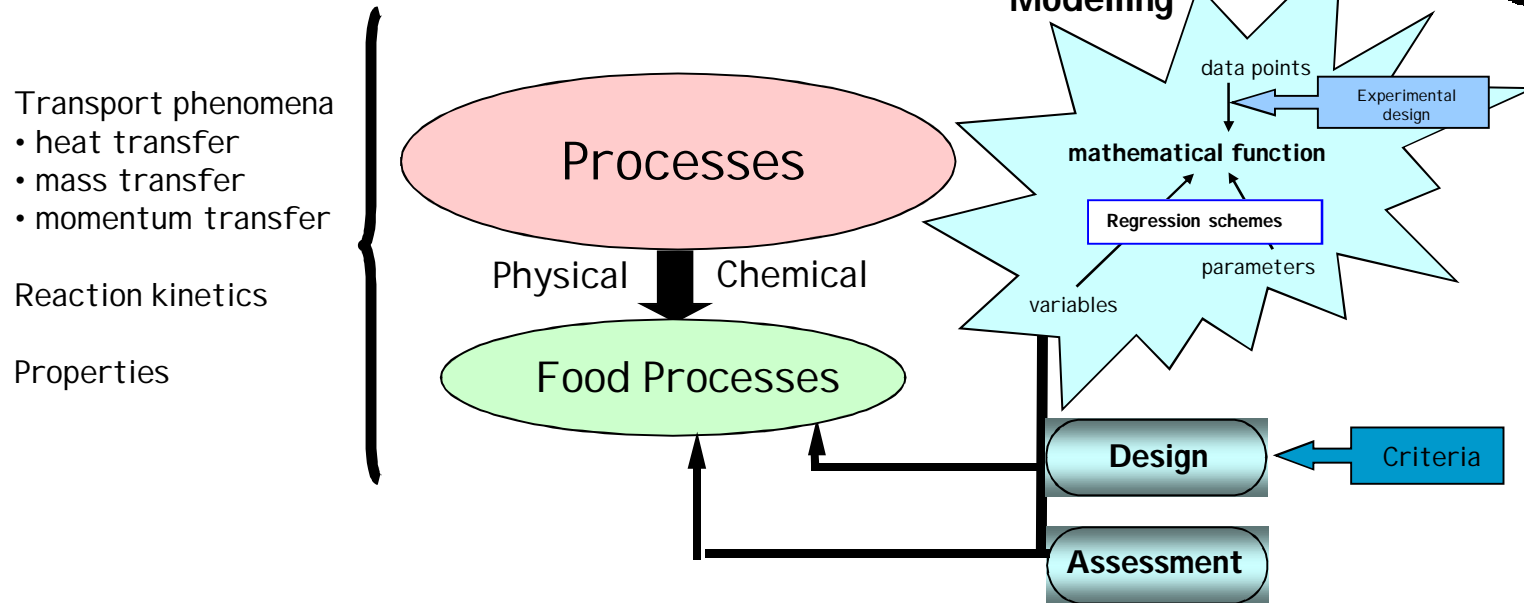
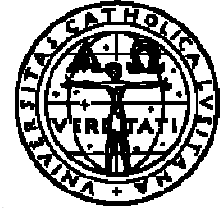
Properties



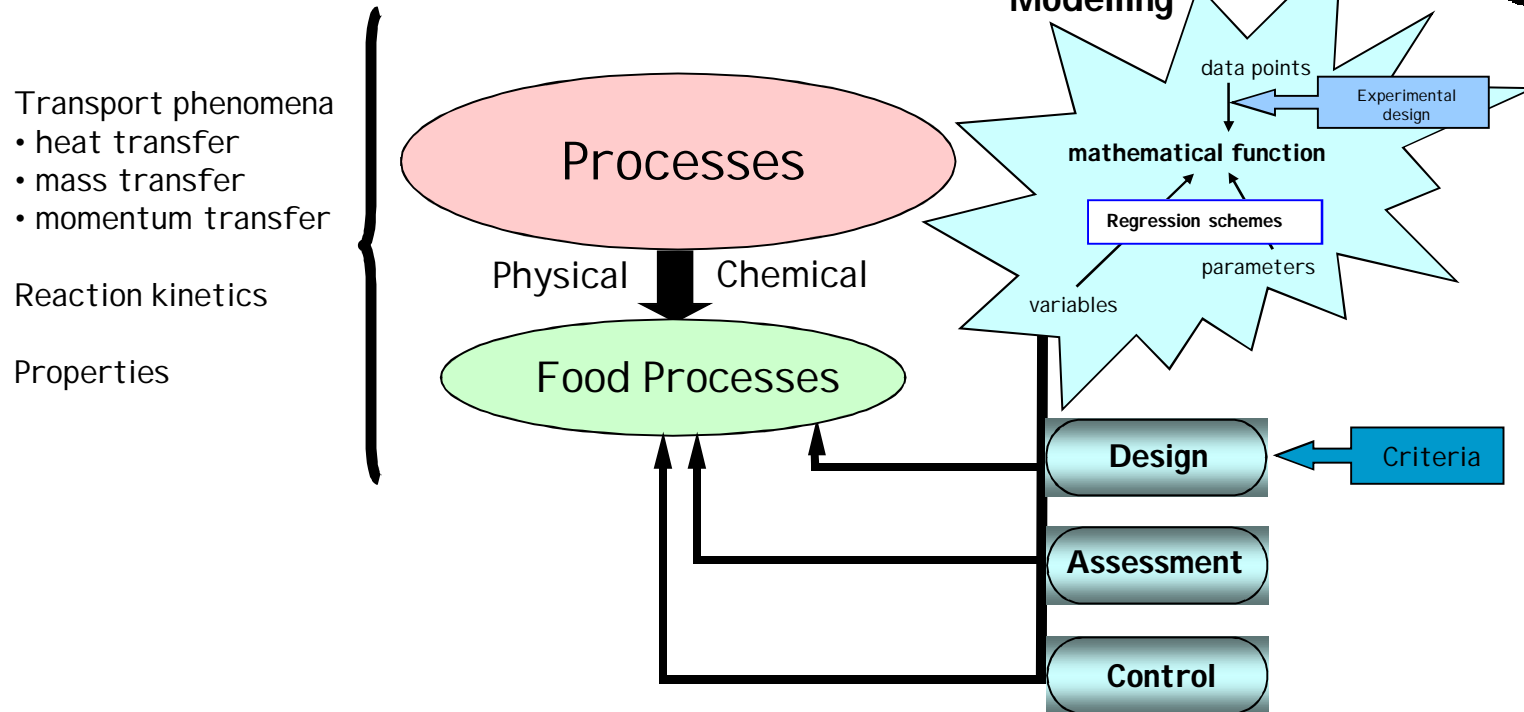
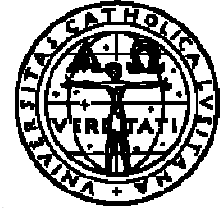
MATHEMATICAL MODELLING



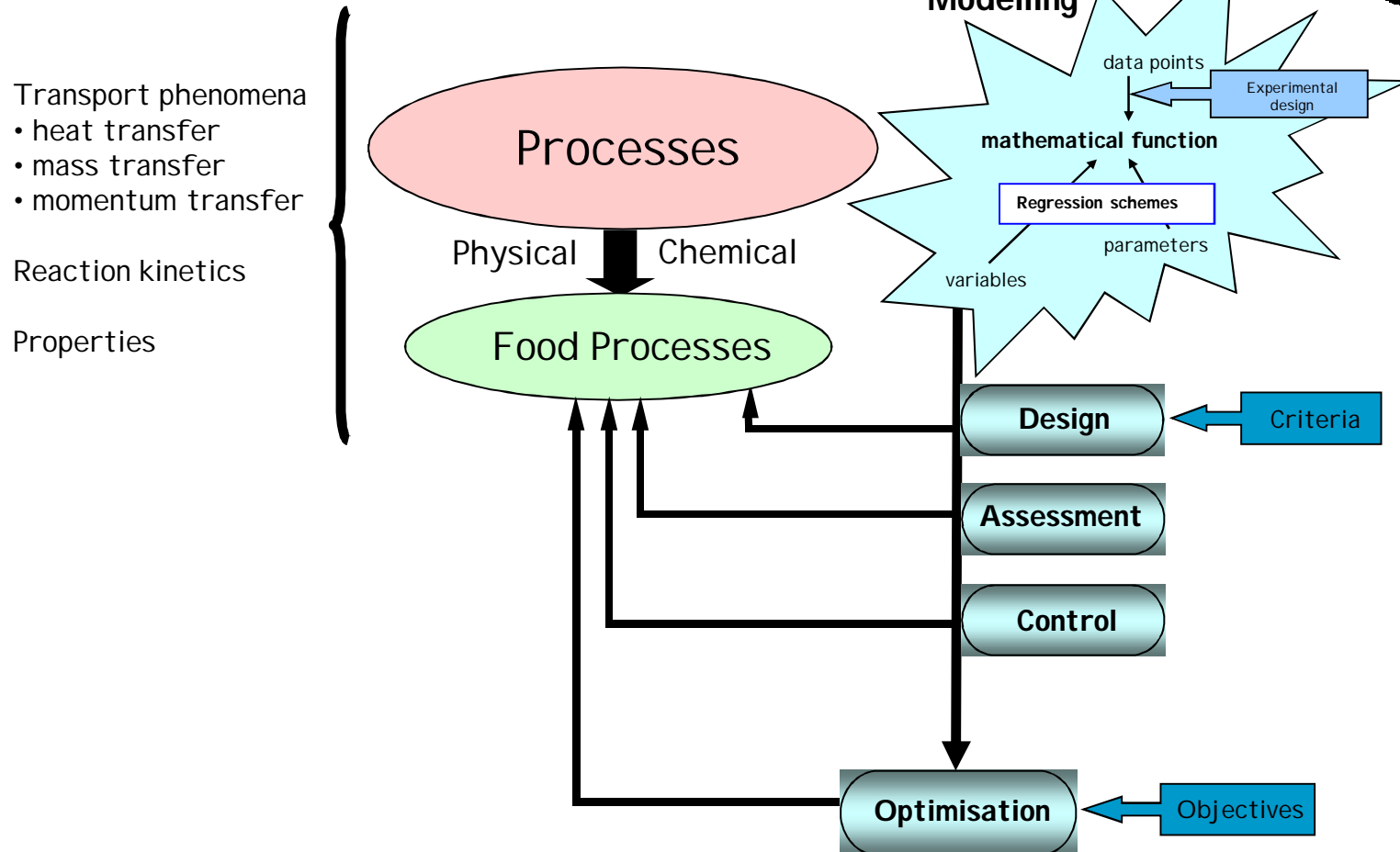
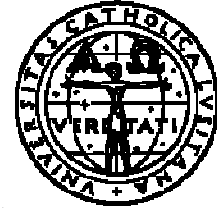
MATHEMATICAL MODELLING



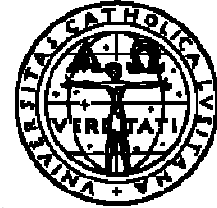
MATHEMATICAL MODELLING



MATHEMATICAL MODELLING



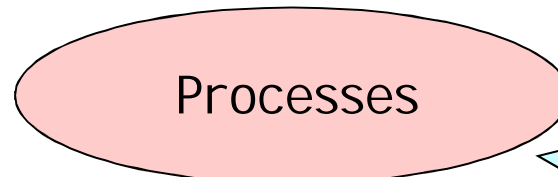
MATHEMATICAL MODELLING



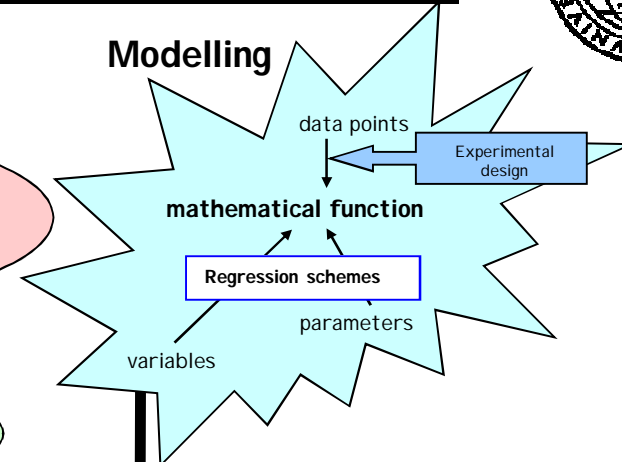
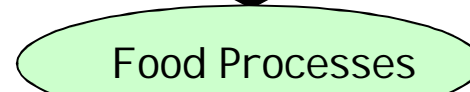
Transport phenomena
• heat transfer
• mass transfer
• momentum transfer

Reaction kinetics

Properties



Physical Chemical



Design

Criteria

Assessment

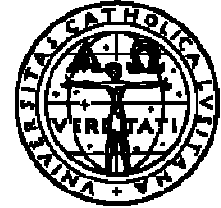
Control

Optimisation

Objectives

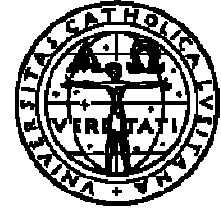


MATHEMATICAL MODELLING

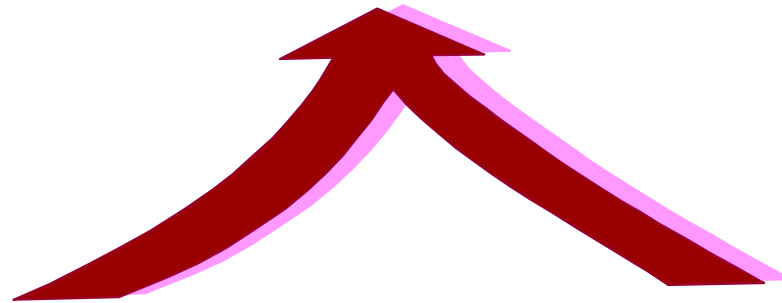


- ◆ Mechanistic models are more complex, but in general allow accurate predictions
- ◆ Empirical models are much simpler, but usually are appropriate to limited practical uses

MATHEMATICAL MODELLING

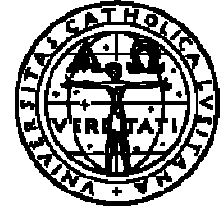


- ◆ Mechanistic models are more complex, but in general allow accurate predictions
- ◆ Empirical models are much simpler, but usually are appropriate to limited practical uses



Balance of the advantages and disadvantages, depending on the final purpose.

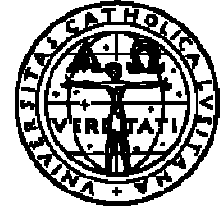
MATHEMATICAL MODELLING



Transport phenomena

- heat transfer
- mass transfer
- momentum transfer

MATHEMATICAL MODELLING



Transport phenomena

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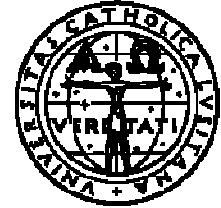
Γ - property

t - time

x, y, z - space coordinates

$$\frac{\partial \Gamma}{\partial t} = \delta \left(\frac{\partial^2 \Gamma}{\partial x^2} + \frac{\partial^2 \Gamma}{\partial y^2} + \frac{\partial^2 \Gamma}{\partial z^2} \right)$$

MATHEMATICAL MODELLING



Transport phenomena

- heat transfer
- mass transfer
- momentum transfer

Generalized diffusion
coefficient

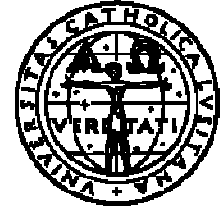
Γ - property

t - time

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$$\frac{\partial \Gamma}{\partial t} = \delta \left(\frac{\partial^2 \Gamma}{\partial x^2} + \frac{\partial^2 \Gamma}{\partial y^2} + \frac{\partial^2 \Gamma}{\partial z^2} \right)$$

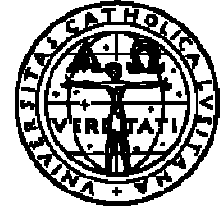
MATHEMATICAL MODELLING



Types of Solutions:

- Analytical
- Numerical

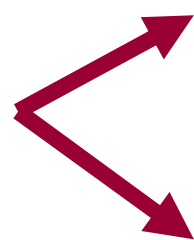
MATHEMATICAL MODELLING



Types of Solutions:

- Analytical

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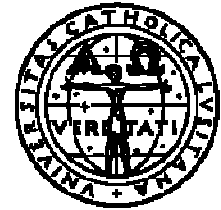


Finite Differences

Finite Elements

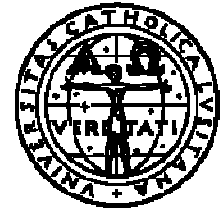


MATHEMATICAL MODELLING



Difficulties in food processes modelling:

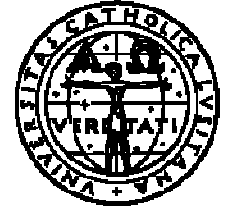
MATHEMATICAL MODELLING



Difficulties in food processes modelling:

- ▀ Dynamic processes

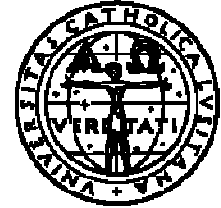
MATHEMATICAL MODELLING



Difficulties in food processes modelling:

- ▶ Dynamic processes
- ▶ Complexity and heterogeneity of products

MATHEMATICAL MODELLING

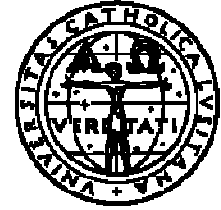


Difficulties in food processes modelling:

- ▶ Dynamic processes
- ▶ Complexity and heterogeneity of products
- ▶ Structural and physicochemical changes



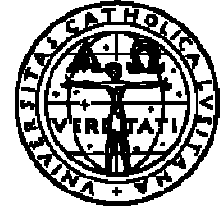
MATHEMATICAL MODELLING



Kinetic Studies:

Allow the quantification of the extension and rate of production/consumption of any substance

MATHEMATICAL MODELLING



Kinetic Studies:

Allow the quantification of the extension and rate of production/consumption of any substance



Safety

MATHEMATICAL MODELLING



Kinetic Studies:

Allow the quantification of the extension and rate of production/consumption of any substance



Safety



Quality

MATHEMATICAL MODELLING

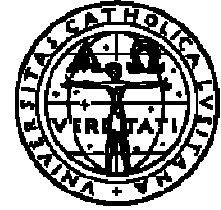


Safety and **Quality** depend on:

Intrinsic factors

Extrinsic factors

MATHEMATICAL MODELLING



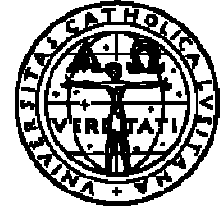
Safety and **Quality** depend on:

Intrinsic factors

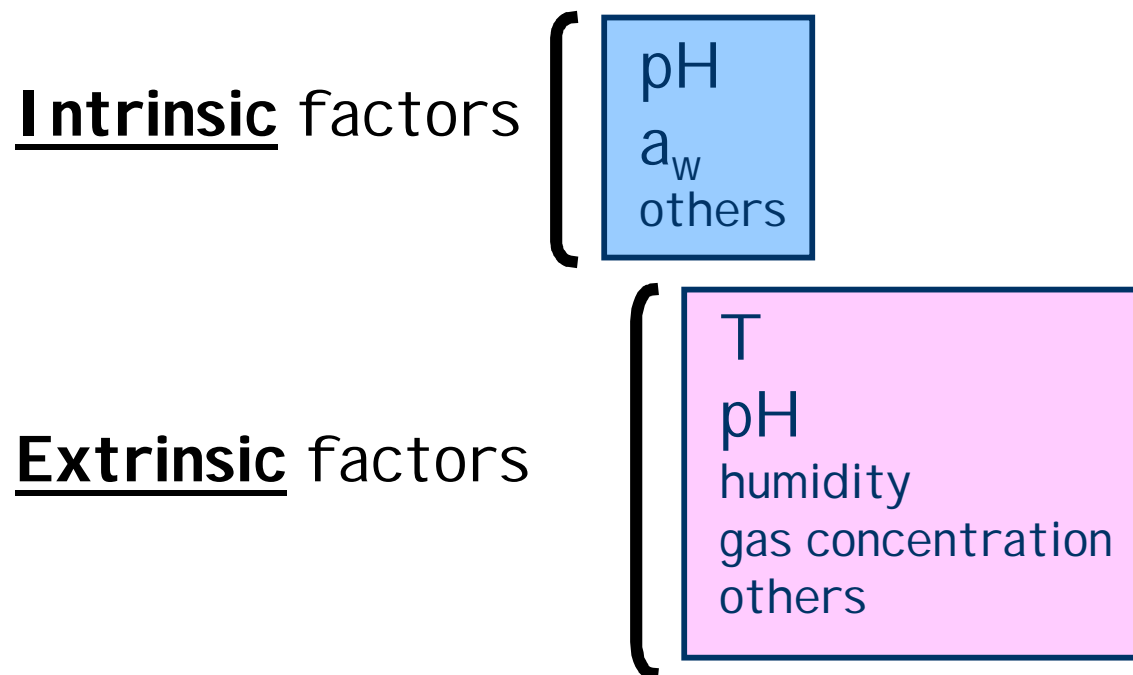
pH
 a_w
others

Extrinsic factors

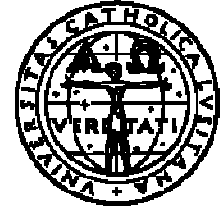
MATHEMATICAL MODELLING



Safety and **Quality** depend on:

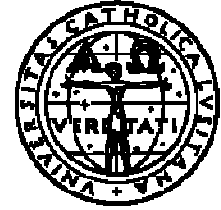


OUTLINE



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EXPERIMENTAL DESIGN AND DATA ANALYSIS



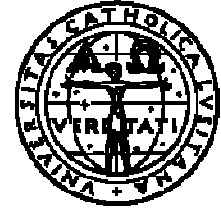
Model Validation:

- Heuristic sampling
- Experimental design

Minimize variance of:

- *predicted response*
- *parameter estimates*

EXPERIMENTAL DESIGN AND DATA ANALYSIS



Data Analysis:

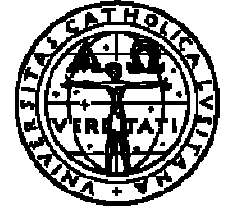
- Regression schemes

$$SSR = \sum_{i=1}^n e_i^2 = \sum_{i=1}^n [y_i - f(x_{ij}, \theta_k)]^2$$

Least-squares
method

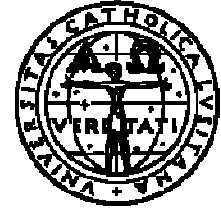
- Analysis of residuals

CONCLUSION



A model is never better than its parameters

OUTLINE



- General Introduction
- Mathematical Modelling
 - Processes
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- Experimental Design and Data Analysis
- ■ Case Studies

1st CASE STUDY



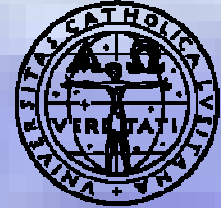
Quality of Frozen Vegetables and Fruits: Influence of Storage

Green Beans

Watercress

Strawberry

Quality of Frozen Vegetables



Storage

- **Storage**
Temperature (-18°C)

Phenomena

- Losses of water
- Recrystalization

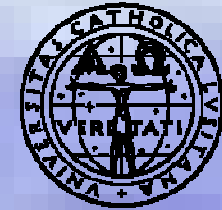
Changes

- Losses of aroma
- Degradation of colour
- Degradation of nutrients
- Losses of texture

**Influence on
Final Product
Quality**

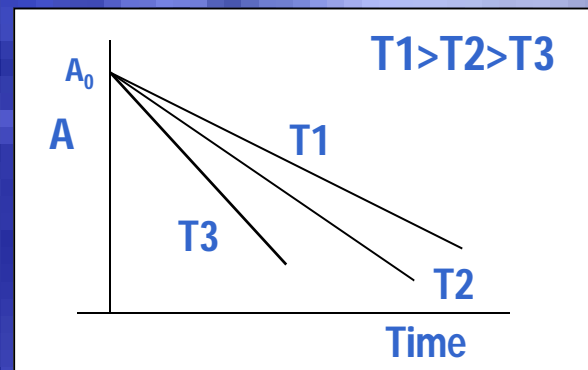
**h Temperature
i Quality**

Quality of Frozen Vegetables



Storage

- **Storage**
Time-Temperature



Product Tolerance

Product Shelf-Life

Quality Factor (A)

Vitamins degradation;
Pigments changes;
Colour changes;
Aroma;
Texture.

Quality of Frozen Vegetables

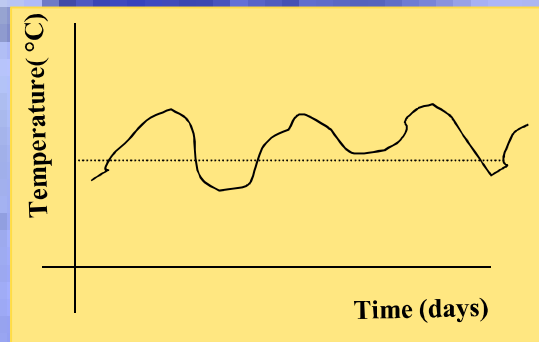


Storage

- Storage Temperature Fluctuations



Factory



Home



Transportation

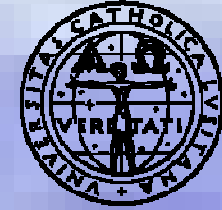


Display / Selling



Transportation

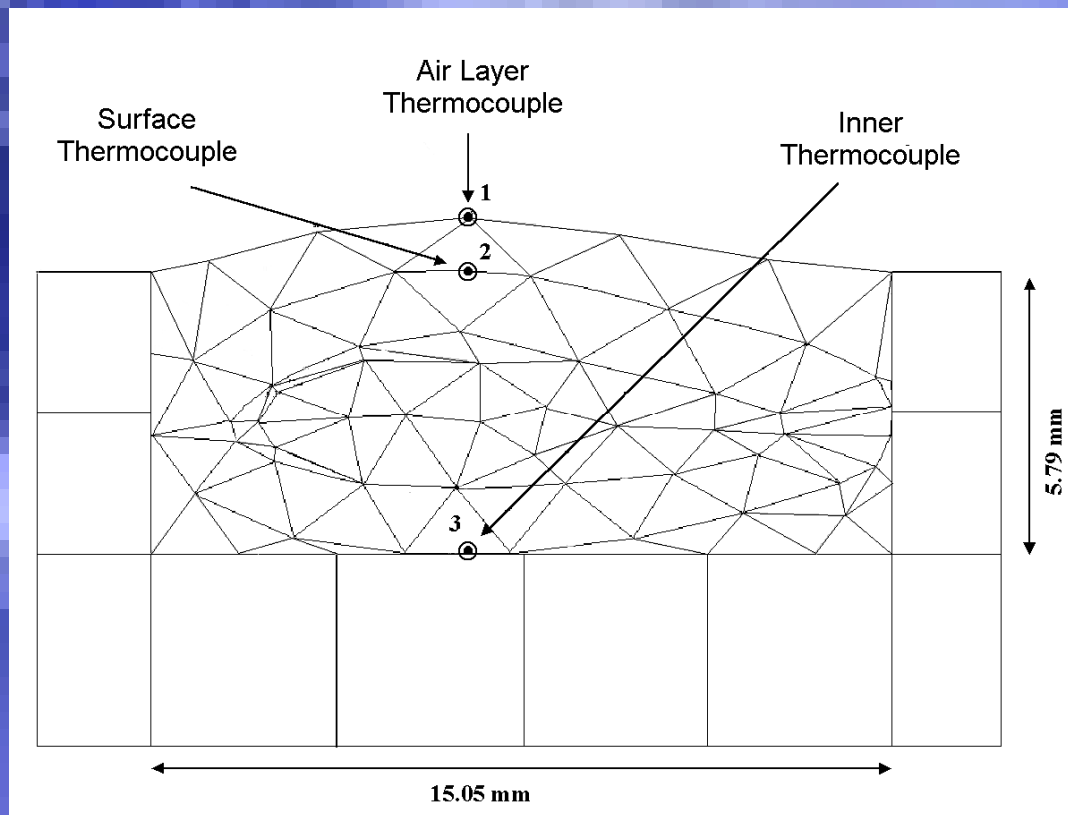
Quality of Frozen Vegetables



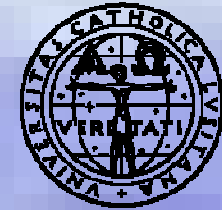
Storage

- **Storage**
Determination of physical properties

Inverse Problem:
Experimental data
against model
predicted data

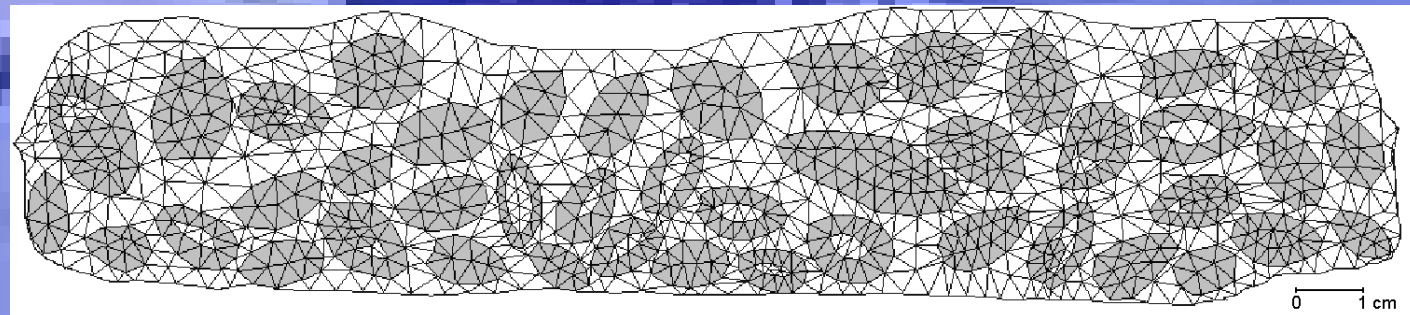


Quality of Frozen Vegetables



Storage

- **Storage**
Frozen Green Beans



**Simulate expected quality retention
along the whole distribution chain**

2nd CASE STUDY



**Integrated approach on pilot
convective drying, solar drying
and microstructural changes**

Introduction



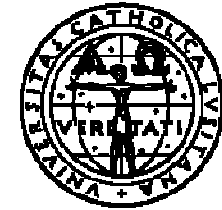
Solar Drying



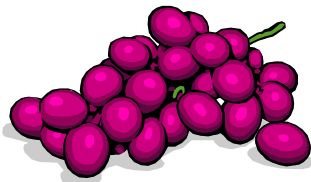
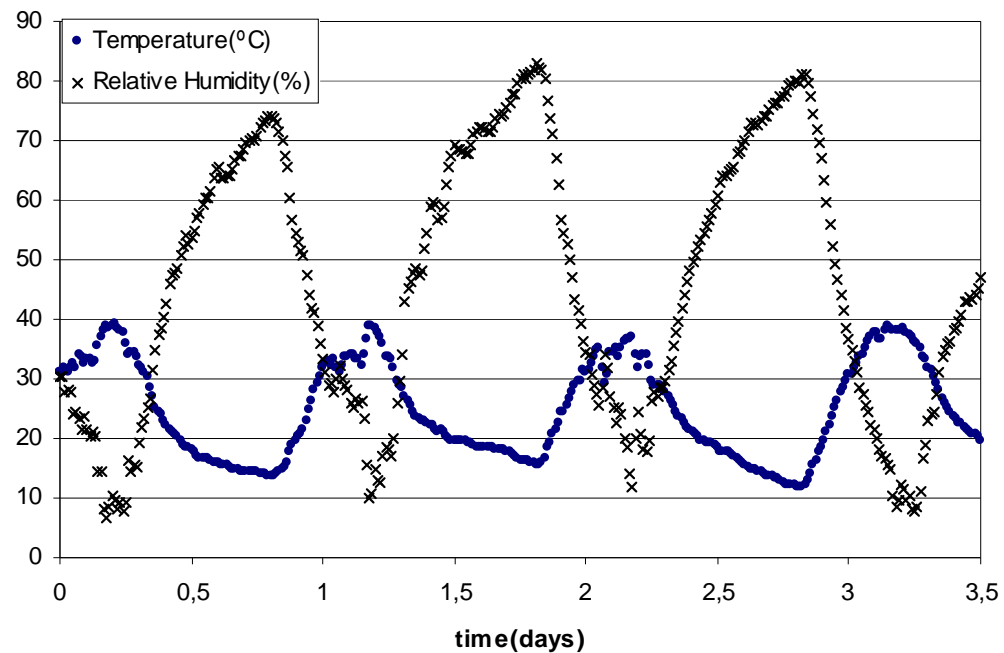
Solar dryer.



Introduction

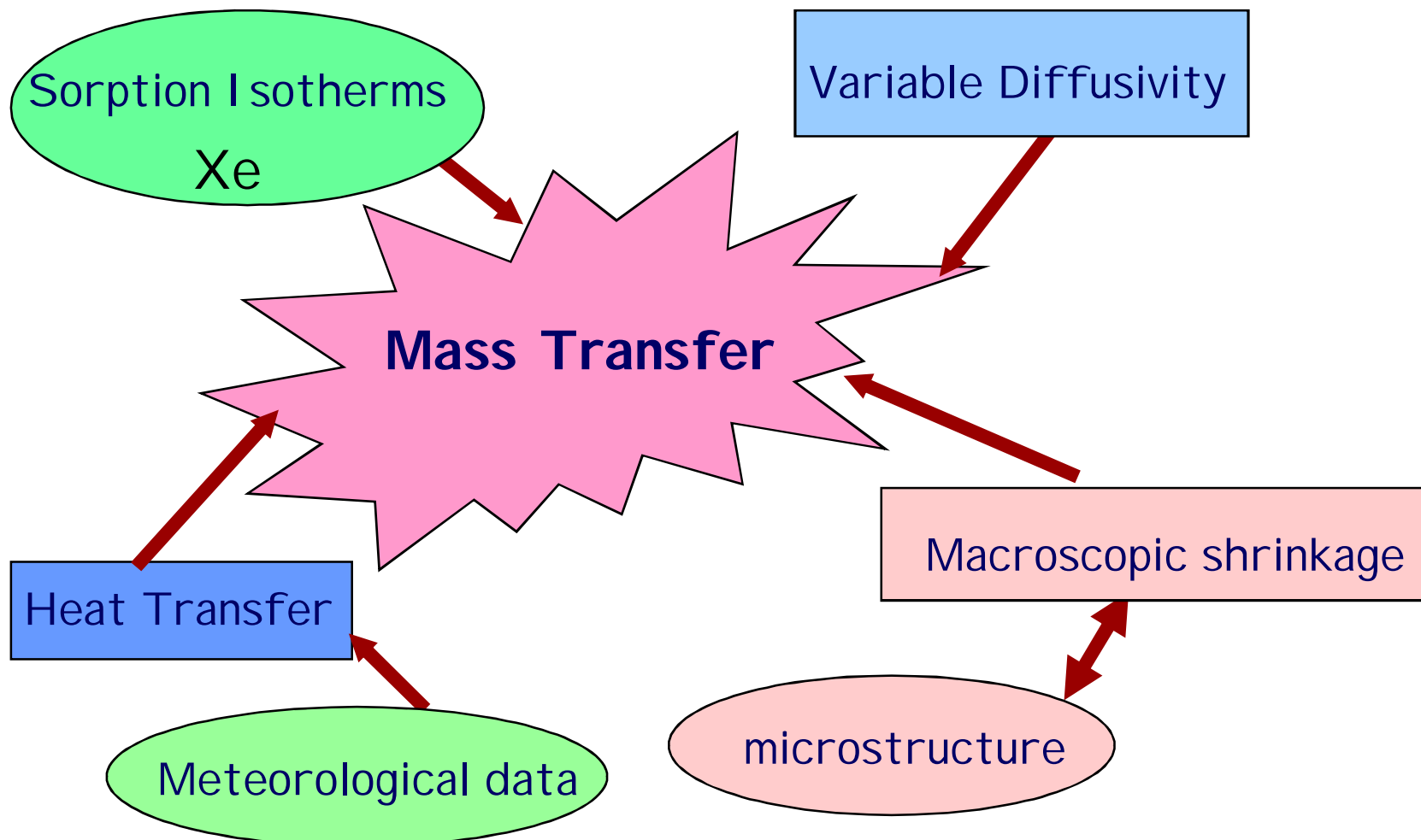
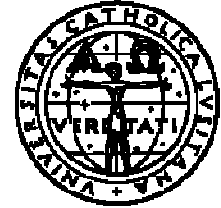


Air conditions inside a solar drier :

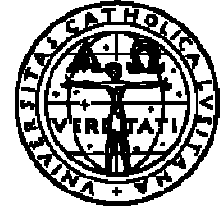


Introduction

Integrated model



Mass Transfer

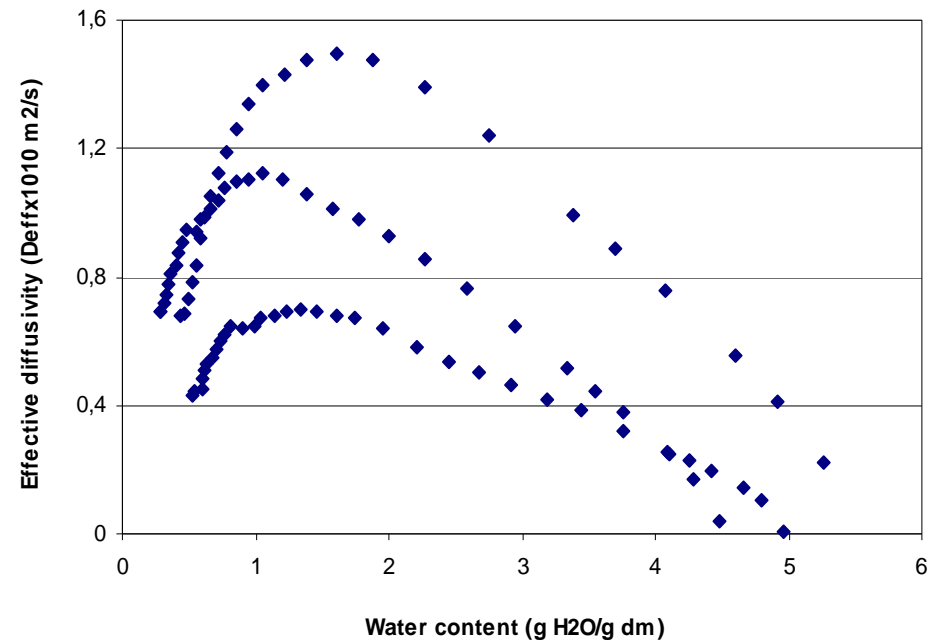


Fick's 2nd law

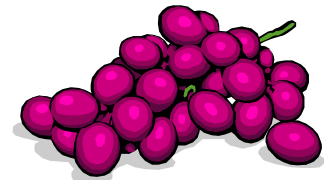
- ◆ Water concentration at the surface constant
- ◆ Sphere:

$$\frac{X - X_e}{X_o - X_e} = \frac{6}{\pi^2} \sum_1^{\infty} \frac{1}{n^2} \exp\left(-n^2 \pi^2 \frac{D_{\text{eff}} t}{r^2}\right)$$

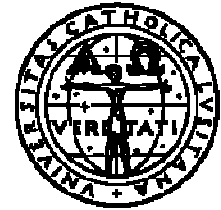
Effective diffusivity



Data similar to Raghavan et al., 1995



Heat Transfer



Global energy balance :

$$\frac{d(m C_p T)}{dt} = \alpha Q_s - hA(T - T_a) - \frac{d(\lambda m)}{dt} - A \varepsilon \sigma (T^4 - T_a^4)$$

energy gained

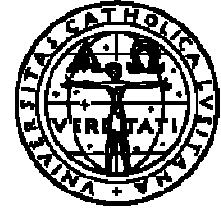
absorbed radiant energy

convective heat loss

evaporation heat loss

radiation heat loss

Shrinkage



Loss of water



shrinkage

reduction in cellular dimensions

Macroscopic Shrinkage

Commonly defined:

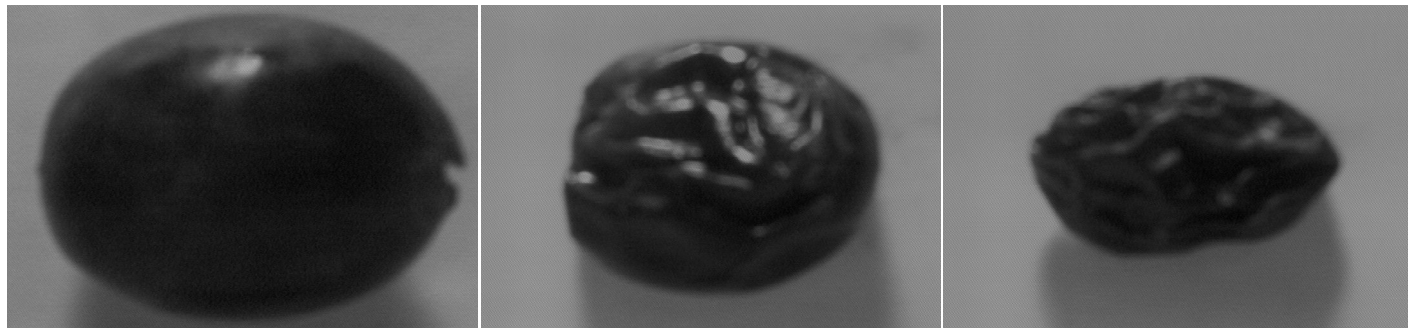
$$\frac{V}{V_0}$$

Macroscopic Shrinkage



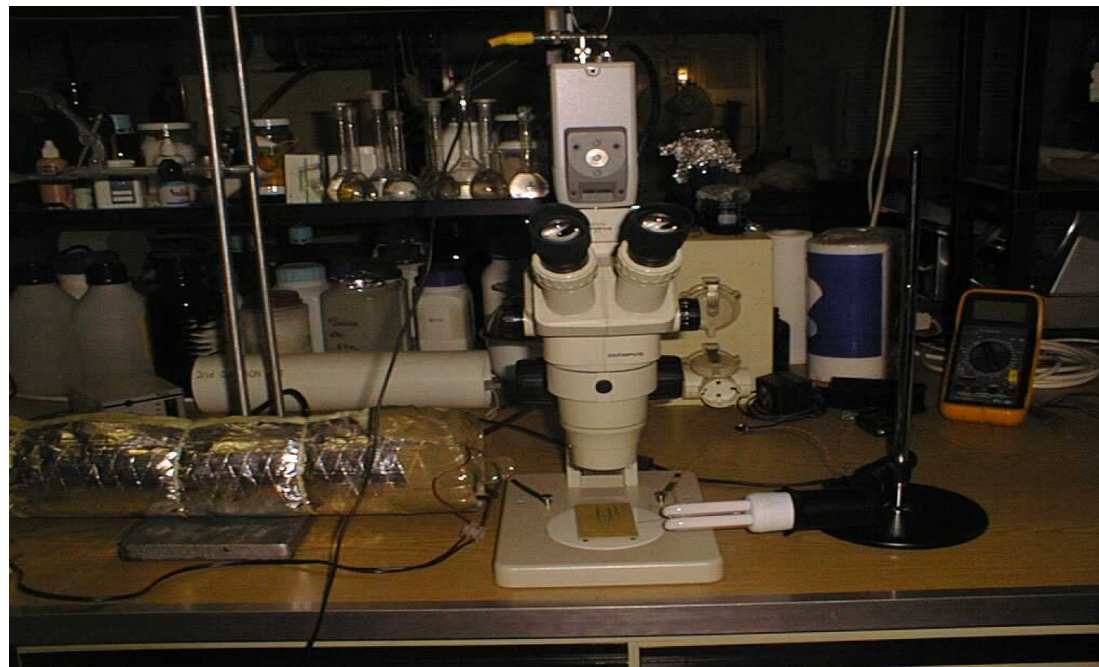
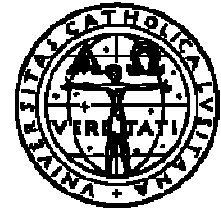
Measurement :

- direct with a calliper
- picnometry with organic solutions
- photography and image analysis:



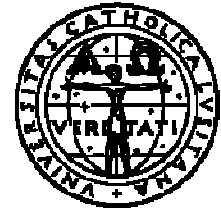
Grape shrinkage under dynamic conditions.

Microscopic Shrinkage

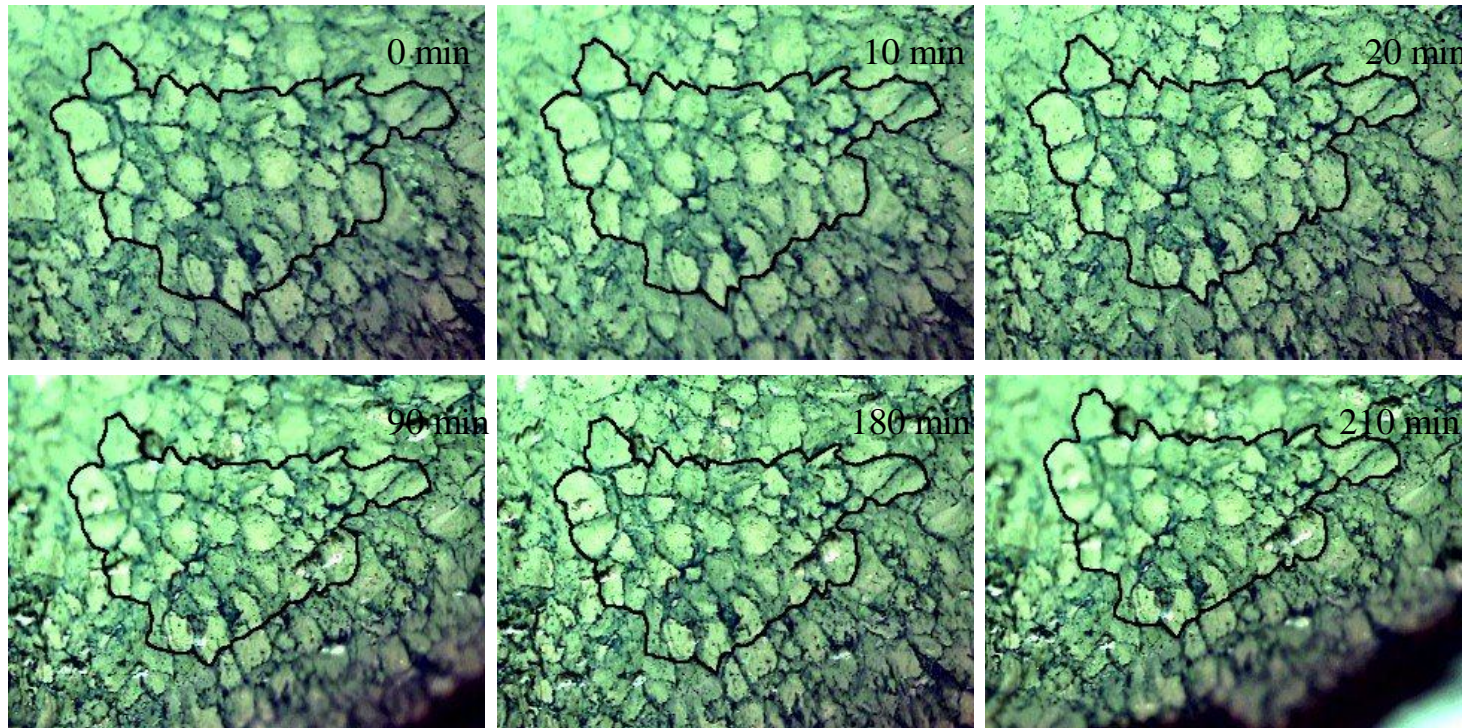


Stereo-microscope with video camera and air-drying tube.

Microscopic Shrinkage

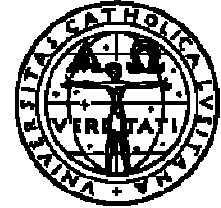


Cellular geometric features quantified by **image analysis**



Images of grape cells shrinkage at 40° C as a function of time.

Final Remarks



- Develop the mathematical basis and considerations for integrating heat and mass transfer phenomena.
 - include variable diffusivity
 - sorption isotherms
 - shrinkage
- Lack of data on thermal properties of foods.
- Microstructure helps understanding drying mechanisms.
- Correlating microstructure, texture measurements and sensory analysis is an attractive area.

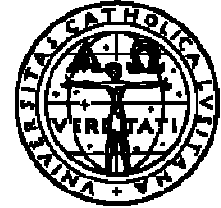
3rd CASE STUDY



**Experimental Validation of Optimal
Sterilisation Conditions for Maximising
Volume Average Quality Retention of
Prepackaged Heating Foods**

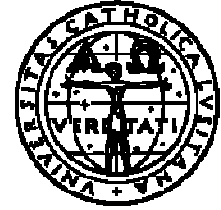


Introduction



Sterilisation or commercial sterilisation - traditional thermal processing based on the application of heat to the food product, by subjecting it to adequate time and temperature in order to destroy heat resistant bacterial spores.

Introduction



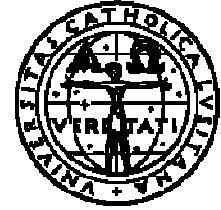
Advantages

- very important thermal process for the food industry
- well established (theoretical and empirical knowledge)
- economic process
- products with long shelf life
- very simple storage and distribution conditions

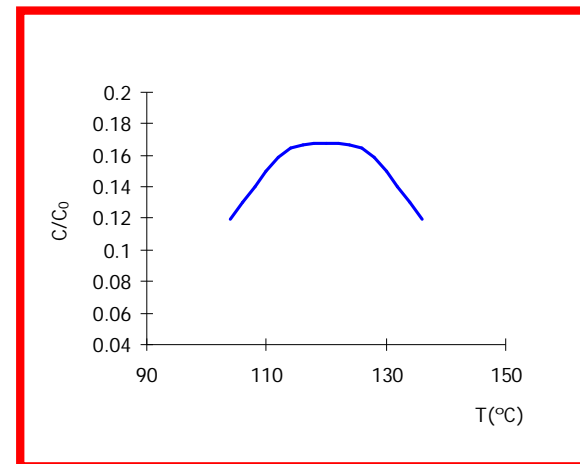
Disadvantages

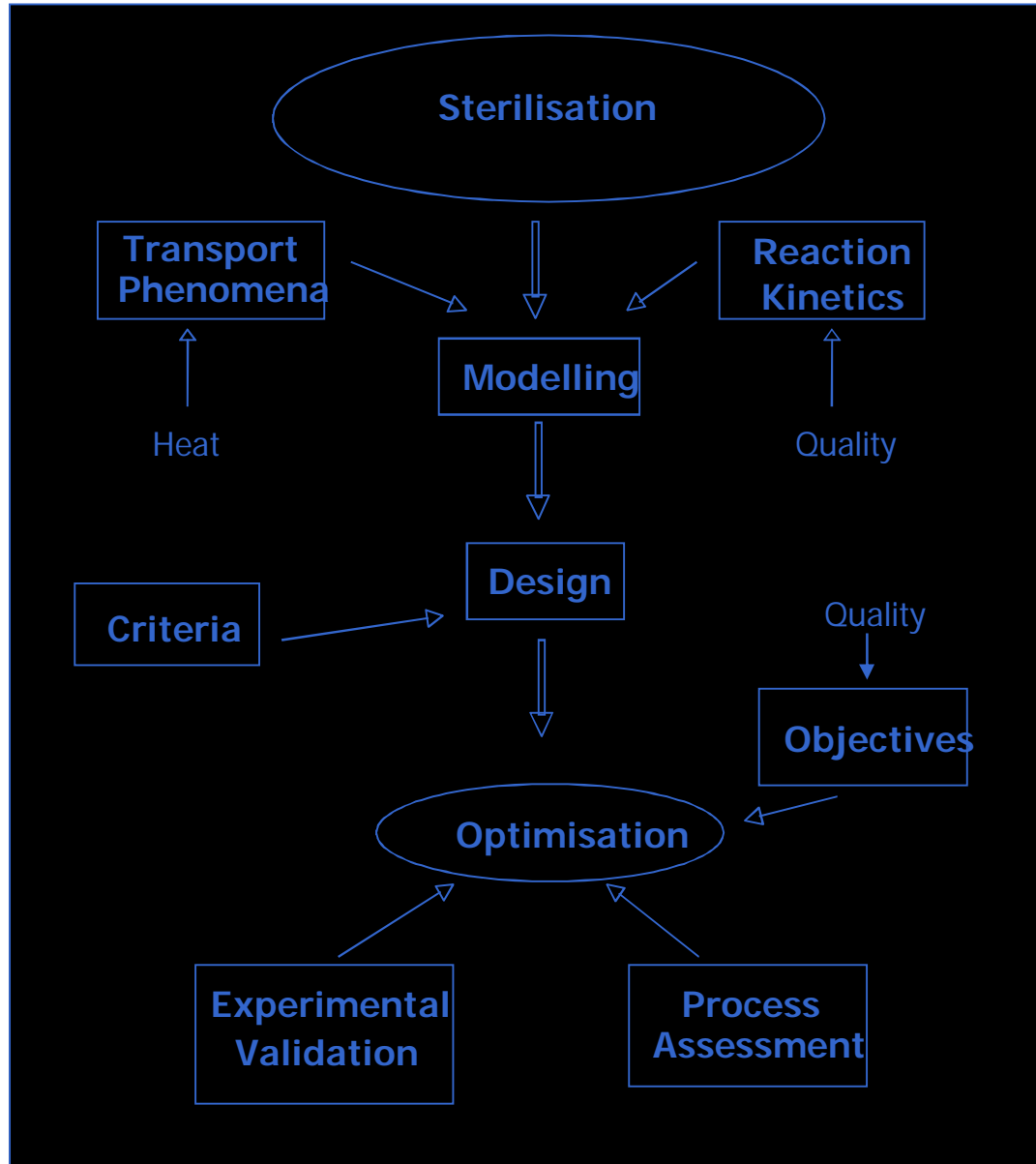
- severe thermal treatment (high temperatures and long times)
- significant losses in nutritional and sensory characteristics of foods

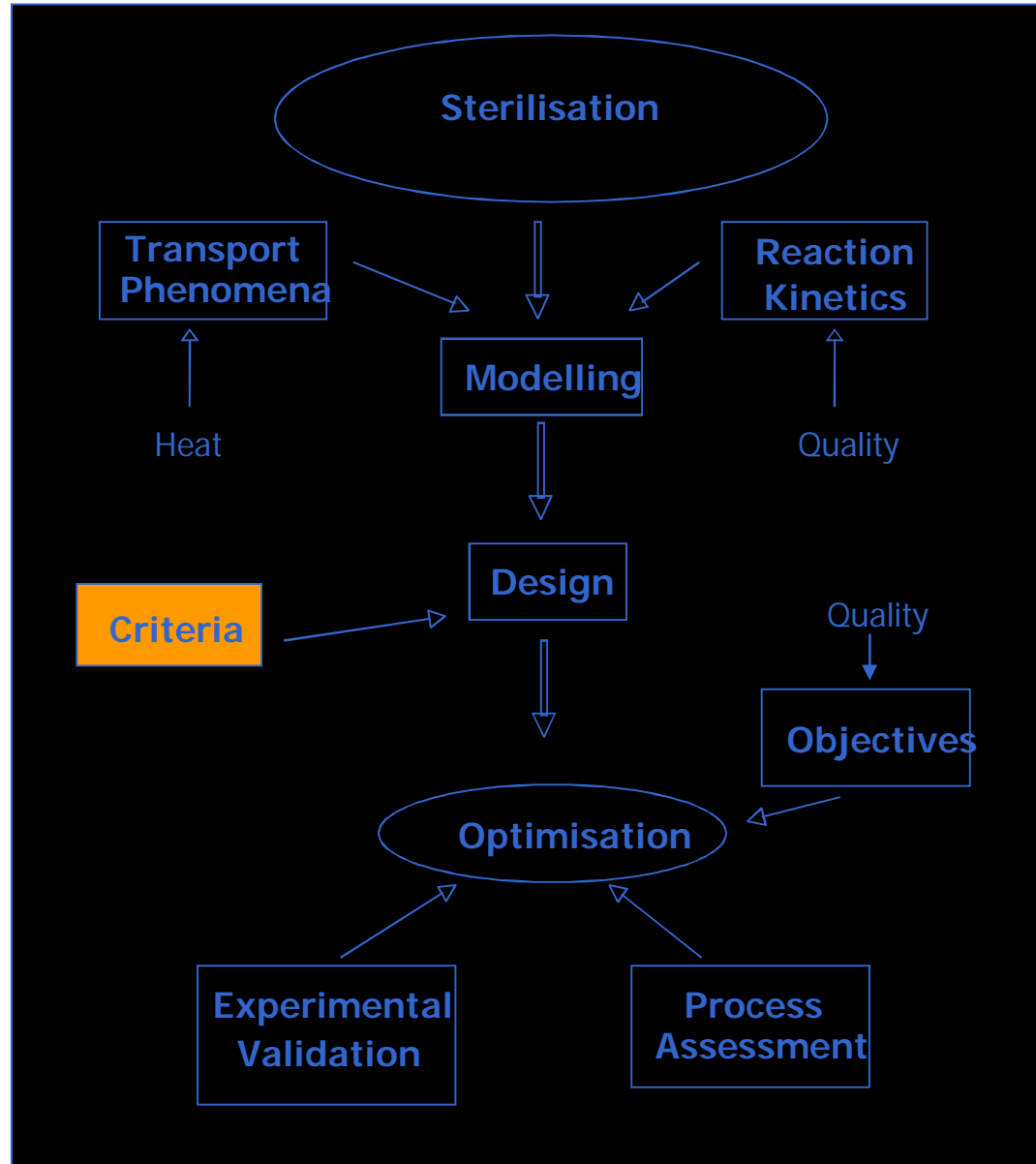
Introduction

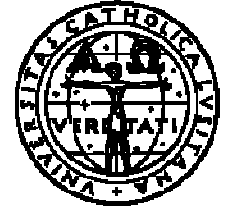


Optimisation - operate the retort at a certain combination of time and temperature, that results in a maximum objective, while guaranteeing the microbiological safety.

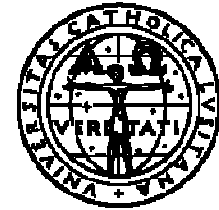








- **Study the effect of different restrictions and objective functions on optimal sterilisation conditions**



Criteria for heat sterilisation

$$F_c = \int_0^{tp} 10^{(T_c - T_{refm})/z_m} dt$$

Sterility value at the geometric centre

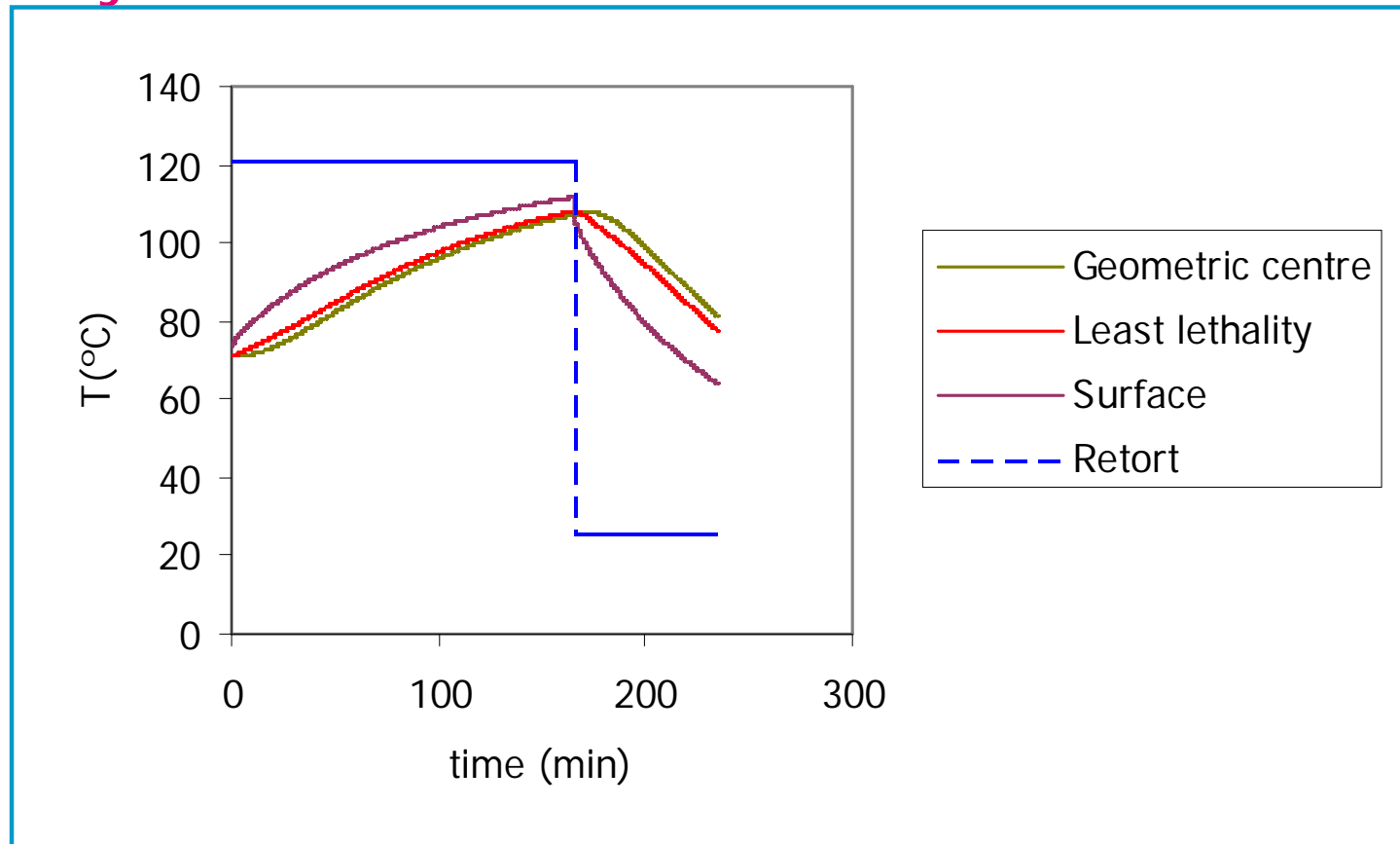
$$F_L = \int_0^{tp} 10^{(T_L - T_{refm})/z_m} dt$$

Sterility value at the LLP

Least Lethality Point (LLP) - point receiving the smallest F_0 value of the whole package

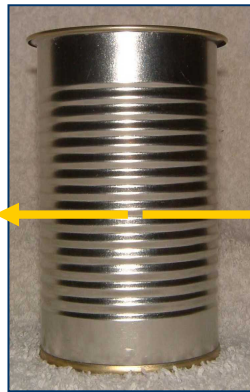
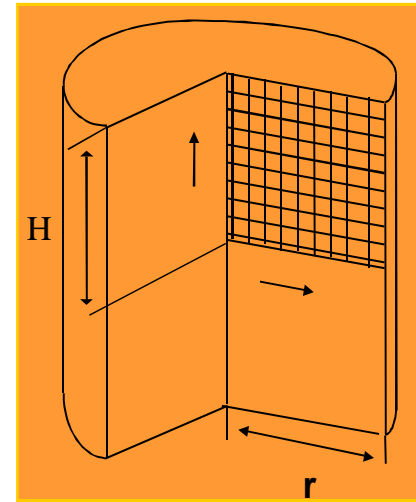


Cylindrical containers





LLP position



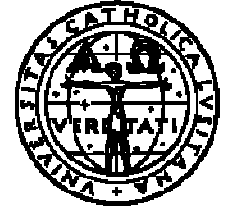
$$0.9 < H/r < 3.0$$



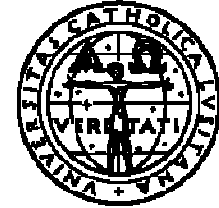
$$\begin{aligned} H/r &= 0.9 \\ H/r &> 3.0 \\ H/r &< 0.1 \end{aligned}$$



$$0.1 < H/r < 0.9$$



- **Study the effect of the sterility value specified at the centre and at the LLP on optimal sterilisation temperatures**



Objective functions

$$(c / c_0)_{surf} = 10^{-\frac{1}{D_{refq}} \int_0^{tp} 10^{(T-T_{refq})/z_q} dt}$$

Surface quality retention

$$(c / c_0)_{ave} = \frac{1}{V_T} \int_0^{V_T} 10^{-\frac{1}{D_{refq}} \int_0^{tp} 10^{(T-T_{refq})/z_q} dt} dV$$

Overall quality retention

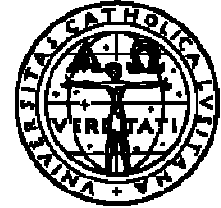
Response variables

Surface quality:

$$(\Delta T_{opt}^{surf} = T_{opt.c}^{surf} - T_{opt.L}^{surf})$$

Volume average quality:

$$(\Delta T_{opt}^{ave} = T_{opt.c}^{ave} - T_{opt.L}^{ave})$$



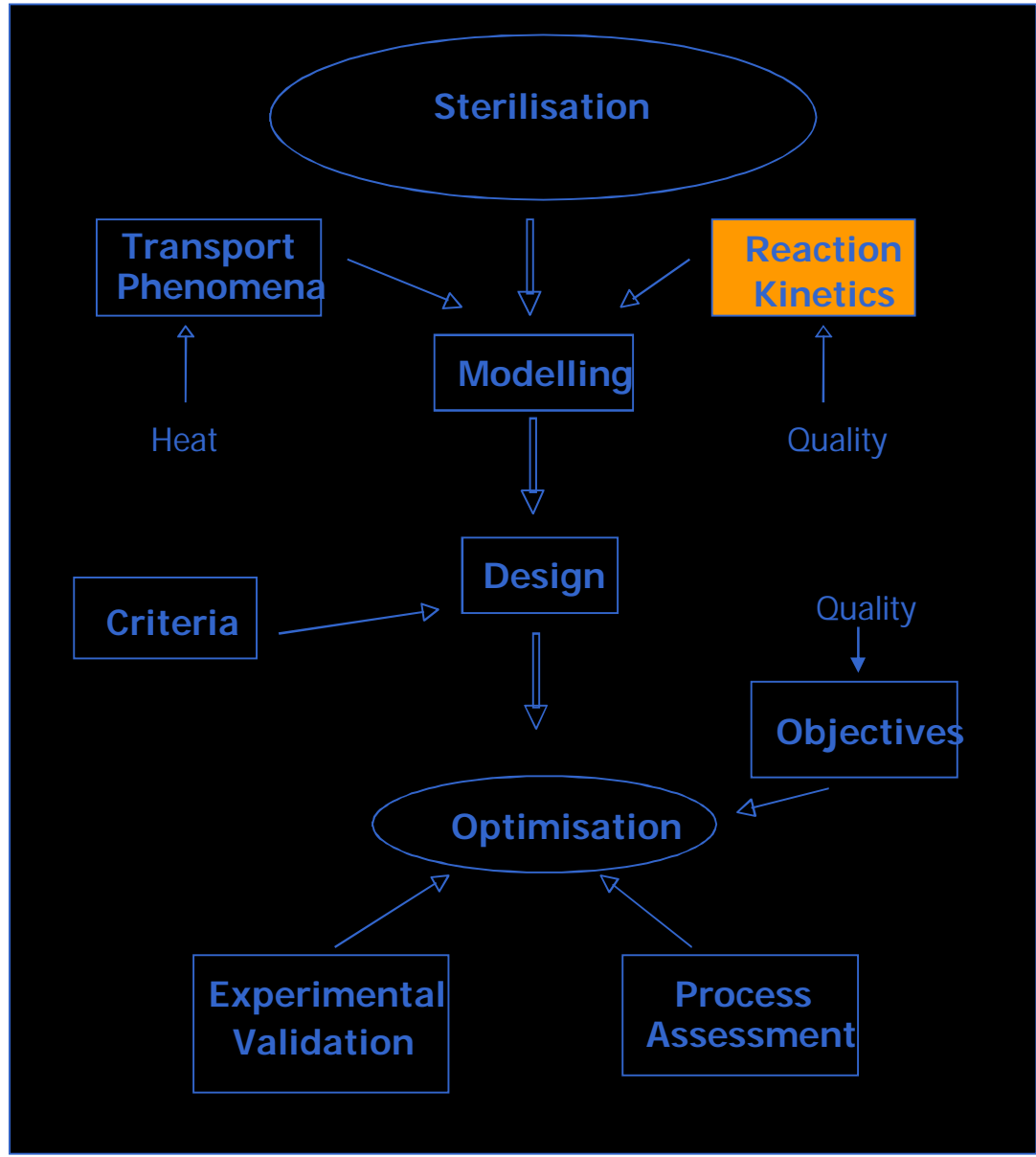
In specific situations:

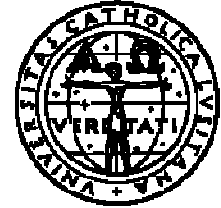
cylindrical containers 4°C

rectangular packages 3°C

**Most adequate optimisation
criterion to use:**

**target sterility value specified
at the geometric centre**





- **Modelling the thermal degradation kinetics of quality attributes**

Peach puree

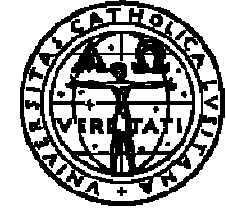


colour and carotenoids

White beans



texture



Thermal death time (TDT) cans



Filled with ~ 10g (d=6 cm, h=0.8 cm)



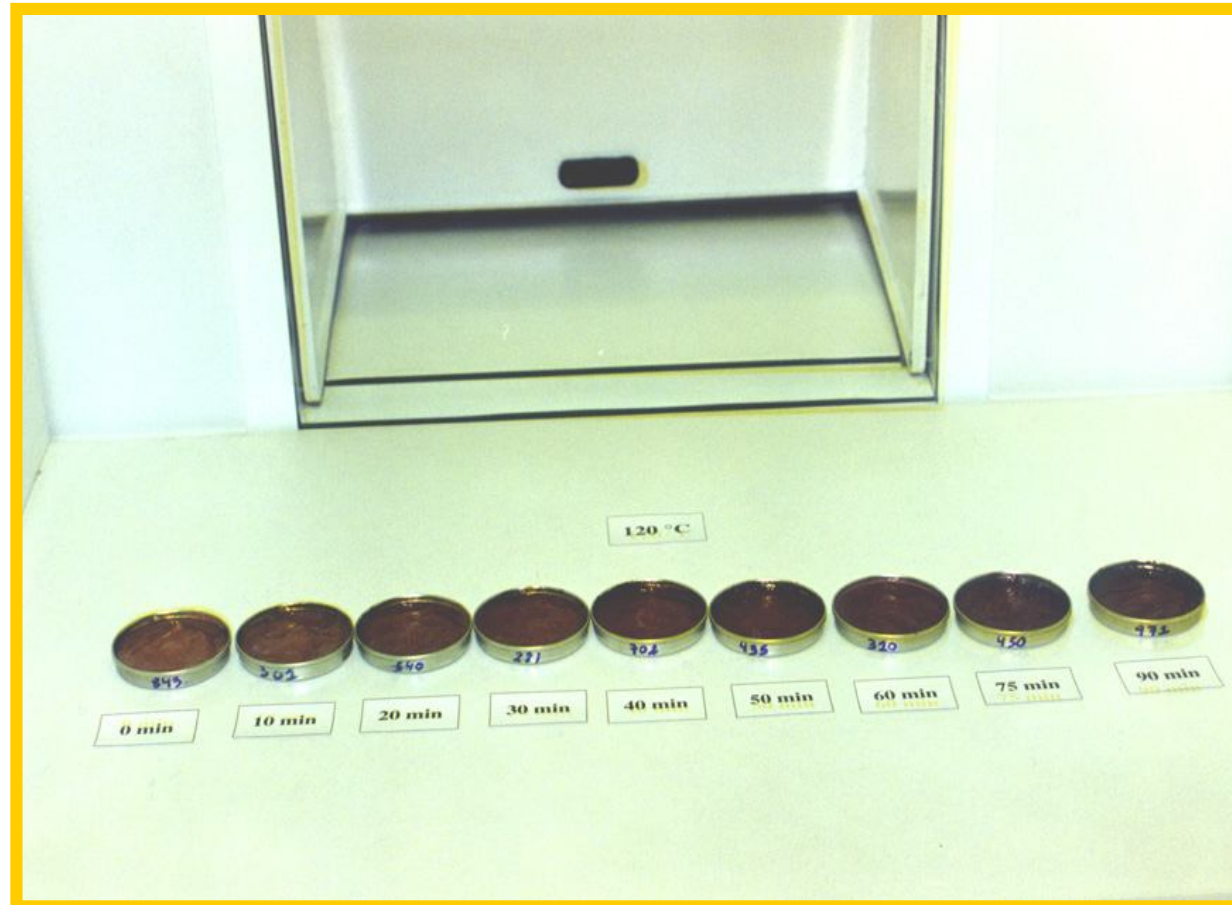
Colour measured by a colorimeter



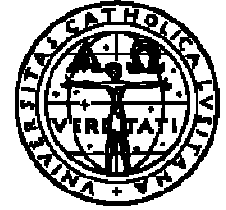
***L, a, b* colour system**



Colour measured by a sensory panel



Kinetic experiments

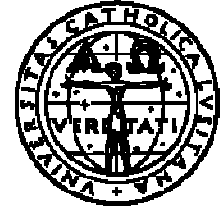


Cans used for kinetics determination of white beans softening



dimensions: $d = 7.1 \text{ cm}$, $h = 2.7 \text{ cm}$

Colour kinetics in peach puree



↓ L -values →

peach puree becomes darker with the increase of heating temperature and time.

↓ b -values
↑ a -values →

peach puree loses its yellowness and becomes more red, when heated.

TCD
La/b →

show to be good indicators of the total colour change of heat treated peach puree.

$$\text{TCD} = \text{Total colour difference} = [(L_0 - L)^2 + (a_0 - a)^2 + (b_0 - b)^2]^{1/2}$$



First order model

$$c = c_0 \exp(-kt)$$

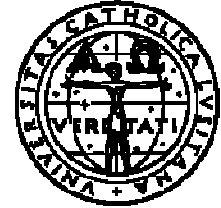


L - value

b - value

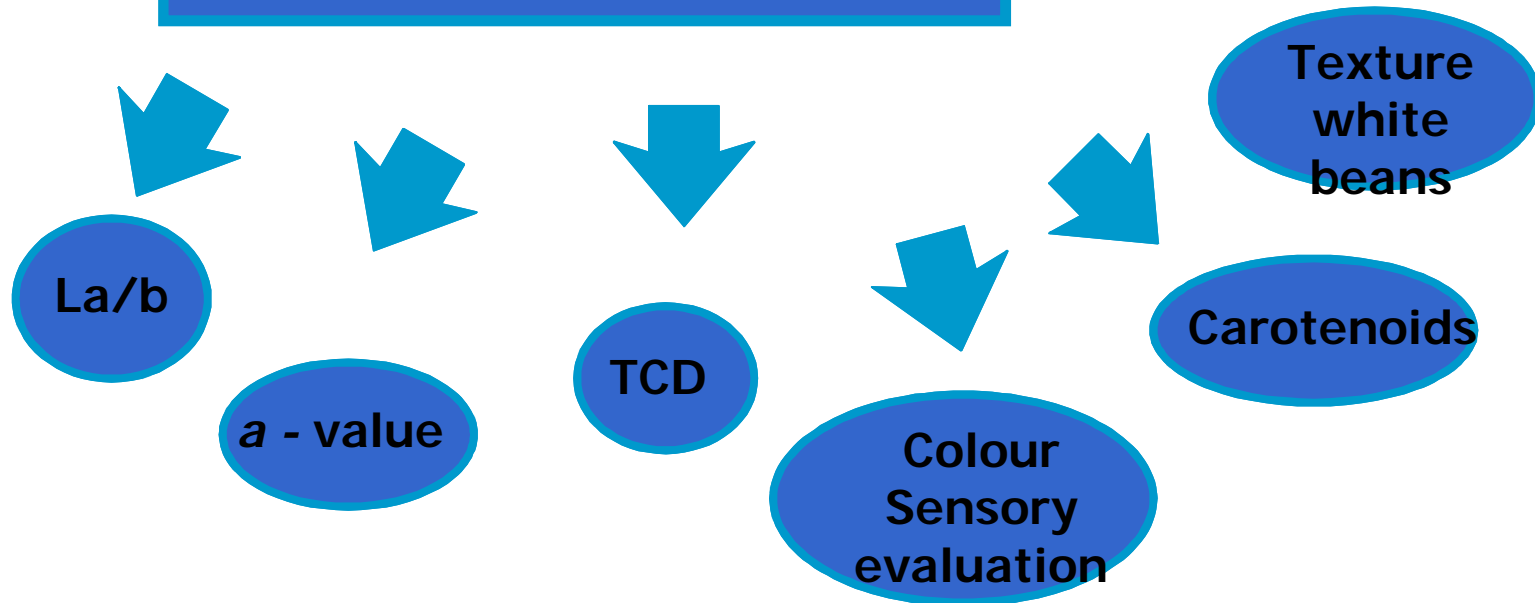
C_0 - initial concentration

k - reaction rate constant



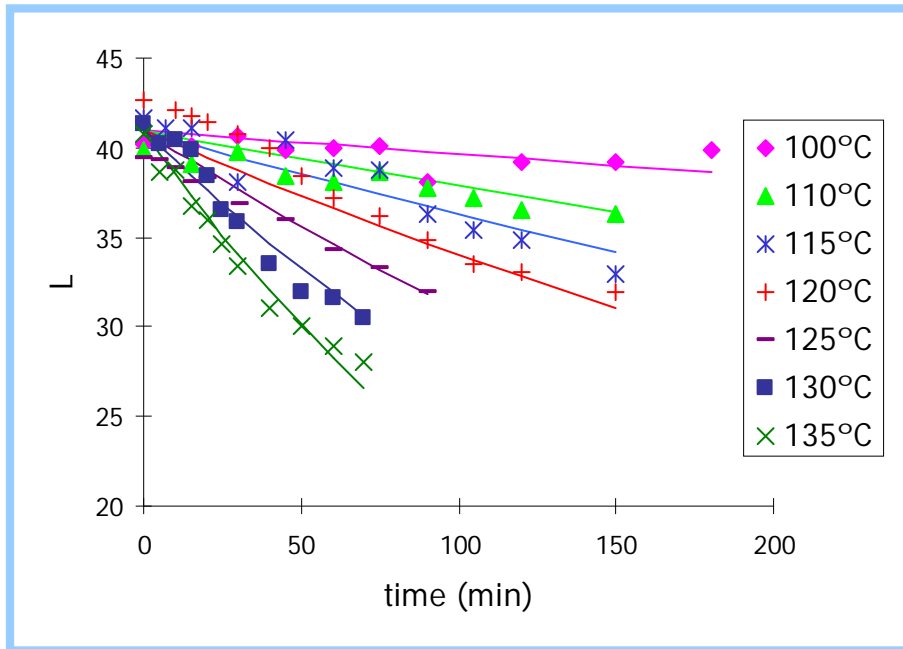
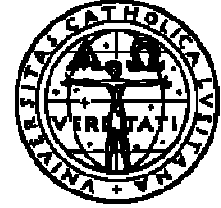
Fractional conversion model

$$\frac{C - C_f}{C_0 - C_f} = \exp(-k t)$$

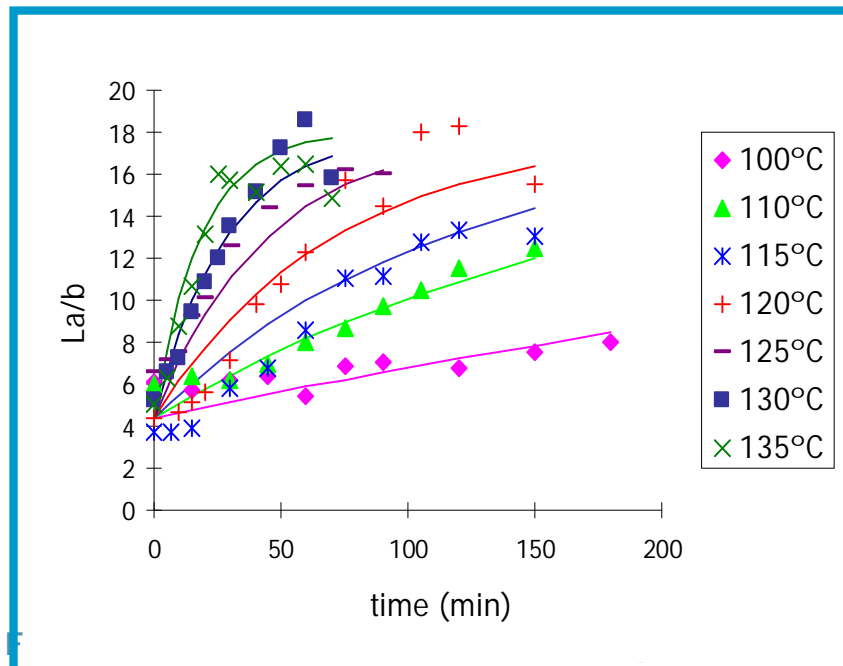


C_f - final concentration

Peach puree kinetic models

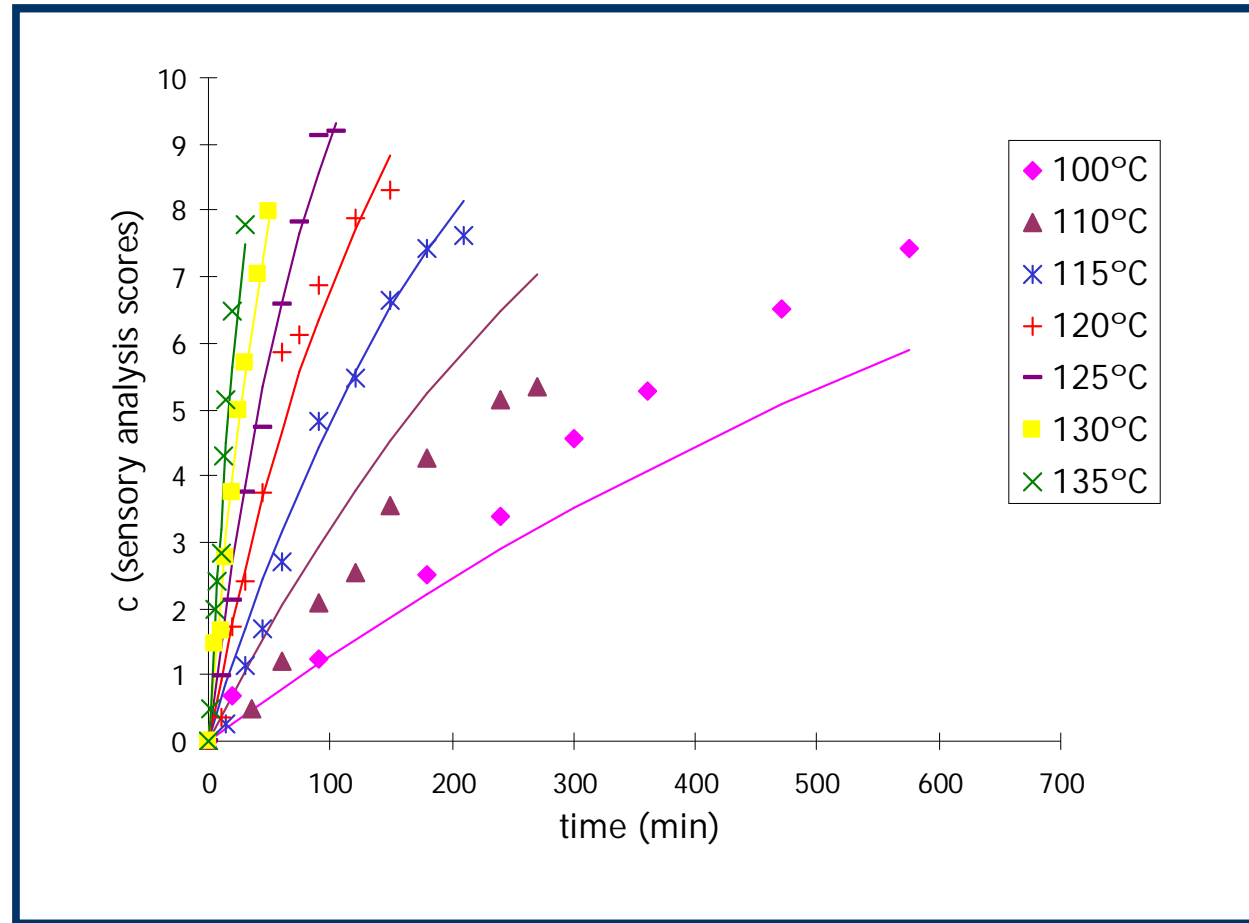
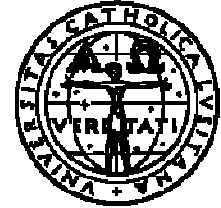


L - values

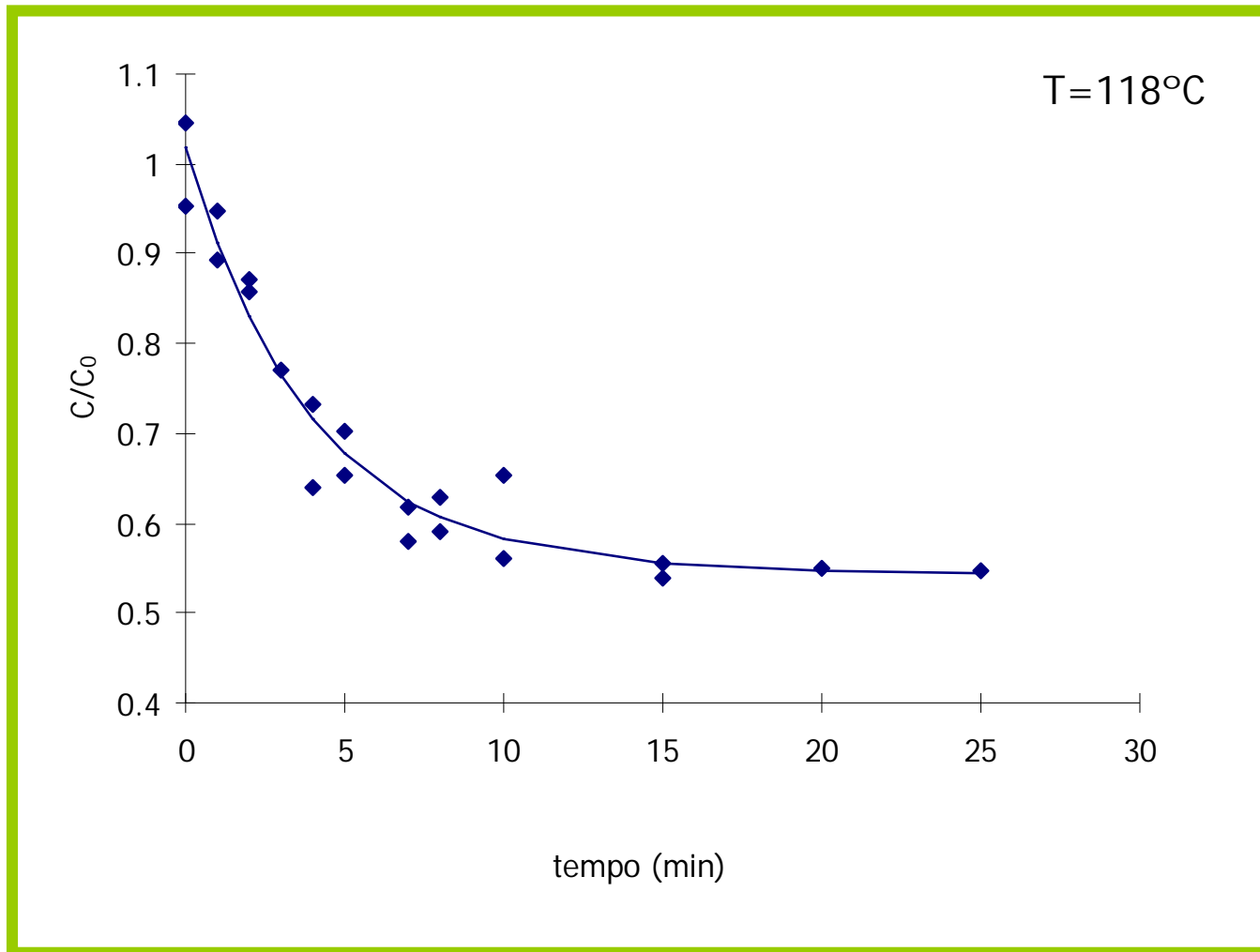


La/b - values

Peach puree kinetic models

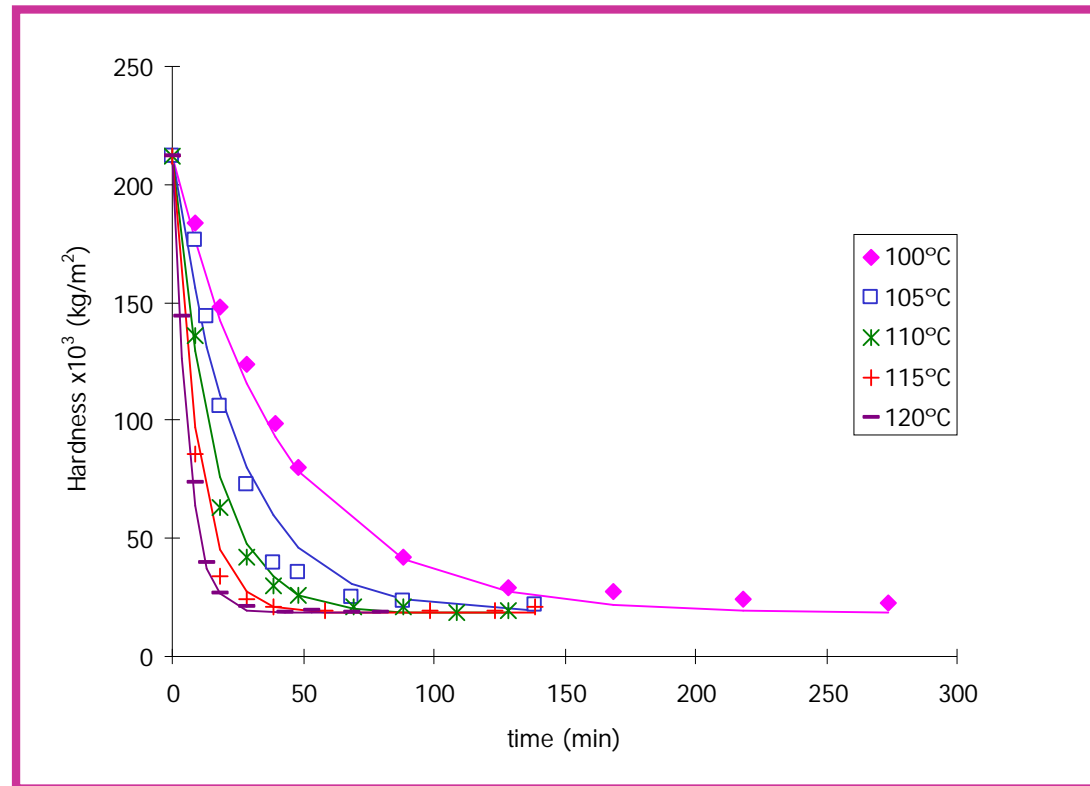


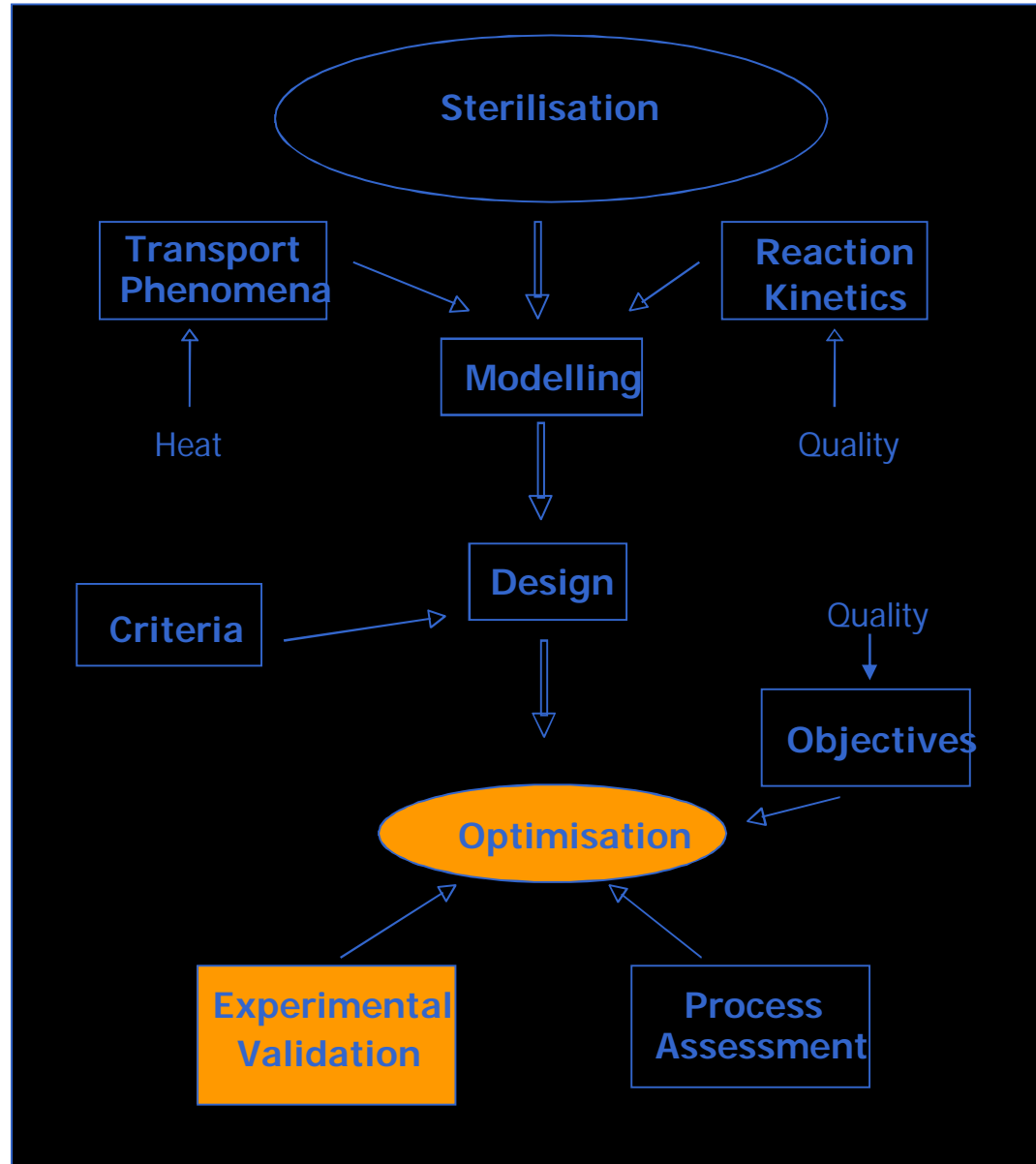
Colour of peach puree evaluated by a sensory panel

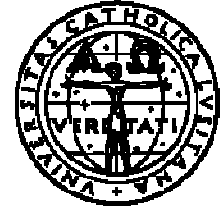


carotenoids

White beans kinetic models







- **Validate experimentally optimal sterilisation conditions for maximising different volume average quality parameters:**

Peach puree



colour and carotenoids

White beans

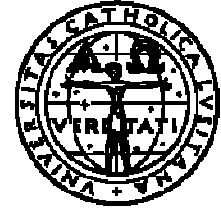


texture

Green beans

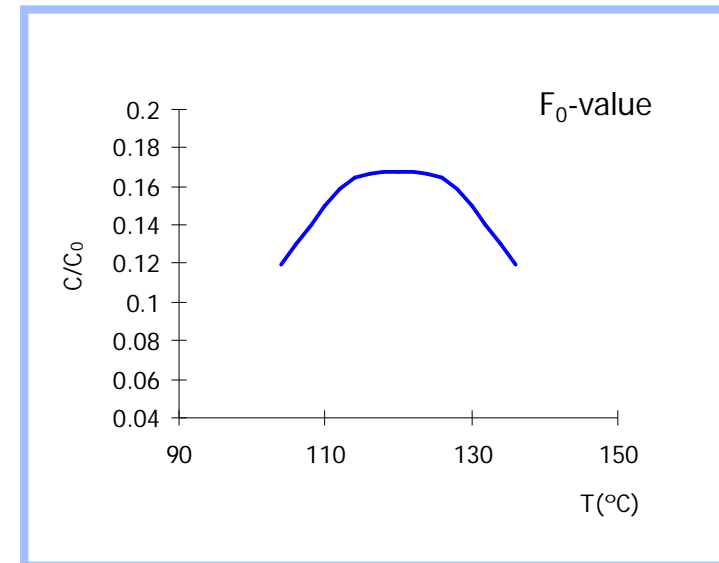


colour



Calculation of optimal sterilisation conditions

- Pascal computer program
- Heat transfer by conduction into cylindrical containers.
- Requires information on kinetic models and heat penetration parameters
- For a certain F_0 value, the computer program calculates equivalent time-temperature processes.

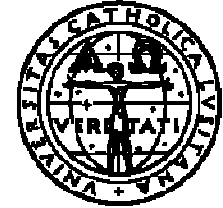


Experimental validation

- Pilot Barriquand Steriflow retort

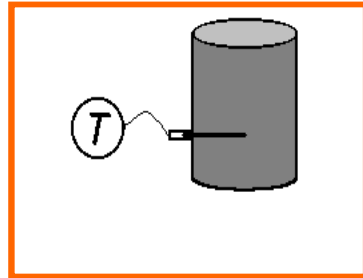
Pilot Barriquand Steriflow retort





Experimental validation

- Heat penetration parameters (f_h and j_h) - Ball's method



$$\log\left(\frac{T - T_\infty}{T_0 - T_\infty}\right) = -\frac{1}{f_h} t + \log j_h$$

- Validation experiments

Peach puree: *colour and carotenoids*

- Metal cans (h=10.4 cm, r=3.65 cm)
- Pure steam
- Static processes
- F_0 value of 3 min
- Colour evaluation: colorimeter and sensory panel
- Carotenoids evaluation: spectrophotometer





Green beans: colour (-a/b)

- Purchased frozen
- Glass jars
- Water cascading
- Static processes
- F_0 value of 3 and 5 min
- Colour evaluation: colorimeter
- kinetics: $D_{121.1^\circ\text{C}} = 21$ min



Hayakawa and Timbers (1977)
z-value = 38.9°C

White beans: hardness

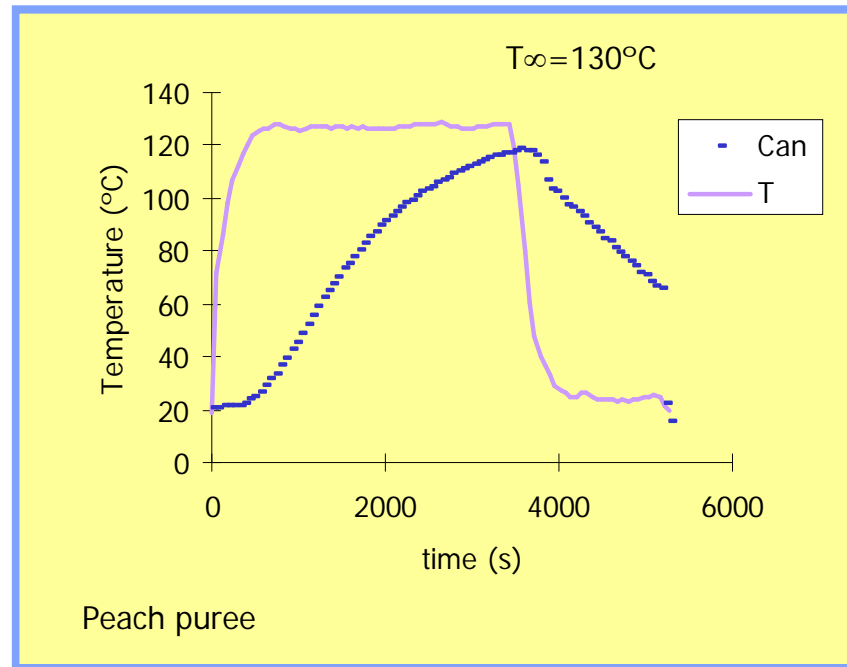
- Glass jars (370ml capacity, h=8.4 cm, d=7.5 cm)
- Water cascading
- Static and end-over-end rotational processes: 0, 4, 7, 10, 15 rpm
- F_0 value of 3 and 5 min
- Hardness evaluation: tenderometer





Heat penetration studies

- Single log-linear behaviour for all food products



- Peach puree: heats by **conduction** ,
- Green and white beans: **mix process convection /**

conduction

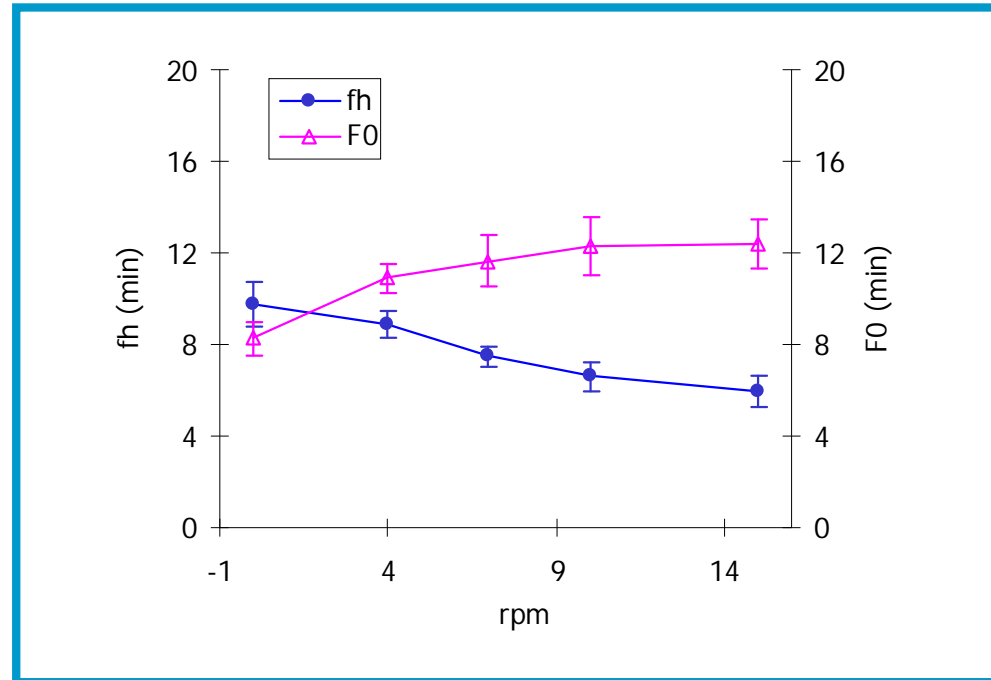
$h = 408 \text{ W}/(\text{m}^2 \text{ K})$ - calculated

$h = \infty \text{ W}/(\text{m}^2 \text{ K})$ - simplification



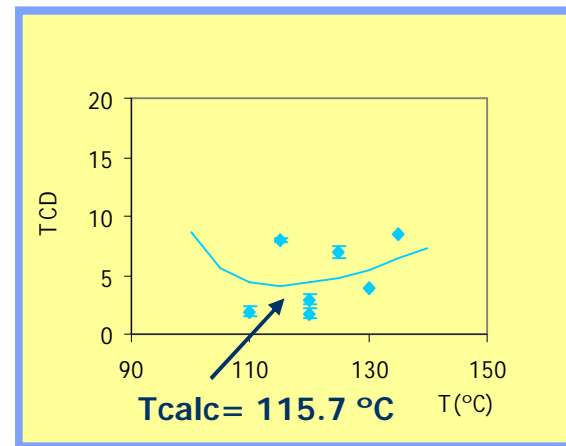
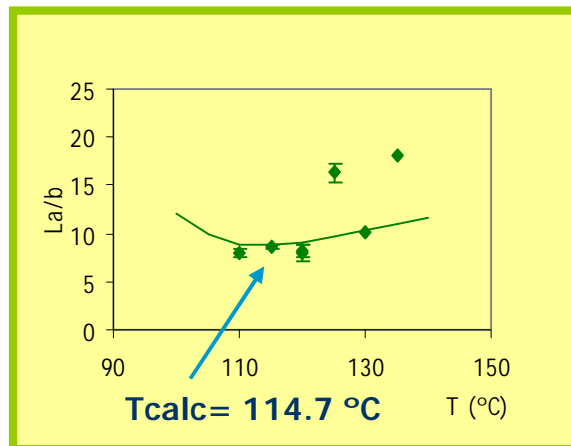
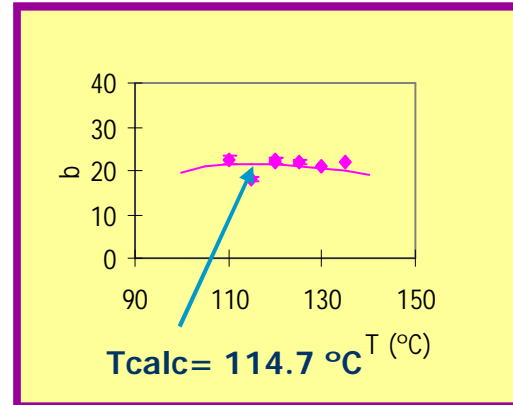
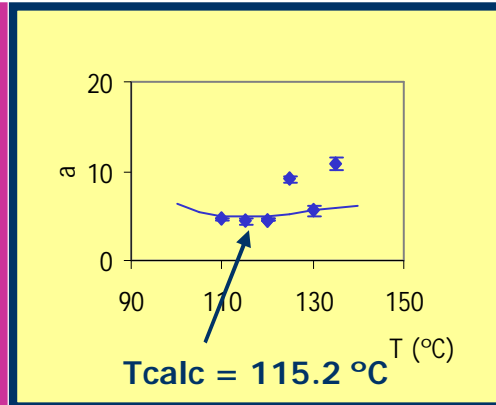
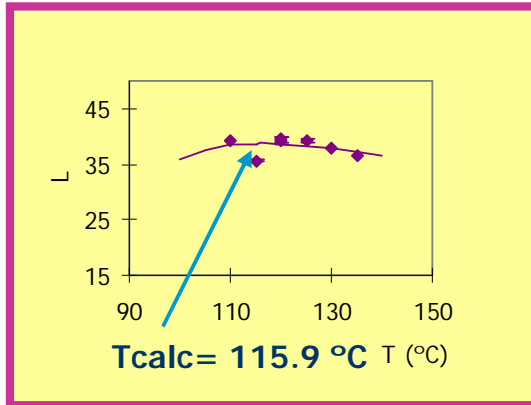
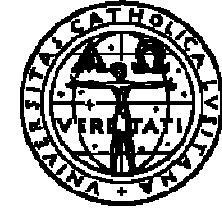
Heat penetration studies

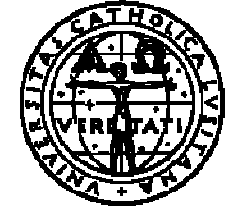
White beans



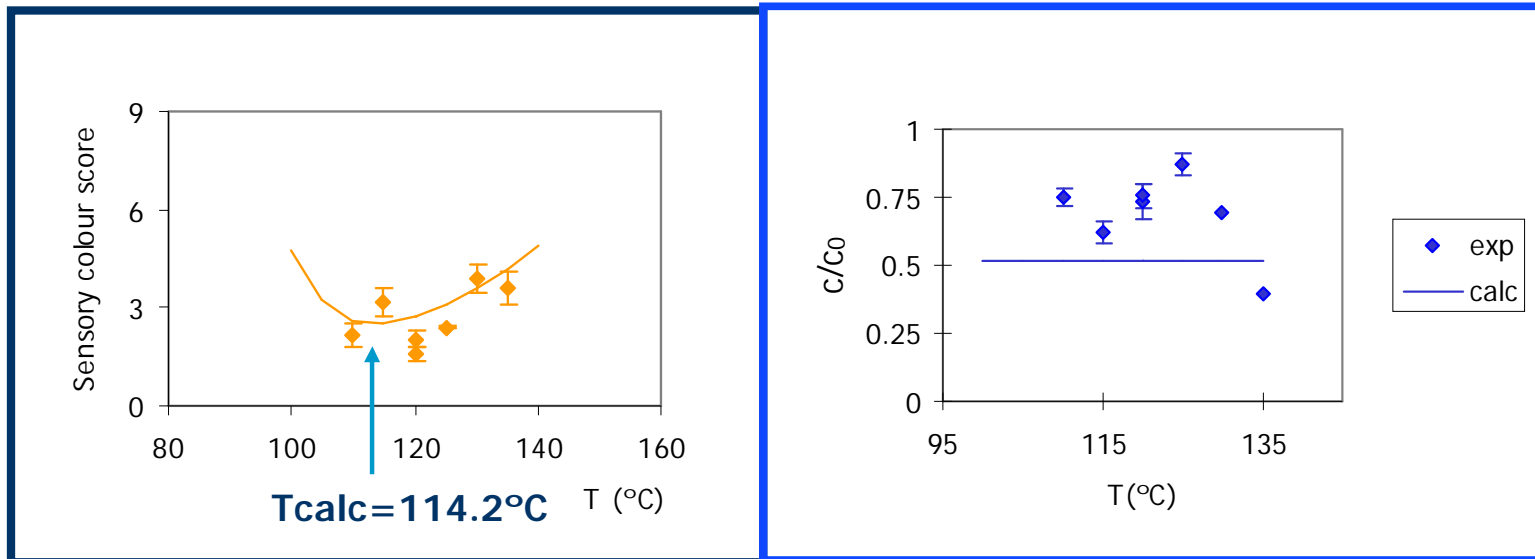
Static and 10 rpm were chosen for further optimisation studies

Peach puree: colour



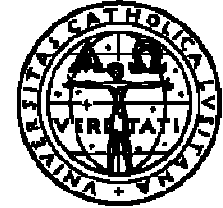


Peach puree

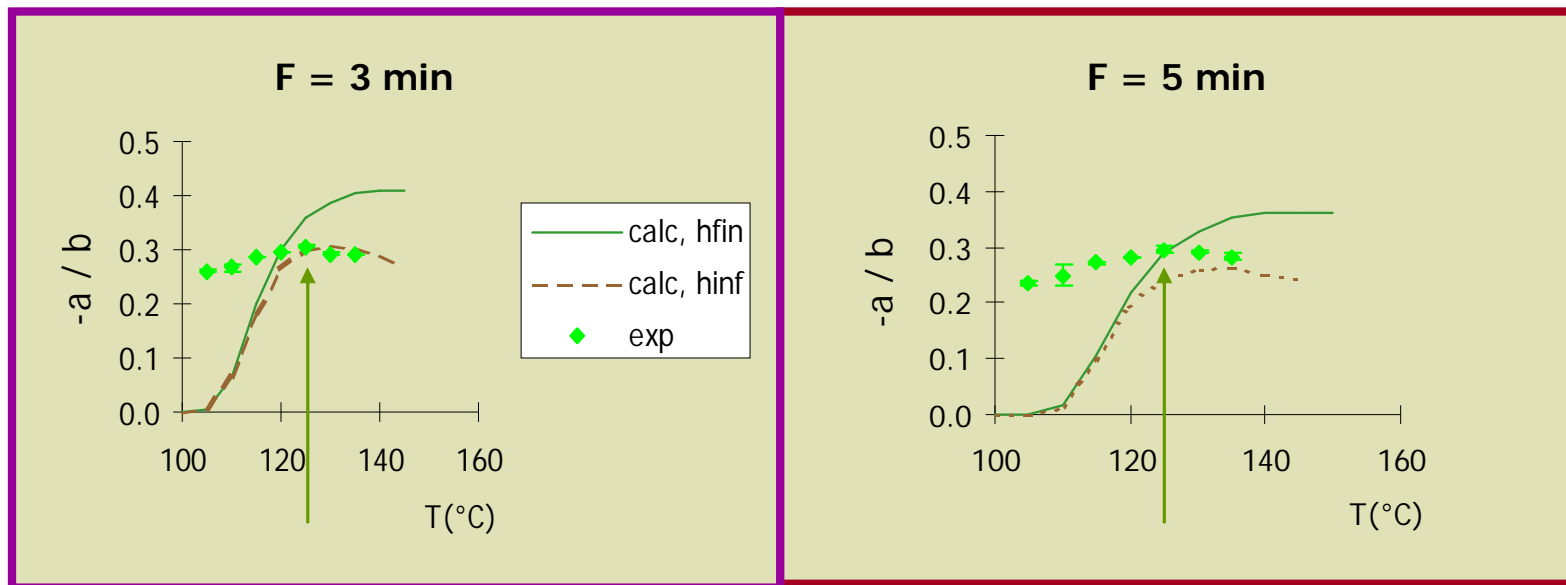


Colour: sensory panel

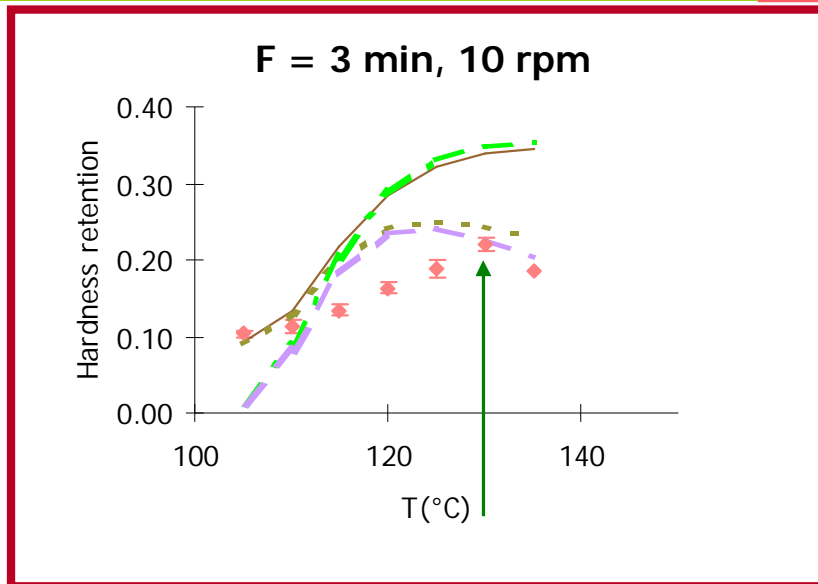
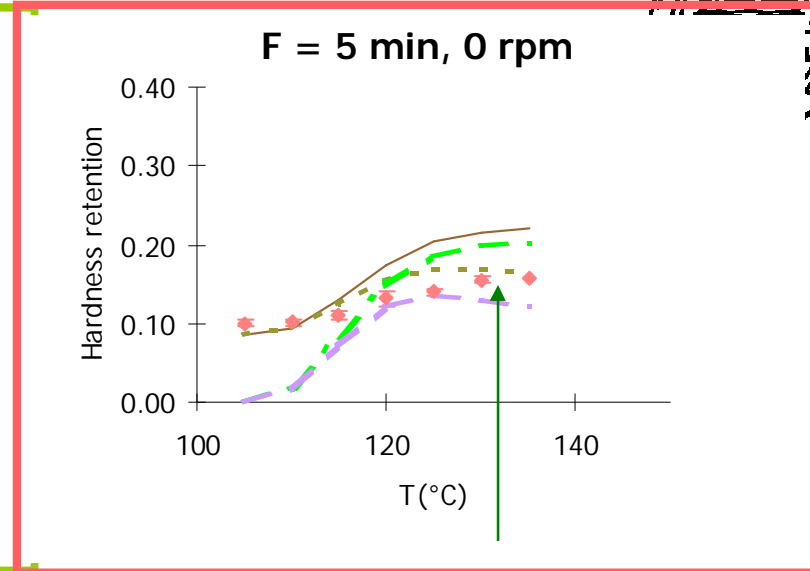
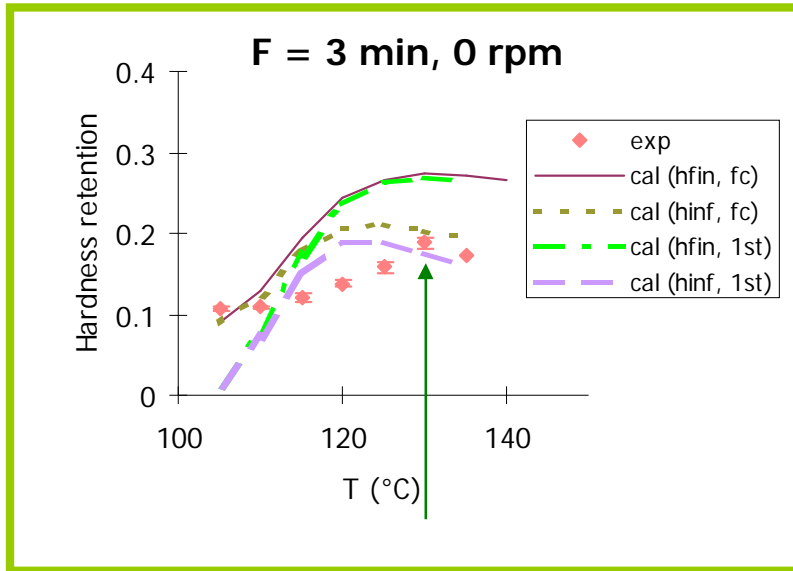
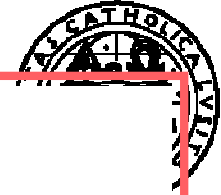
Carotenoids



Green beans: *colour*



White beans: *texture*



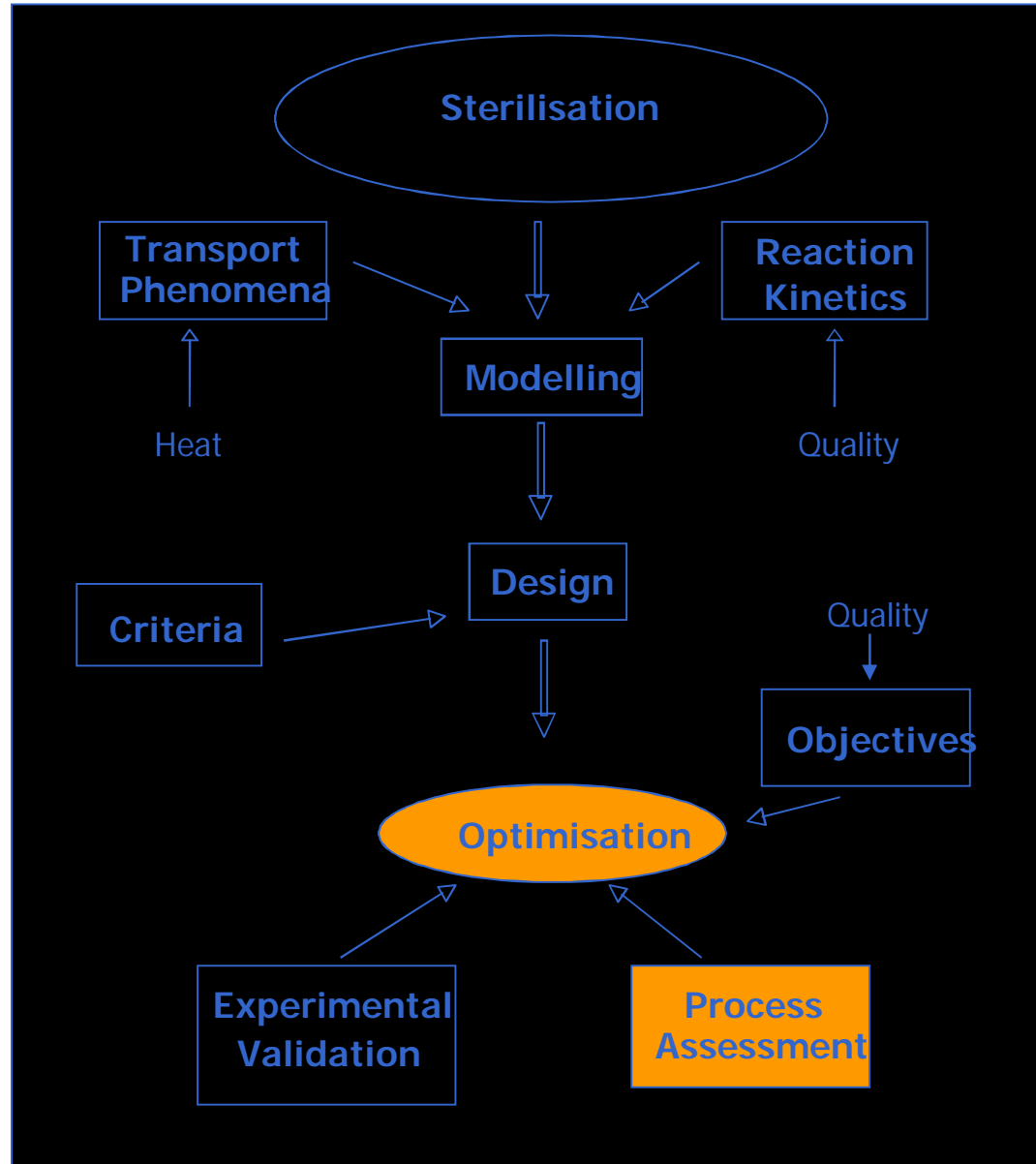
• h finite
F=3 min

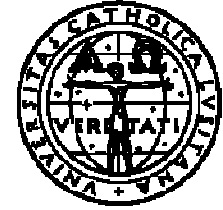
Calculated profile \neq
Experimental profile

• h finite

T_{opt} calc = T_{opt} exp
($\approx 130^\circ\text{C}$)

• type of reaction kinetic model did not significantly affect T_{opt}





- Quantify the effect of uncertainties of some factors on the final quality retention variability of foods and evaluate the impact on process optimisation

White beans



texture

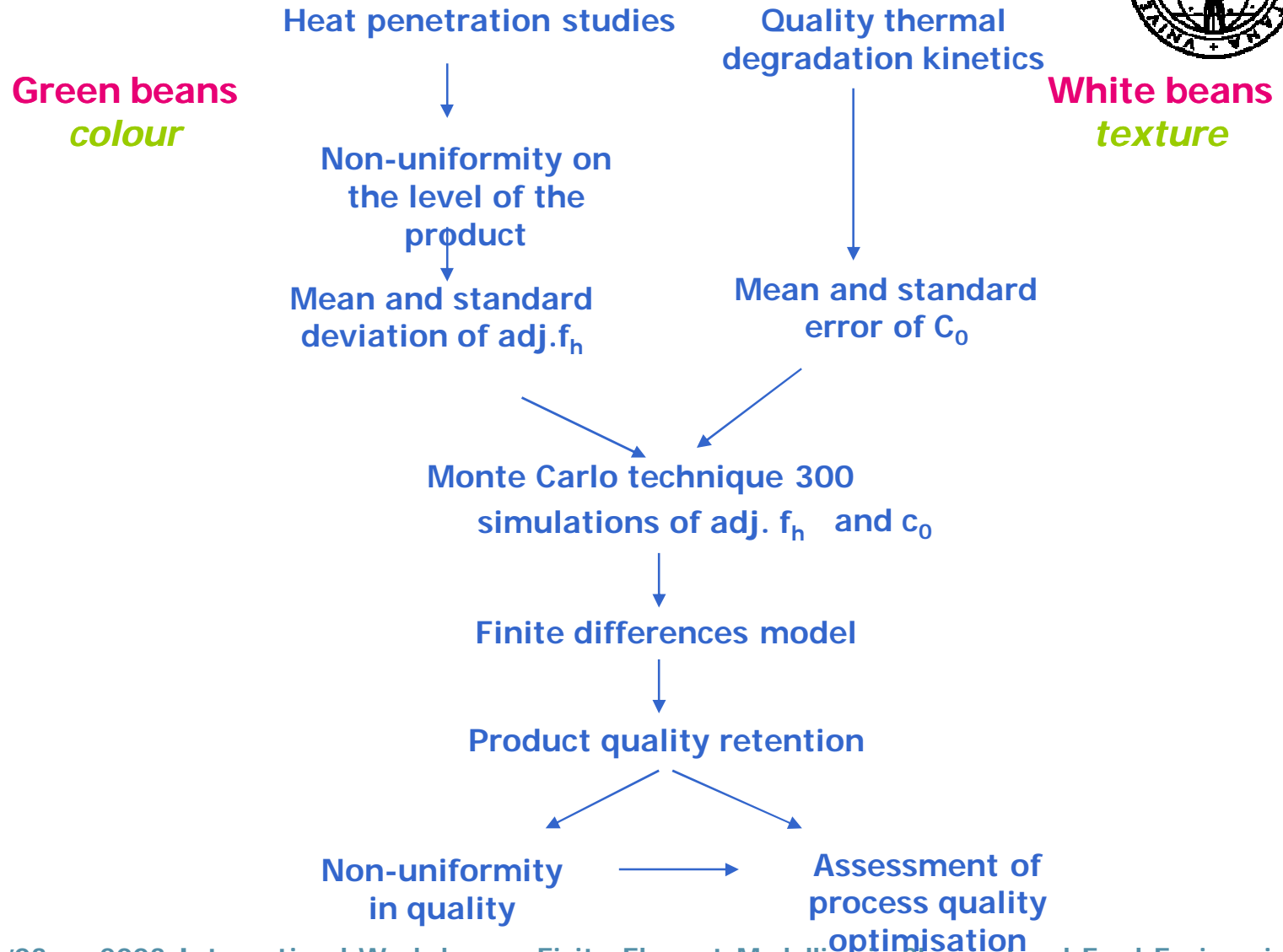
Green beans



colour



Simulation approach





Simulations

Green beans: *colour* (-a/b)

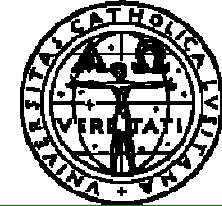
- h finite and infinite
- T_{holding} : 100-160 °C
- Static processes
- F_0 value of 3 and 5 min

White beans: *hardness*

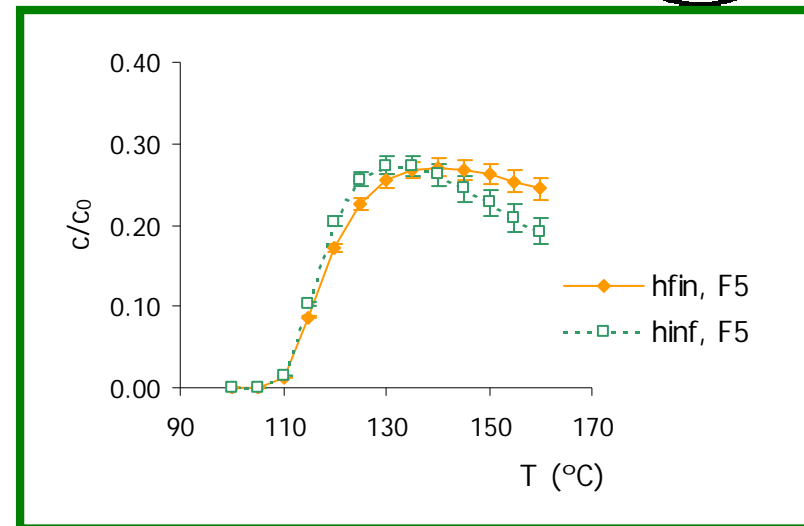
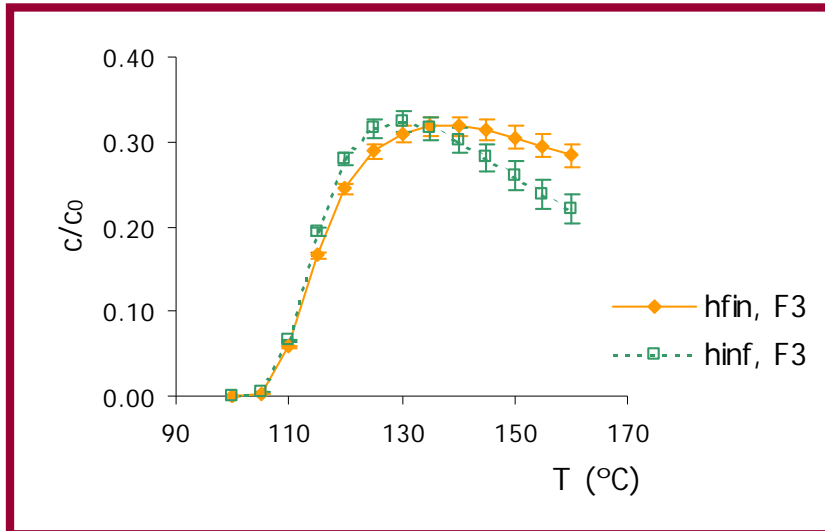
- h finite and infinite
- T_{holding} : 100-160 °C
- Static and 10 rpm
- F_0 value of 3 and 5 min

Statistical analysis

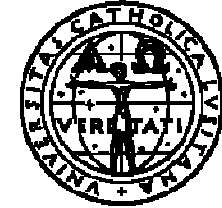
- Three-factor (F_0 , h and T) analysis of variance
- Multiple pairwise comparisons of treatment means, using Least Significant Difference (LSD) at a 5% level of significance



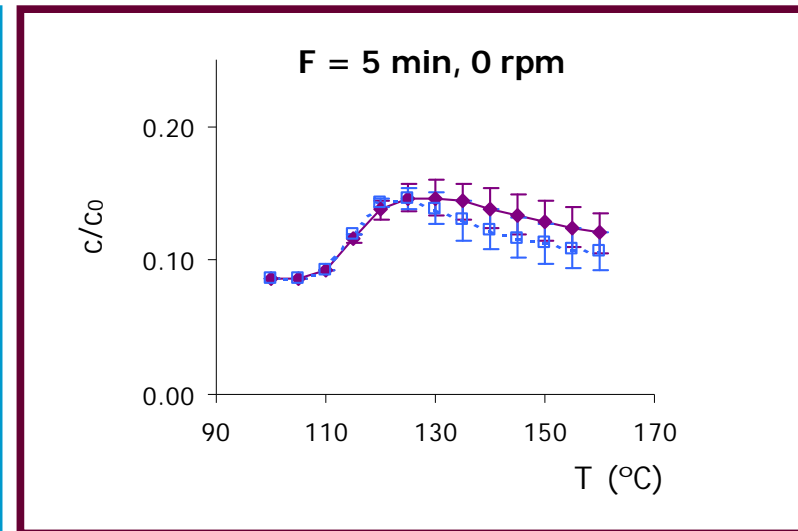
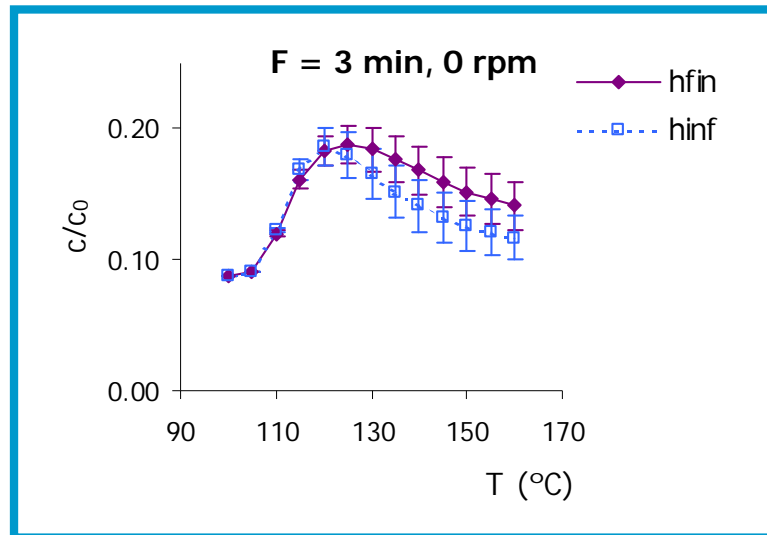
Green beans: *colour retention*



- CV values: 0 to 4.8%
- Optimum temperature range : 130 to 135°C



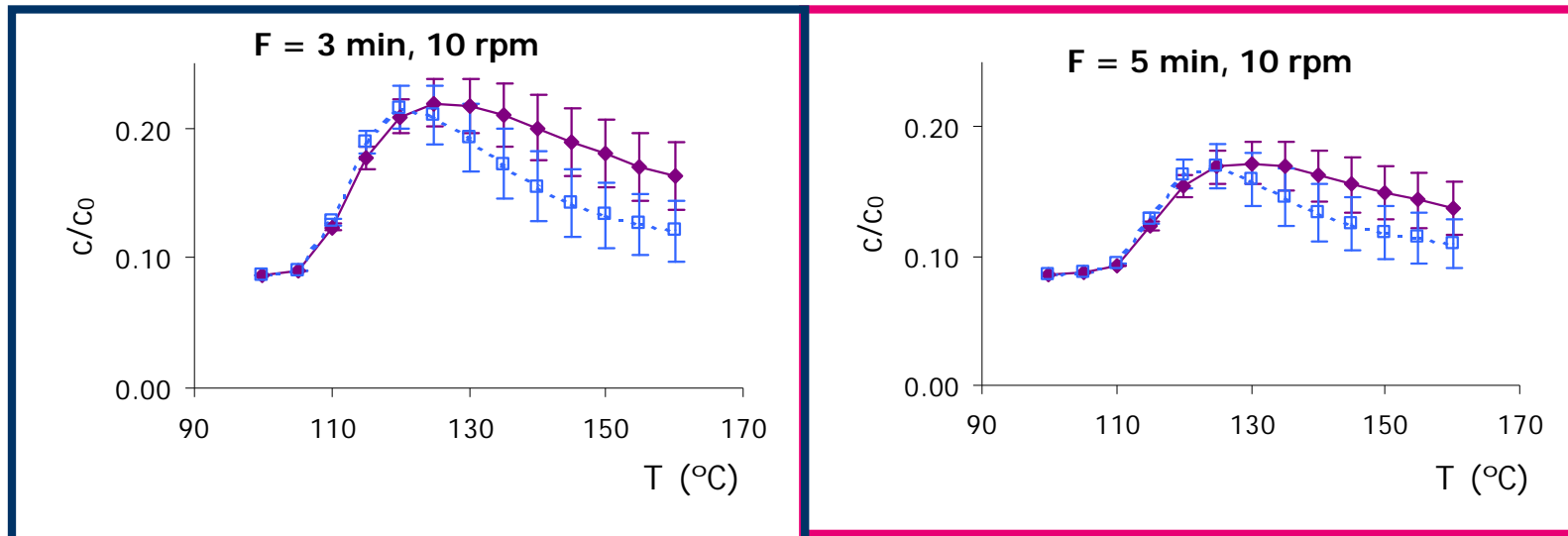
White beans: *texture*



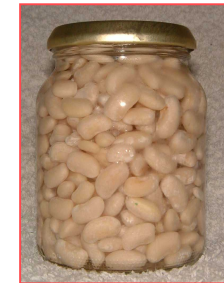
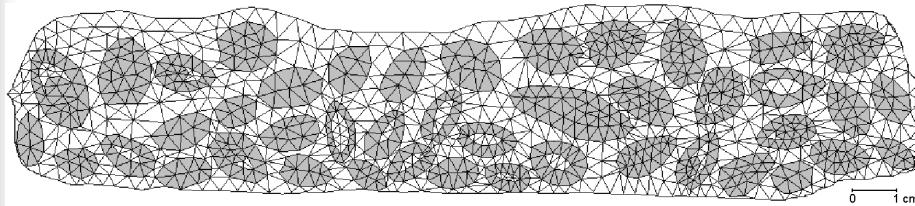
- CV values ranged from 0 to 16%
- Optimum temperature range : 125 to 130°C



White beans: *texture*



- CV values: 0 to 19%
- Optimum temperature range: 120 to 135°C



Thank you

