



**Taxas de Degradação –  
Bases para as ferramentas preditivas**

*Cristina L.M. Silva*

*Teresa S. Brandão*



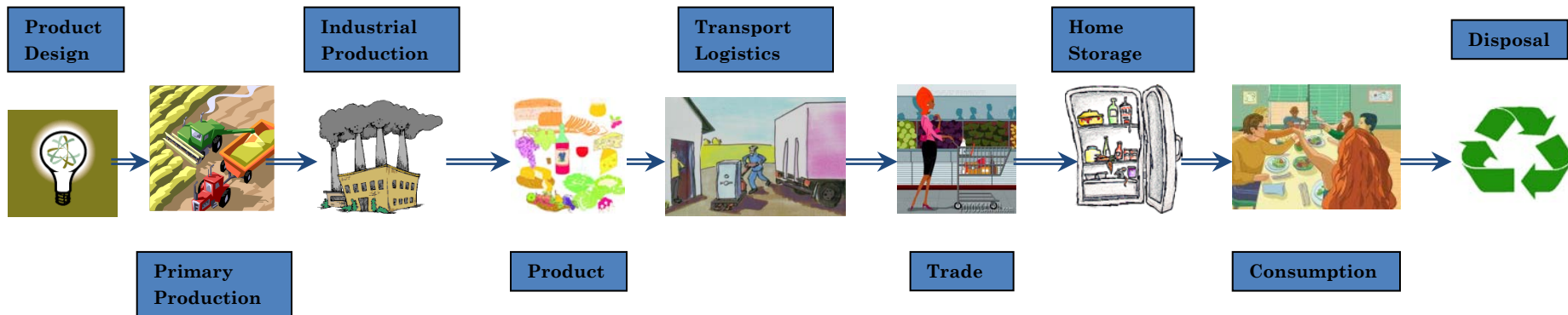
# **Taxas de Degradação – Bases para as ferramentas preditivas**

*Cristina L.M. Silva*

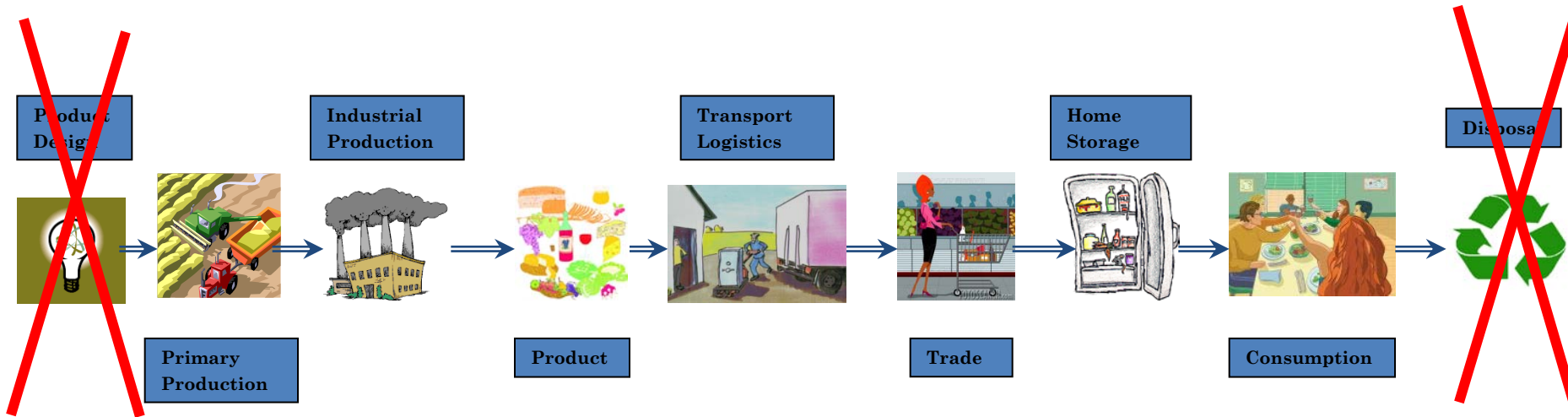
*Teresa S. Brandão*



# Cadeia de Distribuição



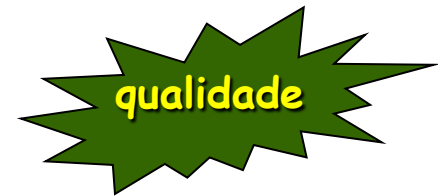
# Cadeia de Distribuição



# Estudo e Definição de Processos

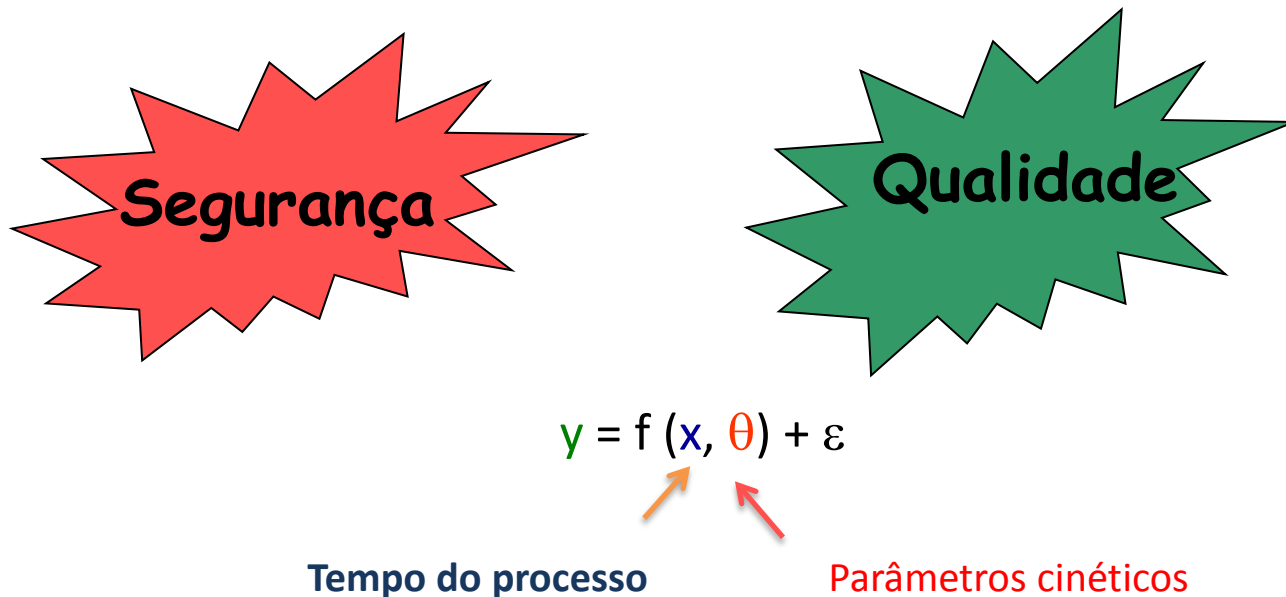


Bacterias patogénicas  
Contaminantes químicos  
...



Textura  
Microestrutura  
Cor  
Vitamin C  
...

# Modelagem Matemática



A extensão e velocidade de produção/degradação de uma característica de segurança ou qualidade pode ser **quantificada**

... assim como **o efeito das condições de processamento** nos parâmetros cinéticos e consequentemente as **respostas finais**

# Modelagem Matemática

alguns conceitos ...

$$y = f(x, \theta) + \varepsilon$$

## Estimativa dos parâmetros

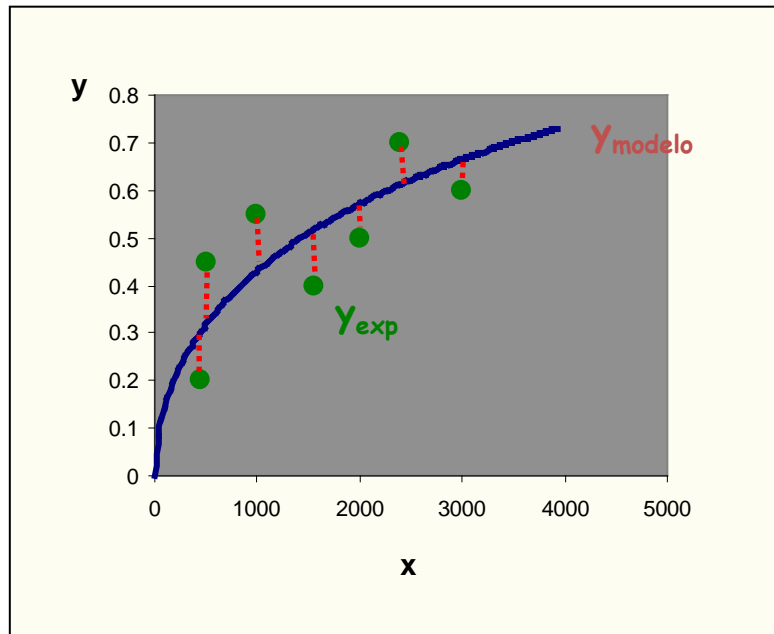
minimização dos desvios entre os valores **experimentais** e os obtidos pelo **modelo**



Precisas ?

$\theta^*$

Exactas ?



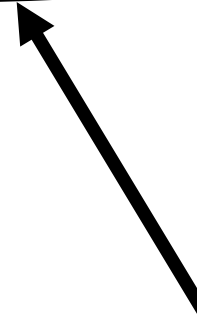
# Modelagem Matemática

**objectivo**

descrição **precisa** e **exacta** das observações

**adequabilidade** do modelo

**qualidade** dos parâmetros





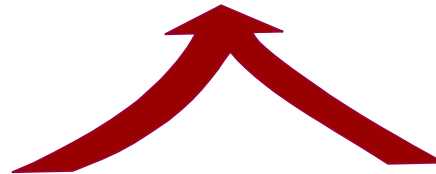
# Modelagem Matemática

## modelos mecanísticos

- ◆ descrição fundamental dos processos físico-químicos envolvidos
- ◆ mais complexos

## modelos empíricos

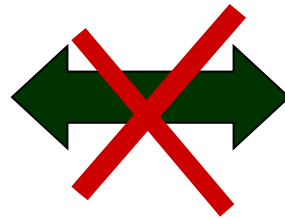
- ◆ *caixa preta*
- ◆ mais simples (ou não!)
- ◆ aplicação prática



ponderar **vantagens** e **desvantagens**  
decisão depende do **objectivo final**

# Modelagem Matemática

complexidade  
matemática



descrição adequada

qualidade

modelo



parâmetros

# Modelagem Matemática

## **vantagens**

- **conhecimento do processo**
- **efeito do processo no produto**
- **controlo das variáveis envolvidas**

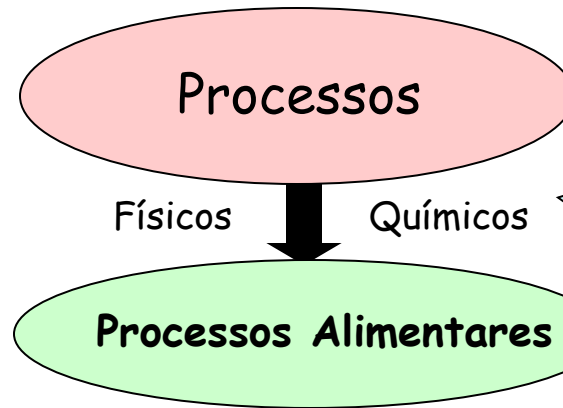
# Modelagem Matemática

Fenómenos de Transferência

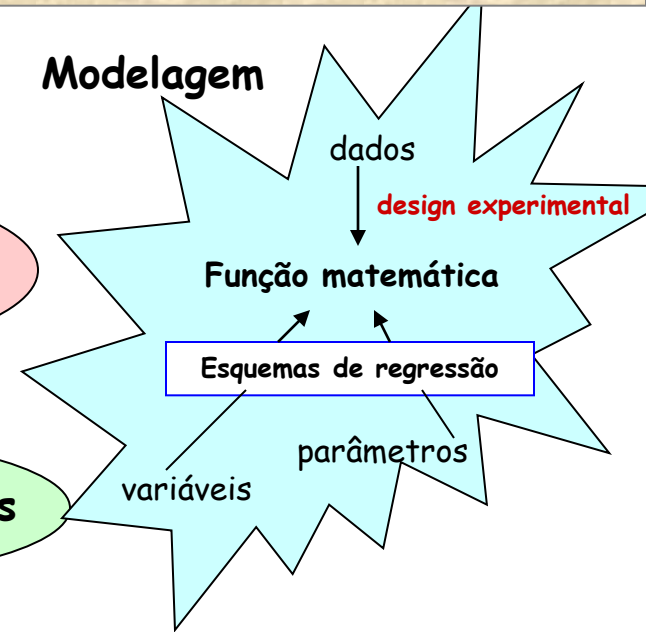
- calor
- massa
- *momentum*

Cinéticas de reacção

Propriedades



Modelagem



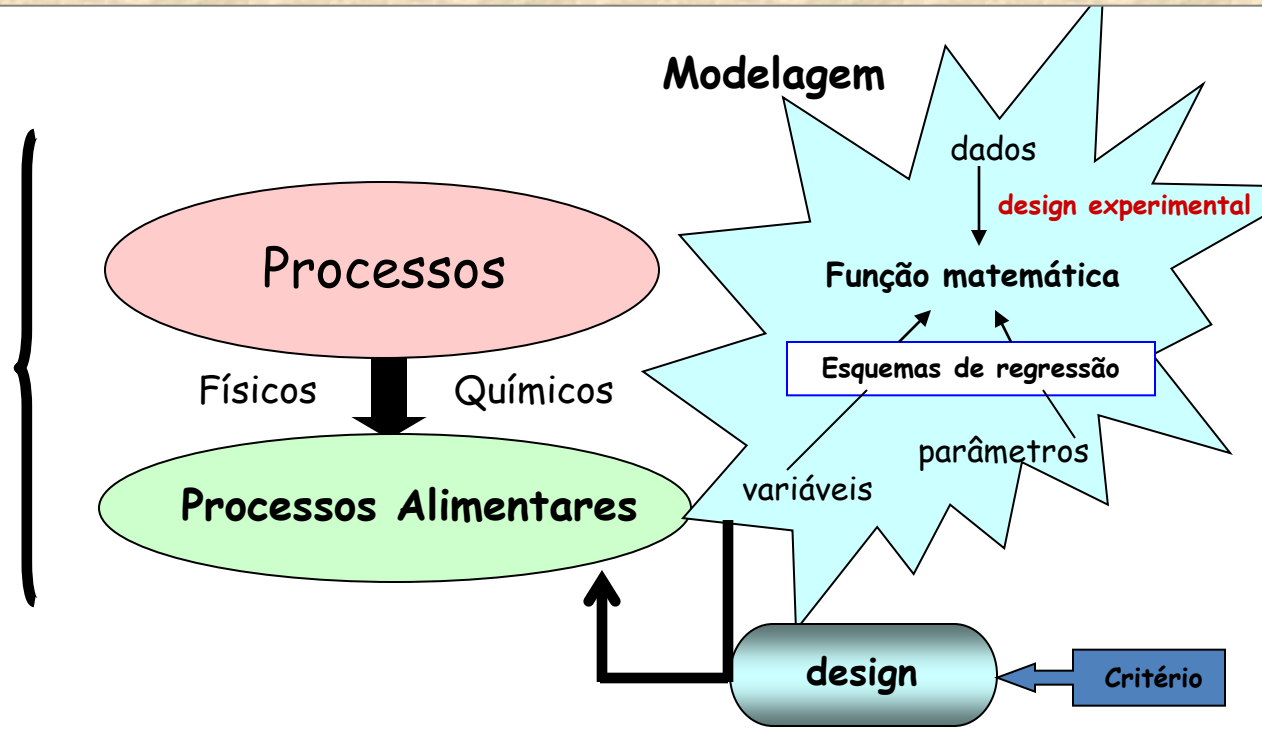
# Modelagem Matemática

Fenómenos de Transferência

- calor
- massa
- *momentum*

Cinéticas de reacção

Propriedades



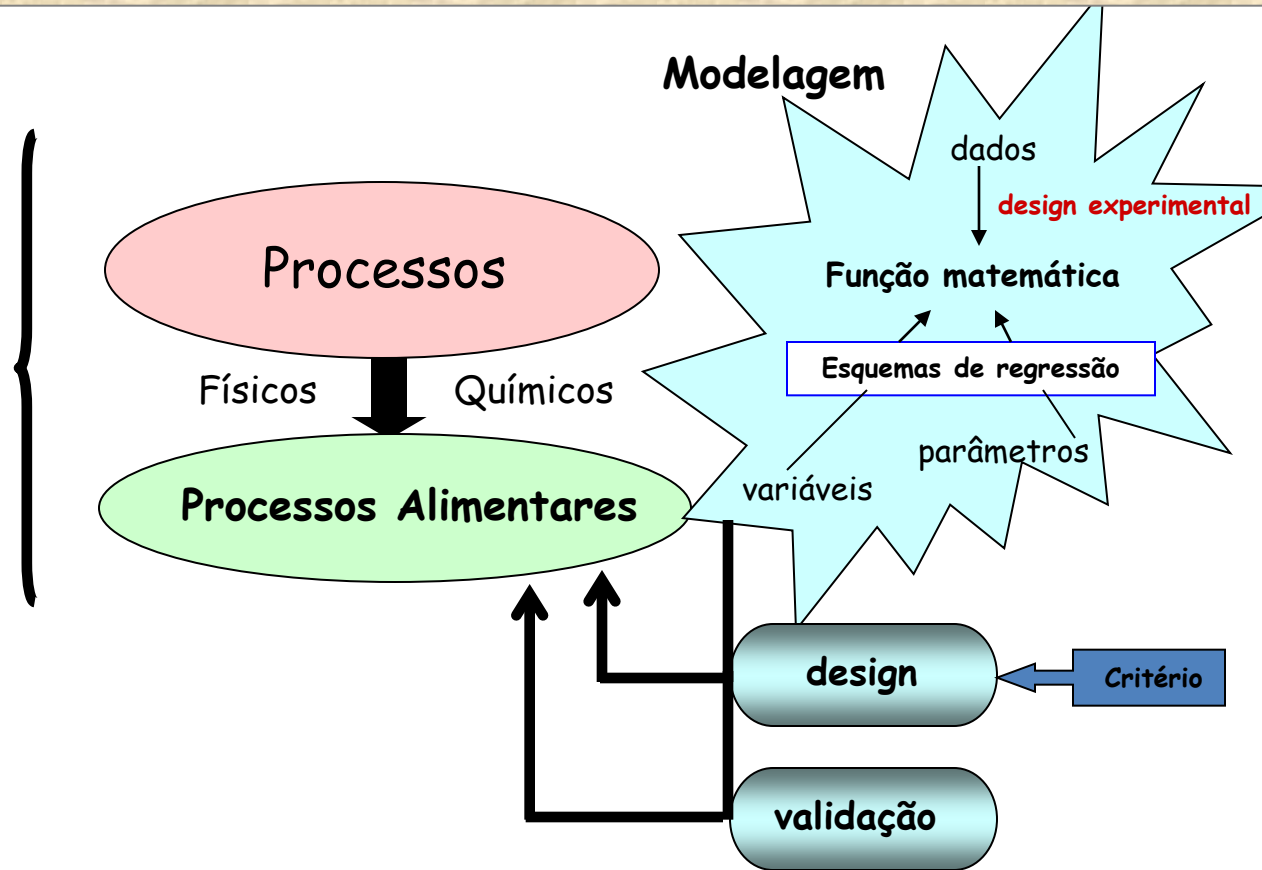
# Modelagem Matemática

Fenómenos de Transferência

- calor
- massa
- *momentum*

Cinéticas de reacção

Propriedades





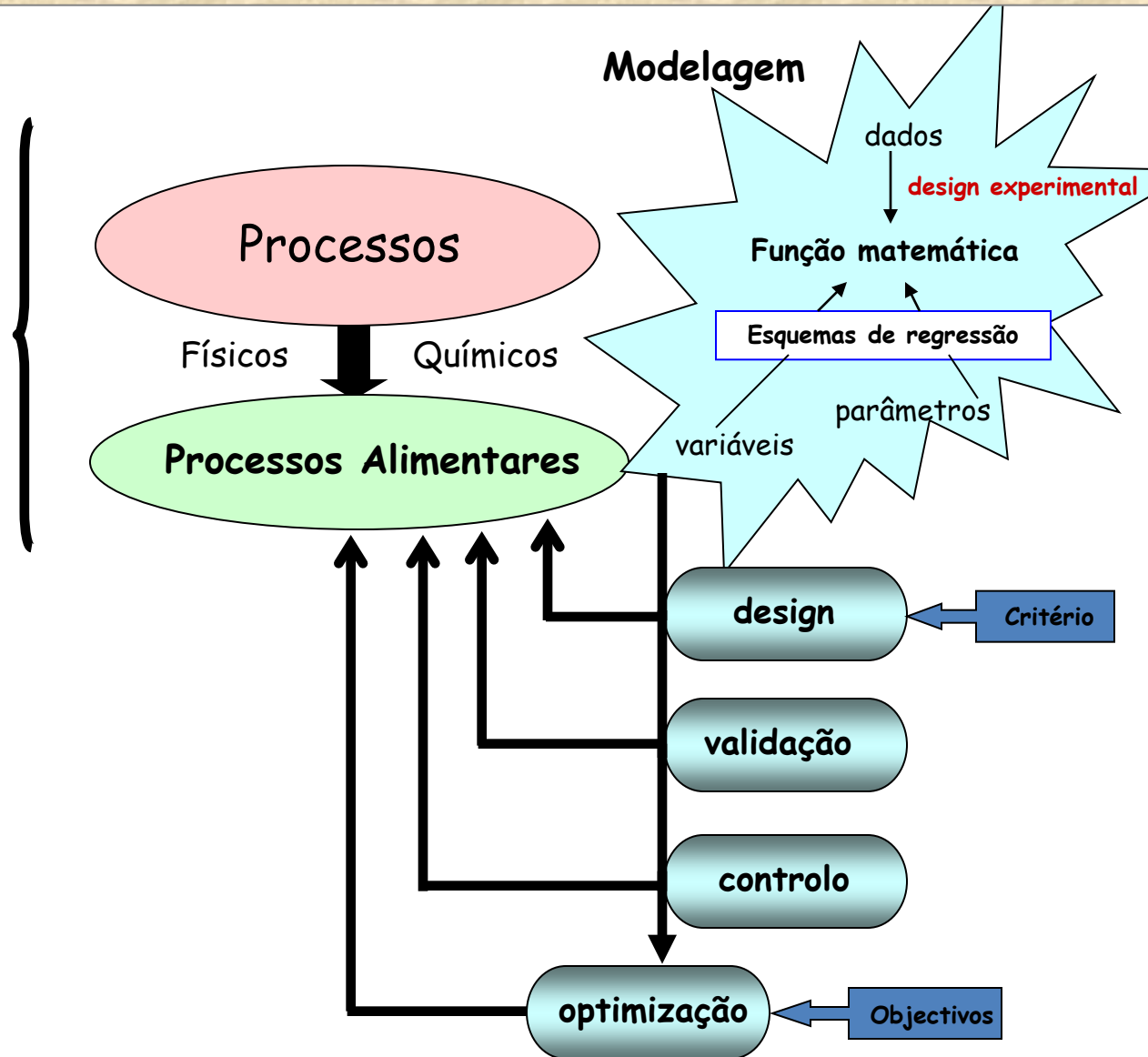
# Modelagem Matemática

Fenómenos de Transferência

- calor
- massa
- *momentum*

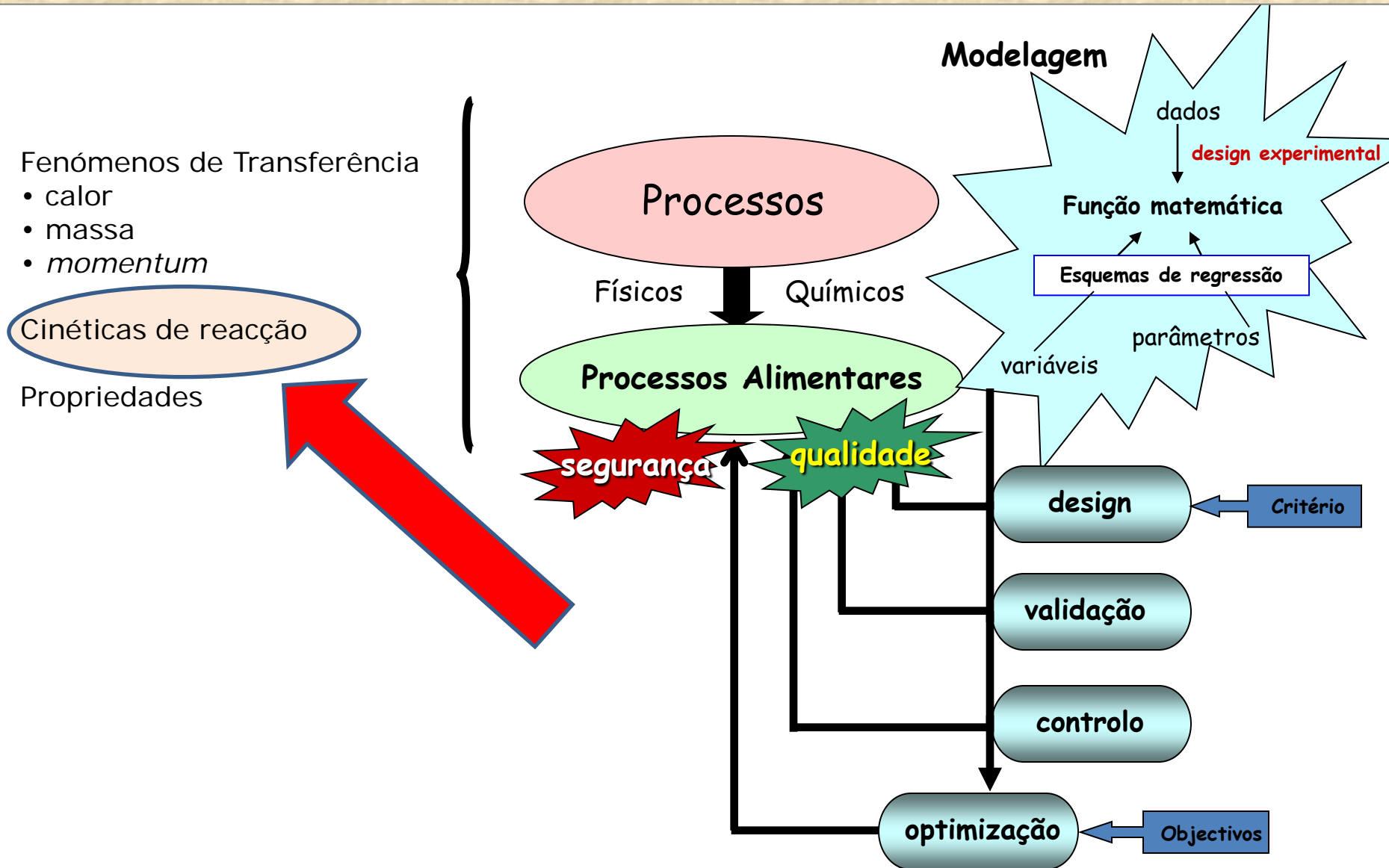
Cinéticas de reacção

Propriedades

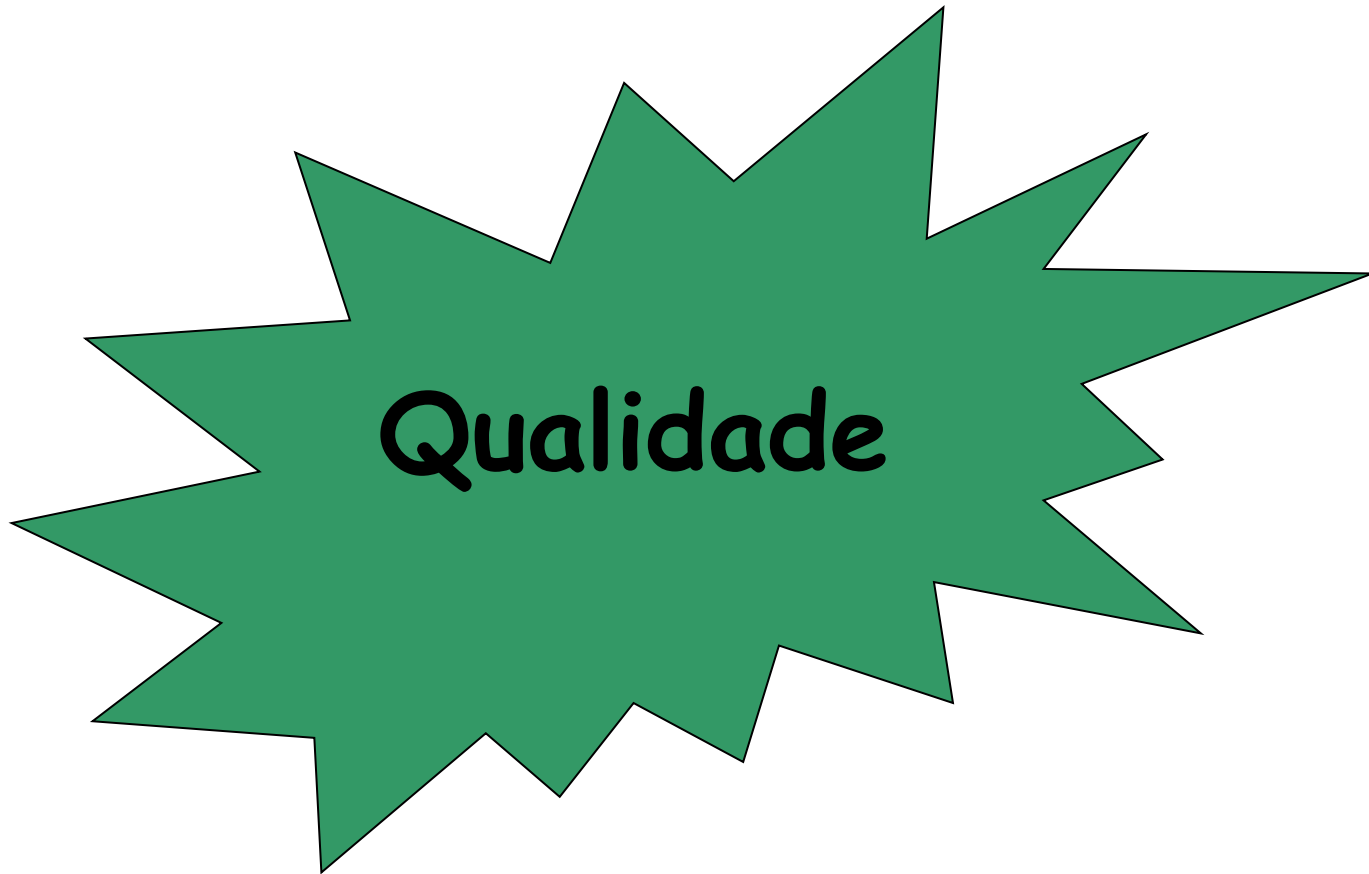




# Modelagem Matemática



# Modelagem Matemática



# Degradação de Qualidade

## Modelos cinéticos

Ordem zero

$$C = C_0 - k_{(T)}t$$

1ª ordem

$$C = C_0 e^{-k_{(T)}t}$$

Fracçãoário

$$\frac{C - C_{eq}}{C_0 - C_{eq}} = e^{-kt}$$

Atributo no tempo t

Valor inicial

Tempo

Energia de activação

T. referência

$$k_{(T)} = k_{ref} \exp\left[-\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right]$$

Const. gases

**Efeito da T em k**  
Lei de Arrhenius

Valor de equilíbrio

# Degradação de Qualidade

**Branqueamento**

**carrots**



*Daucus carota L.*



**Quality**

**pumpkin**



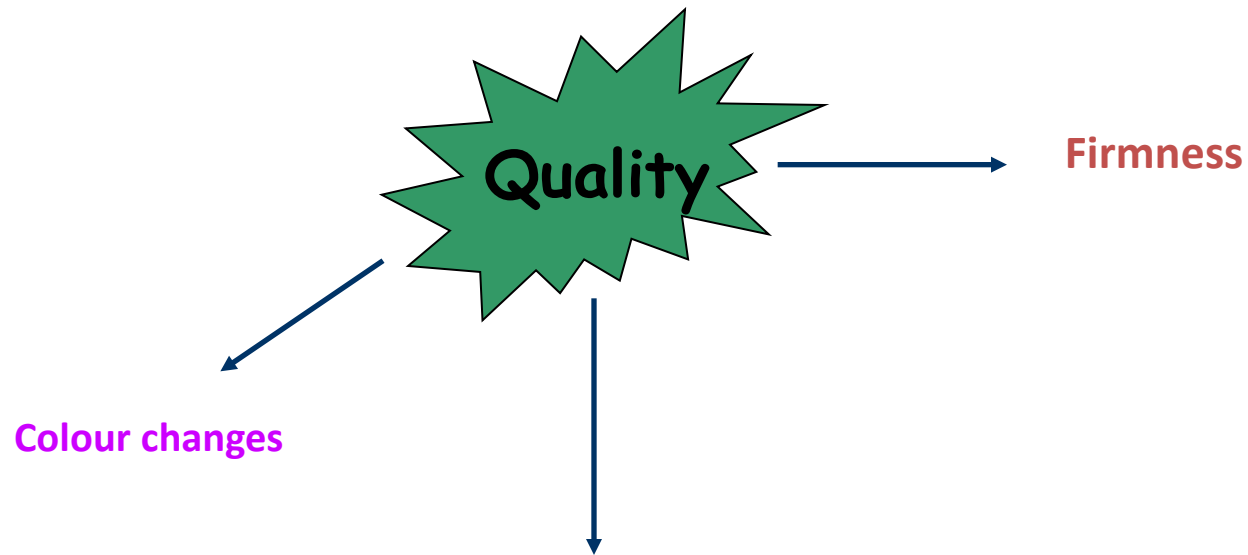
*Cucurbita maxima L.*

**broccoli**



*Brassica oleracea L.*

# Degradação de Qualidade



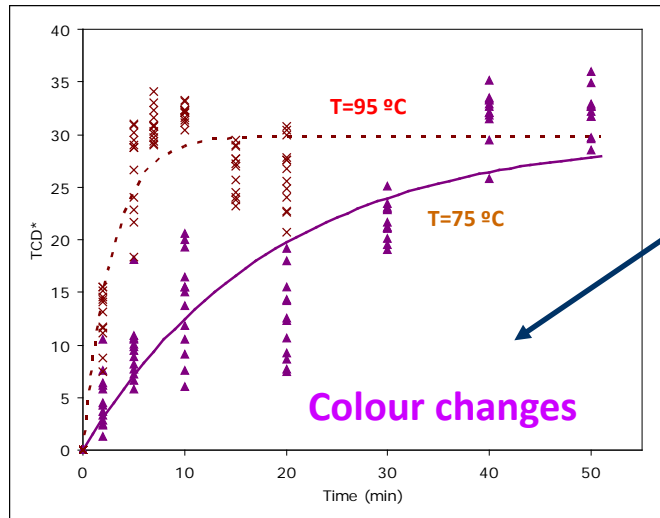
pumpkin



*Cucurbita maxima L.*

# Degradação de Qualidade

Total Colour Difference, Hunter (L,a,b) scale, colourimeter (CR-300, Minolta)



Firmness

Peroxidase

pumpkin



*Cucurbita maxima L.*

# Degradação de Qualidade

Fractional conversion model

$$\frac{TCD - TCD_{eq}}{TCD_0 - TCD_{eq}} = e^{-kt}$$

$k(T) \rightarrow$  Arrhenius



Firmness

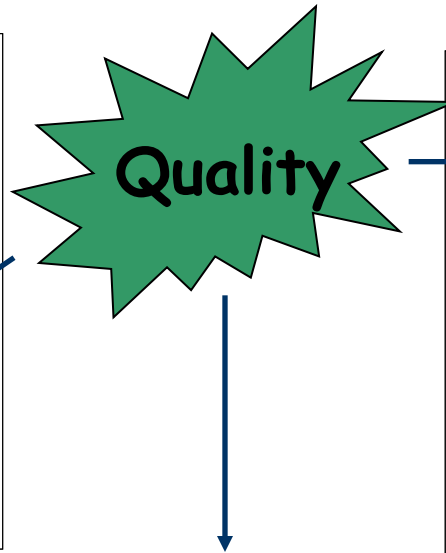
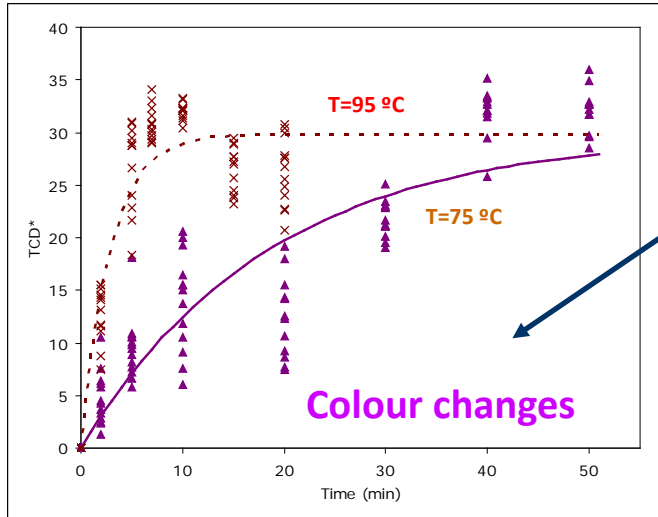
pumpkin

Peroxidase

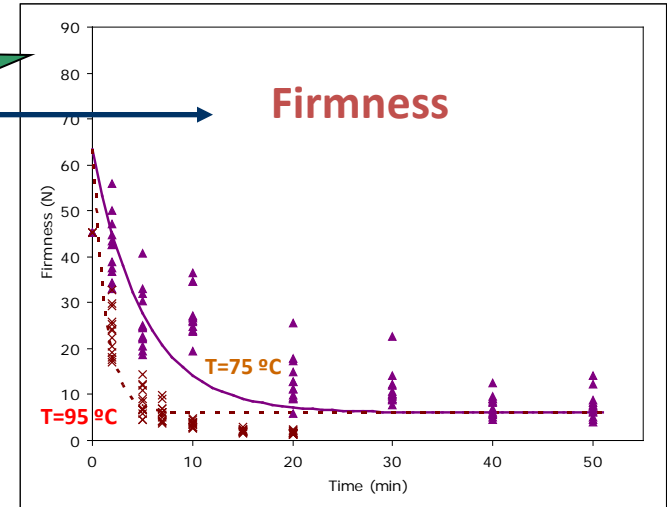


*Cucurbita maxima L.*

# Degradação de Qualidade



Texture Analyser (Stable Micro-System Ltd, Godalming, UK)  
single puncture measurement, 10 mm depth of penetration, velocity of 1.0 mm s<sup>-1</sup>



pumpkin

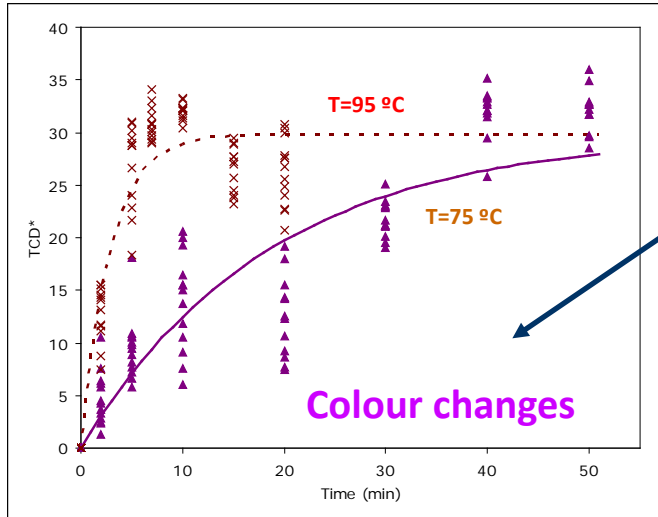


*Cucurbita maxima L.*

Peroxidase



# Degradação de Qualidade



Quality

**Firmness**

Fractional conversion model

$$\frac{\text{Firmness} - \text{Firmness}_{eq}}{\text{Firmness}_0 - \text{Firmness}_{eq}} = e^{-kt}$$

$k(T) \rightarrow$  Arrhenius

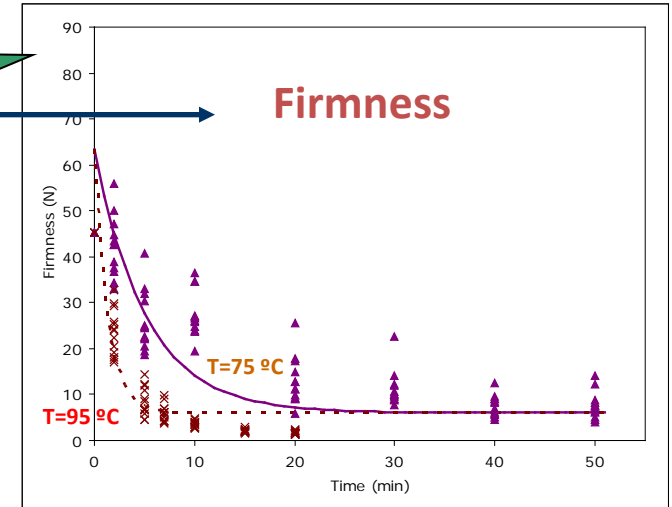
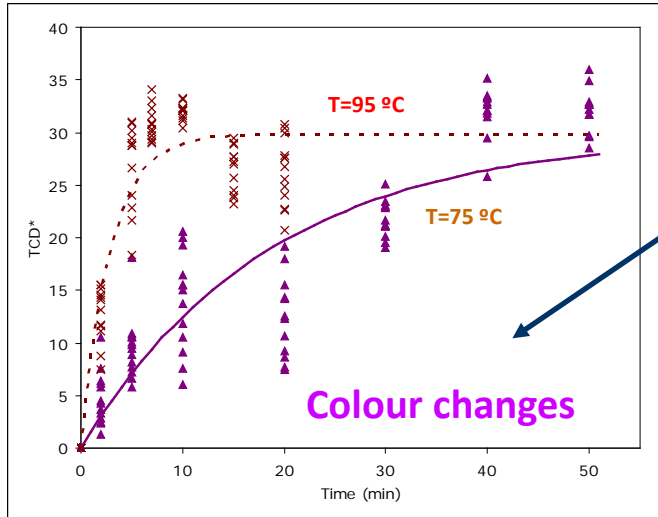
pumpkin



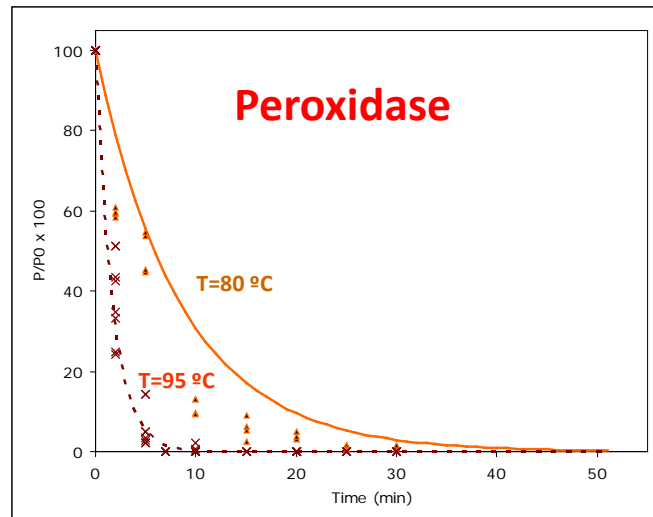
*Cucurbita maxima L.*

Peroxidase

# Degradação de Qualidade

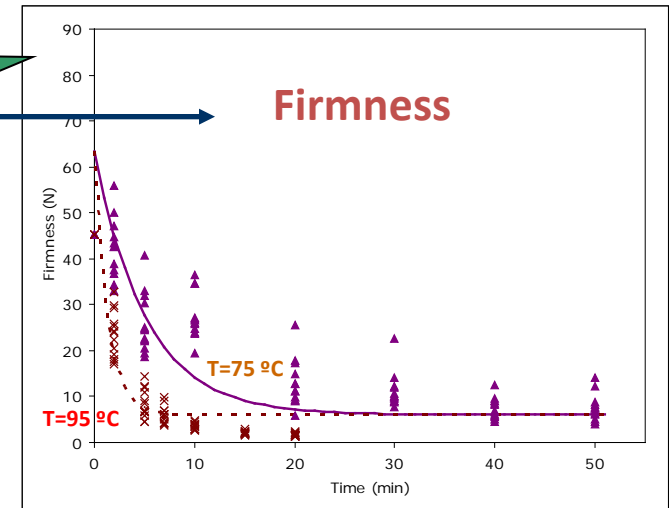
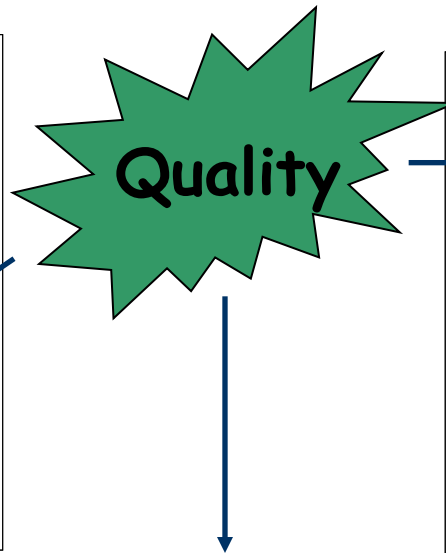
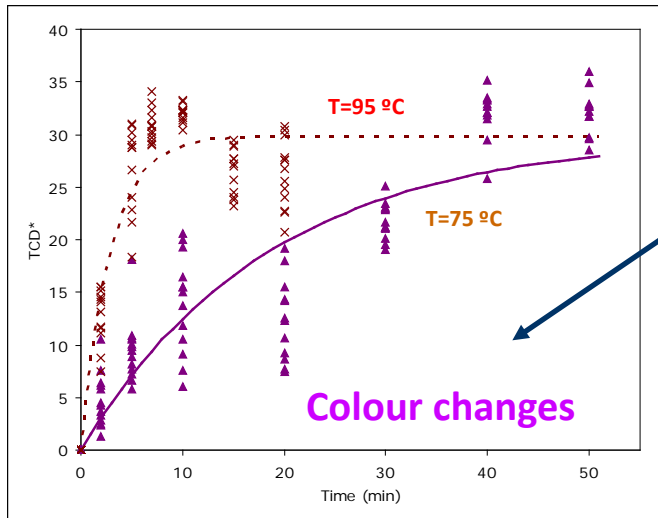


*Cucurbita maxima L.*



Spectrophotometry (Unicom Ltd, Cambridge, UK)

# Degradação de Qualidade



pumpkin



*Cucurbita maxima L.*

Peroxidase

First order kinetics

$$\frac{P}{P_0} = e^{-kt}$$

$k(T) \rightarrow$  Arrhenius

# Degradação de Qualidade

**Modelling** the kinetics of **peroxidase** inactivation and **colour** and **texture** changes of pumpkin during blanching, will allow convenient design of thermal processes



Stabilisation of enzymatic deterioration

Minimisation of quality losses

pumpkin



*Cucurbita maxima L.*

**Blanching conditions**

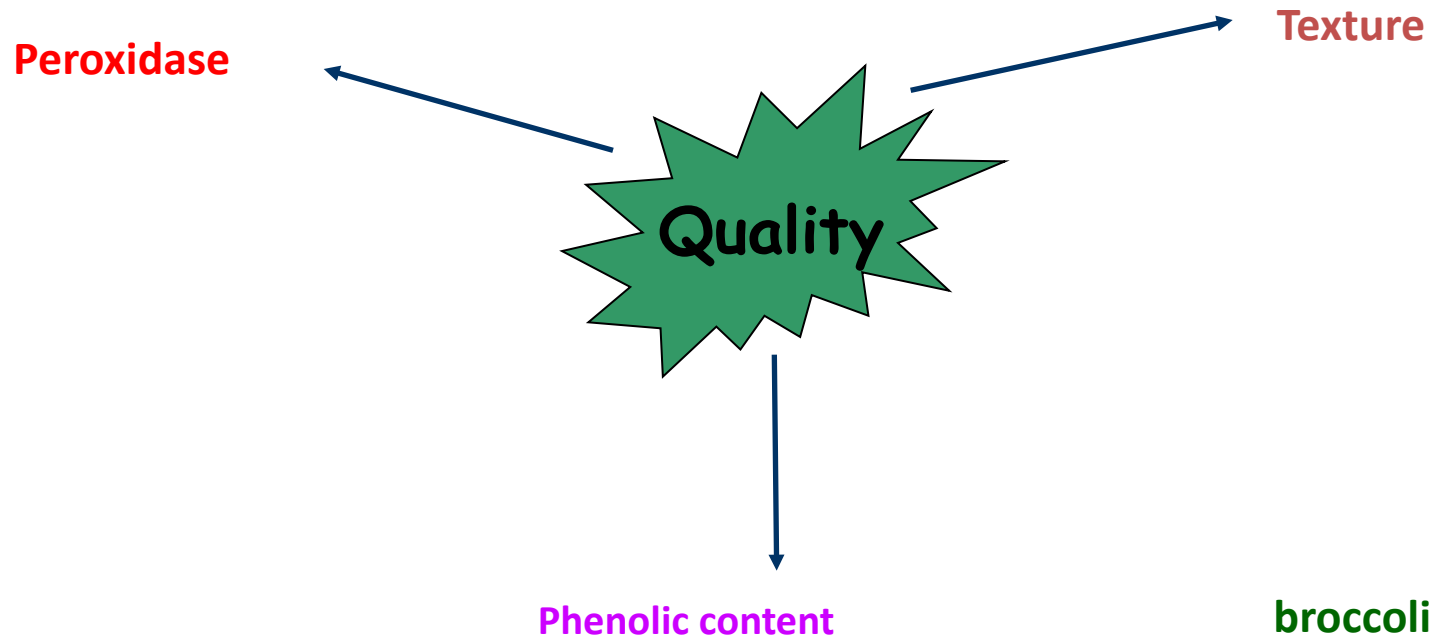
5.8 min at 90 °C

and

3.9 min at 95 °C

... are recommended to decrease 90% of peroxidase activity, ensuring a good retention of colour. Unavoidably, texture is greatly affected (~ 14% was retained).

# Degradação de Qualidade

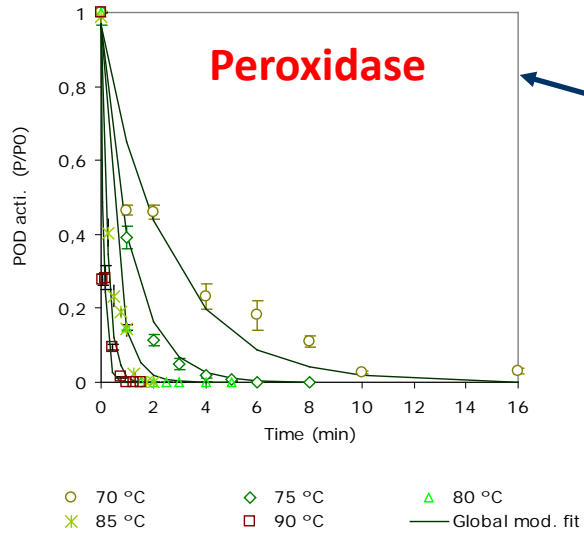


broccoli



*Brassica oleracea L.*

# Degradação de Qualidade



Spectrophotometry (Unicom Ltd, Cambridge, UK)



Texture

Phenolic content

broccoli



*Brassica oleracea L.*

# Degradação de Qualidade

**Peroxidase**

**First order kinetics**

$$\frac{P}{P_0} = e^{-kt}$$

**k(T) → Arrhenius**

**Quality**

**Texture**

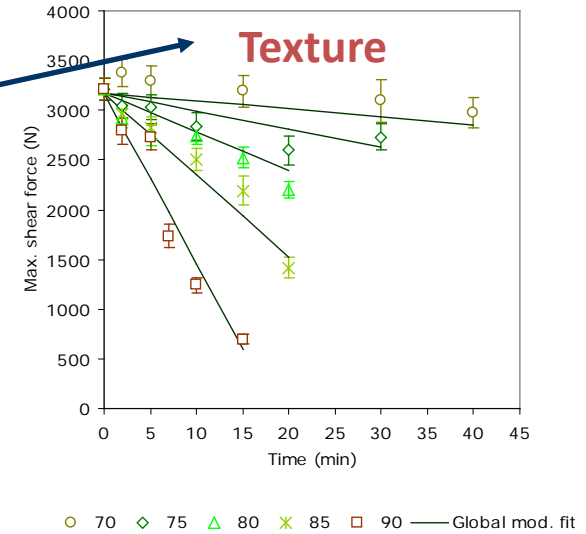
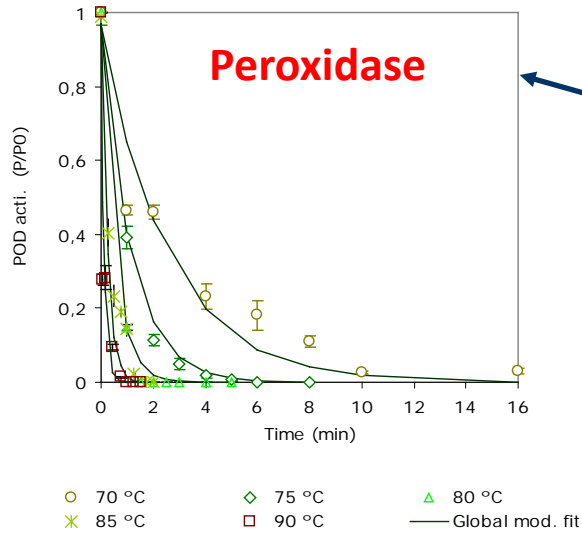
**Phenolic content**

**broccoli**



*Brassica oleracea L.*

# Degradação de Qualidade



Phenolic content

Texture Analyser (Stable Micro-System Ltd, Godalming, UK)  
maximum shear force, test speed 8 mm s<sup>-1</sup>, full-scale load 500 N

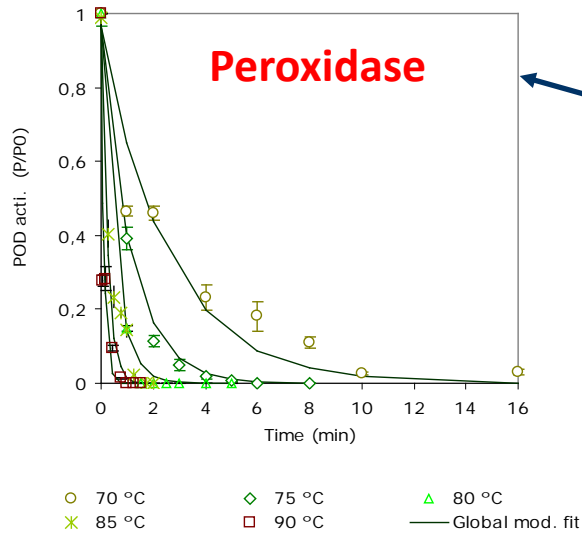
broccoli



*Brassica oleracea L.*



# Degradação de Qualidade



Phenolic content

**Texture**

**Zero order kinetics**

$$\text{Max shear force} = (\text{Max shear force})_0 - kt$$

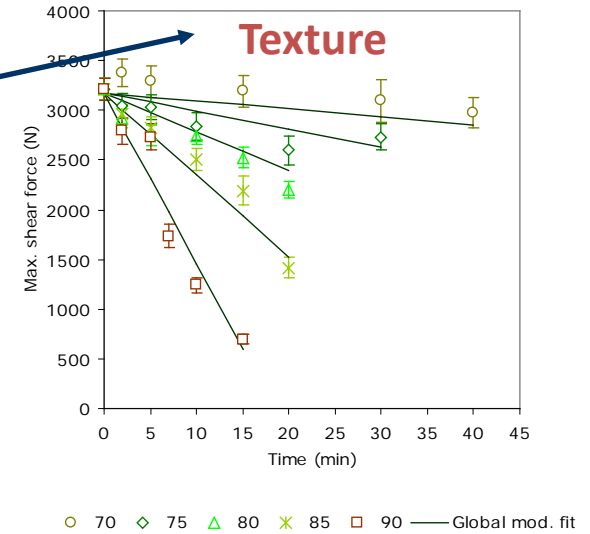
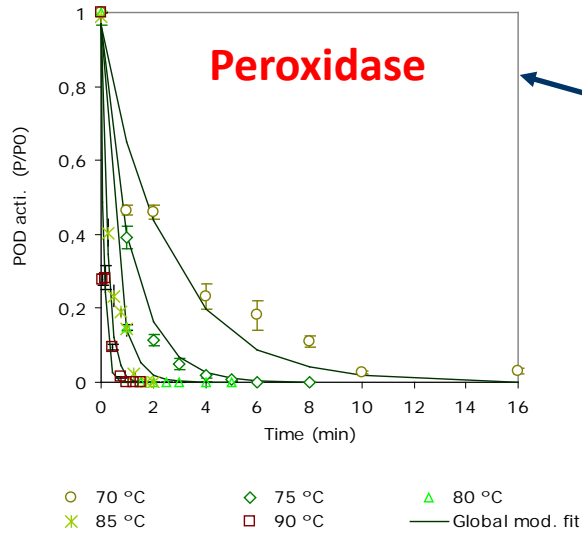
$k(T) \rightarrow$  Arrhenius

broccoli



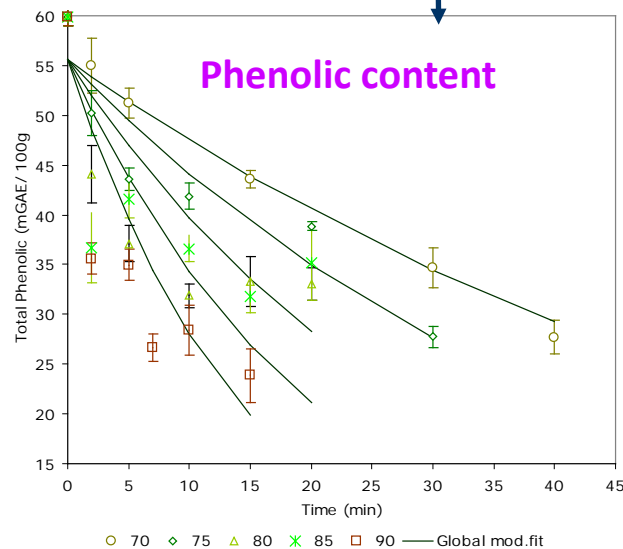
*Brassica oleracea L.*

# Degradação de Qualidade



**Quality**

Spectrophotometry  
(Unicom Ltd, Cambridge, UK)

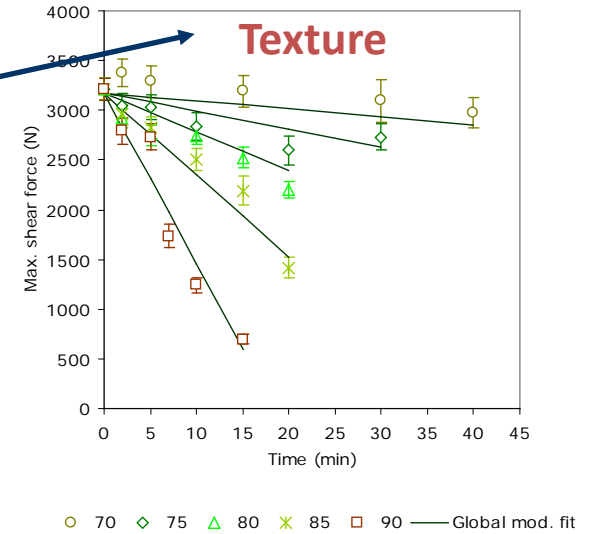
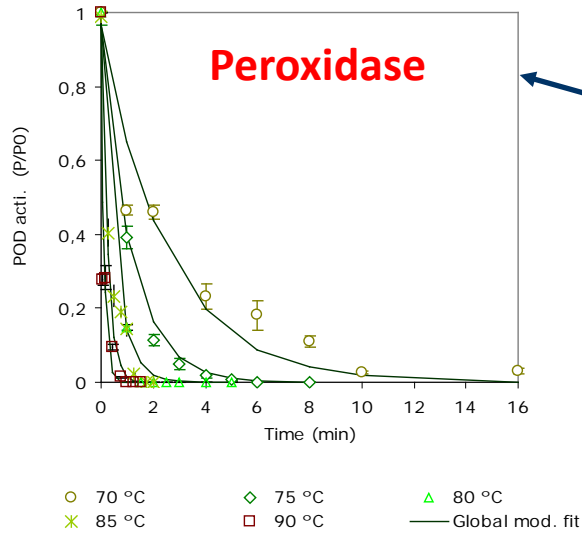


**broccoli**



*Brassica oleracea L.*

# Degradação de Qualidade



Phenolic content

First order kinetics

$$P = P_0 e^{-kt}$$

$k(T) \rightarrow$  Arrhenius

broccoli



*Brassica oleracea L.*

# Degradação de Qualidade

**Modelling** the kinetics of **peroxidase** inactivation and **phenolic content** and **texture** changes of broccoli during blanching, will allow convenient design of thermal processes



Stabilisation of enzymatic deterioration

Minimisation of quality losses

## Blanching conditions

6.5 min at 70 °C  
and  
0.4 min at 90 °C

... are recommended to decrease 90% of peroxidase activity.

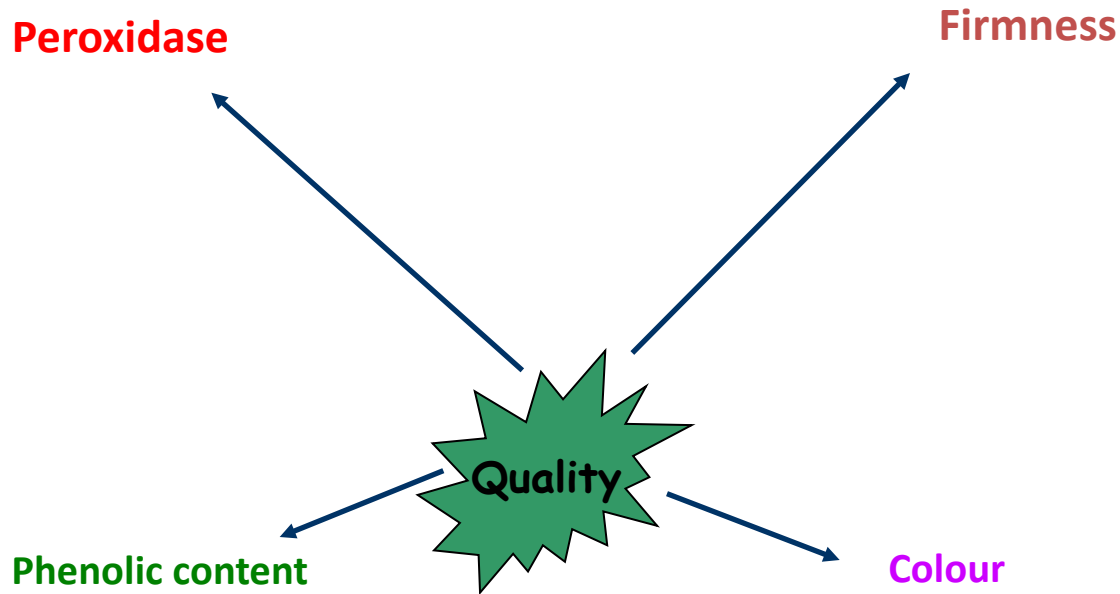
Texture was the most temperature sensitive parameter. Thus, attention should be given to texture against other quality parameters for optimizing thermal processes of broccoli.

broccoli



*Brassica oleracea L.*

# Degradação de Qualidade

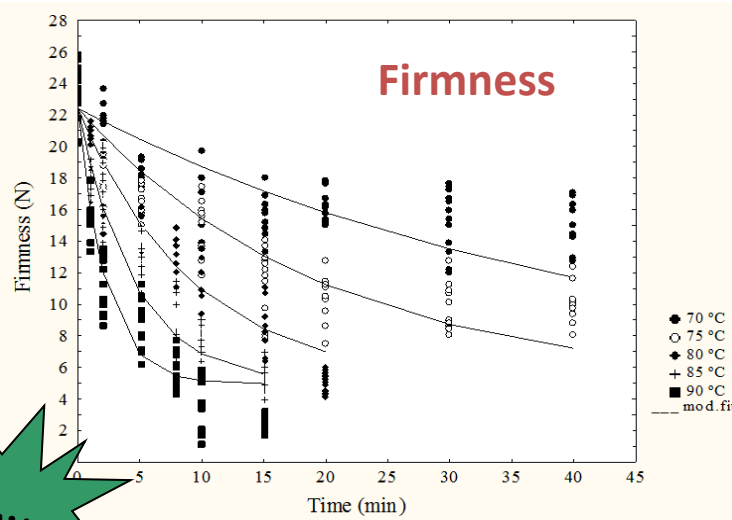
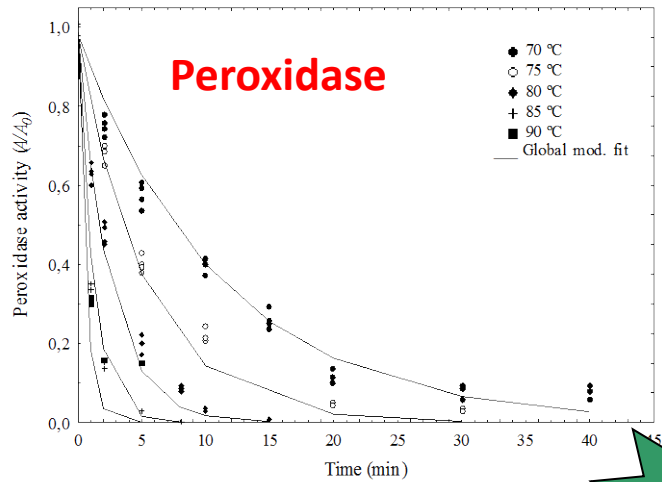


carrots



*Daucus carota L.*

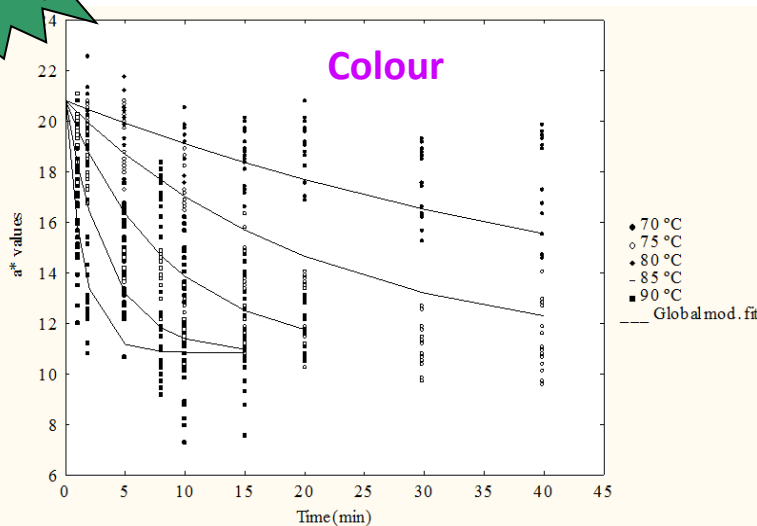
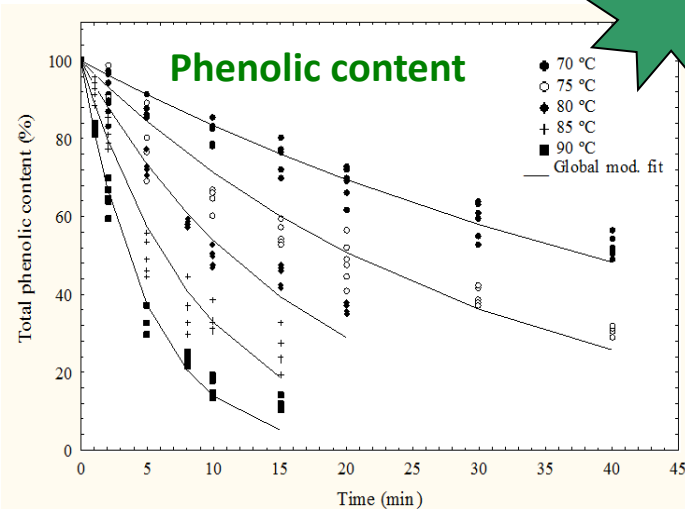
# Degradação de Qualidade



carrots



*Daucus carota* L.



Quality

# Degradação de Qualidade

## Peroxidase

### First order kinetics

$$\frac{P}{P_0} = e^{-kt}$$

$k(T) \rightarrow$  Arrhenius

## Firmness

### Fractional conversion model

$$\frac{\text{Firmness} - \text{Firmness}_{eq}}{\text{Firmness}_0 - \text{Firmness}_{eq}} = e^{-kt}$$

$k(T) \rightarrow$  Arrhenius



carrots

*Daucus carota L.*

Quality

## Phenolic content

### First order kinetics

$$\frac{P}{P_0} = e^{-kt}$$

$k(T) \rightarrow$  Arrhenius

## Colour

### Fractional conversion model

$$\frac{C - C_{eq}}{C_0 - C_{eq}} = e^{-kt}$$

$k(T) \rightarrow$  Arrhenius

# Degradação de Qualidade

**Modelling** the kinetics of **peroxidase** inactivation and **phenolic content**, **colour** and **texture** changes of carrots during blanching, will allow convenient design of thermal processes



carrots

*Daucus carota L.*



**Stabilisation of enzymatic deterioration**  
**Minimisation of quality losses**

**Blanching conditions**

6.0 min at 80 °C

... is recommended to decrease 90% of peroxidase activity, ensuring a good retention of phenolic content (70%). Colour was the most temperature sensitive parameter. Thus, attention should be given to colour against other quality parameters for optimizing thermal processes of carrots.



A large, red, multi-pointed starburst graphic with a black outline, centered on the page. The word "segurança" is written in white, bold, lowercase letters with a black drop shadow inside the starburst.

**segurança**

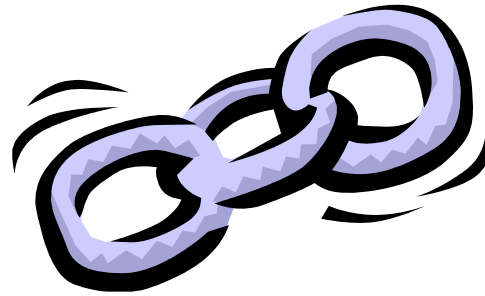
A red starburst graphic with multiple points, containing the text 'microbiologia predictiva' in white.

**microbiologia  
predictiva**

# Modelagem matemática

**microbiologia  
predictiva**

**microbiologia**



**matemática**

**estatística**

## aplicação

- previsão / simulação → rapidez
- desenvolvimento de processos eficazes de inactivação

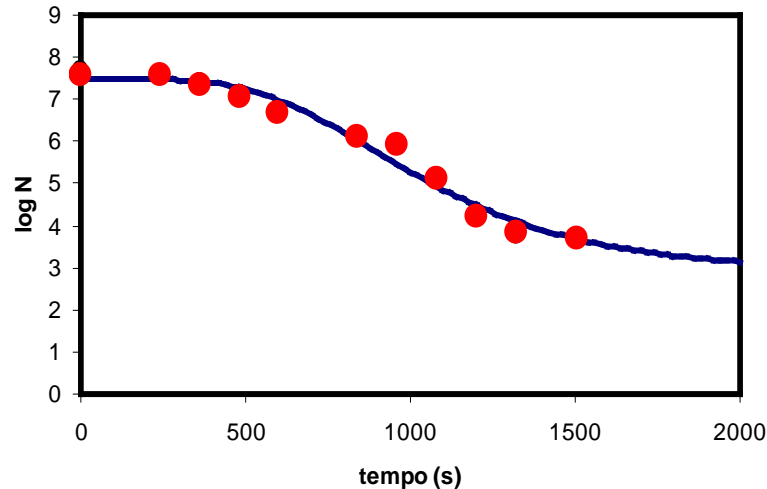


contribuição para **segurança**

## inactivação

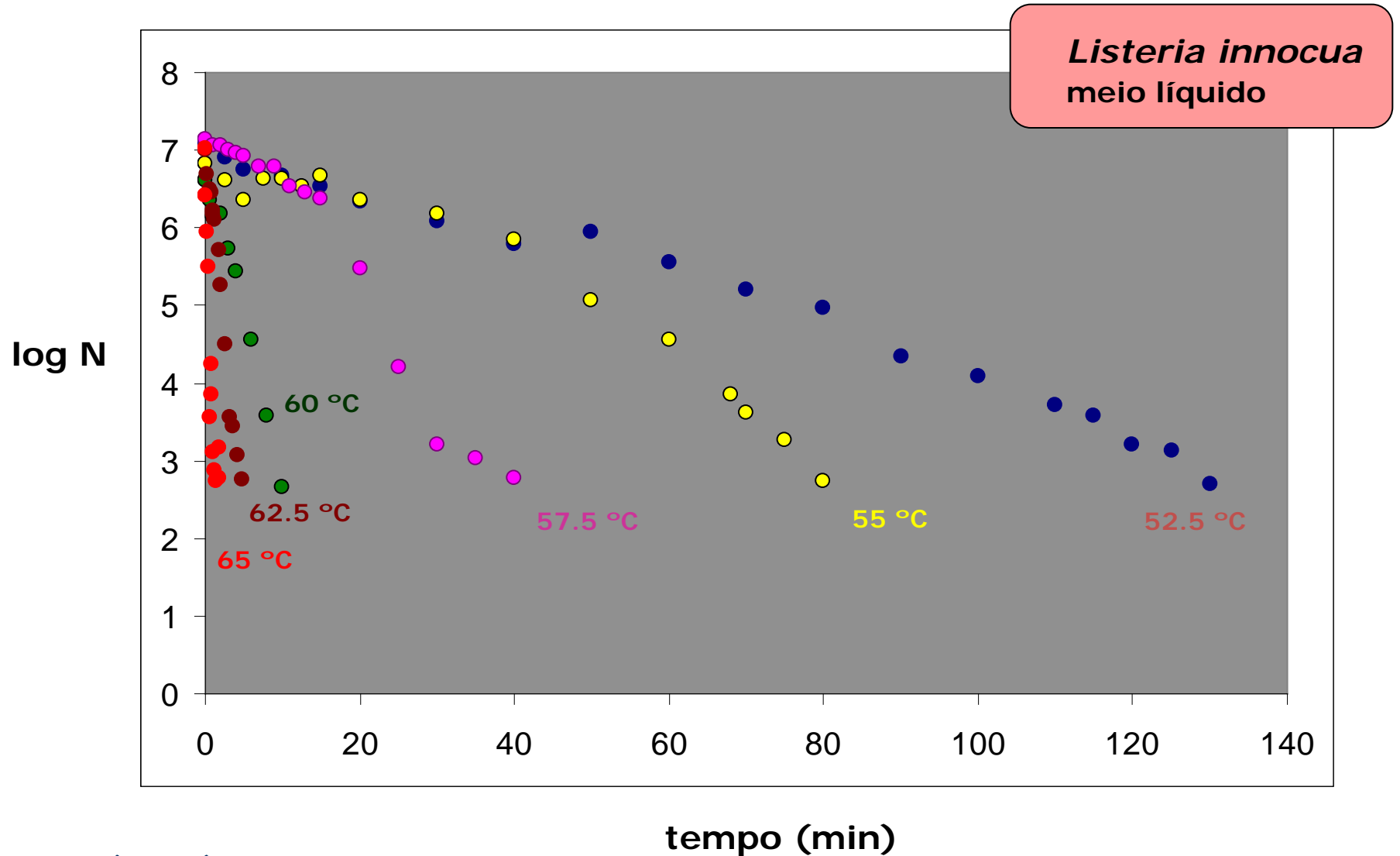


comportamento sigmoidal

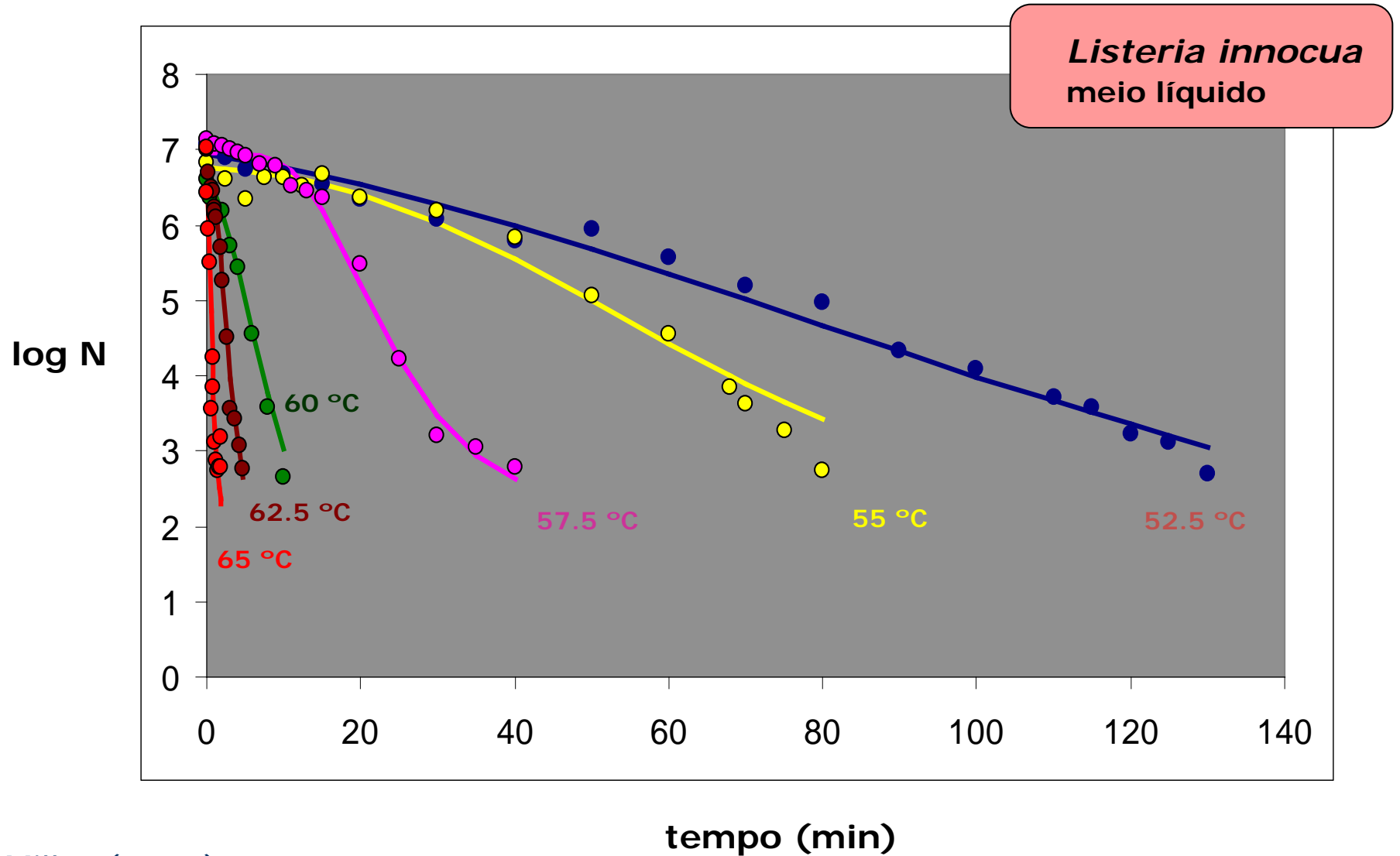


reflece a presença de *agregados* de microrganismos  
ou sub populações mais **resistentes** à **temperatura**  
(ou outro **factor adverso**)

# Exemplos



# Exemplos

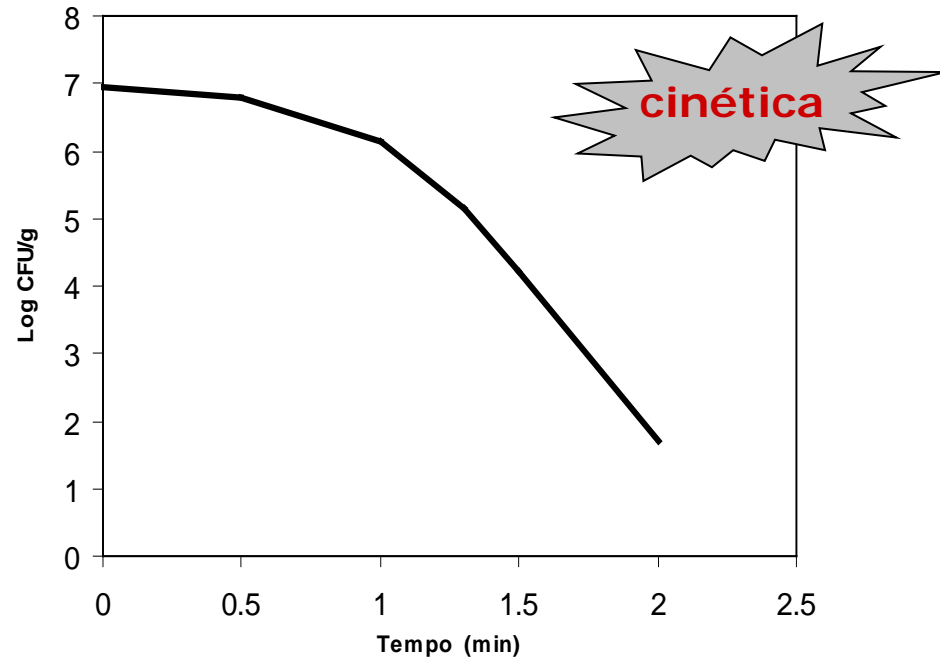


# Modelos matemáticos

❖ primários



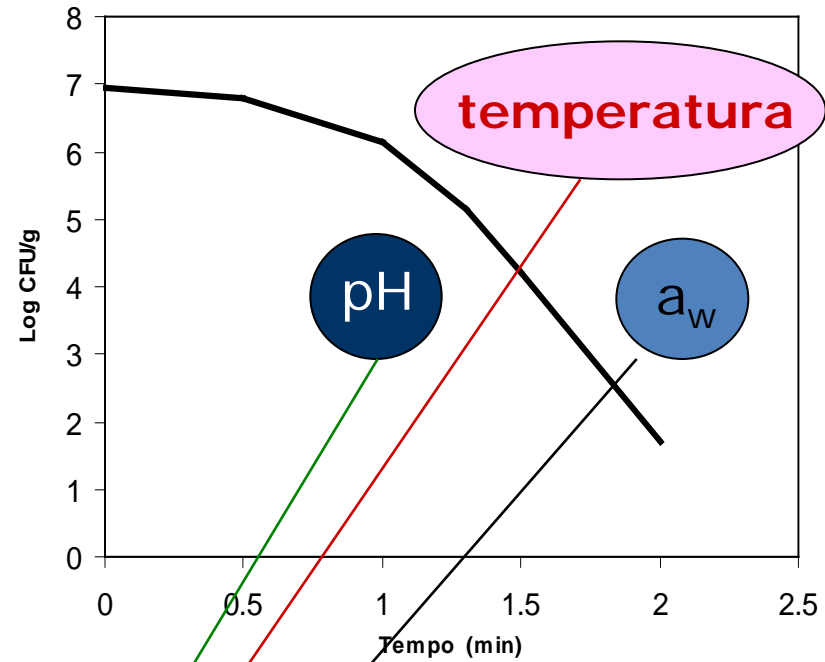
parâmetros





# Modelos matemáticos

❖ primários

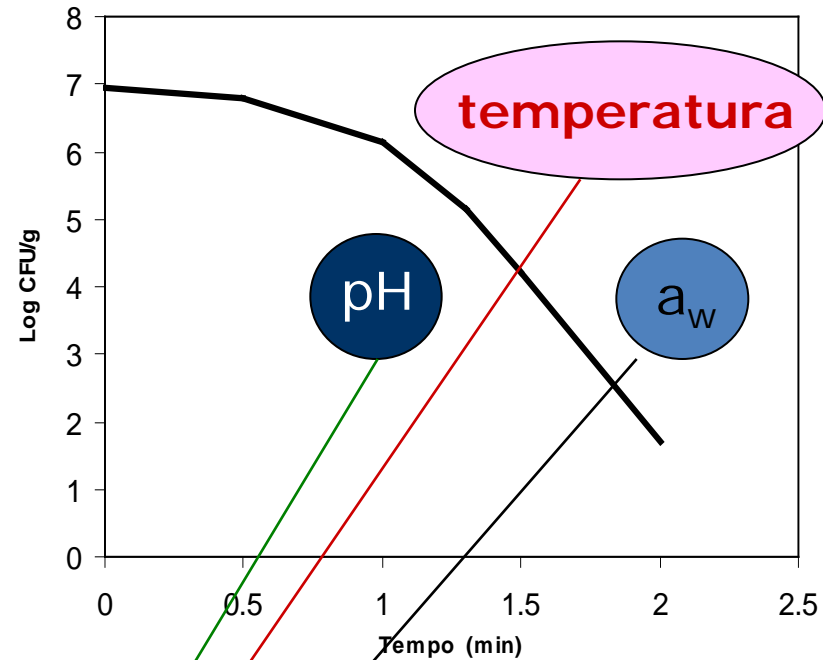


❖ secundários

parâmetros

# Modelos matemáticos

❖ primários

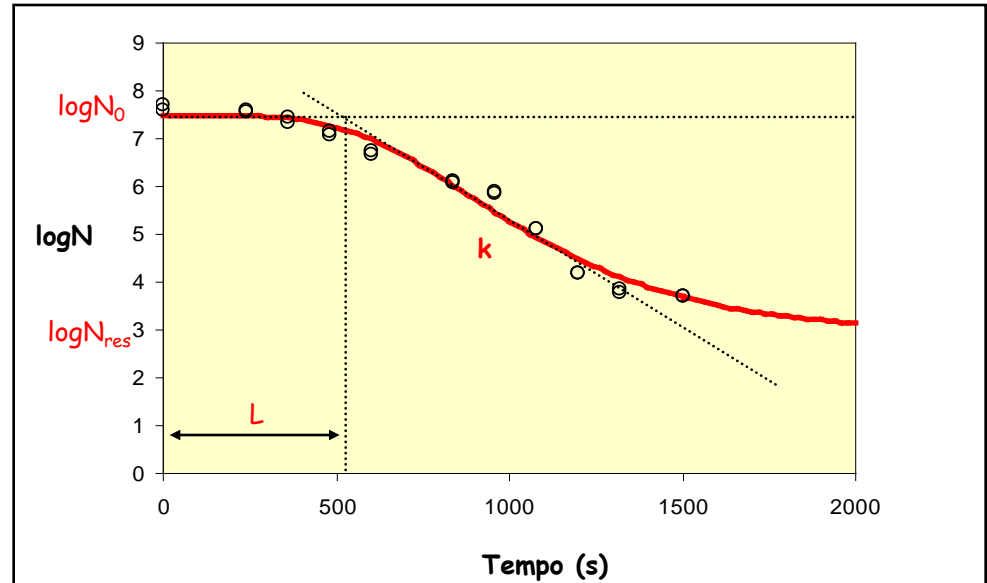


❖ secundários

❖ terciários - integração dos modelos anteriores - **software**  
**parâmetros**

# Modelos de inativação

❖ primários

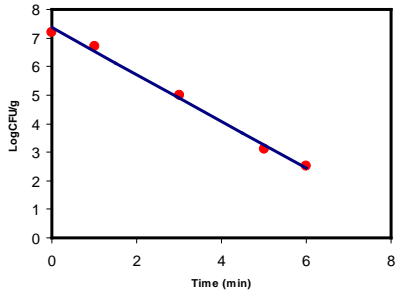


empíricos

fundamentais

# Modelos de inativação

## ❖ primários



$$N = N_0 \exp(-kt)$$

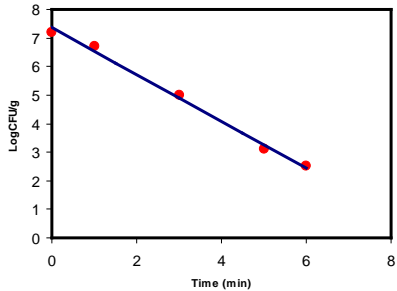


$$\log N = \log N_0 - \frac{t}{D} \quad 1^{\text{a}} \text{ ordem}$$

D – tempo de redução decimal

# Modelos de inativação

## ❖ primários



$$N = N_0 \exp(-kt)$$



$$\log N = \log N_0 - \frac{t}{D}$$

1ª ordem

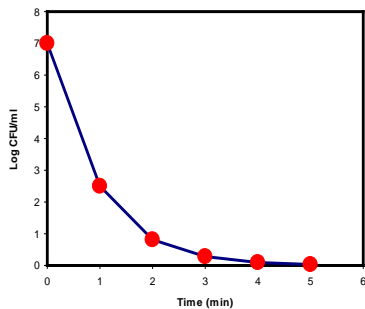
D – tempo de redução decimal

$$\frac{N}{N_0} = F_1 \exp(-k_1 t) + (1 - F_1) \exp(-k_2 t)$$

Cerf  
(1977)

## bifásicos

$F_1$  – fracção de microrganismos inactivados  
 $k_1$  e  $k_2$  – constantes cinéticas

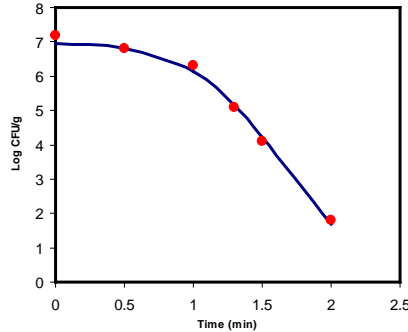


$$\log \frac{N}{N_0} = \log \left( \frac{2F_1}{1 + \exp(k_1 t)} + \frac{2(1 - F_1)}{1 + \exp(k_2 t)} \right)$$

Kamau et al.  
(1990)

# Modelos de inativação

❖ primários



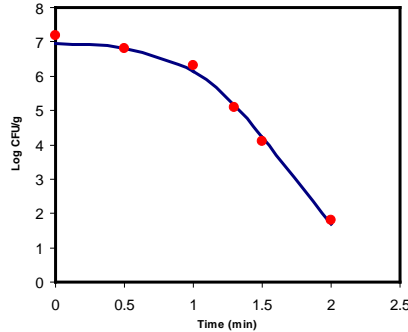
Whiting & Buchanan  
(1992)

$$\log \frac{N}{N_0} = \log \left( \frac{F_1(1 + \exp(-k_1L))}{1 + \exp(k_1(t - L))} + \frac{(1 - F_1)(1 + \exp(-k_2L))}{1 + \exp(k_2(t - L))} \right)$$

L – atraso

# Modelos de inativação

❖ primários



Whiting & Buchanan  
(1992)

$$\log \frac{N}{N_0} = \log \left( \frac{F_1(1 + \exp(-k_1L))}{1 + \exp(k_1(t - L))} + \frac{(1 - F_1)(1 + \exp(-k_2L))}{1 + \exp(k_2(t - L))} \right)$$

L – atraso

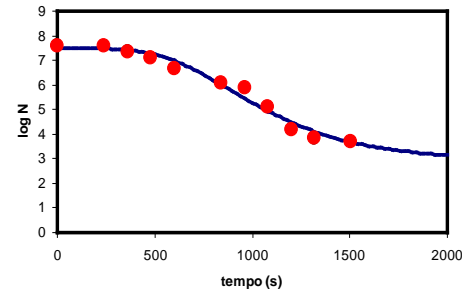
Cole et al.  
(1993)

$$\log N = \alpha + \frac{w - \alpha}{1 + \exp\left(\frac{4\sigma(\lambda - \log t)}{w - \sigma}\right)}$$

Distribuição da sensibilidade ao calor da população dos microrganismos

# Modelos de inativação

❖ primários



Baranyi et al.  
(1993)

$$\frac{dN}{dt} = -k \alpha(t) \beta(t) N$$
$$N(t = 0) = N_0$$

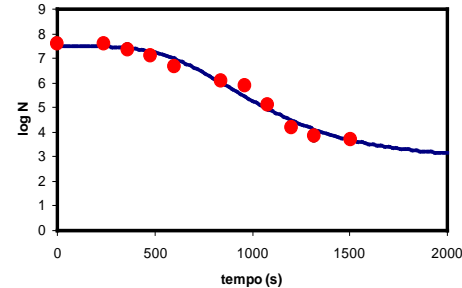
função 'cauda'

função 'atraso'



# Modelos de inativação

❖ primários



Baranyi et al.  
(1993)

$$\frac{dN}{dt} = -k \alpha(t) \beta(t) N$$

$$N(t = 0) = N_0$$

função 'cauda'

função 'atraso'

Geeraerd et al.  
(2000)

$$\frac{dN}{dt} = -k_{\max} k_Q(Q) N$$

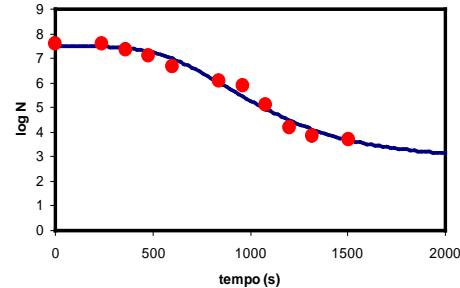
$$\frac{dQ}{dt} = -k_{\max} Q$$

$$\log\left(\frac{N}{N_0}\right) = \log(\exp(-k_{\max} t)) \frac{1 + Q(0)}{1 + Q(0) \exp(-k_{\max} t)}$$

Q – variável relacionada com o estado fisiológico dos microrganismos

# Modelos de inativação

❖ primários



Gompertz

Bhaduri et al (1991)  
Linton et al. (1995, 1996)  
Xiong et al. (1999)



*Listeria monocytogenes*

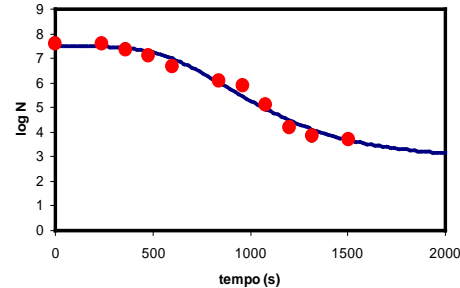
$$\log N = \log N_0 - \log \left( \frac{N_0}{N_{res}} \right) \exp \left( - \exp \left( \frac{k e}{\log \left( \frac{N_0}{N_{res}} \right)} (L - t) + 1 \right) \right)$$



reparameterização para inativação com base em Zwietering (1990)

# Modelos de inativação

❖ primários



## Gompertz

Bhaduri et al (1991)  
Linton et al. (1995, 1996)  
Xiong et al. (1999)



*Listeria monocytogenes*

$$\log N = \log N_0 - \log \left( \frac{N_0}{N_{res}} \right) \exp \left( - \exp \left( \frac{k e}{\log \left( \frac{N_0}{N_{res}} \right)} (L - t) + 1 \right) \right)$$



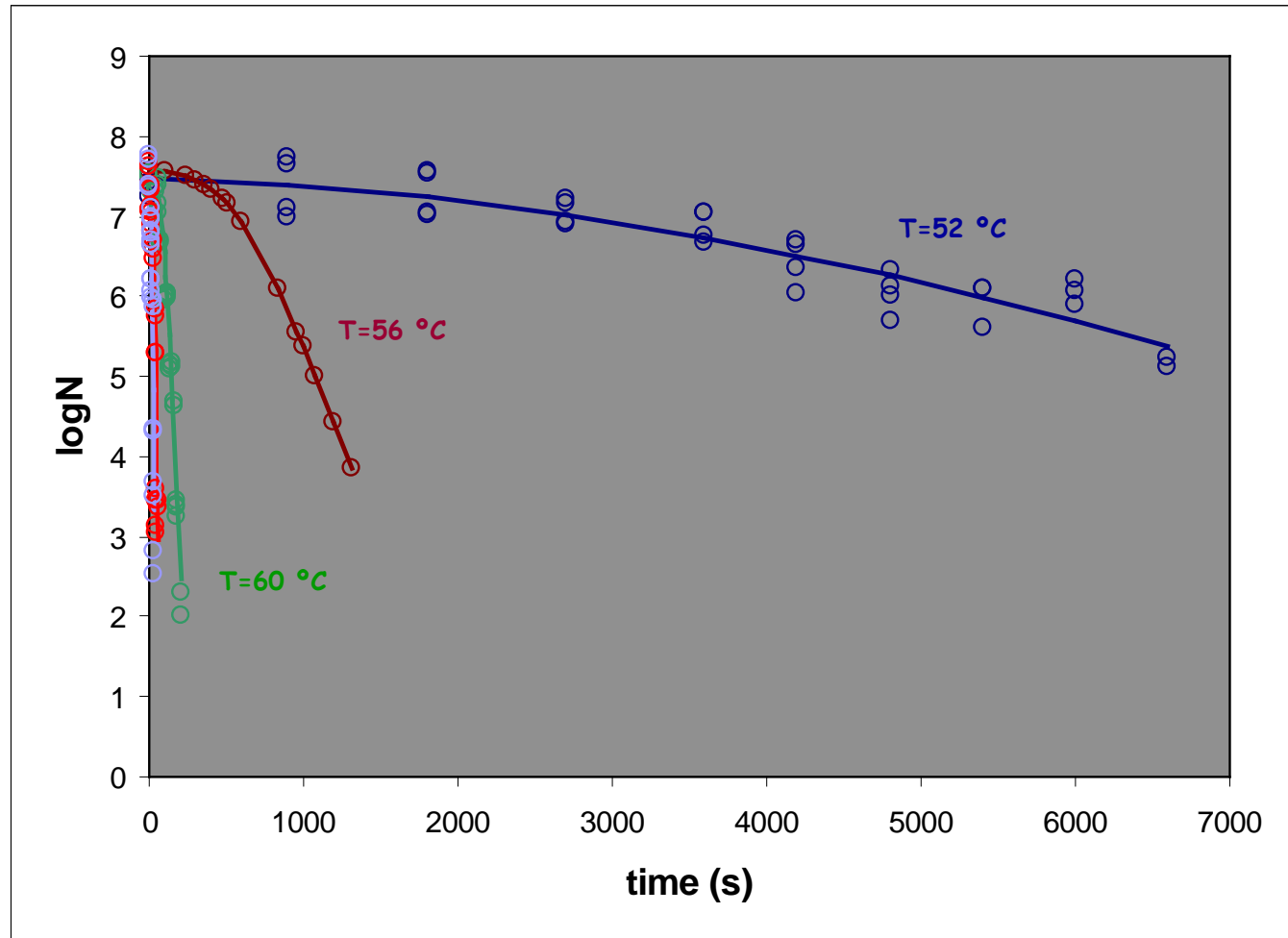
reparameterização para inativação com base em Zwietering et al. (1990)

## Logística

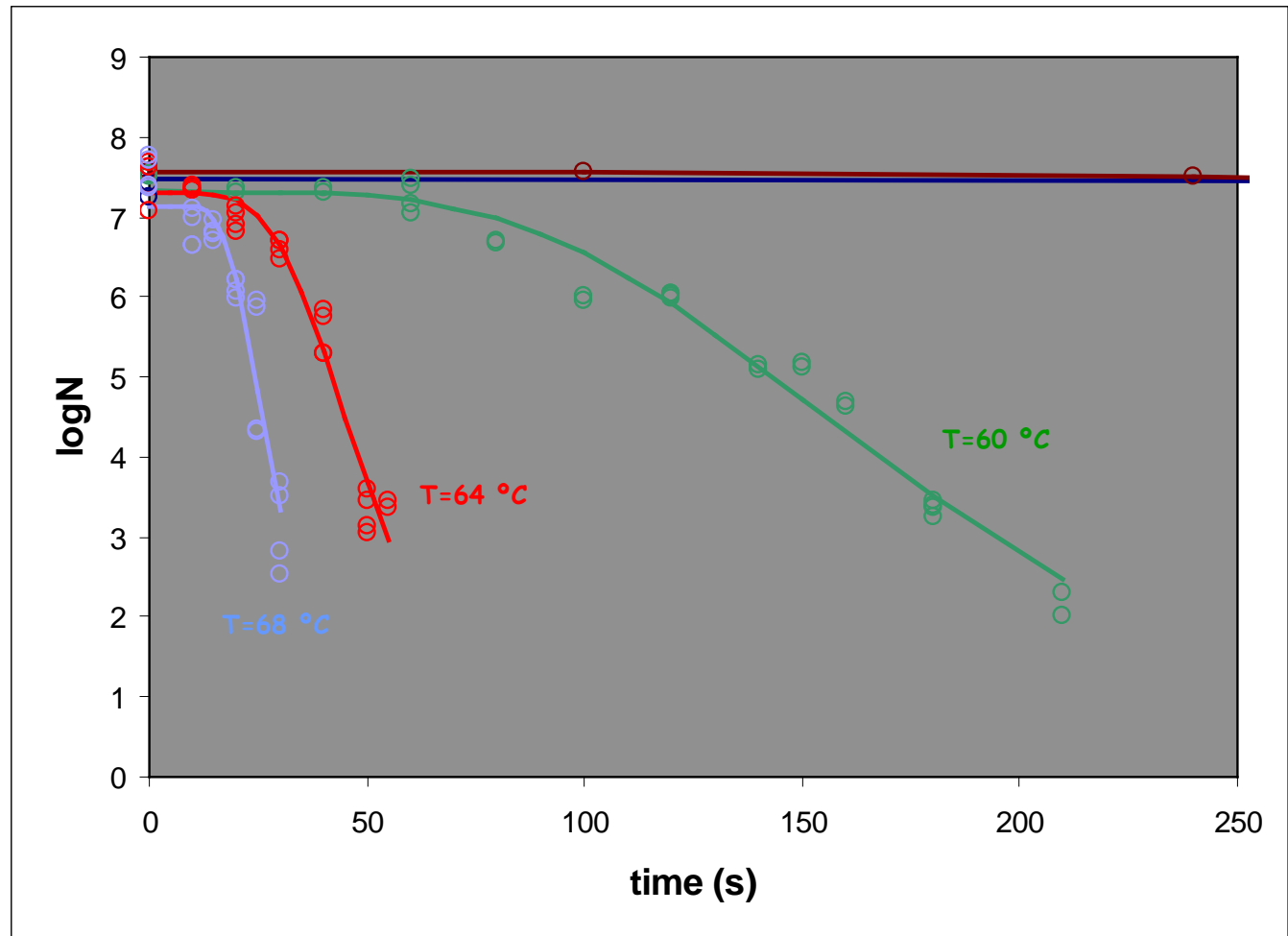
$$\log N = \frac{c}{1 + \exp(k(t - L))}$$

c – constante

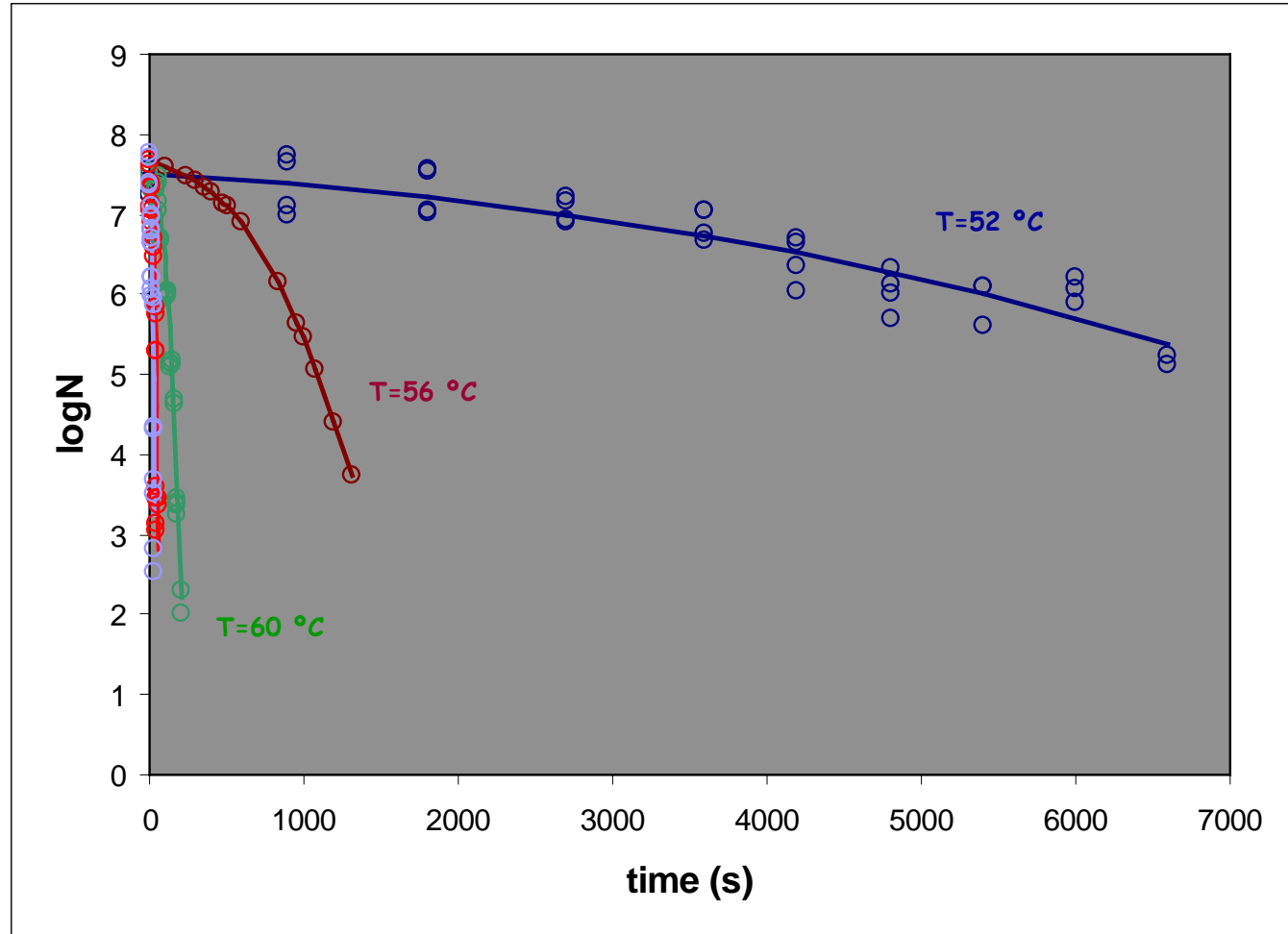
## Gompertz



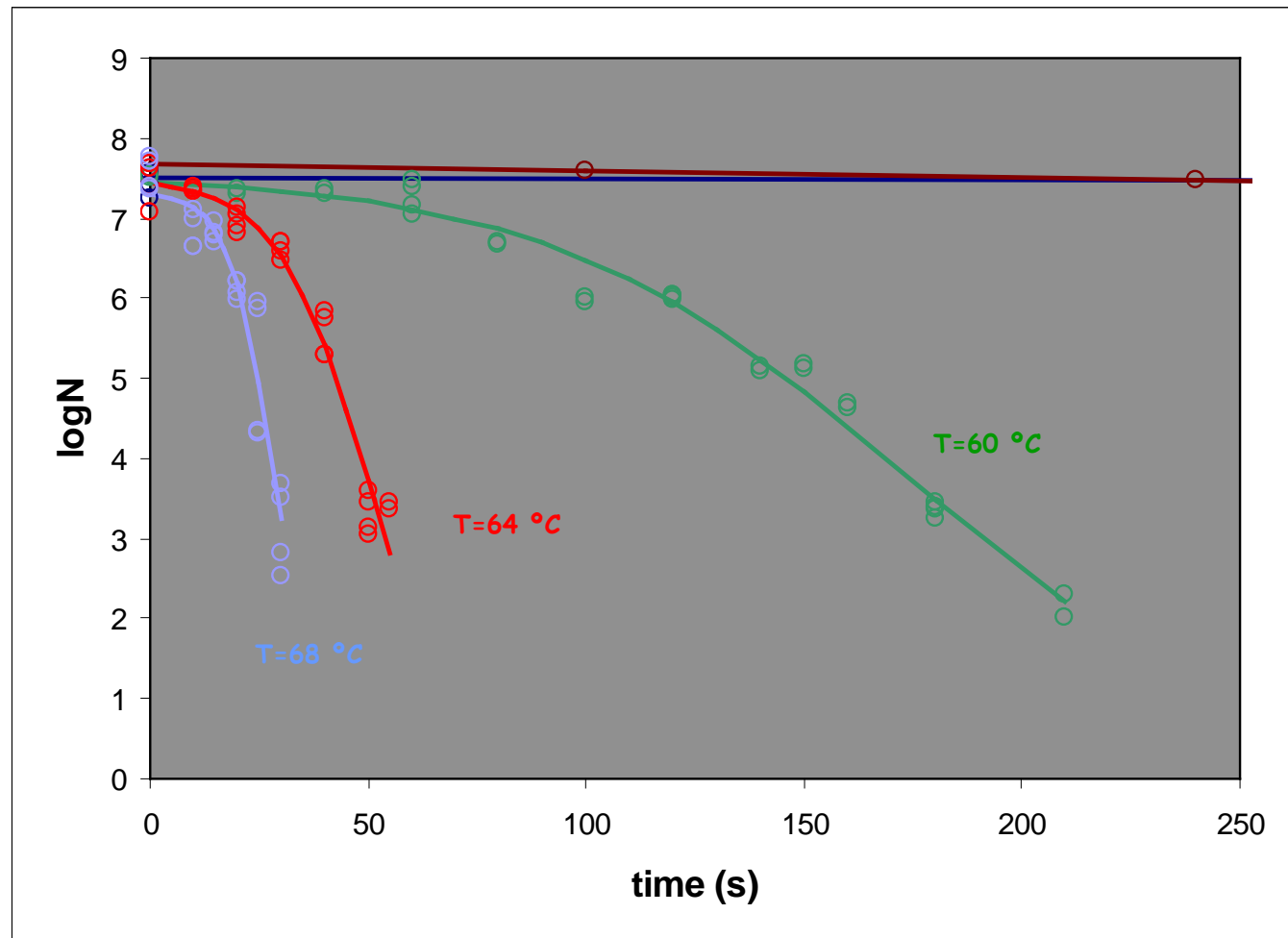
## Gompertz



## Logística

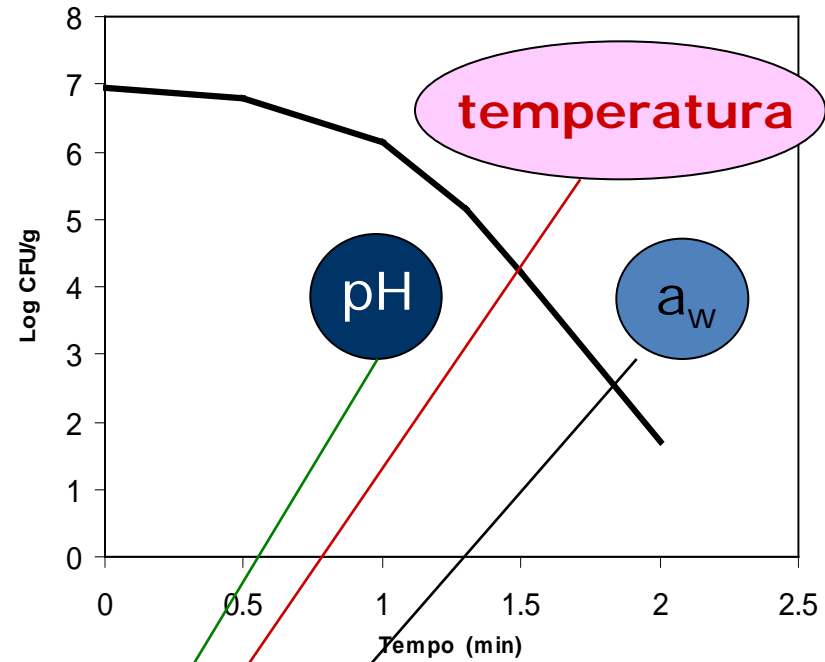


## Logística



# Modelos matemáticos

❖ primários



❖ secundários

parâmetros



# Modelos matemáticos

## ❖ secundários

Arrhenius

$$k = k_0 \exp\left(-\frac{E_a}{RT}\right) \rightarrow \ln k = \ln k_0 - \frac{E_a}{RT}$$

$$k = k_{\text{ref}} \exp\left(-\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right)\right)$$

Davey / Arrhenius modificado

$$\ln k = C_0 + \frac{C_1}{T} + \frac{C_2}{T^2} + C_3 a_w + C_4 a_w^2$$

“Square-root type models”

Ratkowsky *et al.* (1982)

$$\sqrt{k} = b(T - T_{\text{min}})$$

McMeekin *et al.* (1987)

$$\sqrt{k} = b(T - T_{\text{min}}) \sqrt{(a_w - a_{w_{\text{min}}})}$$

Adams *et al.* (1991)

$$\sqrt{k} = b(T - T_{\text{min}}) \sqrt{(\text{pH} - \text{pH}_{\text{min}})}$$

McMeekin *et al.* (1992)

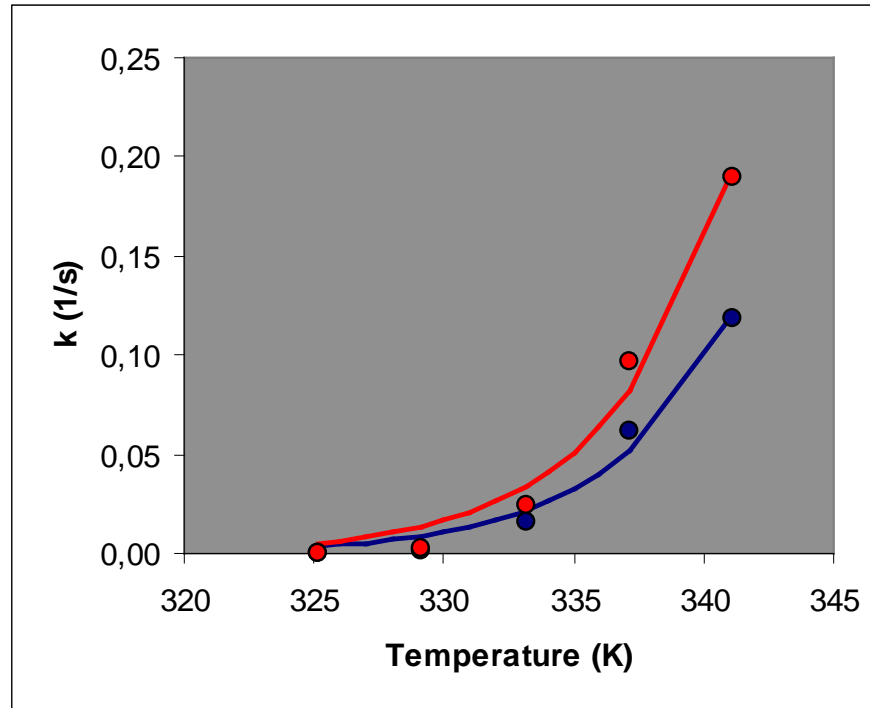
$$\sqrt{k} = b(T - T_{\text{min}}) \sqrt{(a_w - a_{w_{\text{min}}})} \sqrt{(\text{pH} - \text{pH}_{\text{min}})}$$

min – valor mínimo para crescimento

# Exemplos

Data of *L. monocytogenes* Scott A  
(24 hours incubation at 5°C in half cream)

Arrhenius



$$k = f(T)$$

Gompertz

$$k=0.0216 \exp(-203.3/R*(1/T-1/333.15))$$

$$\Delta E_a=28.85 \text{ kJ/mol}$$

$$\Delta K_{ref}=4.58 \times 10^{-3} \text{ s}^{-1}$$

Logística

$$k=0.0337 \exp(-206.6/R*(1/T-1/333.15))$$

$$\Delta E_a=27.56 \text{ kJ/mol}$$

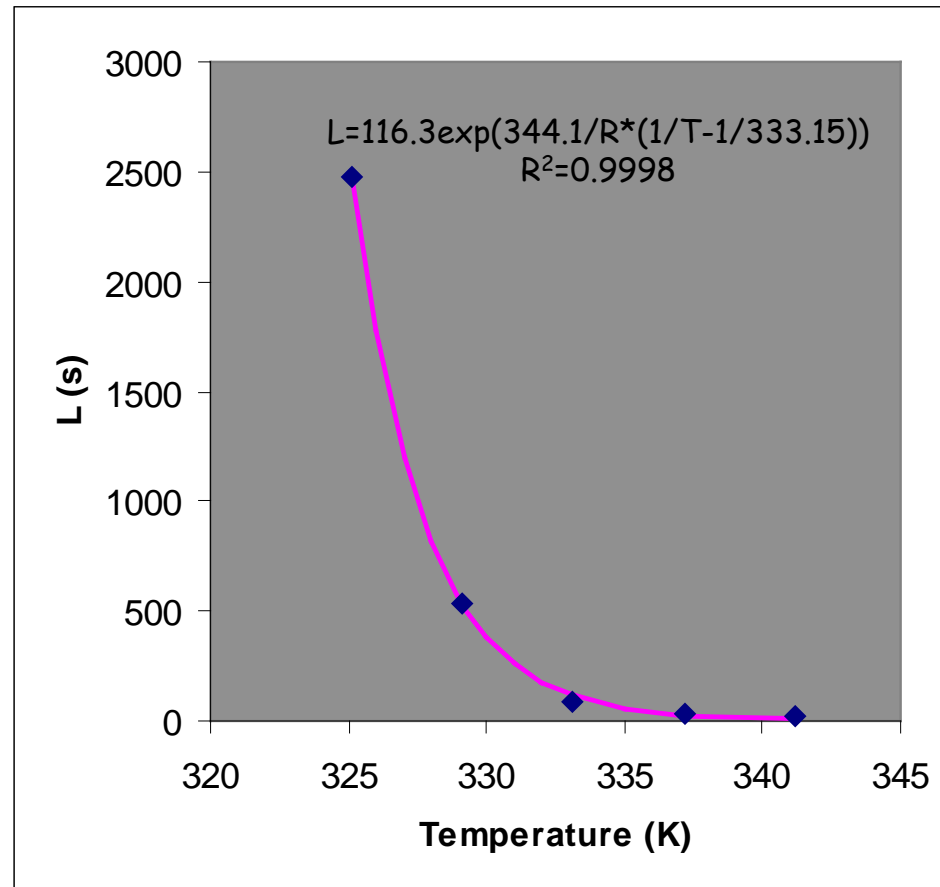
$$\Delta K_{ref}=7.31 \times 10^{-3} \text{ s}^{-1}$$

# Exemplos

Data of *L. monocytogenes* Scott A  
(24 hours incubation at 5°C in half cream)

## Gompertz

atraso = f(T)



$\Delta E_a = 7.485 \text{ kJ/mol}$

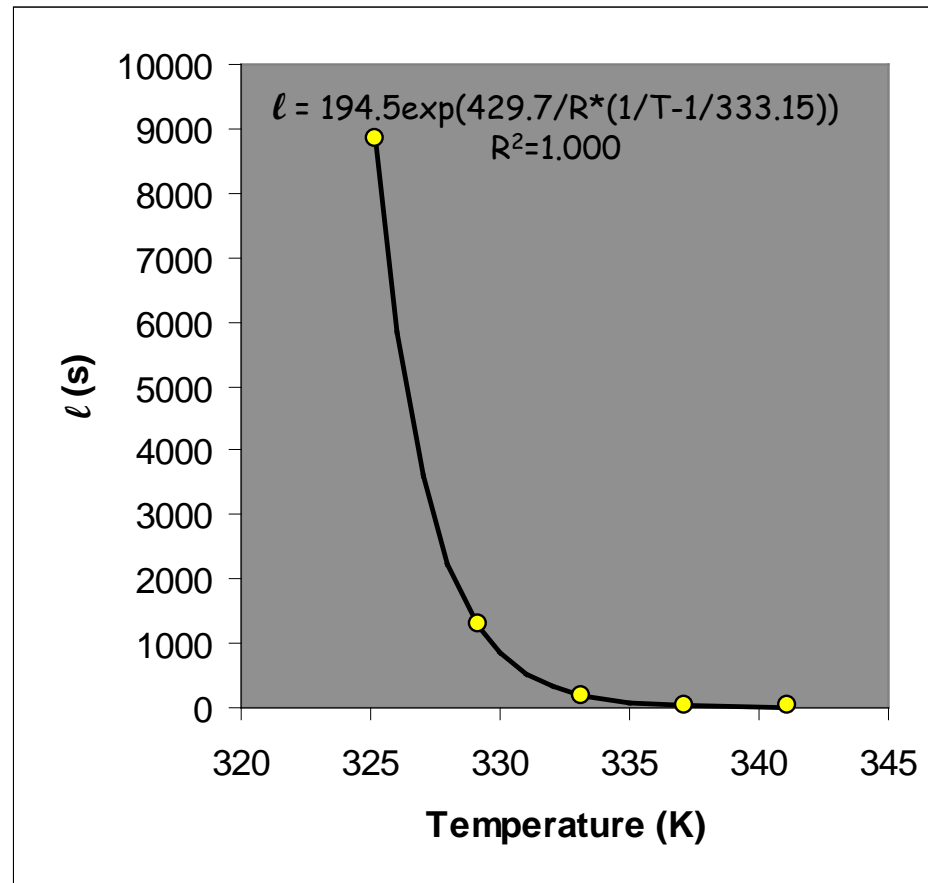
$\Delta L_{ref} = 7.595 \text{ s}^{-1}$

# Exemplos

Data of *L. monocytogenes* Scott A  
(24 hours incubation at 5°C in half cream)

## Logística

atraso = f(T)



$\Delta E_a = 3.591 \text{ kJ/mol}$

$\Delta l_{ref} = 6.154 \text{ s}^{-1}$

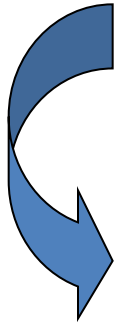
# Modelos matemáticos

Condições variáveis de

temperatura

pH

$a_w$



maior complexidade !!




$$\frac{d(\log N)}{d(\text{tempo})}$$

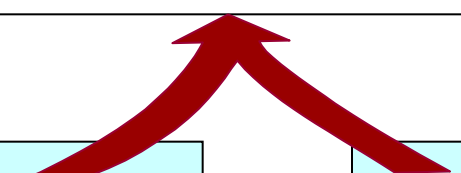
# Modelos matemáticos

## Gompertz

situação dinâmica de temperatura


$$\frac{d(\log N)}{d(\text{tempo})}$$

$$\log N = \log N_0 - \int_0^t \left[ k \exp(1) \exp \left( \frac{k \exp(1)}{\log \left( \frac{N_0}{N_{res}} \right)} (L - t') + 1 \right) \exp \left( - \exp \left( \frac{k \exp(1)}{\log \left( \frac{N_0}{N_{res}} \right)} (L - t') + 1 \right) \right) \right] dt'$$


$$k = k_{ref} \exp \left( - \frac{E_a}{R} \left( \frac{1}{T} - \frac{1}{T_{ref}} \right) \right)$$

$$L = a \exp \left( b \left( \frac{1}{T} - \frac{1}{T_{ref}} \right) \right)$$

# Modelos de inativação

## ❖ terciários

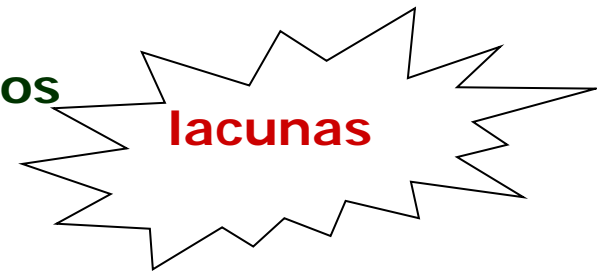
### softwares

crescimento de microrganismos  
previsão de tempo de prateleira



inativação de microrganismos

lacunas

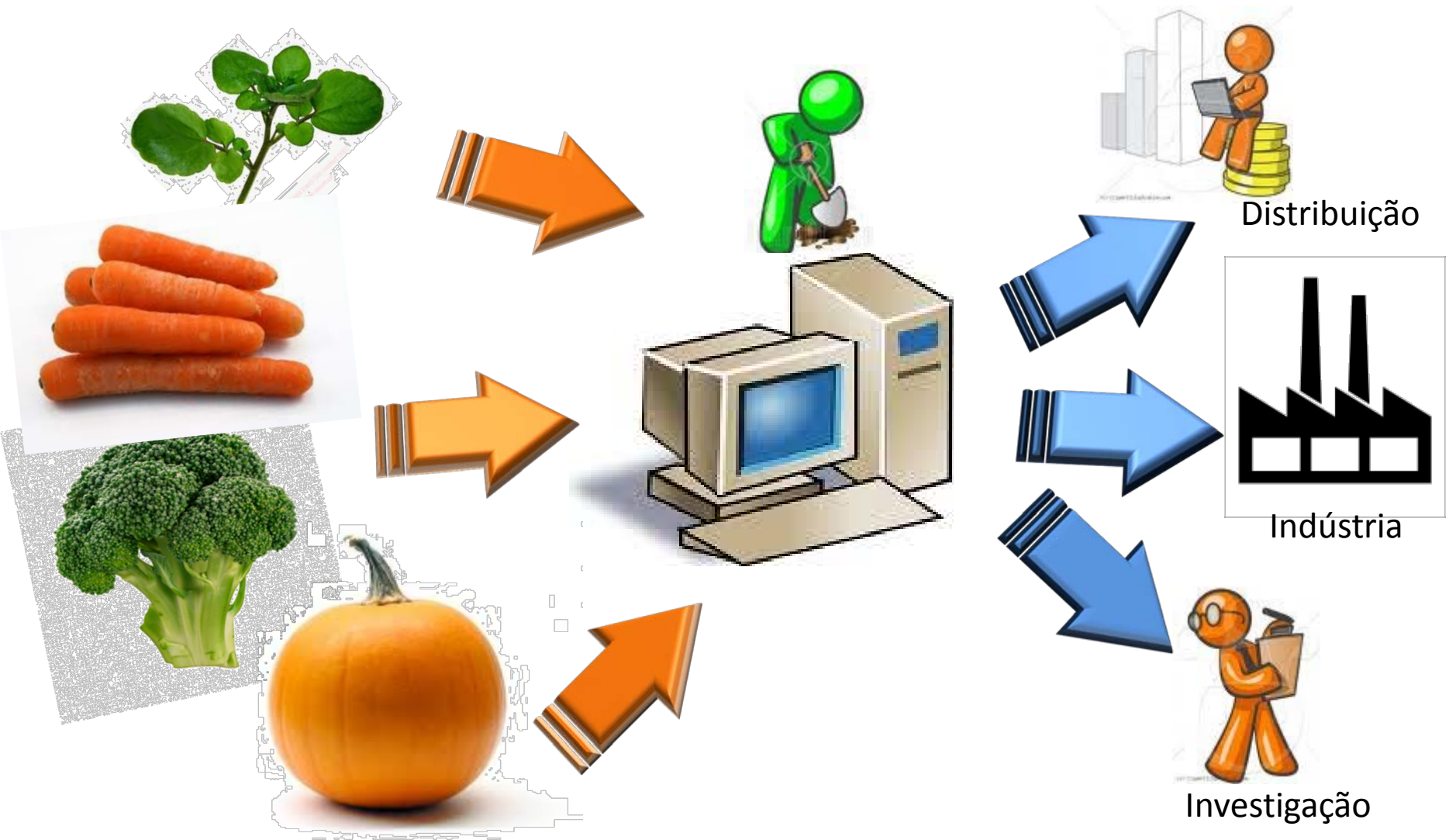


## Limitações

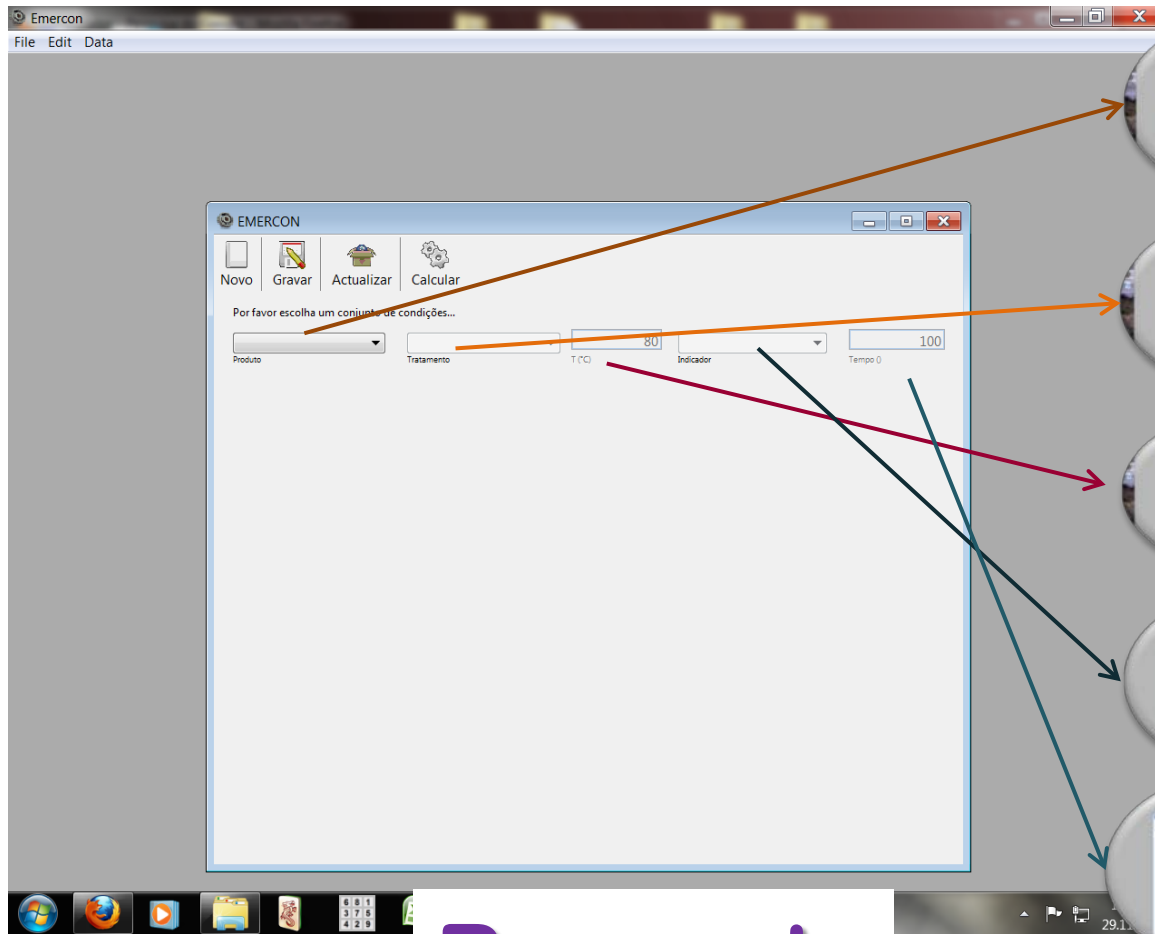
- interações entre microrganismos
- diversidade natural das estirpes
- estrutura complexa dos alimentos
- alimento/microrganismo
- modelagem da fase 'atraso'
- modelagem da fase 'cauda'
- previsões reais com condições ambientais variáveis



# Base de dados



# Base de dados



produto



processo



temperatura



atributo



tempo

## Resposta

(Visual Basic Language)

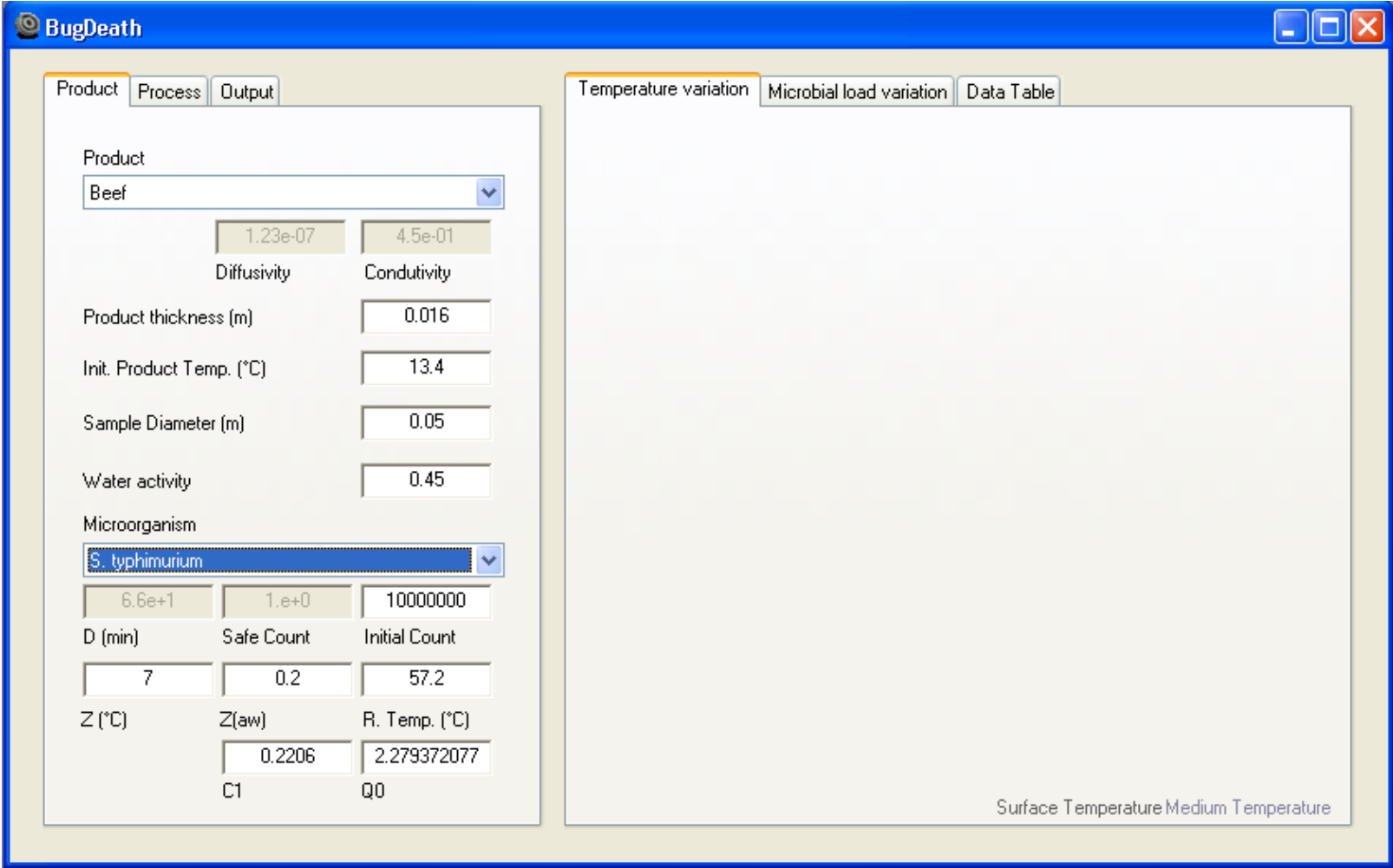
## Software Program



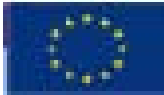
'Bugdeath' - funded by the European Commission under the EC Framework 5;  
Quality of Life and Management of Living Resources Programme



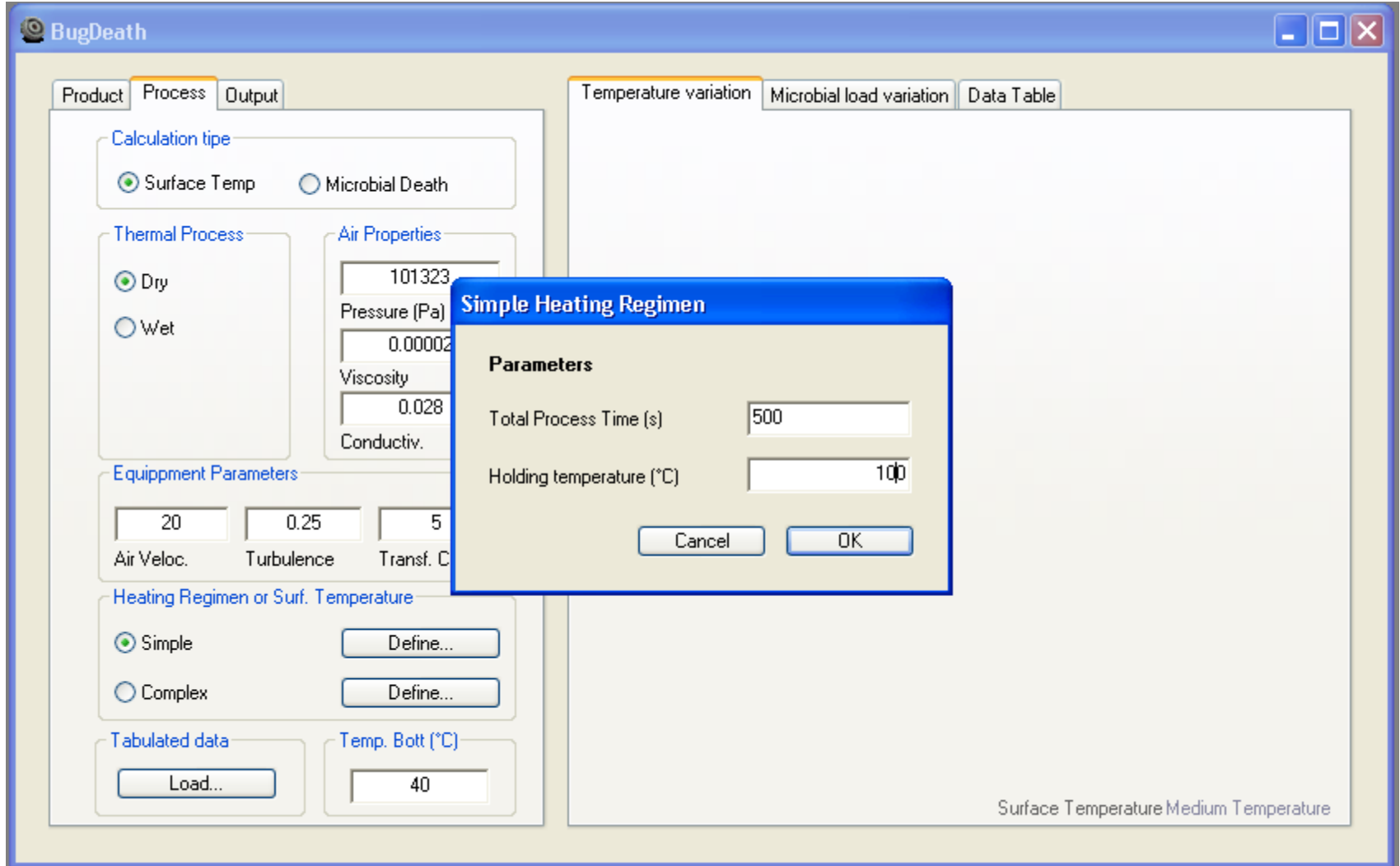
# First screen – product/microorganism



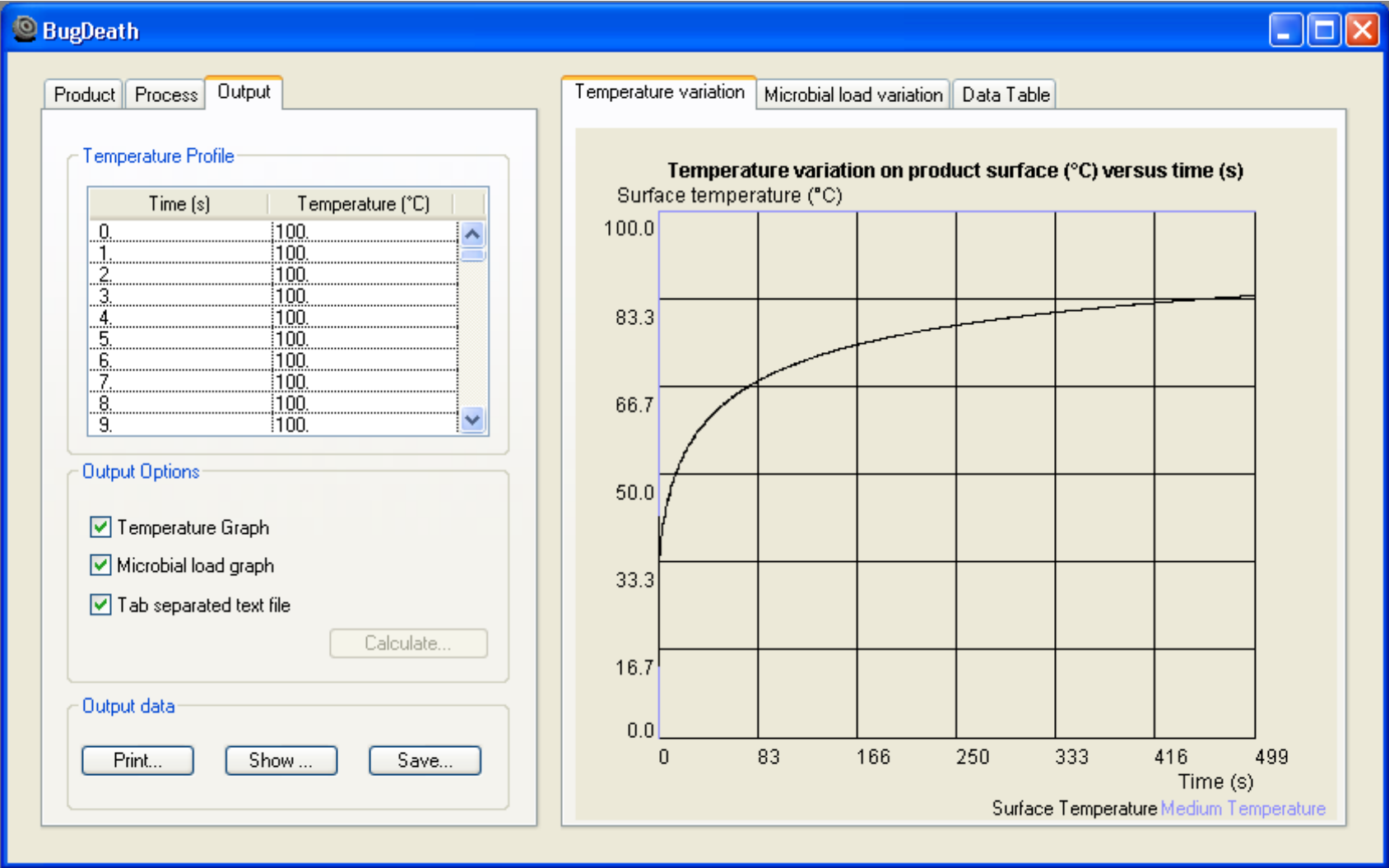
'Bugdeath' - funded by the European Commission under the EC Framework 5;  
 Quality of Life and Management of Living Resources Programme



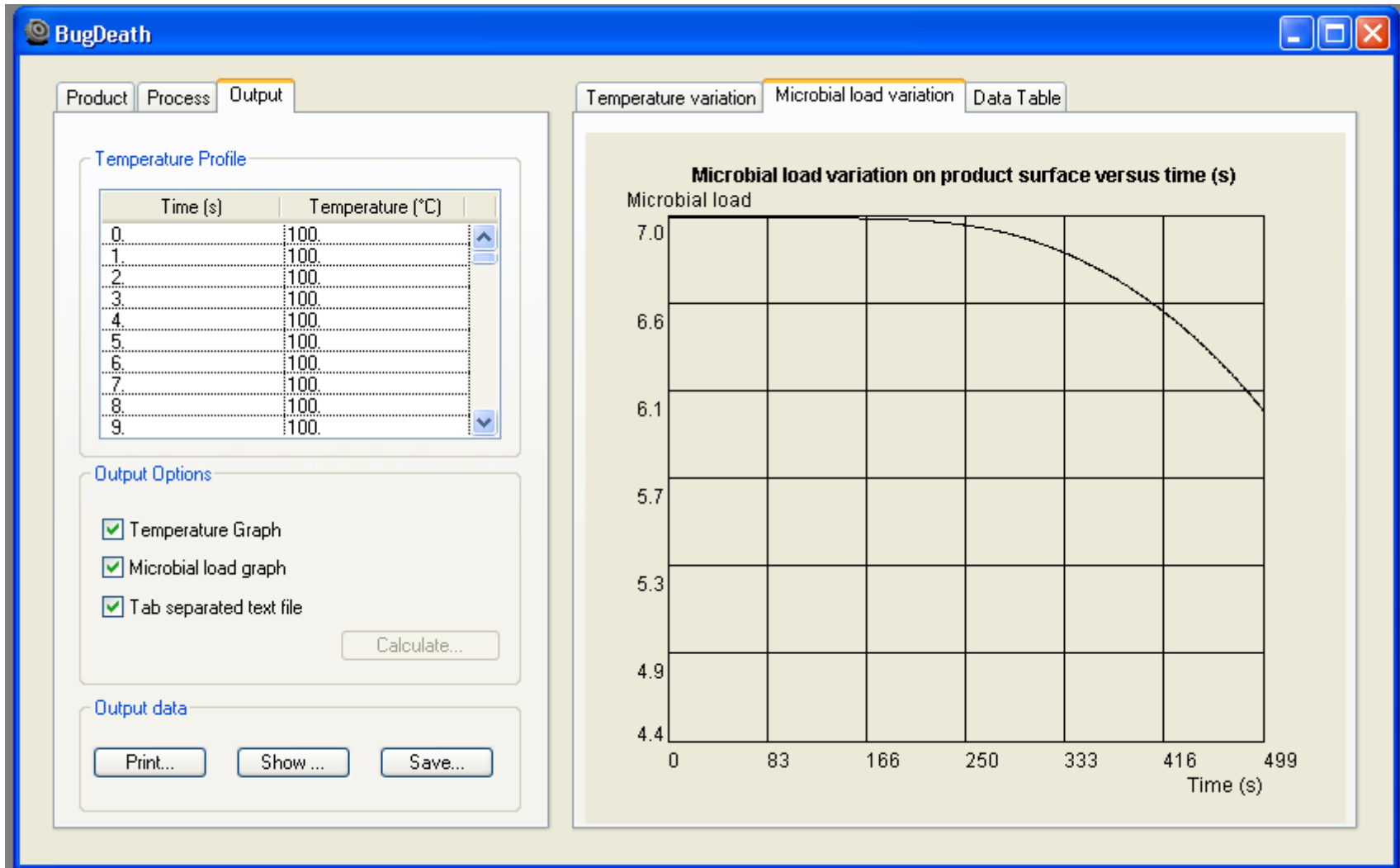
## Second screen – process



# Output – graphic/temperature



# Output – graphic/microbial load



# Output – data table

The screenshot shows the 'BugDeath' software interface. The 'Data Table' tab is active, displaying a table with the following data:

Time (s)	Medium Temp. (°C)	Surface Temp. (°C)	Microbial Load
0	0	14.02522	7
0.6081229	100	39.29868	6.991117
1	100	31.74754	6.991117
1.608123	100	35.68345	6.991117
2	100	36.00534	6.991117
2.608123	100	36.9512	6.991117
3	100	38.14414	6.991117
3.608123	100	38.62585	6.991117
4	100	39.78456	6.991117
4.608123	100	40.16022	6.991117
5	100	41.19636	6.991117
5.608123	100	41.524	6.991117
6	100	42.4504	6.991117
6.608123	100	42.74452	6.991117
7	100	43.58093	6.991117
7.608123	100	43.84836	6.991117
8	100	44.61078	6.991117
8.608123	100	44.85613	6.991117
9	100	45.55682	6.991117
9.608123	100	45.78353	6.991117
10	100	46.43196	6.991117
10.60812	100	46.64271	6.991116
11	100	47.2463	6.991116
11.60812	100	47.44323	6.991116
12	100	48.0079	6.991116
12.60812	100	48.19275	6.991116
13	100	48.72329	6.991115
13.60812	100	48.89746	6.991115
14	100	49.39783	6.991115





**OBRIGADA**

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