Thermal and kinetic parameter estimation and sensitivity analysis for the degradation of anthocyanins in grape pomace

Dharmendra K. Mishra
Kirk D. Dolan
Biosystems & Agricultural Engineering
Michigan State University

Sep. 23, 2008

Application of multiple parameter estimation for the degradation of anthocyanins in low-moisture and high-temperature processed food

Kinetic models often involve two parameters, such as *kr*-*Ea* in arrhenius model, *Dr*-*z* in microbial model

Commercial processes are usually dynamic, i.e. have time-varying temperatures or other variables

commercial processes have more than 2 parameters, because there are multiple variables, such as time, temperature, moisture content, shear rate, pH, pressure, etc.

Objectives

- Simultaneous estimation of kinetic degradation parameters of anthocyanins in grape pomace
- To construct joint confidence region for simultaneously estimated parameters
- Confidence and prediction band for the measured anthocyanins

Mass Average Anthocyanin

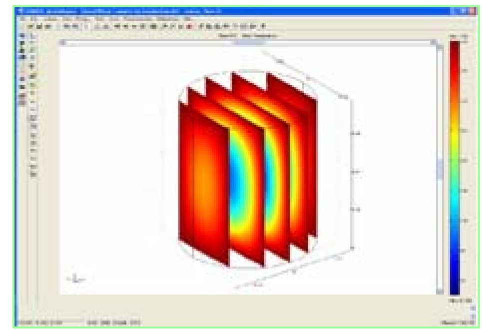
$$C_{pred} = 2C_o \iint e^{-k_r \int_0^t e^{\frac{-E_a}{R}\left(\frac{1}{T(r,z,t)} - \frac{1}{T_r}\right)} dt} \, r \, dr dz$$

Overview of the process

Can Sealing

Retorting at different times

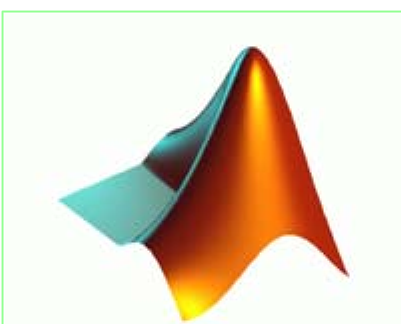
Thermal parameter estimation



Extraction of anthocyanins

HPLC analysis

Kinetic parameter estimation



Estimation of thermal parameter

Two-dimensional axi-symmetric heat conduction

$$\alpha\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right)+\frac{\partial^2 T}{\partial z^2}\right]=\frac{\partial T}{\partial t}$$

$$\alpha(\mathrm{T})=\left(\frac{(\mathrm{T}_2-\mathrm{T})}{(\mathrm{T}_2-\mathrm{T}_1)}\times\alpha_1\right)+\left(\frac{(\mathrm{T}-\mathrm{T}_1)}{(\mathrm{T}_2-\mathrm{T}_1)}\times\alpha_2\right)$$

Boundary Conditions

$$\frac{\partial T}{\partial r}(0,z,t)=0 \qquad T(r,z,0)=T_i \qquad \frac{\partial T}{\partial z}(r,H,t)=0$$

$$-k\frac{\partial T}{\partial r}(R,z,t)=h(T(R,z,t)-T_\infty)$$

$$-k\frac{\partial T}{\partial z}(r,0,t)=h(-T(r,0,t)+T_\infty)$$

Sensitivity Coefficient

- Sensitivity coefficient of a parameter is the first derivative of the function involving the parameter, with respect to the parameter

$$y = f(a, c, x)$$

$\frac{\partial y}{\partial a}$ sensitivity coefficient of a

$\frac{\partial y}{\partial c}$ sensitivity coefficient of c

Scaled Sensitivity

- A scaled sensitivity for parameter can be represented as

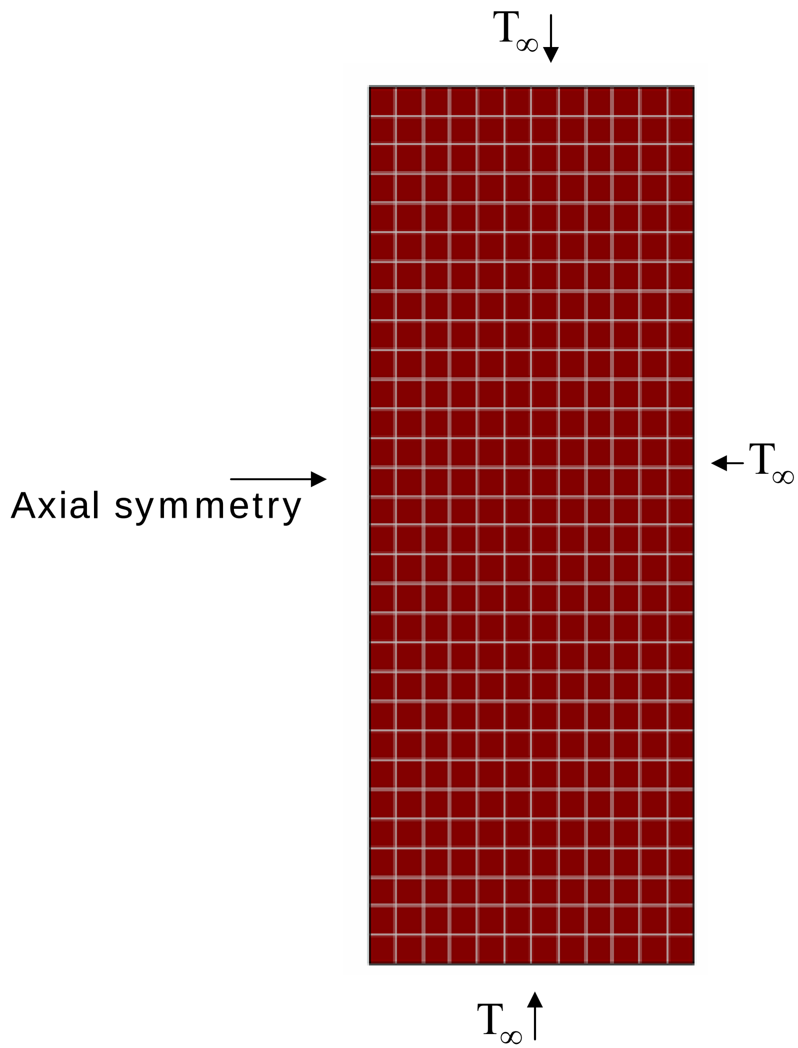
$$X_{p_i} \equiv p_i \frac{\partial y}{\partial p_i}$$

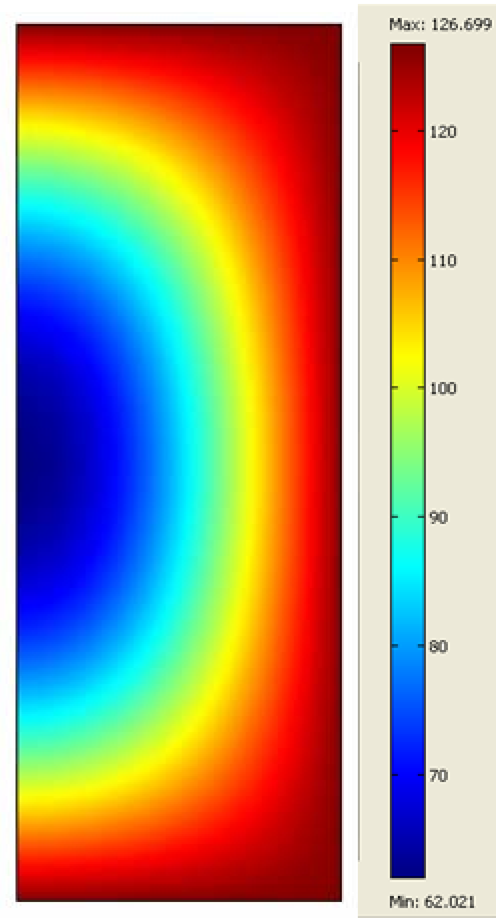
Finite difference method

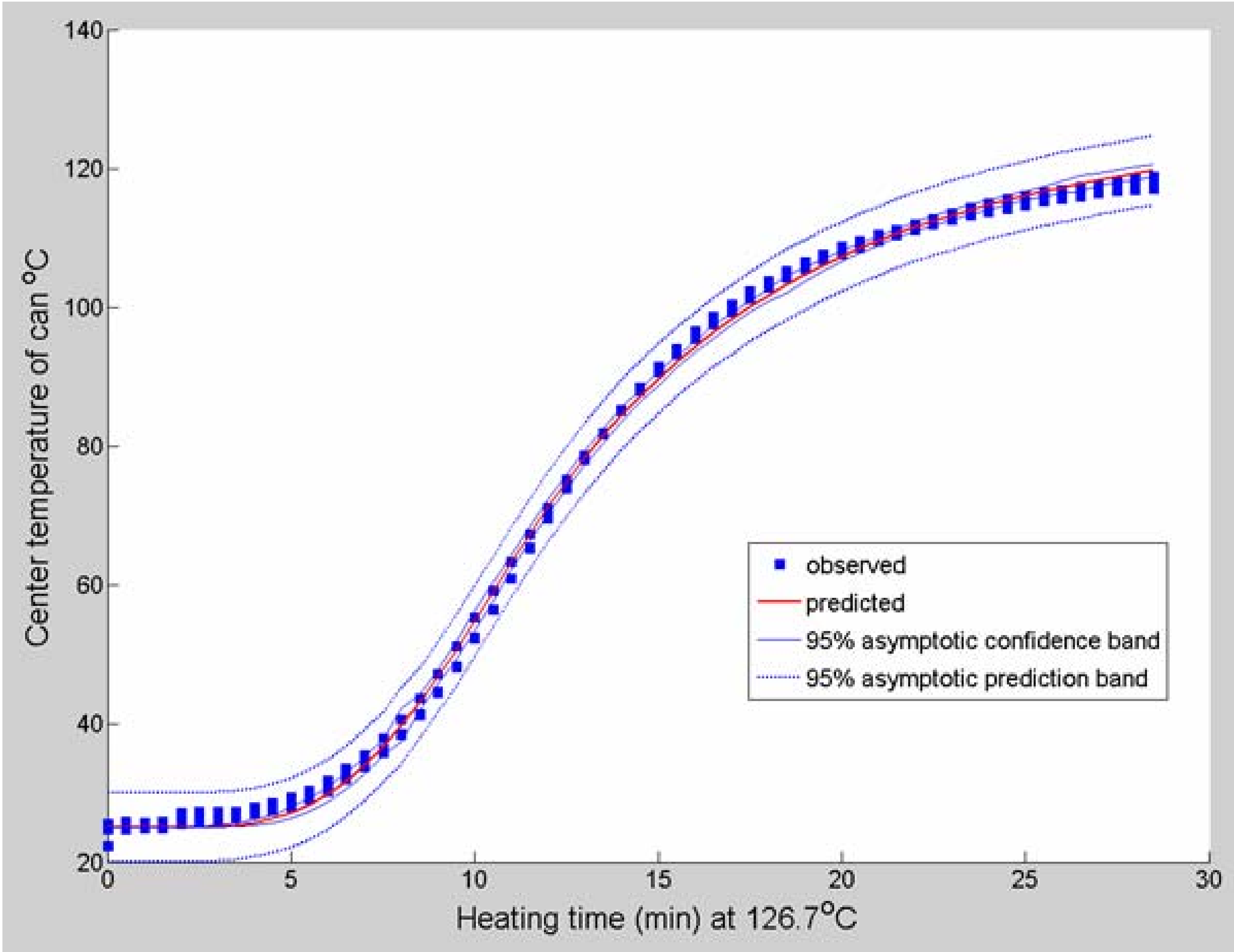
$$X_{p_i} \equiv p_i \frac{y(p_i + \delta b) - y(p_i)}{\delta b}$$

- Useful when comparing several parameters in a model

Temperature Profile of the can

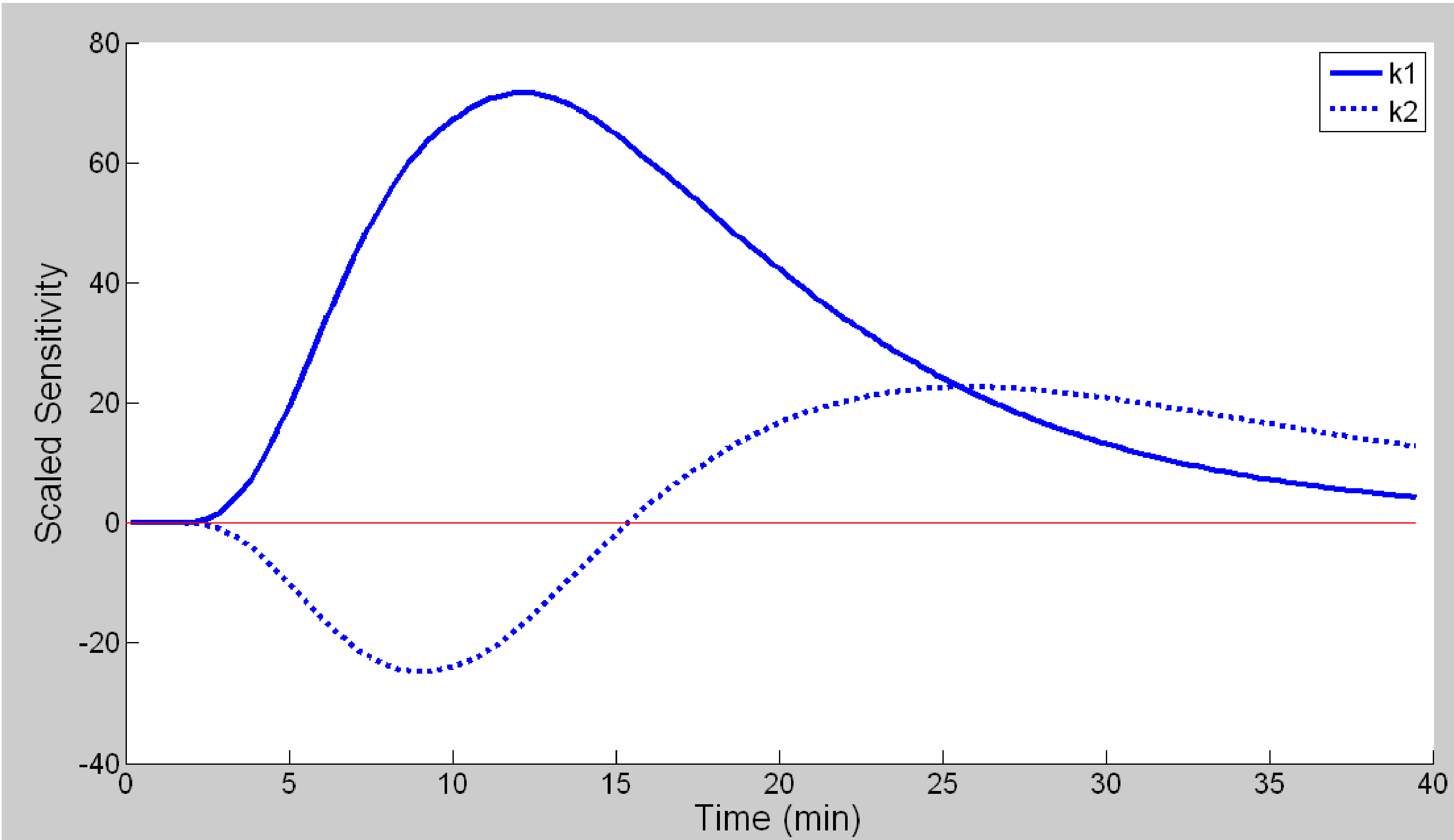






Example of predicted temperature profile from Comsol vs. the observed temperature (triplicate runs) in can used for thermal parameter runs

Scaled Sensitivity of thermal diffusivity parameters



Estimates of thermal diffusivity parameters

Parameter	Parameter Estimates	Standard Error	Correlation coefficient	95% asymptotic confidence interval	RMSE
α_1 at 80 °C	2.32×10^{-7}	0.0054×10^{-7}	0.260	2.31×10^{-7}, 2.33×10^{-7}	2.21
α_2 at 120 °C	2.51×10^{-7}	0.014×10^{-7}		2.49×10^{-7}, 2.54×10^{-7}	

Estimation of Kinetic Parameters

For Low- and intermediate-moisture foods

- First-order model with Arrhenius rate constant

- First-order

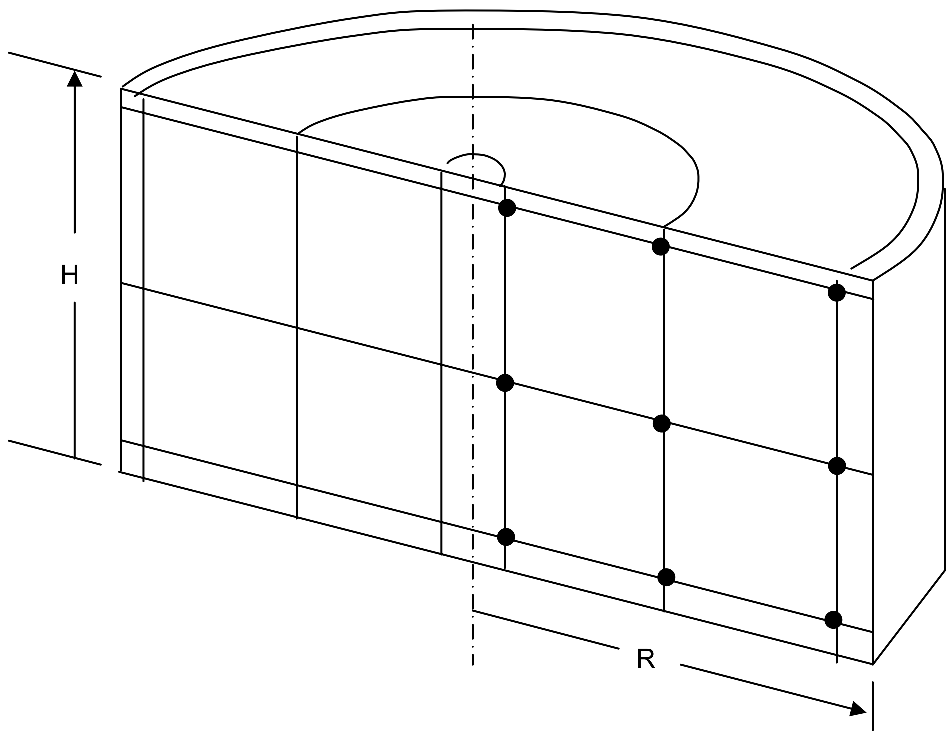
$$\frac{dC}{dt} = -kC$$

- Rate constant

$$k = k_r e^{\left[\frac{-\Delta E}{R}\left(\frac{1}{T(t)} - \frac{1}{T_r}\right)\right]}$$

Estimation of Kinetic Parameters

- Trapezoidal method for Integral over time
- 3-point Gauss method for integral over space



Estimation of Kinetic Parameters

Nlinfit
(α)

$$SSQ = \sum_{i=1}^{n} \left[T_{obs,\, i} - T_{pred,\, i} \right]^2$$

Nlinfit
(K_r, E_a and C_o)

$$SSQ = \sum_{i=1}^{n} \left[\overline{C}_{obs,\, i} - \overline{C}_{pred,\, i} \right]^2$$

Fmincon
(T_r)

Corr(K_r, E_a)

Confidence Intervals

Asymptotic confidence/predicted intervals

for parameters: nlparci(beta, residuals, Jacobian)

for predicted Y value:
nlpredci(model, x, beta, residuals, Jacobian)

Asymptotic prediction interval

nlpredci(model, x, beta, residuals, Jacobian, simultaneousoption, predictionoption)

Kinetic parameters for anthocyanin retention in grape pomace at 42% (wb) moisture content

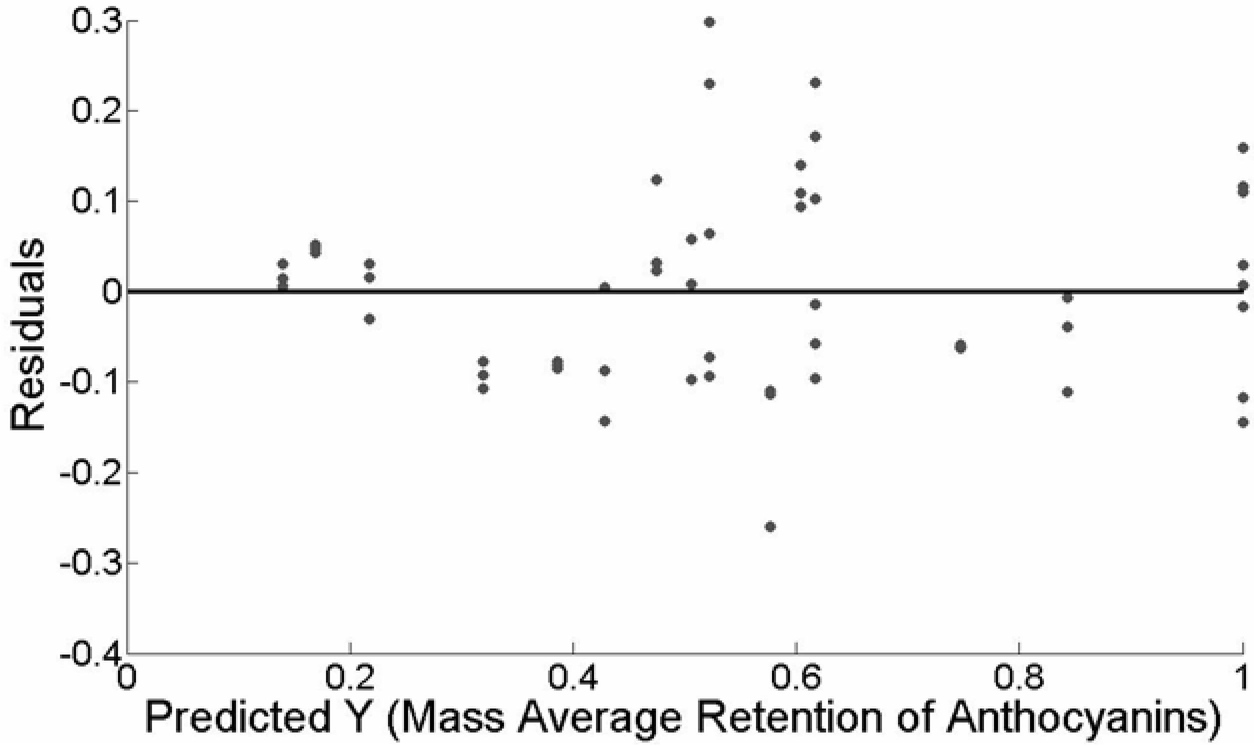
Parameter	No. of Data	Parameter Estimates	Standard Error	Correlation coefficient	95% asymptotic confidence interval	RMSE
k_{113^oC}	42	0.0679 min^{-1}	0.0043	$\rho_{k_r E_a}$ =0.59 ρ_{C_o,E_a} =-0.43 ρ_{k_r,C_o} = 0.66	0.0592, 0.076	0.12
E_a		65.26 kJ/g mol	18.02		28.80, 101.7	
C_o		1.481	0.0413		1.396, 1.564	

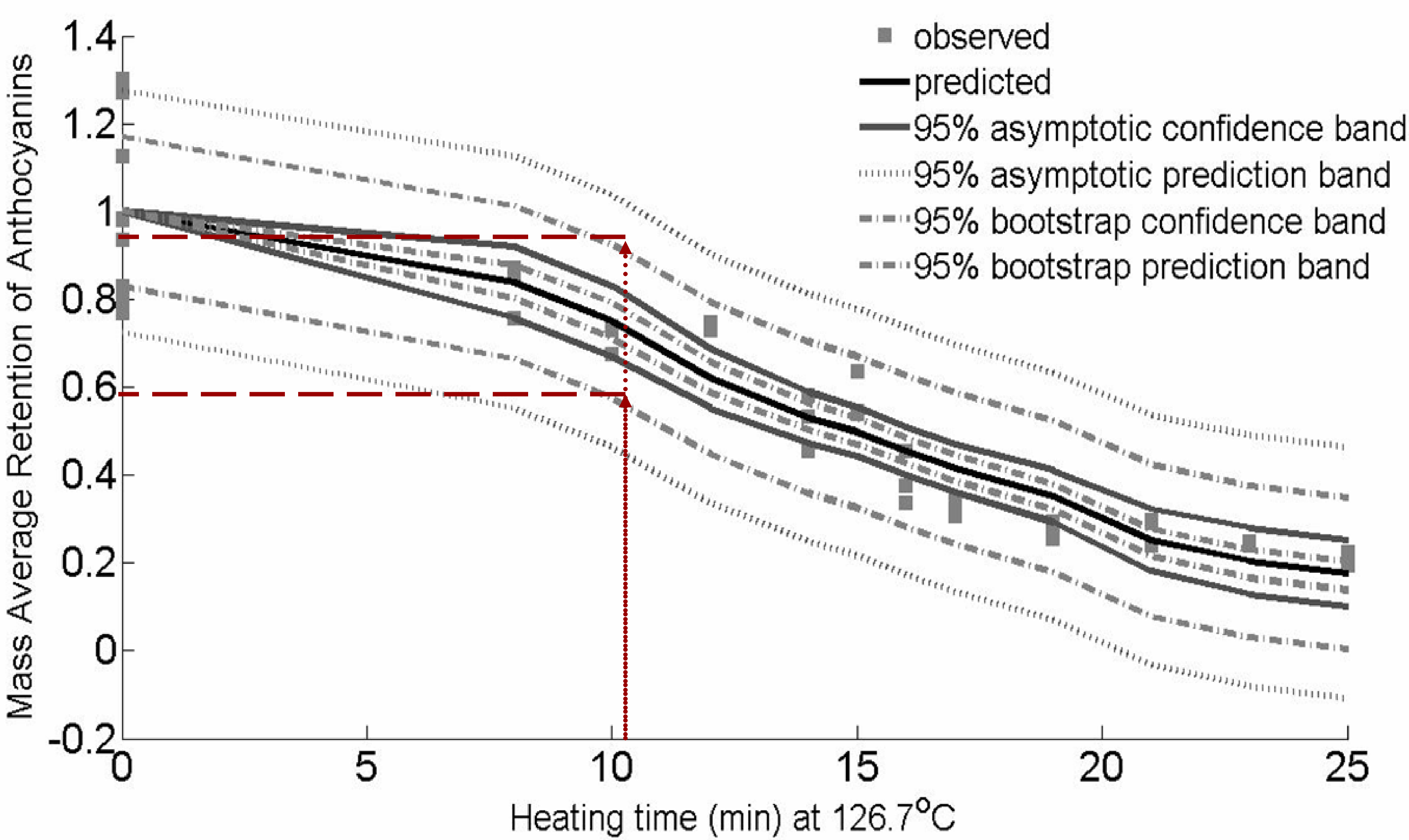
The estimated reference temperature was 113 ^{o}C (confidence interval 96.5,129.6)

Converged value of correlation of rate constant and activation energy was

$$\rho_{k_r E_a} = 1.24e\text{-}005$$

Residual Plot





observed
predicted
95% asymptotic confidence band
95% asymptotic prediction band
95% bootstrap confidence band
95% bootstrap prediction band
Mass Average Retention of Anthocyanins
Heating time (min) at 126.7°C
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
0
5
10
15
20
25

Joint confidence region

1. Bates, 1988

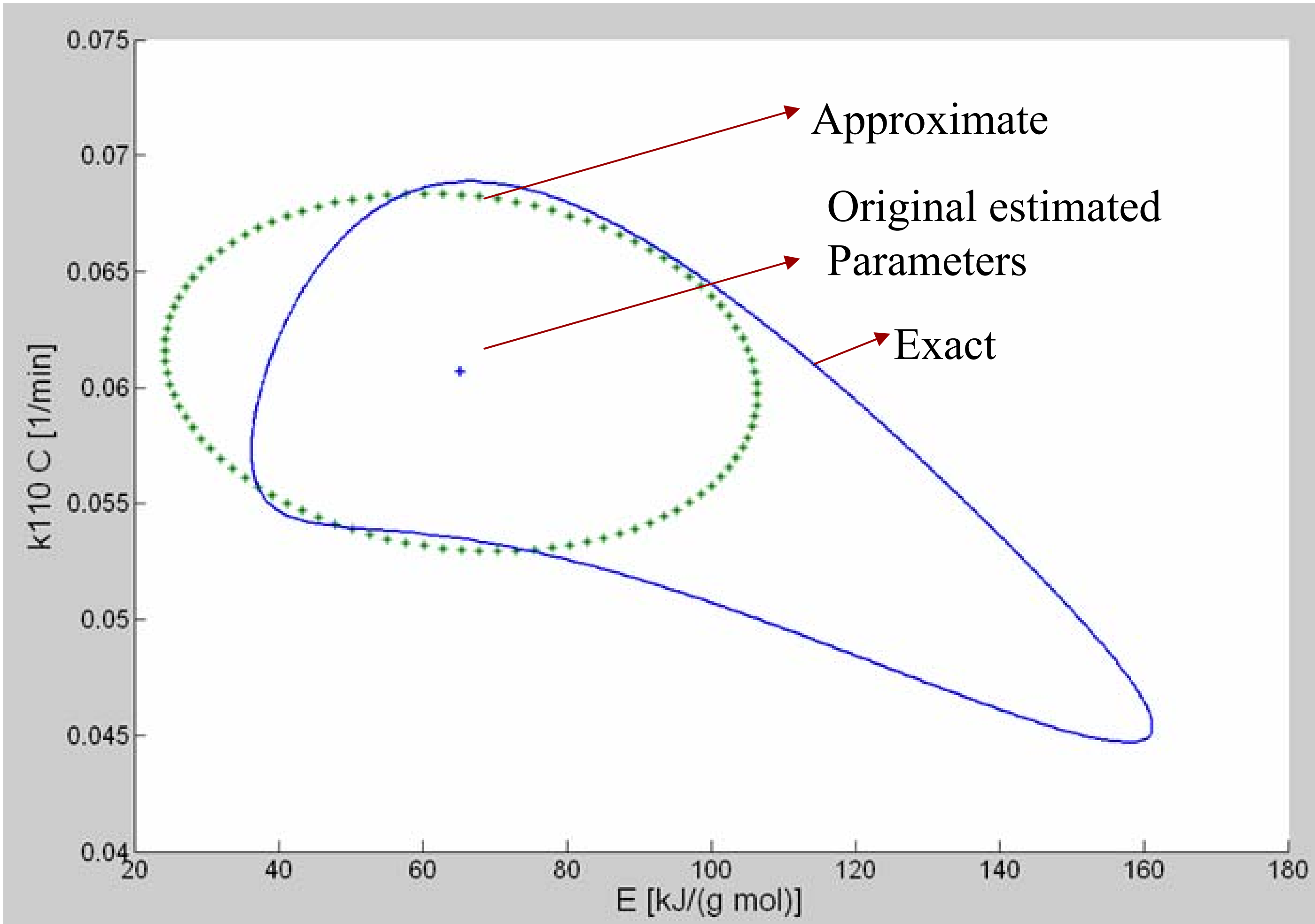
$$(\theta - \hat{\theta})^T \hat{V}_1^T \hat{V}_1 (\theta - \hat{\theta}) \leq ps^2 F(p, N-p; \alpha)$$

Elliptical approximation

2. Motulsky Method

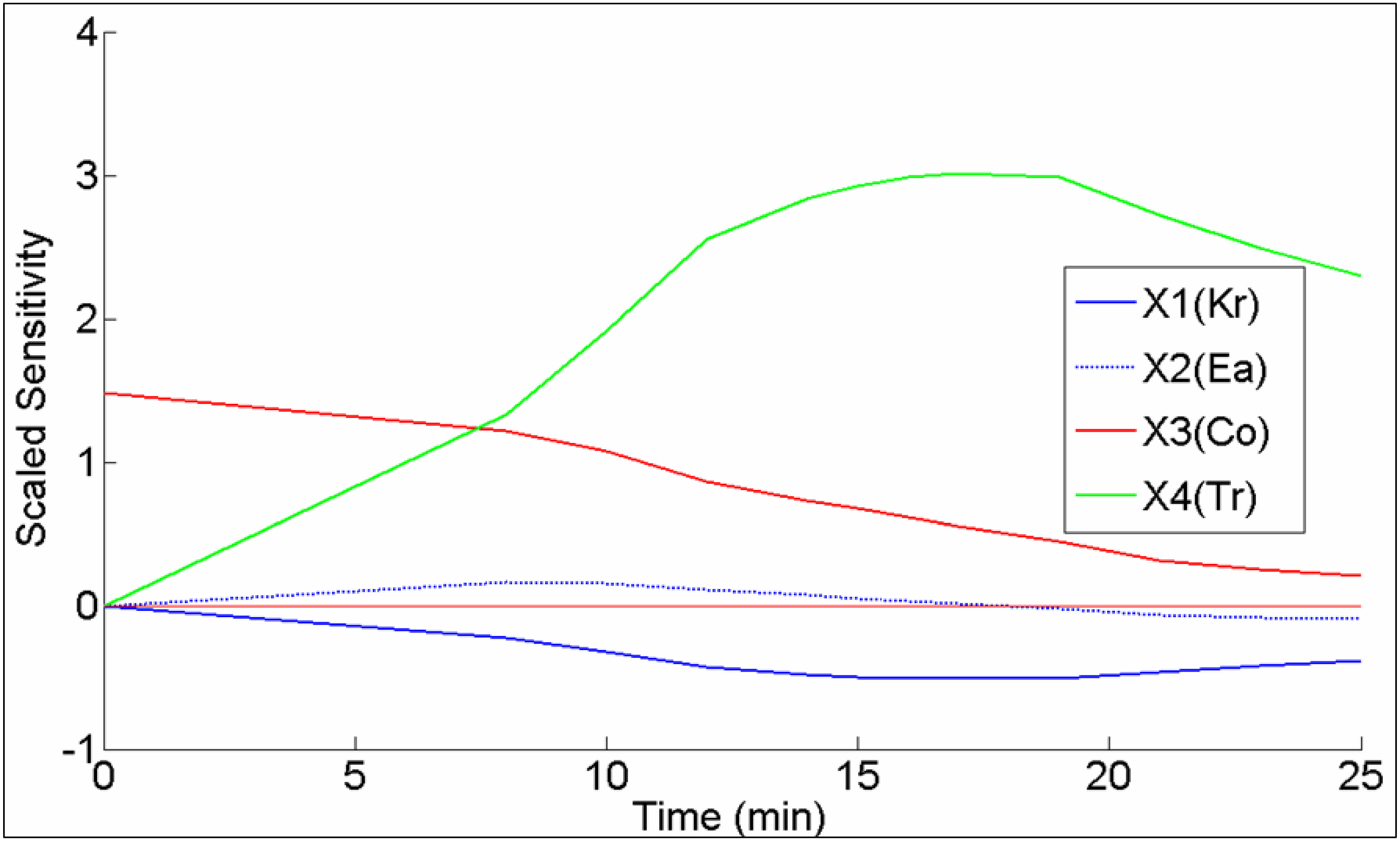
$$SS_{all-fixed} = SS_{best-fit}\left(F\frac{P}{n-P}+1\right)$$

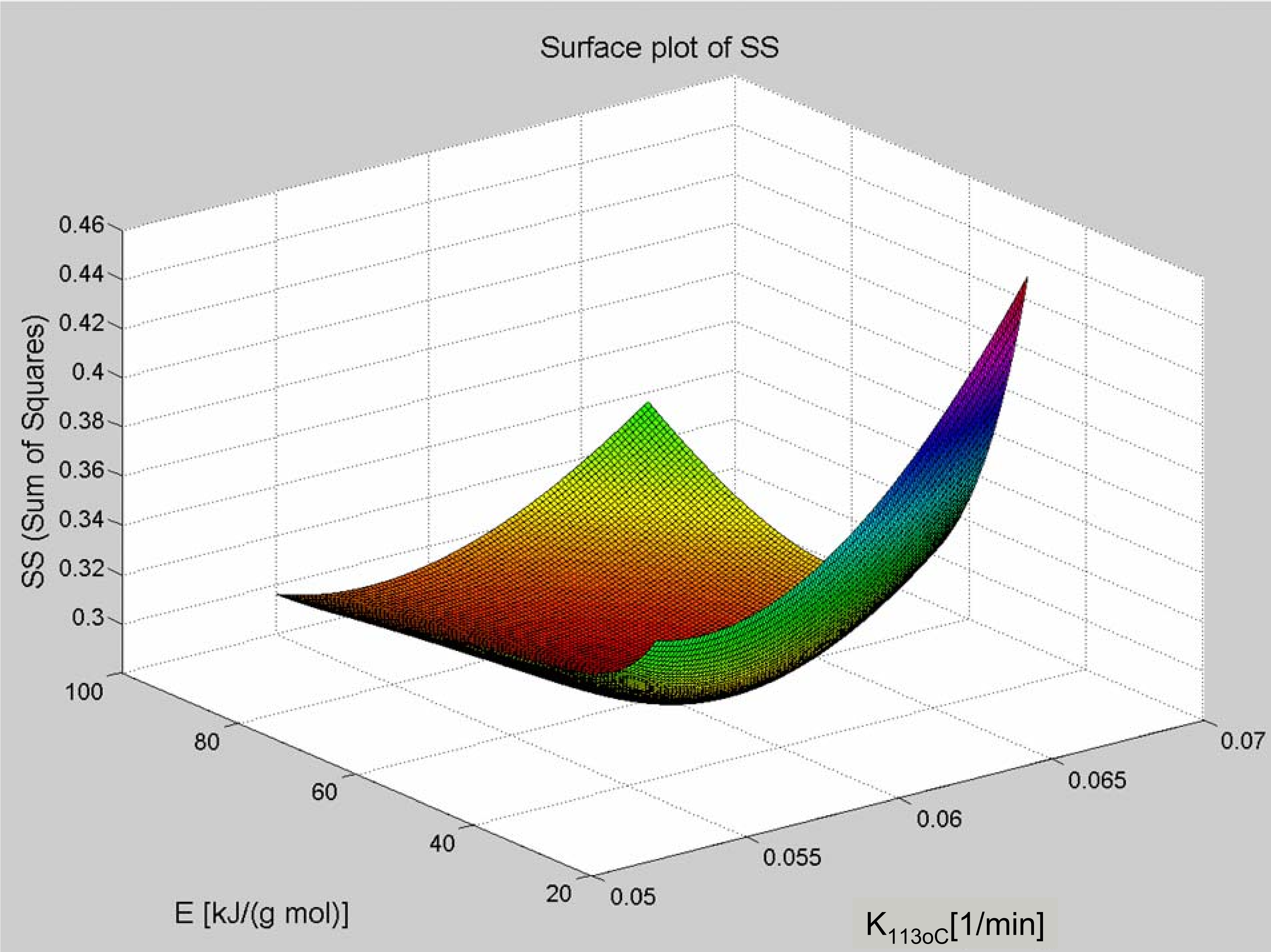
Iterative method



95% joint confidence region using equation and Motulsky method for mass average retention of anthocyanins in grape pomace 42% moisture content (wb) with parameters having correlation coefficient of –0.5.

Scaled Sensitivity





Surface plot of SS
SS (Sum of Squares)
0.46
0.44
0.42
0.4
0.38
0.36
0.34
0.32
0.3
100
80
60
40
20
E [kJ/(g mol)]
0.05
0.055
0.06
0.065
0.07
K113oC[1/min]

Conclusions

The multi parameter approach incorporates the challenges faced in the processing industry, such as the simultaneous effect of temperature and moisture content, and potentially could describe the effect of other factors such as pH, pressure and viscosity

Sensitivity coefficient analysis is helpful in determining whether all the parameters are estimable in the model

Confidence intervals and the joint confidence regions provide useful information about the nature of the parameters and their correlation

Acknowledgements

- Dr. Kirk D. Dolan
- Dr. James V. Beck
- Dr. Lijian Yang

THANK YOU