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Multiresponse modelling of the caramelisation reaction

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OBJECTIVE:

i) review the current understanding of multiresponse modelling

ii) develop a mechanistic multiresponse model able to describe sucrose caramelisation reaction without catalyst in concentrated solutions

INTRODUCTION

Food reactions often do not occur isolated but rather within a chain of complex reactions, all dependent of several different environmental conditions. Measuring several responses of a food system at the same time, using all available information when modelling experimental data and proposing a reaction mechanism, can be a powerful tool. This can be done using multiresponse modelling. This modelling approach enables more precise parameter estimation and realistic model proposes.

Caramelisation is the common name for a group of reactions that occur when carbohydrates are exposed to high temperatures. This reaction differ from Maillard reaction, since no amino groups are involved. It often occurs during the preparation of traditional sucrose syrups and caramels, which are extensively used in confectionery and pastry products.
The caramelisation reaction occurs at high temperatures in the presence or absence of catalysts (acids, basis or salts and impurities). This reaction can be observed both in dilute or concentrated solutions and in the crystal form. Due to the large number of reaction pathways, and even larger number of products formed during caramelisation reaction, kinetic studies based on the caramelisation reaction mechanism are of increased complexity.

THEORETICAL CONSIDERATIONS

MULTIRESPONSE MODELLING

Food scientists often face kinetic problems where more than one response is measured at the same time. In these cases the different responses can be considered as random variables with a multinormal distribution.

Each observation y_{iu} can be expressed as a function of a mathematical model with optimum set of θ_h parameter values:

$$y_{iu} = f_i(\theta_h, x_{iu}) + \varepsilon_{iu} \qquad (1)$$

i=1,…, k measured responses
u=1,…, n experimental runs
h = 1,…,m number of model parameters
ε_{iu} is the experimental random error of the measured response i at observation u.

The joint probability density function of $y_1,\dots,y_k$ for a given experimental data point x_u can then be written as:

$$g(y_1,\dots,y_k) = \frac{1}{(2\pi)^{k/2}\,|\Sigma|^{1/2}} \exp\left[-\frac{1}{2}\sum_{i=1}^{k}\sum_{j=1}^{k}\sigma^{ij}\big(y_i - f_i(\theta_h,x_u)\big)\big(y_j - f_j(\theta_h,x_u)\big)\right] \qquad (2)$$

j is any ≠i
Σ is the variance covariance matrix of y_k
σ^{ij} is the $(i,j)^{th}$ element of the inverse matrix, Σ^{-1}

The probability of making a series of k independent measurements at n distinct x_u points is then:

$$P(Y\,|\,\theta,\Sigma) = \prod_{u=1}^{n} g(y_1,\dots y_k) = \frac{1}{(2\pi)^{nk/2}\,|\Sigma|^{n/2}} \exp\left[-\frac{1}{2}\sum_{i=1}^{k}\sum_{j=1}^{k}\sigma^{ij}\sum_{u=1}^{n}\big(y_i - f_i(\theta_h,x_u)\big)\big(y_j - f_j(\theta_h,x_u)\big)\right] \qquad (3)$$

The marginal posterior probability distribution for the parameters given the observed responses, P(θ|Y), is maximized by minimizing the determinant of the matrix of cross products of the k responses.

$$|\,\upsilon_{ij}\,| = \left|\sum_{u=1}^{n}\big(y_i - f_i(\theta_h,x_u)\big)\big(y_j - f_j(\theta_h,x_u)\big)\right| \qquad (4)$$

The precision of the estimates can be assessed by the contour of the marginal highest posterior density (HPD). The (1-α) HPD interval can be determined by the shortest interval in parameters' space that contains 1-α of the posterior probability.

MECHANISM OF SUCROSE DEGRADATION INTO CARAMEL

In this work we focused on the case where sucrose in very concentrated solutions (above saturation) was heated at high temperatures in the absence of impurities and at neutral pH. Under such conditions, the effect of heat can be assumed similar to the effect of using lower temperatures in acidic conditions and, consequently, an identical reaction mechanism can be considered.

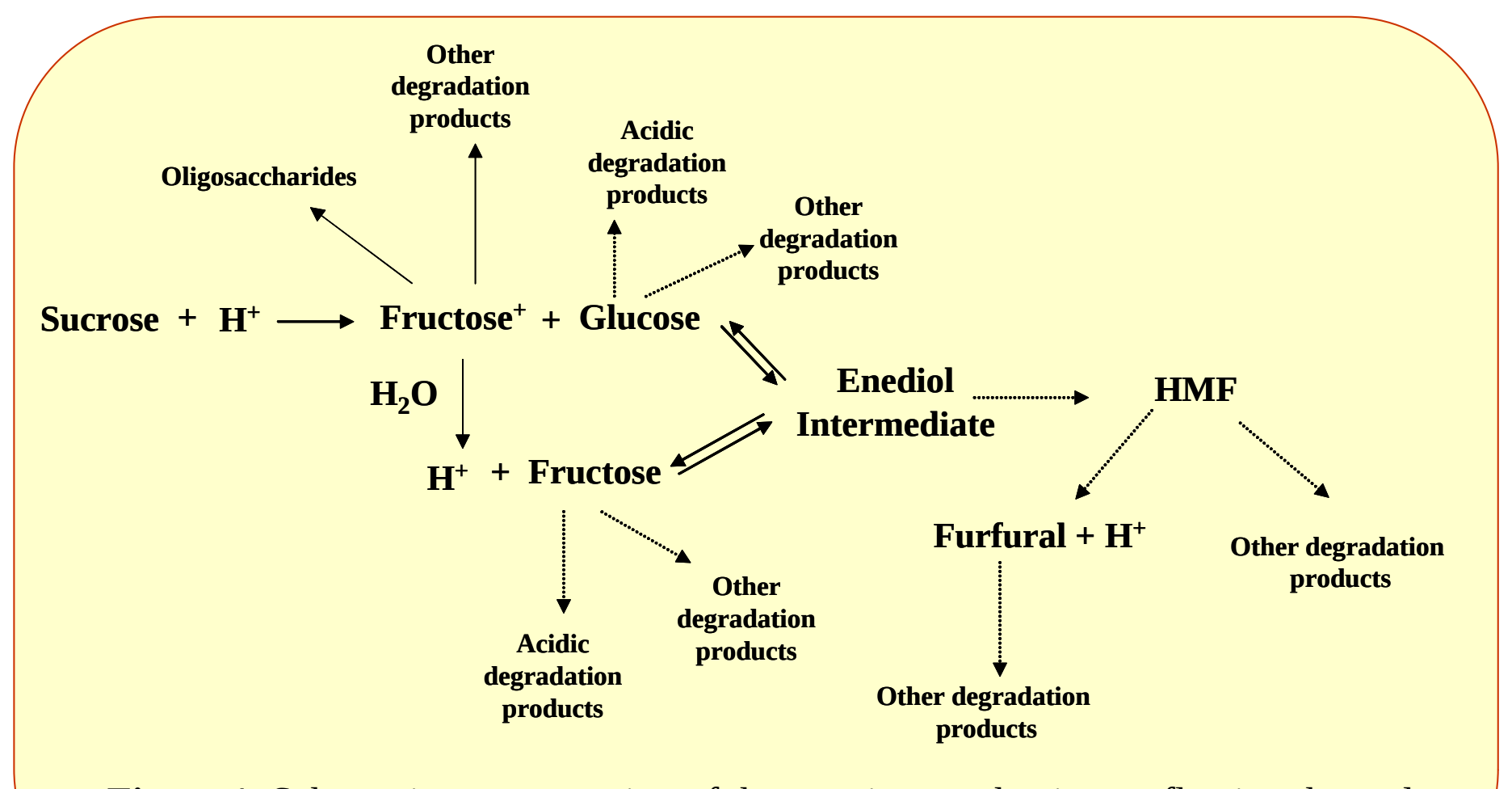

Figure 1. Schematic representation of the reaction mechanism, reflecting the real physical phenomenon of sucrose caramelisation.

1. The first reaction step in the caramelisation reaction is sucrose hydrolysis.
2. Sucrose hydrolysis yields D-glucose and a fructose oxocarbonium ion.
3. This fructose carbocation may:
    - i) react with a water molecule to form fructose and regenerate the catalyst H^+
    - ii) react with another carbohydrate molecule present in solution to form oligosaccharides and anhydro-sacharides
    - iii) undergo non-specific degradation to form a wide range of products, including HMF and organic acids
4. The mechanism of fructose and glucose degradation into HMF is generally accepted to be an open chain β-elimination mechanism that proceeds via an enediol intermediate
5. HMF can be further degraded to products like furfural and 5-methylfurfural

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MATERIALS AND METHODS

EXPERIMENTAL PROCEDURES

Isothermal experiments were performed using different initial sucrose concentration (70 to 87.5 (w/w %)), at different processing temperatures (100 to 180ºC). Sucrose degradation and products formation (fructose, glucose, 5-hydroxymethylfurfural (HMF) and 2-furaldheyde (furfural)) were assessed using HPLC. Evolution of pH was monitored during the reaction.

MODELLING PROCEDURES

Multiresponse modelling was carried out using Athena Visual Studio software (www.athenavisual.com).
The effect of temperature was described by an Arrhenius type dependency of each rate constant, and the effect of water content was included in the kinetic parameters estimation.
Quality of the regression and parameter precision were evaluated, respectively, by the sum of squares residues and the 95% highest posterior density intervals.

RESULTS AND DISCUSSION

PROPOSED REACTION PATHWAY AND MATHEMATICAL MODEL

In order to model the entire sucrose caramelisation reaction, a model was developed by setting up differential equations for each of the possible reaction pathways described in figure 1. However, all lead to inconsistent regression results with the exception of the pathway proposed in figure 2. The corresponding mathematical model is described by equations 5 through 12.

$$\frac{d[Suc]}{dt} = -\,k_1[\mathrm{Sucrose}][H^+] \qquad (5)$$

$$\frac{d[H^+]}{dt} = k_2[\mathrm{Fructose}] + k_4[\mathrm{HMF}] \qquad (6)$$

$$\frac{d[Fru]}{dt} = k_1[\mathrm{Sucrose}][H^+] - k_3[\mathrm{Fructose}] - k_2[\mathrm{Fructose}] \qquad (7)$$

$$\frac{d[Glu]}{dt} = k_1[\mathrm{Sucrose}][H^+] - k_6[\mathrm{Glucose}] \qquad (8)$$

$$\frac{d[HMF]}{dt} = k_3[\mathrm{Fructose}] - k_4[\mathrm{HMF}] \qquad (9)$$

$$\frac{d[Fur]}{dt} = k_4[\mathrm{HMF}] - k_5[\mathrm{Furfural}] \qquad (10)$$

$$\frac{d[Other\ Products_1]}{dt} = k_5[\mathrm{Fur}] \qquad (11)$$

$$\frac{d[Other\ Products_2]}{dt} = k_6[\mathrm{Glu}] \qquad (12)$$

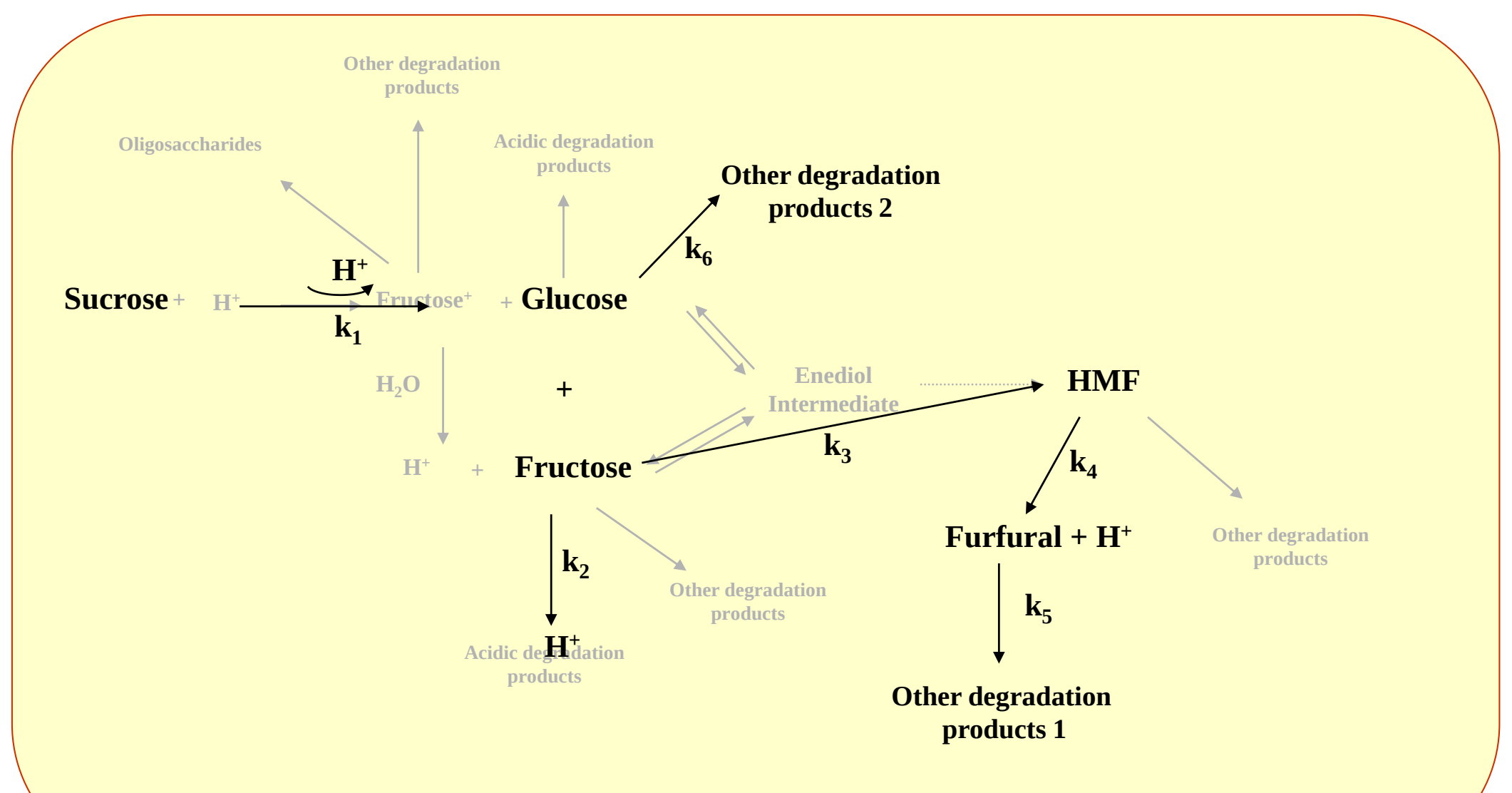

Figure 2. Proposed kinetic mechanism for the caramelisation reaction.

The mechanism proposed in figure 2 is a simplification of the real physical phenomenon, and only takes into account the main reaction pathways. Under different conditions, different pathways may emerge. Model ability to describe experimental data can be observed in figure 3.

TEMPERATURE AND WATER CONTENT EFFECTS

The temperature effect on the reaction was described on rate constants by an Arrhenius type dependency (Eq. 13). Both k_{ref} and Ea for each reaction step were estimated with correspondent 95% HPD intervals, at different water content levels.

$$k_s = k_{ref\ s}\exp\left(-\frac{Ea_s}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right) \qquad (13)$$

s = 1,…6 is the reaction step identification
T_{ref} = 140ºC

No significant effect of water content was observed on Ea_s and $k_{ref\ 2}$.
$k_{ref\ 1,\,3,\,4,\,5\ \mathrm{and}\ 6}$ varied exponentially with water content

A global model with temperature and water content effect was proposed

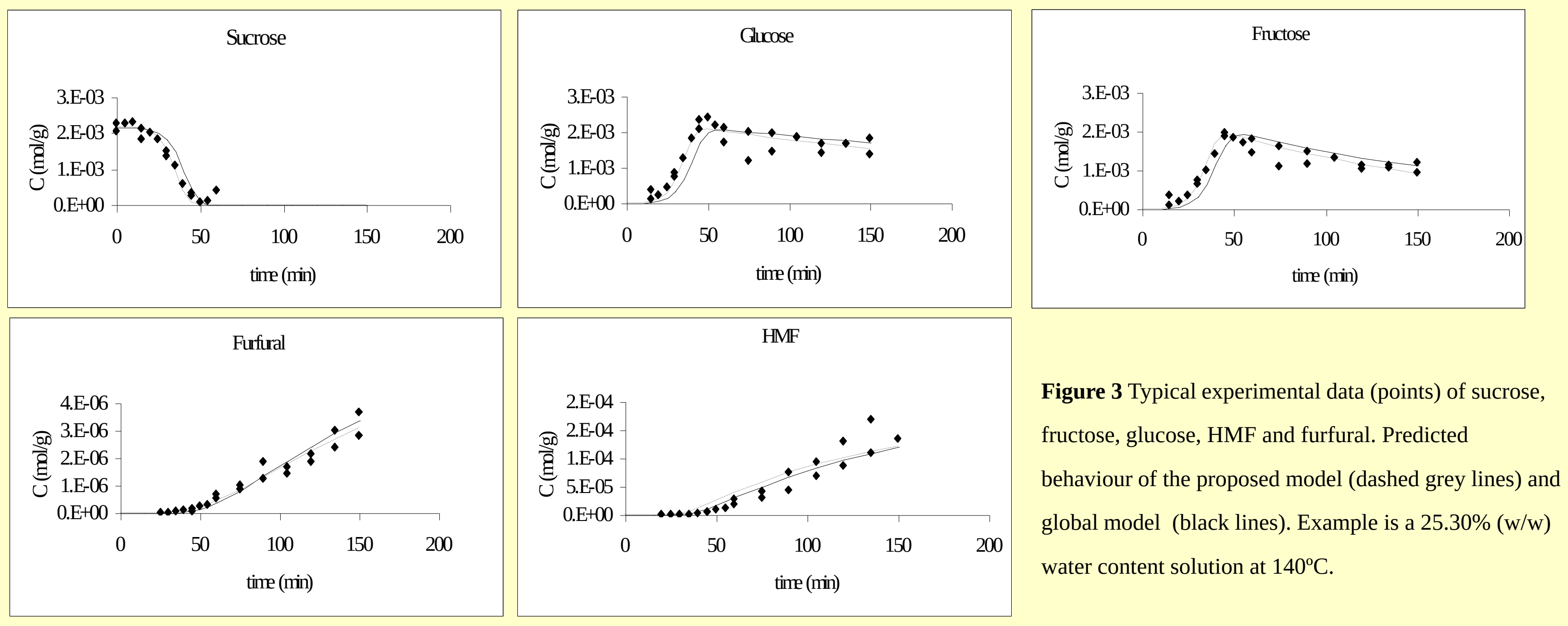

Figure 3 Typical experimental data (points) of sucrose, fructose, glucose, HMF and furfural. Predicted behaviour of the proposed model (dashed grey lines) and global model (black lines). Example is a 25.30% (w/w) water content solution at 140ºC.

FINAL REMARKS

☆ **The proposed reaction pathways and mathematical model describes successfully the experimental data.**

☆ **Temperature and water content effects were included in the model.**

☆ **Satisfactory precision was attained for parameter estimates – 95% HPD intervals varied between 2 and 45% of estimated values.**