Application of the acid hydrolysis of sucrose as a temperature indicator in continuous thermal processes

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Abstract

The hydrolysis of sucrose in an acid medium was used as a temperature indicator to measure holding temperatures in a continuous thermal-processing unit. From a theoretical analysis, target conversion (χ) and errors in both acid concentration and conversion measurements were found to affect significantly the accuracy of predicted temperatures, whereas errors in the determination of the fluid mean residence time did not show a significant effect. For different pasteurisation temperatures ($70°C < T < 86°C$) and flow rates ($4800 < Re < 11,300$), the acid concentration in the medium was adjusted so that different extents of reaction could be tested, as the reaction rate was found to increase exponentially with [H$^+$]. Nitric acid solutions were circulated through the unit, a sucrose solution was continuously fed to the entrance of the holding tube and sucrose concentration was analysed at the half way part and at the exit of the holding tube. The temperature of the holding section was then estimated from the measured conversion. These results compared well with thermocouple measurements, with deviations of less than 4°C for conversions between 0.4 and 0.7, whereas greater errors were obtained for both low and high conversions.

Keywords: Holding; Pasteurisation; Temperature Assessment; Time-temperature indicator

Notation

b	parameter in Eq. (8) (mol^{-1} l)
C	concentration (g l^{-1})
C_0	initial concentration (g l^{-1})
E_a	activation energy (kJ mol^{-1})
[H$^+$]	acid concentration (mol l^{-1})
k_0	pre-exponential factor (min^{-1})
k_{ref}	rate constant at the reference temperature (min^{-1})
m	heating rate (K min^{-1})
Pe	Peclet number
R	universal gas law constant ($R = 8.314$ J mol^{-1} K^{-1})
RTD	residence time distribution
SSR	sum of squares of residuals
t	time (s)
T	temperature (K)
T_0	initial temperature (K)
T_{pred}	predicted temperature (K)
T_{ref}	reference temperature (K)
T_{meas}	measured temperature (K)
TTD	time-temperature distribution
TTI	time-temperature integrator
z	dummy variable in Eq. (4) (E_a/RT)
z_0	dummy variable in Eq. (4) (E_a/RT_0)
z_{ref}	dummy variable in Eq. (5) (E_a/RT_{ref})

Greek letters

κ	parameter in Eq. (8) (min^{-1})
χ	target conversion (%)
τ	mean holding time (min)

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1. Introduction

The main criterion in establishing the efficacy of a thermal process is the microbial safety of the final product (Stumbo, 1973). Mathematical procedures to predict reduction of microorganisms or quality factors in thermal processing are well known, but their accuracy depends, among other factors, on an accurate processing temperature history determination (Hendrickx et al., 1995). Measuring the exact processing temperature during a continuous thermal process using conventional temperature sensors is an intrusive procedure, thus changing the flow characteristics and conduction errors

and temperature gradients in the cross section of the processing system raise additional problems. Alternative on-line methods have been developed to assess the effect of continuous thermal processes on the kinetics of safety and quality factors (Berry, Sing & Nelson, 1989; Weng, 1991). In this framework, several chemical and biochemical indicators have been proposed in the literature, and they were recently reviewed by Hendrickx et al. (1995). Table 1 summarises the reported chemical Time-Temperature Indicators (TTIs). In order to mimic the degradation of a target safety or quality parameter, a TTI must have the same activation energy (Taoukis & Labuza, 1989; Tobback, Hendrickx, Weng, Maesmans & DeCordt, 1992). Typical E_a values for food quality losses vary between 40 and 210 kJ mol^{-1}, while for microbial destruction they range from 210 to 630 kJ mol^{-1} (Taoukis, Fu & Labuza, 1991). Indicators have also been used for the experimental validation of mathematical models that predict temperature profiles in heat exchangers. Ellborg and Trägårdh (1990) developed a model simulating Time-Temperature Distribution (TTD) for non-isothermal flow in a tubular heat exchanger, that was later validated using acid hydrolysis of dextran as a tracer (Ellborg & Trägårdh, 1994).

Lou (1977) first proposed acid hydrolysis of sucrose as a chemical indicator for in-pack thermal processing. Acid hydrolysis of sucrose was further applied in the assessment of the influence of in-pack sterilisation on both volume average and single point (centre and surface) quality (Silva, Oliveira, Lamb, Pinheiro Torres & Hendrickx, 1994). In addition, Adams, Simunovic and Smith (1984) applied this TTI in continuous thermal processes, focusing on UHT temperature ranges. Acid hydrolysis of sucrose was also proposed as a TTI for lower temperature processes, namely continuous pasteurisation (Pinheiro Torres, Oliveira, Silva & Fortuna, 1994), but no validation was presented in the literature.

The development and application of a TTI requires a good knowledge of the TTI kinetics. The kinetics of the acid hydrolysis of sucrose have been studied in batch conditions, both in isothermal and non-isothermal conditions, and it was found that they may be described as a first order reaction, (Honig, 1953; Meade, 1963; Vukov, 1965; Pinheiro Torres et al., 1994)

$$\frac{dC}{dt} = -kC, \quad \frac{C}{C_0} = e^{-kt}, \tag{1}$$

where C is the concentration at time t, C_0 the initial concentration and k is the rate constant.

The rate constant increases with temperature, according to an Arrhenius-like dependence (Vukov, 1965; Lou, 1977; Pinheiro Torres et al., 1994):

$$k = k_0 e^{-(E_a/RT)}, \tag{2}$$

where k_0 is the pre-exponential factor, E_a the activation energy, R the universal gas law constant and T is the absolute temperature.

Sadeghi and Swartzel (1990) and Miles and Swartzel (1995a) compared the kinetic parameters of acid hydrolysis of sucrose at high temperatures and pH 2.5, estimated both with a batch and a continuous flow method. These authors concluded that the kinetic parameters estimated by the two different methods were considerably different, which implies that if the development of this TTI relies only on the classical batch procedure, it may provide unreliable results when applied in the assessment of continuous thermal processes. Furthermore, kinetic parameter estimation greatly depends on the experimental conditions and the extent of reaction in continuous flow processes may also be expected to affect the accuracy of a TTI. Yet, in reported works this value is always selected on the basis of common sense, lacking a theoretical support.

The activation energy was shown to be independent of pH (Vukov, 1965; Pinheiro Torres et al., 1994) and

Table 1
Some proposed chemical indicators (TTI) for application in thermal processing

Indicator	Objective	Application	Validation	Kinetics determination	References
Dextran hydrolysis	Tracer for TTD	Continuous sterilisation	Yes	Yes	Ellborg and Trägårdh (1988)
Sucrose hydrolysis	Safety evaluation	Can sterilization	No	Yes (pH 2.5)	Lou (1977)
Sucrose hydrolysis	Quality indicator	Can sterilization	Yes	Yes (pH 3.5)	Silva (1992)
Sucrose hydrolysis	Safety evaluation	UHT	No	Yes (pH 2.5)	Adams et al. (1984)
Sucrose hydrolysis	Thermal evaluation	UHT	Yes	Yes (pH 2.5)	Miles and Swartzel (1995a)
Blue #2	Thermal evaluation	UHT	Yes	Yes	Miles and Swartzel (1995b)
Immobilised peroxidase	Safety evaluation	Particulate canned foods	Yes	Yes	Weng (1991)
methyl-methionine sulfonium	Safety evaluation	Can sterilization	No	Yes	Berry et al. (1989)
γ-glutamyl transpeptidase	Heat treatment indicator	Milk pasteurisation	No	No	Patel and Willbey (1989)

values between 46.0 and 133.9 kJ mol^{-1} were reported in the literature (Pinheiro Torres et al., 1994). The pre-exponential factor was reported to increase linearly with the acid concentration (Vukov, 1965; Pinheiro Torres et al., 1994). Thus, one may control the reaction rate simply by selecting an adequate pH, thus also controlling the extent of reaction which is achieved during the process.

The main purpose of this work was to assess the applicability of the acid hydrolysis of sucrose for assessing holding temperatures in pasteurisation processes. A theoretical study was also conducted to assess the effect of the reaction extent on the accuracy of the estimated temperatures.

2. Material and methods

2.1. Study of the kinetics of the acid hydrolysis of sucrose

The kinetics of the acid hydrolysis of sucrose were studied in batch conditions. Sixteen non-isothermal experiments were conducted in the range of pH from 0.8 to 1.5, because the lowest value tested in the literature was 2.5. The experiments were conducted as described by Pinheiro Torres et al. (1994), although using a linear temperature increase, from 50°C to 90°C. The heating rate was selected according to pH, so that approximately 90% reduction of the disaccharide was achieved in all experiments (Fig. 1).

2.2. The continuous thermal processing system

Experiments were performed in the holding tube of a pilot plant continuous thermal processing system (Pinheiro Torres & Oliveira, 1993), with a 2.2 cm internal diameter and an upward inclination of 8.3 cm per 1 m tube length. This system was run with nitric acid solutions and tap water as solvent at several processing
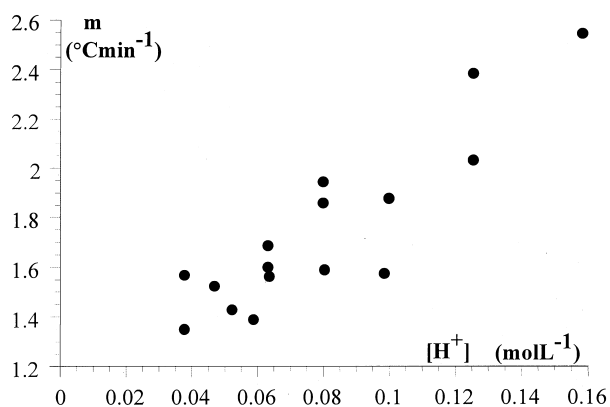

Fig. 1. Heating rates used in the experiments for determination of the kinetics of acid hydrolysis of sucrose, conducted at different pH values.

conditions: holding temperature from 70°C to 86°C and flow rate ranging from 110 to 250 l h^{-1}, corresponding to Reynolds numbers between 4800 and 11,300 and mean holding times up to 5 min. For each set of processing conditions, the acid concentration (0.8 < pH < 1.5) was chosen to provide selected extents of the reaction, as discussed in the Results and Discussion section. The acid concentration was measured using an automatic titrator (Titralab, model 42; Radiometer, Copenhagen, Denmark).

2.3. TTI experiments

A concentrated solution of sucrose (80–100 g l^{-1}) was injected into the flow continuously at the entrance of the holding tube by means of a peristaltic pump. Triplicate samples were taken at three different points of the holding tube, namely right after injection ($L = 0$), at half way ($L = 12.9$ m) and at the exit ($L = 23.6$ m). The samples were immediately immersed in an ice bath to stop the hydrolysis, and were diluted 1:1 with a NaOH 0.5M solution shortly after, to guarantee that no reaction occurred prior to analysis. A portion was kept acidic until total hydrolysis so that total sugars could also be measured. All samples (raw and hydrolysed) were then analysed by the DNS method for reducing sugar determination (Pinheiro Torres et al., 1994). For control, a blank sample taken before injection was also analysed. Sucrose concentrations were obtained by the difference between raw and hydrolysed sample. The initial concentration of sucrose was obtained both from the samples at the holding tube entrance and from the material balance on the injected sucrose, which were in good agreement. Sucrose retention and the corresponding extent of reaction were calculated for both the middle and exit of the holding tube and for each processing temperature.

Meanwhile, the holding temperature was continuously monitored during each experiment at three points next to the sampling ports, and at the entrance and exit of the hold tube, by means of previously calibrated thermocouples type J connected to a data acquisition system. Variations of the measured temperatures along the hold tube were smaller than ±1 K, except for the first and last thermocouples, which had a high conduction error due to their proximity to the heating and the cooling sections, respectively.

2.4. Data analysis

2.4.1. Estimation of the kinetic parameters of the acid hydrolysis of sucrose

The kinetics of the acid hydrolysis of sucrose, under linear increasing temperature conditions, may be described by combining Eqs. (1) and (2):

$$c_t = c_0 \exp \left\{ -k_0 \int_0^t e^{(-E_a/RT(t))} dt \right\}, \tag{3}$$

where $T(t) = T_0 + mt$, being T_0 the initial temperature and m the heating rate.

The integral of Eq. (3) does not have an analytical solution (Rhim, Nunes, Jones & Swartzel, 1989), but an approximation to the exact solution was reported by Nunes, Rhim and Swartzel (1991)

$$c_{pred}(t) = c_0 \exp \left\{ -\frac{k_0 E_a}{mR} \left[\frac{e^{-z}}{z} \frac{(z-4)}{(z^2 + 6z + 6)} \right. \right.$$
$$\left. \left. -\frac{e^{-z_0}}{z_0} \frac{(z_0 - 4)}{(z_0^2 + 6z_0 + 6)} \right] \right\}, \tag{4}$$

where $z = E_a/RT(t)$ and $z_0 = E_a/RT_0$.

This equation may also be written in terms of a finite reference temperature, T_{ref}, with the advantage of improving convergence in the estimation procedure (Nunes et al., 1991)

$$c_{pred}(t) = c_0 \exp \left\{ -\frac{E_a}{mR} \left[\frac{e^{\ln k(z_{ref}-z)}}{z} \frac{(z-4)}{(z^2 + 6z + 6)} \right. \right.$$
$$\left. \left. -\frac{e^{\ln k(z_{ref}-z_0)}}{z_0} \frac{(z_0 - 4)}{(z_0^2 + 6z_0 + 6)} \right] \right\}, \tag{5}$$

where $z_{ref} = E_a/RT_{ref}$.

This equation was found to yield results identical to those obtained from the numerical integration of Eq. (3). It was fitted to the experimental data using 350 K as the reference temperature. Parameters were estimated by non-linear regression using Stata 3.0 Software (Computing Resource Center, Sta. Monica, CA, USA).

2.4.2. Estimation of the holding temperature

The estimation of holding temperatures in a continuous thermal process using the acid hydrolysis of sucrose as a TTI requires the following input: residence time distribution (RTD) of the fluid, acid concentration of the medium, the kinetics of the TTI and its dependence on temperature and acid concentration.

The RTD in holding tubes may be often described by the dispersed plug flow model (Aiba & Sonoyama, 1965; Nassauer & Kessler, 1979; Wennerberg, 1986; Sancho & Rao, 1992), which is characterised by the dimensionless Peclet number. For low viscous fluids, the dispersion is however quite reduced and in many situations the flow approaches a plug flow behaviour (according to Levenspiel (1972), an error below 1% is attained if $0.01 Pe > (k\tau)^2$). In our case $Pe > 670$ and $k\tau < 2.7$, so the mean residence time, τ, was enough to describe the flow. This value was calculated as the ratio between the hold tube volume and the flow-rate.

The holding temperature was predicted (T_{pred}) from the experimental data by combining Eqs. (1) and (2) and

the equation relating the rate constant to [H$^+$], that will be presented in Section 4.

$$T_{pred} = \left\{ \frac{1}{T_{ref}} - \frac{R}{E_a} \ln \frac{-\ln(C/C_0)}{k_{ref}([H^+])\tau} \right\}^{-1}. \tag{6}$$

The accuracy of the prediction, ΔT, was defined as

$$\Delta T = T_{pred} - T_{meas}, \tag{7}$$

where T_{meas} is the temperature measured with thermocouples.

2.5. Simulation procedure

Typical processing parameters were chosen: $T = 80°C$, $\tau = 4$ min. Target conversions, $\chi ((1 - C/C_0) \times 100)$, between 10% and 90% were tested. The [H$^+$] value was calculated by solving Eq. (6) for this variable. Pseudo-experimental values were generated to simulate the variability of experimental measurements, by attributing absolute errors up to 5 s, 0.04 g l^{-1} and 0.01 mol l^{-1}, respectively, to the following variables: τ, C/C_0 and [H$^+$]. These limits were selected taking into consideration the standard deviation that we had observed experimentally in the measurement of these variables. A 3^3 factorial design was performed for these three input variables, considering the maximum levels of error for each variable. T_{pred} was calculated using Eq. (6). Results were analysed with Statgraphics 5.0 (STSC, Rockville, USA).

3. Results and discussion

3.1. Acid hydrolysis of sucrose

The model described by Eq. (5) showed a good fit to the experimental data. The dependence of E_a and k_{ref} on pH values is shown, respectively, in Figs. 2 and 3. The
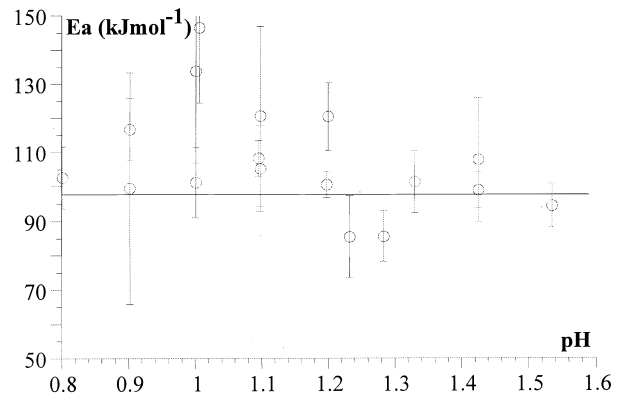

Fig. 2. Dependence of the activation energy on pH. The points correspond to the estimates obtained with the individual fits; the line corresponds to the estimate obtained with the joint regression.
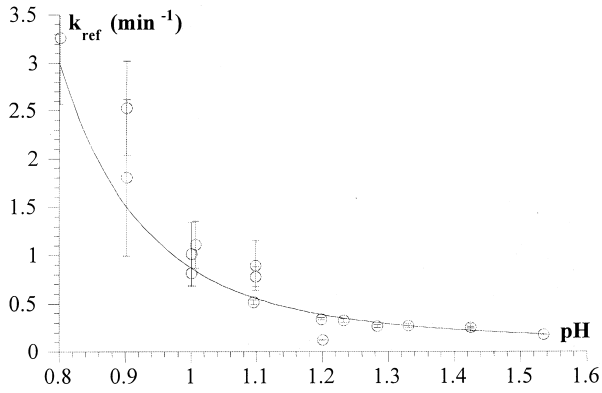
Fig. 3. Dependence of the rate constant on pH. The points correspond to the estimates obtained with the individual fits; the line corresponds to the fit obtained with the joint regression.

95% confidence intervals for each estimate are marked with vertical lines. It can be noted that these intervals have in general a considerable magnitude. The points show some scatter, yet the activation energy does not seem to depend on pH, as expected. The constant rate at the reference temperature shows an exponential decrease with pH. A non-linear regression was then applied to the complete set of experimental data, imposing an activation energy pH independent, and estimating its value, as well as the k_{ref} values for each pH. The SSR obtained was not significantly affected, confirming that the activation energy can be considered as independent of pH. The estimate of the activation energy was 103 kJ/mol and the estimates of k_{ref} are shown in Fig. 4. Although the relationship between k_{ref} and [H$^+$] can be described as linear for the lower [H$^+$] values, as one would expect from theory (Vukov, 1965), it is clear that the effect of increasing [H$^+$] is more pronounced for the higher concentrations tested. Overall, the dependence of k_{ref} on temperature may be described by an exponential model,
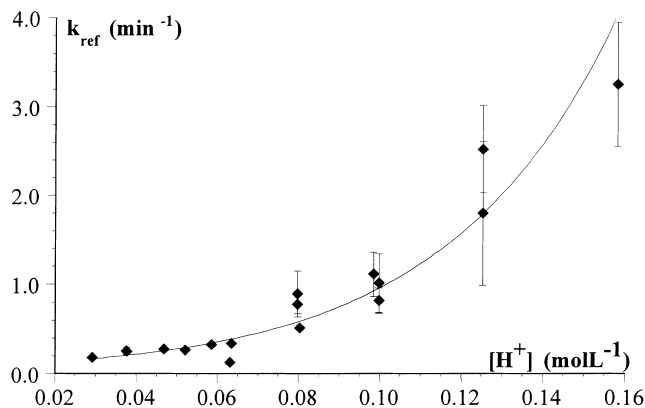

Fig. 4. Dependence of kinetic rate constants at a reference temperature (350 K) on acid concentration, imposing a constant activation energy (estimate value = 103 kJ/mol). The line corresponds to the fit of the data to an exponential equation.
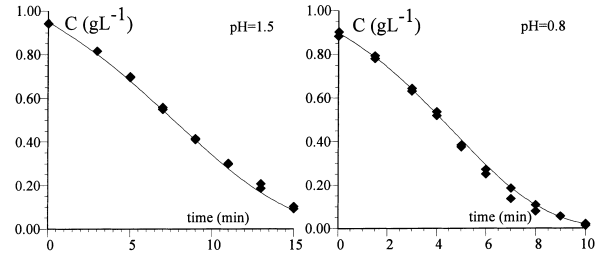

Fig. 5. Fit of the mathematical model (Eq. (3)) to the experimental data of acid hydrolysis of sucrose under non-isothermal conditions, imposing a constant activation energy and an exponential relationship between k_{ref} and [H$^+$] (Eq. (8)).

which shows a quasi-linear behaviour for low [H$^+$] (see Fig. 4).

To improve the precision in parameter estimation, a joint non-linear regression was further applied to the complete set of data, imposing a constant activation energy and an exponential relationship between k_{ref} and [H$^+$]

$$K_{ref} = \kappa \times e^{(b \times [H^+])} \qquad (8)$$

and estimating the activation energy value and the parameters κ and b. The following results were obtained: $E_a = 98 \pm 3$ kJ mol^{-1}, $\kappa = 0.098 \pm 0.002$ min^{-1}, $b = 21.6 \pm 0.5$ mol^{-1} l.

These results are also shown in Figs. 2 and 3. The 95% confidence intervals are not shown because of their very small magnitude. The activation energy lies well within the expected range (Pinheiro Torres et al., 1994; Miles & Swartzel, 1995a). Fig. 5 shows the fit of this model to the experimental data for pH 0.8 and 1.5. Similar fits were obtained for the other pH values tested.

3.2. The effect of the extent of reaction on the accuracy of the TTI

The Anova analysis of the simulated pseudo-experimental data showed that errors in τ did not affect significantly the accuracy of the estimated temperature, whereas errors in [H$^+$] and (C/C_0) were significant at a 95% level. In addition, their effect depended on the target χ.

Figs. 6 and 7 show the influence of the extent of reaction on the predicted temperature, for different levels of errors in [H$^+$] and (C/C_0), respectively. These figures show that positive errors in the experimental values of [H$^+$] or C/C_0 lead to under-estimation of the holding temperature. The effect of experimental errors in the determination of [H$^+$] on the accuracy of predicted temperature decreases as χ increases, ΔT becoming smaller than 0.1°C for levels of conversion above 90%, independent of the error in the measurement of [H$^+$]. This would lead us to the conclusion that one should target at high χ values. On the other hand,
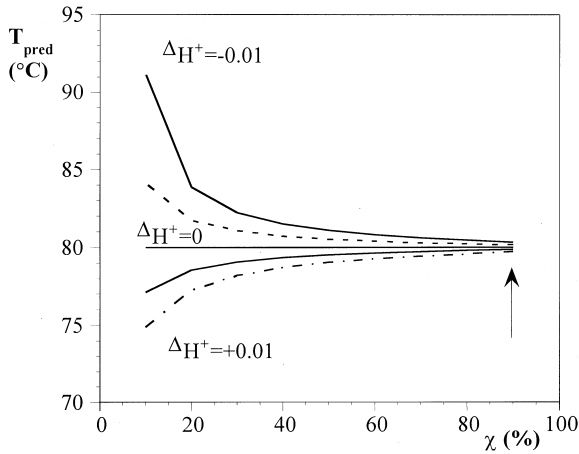
Fig. 6. Influence of target conversion, χ, on the predicted temperature for different levels of experimental error in [H$^+$].
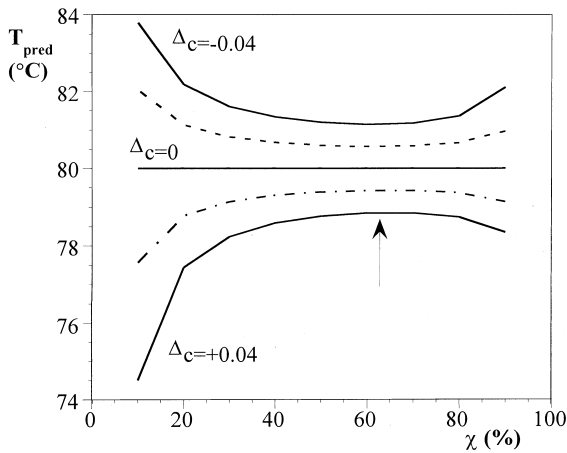

Fig. 7. Influence of target conversion, χ, on the predicted temperature for different levels of experimental error in C/C_0.

Fig. 7 shows that if one considers the error in the measurement of (C/C_0), for χ values below approximately 40%, increasing χ improves temperature prediction between 40% and 80%. No significant influences are detected and further increase of χ actually leads to higher errors in the estimation of the temperature. Therefore, the target conversion should be set to intermediate to high values. Overall, a target conversion from 40% to 70% is recommended. For the set of values used in our simulation, this extent of conversion would lead to ΔT between 0.3°C and 1.8°C, even when both the errors in the measurement of [H+] and (C/C_0) are maximum, respectively, ±0.01 mol l^{-1} and ±0.04 mol l^{-1}.

3.3. Estimation of holding temperatures

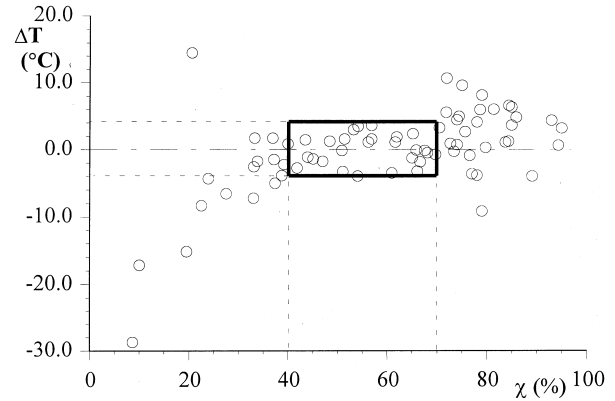Fig. 8 shows the differences between experimentally measured temperatures and predicted values, for differ-

Fig. 8. Influence of reaction conversion, χ, on the accuracy of predicted temperature.
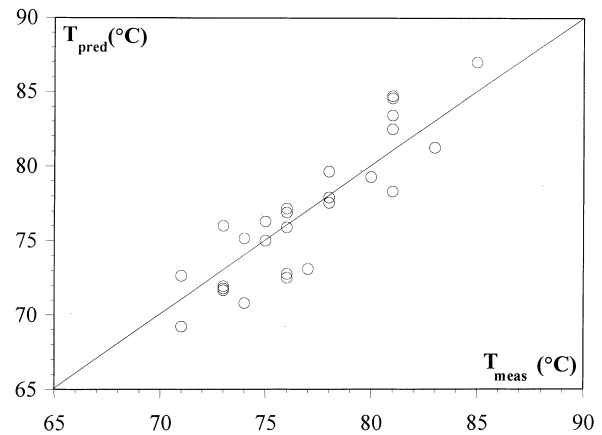

Fig. 9. Relationship between predicted and measured temperatures, for reaction conversions between 40% and 70%.

ent runs, where the experimental conditions were chosen to yield χ from approximately 10% to 95%. One can see that best accuracy (errors below 4°C) was indeed achieved for target conversions within the optimal range above predicted (between 40% and 70%). In general, positive deviations are found for higher conversions, whereas the opposite is found for lower conversions. Fig. 9 shows the relationship between measured and predicted temperatures, where a good agreement is noticed in the range tested.

Table 2 shows the pH values that should be selected to use the acid hydrolysis of sucrose for measuring temperatures accurately ($40\% < \chi < 70\%$) in time-temperature conditions used in continuous thermal processing of some selected products.

4. Conclusions

The activation energy for the acid hydrolysis of sucrose was confirmed to be independent of pH. In opposition to what would be expected from theory, the

Table 2
Estimated pH values required for a 40% and 70% reduction of sucrose during acid hydrolysis, for typical aseptic processing time/temperature conditions

Product	Processing conditions	References	Recommended pH
	77 °C–1 min	Fellows (1988)	0.94–1.12
Fruit juices	95 °C–45 s	Hotchkiss (1989)	1.28–1.87
	100 °C–15 s	Hotchkiss (1989)	1.07–1.35
Beer	71°C–30 s	Hasting (1992)	0.76–0.87
	75°C–20 s	Hasting (1992)	0.75–0.86
Milk HTST	90°C–4 s	Kessler (1988)	0.73–0.84
Concentrated milk	80°C–25 s	Brown (1991)	0.85–1.00

pre-exponential factor was found to increase exponentially with $[H^+]$, although showing a quasi-linear behaviour for pH above approximately 1.1.

The acid hydrolysis of sucrose was successfully applied in the assessment of holding temperatures in continuous thermal processing. Temperature prediction based on kinetic data obtained in batch conditions yielded good results, but proved to be very sensitive to pH and conversion values; thus a large number of samples is advised for obtaining reliable results and low standard errors. Additionally, the target conversion was also confirmed to affect the accuracy of predictions, and values between 40% and 70% are recommended.

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