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Determination of the Kinetic Parameters of a Time-Temperature Integrator for the Flash Pasteurization

Processes for the thermal preservation of beverages in heat exchangers demand for validation methods, especially as performance qualification of a new plant. Particularly in the combination with aseptic filling systems reliable and precise tests are important. A chemical Time-Temperature Integrator (TTI) is expected to measure more accurate, cheaper and faster than conventional microbiological count reduction tests. The acidic hydrolysis of sucrose was investigated as a TTI. For the practical application the calibration of the chemical reaction is necessary in order to find the suitable parameters in terms of the acid and sucrose concentration. For the calibration of the TTI two methods were tested, the isothermal (two steps) and the non-isothermal (one-step) method. The latter revealed as more precise, thus it was used to explore the required kinetic parameters of the reaction. To cover the temperature range from 50 to 78 °C, exemplary for the application of beer pasteurization a sugar concentration of 5 % and acid concentrations between 0.02 and 0.75 mol/L were used. With respect to products with high viscosities such as beverage concentrates a 52 % sugar syrup was used. Here the reaction is faster than with 5 % sugar. According to earlier findings the activation energies of 105.09 ± 1.07 kJ/mol (5 %) and 113.56 ± 0.83 kJ/mol (52 % sucrose) respectively were found. Of deciding importance for the application as TTI is the precise determination of the frequency factor k_0 in dependency on the acid concentration. In case of both sugar concentrations a quasi-linear equation describes this correlation with high precision ($R^2 \geq 0.998$). Herewith earlier indistinct publications could be clarified. With the activation energy and the frequency factor the reaction rate can adjusted by changing the H^+ concentration to different pasteurization intensities as appearing in practice. Because the activation energy of the thermal death of microorganisms is known to be about twice as high as of the TTI only largely, isothermal reactions can be converted in a direct manner. In non-isothermal cases the TTI slightly underestimates the death rate of microorganisms. The transfer of these findings into the practical scale and their verification shall be the subject of upcoming work.

Descriptors: pasteurization, sucrose hydrolysis, Time-Temperature Integrator, kinetic parameter

1 Introduction

The microbial safety of beverages is of great importance for their shelf life. Pasteurization is a widely used technique to accomplish this. To describe the intensity of the pasteurization the Pasteurization Unit (PU) is used. PU´s employed in the practice are often based on outdated data, for example 15-20 PU, typically used for lager beer, arise from a set of publication [1, 2, 3] dated from the early nineteen fifties. Because several factors were not determined precisely, grand safety margins were added. From today´s point of view these data seem no longer to be sufficient [4]. In difference to the conventional approach, the leading objective in this paper is not the microbiologically worst case scenario but also the gentle treatment of the product and consideration of used resources.

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To set the pasteurization parameters time and temperature adequately, the required pasteurization units (PU_{re}) and the effective thermal dosage (PU_{eff}) have to be known [4]. The PU_{re} depend on the number of the present microorganisms, their thermal death kinetics and the accepted risk of surviving microorganisms. The PUeff depend on the applied temperature and exposition time. The common but rough method to estimate the applied PU_{eff} during pasteurization is to calculate with the average or the minimum residence time and the outlet temperature of the holding tube. Due to the effect of residence time and temperature distributions and the unconsidered heating regime in the cooling and heating zones, PU_{eff} is not even closely known in the common use of flash pasteurizers. That is why the applied parameter setting of the pasteurization plant comprises several safety margins.

A practical method to ascertain the effective thermal dosage in flash pasteurization equipment, especially as performance qualification of a new plant is the count reduction test, where a predefined microorganism suspension is introduced into the product stream. The survival rate at the outlet is measured by means of cultivation methods of a sample. From the cell count reduction the PU_{eff} can

be recalculated. In the practice this method is regarded to have a high potential for equipment spoiling caused by high concentrated microorganism suspensions. Moreover the count reduction test comprises imprecisions because of method immanent inaccuracies in microbiological works. A chemical Time-Temperature Integrator (TTI) conducted with a simulant fluid could solve the problems of the count reduction test. Therefor a solution with rheological properties similar to the target product is pasteurized while a reaction is running. The conversion depends on the effective temperature and residence time distribution.

Table 1 Reported kinetic data for acid hydrolysis of sucrose with the dependence of the frequency factor k_0 on the acid concentration.

Reference	Acid	Sucrose	E_A [kJ/mol]	Method	$k_0 = f(c(H^+))$
Leininger [17]	HCl 0.5–4.6 mol/L	20 g/L	108	0–40 °C dilatometric	disproportionately high
Lawrence [18]	HCl 0.5-5.8 mol/L	20 g/L	108	30–60 °C	exponential
Adams [13]	H_2SO_4 pH 2.5	162.5 g/L	106	60–100 °C isothermal	–
Hartofylax [19]	H_2SO_4 0.1–1.0 mol/L	3.42–34.2 g/L	100	45–55 °C batch	linear
Rhim [20]	HCl 0.0005 mol/L	2%	102-106	60–98 °C NI	–
Sadeghi [12]	H_2SO_4 pH 2.5	20%	46 95	110–140 °C batch (isotherm), continuous flow EPM	–
Torres [5]	HNO_3 pH 0.8–1.5	1 g/L	85-145	50–90 °C NI	exponential
Torres [11]	HNO_3 pH 0.8–2.5	1 g/L	85-125	50–90 °C NI	linear
Miles [21]	HCl 0,0005 mol/L	2%	100-117	139–151 °C continuous in a hold tube	

TTI´s have to fulfill particular requirements. First of all the agent should be suitable for use in foodstuffs. The reaction should represent a first order kinetic in order to reduce the calculation complexity. The reaction kinetics should lead to exact results within the time-temperature profile of the pasteurization process, in a manner that the reaction rate is adaptable to the pasteurization process. Overviews of several investigated TTI´s are given by *Torres et al.* [5] and *Hendrickx et al.* [6]. For example the melibiase activity [7, 8], the alkaline destruction of indigo carmine [9], and the hydrolysis of dextran [10] were investigated. The advantages and disadvantages of the investigated TTI´s were discussed in a recent review [4]. The most frequently investigated possible TTI is the acid catalyzed hydrolysis of sucrose [5, 11, 12, 13, 14].

To describe the temperature dependence of a chemical reaction rate the Arrhenius equation is used:

$$k = k_0 \cdot \exp\left(\frac{-E_A}{R \cdot T}\right) \quad (1)$$

In equation 1 k is the reaction rate constant k_0 is the frequency factor, E_A the activation energy, T the absolute temperature and R the universal gas constant. In order to describe the temperature dependence of the reaction the activation energy and the frequency factor have to be known. To describe the destruction of microorganisms analogous values are the decimal reduction time D and the z-value, i.e. the temperature increase that is required to reduce the D-value by one log. The reaction rate constant k can be converted in a D-value:

$$D = \frac{ln\ 10}{k} \quad (2)$$

And the activation energy E_A can be converted in a z-value:

$$z = \frac{T_1 \cdot T_2 \cdot R \cdot ln\ 10}{E_A \cdot} \quad (3)$$

The activation energy shows the temperature dependence of the reaction rate. While the activation energies of chemical reactions range between 50 and 150 kJ/mol, the activation energies of the destruction of microorganisms are between 250 and 400 kJ/mol [15]. This leads to z-values of the microorganisms which are about 2 to 5 fold smaller compared to chemical reactions. However, at a constant temperature this has no effect on the calculation of the effective temperature.

In the literature there are several statements about the reaction rate dependence of the acid hydrolysis of sucrose [11, 16, 17]. The majority of sources state acid concentration independent activation energy whereas the frequency factor varies with acid concentration. An overview about the several statements independent of the application as TTI is shown in table 1.

Since the published findings are not consistent there is a need to investigate the calibration of the acidic sucrose hydrolysis targeted to the application as TTI. Therefore at first two methods are compared: the common isothermal method and a non-isothermal method according to Rhim et al. [20]. With the preferred method the acid concentrations are investigated in more detail. The aim is to establish the acidic hydrolysis of sucrose as TTI adaptable to the several pasteurization conditions.

2 Materials and methods

Strong hydrochloric acid and nitric acid (0.002–0.75 mol/L) were used as catalysts. Solutions were prepared with tap water because it would be more convenient for the later use in a large scale plant, where large amounts of solution are necessary. The final concentrations were controlled by titration with a standard NaOH solution (0.1 mol/L) at the end of the experiment.

Two concentrations of solutions of sucrose (food grade) were used. A 10 %$_{w/w}$ solution was prepared and immediately previous to the test the solution was mixed 1:1 with the acid solution, giving

a resulting concentration of 5 %$_{w/w}$ sucrose. For the higher concentrated test liquid a concentration of 65 %$_{w/w}$ sucrose was prepared. To start the reaction the sucrose solution was mixed 3:1 with the acid solution (resulting in a concentration of 52 %$_{w/w}$). To stop the acid hydrolysis after the desired heating time a NaOH solution was prepared with tap water.

Measuring of sucrose conversion ratio

The conversion ratio χ of the sucrose was measured by means of polarimetry (Krüss, P3002 RS). The polarizing angles of the initial mixture (α_0), of the stopped mixture reaction (α) and the mixture after full conversion (α_∞) were measured for this purpose. All test solutions were mixed in the same ratio with NaOH. The sucrose conversion ratio is calculated by:

$$\chi = 1 - \left(\frac{\alpha - \alpha_\infty}{\alpha_0 - \alpha_\infty}\right) \quad (4)$$

Isothermal method

The isothermal method is a two-step method. At first the reaction rate k is calculated for several temperatures separately, then the activation energy E_A and the frequency factor k_0 (Arrhenius equation 1) are calculated. To determine the reaction rate constant k at a given temperature the sucrose conversion rate after 4 different reaction times was measured as triplicate. For each test 5 mL of the sucrose and the appropriate hydrochloric acid solution (0.2–1.0 mol/L) respectively were preheated (desired temperature between 50 and 78 °C) in a test tube (1.7 x 13 cm) in a tempered water bath. To start the reaction the tempered solutions were filled together and mixed immediately with a vortex and stored in the tempered water bath. The reaction was stopped by transferring the reaction mixture in 10 mL cooled NaOH solution.

The standardized reaction rate constant k^*

$$k^* = \frac{k}{k_{ref}} \quad (5)$$

(with the reference reaction rate k_{ref} =1 s^{-1}) for one temperature is given by the slope of $\ln(1-\chi)$ against the reaction time (calculated by least squares method). E_A and the logarithm of the standardized frequency factor $\ln k^*_0$

$$k^*_0 = \frac{k_0}{k_{ref}} \quad (6)$$

are calculated out of the slope and the ordinate intercept of $\ln k^*$ at the different temperatures plotted against 1/temperature [K-1] respectively [22].

Non-isothermal method

The non-isothermal method is a one-step method because the kinetic parameters can be calculated direct out of the concentration change during a linear increasing reaction temperature. This analysis was performed according to Rhim et al. [20].

The volumes of the sucrose and acid solutions were separately preheated to 3 °C below the starting temperature and then mixed in a double walled beaker glass used as reaction vessel. The vessel was tempered by a thermostatic water bath and mixed by a magnetic stirrer (800 rpm). The temperature of the reaction mixture was measured continuously. Immediately after mixing the temperature was increased in a linear course (stability index $R^2 > 0.995$) at a rate adapted to the acid concentrations of the tested probe. The sampling started when a linear increasing temperature adjusted. In regular intervals (10–12 times) the temperature of the reaction mixture was recorded and 10 mL aliquots were transferred into a vessel with ice water cooled NaOH solution (5 % sugar 1:1; 52 % 1:3) to stop the reaction. For each acid concentration a 3–5 fold determination was carried out.

The calculation of E_A and k^*_0 is based upon the reaction rate (first order law), the Arrhenius relation and the time-temperature relationship. Hence result the following equation [20]:

$$\ln\left(-\frac{1}{C}\frac{dC}{dt \cdot k_{ref}}\right) = ln\,\mathrm{k}^* - \frac{E_A}{R}\frac{1}{T} \quad (7)$$

E_A and k^*_0 are estimated from an Arrhenius type plot of $\ln\left(-\frac{1}{C}\frac{dC}{dt \cdot k_{ref}}\right)$ against $1/T$ (least squares method).

3 Results and discussion

The isothermal method for the determination of kinetic parameters is the classic method routinely used in chemical kinetic studies [20]. However, advantages of the non-isothermal method are the faster performance, the method comprises less sources of error in the performance and every data point is estimated in a continuous manner to generate the kinetic parameters, so there is no loss of information. In a comparative study the more precise method was selected for further investigations.

One of the preconditions was to target a reaction rate that fits to the time-temperature range of the beer pasteurization. Torres et al. [11] recommend a pH value between 0.76 and 0.87 correlating to an H^+ concentration between 0.17 and 0.14 mol/L. In order to compare the two methods, trials at 4 HCl concentrations between 0.1 and 0.5 mol/L were carried out. Therefore the isothermal method was performed at four temperatures between 50 and 78 °C for each HCl concentration. The sucrose concentration (initially 5 %$_{w/w}$) showed a logarithmic decrease over the reaction time corresponding to first order reactions.

The non-isothermal experiments were conducted with a linear increasing reaction temperature, at which the starting and final temperature is set between 35 and 80 °C respectively. Before starting the non-isothermal runs the temperature profile was proven to be linear. The temperature ramp was adapted to the different reaction rates. The target was to cover a wide temperature interval in order to achieve a high degree of accuracy in the slope (E_A) and consequently in the intercept of ordinate ($\ln k^*_0$) in the Arrhenius equation. Furthermore the temperature range of practical pasteurization processes should be met.

The found data for E_A are slightly lower when measured with the isothermal method instead of the non-isothermal method (Table 2). However, in either case the results are within the range of earlier

Table 2 **Standardized frequency factor k^*_0 and activation energy E_A of sucrose hydrolysis catalyzed by HCl. Comparison of the isothermal (IT) and the non-isothermal (NI) method with linearly increasing temperature. E_A is theoretically considered to be constant**

c(HCl) [mol/L]	E_A [kJ/mol]		ln k^*_0	
	IT	NI	IT	NI
0.10	100.5	104.9	29.5	31.1
0.25	92.1	105.68	27.4	32.4
0.38	93.3	103.8	28.1	32.1
0.50	85.0	102.8	25.5	32.1

published data (Table 1). Due to the propagation and combination of method intrinsic errors the dispersion about the mean E_A value measured by the isothermal method is about twice as much as with the non-isothermal method. Thus the accuracy of the calculation of the reaction rate is higher with the non-isothermal method. In consequence of these preliminary trials and the mentioned advantages of the non-isothermal method this method is selected for the further experiments.

In order to investigate more precisely the relationship between the acid concentration and the reaction rate five non-isothermal runs were carried out at each of the 8 concentrations of hydrochloric acid between 0.02 and 0.75 mol/L. In figure 1 the activation energy is plotted against the acid concentration. The mean value of the activation energy is 105.09 ± 1.07 kJ/mol (confidence interval with a probability of 95 %). This variation is considerably small especially compared to earlier publications in which the activation energy ranges between 85 and 125 kJ/mol and the confidence intervals covers 75 to 140 kJ/mol [5, 11].

In figure 2 the experimental data of the non-isothermal method are pictured. Comparing the regression lines for each acid concentration, it can be seen, that the activation energy, shown as slope (Eq. 1), is about the same at all acid concentrations. The differences among the resulting activation energies are marginal. The parallel shift to the right with increasing acid concentration indicates an increase of the ordinate axis intercepts (ln k^*_0). However, the found data represent only a small section of the graphs with distance to the ordinate axis. That means the even small erratic variability of E_A would have a great impact on the extrapolated axis intercept and ln k^*_0 respectively. Therefore regression lines were calculated with a fixed slope representing the average activation energy of all experiments in order to determine the correlation between acid concentration and frequency factor.

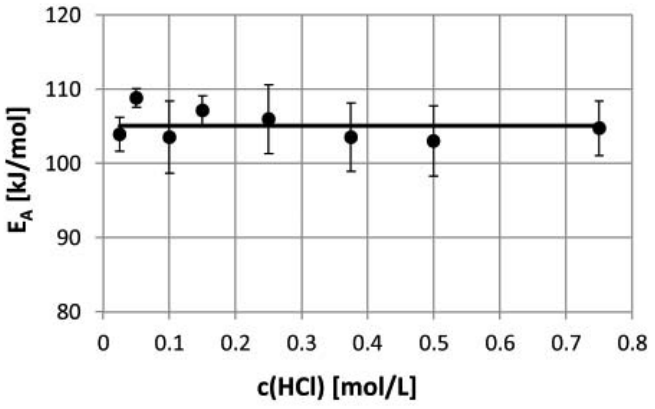

Fig. 1 **Activation energy E_A at various acid concentrations measured with the non-isothermal method, the corresponding 95 % confidence intervals are plotted with vertical lines. The mean value of 105.09 kJ/mol is marked**

In figure 3 the calculated ln k^*_0-values are plotted against the corresponding acid concentration. The found dependency is a logarithmic function (R^2 = 0.999):

$$ln\, k^*_0 = 1.103 \cdot \ln(c^*(H^+)) + 33.709 \quad (8)$$

In order to calculate with dimensionless terms is in equation 8 $c^*(H^+)$ the standardized H^+ concentration and c_{ref} = 1 mol/L is the reference concentration:

$$c^* = \frac{c}{c_{ref}} \quad (9)$$

Taking the antilogarithm leads to:

$$k^*_0 = c^*(H^+)^{1.103} \cdot 4.361 \cdot 10^{14} \quad (10)$$

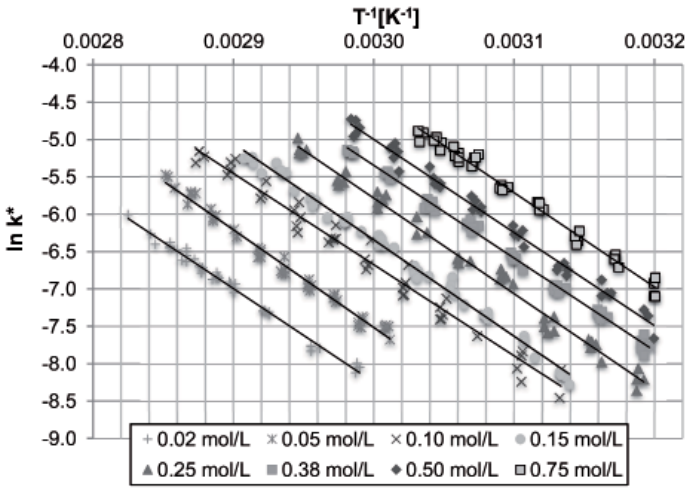

Fig. 2 **Dependency of the standardized reaction rate k^* of the hydrolysis of sucrose catalyzed by HCl on the temperature and the acid concentration (non-isothermal method)**

With an exponent of 1.103 it differs only slightly from a linear expression, but compared with a linear regression (R^2 = 0.991) the regression coefficient is better. Earlier studies represent contradictory conclusions about the functional relation of acid catalyzed sucrose conversion and the acid concentration (Table 1). Torres et al. for example found in their first publication in 1994 a linear correlation within the researched range of 0.003 and 0.158 mol/L acid [11]. In a later publication Torres et al. (1999) introduce an exponential dependency for a similar range [5].

With respect to the corrosive potential of hydrochloric acid additionally nitric acid was investigated as an alternative H^+-ion source. The data resulted from the nitric acid (Fig. 3) confirm the validity of the found equation. Thus equation 10 can hence be used to determine the frequency factor k_0 from the concentration of the H^+-ions between 0.02 and 0.75 mol/L independent of the kind of acid.

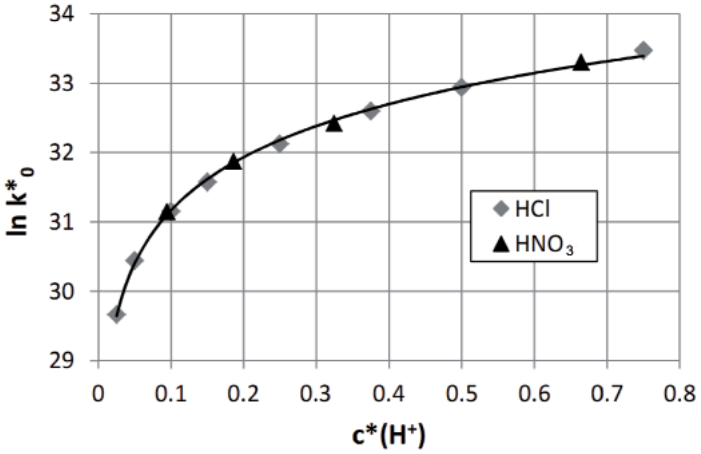

Fig. 3 **Dependency of the logarithmic frequency factor ln k^*_0 of the acid catalyzed hydrolysis of 5 % sucrose on the standardized H^+ concentration $c^*(H^+)$. The regression analysis was performed with the data of HCl by the method of least squares. The validity of the regression was proven by independent experiments with nitric acid**

With the knowledge of k_0 and E_A the acid catalyzed hydrolysis of sucrose can be used as a TTI. The predictability of k_0 as a function of H^+ concentration allows the adapting of the reaction parameters to any feasible process condition in the practical application. Therefor the appropriate H^+ concentration can be calculated from the pasteurization parameter time (t), the absolute temperature (T), a sensible conversion ratio (χ), the measured activation energy (E_A) and the standardized frequency factor (k^*_0) by the following equations:

Transposing (10) leads to

$$c^*(H^+) = \left(\frac{k^*_0}{4.361 \cdot 10^{14}}\right)^{\frac{1}{1.103}} \quad (11)$$

k^*_0 can be calculated by the Arrhenius equation:

$$k^*_0 = \frac{k^*}{\exp\left(\frac{-E_A}{R \cdot T}\right)} \quad (12)$$

The standardized reaction rate (k^*) can be calculated from the targeted conversion rate (χ) and the reaction time (t):

$$k^* = \frac{\ln\left(\frac{1}{1-\chi}\right)}{t * k_{ref}} \quad (13)$$

Thus equation 14 results in:

$$c^*(H^+) = \left(\frac{\ln\left(\frac{1}{1-\chi}\right)}{t \cdot k_{ref} \cdot \exp\left(\frac{12640\ \mathrm{K}}{T}\right) \cdot 4.361 \cdot 10^{14}}\right)^{\frac{1}{1.103}} \quad (14)$$

The targeted conversion rate should be set between 40 % and 70 % to achieve a high accuracy. If the heating and cooling zones have an appreciable influence the targeted conversion in the holding tube has to be reduced. To refer exemplary to the beer flash pasteurization with typical conditions of 71 °C for 30 s [23] and with a set target conversion of 50 % it results that the H^+ concentration must be 0.52 mol/L. The determination of the required acid for the application of the TTI concentration is the first sub-goal. With the known mean residence time now the actual PU can be calculated with the TTI. If additionally the residence time distribution is known the accuracy of the thus determined PU can be even farther improved. Since the residence time distribution depends strongly on the viscosity it is important to perform investigations with different sucrose concentrations and different viscosities respectively. This is particularly important if not only low viscous beverages but also high viscous beverage concentrates are processed.

For the application of beverage concentrates an additional calibration with syrup of 52 % sucrose was carried out. The calibration experiments were conducted between 0.002 and 0.6 mol/L nitric acid. The results indicate a higher activation energy in comparison to the 5 % sucrose concentration with an E_A = 113.56 ± 0.83 kJ/mol. In figure 4 with constant activation energy a logarithmic dependency of the frequency factor can be seen. For the researched interval the following equation results (R^2 = 0.998):

$$ln\ k^*_0 = 1.115 \cdot \ln(c^*(H^+)) + 37.432 \quad (15)$$

To calculate the required acid concentration the following equation can be used:

$$c^*(H^+) = \left(\frac{\ln\left(\frac{1}{1-\chi}\right)}{t \cdot k_{ref} \cdot \exp\left(\frac{-13658\ \mathrm{K}}{T}\right) \cdot 1.806 \cdot 10^{16}}\right)^{\frac{1}{1.115}} \quad (16)$$

As expected the activation energy does not depend on the acid concentration but on the initial sucrose concentration. The consequence for the later practical application is that in case of a change of the sugar concentration a distinct calibration must be performed.

As the activation energy of sucrose as TTI is 105 (5 % sucrose) and 114 kJ/mol (52 % sucrose) a final issue must be discussed. The activation energy of the thermal destruction of microorganism is considerably higher with 250–400 kJ/mol. As long as only one (constant) temperature is considered just as assumed in pasteurizers holding tubes there is no obstacle for the transfer of the TTI results to microbiological effects. If additionally the residence time distribution is taken into account even PU can be derived

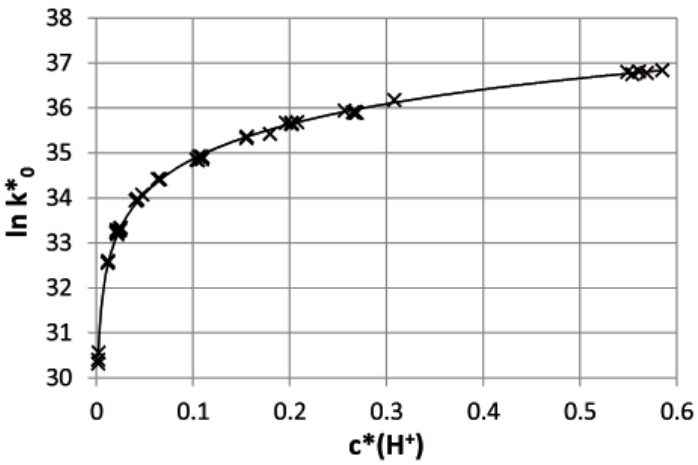

Fig. 4 **Dependence of the standardized logarithmic frequency factor ln k^*_0 of the acid catalyzed hydrolysis of 52 % sucrose on the standardized H^+ concentration. The regression analysis was performed by the method of least squares**

from the TTI quite precisely. However, in case of temperature deviations or ramps as in heating or cooling sections the different activation energies will lead to errors. If thus these sections of a flash pasteurizer are taken into the PU calculation the TTI is not correct but fortunately the results would stay on the safe side. The technical application and the verification is part of a following work.

4 Conclusion

The acidic sucrose hydrolysis as Time-Temperature Integrator (TTI) can serve as an alternative to microbiological count reduction tests to determine the applied Pasteurization Units (PU_{eff}). Therefore it was necessary to find the dependence of the conversion rate on the acid concentration in order to adapt the TTI reaction to any realistic pasteurization condition. Because of the known impact of residence time distributions two equations are provided in this paper with two sucrose concentrations (5 % and 52 %) to have options for low viscous and high viscous products representing beer or soft drinks and beverage concentrates. The experiments revealed that with rising sucrose concentration the activation energy increases slightly whereas the conversion rate increases in a relevant extent. For any other sucrose concentration that may be used it is recommended to execute analogous experiments. The data in this paper show that with regard to the practical application the TTI system with nitric acid can be used without a danger of corrosion and chemical contamination in common stainless steel pasteurizers. The TTI has the potential to be more precise and easier to apply than microbiological count reduction tests.

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