International Journal of Food Engineering

Volume 3, *Issue* 4 2007 *Article* 8

Simplified Kinetics and Colour Formation in Sucrose Solutions Based on A-Dicarbonyl Compounds

Quido Smejkal, *QUIDO-Engineering Berlin*
Thorsten Fiedler, *Pfeifer-Langen KG*
Tomas Kurz, *Technical University of Berlin*
Lothar Kroh, *Technical University of Berlin*

Recommended Citation:
Smejkal, Quido; Fiedler, Thorsten; Kurz, Tomas; and Kroh, Lothar (2007) "Simplified Kinetics and Colour Formation in Sucrose Solutions Based on A-Dicarbonyl Compounds," *International Journal of Food Engineering*: Vol. 3: Iss. 4, Article 8.
DOI: 10.2202/1556-3758.1250

Simplified Kinetics and Colour Formation in Sucrose Solutions Based on A-Dicarbonyl Compounds

Quido Smejkal, Thorsten Fiedler, Tomas Kurz, and Lothar Kroh

Abstract

Colour formation in technical and model sucrose solutions was investigated resulting in a novel kinetic approach of MAILLARD reaction during thermal processing of sugar solutions. Presented results describe new aspects of the non-enzymatic browning reaction (MAILLARD reaction). Two temperature depending pathways of colour formation were found. Both reaction mechanisms are based on the formation of a-dicarbonyl compounds, the key intermediates of colour formation.

Discussing temperature dependence of colour formation, a change on MAILLARD reaction mechanism takes place at 100.4 °C. Above this temperature the colour formation is strongly accelerated. Activation energy of the non-enzymatic browning energy for temperatures from 65 ° to 100.4 °C amounts 77 kJ/mol. In this temperature range, D-glucosone is the most important a-dicarbonyl compound for studied reaction systems. Above 100.4 °C, activation energy is equal to 112 kJ/mol and 3-deoxyosone is the dominant colour formation intermediate. Achieved results bridge the gap between the termination step of a MAILLARD reaction –i.e. of colour formation (represented by its activation energy) and intermediates formation (reaction kinetics). In particular, a change of colour formation mechanism with reaction temperature was confirmed by specific formation of two a-dicarbonyl compounds, responsible for MAILLARD reaction in technical sugar solutions.

KEYWORDS: MAILLARD reaction, a-dicarbonyl compounds, colour formation, kinetics

1. Introduction

The suppression of colour formation and thermal decomposition of sucrose molecules in aqueous sucrose solutions has been major challenges in sugar technology in the last decades. The colorants are formed in almost all periods of sugar manufacture and influence not only technological performance of chemical engineering units, but also the economics of any factory and consequently also sugar prices. Thus, understanding, modelling and prediction of colour formation is of peculiar importance.

The kinetics of colour formation during sugar processing, e.g. evaporation and crystallisation, are influenced by many factors. The most relevant for sugar production are temperature, time, invert sugar concentration and pH-value (Vukov, 1981, Hollnagel, 1998, Van der Poel, 2000).

The mechanism of colour formation in technical sucrose solutions is based on the reaction of reducing sugars D-fructose and D-glucose with an amino compound e.g. γ-aminobutyric acid (GABA), the so-called MAILLARD reaction (Ledl, 1990). In the early stage of the MAILLARD reaction α-dicarbonyl compounds are formed (Westphal, 1985a, 1985 b). The latter are responsible for colour formation in concentrated sucrose solutions (65 %). In sucrose solutions and during several process steps of sugar processing, three major α-dicarbonyl compounds could be determined. These are 3-deoxyosone, D-glucosone and methylglyoxal (Fiedler, 2006).

Regarding a formation of these α-dicarbonyl compounds, a temperature depending reaction pathway could be shown, see Figure 1. At temperatures above 110 °C 3-deoxyosone is the dominant dicarbonyl compound in technical sucrose solutions with max. concentrations up to 640 mg/kg. At temperatures below 100°C D-glucosone is preferably formed. Methylglyoxal takes an intermediate position of these dominant α-dicarbonyl compounds (in relation to the formation of colour) and could not be assigned to any particular temperature range. The concentration of methylglyoxal in studied sucrose solutions is very low and therefore almost no influence on reaction kinetics at chosen process relevant conditions could be found (Imming, 1994, Reinefeld, 1973).

Pioneer studies concerning kinetic modelling of the MAILLARD reaction were based only on colour measurement (Vukov, 1981, Imming, 1994). Later on, kinetic studies with α-dicarbonyl compounds were presented. However, the elucidation of MAILLARD reaction (Martins, 2000, Martins, 2005, Mundt, 2003, Wedzicha, 1995), was mostly related to model solutions and specific reaction conditions far away from process praxis. In sugar production and other food technologies with real sugar solutions, a degradation of sucrose occurs in a wide mixture of reactive components. In above specified reaction step of MAILLARD reaction, amino compounds could react with almost all α-dicarbonyls presented in

the solution. Therefore, the results achieved with model solution systems should be correlated to those of technical sucrose solution, i.e. to results achieved with thick juice. If the results of both reaction systems are comparable, the reaction pathways are the same and the selection of representatives for model solution was correct. The aim of this contribution is to develop a simplified kinetic model for the description of colour formation in technical sucrose solutions (thick juice) at process relevant conditions and to derive its activation energies. The results will be used for a discussion of overall reaction kinetics of MAILLARD reaction.

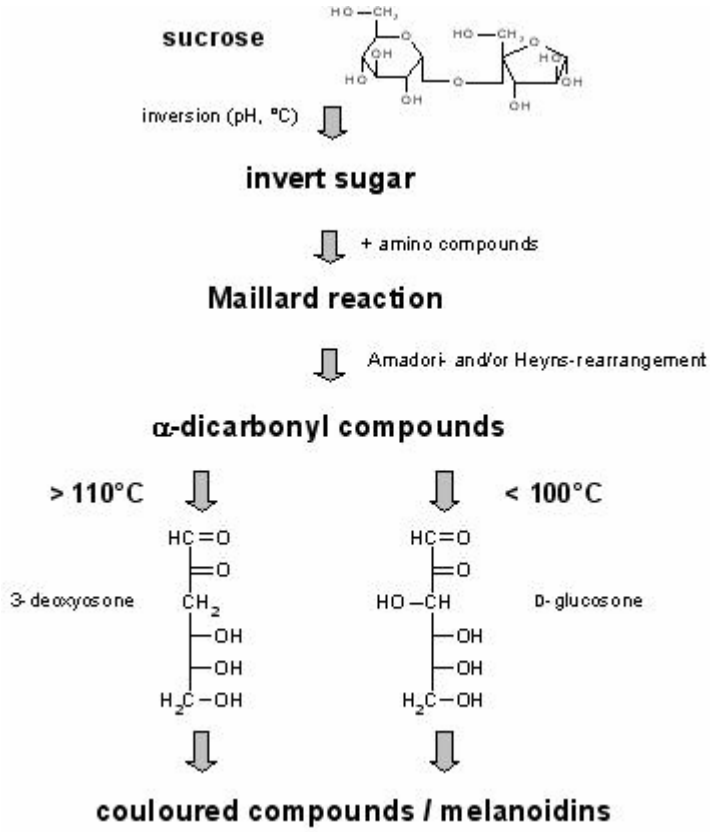

Fig. 1.: Schematic reaction pathway of the colour formation in sucrose solutions.

Achieved results gained by colour formation will be extended with simplified kinetics based on α-dicarbonyl compounds in technical and model sucrose solutions.

DOI: 10.2202/1556-3758.1250

2. Methods and Materials

2.1 Chemicals

D-glucose, D-fructose, sucrose, γ-aminobutyric acid (GABA), acetic anhydride, pyridine, silica, glyoxal, quinoxaline and 1-butanol were obtained from Merck (Darmstadt, Germany), methylquinoxaline and o-phenylenediamine from Fluka (Buchs, Switzerland), toluene Pestanal® from Riedel-de Haën (Seelze, Germany), methanol (HPLC grade), 2,3-diphenylquinoxaline and methylglyoxal supplied by Sigma Aldrich (Steinheim, Germany) and dimethylquinoxaline by Lancaster (Morecambe, England).

2.2 Technical sucrose solution

A diluted thick juice solution (65 %) from sugar production unit (last stage of evaporation) was used as a technical sucrose solution for the corresponding experimental measurements.

2.3 Carbohydrate model-solutions

The used aqueous sucrose MAILLARD reaction solutions contained 65% (w/w) sucrose, 0.1% invert sugar (1:1) and 0.1% GABA, which corresponds to an artificial thick juice. The acidity of the solutions were adjusted to pH = 8. During the reaction, the pH value was not regulated.

2.4 Thermal treatment and derivatization

The solutions were heated in sealed ampoules for up to 300 min at defined temperatures ± 1 °C by means of a thermoblock (Behr Labor Technik, behrotest ET 2). The original samples were used for colour measurement. For quantification of α-dicarbonyls, after a defined reaction time, the samples were stirred with 0.05 mol/L *o*-phenylenediamine to convert α-dicarbonyls into quinoxalines (post-derivatization), which were analyzed after filtration by HPLC-DAD and by GC/MS after acetylation.

2.5 High-performance liquid chromatography with diode array detection (HPLC-DAD)

Degasser: Degasys DG-13000 (Knaur); pump: Shimadzu LC-10 AT; thermostat: 30 °C, Shimadzu CT0-6A; guard column: Nucleosil 120-5 C18 Macherey-Nagel; column: Nucleosil 5 C18 (250 × 4.6 mm); detector: DAD Gynkotek UVD 340S; flow: 1.0 m /min; injection volume: 40 mL; eluent: methanol/water gradient: 0 min – 5 min 30% methanol, 5 min – 12 min 30% – 50%, 12 min – 20 min 50% – 100%, 20 min – 30 min 100% methanol. Quinoxalines prepared from Hollnagel (2000) were used as standards for quantification.

2.6 Gas chromatography/mass spectrometry (GC/MS)

Before quantification, reaction mixture was extracted with 1-butanol. The solvent was dried off and the residue was dissolved in toluene/pyridine (30:1) and acetic anhydride was added (Nedvidek, 1992). Gas chromatograph: Finnigan GCQTM; capillary column: BPX-5 (SGE, 30 m, 0.25 mm ID, 0.5 mm film thickness); carrier gas: helium 4.6; detector: Finnigan Ion Trap Mass Analyzer GCQTM; injection temperature: 270 °C; temperature program: initial temperature 95 °C, hold 1 min, 95–200 °C 15 °C/min, 200 °C 1 min, 200–280 °C 3 °C/min, 280 °C 5 min, 280–300 °C 5 °C/min, 300 °C 5 min. Column effluents were analyzed by selected ion monitoring (SIM). Quinoxalines prepared from Hollnagel (2005) were used as standards for quantification.

2.7 Colour measurement

Mentioned colour of all solutions were measured with a ICUMSA (International Commission for Uniform Methods for Sugar Analysis) method (Reinefelder, 1978) at an absorption wavelength of 420 nm. Abbe-Refractometer: Carl-Zeiss, Jena; Photometer: Novaspec II Pharmacia LKB.

2.8 Modelling of colour formation

The experiments give for any reaction temperature a time-dependence of the colour index which is a linear function for short time periods (Vukov, 1981, Westphal, 1985). That means, the colour formation could be described in a good approximation as a zero-order reaction for the initial conditions of the non-enzymatic browning (Smejkal, 2005). The reaction rate is derived from the slopes of colour increase *dF/dt* (1):

$$\frac{dF}{dt} = k \qquad \text{[IU/min]} \qquad (1)$$

The formal kinetic constants ***k*** [IU/min] were determined for all experimental conditions. The reaction rates of different temperatures allow to calculate the activation energy E_a according to the theory of the reaction kinetics (Westphal, 1985, Imming, 1994), see Equation (2):

$$\frac{\partial \ln k}{\partial \vartheta} = \frac{E_a}{RT^2} \qquad (2)$$

This equation results after integration in the Arrhenius dependence of kinetic constants *k* on temperature:

DOI: 10.2202/1556-3758.1250

$$k = k_{\infty}.\exp\left(\frac{-E_a}{RT}\right) \qquad \ln k = \left(\frac{-1}{RT}\right)E_a + \ln k_{\infty} \qquad [\text{min}^{-1}] \qquad (3)$$

where k_{∞} is the frequency factor. If the natural logarithm of kinetic constant will be plotted against *-1000/RT*, the slope of this dependence represents the activation energy (in [kJ/mol]) of the overall chemical reaction for a given temperature interval.

2.9 Kinetic Modelling of reaction intermediates

Extended kinetic experiments were performed with the aim to elucidate the formation of reaction intermediates by sucrose degradation. The concentration of main intermediates was followed by developed analytical methods. The concentrations as a function of reaction time could be used for the determination of reaction rates. For initial reaction periods the increase of concentration with time can be described by a linear function, if a first-order approach will be used (Vukov, 1981, Smejkal, 2006). From the slopes of concentration differences in reaction time at given temperature, the reaction rate is withdrawn as:

$$\frac{dc_A}{dt} = c_A k \qquad [\text{mg/kg/min}] \qquad (4)$$

and after integration

$$\frac{\ln c_A}{t} = k + const. \qquad [\text{mg/kg/min}] \qquad (5)$$

Resulted kinetic constants enable to calculate the activation energy of the reaction, see above Equations 2 and 3.

3. Results and Discussion

A prediction of colour formation in technical sucrose solutions is very important for operative use in almost every sugar factory. Thus, in a first part of the paper, the results of colour formation in technical and model sucrose solutions will be given. Based on activation energies derived from colour formation experiments in both sugar solutions used, first comparison of reaction mechanism of colour formation in technical and model solution will be withdrawn. However, the colour formation is only the last step of complex MAILLARD reaction in technical sucrose solutions. The thick juice contains a spectrum of minor components, which take part in the studied browning reaction as well.

Thus, later on detailed analytical measurements of chosen intermediates, i.e. of α-dicarbonyl compounds, will be performed. Related to achieved results,

the representatives of α-dicarbonyl (which are believed to be responsible for the colour formation) will be selected for further kinetic experiments. These components will be used for simplified kinetic model of MAILLARD reaction with the aim to confirm the results achieved by experiments with technical sucrose solution.

3.1 Balance of colour formation

3.1.1 Activation energy of colour formation in technical sucrose solution based on colour measurement

The terminating step of non-enzymatic browning experiments were analysed according to Equations 2 and 3 with the aim to calculate the activation energy of the reaction based on colour measurement. Experimental results are listed in an Arrhenius plot in Figure 2.

Activation energy of the non-enzymatic browning reaction amounts for temperatures up to $\vartheta = 100$ °C $E_a = 76.8 \pm 3$ kJ/mol and for temperatures above 100°C $E_a = 112.1 \pm 2.7$ kJ/mol. Activation energy changes at 100.4 °C. The residuals of all measured experimental points used in Figure 2 equal to 0.068 below $\vartheta = 100$ °C and 0.083 above $\vartheta = 100$ °C. The standard experimental deviation remains 0.0768.

The activation energies presented in Figure 2 support the already given assumption of overall reaction mechanism of non-enzymatic browning reaction. The reaction mechanism shifts at 100.4 °C. Above $\vartheta = 100.4$°C the reaction is speeded up and the degradation of sucrose molecules becomes more important. Thus, from technological point of view it is generally desired to reduce the temperature in sugar production, e.g. in evaporation units.

DOI: 10.2202/1556-3758.1250

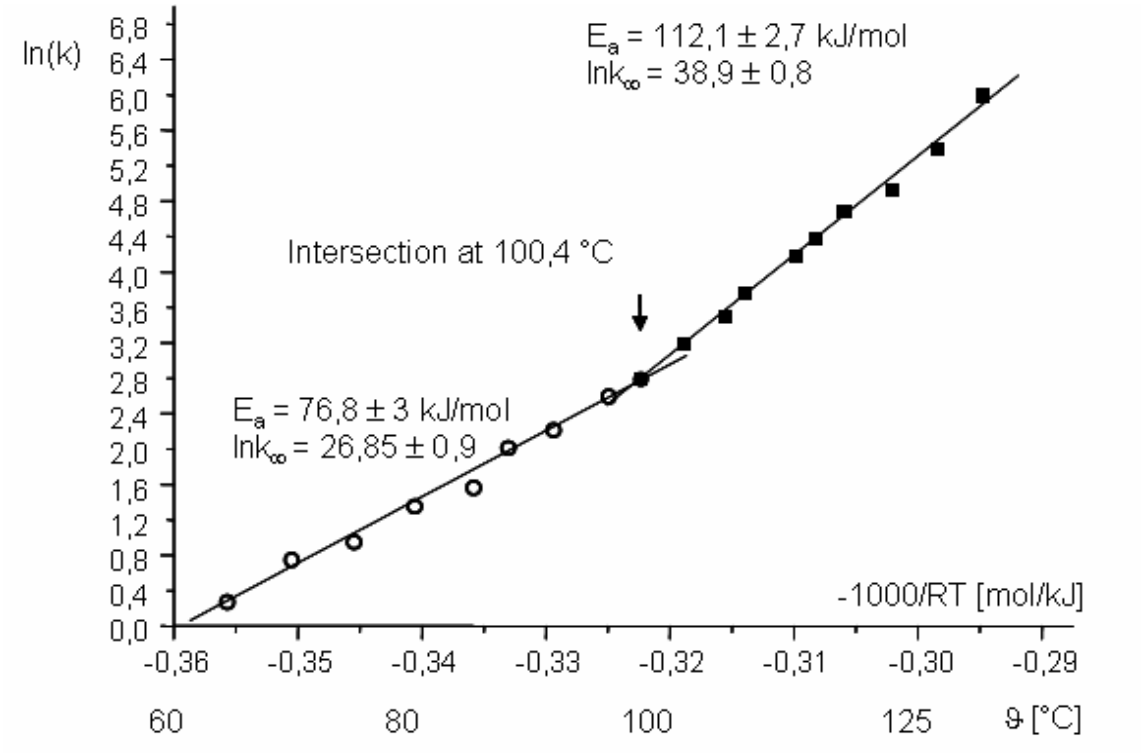

Fig. 2.: Determination of activation energy based on colour measurement; ln (*k)* as a function of -1000/RT, **technical sucrose solution.**

Derived from Fig. 2, a decrease of temperature from 130 °C to 120 °C in evaporation reduces the colour formation with factor of 2.5. Such a temperature reduction improves seriously sugar quality (Smejkal, 2005, Smejkal, 2006) and should be implemented e.g. to the layout of evaporation units.

3.1.2 Activation energy of colour formation in model sucrose solution based on colour measurement

To support the presented shift on derived reaction mechanism, a balance of colour formation was repeated with a model sucrose solution. The composition of the model sucrose solution used in this study is given above in Experimental. From the spectrum of chemical individuals in technical sugar solution only those components were selected, which are believed to be responsible for sucrose degradation. Colour formation in these solutions (and, later on also simplified reaction kinetics of intermediates formation) should later on confirm the selection of these characteristic components.

The aim of activation energy recalculation was focused in simplified reaction mechanism, introduced already in this chapter. If the assumption of reaction pathway is correct, the reaction system will be determined by chosen intermediate in dependence on temperature for both the model as well as for the technical sucrose solution. In a first approach, the intersection on activation energy profile should be found in model solution again. Thus, the results of experiments with model sucrose solution should roughly confirm the shift on reaction mechanism already shown in technical sucrose solution.

Colour formation experiments were repeated with model sucrose solutions. Acquired formal kinetic constants based on colour measurement were plotted in Arrhenius dependence and the results are given in Figure 3.

From Figures 2 and 3 it could be generally concluded that the activation energy of colour formation remains almost the same for both sucrose solutions used. We can state a good agreement between experiments with technical sucrose solution (thick juice) and a model sucrose solution. The intersection on the reaction mechanism in model solution from Figure 3 remains 100.1°C. This value corresponds to 100.4°C found in technical sucrose solution. Moreover, at reaction temperatures below 100 °C, activation energy equals to 77 and 73 kJ/mol, resp.. For $\vartheta > 100$ °C, activation energy amounts 112 and 118 kJ/mol. Pre-exponential factors are comparable in both solutions, too.

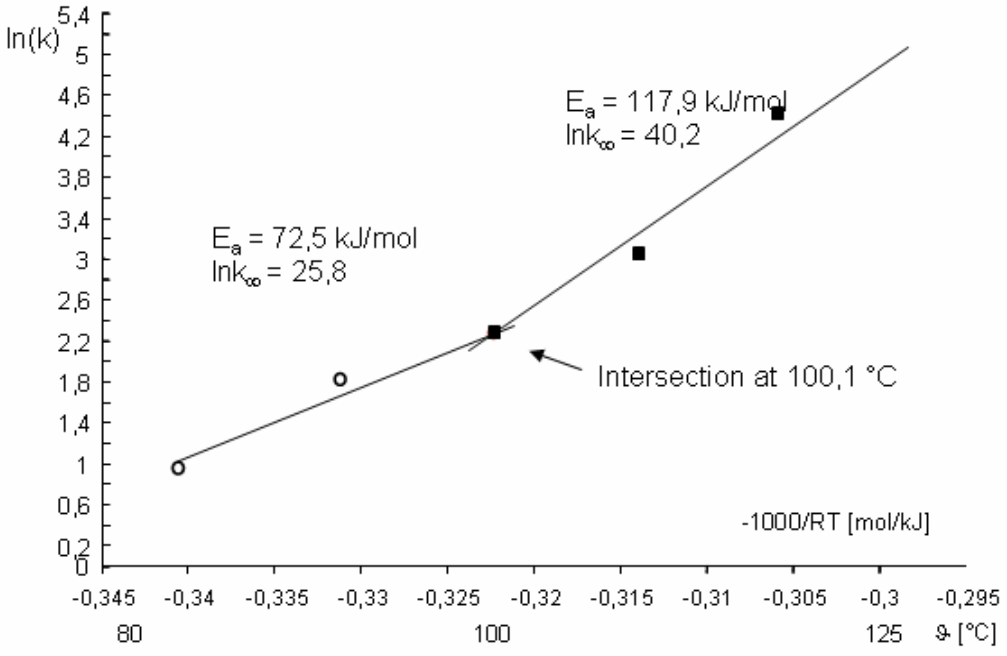

Fig. 3.: Determination of activation energy based on colour measurement; ln (*k)* as a function of -1000/RT**, model sucrose solution.**

DOI: 10.2202/1556-3758.1250

Presented results show that proposed reaction mechanism seems to be reliable. Also the change in the reaction mechanism at roughly 100 °C was found in both studied sucrose solutions.

3.1.3 Key intermediates of MAILLARD reaction in technical sucrose solutions

The discussion above illustrated a reaction mechanism, responsible without any doubt for the last step of non-enzymatic browning reaction, i.e. for colour formation. However, the colour formation consists of a complex of parallel and consecutive reactions and to withdraw the conclusions of reaction pathway from activation energy only is almost impossible. Thus, the kinetics of colour formation was enhanced by the simplified elucidation of intermediates formation according to overall reaction scheme from Figure 1 (Fiedler & Kroh, 2006). The assumption that 3-deoxyosone and D-glucoson are responsible for the colour formation should be confirmed in following discussion.

In Figure 4 the formation of 3-deoxyosone at temperatures between 100 °C and 130 °C is shown. The concentration increases with rising temperature and maximal concentrations of 3-deoxyosone of approx. 640 mg/kg was reached at 130 °C.

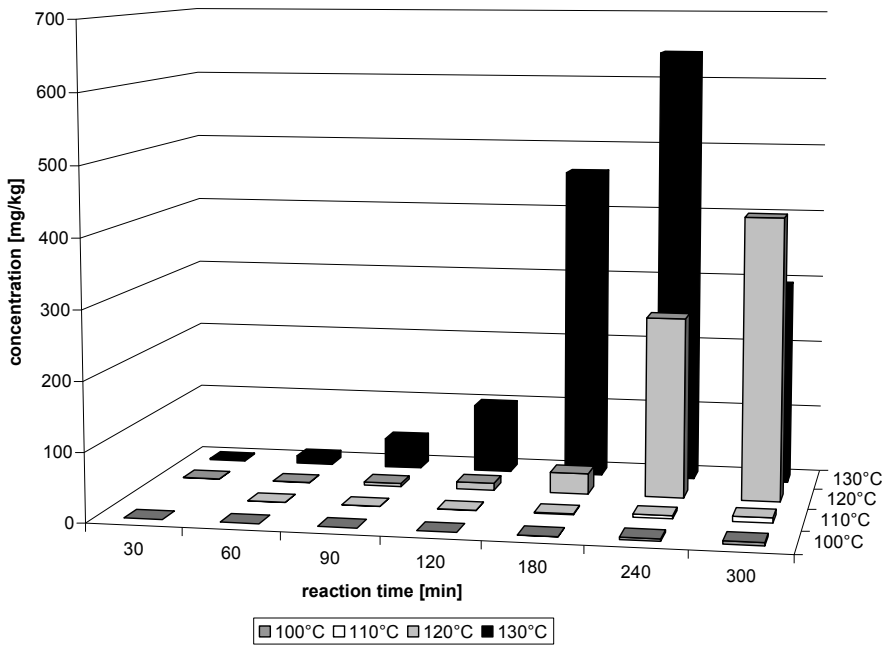

Fig. 4.: Formation of 3-deoxyosone in a technical sucrose solution between 100 and 130 °C.

At temperatures below 100 °C the dominant α-dicarbonyl compound changes from 3-deoxyosone to D-glucosone, see Figure 5. In Figure 5 methylglyoxal is shown, which is formed independently on temperature. However, its concentration remains almost two order lower value compared to D-glucosone (Reinefeld, 1973) in the regarded temperature interval between 80 and 110 °C. The influence of methylglyoxal on the reaction system at these reaction conditions cannot be documented and thus will be neglected (Fiedler & Kroh, 2006).

The concentrations of chosen dominant α-carbonyls changes between 100 °C and 110 °C. At lower temperatures an oxidation mechanism with main product D-glucosone occurs and at temperatures above 110 °C an ionic mechanism with the dominant α-dicarbonyl 3-deoxyosone could be reported (Fiedler & Moritz, 2006, Fiedler & Kroh, 2006). Surprisingly, initial concentration of D-glucosone in technical sucrose solution is almost 60 times higher than initial concentration of 3-Deoxyosone (3-DO) This phenomena supports changing reaction mechanisms after thermal loading of thick juice, first at temperatures above 100°C.

In Figure 5, the shift of the reaction mechanism is presented by dotted (D-glucoson) and full (3-DO) arrows. The formation of 3-DO (full line) is speeded up above 100 °C.

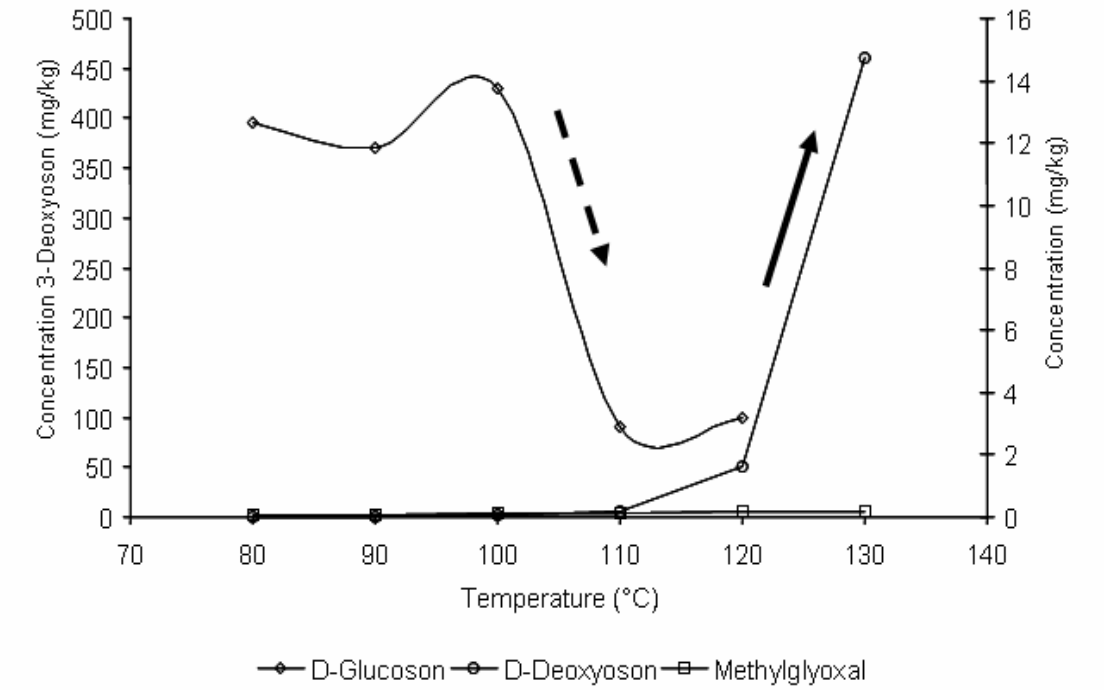

Fig. 5.: Temperature depending change of α-dicarbonyl concentration of thermally treated technical sucrose solutions at 180 min.

DOI: 10.2202/1556-3758.1250

The decrease of D-Glucosone in Figure 5 indicates already at temperature of 100 °C, where the change of reaction mechanism occurs. Between 100°C and 115 °C an intermediate interval can be stated, where both components play an important role. Presented change in reaction mechanism in MAILLARD reaction is supported by the Arrhenius plot from Figure 2 and 3, where the intersection was found at roughly 100 °C. Above shown pathway of dicarbonyl compounds in technical sucrose solutions can be transferred to model sucrose solutions (Fiedler, 2006) and could be correlated to several process units in the sugar production. This phenomena was approved in e.g. in the evaporation station, where a very high concentration of 3-deoxyosone at temperatures above 100 °C was found.

3.2 Simplified reaction kinetics of overall MAILLARD reaction

3.2.1 Formal kinetics of key compounds in technical sucrose solutions

The performed kinetic experiments presented in chapter 3.1 were analysed and from $ln(c_A)/t$ dependencies the kinetic constants at both, given temperature and composition were achieved (see Equations 2 and 3). Experimental temperature interval was divided according to above mentioned activation energy into temperatures above 100 °C ($\vartheta \in$ (100-130) °C) and below 100 °C, i.e. $\vartheta \in$ (80-100) °C.

In following figures, a time-depending formation of reaction intermediates in technical sucrose solutions is given and corresponding kinetic constants are withdrawn. For kinetic evaluation data from Chapter 3.1.3 was used. In Figure 6, a formation of 3-deoxyosone in reaction time at different temperatures is shown.

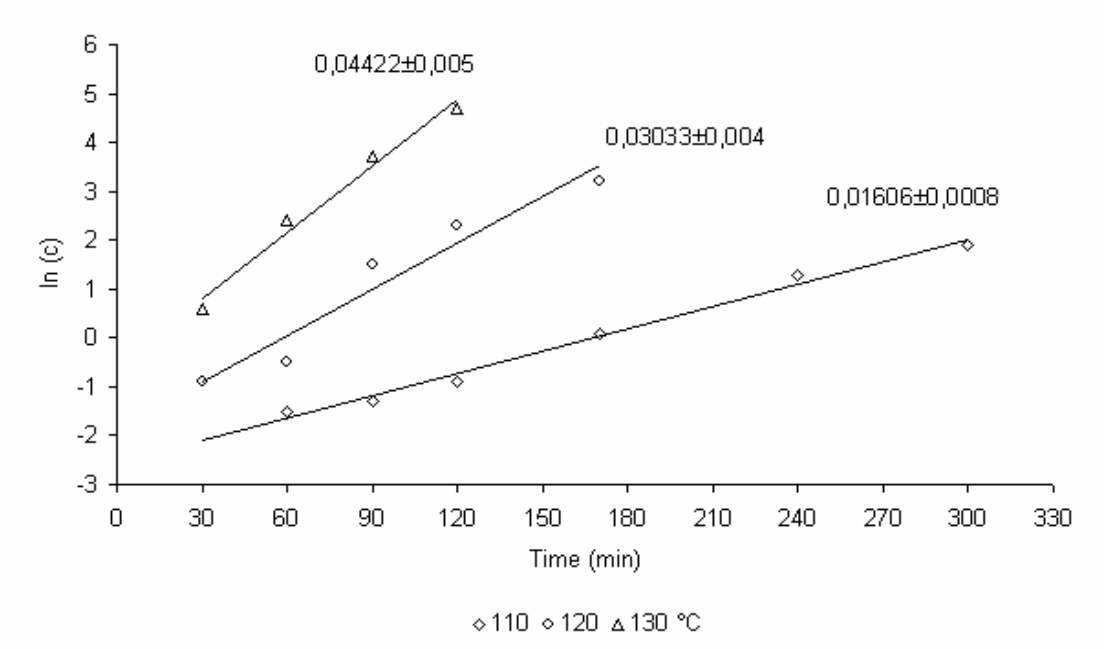

Fig. 6.: Formation of 3-deoxyosone in reaction time; ln (c**)** in (mg/kg) as a function of time (min)**, technical sucrose solution** for $\vartheta \in$ (100-130) °C; $c_{0,3\text{-}DO} = 0.4$ mg/kg

The concentration-dependences were evaluated in *ln (c) versus time* coordinates and repeated for D-glucosone**.** Unfortunately, the concentration of D-glucosone at temperatures below 100 °C as well as at extended technology-relevant times up to 300 minutes is very low. For every reaction temperature, the corresponding slope of linear dependence was analysed. The value of achieved slope is proportional to kinetic constant at given conditions. Evaluated kinetic constants are listed in Table I (see Appendix).

Presented kinetic constants for both 3-deoxyosone and D-glucosone are not directly comparable. The reason therefore are different initial concentrations of 3-deoxyosone ($c_{0,3\text{-DO}}$ = 0,04 mg/kg) and D-glucosone ($c_{0,\text{D-glucoson}}$ = 2.3 mg/kg) in technical sucrose solutions. This is due to the chemical composition of common German thick juices, which were used for experiments. Thus, the results presented in Table I should be taken as a base for an activation energy calculation. Limited temperature interval applied for measurement (process relevant temperatures and retention times) results in increased relative errors of 10 – 15 % with respect to evaluated kinetic constants and consequently to activation energies.

However, considering enormous demand on analysis at very low concentrations of key components and limited pool of reliable experimental conditions, the results are acceptably accurate for target discussion, i.e. for basic elucidation of colorants reaction mechanism in technical sucrose solutions.

The kinetic constants were plotted in an Arrhenius diagram and the activation energies remain:

for 3-deoxyosone	E_A = 92 kJ/mol, and
for D-glucosone	E_A = 78-80 kJ/mol

These values will later on be compared with those from experiments with α-dicarbonyl model-solutions.

3.2.2 Formal kinetics of key compounds in model sucrose solutions

Presented kinetic experiments were repeated with model sucrose solutions. These were performed similarly to those mentioned above in Chapter 3.2.1.

In the beginning, a time-depending formation of 3-deoxyosone was studied and the results are given in Figure 7. Later on, the chemical conversion of model sucrose solution to D-glucosone was monitored and summarised at Figure 8 for a chosen temperature interval.

DOI: 10.2202/1556-3758.1250

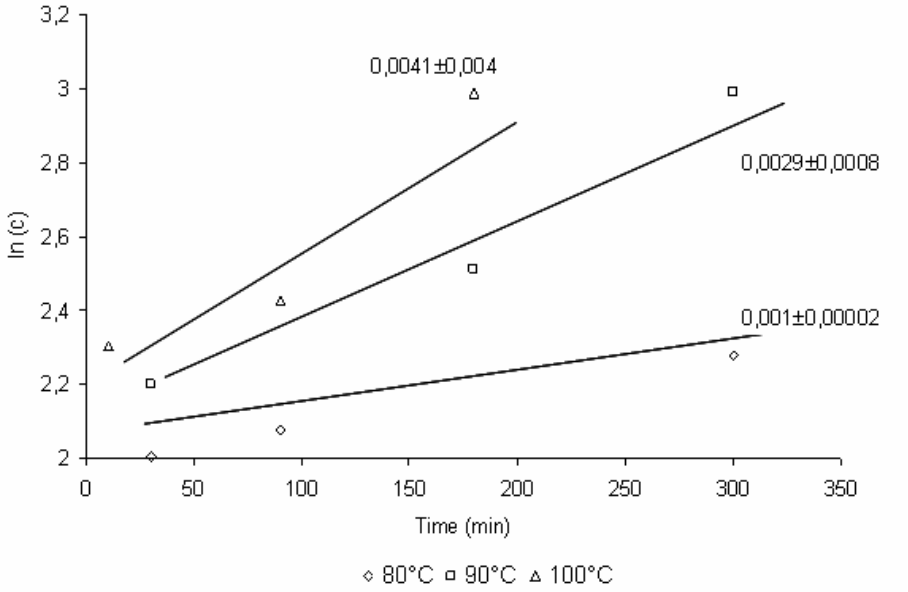

Fig. 7.: Formation of 3-deoxyosone in reaction time; ln (c) in (mg/kg) as a function of time (min)**, model sucrose solution** for $\vartheta \in$ (100-130) °C, $c_{0,3\text{-DO}} = 0.12$ mg/kg

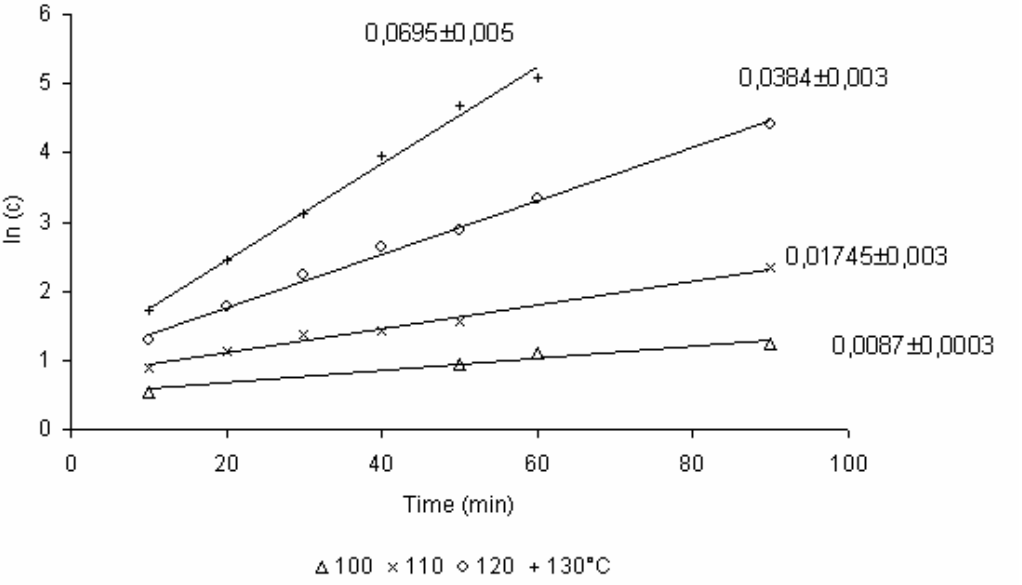

Fig. 8.: Formation of D-glucosone in reaction time; ln (c) in (mg/kg) as a function of time (min)**, model sucrose solution** for $\vartheta \in$ (80-100) °C; $c_{0,\text{D-glucoson}} = 99$ mg/kg

The results from Figures 7 and 8 show the difference in reaction rate of both reaction systems. Below 100 °C, the rates of formation are roughly one order lower compared with the formation of 3-deoxyosone above 100 °C, where the colour formation is speeded up. Kinetic constants of the reaction pathway acquired with model solution are summarised in Table II (see Appendix).

From kinetic constants an activation energy of 3-deoxyosone and D-glucosone formation could be calculated, according to the derivation from Chapter 2. The results are charged with an error of roughly ±10 kJ/mol. An absolute value of activation energy is very difficult to obtain. On contrary - the major aim of this contribution is to show the trends of colour formation at different temperature levels and the measurements were done at comparable conditions. Therefore, the experimental error will be reduced.

Figure 9 supposes an enhanced reaction pathway with activation energies. These were achieved from kinetic experiments listed above and extended with activation energies derived from model sucrose solutions. The activation energy of sucrose degradation to invert sugar (initial step of colour formation) was studied separately (Smejkal, 2005). Presented values are in a good agreement with previous results of various authors (Bohn, 1970, Westphal,1985).

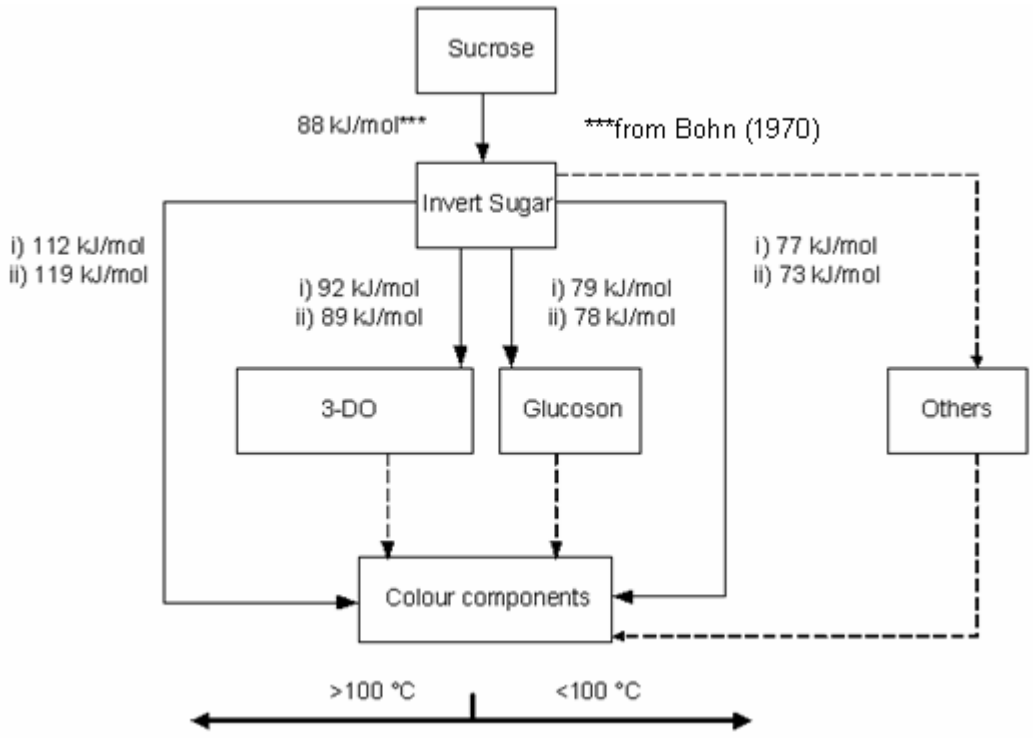

Fig. 9.: Reaction pathway of colour formation, derived from ***i)*** **technical sucrose solution** (thick juice) and ***ii)*** **model solution.**

DOI: 10.2202/1556-3758.1250

From Figure 9 can be concluded that achieved activation energies of colour formation pathway for technical and model solutions are in very good agreement. The formation of both chosen predominant intermediates could be described in technical as well as in a model solution with almost identical activation energies. Despite the problem of a not pronounced formation of 3-DO, the presented simplified kinetic model describes sucrose degradation in technical sugar solutions with acceptable accuracy.

In last years, a lot of complex and not always transparent kinetic models were shown. However, neither an approximation of overall sucrose degradation, nor a kinetic model for technical sucrose solution (thick juice) was presented**.**

Our kinetic study is constrained by two representatives. Therefore, in Figure 9 an imaginative reaction pathway is shown, which is extended by not-yet detected intermediates. A complex study of reaction mechanism in technical sucrose solution could be another aim for further scientific work. Another challenging task is to complete presented reaction pathway from 3-Deoxyoson and D-Glucoson to colour compounds. The preparation of all intermediates has been already described in literature (Fiedler, 2006), nevertheless the acquisition of starting material is still the crucial complication by planning of future experiments.

4. Conclusions

Achieved results comprise practical aspects of colour prediction in sugar production with kinetics study at a simplified reaction system. Our motivation was focused to the balance of colour formation, resulting in reliable elucidation of the last step of MAILLARD reaction. On the other hand, a simplified kinetic model was developed using key intermediates of sugar molecule degradation.

The most important conclusion is the change (shift) of reaction pathway in colour formation at about 100 °C. Above 100°C, the colour formation is speeded up rapidly and the characteristic intermediate changes from D-glucosone to 3-deoxyozone. This phenomena was confirmed independently by balance of colour formation and by formation of chosen dominant α-Dicarbonyl compounds.

5. Appendix

Table I: Kinetic constants of proposed reaction system

Temperature	Kinetic constant (min^{-1})	
(°C)	$k_{1,A}$ 3-deoxyosone	$k_{1,B}$ D-glucosone*
80	n.d.	0.0088
90	n.d.	0.0235
100	0.0048	0.0481
110	0.0161	-
120	0.0303	-
130	0.0442	-

* at temperatures above 100 °C, the decomposition of D-glucosone occurs

Table II: Kinetic constants of proposed reaction system, model sucrose solution

Temperature	Kinetic constant (min^{-1})	
(°C)	$k_{1,A}$ 3-deoxyosone	$k_{1,B}$ D-glucosone*
80	n.d.	0.001
90	n.d.	0.0029
100	0.0087	0.0041
110	0.0174	-
120	0.0384	-
130	0.0695	-

* at temperatures above 100 °C, the decomposition of D-glucosone occurs

6. References

Bohn, K., Untersuchungen über den Saccharoseabbau in alkalischer Lösung bei Temperaturen über 100° C, 1970, Dissertation B, Humboldt Universität zu Berlin

Fiedler Th., Kroh L.W.: Formation of Discrete Molecular Size Fractions of Melanoidins Depending on the Involvement of Several α-Dicarbonyl Compounds, Part 2, *Eur Food Res Technol,* 2006, *in press, online: DOI 10.1007/s00217-006-0442-6*.

Fiedler Th.: Beitrag zur Chemie von α-Dicarbonylverbindungen in der MAILLARD-REAKTION von Saccharose unter der Bildung von Melanoidinen, *Dissertation, Technische Universität Berlin,* 2006, *ISBN 3-8325-1326-4*.

Fiedler Th., Moritz Th., Kroh L.W.: Influence of α-Dicarbonyl Compounds to the Molecular Weight Distribution of Melanoidins in Sucrose Solutions, Part 1, *Eur Food Res Technol,* 2006, *223*, 837-842.

Hollnagel A., Kroh L.W.: Degradation of Oligosaccharides in Nonenzymatic Browning by Formation of α-Dicarbonyl Compounds via a "Peeling Off" Mechanism, *J Agric Food Chem,* 2000, *48*, 6219-6226.

Hollnagel A., Kroh L.W.: Formation of α-Dicarbonyl Fragments from Mono- and Disaccharides under Caramelization and MAILLARD reaction Conditions, *Z. Lebensm. Unters. Forsch. A,* 1998, *207*, 50-54.

Imming R., Bliesener K.-M., Bucholz K.: Chemische Grundlagen der Farbstoffbildung in hochkonzentrierten Saccharoselösungen, *Zuckerindustrie,* 1994, *119*, 915-919.

Ledl F., Schleicher E.: Die MAILLARD-Reaktion in Lebensmitteln und im menschlichen Körper - neue Ergebnisse zu Chemie, Biochemie und Medizin, *Angewandte Chemie,* 1990, *102*, 597-734.

Martins S.I.F.S., van Boekel M.A.J.S.: A Kinetic Model of the Glucose/Glycine MAILLARD Reaction Pathways, *Food Chemistry,* 2000, *90*, 257-269.

Martins S.I.F.S., van Boekel M.A.J.S.: Kinetics of the Glucose/Glycine MAILLARD Reaction Pathways: Influences of the pH and Reactant Initial Concentrations, *Food Chemistry,* 2005, *92*, 437-448.

Mundt S., Wedzicha B.L.: A Kinetic Model for the Glucose-Fructose-Glycine Browning Reaction, *J Agric Food Chem,* 2003, *51*, 3651-3655.

Nedvidek W., Ledl F., Fischer P.: Detection of 5-Hydroxymethyl-2-methyl-3(2H)-furanone and of α-Dicarbonyl Compounds in Reaction Mixtures of Hexoses and Pentoses with Different Amines, *Z. Lebensm. Unters. Forsch. A,* 1992, *194*, 222-228.

Reinefeld E., Schneider F., Westphal K., Tesch K., Knackstedt H.G.: Modellstudien zur MAILLARD-Reaktion in technischen Zuckersäften, *Zucker,* 1973, *26*, 581-588.

Reinefeld E., Schneider F.: "Analytische Betriebskontrolle der Zuckerindustrie" Teil A/B, 1978, *Verlag Dr. Albert Bartens KG*, Berlin.

Smejkal, Q., Schick, R., Fleischer, L.-G.: Influence of reduced temperature during evaporation and crystallization on sugar quality, 2005, SIT Conference Dubai, VAE, Book of Abstracts, Paper 873

Smejkal, Q., Bagherzadeh, A. Schick, R., Fleischer, L.-G., Kurz, T., Overall process model of sugar factory with modified temperature profile along evaporation unit – process evaluation, 2006, FoodSim Series, Juli 2006, Naples, Italy,119-123

Van der Poel P.W., Schiweck H., Schwartz T.: Zuckertechnologie, 2000, *Verlag Dr. Albert Bartens KG*, Berlin.

Vukov K., Pátkai G.: Rechnerische Methode zur Ermittlung von äquivalenten Wärmeeinwirkungszeiten für den Zuckerabbau in Säften, *Zuckerindustrie,* 1981, *106*, 314-318.

Wedzicha B.L., Kedward.: Kinetics of the Oligosaccharide-glycine-sulphite Reaction: Relationship to the Browning of Oligosaccharide Mixtures, *Molecular Nutrition & Food Research,* 1995, *54*, 379-402.

Westphal G., Kroh L.W.: Zum Mechanismus der "frühen Phase" der MAILLARD-Reaktion - 2.Mitt. Folgereaktionen von N-Glycosiden, *Die Nahrung,* 1985, *29*, 765-775.

Westphal G., Kroh L.W.: Zum Mechanismus der "frühen Phase" der MAILLARD-Reaktion - 1.Mitt. Einfluß der Struktur des Kohlenhydrats und der Aminosäure auf die Bildung des N-Glycosids, *Die Nahrung,* 1985, *29*, 757-763.

DOI: 10.2202/1556-3758.1250