Degradation of ascorbic acid during drying processes.

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1. SYNOPSIS

Ascorbic acid has been widely used to indicate the effect of drying on nutritional quality. In a previous study the moisture-dependence of the rate constants for ascorbic acid degradation in Maltodextrin DE12 was determined using isothermal thermal-degradation experiments at different, fixed, water contents. Dynamic drying experiments were then conducted in a convection drying oven. The predictions using the isothermal data were compared with the dynamic results and overall kinetic models were then tested. A re-estimation of the constants was necessary.

2. NOTATION

c=Ascorbic acid concentration (g /g dry solids)
c_o= Initial ascorbic acid concentration (g /g dry solids)
D_r = Decimal reduction time at the reference temperature (min^{-1})
z= Number of °C required to change the D_r-value ten fold (°C)
w= Water content on dry basis (g H_2O /g dry solids)
T_r= Reference temperature (140°C)
Tg_{H2O}= Glass transition temperature of pure water (-135°C)
Tg_{MD12}= Glass transition temperature of the maltodextrin DE12 used in this work (°C)

3. INTRODUCTION

The degradation of temperature-sensitive components in drying processes is a complex phenomenon due to the significant influence of the water content on the decay kinetics. The retention of these components is important for some products such as baby foods where the final nutritional value must be ensured and therefore retention must be maximised.
In literature (1),(2),(3), optimisation has been performed by assuming a given dependence of the rate constants on the water content, normally using empirical models. Accordingly, in a previous paper (4) thermal degradation experiments of ascorbic acid at different water contents in maltodextrin solutions were performed and it was found that the Bigelow model constants' dependence on water content was given by:

$$Dr(w) = 150 - 290w + 269w^2 \quad (1)$$

$$z(w) = 12 + 23w \quad (2)$$

where the reference temperature was 140°C. In drying, where both temperature and water content vary with time, the concentration history of ascorbic acid is given by:

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$$\frac{c}{c_o} = 10^{-\int_0^t \frac{dt}{D(\omega)}};\quad D(\omega) = D_r(\omega)10^{-\frac{T-Tr}{z(\omega)}} \qquad 3$$

The objective of this work was to compare model predictions using equations 1 and 2 with drying experimental data obtained in a convection oven, so that temperature and water content could be contiously monitored. If signigicant deviations were found, the constants in equations 1 and 2 would be re-estimated. An alternative approach to equation 3 could result from applying the concepts of biomaterials science, using the glass transition temperature and WLF equation, as suggested by Nelson (5):

$$\frac{c}{c_O} = 10^{-\int_0^t \frac{dt}{D(\omega)}};\quad D(\omega) = D_r \cdot 10^{-\frac{C_1C_2(T-Tr)}{(C_2+T-Tg)(C_2-(Tg-Tr))}} \qquad 4$$

where Tg is the glass transition temperature of the matrix, which for an essentially binary system (water-maltodextrin) is given by the general equation

$$Tg = \frac{Tg_{H2O}w_{H20} + kTg_{MD12}w_{MD12}}{w_{H2o} + kw_{MD12}} \qquad 5$$

From the data published by Roos and Karel (6), values of k=7.63 and Tg_{MD12}=164°C were obtained. Tg_{H2O} was assumed to be -135°C (6).

4. MATERIALS AND METHODS

Two drying experiments were conducted in a forced convection drying oven (Convection Oven MOV-212F Sanyo Electric Co., Ltd. Japan) at 140°C dry bulb air temperature. Approximately 8 millilitres of a concentrated maltodextrin solution (40% in w/v Glucidex 12, Roquette, France) with 0.012g ascorbic acid/ml (Sigma A-1417) were placed in Petri dishes and weighed. Twenty Petri dishes were used in each experiment and 2 samples were taken at each predetermined time interval. The samples were weighed to determine the moisture content and an aliquot of the product was removed to determine the ascorbic acid concentration.

In order to study the effect of crust formation on the kinetics of ascorbic acid degradation, two additional foam drying experiments were performed, adding egg albumin (Sigma A-5231) in the concentration of 0.04 g/ml to a concentrated solution of maltodextrin (60% w/v). The solution was then foamed using a domestic blade blender, placed in the Petri dishes and dried at 140°C.

Finally, for validation purposes, another experiment was performed at 100°C with a 40% (w/v) maltodextrin solution without egg albumin.

HPLC analysis was performed in a Beckmann HPLC with a 126 Solvent delivery system. A weighed sample was diluted in ultrapure water:methanol (95:5) in a 10 ml volumetric flask and 1 ml of freshly prepared internal standard solution 50 mg/50ml (Isoascorbic Acid Sigma I-0502) was added. The solution was filtered through 0.45 µm Nucleopore Filters (Syrfil 25mm 0.45µm FN) and 10 µl of the solution were injected into the HPLC. The mobile phase was water:methanol (95:5) and 6.82 g/l Dipotassium Phosphate (SIGMA P 3786) and 1.86 g/l Cetrimide (SIGMA T 4762) at a flux of 1.7 ml/min. The column used was Spherisorb ODS18 (250x4.6 mm). Absorbance at 261 nm was measured by a 166 Beckman UV-VIS Detector.

Data analysis was performed using commercial software (Scientist.2.0. MicroMath Scientific Software. Salt Lake City, Utah). The models were used in differential form, integrated using an

internal integration package and compared with the experimental values. The iterative process was carried out firstly by a Simplex minimisation procedure in order to determine speedily the approximate solution region and then by a conventional least squares technique to determine them accurately.

5. RESULTS AND DISCUSSION

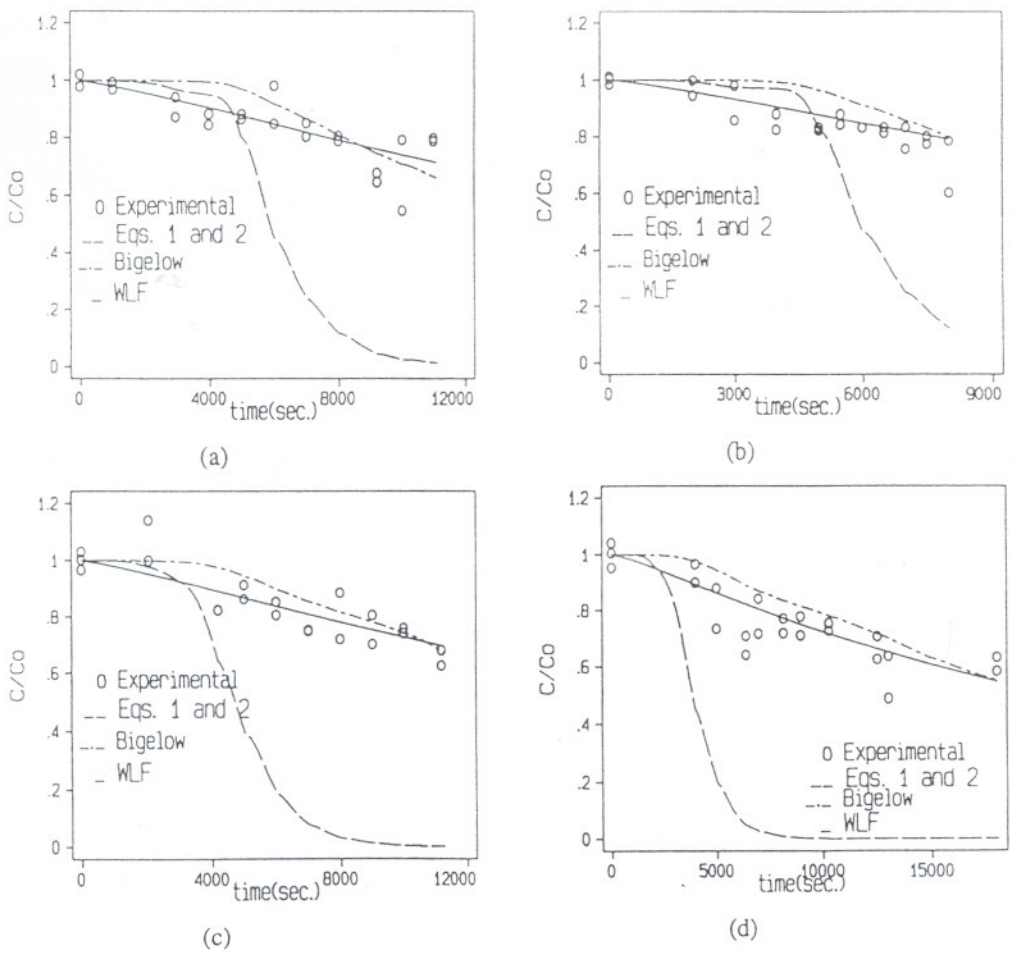

Fig. 1: Experiments performed at 140°C. (a) and (b) without foaming; (c) and (d) with foaming.

Fig. 1 and 2 show the results. The original constants of eqn. 1 and 2 underestimate the stabilisation effect of drying in general. Only in the slowest drying process (fig. 2) was the opposite verified.

Re-estimating the constants, by fitting the whole experimental drying data at 140°C to eqn. 3 yielded new constants:

$$Dr = 588.7 + 4403.3 \cdot \omega - 337.2 \cdot \omega^2 ; z = 38.12 + 3 \cdot \omega \qquad 6$$

The WLF constants were determined in the same way using eqn. 4:
Dr=1141.3; C1=11.2; C2=5060.8

Table 1: Model fitting statistics.

Model	N	SSQ	R^2	Var.	SC
Bigelow	5	0.502	0.991	0.64	2.50
WLF	3	0.355	0.994	0.75	0.28

N= Number of parameters, SSQ=Sum of the squared residuals, Var= Variance explained, SC= Serial Correlation between residuals

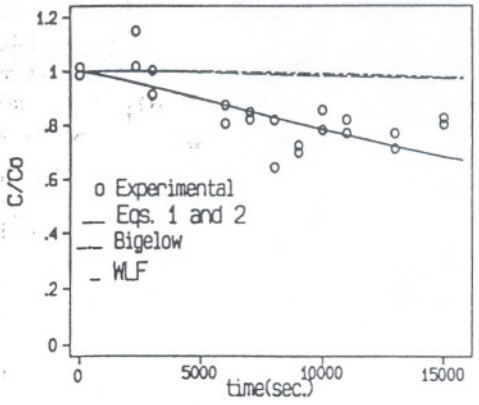

Fig. 2: Experiment performed at 100°C.

The model statistics are shown in table 1. Although the correlation coefficient is good, the serial correlation value indicates some bias on the residuals distribution, which can be observed in fig. 1.

Application of the WLF model yields an equally good correlation coefficient but a much better serial correlation (<1). This improved accuracy is visible in fig. 1. It is worth noting that the WLF model has only 3 constants, while Bigelow's model has 5. Furthermore, the WLF model predicted very well the ascorbic acid degradation at 100°C, while the Bigelow model showed a very poor correlation, as can be seen in fig. 2.

6. CONCLUSION

The degradation of ascorbic acid during drying was described well by the WLF model, better than the use of empirical functions to describe the water content effect on the rate constants.

7. REFERENCES

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