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Honey thermal treatment effects on hydroxymethylfurfural content

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Abstract

The effects of honey thermal treatment on the hydroxymethylfurfural (HMF) content (temperature and time) were studied, during both transient and isothermal heating stages. Assay was carried out with two honey samples whose initial HMF values were 3.9 and 26.6 mg HMF/kg honey. During the transient stage, treatment time ranged between 14 and 60 s, and treatment final temperature ranged between 100 and 160 °C. This study determined that initial HMF concentration did not affect its formation kinetics. HMF content change during the isothermal stage of the thermal treatment was determined at the final temperature of the transient stage and for treatment times up to 90 s, and it follows a kinetic model of pseudo first order. First order rate constants were correlated with temperature by an Arrhenius-type equation. Thus the values of the frequency constant and activation energy were obtained.

Keywords: Honey; Pasteurisation; Crystallisation; Hydroxymetylfurfural; Thermal treatment

1. Introduction

Honey is submitted to thermal treatments for two different reasons: (1) to modify its tendency to crystallisation or delay its appearance and (2) to destroy the micro-organisms which contaminate it.

Honey crystallisation and size of the formed crystals are a function of water content, fructose/glucose ratio and thermal history. Crystallisation has several disadvantages. The most important is the difficulty in handling and pouring; also, dosifiers or filling and packaging machines cannot work properly. Moreover, product presentation is modified and most consumers do not like crystallised honey. If crystallisation takes place when honey is on the shelves, it may cause much inconvenience. When crystallisation occurs after packaging, product extraction is difficult to carry out, especially when it is packed in individual portions for hotel and catering uses. If heated, honey becomes liquid, but if this is not properly done (by heating slowly at low temperatures), it will get damaged. The other disadvantage is the homogeneity loss due to the formation and coexistence of two phases (crystalline and liquid). The latter is formed by water, segregated because of crystal formation, creating, as a result, a higher water activity than that of the original honey. This enables microbial flora, normally present in honey, to develop, with subsequent organoleptic modifications. Honey fermentation is caused by osmophilic flora action on fructose and glucose, producing gaseous carbon dioxide, with foam formation, and ethanol, which, in the presence of oxygen, produces acetic acid. Honey is highly hygroscopic, so water activity also increases if moisture increases.

During beehive handling, and in the extraction operation, honey gets contaminated, generally with mesophiles, aerobics, fungi and yeasts (most of them osmophiles) and with *Clostridium botulinum*. Malan and Marletto (1974) have identified 90 different types of yeasts, belonging to five species. The most frequently isolated were *Torulopsis mogii* and *Saccharomyces rouxii*.

For water activities ranging between 0.65 and 0.60, the osmophilic yeasts (*Saccharomyces rouxii*) and moulds (*Aspergillus echinulatus*) are inhibited (Richardson & Hyslop, 1992). For moisture contents accepted by the Código Alimentario Argentino (CAA, 1997), honey water activity ranges between 0.593 and 0.637. These values inhibit the development of almost all microorganisms present in honey.

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Thermal treatment, applied to honey, may destroy vitamins and bionutrients, and produce a simultaneous decrease in diastase activity and an increase in HMF content. Honey treatment temperature and time must be limited when pasteurising and stabilising it; both diastase activity and HMF content are national and international parameters used as controls so as to limit thermal treatment application.

In Argentina, the CAA stipulates an allowed maximum HMF concentration of 15 mg/kg in honeys with a diastase activity lower than 8% and equal to or higher than 3%, expressed as diastase ratio (DR) on the Gothe scale. On the other hand, HMF can reach the 40 mg/kg maximum value if the DR is higher than 8%. Studies on honey produced in the 1998–1999 period in the Province of Santa Fe (Argentina), carried out by Ré, Tasi, Cazonni, and Tapiz (2000) (unpublished), determined that the HMF mean content was 14.7 mg/kg, with extreme values of 3.5 and 28.7 mg/kg.

HMF can be formed by hexose dehydration in acid media or by the Maillard reaction (Feather, Harris, & Nichols, 1982; Hoseney, 1984). According to Ibarz, Casero, Miguelsanz, and Pagán (1989), HMF formation can be described by a second order kinetics (auto-catalytic), with the following equation as expression model:

$$[HMF]_t = \frac{1}{\frac{1}{[H]_0+[HMF]_0} + \left(\frac{[H]_0+[HMF]_0-[HMF]_0}{([H]_0+[HMF]_0)[HMF]_0}\right)e^{[-k_2 t]}} \quad (1)$$

where:

$[HMF]_t$ = HMF final concentration at time t
$[HMF]_0$ = HMF initial concentration
$[H]_0$ = Hexose initial concentration
t = Thermal treatment time
k_2 = Velocity constant for autocatalytic kinetics of second order (s^{-1})

Considering that the total hexose concentration in honey is higher than the HMF concentration normally present in honey, HMF_0, the HMF formation could follow a first order kinetics, the expression of which is:

$$[HMF]_t = [HMF]_0 e^{(k_1 \cdot t)} \quad (2)$$

where:

k_1 = Reaction rate constant of first order kinetics, (s^{-1})

On the other hand, as the reaction rate constant k_1 is a temperature (T) function, it is feasible to correlate it with T by means of an Arrhenius form equation:

$$k_1 = K_f \cdot e^{-\left(\frac{E_a}{R(T+273^\circ C)}\right)} \quad (3)$$

where

T = Honey temperature (°C)
t = Honey treatment time
K_f = Frequency constant (s^{-1})
E_a = Activation energy (kJ/mol)
R = Gas constant (kJ/mol K)

During heating, two stages can be identified: the transitory or transient stage, which corresponds to an increase in temperature, starting from its initial value and reaching the treatment temperature, followed by the isothermal stage, in which temperature remains constant at the obtained value. There exists a definite time for each of these stages. In the transient stage, time is characteristic and depends on the system properties and heat flow. In the isothermal stage, time is generally fixed according to test targets.

It is important to develop a thermal process capable of achieving pasteurisation and stabilising the crystallisation phenomenon in a single operation. The aim of this work is to evaluate the effects of temperature and time variables of honey thermal treatments during the transient and isothermal stages on HMF concentration, and to determine whether the HMF formation process can be described by a first order kinetic model.

2. Materials and methods

2.1. General

Honey samples with 3.9 and 26.6 mg HMF/kg and 13.8 and 14.0 meq/kg acidity, respectively, were selected, considering HMF values found in the analysed honey (Ré et al., 2000, unpublished) and that the initial acidity influences HMF formation.

Acidity and HMF (by HPLC) contents were determined according to the methods proposed in the Harmonized Methods of Honey European Commission (Bodganov, Martin, & Lüllmann, 1997).

The evaluation of the influence of thermal treatment independent variables on HMF concentration was carried out by experimental designs in which the effects of heating stages were studied separately. First, tests corresponding to the transient stage, and then the isothermal stages were carried out. Final temperature (T), and time (t_t) to achieve T, were taken as independent variables in the transient heating stage; t_t times equal to 14, 26, 42 and 60 s, and temperatures equal to 100, 110, 120, 130, 140, 150 and 160 °C were fixed from previous tests. All tests were started from a standard initial temperature of 25 °C. In the isothermal heating stage, the independent variables were temperature (T) with the same values as the transient stage and treatment time (t) from 0 to 90 s. Both HMF content and HMF relative concentration (HMF_r), were selected as responses; the latter was defined as:

$$[HMF]_r = [HMF]_t/[HMF]_0 \quad (4)$$

Table 1
HMF[a] relative concentration and its standard deviation (δ), as a function of transient stage time (t_t), final temperature (T) and initial HMF concentration[a]

T (°C)	$[HMF]_0$ (mg/kg)	$[HMF]t/[HMF]_0$							
		Elapsed time in transient stage (s) and standard deviation (δ)							
		14	δ	28	δ	42	δ	60	δ
100	3.9	1.0	0.18	1.0	0.17	1.3	0.19	2.6	0.31
	26.6	1.0	0.18	1.1	0.18	1.2	0.17	2.5	0.20
110	3.9	1.0	0.19	1.2	0.17	1.5	0.18	3.0	0.36
	26.6	1.1	0.17	1.3	0.20	1.3	0.18	3.1	0.38
120	3.9	1.1	0.19	1.4	0.17	2.0	0.25	4.8	0.52
	26.6	1.1	0.18	1.5	0.19	2.1	0.31	4.9	0.47
130	3.9	1.2	0.18	1.6	0.18	2.4	0.28	6.3	0.47
	26.6	1.3	0.19	1.8	0.23	3.0	0.33	6.3	0.43
140	3.9	1.4	0.18	1.8	0.21	2.8	0.31	8.4	0.46
	26.6	1.4	0.21	1.8	0.20	2.9	0.33	8.5	0.38
150	3.9	1.6	0.18	2.2	0.25	4.1	0.48	10.6	0.47
	26.6	1.7	0.22	2.1	0.28	4.2	0.50	10.5	0.42
160	3.9	2.4	0.21	4.3	0.47	8.1	0.89	15.4	0.45
	26.6	2.5	0.45	4.2	0.48	8.2	0.45	15.6	0.42

[a] HMF, hydroxymethylfurfural content.

To avoid the decrease of moisture content during thermal treatments, tests were carried out in a close system, consisting of a stainless steel tubing coil of 5 mm internal diameter, hermetically closed at both ends with threaded caps and provided with a micro thermocouple which measured the instantaneous temperature in the core axis of honey contained in the coil.

2.2. Transient heating stage

To determine time and temperature effects on HMF content modification in the transient stage, heating was carried out by coil immersion in a thermostatic and shaking glycerine bath to temperature T. To stop heat action, at the end of t_t, the coil was taken out from the warm bath and immediately submerged in a thermostatic and shaking water bath at 18 °C.

2.3. Isothermal heating stage

To evaluate T and t effects of the isothermal treatments on HMF_r, time t_t, corresponding to the transient stage, was kept constant and equal to 14 s in all tests.

In the applied technique, the coil was submerged in a thermostatic and shaking glycerine heating bath at a certain temperature, in such a way that, after the 14 s, corresponding to the transitory stage, honey reached the temperature, T, fixed for the isothermal treatment. At that moment, the coil was transferred immediately to another heating bath of the same characteristics, which was set at temperature T, corresponding to the isothermal treatment. Once the isothermal treatment time had elapsed, the coil was withdrawn from the hot bath and cooled by immersion, using the same procedure as for the transient stage. The coil transference, from the transient stage bath to the isothermal stage bath, took no longer than two seconds. Both thermal treatment tests, and HMF concentration determination in each test, were carried out in triplicate. Mean values were used in the evaluation of the independent variable action.

To determine whether HMF formation in the isothermal heating stage can be described by a first order kinetic model, adjustment levels of exponential correlations of HMF_r with t were evaluated for each temperature.

3. Results and discussion

The results obtained for the transient heating stage are detailed in Table 1; hence, it can be deduced that initial HMF concentration does not affect the HMF_r modification, both at T and t_t tested intervals. Fig. 1 shows the experimental values, expressed as HMF_r and the adjustment exponential curves corresponding to the isothermal heating stage. The resulting HMF values are due to the isothermal treatment effect only. The HMF formed as consequence of the transient stage, was discounted from the values obtained at the end of the complete transient-isothermal treatment. Table 2 shows the origin ordinates, first order reaction pseudo rate constant and regression coefficients.

High regression coefficients indicate that HMF formation follows first order kinetics. (Eq. 2). The first order reaction pseudo rate constant correlates exponentially with 1/RT, with a regression coefficient of 0.95, yielding the frequency constant and the activation energy of 2.83 s^{-1} and 226 kJ/mol, respectively.

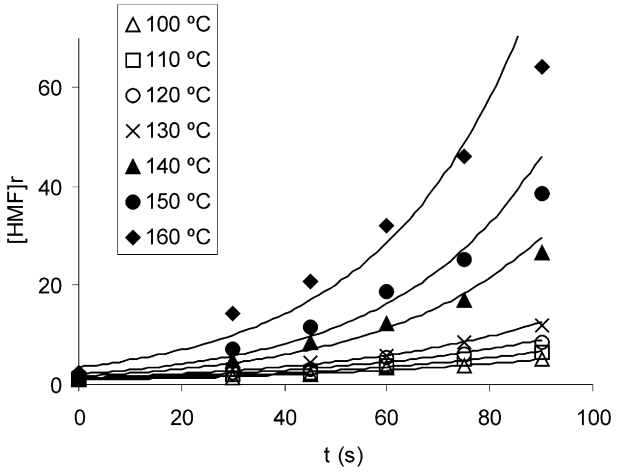

Fig. 1. Hydroxymethylfurfural (HMF) relative concentration variation as function of time and temperature of the isothermal heating stage. Time elapsed in transient heating stage is constant and equal to 14 s.

Table 2
HMF[a] formation kinetics in isothermal heating as a function of treatment temperature, origin ordinates, first order reaction pseudo rate constant and regression coefficients

T (°C)	Origin ordinates	$k_1\ 10^2$ (s^{-1})	r^2
100	0.9343	1.92	0.97
110	0.9908	2.13	0.98
120	1.1687	2.27	0.98
130	1.3404	2.48	0.99
140	1.6677	3.20	0.98
150	2.0970	3.45	0.97
160	3.1511	3.88	0.94

[a] HMF, hydroxymethylfurfural content.

The use of thermal treatments for technological purposes, such as the elimination of crystallisation or pasteurisation, can increase the HMF content. Therefore, treatment time at a given temperature must be as short as possible. If temperatures are higher than 130 °C, even for short times, HMF increase reaches values above these accepted by international standards.

Fig. 1 shows that a 90 s at 130 °C treatment produces approximately the same HMF increase as a 30 s at 150 °C treatment.

Transient heating stage effects are less harmful, but HMF increases reach significantly higher values at high temperatures for longer times. (Table 1)

References

Bodganov, S., Martin, P., & Lüllmann, C. (1997). Harmonised methods of the European honey commission. In B. Vaissière *Apidologie* (pp. 1–59). France: Elsevier.

Código Alimentario Argentino (1997). Metodología Analítica Oficial, Miel. Método 15.8 Determinación de la actividad de la diastasa. Buenos Aires, Argentina: De la Canal y Asociados.

Feather, M. S., Harris, D. W., & Nichols, S. B. (1982). Routes of conversion of D-xilose, hexouronics acids and L-ascorbic acid to 2-furaldehyde. *Journal of Organic Chemistry*, *37*, 1600–1606.

Hoseney, R. C. (1984). Chemical changes in carbohydrates produced by thermal processing. *Journal of Chemical Education*, *61*, 308–312.

Ibarz, A., Casero, T., Miguelsanz, R., & Pagón, J. (1989). Cinéticas de formación de hidroximetilfurfural en concentrado de zumo de pera almacenado a diferentes temperatures. *Alimentaria*, *199*, 81–84.

Malan, C., & Marletto, O. (1974). Blastomiceti da mieli di diversi origini e provenienze. *Annali del' Accademica di Agricoltura di Torino*, *116*, 1–18.

Richardson, T., & Hyslop, D. (1992). Química de los Alimentos. In O. Fennema (pp. 451–464). Acribia SA, Zaragoza, España.