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Modelling of 5-hydroxymethylfurfural photo-degradation by UV irradiation. Influence of temperature and pH

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ABSTRACT

The main aims of this study were (a) to prove that the UV irradiation of juices prevents the formation of 5-hydroxymethylfurfural (HMF), (b) to know the influence of temperature and pH on the UV photo-degradation of the HMF when it is unfortunately present in the juice (for example, after a previous thermal treatment or after a long storage period) and (c) to model this photo-degradation, proposing a reaction mechanism related to the power absorbed by the solution that depends on the HMF concentration.

For these purposes a mid-pressure mercury lamp with emission wavelengths between 250 and 740 nm was used.

Firstly, nectarine juice was irradiated to be sure that HMF was not synthesised. Then, aqueous solutions of 100 $mg \cdot L^{-1}$ HMF at pH 3, 4 and 5 were irradiated at 12, 25, 35 and 45 °C for 120 min. Aliquots were analysed to measure their HMF contents and absorption spectra.

The photo-degradation data fitted well to both zero-order and pseudo-first-order kinetic models and the constant values were similar. The increases in both temperature and pH enhanced the photo-degradation, the optimal conditions inside the ranges studied being 45 °C and pH = 5, when a reduction of 60% of the initial content of HMF was reached.

The spectral radiant power absorbed by the whole solution and the incident spectral radiant power reaching any depth of the reactor were evaluated taking into account the linear spherical emission model and using the Simpson integration method. Its dependence on the HMF concentration was also studied. A three stage degradation mechanism was proposed, matching both the zero-order and pseudo-first-order kinetic models previously obtained.

1. Introduction

5-Hydroxymethylfurfural (HMF) has been identified in many heat-processed foods including fruit juices (Anese, Manzocco, Calligaris, & Nicoli, 2013; Anese & Suman, 2013; Morales, 2009). It is formed in the Maillard reaction as well as during caramelization as the result of dehydration of ketopentoses, particularly in acidic or high-temperature environments (EFSA, 2011; Ibarz, Casero, Miguelsanz, & Pagan, 1989; Lee, Sakai, Manaf, Rodhi, & Saad, 2014). As HMF is not present in fresh fruit and is generated naturally in sugar-containing food during processing, it has become a parameter related to the freshness and quality of foods (Gaspar & Lucena, 2009). High values reveal excessive thermal treatment, inappropriate storage conditions and a likely loss of quality, i.e., loss of L-ascorbic acid, changes in such physical properties as colour, and sensorial characteristics (AIJN, 2001; Chen, Yang, Chen, & Liu, 2009).

In addition, HMF may induce genotoxic and mutagenic effects in bacterial and human cells and promote colon and liver cancer in rats and mice (Glatt & Sommer, 2006; Monien, Engst, Barknowitz, Seidel, & Glatt, 2012; Zhang et al., 1993), although there is no evidence for carcinogenic and genotoxic effects in humans (Abraham et al., 2011; Capuano & Fogliano, 2011; EFSA, 2011).

Given its probable genotoxicity, subchronic toxicity and carcinogenicity, the EFSA considered that it would be prudent to reduce the HMF content as much as technologically feasible (EFSA, 2011). AIJN (2001) recommended a maximum content between 10 and 20 $mg \cdot kg^{-1}$ depending on the fruit juice.

In order to reduce the HMF content in cooked foods, some recent reviews (Anese & Suman, 2013; Anese et al., 2013) summarize the possibilities studied to date. The first option is a temperature reduction in the thermal treatment in order to minimize the synthesis reaction of HMF. It can be achieved by heating at low temperatures and low pressures for long times. Dielectric (radiofrequency and microwave) heating can also be used because heat is generated by the movement of the water molecules in the solution. Thus, a lower temperature is necessary to achieve the desired hygienic and sensory properties. The second option

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is to change some parameters of the cooking process, like substituting or adding some ingredients. The third option consists of removing the HMF synthesised in the cooking process by evaporating the HMF while the food is being cooked in an open vessel or applying a post-treatment like vacuum treatment, ionizing radiation or fermentation.

In the case of non-cooked foods, like fruit juices, some alternative methods have been proposed in order to minimize the synthesis of HMF. These include ultra-high-pressure homogenization (Saldo, Suarez-Jacobo, Gervilla, Guamis, & Roig-Sauges, 2009), high hydrostatic pressure (Vervoort et al., 2012) or UV light treatment (Bule et al., 2010).

The UV light treatment method is known to be an alternative to the traditional thermal pasteurization in liquid foods, fresh juices, and beverages (Ibarz, Garvin, Azuara, & Ibarz, 2015; Ibarz, Garvín, & Falguera, 2015). Its effectiveness at inactivating microorganisms, enzymes and degrading mycotoxins was proved (Falguera, Pagán, Garza, Garvín, & Ibarz, 2011b). Moreover, it requires very little energy compared to thermal pasteurization processes (Keyser, Muller, Cilliers, Nel, & Gouws, 2008; Koutchma, 2009) and preserves the original colour of the food (Tran & Farid, 2004). Taking into account that this treatment does not need to work at high temperatures, it can be proposed as a potential treatment of liquid foods to replace the traditional thermal treatment in order to avoid the synthesis of HMF and also to degrade the HMF once it is present.

Therefore, the main aims of this study were: (a) to prove that the UV irradiation of juices avoids the formation of HMF, (b) to establish the influence of temperature and pH on the photo-degradation of the HMF by UV irradiation, when it is unfortunately present in the juice (for example, after a previous thermal treatment or after a long storage period) and (c) to model this photo-degradation, proposing a reaction mechanism related to the power absorbed by the solution that depends on the HMF concentration.

2. Materials and methods

2.1. Irradiation model

When a solution is irradiated with electromagnetic radiation, part of the energy is absorbed. The ability to absorb radiation can be known by defining the absorbance as the logarithm of the ratio between the incident (P_λ^0) and the transmitted (P_λ) spectral radiant power at wavelength λ. Taking into account the base of the logarithm, two definitions of absorbance are possible:

$$A_{10}(\lambda) = \log\frac{P_\lambda^0}{P_\lambda}; A_e(\lambda) = \ln\frac{P_\lambda^0}{P_\lambda}. \tag{1}$$

Spectrophotometers usually measure the absorbance as A_{10}, while the model equations usually use A_e. The relation between both terms is $A_e = A_{10} \cdot \ln 10$.

Lambert–Beer proposed a linear relation between the absorbance at a fixed wavelength and concentration of the absorber substance

$$A(\lambda) = \varepsilon_\lambda \cdot C_A \cdot D_S = \mu_\lambda \cdot D_S \tag{2}$$

where $A(\lambda)$ is the absorbance at wavelength λ, ε_λ the molar extinction coefficient at the same wavelength, C_A the concentration of the absorber substance, D_S the length of the path of light through the solution and μ_λ the absorption coefficient (which corresponds to the product of ε_λ and C_A).

Considering Lambert–Beer's law, the e-base absorbance, a plane photo-reactor with a linear lamp (Fig. 1) and a linear spherical emission model, the next equations (each parameter is shown in Fig. 1 and/or defined below in the Nomenclature section) are obtained (Garvin, Ibarz, & Ibarz, 2015; Ibarz, Garvin, Azuara, et al., 2015; Ibarz et al., 2014):

a. The incident spectral radiant power reaching a specific point inside the solution:

$$P(x,y,z) = \sum_\lambda P_\lambda(x,y,z) = \sum_\lambda \frac{W_\lambda/L}{4\pi D^2}\int_{y_L=y_0}^{y_L=y_0+L} \exp\left(-\mu_\lambda \frac{z}{\sin\beta}\right) dy_L \tag{3}$$

being

$$D^2 = (x-x_0)^2 + (y-y_L)^2 + (z+z_0)^2 \tag{4}$$

and

$$\sin\beta = \frac{z_0+z}{D}. \tag{5}$$

b. The incident spectral radiant power for a specific depth (z) of the reactor is obtained by integrating Eq. (3) for all the x and y values for the specific z value:

$$P(z) = \int_{x=0}^{x=A}\int_{y=0}^{y=B} P(x,y,z)dxdy = \sum_\lambda \frac{W_\lambda/L}{4\pi}\int_{x=0}^{x=A}\int_{y=0}^{y=B}\int_{y_L=y_0}^{y_L=y_0+L} \frac{e^{-\mu_\lambda \frac{z}{\sin\beta}}}{D^2} dy_L dydx. \tag{6}$$

The values of $P(z)$ for $z = 0$ and $z = C$ are the incident radiation power on the surface ($P(0)$) and at the bottom of the reactor ($P(C)$), respectively. Although the total radiation power absorbed by the solution depends on the incident radiation power at the surface of the reactor, only a fraction of this incident radiation power is absorbed. In fact, not even the incident radiation dose on the surface could be absorbed.

Considering a point (x',y',z') at an infinitesimal distance from (x,y,z), the spectral radiant power reaching this point after following this infinitesimal path (d_S) is:

$$P_\lambda(x',y',z') = P_\lambda(x,y,z)\exp(-\mu_\lambda d_S) \tag{7}$$

being

$$d_S = \frac{dz}{\sin\beta}. \tag{8}$$

2.1.1. Diluted solutions

In the case of diluted solutions, where the values of μ_λ are low, this equation can be simplified as (Ibarz, Garvín, & Falguera, 2015; Ibarz et al., 2014; Keyser et al., 2008):

$$P_\lambda(x',y',z') \approx P_\lambda(x,y,z)[1-\mu_\lambda d_S]. \tag{9}$$

The infinitesimal spectral radiant power absorbed by the solution between the points separated by an infinitesimal distance is:

$$dP_{abs,\lambda}(x,y,z) = P_\lambda(x,y,z) - P_\lambda(x',y',z') \approx P_\lambda(x,y,z)(\mu_\lambda d_S). \tag{10}$$

Thus, for low light absorber concentrations, the spectral radiant power absorbed by the whole solution and the whole lamp per volume unit is:

$$P_{abs} = \frac{1}{V}\sum_\lambda \int_{x=0}^{x=A}\int_{y=0}^{y=B}\int_{z=0}^{z=C}\int_{y_L=y_{0+L}}^{y_L=y_0} \frac{W_\lambda/L}{4\pi D^2}\exp\left(-\mu_\lambda \frac{z}{\sin\beta}\right)\mu_\lambda \frac{dz}{\sin\beta} dy_L dxdydz. \tag{11}$$