Journal of Food Engineering 191 (2016) 67–76

Contents lists available at ScienceDirect

Journal of Food Engineering

journal homepage: www.elsevier.com/locate/jfoodeng

Effect of the concentration on the kinetic model of the photo-degradation of 5-hydroxymethylfurfural by UV irradiation

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ARTICLE INFO

Article history:
Received 19 June 2015
Received in revised form
11 February 2016
Accepted 27 June 2016
Available online 1 July 2016

Keywords:
UV
Radiation
Photo-degradation
Juice
HMF
Treatment

ABSTRACT

The aim of this work was to study the effect of the initial concentration on the photo-degradation kinetics of 5-hydroxymethylfurfural (HMF) and develop different mathematical models for HMF photo-degradation related to the radiation absorbed by the solution. For this purpose, a mid-pressure mercury lamp with emission wavelengths between 250 and 740 nm was used. Aqueous solutions of 25 and 100 mg L^{-1} of HMF (pH 4) were irradiated at 12, 25, 35 and 45 °C. Then, aqueous solutions of 1 and 100 mg L^{-1} of HMF (pH 3, 4 and 5) were irradiated at 25 °C. The treatments were applied for 120 min. Aliquots were analysed to measure their HMF content and absorption spectra.

The spectral radiant power absorbed by the solution was evaluated taking into account the linear spherical emission model and using the Simpson integration method. Its dependence on the HMF concentration was studied. Considering specific narrow ranges of concentrations, the function can be defined by linear equations.

A three-stage degradation mechanism was proposed from which, considering different relations between the absorbed radiation and the concentration, three different kinetic models were obtained: first-order, zero-order and pseudo first-order.

1. Introduction

5-hidroxymethylfurfural (HMF) has been identified in many heat-processed foods (Morales, 2009). It is formed in the Maillard reaction as well as during caramelization as the result of hexose dehydration under acidic or high-temperature environments (EFSA, 2011; Ibarz et al., 1989). Its impact on human health is a contentious topic since The International Agency of Research on Cancer declared this compound “possibly carcinogenic to humans” (Anese et al., 2013; Kowalski, 2013). Although there is no evidence for carcinogenic and genotoxic effects in humans (Abraham et al., 2011; Capuano and Fogliano, 2011) the EFSA (2011) considers that it would be prudent to reduce the content of HMF.

The content of HMF has also been a quality parameter for fruit juices since high values reveal an excessive thermal treatment, inappropriate storage conditions and a likely loss of quality. The Association of the Industry of Juices and Nectars from Fruit and Vegetables for the European Union has recommended a maximum value of 10 mg L^{-1} in orange juice and 20 mg L^{-1} in apple juice (AIJN, 2001).

Several technologies have been studied aimed at reducing the content of 5-hydroxymethylfurfural in non-cooked foods, like fruit juices: e.g. ultra-high-pressure homogenization (Saldo et al., 2009), high hydrostatic pressure (Vervoort et al., 2012) and adsorption with activated carbon (Carabasa et al., 1998).

Ultraviolet treatment is known to be an alternative to traditional thermal pasteurization in liquid foods, fresh juices, and beverages. Its effectiveness at inactivating microorganisms and enzymes was proved (Guerrero-Beltrán and Barbosa-Cánovas, 2004; Ibarz et al., 2015a). Moreover, it requires very little energy compared to thermal pasteurization processes (Keyser et al., 2008) and preserves the colour of the original food (Tran and Farid, 2004). UV light has also been applied to degrade undesirable substances such as dyes, herbicides and antibiotics in wastewaters (El-Moselhy, 2009; Orellana-García et al., 2014; Santos et al., 2015) and mycotoxins in fruit juices (Ibarz et al., 2014; 2015b).

The photo-degradation of HMF was studied in a previous work (Aguilar et al., 2015). This concluded that UV radiation is a useful alternative treatment to the thermal method. When a fruit juice goes through UV radiation in order to eliminate microorganisms,

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http://dx.doi.org/10.1016/j.jfoodeng.2016.06.026

HMF is not generated. Moreover, if HMF were present in the juice, for example after a previous thermal treatment or after a long storage period, UV radiation would be a useful treatment method to eliminate HMF. This study was done at an initial HMF concentration of 100 mg L^{-1}. As the range of HMF concentrations found in commercial fruit juices is very wide, from 0.08 to 91.5 mg L^{-1} (Álvarez et al., 2014; Lee et al., 2014), the aim of this work was to study the effect of the initial HMF concentration on the photo-degradation kinetic model.

2. Materials and methods

2.1. Irradiation model

When a solution is irradiated with electromagnetic radiation, part of the power emitted by the lamp reaches the surface of the solution and only a part of this can be absorbed. Only a fraction of the absorbed radiation can cause any reaction, this fraction being the quantum yield of the total absorbed radiation. In fact, the incident radiation on the surface of the solution could not be absorbed at all; and even in the case of part of the radiation being absorbed, no reaction would take place if the quantum yield were nil.

Considering Lambert-Beer's law, the *e*-base absorbance, a plane photo-reactor with a cylindrical lamp (Fig. 1) and a linear spherical emission model, Ibarz et al. (2014) and Garvín et al. (2015) obtained the following equations (each parameter is shown in Figs. 1–2 and/or defined below in the nomenclature section):

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

$$P(x,y,z) = \sum_{\lambda} \frac{P_{emit,\lambda}/L}{4\pi D^2} \int_{y_L=y_0}^{y_L=y_0+L} \exp\left(-\mu_\lambda \frac{z}{\sin\beta}\right) dy_L \qquad (1)$$

b. The incident spectral radiant power for a specific depth (z) of the reactor is obtained by integrating eq. (1) for all the x and y values for the specific z value:

$$P(z) = \sum_{\lambda} \frac{P_{emit,\lambda}/L}{4\pi} \int_{x=0}^{x=A} \int_{y=0}^{y=B} \int_{y_L=y_0}^{y_L=y_0+L} \frac{e^{-\mu_\lambda \frac{z}{\sin\beta}}}{D^2} dy_L dy dx \qquad (2)$$

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.

c. Spectral radiant power absorbed

c1. In the case of diluted solutions, when the values of μ_λ are low ($\mu_\lambda = \varepsilon_\lambda \cdot C$), the spectral radiant power absorbed per volume unit can be calculated using the following simplified equation:

$$P_{abs} = \frac{1}{V} \sum_{\lambda} \int_{x=0}^{x=A} \int_{y=0}^{y=B} \int_{z=0}^{z=C} \int_{y_L=y_0}^{y_L=y_{0+L}} \frac{P_{emit,\lambda}/L}{4\pi D^2} \exp\left(-\mu_\lambda \frac{z}{\sin\beta}\right) \mu_\lambda \frac{dz}{\sin\beta} dy_L dx dy dz \qquad (3)$$

c2. For any concentration, particularly for high concentration values, when the values of μ_λ are high, the spectral radiant power absorbed per volume unit has to be evaluated without any simplification. In order to facilitate the solution, it is useful to divide the reactor into a number of layers n (Fig. 2) (Garvín et al., 2015):

$$P_{abs} = \frac{1}{V} \sum_{\lambda} \sum_{i(z)=1}^{i(z)=n} \int_{x=0}^{x=A} \int_{y=0}^{y=B} \int_{y_L=y_0}^{y_L=y_0+L} \frac{P_{emit,\lambda}/L}{4\pi D^2} dy_L \left[e^{-\mu_\lambda D_{i-1}} - e^{-\mu_\lambda (D-D_0)}\right] dx dy \qquad (4)$$

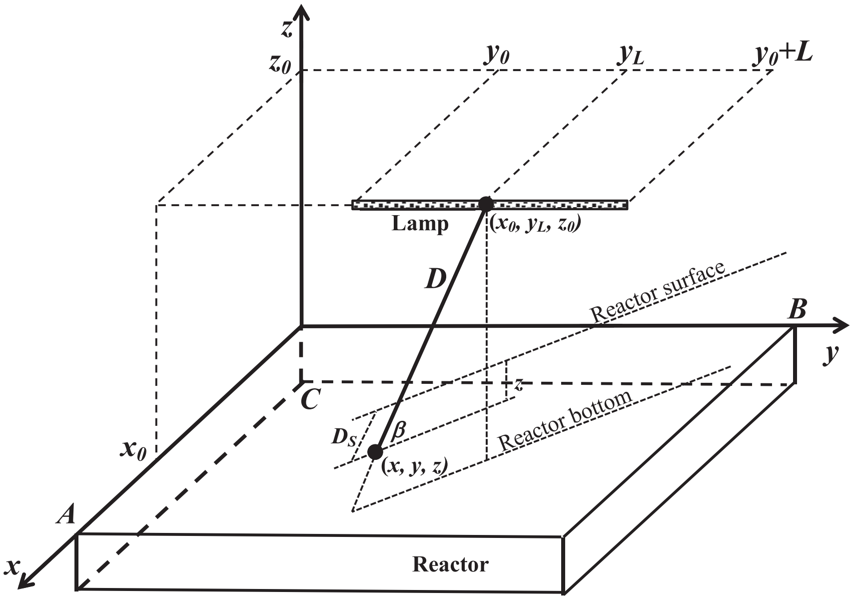

Fig. 1. Scheme of a plane photo-reactor.