Simulation of an active packaging with catalytic oxidation of ethylene for 'Cavendish' banana

Simulación de un empaque activo con oxidación catalítica de etileno para banano 'Cavendish'

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ABSTRACT

In the ripening and senescence of fruits, ethylene plays a major role and therefore, its control is essential to extend the shelf-life of these products. In this study, the kinetics of catalytic oxidation of ethylene was experimentally determined for a catalyst of gold nanoparticles supported on cerium oxides and the use of this was simulated in a perforated rigid packaging system for 'Cavendish' bananas. According to the simulations performed, for 1 kg of fruit in the active packaging 5.931 g of the obtained catalyst are needed to reduce 99% of the ethylene concentration at 12°C and with constant concentrations of 0.072 of O_2 and 0.178 of CO_2 (in molar fraction).

Key words: mathematical models, gas exchange, storage, catalysis, preservation.

RESUMEN

En los procesos de maduración y senescencia de frutas el etileno juega un papel principal, por lo que el control de la cantidad de etileno es indispensable para extender la vida útil de los productos. En este trabajo, se determinó experimentalmente una cinética de oxidación catalítica de etileno para un catalizador de nano-partículas de oro soportadas en óxido de cerio, y se acopló en la simulación de un sistema de empaque rígido activo para banano 'Cavendish'. De acuerdo a las simulaciones, para 1 kg de fruta en el empaque activo se requieren 5,931 g del catalizador a base de oro, para reducir hasta 99% de la concentración de etileno a 12°C y con concentraciones constantes de O_2 y CO_2 iguales a 0,072 y 0,178 (en fracción molar) respectivamente.

Palabras clave: modelos matemáticos, transferencia de masa, almacenamiento, etileno, preservación.

Introduction

Ethylene has a critical role in the development and ripening of climacteric fruits. In these fruits, there is a rapid increase in the autocatalytic production of ethylene resulting in the activation of a number of genes responsible for structural changes, variations of pH, development of flavor compounds, degradation of chlorophylls, synthesis of carotenoids and softening (Barry and Giovannoni, 2007; Mendoza *et al*., 2016). In non-climacteric fruits, there is no abrupt increase in ethylene production although in some products, there can be a residual production of ethylene and an effect on some of the ripening processes (Barry and Giovannoni, 2007).

Given the importance of ethylene in ripening and senescence in fruits, many methods to control it have been evaluated: changes in the expression of precursor genes responsible of its production, application of inhibitors as 1-methyl-cyclopropene (1-MCP) or silver thiosulfate, cooling and use of modified atmospheres to slow down its production rate (Mendoza *et al.,* 2016). However, usual control methods can present some difficulties in their implementation, in terms of cost, period of effectiveness, subsequent product damage or removal capacity, so it is convenient to explore new possibilities (Jiang *et al.,* 2013).

An alternative with implementation possibilities is the active removal of ethylene in the atmosphere surrounding the product by catalytic oxidation reactions. Several processes have been proposed to catalytic ethylene oxidation, however the temperatures at which the catalysts are effective were too high to have application in fruits preservation. Recently, platinum and gold nanoparticles base catalysis were used in the elimination of ethylene at under-ambient temperatures (Jiang *et al*., 2013).

In this paper, the kinetics of total oxidation of ethylene on gold nanoparticles supported on cerium oxide was experimentally developed and this kinetics was used to simulate the evolution of the ethylene concentration in the headspace of a rigid packaging containing 'Cavendish' bananas.

ISSN: 2539-4142 Doi: 10.15446/agron.colomb.sup.2016n1.58276

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Materials and methods

The kinetics of oxidation of ethylene using a gold supported on cerium oxide catalyst was experimentally obtained at various temperatures and used in simulations to represent the evolution of ethylene in the headspace of a rigid active packing with perforations under different conditions. For run the simulations, available data from literature were used to represent the gas exchange through the perforations in the packaging and the respiration and ethylene production of banana fruits (cv. Cavendish).

Catalyst preparation and estimation of the oxidation kinetics

The CeO_2 was prepared by the pseudo-sol-gel method, based on thermal decomposition of metallic propionates (Vargas *et al.*, 2005). Au particles were deposited using the anionic exchange method (Ivanova *et al.,* 2006), where an aqueous solution $1x10^{-3}$ M of $HAuCl_4$ (Sigma Aldrich) was adjusted to pH = 6.0 with NaOH 0.5 M, was heated to 70°C and then the support was added and mixed by 1.5 h. The catalyst was obtained by filtering the resulting solution, washing, dried overnight, and calcined in air at 300°C for 4 h, using a heating ramp of 2°C min^{-1}. An Au loading of 1% w/w was obtained.

To obtaining the kinetic data, a continuous tubular glass reactor packed with 0.2 g of catalyst was used. Ethylene and oxygen concentration was changed between 0.5-3.0 x 10^{-4} and 0.21-0.27 (mole fraction) respectively, and temperature was varied between 30-90°C.

In the packed tubular reactor, r_{C2H4} corresponds to the change in the molar flow of ethylene with respect to the catalyst weight used in the experiments. To fitting experimental data and describe the oxidation of ethylene, r_{oxC2H4}, the following rate kinetics was used (Russo *et al.*, 2015):

$$r_{ox\,C_2H_4} = \frac{k y_{C_2H_4} y_{O_2}^{0.5}}{\left(1 + k_{C_2H_4} y_{C_2H_4} + k_{O_2} y_{O_2}\right)^2} \quad (1)$$

Where y_{C2H4} is the ethylene concentration, y_{O2} is the oxygen concentration and k is a kinetic constant and k_{C2H4}, k_{O2} are adsorption constants for C_2H_4 and O_2. The kinetic parameters in equation 1 were estimated using the Simpson's method for solving integrals and performing a regression by the least squares method.

The dependence on temperature of k, k_{C2H4} and k_{O2} s was described using the Arrhenius' law:

$$k_i = k_{i,\,ref} EXP\left(-\frac{Ea_i}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right) \quad (2)$$

Where k_i is the kinetic parameter, k_{iref} is the reference value at T_{ref} and E_{ai} is the activation energy. The parameters were estimated by linear regression of equation 2.

Simulation of the active packaging system

In a rigid packaging with low or non-permeability to gases, it is necessary to make perforations in order to compensate the fruit respiration, trying to maintain a low O_2 level but avoiding this to be less than 1-3% to not induce deterioration (Castellanos *et al.,* 2016). For an active rigid packaging with perforations, the evolution of the ethylene level depends on the transfer of this gas through the perforations, its generation by the fruit and its active removal due a catalyzed reaction of oxidation. This process can be represented by the following equation:

$$V\frac{dy_{C_2H_4}}{dt} = K_{TRC_2H_4}\left(y^{out}_{C_2H_4} - y_{C_2H_4}\right) + \frac{N\pi d^4\left(P_{out} - P\right)}{128\mu L h} y_{C_2H_4} + r_{C_2H_4}W - r_{ox\,C_2H_4}W_{cat} - \frac{V}{P}\frac{dP}{dt} y_{C_2H_4} \quad (3)$$

Where K_{TRC2H4} is the ethylene transmission rate through the perforations, (P_{out}-P) is the pressure differential between the external atmosphere and the packaging headspace (Poiseuille's Law), r_{C2H4} is the ethylene production rate by the fruit and r_{oxC2H4} is the rate of ethylene oxidation. W is the fruit weight, V is the headspace volume, and N, d and L are number, the diameter and the effective length respectively of the perforations, μ is the air viscosity and W_{cat} is the catalyst weight included in the packing and used to oxide the ethylene. For O_2, CO_2 and N_2 similar equations as equation 3 can be written using the appropriated parameters. For this study, the parameters of ethylene production and respiration of banana fruits and the transmission rates for the different gases were previously reported by Castellanos *et al.* (2016) and Mendoza *et al.* (2016).

To perform the simulations, once the parameters for equations 1-3, were determined for C_2H_4, O_2, CO_2 and N_2, the complete system of gas-balance differential equations was numerically solved as described earlier (Mendoza *et al.,* 2016). A rigid packaging of high density polyethylene (HDPE) 1mm thick and with five perforations of 1 mm effective diameter was designed and simulated to pack 1 kg

of bananas at 12°C and 74.67 kPa. The headspace volume was 3000 cm^3 and the equilibrium concentrations (mole fraction) were 0.072 of O_2 and 0.178 of CO_2. In the simulations, the load of catalyst (W_{cat}) influence on y_{C2H4} was evaluated, to determine different percentages of removal inside the packaging system.

Results and discussion

Kinetic data

The kinetic parameters for equations 1-2 are shown in table 1. The obtained parameters have a good degree of fit with the experimental data according to the R^2_{adj} of 0.89. The activation energies for each parameter indicate a direct temperature-dependence of the kinetic parameters, even though, Au supported CeO_2 catalyst continue to be active at typical storage temperatures for fresh produce as shown below.

TABLE 1. Kinetic parameters of oxidation of ethylene with an Au (1%) supported CeO_2 catalyst (equations 1-2).

Kinetic parameters	
T_{ref} (°C)	60
k_{ref} ($cm^3\ kg_{catalyst}^{-1}\ d^{-1}$)	8.28×10^4
E_a (k_{ref}) (kJ mol^{-1})	19.46
$k_{C2H4ref}$ (mol mol^{-1})	3.93×10^3
E_a ($k_{C2H4ref}$) (kJ mol^{-1})	6.3
k_{O2ref} (mol mol^{-1})	9.2
E_a (k_{O2ref}) (kJ mol^{-1})	21.79
R^2_{adj}	0.89

Packaging simulations

In the rigid packaging with perforations, the ethylene concentration in the headspace increased due the ethylene production by the fruit and then a steady value is achieved when the ethylene produced is continuously transferred outside the packing system. This process is shown in figure 1 with a solid line. By including the catalyst, the ethylene concentration decreases according to the weight of the former; 0.073 g are needed to reduce the concentration to 50%, 0.562 g for 90% and 5.931 g for 99% as shown with dotted lines in figure 1.

Considering that ethylene can have effects on fruit ripening at concentrations between 0.1-1 × 10^{-6} (in molar fraction) (Barry and Giovannoni, 2007), in the case of banana fruits used in the simulation a reduction of at least 90% would be required for the active packaging system to be effective in preserving the product. In any case, the low amounts of catalyst required per weight of fruit would enable its use in these systems. But, experimental validation tests are needed to determine the actual catalyst efficiency and the maximum ethylene levels to delay ripening.

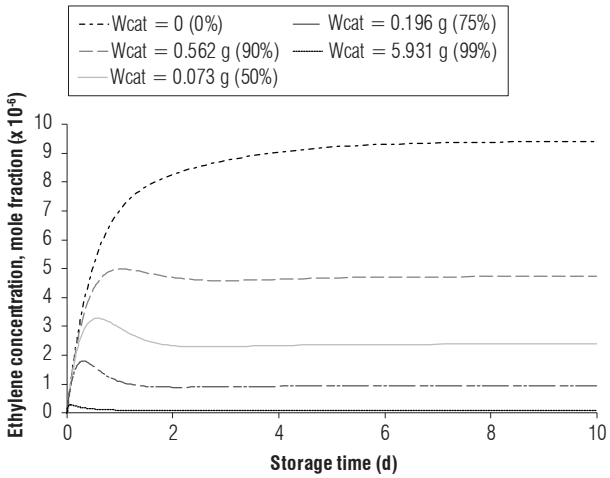

FIGURE 1. Evolution of the ethylene concentration in the packaging headspace with different catalyst weights. The percentage of reduction in the ethylene concentration is stated between brackets.

Conclusions

A gold supported cerium oxide catalyst to remove ethylene was used in the catalytic oxidation of ethylene. From the simulation data, the use of a gold base catalyst can be effective for reduce the ethylene concentration in the headspace of a perforate active packaging for banana fruits.

The data obtained in this study can be used to develop and validate a packaging system with active removal of ethylene to preserve fresh produce.

Literature cited

Barry, C.S. and J.J. Giovannoni. 2007. Ethylene and fruit ripening. J. Plant Growth Regul. 23, 143-159. Doi: 10.1007/s00344-007-9002-y

Castellanos, D.A., J. P. Cerisuelo, P. Hernández-Muñoz, A.O. Herrera, and R. Gavara. 2016. Modelling the evolution of O_2 and CO_2 concentrations in MAP of a fresh product: application to tomato. J. Food Eng. 168, 84-95. Doi: 10.1016/j.jfoodeng.2015.07.019

Ivanova, S., V. Pitchon, and C. Petit. 2006. Application of the direct exchange method in the preparation of gold catalysts supported on different oxide materials. J. Mol. Catal. A: Chem. 256, 278-283. Doi:10.1016/j.molcata.2006.05.006

Jiang, C., K. Hara, and A. Fukuoka. 2013. Low-temperature oxidation of ethylene over platinum nanoparticles supported on mesoporous silica. Angew. Chemie 52, 6265-6268. Doi: 10.1002/anie.201300496

Mendoza, R., D.A. Castellanos, J.C. García, J.C. Vargas, and A.O. Herrera. 2016. Ethylene production, respiration and gas exchange modelling in modified atmosphere packaging for banana fruits. Intl. J. Food Sci. Technol. 51, 777-788. Doi: 10.1111/ijfs.13037

Russo, V., T. Kilpiöa, J. Hernandez-Caruccia, M. Di Seriob, and T.O. Salmia. 2015. Modeling of microreactors for ethylene epoxidation and total oxidation. Chem. Eng. Sci. 134, 563-571. Doi: 10.1016/j.ces.2015.05.019

Vargas, J.C., S. Libs, A. Roger, and A. Kiennemann. 2005. Study of Ce-Zr-Co fluorite-type oxide as catalysts for hydrogen production by steam reforming of bioethanol. Catal. Today 107-108, 417-425. Doi:10.1016/j.cattod.2005.07.118