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Model for the calculation of the ethylene concentration with apples under different storage conditions*

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Jirí Létal and Jan Goliáš

Horticultural Faculty
Mendel University of Agriculture and Forestry Brno
CZ-69144 Lednice, Valticka 337

The dynamics of the ethylene concentration with apples in an experimental storage chamber under ambient atmosphere is described. To obtain an atmosphere with low ethylene concentration a catalytic oxidation of ethylene was used. The efficiency of the catalytic unit (filled with granules of palladium and copper oxide is 90 to 95 % depending on the flow of ambient atmosphere through the unit. The catalytic temperature is 320 °C. The mathematical model of ethylene dynamics is based on differential equations of first order and coincides well with experimental data. The mathematical model includes the following parameters: chamber volume, amount of fruit and their production of ethylene, efficiency of the catalytic unit and the flow of atmosphere through the unit. The mathematical equations allow the prognosis of the development of ethylene concentration in the case of continual oxidation of ethylene. For apples and the chosen experimental chamber the limit concentration of ethylene was 20 µl/l. This catalytic system seems to be useful especially for horticultural products with low production of ethylene of up to 5 µl/kg/h otherwise the flow rate of atmosphere through the catalytic unit should be much higher.

Berechnungsmodell für den Verlauf der Ethylenkonzentration bei Äpfeln unter verschiedenen Lagerungsbedingungen. *Äpfel wurden in einer Lagerzelle unter Umgebungsatmosphäre gelagert und die Veränderung der Ethylenkonzentration gemessen. Um die Ethylenkonzentration in der Lagerluft zu verringern, wurde eine katalytische Ethylen-Oxidation angewandt. Die Katalyse-Einheit war mit einem Granulat aus Palladium und Kupferoxid befüllt, die Katalyse-Temperatur war 320 °C, und in Abhängigkeit von der Durchflussrate betrug die Wirksamkeit 90 bis 95 %. Das Berechnungsmodell für den Verlauf der Ethylen-Konzentration basiert auf Differenzialgleichungen erster Ordnung und korreliert gut mit den Untersuchungsergebnissen. Das Modell schließt die folgenden Parameter mit ein: Kammervolumen, eingelagerte Obstmenge und deren Ethylenproduktion, Leistung der Katalyse-Einheit und Durchflussrate der Lagerzellenluft durch die Einheit. Die mathematischen Gleichungen ermöglichen eine Prognose des Ethylen-Konzentrationsverlaufes im Falle einer kontinuierlichen Ethylen-Oxidation. Bei Äpfeln in der ausgewählten Lagerzelle lag die höchste Ethylen-Konzentration bei 20 µl pro Liter. Dieses Katalyse-System erscheint besonders brauchbar für Früchte mit einer geringen Ethylen-Produktion von bis zu 5 µl pro Kilogramm und Stunde, ansonsten müsste die Durchflussrate durch die Katalyse-Einheit stark erhöht werden.*

Modèle de calcul du développement de la concentration d'éthylène des pommes dans des conditions de stockage différentes. *Des pommes ont été stockées dans une cellule de stockage sous atmosphère ambiante, et le changement de la concentration d'éthylène a été mesuré. Une oxydation catalytique d'éthylène a été utilisée afin de réduire la teneur en éthylène de l' air de stockage. L' unité de catalyse était remplie d' un granulat de palladium et d' oxyde de cuivre, la température de catalyse s'élevait à 320 °C et l' efficacité se situait entre 90 et 95 %, en fonction du débit. Le modèle de calcul du développement de la concentration d'éthylène est basé sur des équations différentielles de premier ordre et présente une bonne corrélation avec les résultats des examens. Le modèle tient compte des paramètres suivants : volume de la cellule de stockage, quantité de fruits stockés et leur production d'éthylène, puissance de l' unité de catalyse et débit dáir de la cellule de stockage à travers l' unité. Les équations mathématiques permettent de procéder à un pronostic du développement de la concentration d'éthylène dans le cas d' une oxydation continue d'éthylène. Pour les pommes dans la cellule de stockage choisie, la concentration maximale d'éthylène était de 20 µl par litre. Ce système semble particulièrement utile pour des fruits présentant une faible production* *d'éthylène, allant jusqu'à 5 µl par kilogramme et heure ; dans le cas contraire, il faudrait fortement augmenter le débit dáir à travers l' unité de catalyse.*

The role of ethylene in the initiation of fruit ripening is well known and its influence on artificial ripening of fruits is documented. Ethylene, which is a maturation phytohormone, appears to be an essential indicative factor for the acceleration of fruit senescence (Lelievre et al. 1997; Graell and Recasens, 1992; Blanpied, 1986) especially in the case of climacteric fruits (Gorny and Kader, 1996; Halder-Doll and Bangerth, 1987). The chemical inhibition of ethylene synthesis has also been used under different partial pressure of oxygen atmosphere (Brackmann and Saquet, 1999; Streif and Bangerth, 1978). In conventional storage chambers it is possible to maintain a low concentration of ethylene by regular periodical ventilation of atmosphere. The lowest concentration of ethylene in ventilated chambers depends on the amount of stored products, their ethylene production and the amount of ventilated air (Sherman, 1985; Goliáš and Novák, 1986).

In case of chambers with controlled atmosphere (CA) and ultra-low oxygen atmosphere (ULO) periodical washing with nitrogen should be carried out. CA-(ULO-) chambers are highly gas-tight, which causes the accumulation of ethylene even when some ethylene is absorbed in a carbon dioxide scrubber. Some activated carbon scrubbers which are used to remove carbon dioxide from CA-rooms are about ten times more effective in reducing the ethylene level in the ambient atmosphere compared to dry lime (Dilley, 1983).

The chemical sorption of ethylene by potassium permanganate are only suited for small storage rooms since the activity of the chemical is rapidly diminished and must be replaced several times during the storage period (Wojtechowski et al., 1985; Liu et al., 1986). High temperature catalytic oxidation of ethylene with relatively expensive catalytic powder is based on platinum, copper or copper/zinc compounds. The catalysis seems to be more effective with comparison to chemical sorption with potassium permanganate (El Blidi et al., 1993).

Several reports have indicated significant benefits of ethylene removal in CA storage like improvement of compactness, decrease of storage scald (Wang and Dilley, 2000; Dover, 1985; Graell and Recasens, 1992) and other physiological disorders like senescent breakdown (Liu, 1977) as well as core flush (Little et al., 1985).

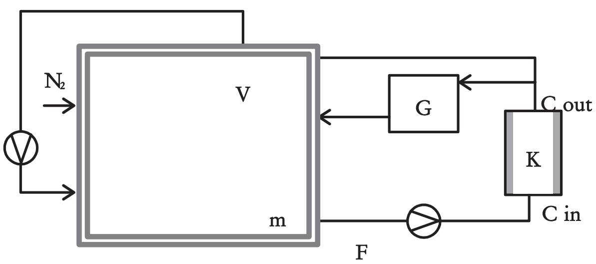
The objective of this work was to demonstrate a decrease of ethylene in ambient atmosphere in an experimental storage chamber by catalysis and to describe the dynamics of ethylene by mathematical equations. Apples of the varieties 'Golden Delicious' and 'Spartan' were stored with and without ULO conditions.

Material and methods

Experimental scheme

Apples of the varieties 'Golden Delicious' and 'Spartan' with weight *m* (kg) were stored in an experimental hermetic chamber. The atmosphere of the chamber with an effective volume *V* (l) was pumped through the catalytic scrubber *K* with the flow rate *F* (l/h). Input and output concentrations of ethylene were C_{in} and C_{out}, respectively, these values were used to calculate the efficiency of the catalytic oxidation η . The actual ethylene concentration in the low-ethylene atmosphere of the ethylene scrubber was analysed by measuring its occurence in the *G*-vessels trough which gas percolated at a defined volume rate (see Fig.1). When the chamber was hermetically closed, the starting point of catalytic oxidation was denoted as t_0.

Fig. 1: Scheme of scrubbing of ethylene in CA chamber by catalytic unit



The actual parameters of the experimental unit were as follows:

F - flow rate of atmosphere 120 l/h

V - effective volume of the chamber 1050 l

m - amount of fruit 50 kg

G - production of ethylene by fruit 41 µl/kg/h

$\eta = 1 - c_{out} / c_{in}$ - efficiency of catalytic unit 90 %

t_0 - starting point of catalysis 100 h

Measuring of the ethylene concentration

1 ml of sample was taken from the ambient atmosphere of the hermetic chamber and injected into the gas chromatograph which was equipped with a 1.2 m column filled with Porapak Q. The working temperature of the column was 78 °C with a flow rate of 12 ml/min of helium. The external calibration was done with a gauge gas, which had a concentration of 110.7 µl/l. The resulting concentration of ethylene was computed by the equation

$$c_i = \frac{A_i}{A_s} \cdot \frac{\nu_s}{\nu_i} \cdot c_s \qquad (\mu l/l) \qquad (1)$$

where:
A_i - area of ethylene peak in the sample (mV.s)
A_s - area of ethylene peak in the gauge gas (mV.s)
v_i - volume of injected sample (ml)
v_s - volume of injected standard (ml)
c_s - concentration of standard (µl/l)
Calculation of the input and output concentrations of ethylene in the catalytic unit were done similarly.

Measuring the production of ethylene by fruits

Each fruit was stored in a separated and hermetic unit with a volume of 500 ml. Using a needle valve and a capillary flow-meter, percolated gas from ethylene scrubber was passed through the storage unit with a flow rate of 30 ml/min. The air in a capillary tube was analyzed for its content of ethylene. The total production of ethylene G (µl/kg per hour) by the fruit was computed using the concentration of ethylene in percolated gas (c_i), flow rate and the weight of the fruit.

Experimental material

For the experiments apples of the two varieties 'Golden Delicious' and 'Spartan' were used. Just after harvest fruit were put into a ventilated storage chamber at a temperature of +3 °C. After half of storage time, the investigated fruit (50 kg) were placed into a hermetic chamber (volume 1050 l) and an equilibrium state between the ethylene released from the fruit and the inner atmosphere of the chamber set in. In the case of low-oxygen atmosphere pure nitrogen was pumped from a pressure tank into the storage chamber.

Catalytic oxidation of ethylene

The catalytic unit (Typ CHEROX, Fa. Chemopetrol, Litvínov, Czech Republic) was based on a ceramic skeleton of small hollow cylinders with external diameter and height of 5 mm. These ceramic granules were coated with 0.2 % of palladium and 3 % of copper oxide. The working temperature of the catalytic unit was 320 °C. For measuring the efficiency of the catalytic oxidation two different contents of catalytic granules - 28 g and 75 g - were tested with defined flow rates and 6.6 kg of apples.

Results

Theoretical model description of the ethylene dynamics

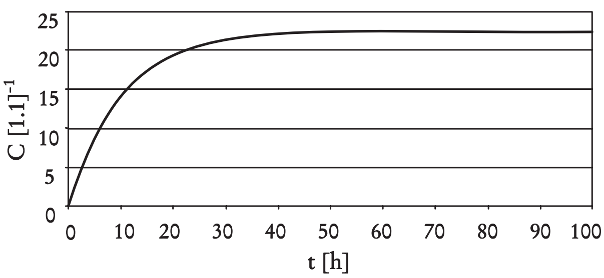
If ethylene is not continually ventilated, its concentration increases during storage. The ethylene dynamics in a chamber with ventilation of inner atmosphere or removal of ethylene by adsorption or a catalytic unit is described by the following differential equation

$$\frac{dC(t)}{dt} \quad \frac{dC(t)}{dC(t)} = (mG\text{-}F'C(t)) \qquad (2)$$

with the following graphical representation (Graph 1).
In the case of catalytic oxidation the parameter F' can be calculated with formulas 3 and 4.

$$F' = F \cdot \eta \qquad (3)$$

F' - flow rate of percolated gas through the catalytic unit
η - efficiency of catalysis



Graph 1: Development of ethylene concentration in the storage chamber in the case of continuously ethylene scrubbing

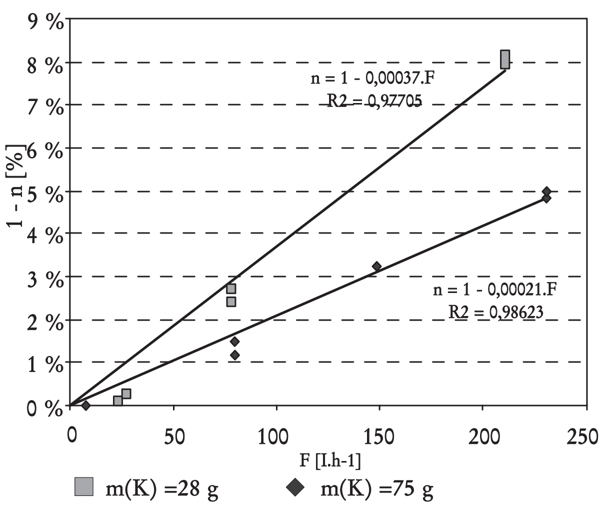
$$\eta = 1 - c_{out} / c_{in} \quad (4)$$

c_{in} - input concentration of ethylene
c_{out} - output concentration of ethylene

Efficiency of catalytic oxidation of ethylene for different flow rates

For different amounts of catalytic granules and flow rates a linear relationship between the efficiency of catalysis h and the flow rate *F'* of percolated gas through the catalytic unit exists. This relationship is shown in the graph 2 and can be expressed by the equation 5:

$$\eta = 1 - k \, . \, F \quad (5)$$



Graph 2: Relationship between the efficiency of catalysis η and flow rate *F* (l/h) for two different amounts of catalytic granules (m_0 = 28 g and m_1 = 78 g)

Comparing the experimental values, constant *k* depends on the size of the catalytic unit. The linear relationship between Δη (difference in the efficiency of catalysis) and the increase of weight of granules Δ*m* can be expressed in the following way:

$$\Delta\eta = k \, . \, F. \, \Delta m \quad (6)$$

Under our experimental conditions the estimations were k = 0,0034 and the efficiency of catalysis was η = 90 % for F = 120 l/h.

Development of ethylene concentration under delayed catalysis

Including the substitution $F' = F \, . \, \eta$ and starting point of catalysis $t = t_0$, the dynamics of ethylene in the storage chamber can be expressed by a modification of equation (2). For actual concentration of ethylene C(t) in time *t* equation (2) can be transformed into formula (7).

$$C(t) = \left(C_0 - \frac{mG}{F\eta} \right) e^{\frac{F\eta}{V}(t_0 - t)} + \frac{mG}{F\eta} \quad (7)$$

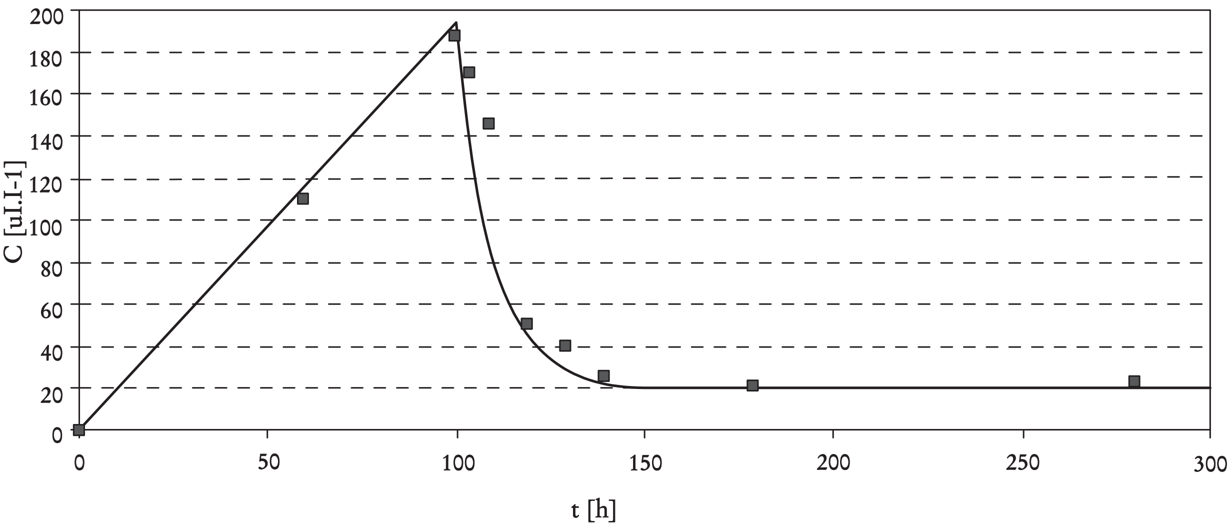
After starting the catalytic oxidation of ethylene the gas equilibrium is determined by the expression $mG / F\eta$. Thus, the limit concentration $C(t)=C$ can be expressed as

$$F = \frac{mG}{F\eta} \quad (8)$$

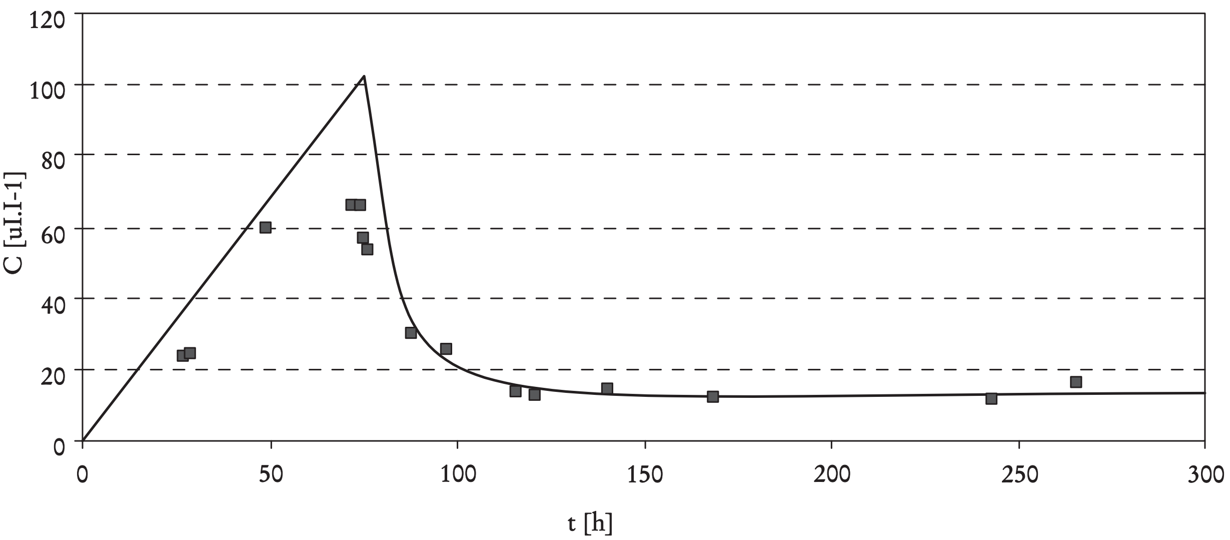
For t_0 = 100 h and according to equation (2) spontaneous production of ethylene was followed by a decrease of ethylene in the atmosphere. Theoretical values are described by the equation (7). The consistency of a theoretical model with experimental values is shown in graph 3.

Catalytic oxidation of ethylene under ULO atmosphere

As it is shown in graph 4, maintenance of low-oxygen atmosphere by washing with pure nitrogen causes a decrease of the ethylene concentration.
The theoretical model does not include the influence of maintaining ULO atmosphere (towards 0.9 % of O_2) at a concentration of ethylene in the atmosphere. Therefore at the beginning of the experiment the effective ethylene concentration was lower than the theoretical one - see graph 4. After the start of catalytic oxidation of ethylene good coincidence of the calculated values with experimental values is evident.



Graph 3: Development of ethylene concentration in the storage chamber



Graph 4: Development of ethylene concentration in case of continuous catalytic oxidation of ethylene and decreasing oxygen concentration. Starting point of catalytic oxydation was t_0=75 h

Application of a prognosis model for the ethylen concentration under practical storage conditions for products with medium ethylene production

In practice the weight of apples in CA chambers with volumes of up to 1200 m^3 varies in hundreds of tons (in large-volume boxes). For example a total amount of stored fruit m = 120 t and a weight of catalytic granules m_K = 120 kg with the efficiency η = 90 % and a flow rate of ambient atmosphere F = 200 m^3/h is supposed. According to equation (7) the concentration of ethylene will be stabilized on the level C = 5,5 µl/l after 50 h in the case of continuous catalytic oxidation of ethylene. Corresponding to storage of apples in cold chambers an ethylene production of G = 8 µl/kg per hour was suggested (Kader, 1992).

Low-ethylene atmosphere for products with low ethylene production

The described catalytic system is useful especially for horticultural products with low production of ethylene. Root vegetables e.g. produce less than 1 µl/kg of ethylene per hour (MALMARY et al., 1993). With such vegetables and application of continuous catalytic oxidation of ethylene it should be possible to maintain the limit concentration of ethylene below 0,8 µl/l (see equation (7)). By doubling the flow rate through the ethylene scrubber two times, it should be possible to maintain the limit concentration of ethylene below 0,3 µl/l.

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