

## **A Kinetic Model for Predicting Temperature in Modifier Atmosphere Packaging (MAP) for Hung Yen Longan**

**Ho Huu Phung<sup>†\*</sup>, Nguyen Viet Dung<sup>†</sup>, Nguyen Thi Minh Nguyet<sup>‡</sup>, & Nguyen Thi Hue<sup>‡</sup>**

<sup>†</sup>School of Heat Engineering and Refrigeration, Hanoi University of Science and Technology, 01 Dai Co Viet, Hai Ba Trung, Hanoi, Vietnam, 10000

<sup>‡</sup>Vietnam Institute of Agricultural Engineering and Post-Harvest Technology, 60 Trung Kinh, Trung Hoa, Cau Giay, Hanoi, Vietnam, 10000

\*Corresponding Author Email: phung.hohuu@hust.edu.vn

**ABSTRACT:** Controlling the temperature inside package is important for ensuring the quality, as well as the shelf life of the fresh fruits in the modified atmosphere package (MAP). In this paper, a kinetic model for predicting the temperature in MAP was developed. The model was based on system of differential equations of respiration heat (a Michaelis-Menten type equation), energy balances and gases transport phenomena across the package. The system equations were solved numerically using 4th-order Runge-Kutta method. The applicability of the model to in predicting temperature of MAP containing Hung Yen Longan was successfully verified with the experiment data for various types of packaging film.

**KEYWORDS:** Longan; Respiration-Transpiration; Energy balances-gases transport phenomena; MAP

### **INTRODUCTION**

Hung Yen Longan is one of eleven fruits which have the high export potential of Vietnam. However, the present technology to preserve fresh Longan after harvesting is still inadequate which leads to great loss and limitation of preservation time for export and domestic demand. To tackle this problem, low-temperature preservation technology combined with MAP which has many advantages, such as minimizing the chemical used in storage, low cost and low energy consumption, is one of the promising solutions.

The decisive factor to apply MAP technology is to control the microclimate parameters of the environment surrounding fresh produce in the packaging including: gas concentration, the average temperature of the mixture gas and the relative humidity and condensate inside the package that appears in storage time. In which, the two first parameters are used to design, package and control storage temperature. The last parameter is used to predict the relative humidity, condensate amount in packaging, which is a factor that promotes the growth of microorganisms and influence to the quality of foods.

In the past, several MAP models have been proposed in literature. But most of them are developed based on two main approaches included the empirical method (Yang and Chinnan (1988), Camerol (1989), Talasila (1992)) and reactive kinetic form of Enzim method or Michaelis-Menten oxidation reaction rate equation (Lee (1991)). The empirical method has some disadvantages since the model does not reflect the mutual influence of gas components to the respiration intensity of the preserved produce, thus the results could not archive the high accuracy. In the contrary, the other model show more advantages since it reflects the nature of respiration. Based on the proposal of Yang and Chinnan (1988), Lee (1991) has proposed the method using Michaelis-Menten equation.

Recently, describes the process of evaporation of water from the surface of the fruit by using the Dalton-type respiratory diffusion equation of produce in the MAP package [2]. However, this model does not reflect the physical nature of evaporation process of water from the surface of the fruits that is closely related to the respiration even when the relative humid reaches to saturation state. Using the other approach, demonstrated evaporation of surface water using the enthalpy equilibrium equation of the first thermal law combined with the respiratory model of produce in MAP [1, 3]. However, to apply the MAP efficiency, a respiration model which include the effect of oxidize and carbonic concentration and temperature is still needed.

In Vietnam, the method of preserving produce in MAP, especially for Longan, is limited such as the work by Hung et al. (2007), which reported a lot of experimental data but still lack of a respiration model in MAP [13].

In this work, the authors developed a respiratory model for Hung Yen longan using Michaelis-Menten equation with the factors of respiratory inhibition. The model was then compared and evaluated with the experimental results to archive the best prediction.

## MODEL DEVELOPMENT

### Respiration model

The simple form of respiration equation is defined as following:



Applying to the respiratory case of fruits in MAP, then the respiration intensity can be considered as the reaction rate of the oxidation of glucose and other organic compounds in fruits. In which,  $O_2$  is considered as a reactant, then according to the Michaelis-Menten model, we can determine the respiration rates as following:

$$R_{O_2} = \frac{V_{mO_2} \cdot [O_2]}{K_{mO_2} + [O_2]} \quad (2)$$

For some fresh fruits, both  $O_2$  and  $CO_2$  concentrations have the effect of inhibiting respiratory reactions, affecting the quality and life time of fresh produce [2]. Chang et al. (1991) proposed three type of inhibition of enzyme reaction rates included competitive inhibition, uncompetitive inhibition, non-competitive inhibition.

Based on the above three types of inhibition rates, have proposed the four types of inhibition in an enzyme kinetics models [2].

The type of "competitive inhibition" occurs when both the inhibitor and the reactant work together, when the  $CO_2$  concentration is high, the concentration of  $O_2$  increases strongly the intensity of  $O_2$  absorption. The model of competitive influence is described as follows:

$$R_{O_2} = \frac{V_{mO_2} \times [O_2]}{[O_2] + K_{mO_2} \times \left(1 + \frac{[CO_2]}{K_{mcO_2}}\right)} \quad (3)$$

Uncompetitive type occurs when  $CO_2$  inhibitors do not react with enzymes, but react with enzyme-reactive compounds. In this case, increasing the concentration of  $O_2$  at a high concentration of  $CO_2$  hardly affects the consumption of  $O_2$ . The model with non-competitive inhibition is described as follows:

$$R_{O_2} = \frac{V_{mO_2} \times [O_2]}{K_{mO_2} + [O_2] \times \left(1 + \frac{[CO_2]}{K_{muO_2}}\right)} \quad (4)$$

The "non-competitive" approach occurs when the reaction is inhibited both with enzymes and enzyme-substrate mixtures. This results, at high  $CO_2$  concentrations, that the intensity of  $O_2$  absorption will be in the range between the values obtained from the two inhibitory models described above. Non-competitive inhibition model is described in the following form:

$$R_{O_2} = \frac{V_{mO_2} \times [O_2]}{(K_{mO_2} + [O_2]) \times \left(1 + \frac{[CO_2]}{K_{mnO_2}}\right)} \quad (5)$$

In the enzymatic reactions described above, only one enzyme is involved. However, in fact, the respiratory process has many enzymes that act together. This means that a "synthetic" form is needed to describe the change in gas concentration, which can combine both types of competition inhibition and non-competitive inhibition. This type of inhibition is called a combination inhibition and is described as follows:

$$R_{O_2} = \frac{V_{mO_2} \times [O_2]}{K_{mO_2} \left(1 + \frac{[CO_2]}{K_{mcO_2}}\right) + [O_2] \times \left(1 + \frac{[CO_2]}{K_{muO_2}}\right)} \quad (6)$$

These four inhibition models will be tested for Hung Yen Longan. Then we evaluate the above models according to the level of applicable for Hung Yen Longan.

Temperature model

The internal heat source,  $Q_{int}$  is the respiratory heat of produce and can be determined as follows:

$$Q_{int} = Q_s \cdot W_s \quad (7)$$

Where,  $Q_s$  is the respiration heat and determined from equation (1). Assume that the respiratory intensity is the average of  $O_2$  consumption and  $CO_2$  evolution, then,  $Q_s$  is calculated as follows:

$$Q_s = \left( \frac{2816}{6} \right) \times \left( \frac{R_{O_2} + R_{CO_2}}{2} \right) \times \alpha \quad (8)$$

Above equation is proposed by Kang và Lee. Factor  $\alpha$  is considered as the convert factor from respiratory heat to energy and ranged from 0,8 to 1 (Burton, 1982; Powrie & Skura, 1991)

Factors  $R_{O_2}$  and  $R_{CO_2}$  is oxygen absorption intensity and carbonic emission intensity, respectively.  $R_{O_2}$  and  $R_{CO_2}$  can be calculated as follows [2÷5].

The convection heat exchange between the produce surface and the gas inside the package is expressed as follows:

$$Q_{ext} = h_s A_s (T_i - T_s) \quad (9)$$

The thermal equilibrium equation for fresh produce is built including the following thermal components: internal heat (respiratory heat), surface convection heat, latent heat of moisture escaping on the surface and current heat increases the fruit temperature [4]. The equation can be summarize as follows:

$$Q_s W_s + h_s A_s (T_i - T_s) = \dot{m}_1 \lambda + W_s C_s \frac{dT_s}{d\tau} \quad (10)$$

where,  $m_1$  is the evaporation rate from the fresh produce surface to the free gas layer in the package,  $\lambda$  is the vaporized latent heat and  $C_s$  is the specific heat capacity of produces.

During the preservation, we can consider  $T_i$  approximately equals  $T_s$ , then the equation (10) can be rewritten in a simple form as follows:

$$Q_s W_s = \dot{m}_1 \lambda + W_s C_s \frac{dT_s}{d\tau} \quad (11)$$

The energy balance equation inside the package is defined as follows [4]:

$$Q_s W_s + h_p A_p (T_o - T_i) = \dot{m}_2 \lambda + W_s C_s \frac{dT_s}{d\tau} + W_a C_a \frac{dT_s}{d\tau} \quad (12)$$

For the initial conditions:  $T_i = T_s$ , i at  $\tau = 0$ , from equation (12), change the gas temperature in the package is determined as follows:

$$\frac{dT_s}{dt} = \frac{Q_s W_s - \dot{m}_2 \lambda - h_p A_p (T_i - T_o)}{W_s C_s + W_a C_a} \quad (13)$$

where,  $h_p$  is the convective heat transfer coefficient of the packaging surface and is determined according to [4].

In summary, the temperature model consists of four nonlinear differential equations (2÷5), (16) and (13). This system is solved based on the 4th Runge-Kutta numerical method using Matlab software.

## MATERIALS AND METHODS

### Experimental subject

The subject of experiment is Hung Yen Longan. The experiment was conducted with the untreated longan fruit with the time from harvest to experiment is within 24 hours. Experimental samples were tested at the second level of maturity. Fruit were treated before preservation included removing fruits that are not properly ripened, crushed, scratched, rotten worms due to illness, birth; choosing fruit evenly for each experimental batch and cleaning mechanical impurities on the fruit surface. The fruit is stabilized in a cool place for a minimum of 12 hours and up to 24 hours before being tested. The sample of subject is shown in Figure 1.



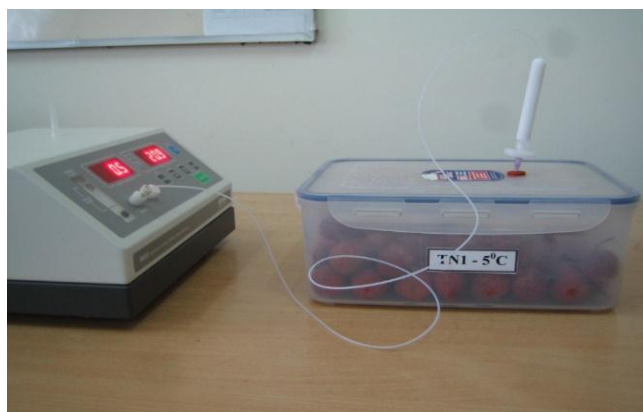
**Figure 1.** Sample of Longan

### Testing method

The method of measuring respiration rate is to measure the respiratory intensity of fresh produce in a closed system. The closed system method is performed by measuring  $O_2$  and  $CO_2$  concentrations over time in a closed container containing produce. This method is suitable for fruits and vegetables with low respiration rate and short experimental time.

The experiment was conducted in temperature mode  $4^\circ C$ . The weight of each test sample is 1.0 kg putting in a plastic container with a sealed lid and the free volume of 5000 ml, as shown in Figure 2.

The testing procedure is taken in step by step included determining the weight of material sample  $W_s$  and determining the free volume  $V$  by overflowing method. The initial and final measurements are displayed directly on the 6600 Headspace Oxygen / carbon dioxide Analyzer ( $O_2$ ,  $CO_2$ ) screen. The material is measured for 96 hours with recording interval of 2 hours.



**Figure 2.** Closed system

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In order to ensure the reliability of the measurement results, the experiments were repeated 3 times and the results were analysed by the centralized method.

## RESULTS AND DISCUSSIONS

### Respiration model

Table 1 shows the parameters for respiration model at  $4^\circ C$  using Matlab. These values are used to identify respiration models according to 4 equations (2÷5), where the  $O_2$  and  $CO_2$  concentrations over time, produce weight, and free volume in closed systems were determined by experimental results.

**Table 1.** The respiration model parameters for  $T = 4^{\circ}\text{C}$ 

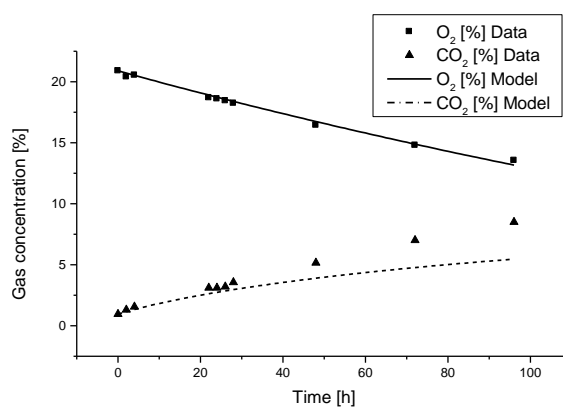
Models		$V_m$	$K_m$	$K_{mc}$	$K_{mu}$	$K_{mn}$
1	O <sub>2</sub>	5.7439	3.5887	3.7896	-	-
	CO <sub>2</sub>	8.9482	2.3870	0.2613	-	-
2	O <sub>2</sub>	27.6361	99.8063	-	19.7516	-
	CO <sub>2</sub>	8.4590	0.0001	-	2.1505	-
3	O <sub>2</sub>	6.5630	7.1096	-	-	27.2597
	CO <sub>2</sub>	8.4588	0.0001	-	-	2.1507
4	O <sub>2</sub>	5.0387	0.3726	12.9079	20.3545	-
	CO <sub>2</sub>	8.6355	0.4549	80.7827	2.1123	-

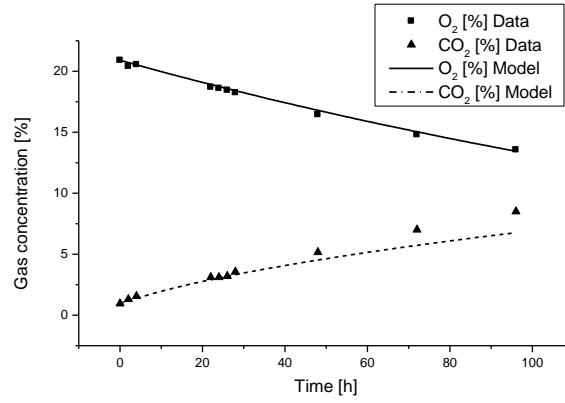
Model 1: Competitive; Model 2: Uncompetitive;

Model 3: Noncompetitive; Model 4: Combination.

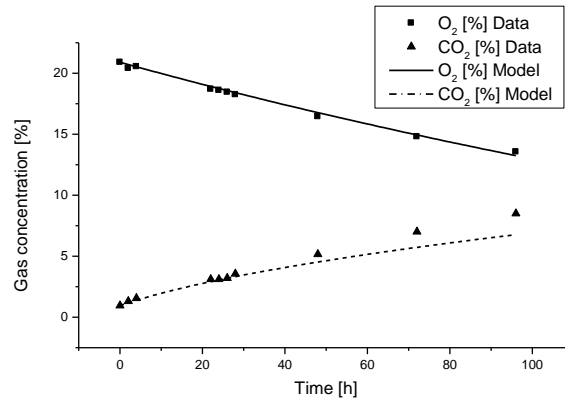
#### Validation of the respiration models

The parameters of the respiration model in Table 1 were verified by comparing the predicted gas concentration from the respiration model and the experimental results of preserving the label in the closed system at a temperature of  $4^{\circ}\text{C}$ . The predicted gas concentration from the equation (2 ÷ 5), using the Runge-Kutta method, is simulated from the Fig.3 to Fig.6.

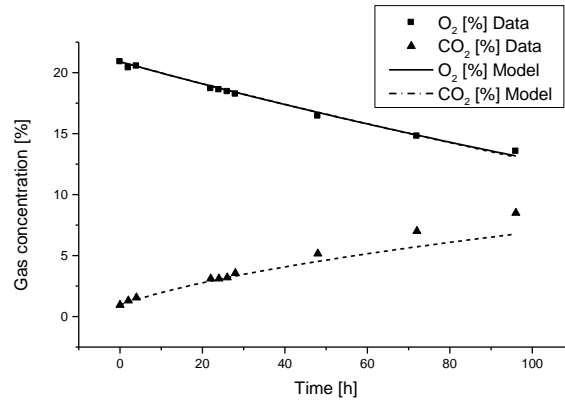

**Figure 3.** Validation of Competitive Model



**Figure 4.** Validation of Uncompetitive Model



**Figure 5.** Validation of Noncompetitive Model



**Figure 6.** Validation of Combination Model

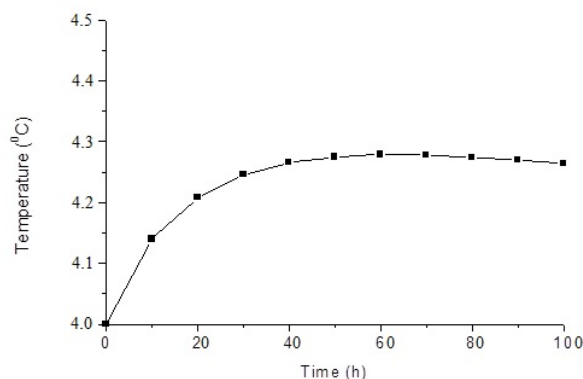
The results from the validation model show that:

- [O<sub>2</sub>], [CO<sub>2</sub>] determined from the models show the good agreement with  $R^2_{O_2} > 0.99$  and  $R^2_{CO_2} > 0.69$ .
- The average relative errors for model 1 with [O<sub>2</sub>] is 1.01%, [CO<sub>2</sub>] is 17.25%. And square error  $R^2_{O_2} = 0.9921$  and  $R^2_{CO_2} = 0.6964$ .
- The average relative errors for model 2 with [O<sub>2</sub>] is 0.95%, [CO<sub>2</sub>] is 8.50%. And square error  $R^2_{O_2} = 0.9929$  and  $R^2_{CO_2} = 0.9060$ .
- The average relative errors for model 3 with [O<sub>2</sub>] is 1.04%, [CO<sub>2</sub>] is 8.50%. And square error  $R^2_{O_2} = 0.9921$  and  $R^2_{CO_2} = 0.9060$ .

- The average relative errors for model 4 with  $[O_2]$  is 1.10%,  $[CO_2]$  is 8.50%. And square error  $R^2_{O_2} = 0.9902$  and  $R^2_{CO_2} = 0.9058$ .
- Model 2 - uncompetitive show the best prediction with  $R^2_{O_2} = 0.9921$  and  $R^2_{CO_2} = 0.9060$ ; The average relative errors, respectively:  $[O_2] = 0.95\%$ ,  $[CO_2] = 8.5\%$ , and the maximum relative errors for  $[O_2]$  is 2.10%, and for  $[CO_2]$  is 20.42%.

#### Validation of temperature model

Figure 7 illustrates the temperature field of the gas in the closed system. The results of the prediction model give the approximate results with experimental data. Thus, the application of respiration model for Hung Yen longan has been successfully verified in closed systems.



**Figure 7.** Temperature inside close system ( $t_{mt} = 4^\circ\text{C}$ )

#### CONCLUSIONS

In this paper, the respiration models for Hung Yen longan in MAP have been demonstrated. In four Michaelis-Menten models, the uncompetitive, in general, shows the best prediction with the  $R^2_{O_2} = 0.9921$  and  $R^2_{CO_2} = 0.9060$ , and the relative errors are smaller than 2.1% for  $O_2$  and smaller than 20.42% for  $CO_2$ . These are quite convincing results.

Moreover, respiration-evaporation model built on the basis of Michaelis-Menten formula combined with differential equations to express the energy equilibrium process shows the small errors. Based on that, the gas concentration prediction results, the temperature in the packaging are highly accurate and can explain the actual process.

In summary, the proposed model in present study allows to shorten the time in designing of a suitable MAP package for the characteristics of each seasonal fruit, aiming to increase quality and extend the shelf life of fresh produce in actual production.

#### NOMENCLATURES

- $[CO_2]$  : carbon dioxide concentration (%);
- $[O_2]$  : oxygen concentration (%) ;
- $K_m$  : Michaelis constant;
- $K_{mc}$  : inhibition constant for competitive model;
- $K_{mu}$  : inhibition constant for uncompetitive model;
- $K_{mn}$  : inhibition constant for noncompetitive model;
- $R_{O_2}$  : respiration rate in  $O_2$  consumption ( $\text{ml kg}^{-1} \text{h}^{-1}$ );
- $R_{CO_2}$  : respiration rate in  $CO_2$  evolution ( $\text{ml kg}^{-1} \text{h}^{-1}$ );
- $T$  : Preservation temperature ( $^\circ\text{C}$ );
- $T_i$  : temperature inside package ( $^\circ\text{C}$ )

$T_o$	: temperature outside package ( $^{\circ}\text{C}$ )
$T_s$	: temperature on surface of produce ( $^{\circ}\text{C}$ )
$T_{ii}$	: initial temperature inside the package ( $^{\circ}\text{C}$ )
$t$	: time (h);
$V$	: free volume (ml);
$V_{mO_2}$	: maximum $O_2$ consumption rate ( $\text{ml kg}^{-1} \text{h}^{-1}$ );
$V_{mCO_2}$	: maximum $CO_2$ evolution rate ( $\text{ml kg}^{-1} \text{h}^{-1}$ );
$W_s$	: weight of produce (kg).

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