A MATHEMATICAL MODEL FOR PREDICTING OPTIMAL MICRO-PERFORATED PACKAGING

By

Jin Zhang

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

Packaging-Master of Science

2015
ABSTRACT

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Micro-perforated packaging has been known to maintain the quality of fresh produce by increasing gas exchange volume through polymer films. Even though by far several mathematical models have been proposed to predict gas exchange process of micro-perforated films, to the best of author's knowledge, there are no statistical methods used to analyze the models themselves. Therefore, the aim of this research was to employ inverse problem technique (ordinary least square, sequential and bootstrap methods) to model gas exchange process of micro-perforated packaging based on a different approach, and to assess the validity of the prediction. The prediction model involved hydrodynamic flow (minor head loss theory) and diffusion flow (total pressure gradient ≠ 0). To better predict hydrodynamic flow, the entrance shape of micro perforations was analyzed under SEM. To test the prediction model, experimental data sets were evaluated together with a published data set. The predicted results had high agreement with both data groups, and all the predicted values fell within the asymptotic and bootstrap confidence and prediction bands showing the reliability of the model. Besides, the condition number (cond(J) =1) and bootstrap residual analysis further verified the validity of the model. Due to the slight difference from the reference boundary values, parameters in the model were also accurately estimated by inverse problem technique.
I dedicate this thesis to my dear parents
ACKNOWLEDGEMENTS

It took me long time to reach the end of this research. Absolutely, without the endless help from my professors, friends and family members, I would never ever finish this journey.

First of all, I would like to express my sincere gratitude to Dr. Joseph Hotchkiss for his patience and guidance during the past years. With his continual help, I gradually established systematic thinking for studying this research. I appreciate his trust in my research plan and his valuable support to my experiments.

Secondly, genuine thanks go to my committee members, Dr. Giles Brereton, Dr. Eva Maria Almenar Rosaleny and Dr. Randolph Beaudry, for their agreement on offering me an opportunity to initiate this research and sharing their works and experience to help me understand the fundamental knowledge regarding this research.

Thirdly, special thanks to Professor Kirk David Dolan in the department of Food Science and Human Nutrition for his kind help and priceless suggestions to improve my Matlab program.

Fourthly, thank you very much to Professor Susan Selke. Whenever I was under great pressure, she always considerately cared about my situation and kindly motivated me. I am lucky to have her as one of my professors.

Besides, I would like to thank my lovely friends, Hayati Samsudin, Woranit Muangmala, Noor Zainah Adzaly, Yanzhe Wu and Yangyang Huang for standing by me,
encouraging me and helping me pull through all the difficulties. I feel blessed to have them accompanying me during my tough time. We shared tears and joys. We encouraged each other. I am grateful to have them as my friends.

Last but not least, the deepest appreciation is extended to my beloved parents, Yayan Liu and Yang Zhang, for never questioning my choices and always fully supporting me throughout my life. Also, I want to thank to my grandparents on my mother’s side. They are my spiritual motivation to keep moving forward.

Jin Zhang
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KEY TO SYMBOLS

\( \frac{dC_A}{dx} \)  Concentration gradient of gas A (kg/ m^4)

\( C_{tot} \)  Total molar concentration of fluid species 1, 2, …, n (mol/L)

\( D \)  Pipe diameter (m)

\( D_{AB} \)  Molecular diffusion coefficient (m^2/hr)

\( D_{KA} \)  Knudsen diffusion coefficient for gas A (m^2/hr)

\( D_{KB} \)  Knudsen diffusion coefficient for gas B (m^2/hr)

\( D_{ij} \)  Stephan-Maxwell diffusion coefficient (m^2/hr)

\( D_{O_2N_2} \)  Diffusion coefficient of the gas mixture of O_2 and N_2 (m^2/hr)

\( D_{O_2CO_2} \)  Diffusion coefficient of the gas mixture of O_2 and CO_2 (m^2/hr)

\( F \)  Hydrodynamic flow (m^3/hr)

\( J_i \) and \( J_j \)  Individual fluxes of fluid species \( A_i \) and \( A_j \) (m^3/hr)

\( K \)  Coefficient of minor head loss

\( \ell \)  Pipe length (m)

\( M_A \) or \( M_B \)  Molar mass of component A or B (kg/mol)

\( N \)  Total number of micro pores in polymer films

\( N_A \)  Diffusion flux of gas A (m^3/hr)

\( N_B \)  Diffusion flux of gas B (m^3/hr)

\( N_{A'} \)  Combined diffusion and hydrodynamic flow of gas A (m^3/hr)

\( N_{B'} \)  Combined diffusion and hydrodynamic flow of gas B (m^3/hr)

\( N_{A^*} \)  Combined diffusion and hydrodynamic flow of gas A passing through micro perforations (m^3/hr)
$N_B^\ast$  Combined diffusion and hydrodynamic flow of gas B passing through micro perforations (m$^3$/hr)

$OTR_{static}$  Oxygen transmission rate obtained by static experimental method (m$^3$/m$^2$•hr)

$OTR_{flow}$  Oxygen transmission rate obtained by static flow through method (m$^3$/m$^2$•hr)

$p$  Difference of pressure at the ends of micro perforations (dyne/cm$^2$)

$P_{1A}$ and $P_{2A}$  Partial pressure of gas A at the top and bottom part of a micro perforation (Pa)

$P_{1B}$ and $P_{2B}$  Partial pressure of gas B at the top and bottom part of a micro perforation (Pa)

$\Delta P$  Total pressure difference between both ends of a micro perforation (Pa)

$P$  Pressure (Pa)

$P_{CO_{2,1}}$ and $P_{CO_{2,2}}$  Partial pressures of carbon dioxide in air and inside a micro perforated packaging respectively (Pa)

$P_{O_{2,1}}$ and $P_{O_{2,2}}$  Partial pressures of oxygen in air and inside a micro perforated packaging (or a glass jar) respectively (Pa)

$P_{N_{2,1}}$ and $P_{N_{2,2}}$  Partial pressures of nitrogen in air and inside a glass jar respectively (Pa)

$Q$  Volume flow rate (hydrodynamic flow) (m$^3$/m$^2$•hr)

$-\frac{\partial p}{\partial x}$  The negative gradient of hydrostatic pressure (Pa/m)

$r$  Radius of a micro perforation (m)

$R$  Gas constant (J/ K•mol)

$RR_{O_2}$  Respiration rate of oxygen consumption (m$^3$/kg•hr)

$RR_{CO_2}$  Respiration rate of carbon dioxide generation (m$^3$/kg•hr)

$t$  Time (hrs)
\( T \)  
Temperature (Kelvin)

\( \mu \)  
Dynamic viscosity (m\(^2\)/s)

\( \mu_i \)  
Chemical potential of species \( A_i \) (J/kg)

\( v \)  
Rate of volume movement (m\(^3\)/hr)

\( v_{av} \)  
Average velocity of fluid flow (m\(^3\)/hr)

\( \chi_i \) and \( \chi_j \)  
Molar fractions of fluid species \( A_i \) and \( A_j \)

\( \chi_i \)  
The \( i \)th sensitivity coefficient

\( \chi_i' \)  
The \( i \)th scaled sensitivity coefficient

\( X \)  
Length of a micro perforation (m)

\( y_A \)  
Mole fraction of gas A

\( y_{A1} \) and \( y_{A2} \)  
Mole fractions of gas A at both ends of a micro perforation

\( y_{O2,air} \)  
Molar fraction of oxygen in air

\( y_{CO2,air} \)  
Molar fraction of carbon dioxide in air

\( y_{O2,jar} \)  
Molar fraction of oxygen inside a glass jar

\( y_{N2,jar} \)  
Molar fraction of nitrogen inside a glass jar

\( y_{CO2,hs} \)  
Molar fraction of carbon dioxide in the headspace of a micro-perforated packaging

\( y_{O2,hs} \)  
Molar fraction of oxygen in the headspace of a micro-perforated packaging

\( y_{N2,hs} \)  
Molar fraction of nitrogen in the headspace of a micro-perforated packaging

\( V_A \) or \( V_B \)  
Atomic diffusion volume of component A or B (m\(^3\))

\( V_{hs} \)  
Headspace volume of a micro-perforated packaging (m\(^3\))

\( V_{jar} \)  
The volume of a glass jar (m\(^3\))
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$W$</td>
<td>Product weight (kg)</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Gas flux ratio</td>
</tr>
<tr>
<td>$\eta^*$</td>
<td>Dependent variable</td>
</tr>
<tr>
<td>$\beta$</td>
<td>A parameter vector</td>
</tr>
<tr>
<td>$\beta_i$</td>
<td>The $i$th parameter in a parameter vector</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>End correction factor</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Coefficient of viscosity (poise or dyne\cdot s/cm$^2$)</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Fluid density or fluid concentration (kg/ m$^3$)</td>
</tr>
</tbody>
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## KEY TO ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>MAP</td>
<td>Modified atmosphere packaging</td>
</tr>
<tr>
<td>Nlinfit</td>
<td>Non-linear regression</td>
</tr>
<tr>
<td>HDPE</td>
<td>High density polyethylene</td>
</tr>
<tr>
<td>OLS</td>
<td>Ordinary least square</td>
</tr>
<tr>
<td>PLA</td>
<td>Polylactic acid</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
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</table>
CHAPTER ONE:

Literature Review

1.1 Background

For fresh produce (fresh vegetables and fruits) with high respiration rate, color changes, texture alteration, off-flavor and odor development, mold growth, and nutrient loss are major issues occurred during transportation and storage (Valentas, Rotstein, & Singh, July, 1997). The rates of these deteriorating activities are significantly influenced by temperature, relative humidity, and atmosphere.

To reduce the rate of deterioration of respiring produce, a number of approaches have been implemented including temperature control (Fennema, Powrie, & Marth, 1973), optimization of gas composition (O₂, CO₂ and H₂O) surrounding food produce (Zagory & Kader, 1988, 1989) and reduction in physical damage of fresh produce (Montanez, Rodriguez, Mahajan, & Frias, 2010). Besides, packaging technology is commercially used to mitigate several aforementioned deteriorating activities.

1.2 Modified Atmosphere Packaging

Modified atmosphere packaging (MAP) is widely applied for fresh vegetables and fruits. It refers a sealed polymer packaging filled with a gas mixture with its composition (the percentages of O₂ and CO₂) that is different from normal air (Robertson, 2006; Zhuang, Barth, & Cisneros-Zevallos, 2014). The modified gas mixture normally contains high percentage of CO₂ (around 10% to 15%) (Breese et al., 2010) and low percentage of O₂ (but can not lower than 1%) (Almenar et al., 2006) to slow down deterioration process and ensure quality consistency of fresh produce inside the polymer packaging. Under this scenario, the modified gas mixture prolongs the shelf life of packaged produce (Salvador,
Jaime, & Oria, 2002). Except lengthening life span of fresh produce, other advantages of MAP are shown in Table 1.1.

MAPs can be categorized into two groups based on their gas modification process: active MAP and passive MAP. Active MAP technology uses a gas flux with predetermined gas composition to replace the air inside a packaging. Except gas replacement method, packaging processors add absorbers, scavengers or emitters into active MAPs to achieve desired gas composition (Breese et al., 2010). In passive MAPs, the modified gas composition is resulted from respiration or other metabolic activities of packaged fresh produce (Robertson, 2012). For both active and passive MAPs, permeability of packaging films makes contribution to the modification of inside gas composition as well.

Permeabilities of different packaging films are not same. Generally, the permeability of O₂ of a packaging film is smaller than the permeability of CO₂ of the film (Breese et al., 2010). The permselectivity (the ratio of CO₂ permeability coefficient to O₂ permeability coefficient of a polymer packaging) of a packaging film normally varies from 4 to 6 (Al-Ati, 2002). For packaged fresh produce with high respiration rate, O₂ consumption and CO₂ accumulation inside MAPs progress at fast speed. Within a short time period, dramatically reduced O₂ inside the packaging and a large amount of permeated CO₂ (since the permselectivity of polymer packaging ranges from 4 to 6) through the packaging create an inside environment with low concentration of O₂ and comparatively low concentration of CO₂ (Zagory, 1997). As a consequence, anaerobic activity will be initiated to accelerate degradation process of the inside fresh produce and thus shorten the shelf life of the packaged produce.
Table 1.1 Advantages of Modified Atmosphere Packaging (Sivertsvik et al., 2002, Chap 4)

<table>
<thead>
<tr>
<th>Advantages</th>
</tr>
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<tbody>
<tr>
<td>• Shelf-life increase by possibly 50–400%</td>
</tr>
<tr>
<td>• Reduced economic losses due to longer shelf-life</td>
</tr>
<tr>
<td>• Decreased distribution costs, longer distribution distances and fewer deliveries required</td>
</tr>
<tr>
<td>• Provides a high quality product</td>
</tr>
<tr>
<td>• Easier separation of sliced products</td>
</tr>
<tr>
<td>• Centralized packaging and portion control</td>
</tr>
<tr>
<td>• Improved presentation – clear view of product and all-around visibility</td>
</tr>
<tr>
<td>• Little or no need for chemical preservatives</td>
</tr>
<tr>
<td>• Sealed packages, barriers against product re-contamination and drip from package</td>
</tr>
<tr>
<td>• Odorless and convenient packages</td>
</tr>
</tbody>
</table>

1.3 Micro-perforated Packaging

1.3.1 Introduction

Micro-perforated packaging is classified as passive MAP. It is designed for fresh produce with high respiration rate. By making micro perforations (size range: 40 \( \mu m \) to 200 \( \mu m \) in diameter) (Sandhya, 2010) in the polymer films of MAPs, packaging processors create channels for exchanging \( O_2 \) and \( CO_2 \) between the inside and outside packaging environment. Consequently, aerobic activity of packaged fresh produce can be maintained. Since the ratio of gas exchange rate of \( CO_2 \) to \( O_2 \) through micro-perforated packaging films is improved close to 1, when the concentration of \( O_2 \) inside micro-perforated packaging reaches desired low level (\( O_2 \) concentration level varies according to specific type of food product), the inside \( CO_2 \) concentration accumulates at a relatively high level (within the \( CO_2 \) tolerance) (Breese et al., 2010; Gontard & Guillaume, 2010;
Zagory, 1997). The goals concerning degradation deceleration and quality assurance for the packaged fresh produce with high respiration rate can thus be achieved.

Mechanical needle, electrostatic discharge, laser and mineral fillings are the techniques packaging processors currently employed to make micro-perforated packaging. Among them, laser is widely applied due to its easiness to change the number and size of micro perforations in polymer films. Depending on specific storage and marketing conditions, the number and size of micro perforations in polymer packaging change in accordance with individual cultivar to keep produce quality. Other than developing efficient techniques to make micro perforations, packaging researchers also focus on revealing the relationship between the gas exchange volume through micro perforations in packaging films and the number, size and shape of the micro perforations by developing mathematical models. They proposed their mathematical models by presenting the agreement between their experimental results and the theoretical values computed by their models regarding gas exchange process through micro-perforated packaging, but by far, there are no statistical methods presented to support the solidity of the formulae those models employed.

1.3.2 Factors Influencing the Performance of Micro-perforated Packaging

Different produce has different physiological attribute. Based on the unique characteristics, micro-perforated packaging needs to be modified to meet particular requirements. There is no universal micro-perforated packaging, namely a fixed number of micro-perforations with a fixed diameter for all types of produce. In most cases the following aspects are considered as major factors affecting the performance of micro-perforated packaging:
(1) The number and diameter of micro perforations. These two variables directly control the volume of gases exchanging through micro perforations in packaging films. The gas exchanging volume is proportional to the number and diameter of micro perforations.

(2) The effective length of micro perforations. The thickness of polymer films determines the length to a large extent. To obtain more accurate value of effective gas flow distance, end correction factors of micro perforations in packaging films should be put into consideration.

(3) The entrance shape of micro perforations. Micro perforations with top ends surrounding by debris of polymers will introduce high air resistance and thus have less gas volumes passing through micro perforations comparing to those have flat edges of entrances.

(4) Consistency of the shape of micro perforations. It is hard to precisely adjust the gas composition inside a micro-perforated packaging with various sizes of micro perforations. In this case, the product quality of any fresh produce bagged into the package will be difficult to maintain.

(5) Respiratory activity of produce. O₂ consumption and CO₂ generation of fresh produce influence gas exchanging process through micro perforations.

To attain an optimal micro-perforated packaging for each produce, simply considering one aspect above will have great difficulty to achieve the goal. Only with thorough consideration, one may obtain a packaging solution, which will meet the requirements of the packaged produce.
1.3.3 Techniques for Making Micro perforations

1.3.3.1 Mechanical Needle

Rolls of small needles are usually made of stainless steel. As polymer films are being fed under the rolls, the needle drums press films to make micro perforations. While making perforations, the needles can be either heated or kept at room temperature (Chow, 2003). By using this method, it is more possible to have micro perforations with elliptical shape instead of round shape. Besides, if micro perforations with different densities or different sizes are required, packaging processors have to spend extra time fabricating new drums.

1.3.3.2 Electrostatic Discharge

“A packaging film is passed through high electrostatic voltage. Sparks are generated through the film, causing micro holes.” (Chow, 2003) Controlling the density of micro-perforations is the toughest job since packaging processors lack the accessibility to manually manipulate the electrostatic discharge process.

1.3.3.3 Laser

Compared to the approaches above, laser perforation is a lately introduced method. While perforating, a beam of laser light heats a polymer film until the temperature high enough to melt and eventually vaporize the film to make a micro perforation. This entire process happens within a second to obtain a micro perforation with both ends that are similar to round shape. Also, the density of micro perforations is controllable by activating laser light for different times to pierce through polymer films. Except swift process and controllable density of micro perforations, this laser technic also can make micro holes with difference sizes. Based on the demand of a specific produce, packaging
processors only need to adjust the intensity of laser light to perforate a particular size of perforation.

In order to study the improvement and influence of micro-perforated packaging on fresh perishables with high respiration and transpiration rates, laser perforation became a popular choice of packaging researchers. Only a few packaging researchers selected mechanical needle or electrostatic discharge as the way making their micro-perforated films for experimental uses (Ghosh & Anantheswaran, 2001; Samsudin, 2010).

**1.3.3.4 Mineral Filling**

According to a patented film making technology (obtained by Albert Fisher, Inc.), a large amount of mineral fillers, such as crushed calcium carbonate, are added during film extrusion process, as a result, the embedded fillers not only create micro channels or micro perforations in the polymer films, but also they change polymer characteristics, such as transparency and stiffness (Gates, 2010; Mangaraj, Goswami, & Mahajan, 2009).

**1.4 Theory of Gas flow through Micro Perforations**

Gas flux passing through micro perforations involves two general mechanics: diffusion flow and hydrodynamic flow.

**1.4.1 Diffusion Flow**

Several models of diffusion flow through micro perforations have been developed depending on specific conditions:

**1.4.1.1 Stefan-Maxwell’s Diffusion Law**

Stefan-Maxwell diffusion law is a complicated model. Scientists James Clerk Maxwell and Josef Stefan aimed at using this system to predict diffusion phenomenon of
a gas mixture of n species (Maxwell, 1868). In other words, this theory explains fluid diffusion flow with multicomponent, and it can be defined by Equation 1.1 (Bothe, 2011).

\[
\frac{x_i}{RT} \text{grad} \mu_i = - \sum_{j \neq i} \frac{x_j I_i - x_i I_j}{c_{tot} D_{ij}} \quad \text{for } i = 1, \ldots, n.
\]

(Equation 1.1)

Where

- \(x_i\) and \(x_j\) = Molar fractions of fluid species \(A_i\) and \(A_j\);
- \(\mu_i\) = Chemical potential of species \(A_i\);
- \(I_i\) and \(I_j\) = Individual fluxes of fluid species \(A_i\) and \(A_j\);
- \(c_{tot}\) = Total molar concentration of fluid species 1, 2, \ldots, n;
- \(D_{ij}\) = Stephan-Maxwell diffusion coefficient;
- \(R\) = Gas constant;
- \(T\) = Temperature;

1.4.1.2 Knudsen Diffusion Flow

As shown in Figure 1.1, airflow (composed of gas A and B) diffuses though a short micro perforation, \(P_1\) and \(P_2\) are constant total pressures at both ends of the perforation, \(D\) and \(L\) are the diameter and the thickness of the perforation respectively.

If the total pressures \(P_1\) and \(P_2\) are equal to each other, and the ratio of the perforation diameter to the mean free path of a gas molecule, \(\lambda\), is less than 0.2, Knudsen diffusion flow will occur. This type of diffusion describes the phenomenon that rather than collide with each other, gas molecules frequently collide with internal wall of perforations under
zero total pressure gradient, and it can be defined by Equation 1.2 and 1.3 (Knudsen, 1909; Knudsen & Fisher, 1910; Youngquist, 1970):

\[ N_A = - \frac{D_{KA}}{RTL} (P_{1A} - P_{2A}) \]  
(Equation 1.2)

\[ N_B = - \frac{D_{KB}}{RTL} (P_{1B} - P_{2B}) \]  
(Equation 1.3)

Where

\( N_A \) = Diffusion flux of gas A;
\( N_B \) = Diffusion flux of gas B;
\( D_{KA} \) = Knudsen diffusion coefficient for gas A;
\( D_{KB} \) = Knudsen diffusion coefficient for gas B;
\( P_{1A} \) and \( P_{2A} \) = Partial pressure of gas A at top and bottom part of the tube;
\( P_{1B} \) and \( P_{2B} \) = Partial pressure of gas B at top and bottom part of the tube;
\( R \) = Gas constant;
\( T \) = Temperature in Kelvin;
To determine mean free paths of gas molecules under specific conditions, some researchers have computed the values for a variety of gas species. Also, Roy et al. (Roy, Raju, Chuang, Cruden, & Meyyappan, 2003) established a formula for researchers to determine the values (Equation 1.4):

$$\lambda = \frac{16\mu}{5\rho \sqrt{2\pi RT}}$$

(Equation 1.4)

Where

$$\mu = \text{Dynamic viscosity;}$$

$$\rho = \text{Fluid density;}$$

$$R = \text{Gas constant;}$$
\[ T = \text{Temperature}; \]

1.4.1.3 Transitional Diffusion Flow

If keep the environmental conditions of Knudsen diffusion, but change the gas species or the diameter of the micro perforation until the ratio of \( D / \lambda \) falls between 0.2 and 20, then, transitional diffusion flow will take place. The diffusion flux of gas A, thus, can be defined by Equation 1.5 or 1.6 (Scott & Dullien, 1962):

\[
N_A = \frac{-D_{AB} \frac{dC_A}{dx} + (N_A + N_B)\gamma_A}{1 + \frac{D_{AB}}{D_{KA}}}
\]

(Equation 1.5)

Or

\[
N_A = \frac{-1}{1 - \alpha \gamma_A} \cdot \frac{dC_A}{dx} + \frac{1}{D_{AB}} + \frac{1}{D_{KA}}
\]

(Equation 1.6)

Where

\[ D_{AB} = \text{Molecular diffusion coefficient}; \]

\[ \frac{dC_A}{dx} = \text{Concentration gradient of gas A}; \]

\[ \gamma_A = \text{Mole fraction of gas A}; \]

\[ \alpha = \text{Gas flux ratio}; \]

1.4.1.4 Ordinary Molecular Diffusion Flow

If keep the environmental conditions of Knudsen diffusion, but change the gas species or the diameter of the micro perforation until the ratio of \( D / \lambda \) greater than 20,
then, ordinary molecular diffusion flow will happen. The diffusion flux of gas A, in this case, can be described as in Equation 1.7 or 1.8 (Youngquist, 1970):

\[
N_A = -D_{AB} \frac{dC_A}{dx} + (N_A + N_B)y_A
\]

(Equation 1.7)

Or

\[
N_A = \frac{D_{AB}P}{RTL \alpha} \ln \left[ \frac{1 - \alpha y_{A1}}{1 - \alpha y_{A2}} \right]
\]

(Equation 1.8)

Where

\( y_{A1} \) and \( y_{A2} \) = Mole fractions of gas A at both ends of a micro perforation;

1.4.1.5 Diffusion Flow at Total Pressure Gradient ≠ 0

When pressure difference is introduced to the top and bottom ends \((P_1 \neq P_2)\) of the micro perforation in Figure 1.1, diffusion flow and hydrodynamic flow should be considered together to evaluate gas flux through the perforation. The formulations used for determine transitional diffusion flow can be applied here to assess diffusion flow under total pressure gradient \(\neq 0\). Considering hydrodynamic flow and diffusion flow occur at same time, gas flux A can be defined by Equation 1.9 (Youngquist, 1970):

\[
N_{A}' = \frac{-D_{AB} \frac{dC_A}{dx}}{1 + \frac{D_{AB}}{D_{KA}} - \alpha y_A} + \frac{FY_A}{1 + \frac{D_{AB}}{D_{KA}}}
\]

(Equation 1.9)
And gas flux B can be determined by Equation 1.10:

\[ N'_B = -\frac{D_{AB} (1 - \alpha) \frac{dC_B}{dx}}{1 + \frac{D_{AB}}{D_{KA}} - \alpha y_A} + \frac{Fy_B}{1 + \frac{D_{AB}}{D_{KB}}} \]

(Equation 1.10)

Where

\[ N'_A = \text{Combined diffusion and hydrodynamic flow of gas } A; \]
\[ N'_B = \text{Combined diffusion and hydrodynamic flow of gas } B; \]
\[ F = \text{Hydrodynamic flow}; \]

To determine a gas flux (\(N'_A\) or \(N'_B\)) in a binary diffusion flow, the gas flux ratio, \(\alpha\), should be inversely proportional to the square root of its molecular weight (Kosov, 1982; Spiegler, 1966)

1.4.1.6 End Correction of Diffusion Flow

Stefan’s Law of 1881 states that while airflow diffusing through small apertures, the diffusion is not only proportional to the diameter of the apertures, but also, it is proportional to the difference in density measured between the underside of the pore and a point some distance away from it (Willmer & Fricker, 1996). This statement reflects the fact that normally the density of diffusion flow can be known at a point some distance away from ends of micro perforations, it is not reasonable to evaluate the diffusion flow based on the length and diameter of micro perforations only.

To examine diffusion gas flux, ‘effective diffusive pathway (\(L_{eff}\))’ should be applied. The ‘effective diffusive pathway’ refers to a micro perforation with the same cross sectional area as the actual perforation but greater length (Figure 1.2). The difference
between ‘effective diffusive pathway’ of the micro perforation and its actual length is called ‘end correction’. Its value is controlled by the diameter of the micro perforation. (Meidner & Mansfield, 1968).

**Figure 1.2** Schematic of Effective Length of Diffusion Flow (Modified from Paul & Clarke, 2002)

1.4.2 Hydrodynamic Flow

Hydrodynamic flow presents when total pressure difference along the micro perforation in Figure 1.1 exists ($P_1 \neq P_2$). It is studied for understanding fluid flow, driven by total pressure gradient, moving along tubes or pipelines.
1.4.2.1 Poiseuille’s Law

In 1840, French physiologist and physician, Poiseuille Jean-Léonard-Marie, developed Poiseuille’s law. The purpose of developing this law was to understand blood movement circulating vessels. During the experiment, Poiseuille found that the rate of fluid flow was a result of pressure difference along blood vessels, and to determine the velocity of the fluid flow moving along the long vessels, the value of the radius of vessels to the power of four \((r^4)\) must be known. Since then, Poiseuille’s law became well known due to its application in evaluating laminar flow through cylindrical and capillary tubes (Equation 1.11, Kirkham, 2004):

\[
\nu = \frac{\pi pr^4}{8X\eta}
\]

(Equation 1.11)

Where

\(\nu\) = Rate of volume movement;
\(p\) = Difference of pressure at the ends of the tube;
\(r\) = Radius of the tube;
\(X\) = Length of tube;
\(\eta\) = Coefficient of viscosity;

If convert the unit of coefficient of viscosity by applying Newton’s law, Poiseuille’s law can also be stated as in Equation 1.12 (Kirkham, 2004):

\[
\nu = -\left(\frac{\pi pr^4}{8\eta}\right)\frac{\partial P}{\partial X}
\]

(Equation 1.12)
Where

\[ r = \text{Radius of the capillary tube}; \]
\[ \eta = \text{Viscosity coefficient of the solution}; \]
\[ -(\partial P/\partial X) = \text{The negative gradient of the hydrostatic pressure}; \]

In the field of fluid mechanics, engineers modified Poiseuille’s law to study laminar flow passing through pipes as in Equation 1.13 (Munson et al., 2009):

\[ Q = \frac{\pi D^4 \Delta P}{128 \mu \ell} \]

(Equation 1.13)

Where

\[ Q = \text{Volume flow rate (hydrodynamic flow)}; \]
\[ D = \text{Pipe diameter}; \]
\[ \Delta P = \text{Total pressure difference at each end of pipe}; \]
\[ \mu = \text{Dynamic viscosity}; \]
\[ \ell = \text{Pipe length}; \]

1.4.2.2 Minor Head Loss

Hydrodynamic flow going through tubes generally causes two types of head loss: major head loss denoted as \( h_{L\text{major}} \) and minor head loss denoted as \( h_{L\text{minor}} \). Frictional effect influences major head loss. Minor head loss results from entrance shape and/or area changes of flowing path. The classifications of “major” and “minor” do not mean that one type of head loss is always important than the other one. When hydrodynamic flow goes along long and straight tubes, major head loss dominates total head loss; If
hydrodynamic flow travels through short tubes, then minor head loss will play crucial role (Fox, McDonald, & Pritchard, 2003).

The formula established for determining minor head loss is defined as in Equation 1.14 (Munson et al., 2009):

\[ \nu_{av}^2 = \frac{2\Delta P}{K \times \rho} \]

(Equation 1.14)

Where

\( \nu_{av} \) = Average velocity of fluid flow;
\( \Delta P \) = Total pressure difference at each end of pipe;
\( \rho \) = Concentration of fluid flow;
\( K \) = Coefficient of minor head loss;

There is no universal value for loss coefficient, K, fitting in any situation when minor head loss dominates. K can be determined by conducting experiments for each case, and it depends on the geometric pattern of entrance shape of a short tube. Figure 1.3 shows three typical entrance geometries. \( K \approx 0.8 \) when the tube entrance pattern belongs to the category of ‘Reentrant’; \( K \approx 0.5 \) if the tube entrance shape is grouped into ‘square-edged’; For the third condition, if the tube entrance has slightly rounded shape from cross sectional view, then \( K \approx 0.2 \), and if the entrance has well-rounded shape, \( K \approx 0.04 \). All the estimations above are derived from experimental data (Munson et al., 2009).
1.5 Current Works on Micro-perforated Packaging

Several packaging researchers have spent years on examining and evaluating the properties of micro-perforated packaging. Some of them focused on gas exchanging rates across micro perforated films with different thickness; Some of them assessed the influence of micro perforations with different sizes on gas exchanging rates through micro perforated films; The others aimed at developing mathematical models for produce to predict gas concentration change inside micro perforated packaging with time increasing.
1.5.1 Effective Diffusion pathway

During past twenty years, some packaging researchers conducted experiments to determine ‘effective diffusive pathway’ for micro perforations in polymer films. They introduced ‘end correction factors’ into their computations to establish the relationship between diameters of micro perforations and ‘end correction’ (the product of a ‘end correction factor’ and a diameter of a micro perforation is equal to ‘end correction’).

In 1994, Renault et al. (Renault, Houal, Jacquemin, & Chambroy, 1994b) emphasized the importance of introducing ‘end correction factors’ into the prediction of gas exchange rates through micro perforated packaging. They explained that the air resistance near the ends of micro perforations, resulted from accumulated polymer deposits around the ends of micro perforations, was the primary factor leading to the difference between predicted and experimental values of gas exchanging rates through micro perforated packaging. Only when introducing an ‘end correction factor’ into their evaluation, could they obtain predicted results within acceptable variance.

Table 1.2 listed experimental values of ‘end correction factors’ proposed by packaging researchers. They determined the factors by testing perforations in various sizes. Among the following evaluations, the size of perforations tested by González et al. in 2008 fell into the range of micro perforations made by packaging processors for current commercial uses.
Table 1.2 End Correction Factors Evaluated for Films With Different Thickness

<table>
<thead>
<tr>
<th>Film Thickness (L) and Diameters (D) of Micro Perforations</th>
<th>End Correction Factors $\gamma$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L = 20 \mu m, d = 2 mm;$</td>
<td>$\gamma = 0.5$</td>
<td>Fishman et al. (1996)</td>
</tr>
<tr>
<td>$0.00284 \text{ cm} \leq L \leq 0.102 \text{ cm}$</td>
<td>$\gamma = \frac{7}{6}d$</td>
<td>Paul et al. (2002)</td>
</tr>
<tr>
<td>$0.0762 \text{ cm} \leq D \leq 0.127 \text{ cm};$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$29 \mu m \leq L \leq 57 \mu m;$</td>
<td>$\gamma = 0.56$ for $\text{O}_2$;</td>
<td>González et al. (2008)</td>
</tr>
<tr>
<td>$40 \times 30 \mu m \leq D$</td>
<td>$\gamma = 0.46$ for $\text{CO}_2$;</td>
<td></td>
</tr>
<tr>
<td>$\leq 350 \times 110 \mu m;$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1.5.2 The Influence of the Dimension of Micro Perforations on Gas/Vapor Exchanging Rates

In 2003, Del-Valle et al. (Del-Valle, Almenar, Lagaron, Catala, & Gavara, 2003) concluded that gas flux going through one micro perforation with diameter of $2d$ could not have the same gas exchanging rate as the flux going through four micro perforations with diameter of $d$. This implied that gas exchanging rate through micro perforations was related to perimeter of micro perforations rather than area. Also, they stated that this relationship would be more noticeable when the diameter of micro perforations is larger than the thickness of micro perforated films.

In 2010, Gates (Gates, 2010) mentioned that no water vapor flowing through micro perforations with diameter smaller than $200 \mu m$ could be detected. Possibly, if increased the diameter of micro perforations up to $250 \mu m$ or even larger, water vapor through micro perforations would be detected. However, he did not offer any detailed explanation or experimental data to support his point of view, and his conclusion was contrary to the
experimental results obtained by Del-Valle’ group. This research group did successfully detect water vapor exchanging through micro perforations with 225 \( \mu m \) in diameter.

1.5.3 Mathematical Models for Micro-perforation Studies

Since 1991, packaging researchers started conducting experiments to study gas composition changing process inside micro-perforated packages (Del-Valle et al., 2003; Emond, Castaigne, Toupin, & Desilets, 1991; Fishman, Rodov, & Ben-yehoshua, 1996; Ghosh & Anantheswaran, 2001; González, Ferrer, Oria, & Salvador, 2008; González, Ferrer., Oria, & Salvador, 2009; Hirata, Makino, Ishikawa, Katsuura, & Hasegawa, 1996; Renault, Souty, & Chambroy, 1994a). By employing theoretical laws regarding diffusion flow and hydrodynamic flow, they established mathematical models to predict gas exchanging rates through micro-perforated films. Table 1.3 listed 7 prediction models. Even though different laws applied in these models, all the predicted values were reported having agreement with corresponding experimental results.
Table 1.3 Available Mathematical Models for Gas Exchange Prediction

<table>
<thead>
<tr>
<th>Applied Law and Model</th>
<th>Nomenclature</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modified Fick’s law:</td>
<td>$x_t = x_\alpha - (x_\alpha - x_0)e^{(K_p^*t/v)}$</td>
<td>Emond et al. (1991)</td>
</tr>
</tbody>
</table>
|                                                           | $x_t$ and $x_0$ are volumetric fractions of gas “i” inside the package at time $t$ and time 0 respectively;  
  $x_\alpha$ is volumetric fraction of gas “i” outside the package;  
  $K_p^*$ is effective permeability of gas “i” through perforations;  
  $V$ is the package total free volume;                                                                 |                         |
| Stephan Maxwell law:                                      | $-\frac{P}{RT} \frac{\partial Y_i}{\partial x} = \sum_{i\neq j}^{\infty} \Phi_{pi}Y_j - \Phi_{pj}Y_i$                                                                                              | Renault et al. (1994)   |
|                                                           | $P$ is total gas pressure;  
  $Y_i$ and $Y_j$ are molar fraction of gases “i” and “j”;  
  $\Phi_{pi}$ and $\Phi_{pj}$ are molar fluxes of gases “i” and “j” though a perforation;  
  $D_{ij}$ is binary diffusion coefficient;                                                                 |                         |
| Graham’s law and Fick’s law:                             | $Q = q_1 + q_2$;  
  $q_1 = S(\mu_1 - \mu_2)$;  
  $\frac{P \times A}{L} (p_1 - p_2)$;  
  $S$ is total area of the perforations;  
  $L$ is film thickness;  
  $A$ is effective area of the film;  
  $P$ is gas permeability coefficient;  
  $p_1$ and $p_2$ are gas pressures at both sides of polymer films;  
  $\mu_1$ and $\mu_2$ are the amount of gas molecules colliding with unit area per unit time at the gas pressures $p_1$ and $p_2$. | Hirata et al. (1996)     |
<table>
<thead>
<tr>
<th>Table 1.3 (cont’d)</th>
<th>J = − \frac{D(C - C_A)}{L_h};</th>
<th>D is diffusion coefficient of gas in air; C is partial concentration of the examined gas in packaging; C_A is oxygen concentration in ambient atmosphere; L_h is the sum of film thickness and radius of the perforation;</th>
<th>Fishman et al. (1996)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Diffusion flow and Poseuille’s law:</td>
<td>L is the thickness of polymer film; d is the diameter of micro pores; D_A, mix diffusivity coefficient of gas “A” in a gas mixture; y_A,1 molar fraction of gas “A” outside the packaging, at time 0; y_A,2(t) molar fraction of gas “A” inside the packaging, at time t; ( \sum_i J_{h,i} ) is net diffusional flow;</td>
<td>Del-Valle et al. (2003)</td>
</tr>
<tr>
<td></td>
<td>[ \Delta V_A = \frac{\pi d^2}{4L + 2d} D_{A,mix} (y_A,1 - y_A,2) \Delta t + y_A,1 \text{ or } 2 \sum_i J_{h,i} ]</td>
<td>Fick’s law:</td>
<td>González et al. (2008)</td>
</tr>
<tr>
<td></td>
<td>[ C_i - C_{i,\text{out}} = (C_i,0 - C_{i,\text{out}}) e^{-\frac{TR_i}{V}} ]</td>
<td>Ci and Ci, out are the volumetric fraction of gas “i” inside and outside the package; TR_i is gas transmission rate;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Diffusion flow and Poiseuille’s law:</td>
<td>p_i and p_{i,\text{out}} are partial pressures of gas “i” inside the package and outside the package respectively; P is pressure; J_{h,i} is flow of gas “i” through the holes; TR_i is gas transmission rate; J_{p,i} is hydrodynamic flow of gas “i” (based on the principle of Poiseuille’s law);</td>
<td>González et al. (2009)</td>
</tr>
<tr>
<td></td>
<td>[ J_{h,i} = \frac{n p_i \sum_{i=1}^{n} J_{h,i} - TR_i (p_i - p_{i,\text{out}})}{RT} + J_{p,i} ]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

All the researchers referred above, except Hirata et al., agreed that temperature, polymer thickness, the diameter of micro perforations did influence gas flux traveling through micro perforations. Hirata et al. used Graham’s law to prove that the contribution
of diameter of micro perforations could be “assumed as naught”. Therefore, they did not introduce diameter as a variable into their evaluation.

Among these researchers, Hirata et al., Emond et al., and Renault et al. didn’t solely take gas flux through micro perforations into consideration, along with this, they included gas permeation across polymer films into their researches as well.

As for the sizes of micro-perforated samples tested for above models, both macro and micro perforations were used. Table 1.4 included the sizes of perforations tested in all those models. According to the table, Emond et al. and Fishman et al. selected the sample sizes that were far more bigger than the range of micro perforations (from 40 to 200 µm in diameter) currently used in packaging field, while the other researchers did evaluate micro perforations within the range from 40 to 200 µm in diameter.

Table 1.4 Various Micro-perforated Samples Applied in Available Models

<table>
<thead>
<tr>
<th>Micro-perforation Sizes (Diameter)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>From 6000 to 11000 µm</td>
<td>Emond et al. (1991)</td>
</tr>
<tr>
<td>From 85 to 250 µm</td>
<td>Hirata et al. (1996)</td>
</tr>
<tr>
<td>2000 µm</td>
<td>Fishman et al. (1996)</td>
</tr>
<tr>
<td>80 µm</td>
<td>Renault et al. (1994)</td>
</tr>
<tr>
<td>From 40×30 to 350×110 µm</td>
<td>González et al. (2008)</td>
</tr>
<tr>
<td>From 90×50 to 200×100 µm</td>
<td>González et al. (2009)</td>
</tr>
<tr>
<td>225 µm</td>
<td>Del-Valle et al. (2003)</td>
</tr>
</tbody>
</table>

To validate predicted values estimated by mathematical models, researchers, in most cases, preferred static than flow-through method to collect experimental data with respect to the gas changing process inside micro-perforated containers.

As shown in Figure 1.4 (the apparatus setup might be modified by different packaging researchers), in static method, a micro-perforated film was attached at the top
of a container. On the body of the container, there were three ports: inlet port, outlet port and sampling port. The inlet and outlet ports were designed for allowing sweeping gas (nitrogen or helium) to flush out air inside the container. The sampling port was used to withdraw sample gas from the container at each predetermined time interval. At the beginning of a test, sweeping gas was used, then, the inlet and outlet ports were blocked immediately, after every predetermined time interval, a small amount of gas inside the container was sampled from the sampling port by using a syringe for gas composition analysis. In flow-through method (Figure 1.5), a micro-perforated film separated a container into two compartments. Both compartments have a pair of inlet and outlet ports. The upper pair was used for flushing tested gas (oxygen and/or carbon dioxide) through the upper compartment, the lower pair was used for allowing sweeping gas (nitrogen or helium) to continuously take sample gas out of the lower compartment. For each test, the gas composition of sweeping gas mixed with sample gas was analyzed at every predetermined time spot.

Compared to flow-through method, static approach provided more actual values, but the time spent for a complete test (around several days) was considered as its downside. Flow-through method did significantly cut down the time (around 2 hours), however, experimental data with less preciseness were observed (Ghosh & Anantheswaran, 2001).
**Figure 1.4** Schematic of Static Method Setup

**Figure 1.5** Schematic of Flow-through Method Setup
To obtain precise values in much shorter time span, Ghosh and Anantheswaran in 2001 developed a regression equation to interpret the relationship between static and flow-through gas exchanging rates (Equation 1.15).

\[ OTR_{static} = 1.02 OTR_{flow}^{0.964} \]

(Equation 1.15)

They proposed that it was timesaving to run flow-though system firstly to get experimental data, and then to apply the regression equation to obtain accurate experimental values. By testing micro perforations within the range of 96 to 247\,\mu m in diameter (film thickness: 50.7\pm3.23 to 76.9\pm1.61\,\mu m), Ghosh and Anantheswaran proved that their predicted gas exchange rates had agreement with their experimental data determined by Equation 1.15. By far, there were no other researchers further verify that Equation 1.15 was applicable for testing micro perforations in polymer films.

1.6 MATLAB® program simulation

Matlab® is a numerical analysis software. It paves an efficient and reliable way to study mathematical models. To provide more insights for researchers to evaluate their models, Matlab® modeling programs are coded into two parts: forward problem and inverse problem. In forward problem part, the method of scaled sensitivity coefficient is incorporated. By employing this, researchers will know the relationship between the dependent variables of their models and the involved parameters, and the approaches for parameter estimation in inverse problem part can be thus determined. In inverse problem part, numerical analysis methods such as ordinary least square, sequential estimation and bootstrap are included for parameter estimation and dependent variable prediction. Aside
from these, each method analyzes mathematical models from different aspect to indicate the reliability of tested models.

In previous works, there is no publication reported employing Matlab® software to study modeling regarding micro-perforated packaging. Therefore, this research introduced Matlab® into the field of micro-perforated packaging for gaining more insights.

1.6.1 Forward Problem

1.6.1.1 Sensitivity Coefficient and Scaled Sensitivity Coefficient

A mathematical model typically incorporates one or more parameters for establishing a connection between independent and dependent variables. In order to further understand the mathematical model, taking the first derivative of dependent variable with respect to involved parameter(s) is strongly recommended. This first derivative is named as sensitivity coefficient (Equation 1.16, Beck & Arnold, 1977):

$$X_i = \frac{\partial \eta^*}{\partial \beta_i}$$

(Equation 1.16)

Where

- $X_i =$ The $i$th sensitivity coefficient;
- $\eta^*$ = Dependent variable;
- $\beta =$ A parameter vector;

It functions as an indicator to present the magnitude of reactivity of the dependent variable to perturbing parameters. The larger the magnitude, the more sensitive the parameters to the dependent variable are. The notable perturbation helps researchers to
know within which range of independent variable, more useful experimental data can be collected accordingly while conducting experiments (Grijspeerdt & Vanrolleghem, 1999).

If two or even more sets of sensitivity coefficients are found correlated to each other, then it is impossible to estimate all the parameters at the same time, more efforts and time have to be spent on parameter estimation.

To observe and compare the reactivity of each parameter together at the same scale, a scaled sensitivity coefficient plot is needed, and the scaled sensitivity coefficient is defined as in Equation 1.17:

\[ X_i' = \beta_i \frac{\partial \eta^*}{\partial \beta_i} \]  

(Equation 1.17)

On this plot, a scaled sensitivity coefficient curve with the maximum response to the dependent variable implies that the parameter this curve represents should be the most accurate one (smallest relative error) estimated by the approaches in inverse problem part. Correlated sensitivity coefficient curves indicate the identical responses of dependent variable to the parameters. As a result, the difficulty of parameter estimation will be significantly increased (Dolan & Mishra, 2013).

1.6.2 Inverse Problem

1.6.2.1 Parameter Estimation

Parameter estimation is a statistical evaluation process to determine values of constants included in a mathematical model by using experimental data (values of dependent variable). This process is commonly known as inverse problems (Beck & Arnold, 1977). In most cases, manually estimating parameters is complicated and time consuming. It requires researchers to search and check potential statistic methods, test the
methods and then determine the most suitable approach for their calculations. For modeling study, researchers may need to run extra experiments to determine parameter of interest first. Even in some situations, researchers can find reference values for their parameters, the available data may not reflect the real conditions of the researchers’ experiments. Using Matlab® software to program modeling saves researchers from this time consuming and complicated situation. It provides an efficient way for researches to obtain the estimations. Parameters of interest can be evaluated together with prediction process of dependent variable. The built-in statistical coding of Matlab® software helps researchers compute the values in a reliable manner.

1.6.2.2 Ordinary least square (OLS)

OLS is one of the common methods in Matlab® for parameter estimation. It uses non-linear regression (known as Nlinfit for short) command built in Matlab® software. Except generating the values for parameters, standard errors and standard deviations, confidence band, prediction band, and an evaluation value called condition number cond(J) reflect the reliability and the validity of a mathematical model.

1.6.2.3 Sequential estimation

According to Beck (1977) and Dolan (2013), the sequential estimation method formed by applying the matrix inversion lemma based on the Gauss minimization method. Other than computing the same type of data generated by OLS, the crucial reason for employing this approach is that this method can examine experimental duration packaging researchers spent on their tests by analyzing parameters fluctuation trend within the range of independent variable. This examination helps researches schedule enough experimental time, that is, they need to perform their tests to the time
when the fluctuation trend of parameters reaches a constant. This valuable analysis is very helpful for researches to optimize their experiment design.

**1.6.2.4 Bootstrap**

Bootstrap is built based on Monte Carlo methods. To estimate the value of dependent variable, Bootstrap method randomly samples numbers of sets of data to form fictional data groups. Normally, 1000 times of random sampling is suggested for predicting dependent variable with more precise value. Compared to nlinfit, the narrowed confidence and prediction bands of dependent variable are considered more accurate by reason of the large quantity of sample data (Mishra, Dolan, & Yang, 2011).
CHAPTER TWO:

Objectives

The goals of this research were:

(1) Develop a predictive model of gas flow through polymer films containing micro perforations (within 40~200 μm in diameter) used for fresh produce packaging.

(2) To test the predictive model using micro-perforated films.

(3) To test the predictive model by applying experimental data published by other researchers.
CHAPTER THREE:

Materials and Methods

3.1 Materials

3.1.1 Sample Films

High density polyethylene, HDPE, film was provided from Printpack, Inc. (Jackson, TN, specification number: 190 B559-722 (Z294)). This film was specially designed for food packaging. The thickness of the film was 49.00 ± 0.0023 μm, determined by averaging five measurements with a TMI digital micrometer (Ronkonkoma, NY, model number: 49-70-01-001).

Biaxially oriented polylactic acid, PLA, film (Ingeo™ biopolymer 4042D) was obtained from NatureWorks, LLC (Minnetonka, MN). The thickness of this film was 42.60 ± 0.0023 μm, determined by averaging five measurements with a TMI digital micrometer (Ronkonkoma, NY, model number: 49-70-01-001).

3.1.2 Micro-tool

The Micro-tool used for making micro-perforations was acquired from Ted Pella, Inc. (Redding, CA). This instrument had two components: a stainless steel micro-tool handle (product number: 13675, length: 120mm, color: gold), and a long micro-needle (product number: 13061) mounted in an anodized tool cone. The micro-needle was made from first grade hardened tool steel with a shank size of 120 μm.

3.1.3 Gas Measurement Container

Cylindrical glass containers (260 ml Mason jars with silver vacuum seal lid, wide mouth, Collection Elite) were purchased from Ball Brothers Glass Manufacturing
Company (Broomfield, CO). These jars were used for examining gas exchanging process through micro-perforated sample films.

To make gas inlet and outlet ports on the lids of the glass jars, rubber vial stoppers were acquired from Zicis Group LLC (product model: 13RBS-Red-100, outer rim-to-rim diameter: 13mm, color: red). This type of stopper was designed for serum vials with 7mm mouth in diameter.

3.1.4 Gas Measurement Syringe

To examine gas composition inside the glass jars at each predetermined time interval, a Supelco 100 µl gastight syringe was ordered (product number: 509531, needle size: 23 gauge). This syringe was made by Sigma-Aldrich Corporation (Bellefonte, PA).

3.2 Methods

3.2.1 Sample Preparation

A HDPE and a PLA sample film with the surface area of $9.5 \times 10^{-3} \text{ m}^2$, a polystyrene board (thickness: $2.0 \times 10^{-2} \text{ m}$) with the area of $3.38 \times 10^{-2} \text{ m}^2$, and the micro-tool were conditioned at room temperature for 12 hours before making micro perforations. After conditioning, the sample films were attached to the polystyrene board by using pushpins and transparent tape, then, the micro-tool was vertically held to slowly pierce through the sample films to make approximately 35 micro perforations on each film at random locations.

3.2.2 Micro perforations under SEM

The sample films were prepared for SEM observation by:

(1) At room temperature, five small pieces of films with the area of $1.0 \times 10^{-4} \text{ m}^2$ each were cut from each sample film by using utility knife, and at least four
micro holes were contained on each small film. Among the five small pieces of HDPE or PLA films, three were prepared for cross sectional observation and two were prepared for top and bottom side observations.

(2) Three aluminum SEM specimen stubs (diameter: 25mm) were placed into liquid nitrogen for around ten minutes.

(3) To minimize deformation of the cross-sectional shape of micro perforations, three small pieces of HDPE films and three small pieces of PLA films were immediately placed on the SEM specimen stubs after removing from liquid nitrogen then cutting micro perforations through the center by using razor blade.

(4) The last step was adding conductive coating on polymer film. All sample films were treated by NEOC-AT Osmium Coater (Meiwafosis Co., Ltd., Osaka, Japan). Osmium plasma coating was chosen to provide finer resolution.

SEM photos were achieved by placing both the cut and uncut small films into the chamber of JEOL JSM 6610LV. 13 (JEOL, Tokyo, Japan). The top, bottom and cross sectional views of micro pores were visualized under accelerating voltage at 10 kV.

3.2.3 Gas Exchange Measurement

In the gas exchange experiment, glass jars were used as gas exchange containers. On the lid of each container, there were three ports. Two ports in same size (6 mm in diameter) were designed as gas inlet and gas outlet ports. In order to flush the container and take gas samples by using the gastight syringe, two rubber vial stoppers were placed into the ports, and waterproof silicon sealant were added at the rims of the stoppers to
prevent air leakage. The third port (13 mm in diameter) was used for attaching the micro-perforated HDPE film with epoxy glue (Figure 3.1).

At the beginning of the experiment, the micro-perforated films were fully covered by non-porous aluminum foils. Pure nitrogen was then injected from gas inlet port for flushing the glass jars until the gas composition inside the containers was ≈ 100% nitrogen. To prevent high gas pressure accumulated inside the jars and to provide exits for flush gas, the lids of the containers were loosely closed, in addition, a 18-gauge-syringe needle was inserted into gas outlet port. After flushing, the 18-gauge-syringe needle was immediately removed and the lids were tightly closed. The containers were finally kept in a temperature (23°C) and relative humidity (50%) controlled chamber under 98300 Pa environmental pressure.

At every predetermined time interval (8 hours), 100 µl gas inside each glass jar was taken from the gas outlet port. The composition of each gas sample was analyzed by a TRACE™ GC Ultra gas chromatograph (Fisher Scientific Inc, Waltham, MA) with a thermal conductivity detector (TCD) and a Supelco Carboxen 1010 PLOT capillary column (Size: 30 m (L) × 0.53 mm (I.D.), material: fused silica). Initially, the temperature of the GC oven was maintained at 45°C for 4 minutes. It then climbed up to 190°C at a ramp of 60°C/min. The temperature stayed at 190°C for 1.3 minute. 200°C and 250°C were set as the temperatures for the GC injector and detector. To quantify the gas composition of each sample, previously prepared calibration curves were employed (See appendices A and B). The final experimental results presented are the average values of three replicates.
Figure 3.1 Schematic (topside view) of the gas measurement container used for testing micro-perforated films

3.2.4 Mathematical Model

A model of gas transmission through micro perforations in packaging films was developed using MATLAB® R2012b (version 8.0, the MathWorks, Inc., MA, USA).

To predict gas exchanging process through micro-perforated packaging, the MATLAB® modeling program was coded by following steps:

3.2.4.1 Forward problem

Scaled sensitivity coefficient was employed to evaluate the magnitude of reactivity of the dependent variable to the perturbing parameter. By doing this, the parameter with
the most accurate estimation was revealed, the useful range of experimental time for researchers to collect data was known, and the correlation between sensitivity coefficient curves and the dependent variable was presented to indicate the methods needed to be applied in the second part of MATLAB® modeling program.

3.2.4.2 Inverse problem

In this part, three mathematical methods were employed to determine the parameters of the gas transmission model, to predict gas-changing process inside micro-perforated packaging, and to evaluate the reliability of the mathematical model:

3.2.4.2.1 Nlinfit

Purpose: parameter estimation, prediction of gas transmission and evaluation of reliability of the prediction model according to computed condition number cond(J) and computed confidence and prediction bands of prediction curves.

3.2.4.2.2 Sequential estimation

Purpose: estimating parameters and evaluating stability of the parameters of interest within the range of independent variable.

3.2.4.2.3 Bootstrap

Purpose: based on 1000 loops of computation to further estimate the modeling parameters, to predict gas transmission process and to evaluate the reliability of the prediction model according to generated asymptotic confidence and prediction bands and 95% of bootstrapping confidence and prediction bands of prediction curves.

3.2.5 Prediction Evaluation

There were two sets of data used for the predictive modeling program: a) a set of experimental data obtained from a gas exchange experiment, and b) a set of experimental
data published by other packaging researchers.

To test the reliability of the prediction model by using other packaging researchers’
experimental results, a group of observed values published by González et al. in 2009
were selected. In this experiment, the known values were:

- ‘Calante’ peach was selected as the evaluated produce. For this product, the
  respiratory properties in terms of carbon dioxide generation and oxygen
  consumption rates were directly adopted from the published paper (González et
  al., 2009).
- Product weight was 0.25 kg.
- The storage temperature for the produce was assumed to be steady at 277.15 K.
- The storage relative humidity was 80%.
- At initial stage, the gas composition inside packaging was identical as that of
  the atmosphere.
- Table 3.1 listed the characteristics of micro-perforated packaging used by
  González et al..

Table 3.1 Characteristics of micro-perforated packaging used by González et al. (2009)

<table>
<thead>
<tr>
<th>Film</th>
<th>Thickness (m)</th>
<th>Headspace Volume (m$^3$)</th>
<th>Environmental Pressure (Pa)</th>
<th>Number of Micro Perforations</th>
<th>Micro Perforation Dimension (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE</td>
<td>4.00×10$^{-5}$</td>
<td>4.50×10$^{-4}$</td>
<td>98792</td>
<td>2</td>
<td>90×50</td>
</tr>
</tbody>
</table>
3.2.6 Effective or Equivalent Circular Diameter

Other than evaluating the validity of the prediction model, the influences of perimeter and area of oval-shaped micro perforations on the prediction of gas exchange volume through micro perforations were evaluated.

For either $O_2$ increasing or $CO_2$ decreasing process inside micro-perforated packaging, two prediction curves under the same environmental condition were plotted together with the experimental data of the ‘Calante’ peach. One of the prediction curves was generated based on the effective diameter of micro perforations with the same perimeter as the actual micro perforations (90×50 $\mu m$), the other prediction curve was generated based on the effective diameter of micro perforations with the same area as the actual perforations. Then, at the same time spots, the predicted values on both prediction curves were compared to the corresponding experimental points. Finally, a conclusion regarding the dependence of the prediction of gas exchange volume on perimeter or area of micro perforations was drawn.
CHAPTER FOUR:

Results and Discussion

4.1 Characterization of Micro Perforations

4.1.1 SEM Images

Figure 4.1 to Figure 4.4 showed the SEM images of both top and bottom ends of the micro perforations in the HDPE and PLA sample films. On Figure 4.1 and Figure 4.2, it was obvious that the issue of heavy polymer deposit around topside of micro perforations had been avoided by applying the methods described in chapter three, however, this approach did not successfully prevent polymer deposit piling surround the bottom end of micro perforations, especially, on the HDPE films this phenomenon was evident (Figure 4.3). Despite this, these micro perforations were more uniform and less deformed than those micro perforations reported in references (Ghosh & Anantheswaran, 2001; González et al., 2008).

**Figure 4.1** Topside view of micro perforation under SEM (HDPE)
**Figure 4.2** Topside view of micro perforation under SEM (PLA)

![Topside view of micro perforation under SEM (PLA)](image)

**Figure 4.3** Bottom side view of micro perforation under SEM (HDPE)

![Bottom side view of micro perforation under SEM (HDPE)](image)
Figure 4.4 Bottom side view of micro perforation under SEM (PLA)

Figure 4.5 and Figure 4.6 showed the cross-sections of micro perforations in HDPE and PLA sample films under SEM. At the central of the figures, the images visualized in light gray scale were the cross sections of micro perforations, and the polymer films located at the left and right sides of the cross sectional parts.

Both images further proved that polymer residuals did exist at the bottom ends of micro perforations resulted in lengthened pathway of transmitted gas flux, even though there was no polymer deposit around the topside entrances. For the micro perforations in HDPE films, the tube length was elongated to 57.5 ± 2.09 µm (the thickness of polymer deposit accumulating at the bottom ends included). For the micro perforations in PLA films, the tube length was stretched to 67.9 ± 0.56 µm (the thickness of polymer deposit accumulating at the bottom ends included). These extended pathways of micro perforations implied that it should be not correct to only consider packaging film thickness as the distance of gases flowing through micro perforations. The actually pathway of gas flux was longer.
**Figure 4.5** Cross-sectional view of micro perforation under SEM (HDPE)

![Image of HDPE micro perforation](image1)

**Figure 4.6** Cross-sectional view of micro perforation under SEM (PLA)

![Image of PLA micro perforation](image2)
While trying to cut micro perforations to observe cross sections, the SEM specimen stubs pretreated by liquid nitrogen temporarily froze the sample films placed on them. This proposed method did effectively avoid film distortion, but two problems were emerged. The technic indeed enhanced the stiffness of polymer films, nevertheless, it leaded to significantly hazed polymer surface. In this situation, it was tough to cut the films right at the middle of every targeted micro perforation, unqualified sample perforations were thus detected under SEM. Besides, the razor blade deformed a couple of cross sections, qualified samples were, in this case, lessened. In future works, an advanced method may be needed for better understanding the geometric properties of micro perforations.

Table 4.1 recorded the average diameters of micro perforations in the HDPE and PLA sample films. Due to the issues explained above, only 4 micro perforations could be counted in the PLA samples, and 12 cross sections were identified in the HDPE samples.

Table 4.1 Diameters of Micro-perforations on HDPE and PLA films

<table>
<thead>
<tr>
<th></th>
<th>HDPE</th>
<th>PLA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perforation Numbers</td>
<td>12</td>
<td>4</td>
</tr>
<tr>
<td>Average Diameter</td>
<td>54.92 µm</td>
<td>110.50 µm</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>8.46 µm</td>
<td>4.60 µm</td>
</tr>
</tbody>
</table>

The significant variance between the diameters of micro perforations in the two types of films indicated that surface tension of polymer film, polymer processing procedure,
orientation of polymer films or additives in polymer films may influence the size of micro perforations and thus the volume of gas transmission.

4.1.2 Evaluation of Minor Head Loss Coefficient $K$

Since the entrance shapes of micro perforations presented in Figure 4.5 and 4.6 had no exact counterparts shown in Figure 1.3, it was merely reasonable to infer that the values of minor head loss coefficients, $K_s$, for both types of the micro tubes should be around 0.04 to 0.2. The MATLAB® modeling program could further determine more precise values while predicting gas transmissions volume through the micro-perforated polymer films.

4.2 Predictive Model

4.2.1 Mathematical Model

In 1994, Renault et al. (Renault et al., 1994a) recorded that during their experiment of micro-perforated packaging, the pressure difference (between the surrounding environment and inside packaging) caused by a small volumetric decrement of examined packaging could be frequently observed. This phenomenon indicated that during the gas transmission process through micro-perforated packaging, hydrodynamic flow and diffusion flow existed at the same time. This inference agreed with the standpoint proposed by Paul et al. (Paul & Clarke, 2002) and Del-Valle et al (Del-Valle et al., 2003). On account of this, the formulae used for determining gas diffusion flow at nonzero pressure gradient (Equation 1.5, 1.6 and 1.7) should be applied for this research.

While considering hydrodynamic flow and diffusion flow together as the total gas flux traveling through micro perforations in packaging films, Equation 1.9 and 1.10 were regarded as the suitable formulae:
For gas A in a gas mixture (Youngquist, 1970):

\[
N'_A = \frac{-D_{AB} \frac{dC_A}{dx} + F y_A}{1 + \frac{D_{AB}}{D_{KA}} - \alpha y_A} + \frac{D_{AB}}{D_{KA}}
\]

(Equation 1.9)

And for gas B in the gas mixture:

\[
N'_B = \frac{-D_{AB} (1 - \alpha) \frac{dC_B}{dx} + F y_B}{1 + \frac{D_{AB}}{D_{KA}} - \alpha y_A} + \frac{D_{AB}}{D_{KB}}
\]

(Equation 1.10)

For this research, when gas transmission process of micro-perforated packaging reached steady state, Equation 1.9 and Equation 1.10 could be integrated as Equation 4.1 and 4.2:

For gas A in a gas mixture:

\[
N_A^* = \frac{\pi D^2}{4} D_{AB} \frac{(P_{1A} - P_{2A})}{RT(L + \gamma D)} + \frac{Q \times y_A}{1 + \frac{D_{AB}}{D_{kA}} - (\alpha) y_A}
\]

(Equation 4.1)

For gas B in the gas mixture:

\[
N_B^* = \frac{\pi D^2}{4} D_{AB} (1 - \alpha) \frac{(P_{1B} - P_{2B})}{RT(L + \gamma D)} + \frac{Q \times y_B}{1 + \frac{D_{AB}}{D_{kA}} - (\alpha) y_A}
\]

(Equation 4.2)

Where

\[N_A^* = \text{Combined diffusion and hydrodynamic flow of gas A passing through micro perforations;}\]
\[ N_B^* = \text{Combined diffusion and hydrodynamic flow of gas B passing through micro perforations;} \]

\[ Q = \text{Volume flowrate;} \]

\[ \gamma = \text{End correction factor;} \]

In 2008, González et al. (González et al., 2008) experimentally determined ‘end correction factors’ for micro perforations within the range of \(40 \times 30 \text{ µm} \leq D \leq 350 \times 110 \text{ µm}\). They proposed that their ‘end correction factors’ (0.56 for \(O_2\) and 0.46 for \(CO_2\)) resulted in better prediction curves of gas transmission flux through micro perforations. As the dimension of the micro perforations González’s group evaluated fell within the dimension range of the micro perforations commercially used in packaging films (\(40 \leq D \leq 200 \text{ µm}\)), the value of ‘end correction factor’ for \(O_2\) suggested by González et al. was thus introduced into this prediction model for the evaluation. For the ‘end correction factor’ for \(CO_2\), 0.46 was used for evaluating gas exchange experiment and 0.44 (González et al. proposed in 2009) was used for evaluating González’s experimental data.

To determine the hydrodynamic flow \(F\) in Equation 1.9 and 1.10, the gas law about minor head loss fits better in the case of micro-perforated packaging than Poiseuille’s law. Poiseuille’s law is only valid for laminar fluid flow. It focuses on fluid flow going through long and straight pipes. The ratio of the length of a pipe (\(L\)) to its diameter is no less than 20 (Marquardt, 2009). As the schematic presented in Figure 4.7a, when a gas flux travels through a long pipe, the fluid flow gradually forms a fully developed parabolic velocity profile owing to gas viscosity and shear stress. Under this circumstance, the flowing gas flux at pipe wall has the smallest speed (zero), and its
velocity increases to the largest rate at the centerline of the pipe. Eventually, the flow possesses characteristics of laminar flow (Fox et al., 2003).

Unlike the model of Poiseuille’s law, the tube type applied in the study of minor head loss is different. Like the graphic shown in Figure 4.7b, the diameter of tubes in this case is comparatively larger than the length of the tubes, hence, gases flowing through such tubes or pipes are possibly hard to have velocity profiles with fully developed parabolic shape due to the limited pathway.

Talking about the micro perforations in packaging films, the length of the micro perforations is limited. It is normally less than the diameter of the micro perforations ($40 \leq D \leq 200 \mu m$). Because of this fact, the theory of minor head loss was employed into this mathematical model for predicting hydrodynamic flow.
Figure 4.7 Schematic of Poiseuille’s Model and Minor Head Loss Model

a. Poiseuille’s Pipe Model (Munson et al., 2009)

b. Minor Head Loss Model

For the convenience, the equation regarding using minor head loss (Equation 1.14) to determine hydrodynamic flow through one short tube can be modified as Equation 4.3:

\[
Q = \frac{\pi D^2}{4} \sqrt{\frac{2\Delta P}{\rho K}}
\]

(Equation 4.3)

If combine Equation 4.1, 4.2 and 4.3, gas flux going through micro-perforated polymer films could be defined as:
For gas A in a gas mixture:

\[
N_A^* = \frac{\pi D^2}{4} D_{AB} \frac{(P_{1A} - P_{2A})}{RT (L + \gamma D)} + \frac{\pi D^2}{4} \frac{2 \Delta P}{\rho K} \times y_A
\]

\[
1 + \frac{D_{AB}}{D k_A} - (\alpha) y_A
\]

(Equation 4.4)

For gas B in the gas mixture:

\[
N_B^* = \frac{\pi D^2}{4} D_{AB} (1 - \alpha) \frac{(P_{1B} - P_{2B})}{RT (L + \gamma D)} + \frac{\pi D^2}{4} \frac{2 \Delta P}{\rho K} \times y_B
\]

\[
1 + \frac{D_{AB}}{D k_A} - (\alpha) y_A
\]

(Equation 4.5)

To evaluate the experimental data obtained from the gas exchange experiment, it was assumed that O\textsubscript{2} and N\textsubscript{2} were the targeted gases, uniformly spread inside the entire glass jars. The hydrodynamic flow together with the diffusion flow though micro perforations in the HDPE films contributed 100% of gas exchange volume between outside environment and inside environment of the glass jars. In other words, the gas exchange volume across polymer films was regarded as negligible.

Hence, Equation 4.4 and Equation 4.5 could be defined as:

For gas flux of O\textsubscript{2} through micro perforations:

\[
N_{O_2} = -\frac{N \pi D^2}{4} \times D_{O_2} N^2 \frac{(P_{O_2,1} - P_{O_2,2})}{RT (L + 0.56D)} + \frac{N \pi D^2}{4} \frac{2(P_1 - P_2)}{\rho K} \times y_{O_2,hs}
\]

\[
1 + \frac{D_{O_2} N^2}{D k_{O_2}} - (\alpha) y_{O_2,hs}
\]

(Equation 4.6)
For gas flux of N\textsubscript{2} through micro perforations:

\[
N_{N_2} = -\frac{N\pi D^2}{4} \times D_{O2N_2} (1 - \alpha) \frac{(P_{N_2,1} - P_{N_2,2})}{RT(L + \gamma D)} + \frac{N\pi D^2}{4} \frac{2(P_1 - P_2)}{\rho K} \times y_{N_2,hs} \frac{1 + \frac{D_{O2N_2}}{DK_{O2}}}{1 + \frac{D_{O2N_2}}{DK_{N_2}}}
\]

(Equation 4.7)

Where

\[y_{O_2,hs} = \text{Molar fraction of oxygen in headspace;}
\]
\[y_{N_2,hs} = \text{Molar fraction of nitrogen in headspace;}
\]
\[P_{O_2,1} \text{ and } P_{O_2,2} = \text{Partial pressures of oxygen in air and inside the glass jars respectively;}
\]
\[P_{N_2,1} \text{ and } P_{N_2,2} = \text{Partial pressures of nitrogen in air and inside the glass jars respectively;}
\]
\[D_{O2N_2} = \text{Diffusion coefficient of the gas mixture of O}_2 \text{ and CO}_2;
\]
\[N = \text{Total number of micro pores in polymer films;}
\]

Finally, gas-changing process inside the glass jars could be defined as:

For the gas dynamics of O\textsubscript{2}:

\[V_{O_2,jar(t)} = V_{jar} \times y_{O_2,hs}
\]

\[= V_{jar} \times y_{O_2,hs} + t(\frac{-N\pi D^2}{4} \times D_{O2N_2} \frac{(P_{O_2,1} - P_{O_2,2})}{RT(L + 0.56D)} + \frac{N\pi D^2}{4} \sqrt{\frac{2(P_1 - P_2)}{\rho K}} \times y_{O_2,hs} \frac{1 + \frac{D_{O2N_2}}{DK_{O2}}}{1 + \frac{D_{O2N_2}}{DK_{N_2}}})
\]

(Equation 4.8)
For the gas dynamics of $N_2$:

$$V_{N_2,\text{jar}}(t) = V_{\text{jar}} \times y_{N_2,hs}$$

$$+ t \left( -\frac{N\pi D^2}{4} \times D_{O_2N_2} (1 - \alpha) \left( \frac{P_{N_2,1} - P_{N_2,2}}{RT(L + yD)} \right) + \frac{N\pi D^2}{4} \sqrt{\frac{2(P_1 - P_2)}{\rho K}} \times y_{N_2,hs} \right)$$

(Equation 4.9)

Where

- $V_{\text{jar}}$ = The volume of the glass jar;
- $y_{O_2,\text{jar}}$ = Molar fraction inside the glass jar;
- $y_{N_2,\text{jar}}$ = Molar fraction inside the glass jar;
- $\gamma$ = End correction factor for nitrogen passing through micro perforations;
- $t$ = Time;

Similarly, to evaluate González et al.’s experimental data, it was assumed that $O_2$ and $CO_2$ were the targeted gases, uniformly spread inside the entire package. The hydrodynamic flow together with the diffusion flow through micro perforations in packaging films contributed 100% of gas exchange volume between outside environment and inside environment of packaging. In other words, the gas exchange volume across polymer films was regarded as negligible.

If considering respiratory activity of a produce inside micro-perforated packaging, then Equation 4.4 and Equation 4.5 could be defined as:
For gas flux of $O_2$ through micro perforations:

$$N_{O_2} = \frac{N\pi D^2}{4} \times D_{O_2} \left( \frac{P_{O_2,1} - P_{O_2,2}}{RT(L + 0.56D)} \right)$$

$$1 + \frac{D_{O_2} D_{O_2}}{D_{k_{O_2}}} - (\alpha)y_{O_2,hs}$$

$$+ \frac{N\pi D^2}{4} \sqrt{\frac{2(P_1 - P_2)}{\rho K}} \times y_{O_2,hs}$$

$$1 + \frac{D_{O_2} D_{O_2}}{D_{k_{O_2}}} - RR_{O_2} W y_{O_2,hs}$$

(Equation 4.10)

For gas flux of $CO_2$ through micro perforations:

$$N_{CO_2} = \frac{N\pi D^2}{4} \times D_{CO_2} \left( 1 - \alpha \right) \left( \frac{P_{CO_2,1} - P_{CO_2,2}}{RT(L + 0.44D)} \right)$$

$$1 + \frac{D_{CO_2} D_{CO_2}}{D_{k_{CO_2}}} - (\alpha)y_{O_2,hs}$$

$$+ \frac{N\pi D^2}{4} \sqrt{\frac{2(P_1 - P_2)}{\rho K}} \times y_{CO_2,hs}$$

$$1 + \frac{D_{CO_2} D_{CO_2}}{D_{k_{CO_2}}} + RR_{CO_2} W y_{CO_2,hs}$$

(Equation 4.11)

Where

$y_{CO_2,hs} = \text{Molar fraction of carbon dioxide in headspace;}

P_{CO_2,1} \text{ and } P_{CO_2,2} = \text{Partial pressures of carbon dioxide in air and inside the packaging respectively;}

D_{O_2} = \text{Diffusion coefficient of gas mixture of } O_2 \text{ and } CO_2;\n
RR_{O_2} = \text{Respiration rate of oxygen consumption;}

RR_{CO_2} = \text{Respiration rate of carbon dioxide generation;}

W = \text{Product weight;
Finally, gas-changing process inside micro-perforated packaging for fresh produce could be defined as:

For the gas dynamics of $\text{O}_2$:

$$ V_{O_2,hs(t)} = V_{hs} \times y_{O_2,air} $$

$$ = \frac{N \pi D^2}{4} \times D_{O_2CO_2} \frac{(P_{O_2,1} - P_{O_2,2})}{RT(L + 0.56D)} + t\left(1 + \frac{D_{O_2CO_2}}{Dk_{O_2}} - (\alpha)y_{O_2,hs}\right) $$

$$ + \frac{N \pi D^2}{4} \sqrt{\frac{2(P_1 - P_2)}{\rho K}} \times y_{O_2,hs} $$

$$ + \frac{RR_{O_2} W y_{O_2,hs}}{1 + \frac{D_{O_2CO_2}}{Dk_{O_2}}} \right) $$

(Equation 4.12)

For the gas dynamics of $\text{CO}_2$:

$$ V_{CO_2,hs(t)} = V_{hs} \times y_{CO_2,air} $$

$$ = \frac{N \pi D^2}{4} \times D_{CO_2CO_2} (1 - \alpha) \frac{(P_{CO_2,1} - P_{CO_2,2})}{RT(L + 0.44D)} + t\left(1 + \frac{D_{CO_2CO_2}}{Dk_{CO_2}} - (\alpha)y_{O_2,hs}\right) $$

$$ + \frac{N \pi D^2}{4} \sqrt{\frac{2(P_1 - P_2)}{\rho K}} \times y_{CO_2,hs} $$

$$ + \frac{RR_{CO_2} W y_{CO_2,hs}}{1 + \frac{D_{CO_2CO_2}}{Dk_{CO_2}}} \right) $$

(Equation 4.13)
Where

\[ V_{hs} = \text{Headspace volume of micro-perforated packaging;} \]
\[ y_{O_{2,air}} = \text{Molar fraction of oxygen in air;} \]
\[ y_{CO_{2,air}} = \text{Molar fraction of carbon dioxide in air;} \]

### 4.2.2 Parameters of interest

In Equation 4.8 and 4.9, the parameters of interest are:

- \( Dk_{O_2} \), Knudsen diffusion coefficient of \( O_2 \)
- \( Dk_{N_2} \), Knudsen diffusion coefficient of \( N_2 \)
- \( D_{O_2N_2} \), Diffusion coefficient of the gas mixture of \( O_2 \) and \( CO_2 \)
- \( K \), Minor loss coefficient
- \( \gamma \), End correction factor for nitrogen passing through micro perforations.

In Equation 4.12 and 4.13, the parameters of interest are:

- \( Dk_{O_2} \), Knudsen diffusion coefficient of \( O_2 \)
- \( Dk_{CO_2} \), Knudsen diffusion coefficient of \( CO_2 \)
- \( D_{O_2CO_2} \), Diffusion coefficient of gas mixture of \( O_2 \) and \( CO_2 \)
- \( K \), Minor loss coefficient

### 4.3 Evaluation of Prediction Model

#### 4.3.1 Gas Exchange Experiment

In the gas exchange experiment, gas transmissions through 2 and 3 micro perforations in the HDPE sample films were tested respectively (See appendix C for experimental data of the gas exchange experiment) to evaluate Equation 4.8 and 4.9. Figure 4.8 and 4.10 showed \( N_2 \) changing process inside the glass jars, and Figure 4.9 and Figure 4.11 presented \( O_2 \) changing process inside the glass jars. According to these
Figures, the mathematical model (Equation 4.8 and 4.9) predicted that at 88\textsuperscript{th} hour, the gas composition inside the glass jars with 2 micro perforations in the sample films would reach steady state. This agreed with the experimental results. For the glass containers with 3 micro perforations in the HDPE films, the experimental observations proved that the mathematical model predicted the correct time for O\textsubscript{2} reaching steady state, but there was a small gap between the observed and the predicted times for N\textsubscript{2} getting to steady state. The theoretical value lagged around 3-hour behind. Also, different dropping speeds of the N\textsubscript{2} volume inside the glass jars with 3 micro holes in the HDPE sample films were noticed in Figure 4.10 (0 to 20 hours). While testing the micro perforated films, every amount of examined gas (target volume: 100\(\mu\)l) withdrawn from the glass jars, sampling speed at each time (comparatively faster sampling speed could cause unexpected fluctuation of pressure gradient along the micro perforations), and consistency of the GC analysis were considered as major aspects brought about variances, which might explain the predicted quicker speed of N\textsubscript{2} depletion and other differences between the experimental and predicted results in Figure 8 to Figure 11.

In spite of these facts, the 90\% prediction band computed by the mathematical model incorporated all the observation data, and the predicted N\textsubscript{2} reducing curve located at the centerline of the 99\% confidence band showing its small difference from the sample mean of N\textsubscript{2} data (Figure 4.12).

The estimations of the parameters of interest (Table 4.2) further proved the reliability of the mathematical model (Equation 4.8 and 4.9). The analyzed result of minor head loss coefficient, K, supported aforementioned estimation—the coefficient of the micro perforations in HDPE sample films should be between 0.04 and 0.2. As the estimation
was closer to 0.04, it further implied that the entrance shape of the micro perforations could be categorized into well-rounded group.

In 1966, Fuller et al. (Fuller, Shettler, & Giddings, 1966) proposed a method to determine diffusion coefficient for gas mixture at low pressures (Equation 4.14). This well known equation indicated that the diffusion coefficient, $D_{AB}$, should be proportional to temperature, $T$, and inversely proportional to pressure, $P$. Based on this, the diffusion coefficient, $D_{O_2N_2}$, in Equation 4.8 and 4.9 equaled to 7.60e-01 $m^2/hr$ which was close to the corresponding estimation (7.22e-01 $m^2/hr$) computed by the prediction model.

\[
D_{AB} = \frac{0.10137 T^{1.75} \left( \frac{1}{M_A} + \frac{1}{M_B} \right)^{0.5}}{P \left[ (\sum v_A)^{1/3} + (\sum v_B)^{1/3} \right]^2}
\]

(Equation 4.14)

Where

- $T$ = Temperature;
- $M_A$ or $M_B$ = Molar mass of component A or B;
- $P$ = Pressure;
- $V_A$ or $V_B$ = Atomic diffusion volume of component A or B;

While checking the standard errors and standard deviations (Table 4.2), the small numbers indicated the narrowed distribution of sample values of parameters, and the small variance between the estimated values and the true mean values of the corresponding populations of the parameters. In this case, the reliability of the predicted model itself was, again, proved.

According to elementary kinetic theory, the Knudsen diffusion coefficient of a gas in a binary gas mixture is inversely proportional to the square root of its molecular weight.
(Kosov, 1982; Spiegler, 1966). On account of this, the theoretical ratio of $D_{K_{O_2}}$ to $D_{K_{N_2}}$ should be 0.93, which was close to the corresponding ratio (i.e. 0.95) of the estimated coefficients.

Directly estimating end correction factor of diffusion flow, $\gamma$, while generating prediction curves for tested gases is another advantage of this MATLAB® modeling program. In the gas exchange experiment, the end correction factor of $N_2$ diffusion flow was an unknown value. There was no reference number could be used. If employed other modeling methods to predict gas exchange process, preliminary experiment would have to be done to determine the value of $\gamma$ first. The MATLAB® prediction coding of this research did not need the extra work. Parameter estimation and prediction curve generation were completed during the same time. For this experiment, the value of $\gamma$ directly calculated from the prediction of $N_2$ increasing process inside the glass jars with 3 micro perforations in the HDPE sample films. The standard error and standard deviation were used for checking accuracy of the estimation.
Figure 4.8 N\textsubscript{2} Changing Process inside the Glass Jar (2 micro perforations; ■, experimental value; -•- predicted value; + experimental value of control sample (HDPE film with 0 micro perforation))

Figure 4.9 O\textsubscript{2} Changing Process inside the Glass Jar (2 micro perforations; ■, experimental value; -•- predicted value; + experimental value of control sample (HDPE film with 0 micro perforation))
Figure 4.10 \( \text{N}_2 \) Changing Process inside the Glass Jar (3 micro perforations; ■, experimental value; –– predicted value; + experimental value of control sample (HDPE film with 0 micro perforation))

![Graph](image1)

Figure 4.11 \( \text{O}_2 \) Changing Process inside the Glass Jar (3 micro perforations; ■, experimental value; –– predicted value; + experimental value of control sample (HDPE film with 0 micro perforation))

![Graph](image2)
Figure 4.12 N₂ Changing Process inside the Glass Jar (3 micro perforations; ■, experimental value; – – predicted value; + experimental value of control sample (HDPE film with 0 micro perforation); –.– 99% confidence band; … 90% prediction band)

Table 4.2 Parameter Estimation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$D_{O2N2}$ ($m^2/hr$)</th>
<th>$D_{KO2}$ ($m^2/hr$)</th>
<th>$D_{KN2}$ ($m^2/hr$)</th>
<th>$K$</th>
<th>$Y$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Estimated Value</td>
<td>7.22e-01</td>
<td>7.67e-04</td>
<td>8.11e-04</td>
<td>4.51e-02</td>
<td>8.91e-01</td>
</tr>
<tr>
<td>Standard Error</td>
<td>2.70e-04</td>
<td>6.94e-09</td>
<td>6.77e-10</td>
<td>4.18e-06</td>
<td>7.84e-09</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>1.01e-03</td>
<td>2.60e-08</td>
<td>2.53e-09</td>
<td>1.57e-05</td>
<td>2.93e-08</td>
</tr>
</tbody>
</table>

4.3.2 Assessment by Using Other Packaging Researchers’ Experimental Data

To examine the reliability of the prediction model (Equation 4.12 and 4.13) by using other packaging researchers’ experimental data, a group of experimental result published by González et al. (González et al., 2009) was used. Not only computed predicted values,
the programmed mathematical model also estimated the parameters of interest and proved the reliability of the model itself based on statistical analysis.

4.3.2.1 Forward problem

4.3.2.1.1 Scaled sensitivity coefficient

Figure 4.13 and 4.15 showed the plots of scaled sensitivity coefficient for CO$_2$ and O$_2$ changing process inside the micro-perforated packaging. In Figure 4.13, the total span of the dependent variables along y-axis, $V_{CO_2}$, was around $8 \times 10^{-5}$. Among all the curves of scaled sensitivity coefficient, the maximum magnitude of $X'_{DKCO_2}$ (around 90th hour) was 93.75% of the total span of $V_{CO_2}$. Given this fact, Figure 4.13 referred that the estimation for $D_{KCO_2}$ by the prediction model should be the easiest one with most accuracy. If took absolute value of the magnitude, the second easiest one shown in Figure 4.13 would be $D_{O_2CO_2}$ (because the coefficient curve of $D_{O_2CO_2}$ was in the opposite direction to the direction of the prediction curve). In Figure 4.15, the estimation with the smallest difficulty should be $D_{KO_2}$ ($X'_{DKCO_2}$ was 63.80% of the total span of $V_{O_2}$), $D_{O_2CO_2}$ still ranked at the second place. Besides, to estimate the parameters of interest in the prediction model with smallest error and hence to obtain optimal prediction curves, the scaled sensitivity coefficient suggested the micro-perforated experiment should be lasted around 90 hours (the time when the parameters of interest present the maximum magnitude to the prediction curves).

When calculated the ratio of each pair of the scaled sensitivity coefficients (Figure 4.14 and 4.16), correlations between parameters were found. The small range of the ratios indicated that during the gas changing process happening inside the micro-perforated packaging, the hydrodynamic flow and diffusion flow passing through the micro
perforations in the polymer films influenced each other. This indication supported by fact. From the point of time $t = 0$ hour, the produce inside the micro-perforated packaging started consuming $O_2$ and generating $CO_2$. In this way, the respiration activity induced $O_2$ and $CO_2$ concentration differences across the micro-perforated packaging film. Due to the concentration differences, diffusion flows of $O_2$ and $CO_2$ exchanging through the micro perforations were introduced to compensate the differences. In spite that the pressure surrounded the produce inside the micro-perforated packaging kept at constant, pressure gradient existed near the ends of micro perforations in the packaging film. Hence, hydrodynamic flow was also initiated to adjust the gas composition fluctuation. As time increasing, the gas compositions of $O_2$ and $CO_2$ gradually reached steady state, and the gas composition fluctuation eventually decreased to a negligible aspect. Owing to this correlation fact, simultaneously estimating all the parameters of interest by the prediction model would be hard. The solution to deal with the correlated scaled sensitivity issue was to estimate the parameters separately by employing the programmed prediction model of this research.
Figure 4.13 Scaled Sensitivity Coefficients for the Prediction of Carbon Dioxide Changing Process inside Micro-perforated Packaging
**Figure 4.14** Correlations Between the Parameters of Carbon Dioxide Changing Process inside Micro-perforated Packaging Prediction ($\beta_1 = Dk_{O_2}, \beta_2 = K, \beta_3 = Dk_{CO_2}, \beta_4 = D_{O_2CO_2}$)
Figure 4.15 Scaled Sensitivity Coefficients for the Prediction of Oxygen Changing Process inside Micro-perforated Packaging
Figure 4.16 Correlations Between the Parameters of Oxygen Changing Process inside Micro-perforated Packaging ($\beta_1 = Dk_{O2}, \beta_2 = K, \beta_3 = D_{O2CO2}$)

4.3.2.2 Inverse Problem

4.3.2.2.1 Nlinfit

As the first part of inverse problem, Nlinfit was programmed to generate prediction curves for gas composition changing process inside the micro-perforated packaging (Figure 4.17 and 4.18) and to estimate parameters of interest in Equation 4.12 and 4.13 (Table 4.3).

Along with the prediction curves, 95% prediction bands for the experimental data and 95% confidence bands were computed. In either of the figures, the predicted curves
highly agreed with the experimental results. All the prediction bands incorporated all the observed data, and every predicted curve located at the centerline of the confidence bands showing its small difference from the mean values of the corresponding experimental data.

Different from sequential and bootstrap methods, Nlinfit could compute a reference value called condition number, $\text{cond}(J)$ ($J$ referred Jacobian matrix), to indicate the accuracy of the predicted gas changing curves computed by the prediction model. For this prediction, the condition number was 1. Because the value was much smaller than 1 million, it implied that the Jacobian matrix of the prediction model was well conditioned, in other words, the mathematical model itself could be relied.

Figure 4.17 95% Confidence and Prediction Bands for Carbon dioxide Prediction Curve based on Each Parameter Estimation

![Figure 4.17 95% Confidence and Prediction Bands for Carbon dioxide Prediction Curve based on Each Parameter Estimation](image)

a. $D_{K02}$
Figure 4.17 (Cont’d)

b. $D_{O2CO2}$

c. $K$
Figure 4.17 (Cont’d)

d. $D_{KCO_2}$
Figure 4.18 95% Confidence and Prediction Bands for Oxygen Prediction Curve based on Each Parameter Estimation

a. $D_{K_{O2}}$

b. $D_{O_2CO_2}$
4.3.2.2.2 Sequential estimation

Other than evaluating parameters of interest (Table 4.3), sequential method was used for examining the stability of the parameter of interest within the experimental duration. Figure 4.19 and 4.21 presented the parameters fluctuation trends during $O_2$ decreasing and $CO_2$ increasing process. Compared to other parameters, $D_{KCO_2}$ had the largest range of oscillation while the volume of $CO_2$ climbing inside the micro-perforated packaging, and $D_{KO_2}$ had the greatest fluctuation while the volume of $O_2$ reducing inside the micro-perforated packaging. When plotted all the sequential normalized curves on the same scale (Figure 4.20 and 4.22), it was clearly to see that all the fluctuation trends finally approached to 1.0 at the time $t = 120$ hours, which evidenced the enough experimental time the packaging researchers arranged for this experimental.
Figure 4.19 Sequential Normalized Plots for Each Parameter (Carbon dioxide Prediction)

a. $D_{KO2}$

b. K
Figure 4.19 (Cont’d)

c. $D_{KCO2}$

d. $D_{O2CO2}$
Figure 4.20 Sequential Normalized Plot for All the Parameters on the Same Scale
(Carbon dioxide Prediction)
**Figure 4.21** Sequential Normalized Plots for Each Parameter (Oxygen Prediction)

a. $D_{K_{O2}}$

b. $K$
Figure 4.21 (Cont’d)

c. $D_{O_2CO_2}$
Figure 4.22 Sequential Normalized Plot for All the Parameters on the Same Scale (Oxygen Prediction)

4.3.2.2.3 Bootstrap estimation

The parameters of interest evaluated by bootstrap method had the same estimations as the values computed by nlinfit approach. Like aforementioned, the primary advantage of bootstrap method was its large sample pool created by employing Monte Carlo theory. For this prediction, the number of sample data was increased up to 6000 data points (1000 groups of sample data and 6 points per group). In this case, the computed 95% bootstrap prediction and confidence bands should be closer to the true values of the corresponding populations, because the enlarged sample pool decreased the variance between the sample mean and the true mean of the gas exchanging data. In other words, bootstrap method had the ability to generate narrower prediction and confidence bands than the bands shown in Figure 4.17 and 4.18.
Figure 4.23 and 4.24 were the bootstrap plots. Together with these plots, the 95% prediction bands and 95% asymptotic confidence bands in Figure 4.17 and 4.18 were drawn for comparison. Even though the bands were narrowed, the prediction bands still incorporated all the observed data, and the predicted curves were within the confidence bands to evidence that even compared the true mean values, the prediction curves still had high reliability.

To further examine the reliability of the prediction model of this research, residuals between the predicted (based on Monte Carlo theory) and sample data were calculated and analyzed. Figure 4.25 and 4.26 showed the residual plots and analyzed results for both O₂ and CO₂ predictions. In the scattered plots, the residuals were widely spread, and no systematic fan-shaped trend could be noticed. If more proof needed to confirm the absence of residual trend, small time interval (<20 hours) used for testing the micro-perforated packaging would be suggested to collect more sample data. In the histogram charts, the variances and means of the residuals were very close to zero (shown in residual analysis) and the values of log likelihood were high. These results verified the nearly normal independent distributed residuals and further escalated the reliability of the prediction model itself from statistical aspect.
Figure 4.23 95% Bootstrap Confidence Bands and Prediction Bands for Carbon Dioxide Prediction Curve based on Each Parameter Estimation

![Graph showing 95% Bootstrap Confidence Bands and Prediction Bands for Carbon Dioxide](image)

a. \( D_{KO2} \)
Figure 4.23 (Cont’d)

b. $D_{KCO_2}$

c. $D_{CO_2O_2}$
Figure 4.23 (Cont’d)
Figure 4.24 95% Bootstrap Confidence Bands and Prediction Bands for Oxygen Prediction Curve based on Each Parameter Estimation

a. $D_{K02}$

b. $D_{O2CO2}$
Figure 4.24 (Cont’d)

c. K
Figure 4.25 Residual Analysis (Carbon Dioxide Prediction)

a. Histogram Chart (based on bootstrap data points)

<table>
<thead>
<tr>
<th>Distribution:</th>
<th>Normal</th>
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<tr>
<td>Log Likelihood:</td>
<td>63847.2</td>
</tr>
<tr>
<td>Domain:</td>
<td>(-\infty &lt; y &lt; \infty)</td>
</tr>
<tr>
<td>Mean:</td>
<td>(6.52994 \times 10^{-7})</td>
</tr>
<tr>
<td>Variance:</td>
<td>(3.34787 \times 10^{-11})</td>
</tr>
</tbody>
</table>

b. Residual Analysis
c. Scattered Plot (based on experimental data points)
**Figure 4.26** Residual Analysis (Oxygen Prediction)

**a. Histogram Chart**

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<td>Domain:</td>
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<td>Mean:</td>
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</tr>
<tr>
<td>Variance:</td>
<td>$8.82028e-12$</td>
</tr>
</tbody>
</table>

**b. Residual Analysis**
4.3.3 Parameter Estimation

Table 4.3 listed the estimations of parameters of interest of the mathematical model (Equation 4.12 and 4.13). Although three statistical approaches were employed to estimate the parameters, there was no significant deviation among the estimated values computed by each statistical method. The smallest standard error and standard deviation of $D_{K\text{CO}_2}$ (Table 4.3) verified the indication of the scaled sensitivity coefficient plot in forward problem part—the estimation of $D_{K\text{CO}_2}$ (Knudsen diffusion coefficient of CO2) should be the most accurate number computed by the prediction model. The small standard deviation revealed a narrow sample distribution of $D_{K\text{CO}_2}$, and thus the evaluated value was very close to the sample mean of $D_{K\text{CO}_2}$. Also, the small standard
error served as an estimator to prove that there was a tiny difference between the estimated $D_{KCO_2}$ and the population mean of $D_{KCO_2}$. Followed $D_{KCO_2}$, $D_{KO_2}$ was the second accurate value. When calculated the ratio of the evaluated $D_{KO_2}$ to $D_{KCO_2}$, the result (i.e. 1.15) agreed with the corresponding theoretical value (i.e. 1.17) based on elementary kinetic theory (Kosov, 1982; Spiegler, 1966).

To check the accuracy of the evaluated diffusion coefficient of gas mixture, $D_{O_2CO_2}$, Equation 4.14 was again employed. The theoretical value was $5.25e-01 \, m^2/\text{hr}$, which was same as the value estimated by Sequential method, and only had $2.00e-02$ difference compared with the results evaluated by Nlinfit and Bootstrap approaches.

The estimation of minor head loss coefficient, $K=1.99e-01$ or $2.00e-01$, clarified that the cross sectional shape of the micro perforations tested in González et al.’s research belonged to slight-rounded group. Wherefore, if tested González et al.’s micro-perforated samples together with the micro-perforated samples used in previous gas exchange experiment (Assume except the cross sectional shape of both types of the micro perforations, the other experimental values were same), the flow rate of hydrodynamic flow through the micro perforations used in the gas exchange experiment would be around 3.4 times more than the corresponding rate of González’s samples. Hence, cross sectional shape of micro perforations in polymer films would significantly influence hydrodynamic flow through micro-perforated packaging.
Table 4.3 Parameter Estimation

<table>
<thead>
<tr>
<th></th>
<th>$D_{KCO_2}$ (m$^2$/hr)</th>
<th>$D_{KCO_2}$ (m$^2$/hr)</th>
<th>$D_{O_2CO_2}$ (m$^2$/hr)</th>
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</thead>
<tbody>
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<td></td>
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<td>Sequential</td>
<td>Bootstrap</td>
</tr>
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<td>Value</td>
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<td>7.63e-03</td>
<td>7.62e-03</td>
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<td></td>
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<tr>
<td></td>
<td>OLS</td>
<td>Sequential</td>
<td>Bootstrap</td>
</tr>
<tr>
<td>Value</td>
<td>6.63e-03</td>
<td>6.63e-03</td>
<td>6.63e-03</td>
</tr>
<tr>
<td>Standard Error</td>
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<td>Bootstrap</td>
</tr>
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<td>Value</td>
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<td>5.25e-01</td>
<td>5.23e-01</td>
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<td>Bootstrap</td>
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<td>Standard Deviation</td>
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4.4 Effective or Equivalent Circular Diameter

The diameter of micro perforations is a crucial variable to predict gas exchanging process. Due to the limitation of current technology, packaging researchers, in some cases, obtain elliptical micro perforations in polymer sample films instead of round micro perforations. To predict gas exchanging rate through those elliptical micro perforations, packaging researchers need to determine effective or equivalent circular of the elliptical micro perforations, and then to use the effective or equivalent circular diameter for predictions. Effective or equivalent circular refers to round micro perforations with same area or perimeter as the elliptical micro holes.
How to determine the effective or equivalent circular? Should packaging researchers use same area or same perimeter to determine the effective or equivalent circular? Which one will help packaging researchers predict more accurate values, circular with same area or circular with same perimeter? In 2003, Del-Valle’s group (Del-Valle et al., 2003) proposed that perimeter of micro perforations rather than area of micro perforations affected the gas transmission rate through their micro-perforated samples, but no other references discussed the effect in detail.

As the last part of this research, both types of effective circular diameter (based on same area and same perimeter) were used to predict the gas changing process for González’s experimental data (Figure 4.27 and 4.28). Figure 4.27 showed that the prediction curve generated by using effective circular diameter based on the same area matched the experimental results from 0 to 22 hours. After 22 hours, there was no predicted value close to the experimental data, whereas, the prediction curve generated by using effective circular diameter based on the same perimeter agreed with most of the experimental results. If compared the estimated values to the observed data (Table 4.4), the predicted values based on same perimeter had 7.57% deviation in average to the observed data, the predicted values based on same area enlarged the deviation up to 20.10%. Particularly at the last data point, the predicted values based on same area had the deviation as great as 57.32%.

The difference caused by these two types of effective circular diameter was even apparent in the predictions for CO₂ (Figure 4.28 and Table 4.5) Since the very beginning, the prediction based on same area underestimated CO₂ changing process inside the micro perforated packaging. No predicted value closed to the experimental data, and the
average deviation was three times than the deviation of predicted values based on same perimeter to the observed data.

According to above analysis, effective or equivalent circular based on same perimeter of elliptical micro perforations in polymer films was suggested to determine effective circular diameter. Using effective circular diameter based on same area of micro holes might lead to underestimated or overestimated prediction.

**Figure 4.27** O₂ Changing Process inside Micro-perforated Packaging
Table 4.4 Comparisons between Experimental and Predicted Values (O₂)

<table>
<thead>
<tr>
<th>Time (hrs)</th>
<th>Oxygen Volume inside Micro Perforated Packaging (m³)</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental Data</td>
<td>Predicted Value (Same Perimeter)</td>
</tr>
<tr>
<td>0</td>
<td>9.43E-05</td>
<td>9.43E-05</td>
</tr>
<tr>
<td>22.5</td>
<td>6.21E-05</td>
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</tr>
<tr>
<td>45</td>
<td>4.14E-05</td>
<td>3.72E-05</td>
</tr>
<tr>
<td>65</td>
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<tr>
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<td>7.57%</td>
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Figure 4.28 CO₂ Changing Process inside Micro-perforated Packaging
Table 4.5 Comparisons between Experimental and Predicted Values (CO$_2$)

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<th>Time (hrs)</th>
<th>Carbon Dioxide Volume inside Micro Perforated Packaging (m$^3$)</th>
<th>Ratio</th>
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</thead>
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<td>Predicted Value (Same Perimeter)</td>
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<td>8.10E-05</td>
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<tr>
<td><strong>Average</strong></td>
<td><strong>10.33%</strong></td>
<td><strong>28.63%</strong></td>
</tr>
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</table>
CHAPTER FIVE:

Conclusion and Future Work

5.1 Micro Perforations

In this research, the approach used for making micro perforations improved the geometric shape of the topside entrance. In this case, air resistance reduced while air flux from outside environment entered into micro perforations in the sample films. However, the lengthened pathway of gas flux still existed due to the perceived polymers deposited around the bottom ends of the micro perforations.

To correctly predict hydrodynamic flow through micro-perforated films, cross sectional view of micro tubes is needed. The cross-sectional view of micro perforations could hint packaging researchers to assess the range of minor head loss coefficient, K, and thus to obtain closer predictions to the experimental data by using the mathematical model of this research.

While measuring micro perforations under SEM, significant difference between the diameters of micro perforations in the HDPE and PLA films was noticed. As the same experimental conditions and treatment applied for making micro perforations in both types of films, surface tension of polymer films, processing procedure, orientation of polymer films and types of additives mixed into polymer films were considered as the factors, which might result in different sizes of micro perforation and thus could influence gas exchange volume.

5.2 Prediction Model

Matlab® program, at first time, was introduced into packaging field to predict gas changing process inside micro-perforated packaging. Unlike the other mathematical
models, the programmed prediction model of this research not only computed prediction curves for gas changing process inside micro-perforated packaging, it also proved the reliability of the mathematical model itself based on various data generated by different statistical analysis methods. Besides, the prediction model of this research could be used to examine experimental duration. With an analyzed experimental duration, packaging researchers could reasonably operate their experiments to collect enough data for their researches. More importantly, this Matlab® prediction model saved researchers time on performing extra experiments to determine unknown parameters. Generating predicted gas changing curves and estimating unknown parameters could be completed during the same process, researchers do not need to design preliminary works especially for parameter estimation, and the computed statistical data, like standard error, standard deviation, etc., could be used for checking the accuracy of parameter estimation.

5.3 Predicted Results

In this research, a new mathematical model was established for predicting gas changing process inside micro perforated packaging by using Matlab® program. To test the reliability of the prediction model, experimental data obtained from a self-performed experiment and from other packaging researchers’ experiment were adopted.

In the self-performed experiment, almost all the predicted data agreed with experimental values. Higher agreement existed between the observed data and the predicted gas changing process inside the glass jars with 2 micro perforations in the HDPE sample films. The prediction curves correctly anticipated the time span used for the gas composition reaching steady state. A small variance was noticed between the predicted data of N₂ changing process inside the glass jars with 3 micro perforations in
the HDPE sample films. The amount of examined gas withdrawn from the containers at each time, the sampling speed, and the consistency of GC analysis were considered as the major aspects brought about the variance. While computing prediction curves, the mathematical model also estimated the correct values of parameters of interest. The small standard errors and standard deviations further proved the parameter estimation and the prediction model.

To manifest the prediction model is applicable for other micro-perforated tests, experimental data published by other packaging researchers were used. The prediction curves agreed with the experimental data, and the estimated parameters shown similar values as theoretical values. In addition, the reliability of the prediction model itself was verified by generating the following information:

- Scaled sensitivity coefficient. The plot of scaled sensitivity coefficient revealed the correlation between hydrodynamic flow and diffusion flow, which could be supported by theoretical concepts.
- Nlinfit. This statistical method a) correctly estimated the parameters of interest, b) verified the reliability of the prediction model by computing the condition number of Jacobian matrix, and c) computed 95% prediction and 95% asymptotic confidence bands, which supported the prediction values.
- Sequential. Except correctly estimated the parameters of interest, this mathematical method examined the proper experimental duration spent on testing the micro-perforated samples.
- Bootstrap. This statistical section employed Monte Carlo theory to a) correctly estimate the parameters of interest, b) analyze and present a non-trend residual plot.
proving the reliability of the prediction model, and c) compute more precise prediction and confidence bands. Even in this case, the prediction curves computed by the prediction model still shown their small deviations.

Also, the predicted results explained that to predict gas flux through elliptical micro perforations in packaging films, diameter of effective circular with the same perimeter as the micro perforations was recommended to obtain better estimations.

5.4 Future Work

In this research, a gas exchange prediction model was developed for micro-perforated packaging. Also, most crucial factors, which could significantly affect the prediction of gas exchange process through micro perforations in polymer films, were studied. However, limitations and missing parts still exist and may need to be addressed in future work.

- Although clear cross-sectional view of micro perforations in polymer films was observed under SEM by employing the proposed method of this research, some micro-perforated samples were destroyed during the sample preparation process, hence, an advanced technic will be applauded to observe cross sections of micro perforations without leaving any deformation.

- To further verify the reliability of this gas exchange prediction model, experiments regarding different types of fresh produce bagged with micro-perforated packaging under different storage conditions need to be performed and analyzed.

- Other variables, such as ethylene production of fresh produce and water vapor content inside micro-perforated packaging, may be included into the prediction model to generate gas exchanging curves closer to real packaging situations.
APPENDICES
Appendix A Oxygen Calibration Curve of GC-TCD

Figure A Oxygen Calibration Curve of GC-TCD

\[ y = 34473x \]
\[ R^2 = 0.96426 \]
Appendix B Nitrogen Calibration Curve of GC-TCD

Figure B Nitrogen Calibration Curve of GC-TCD

\[ y = 110498x \]
\[ R^2 = 0.99973 \]
Appendix C Experimental Data of Gas Exchange Research

Table C Experimental Data of Gas Exchange Research

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<th>Inside N₂ (m³)</th>
<th>Control Sample for O₂ (m³)</th>
<th>Control Sample for N₂ (m³)</th>
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a. HDPE Sample Films with 2 Micro Perforations
Table C (Cont’d)

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<th>Control Sample for O&lt;sub&gt;2&lt;/sub&gt; (m&lt;sup&gt;3&lt;/sup&gt;)</th>
<th>Control Sample for N&lt;sub&gt;2&lt;/sub&gt; (m&lt;sup&gt;3&lt;/sup&gt;)</th>
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b. HDPE Sample Films with 3 Micro Perforations
REFERENCES


