This is to certify that the

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EFFECT OF ETHANOL VAPOR ON THE OXYGEN PERMEABILITY OF PACKAGING POLYMER FILMS

By

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ABSTRACT

EFFECT OF ETHANOL VAPOR ON THE OXYGEN PERMEABILITY OF PACKAGING POLYMER FILMS

By

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In this study, the steady state oxygen permeance of selected films were determined under 0 ppm, 1 ppm and 7 ppm ethanol vapor conditions. The oxygen permeability test were carried out by using a modified Oxtran 100 permeability tester. This modification included the use of tenax as ethanol adsorbent which prevent ethanol vapor from exposing to the coulometer sensor of the Oxtran. The result revealed that there was no significant effect of ethanol vapor in the concentration range of 0-1 ppm (wt/vol) on the oxygen permeability of selected polymer film within 24 hour period.

To My Family.

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INTRODUCTION

In the past, the production of packaging materials was based exclusively on "natural" materials such as wood, cotton, sand, and metal. However, synthetic polymeric materials that were developed mainly after 1930, are now increasingly playing an important role in the packaging industry. These polymeric materials have some advantages and disadvantages compared to other packaging materials. The advantages include the versatility that these materials offer to the packaging designer, light weight compared to glass and metal packaging, and resistance to breakage. However, polymeric packaging materials are semi-permeable and are therefore able to interact with small molecules such as gases, water, and organic vapors. Specifically, polymeric materials exhibit physico-chemical interactions with small permeant molecules based on sorption and diffusion mechanisms.

Polymer-permeant interactions have important practical effects since polymeric packaging materials may change its original properties during the shelflife of the package. It is important therefore, to understand the mass transfer behavior of the product-package system in order to better apply a specific behavior of package/product system. This

behavior includes the sorption, diffusion, desorption, and evaporation of the permeant molecules coming from the product as well as from the external environment.

The use of polymeric packaging material for Modified Atmosphere Packaging and Controlled Atmosphere Packaging (MAP/CAP) of respiring foods -e.g., fresh produce - presents a technical challenge to packaging and food technologists. In the normal aerobic respiration of produce, oxygen is consumed as carbohydrates are converted to carbon dioxide, and water, to produce energy. One of the objectives of MAP/CAP is to extend the shelflife of produce by reducing the rate of respiration of the product, which reduces the rate of substrate depletion, carbon dioxide production, oxygen consumption and energy release (Zagory et al. 1988). The result of this controlled metabolism, is a potentially longer shelflife. The rate of respiration and the metabolic pathway of respiration are subject to both internal and external influences such as temperature and oxygen concentration. The respiration rate can change during the natural processes of ripening, maturity, and senescence.

The rate of respiration is sensitive to changes in oxygen concentration below 8% and carbon dioxide above about 1%. If oxygen concentration is reduced or carbon dioxide concentration is elevated beyond the critical concentration levels required by the product, the physiological activity

associated with anaerobic respiration will increase (Zagory et al. 1988). This anaerobic activity triggers several chemical reactions that normally produce aldehydes, alcohols, and other volatile chemicals (Kader, 1986). Once the anaerobic process is developing the product will require a more oxygenated environment. This will require a higher value of the oxygen permeability of the packaging material.

Several alternatives may be considered in order to supply adequate oxygen at the required time, ie., when the produce goes from an anaerobic to an aerobic phase. One is to develop biosensors to be used to indicate the anaerobic condition, however, these biosensors have not been successfully developed yet. The other alternative is the removal or partial elimination of packaging material used during the anaerobic condition after a pre-determined period of time.

However, as mentioned earlier, organic volatile compounds such as aldehydes and alcohols are generated during the anaerobic phase of the package shelflife. Since the mass transport characteristics of permeants such as oxygen through polymeric materials may be affected by the sorption of organic vapor by the polymer, it is reasonable to investigate, oxygen permeability changes due to the presence of such volatile organic on selected polymeric samples. If

oxygen permeability of a given film is increased, by the presence of organic vapors such as ethanol, it may be possible to use the presence of volatile compounds produced during the beginning of the anaerobic respiration, to increase the flux of oxygen into the package.

Most of the permeability studies on polymeric packaging material have been focused on determining the basic permeability parameter, ie., sorption, diffusion, and permeability coefficients of a single penetrant in mostly pure or uncontaminated polymers. However, the study about effects of organic vapors on the oxygen permeability of polymer membrane is very limited. This project focuses on describing the effect of ethanol which is the by-product from anaerobic respiration on the oxygen permeability properties of polymers. A major concern is the level of ethanol concentration in the head-space that may affect the oxygen permeability of the membrane.

The objective of this research was:

1. To develop a test apparatus to study the effect of ethanol vapor on the oxygen permeability. This will include a modification of an OXTRAN permeability tester.
2. To experimentally determine the effect of ethanol vapor on the oxygen permeability of selected polymer films as a function of ethanol vapor concentration.

LITERATURE REVIEW

DIFFUSION MODELS

In 1866, Graham postulated that the mechanism of the permeation process included (a) sorption-solution of the penetrant in the high concentration surface of the membrane, (b) diffusion through the membrane by colloidal diffusion, followed by, (c) desorption-evaporation from the downstream membrane surface.

The sorption process can be explained phenomenologically as the distribution of the penetrant between two or more phases to include adsorption, absorption, incorporation into micro-voids, cluster formation, solvation-shell formation and other modes of mixing (Roger, 1985).

Penetrant molecules may experience more than one concurrent or sequential mode of sorption in a given polymer material. The distribution of penetrant between different modes of sorption may change with changes in sorbed concentration, temperature, swelling-induced structural states, time of sorption to equilibrium, and other factors.

Most of the early studies on the permeation of molecules

through polymeric films were concerned mostly with rubbery polymers. However, since plastic and glassy polymers are produced in large quantity and are very popular in the packaging industry, there has been a tremendous research effort to try to describe the permeation phenomena of these polymers. It was found that in all types of polymers , the permeation mechanism through a homogenous membrane, in the absence of gross defects involves sorption of penetrant in the polymer, diffusion through the membrane followed by evaporation from the surface into the ambient phase. The diffusion of penetrants in the polymer membrane can be portrayed as a sequence of unit diffusion steps or jumps. This unit diffusion involves a cooperative rearrangement of penetrant molecule and its surrounding polymer chain segments. It is not necessary that, in the polymer structure, an intrinsic hole exists in between two successive penetrant positions. However, a certain number of van der Waals type or other interactions between the component molecule and chain segment must be broken to allow a rearrangement of the local structure. Energy is required for this rearrangement (or hole formation) against the cohesive forces of the medium and effective movement of the penetrant for a successful jump (Comyn, 1985).

In a polymer above its gas transition temperature, hole density fluctuates as a result of thermal fluctuation. Diffusion thus depends on the relative mobilities of

penetrant molecules and polymer chain segments as they are affected by changes in size, shape, concentration component interactions, temperature and other factors which affect polymeric segmental mobility. The overall transport process in a polymer therefore depends on polymer chain segmental mobility and defect structures, such as void, microcracks and other non-thermodynamic variations in polymer structure and morphology. This includes spherulitic and lamellar boundary regions in semi-crystalline polymers and permanent or transient voids (excess free volume, frozen hole, etc.) found in glassy polymer (Roger, 1985).

In 1879, Von Wroblewski showed that the solution of gases in rubber followed Henry's law , Figure 1, Equation(1),

$$C = kp \qquad (1)$$

C = Penetrant concentration in the polymer at equilibrium.(cc(stp)/cc.polymer)

k = Bunsen solubility coefficient. (cc.(stp)/cc.atm.)

p = Fixed gas pressure on the polymer.

Henry's law simply states that the concentration of penetrant in the polymer, C, is directly proportional to the gas pressure or the concentration of gas, p, on the polymer.

Fick's first law is the fundamental law of diffusion (Comyn, 1985). It states that the flux, J, in the x-direction is

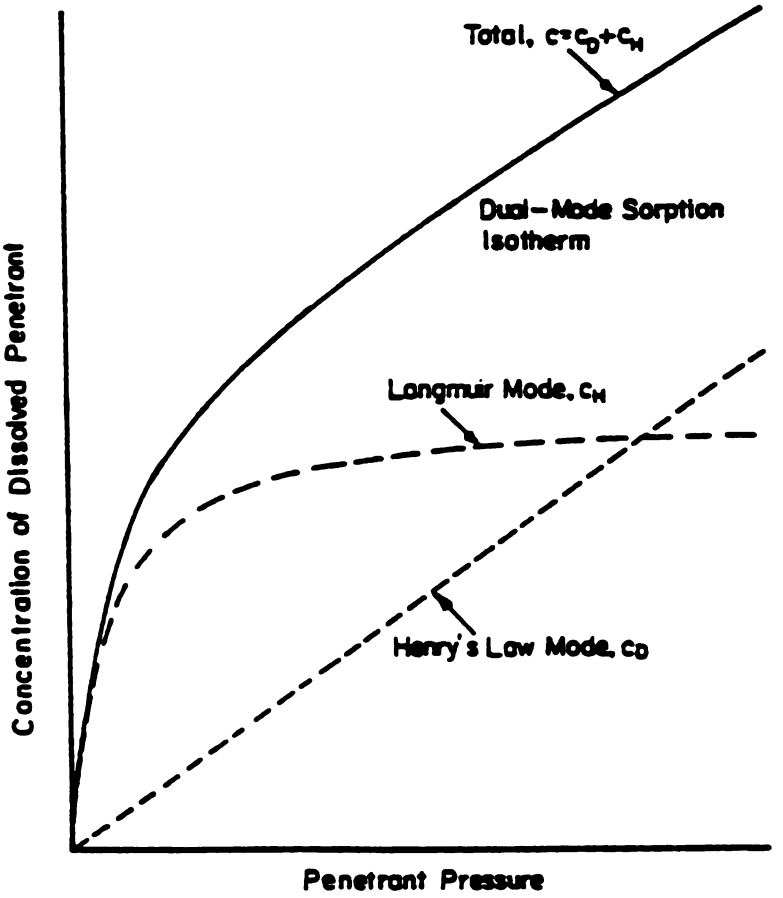


Figure 1: Typical Dual-Mode Sorption Isotherm and its Component (Stern and Trohalaki, 1990)

proportional to the concentration gradient ($\partial c/\partial x$)

$$J = - D \, \partial c/\partial x \qquad (2)$$

The diffusion coefficient, D (sq.cm/sec), may or may not be independent of the concentration of gas in the membrane. Diffusion behavior, in which D is only a function of temperature and permeant concentration but not the time of the permeation process, is called Fickian diffusion.

When Henry's Law is obeyed, the steady-state flux can be expressed by combining the Henry's law and Fick's law, the relationship between permeability, diffusivity and gas solubility becomes

$$J = \frac{kD\Delta p}{l} = \frac{P\Delta p}{l} \qquad (3)$$

$$P = kD \qquad (4)$$

J = Steady state permeation flux is the amount of substance diffusing across unit area in unit time.

p = Pressure difference between top and bottom faces of the membrane.

P = Steady state permeability which has typical units of cc(stp)cm)/(sec.sqcm.atm.

An increase in temperature provides energy for a general increase in segmental motion. The effect of an increase in temperature may also be expressed in terms of the increase in free volume (Roger, 1985).

For the frequently observed ideal behavior noted in organic rubbers the diffusion coefficient varies with temperature by an Arrhenius relationship:

$$D = D_o \exp(-E_d/RT) \qquad (5)$$

D_o = Pre-exponential factor

E_d = Activation energy for diffusion (Cal)

R = Gas constant (Cal/degree.mole)

T = Absolute temperature (degree Kelvin)

Studies of transport of penetrants in glassy polymers revealed that the sorption behavior in the polymer is more complicated than that represented by Henry's Law. These models include dual-sorption modes for permanent gas and the extension of this model in the case of plasticized penetrant-polymer system.

Dual Mode Sorption Models

Langmuir-Henry's Law Model

The mechanisms of gas diffusion are different at temperatures above and below the glass-transition

temperature, Tg, of the polymer, ie., when the polymers are in their "rubbery" or " glassy" state, respectively (Stern et al. 1990).

Michael et al. (1963) proposed a two-mode sorption model. This model postulates that a gas dissolved in a glassy polymer consists of two distinct molecular populations:

1. Molecules dissolved in the polymer by a mechanism described by Henry's Law, and
2. Molecules dissolved in a limited number of fixed, pre-existing microcavities, or a fixed sites, in the polymer matrix, described by the Langmuir equation C_H.

The concentration of molecules dissolved by the simple dissolution process, C_d, is related to the penetrant equilibrium pressure, p, by a Henry's law isotherm as in equation 1.

$$C_d = kp \qquad (1)$$

The concentration of molecules dissolved in microcavities, C_H, is described by the Langmuir equation:

$$C_H = \frac{C'_H bp}{1+bp}$$

(6)

Where C_H' is a "Langmuir Saturation" constant, and

b is a " Langmuir affinity constant

The total concentration of the dissolved penetrant C, at a given p and temperature is then obtained from the linear combination of the two populations and given by the sum of equations (1) and (6).

$$C=C_D+C_H=kp+\frac{C_H'bp}{(1+bp)} \tag{7}$$

Typical dual-mode sorption isotherm and its compounds are shown in Figure 1 (Stern et al., 1990).

The permeability coefficient, P, for gas transport across a glassy polymer membrane is then given by the relation:

$$\bar{P}=kD_D\frac{(1+FK)}{1+bp} \tag{8}$$

$$F=\frac{D_H}{D_D} \tag{9}$$

$$K=\frac{C_H}{k} \qquad (10)$$

D_H and D_D = mutual diffusion coefficients of the two penetrant populations of concentration C_H and C_D, respectively.

The formulations of the sorption models presented assume that the solubility of the penetrant gas in a polymer is very low, and that consequently the polymer is not plasticized to any significant extent by the penetrant. However, for many penetrant-polymer system, D is not a constant but rather is a function of concentration or in some cases the elapsed time. The concentration dependence is a consequence of the plasticising action of sorbed penetrant and/or various mechanisms which localise a portion of the sorbed penetrant. For example, the permeation of gases with higher critical temperatures, such as organic vapors and water vapor, exhibit sufficiently high solubilities to plasticize glassy polymers which therefore can not be described by using only the previous discussed sorption models.

Flory-Huggins Model

In general, the diffusivities of penetrants that swell glassy and rubbery polymers increase with concentration.

The sorption isotherms are normally well-described by the Flory-Huggin equation instead of Henry's Law as shown for a general case in Figure 2.

The isotherm represents a preference for penetrant-penetrant pairs to be formed such that the solubility coefficient increases continuously with pressure. There are two principal physical interpretations of this behavior. One is that the first molecules sorbed tend to loosen the polymer structure locally and make it easier for subsequent molecules to enter in the neighborhood of the first rather than to go elsewhere.

This interpretation implies that the sorbed penetrant effectively plasticises the polymer and the Flory-Huggin isotherms are observed when a liquid or vapor penetrant is a strong solvent or swelling agent for the polymer (Roger, 1985).

Another physical interpretation of this behavior is represented by the systems in which the interactions among penetrant are stronger than the interactions between polymer and penetrant. As a result the stable sorption sites of primary penetrant on the polymer will be the sites for the sorption of consequent penetrants on the polymer. Therefore, the sorption concentration increase with increasing clustered molecules. However, in this behavior,

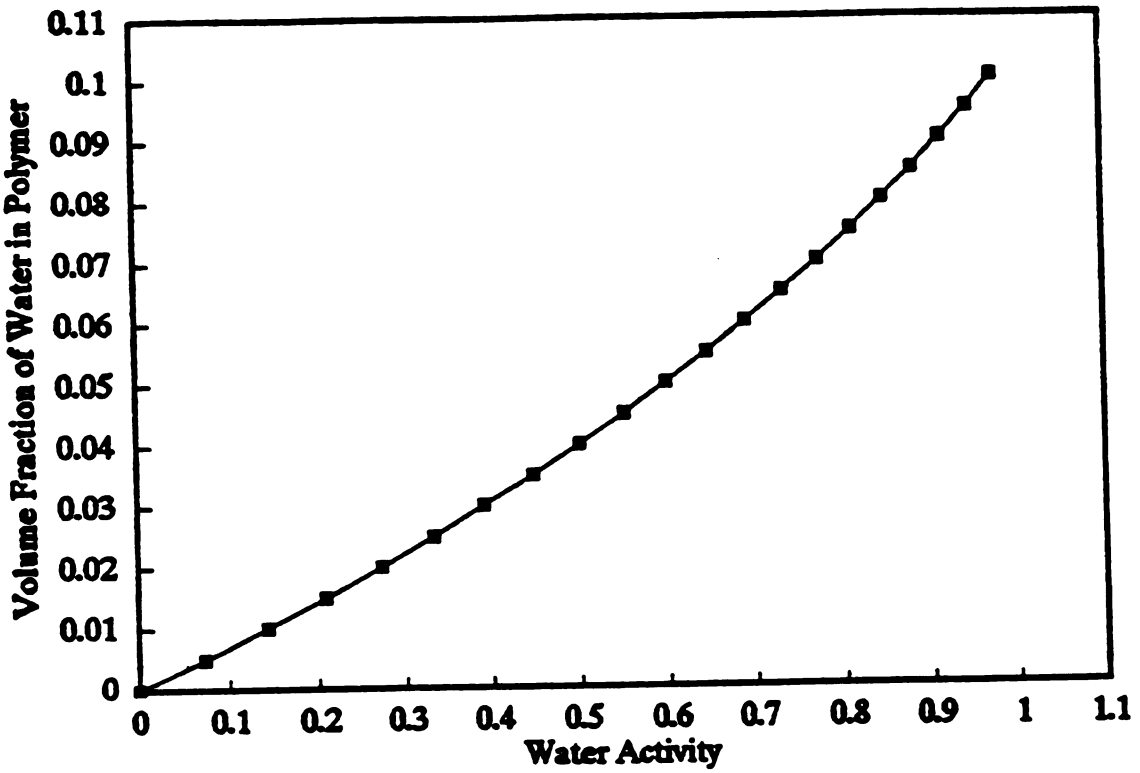


Figure 2: Flory–Huggins Sorption Isotherm
Nylon 6I/6T and water vapor at 23 C

it would be expected that the diffusion coefficient would decrease with increasing C (Roger, 1985).

Langmuir-Flory-Huggin Model

Hernandez et al. (1992), had studied the effect of sorbed water on the oxygen permeability of Nylon 6I/6T films. The authors found that as water content in polymer increased, the oxygen diffusion coefficient increased, and the solubility of oxygen decreased. However, the decrease in the oxygen solubility was more significant than the increase of the diffusion coefficient. The authors proposed a dual mode sorption model based on Langmuir and Flory-Huggins mechanism. At water activities below 0.1, water preferentially chemiabsorbs to amide bonds although only a low mole fraction of the total hydrogen bonding sites on the polymer are occupied. At higher water activities, the model predicts that water molecules cluster among themselves. This mechanism results in an increased capacity of polymer to accommodate water molecules and therefore oxygen permeability decreases. This study suggested that a distribution of sites for each penetrant was present with in the polymer matrix. The study also indicated that not only is there competition for Langmuir sites, but the availability of these sites depends on the type of molecules and more specifically on the size of penetrant.

This phenomenon of size distribution of sorbed molecules

appears to take place also within other polymers and sorbants. For example, Gedraitte et al [7] reported a size distribution of additive sorption centers in polyethylene. The authors found that the sorption of various additives by high density and low density polyethylene such as hexane and isopropanol obeyed the Langmuir sorption law.

These results, coupled with the availability of the model described by the equation indicate, in principle, that the permeability of oxygen should be affected by the presence of organic molecules sorbed by a polymeric matrix.

PERMEABILITY MEASUREMENT

There are two test methods which provide quantitative measurement for the rate of diffusion of gases or vapors through polymer membranes: the isostatic method and the quasi isostatic method.

In the first method, the test system allows for the continuous collection of permeation data on vapor or gas through a polymer membrane from the initial time zero to steady-state condition, as a function of temperature and permeant concentration. An example of equipment using this method is OXTRAN 100 permeability tester which was used in this study. The instrument consists of a measuring cell divided into two sections by the film which will be tested.

The upper cell is the high oxygen concentration chamber, oxygen will permeates through the tested film to the lower chamber which then will be conveyed to the sensor by the carrier gas. The sensor consists of an electro-chemical cell made of nickel, cadmium and graphite that is immersed in a basic electrolyte. Oxygen will react with cadmium under high humidity and release electric current which then will produce voltage when it is connected to a suitable resistance and the voltage can be recorded. This value can be converted to permeance value by multiplying with a conversion factor.

In the second method the permeated gas is accumulated and monitored as a function of time. Daynes in 1920 (2) showed that, solubility coefficient, D is related to the time required to achieve steady state permeation through an initially degassed membrane (so-called " Diffusion lag time", θ).

As shown in equation (11), the time lag is quantitatively related to the diffusion coefficient and membrane thickness,l, for the simple case where both k and D are constants

$$D=\frac{l^2}{6\theta} \qquad (11)$$

PERMEATION OF MIXTURE

Research involving the permeation process of organic vapor has been mostly focused on single component organic vapor/polymer systems (Rogers et al., 1960, Gilbert et al., 1983, Niebergall et al., 1978., Zobel, 1982, Rogers,1964, Baner et al., 1968, Hernandez et al., 1986, Mohney et al., 1988, and Liu et al., 1986). These studies provided crucial information about the permeation mechanism of organic penetrants in polymer membranes.

Laine et al. (1971), conducted a study on organic vapor permeability of polyethylene film. The result revealed that in polyethylene, which is nonpolar, the permeability is lowest for polar components and highest for nonpolar components.

A number of studies involving the permeation of mixed gas have been conducted. One of the early studies was carried out by Alexejev et al. (1927), who conducted studies on the permeation of pure carbon dioxide, oxygen, acetylene, nitrogen and air, and their mixtures in a wide variety of compositions through rubber membranes. The study showed that the permeation rate of gas mixture was equal to the sum of the rates of its constituents. Meyer et al. (1957), found no effect of one penetrant gas on another, however, the time taken to establish the steady state increased when

gas mixtures were used.

The research of Pye et al. (1976), confirmed the previous study which revealed that in the study system which involves noninteractive materials, gases permeate independently of each other even at very low partial pressures. Their results are in agreement with those of Stannett et al. (1957), Stern (1972) and Rogers (1965).

According to Pye et al., the permeability of a membrane to a component A may be reduced due to the sorption of a second component B in the polymer which therefore effectively reduces the microvoid content of the film and the path for the nonreactive gases.

Chern et al. (1983), conducted research in "second component" effects in sorption and permeation of gases in glassy polymers, which revealed that the carbon dioxide flux through Kapton polyimide was depressed by the presence of water vapor. This study suggests that competition of mixed penetrants for sorption sites an transport pathways associated with unrelaxed volume in glassy polymers is a general feature of gas/glassy polymer systems.

Lui et al. (1988), and Delassus et al. (1988), both found that water vapor exhibited strong interactive effects with moisture sensitive materials (EVAL and EVOH). This was due

to the plasticizing effect of the sorbed water which resulted in the increase of the permeability of the other components. However, Landois-Garza et al. (1988), who studied the permeation of PVOH film by ethyl esters, postulated a trend toward lower permeability values as relative humidity increased. This finding was contrary to the work of Liu et al. (1988), and Delassus et al. (1988). The authors explained that the decrease in permeability was mainly a result of the lowering of the solubility as relative humidity increased due to a competition effect between the water molecules and the ethyl ester molecules. The highly polar water molecules were able to compete more effectively than the nonpolar ethyl ester molecules for absorption sites of the also polar PVOH.

Hensley et al. (1991), conducted a study on the permeability of binary organic vapor mixtures through polypropylene film. The results showed that, independently, the organic vapors showed concentration dependency for both permeation and diffusion characteristics. For binary mixtures, the total permeation rate of the mixture was much higher than that of the pure components.

Sadler et al. conducted a research on "Oxygen permeability of low density polyethylenes as a function of limonene absorption: An approach to modeling flavor scalping. The study suggests that oxygen permebility might provide

information on volatile scalping. That is the increasing of oxygen permeation would reflect absorption of volatiles, and the desorption of volatile would reduce oxygen permeabilty.

Thalmann (1990), studied the sorption of solvents in plastics and solvent desorption and retention. The solvents included methanol, ethanol, n-propanol, and ethyl acetate. Thalmann conducted the sorption experiments in the vapor phase in a closed desiccator with special cover. The change in weight was measured continuously as time increased. Sufficient solvent was placed in the lower part of the desiccator to ensure a vapor-saturated atmosphere. The plastic samples were suspended on a microbalance. As soon as the samples were fixed and the desiccator closed, the weight registration started with an initial zero adjustment. The sorption experiments were continued until they reached an approximate equilibrium of saturation. The sorption of each polymer is shown in Table 1.

The above review describes the permeability studies of various conditions which reveal that permeability mechanism of small molecules through polymer membranes depends on penetrant-polymer interaction in both sorption state and diffusion state. And this leads to the assumption that the presence of organic molecules sorped by polymeric matrix may affect oxygen permeability of a polymer. The trends of such an effect is not yet confirmed which can involve either

organic molecules plasticizing a polymer as in the Flory-Huggin model and results in higher oxygen permeability or the competition between organic molecules and oxygen molecules. This study is an attempt to clarify the above assumption through measuring oxygen permeability of various polymer films in the presence of a low concentration ethanol vapor.

MODIFIED ATMOSPHERE CONDITION

The specific optimum levels of O_2 and CO_2 have been studied and reported by many researchers (Kader, 1980). Research on packaging materials is important today because the final package will have to allow enough O_2 to pass through and reach the product in order to eliminate the potential of anaerobic condition. This should be done at such a rate that the O_2 concentration in the headspace is maintained at a much lower level than atmospheric O_2 which will result in the desired quality maintenance. In addition, CO_2 permeability should be such that enough CO_2 is vented out of the package while the optimum level of CO_2 maintained inside.

Although many plastic films are available for packaging purposes, relatively few have been used to wrap fresh produce. Even fewer have gas permeabilities that make them suitable to use for MAP/CAP. Because O_2 content in a MAP/CAP is typically being reduced from an ambient 21% to

2-5% within the package, there is a danger that CO_2 will increase from ambient 0.03% to 16-19% in the package. This is because normally, this is a one-to-one correspondence between O_2 consumed and CO_2 produced. Because this high level of CO_2 would be injurious to most fruit and vegetables, an ideal film must let more CO_2 exit than it lets O_2 enters. The CO_2 permeability should be somewhere in the range of 3-5 times greater than the oxygen permeability. The O_2 and CO2 permeabilities of films available for packaging fresh produce are as shown in Table 2.

Table 1: Ethanol Sorption Test Data of Polymer Films (Thalmann, 1990)

Film	Temperature (°C)	Weight increase		
		mg	mg dm_2	%
LDPE	49.1	3.28	2.10	0.43
OPP	25	8.46	4.13	1.13
	50	4.46	2.85	0.78
PS	26.1	32.57	20.84	3.63
	50	35.36	22.63	4.02
Rigid PVC	25	19.12	12.24	2.35
	50	42.91	27.46	5.34
PTEP	49.3	14.72	9.42	2.74

Table 2: Permeabilities of Films Available for Packaging Fresh Produce (Zagory et al., 1988)

Film Type	Permeabilities (cc./m2.mil.day.atm.)	
	Carbon dioxide	Oxygen
Polyethylene		
Low Density	17,700-77,000	39,00-13,000
Polyvinyl		
Chloride	4,263-8,138	620-2,248
Polypropylene	7,700-21,000	1,300-6,400
Polystyrene	10,000-26,000	2,600-7,700
Saran	52-150	8-26
Polyester	180-390	52-130

MATERIAL AND METHODS

MATERIALS

Polymer Films

- PET (Mylar 50K 23) 0.7 mil (Du Pont Co., Chemicals & Pigment Dept., Wilmington, DE)
- Saranex 2.0 mil (Dow Chemical, Midland, MI)
- LDPE 1.5 mil (unknown source)
- Poly propylene (0% ceramic 0.9 mil, 3% ceramic 1.4 mil, and 7% ceramic 1.8 mil provided by Kwang-Ho Lee of STC Corporation, Kyoungki, Korea)
- Poly vinylchloride 1.0 mil (Mobil Polymer US.Inc., Norwalk, CT)
- Oriented Polystyrene 1.0 mil (unknown source)
- Ethylene vinyl acetate co-polymer 0.8 mil (unknown source)
- Cellulose acetate 0.8 mil (unknown source)
- Polyvinyl acetate 1.0 mil (unknown source)
- Poly vinyl butyral 1.0 mil

Poly (vinyl butyral) films (PVB) were casted from a solution prepared by dissolving Poly(vinyl butyral) powder which consisted of 19% hydroxyl/ 1% acetate / 80% butyral (Scientific Polymer Products Inc., Ontario, NY) in absolute ethanol until saturated. The saturated solution was extended

on a polyethylene film by using coating bar number 34. The solvent was evaporated at room temperature for 24 hours and then was put in a vacuum oven (set at 50°C) for 4 hours. The poly(vinyl butyral) layer was easily removed from the polyethylene film, the thickness was measured as 1.0 mil.

- Polyethyl acrylate

Prepared by coating a bleached kraft paper (4.2 mil) with polyethylene acrylate 18% solution in toluene (Scientific polymer products, Inc., Ontario, NY). A coating bar No. 34 was used for extending the polymer solution on the paper surface. The coated material was left at room temperature, under hood for 24 hours. It was dried in a vacuum oven set at 50°C for 4 hours. The total thickness of the coated material is 4.3 mil.

Gas

- Nitrogen gas

  High purity dry nitrogen was provided by AGA Gas, Inc. (Cleveland, OH)

- Carrier Gas

  Nitrogen dry grade gas containing 1% Hydrogen, supplied by AGA Specialty & Medical Gases Division (Maumee, OH)

- Permeant

  Oxygen supplied in the form of compressed air (O_2 partial pressure equals 0.21 atm), obtained from AGA Gas, Inc. (Cleveland, OH).

Chemicals

- 1, 2-dichlorobenzene
  HPLC grade, Aldrich Chemical Co. Inc., (Milwaukee, WI)
- Ethyl Alcohol USP, Absolute - 200 proof, Midwest Grain Co. of Illinois, (Pekin, IL).
- Tenax GC 35760 Mesh, Alltech Associated, Inc., (Deerfield, IL).

PROPERTIES OF POLYMER SAMPLES

1. Low-Density Polyethylene (LDPE)

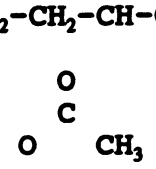
This is a thermoplastic polymer produced by the polymerization of ethylene gas. Its molecular structure of this polymer can be represented as:

$$-\!\!-[CH_2]-\!\!-_n$$

The polymer is obtained from a non-catalytic high-pressure process, therefore, it has a branched structure. The degree of crystallinity in LDPE is a function of the amount of short chain branching, normally in the range of 30% to 40%. This polymer has good oil resistance because of the non-polar structure and also is a good water barrier. However, it is a poor barrier to most other gases. For instance, the oxygen permeability coefficient is between 6,000-15,000 cc.mil/day.m^2.atm. The glass transition temperature is -120°C and PE is a polymer which sorbs large

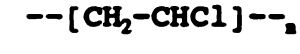
amount of organic vapors. This is a inexpensive polymer widely used in the packaging industry.

2. Ethylene-Vinyl Acetate copolymer (EVAc)



Ethylene-vinyl acetate copolymers include a board range of thermoplastic material with vinyl acetate constants from below 5 to 50% incorporation. Compared to other polyolefins such as LDPE, EVAc is more polar and less crystalline. As the vinyl acetate (VA) content increases the low-temperature flexibility and impact resistant increases but the barrier properties decreases. Above 50% VA incorporation, EVAc is totally amorphous.

3. Polyvinyl Chloride (PVC)



This polymer has atactic stereochemical configuration, therefore, it is amorphous. However, because of the polarity of the chloride groups is high, the polymer chains are tightly packed (Tg= 87°C). Stabilizer are always added to stabilize PVC since it tends to degrade at high

temperature. The barrier properties depends on how much it is plasticized, usually, oxygen barrier is low. PVC has excellent clarity, and is among the lowest priced film.

4. Vinylidene Chloride Copolymer

Saran is a copolymer of vinylidene chloride (VDC) with vinyl chloride, acrylates, or nitriles. The choice of comonomer significantly affects the properties of the resulting polymer. The important attributes of copolymers are their low permeability to gases and liquids and also high chemical resistance. Saran is used in food packaging as barrier to moisture, flavorants, and odors.

5. Polypropylene (PP)

$$--[CH_2-\underset{CH_3}{CH}]--_n$$

The most common commercial form of PP is isotactic PP which allows crystal formation (60% crystallinity). The crystalline nature gives it good solvent and heat resistance. The Tg of PP is about 10°C which is higher than PE because of the large methyl substituent group. Oxygen permeability is about 2,400-4,000 cc.mil/m^2.day.atm. PP has good clarity, its high melting point makes it suitable for heat-processed product, and it is among the lowest-priced transparent film. The ceramic filled PP is developed in Korea and was kindly obtained from Dr. K Yam of Rutgers

University

7. Polystyrene (PS)

$$--[CH-CH_2]--_n$$

Crystal PS is an amorphous polymer made from the addition polymerization of styrene monomer. The Tg of PS is relatively high (about 90°C). This is because the phenylene group, though it is not polar, is bulky which prohibits chain mobility. It has good optical properties. The high moisture and gas transmission rates are very desirable for fresh produce and baked goods.

8. Polyethylene terephthalate (PET)

This polymer is a condensation polymer generally between ethylene glycol and terephthalic acid with the structure as below:

$$--[C(=O)-\text{C}_6\text{H}_4-C(=O)-O-CH_2-CH_2-O]--_n$$

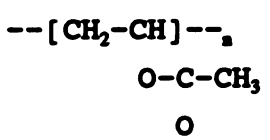
The ring structure of the back-bone chain provides the rigidity of this polymer. Thus it exhibits a high transition temperature (Tg = 73-80°C, Tm = 246-265°C). Carbonyl groups provide high molecular force, therefore, it exhibits high barrier properties. The oxygen permeability

is about 50-100 cc.mil/day.m_2.atm. It also has good chemical resistance and good transparency. Its cost is rather high.

9. Cellulose Acetate

Cellulose Acetate is an acetic acid ester of cellulose. The moisture sensitivity is less than that of Cellophane. It is nearly always used plain, without a heat-seal coating plasticizers are frequently added to improve its impact strength. Moisture and gas barrier of this material are poor (oxygen permeability coefficient is about 1000-3000 cc.mil/sqm.day.atm.).

10. Polyvinyl Acetate



This polymer is amorphous because of atactic stereochemical configuration. Tg of this polymer is about 28-31°C. This polymer is soluble in organic solvent, eg. esters, ketones etc., but it is insoluble in the lower alcohol (excluding methanol), water and nonpolar liquid such as ether.

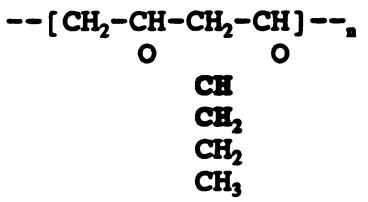
11. Polyethyl Acrylate

Polyethyl acrylate is an acrylate ester which is an unsymmetrically substituted ethylene. This polymer is a

rubberlike, soft and extensible polymer with Tg = -24°C.

12. Polyvinyl Butyral (PVB)

Polyvinyl butyral is a member of the polyvinyl acetal family, made by reacting polyvinyl alcohol with butyraldehyde, with some unreactive PVA groups retained in the polymer. It is soluble in alcohol and the structure is shown below:



METHODOLOGY

The oxygen permeance of the film samples was determined in accordance with ASTM Standard D 3985-81 "Oxygen Gas Transmission Rate Through Plastic Film and Sheeting Using A Coulometric Sensor". The studies were carried out on an Oxtran 100 Permeability tester (Modern Controls, Inc., Elk River, MN), whose operation is based on the isostatic method. Since the oxygen sensor of the Oxtran can be damaged by high concentration of oxygen, the surface area of high oxygen permeance film had to be reduced. This was achieved by utilizing a impermeable mask that reduced the exposed area of the film by a factor of 10.

The Oxtran 100 oxygen permeability tester was modified to prevent the ethanol vapor used during permeability tests from being conveyed by the carrier gas to the coulometer sensor. By preventing the ethanol vapor from contact with the oxygen sensor, potential damage of the sensor was avoided. Possible effects of the presence of ethanol vapor in the sensor could be damage to the sensor or interference with the permeability output.

A trapping agent was used to retain the ethanol vapor in the carrier gas and was placed after the permeability cell and before the sensor. The trapping agent must have a known ethanol sorption capacity and it must not absorb oxygen gas. Tenax was the trapping agent selected, and the following tests were performed:

1. Determination of oxygen absorptivity of tenax.
2. Determination of ethanol sorption capacity of tenax.

These tests are described in Appendix 3 and Appendix 4, respectively.

Results of the oxygen absorptivity test indicated that tenax does not retain oxygen. The ethanol absorption capacity of tenax was determined to be 657 μg ethanol/g of tenax at 6 ml/min of flow. However, the absorption capacity might be changed as a function of the flow rate of ethanol stream. Calculation for amount of tenax necessary for each ethanol

concentration is presented Appendix 5.

The Oxtran apparatus was modified by connecting a glass tube containing the tenax to the "Package Test Fitting" connection as indicated in Figure 3. In this way, tenax was able to trap ethanol vapor from the carrier gas which conveyed the oxygen permeated in the presence of ethanol vapor before going to the sensor.

The concentrations of ethanol vapor used in this study were based on studies conducted by Dr. A. Cameron (Horticulture Department, Michigan State University) on fresh fruits. The value of the ethanol vapor concentrations tested in this study corresponded to the head-space equilibrium vapor concentration of a ethanol in water 100 ppm (volume/volume). The determination of equilibrium head-space ethanol vapor concentration of the ethanol/water solution is described in Appendix 2, which reveals that for a solution of 100 ppm Ethanol in water, a concentration of ethanol in headspace equal to about 1 ppm (weight/volume) is obtained. In this study, the oxygen permeability through the films was determined in the presence of 1 and 7 ppm ethanol vapor (wwt/V). The ethanol vapor concentration are expressed through out in ppm (mass/volume), vapor in gas (nitrogen or air), where 1 ppm equal 1 μg ethanol per cm^3 of gas mixture, at 1 atm at 21 °C. Prior to each permeability test, the tested film sample was mounted in the permeability cell,

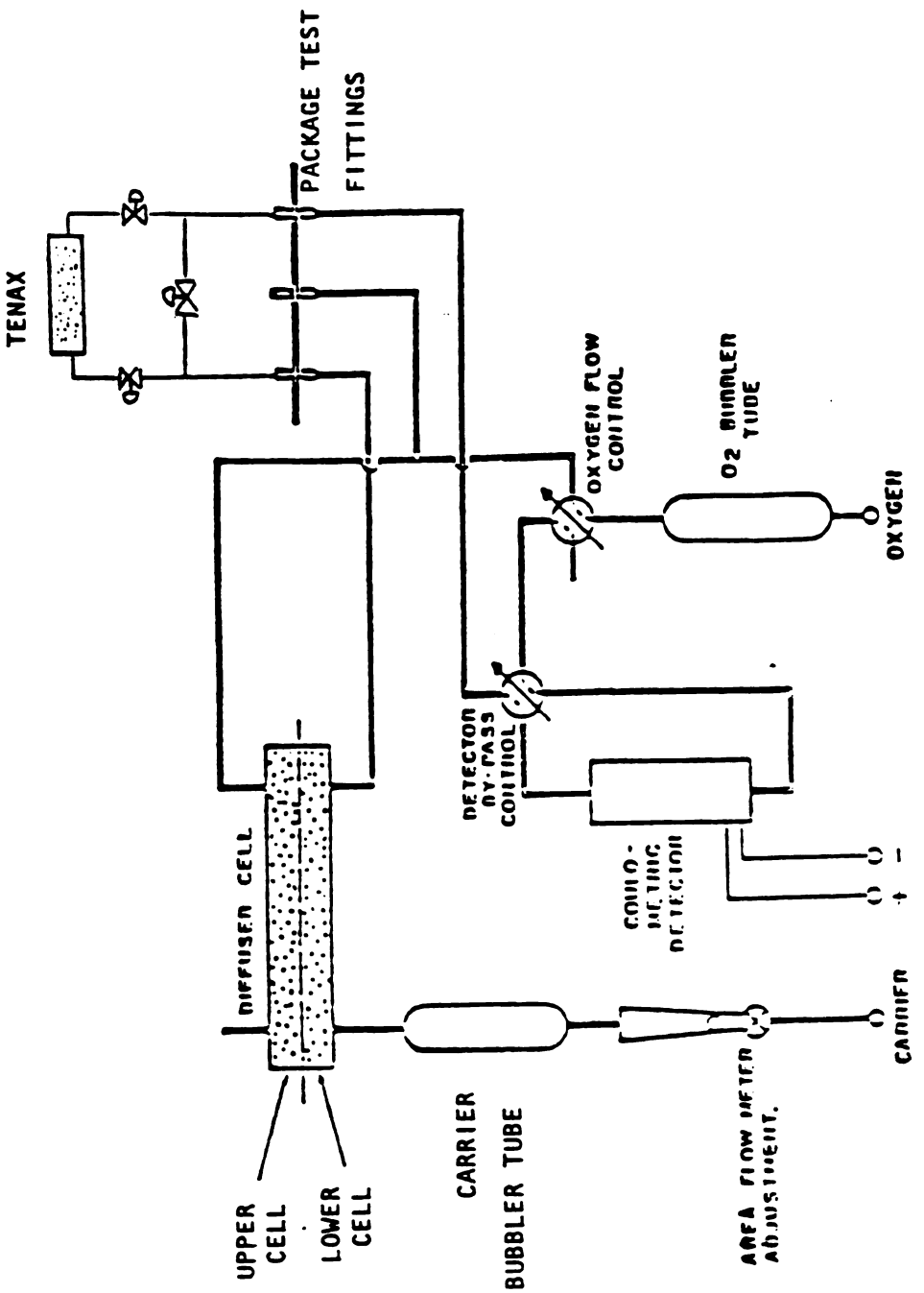


Figure 3: Modified OXTRAN 100 Diagram

both surfaces of the sample were preconditioned by being exposed to ethanol vapor stream for about 24 hours. During the permeability tests, air with adjusted ethanol vapor concentration was flowed through the upper chamber of the permeability cell throughout the test.

The gas streams containing the ethanol vapor were generated by using an ethanol generator apparatus. The required concentration was obtained by blending a stream of pure gas with another gas stream of the same gas that bubbled in chemically pure liquid ethanol. A controlled flow of pure gas (nitrogen or air) was bubbled through pure liquid ethanol in a gas-washing bottle to generate a mixture of gas and ethanol vapor. To adjust the required ethanol vapor concentration stream, a fraction of this gas mixture was vented out to decrease the excessive flow and the rest was mixed by the pure gas and adjusted to the required value. The flow of gas streams was measured by flow meters and could be adjusted by needle valves. Ethanol concentration of the gas stream was monitored by withdrawing a sample from the sampling port and injecting the sample into the GC. The ethanol calibration curve of the GC is as shown in Appendix 1. The schematic of the ethanol generator is as in Figure 4.

The experimental method to measure the effect of ethanol on oxygen permeability of the film samples is as follows.

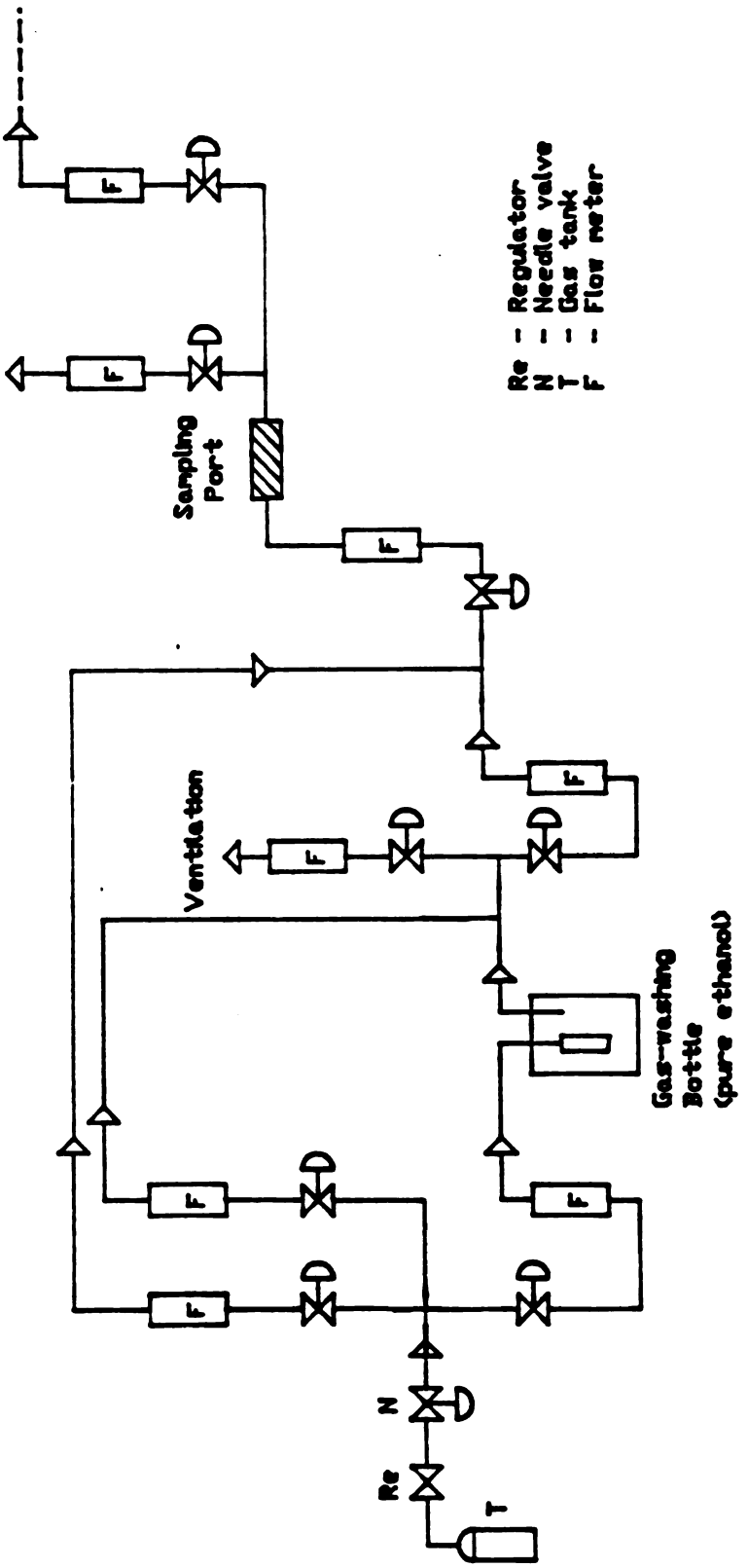


Figure 4: The Schematic of Ethanol Vapor Generator System

1. The test was conducted to determine the conversion factor which was used in calculating the permeance. (The procedure is as shown in Appendix 6.)
2. Before conducting the permeability test, the tenax system was prepared by eliminating oxygen from the system. This was done by flowing the carrier gas (1% hydrogen balance nitrogen) through the system until zero steady baseline was obtained. The system was thoroughly checked for leakage and was kept closed to maintain its conditions.
3. Free-ethanol permeability measurement was conducted by the conventional procedure and bypassing tenax system.
4. For oxygen permeability measurements in the presence of ethanol, the tested film was preconditioned in the ethanol vapor stream for 24 hours. This preconditioning was carried out by passing the required ethanol vapor stream into both sides of permeability cell on which tested film was mounted. This was achieved by connecting the ethanol vapor generator, in which nitrogen was used as the pure gas, at the carrier gas inlet of the Oxtran. The final flow was adjusted to about 16 ml/min. The Oxtran was set at bypass sensor, therefore, both surfaces of the sample would be exposed by ethanol at adjusted concentration (the flow diagram is as in Figure 5).
5. The oxygen permeability test was conducted in the presence of ethanol by using an air-ethanol mixture as

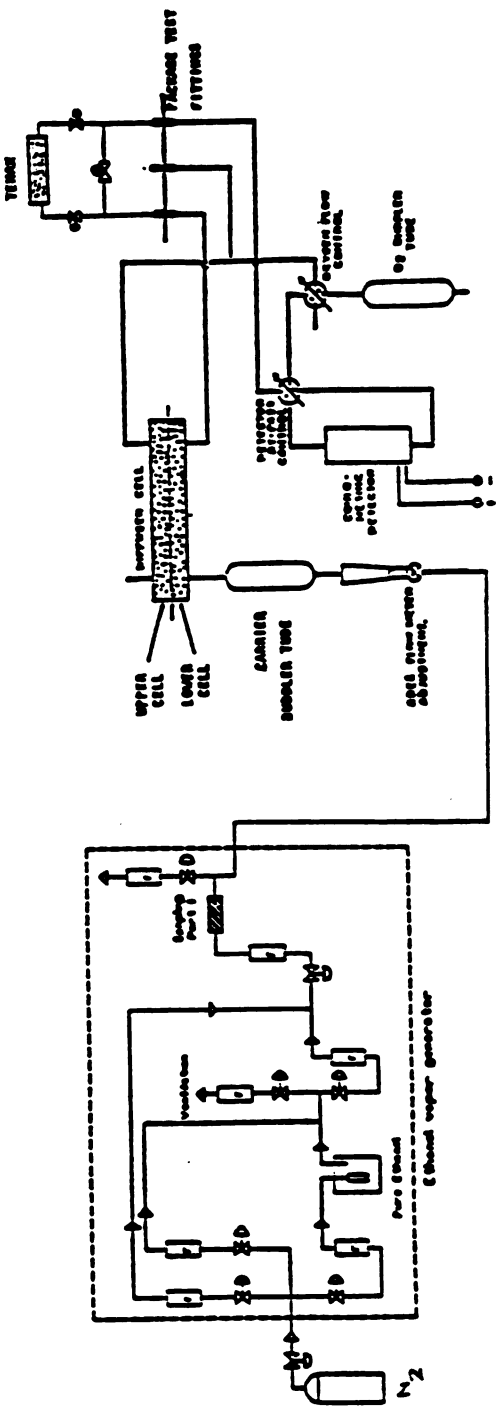


Figure 5: Diagram of Preconditioning System

a permeant vapor. This was obtained by connecting the ethanol generator system, using air as the pure gas, to the oxygen inlet of the Oxtran (the schematic is as in Figure 6), the final flow was adjusted to about 16 ml/min. With this setting, ethanol vapor in air flowed through the upper chamber. The permeability test was then conducted in the conventional procedure, except that the tenax system was used.

6. The output from the recorder which is in voltage units was converted to permeance units that are in cc/day.m^2.atm. by multiplying the volt response times the conversion factor (from Appendix 6) and dividing by the partial pressure of oxygen in air. The equation is as follows;

$$Permeance = \frac{VoltageResponse \times 15.53 \times 10}{0.21}$$

7. The above experimental method was applied to both 1 ppm and 7 ppm concentration levels of ethanol in the permeation stream, except that a different amount of tenax was used in each case. However, in the case of 7 ppm ethanol concentration, an excessive drop of pressure through the tenax system was experienced. This was a result of the large amount of tenax needed (8 g). The problem was avoided by loosely packing

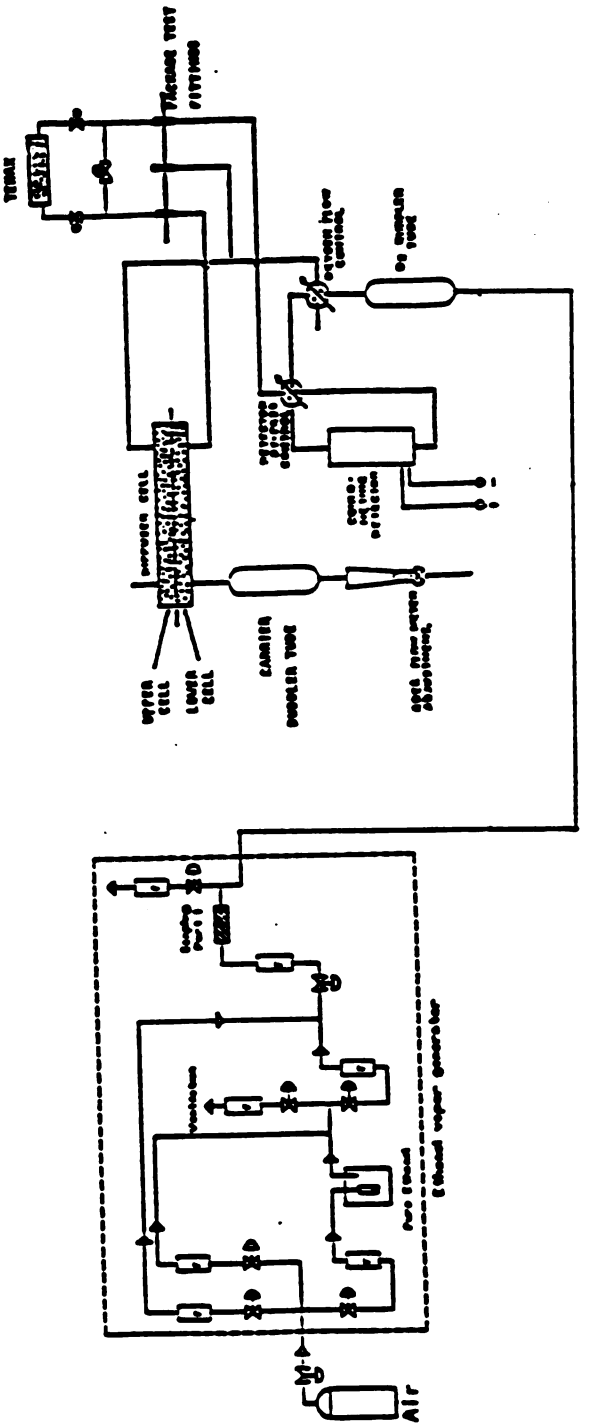


Figure 6: Diagram of Oxygen Permeability Test System in the Presence of Ethanol

the tenax in a cylinder, layers of tenax powder were alternated with layers of glass wool. This provided an acceptable drop in pressure. However, to protect the coulometric sensor, only steady state transmission was recorded.

8. The estimated percent error of each test was calculated by calculating the percent deviation from three permeability tests of a selected LDPE film sample as shown in Appendix 8.

RESULT AND DISCUSSION

In this study, the effect of ethanol vapor on the oxygen permeability of selected polymeric film was evaluated under different ethanol vapor concentration values. To carry out this study, an Oxtran 100 oxygen permeability tester was modified to use a trapping agent to retain ethanol vapor before reaching the oxygen sensor. Preliminary experiment have shown that tenax, the trapping agent, does not absorb oxygen, thus, producing no interference with oxygen measurements. Ethanol vapor which was presented in the permeability cell during the permeability test was trapped by the tenax from the carrier gas stream, leaving the carrier gas to convey the permeated oxygen to the coulometer sensor. The tests were conducted at dry condition (0% relative humidity) to avoid any effect of the water molecule on the polymer and the tenax. In this study, the equipment was designed for low ethanol concentration (below 20 ppm).

The oxygen permeability under three different ethanol vapor concentrations (ie., 0, 1, and 7 ppm, weight/volume) were measured. The experimental data for each polymer under ethanol concentrations of 0 ppm and 1 ppm are presented in Tables 9 to 32 (see Appendix 7). The graph comparing oxygen

permeance of both ethanol conditions of PP (3% ceramic) film is shown in Figures 7 which reveal that the experiments conducted under 1 ppm ethanol conditions required longer time to establish steady state as compared to those of 0 ppm ethanol vapor conditions. This due to the fact that the connection of tenax to the Oxtran not only increased the pathway between permeation cell to the sensor but also resisted the flow of the gas stream.

To determine the effect of the pathway on the time to establish steady state, oxygen permeability under 0 ppm ethanol vapor and 1 ppm ethanol vapor conditions of polypropylene (3% ceramic) were determined by using tenax system. The respective graphs of permeance value versus time are presented in Figure 8. This permeance profile was compared to that in Figure 7 which was the permeance profile of the same polymer under 0 ppm and 1 ppm ethanol conducted by using a different pathway. The profiles reveal that by using the same pathway, the time to establish the steady state permeance of 0 ppm ethanol was increased compared to that of non-tenax system. Therefore, the time to establish steady state can be compared by modified Oxtran by using the same pathway, however, in this study only steady state permeability will be considered.

Due to fluctuations in room temperature, the permeability of each condition was conducted under slightly different

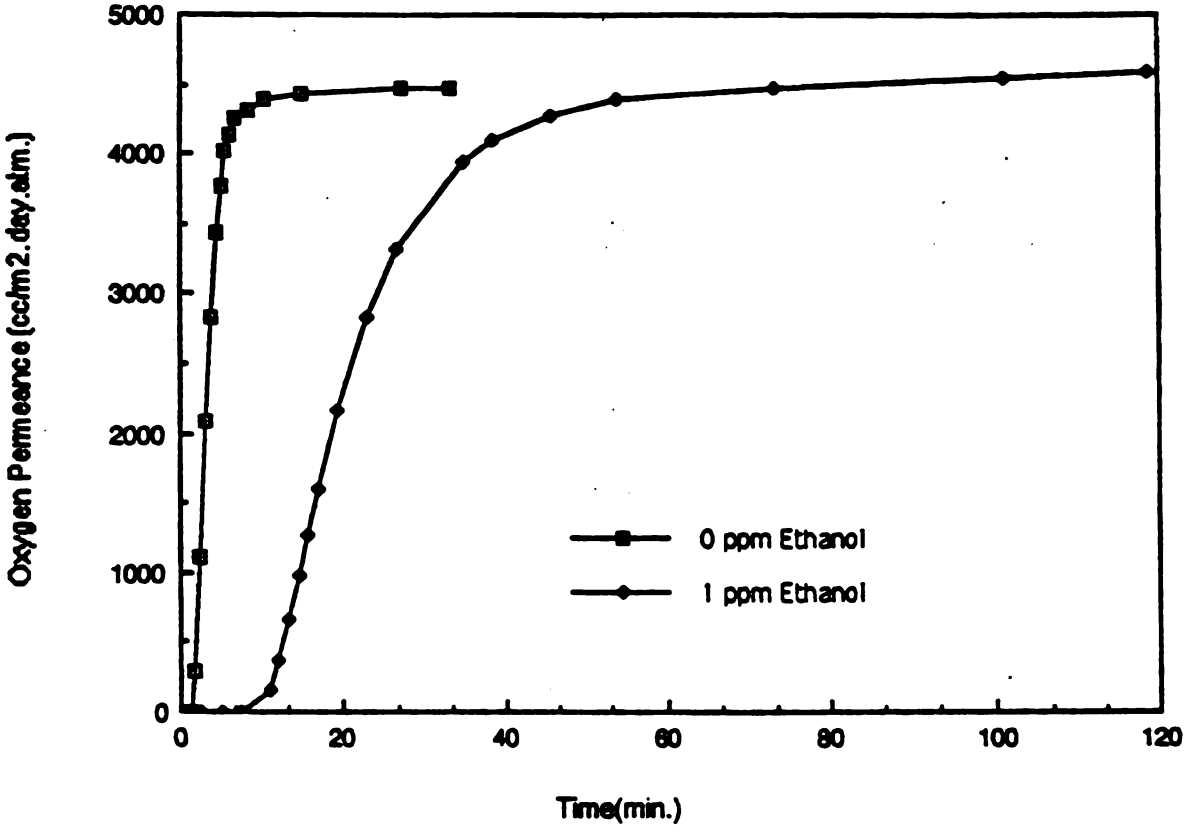


Figure 7: Oxygen Permeance of PP 3 % Ceramic 1.4 mil at 23 C for 0 and 1 ppm Ethanol Condition

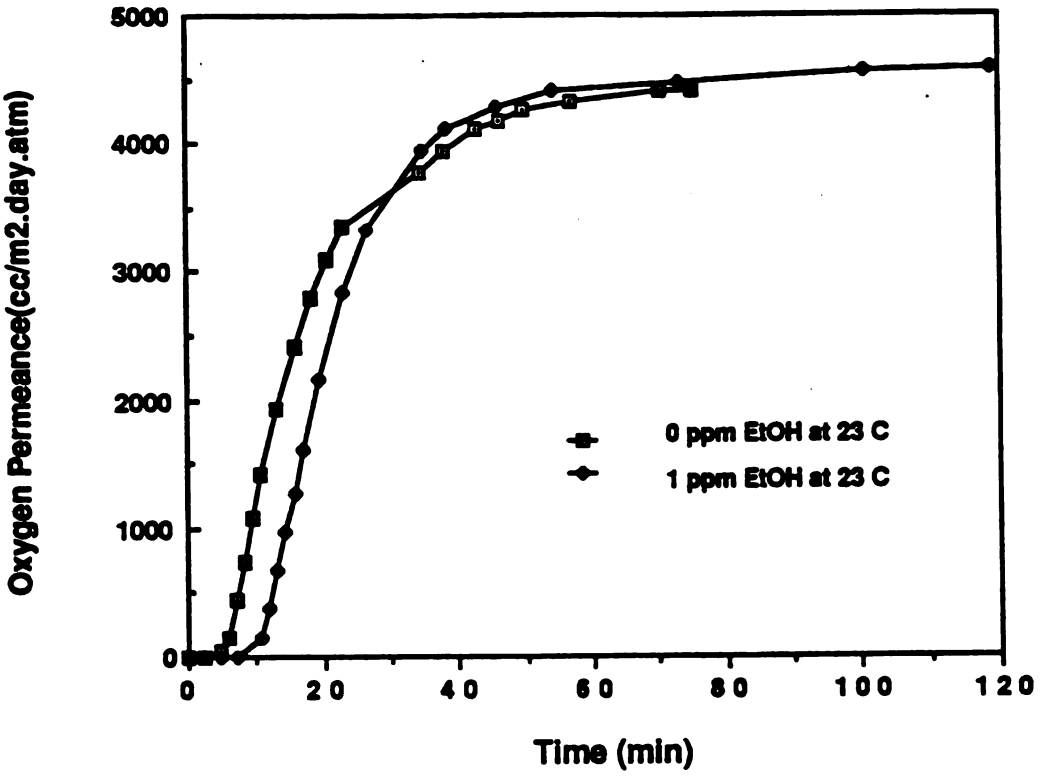


Figure 8: Oxygen Permeance of PP (3% Ceramic), Tenax Pathway

temperature values. To compare the steady state permeance values among the different ethanol conditions and polymer films, values of steady state permeance were normalized at 24 °C based on the Arrhenius equation;

$$P_1 = P_2 \exp\left[\frac{E}{R}\frac{(T_1 - T_2)}{(T_1 T_2)}\right]$$

where, E = Activation Energy of polymer(cal/mole)

R = Gas constant = 1.98 (cal/Kelvin.mole)

T_1, T_2 = Absolute temperature 1 and 2 (Kelvin)

P_1, P_2 = Oxygen permeance at absolute temperature 1 and 2, respectively (cc./sqm.day.atm.)

Normalized oxygen permeance values are as shown in Table 5 which shows only small difference of oxygen permeation for the film samples, between the 1 ppm ethanol and non-ethanol condition within 24 hours period. The percent difference is in range of -13 to 2 percent.

For the case of 7 ppm, only the steady state was considered in this test to avoid excessive exposure of ethanol to the sensor, the results are shown in Table 4. The steady state permeance values shown in Table 4 were also normalized to

values at 24 °C as presented in Table 5, these values show a more significant effect of ethanol on the oxygen permeance at 7 ppm ethanol conditions. In the case of PET, although in the first experiment the oxygen permeance at 7 ppm ethanol vapor concentration showed a significant increase, a second experiment indicated only 5% difference between 1 ppm and 7 ppm ethanol condition. Therefore, the effect of 7 ppm ethanol vapor on the oxygen permeability in PET films is not conclusive and further studies are necessary to confirm any effect.

Table 3: Oxygen Permeance of Polymer Film Samples at 0 ppm and 1 ppm (wt/vol) Ethanol Vapor (0% RH)

Film	Thickness (mil)	0 ppm EtOH		1 ppm EtOH	
		T(°C)	Permeance (cc/m2.day.atm)	T(°C)	Permeance (cc/m2.day.atm)
PET	0.7	24	22	24	19
Saran	2.0	24	10	24	10
LDPE	1.5	23	4500	24	4700
PVC	1.0	24	7500	24	7300
PS	1.0	23	4100	24	3800
EVA	0.8	24	10900	24	11000
Cellulose Acetate	1.0	24	2600	24	2500
PVA	1.0	26	860	24	800
Polyvinyl Butyral	1.0	23	3100	22	2700
PP 0%Ceramic	0.9	23	4500	23	4300
PP 3%Ceramic	1.4	23	4500	23	4600
PP 7%Ceramic	1.8	21	2200	23	2200

Table 4: Oxygen Permeance of Polymer Film Samples at 0 ppm and 7 ppm (wt/vol) Ethanol Vapor (0% RH)

Film	Thickness	Without EtOH		With EtOH	
	(mil)	T(°C)	Permeance (cc/m2.day.atm)	T(°C)	Permeance (cc/m2.day.atm)
PET	0.7	22	16	24	27
		23	20	23	21
Saranex	2.0	24	10	22	8
LDPE	1.5	23	4500	22	4200
PVC	1.0	24	7500	22	6900
PS	1.0	23	4100	24	3800
EVA	0.8	24	10900	22	10000
Cellulose Acetate	1.0	24	2600	23	1900
PVA	1.0	26	860	23	590
Polyvinyl Butyral	1.0	23	3100	22	2500
PP 0%Ceramic	0.9	23	4500	22	4100
PP 3%Ceramic	1.4	22	3700	22	3700
PP 7%Ceramic	1.7	21	2200	23	2100
Polyethyl Acrylate coated on paper	4.2	23	54E05	22	53E05

Table 5: Normalized Values of Oxygen Permeance of Polymer Films at 24 °C (Calculated by using Arrhenius Equation)

Film	Steady state permeance cc/m2.day.atm)			ΔPermeance* of 7 ppm
	0 ppm EtOH	1 ppm EtOH	7 ppm EtOH	(%)
PET	22	19	-	-
	18	-	27	50
	21		22	5
Saranex	10	10	10	0
LDPE	4600	4700	4700	0
PVC	7200	7000	7800	8
EVA	10900	10800	10900	0
Cellulose Acetate	2500	2500	2000	-20
PVA	760	800	640	-16
Polyvinyl Butyral	3200	3000	2800	-13
PP 0% Ceramic	4700	4600	4600	0
PP	4800	4800	-	-
3% Ceramic	4100	-	4100	-15
PP 7%Ceramic	2600	2400	2300	-12

* Based on oxygen permeance of 0 ppm ethanol condition.

CONCLUSIONS

1. An apparatus was designed and built to test the effect of organic vapors on the permeability and diffusion, coefficient of oxygen. The same approach can be employed for other gases such as carbon dioxide.

2. There was no significant effect of ethanol vapor in the concentration range of 0-1 ppm (weight/volume) on the oxygen permeability of selected polymeric film within a 24 hour period. However, the effect of ethanol vapor at concentration higher that 1 ppm still need a further study.

BIBLIOGRAPHY

BIBLIOGRAPHY

Baer, E. (1964). Engineering Design of Plastics. Polymer science and engineering series., Reinhold publishing corp. New York.

Brandrup, J., and Immergut, E.H., editor. (1975). Polymer Handbook, 2nd ed., A Wiley-interscience.

Chern, R.T., Koros, W.I., Senders, E.S., and Yui, R. (1988). "Second component" effects in sorption and permeation of gases in glassy polymers. Journal of membrane science, 15:157 (1983).

Comyn, J. (1985) Polymer Permeability, Elsevier Applied Science Publishers, New York.

Delassus, P.T., Strandburg, G., and Howell, B.A. (1988). Flavor and aroma permeation in barrier film: the effects of high temperature and high humidity. Tappi Journal, Nov. pp.177.

Gedraitite, G.B., Marin, A.P., and Shlyapnikov, Y.A. (1989). The Size distribution of additive sorption centers in polyethylene. Eu. Polymer J., 25:31-41.

Hanlon, J.F. (1984). Handbook of Packaging Engineering (2nd ed.). Mc Graw-Hill, Inc.

Hensley, T. M. (1991). The Permeability of Binary Organic Vapor Mixtures through a biaxially oriented polypropylene film. M.S. Thesis. Michigan State University, E. Lansing, MI.

Hopfenberg, H.B., and Stennett, V. The Diffusion and Sorption of Gases and Vapours in Glassy Polymers. The physics of glassy polymers., pp.504-547.

Encyclopedia of polymer science and engineering (2nd.ed.), Herman, F.M. et al., editor,(John Wiley & Sons,1989).

Hernandez, R.J., Gaicin, J.R., and Grulke, E.A. (1992). The Sorption of Water Vapor by an Amorphous Polyamide. Journal of Membrane Science. 65:187-199

Huang, R.Y.M., and Lin, V.J.C. (1968). Separation of liquid mixtures by using polymer membranes. I. Permeation of binary organic liquid mixtures through polyethylene. Journal of Applied Polymer Science., 12:2615.

Laine, R. , and Osburn, J.O. (1971). Permeability of Polyethylene Film to Organic Vapor. Journal of Applied Polymer Science., 15:327.

Landois-Garza, J., and Hotchkiss, J.H. (1988). Permeation of High-Barrier Films of Ethyl Esters. Food and packaging interaction, ASC symposium series 356. Hotchkiss,J.S., editor., American Chemical Society, Washington, DC.

Lui, K.J., Gaicin,J.R., and Hernandez, R.J. (1988). The effect of relative humidity on the permeability of toluene vapour through a multi-layer coextruded film containing hydrophilic layers. Packaging Technology and Science,1:57-65.

Pye, D.G., Hoehn, H.H., and Panar, M. (1976). Measurement of Gas Permeability of Polymers. II Apparatus for determination of permeabilities of mixed gases and vapors. Journal of Applied Polymer Science, 20:287.

Roger, C.E., Stannett, V., and Szwarc, M. (1960). The Sorption, Diffusion, and Permeation of Organic Vapors in Polyethylene. Journal of Polymer Science., 45;61.

Stennett, V., et al.,"Recent Advances in Membrane Science and Technology", pp 69-121.

Stern, S.A., and Trohalaki, S. (1990). Fundamentals of Gas diffusion in Rubbery and Glassy Polymers. Barrier Polymers and Structures, Koros, W.J.,editor, ASC symposium series 424, pp. 22-59, American Chemical Society, Washington, DC.

Thalmann, W.R. (1991). Sorption of Solvents in Plastics and Solvent Desorption and Retention. Packaging Technology and Science, 3:67-82.

Zagory, D. and Kader, A. (1988). Modified Atmosphere Packaging of Fresh Produce. Food Technology, September, pp 70-77.

APPENDICES

Appendix 1

Ethanol Calibration Curve for Gas Chromatography

Instrument: Hewlett Packard 5890A Gas Chromatography

Column - Supelco Wax 10

Cabowax 20 M

Condition - Oven temperature 80 °C

- Initial temperature 80 °C
- Initial time 1 minute
- Rate 4 degree/min.
- Final time 0
- Final temp 150 °C
- Flow 27.1
- Range 3
- ATT 0

Reagent: 1. 1,2-dichlorobenzene maximum impurities and specifications 98%, EM Science, Gibbstown, NJ.

2. Ethyl Alcohol USP absolute 200 Proof, Midwest Grain Co., IL.

Density 0.7836 gm/ml at 21 °C.

Procedure: 1. Prepared standard ethyl alcohol solution at various concentration (ie. 4 ppm, 10 ppm, 20 ppm, 40 ppm, 60 ppm, 80 ppm, and 100 ppm (volume/volume)) by using

1, 2- dichlorobenzene as the solvent.

2. Inject .5 μl of prepared solution into the

GC. (The retention time of ethyl alcohol is about 1.68 minutes.)

3. Plotted graph between quantity of ethanol injected versus area response.

Result :

Table 6: Ethanol Calibration Data for Gas Chromatography(1)

Conc.of ethanol (ppm.V/V)	Volume of ethanol injected $*10^9$(ml)	Quantity of ethanol injected $*10^9$(g)	Average area response (area unit)
0	0.0	0.0	0
4	2.0	1.6	1101
10	5.0	3.9	2785
20	10.0	7.8	4174
40	20.0	15.7	7628
60	30.0	23.5	14034
80	40.0	31.3	15112
100	50.0	39.2	23423

Standard curve of quantity of ethanol injected versus area response is as shown in Figure 9. The linear relationship between quantity of ethanol injected and area response is as equation ; $Y = -27.16 + 556.70\ X$

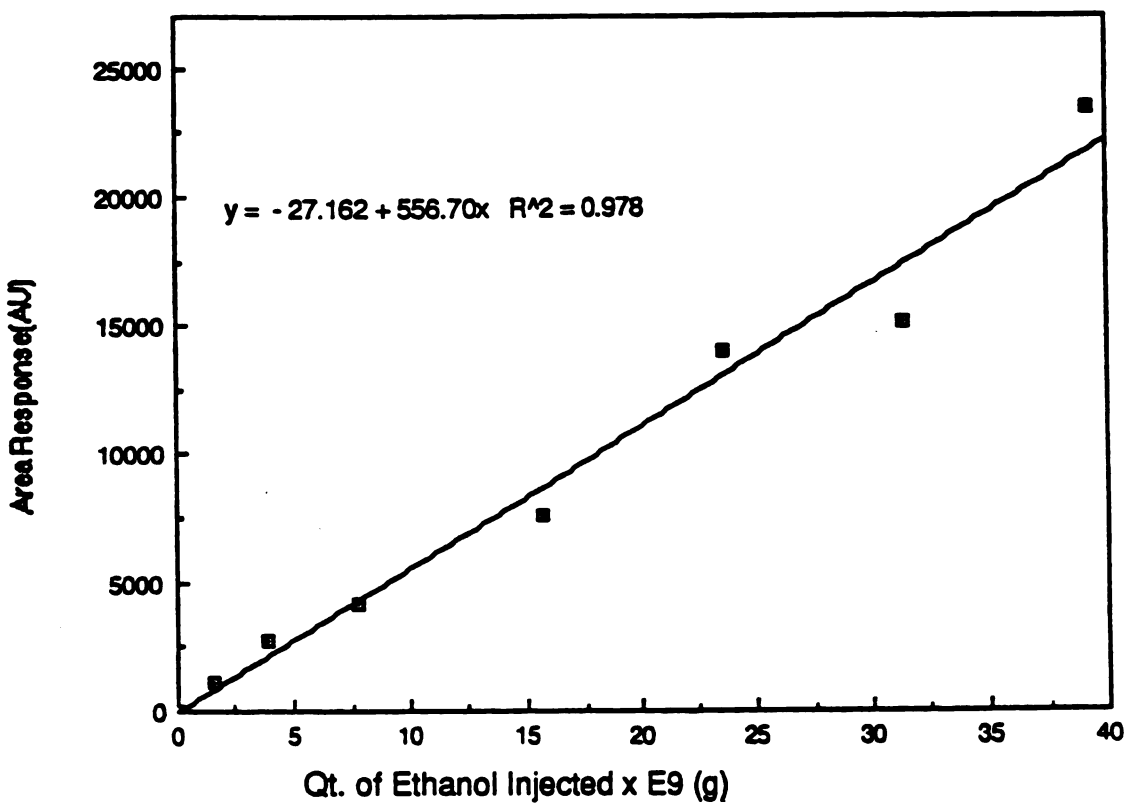


Figure 9: Ethanol Calibration Curve for the GC (1)

Table 7: Ethanol Calibration Data for Gas Chromatography(2)

Conc.of ethanol (ppm.V/V)	Volume of ethanol injected $*10^9$(ml)	Quantity of ethanol injected $*10^9$(g)	Average area response (area unit)
0	0	0.0	0
4	2	1.6	1401
10	5	306	3471
20	10	7.8	5879
60	30	23.5	20792
100	50	39.2	37588

Graph plotted between quantity of ethanol injected and area response is as shown in Figure 10. The linear relationship is as equation:

$$Y = - 547.5 + 952.8 X$$

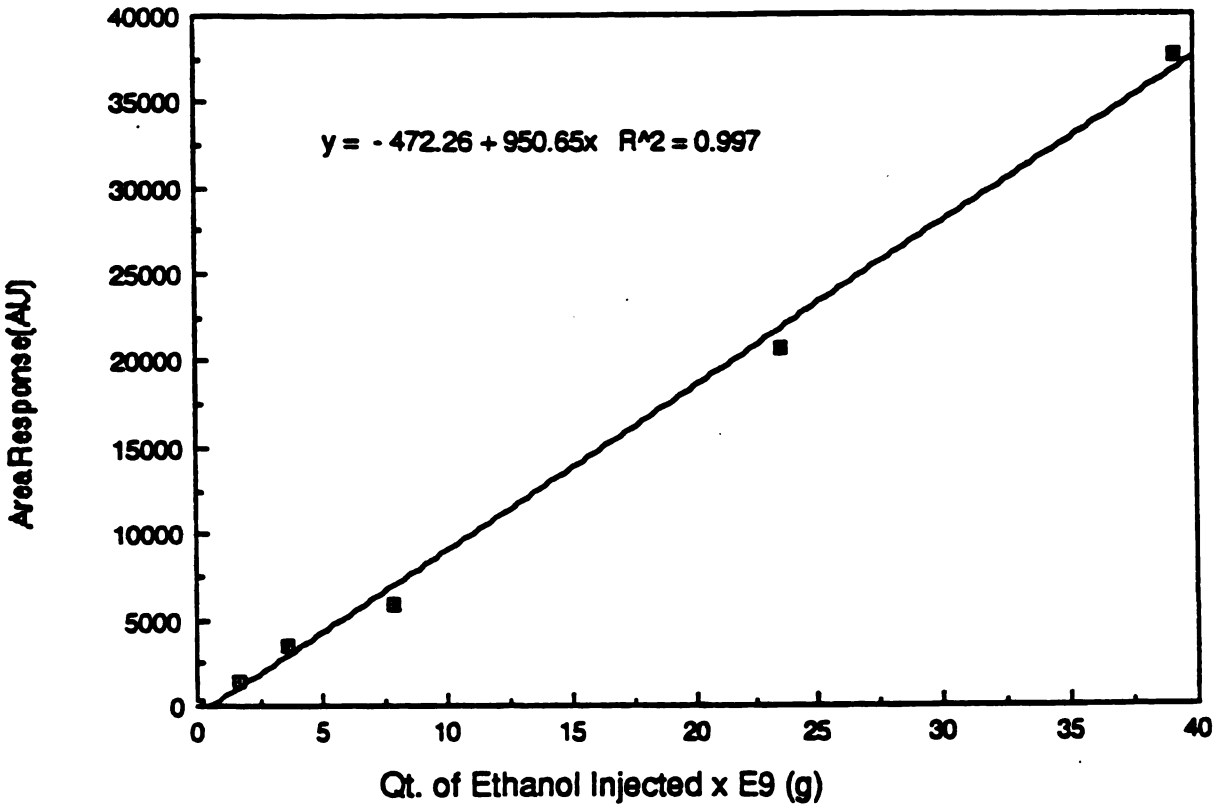


Figure 10: Ethanol Calibration Curve for the GC (2)

Appendix 2

Determination of Equilibrium Concentration of Ethanol in the Head-Space

Procedure:

1. Prepared aqueous solution of different concentration of ethanol (0.05%, 0.075%, 0.1% 0.125%, 0.50%, and 1.0%) by using distilled water and placed in septa seal vial.
2. Kept this solution in room temperature for 2 weeks.
3. Injected 100 μl of the headspace of each solution into the GC.
4. Calculated concentration of ethanol in head-space using standard curve (Figure 20.)

$$Y = - 27.16 + 556.70 * 10^{-9} X$$

Result. Table 8: Equilibrium Concentration of Ethanol in the Head-Space at 21 °C

Conc. of etOH sample(%byVol)	Area response (Area Unit)	Quantity inj. $*10^9$(g)	Conc. of in head-space (μg./ml)
0.051	4426	7.9	.079
0.075	6162	11.1	.111
0.100	7561	13.6	.136
0.126	9792	17.6	.176
0.500	41564	74.7	.747
1.000	78934	141.8	1.418

Graph plotted between equilibrium concentration of ethanol in headspace versus concentration of ethanol solution is as shown in Figure 11. The linear relationship is as equation:

$$Y = 3.760E\text{-}03 + 1.427X$$

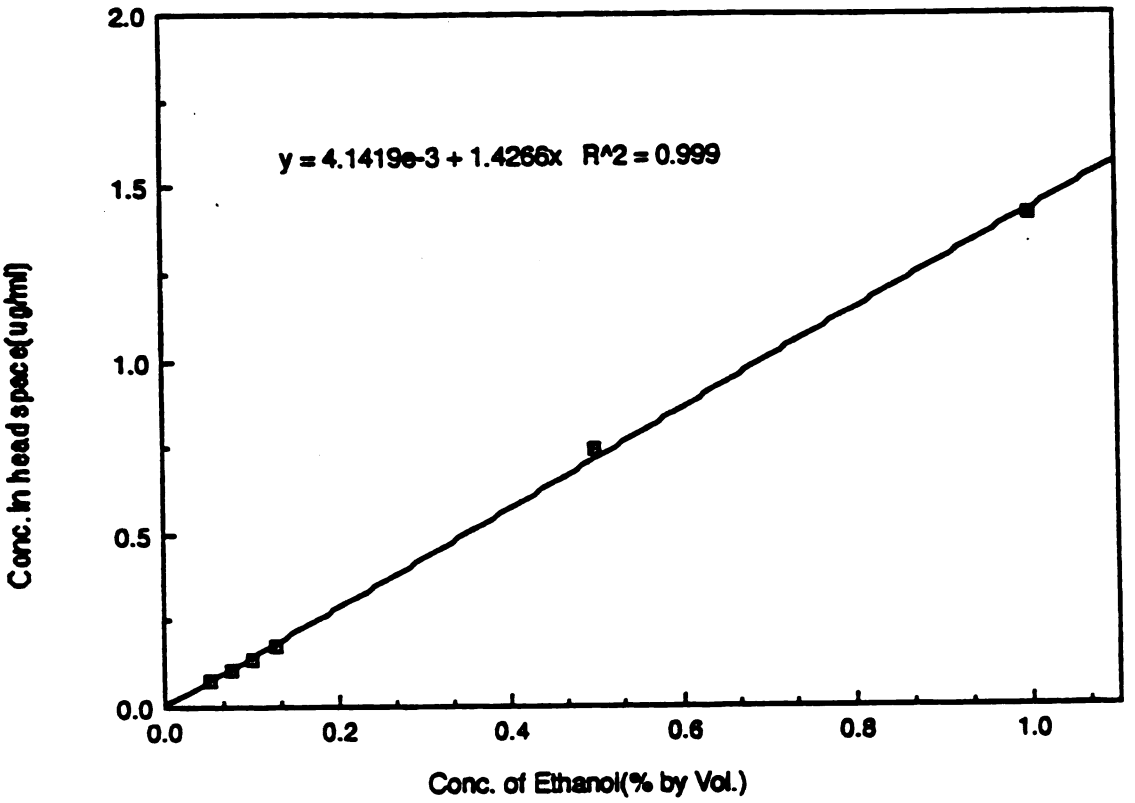


Figure 11: Equilibrium Concentation of Ethanol in the Headspace

Appendix 3

Oxygen Absorptivity of Tenax

Instrument: - Mocon Oxtran 100 Permeability Tester

- Linseis L6512 recorder.

Material: Standard reference Material 1470 Polyester film for gas transition from US Department of Commerce National Bureau of Standards, Washington, D.C. Permeance = 69.104 $cc/m^2.day.atm$.

Procedure:

1. Calibrate the Oxtran 100 by using standard Reference Material 1470.
2. Connect the tenax at the package test fittings as the schemetic in Figure 3, tenax was connected before the stream of carrier gas go to the sensor, measure the permeability of standard film again. The condition which was used in this test is dry condition at room temperature.
3. Compare the permeability of the standard film by using the system with tenax and without tenax.

Result:

Condition	Permeability output (mV)
With tenax	5.1
Without tenax	5.1

From the result reveal that at dry condition, room temperature, if tenax does absorb oxygen, it does not affect the final reading.

Appendix 4

Ethanol Sorption Capacity of Tenax

Instrument: Hewlett Packard 5890A Gas Chromatography
Column - Supelco Wax 10, Cabowax 20M
Condition - The same as in Appendix 1

Procedure: (Schematic of the system is as in Figure 12.)

1. Close the tenax system, adjust the concentration until close to 1 μg/ml. The concentration is determined by withdrawing 500 μl. gas from sampling port 1 by using a gas-tight-syringe and inject the sampling gas into the GC.
2. After get the desire ethanol concentration, then open the needle valve to let the ethanol vapor pass through the tenax.
3. Sampling the gas from sampling port 2. Determine the concentration until get the consistent concentration.

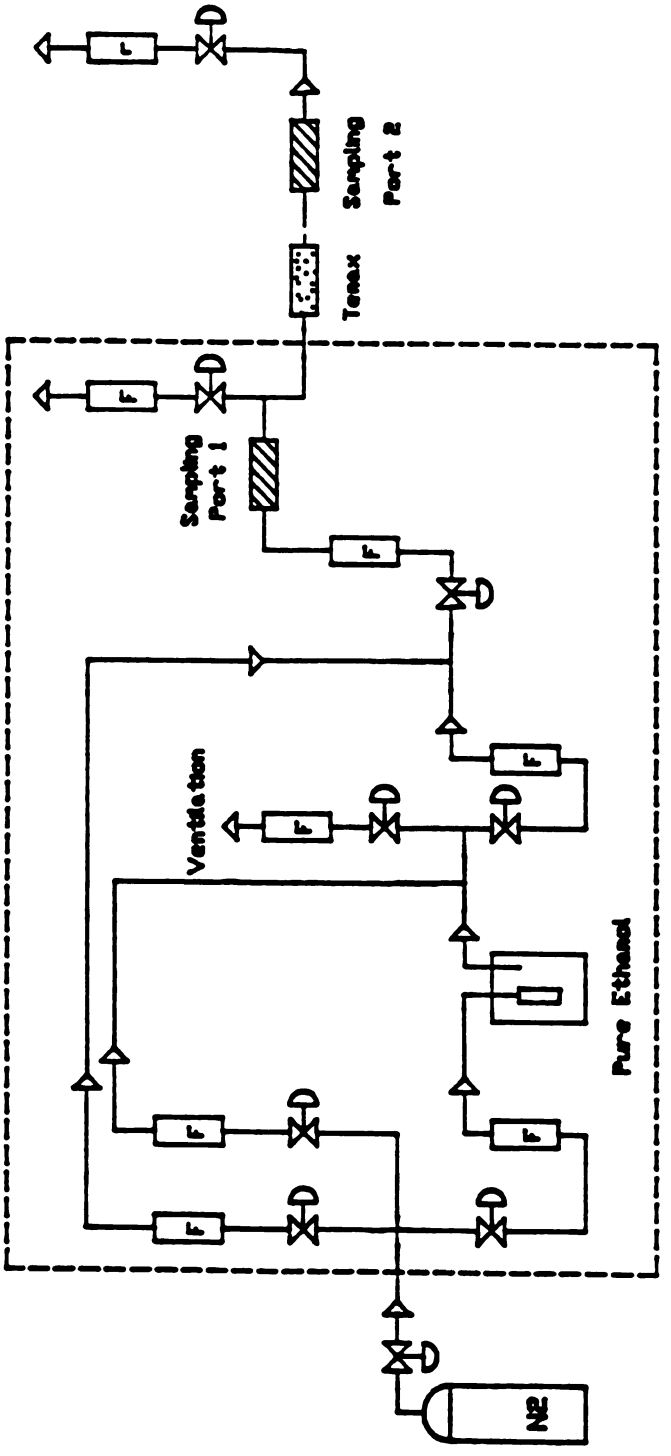


Figure 12: Schematic of Diagram for Determining Ethanol Sorption Capacity of Tenax

Result Table 9: Ethanol Sorption Capacity Data of Tenax at 21 °C

Time (min.)	Sampling Port 1 Area Response(AU)	Sampling Port 2 Area Response(AU)	Conc. of etOH in port 2 (μg/ml)
3	-	332	.00079
8	-	378	.00079
12	589310	-	-
18	-	314	.00066
24	597460	-	-
29	-	333	.00069
36	-	274	.00058
41	575940	-	-
46	-	319	.00067
53	-	379	.00079
62	-	328	.00067
69	-	3128	.000660
73	-	83799	.18858
77	-	469240	.985
82	-	569310	1.20
87	586510	-	-
93	-	600770	1.26
106	564750	-	-
118	-	610710	1.28

Graph plotted between concentration of ethanol in the sampling port 2 (μg/ml) versus time (min) is presented in Figure 13.

From the test result obtained, the average original concentration of ethanol (concentration of ethanol in sampling port 1) before the tenax is 1.2 μg/ml a with standard deviation .02 μg/ml. The time before the ethanol concentration in sampling port 2 started increasing was about 60 minutes.

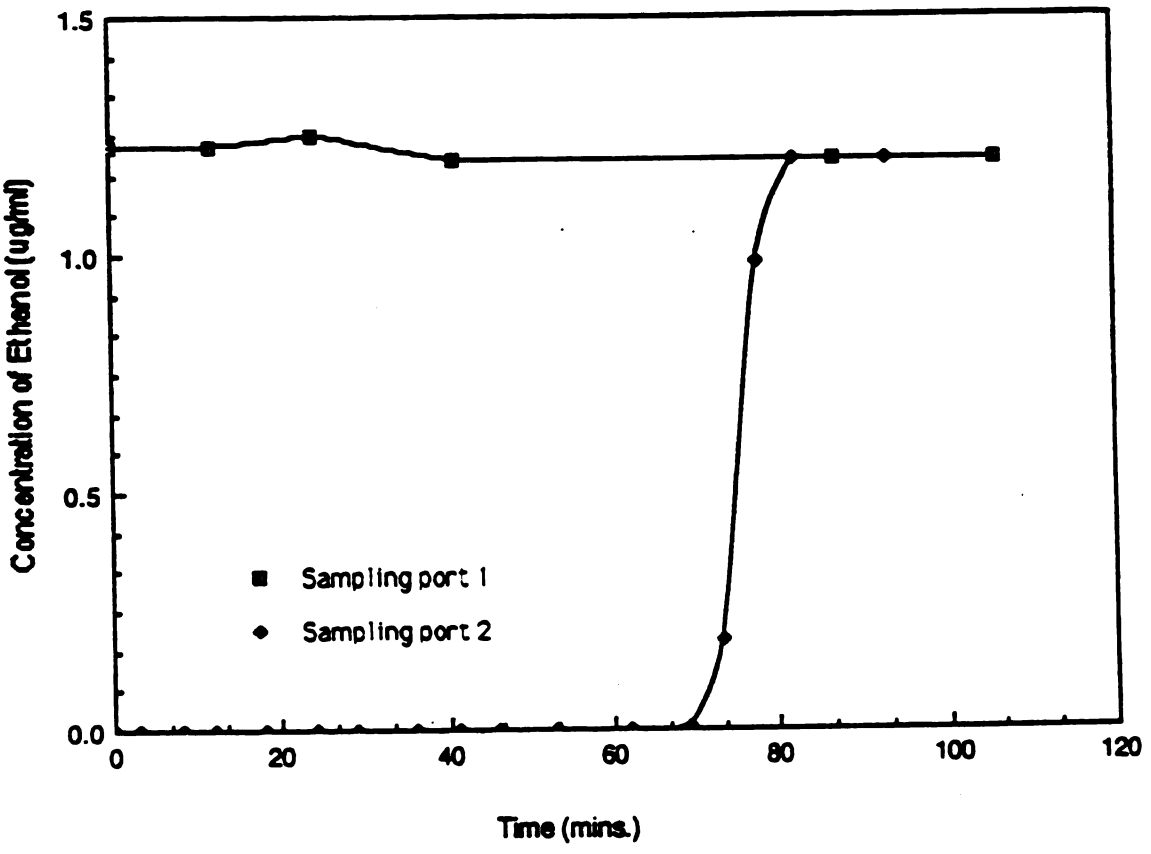


Figure 13: Ethanol Sorption Capacity of Tenax

Gas flow in the tenax system was equal to 5.84 ml/min of gas. Total amount of tenax was about 0.64 g. Therefore, total amount of ethanol absorbed in the tenax at saturation was, W_a = 5.84 ml/min * 60min * 1.2 μg/ml = 420.48 μg.

Absorption capacity = A_c = W_a./0.64 g.tenax.

= 657 μg.ethanol/g.tenax.

Appendix 5

Calculation for Amount of Tenax for Each Ethanol Concentration

From Appendix 4, the estimated capacity of tenax is equal to 657 μg ethanol/g tenax. The calculation for each concentration is as follows;

1.2 ppm Ethanol,

Gas flow rate to the sensor is about 10 ml/min.

Estimated duration of test is about 120 mins.

Estimated amount of ethanol which would flow through tenax through out the test, W_E = 10 ml/min * 120 min * 1.2 μg/ml

W_E = 1440 μg

Therefore, the least amount of tenax should be used is

W_T = 1400 μg* g of tenax / 657 μg

W_T = 2.2 g tenax.

In the permeability test amount of tenax used is 2.4 g

7 ppm Ethanol;

Gas flow rate to the sensor is about 10 ml/min.

Estimated duration of test is about 120 mins.

Estimated amount of ethanol which would flow through tenax through out the test, W_E = 10 ml/min * 120 min * 7 μg/ml.

W_E = 8400 μg.

Therefore, the least amount of tenax should be used is

$$W_T = 8400\ \mu g * g \text{ of tenax} / 657\ \mu g$$

$$W_T = 13 \text{ g tenax.}$$

In the permeability test only 8 g of tenax was used because too much amount of tenax will prohibit the flow. Therefore, for 7 ppm ethanol, only steady state transmission was measured.

Appendix 6

Determination of the Conversion Factor for the Oxtran

Condition: 22 °C, 0% relative humidity.

Material and equipment:

- Standard reference material 1470 for gas transmission with known permeability of 69.104 cc./m2.day.atm.
- Mocon Oxtran 100 Oxygen Permeability tester, load resistor 53 ohm.

Procedure:

- Conduct the permeability test of the standard reference sample.
- Calculate oxygen transmission of 1 mV output.

Result and discussion:

The permeability of this standard was equal to 4.45 mV.

Therefore, the conversion factor C

$$C = 69.104 \text{ cc/m2.day} / 4.45 \text{ mV}$$

$$C = 15.53 \text{ cc/m2.day.}$$

The transmission output from the Oxtran in mV unit can be converted to permeance value in unit cc oxygen/m2.day.atm., as follow;

Permeance = Response output (mV)* Conversion factor* Area conversion factor/ Partial pressure of oxygen.

Area conversion factor; non-masked sample = 1

masked sample = 10

Partial pressure of oxygen = .21 atm

Appendix 7

Oxygen Permeance Data under 0 ppm and 1 ppm Ethanol at 0% RH

Table 10: Oxygen Permeance of Polystyrene 1.1 mil at 23 °C (0% ethanol).

Time (min)	Recording Output (mV)	Oxygen Permeance (cc/m2.day.atm)
0.0	0.00	0.00
1.2	0.10	75.54
1.8	1.00	745.44
2.4	2.80	2087.23
3.0	3.80	2832.67
3.6	4.65	3466.29
4.2	4.95	3689.93
4.8	5.15	3839.02
6.0	5.25	3913.56
7.2	5.30	3950.87
13.2	5.40	4025.38
56.4	5.45	4062.65
79.2	5.50	4099.95

Table 11: Oxygen Permeance of Polystyrene 1.1 mil at 24 °C (1 ppm Ethanol)

Time (min)	Recording Output (mV)	Oxygen Permeance (cc/m2.day.atm)
0.0	0.00	0.00
6.6	0.00	0.00
11.4	0.00	0.00
13.8	0.10	74.54
16.2	0.45	335.45
18.6	1.00	745.44
21.0	1.50	1118.16
24.6	2.30	1714.51
29.4	3.10	2310.86
33.0	3.55	2646.31
40.2	4.20	3130.85
43.8	4.40	3279.94
51.0	4.70	3503.57
55.8	4.80	3578.11
61.8	4.90	3652.66
66.6	5.00	3727.20
71.4	5.05	3764.47
83.4	5.10	3801.74
96.6	5.15	3839.02

Table 12: Oxygen Permeance of Saranex 2 mil at 24 °C (0 ppm Ethanol)

Time (min)	Recording Output (mV)	Oxygen Permeance (cc./m2.day.atm.)
0.0	0.000	0.00
1.2	0.000	0.00
2.4	0.000	0.00
3.0	0.000	0.00
4.2	0.005	0.37
5.4	0.020	1.49
6.6	0.045	3.35
7.8	0.070	5.22
8.4	0.080	5.96
9.0	0.090	6.71
10.8	0.110	8.19
12.0	0.120	8.95
14.4	0.130	9.69
21.6	0.140	10.44
32.4	0.140	10.44

Table 13: Oxygen Permeance of Saranex 2 mil. at 24 °C (1 ppm Ethanol)

Time (min)	Recording Output (mV)	Oxygen Permeance (cc./m2.day.atm.)
3.6	0.00	0.00
7.2	0.00	0.00
9.6	0.00	0.00
12.0	0.00	0.00
14.4	0.00	0.00
20.4	0.02	1.12
24.0	0.04	2.61
27.6	0.06	4.09
30.0	0.07	4.85
32.4	0.08	5.59
34.8	0.07	6.34
38.4	0.10	7.08
43.2	0.11	7.83
49.2	0.12	8.57
60.0	0.13	9.32
84.0	0.14	10.06
105.6	0.14	10.44
109.2	0.14	10.44

Table 14: Oxygen Permeance of PET 0.7 mil at 24 °C (0 ppm Ethanol)

Time (min)	Recording Output (mV)	Oxygen Permeance (cc/m2.day.atm)
0.0	0.000	0.00
2.4	0.000	0.00
3.6	0.000	0.00
4.8	0.005	0.37
7.2	0.025	1.86
10.8	0.070	5.22
15.6	0.120	8.95
18.0	0.140	10.45
20.4	0.160	11.93
25.2	0.190	14.16
28.8	0.210	15.65
33.6	0.230	17.15
37.2	0.240	17.86
42.0	0.250	18.64
46.8	0.260	19.38
52.8	0.270	20.13
62.4	0.280	20.87
79.2	0.290	21.62
93.6	0.295	21.99
99.6	0.295	21.99

Table 15: Oxygen Permeance of PET 0.7 mil at 24 °C (1 ppm Ethanol)

Time (min)	Recording Output (mV)	Oxygen Permeance (cc/m2.day.atm)
0.0	0.000	0.00
2.4	0.000	0.00
4.8	0.000	0.00
8.4	0.000	0.00
10.8	0.000	0.00
16.8	0.000	0.00
21.6	0.005	0.37
25.2	0.020	1.49
27.6	0.030	2.24
30.0	0.040	2.98
36.6	0.060	4.47
40.2	0.080	5.96
46.2	0.110	8.19
48.6	0.120	8.95
53.4	0.040	10.44
61.8	0.070	12.67
67.8	0.190	14.16
72.6	0.200	14.91
77.4	0.210	15.65
83.4	0.220	16.39
89.4	0.230	17.15
99.0	0.230	17.89
113.4	0.250	18.64
127.8	0.255	19.01
142.2	0.260	19.38
148.2	0.260	19.38

Table 16: Oxygen Permeance of LDPE 1.5 mil at 23 °C (0 ppm Ethanol)

Time (min)	Recording Output (mV)	Oxygen Permeance (cc/m2.day.atm)
0.0	0.00	0.00
0.6	0.00	0.00
1.2	0.20	149.09
1.8	1.35	1006.34
2.4	2.90	2161.78
3.0	4.00	2981.76
3.6	4.80	3578.11
4.2	5.20	3876.29
4.8	5.50	4099.92
5.4	5.70	4249.01
6.0	5.75	4286.28
7.2	5.85	4360.82
8.4	5.90	4398.09
15.6	5.95	4435.37
26.4	6.00	4472.64
32.4	6.00	4472.64

Table 17: Oxygen Permeance of LDPE 1.5 mil at 24 °F (1 ppm Ethanol)

Time (min)	Recording Output (mV)	Oxygen Permeance (cc/m2.day.atm)
0.0	0.00	0.00
2.4	0.00	0.00
4.8	0.00	0.00
7.2	0.00	0.00
9.6	0.05	37.27
10.8	0.20	149.09
13.2	0.90	670.89
14.4	1.30	969.07
15.6	1.75	1304.52
16.8	2.20	1639.97
18.0	2.60	1938.14
19.2	3.00	2236.32
20.4	3.30	2459.95
21.6	3.65	2720.86
22.8	3.95	2944.49
25.2	4.44	3309.75
27.6	4.85	3615.38
30.0	5.15	3839.02
33.6	5.50	4099.92
38.4	5.80	4323.55
43.2	6.00	4472.64
48.0	6.10	4547.18
58.8	6.20	4621.73
81.6	6.30	4692.27

Table 18: Oxygen Permeance of Cellulose Acetate 1 mil at 24 °C (0 ppm Ethanol)

Time (min)	Recording Output (mV)	Oxygen Permeance (cc/m2.day.atm)
0.0	0.00	0.00
0.6	0.00	0.00
1.8	0.60	447.26
2.4	1.45	1080.89
3.0	2.35	1751.78
3.6	2.75	2049.96
4.2	3.05	2273.59
4.8	3.20	2497.22
9.0	3.40	2534.49
32.4	3.45	2571.77

Table 19: Oxygen Permeance of Cellulose Acetate 1 mil at 24 °C (1 ppm Ethanol)

Time (min)	Recording Output (mV)	Oxygen Permeance (cc/m2.day.atm.)
0.0	0.00	0.00
2.4	0.00	0.00
4.8	0.00	0.00
6.0	0.00	0.00
8.4	0.25	186.36
10.8	0.88	652.26
13.2	1.48	1103.25
14.4	1.73	1289.61
15.6	1.95	1453.61
16.8	2.15	1602.69
18.0	2.30	1714.51
19.2	2.45	1826.31
21.6	2.68	1997.78
24.0	2.85	2124.50
26.4	2.98	2217.68
30.0	3.10	2310.86
34.8	3.20	2385.41
37.2	3.25	2422.68
44.4	3.30	2459.95
49.2	3.33	2482.32
66.0	3.35	2497.22
118.8	3.38	2519.59

Table 20: Oxygen Permeance of Polyvinyl Acetate 0.8 mil at 26 °C (0 ppm Ethanol).

Time (min)	Recording Output (mV)	Oxygen Permeance (cc/m2.day.atm)
0.0	0.00	0.00
0.6	0.00	0.00
1.8	0.25	186.36
2.4	0.58	428.63
3.0	0.83	614.99
3.6	0.95	708.17
4.2	1.03	764.08
4.8	1.08	801.35
6.0	1.10	819.99
10.8	1.13	838.62
22.8	1.15	857.26

Table 21: Oxygen Permeance of Polyvinyl Acetate 0.8 mil at 24 °C (1 ppm Ethanol)

Time (min)	Recording Output (mV)	Oxygen Permeance (cc/m2.day.atm)
0.0	0.00	0.00
1.2	0.00	0.00
2.4	0.00	0.00
3.6	0.00	0.00
4.8	0.00	0.00
6.6	0.05	37.27
7.8	0.15	111.82
9.0	0.29	216.18
10.2	0.41	305.63
11.4	0.52	387.63
12.6	0.61	454.72
13.8	0.69	514.35
15.0	0.75	559.08
16.2	0.80	596.35
17.4	0.85	633.62
18.6	0.88	655.99
19.8	0.91	678.35
21.0	0.94	700.71
22.2	0.96	715.62
23.4	0.98	730.53
25.8	1.01	752.89
27.0	1.02	760.35
34.2	1.04	775.26
40.2	1.05	782.71
48.6	1.06	790.17
67.8	1.07	797.62
87.0	1.07	797.62

Table 22: Oxygen Permeance of Polyvinyl Butyral 1 mil at 23 °C (0 ppm Ethanol)

Time (min)	Recording Output (mV)	Oxygen Permeance (cc/m2.day.atm)
0.0	0.00	0.00
1.2	0.05	37.27
2.4	1.50	1118.16
3.6	2.90	2161.78
4.8	3.45	2571.77
6.0	3.60	2683.58
7.2	3.70	2758.13
8.4	3.75	2795.40
9.6	3.77	2810.31
12.0	3.80	2832.67
21.6	3.90	2907.22
30.0	3.95	2944.49
38.4	4.00	2981.76
54.0	4.05	3019.03
69.6	4.10	3056.30
70.8	4.10	3056.30

Table 23: Oxygen Permeance of Polyvinyl Butyral 1 mil at 22 °C (1 ppm Ethanol)

Time (min)	Recording Output (mV)	Oxygen Permeance (cc/m2.day.atm)
0.0	0.00	0.00
4.8	0.00	0.00
9.6	0.00	0.00
10.8	0.05	37.27
12.0	0.15	111.82
14.4	0.60	447.26
16.8	1.10	819.98
19.2	1.50	1118.16
22.8	2.00	1490.88
26.4	2.40	1789.06
30.0	2.70	2012.69
33.6	2.90	2161.78
38.4	3.10	2310.86
42.0	3.20	2385.41
46.8	3.30	2459.95
54.0	3.40	2534.49
73.2	3.50	2609.04
124.8	3.55	2646.31

Table 24: Oxygen Permeance of Ethylene Vinyl Acetate 0.8 mil at 24 °C (0 ppm Ethanol)

Time (min)	Recording Output (mV)	Oxygen Permeance (cc/m2.day.atm)
0.0	0.00	0.00
0.6	0.00	0.00
1.2	0.30	223.63
1.8	2.40	1789.06
2.4	5.40	4025.38
3.0	8.40	6261.69
3.6	10.30	7678.03
4.2	11.60	8647.10
4.8	12.50	9318.00
5.4	13.00	9690.72
6.0	13.40	9988.89
6.6	13.70	10212.53
7.2	13.80	10287.07
10.8	14.20	10585.25
19.2	14.40	10734.34
32.4	14.50	10808.88
55.2	14.60	10883.42

Table 25: Oxygen Permeance of Ethylene Vinyl Acetate 0.8 mil at 24 °C (1 ppm Ethanol).

Time (min)	Recording Output (mV)	Oxygen Permeance (cc/m2.day.atm)
0.0	0.00	0.00
2.4	0.00	0.00
4.8	0.00	0.00
6.0	0.00	0.00
8.4	0.40	298.18
9.6	1.00	745.44
10.8	2.10	1565.42
12.0	3.50	2609.04
13.2	4.70	3503.57
14.4	5.80	4323.55
15.6	7.10	5292.62
16.8	8.00	5963.52
18.0	8.90	6634.42
20.4	10.30	7698.03
22.8	11.40	8498.02
26.4	12.60	9392.54
28.8	13.20	9839.81
33.6	14.00	10436.16
38.4	14.50	10622.52
43.2	14.80	11032.51
54.0	15.10	11256.14
66.0	15.20	11130.69
98.4	15.10	11256.14
109.2	15.10	11256.14

Table 26: Oxygen Permeance of Polyvinyl Chloride 1.0 mil at 24 °C (0 ppm Ethanol)

Time (min)	Recording Output (mV)	Oxygen Permeance (cc/m2.day.atm)
0.0	0.00	0.00
0.6	0.00	0.00
1.2	0.00	0.00
1.8	1.60	1192.70
2.4	3.20	2385.41
3.0	5.40	4025.38
3.6	7.10	5292.62
4.2	8.20	6112.61
4.8	8.80	6559.87
5.4	9.20	6858.05
6.0	9.20	7081.68
6.6	9.50	7156.22
7.2	9.60	7230.77
9.6	9.80	7305.31
13.2	9.90	7379.86
37.2	10.00	7454.40
48.0	10.00	7454.40

Table 27: Oxygen Permeance of Polyvinyl Chloride 1.0 mil at 24 °C (1 ppm Ethanol)

Time (min)	Recording Output (mV)	Oxygen Permeance (cc/m2.day.atm)
0.0	0.00	0.00
2.4	0.00	0.00
4.8	0.00	0.00
7.2	0.30	223.63
8.4	1.00	745.44
9.6	1.90	1416.34
10.8	2.80	2087.23
12.0	3.80	2832.67
13.2	4.60	3429.02
14.4	5.40	4025.38
16.8	6.70	4994.45
19.2	7.60	5665.34
21.6	8.20	6112.61
25.2	8.80	6559.87
28.8	9.20	6858.05
32.4	9.40	7007.14
38.4	9.60	7156.22
50.4	6.70	7230.77
66.0	9.80	7305.31

Table 28: Oxygen Permeance of Polypropylene 0% Ceramic 0.9 mil at 23 °C (0 ppm Ethanol)

Time (min)	Recording Output (mV)	Oxygen Permeance (cc/m2.day.atm)
0.0	0.00	0.00
0.6	0.00	0.00
1.2	0.05	37.27
1.8	0.80	596.35
2.4	2.05	1490.88
3.0	3.30	2459.95
3.6	4.20	3130.85
4.2	4.80	3578.11
4.8	5.20	3876.29
5.4	5.45	4062.65
6.0	5.60	4174.46
6.6	5.70	4249.01
7.2	5.80	4323.55
9.6	5.90	4398.09
15.6	5.95	4435.37
26.4	6.00	4472.64
31.2	6.00	4472.64

Table 29: Oxygen Permeance of Polypropylene 0% Ceramic 0.9 mil at 23 °C (1 ppm Ethanol)

Time (min)	Recording Output (mV)	Oxygen Permeance (cc/m2.day.atm)
0.0	0.00	0.00
2.4	0.00	0.00
4.8	0.00	0.00
7.2	0.00	0.00
9.6	0.15	111.82
12.0	0.95	708.17
13.2	1.45	1080.89
14.4	1.90	1416.34
16.8	2.70	2012.67
20.4	3.60	2683.58
25.2	4.40	3279.94
28.8	4.80	3578.11
31.2	5.00	3727.20
34.8	5.20	3876.29
37.2	5.30	3950.83
62.6	5.70	4249.01
79.4	5.75	4286.28

Table 30: Oxygen Permeance of Polypropylene 3% Ceramic 1.4 mil at 23 °C (0 ppm) Ethanol

Time (min)	Recording Output (mV)	Oxygen Permeance (cc/m2.day.atm)
0.0	0.00	0.00
1.2	0.00	0.00
1.8	0.40	298.18
2.4	1.50	1118.16
3.0	2.80	2087.23
3.6	3.80	2832.67
4.2	4.60	3429.02
4.8	5.05	3764.47
5.4	5.40	4025.38
6.0	5.55	4137.19
6.6	5.70	4249.00
8.4	5.80	4323.55
10.2	5.90	4398.09
15.0	5.95	4435.37
27.0	6.00	4472.64
33.0	6.00	4472.64

Table 31: Oxygen Permeance of Polypropylene 3% Ceramic 1.4 mil at 23 °C (1 ppm Ethanol)

Time (min)	Recording Output (mV)	Oxygen Permeance (cc/m2.day.atm)
0.0	0.00	0.00
2.4	0.00	0.00
4.8	0.00	0.00
7.2	0.00	0.00
10.8	0.20	149.29
12.0	0.50	372.72
13.2	0.90	670.89
14.4	1.30	969.07
15.6	1.70	1267.25
16.8	2.15	1602.69
19.2	2.90	2161.78
22.8	3.80	2832.67
26.4	4.45	3317.21
34.8	5.30	3950.83
38.4	5.50	4099.92
45.6	5.75	4286.28
54.0	5.90	4398.09
73.2	6.00	4472.64
100.8	6.10	4547.18
118.8	6.15	4584.46

Table 32: Oxygen Permeance of Polypropylene 7% Ceramic 1.8 mil at 21 °C (0 ppm Ethanol)

Time (min)	Recording Output (mV)	Oxygen Permeance (cc/m2.day.atm)
0.0	0.00	0.00
0.6	0.00	0.00
1.2	0.00	0.00
1.8	0.25	186.36
2.4	0.80	596.35
3.0	1.50	1118.16
3.6	2.00	1490.88
4.2	2.35	1751.78
4.8	2.55	1900.87
5.4	2.70	2012.69
6.0	2.75	2049.96
6.6	2.80	2087.23
16.8	2.90	2161.78
21.6	2.90	2161.78

Table 33: Oxygen Permeance of Polypropylene 7% Ceramic 1.8 mil at 23 °C (1 ppm Ethanol)

Time (min)	Recording Output (mV)	Oxygen Permeance (cc/m2.day.atm)
0.0	0.00	0.00
2.4	0.00	0.00
4.8	0.00	0.00
7.2	0.00	0.00
8.4	0.10	74.54
9.6	0.40	298.18
10.8	0.70	521.81
12.0	1.00	745.44
13.2	1.25	931.80
14.4	1.50	1118.16
15.6	1.70	1267.25
16.8	1.90	1416.34
20.4	2.30	1714.52
24.0	2.50	1863.60
28.8	2.70	2012.69
32.4	2.80	2087.23
40.8	2.90	2161.78
51.6	2.95	2199.05
68.4	3.00	2236.32

Table 34: Oxygen Permeance of Polypropylene 3% Ceramic 1.4 mil at 23 °C (0 ppm Ethanol, Tenax Pathway).

Time (min)	Recording Output (mV)	Oxygen Permeance (cc/m2.day.atm)
0.0	0.00	0.00
2.4	0.00	0.00
4.8	0.05	37.27
6.0	0.20	149.09
7.2	0.60	447.26
8.4	1.00	745.48
9.6	1.45	1080.89
10.8	1.90	1416.34
13.2	2.60	1938.14
15.6	3.25	2422.68
18.0	3.75	2795.40
20.4	4.15	3093.58
22.8	4.50	3354.48
34.2	5.05	3764.47
37.8	5.30	3950.83
42.6	5.50	4099.92
46.2	5.60	4174.46
49.8	5.70	4249.01
57.0	5.80	4323.55
70.2	5.90	4398.09
75.0	5.90	4398.09

Appendix 8

Determination of the Repeatability of the Experiments

The repeatability of the experiments was estimated by determining the oxygen permeance of a masked sample of LDPE 1.5 mil three times (at 23 °C, 0% RH). The oxygen permeance data is as shown below.

Trail	Oxygen Permeance ($cc/m^2.day.atm$)
1	4524
2	4289
3	4252
Average	4355

The estimated percent standard error is 3%.

Appendix 9

Table 35: Activation Energy of Polymer Samples (Polymer Handbook, 1975)

Film	Activation Energy (cal/mole)
PET	7,690.50
SARAN	15,833.30
LDPE	10,738.10
PVC	13,238.10
EVAc	13,357.10
Cellulose Acetate	4,976.20
PVAc	13,557.10
PVB*	11,904.76
PP	11,357.10

* Estimated value