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Hexanal Vapor to Control Decay of Sliced Apples in Modified-Atmosphere Packages Using Metallocene Film

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HEXANAL VAPOR TO CONTROL DECAY OF SLICED APPLES IN MODIFIED-ATMOSPHERE PACKAGES USING METALLOCENE FILM

By

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ABSTRACT

HEXANAL VAPOR TO CONTROL DECAY OF SLICED APPLES IN MODIFIED-ATMOSPHERE PACKAGES USING METALLOCENE FILM

By

Jeffrey J. Wolford

Simple modified atmosphere packaging (MAP) fails to protect fresh produce from decay like in the case of apple slices. The incorporation of natural organic volatile compounds in MAP has proved to be effective in the overall produce quality. The use of natural preservatives in MAP can minimize color change, browning, and texture change while retarding senescence and enhancing aroma biosynthesis.

Sliced apples were placed in MAP with less than 20^{-6} mol·L^{-1} hexanal vapor in the headspace. Consumption of hexanal vapor by apple tissue was determined by a continuous flow method, the sorption and permeability of hexanal into Exxon Exact™ 4151 film were determined by electrobalance and permeation. Effect of hexanal vapor in minimizing texture change, color change, and browning was evaluated at selected hexanal concentrations.

The hexanal consumption rate (C) was found to be dependent on concentration of hexanal (H) in the headspace according to following equation: $C = 0.2216H + 0.0378$. Permeability of hexanal to Exxon Exact™ 4151 film was found to be 4.2×10^{-14} Kg·m·$m^{2\,-1}$·sec^{-1}·Pa^{-1}. Results show minimized browning texture loss and increased production of aroma compounds.

To my mother, Keron M. Wolford

For her sacrifices, undying support, and hope that I would someday finally finish college

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INTRODUCTION

The potential market for packaged fresh cut apples is anticipated to be tremendous. Unlike other minimally processed fruits, apples have been restricted by problems such as moisture loss, browning, texture change, and microbial decay. Such decay often occurs within the 14 days necessary for distribution and retailing. While modified atmosphere packaging deals with some of these problems by use of a "hurdle approach", it does not adequately solve all dilemmas.

Ketones, aldehydes, and acids are among a group of natural compounds that are capable of retarding decay of whole fruits. Nonetheless, literature on the effect of natural volatiles on sliced fruit is limited.

The goal then, was to develop a method to generate hexanal vapor in the headspace of a sealed modified atmosphere package and study the effect on decay. This involved construction of flow through exposure systems to study the "consumption" of hexanal vapor by the apple tissue and the permeation to a metallocene catalyzed film. The generation of hexanal vapor in the headspace was accomplished by a release pouch. The headspace concentration needed to be balanced to account for losses to consumption and permeation while still maintaining a concentration that proved effective in retarding decay of the fruit tissue. A gas chromatography method to quantify vapor concentration in the headspace was developed and utilized.

This research chose hexanal as a natural organic vapor with low toxicity and ease of vapor generation. Research was carried out in three sections: the consumption of hexanal by fruit tissue, the permeability of hexanal to a polymer, and evaluation of the effect of hexanal in a MAP to minimize texture loss and browning.

CHAPTER 1

LITERATURE REVIEW

Fresh-cut fruits

As food health trends continue to dominate the eating behavior of many Americans, the market for fresh fruit continues to grow accordingly. Despite the side trend of the common "luxuries" of high fat gourmet ice cream and whipped cream laden cappuccinos, demand for fresh produce remains high, thanks in part to the work of such organizations as the American Cancer Society in educating society of the links of a healthy diet with reducing the risk of several major diseases.

The International Fresh-cut Produce Association claims that fresh-cut produce is the fastest growing segment of the exploding market for fresh fruits and vegetables. The USDA's Economic Research Service estimates that each American consumed about 300 pounds of fresh fruits and vegetables in 1996. Sales of fresh-cuts in the United States are projected to increase from $5.8 billion in 1994 to $19 billion by 1999 (Stanley, 1997). This growth has been fueled wholly by consumer demand, whose needs cannot be appeased with conventionally processed products such as canned, frozen, and dried foods. Consumer taste now includes a large dose of health consciousness resulting in about a 10 percent rise in total fruit consumption between 1978 and 1988 (Cook, 1992). Seventy three percent surveyed named a balanced diet as a primary reason for eating more fresh fruit (Segal, 1988). Fresh-cut produce, such as carrots, cauliflower, and broccoli, has become a hot item with consumers – not just in the United States, but worldwide (Stanley, 1997).

Fresh-cut products, which we used to call lightly or minimally processed, have been around for years, but the types and quantity have expanded tremendously over the past decade (Stanley, 1997). Concern over the use of pesticides, preservatives, artificial colors, and additives have driven the demand for a more wholesome approach. Processing is now limited to the very steps that would be done in the home kitchen: washing, sorting, trimming, peeling, and cutting. When you cut produce, you leave a large surface area exposed to air without any skin for protection against loss of water and attack by microorganisms, and the produce must be shipped-sometimes for several days- which makes shelf life vitally important (Stanley, 1997).

The most crucial problem for fresh-cut fruits is the undesirable physical, chemical, and physiological changes. The act of cutting fruit tissue destroys cellular integrity and compartmentalization of enzymes and substrates, resulting in the formation of secondary metabolites and unsightly browning. In addition senescence and off-flavors may be enhanced (Burns, 1995) and more importantly fungal and bacterial contamination can occur on the cut surface.

Before fresh-cut products are ready to be marketed, the above problems need to be eliminated or minimized. Several approaches have been used to solve these problems including: selective cultivars that are able to withstand minimal processing while maintaining quality; temperature and humidity control; chemical treatments; edible coatings; and modified atmospheres.

Each fruit has its own specific post-processing problems that call for specific preservative measures.

Reception to fresh-cut fruit appears to be very favorable. According to a recent survey, 52 percent of households reported they would purchase one or more fruits more frequently if they were more convenient to prepare (Hoag, 1995). While precut apples are not yet readily available, demand is expected to increase rapidly once an acceptable product is developed (Hoag, 1995). Produce accounts for 10% of supermarket sales, and ranks as the No. 1 reason consumers choose one store over another (Spethmann, 1995).

While the need for minimally processed fruits was foreseen well over a decade ago, no one could predict the demand that would result. MAP and value added products represent new technologies that use packaging to extend shelf life but marketing considerations are also important (Barmore, 1987).

Developmental problems of fresh-cut apples

Browning

Browning reactions are detrimental to quality and curb the consumer acceptance of minimally processed apple products (Monsalve-González, 1995). Research on minimally processed apple slices has focused on methods to inhibit browning, due to the ban on use of sulfur dioxide (FDA 1987).

Browning in apples begins immediately after cutting the fruit skin (Nicoli, 1993). Disruption of the cells at the cut surface leads to discoloration by allowing phenolic substrates and the enzyme polyphenol oxidase (PPO) to come into contact (Brecht, 1995). A number of chemical treatments have been suggested to reduce browning from slicing, most of which are antioxidants. $Ca(OCl)_2$ is more effective than NaOCl in reducing browning on apples (Brecht, 1995). Other chemical treatments for reducing browning include ascorbic acid, chlorine, meta-bisulfite and 4-hexylresorcinol. Meta-bisulfite and 4-hexylresorcinol are the most effective of those listed. 4-Hexylresorcinol has proven useful in inhibiting browning reactions in stored apples preserved by combined methods (Monsalve et al., 1993). Recent research in edible coatings derived from seaweed has shown the ability to reduce respiration of fresh-cut apples. Alginic acid from seaweed preserves apple slices up to 8 days without browning, which is significantly better than the 2-3 days provided by salts of vitamin C (Stephens, 1994). A modified atmosphere consisting of 1-3% oxygen and 3-5% carbon dioxide is able to retard browning and maintain quality of whole apples (Barrett, 1989). However, while modified atmosphere (1% O_2 and 5-20% CO_2) significantly reduces browning relative to air control, the level of browning is still objectionable (Lakakul, 1994). Extreme variations of atmosphere, with oxygen below 0.5% and carbon dioxide in excess of 20%, effectively control browning but at the cost of damaging the fruit tissue. Temperature also affects the rate of discoloration. As temperature decreases, oxidation occurs at reduced rates. Ascorbic acid and citric acid are effective in

reducing browning of fresh-cut fruit surface, but may cause undesirable flavor changes (Anonymous, 1996).

Genetic research has proposed changing plant DNA to eliminate browning and all its associated problems. The researchers have inserted a reverse copy of the PPO gene into their potatoes, leaving them with less than 10 percent of the PPO activity of ordinary potatoes-so they do not turn brown (Thwaites, 1995). If trials are considered a success, other fruits and vegetables–including apples, beans, lettuce and grapes-will follow.

Moisture loss

Loss of moisture is a major cause of quality degradation in sliced apples causing diminished weight, unfavorable appearance due to shriveling, and poor mouth feel due to a loss of crispness and juiciness. Moisture loss results from a gradient between saturated atmosphere within the intercellular spaces and the less saturated external environment. Water vapor migrates primarily through openings or injuries in the fruit skin, and is affected by both internal and external factors. Internal factors include morphological and anatomical characteristics of the fruit, surface to volume ratio, surface injuries or cutting, maturity stage, etc. External factors include temperature, relative humidity, air movement, and atmospheric pressure. Cutting of apple fruit causes surface injury and raises the surface to volume ratio allowing more air to come in contact with the apple tissue therefore providing a vehicle for rapid water vapor loss. Surface coatings, including waxes, have been used to

prevent moisture loss for certain products. However, consumers commonly refuse any such measure that alters the appearance or texture. Consumer preference and numerous technical difficulties with edible coatings has resulted in the common use of packaging materials that provide good water vapor barrier properties to minimize moisture loss.

Texture change

Texture change is associated with senescence and loss of fruit firmness. The softening of fruit tissue stems mainly from water loss, decreasing the internal cellular pressure. Increasing the calcium content of fruit can reduce the amount and speed of texture change and furthermore, is able to reduce susceptibility to physiological disorders (Kader, 1992). However calcium treatments can affect flavor, giving a salty taste to the produce (Hanson et al., 1993).

Microbial decay

When a piece of whole produce is cut, nutrients are exposed that can feed microorganisms, and the increased surface area allows more growth (Anonymous, 1996). Fungal contamination can occur during either harvesting or processing. If processing equipment is not properly sanitized, the cut slices could be inoculated with microorganisms during processing. When most organisms attack fruit, they induce the following effects on the host including physical injury, physiological breakdown, texture change, and off flavor.

Importantly, even a small lesion can result in a complete loss of value, therefore the tolerance limit for decay in any fresh product is zero.

The primary cause of spoilage in whole apples is *Penicillium expansum* Link and *Botrytis cinerea* Pers. (Singleton, 1987; Snowdon, 1990). Blue mold rot caused by *P. expansum* is extremely destructive to apple fruits. The symptoms are soft, watery, light brown lesions, which undergo rapid enlargement at temperatures between 20 and 25°C. As the lesion grows, the decay portion can be easily separated from the surrounding sound tissue. It then becomes pale blue as sporulation occurs. *P. expansum* is generally regarded to be a wound parasite and infection commonly follows rough handling and washing procedures after harvest. Infection can occur even at 0°C, although the decay proceeds slowly at cold storage temperatures.

Gray mold rot caused by *B. cinerea* is light to dark brown in color. Gray mold lesions are characteristically less soft than those of blue mold and have a well defined margin, but rotted tissue cannot be neatly separated from the surrounding healthy tissue. Lesions become covered with gray sporulating mycelium at optimum humidity. Under humid conditions, infections often occur via wounds sustained during harvesting and handling. Rotting can proceed even at –1°C. Decay can spread to adjacent healthy fruit at this low temperature, but its growth rate is very low (Kiss, 1984; Sommer et al., 1992). The temperature range for optimal growth is 22-25°C. *B. cinerea* can infect the sepals of apple flowers and live in latent conditions inside the tissue until fruit maturation (Tronsmo, 1977). It is unable to grow in unripe fruit but will begin to

grow as the fruit matures. *B. cinerea* is a facultative parasite on several vegetables and fruits, such as strawberry, raspberry, blueberry, grape and apple. Interestingly, human pathogenesis by *B. cinerea* has also been reported (Beaumont et al., 1985). The number of *B. cinerea* spores on both outside and inside the dwellings has been correlated with the contraction of asthma (chronic coughing). In addition, *Botrytis* extracts are active in the skin test on asthmatic patients showing a high sensitization rate comparable to that of *Aspergillus fumigatus*.

Perhaps the biggest risk to consumers is the growth of harmful bacteria without any of the customary warning signs. For example, an experiment showed that modified atmosphere packaging could extend shelf life by a week with the sensory quality preserved. Nevertheless, during that period, the pathogen Listeria monocytogenes continued to grow. Several parasites can be transmitted by produce, including Giardia lamblia and Cryptosporidium (Anonymous, 1996). A variety of other pathogens may be found on fruit and vegetable products, including Salmonella and *Shigella spp.*, *enteropathogenicia*, *Yersinia entercolitica*, *Staphylococcus aureus*, and others (Breidt and Fleming, 1997). Extending the shelf life of refrigerated foods might increase risks in packaged produce in at least three ways. First, increasing the time in which food remains acceptable (edible) increases the time in which even slow growing pathogens can develop to significant numbers or produce toxin. This is especially true for pathogens that can grow, albeit slowly at 3 to 8°C. Secondly, MAP can retard the development of competing spoilage

organisms and thereby allow or enhance pathogen growth. Thirdly, packaging respiring produce in MAs could alter the atmosphere such that the growth of pathogens is stimulated (Hotchkiss, 1992). For example, CO2 has been reported to enhance toxigenesis by *C. botulinum* (Foegeding, 1983).

Methods for controlling decay of fresh-cut apples

Minimal processing often increases perishability rather than making products more stable (Rolle and Chism, 1987; Shawfelt, 1987). Several problems including browning, moisture loss, texture change, and decay have hindered the development of fresh-cut apples. However, control treatments for each of these problems exists. A good scheme is to combine two or more of these preserving treatments on the assumption that their effects are synergistic. This approach has been called the "hurdle approach", since the degradation process must overcome the hurdle of the preserving treatment. The aim is to use treatments that have additive effects, so that the rate of degradation is diminished by the presence of more hurdles (Huxsoll and Bolin, 1989).

Different cultivars are best suited to address individual problems experienced with fresh-cut apples. However, no single cultivar appeared most suitable for minimal processing. One cultivar with an advantage in one parameter may have no advantage with respect to another parameter (Kim, 1993).

There are several possibilities for controlling decay of apple slices. Fungal inoculum and activity can be minimized during both preharvest and postharvest. Fungicidal sprays are often applied in the field to control infection. However, the use of chemical fungicides was limited by increasing fungal resistance and chemical residue on the fruits (Eckert and Ogawa, 1988). For minimally processed products, chlorine, usually in the form of calcium or sodium hypochlorite, is used for reducing fungal decay in many kinds of fruits and vegetables. The most common concentration is 50-125$\mu g \cdot L^{-1}$. For lightly processed products, strict hygiene in both orchard and packinghouse, during handling and light processing, would be critical (Huxsoll, 1989). Other potential methods (chemicals, preservatives, reducing water activity with sugar or salt) have also been used to retard decay.

Irradiation is another method of extending shelf life of fresh produce that offers several benefits. Irradiation is a "cold" treatment that achieves its effects without raising the food's temperature significantly, leaving the food closer to its unprocessed state. By not using high temperatures, irradiation minimizes nutrient losses and changes in texture, color, and flavor (Morrison, 1992). Strawberries maintained their fresh appearance and market quality for 22 days instead of the usual 3 to 5 days and most consumers were indifferent about the irradiation treatment. However, government regulations require irradiated food to carry the international logo for irradiated food. One limiting factor is that irradiating fresh produce with sufficient dosage to control microbial activity can cause softening, increase sensitivity to chilling injury, cause uneven ripening,

and decay. Unlike other treatment methods, irradiation does not provide any residual protection, and relies on packaging to prevent recontamination.

Temperature control is the oldest yet still most important technique to act on microbial decay. Fungal growth slows sharply at lower temperatures. Lowering the temperature by a single degree (Celsius) effectively increases the lag time and significantly slows the rate of reproduction of microorganisms (Elliot and Michener, 1965; Will et al., 1989). Low storage temperature also reduces respiration rate, chemical reaction rate, enzymatic quality loss, and slows ethylene production, each of which contributes to extending storability. However, this does not apply to psychrophilic microorganisms, which are still able to thrive in such conditions. Consequently, temperature control of fungal decay has some limits. Controlled atmosphere also has the potential to decrease fungal growth rates. Decay in strawberry fruit will be reduced when stored under low oxygen and high carbon dioxide. *B. cinerea* on strawberry is dramatically controlled at 0.5% oxygen, but fruits are injured (Couey et al., 1966; Couey and Wells, 1970). Besides the potential for damaging low O2 levels to be generated in MA packages, there is also a concern of the growth of anaerobic pathogens, such as *Clostridium botulinum*.

To control pathogenic bacteria in fresh-cut produce, the use of lactic acid bacteria has been recently used. The objective in using biocontrol cultures is not to ferment foods, but to control the microbial ecology through competitive inhibition of pathogenic bacteria (Breidt and Fleming, 1997). This method should only be considered a supplement to good manufacturing practices and

an enhancement to existing hurdle technology, not substitute for proper handling and packaging of minimally processed produce.

Most of the aforementioned approaches are insufficient because of relative effect, chemical toxicity, unacceptable residues, incomplete inhibition of decay, complicated methods, etc. In this research, a new technology of using natural volatiles from fruits to retard decay (including fungal decay) will be investigated. The concept is that a natural compound, already produced by the fruit, could reduce decay without adversely affecting fruit flavor and possibly enhance aroma compound synthesis.

All of these measures are easily defeated if distribution is not optimized. Even a well produced product will lose value if it takes too long to deliver to market. Yet, even a fast delivery to market can be made worthless if distribution conditions are less than ideal. Fresh produce is extremely susceptible to chill injury, physical damage, and accelerated degradation at higher temperatures.

Use of organic vapors to retard decay

Several natural fruit volatiles have been found to retard decay of fresh fruits. Among these biologically active compounds are aldehydes such as acetaldehydes, hexanal, (E)-2-hexenal, nonanal, and benzaldehyde, ketones such as 2-nonanone, and σ-pentylpyranone, acids such as acetic acid, benzoic acid, and ascorbic acid, alcohols such as 1-hexanol, Z-3-hexen-1-ol, benzyl alcohol, and others (Leepipattanawit, 1996).

Acetaldehyde is a biologically active natural volatile compound that has a minor role in the flavor of fruits and vegetables. This compound is used as a flavoring agent, can be used as a chemical index of fruit ripening (Hayes, 1963), and is approved by EPA as a food additive. However, it was decried as a highly toxic compound, suspected carcinogen, human systemic irritant by inhalation, skin and eye irritant and flammable liquid (Lewis, 1992). Decay of fresh raspberries inoculated with *Botrytis cinerea* Pers. ex. Fr can be inhibited by acetaldehyde vapor treatment (Prasad and Stadelbacher, 1973; Prasad and Stadelbacher, 1974). Exposing the fruits to acetaldehyde vapor at 0.25% or 0.5% for 70 minutes is as effective in retarding fungi as at 1% or greater concentration. At concentrations of 0.5% and below, off-flavors are not detected. Decay of fresh strawberries, caused by *B. cinerea* or *rhizopus stonifer* Ehr. ex. Fr. is also controlled by fumigation with acetaldehyde vapor (Prasad and Stadelbacher, 1974). Treatments with concentrations of 1%, 4% and greater for 30, and 60 minutes kills conidia of the fungi. Treatment with 1% acetaldehyde is suggested as a practical control measure because it does not affect the quality of the berries. Stadelbacher and Prasad (1974) also studied the effect of acetaldehyde vapor on decay of apples inoculated with *Penicillium expansum*. Inoculated apples and culture media were exposed to acetaldehyde vapor concentrations of 5% for 180 minutes, 1% for 120 minutes, 2% for 60 minutes, and 3% for 30 minutes. Fungal spores treated with acetaldehyde do not germinate in 21 days at 21°C on the culture media and fruits. Importantly, treated fruit do no exhibit lenticel or skin injury. Acetaldehyde

vapor is highly effective in killing the P. *expansum conidia* and mycelium on culture media and fruits. Acetaldehyde residues are not detected within 21-day incubation after 8-10 day fumigation.

The effects of sixteen volatile compounds occurring naturally in fruits on spore germination and growth of *Monilinia fructicola* Pers. ex. Fr. and *B. cinerea* were studied (Wilson et al., 1987). Benzyl acetate, benzyl alcohol, δ-caprolactone, α-decalactone, δ-decalactone, δ-octalactone, methylsalicylate and δ-valerolactone inhibited spore germination of both fungi at 1250μL·liter^{-1}. Benzaldehyde vapor entirely suppressed spore germination of *B. cinerea* at 25 μL·liter^{-1} and *M. fructicola* at 125 μL·liter^{-1}. Complete inhibition of fungal growth can be obtained by a benzaldehyde, methylsalicylate, or ethyl benzoate treatment concentration of 370 μL·liter^{-1}.

Chambers (1990) found that benzyl alcohol could control *Botrytis cinerea* rot on package grapes during storage but its efficacy is less than that of SO_2. Benzyl alcohol was not considered an acceptable treatment because of a physiological disorder that was induced and an off-taste imparted to the fruit.

Hamilton-Kemp et al. (1992) and Andersen et al. (1994) found wounded leaves produce a number of aldehydes, including 6-carbon and 9-carbon compounds via the action of lipoxygenase (Hildebrand, 1989). Of the C-6 and C-9 compounds released from tomato leaf, 5.2 μl·liter^{-1} of 2-hexanal, 268.7 μl·liter^{-1} of hexanal, 47 μl·liter^{-1} of 2-nonenal, and 44.8 μl·liter^{-1} of nonanal completely inhibit hyphal growth of *B. cinerea*. *Alternaria alternata* (FR.) Keissl.

Growth is completely suppressed by 8.3 $\mu l \cdot liter^{-1}$ of 2-nonenal. However, other compounds, including terpene hydrocarbons 2-carene and limonene, have no significant effect on hyphal growth. Urbasch (1984) found that E-2-hexenal is more effective than hexanal on growth of cultured *B. cinerea*. She consequently studied the effect of the corresponding unsaturated alcohol, E-2-hexen-1-ol, which was found to inhibit spore germination and fungi growth of *B. cinerea*. (Deng et al. 91993) studied the effect of 6-carbon aldehydes and alcohols from the lipoxygenase/hydroperoxide pathway on *Escherichia coli* TB1, *Pseudomonas Syringae* pv. *Tabaci* Deall, and *P. Syringae* pv. *angulata* Deall. They found (E)-2-hexenal vapor completely inhibits proliferation of both *P. syringae* (101 $\mu l \cdot liter^{-1}$) and *Escherichia coli* TB1 (165 $\mu l \cdot liter^{-1}$). In addition, 2-hexen-1-ol prevents growth of *P. syringae* pv. (246.4 $\mu l \cdot liter^{-1}$) and *E. coli* (515.2 $\mu l \cdot liter^{-1}$). *P. syringae* pv. *angulata* is the most sensitive of the organisms tested, being inhibited by as little as 7 $\mu l \cdot liter^{-1}$ (E)-2-hexenal. Unsaturated volatiles showed a greater inhibitory effect than saturated volatiles (Hatanaka, 1987).

The essential oils used in medicinal drugs for controlling harmful insects were studied for their antifungal activity against the soil-borne pathogens and the foliar pathogen *B. cinerea*. Shimoni et al. (1993) found essential oils extracted form *Majorana syriaca* (origanum), *Satureja thymbra* (savory), *Micromeria fruticosa* (savory), and *Salvia trioba* (saga), which are aromatic wild plants growing in Israel, to have antifungal properties. Extracts of

these herbs were found to inhibit the growth of *B. cinerea* by 40% and *Fusarium oxysporum* f. sp. *vasinfectum, Macrophomina phaseolina*, and *Exserohilum turcicum* by 100%.

Acetic acid was tested for its antifungal activity on apple fruits (Sholberg and Gaunce, 1995). The spores of *B. cinerea* and *P. expansum* do not germinate after treatment with 2.7 and 5.4 mg liter^{-1} (1008 and 2016 µl·liter^{-1}) at 2 and 20°C. Use of acetic acid at fungicidal concentration causes no apparent phytotoxic effect on fruit.

Vaughn et al. (1993) studied the effect of fifteen volatiles produced by raspberries and strawberries during ripening on fungal decay. They indicated that five compounds including benzaldehyde, 1-hexanol, E-2-hexenal, Z-3-hexen-1-ol, and 2-nonanone completely inhibited all fungi on fruit at 400 µl·liter^{-1}. Of these compounds, benzaldehyde at 40 µl·liter^{-1} can completely inhibit *A. alternata*, *B. cinerea* and *Coletotrichum gloeosporioides* spp. The other compounds such as 1-hexanol, E-2-hexenal, and 2-nonanone also inhibit the indicated fungi at 100 µl·liter^{-1}.

Hexanal

To date the vast majority of research on hexanal is related to the meat industry and its concern of hexanal as an indicator of the flavor deterioration of meat and meat products (Shahidi, 1994). However, more research is being conducted on the use of natural organics with minimally processed produce.

Six-carbon (C_6) aldehydes have been found to inhibit the hyphae growth of *Alternaria alternata* and *Botrytis cinerea* (Hamilton-Kemp, 1992). Besides beneficial antifungal properties, hexanal is also been proven to enhance aroma biosynthesis in sliced apples. Six-carbon aldehydes are also important precursors for the formation of C_6 esters, which are among the most abundant volatile compounds in apple, pears, and bananas and contribute to typical fruity odors (Paillard, 1986, 1990). Hexanal was actively converted to aroma volatiles in 'Jonagold' and 'Golden Delicious' apple slices (Song, 1996).

Factors that influence the selection of natural volatiles to control fruit decay might be expected to include low plant and mammalian toxicity, a pleasant or unobjectionable odor, resistance to rapid decomposition, commercial availability, and adequate volatility (Buckingham, 1994; Lewis, 1992). For these reasons, we selected to examine the suitability of hexanal as a natural volatile for decay control of apple slices. Most reports on the use of natural volatiles to control decay were on whole fresh fruits. Few prior investigations have been conducted on volatiles to control decay of fresh-cut apples. In that regard, research in this area is scarce and very much needed.

Metallocene films

Although structural design and food processing methods have changed over the past few years, the films themselves have only undergone only minor tweaking and processing variations such as perforation and gauge adjustments. There still exists a need for more specially tailored polymer

resins. Metallocenes have been proved to impart improved properties over classic polyethylene. Now with metallocene catalysts discovered in the 1980s, producers can refine, even design, the structure of polymers (Thayer, 1995).

Modified atmosphere packaging is one area that could greatly benefit from new, specialized films. The increasing requirements for longer shelf life at the retail level for fresh produce will favor new packaging materials; i.e., the metallocene plastomers with higher O_2 and CO_2 transmission rates represent another market opportunity for the metallocene PE resins (Unterreiner, 1996). Despite processing problems being currently experienced by converters and initial high costs associated with a new technology, it is only a matter of time before the preferred properties of metallocenes make them the resin of choice. By 2005 about 37% of the low-density polyethylene market will be replaced by metallocene resins (Colvin, 1997).

CHAPTER 2

CONSUMPTION OF HEXANAL VAPOR

BY GOLDEN DELICIOUS APPLE FRUIT TISSUE

MATERIALS AND METHODS

Materials

Plant material

'Golden Delicious' apple fruits were obtained from a local supermarket and stored at 1°C until used. Fruit was removed from cold storage and allowed to equilibrate to ambient temperature (23°C) which took approximately 1 hour. Each apple was rinsed with distilled water and sliced into wedges that weighed 15-20 g per pair of wedges, and placed in exposure chambers with hexanal vapor and a control chamber without hexanal.

Hexanal

97% pure Hexanal (*Caproaldehyde*) was obtained from Aldrich Chemical Company, Inc. (Milwaukee, WI) and stored at 4°C until used.

Squalane

Squalane (2,6,10,15,19,23 Hexamethyl-tetracosane) was obtained from Aldrich Chemical Company, Inc. (Milwaukee, WI) and stored at 4°C until used.

Methods

Flow-through exposure chamber

A flow-through vapor exposure system was constructed (Figure 1). The inlet air was filtered by in-line microbial filters (0.45 µm pore size) obtained from Alltech Associates, Inc. (Deerfield, IL) and humidified by bubbling the air through

sterilized water (tap water boiled for 10 minutes). The system consisted of four parallel systems (labeled A, B, C, & D(control)) which only differed in hexanal concentration due to different gas flow rates.

A glass vapor generator containing a mixture of hexanal and squalane was used to create hexanal vapor by bubbling nitrogen through liquid hexanal. The resulting hexanal vapor was then mixed with the sterilized air to reduce the vapor concentration. The concentration of hexanal vapor was coarsely controlled by regulating the air and nitrogen flow and also adjusting the squalane:hexanal ratio in the vapor generator. Gas flows were adjusted with glass microbore capillary tubes in combination with a Scientific pressure regulator (South Plainfield, NJ). The concentration of hexanal is expressed in moles of hexanal per liter of air at STP. Due to its high boiling temperature, hexanal was mixed with squalane (a non-volatile oil) and the vapor generators were placed in an ice bath to lower the vapor pressure and keep the hexanal vapor from saturating the exiting nitrogen gas. These steps were necessary in order to produce concentrations lower than 25×10^{-6} mol·L^{-1}.

Air containing hexanal vapor was directed into the exposure chambers with 3mm flexible Teflon tubing, which was impermeable to hexanal. The flow rate through the exposure chambers ranged from 15 to 120 mL·min^{-1}. Treatment concentrations of hexanal ranged from 0.35×10^{-6} to 11.02×10^{-6} mol·L^{-1} at 23°C, from 0.78×10^{-6} to 13.75×10^{-6} mol·L^{-1} at 10°C, and 2.06×10^{-6} to 20.19×10^{-6} mol·L^{-1} at 5°C. The concentration of hexanal vapor was measured by taking a gas sample from the integral glass sampling port fitted with

a Teflon-lined septum at the inlet and outlet of the exposure chamber. Outlet flow was directed to a fume hood using 1/4 inch flexible tubing. Steady state hexanal concentration in the headspace of the exposure chamber was reached in less than 30 minutes and consumption reached steady state in 8-10 hours.

Trials were started by allowing the vapor generators to cool for 30 minutes in the ice bath, starting the nitrogen flow and allowing the system to equilibrate for another 30 minutes. At this point the apples where sliced, weighed, and placed in the exposure chambers.

Hexanal analysis

Hexanal vapor concentration was quantified by sampling the inlet and outlet gas streams of the exposure chambers and analyzing with a gas chromatograph (Shimadzu model GC-4CM) fitted with a 2 meter column packed with 10% DEGS-PS, 80/100 Supelcoport. The column was maintained at 110°C. Nitrogen was used as a carrier gas at a flow rate of 40 $mL \cdot min^{-1}$. Air flow rate was 15 $mL \cdot min^{-1}$ and hydrogen flow rate was 20 $mL \cdot min^{-1}$ Samples were taken with a Hamilton 500 µL gas tight syringe (model 1750) and output was recorded on a Linear chart recorder (model 1201-0000). Concentration was determined by comparison of output with that of a standard.

Consumption

Hexanal vapor concentrations were determined for inlet, outlet and difference (inlet-outlet) air flows. Consumption values were determined with the

following equation:

$$C = f \cdot h \cdot w^{-1} \qquad (1)$$

C = Consumption rate ($mol \cdot g^{-1} \cdot sec^{-1}$)
f = flow rate ($mL \cdot min^{-1}$)
h = hexanal consumed ($mol \cdot L^{-1}$ air)
w = weight of fruit tissue (grams)

Aroma assessments

Sampling of aroma compounds was conducted in the manner outlined by Song (1996): A solid-phase micro-extraction (SPME) device fitted with a fiber coated to a thickness of 100 µm with polydimethylsiloxane was inserted through a Teflon lined septum of the exposure chamber outlet.

Identification of the aroma compounds was confirmed by comparing mass spectra with a standard of known composition and by comparison to spectra in the National Institute for Standard Technology (NIST) mass spectra library (Search version 1.0).

RESULTS AND DISCUSSION

Standard calibration curve

The relationship between the GC response and hexanal vapor concentration was linear (Figure 2) according to the following equation:

$$Y=22.51X + 13.90 \quad (2)$$

where X is the hexanal concentration ($mol \cdot L^{-1}$) and Y is the GC response. The coefficient of determination (r^2) was 0.9413 and coefficient of variation was 57%.

Statistical Analysis

Statistical analysis was run on data to study the possible interaction effect of temperature, system, and concentration on the consumption rate of hexanal vapor by golden delicious apple tissue. Each factor was analyzed individually as well as together to examine possible cross interaction or synergistic effect. SAS (Release 6.12) was used to conduct analysis of covariance with generalized linear modeling.

Effect of temperature on hexanal consumption

The relationship between hexanal headspace concentration and consumption rate at each temperature (5, 10, 23°C) was plotted and statistically analyzed. A plot of all the raw data is presented in Figure 3. No significant effect ($\propto$ = 0.05) of temperature on the consumption rate was found at the temperatures tested (Figure 4).

Research into the consumption of hexanal by fruit tissue and understanding of the mechanics behind it is very limited. It is uncertain why temperature seems to have no effect on consumption. One possible explanation is that they enzymatic reactions that are responsible for consumption are not temperature sensitive or that we are operating at a too small of a range to see a significant effect. It should not be assumed that lowering the temperature to a value close to 0°C necessarily reduces the activity of all enzymes (Fennema, 1985).

However, it is also likely is that this may be due to the large variability (inherent to biological systems) between temperatures. Therefore, the actual difference is masked by the overlapping variation between temperature data sets.

Effect of system on hexanal consumption

Although each parallel exposure chamber was identical with the exception of flow rate (and therefore produced hexanal concentration), graphs of the raw data suggested that there was a slight chance of interaction (grouping). Hexanal concentration is generated by flowing nitrogen gas through a liquid squalane:hexanal mixture, therefore concentration is dependant on the rate of nitrogen flow. Since the flow rate is considered in the consumption equation, all consumption results are normalized for flow rate. Effect of individual exposure system on the consumption rate was found highly insignificant ($\propto = 0.05$) at the temperatures tested (Table 1). This interaction concern was eliminated upon review of the statistical analysis.

Effect of hexanal headspace concentration

Hexanal headspace concentration was the only factor that had a highly significant effect ($\propto = 0.05$) on the consumption rate of hexanal by golden delicious apple tissue (Tables 1 and 2). Consequently, an overall linear regression equation was fitted, disregarding temperature and system. The

consumption rate was found to be linear with hexanal vapor concentration according to the following equation:

$$Y = 0.2216X + 0.0378 \qquad (3)$$

where X is the hexanal concentration ($mol \cdot L^{-1}$) and Y is the consumption rate in $mol \cdot g^{-1} \cdot sec^{-1}$. The coefficient of determination (r^2) was 0.516331 and coefficient of variation was 70%.

Table 1. Type III Sum of Squares for ANOVA with single factor of headspace concentration

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Conc	1	35.09254528	35.09254528	35.23	0.0001

Effect of hexanal on aroma production

Hexanal concentration was found to have an effect on aroma compound production up to an undefined 'saturation' point (Figure 7). Conversion was found to be sensitive to mass delivery rate through the exposure chamber. Mass delivery rate is defined as the product of hexanal concentration and flow rate, results given in units of $mol \cdot sec^{-1}$. Samples were only taken twice and there is insufficient data to fully examine this interaction. A mass spectra of a sample is shown in Figure 8. Despite the brevity of the study, the trendline is supported by the fact that despite increasing amounts of hexanal in the headspace, aroma production did not increase after a 'saturation' point.

Analysis focused on six prominent compounds: 1-hexanol, hexanoic acid, acetic acid-hexyl ester, butanoic acid-hexyl ester, butanoic acid-2-methyl-hexyl

ester, and hexanoic acid-hexyl ester. All compounds showed a marked increase upon contact with hexanal vapor (Table 3). 1-Hexanol had the biggest increase (18-27%) while the remaining compounds were in the range of 0.01-0.99% (Figures 5 and 6). Although compounds (besides 1-hexanol) were relatively small in terms of percentages, they still represent a 8-469 fold increase over the control.

There was no differentiation between 1-hexanol produced via hexanal conversion by apple tissue and possible production due to hexanal reduction by atmospheric oxygen.

Table 2. Type III Sum of Squares for ANOVA with multiple factors

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Conc	1	4.95462990	4.95462990	5.17	0.0335
System	2	0.14917512	0.07458756	0.08	0.9253
Temp	2	1.78102251	0.89051126	0.93	0.4103
Conc*Temp	2	1.18211736	0.59105868	0.62	0.5490
Conc*System	2	1.02040695	0.51020347	0.53	0.5947
System*Temp	4	2.86525156	0.71631289	0.75	0.5703

Table 3. Conversion of hexanal in headspace to selected aroma compounds by golden delicious apple tissue

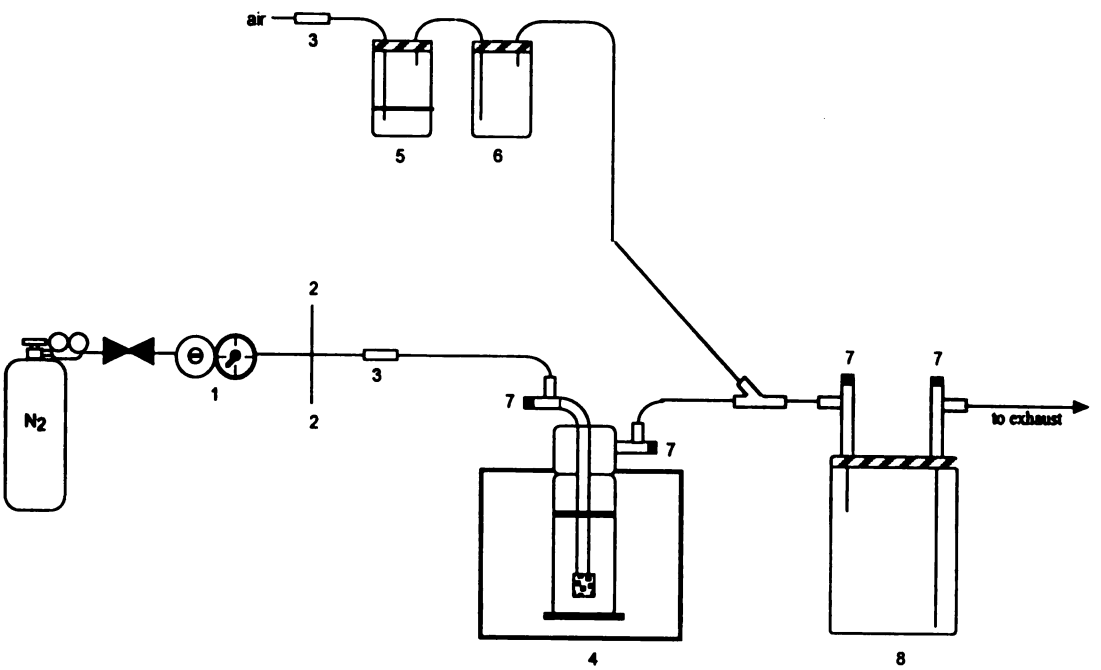
System	Supplied Hexanal ($mol \cdot sec^{-1}$)	Aroma Compound	aroma ($mol \cdot L^{-1}$)	production rate ($mol \cdot sec^{-1}$)	% conversion
		Aroma			
A	3.25E-08	1-Hexanol	3.29E-06	5.90E-09	18.13%
A	3.25E-08	Hexanoic Acid	8.42E-08	1.45E-10	0.45%
A	3.25E-08	Acetic acid, hexyl ester	2.35E-08	4.02E-11	0.12%
A	3.25E-08	Butanoic Acid, hexyl ester	1.86E-08	3.23E-11	0.10%
A	3.25E-08	Butanoic acid, 2-methyl-, hexyl ester	1.13E-08	2.09E-11	0.06%
A	3.25E-08	Hexanoic acid, hexyl ester	3.86E-08	6.44E-11	0.20%
				Total	19.06%
B	3.81E-09	1-Hexanol	2.29E-06	8.64E-10	22.66%
B	3.81E-09	Hexanoic Acid	7.28E-09	2.60E-12	0.07%
B	3.81E-09	Acetic acid, hexyl ester	5.38E-08	1.88E-11	0.49%
B	3.81E-09	Butanoic Acid, hexyl ester	1.88E-08	7.14E-12	0.19%
B	3.81E-09	Butanoic acid, 2-methyl-, hexyl ester	7.75E-10	2.79E-13	0.01%
B	3.81E-09	Hexanoic acid, hexyl ester	2.14E-08	7.61E-12	0.20%
				Total	23.62%
C	5.94E-09	1-Hexanol	1.61E-06	1.61E-09	27.05%
C	5.94E-09	Hexanoic Acid	1.00E-08	1.00E-11	0.17%
C	5.94E-09	Acetic acid, hexyl ester	5.89E-08	5.89E-11	0.99%
C	5.94E-09	Butanoic Acid, hexyl ester	1.88E-08	1.88E-11	0.32%
C	5.94E-09	Butanoic acid, 2-methyl-, hexyl ester	9.63E-10	9.63E-13	0.02%
C	5.94E-09	Hexanoic acid, hexyl ester	2.29E-08	2.29E-11	0.39%
				Total	28.93%
D*		1-Hexanol	0.00E+0	0.00E+00	
D*		Hexanoic Acid	0.00E+0	0.00E+00	
D*		Acetic acid, hexyl ester	5.62E-09	2.34E-12	
D*		Butanoic Acid, hexyl ester	1.65E-10	6.88E-14	
D*		Butanoic acid, 2-methyl-, hexyl ester	0.00E+0	0.00E+00	
D*		Hexanoic acid, hexyl ester	8.06E-10	3.36E-13	

* hexanal-free control

Table 4. Consumption test conditions for aroma analysis

Date	System	Hexanal ($mol^{-6} \cdot L^{-1}$)	flow ($L \cdot min^{-1}$)	Temperature (C)
6.29.98	A	8.8	0.111	5
7.24.98	A	9.75	0.1	10
6.29.98	B	5.12	0.025	5
7.24.98	B	5.04	0.02	10
6.29.98	C	2.06	0.06	5
7.24.98	C	3.88	0.06	10
6.29.98	D	0	0.025	5
7.24.98	D	0	0.025	10

Figure 1. Flow through exposure system



1 Pressure regulator
2 Parallel system
3 Glass capillary
4 Hexanal vapor generator (in ice bath)
5 Air stream humidifier
6 Water condensation trap
7 Sampling port
8 Exposure chamber

Figure 2. Calibration curve for hexanal

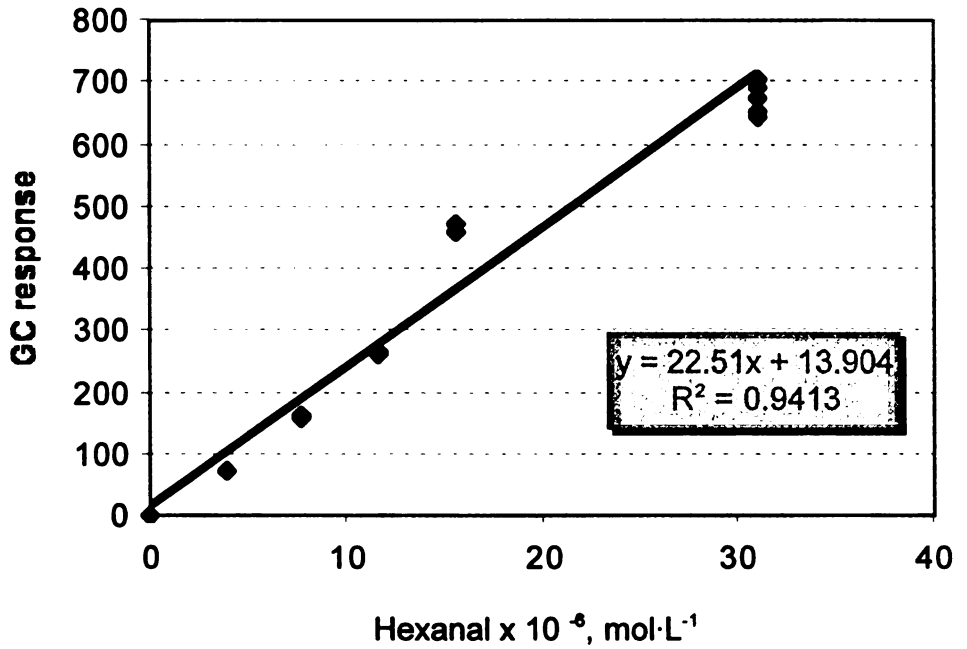


Figure 3. Hexanal headspace concentration vs. hexanal consumption by golden delicious apple tissue for various temperatures

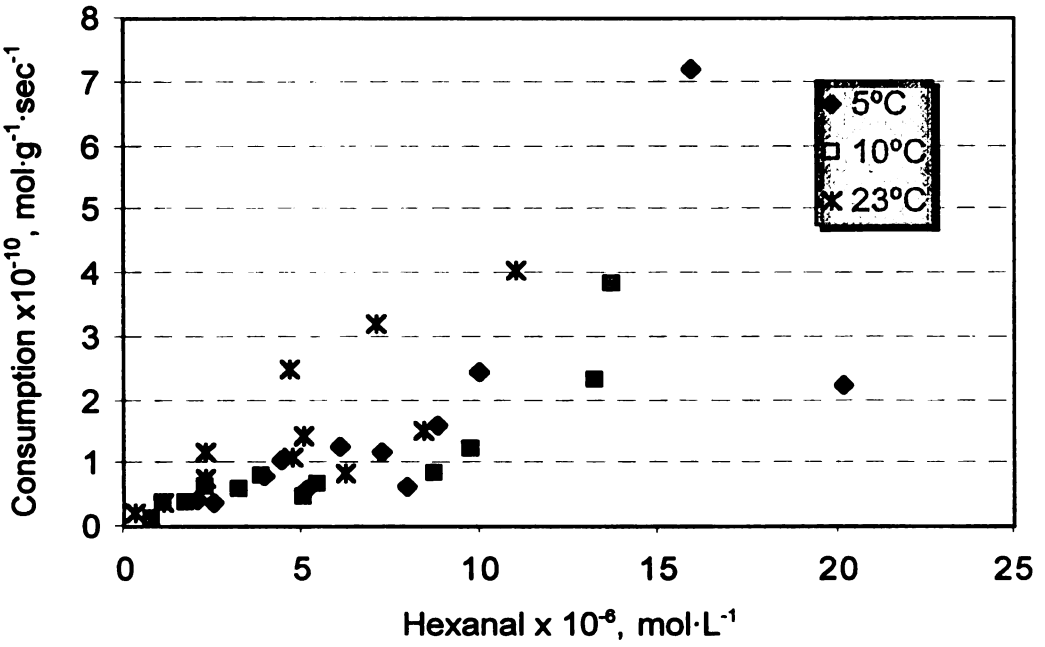


Figure 4. Effect of hexanal headspace concentration on hexanal consumption by golden delicious apple tissue for various temperatures and statistical model

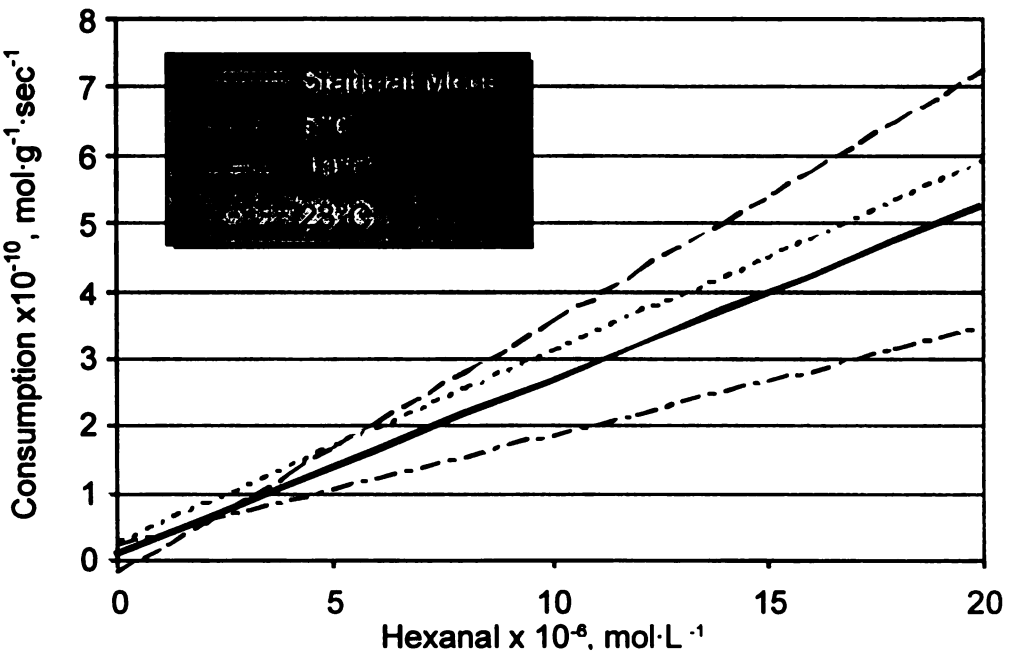


Figure 5. Effect of hexanal delivery rate on conversion to 1-hexanol

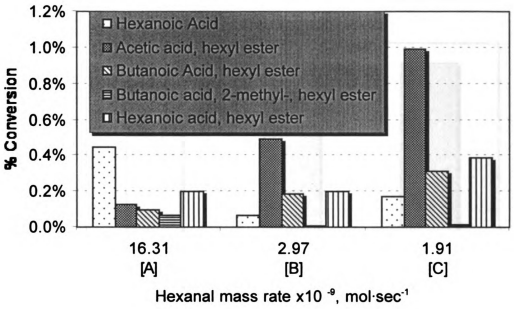


Figure 6. Effect of hexanal delivery rate on conversion to selected aroma compounds

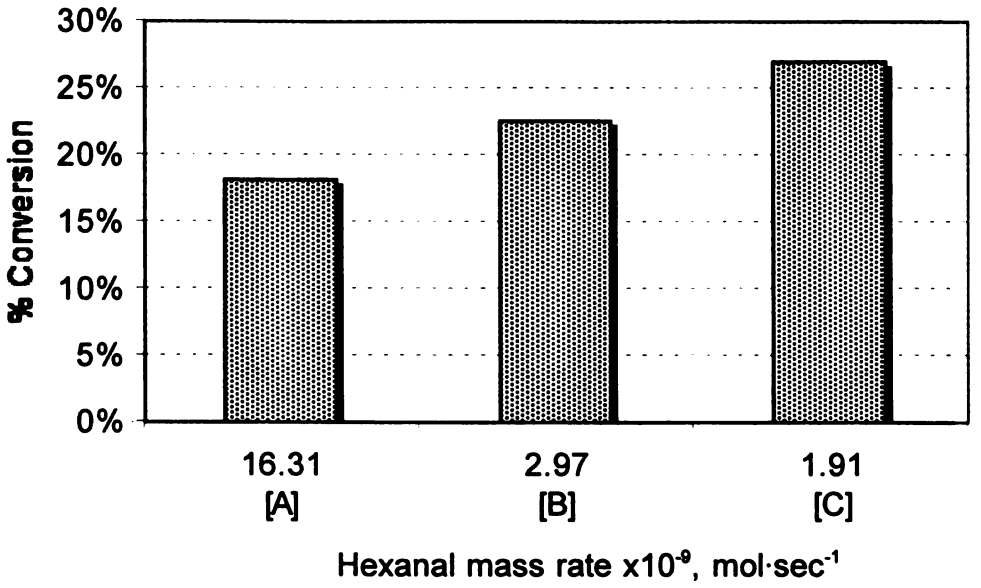


Figure 7. Effect of mass rate on conversion of hexanal to aroma compounds by golden delicious apple tissue

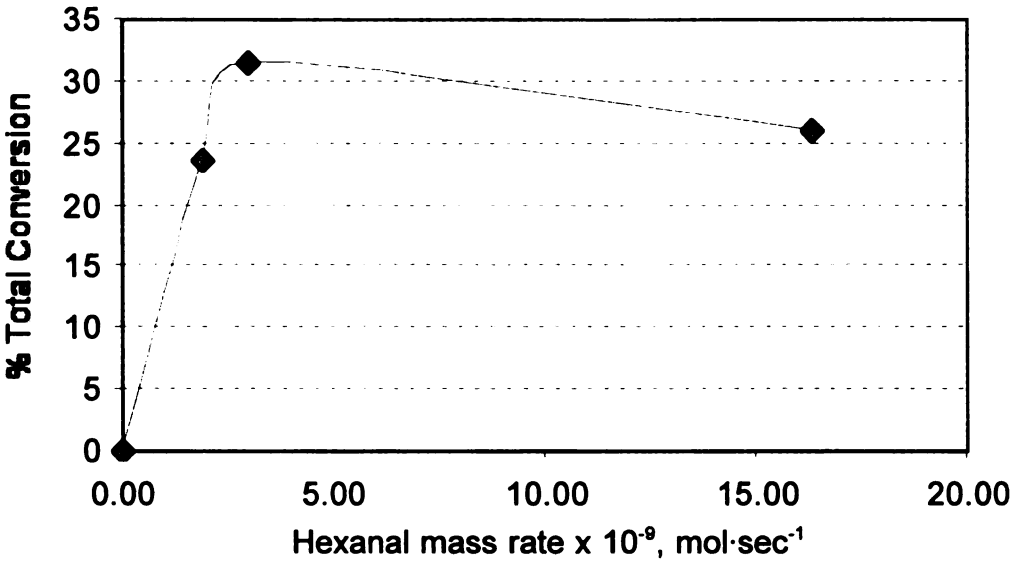
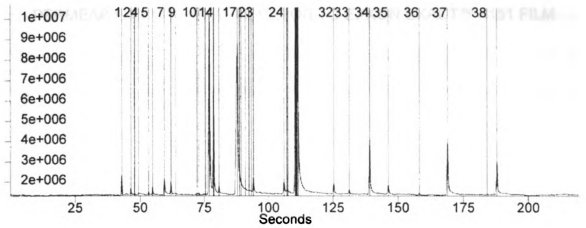


Figure 8. Mass spectra of aroma compounds produced by consumption of hexanal by golden delicious apple tissue



CHAPTER 3

PERMEABILITY OF HEXANAL VAPOR TO EXXON EXACT™ 4151 FILM

Sorption

The Henry's law solubility coefficient (S) is the quantity of permeant molecules dissolved into a polymer matrix per unit of polymer mass or volume at equilibrium conditions of a given sorbate partial pressure and temperature. A large S implies a tendency for the penetrant molecules to dissolve into and be retained in the polymer. Sorption is derived from the following equation:

$$S = \frac{c}{p} \qquad (4)$$

where c is the concentration of the permeant in the polymer and p is the permeant partial pressure in the gas phase.

Sorption relates to the condensation, penetration and dispersion of penetrant molecules into the polymer matrix and includes adsorption (surface attachment), adsorption (access to the polymer matrix), incorporation into microvoids, cluster formation and other modes of mixing (Rogers, 1985).

Braunauer (1994) explains the tendency for gas molecules to adsorb to the surface of solids on the basis of reducing the free surface energy. The rate of sorption is often very fast –granular Darco G (adsorbent activated charcoal) adsorbs three hundred times its own volume of nitrogen gas at –183°C in under one minute. However the fast adsorption stage is often followed by a slow absorption process.

Diffusion

Diffusion describes the process where a permeant molecule moves within the polymer structure across a concentration gradient. It is also a measure of the

length of time required for a permeant/polymer combination to reach a steady state condition. Diffusion rate is influenced by permeant size, shape, and interaction with the polymer. The diffusion process is described by Fick's first law:

$$F = -D\frac{\delta c}{\delta x} \quad (5)$$

where F is flow *or flux* of penetrant per unit area, expressed as the mass of diffusing species per unit area of polymer film per unit time (t); c is the concentration of the penetrant in the film expressed in the same unit of mass of diffusing species per unit of volume or mass of the polymer; D is the diffusion coefficient, in length/time; x is the distance in the direction of the penetrant transport (Crank, 1975). The diffusion coefficient (D) is a proportionality constant, however for many penetrant/polymer systems, D is not a constant but a function of a concentration, or time. Low-molecular weight permeants in solid polymers exhibit diffusion coefficient values ranging from 1×10^{-12} to 1×10^{-18} m^2s^{-1} (Hernandez, 1996).

Permeability

Permeation is the diffusional molecular exchange of gases, vapors, or liquid permeants across a plastic material which is devoid of imperfections such as cracks and perforations (Hernandez, 1996). Permeability is the product of the thermodynamic parameter of solubility and the kinetic parameter of diffusion.

The permeability coefficient describes the transport rate of permeant across a film at steady state. Therefore the degree to which the molecular

species is soluble in the polymer and the rate of diffusion through the polymer matrix, prior to desorption on the exterior surface, determines the film's permeability to the permeant species. The permeability coefficient will therefore depend on the temperature and physio-chemical properties of the polymer and permeant.

The driving force for permeation of gases and vapors through a polymer film is the difference in concentration or partial pressure of the test gas or vapor between each side of the film. Partial pressure is used because it is more easily measured according to Henry's law. Dalton's law defines partial pressure as the pressure exerted by a constituent gas in a mixture of gases where the total pressure exerted is the sum of the partial pressure for each constituent gas. Therefore the rate of permeation of a constituent permeant through a polymer film is a function of its partial pressure difference across the film. The resultant concentration gradient drives a flow of permeant molecules from the high concentration side to the low concentration side of the film. Figure 9 illustrates a model for gas or vapor permeability through a plastic packaging film. The units used in this study are based on the SI system: Kg m m^{-2} s^{-1} Pa^{-1}.

MATERIALS AND METHODS

Materials

Metallocene film

Metallocene catalyzed ethylene-hexene copolymer film (Exact™ 4151) was donated by Exxon Chemical. Material was supplied in sheet form measuring 11 inches x 8.5 inches x 1.2 mil (30.5μm) thick (table 5). Film was carefully handled with dedicated tweezers and samples were cut using dedicated scissors. Care was taken to avoid sample contamination by dust or oils via direct skin contact.

Hexanal

Hexanal (97% Purity) was obtained from Aldrich Chemical Company, Inc Milwaukee, WI). It was stored at 4°C until used.

Squalane

Squalane (2,6,10,15,19,23 Hexamethyl-tetracosane) was obtained from Aldrich Chemical Co. (Milwaukee, WI) and stored at 4°C until used.

Compressed Gas

Nitrogen, compressed air, helium, and hydrogen were obtained from AGA Gas Inc. (Cleveland, OH).

Methods

Sorption measurement by gravimetric method

Sorption experiments were conducted in a Cahn Electrobalance which continually records weight change of a film sample with time. This instrument is very good for measuring the small weight increases in films sorbing organic vapors. Many researchers have studied sorption of organic vapors utilizing an electrobalance (Hernandez et al., 1986; Baner, 1987).

The electrobalance is comprised of a balance beam and highly sensitive weighing unit which converts torque to current. As weight increases, the greater the torque and thus larger current is required to maintain the balance beam in a horizontal position. The amount of current is therefore proportional to the weight suspended from the balance beam.

The electrobalance is contained within a glass vessel, and the film sample is suspended from the balance beam wire enclosed in the hangdown tube. This isolates the instrument from the external environment, thus experiments can be conducted under a controlled gaseous or vapor atmosphere.

The electrobalance hangdown tube was placed in a Thermotron temperature controlled chamber (Model SM-8-SH, Thermotron Industries, Holland, MI). The electrobalance was connected to a Digital Interface which converts the analog signal to a digital format enabling connection to a computer installed with software for recording, analyzing, and displaying weight data. Data was exported to spreadsheet software for analysis.

Since the electrobalance is very sensitive to mechanical shocks and vibration, it rests on a wall mounted brace system over the chamber, with the hangdown tube entering the chamber through an overhead equipment port. The electrobalance and hangdown tube are not in physical contact with the environmental chamber to prevent vibrations and shocks from interfering with electrobalance operation.

Hexanal vapor is generated by bubbling nitrogen gas through a mixture of squalane and hexanal in a glass vapor generator that rests in an ice bath. Ice was replenished every 14-16 hours to maintain the vapor generator at 0°C. As with consumption experiments, this was helpful to keep the hexanal vapor from saturating the exiting nitrogen gas and produce concentrations lower than 25 x 10^{-6} mol·L^{-1}. The hexanal vapor stream flowed into the hangdown tube, surrounding the film sample and then into a fume hood (Figure 10).

Small rectangles of Exact™ film, weighing 40-50 mg, were cut with dedicated scissors and placed on the balance beam wire in the hangdown tube with dedicated tweezers. Dry nitrogen was flowed through the system overnight to degas the film samples and remove any condensation or vapor in the hangdown tube.

Tests were started by allowing the vapor generator to cool for 30 minutes in the ice bath, starting the nitrogen flow through the vapor generator and allowing the system to equilibrate for another 30 minutes. The system was constructed so dry nitrogen and hexanal streams could flow simultaneously, exiting through separate exhaust lines. When the vapor generator was

sufficiently chilled, the weight of the film sample was recorded, and the balance tarred. Then the dry nitrogen flow was ceased and the hexanal vapor flow was directed into the hangdown tube with immediate initiation of computer weight recording.

Sorption profiles at 25 and 5°C were obtained by continuous recording (10 minute intervals) of weight gain until sorption steady state was reached. To ensure that a valid steady state had been reached, tests were allowed to continue and data examined for deviations from equilibrium values. No significant deviations from steady state values were observed.

The equilibrium solubility value is the ration of weight of permeant retained in the polymer sample (at steady state) to the initial polymer sample weight at the vapor partial pressure of test conditions (expressed in gram per gram). The weight increase of the polymer sample due to sorption of hexanal vapor was constantly monitored by the computer which is digitally interfaced with the electrobalance.

A first estimation of the diffusion coefficient was carried out using the half-sorption time ($t_{0.5}$) obtained from interpolating $M_{ss} = 0.5$ from experimental data of M_t/M_{ss} versus time and substituting this value into the following equation:

$$D_s = \frac{0.049l^2}{t_{0.5}} \qquad (6)$$

where $t_{0.5}$ is the time required to reach half of the steady state sorption value when M_t/M_{ss} =0.5 as shown in figure 11.

A sorption curve was found by substituting the experimental diffusion coefficient value into the following equation and calculated values of weight increase were obtained from the following equation:

$$\frac{M_t}{M_{ss}} = 1 - \frac{8}{\Pi^2}\left[\exp\left(\frac{-D_s \cdot \Pi^2 \cdot t}{l^2}\right) + \frac{1}{9}\exp\left(\frac{-9D_s \cdot \Pi^2 \cdot t}{l^2}\right)\right] \quad (7)$$

where M_t is the quantity of permeant sorbed by the film at time t; M_{ss} is the equilibrium sorption level at steady state, after infinite time; t is the time to reach M_{ss}; l is the film thickness.

A sums of squares analysis between the experimental and calculated M_t/M_{ss} as a function of time was implemented to obtain the "best fit" diffusion coefficient (D).

The permeability was obtained from the following equation:

$$P = D \times S \quad (8)$$

Where P is the permeability coefficient, D and S are the diffusion and solubility coefficients, respectively. This relationship is valid when the diffusion coefficient is concentration independent and the solubility coefficient follows Henry's law. Henry's law states that the permeability coefficient is a function of the penetrant molecules solubility in the polymer and their diffusion rate across the polymer and is defined in equation 7.

Isostatic gravimetric dish method

Packages consisted of an aluminum dish, steel reinforcement rings, polymer film, and office supply binder clips (Figure 15). A thin layer of vacuum grease was applied to the lip of the aluminum dish and metallocene film placed

over the top of the dish, gently pressing at the edges to ensure a seal. Steel rings were placed on top of and beneath the sealing edge of the dish and clamped with 3/4" binder clips, pulling gently on the film to eliminate wrinkles. The packages used are the identical packages later utilized for modified atmosphere testing.

Sampling ports were created by drilling a 1/16" hole in the side of the dish and covering it with pure silicone caulk. After drying for 48 hours, the caulk provided a tight seal that would reseal when the syringe was removed after taking a sample of headspace.

Approximately 5 mL of liquid hexanal was placed in six dishes (three with sampling ports), sealed with Exact™ 4151 film, and placed in a fume hood. Weights of three dishes (without sampling ports) were recorded and plotted as weight per time.

. The hexanal headspace concentration of the three dishes with sampling ports were sampled at the same intervals as weighings. 5 ml of hexanal provided enough liquid to saturate the headspace of the dish with hexanal vapor. Concentration was determined using the ideal gas law as follows:

$$p = \frac{n}{v} \cdot R \cdot T \quad (9)$$

where: p = vapor pressure (converted to Pa)

n/v = concentration ($mol \cdot L^{-1}$)

R = ideal gas law constant ($L \cdot atm \cdot K^{-1} \cdot mol^{-1}$)

T = temperature (Kelvin)

The concentration vapor pressure was calculated as an average of all data points.

Permeability was then calculated using the following equation:

$$P = \frac{q}{t} \cdot \frac{l}{A \cdot \Delta p} \qquad (7)$$

Where: q/t = slope of weight loss/time ($Kg \cdot sec^{-1}$)

l = film thickness (M)

A = film area (M^2)

Δp = concentration partial pressure (Pa)

Hexanal analysis

Hexanal vapor concentration was quantified by sampling the gas flow of the hangdown tube or package headspace and analyzing with a gas chromatograph (Hewlett Packard Model 6890) fitted with a 30 m long column. A complete list of GC settings is presented in Table 6. Samples were taken with a Hamilton 500 µl gas tight syringe (model 1750) and output was recorded on Hewlett Packard 6890 integrator. Concentration was determined by comparison of output with that of a standard.

RESULTS AND DISCUSSION

Standard calibration curve

The relationship between the GC response and hexanal vapor concentration was linear (Figure 12) according to the following equation:

$$Y = 9.968\,X - 6.81$$

where X is the hexanal concentration ($mol \cdot L^{-1}$) and Y is the GC response. The coefficient of determination (r^2) was 0.9954 and coefficient of variation was 8%.

Sorption by gravimetric method

Sorption experiments were conducted at 5 and 25°C and at partial pressures ranging from 70 to 84 Pa. The sorption experiment was conducted twice at 25°C to prove reproducibility of results.

The computer software was limited by a maximum of 168 hours of data recording. This required a manual restart of the program at the time of program self-termination in order to carry out an experiment longer than this time limit. This presented a problem of a small recording delay upon the restart of data recording an joining of separate data sets.

Sorption curves for hexanal obtained in the above testing descriptions are presented in Figures 13 and 14. The sorption curves are plotted as M_t versus time, where M_t is the weight gain, in mg, at time *t*. Experimental data points are superimposed on the theoretical curve calculated from equation 7, using the best fit of the diffusion coefficient from the sum of squares method. Since the fit of experimental and theoretical curves generally agree with each other, a Fickian

diffusion process can be assumed. Half time steady state sorption ($t_{0.5}$) was reached within approximately 7 hours at 25°C and 83 hours at 5°C. As temperature and hexanal partial pressure increased, an equilibrium steady state was reached more rapidly, therefore $t_{0.5}$ values decreased.

The sorption coefficient values decreased and diffusion coefficient values increased as temperature increased. Temperature has a varying effect on the solubility and diffusion coefficients and can act upon the permeability coefficient either way, depending on the overall effect of S and D. The effect of temperature on the solubility coefficient can be represented by an Arrhenius-type relationship:

$$S = S_o \exp(-\Delta H_s / RT) \qquad (12)$$

where ΔH_s is the heat of solution for the permeant gas, R is the gas constant and T is the temperature (in Kelvin). ΔH_s is the sum of the molar heat of condensation ΔH_c and the molar heat of mixing ΔH_m:

$$\Delta H_s = \Delta H_c + \Delta H_m$$

For gases well above their critical point at room temperature (i.e. hydrogen, oxygen, and nitrogen), the heat of solution is small and positive, therefore S increases slightly with temperature. For easily condensable organic vapors, the heat of solution is always negative and therefore S decreases with increasing temperature (Braunauer, 1965),

The effect of temperature on the diffusion coefficient can also be represented by and Arrhenius type equation:

$$D = D_o \exp(-E_D / RT) \qquad (13)$$

where the activation energy for the diffusion process (E_D) is always positive and therefore D will always increase with temperature.

Since the permeability coefficient is a product of the diffusion and solubility coefficients, it will be effected by E_D and ΔHs. In this case, the heat of solution is not large enough to overshadow the influence of the diffusion activation energy, therefore the permeability coefficient increases with a temperature increase. The diffusion, solubility, and permeability coefficients are listed in Tables 7 and 8.

Isostatic gravimetric dish permeability values

The permeability of hexanal to Exact™ 4151 film was found to be 4.2 x 10-16 kg·m·m-2·sec-1·Pa-1 at both 25 and 5°C, despite the difference of hexanal partial pressure (1,000 and 505 Pa, respectively).

Permeability values were found to be higher than those derived from the gravimetric sorption technique. This is expected due to the higher partial pressure values of hexanal used in this technique. Due to the nature of the technique, differences in permeability coefficient values between test temperatures were not distinguished.

Dish weight as a function of time for 23 and 5°C are shown in Tables 9 and 10 and graphically in Figures 16 and 17.

One drawback to this method is the lack of sensitivity when compared to the sorption gravimetric method. Both methods collect data by devices that measure weight. However, the digital balance used in this methods has a small sensitivity of 0.00005 grams when compared to the electrobalance (0.00000005

g). It is the lack of sensitivity that provides such similar results between 25°C and 5°C, where we expect a difference in permeability between the temperatures. This difference is evident in the permeability values obtained from the sorption gravimetric results.

It is also only possible to conduct tests of permeates that are at saturation partial pressure. In the case of hexanal, the saturation partial pressure creates a concentration well above the consumption threshold of golden delicious apple tissue. As previously discussed, this causes physiological damage to the tissue, most evident by development of a red tint in the fruit peel.

However, the method is not without benefit. The most obvious is the speed at which the test can be set up and conducted. This provides for the possibility of several tests in the time it would take to conduct one with the sorption gravimetric method.

Table 5. Characteristics of Exact™ 4151

Thickness	0.0000305 m (1.2 mil)
Oxygen Transmission Rate*	8.35×10^{-17} $kg \cdot m \cdot m^{-2} \cdot sec^{-1} \cdot Pa^{-1}$
Carbon Dioxide Transmission Rate	4.13×10^{-17} $kg \cdot m \cdot m^{-2} \cdot sec^{-1} \cdot Pa^{-1}$
Melt flow index* ASTM D-1238	2.2 $g \cdot 10\ min^{-1}$
Density*	0.895 $g \cdot cc^{-1}$
DSC Peak Melting Temperature*	201°F (94°C)
Tensile Strength @ yield* ASTM D-882 psi (MPa)	MD 990 (6.8) CD 600 (4.1)
Tensile Strength @ break* ASTM D-882 psi (MPa)	MD 11,400 (78.5) CD 8,730 (60.0)
Elongation @ break* ASTM D-882	MD 280% CD 590%
Elmendorf Tear Strength* ASTM D-1922 ($g \cdot mil^{-1}$)	MD 80 CD 280
Dart Drop Impact* ASTM D-1709(A) ($g \cdot mil^{-1}$)	1420

* Exxon Chemical, 1998.

Table 6. Settings for HP 6890 Gas Chromatograph

Parameter	Setting
Initial Temperature (°C)	100
Heating Rate (°C min-1)	55
Final Temperature (°C)	250
Detector Temperature (°C)	250
He carrier gas flow rate (cc min-1)	1.9
Air flow rate (cc min-1)	450
H gas flow rate (cc min-1)	40
Elution Time (min)	6.22
Column	Supelco SPB-5 Capillary30m 0.32mm ID 0.25 film thickness

Table 7. Sorption and Diffusion Coefficients of hexanal in Exact™ metallocene films

Temperature (°C)	Sorption Coefficient (Pa^{-1})	Diffusion Coefficient ($m^{-2} \cdot sec^{-1}$)
25	2.7×10^{-5}	1.9×10^{-15}
25	4.8×10^{-5}	1.9×10^{-15}
5	1.6×10^{-4}	1.5×10^{-16}

Table 8. Permeability coefficient of hexanal through Exact™ metallocene films

Method	Temperature (°C)	Hexanal Partial Pressure (Pa)	Permeability $kg \cdot m \cdot m^{-2} \cdot sec^{-1} \cdot Pa^{-1}$
Gravimetric sorption	25	84	8.1×10^{-17}
Gravimetric sorption	25	81	4.6×10^{-17}
Gravimetric sorption	5	70	2.3×10^{-17}
Isostatic dish	23	1000	4.2×10^{-16}
Isostatic dish	5	505	4.2×10^{-16}

Table 9. Isostatic gravimetric dish weight values at 23°C

	weight (g)		
Hour	Rep 1	Rep 2	Rep 3
0	100.47	101.25	100.82
12	99.506	100.34	99.901
14	99.369	100.21	99.770
15	99.307	100.17	99.713
17	99.205	100.08	99.614
19	99.110	100.00	99.523
20.5	99.041	99.948	99.458
24	98.937	99..868	99.358
35	98.756	99.735	99.182
36	98.747	99.728	99.173
slope ($g \cdot hr^{-1}$)	0.0428	0.0371	0.041
r^2	0.920	0.897	0.921

Table 10. Isostatic gravimetric dish weight values at 5°C

	weight (g)		
Hour	Rep 1	Rep 2	Rep 3
0	103.98	105.61	102.97
12	103.82	105.47	102.76
14	103.78	105.44	102.68
23	103.62	105.29	102.46
31.5	103.46	105.15	102.27
33.5	103.42	105.11	102.22
36	103.37	105.07	102.16
slope ($g \cdot hr^{-1}$)	0.0173	0.0155	0.0227
r^2	0.997	0.996	0.999

Figure 9. Permeability model for gas transfer through a polymer film (adapted from Giacin and Hernandez, 1996)

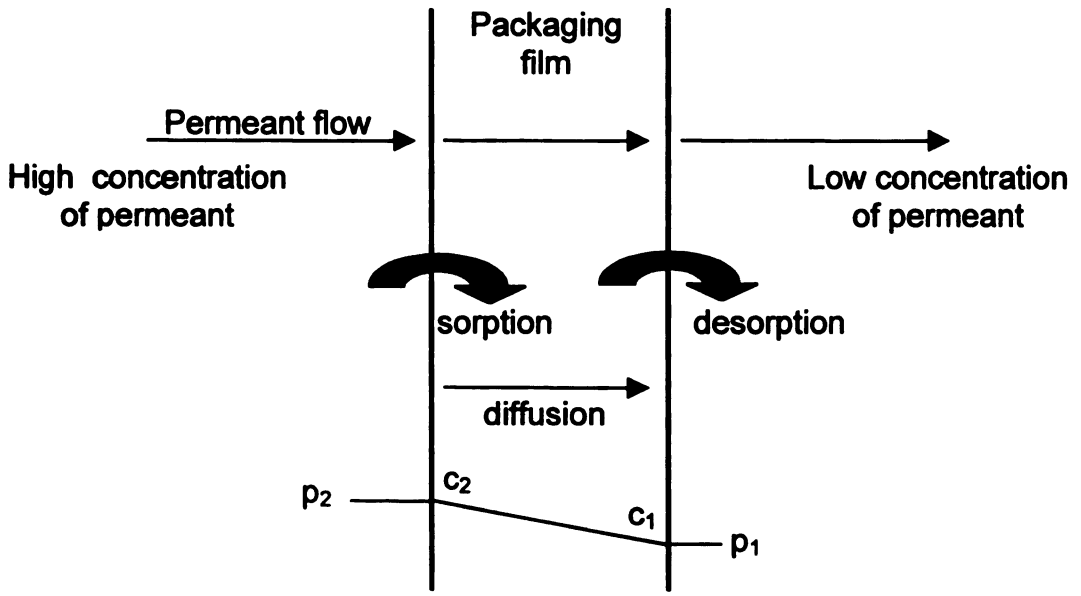


Figure 10. Flow through system for Cahn D200 Digital Electrobalance

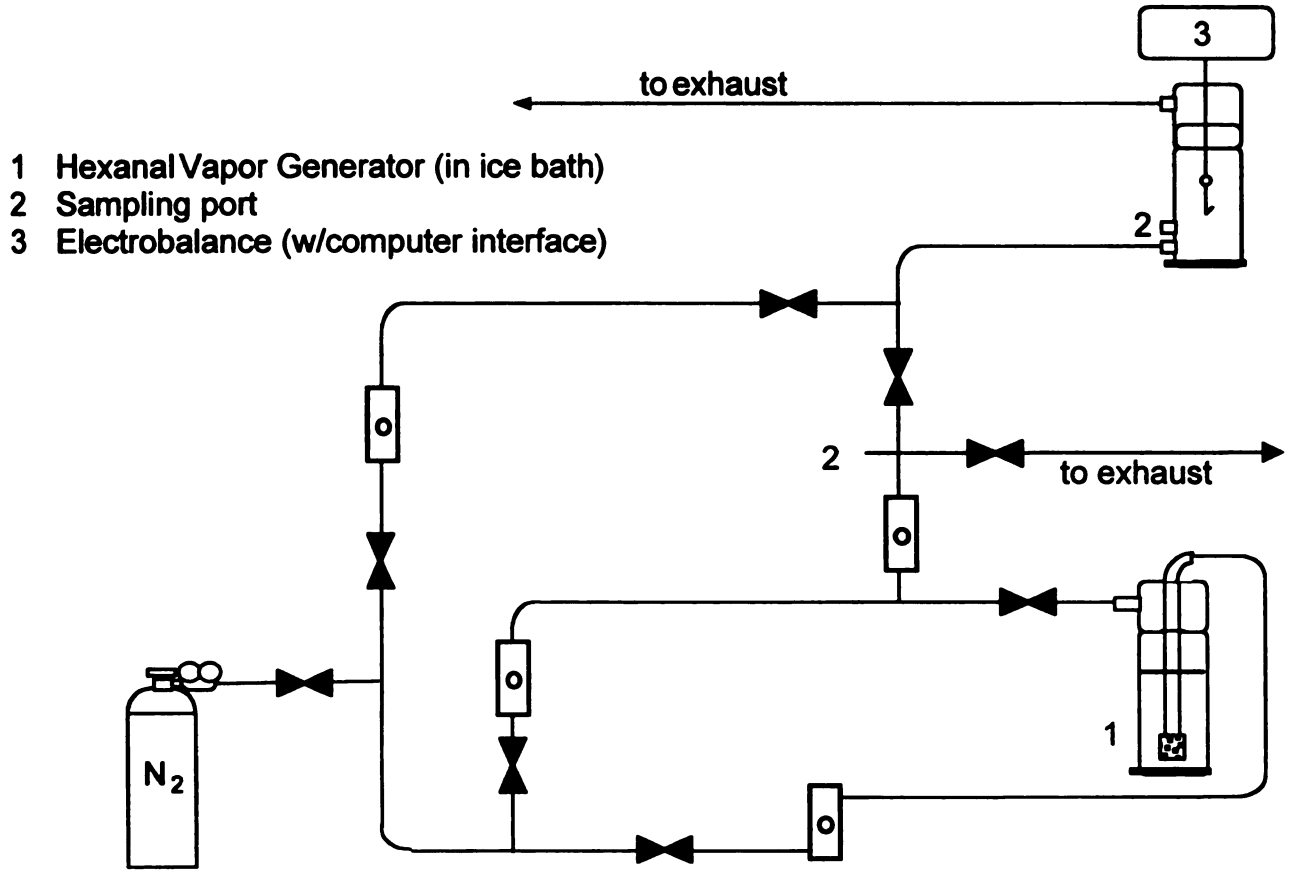


Figure 11. General Sorption profile curve illustrating determination of half-time sorption value ($t_{0.5}$) from stead state sorption value (M_{ss})

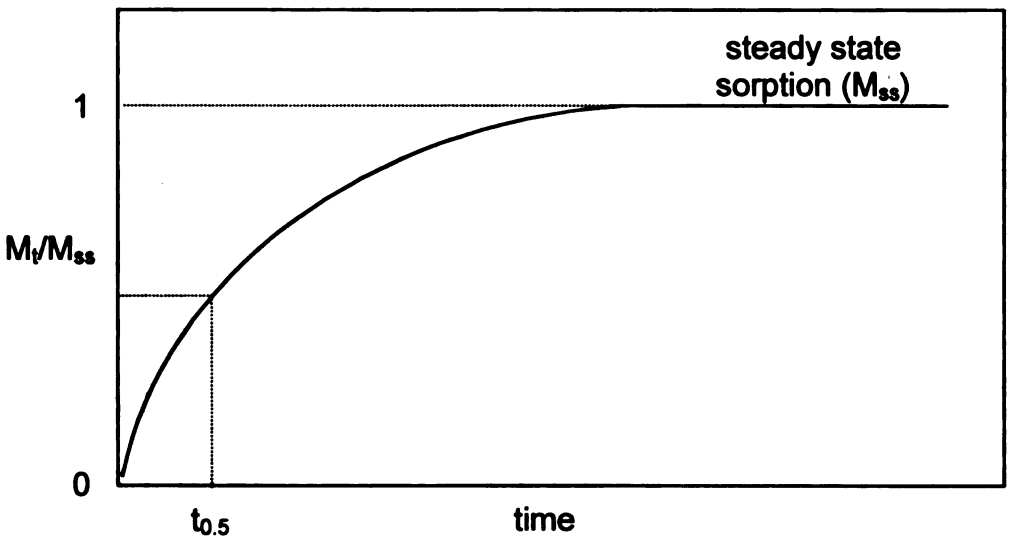


Figure 12. Calibration curve for hexanal on HP 6890 GC

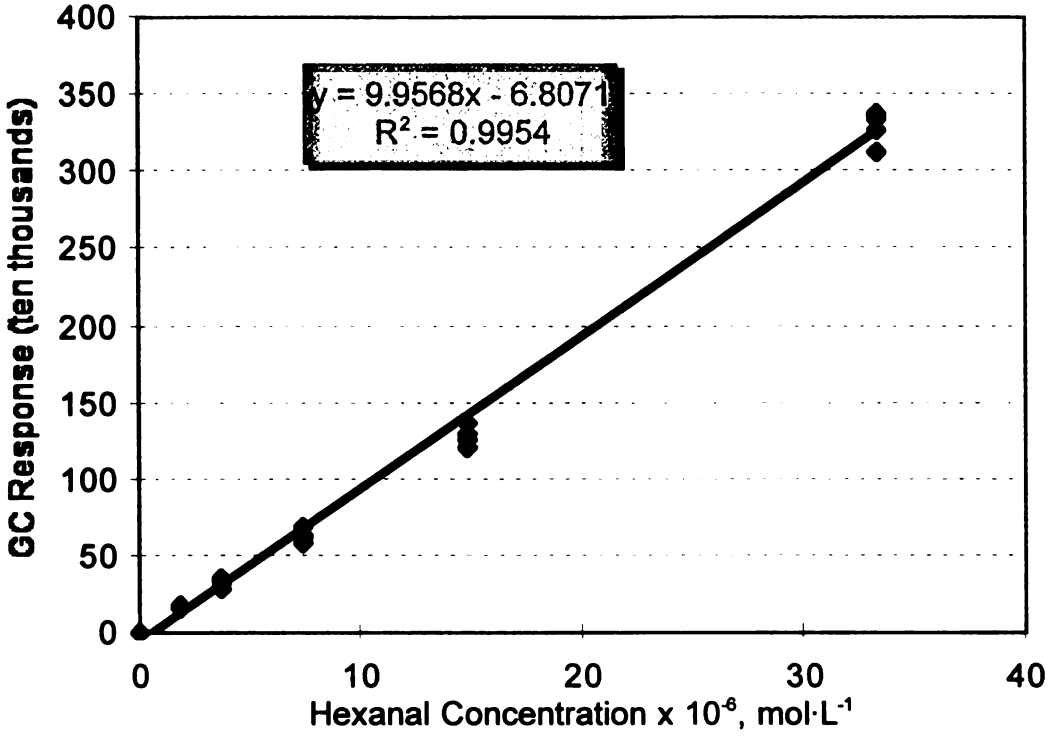
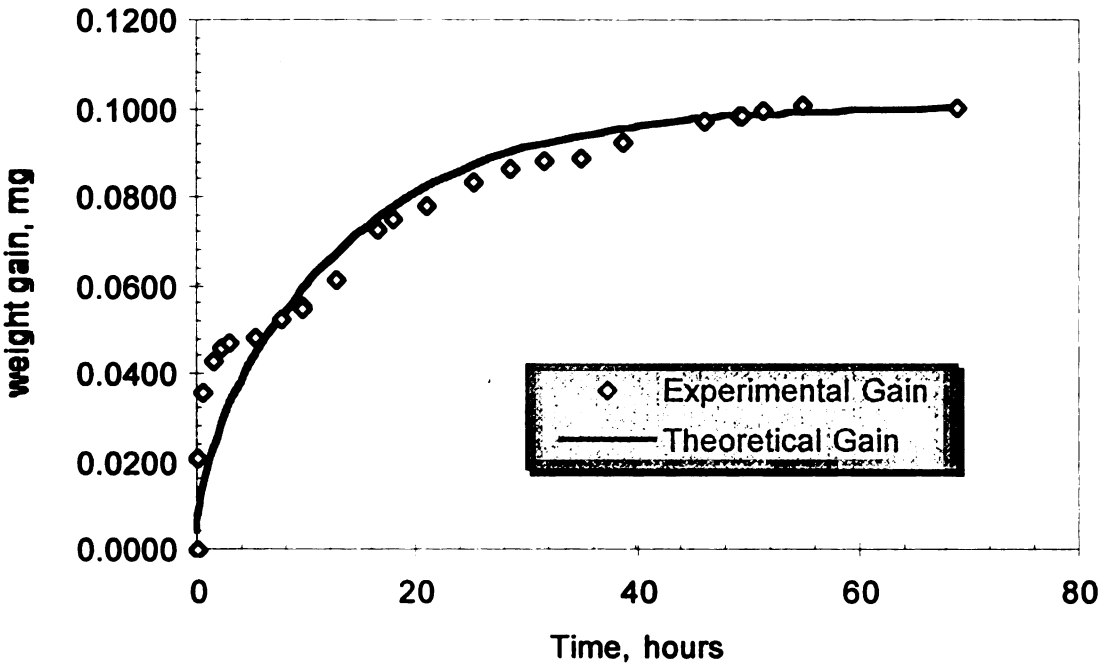


Figure 13. Sorption profile curves for hexanal with Exxon Exact™ 4151 at 25°C



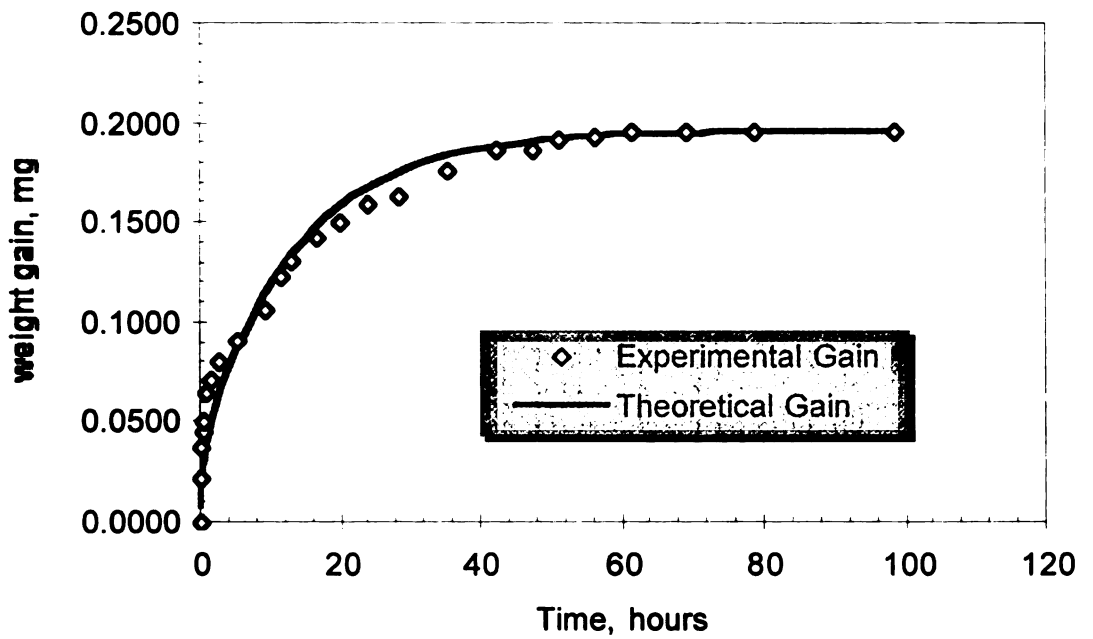


Figure 14. Sorption profile curve for hexanal with Exxon Exact™ 4151 at 5°C

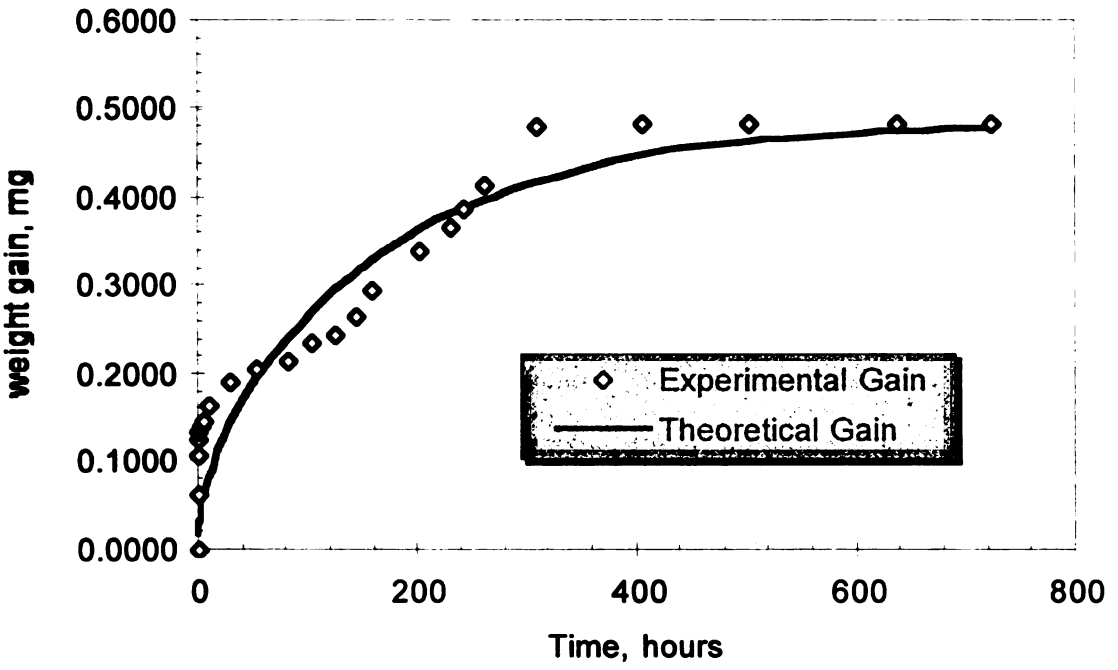
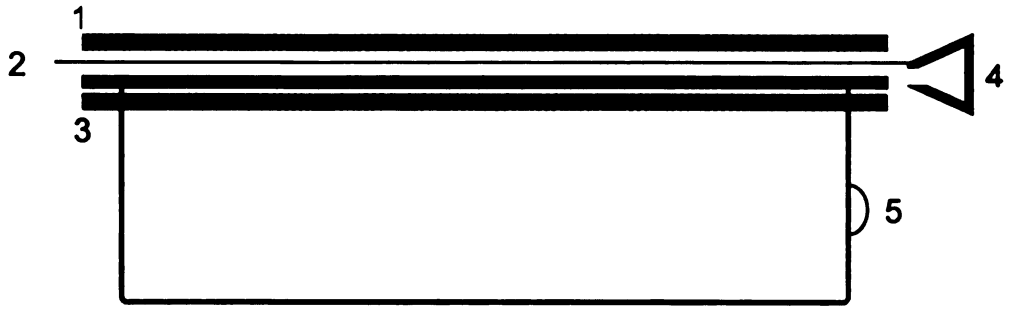


Figure 15. Isostatic gravimetric dish diagram (side view)



1. Top reinforcement ring
2. Test film
3. Bottom reinforcement ring
4. Binder clip
5. Sampling port

Figure 16. Isostatic gravimetric dish weight loss due to permeation at 23°C

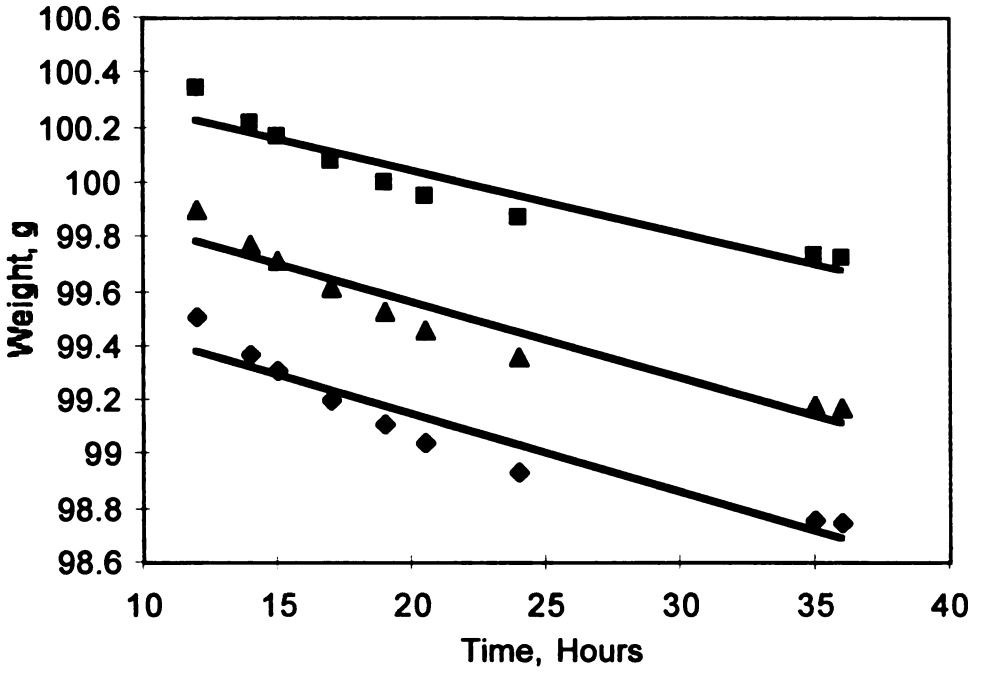
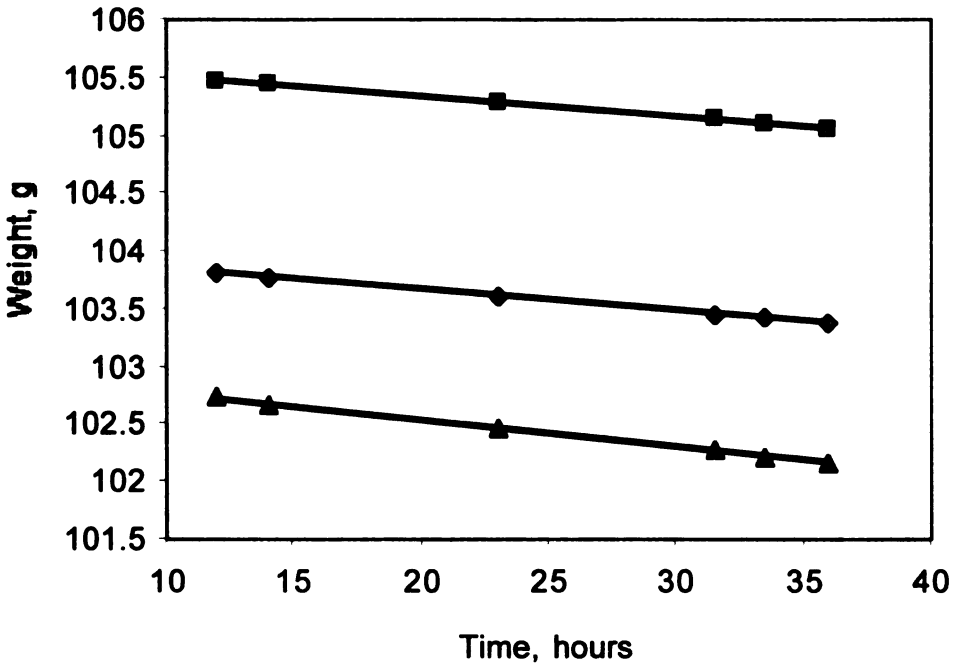


Figure 17. Isostatic gravimetric dish weight loss due to permeation at 5°C



CHAPTER 4

HEXANAL VAPOR IN MODIFIED ATMOSPHERE PACKAGING

MATERIALS AND METHODS

Materials

Plant material

'Golden Delicious' apple fruits were obtained from a local supermarket and stored at 1°C until used.

Metallocene film

Exact™ 4151 metallocene catalyzed ethylene-hexene copolymer film was obtained from Exxon Chemical. This particular film was chosen due to the properties created by the improved control of single site metallocene catalysts used during the polymerization process. Such improvements are: narrower molecular weight distribution (MWD), increased dart impact strength, lower film haze, and higher oxygen, carbon dioxide, and water vapor transmission rates.

Low density polyethylene film

Low density polyethylene film was obtained from Dow Chemical.

Hexanal

Hexanal (97% Purity) was obtained from Aldrich Chemical Company, Inc. (Milwaukee, WI) and stored at 4°C per supplier recommendation until used in release pouches of the modified atmosphere package.

Squalane

Squalane (2,6,10,15,19,23 Hexamethyl-tetracosane) was obtained from Aldrich Chemical Co. (Milwaukee, WI) and stored at 4°C until used in release pouches of the modified atmosphere package.

Methods

Hexanal vapor generation in package headspace

Generation of hexanal vapor in package headspace was achieved by placing a LDPE pouch filled with a squalane:hexanal mixture in sealed packages and allowing the headspace to equilibrate. The pouches were constructed of LDPE and sealed with an impulse sealer. Hexanal concentration in the headspace was quantified by taking aliquot samples with a gas tight syringe. Squalane:hexanal ratios and pouch surface areas were adjusted to generate equilibrium headspace concentrations between 10.3×10^{-6} and 18.6×10^{-6} $mol \cdot L^{-1}$. Compensations in area where made for the fact that Exact™ has roughly twice the permeability to hexanal compared to LDPE.

Package seal integrity

Packages were sealed in the manner described in chapter 3 and held submerged under hot water to check for leakage of the expanding headspace air around the seal and the sampling port. Packages were also filled with 5mL of liquid hexanal and sealed with non-permeable aluminum foil (in place of polymer film) and weighed periodically to detect leakage of hexanal.

Modified atmosphere packaging

Whole apple fruits were removed from cold storage and allowed to equilibrate to ambient temperature (23°C) which took approximately 1 hour. Each apple was rinsed with distilled water and sliced into wedges that weighed

30-35 g per wedge. The apple wedges were placed in modified atmosphere packages with a hexanal vapor release pouch and sealed as described in chapter 3 (Figure 17). For control, packages without hexanal release pouches were used. Due to limited materials, only eight packages (including 3 control) were assembled.

Packages were placed in a fume hood at ambient temperature (23°C) for 48 hours. Hexanal headspace concentration was evaluated every 24 hours by sampling the package headspace and analyzing it in a Hewlett Packard Model 6890 gas chromatograph fitted with a 30 m long column (SPB-5). Samples were taken with a Hamilton 500 µl gas-tight syringe (model 1750) and area response was recorded on Hewlett Packard 6890 integrator. The hexanal concentration was determined by comparison of output with that of the regression equation of the calibration curve (Figure 11).

Texture analysis of apple wedge

Apple texture was quantified by use of a Gauge-R durameter (Chatillon, NY USA) fitted with a 2mm tip. The durameter was pressed against the fruit tissue, gradually increasing pressure until the probe resistance was equal to the firmness of the tissue and the probe tip pierced the tissue. Results were recorded as grams of force. Measurements are reported from three locations on the tissue (excluding peel) selected at random and then averaged.

Color/browning analysis

The surface color of the cut fruit was measured with a Minolta Chroma Meter (Model CR-300). The Chroma Meter was calibrated with standard white tile to confirm working status. Results were printed in the Yxy color scale via a small dot matrix printer attached to the Chroma Meter. Measurements are reported from three locations on the tissue (excluding peel) selected at random and then averaged.

Only the Y value, indicating hue or lightness was considered. The Y values were averaged and then converted to a similar measurement of L* from the Lab scale (1976) using the following equation:

$$L^* = 116\left(\frac{Y}{Y_o}\right)^{1/3} - 16 \qquad (14)$$

Where Y is the value from the Yxy scale, and $Y_o = 100$, based on the "C" light source index.

Statistical Analysis

Data recorded from texture and color analysis was input into a spreadsheet program and then imported into SAS (Release 6.12). SAS was used to conduct an analysis of covariance with generalized linear modeling. Data was grouped as either control (hexanal free) or treatment. The goal was to prove if the two groups (treatment and control) were statistically significantly different from each other.

RESULTS AND DISCUSSION

Hexanal generation pouches

Hexanal release pouch area was calculated to produce headspace concentrations around 20 x 10^{-6} mol·L^{-1} in order to compensate for fruit tissue consumption and permeation loss. However, these compensations were not enough to create the hexanal headspace concentrations needed and were already as low as 5 x 10^{-6} mol·L^{-1} after 24 hours and continued to drop rapidly.

This is most likely due to depletion of hexanal in the release pouch, since all other forms of loss have been considered. The remote possibility of absorption of hexanal vapor by the thin layer of vacuum grease used in sealing the package is negligible if it does exist.

For a package at a steady state hexanal headspace concentration, the flow of hexanal from the release pouch must be equal to the sum of hexanal lost to consumption and permeation from the package (Equation 15) in order to maintain a constant hexanal headspace concentration.

$$F_1 = F_2 + F_3 \qquad (15)$$

Where F_1 is the hexanal produced by the hexanal release pouch and F_2 and F_3 are the losses due to fruit consumption and package permeation, respectively (Figure 18) . All flows are listed in mol·sec^{-1}.

The concentration of hexanal vapor in the package headspace (C_{HS}) at any time is the value at steady state (q_{ss}) that follows the preceding transient state (q_{ts}). Steady state is the "equilibrium" value of the target hexanal headspace concentration required to be maintained. Values of flow rates given

in equation 15 at various hexanal "equilibrium" concentrations are listed in Table 13. As seen, values of F_3 are less than 1/1000 of F_2 and due to the difficulty to control the rate of generation of hexanal, equation 15 can be reduced to $F_1 = F_2$. Therefore, the generation of hexanal only needs to supply a hexanal concentration equal to that of the consumption rate. This also indicates that the Exact™ 4151 is a significant barrier to hexanal and, for all practical purposes, prevents the depletion of hexanal from the headspace, at least when compared with the consumption rate. Although F_3 is very small compared to F_1, it may produce a significant aroma from the package due to permeation.

The generation of constant hexanal vapor concentration in a sealed package proved to be a difficult portion of the experiment, especially for a long duration. Reported devices for the generation of organic vapor have been accomplished through a flow through system. Flow through systems are usually able to control the concentration by manipulation of the gas flow rate through the vapor generator. In the case of hexanal, due to its high volatility, it was necessary to include an ice bath and incorporation of squalane in the flow through system. The ice bath was needed to decrease the temperature at which hexanal volatilizes and therefore reduce the rate of evaporation. The inclusion of squalane reduced the partial pressure of hexanal. The combined effect of low temperature and mixture with squalane resulted in a decreased partial pressure of hexanal that facilitated the generation of concentrations well below levels damaging to the fruit tissue.

Hexanal vapor saturation posed two problems in that hexanal condensed to liquid form and clogged gas lines of the flow through exposure system and saturation concentrations were well above the 20 x 10^{-6} mol·L^{-1} threshold that invoked physiological damage to the fruit tissue.

Package seal integrity

The testing of the package seal did not produce any evidence of leaks either around the film seal or the sampling port with either detection method. When placed under hot water, the plastic bulged due to the increase of internal pressure due to temperature but did not show any leaks even when force was applied by hand to the polymer to add additional pressure. The weight remained constant (within 10 fold of instrument sensitivity) with the second method. This is especially evident when compared to the weight loss recorded in the isostatic dish method discussed in chapter 3.

Modified atmosphere packaging

Packaging for fresh cut produce must be permeable enough to take in the exact amount of required oxygen and exhale the excess carbon dioxide. However, this film has permeability values (Table 5) that are much higher than needed for this fruit and is more appropriately suited for much higher respiring products such as broccoli and peas. Film selection was made from a select few pilot plant productions of Exact™ films. Despite the extremely high oxygen transmission rate (OTR) and carbon dioxide transmission rate (CTR) of the film,

the apple slices maintained themselves rather well, even in the control (hexanal free) packages.

Moisture loss (water loss) was minimal in the test packages as all of the apple slices still had slight surface moisture and none showed signs of shriveling. Water vapor transmission rate (WVTR) was not tested nor was a value provided by Exxon. Moisture loss is a concern from a marketability/sensory standpoint. Water loss is a main cause of deterioration because it results not only in direct quantitative losses (loss of salable weight), but also in losses in appearance (wilting and shriveling), textural quality (softening, flaccidity, limpness, loss of crispness and juiciness, and nutritional quality (Kader, 1992).

Confirming the observation of the enhanced aroma biosynthesis discussed in chapter 2, aroma compounds could be detected emanating from film surface of the unopened treatment packages as a result of the permeation process. This was not detected for the hexanal free control packages. Although not scientifically proven, when asked, three randomly selected individuals confirmed by smell the permeation of aroma. Packages were taken out of the lab to avoid sensory influences from other aromatic substances present in the laboratory and fume hood.

Texture

Hexanal treatment proved to be useful in preserving the initial texture of apple slices. Differences in texture values between treatment and control (hexanal free) packages was found to be statistically significant (α=0.01). The

statistical analysis is listed in Table 11 and the complete data set is shown in Table 14

Table 11. Type I and III Sums of Squares for ANOVA of texture analysis results

Source	DF	Type I SS	Type III SS	Mean Square	F Value	Pr > F
Texture	2	367850.133	367850.133	183925.07	518.13	0.0001

Color

The presence of hexanal vapor in the MAP helped to preserve the initial color of the apple tissue. Color change is defined here as the enzymatic browning that occurs as a result of mechanical injury. Mechanical injury in this case is invoked by minimal processing (i.e. slicing) of the fruit tissue. These reactions may be considered desirable in certain instances, e.g., tea fermentation, but are generally undesirable in postharvest fruits and vegetables (Fennema, 1985).

Color as perceived has three dimensions: hue, chroma, and lightness. Chromaticity includes hue and chroma (saturation), specified by two chromaticity coordinates. Since these two coordinates can't describe a color completely, a lightness factor must also be included to identify a specimen color precisely.

In the Yxy color system (Commission Internationale de l'Eclairage, 1931), Y is a lightness factor expressed as a percentage based on a perfect reflectance of 100% and x and y are the chromaticity coordinates. Equal distances in the Yxy system do not represent equal differences in color as perceived. The CIE

1976 Lab color system was also used because it more closely represents human sensitivity to color. In either system, Y and L* both represent a lightness variable.

Differences in color values (lightness) between treatment and control (hexanal free) packages was found to be statistically significant (α=0.01). The statistical analysis is listed in the Table 12 below and the complete data set is shown in Table 15.

Table 12. Type I and III Sums of Squares for ANOVA of color analysis results

Source	DF	Type I SS	Type III SS	Mean Square	F Value	Pr > F
Avg Y	2	20121.23	20121.23	10060.62	94.98	0.0001
Avg L*	2	48565.30	48565.30	24282.65	10466.8	0.0001

Table 13. Mass balance flow rates at various hexanal headspace concentrations

Headspace hexanal ($mol \cdot L^{-1}$)	Mass Balance Flow Rates ($mol \cdot sec^{-1}$)			Steady State hexanal ($mol \cdot L^{-1}$)
C_{HS}	F_1	F_2	F_3	q_{ss}
2.00E-06	9.4504E-10	9.4501E-10	2.6944E-14	9.4504E-10
5.00E-06	9.4510E-10	9.4503E-10	6.7359E-14	9.4510E-10
8.00E-06	9.4515E-10	9.4504E-10	1.0777E-13	9.4515E-10
1.00E-05	9.4519E-10	9.4506E-10	1.3472E-13	9.4519E-10
1.20E-05	9.4523E-10	9.4507E-10	1.6166E-13	9.4523E-10
1.50E-05	9.4529E-10	9.4508E-10	2.0208E-13	9.4529E-10
1.80E-05	9.4534E-10	9.4510E-10	2.4249E-13	9.4534E-10
2.00E-05	9.4538E-10	9.4511E-10	2.6944E-13	9.4538E-10
2.50E-05	9.4548E-10	9.4514E-10	3.3680E-13	9.4548E-10

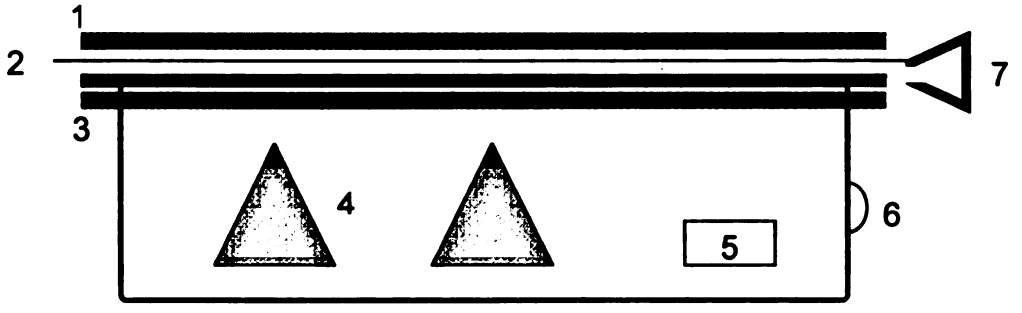
Table 14. Texture analysis results

Group	Label	Texture (grams)			Avg
		Rep 1	Rep 2	Rep 3	
Treatment	Pkg 1	240	225	250	238
Treatment	Pkg 2	265	240	305	270
Treatment	Pkg 3	215	210	220	215
Treatment	Pkg 4	225	230	215	223
Treatment	Pkg 5	265	250	255	257
Control	Pkg 6	175	165	155	165
Control	Pkg 7	175	150	160	162
Control	Pkg 8	130	180	165	158

Table 15. Color analysis results

Group	Label	Color (Yxy scale)			Avg Y
		Rep 1	Rep 2	Rep 3	
Treatment	Pkg 1	Y 56.66 x 0.3609 y 0.3772	Y 53.78 x 0.3574 y 0.3707	Y 56.86 x 0.3653 y 0.3826	55.77
Treatment	Pkg 2	Y 58.85 x 0.3529 y 0.3682	Y 59.57 x 0.3520 y 0.3693	Y 57.98 x 0.3583 y 0.3746	58.80
Treatment	Pkg 3	Y 56.16 x 0.3581 y 0.3719	Y 59.08 x 0.3534 y 0.3703	Y 51.11 x 0.3595 y 0.3742	54.55
Treatment	Pkg 4	Y 56.88 x 0.3514 y 0.3666	Y 57.21 x 0.3504 y 0.3642	Y 52.71 x 0.3660 y 0.3783	56.03
Treatment	Pkg 5	Y 56.79 x 0.3622 y 0.3780	Y 57.58 x 0.3566 y 0.3699	Y 52.45 x 0.3626 y 0.3777	55.61
Control	Pkg 6	Y 43.21 x 0.3819 y 0.3863	Y 43.85 x 0.3810 y 0.3887	Y 45.24 x 0.3763 y 0.3889	44.10
Control	Pkg 7	Y 46.13 x 0.3867 y 0.3950	Y 45.73 x 0.3827 y 0.3913	Y 51.81 x 0.3722 y 0.3844	47.89
Control	Pkg 8	Y 51.26 x 0.3771 y 0.3881	Y 51.19 x 0.3778 y 0.3898	Y 52.43 x 0.3746 y 0.3849	51.63

Figure 18. Modified Atmosphere Test Package diagram (side view)



1. Top reinforcement ring
2. Test film
3. Bottom reinforcement ring
4. Fruit tissue
5. Hexanal release pouch
6. Sampling port
7. Binder clip

Figure 19. Mass flow diagram of hexanal in packaging system

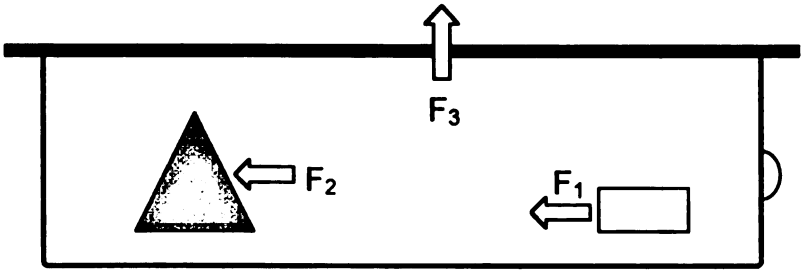


Figure 20. Golden delicious apple tissue after 48 hours with hexanal treatment and hexanal-free control

Treatment Hexanal-free control

CONCLUSIONS

Hexanal vapor proved useful in preserving texture, retarding enzymatic browning, and enhancing aroma biosynthesis of golden delicious apple tissue in MAP constructed with metallocene films.

Golden delicious apple tissue was found to "consume" hexanal vapor as a linear function of headspace hexanal vapor concentration. Consumed hexanal vapor is thought to be metabolized by an undetermined enzymatic process into numerous aroma compounds.

Exxon Exact™ 4151 metallocene film was found to be highly permeable to hexanal vapor. Permeability coefficients were found to be in the range of 8×10^{-17} to 2×10^{-16} $Kg \cdot m \cdot m^{-2} \cdot sec^{-1} \cdot Pa^{-1}$.

The use of hexanal vapor in the headspace of MAP of sliced golden delicious apples retarded browning and preserved texture. In both cases, it was shown that the treated samples showed marked improvement over untreated controls. The difference of quantitative analysis was statistically significant at $\alpha=0.01$.

The generation of steady concentrations of hexanal vapor in the headspace of a sealed package proved to be difficult. The use of hexanal vapor in MAP presents a very interactive, complex, and sensitive system. While a temperature increase would increase fruit respiration and increase permeability, it would not have an effect on the consumption rate of hexanal by the fruit tissue.

Provided the delivery of constant hexanal vapor concentration in the MAP headspace is under control, hexanal vapor is a useful tool in a hurdle approach to the preservation of minimally processed fresh-cut apple slices.

FUTURE RESEARCH

This research continues to explore the relatively new idea of using organic vapor in modified atmosphere packaging. However, in combination with the handful of research projects conducted so far, there is still a vast body of knowledge that remains unexplored. Use of such a system in MAP requires further understanding of many interactive and cross-linked components. Below are just a few areas that could greatly benefit the science of food packaging:

- Effect of hexanal vapor on film oxygen and carbon dioxide transmission rates
- Effect of hexanal vapor on respiration rates of fresh produce
- Effect of hexanal vapor on cultivars other than Golden Delicious
- Effect of hexanal vapor on other fruits
- Methods to Generate of steady concentration organic vapors in closed packaging
- Further examination of role of hexanal vapor in aroma compound generation
- Residual effect of organic vapor in MAP of fresh produce
- Sensory analysis of fresh produce treated with organic vapor
- Shelf life studies of fresh produce treated with organic vapor

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