DEVELOPMENT OF ACTIVE PACKAGING TRAYS WITH ETHYLENE REMOVING CAPACITY

By

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ABSTRACT

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Active packaging is an innovative packaging solution to recent consumer demands for fresher and safe produce for longer periods. Ethylene-removing packaging can take away ethylene from the produce surroundings delaying ethylene’s detrimental effects and thereby leading to an increase in shelf life.

The focus of the present work was to develop a tray with ethylene removing capacity. Ethylene scavengers (potassium permanganate, two activated carbons, two zeolites, metal-organic frameworks) were characterized by studying their ethylene removing capability under temperature (23 ^{o}C and 4 ^{o}C) and humidity (< 5%, 55%, and 100% RH) conditions, while petroleum-based and bio-based plastics were compared by measuring their barrier properties. Thermoformed trays were developed with selected scavenger and plastic characterized for their ethylene scavenging capacity, thermal, mechanical, and barrier properties and evaluated for packaging application in produce.

Trays were developed with activated carbon as the scavenger as it had good ethylene removing capacity at ≥ 55% RH, low density polyethylene was selected as the polymer of choice because of its barrier properties. Thermoformed trays able to adsorb ethylene were developed with 10% activated carbon and no differences in terms of thermal, mechanical and barrier properties were obtained compared to trays without activated carbon. Further studies on the ethylene removing capacity of the developed trays need to be carried out.

Dedicated to my husband
Chinmay Naphade

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When I wanted to write this section, I was at loss of words of how to communicate the gratitude I felt and like for most other things, I went to Google! I found my answer on Google Scholar which says, “Stand on the shoulder of giants”. This thesis would not have been possible without my research advisor, committee, research team, family and friends. Firstly, I am extremely thankful to my advisor Dr. Eva Almenar (School of Packaging, Michigan State University) for her never-ending support, guidance and motivation to keep this research going. She had been an excellent mentor and teacher particularly in putting the domains of both food and packaging together. She also constantly helped me improve myself in scientific writing, communication and analytical skills. Moreover, I am extremely thankful to my committee members, Dr. Susan Selke (School of Packaging, Michigan State University) and Dr. Randy Beaudry (Department of Horticulture, Michigan State University) for their time commitment, expertise and suggestions.

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INTRODUCTION

1.1 Introduction

In recent years, consumer expectations and demands have changed owing to an increase in technological, scientific, and social innovations. In terms of food, today's consumer expects freshness, safety, healthiness, and minimal processing (Singh et al., 2011). These new requirements are putting huge demands on the food packaging industry and are major driving forces to provide new packaging solutions (Ghaani et al., 2016). Active packaging (AP) is one of the innovative solutions to mounting consumer requirements. AP is a packaging technology where certain additives are intentionally incorporated into the packaging material or placed within the packaging container to interact directly with the perishable product to extend its shelf life. AP differs depending on the type of additive: oxygen scavenger, ethylene adsorber, drip absorber, flavor absorber, etc (Almenar et al., 2006).

Ethylene-removing packaging is a type of AP that intentionally and dynamically modifies the ethylene levels within the package through use of scavenging compounds (Almenar et al., 2006). This lowering or removing of ethylene is essential in the case that ethylene acts as a ripening hormone (climacteric fruits) and/or leads to detrimental effects such as excessive softening of fruits, abscission of leaves and flowers, toughening of vegetables, and increased pathogen susceptibility (Zagory 1995). Compounds such as potassium permanganate ($KMnO_4$), activated carbon, zeolites, and metal-organic frameworks (MOFs) have been reported to be effective in removing ethylene (Keller et al., 2013; Martínez-Romero et al., 2007; Zhang et al., 2016). $KMnO_4$ is highly effective in removing ethylene and consequently, it has been widely studied and commercialized as an ethylene remover (Keller et al., 2013). Activated carbon varies in ethylene removing capacity depending on its format. Powdered activated carbon (PAC) and granulated activated carbon (GAC) adsorb more ethylene than carbon fibers (Bailen et al., 2007). The former two are also easily available and regenerated (Martínez-Romero et al., 2007). Like activated carbon, different forms of zeolites are available. They differ in structure and origin (natural vs synthetic), which leads to differences in ethylene removing capacity. Among these, the synthetic zeolite 4A and the natural zeolite clinoptilolite (CL) have shown promising ethylene removing capacities (Szwedzińska, 2015; Erdoğan et al., 2008). In contrast, Peiser & Suslow (1998) reported that CL did not adsorb ethylene. MOFs are a new class of synthetic porous compounds that can selectively adsorb and desorb many volatile molecules including ethylene (Kuppler et al., 2009; Li et al., 2011). In agreement, Chopra et al. (2017) reported that Basolite C300 and Basolite 520 can sorb, store, and release ethylene, with Basolite C300 being more effective. Zhang et al. (2016) reported that copper terephthalate (CuTPA) MOF can adsorb and release up to 654 ppm of ethylene.

The main mechanisms of action for the aforementioned scavenging compounds are ethylene adsorption (activated carbon, zeolites, and MOFs) and ethylene oxidation ($KMnO_4$) (Pereira de Abreu et al., 2012; Lopez Rubio et al., 2004; Zagory 1995; Chopra et al., 2017). The former mechanism is highly affected by temperature, humidity, adsorbate concentration, magnitude and distribution of pore volume (pore structure), surface chemistry, and molecules competing for the adsorption sites with ethylene like oxygen (O_2) and carbon dioxide (CO_2) (Martínez-Romero et al., 2007; Keller et al., 2013; Chopra et al., 2017). Although all these factors are important, getting to know about the effects of combinations of temperature and humidity including those occurring during the postharvest period on the scavenging capacities of these compounds can help selecting the best scavenger, thereby contributing to the advancement of ethylene-removing packaging. Currently, there is a lack of comparative data for the scavenging capacity among these compounds at the aforementioned conditions (Keller et al., 2013; Zagory 1995). Besides the type of scavenger, another factor key for creating adequate ethylene-removing packaging is the type of packaging material since its barrier properties define the contents of ethylene, O_2, CO_2, and water vapor in the package headspace, all molecules that affect ethylene scavenging capacity.

The current methods for developing an ethylene removing AP are either through placing the active compound inside the package along with the product (e.g., sachets) or by making the active compound a part of the packaging material itself (Almenar, 2018). Wilson et al. (2018) found that consumers prefer to use packages without sachets rather than the ones with sachets. However, the addition of an active compound to the packaging material can alter its properties and hence it is important to characterize the thermal, mechanical, and barrier properties of any developed material.

Cherry tomatoes are climacteric fruits (require the action of ethylene for ripening) and are generally harvested when deep red and destined directly to fresh market. They are usually held at typical retail outlet display temperatures, which are around 20 ^{o}C and are generally packaged in rigid clamshell containers. Ethylene-removing packaging has been shown to extend the shelf life of tomatoes. Tas et al. (2017) reported that composite films made of halloystic nanotubes and polyethylene retained tomato firmness for 10 days. Maneerat, & Hayata (2008) observed that titanium dioxide coated films reduced the ethylene content by 88 %. Salamanca et al. (2014) found that the combination of $KMnO_4$ and zeolite when placed as a sachet in a thermoformed polyethylene terephthalate container can reduce weight loss and retained firmness and soluble solids content.

Most of the aforementioned studies on tomatoes have been carried out with active compounds (halloystic nanotubes, zeolites, $KMnO_4$, titanium dioxide) in sachets, films, or corrugated boards. However, no studies have been carried out on rigid containers such as trays that are more commonly used for packaging delicate fruits such as cherry tomatoes and other climacteric fruits. Hence the present study was carried out with following objectives.

1.2 Objectives

The ultimate objective of this study is to develop a tray with ethylene removing capacity for produce packaging. To achieve this objective, the following specific objectives were proposed:

- Identify an ethylene scavenger and a packaging material for development of a tray with ethylene removing capacity.
    - Selection of scavenger: Different ethylene scavengers ($KMnO_4$, MOF, GAC, PAC, CL and 4A) were tested for their ethylene removing capability at different combinations of temperature (23 ^oC and 4 ^oC) and relative humidity (<5 %, 55 % and ~100 % RH). Shortlisted scavengers were studied for ethylene removing capability in the presence of competing molecules (O_2 and CO_2).
    - Selection of packaging material: The permeability of petroleum-based (LLDPE, LDPE, PP, nylon) and bio-based (PLA, carbohydrate- and protein-based) plastics to ethylene and water was tested.
- Develop an ethylene-removing tray using the thermoforming process and characterize the properties of the developed tray (ethylene scavenging capacity, mechanical, barrier, thermal, thickness profile).
- Study the possible use of the developed ethylene-removing tray to package produce using cherry tomatoes.

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Chapter 2

LITERATURE REVIEW

2.1 Ethylene in produce

Ethylene is a gas molecule with two carbon atoms linked by a double bond. Ethylene is common in the environment due to its artificial and natural production. Ethylene is naturally generated by produce and several species of bacteria and fungi (Zagory, 1995). In produce, ethylene is formed during ripening, mechanical injury, and diseased conditions (Zagory, 1995) through a complex metabolic pathway of enzymatic action on the amino acid methionine. Methionine is converted to S-adenosyl-methionine (SAM) by the addition of adenine and consumption of adenosine triphosphate. SAM is transformed to 1-aminocyclopropane-1-carboylic acid (ACC) by the enzyme ACC synthase (ACS) and generates 5-methylthioadenosine (MTA) as a by-product. ACC is oxidized to ethylene by ACC oxidase and MTA is recycled to produce methionine (Martinez et al., 2007).

Climacteric fruits (e.g., tomato, apple, peach, and banana) are characterized by rapid ripening, high respiration and high ethylene production. Whereas non-climacteric fruits (e.g. citrus, grape, and strawberry), ripening does not occur after harvest little or no ethylene is produced (Zagory, 1995). In both, climacteric and non-climacteric fruits, ethylene can have negative effects during postharvest storage. Furthermore, beneficial or detrimental changes caused in produce by ethylene depend on the type and ripening stage. Beneficial effects of ethylene include stimulation of ripening in climacteric fruits, color development through pigment (anthocyanin and lycopene) synthesis, chlorophyll degradation (degreening), and enhancement of flavor. Detrimental effects of ethylene can be excessive softening of fruits, production of bitter compounds, abscission of leaves and flowers, hastened toughening of vegetables, increased pathogen susceptibility, promotion of discoloration, sprouting stimulation, changes in shape, formation of bitter compounds and russet spotting (Saltveit, 1999). These undesired changes often occur due to exposure to the ethylene produced by adjacent produce and/or to the ethylene generated as a pollutant in greenhouse locations, storage, and transportation. Thus, it is crucial to reduce surrounding ethylene in addition to inhibiting ethylene biosynthesis in order to minimize its impact on produce (Zagory, 1995).

Different approaches have been used to inhibit ethylene biosynthesis including the use of (1) compounds that compete with ethylene for either ethylene receptor binding sites or ethylene precursors, (2) compounds and specific types of irradiation that inhibit the activity of ethylene-forming enzymes, and (3) specific types of storage like controlled atmosphere and hypobaric storage.

With regard to controlled atmosphere, exposure to a low O_2 concentration inhibits ethylene production (Gorny & Kader, 1997) while concentrations of O_2 greater than 21% (air) have been reported to alter ethylene production in a way that enhances ethylene-induced physiological disorders in a variety of crops including pears, potato tubers, tomatoes, and lettuce (Creech, et al., 1973). O_2 participates in the oxidation of ACC to ethylene and the details of the mechanism can be found in Dilley et al. (2013). In contrast, CO_2 has been shown to be a competitive inhibitor of ethylene action by displacing ethylene from its receptor site (Burg & Burg, 1967). Burg & Burg (1967) reported that 1.55% CO_2 reduces ethylene action by 50%. In agreement, Colelli, et al., (1991) also reported less ethylene production when produce is exposed to CO_2-enriched atmospheres. The mechanism of CO_2 on inhibiting ethylene action is not yet fully understood (Beaudry, 2010).

2.2 Ethylene-removing packaging

2.2.1 Overview

Technologies like controlled atmosphere have been used for several decades and therefore, they could be considered today as conventional or mature technologies used to control ethylene. Recently, considerable research has been carried out to develop technologies to reduce the ethylene produced or its biosynthesis. Packaging technologies like modified atmosphere packaging (MAP) can expose the produce to depleted O_2 and/or enriched CO_2 amounts like controlled atmosphere does and thus, MAP can reduce ethylene synthesis and action (Beaudry, 1999; Zagory & Kader, 1988). However, the required gaseous composition will most likely not be maintained at an optimal level like in controlled atmosphere due to the changes over time caused by the interplay between produce respiration and packaging material permeability. Additionally, the resulting gaseous composition may not be the most beneficial for the produce in terms of physiological responses other than ethylene.

Active packaging (AP) is a relatively new packaging technology compared to MAP. AP can be defined as a packaging technology where certain additives, known as "active compounds", are incorporated into the packaging material or placed within the packaging container in order to interact directly with the perishable product and/or its environment to extend its quality and/or safety (Almenar, 2018). The current mechanisms to make packages active are: (1) placing the active compound inside the package along with the product to be packed (e.g., sachets and labels), and (2) making the active compound part of the materials that form the package itself (e.g., blended in the bulk polymer matrix, applied to the package as a coating, integrated in the ink used for printing) as shown in Figure 2.1. In the last decade, there has been a shift towards direct incorporation of the active compound into the packaging material since this allows manufacturers to continue using the packing equipment commonly used for non-active packaging and consumers to appreciate not having foreign objects within the package that could be ingested by mistake (Almenar, 2018). Supporting the latter, Wilson et al. (2018) found through a consumer sensory evaluation that consumers like packages with sachets less than packages without sachets.

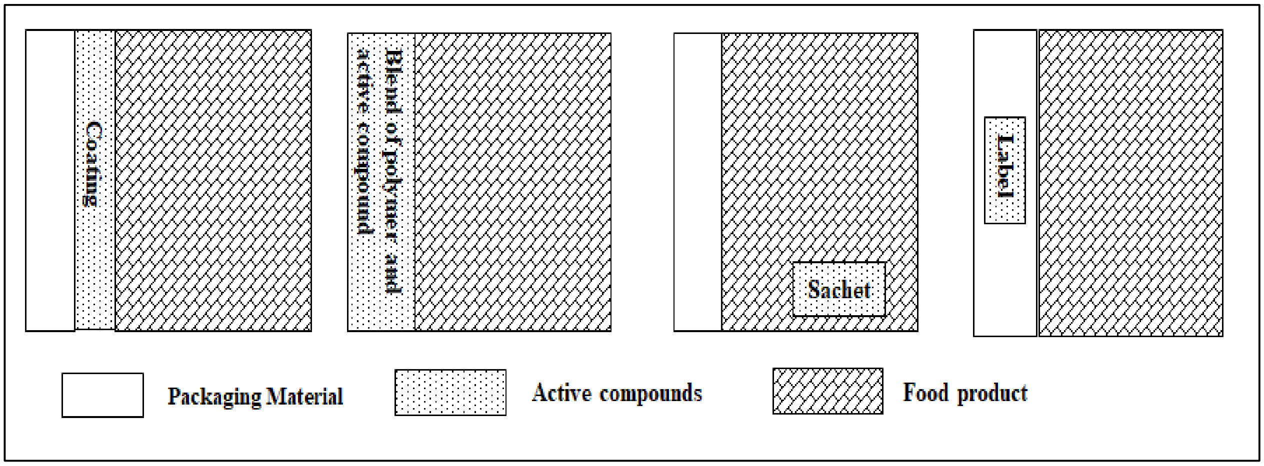

Figure 2.1 Different types in which active packaging can be used (adapted from Awalgaonkar and Almenar (2018))

Active packaging with ethylene removing capacity, a.k.a. ethylene-removing packaging, can be defined as a type of active packaging that can counteract the action of ethylene due to the presence of compounds that can adsorb, absorb, or chemically alter ethylene (Almenar, 2018).

2.2.2 Classification of ethylene-removing packaging

Ethylene-removing packaging can be classified into two types depending on the basic mechanism of action of the compound used to remove ethylene: oxidation or adsorption/absorption. Each type can subsequently be divided into subtypes based on the used compound, which generally represent a whole family instead of a single compound. For example, zeolites used to develop ethylene-removing packaging can have a natural origin (Coloma et al.,

2014) or be synthetic (Szwedzińska 2015). These subtypes can be further split depending on the nature of the compound as discussed above. Figure 2.2 provides an overview of this classification.

The mechanism of action, integration into the package, advantages and disadvantages, combination with other compounds, combination with other shelf-life extending technologies, applications, and commercial and academia progress made for each of these types of ethylene-removing packaging are covered below.

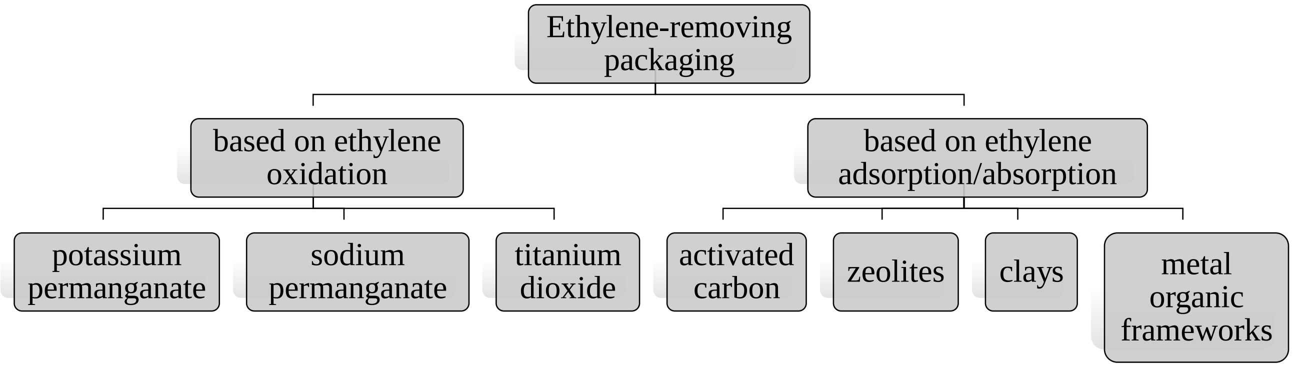

Figure 2.2 Classification of ethylene-removing packaging (adapted from Awalgaonkar and Almenar (2018))

2.2.3. Types

2.2.3.1 Ethylene-removing packaging based on ethylene oxidation

Ethylene oxidizes to carbon dioxide and water irreversibly. Potassium permanganate can oxidize ethylene and thus, ethylene-removing packaging using potassium permanganate ($KMnO_4$) has been developed and its effect on produce shelf life has been studied extensively. $KMnO_4$ attacks the double bond in the ethylene molecule to oxidize it. Ethylene when oxidized by $KMnO_4$ initially forms acetaldehyde, followed by acetic acid, and finally produces carbon dioxide and water. The redox reaction caused by $KMnO_4$ results in its change in color from purple (MnO_4^- ions) to brown (MnO_2). The evolution of the integration of $KMnO_4$ into the package has been from being placed on trays or dishes to in sachets, and finally blended into the polymer bulk to make it part of the packaging film. Regardless, $KMnO_4$ is always incorporated onto inert carriers prior to its integration into the package. These carriers serve to increase the surface area of $KMnO_4$ in contact with the ethylene and make an easily handled solid scrubber. However, the quantity of $KMnO_4$ that can be incorporated is about 4-6% of the inert carrier, and the resulting mixture does not have the same effectiveness as the oxidizer alone. This results in the need for large amounts of impregnated material to achieve the desired scrubbing results (Ahvenainen, 2003). According to Álvarez-Hernández et al. (2018), the selection of the inert carrier depends on characteristics such as surface area, size, material type, shape, and ethylene adsorption ability. Examples of $KMnO_4$ carriers include aluminum oxide, silica gel, vermiculite, celite, and perlite (Saltveit, 1980). A discussible of the physical properties of these and other materials used as carriers for $KMnO_4$ including pore volume, pore size distribution, surface area, and effectiveness in extending produce shelf life can be found in Álvarez-Hernández et al. (2018).

The work done with trays and dishes can be considered as a way to prove the effectiveness of packages containing $KMnO_4$ in reducing ethylene in the headspace and extending fruit shelf life (Shorter, et al., 1992; Szczerbanik, et al., 2005) but not the development of packaging feasible for supply chain conditions. The effectiveness of $KMnO_4$ when integrated into the package in the form of sachets and films has been evaluated during the last decade. Active packages that use $KMnO_4$ as an active compound to scavenge ethylene are compiled and described in Table 2.1. Generally speaking, the fruits in the active packages had lower ethylene and CO_2 production, less weight loss, higher firmness retention, lower soluble solids content (SSC) increase, higher titratable acidity (TA), and less sugar accumulation and decay incidence compared to identical packages without the oxidizer.

$KMnO_4$ is used due to its high effectiveness in scavenging ethylene generated by climacteric fruits. It can be found in the form of sachets and films for placement inside packages, storage facilities, and transportation vehicles and in the form of sprays and filters for other applications. The integration of $KMnO_4$ into the package in the form of sachets or as a part of multilayer films has solved the toxicity issue associated with $KMnO_4$. This is the reason $KMnO_4$ is commercially used although it is caustic in nature. Commercial scavengers based on $KMnO_4$ that are currently used by industry are tabulated in Table 2.2. Some of them have been evaluated and validated by academia. For example, Shorter et al. (1992) reported that Granny Smith apples held in PE bags containing Purafil had less bitter pit and superficial scald, which the authors attributed to the ethylene removal by Purafil. Advantages and disadvantages of using $KMnO_4$ as ethylene oxidizer in active packaging are compiled in Table 2.3.

Active packaging containing $KMnO_4$ combined with other shelf-life extending compounds has also been developed. The effect of the mix has been shown to be beneficial or not on a case-by-case basis. $KMnO_4$ and 1-MCP inside LDPE bags resulted in higher ethylene content that increased physiological disorders such as yellowing, flesh browning, and core browning in Japanese pears compared to LDPE bags with only $KMnO_4$ (Szczerbanik et al., 2005). Active packages containing $KMnO_4$ sachets and sorbitol sachets were evaluated on the removal of volatiles associated with off-odors in packaged broccoli (DeEll, et al., 2006). The authors concluded that sorbitol and $KMnO_4$ combined in specific amounts could be used to remove off-odors like acetaldehyde and ethanol and to maintain appearance and texture, thus, extending broccoli quality and marketability

Table 2.1 Ethylene-removing packages based on $KMnO_4$ created during the last decade and their effects on produce shelf-life extension.

Integration technique	**Active compound amount**	**Inert carrier**	**Packaging format**	**Packaging material**	**Produce**	**Storage conditions**	**Effect**	**Reference**
Sachet	Not specified	Not specified	Box	Corrugated fiber board	Sapota	27-32°C & 65-75% RH.	Lower ethylene and CO_2 production, less weight loss, higher firmness retention, lower SSC increase, higher TA, less sugar accumulation and decay incidence in mature and half-ripe fruits but not in ripe fruits. Extended marketable life up to 13 days for mature-state sapota.	Bhutia, et al., 2011
Sachet	5ml	Vermiculite (5g)	Bags	LDPE (0.15mm)	Banana	19-25°C	Treated samples prevented change in peel color and obtained a shelf life extension of 62 days compared with 55 days of untreated bananas	Hassan, et al., 2005

Table 2.2 Commercial ethylene scavengers in their available formats (adapted from Awalgaonkar and Almenar (2018))

Active ingredient	**Carrier**	**Format**	**Commercial name**	**Manufacturer**	**Manufacturer's website**
$KMnO_4$	Alumina pellets	Sachet	Purafil	Purafil, Inc., USA	https://www.purafil.com/products/chemical-filtration/filtration/sachet/ accessed on 9 June 2018
	Silica	Sachet	Greenpack	Rengo, Co., Japan	http://www.rengo.co.jp/english/products/cardboard.html accessed on 9 June 2018
	Zeolite	Sachet	EC-3+	Ethylene Control, Inc., USA	https://www.ethylenecontrol.com/products/sachets/ accessed on 9 June 2018
	Activated alumina beads	Film, carton liner, pallet cover	PrimePro®	DeltaTrak®, Inc., USA	https://www.deltatrak.com/products/ethylene-absorbers accessed on 9 June 2018
Zeolite	None	Films	Dry Pak's line, Peak Fresh®	Dry Pak Industries, Inc., USA	http://www.drypak.com/ethyleneAbsorbers.html accessed on 9 June 2018
	None	Filter, pad, label	It's Fresh!	It's Fresh! Inc, USA	http://www.itsfresh.com/default.asp?contentID=701 accessed on 9 June 2018
Activated carbon	None	Sachet	Ethylene adsorber	Vamsha Nature Care, India	http://vamshacare.com/ethylene-absorber accessed on 9 June 2018

Table 2.3 Advantages and disadvantages of ethylene oxidizers and scavengers in active packaging (adapted from Awalgaonkar and Almenar (2018))

Ethylene oxidizer/scavenger	**Advantages**	**Disadvantages**
Potassium permanganate	Highly effective in scavenging ethylene compared to other scavengers such as activated carbon, zeolites, metal organic frameworks, clay[a, d, c] Commercially available compared to sodium permanganate and titanium dioxide[a] Irreversible interaction with ethylene[b] Continuous reaction until saturation[b]	Rapidly consumed, needs frequent replacement Needs an inert carrier[a,b,c] Purple color of KMnO4 may not be aesthetically pleasing[c] Caustic nature[c], careful handling required during transportation and storage[b] Efficiency of ethylene oxidation is dependent on relative humidity conditions[d]
Activated carbon	Regeneration possible[a] environmentally friendly nature[b] Surface area (BET 1,120 m^2/g) available for adsorption[c] Relatively cheap production and low cost[b] Good porosity[a] and non-toxic[a] Ease of availability[b]	Efficiency of ethylene adsorption is dependent on temperature and relative humidity conditions[f] Can adsorb other compounds such as oxygen, carbon dioxide, and organic compounds[b,f]
Zeolite	Non-toxic[c] Environmentally friendly[c] Surface area (BET 320m^2/g) available for adsorption[a] Low cost[d] Regeneration possible[d]	Can adsorb/absorb other compounds such as oxygen, carbon-dioxide, and organic compounds[b,] Efficiency of ethylene adsorption is dependent on relative humidity conditions[d] Low ethylene adsorption capacity (1.3-19.6mmol/kg)[a] Lack significant ethylene adsorbing capacity when embedded in films[a]
Metal-organic frameworks	Exceptionally high surface area available for adsorption (BET 1,500-2,100m2/g)[e] Regeneration possible[e]	Efficiency of ethylene adsorption is dependent on relative humidity conditions

a= Keller et al., 2013; b=Martínez et al., 2007; c= Zagory, 1995; d=Álvarez-Hernández et al., 2018; e = DeEll et al., 2006; f=Bailen et al., 2007.

2.2.3.2 Ethylene-removing packaging based on ethylene adsorption/absorption

Adsorption is a surface phenomenon in which a particle is held on the surface of a solid material (Martínez et al., 2007). In contrast, absorption is a bulk phenomenon where the particle is held inside the solid material (Keller & Staudt, 2005). Activated carbon/charcoal, zeolites and metal-organic frameworks can adsorb/absorb ethylene and thus, they have been used to develop ethylene-removing packaging as discussed below.

2.2.3.2.1 Activated carbon

Any carbonaceous material can be used to make activated carbon (AC). The choice of material is dependent on parameters such as low inorganic matter, ease of activation, ready availability, lower cost, and lower degradation (Martínez et al., 2007). The most common materials used for activated carbon production are wood, fruit shells, fruit stones, apple pulp, wheat, cotton stalks, viscose rayon, and coal (Puziy et al., 2002). AC is widely used in many fields as an efficient and versatile adsorbent including as a purification agent, gas adsorber, decolorizing agent, and taste-odor removing agent (Martínez et al., 2007). The use of AC as an ethylene scavenger can be dated back to the 1940s when Southwick & Smock (1943) used brominated charcoal to remove ethylene from the storage atmosphere, which resulted in the reduction of scald and a considerable lengthening of the shelf life of McIntosh apples in controlled atmosphere storage (2-3 months).

AC differing in particle size has been used for ethylene scavenging. Granular, powdered, and fiber AC are the most common forms. Recently, carbon based nano-particles have been investigated for ethylene adsorption capacities. The particle size of AC affects its ethylene removal capacity due to differences in surface area, porosity, and activation efficiency. Bailen et al. (2007) reported that granular AC (20-60 mesh) can adsorb 70% of available ethylene while powdered AC

(100-400 mesh) can only adsorb 40%. Liu et al. *(*2006) found that carbon nano-particles could scavenge between 64-100 ppm of ethylene. Other factors affecting the capacity of AC to remove ethylene include impregnation with catalyst (e.g, palladium; increases adsorption), ethylene concentration (the higher the concentration the more the adsorption), heat treatment (increases adsorption), activation with H_2 (increases adsorption), etc. (Liu et al., 2006). Ethylene adsorption of granular AC follows a Langmuir isotherm (Bailen et al., 2007), which means that ethylene accumulates as a monolayer on the surface of the adsorbent. The area available for adsorption depends on the particle size of AC and the use of an activation treatment. Keller et al. (2013) reported that the AC surface area available for adsorption ranges between 827 and 1120m^2/g.

AC scavenges ethylene through adsorption. The pore size of AC plays an important role in the adsorption process. A pore diameter greater than 3.9Å (kinetic diameter of ethylene) is essential for ethylene adsorption (Szwedzińska, 2015). The ability and efficacy of AC depends on factors like surface chemistry, surface area, pore volume, temperature, and relative humidity, etc. (Martínez et al., 2007). Major advantages of AC as ethylene scavenger include its environmentally friendly nature, low toxicity, availability, and low cost. However, its non-specific nature of adsorption is a major limitation for its widespread use. Table 2 3 provides a detailed list of the advantages and drawbacks of AC as ethylene scavenger.

AC has commonly been integrated into the package through sachets. However, two recent studies report the integration of AC into the packaging medium. Sothornvit (2012) incorporated rice straw and activated carbon to the pulp mixture during the paper making process to create paper sheets with an ethylene scavenger. When the sheets were tested for ethylene adsorption, almost 70% of ethylene was adsorbed in the first hour, and the maximum ethylene adsorption was 77%. The researchers claim that an application of AC-rice straw papers would be as a separate bag or wrapper or as a laminate inside a carton to extend the shelf life of fruits. It is worth noting that the authors chose paper instead of plastic as a polymer substrate since plastics have commonly been selected as material for active packaging creation. Table 2 4 provides examples of shelf life studies that evaluate AC as an ethylene scavenger. The combination of active packages containing AC with other shelf-life extending technologies has also been reported in the literature as shown in Table 2.4. Sachets containing adsorbers based on AC are commercialized as shown in Table 2.2. They can be placed inside packages to create active packages.

2.2.3.2.2 Zeolites

Zeolites are microporous three-dimensional framework structures of crystalline aluminosilicates. Zeolites have negative charges on their framework that are balanced with alkali or alkali earth ions (Patdhanagul et al., 2012). The pore size of zeolites ranges from 3 to 12 Å, providing them with the ability to adsorb many chemicals including ethylene.

Table 2.4 Ethylene-removing packages based on ethylene adsorption/absorption created during the last decade and their effects on produce shelf-life extension

Active Compound	**Active compound amount**	**Integration technique**	**Packaging format**	**Packaging material**	**Produce**	**Storage conditions**	**Effect**	**Reference**
AC granulated	5g	Sachet	Bags	Oriented polypropylene	Tomato	8°C and 90% RH with 8 kPa for O_2 and 7kPa CO_2	MAP and granulated AC treated with Pd, led to lower ethylene concentration, treated tomatoes exhibited a reduction in color, softening and weight loss	Bailen et al., 2006
AC and $PdCl_2$–$CuSO_4$	10,20, 30g/kg of broccoli	Sachet	Pouch	Polyethylene (0.05 mm)	Broccoli	20°C and 90% RH	Delay yellowing and quality loss, reduced ethylene production and ethylene producing enzymes	Cao et al., 2015
AC powdered, granulated	1.25g/lit	Sachet	Porous paper	Glass Jars	Tomato	20°C	Significant reduction in softening and color changes in tomatoes	Bailen et al., 2007

Table 2.4 (Cont'd)

AC, palm shell charcoal	40% w/w	Liner and edium of box	Corrugated board	Kraft paper	Tomato	27°±1°C	Delayed rate of ripening, color change, shriveling and water loss observed in tomatoes treated with activated charcoal	Taechutrakul 2009
AC	10g	Paper packet		Metal tray with glass cover	Kiwi slices, Spinach, Banana slices	20°C	Retained fruits firm for longer time, , degradation of chlorophyll minimized	Abe & Watada 1991
Zeolite (Tazetut 50% of aluminosilicate minerals)	8% w/w	Film	Film	Polyethylene	Broccoli	4°C and 75% RH for 20 days	Delayed weight loss, chlorophyll degradation, stem hardening. Shelf life increased by 15 days	Esturk et al., 2014
Zeolite	2%	Film	Film	Zeolite melt blended with LDPE	Banana	Not specified	Improved quality attributes and better preservation in bananas	Li et al., 2012

Due to cation exchange capacity, molecular sieving, and adsorption, zeolites can be used to remove ethylene (Limtrakul et al., 2001; Suslow, 1997). Zeolites have been reported to have a low ethylene adsorption capacity (1.3-19.6mmol/kg) (Keller et al., 2013); however, this can be modified by cationic agents. Sue-aok et al. (2010) studied the modification of NaY zeolite caused by several ions including potassium (K-NaY), rubidium (Rb-NaY), and cesium (Cs-NaY). The modified zeolites adsorbed more ethylene and followed the pattern K-NaY > Rb-NaY > Cs-NaY >NaY. Zeolites are environmentally friendly and non-toxic. However, they have a low ethylene sorption capacity. Table 2.3 lists advantages and drawbacks associated with using zeolites as ethylene scavengers.

Ethylene can be absorbed within the zeolite framework and adsorbed on the surface of the zeolite framework (Coloma et al., 2014). For natural zeolites, a large pore diameter (12Å) favors ethylene (kinetic diameter 3.9 Å) to pass through zeolite pore openings and be absorbed within the zeolite framework (Szwedzińska 2015). There two theories to explain this phenomenon. The first one assumes that a cation-π interaction occurs between the π-electrons of the double bond of ethylene and metal cations. It involves s-donation and p* back-donation between the metal cations and the π orbital of ethylene. The second theory involves a CH-O interaction, resulting from hydrogen bonding between hydrogen atoms of ethylene and oxygen atoms at the zeolite surface (Coloma et al., 2014).

Only the blending of zeolites with polymer matrixes has been studied as integration technique. Dirim et al. (2001) studied various methods to manufacture a PE film containing zeolite. These methods were addition of zeolite to molten PE, coating PE beads with zeolite, extrusion of PE with zeolite, and hot pressing of co-extruded zeolite-PE film. Among all these methods, the latter was found to be most effective for produce shelf-life extension. Coloma et al. (2014) obtained a 37% reduction in ethylene concentration when the authors evaluated a LDPE film containing 10% zeolite (Zn-Ch). Ethylene permeability for a double layer composite film, prepared by laminating LDPE and poly[styrene-b-(ethylene-co-butylene)-b-styrene] (SEBS) modified with zeolite, was improved due to enhanced adsorption of ethylene by the incorporated zeolite and the dispersion of the zeolites (Monprasit et al., 2011). The combination of active packages containing zeolites with other shelf-life extending technologies has also been reported in the literature. Thermoformed PET containers containing zeolites combined with KMnO4 in amounts of 0, 0.5, 1.0, or 1.5% each when evaluated on the shelf life of 'Chonto' tomato showed that several of the combinations of scavenger and oxidizer were able to delay tomato ripening. However, each combination enhanced a different quality attribute (Salamanca et al., 2014). Sachets and films containing zeolites for creation of packages able to scavenge ethylene are commercially available. Table 2 lists some manufacturers of the aforementioned formats.

2.2.3.2.3 Metal-Organic Framework (MOFs)

MOFs are a new class of synthetic porous materials, consisting of metal ions or ion clusters bound to organic molecules to form a porous structure. The combination of different organic and inorganic building blocks gives flexibility in terms of pore size, shape, and structure (Kuppler et al., 2009). Li et al. (2009) reported that MOFs have an exceptionally high surface area (1,000–3,000 m^2 /g or more). In addition, they have a greater adsorptive surface per gram (BET) than zeolites (320 m^2/g) and activated carbon (827-1,120 m^2/g) (Table 2.4). MOFs can selectively adsorb volatile compounds such as ethylene (Kuppler et al., 2009; Chopra et al., 2017). Chopra et al. (2017) reported that MOFs did not adsorb ethylene very efficiently if water is present in the surrounding environment. The authors also reported that MOFs can be successfully used for ethylene releasing applications. Zhang et al. (2016) and Zhang & Luo (2017) investigated the effectiveness of MOF for on-demand ripening. They found that 50 mg of copper-based MOF can adsorb and release up to 654 µl/l of ethylene in a 4L container. It is worth to note that if the hydrophilicity of MOFs is controlled, then they have potential to be used in ethylene scavenging applications where high relative humidity is present. MOFs scavenge ethylene due to adsorption (Chopra et al., 2017). While the mechanism is not yet proven, modelling by Li et al. (2009) suggests that electrostatic interactions take place between the partial positive charges of coordinately unsaturated metal sites and the π-electrons of the double bond in ethylene molecules. Advantages and drawbacks of using MOFs as ethylene scavengers are compiled in Table 2.3.

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CHAPTER 3

Identification of ethylene scavenger and packaging material for development of a tray with ethylene removing capacity

3.1 Materials

3.1.1. Scavengers

Metal organic framework (MOFs) (Basolite® C300) was obtained from the German branch of BASF (Ludwig, Germany). Powdered activated carbon (PAC) (100 mesh particle size) and potassium permanganate ($KMnO_4$) were obtained from Sigma-Aldrich (St. Louis, Missouri, USA). Granulated activated carbon (GAC) (8-12 mesh particle size) derived from coconut was obtained from Capital Scientific (Austin, Texas, USA). Clinoptilolite (CL) was procured from Liquid Zeolite Company Inc. (Cedar Grove, NJ, USA), 4A zeolite was obtained from UOP LLC., A Honeywell Company (Des Plaines, IL, USA). These scavengers are shown in Figure 3.1 and their properties as claimed by the manufacturers are listed in Table 3.1. Desiccant was obtained from W.A. Hammond Drierite Co. LTD (Xenia, OH, USA). Certified gas cylinders containing 500 ppm of ethylene balanced in N_2 and a gas mixture of 40% O_2, 40% CO_2 balanced in N_2 were provided by Airgas (Radnor, PA, USA).

3.1.2. Films

Low density polyethylene (LDPE 0.030-mm thickness), linear low density polyethylene (LLDPE 0.025-mm thickness), polypropylene (PP 0.020-mm thickness), nylon (0.012-mm thickness), and polyethylene terephthalate (PET 0.013-mm thickness) films were donated to the School of Packaging by Dow Chemicals (Midland, MI, USA). Polylactic acid (PLA) film (0.040-mm thickness) was obtained from EVLON EV-HS1 (BI-AX International Inc., Wingham, ON, Canada).

Table 3.1 Properties of scavengers used in the study.

Scavengers	**Metal Constituents**	**Pore radius (Å)**	**Langmuir surface area (m^2/g)**	**BET surface area (m^2/g)**
PAC	-	4-10[1]	1070[2]	741[2]
GAC	-	4-10[1]	1252[2]	747[2]
MOF	Cu	5.0[3]	1520[3]	1470[3]
CL	K, Ca, Na	5.5 [4]	169.8 ± 17.8[4]	31.4 ± 5.4[4]
4A	Na	2.3[4]	171.3 ± 79.4[4]	48.0 ± 26.0[4]

Sources: [1]Ding et al. (2008); [2]Yener et al. (2008); [3]Kathuria (2013); [4]Szwedzińska (2015).

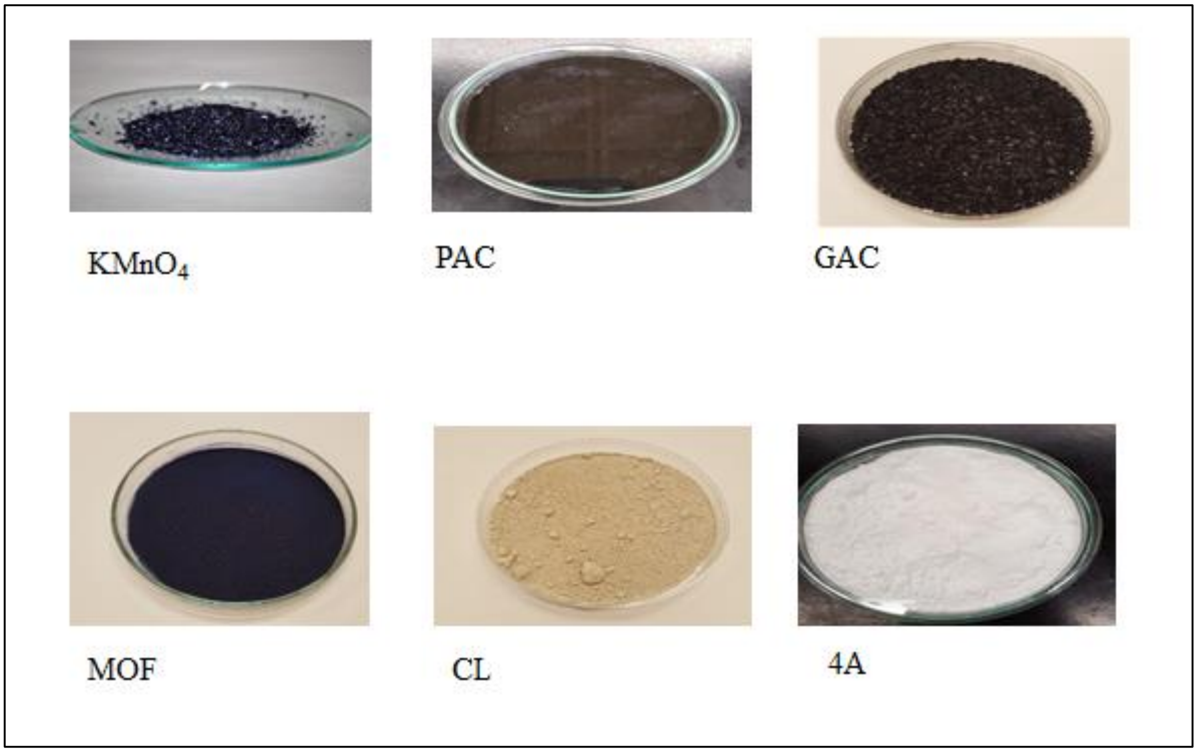

Figure 3.1 Images of scavengers used for the study.

3.2. Methods

3.2.1 Activation of scavengers

MOF (Basolite® C300) was subjected to a vacuum oven (VWR, Pennsylvania, USA) and set at 140 °C between 10 and 20 mm Hg for at least 8 hours. Activated carbons (PAC, GAC) and zeolites (CL and 4A) were activated in the aforementioned oven at 110 °C and 25mm Hg for at least 8 hours. After activation, samples were stored in sealed glass vials (Weaton™ 20-mL glass with polypropylene caps, Fisher Scientific, Pittsburgh, PA, USA) until use.

3.2.2 Assay systems

About 0.5 grams of scavenger was placed into 250-ml glass jars with aluminum closures containing a central hole covered with a septum. The jars were then injected using a gastight syringe (Supelco Analytical, California, USA) with 500 ppm of ethylene balanced in N_2 to obtain 5 µl of ethylene. Relative humidity (RH) conditions of <5 %, 55 % and 100 % RH were generated inside the jars by using a desiccant, ambient RH, and a small vial with deionized water, respectively. In another study, the jars were flushed with a mixture of 40 % O_2, 40 % CO_2, and 20 % N_2 prior to closure and injection with ethylene (same as above) and only high RH conditions were generated.

3.2.3 Storage conditions

Two temperatures, 23 ± 2 ºC and 5 ± 2 ºC were used to mimic the produce supply chain. The different temperatures were attained by placing the jars in an environmental chamber (Environmental growth chambers, Chagrin, Ohio, USA).

3.2.4 Adsorption measurements

3.2.4.1 Ethylene adsorption

Ethylene levels were measured by withdrawing an amount of 100 µL from each jar using the gastight syringe and septum described in section 3.2.2. The gas was injected into the splitless port of a gas chromatograph (HP 6890 series GC) equipped with a Carboxen TM 1010 Plot fused silica capillary column (30 m X 0.53 mm) (Supelco, Bellefonte, California, USA) and a flame ionization detector. The oven and injector temperatures were set to 150 °C and 220 °C, respectively. Ethylene levels in µl were quantified using a standard curve with the following regression equation: $y = 6E\text{-}14x^2 + 3E\text{-}08x + 5E\text{-}05$. Ethylene sorption was tested every 24 hours until maximum sorption was reached or there was a suspicion of leakage. Otherwise, ethylene withdrawal was carried out for five days. Three replicates of each scavenger type were used. % ethylene adsorption was calculated as shown below and was then normalized for the weight of the scavenger.

$$\%\,Ethylene\ adsorption = \frac{(Initial\ concentration\ in\ \mu l - Final\ concentration\ in \mu l)}{Initial\ concentration\ in\ \mu l} * 100$$

where: Initial concentration indicates the concentration of ethylene in µl at t=0 and Final concentration indicates the concentration of ethylene in µl at a specific time t.

3.2. CO_2 and O_2 adsorption

The amounts of O_2 and CO_2 in the jar headspace were measured using the Check Point 3 (Mocon, Ametek Instruments, Minneapolis, USA). 1 ml of gas sample from each jar was withdrawn through the septum of the lid every 24 hours for 5 days. Three replicates of each scavenger type were used. % O_2 and CO_2 adsorption were calculated similarly to ethylene.

3.2.5 Barrier properties

Water vapor transmission rates (WVTR) of the films listed in section 3.2.2 were measured in accordance with ASTM F1249-05 (ASTM, 2005) using a Permatran W Model 3/33 water permeability analyzer (MOCON, Minneapolis, MN, USA). Three films of each material were tested at 23 °C and 100 % RH.

A setup was created to measure ethylene permeation (Figure 3.2). A permeation cell was used. The film was mounted separating the cell into two halves. The system consisted of test gas (15,000 ppm of ethylene + air) flowing at 0.125 ml/sec through the upper half of the cell (donor chamber) while the carrier gas (air) flowed at 0.667 ml/sec through the lower portion (receiver chamber). The ethylene permeated into the receiver chamber was withdrawn using a 1-ml gas syringe and was injected into a GC (Carle Series 400 AGC; Hach Co., Loveland, CO, USA) equipped with a flame ionization detector and coupled with a 6-m-long x 2-mm-i.d. stainless steel column packed with activated alumina. The ethylene detection limit of the GC was 0.005 µl/l. Ethylene concentrations were calculated relative to a certified standard (Matheson Gas Products, Chicago, Il, USA) with a concentration of 0.979 µl/l. Three films of each material were tested at 23 °C and 55% RH.

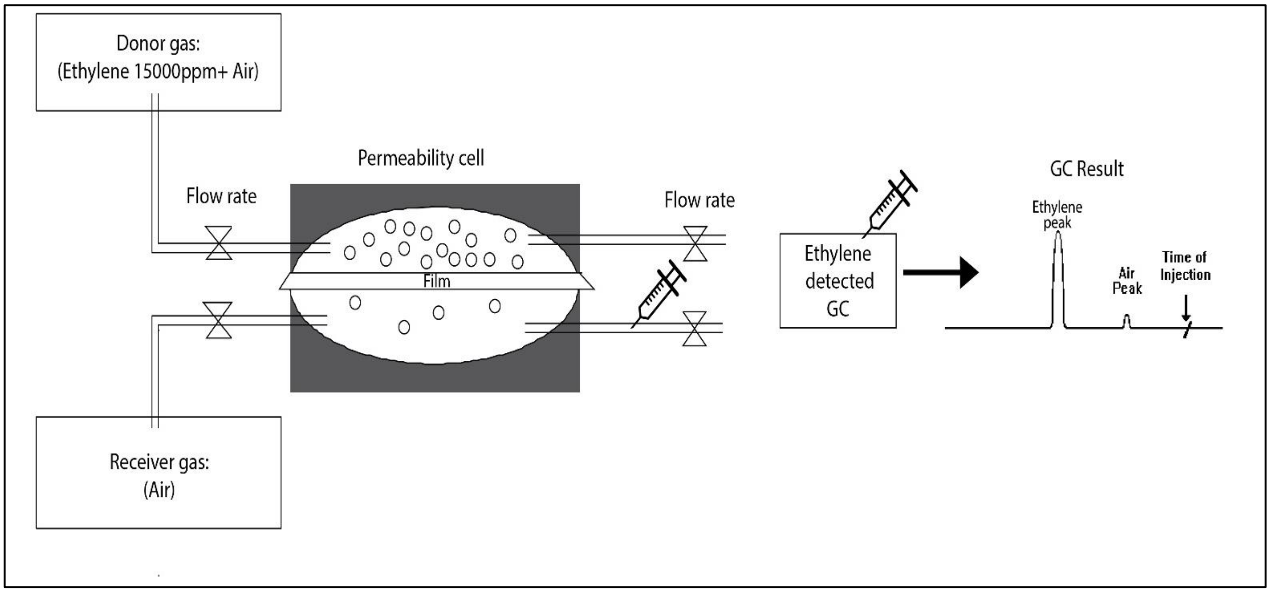

Figure 3.2 Schematic representation of the system used to measure ethylene permeation.

3.2.6 Statistical analysis

To compare the effect of type of scavenger, time, temperature, and relative humidity the statistical model included these parameters and their interactions as fixed factors, and the replicates used for the analysis as a random factor. There was a minimum of three replicates per treatment. All evaluated factors and their interactions were determined through a general linear model using the statistical software Minitab 17 (State College, PA, USA) and Tukey's test at 0.05 level was used for statistical significance. In all analyses, the assumptions of normality of statistical errors and homogeneity of variances were checked and met for avoiding biasing results from uncontrolled factors and thus for improving the generalizability and reproducibility of this study's findings. For the adsorption study in presence of O_2 and CO_2 and for barrier properties the statistical analyses was performed using a univariate analysis of variance (ANOVA) with the statistical software Minitab 17 (State College, PA) and Tukey's test at 0.05 level for statistical significance.

3.3 Results and discussion

3.3.1 Effects of temperature and relative humidity on the sorption capacity of ethylene scavengers

The results obtained by subjecting the scavengers (KMnO4, MOF, PAC, GAC, CL, 4A) to the temperatures 4 ± 2 ^{o}C and 23 ± 2 ^{o}C and the relative humidity conditions <5 % RH, 55 %RH, 100 %RH are shown in Figure 3.3

3.3.1.1 $KMnO_4$

At RH conditions of 55 % and higher, $KMnO_4$ had a greater ethylene oxidizing capacity at 23 ^{o}C than at 4 ^{o}C until day 3, after which no statistically significant results were obtained. Lidster et al. (1985) also reported that ethylene removal by $KMnO_4$ increases with time and temperature. After 5 days, $KMnO_4$ oxidized 97 % of the ethylene at RH of 55 % and higher, while it showed lower activity in the range of 60 % (4 ^{o}C) and 70 % (23 ^{o}C) at < 5 % RH. Lidster et al. (l985) also reported higher ethylene removal capacity for $KMnO_4$ at high RH (90~96 %), which was attributed to the moisture requirement for reaction between ethylene and $KMnO_4$ crystals. In comparison with all other scavengers, $KMnO_4$ had the highest ethylene removing capacity at 100 % RH and 23 ^{o}C. These conditions are prevalent for a few climacteric fruits but not for most.

3.3.2.2 Activated carbon

Temperature influenced the ethylene removing capacity of both GAC and PAC. Higher adsorption was observed at 5 ^{o}C than at 23 ^{o}C regardless of the RH. The difference was much larger when RH increased. In contrast, Martinez-Romero et al. (2007) reported that temperature (2 ^{o}C vs. 20 ^{o}C) does not affect the ethylene adsorption of activated carbons. Ethylene adsorption was about 80 % at 4 ^{o}C regardless of the RH. However, ethylene adsorption decreased with increasing RH at 23 ^{o}C. This is most likely due to more water molecules surrounding the scavenger at 23 ^oC compared to 4 ^oC as water pressure increases with increasing temperature (Kessler, 2006). Furthermore, water instead of ethylene adsorption was favored due to the smaller kinetic diameter of water (2.65 Å) compared to ethylene (3.9 Å). Nature of activated carbon (GAC and PAC) showed differences in the first 24 hours only at 100% RH, with GAC being able to adsorb more ethylene. In agreement with these results, Bailen et al. (2007) found that PAC (40%) had a lower ethylene adsorption compared to GAC (70%). However, the authors reported the difference happening at ambient RH instead of at high RH like in this study. The difference between the two studies could be the use of different sources of activated carbon that led to different BET surface areas and/or the use of different activation conditions. Both activated carbons desorbed more than half of the trapped ethylene after 48 hours at 100 % RH and 4 ^oC but not at other combinations of temperature and RH. Among the scavengers considered in this study, the ethylene removing capacity of activated carbon was the highest at 4 ^oC and RH of 55 % and higher (conditions surrounding climacteric fruits and other types of commodities) for the first 48-72 h. At 23 ^oC, activated carbon still showed more ethylene removing capacity than zeolites but not than $KMnO_4$ at RH of 55 % and higher and MOF at RH of 55% and lower. GAC was the second best ethylene remover at high RH regardless of the RH.

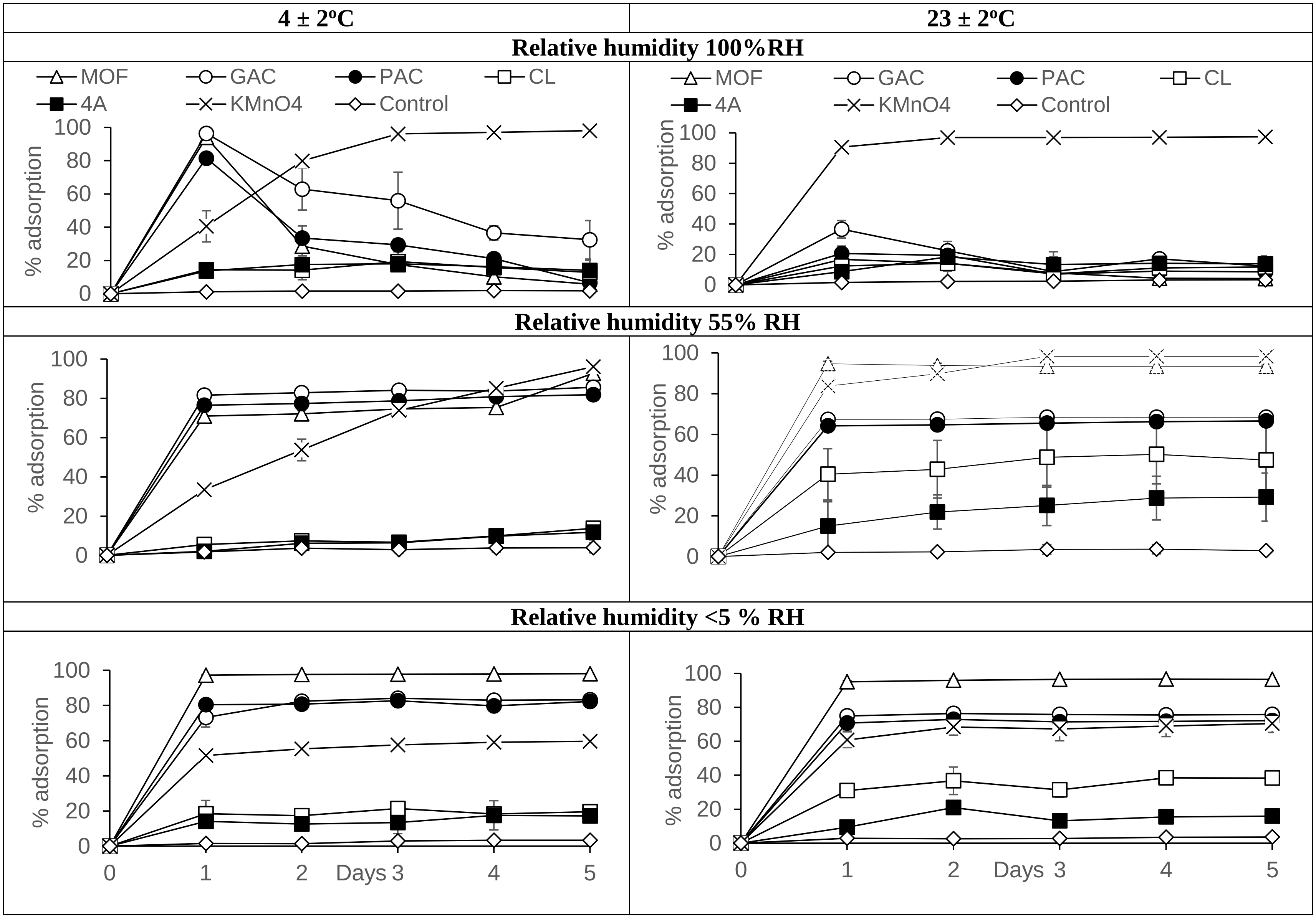

Figure 3.3 Impact of temperature and relative humidity on the ethylene removing capacity of six scavengers.

3.3.2.3 Zeolite

According to Figure 3, CL has ethylene removing capacity. This is in agreement with Erdoğan et al. (2008) but not Peiser & Suslow (1998). In fact, CL had higher ethylene removing capacity than 4A. This could be attributed to its larger pore diameter compared to 4A. Furthermore, the two zeolites differ in metal constituents and these seem to play a role in ethylene removal. CL consists of K^+, Ca^+ and Na^+ ions whereas 4A consists of Na^+ ions. The adsorption of ethylene by CL has been attributed to the interactions between the K^+ ions and ethylene and strong quadropole moment and interaction between divalent Ca^{2+}ions with the ethylene double bond (Erdoğan et al., 2008). Temperature and RH influenced the ethylene removing capacity of CL but did not of 4A. Ethylene adsorption by CL was lower at 4 ^oC than at 23 ^oC and decreased with increasing RH. Ethylene adsorption was expected to be lower at 23 ^oC because of more water molecules. This could be explained by zeolites being able to remove ethylene by adsorption and absorption instead of only adsorption like the other scavengers. The details of this mechanism can be found in Chapter 2 (literature review). Among all compared scavengers, zeolites exhibited the lowest ethylene removing capacity. The evaluated zeolites were in their natural form and not modified. However, an improvement in their ethylene removing capacity can be obtained when treated with cationic agents and surfactants (Sue-aok et al., 2010, Patdhanagul et al., 2010, Erdoğan et al., 2008).

3.3.2.4 MOF

Temperature did not have a consistent impact on ethylene removing capacity of MOF but RH did. Like activated carbons and zeolites, MOF's ethylene adsorption capacity decreased with increasing RH, which can be attributed to more water molecules competing for the same adsorption sides as ethylene. The ethylene removing capacity of MOF at low relative humidity (~96 %) was comparable to that of $KMnO_4$ at high RH (~93 %) at both temperatures. At ambient and low RH, equilibrium was reached within the first 24 hours. At high RH, ethylene adsorption was ~95 % at 4 ºC and ~15% at 23 ºC after 24 hours. However, the trapped ethylene was then desorbed and reached values of less than 5 % at both temperatures. In agreement with these results, Chopra et al. (2017) reported a high affinity of MOF towards ethylene in the absence of water and low ethylene adsorption by MOF in the presence of water. The authors also reported that ethylene sorption was complete within one or two hours. Among the studied scavengers, MOF's ethylene removing capacity was more than $KMnO_4$, activated carbon, and zeolites at < 5 % RH.

Based on the results discussed above, the ethylene removing capability of the scavengers is highly diminished with increasing RH except for $KMnO_4$, which was able to retain its high ethylene removing capacity at high RH due its oxidative mechanism compared to an adsorption mechanism. However, as mentioned in the literature review, certain drawbacks of $KMnO_4$, such as its caustic nature and need for careful handling during storage require the study of alternative scavengers (e.g., adsorption-based scavengers) to replace $KMnO_4$. Among the studied adsorption-based scavengers, zeolites have a low ethylene adsorption capacity compared to activated carbon and MOF. Consequently, zeolites and $KMnO_4$ were excluded and MOF and PAC were shortlisted for a further study on competitive adsorption of ethylene in the presence of competing molecules like CO_2 and O_2. The study was carried out because CO_2, and O_2 not only can compete for the same adsorption sites but are also present in produce surroundings (e.g., package headspace).

3.3.2 Effect of competitive adsorption (CO_2, O_2 and water) on ethylene adsorption

The ethylene adsorption of PAC and MOF was studied in the presence of competing molecules such as CO_2, O_2, and water. Three replicates of jars were used for the study, however leakage was suspected in one set of jars and hence the reported data is only for two sets of jar samples. The % ethylene and % CO_2, were calculated using the formula mentioned in 3.2.4. No adsorption of O_2 was observed by MOF and PAC. The results obtained for ethylene and CO_2 after 5 days of storage at 23 ^{o}C and 100 % RH are presented in Table 3.2. Both scavengers were able to adsorb ethylene and carbon dioxide simultaneously. Both MOF and PAC adsorbed CO_2 in the presence of water and ethylene. It could be that the co-adsorbed water molecules enhanced CO_2 adsorption. Yazaydiyan et al. (2009) and Burtch et al. (2014) both reported an enhancement of CO_2 adsorption in the presence of water. Both scavengers were able to adsorb ethylene when CO_2 and water were present.

However, the effect of CO_2 on ethylene adsorption was different depending on the scavenger type. CO_2 had no effect on the adsorption of ethylene by PAC. However, the competing molecule increased the adsorption of ethylene by MOF. This could be attributed to different host-guest affinities that depend on host sides (Li et al., 2011). This variability in ethylene adsorption among scavengers in the presence of competing molecules has already been reported. Chopra et al. (2017) reported a decrease in the amount of ethylene adsorbed by Baseolite® C300 but not by Baseolite® A520 and Zeolite Z13X, which showed the same capability to adsorb ethylene.

Table 3.2 Competitive adsorption of CO_2 and ethylene of MOF and PAC at 23°C and 100% RH

Scavenger	**Ethylene adsorption (%)**		**CO_2 adsorption (%)**
	Condition: 5µl of ethylene and high RH	Condition: 40% CO_2, 40% O_2, 5µl ethylene and high RH	Condition: 40% CO_2, 40% O_2, 5µl ethylene and high RH
MOF	3.28	9.98	9.01
PAC	8.54	7.21	8.32

3.3.3 Barrier properties

From Figure 3.3 and Table 3.2, it can be inferred that PAC and MOF have more affinity towards water than CO_2 and ethylene. So, for developing an ethylene-removing packaging, it is essential to have a packaging material with good barrier properties to water as produce generates a high RH condition inside the package. On the other hand, a weak permeability to ethylene is also desired. It is important that the gas permeates through the film to reach the scavenger. Hence, several petroleum-based and bio-based films were tested for their permeability to water and ethylene and the results are presented in Table 3.3. The petroleum-based polyolefin films (LDPE, LLDPE, PP) had lower permeability to water than the other petroleum-based and bio-based films. PET had moderate permeability to water while nylon and the bio-based films (PLA, carbohydrate-based and protein-based) have poor water barrier properties. Ethylene was only detected in the case of the LDPE, LLDPE, and PP films indicating they are relatively poorer barriers to ethylene than the other films. The none detection of ethylene in case of the other films shows that these have good barrier to ethylene.

Table 3.3 Water and ethylene permeability of various petroleum-based and bio-based films.

Film	**Thickness (mm)**	**Water vapor permeability * 10^{-16} (Kg. m/m^2 sec Pa) @ 23°C and 100%RH**	**Ethylene permeability *10^{-17} (Kg. m/m^2 sec Pa) @ 23°C and 55%RH**
LDPE	0.030	4.551±0.145a	2.775±1.388a
LLDPE	0.025	2.849±0.078a	2.111±1.065a
PP	0.020	1.754±0.031a	1.533±1.387a
PET	0.013	10.484±1.50a	Below measurable quantity
Nylon	0.012	104.012±4.33b	Below measurable quantity
PLA	0.040	221.007±7.99c	Below measurable quantity
Yam-based [1]	0.070	20827±3184d	Below measurable quantity
Egg white-based [2]	0.110	21458±8790d	Below measurable quantity

[1]Pranata et al. (2018); [2]Guimarães et al. (2018). Means within the same column with a same letter are not statistically different at $p < 0.05$.

Wang et al. (1998) studied ethylene permeation for LDPE and LLDPE and reported similar ranges for the two polymers in terms of ethylene permeation results. For developing ethylene-removing packaging, a plastic with poor barrier to ethylene and a decent barrier to water would be ideal. Based on these criteria, plastics like LDPE, LLDPE, and PP could be used for creation of ethylene-removing packaging.

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CHAPTER 4

Development and characterization of an ethylene removing tray and its validaton for produce packaging applications

4.1 Materials

Low density polyethylene (LDPE) resin (melt flow index of 24 g/10 min, density 0.913g/cm^3) were procured from LyondellBasell and LDPE film (0.04-mm thickness) was supplied by Dow Chemicals (Midland, MI, USA). Powdered activated carbon (100 mesh particle size) was purchased from Sigma Aldrich (St Louis, MO, USA). Cherry tomatoes (*Solanum lycopersicum* var. cerasiforme*)* were purchased from a local grocery store (East Lansing, MI, USA). They were transported to the School of Packaging and were then sorted by color and size and any damaged or rotten fruits were removed, all at ambient conditions. Certified gas cylinder containing 500 ppm of ethylene balanced in N_2 was provided by Airgas (Radnor, PA, USA).

4.2 Methods

4.2.1 Tray development

Activated carbon (AC) was conditioned prior to processing using a vacuum oven (VWR, Pennsylvania, USA) for 4 h at 110 °C followed by 4 h at 200 °C and was then stored in a desiccator until use. Specific quantities of LDPE resin and AC (5%, 10%, and 20% w/w) (Step 1; Figure 4.1) were weighed (Adventurer™ precision balance, OHAUS, Pine Brook, NJ, USA) and mixed (Step 2; Figure 4.1) using a three-piece mixer (Brabender, Duisburg, Germany) at 160 °C for 3 min. Amounts of ~11g of each of the LDPE/AC mixtures were compression molded into sheets with thicknesses between 350 µm and 420 µm using a hydraulic press (model 0L488-C, PHI, City of Industry, CA, USA) at a pressure of 20,000 psi and a temperature of 120 °C for 7 min (Step 3;

Figure 4.1). The formed sheets (Step 4; Figure 4 1) were stored in a desiccator at 23°C (Step 5; Figure 4.1) until these were shaped into trays using a vacuum thermoforming machine (LABFORM® Model 1620, Hydrotrim thermoformer, New York, NJ, USA). The heating phase was carried out for 1 minute and the thermoforming phase for about 45 seconds. A temperature of 120 °C was maintained during the whole thermoforming process (Step 6; Figure 4.1). A minimum of six trays containing only LDPE (controls) and six trays containing AC in concentrations of 5%, 10%, and 20% were produced. Figure 4.2 shows a control tray and a tray containing AC.

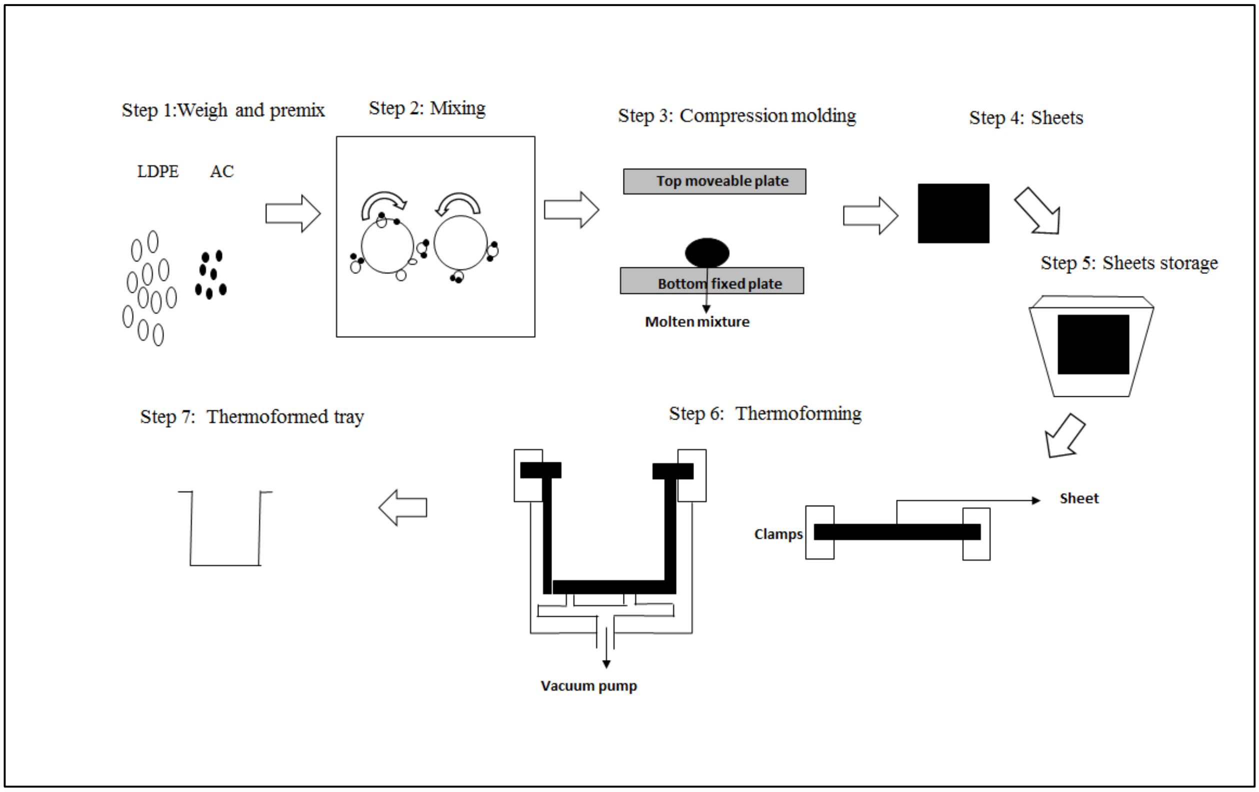

Figure 4.1 Schematic representation of the preparation of the thermoformed trays

Figure 4.2 Control tray (left) and a tray containing AC (right).

4.2.2 Tray selection

The trays containing AC produced in section 4.2.1 were tested for their ethylene adsorption capacity. The assay systems consisted of 250-ml mason jars with one tray each, it was flushed with N_2 containing 20 ppm of ethylene for 1 min prior to their closure. The lids were previously modified by cutting a central piece out that was covered with a snap-fit rubber septum. The assay systems were stored at 23 ^oC and 100 % RH. Amounts of 100 µL of jar headspace were withdrawn throughout the lid septum every 24 h for 5 days using the gastight syringe (Supelco Analytical, California, USA). The gas was injected into the splitless port of a gas chromatograph (HP 6890 GC, Agilent Technology, Palo Alto, California, USA) equipped with a flame ionization detector and a Carboxen TM 1010 Plot fused silica capillary column (30 m X 0.53 mm) (Supelco, Bellefonte, California, USA). The oven temperature was 150°C and injector and detector temperatures were set to 150 °C and 220 °C, respectively. The splitless flow was 3.0. Ethylene levels were quantified using a previously prepared standard curve with the following regression equation: $y = 6E\text{-}14x^2 + 3E\text{-}08x + 5E\text{-}05$. The results are presented as adsorbed ethylene/g of tray.

4.2.3 Tray characterization

The control trays (LDPE) and the trays containing AC selected in section 4.2.2 were compared in terms of thickness profile and thermal, mechanical, and barrier properties.

4.2.3.1 Thickness

Sheet thickness (Step 4, Figure 4.1) was determined with a TMI 549 M micrometer (Testing Machines Inc., Amityville, NY, USA) in accordance with ASTM D374 - 99 (ASTM, 2016). The thickness profiles (wall, edge, bottom, and trim) of the trays (Step 7, Figure 4.1) were obtained using a Magna-Mike Model 8000 thickness gauge (Panametrics, Waltham, MA. USA). At least six samples of each type of tray were measured. The results are presented in mm.

4.2.3.2 Thermal characterization

The thermal transitions of the neat LDPE and LDPE/AC sheets (Step 4; Figure 4.1) were determined using a Q100 Differential scanning calorimeter (TA Instruments, New Castle, DE, USA). The temperature calibration of the equipment was performed in accordance with ASTM E967-03 (ASTM, 2003a) and the heat flow calibration was performed in accordance with ASTM E968-02 (ASTM, 2002). Degree of crystallinity (% X_c) was obtained from the ratio between the heat of fusion samples (ΔHm) and heat of fusion 100% crystalline LDPE (277.1 J/g) as reported by Brandrup, Immergut, & McDowell (1975) but taking into consideration the percentage weight of the LDPE present in the sheets (X_{LDPE}):

$$\%\, Crystallinity = \%\, X_C = \left(\frac{\Delta Hm}{277.1 * X_{LDPE}}\right) * 100$$

Between 5 mg and 8 mg of LDPE and LDPE/AC sheets were used for each run. Samples were heated from 5 °C to 210 °C at a rate of 10 °C/min. Three replications of each type of sheet were tested. The results are presented as % crystallinity.

4.2.3.3 Mechanical characterization

The control trays and the trays containing AC selected in section 4.2.2 were subjected to compression tests in order to determine the effect of the addition of the AC on the mechanical properties of the material since the trays did not differ in design. Measurements were carried out using an Instron Universal Testing Machine (Model 5565, Instron, Norwood, MA, USA) with a crosshead speed of 5 mm/min and a gauge length of 30 mm. Ten trays of each type were used and the results are presented as compressive force (N) and extension (mm).

4.2.3.4 Barrier properties

Water vapor transmission rates (WVTR) of the aforementioned sheets were measured in accordance with ASTM F1249-05 (ASTM, 2005a) using a Permatran W Model 3/33 water permeability analyzer (Mocon, Minneapolis, MN, US). Three sheets of each type were tested at 23 ^{o}C and 100 % RH. Oxygen transmission rates (OTR) of the sheets were measured in accordance with ASTM D3985-05 (ASTM, 2005b) using an 8001 Oxygen permeation analyzer (Mocon, Minneapolis, MN, US). Three sheets of each type were tested at 23 ^{o}C and 0 % RH. All samples were masked with an adhesive type aluminum foil (McMaster-Carr, Aurora, Ohio, US), leaving an uncovered test area of 3.14 cm^2. The results are presented as permeability units (kg. m/m^2 sec Pa).

4.2.4 Shelf-life study

Quantities of approximately 75 grams of cherry tomatoes were weighed (Adventurer™ precision balance, OHAUS, Pine Brook, NJ, USA) and placed inside the control trays and the trays containing AC selected in section 4.2.2. The trays were wrapped with LDPE film that had all its sides heat sealed using an impulse sealer (Ceratek, Sencorp SystemsInc., Hyannis, MA, USA) for 5 seconds. A silicone septum was attached to the corner of each package to withdraw the headspace gases. Figure 4.3 shows the developed packaging systems. All packages were kept at 23 ºC and 55% RH for 9 days. Physiological, physico-chemical, and microbial evaluations were performed every 3 days. Six packages of each material were evaluated at each testing day.

Figure 4.3 Packaging systems with and without trays containing AC.

4.2.4.1 Physiological evaluations

The in-package headspace composition (CO_2 and O_2) was measured using Check Point 3 (Mocon, Ametek Instruments, Minneapolis, USA). 1-ml syringe of the gas headspace was withdrawn through the septum patched on the package. The concentration of the headspace gases

CO_2 and O_2 is reported in percentage. Ethylene content was measured according to the method described in 4.2.2 but using packages instead of glass jars.

The weight of each package of cherry tomatoes was measured on day 0 and on each sampling day using a balance (Adventurer™ precision balance, Ohaus, NJ, USA). Weight loss was determined by subtracting the final weight from the initial weight divided by the result from the subtraction of the packaging material weight from the initial weight. Weight losses are reported in percent.

4.2.4.2 Physico-chemical evaluations

The cherry tomatoes of each package were blended for 30 s using a common blender (Hamilton Beach, NC, USA). Soluble solids in the tomato juice were determined using a refractometer (RHB-32ATC, Cole-Parmer Instruments, IL, USA). The refractometer was calibrated prior to each measurement. Three measurements were taken for each sample and the results are reported in ^{o}Brix.

4.2.4.3 Microbiological evaluations

Fungal growth was visually estimated on each individual fruit immediately after opening the packages. Any cherry tomato with visible fungal growth was considered to be decayed. The results were expressed as percentage of decayed cherry tomatoes.

4.2.5 Statistical analysis

All statistical analyses were performed using univariate analysis of variance (ANOVA) with the statistical software Minitab 17 (State College, PA) and Tukey’s test at 0.05 level for statistical significance. In all analyses, the assumptions of normality of statistical errors and homogeneity of variances were checked and met for avoiding biasing results from uncontrolled factors and thus for improving the generalizability and reproducibility of this study's findings.

4.3 Results and discussion

4.3.1 Tray selection

The developed trays differing in AC concentrations (0 %, 5 %, 10 %, 20 % w/w) are shown in Figure 4.4. The ethylene removing capacity of these trays present in the jars after 5 days is shown in Figure 4.5. The control tray (LDPE tray) was able to adsorb 1.105 ppm/g of tray when exposed to an ethylene concentration of 20 ppm. Similarly, García-García et al. (2013) reported that thick LDPE films (0.07 mm) adsorbed 2.755 ppm of ethylene in 15 days. Significant differences ($P < 0.05$) in ethylene adsorption capacity were observed between the LDPE tray and the LDPE/10% AC and LDPE/20% AC trays. The latter two absorbed twice as much ethylene as the LDPE tray. The LDPE/10% AC and LDPE/20% AC trays did not differ in ethylene adsorption capacity but in uniformity. The trays with 20% AC developed some micro-cracks and small voids. These could have resulted from the formation of clusters and agglomerations by the AC due to its high concentration that restricted the LDPE chain mobility during thermoforming. Development of cracks and voids was also reported by Chodak & Krupa (1999) when the authors studied the addition of carbon black to polyethylene. Based on the higher ethylene adsorption capacity and the even trays, the LDPE/10% AC trays were selected for further characterization.

LDPE tray	
LDPE/5% AC tray	
LDPE/10% AC tray	
LDPE /20% AC tray	

Figure 4.4 Trays developed with LDPE and 0%, 5%, 10%, and 20% activated carbon.

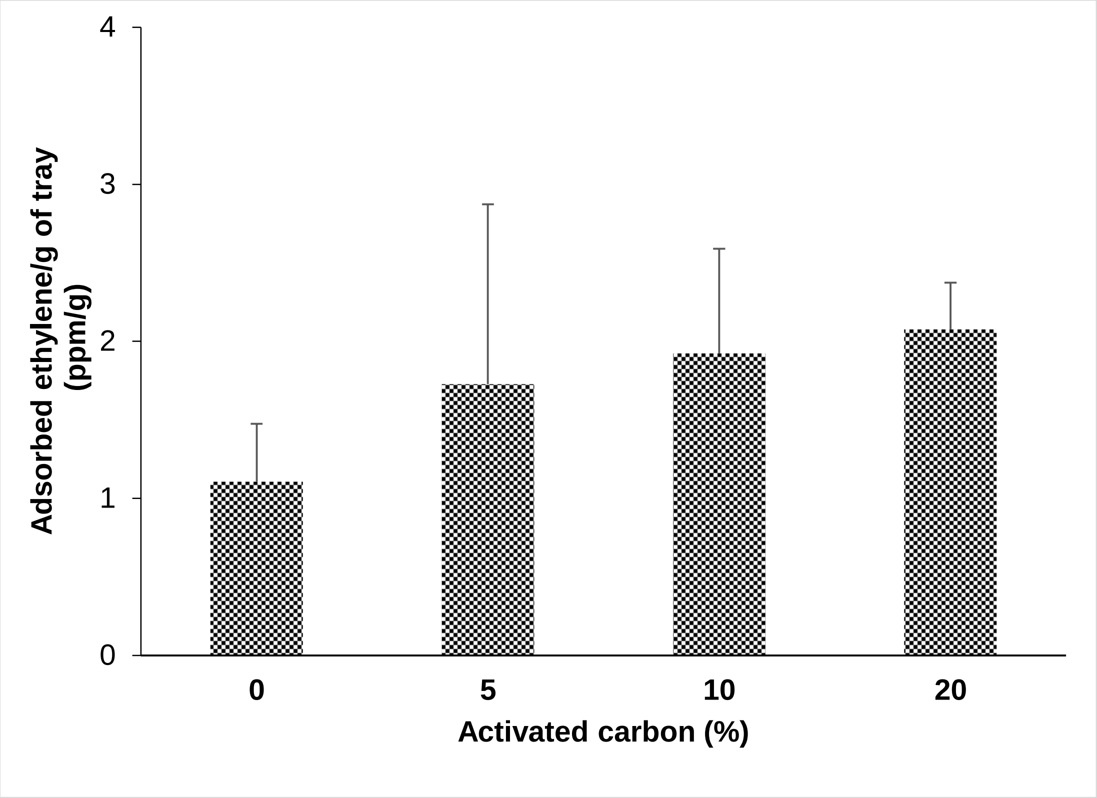

Figure 4.5 Ethylene adsorption after 5 days by developed trays containing 0%, 5%, 10% and 20% of AC.

and a shelf-life study. Furthermore, the selection of this type of tray led to the use of a tray where 10% of the LDPE resin is replaced with a material obtained from agricultural waste.

4.3.2 Tray characterization

4.3.2.1 Thickness

As shown in Table 4.1, the thickness of both trays varied significantly ($P < 0.05$) based on the part of the tray. Wall thickness was higher than corner and bottom thicknesses in both LDPE and LDPE/10% AC trays. Buntinx, et al. (2014) and Throne (2008) attributed the non-uniform thickness of a tray to a variety of processing parameters in the thermoforming process including sheet temperature, type of mold, depth of mold, mold temperature, heating time, thermoforming pressure, and differential stretching. Also, the authors mentioned that the thinning observed in the corners and bottom of a tray is a major drawback for thermoforming. No differences were observed between the thicknesses of sheet and trim indicating that the non-uniformity in thickness occurs when the heated sheet is deformed into the mold. The addition of 10% AC did not affect the thickness in sheet, trim, and corner. However, differences ($P < 0.05$) were observed in the thicknesses of the walls and bottoms, which thinned with the addition of the AC. This could be explained by different levels of deformation that parts of the sheet have to undergo to reach the furthest ends of the mold (Martin & Duncan 2007). Due to the mold design, as the tray becomes deeper, thinning is observed in the corners and the bottom

4.3.2.2 Thermal characterization

The % crystallinity of the LDPE and LDPE/10% AC sheets are shown in Table 4.2. These thermal properties were not altered due to the presence of AC. This could be due to the saturation of the nucleating action of AC occurring at higher loading (10 %). At such high amounts, AC interferes with the crystal growing process and hence an increase in crystallinity was not observed (Trujillo et al., 2007). Karsli & Aytac (2011) observed a decrease in crystallinity for short carbon fiber reinforced polypropylene composites. The difference could be attributed to the lower concentration of carbon (2.5-5%) and the increased interfacial interaction between polymer matrix and the carbon due to the use of a fiber format.

4.3.2.3 Mechanical characterization

The compressive force (N) and extension (mm) of the tray did not change with the addition of AC as shown in Table 4.2. The compressive force was approx. 7.90 N and the extension was 15 mm. The identical mechanical properties of the trays can be attributed to their same % crystallinity and corner thickness. Contrary to what one might expect, differences in wall thickness did not lead to different compressive forces and extensions. There are not results for trays loaded with AC in the literature for comparison purposes. For films, Khalil et al. (2007) observed higher tensile strength for cast polyester resin loaded with 10% AC compared to the neat casted material.

4.3.2.4 Barrier properties

The water permeability and oxygen permeability of the trays were determined due to their effect on the concentration of water and oxygen inside the package headspace. As reported in Table 4.2, the LDPE/10% AC and LDPE trays had the same permeability to water (approx. 5×10^{-16} $kg.m/m^2$ s Pa). Zagory (1995) reported that polymers with open pore spaces created by addition of compounds such as zeolites can alter the gas/vapor exchange properties of the polymers. Dirim et al. (2004) showed that LDPE films with embedded zeolites had less permeability to water than the neat films, which was attributed to the porous structure and water sorption capacity of zeolites. Although AC is porous and has water sorption capacity (Bailen et al., 2006), a decrease in water permeability was not observed due to no differences in crystallinity between the LDPE/10% AC and LDPE sheets. Similar to water permeability, the developed LDPE/10% AC and LDPE trays did not show differences in oxygen permeability (approx. 5×10^{-17} $kg.m/m^2$ s Pa). The reasoning is the same as that for water.

Table 4.1 Thickness profile of the sheets and the developed tray

Sample	**Thickness (mm)**				
	Sheet	Tray			
		Wall	Corner	Bottom	Trim
LDPE	0.397±0.025aA	0.351±0.033aA	0.207±0.042cB	0.275±0.040dC	0.378±0.047aA
LDPE/10% AC	0.393±0.022aA	0.311±0.013bB	0.190±0.030cC	0.227±0.042cD	0.389±0.029aA

Means with same lowercase letters within the same column are not significantly different based on the ANOVA results at 5% significant level. Means with same uppercase letters within the same row are not significantly different based on the ANOVA results at 5% significant level.

Table 4.2 Thermal, mechanical, and barrier properties of the LDPE tray and LDPE/10% AC tray.

Sample	**Thermal properties**		**Mechanical properties**		**Barrier properties**	
	T_m	Crystallinity (%)	Compressive force (N)	Extension (mm)	Water vapor permeability $*10^{-16}$ (Kg m/m^2 s Pa)	Oxygen permeability $*10^{-17}$ (Kg m/m^2 s Pa)
LDPE tray	131.12±0.222a	54.57±0.655a	7.900±2.014a	15.023±0.008a	5.037±1.734a	4.561±1.935a
LDPE/10% AC tray	130.85±0.521a	54.06±0.884a	7.839±2.597a	15.019±0.008a	5.116±3.984a	5.560±3.366a

Means with same lowercase letters within the same column are not significantly different based on the ANOVA results at 5% significant level.

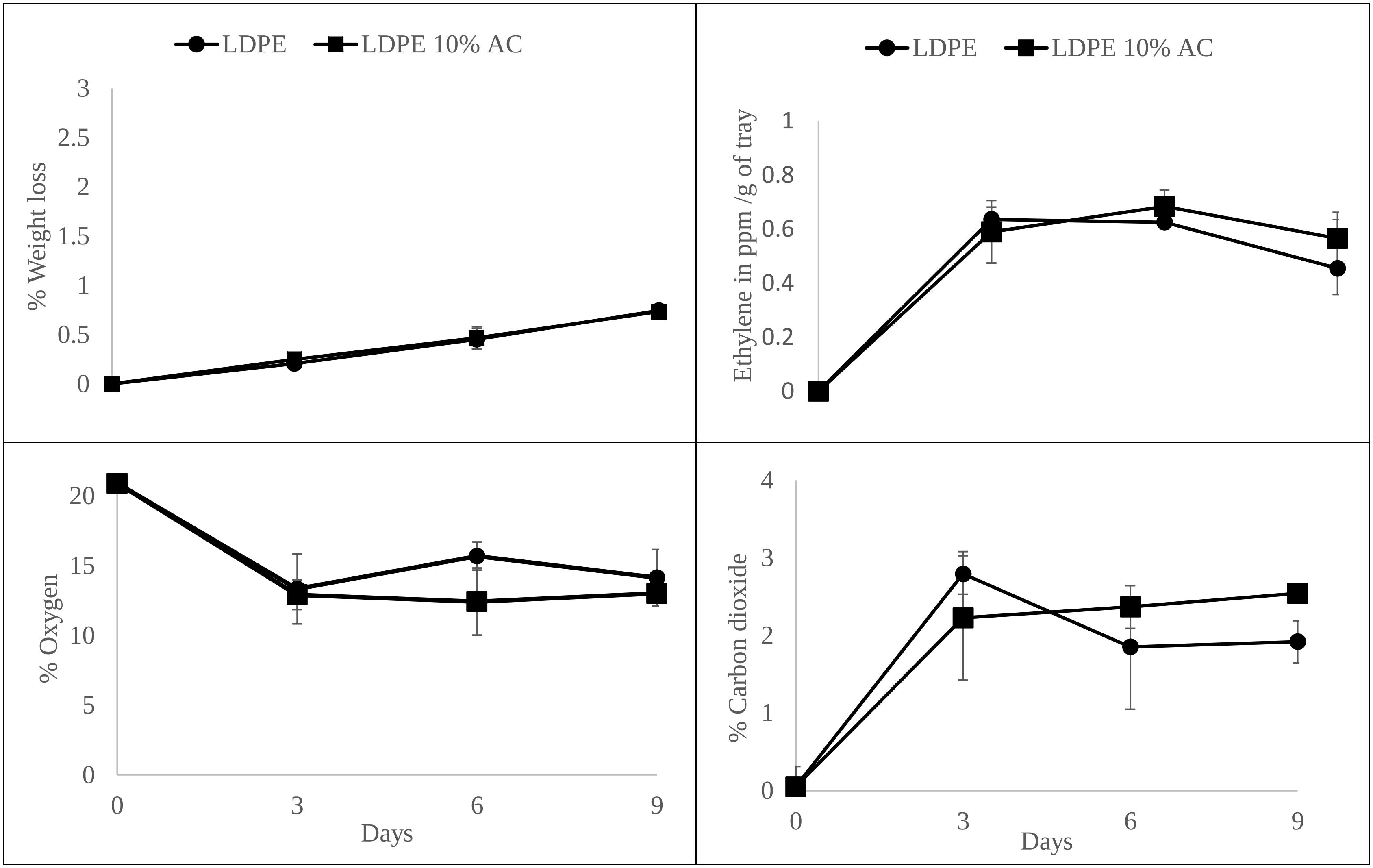

Figure 4.6 Shelf-life study parameters of cherry tomatoes packaged in LDPE and LDPE/10% AC trays and stored at 23ºC and 85% RH for 9 days.

4.3.3. Shelf-life study

4.3.3.1 Physiological evaluations

Figure 4.6 shows the evolution of weight loss for cherry tomatoes packaged in LDPE and LDPE/10% AC trays and stored at 23°C and 85% RH for 9 days. In both packaging systems, weight loss was directly proportional to the storage time and was less than 1% after 9 days. This can be attributed to both packaging systems being wrapped with a good barrier to water like LDPE film and no adsorption of water by the trays containing AC. The observed results are similar to the ones reported by Bailen et al. (2006) who reported a <1% weight loss for tomatoes when packaged in bags with 5 g of sachets containing AC. Taechutrakul et al. (2008), however, observed a weight loss of > 9% for tomatoes packaged in corrugated boxes containing AC and palm shell charcoal. They reported that the higher weight loss compared to the controls was due to the greater water absorption by AC. Transpiration in cherry tomatoes results in shriveling rendering the fruit unacceptable, which did not happen with the developed package.

Figure 4.6 illustrates the changes in O_2 and CO_2 content within the packaging systems with LDPE trays and with LDPE/10% AC trays. In both packaging systems, O_2 content decreased and CO_2 content increased due to the respiration of the cherry tomatoes. After day 3, no further changes in gas concentration were observed due to the equilibrium reached between the respiration of cherry tomatoes and diffusion of gases through the LDPE film. Fagundes et al. (2015) observed similar equilibrium in cherry tomatoes after 100 hours of storage at 5°C. The equilibrium was attained earlier (within 72 hours) in this study due to the higher temperature (23 °C). No statistically significant differences in O_2 and CO_2 contents were observed between the two packaging systems except for a slight increase in the CO_2 content (0.5 %) of the packaging systems with LDPE/10% AC trays at day 9. No differences in O_2 content were observed in the presence of

10 % AC. Salveit (1997) observed that 3–5 kPa O_2 (minimum) and 3–5 kPa CO_2 (maximum) was the best gas combination for red tomatoes under controlled atmosphere storage conditions while Ben-Yehoshua et al. (2005) recommended 3–5% CO_2 and 3–5% O_2 for ripe tomatoes in modified atmosphere storage.

Figure 4.6 illustrates the evolution of ethylene in the headspace of the packaging systems with LDPE trays and with LDPE/10% AC trays. In both packaging systems, ethylene content increased due to the production of ethylene by the cherry tomatoes. No differences in ethylene content were observed in the presence of 10 % AC. Based on the results obtained in chapter 3, the ethylene adsorption by AC under medium and low RH and 23 ^oC occurs within the first 24 hours. Hence, the saturation of AC could have happened before day 3, when the first measurements were taken. Therefore, the initial data on ethylene adsorption was missed and not many significant changes were observed after that. Differences were observed in the amount of ethylene adsorbed in the concentration study compared to the shelf-life study because during the former the trays were studied in glass jars. Also, higher amounts of ethylene (20 ppm) and CO_2 (40%) were present in the jars compared to the packages. The trays have a potential to adsorb ethylene. Therefore, further studies are necessary to find correlations between the amount of AC, ethylene adsorption, and its applications in extending produce shelf life.

4.3.3.2 Physico-chemical evaluations

The soluble solids content of the packaged cherry tomatoes stored at 23^oC and 85% RH for 9 days is presented in Table 4.3. An increase in the total soluble solids content was observed in both LDPE and LDPE/10% AC trays. Significant differences were obtained between the two trays. An increase in soluble solids concentration is associated with ripening of fruit as the days proceed (Martinsen, & Schaare, 1998).

Table 4. 3 Changes in total soluble solids content of cherry tomatoes packaged in LDPE and LDPE/10% AC trays and stored at 23ºC and 85% RH for 9 days.

Sample	**ºBrix**		
	Day 3	Day 6	Day 9
LDPE tray	6.140±0.054a	6.880±0.044a	6.925±0.095a
LDPE/10% AC tray	6.320±0.109b	6.720±0.083b	7.285±0.083b

Means with same lowercase letters within the same column are not significantly different based on the ANOVA results at 5% significant level.

4.3.3.3 Microbiological evaluations

Figure 4.7 shows the fungal growth of cherry tomatoes packaged in LDPE and LDPE/10% AC trays and stored at 23ºC and 85% RH after 6 days. 2.85% of the tomatoes presented fungal growth in the LDPE 10% AC trays while a higher damage rate of 8.57% was observed in the LDPE trays. However, no microbial growth was observed in any of the trays at days 3 and 9. The unusual fungal decay on day 6 may be due to the higher microbial load on the tomatoes tested in that day.

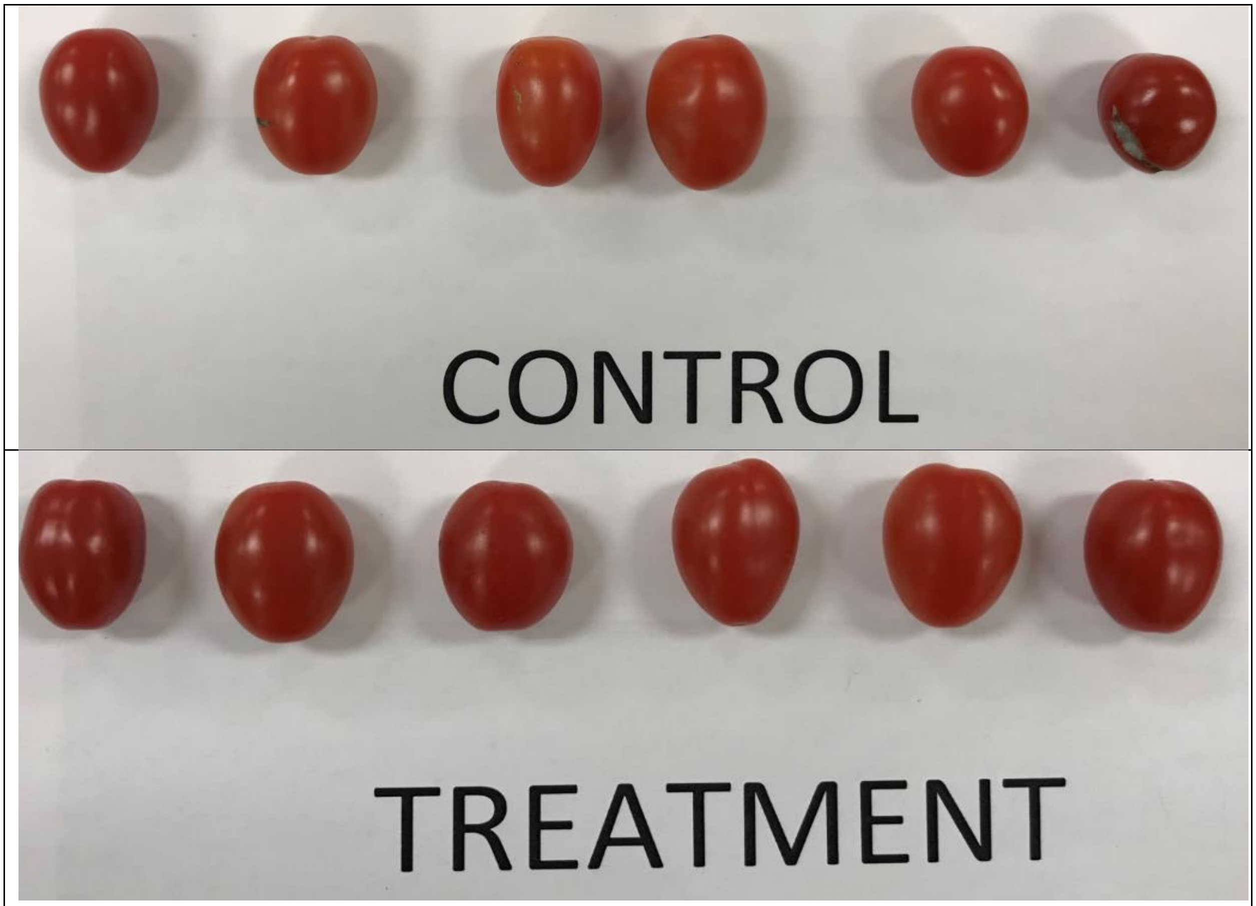

Figure 4.7 Microbiological evaluation of the cherry tomatoes packaged in LDPE and LDPE/10% AC trays and stored at 23^{o}C and 85% RH after 6 day

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CHAPTER 5

CONCLUSIONS

5.1 Conclusions

The following conclusions were drawn from the study, among the tested scavengers (potassium permanganate, two activated carbons, two zeolites and metal organic frameworks), activated carbon was selected because it had second best ethylene scavenging capacity at high RH regardless of the temperature. Activated carbon can be easily obtained from agricultural waste and is approved for food contact by the FDA contrary to potassium permanganate, which is not used for direct contact with food products. Among the tested petroleum-based and bio-based plastics, low density polyethylene was chosen as the packaging material because of its adequate barrier to both water and ethylene. A thermoformed tray containing 10% activated carbon was developed. The developed tray had similar of thickness profile, thermal, mechanical, and barrier properties compared to the tray without the activated carbon and showed ethylene removing capability. Cherry tomatoes could be packaged and commercialized in the developed trays, however, further studies on the effect of the developed ethylene removing trays on the shelf life extension needs to be carried out.

5.2 Future work

Activated carbon has been proven to have ethylene removing capacity, it can be further enhanced by the treatment of certain catalysts and metal ions such as palladium (Pd) etc. In terms of developing a tray further studies are required to optimize and reach the maximum concentration of activated carbon that could replace the polymer. For tray design, transparent lids could be developed for the tray, also different sizes and shapes could be explored by changing the mold design used in the thermoformer. Also, extrusion processing instead of compression molding could be considered for forming the sheets used for tray development. Also the potential of micro perforating the sheets could be considered for balancing the gas composition and package headspace. The developed trays are black in color that gives a good contrast on packaging on produce such as cherry tomatoes. Studies on how does color of package (transparent, white, black) influence consumer behavior could be carried out.