PREDICTIVE MODELING OF PECAN QUALITY DURING COMMERCIAL STORAGE AND DISTRIBUTION

by

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(Under the Direction of Fanbin Kong)

ABSTRACT

Pecan is a high fat hickory nut which is susceptible to rapid physical and chemical deterioration, affected by post-harvest conditions. Some of the external factors such as relative humidity (RH), temperature of the surrounding environment and storage duration are the major factors affecting pecan quality. The aim of the project is to study quality changes during storage. Three cultivars (Stuart, Pawnee and Desirable) were stored at various temperatures (0°C to 40°C), relative humidity (RH, 30% to 90%) and packaging materials (LDPE, PE, laminate, PE-Nylon). The effect of environmental conditions was studied and changes in pecan color, texture and lipid oxidation status during storage was explored. For the first time, effect of RH on pecan color was explored. It was recorded that under high RH conditions (>50%), rate of color deterioration increased, and pecans turned dark brown as opposed to reddish brown under low RH conditions (<50%). The extent and difference in storage stability under varying environmental condition was explored via sensory evaluation. The pecans stored in metallic laminates (with N_2 flushing) experienced least color, aroma, texture and lipid oxidation degradation (even under extreme conditions i.e., 40°C storage temperature) followed by PE-Nylon (vacuum

packed) and LDPE. The computer-aided predictive models were developed to estimate changes in pecan quality (color, texture, lipid oxidation status and sensory) at different storage and packaging conditions. For the first time, artificial neural network model was developed, capable of estimating sensory perception score (from human's perspective) based on concentration of volatile compounds present in pecans and/or generated during storage. These models has been made available online for free use to researchers, pecan growers and processors. This information will allow pecan growers and processors to select best storage conditions and packaging methods for improved quality and extended shelf life of pecan products. The results from this project will contribute to a more consistent and sustainable supply of pecan and ensure that the US pecan industry remains competitive in the international marketplace.

INDEX WORDS: Quality, pecan, storage, oxidation, texture, lipid, neural, color, sensory

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DEDICATION

To my family,

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CHAPTER 1

INTRODUCTION

The U.S. is the world's leading producer of pecans, contributing 40-50% of the world's pecan production where Georgia (US) alone produces one-third of pecans sold in the world market (Worley, 1994). After harvest, various environmental conditions during storage and distribution can adversely impact the quality of nutmeats. Pecans are subjected to various storage conditions during transportation, storage, and distribution post harvest. A big amount of Georgia grown pecans are exported to other countries in which pecans may encounter adverse storage conditions, and the quality can deteriorate significantly during the long-time transportation and storage.

The shelf life and quality of pecans depend on compositional as well as external factors. Color darkening, lipid oxidation and the resultant rancidity flavor, and texture degradation (loss in crispness and crunchiness) are the major issues relating to inferior pecan quality. Relative humidity (RH), temperature of the surrounding environment, storage duration, and packaging methods are the major factors contributing to the physical, chemical and biological reactions in pecans and the subsequent quality changes (Brison, 1945). Different pecan cultivars may have varying storability due to their different composition (Thewes et al. 2021). Processing methods such as conditioning and roasting, may also affect the pecan storability.

In pecans, the antioxidants and bioactive compounds such as phenolic acids, gamma tocopherols, anthocyanidins etc. possess health benefit effects that are useful for

maintaining healthy human body. A clinical study done by Rajaram et al 2001 investigated the effect of pecans rich in monounsaturated fat as an alternative to the Step 1 diet in modifying serum lipids and lipoproteins in men and women with normal to moderately high serum cholesterol. The authors recommended pecans as a part of prescribed cholesterol lowering diet of patients or habitual diet of healthy individuals. It is crucial to ensure that pecan quality is preserved during the processing, handling, and storage and also, to understand how these factors affects nutritional quality of pecan.

The work done on assessing the quality changes of pecans during storage is very limited. Erikson et al (1994) conducted a study in which raw and roasted almonds were stored at 24˚C and RH of 55%, 65%, respectively and a predictive relationship for rancid aroma, rancid flavor and crunchiness was developed using instrumental measurements. Oro et al. (2008) evaluated two packaging methods, i.e., polypropylene (PP) plastic containers and nylon-polyethylene plastic films under vacuum, on the quality of pecan kernels stored at 23°C for up to 150 days. Dull and Keys (1988) also studied effect of various packaging materials and methods on pecan quality stored at 24°C, 60% RH under continuous lighting for 6 months simulating market display conditions. These studies indicated proper packaging can help maintain good quality of pecans by reducing moisture migration and oxygen transferred from ambient environment. A storage study was done Magnuson et al 2015 to evaluate changes in the flavor profiles of 16 different pecan varieties as kernels aged at room temperature. The authors found an interaction between time and cultivar for rancidity, bitterness, and sweetness. The rancidity, bitterness, and sourness increased over time for all 16 cultivars while sweetness decreased for all cultivars.

Anzaldúa-Morales et al. 1999 studied the effect of freezing rates, storage temperature, and thawing rates on texture of pecan kernels using texture profile analysis (TPA). The authors concluded that freezing and thawing at high rates had the least effect on pecan texture. Even though abovementioned studies try to address changes in pecan quality, the variables and levels chosen do not reflect actual transportation and storage conditions. In most of the studies, pecans were kept at ambient temperature (20-25°C) and RH conditions (55-65%). Moreover, the cultivars or varieties of pecan chosen for previous studies were based on the availability rather than economic importance. This project aims to investigate pecan quality changes at various storage conditions and develop mathematical and probabilistic model to understand the impact of temperature on pecan quality. The storage conditions will cover higher temperature range (temperature: up to 40˚C, RH: up to 90%, storage duration up to 500 days) that may occur during commercial storage and transportation.

The **central hypothesis** for this investigation was that the quality of pecans will undergo changes depending on storage temperature and RH. In addition to that, the rate of deterioration of pecan quality would vary with different packaging material, conditioning methods and modified atmosphere. The lipids in pecan would deteriorate due to oxidation, color will darken, and texture will change (depending on environmental conditions). To test our central hypothesis, following objectives were proposed:

1. To study the effects of temperature (up to 40 °C), RH (up to 90%), packaging material (Low Density Polyethylene [LDPE], Polypropylene [PP], Polyethylene [PE]PE-Nylon and laminates), modified atmosphere (air, vacuum, and N_2) and conditioning on color, texture lipid oxidation status and sensory properties of pecans

2. To develop mathematical and probabilistic model capable of predicting the changes in pecan quality (color, texture, lipid oxidation and sensory attributes) due to varying environmental and processing conditions during storage.

The long-term objective is to help Georgia pecan growers (and eventually US) to increase the market share of their product globally. As United States pursue selling more pecans internationally, this research will aid in improving and maintaining the pecan quality during long time transportation and distribution, which is critical for US pecan to remain competitive in the international marketplace.

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CHAPTER 2

LITERATURE REVIEW

EFFECTS OF POSTHARVEST HANDLING AND STORAGE ON PECAN QUALITY[1]

[1] Prabhakar, H., Sharma, S., Kong, F. 2020. *Food Reviews International*. 1-28. Reprinted here with permission of the publisher.

Abstract

The United States is the world's leading producer, consumer and exporter of pecans and currently experiencing high demand for pecans from countries around the world. Environmental factors such as temperature, RH, light, etc. under pecan storage, transportation, and distribution can adversely affect its quality attributes such as color, texture, oil quality, and phytochemical content. The diminished pecan quality reduces consumer acceptability, hurting the profits of growers and processors. With over 1000 varieties, pecan is one of the most scantily examined research topics for its commercial importance, quality changes, and alteration in the phytochemical profile including degradation of phenolic and liposoluble compounds. Most importantly, there is no review that critically analyzes and discusses the changes in pecan quality during storage. This review scrutinizes the factors influencing the quality of pecans, the underlying concepts, and explanation of the causation of these transitions. The central objective is to provide a comprehensive analysis of work done on pecan quality so far and propose some future research ideas. This thorough piece of work is intended to serve the US pecan industry by helping them understand the scientific bases of quality change in pecans and suggest for them some methods to improve the pecan quality.

Introduction

Carya illinoinensis (Wangenh.) K. Koch, commonly known as pecan, is a native plant species found in the United States (US) that has been transformed into a notable horticultural crop [1]. The US is the world's leading producer of pecans, contributing to 80% of the world's total pecan production. Pecan is one of the native crops to US (viz. potatoes, corn, sweet potatoes, beans etc.) which are cultivated commercially outside the US. Many countries such as Mexico, Australia, South Africa, Israel, Brazil, Argentina, Peru, China and Uruguay, have a climate suitable for growing pecan thus, competing with US pecans in the international market [2]. During the last decade, the US pecan crop production varied between 250 & 300 million lbs, corresponding to a value of 560 to 700 million USD [3]. Inside the US, commercial pecan production has been reported in 15 states viz. Alabama, Arkansas, Arizona, California, Florida, Georgia, Kansas, Louisiana, Missouri, Mississippi, North Carolina, New Mexico, Oklahoma, South Carolina, and Texas. Georgia has been the highest pecan producing state in the US for a long time, contributing over one-third of the total pecan production in the country. However, a more recent report published by NASS[3] stated that New Mexico has taken the number one spot in the US as a pecan producing state. New Mexico has produced 96.6 million pounds of pecan in 2019, followed by Georgia at 69.0 million pounds. In 2018, Georgia state was hit by Hurricane Michael which destroyed most of the older pecan bearing trees, adversely affecting the yield in the subsequent years. Despite the bad weather, 2019 pecan production in US was up by 14% from the previous year.

The pecan per capita consumption in the US has held nearly constant over the past several decades, ranging from 0.3 pounds to 0.6 pounds, making the US the highest

pecan consuming country in the world [4]. In 2019, approximately 45% of pecans grown in the US were exported to other countries, valuing over 470 million USD [5]. Major buyers of US pecans include Mexico, Hong Kong, Canada, Netherlands, Vietnam, China, UK, Israel, Germany, and France [5,6]. In 2019, the import price of shelled pecan varied from $3.00 to $4.50/lbs [5]. Western Schley, Stuart, Desirable, Wichita, Sumner and Pawnee were the major cultivars of pecans traded in the market. These cultivars possessed high disease resistance, high yield, and high percent kernel after shelling, turning in more profits for growers and processors.

Newly planted pecan trees can take anywhere between 5 to 10 years before producing nuts [6]. The pecan trees are alternate bearing which means the plant will give high yield every alternate year. Although alternate bearing is internally regulated by the plant, however, poor orchard management can affect by cycle resulting in lower yield from pecan trees. Sparks [7] suggested several management practices for better yield including control on insects and diseases, extensive use of irrigation, optimum sunlight exposure and correction of zinc, potassium, nitrogen, and magnesium that can help in maintaining a commercial pecan orchard. With an ensured and nearly constant supply of pecans throughout the year due to modern farming practices, growers want to be definitive on determining the time of the year to sell their pecans. Thus, many pecan growers have shown inclination towards harvesting and storing nuts for later sale to maximize profits, avoid deterioration of surplus harvest and ensure a constant supply of pecan both within and outside the US [3]. It has been anticipated that over 50 percent of the 2020 season's crop will go into cold storage [8].

After harvest, pecans are subjected to varying environmental conditions during its storage, transportation, and distribution for both domestic and international trade. During transit, pecans may encounter adverse storage conditions where the pecan quality deteriorates significantly. Figure 2.1 presents a summary of the different factors that affect the quality of pecan. Color darkening, lipid oxidation, and the resultant rancidity flavor, and texture degradation (loss in crispness and crunchiness) are the major issues related to inferior pecan quality [9]. There are several factors that can contribute to the changes in pecan quality during storage, including composition (Moisture, lipid content, phytochemicals including flavonoids, lipid-soluble compounds, minerals, phenols), processing (conditioning, drying, freezing, moisture adjustment, lipid extraction), packaging (types of packaging, modified atmosphere), and environmental conditions (relative humidity, temperature, oxygen, light). This review aims to provide insights into physical and chemical changes occurring in pecans due to these factors. Most of the research discussed in this review is over twenty years old. This is because very few organizations other than US Department of Agriculture (USDA) have actively published on pecan quality. Even though extensive research has been done on pecan quality changes, there are still numerous aspects that are left unexplored. The literature does not explain well the scientific phenomena involved in the changes occurring in the overall quality of pecans and difference in quality attributes across different commercially important varieties. An understanding of the expected changes in pecan quality during storage can help growers and processors select the right kind of environmental and packaging conditions to achieve enhanced shelf life of the pecan kernels. Discussion addressing these concerns is likely to help in designing of the future studies on pecans. The growing

importance of mathematical modelling and the scope for implementing regression and kinetic models to predict changes in pecan quality during processing and storage is discussed.

Pecan Harvesting

Since harvested pecans can have moisture levels as high as 30% [10], drying them quickly is essential to retard changes in their quality. Despite the antimicrobial properties that pecan shell has [11], the mechanically harvested pecans falling on the soil must be collected immediately to prevent initiation of potential mold growth due to the increase in moisture of pecan. Thus, the first goal of the grower should be to remove pecans from the orchard floor at the earliest and dry them quickly. This prevents the chance of mold growth in pecans due to the decrease in water activity (aw) [12]. Pecan is most susceptible to mold growth, specifically Aspergillus spp. [13] and Penicillium spp. [14] and it has been traditionally advised for processors to bring the pecan nutmeats to the moisture level of 4.5% or lower before storage to control mold growth [15]. However, it has been argued that using aw is a much more reliable indicator of mold growth instead of moisture content. Beuchat[16] demonstrated how pecans, having moisture content between 4.5 to 5.7%, had the aw < 0.68 and did not exhibit any mold growth. The differences in moisture content and resultant moisture activity across different pecan types can be attributed to the varying levels of lipid content occurring naturally in these pecans (Table 2.1).

Color of Pecans

The color of pecan has been conventionally used as a measure of the overall quality of the kernel. It is considered as the main indicator of freshness and quality [17]. The wholesale distributors and retailers ranked color of pecans as the top-quality criteria [18]. The United

States Department of Agriculture (USDA) has developed rubber pecan models (Pec-MC-1-1968) based on four-color standards for pecans namely golden, light brown, medium brown, and dark brown [19]. Thompson et al. [20], however, considered the established USDA grades inadequate and argued that the defined standard was established for extremely poor-quality kernels. The authors suggested a simplified Munsell color rating system (Hue, Chroma, Value) with six color classes instead of four, which could be better suited for the pecan industry. Several techniques have been used in previous research to quantify pecan color. Hunter colorimeter instruments have been the most suited equipment to objectively measure the color of pecans in terms of lightness or value, hue (shade or color), and chroma (color intensity). Furthermore, a (- a, green to +a, red) and b (-b, blue to +b, yellow) are two other instrument parameters that indirectly reflect the visually informative parameters of hue and chroma [20].

The association of dark color or discoloration in pecans as marker of poor quality has been discouraged by the researchers for quite some time. Dark color does not necessarily indicate poor kernel quality and a light color does not always indicate good quality pecan [21]. The characteristic golden-brown color of a pecan kernel is due to its pigments, which absorb and reflect lights in various wavelengths of the visible spectrum [22]. Carotenoids and flavonoids are the most commonly found pigments in the nuts [23,24]. Investigation has revealed that leucocyanidin and leucodelphinidin are the major flavonoids and carotene and xanthophyll are the major carotenoids responsible for the characteristic golden yellow color of pecans [23,25]. As these pigments react with oxygen present in the air, oxidized compounds are formed which impart discoloration to pecans [26]. Also, there is no reported evidence of any association between off-flavor and

development of dark color in pecans [27]. Despite this revelation, kernel color continues to remain a primary factor in the judgement of the quality of pecans. As long as the present color-based price structure remains intact, the growers will always attempt to provide light golden-colored pecan kernels to consumers [28]. Various pre and post- harvest factors affecting pecan color have been presented in Table 2.2. The effects of several extrinsic (temperature, processing, oxygen, etc.) and intrinsic (variety and phytochemicals) factors affecting pecan color are summarized below:

Temperature:

The oxidation of pigments resulting in discoloration is one of the several chemical reactions that occur in the pecan's matrix during storage. The rate of these chemical reactions increases with temperature; this causes discoloration in pecans early on [29]. Besides the exposure of kernels to temperatures greater than 37.8°C, or prolonged heating periods has been shown to darken the pecan color [30]. Figure 2.2 (unpublished data) depicts the differences in color of pecans stored under different conditions. As a matter of fact, the post-harvest storage of pecans under freezing and refrigerating conditions have little to no effect on pecan color [31]. Blackmon [32] analyzed the changes in pecan (Stuart and Curtis) color during storage at freezing (-17.8°C) and room temperature (22°C). At higher temperatures (22°C), the pecan color started to darken, accompanied by an increase in red or orange hue, which resulted in the color change from tan to reddish-brown. Furthermore, the influence of the temperature on shelled pecans was greater than the in-shell pecans; the shelled nuts developed relatively darker color than in-shell nuts at room temperature. No significant deteriorative changes occurred in shelled and in-shell pecans at freezing

temperature. Wright [31] also conducted a series of storage tests on unshelled and shelled pecans (Schley). The pecans were exposed to air having 75% RH and temperatures varying from 32°F (0°C) to 70°F (21.1°C) for a duration of 3 to 30 months. The shelled pecans kept at room temperature darkened in only 4 months. Contrary to this, pecans stored under refrigeration and freezing temperature experienced infinitesimal color change. The shelled pecans stored under refrigeration did not experience a significant change in quality attributes for up to 3 years. The idea of using low temperature, in combination with other processing techniques, was also studied to measure the degree of effectiveness in preserving the original characteristics of pecans at freezing temperatures [29]. The pecans (Schley) harvested in 1962, was stored in hermetically sealed can at -20°C for 25 years. The same crop, harvested in 1986, was sealed, stored in a dark place at -20°C for 10 months, and used as a control. The instrumental analysis revealed that total change in color (ΔE) increased, and the hue angle diminished significantly with time (from a statistical viewpoint). However, the observations obtained from the sensory evaluation showed that the panelists could not find any difference in the appearance of the treatment and control. The pecans experienced minimum physical, chemical, and biological changes after 25 years of long storage. Likewise, the influence of temperature on color has been reported in other nuts. The hazelnuts (filberts) stored at room temperature experienced a higher rate of quality degradation than the hazelnuts stored at refrigeration (4°C) and freezing temperatures (0°C); the color changed from brown to reddish-brown at a higher temperature [31]. The three varieties of walnuts (Chandler, Hartley, and Loli) stored at freezing (0°C) and room temperature (20°C) had a similar effect on the color; the temperature significantly influenced the lightness (L*), hue (h°), and whiteness index (WI)

of all three cultivars of walnuts [33]. Walnuts stored at 0°C exhibited higher L*, h°, and WI values than those stored at 20°C, indicating that lower temperature abated color darkening in the walnuts.

***Conditioning*:**

Wet conditioning:

Albeit the lower temperature is beneficial for conserving pecan quality, exposing pecans to high temperatures for the shorter duration can lengthen the pecan storage life. Wet conditioning is a pre-requisite for shelling, which involves adding moisture and heat to the pecan kernel, to improve the yield of kernel halves [34]. The moisture content of in-shell pecans increases from 4% to 8% which aids in cracking of the shell [9]. The traditional process includes soaking the pecans in 85°C water or treating them with steam for 3-5 min and holding them for 20 min at ambient conditions before shelling [35]. The heat treatment during conditioning sanitizes the outer shell, making them more pliable, and preventing them from breaking into pieces during cracking [34]. It also inactivates certain hydrolytic and oxidative enzymes present in the pecan matrix which can promote rancidity of pecan [36]. Even though the conditioning methods increase the shelling yield, reduce the cracking of pecan halves, and deactivates deteriorative enzymes, pecan kernels may darken due to exposure to high temperatures [34]. Forbus Jr. and Senter [35] investigated the color change in pecans (Stuart and Schley) due to different wet conditioning treatments viz. soaking in-shell pecans for 1 hour in 21°C chlorine water (concentration-1000 ppm) and holding for 12 hours under ambient conditions before cracking; soaking in-shell pecans for 3 minutes in 85°C water bath and holding for 20

min at ambient conditions before cracking; and subjecting to atmospheric-steam in retort for 3 min and holding for 20 min at ambient conditions before cracking.

The authors examined the change in color as a/b ratio. A larger a/b ratio denotes a darker orange color [37], which indicates the color transition from bright yellow to dark red/brown. The a/b ratios were significantly higher for steam treated pecan as compared to the rest of the treatments, demonstrating deleterious effects of heat on pecan color. However, the rate of deterioration of pecan quality remained unaffected even after conditioning. The exposure of in-shell pecans to steam caused an initial darkening of kernels; however, the degree of color change was not significant enough to affect its selling price [28].

Dry conditioning:

Tannins are one of the major flavonoids in pecan shells and have been reported to be present in a much higher quantity than pecan kernel [38a]. The exposure of in-shell pecans to water (during wet conditioning) causes leaching of tannins from the lining or middle partition of the shells to kernels. The leached tannins contribute towards change in hue, imparting dark brown color and bitter taste, highlighting the role of water in the total color change of pecans [34,39]. It has been propounded that heating the in-shell pecans in the absence of water is one way to minimize or prevent the darkening caused by tannins. The dielectric heating was posited as a processing technique suitable for the dry conditioning of pecans. Dielectric heating or radiofrequency heating is an innovative technique, where electromagnetic energy is transferred directly into a food product, initiating volumetric heating (heating via the volume of liquid in food) due to frictional

interaction between molecules. Senter et al. [40] exposed pecan kernels to dielectric heating for 1, 2, and 2.5 min at 43 MHz. Internal temperature (IT) was measured using thermocouple; average internal temperature (IT) attained for the exposure of 1, 2 and 2.5 minutes at 43 MHz was 88°C, 136°C, and 156°C, respectively. Dry conditioned pecans were compared with wet conditioned pecans (steam treatment for 4 min, IT-93°C) and the change in pecan color was assessed. The Hunter color values (Lab) indicated that the dielectrically heat-treated pecans kernels were lighter (higher L value) and brighter yellow than the steam treated pecans. This experiment validated the role of water in the darkening of pecans, provided a solution for the undesirable color change, and demonstrated the feasibility of using innovative processing techniques for conditioning of in-shell pecans.

***Cultivar*:**

The cultivars do not only affect the chemical composition of pecan but also certain physical properties like pecan's color. Kays and Wilson [41] undertook a study to investigate different shelled and unshelled pecan cultivars (Desirable, Schley, Shawnee, Stuart, Mohawk, 48-15-3, Chickasaw, Caddo, and Cherokee) for their resistance towards deleterious color changes during 12 weeks storage at a temperature varying from 23.9 to 26.7°C (75-80°F) under unspecified RH. The data revealed that the order of highest to lowest intensity bright yellow color of freshly picked samples was Schley > Stuart~ Shawnee> Caddo> Cherokee> Desirable> Chickasaw> 45-15-3> Mohawk. In general, shelled pecans exhibited a greater decline in color quality than in-shell pecans. Schley, Cherokee, Caddo, and Stuart exhibited relatively high rates of color degradation whereas

Mohawk, 48-15-2, and Shawnee displayed the lowest change in color values over 12 weeks of storage for both the shelled and unshelled pecans. An independent study by Forbus Jr. et al. [35] published similar observations and revealed that a/b ratio for the Schley was higher at the beginning of storage study and increased at a more rapid rate than Stuart, underlining that Schley was more susceptible to color darkening than Stuart. This difference in gradual color degradation shed some light on cultivar's innate resistance towards the breakdown of pigments such as flavonoids and carotenoids.

***Liposoluble-compound Content*:**

It has been argued that the presence and modification of lipid-soluble compounds are somewhat responsible for contributing to the total color of pecans. γ(gamma)- tocopherol is one of the most potent lipid-soluble antioxidants present in pecans, which forms a red-colored compound (chroman-5,6-quinone) upon oxidation [42]. Pecans have also been reported to contain another lipid-soluble color compound known as carotenoids [23]. As these phytochemicals are colored chemical compounds, theoretically, their removal could cause color change in pecans. Yao et al. [43] investigated the extent of color change in different cultivars (Stuart, Desirable, and Schley) by correlating lightness and hue with γ-tocopherol content. Cultivars were stored at 23.9°C and 60-70% RH and 0.6°C and 75% RH for 12 months. The authors found a very low positive correlation between tocopherol levels and Hunter color parameters in pecans stored at 0.6°C. Contrary to this, a moderate to strong positive correlation was found between the concentration of γ-tocopherol and Lightness (L), hue, and saturation index in all three cultivars stored at 23.9°C. The study

suggested that change in the concentration of γ-tocopherol in cultivars could explain the change in color and their intensity of pecans during storage at room temperature.

As these lipid-soluble color compounds undergo change or are extracted from the pecan matrix, their effect started to become visible on the color of pecans. Pecan nutmeats became more whitish in appearance as the more oil was removed from the pecans [44]. The percent oil removed tends to affect the lightness and intensity of color; both lightness and chroma values have been reported to increase with as more the amount of lipid extracted from the pecans goes higher. The hue or color might shift slightly away from bright yellow. A similar experiment has been conducted with other nuts and the outcomes were strikingly similar. Walnuts and pecans belong to the common plant family of Juglandaceae and share a lot of similarities in terms of physical and chemical characteristics. The difference in the color of full-fat walnuts and reduced- fat walnuts was very prominent [45]. The lightness or whiteness was significantly higher in the reduced-fat walnuts than the full-fat walnuts. The testa or outer yellow layer of reduced lipid pecans had lower hue value (in degrees) than unextracted pecans; the color deviated from bright yellow to dark red due to the formation of chroman-5,6- quinone (an oxidation product of γ-tocopherol). The long-term storage of nuts under inappropriate conditions could also induce unwanted color change due to oxidation and transformation of lipid-soluble phytochemicals (Table 2.2).

***Oxygen*:**

Kays and Wilson [26] emphasized on the influence of oxygen on the color of pecans. The study concluded that a higher concentration of oxygen leads to darker kernels. The

presence of oxygen is suitable for the formation of phlobaphenes, a condensed tannin formed via oxidation and polymerization of leucocyanidin and leucodelphinidin [25]. As the concentration of phlobaphenes in pecans builds up, a characteristic dark brown color starts to develop [45] which diminishes the visual appeal of pecans. This effect is more pronounced at higher temperature and oxygen concentration [46]. Since oxygen seems to be an important part of the reaction, replacing it with other gas(es) or eliminating it would significantly delay the color change in pecans.

***Light*:**

Heaton and Shewfelt [47] studied the effects of light exposure on the color of pecans. The pecans were exposed to various light sources including sunlight, fluorescent light, and cool white light in flexible pouches; pecans stored in the sunlight for the duration of 24 hours experienced significant darkening whereas pecans kept under cool white fluorescent light were relatively less darkened. Santerre [9] expounded that the cool white light radiated by the light source consists of narrow spectrum of ultraviolet radiations (as compared to sunlight). The UV radiations can cause pigments to degrade, and form impart dark color to pecans. Hence, the pecans stored under cool white light experienced relatively less color change than the pecans stored under sunlight.

Texture of Pecans

Like color, the texture is another robust indicator of pecan quality. Bourne [48] defined food texture as the association of physical attributes discerned from food structure by human senses, such as touch, deformation & disintegration (mouthfeel), and flow of the

food under a force, measured objectively as a functions of mass, time, and distance. Biting into the pecans and not finding them crispy or crunchy can discourage the buyers from consuming it. This makes the texture a critical quality parameter in the pecan market as it can sway consumer's decisions to purchase. Furthermore, the texture of pecans is an important factor for food processors as well, since the quality of their products (e.g., baked goods) may depend largely on the texture of raw materials of the final product [49]. An instrumental method (especially empirical techniques) must reflect considerations of what consumers perceive when they eat the food [50,51]. This first impression is very important in the detection and description of the texture. The order for the detection of textural properties by human senses is as follows; touch, first bite, the second bite, chewing, swallowing, and residual sensations [51]. Before 1987, there was not any definite method to objectively measure the pecan texture. Most researchers were relying on sensory panelists to evaluate the pecan's texture, which was not a standalone method for comparing the outcomes of change in pecan texture reported by different studies. Resurreccion and Heaton [52] came up with a method for objective texture evaluation to study any distinction in early and traditionally harvested pecans. The authors used Instron Universal Testing Machine (Model 1122, Canton, MA) to conduct a puncture test and calculated the shear force (in Newtons/g) required to cut the pecans halves using a blunt blade attachment. A trained panel evaluated the pecans on the 5-point hedonic scale and the observations were compared with objective analysis. Even though the study found a moderately strong correlation between objective and subjective analysis, the method used in the experiment was argued upon as certain facets were not very clear. Pecans are non-uniform, irregular, and have semi-infinite geometry. These small irregularities on the surface of the test

product have the potential to give large errors during deformation [48], rendering the test method less accurate. So, it was suggested that using a uniformly sized sample from the product of interest can give a precise and accurate objective measurement [53]. A uniform pecan sample for texture analysis could be prepared by driving a cork borer through pecan kernel (perpendicularly) and taking out cylinders of uniform dimensions. Ocon et al. [53] analyzed the cylinders were taken out from the four different cultivars of pecans (Western Schley, Wichita, Mahan, and Barton) for texture via texture profile analysis (TPA), compression, puncture and bending tests using Texture Analyser TA-XT2 ® (Texture Technologies Corporation, Scarsdale, New York/Stable MicroSystems, Haslemere, Surrey, UK). A strong correlation was found between instrumental and sensory analysis. The authors concluded that compression, TPA, and puncture came closest to determining the texture of pecans for all four varieties when compared with sensory evaluations [53]. TPA is one of the most commonly used tests for texture analysis which mimics the compression of food in-between human jaws. This compression test can quantify numerous textural parameters including fracturability, cohesiveness, springiness, chewiness, gumminess, etc. The choice of selecting the parameters is of utmost importance and should be based on the nature of the food product. Majority of the papers published on nuts have used chewiness and gumminess as two of their TPA parameters to evaluate the texture of nuts. Even though the gumminess and chewiness both measure the force required to chew the food product before swallowing, their use depends on the nature of the food product. Where gumminess is suitable for semi-solid foods and cohesiveness for solid foods, this makes these attributes mutually exclusive and cannot be used together. Thus, this review will not discuss the reported effects on the gumminess as it is not an appropriate TPA

parameter for pecan and other nuts, the main factors responsible for change in pecan texture, such as, removal or addition of moisture, oil content, freezing and thawing, are discussed below:

Drying:

To prevent mold growth in shelled pecan kernels, various combinations of temperature, RH, and airflow have been suggested to bring the moisture content from 8% to 4.4% [54]. Chinnan [10] determined the drying rate for in-shell pecans (Stuart) by keeping them at 34°C (95°F), 48% equilibrium RH, and an airflow of 100 ft/min (32 m/min). The moisture content has been shown to affect the texture of food products such as wheat, rice, and several seeds [56,57,58]. The same is true for pecan as moisture plays an important role in defining its texture. With an increase in moisture in pecans, an increase in hardness, a decrease in cohesiveness, and a decrease in springiness had been observed [58]. Below 2.0 % moisture, the pecan kernels become too fragile and might experience breakage during handling and storage [59].

Freezing and Thawing:

Pecans stored at sub-freezing temperatures become brittle and susceptible to damage during handling and transportation. Anzaldúa-Morales et al. [60] experimented to study the effects of freezing methods on pecan texture. The authors concluded that hardness was strongly affected by moisture content. The high moisture (8.5% and 9.6%) and fast freezing pecans became slightly harder. The moisture content also exerted a significant effect on the chewiness of pecans. High moisture pecans were 25-40% less cohesive than low

moisture pecans (2.5% and 2.9%). The authors suggested using fracturability/hardness ratio to study the effects of freezing treatment on pecans. The water sprayed pecans had slightly higher ratios (0.88-0.99) over unsprayed pecans (0.76 - 0.88). Frozen pecans had similar fracturability/hardness ratio as pecans that were never frozen.

Surjadinata et al. [61] studied the effects of freezing, thawing rate, and multiple freeze/thaw cycles on pecan texture at two different levels of moisture content (3% and 5%). The different rate of thawing was obtained by blowing air at 25°C and a velocity of 5.5 m/s (fastest, 29 min) or 3.3 m/s (fast, 35 min) over the bags of pecans, placing bags of pecans 10-mm thick bubble wrap (medium, 78 min) and 25-mm fiberglass blanket insulation (slow, 162 min). The samples for texture analysis were prepared as suggested by Ocon et al. [53], with some modifications and were analyzed using TPA in combination with sensory evaluation by trained panelists. TPA and sensory texture measurements indicated that initial moisture content before freezing had a significant effect on fracturability; the pecans with 3% moisture content fractured much early, indicating their brittle nature. The pecans exposed to slow thawing had the lowest fracturability compared to the control (pecans without any treatment) and pecans experiencing the fastest thawing. For TPA, pecans with 3.0% moisture content are harder and more cohesive than pecans with 5.0% moisture content. However, the observations from the sensory evaluation were not in agreement with instrumental analysis. The authors pointed out that the sample was cut out of the interior of the pecan's nutmeat without the skin as compared to whole pecans where the panelists bite through the skin and meat of the entire intact pecan kernel. Additionally, the orientation of samples drawn from pecan kernel was different from what was stated in the original method. The authors also concluded that the thawing rate had

little or no impact on the texture of pecan with 3.0 % moisture whereas slow thawing rate had detrimental effects on pecans with 5.0 % moisture content. Overall, the thawing rate had little or no impact on pecan texture, and multiple freeze/thaw cycles affect pecan texture significantly, especially for pecans at higher moisture content.

Moisture addition and oil removal:

The change in the lipid content of pecans can affect their textural properties. The experiments have shown that with an increasing amount of lipid removal, pecan's texture starts to change during freezing and storage [58]. The results showed that the hardness decreased linearly by 24 to 88% of the original value as the higher amount of lipids are removed from the pecan matrix. Oil removal seems to have no impact on chewiness of pecans, however, it affected the cohesiveness of pecans by decreasing its value by 40-60% when compared to untreated pecans. An increase in oil removal also leads to early fracturing of the sample. It has been reported that longer exposure to the extraction process and higher oil removal will lead to cracked and broken kernels [62]. Anzaldúa-Morales et al. [63] tried to restore pecan texture by altering the moisture content of reduced oil pecan kernels. The moisture of full-oil and 25% reduced-oil pecans (Western Schley) was adjusted, varying from 2.43% to 19.85% by allowing them to come to equilibrium with the moisture in the air or by directly spraying them with water. TPA revealed that the kernel's hardness decreased with an increase in moisture whereas, at higher moisture levels, pecan stopped showing signs of fracturing. Springiness increased and brittleness decreased with an increase in moisture content. At high moisture levels (>15%), pecan exhibited plastic consistency, resulting in more recovery after compression. The authors were successfully

able to restore most of the original textural attributes of pecans by bringing pecan's moisture to 5%.

Lipids in Pecans

Pecans are predominantly composed of lipids. According to the USDA FoodCentral database, pecan contains 13.86% carbohydrates (dietary fiber-9.6%), 9.17% protein, and 71.97% fat [64]. Pecans are predominantly composed of lipids. As per Reference Amounts Customarily Consumed (RACC), 1 ounce or 28 grams of pecan contains, 20.0g fat, 3.9g carbohydrates (dietary fiber - 2.7g), 2.6g protein, vitamins (vitamin B6) and minerals (Iron, Calcium, Magnesium, etc.). Total fat from a serving of pecan can provide around 27% of the daily value of fat, making it an excellent source of fat. The lipid profile and lipophilic components in oil are gaining attention due to their impact on human health [67,68]; studies have indicated that the pecan oil can lower the risk of cardiometabolic diseases in obese adults [69].

Fatty acid profile of pecan oil:

A great deal of research has been conducted to determine the lipid composition of pecans; Table 2.1 summarizes lipid content and fatty acid of various cultivars of pecans grown at different locations and their methods of oil extraction. The pecans primarily contain hexadecenoic or palmitic acid (C16:0), octadecanoic or stearic acid (C18:0), octadecenoic or oleic acid (ω-9, C18:1), octadecadienoic or linoleic acid (ω-6, C18:2), and octadecantrienoic or linolenic acid (ω-3, C18:3) [9]. These fatty acids constitute almost 98% of total fatty acids in pecans. Additionally, the pecans contain small amounts of short-chain fatty acids such as decanoic or capric acid (C10:0), dodecanoic or lauric acid (C12:0),

dodecenoic or lauroleic acid (C12:1), tetradecanoic or myristic acid (C14:0), and tetradecenoic or myristoleic acid (C14:1).[17] The triacylglyceride (TAG), diacylglyceride (DAG) and monoacylglyceride (MAG) content in pecans vary from 95 to 99%, 0.3 to 1.56%, and 0.9 to 1, respectively [17]. These acyl glyceride molecules chiefly consist of palmitic acid, stearic acid, oleic acid, linoleic acid, and linoleic acid [47,70]. Furthermore, these attributes also play an important role in determining the rate of quality degradation. Different factors affecting the lipid profile, functionality, and stability of lipids in pecans have been discussed below.

Factors affecting lipid content and fatty acid profile of pecan oil:

Heaton et al. [71] measured the pecan oil content and its composition from six growing locations (Texas, Louisiana, Georgia, Florida, Mississippi, and Oklahoma) with oil content varying from 61.5% to 76.3%. Even though this is the most extensive study done on determining oil content in pecans, some studies have reported the oil content levels as low as 53% (Table 2.1). Several factors can affect the biosynthesis total oil content of pecan. The lipid synthesis in pecans does not occur at a constant rate and vary depending on the growth stage of pecan tree. It has been reported that the pecan trees in central Georgia experience an increase in lipid biosynthesis approximately a month prior to harvest in September.[55] Wood and McMeans [72] asserted that the nuts harvested before November in some regions had higher levels of oil as compared to pecan traditionally harvested after November. The rate of lipid synthesis and quantity of oil formed in pecan kernel depends on environmental and climatic conditions such as excessive rain and drought, strong winds, reduced sunlight exposure, or damage inflicted by insects, rodents,

birds or molds that occur during lipid synthesis.[9] The fatty acid profile also varies because of location and growing condition [73]; however, it was determined that the difference in concentration of fatty acids is chiefly because of nitrogen fertilizer application [71]. Pecan trees that received low levels of nitrogen for 9 years had a significantly higher concentration of C18:1 but a significantly lower level of C18:2.

Moisture:

The lipid degradation could occur generally by lipid oxidation and lipid hydrolysis. The latter results in the formation of free fatty acid (FFA) either by chemical or enzymic action. This phenomenon generally occurs in the presence of moisture, either due to moisture in matrices of food component or amassed from the surrounding environment. Previous research has shown that the free fatty acid content of pecan increases significantly when stored above refrigeration temperature [21]. The rate of increase in FFA differs during the storage of pecan oil versus oil obtained from stored pecan kernel. It has been reported that the stored pecan oil experiences a very low change in FFA [70,74]. However, the oil obtained from stored pecans had higher levels of FFA by the end of the storage period because of the presence of moisture in pecan kernel, [38,47] which can cause hydrolysis of TAG molecules and form FFA. The pecans consist of vacuoles that are responsible for the containment of the oil inside the pecans. The rupturing of these oil vacuoles, by any means (such as physical damage to pecan kernel, lipid extraction, etc.), could lead to the release of oil in the pecan matrix. The released pecan oil encounters moisture, inducing the hydrolytic rancidity. The pecans having reduced oil levels (achieved via SC-CO_2) have been reported to have higher levels of FFA at the end of ambient temperature storage than

normal or full oil pecans [47]. During SC-CO_2, even though oil cannot be fully extracted, the process can damage the cell structure, resulting in the release of oil, which, after coming in contact with moisture, induces the hydrolytic rancidity. Kanamangala et al. [47] reported that the FFA in the pecan oil had more saturated fatty acids (palmitic and stearic) than the reduced-lipid pecans throughout storage. Both palmitic acid and stearic acid increased in unextracted pecans during storage. This finding was in contrast to the observation made by Erickson [70]; the free fatty acids were higher in linoleic acid (C18:2), palmitic acid (C16:0) and lower in oleic acid (C18:1) than the TAG fraction. Kanamangala et al. [47] accounted these differences for applied lipid extraction (2 chloroform: 1 methanol vs SFE) and lipid class separation (thin layer chromatography vs aminopropyl bonded phase columns) procedures.

Oxygen:

Development of primary oxidation products –

Apart from degradation by water/moisture, the oil is also susceptible to oxidation because of the presence of oxygen in the air. The lipid oxidation involves the continuous formation of hydroperoxides TAG, the primary oxidation compounds, followed by further reactions of hydroperoxides forming simpler non-volatile and volatile secondary oxidation compounds [75]. The unsaturated fatty acids such as oleic, linoleic, and linolenic acid are highly susceptible to oxidation [76]. Higher the double bond count, the more readily the fatty acid will be degraded via oxidation to form unstable hydroperoxide compounds.

The formation of primary oxidant compounds in pecan oil has been reported to increase during the storage. Fourie and Basson [77] stored pecan at 30°C at 55% relative

humidity for 16 weeks and observed a linear increase in peroxide value (0.6 to 4.9 meq/kg of oil) with time. A similar trend was reported by Forbus and Senter [38]. Forbus Jr et al. [78] stored Stuart at 21°C and 65% RH for 12 weeks and observed an increase in PV from 0.15 to 0.55 meq/kg of oil, with exception of linearity in increase. Mcglamery and Hood [79] conducted an experiment to devise a method capable of inhibiting enzymatic activity and preserve desirable characteristics. The in-shell pecans were treated at 177°C (until the internal temperature reached 80°C) followed by immediate cooling. Another treatment was to heat pecans at 177°C, dip the heated shells in mineral oil (kept at 80°C) for 60 seconds, followed by immediate cooling. All treatments were stored for 24 weeks at ambient conditions. The peroxide value (PV) of the oils of the untreated pecans and the hot air treated nuts increased with time. The PV of in-shell pecan dipped in mineral oil did not change significantly during storage. Whenever a limited supply of oxygen is available, the formation of peroxide will gradually fall off as the free oxygen is consumed [80]. During dry heat treatment, the oxygen inside the shell was driven out through micropores of shell because of vapor formation inside pecans. With time, oxygen can enter back through shells which explains the slight increase in peroxide value in dry heat-treated in-shell pecans. The mineral oil treatment blocked the microspores, thus preventing entry of air back into the shell. As discussed previously, the degree of lipid deterioration differs for the stored pecan oil and oil extracted from stored pecans. Oro et al. [74] stored cold-pressed oil at room temperature for 120 days. For the first 75 days, the peroxide value of pecan oil increased from 0.55 to 7.23 meq/kg of oil. The stored oil tends to have a higher rate of PV increase than oil inside pecans because of the presence of numerous chemical compounds contributing to resistance in lipid deterioration, as discussed later in this review.

Subsequently, the levels of peroxide value declined due to hydroperoxide decomposition [81]. These unstable, oxidation intermediate structures degrade to form elementary compounds, also known as secondary oxidation compounds, responsible for imparting off-flavor and off-odor to food products containing oil.

Development of secondary oxidation products –

Although the original causes and the consequences of oxidative and hydrolytic degradation processes are considerably different, they seem to interact with each other and contribute to the reduction of the oil storage stability by pushing the oxidation reaction forth. The hydroperoxides are the unstable intermediates in the autoxidation reaction and form secondary oxidation products. FFAs, formed from hydrolytic rancidity, are more susceptible to autoxidation than esterified fatty acids and can break down to form simpler chemical structures, which can greatly alter the taste and aroma of oil. Some researchers have reported that FFA also acts as a pro-oxidant, which accelerates the rate of decomposition of hydroperoxides [82]. FFAs are concentrated on the surface of edible oil and have a hydrophilic and a hydrophobic group in their structure. Because of this molecular arrangement, the surface tension of oil decreases, enhancing the diffusion rate of oxygen into the oil [83].

Just like hydroperoxides, the levels of secondary oxidation products increase during storage. Pyriadi et al. [81] observed an increase in TBA value in eight different pecan cultivars stored at 60°C for 14 days and reported detectable rancidity development on the 9th day of storage. Another study by Senter et al. [84] evaluated the profile of volatiles developed in pecan for 12 weeks storage at 21°C and 65% RH using gas-liquid

chromatography (GLC). Regression analysis revealed a strong positive linear relationship between storage span and volatile concentration. The sensory panelists also detected some off-flavors and off-odors in pecan, leading to a decrease in sensory score. Furthermore, the authors found a strong negative correlation between sensory scores and volatile compounds ($r = -0.86$ to -0.95), suggesting that quantifying the secondary compounds would help in better assessment of pecan acceptability during storage. Miraliakbari and Shahidi[85a] conducted a study to evaluate the oxidative stability of different types of tree-nut oils at 60°C for 12 days. Oxidation led to the formation of various secondary oxidation products. The hexanal and nonanal were the extensively detected headspace volatiles in pecans. The authors also reported elevated levels of PV and conjugated dienes (CD). A study on raw and roasted pecans stored at 24°C in 55% to 65% RH revealed that TBA value accurately predicted the sensory scores for roasted pecans whereas CD and PV were more appropriate indicators for predicting rancid flavor and aroma in raw pecans [86]. Some researchers detected an association between primary oxidation products and sensory modalities (taste and aroma) of pecans during storage [32,38,44,77]. Because techniques like TBARS and p-anisidine value are not as accurate as chromatographic techniques in detecting secondary oxidation products, it is advisable to use primary oxidation and secondary oxidation products estimation techniques mutually to get a better understating of oxidation status of oil. As the oxidative deterioration process proceeds, the levels of undesirable chemical compounds, and the sensory properties start to change.

Minerals:

Pecans contain certain intrinsic elements, such as minerals, that can potentially promote lipid oxidation (pro-oxidants). Many metals such as Cu, Fe, Co, Cr, Zn, Pb, Ca, and Mg have been proclaimed to accelerate the oxidation of oil [87]. Senter [88] conducted a study to determine the mineral content in 10 different cultivars of pecans. The author found a significant difference in mineral content among cultivars. The average values for Cu, Fe, Cr, Mn, B, Zn, Ba, P, K, and Ca in pecan were 1.08, 2.20, 1.20, 3.28, 0.62, 7.02, 0.56, 450, 460 and 5.8 mg/100 g of dry nut meat, respectively. The difference in mineral content implies that there might be some variation in speed with which the lipid oxidation occurs during storage in different cultivars.

Phytochemicals in Pecans

This review discusses numerous studies where the change in the chemical composition of oil with storage and sensory evaluation scores were correlated. However, most of the studies did not talk about innate components of pecans that could be responsible for abating the rancidity of oil. Pecan contains a lot of important phytochemicals that can benefit human health [89]. The pecan contains phenolic and non-phenolic compounds, responsible for imparting antioxidant activity and neutralizing free radicals. The free radicals can trigger deterioration of oil leading to the formation of carbonyl compounds and causing the development of off-flavors. Some of these phytochemicals include carotenoids, flavonoids, and simple phenols (Fig. 2.3). The varying levels of these phytochemicals in cultivars could be considered as one of the many factors affecting the storage stability of pecans. Forbus Jr and Senter [38] observed the difference in the rate of formation of hydroperoxides in

Stuart and Schley stored at 21°C and 65% RH after different conditioning treatments. Senter and Forbus Jr. [90] demonstrated the effects of varieties on the rate of rancidity when Schley, Halbert, and Seedlings were stored at 30°C for 24 weeks. These authors emphasized that apart from the storage conditions (temperature, relative humidity, packaging material, etc.), the quality of pecan is also influenced by their indigenous chemical properties. According to USDA database for flavonoids, proanthocyanidins, ORAC and total phenols [91a,b,c], pecans contain 18.02 mg/100 g fresh weight of anthocyanidins, 494.1 mg/100 g fresh weight of proanthocyanin or condensed tannins, 17524 µmol TE/100 g fresh weight of ORAC value (antioxidant activity) and 2016 mg/100 g fresh weight of total phenols. These are general values and not cultivar specific because limited studies are available on phytochemicals content for different varieties of pecans. Table 2.3 summarizes phytochemicals of some of the pecan varieties that have been reported to date in the literature.

Phenolics are a major phytochemical class in pecans, consisting of molecules with one or more phenolic groups, also known as polyphenols. The polyphenols are assessed using the Folin–Ciocalteu assay, to measure total phenols or total polyphenols in the substrate [95]. Flavonoids are a subclass of phenolics which is further divided into following subclasses: flavonols, flavones, flavanones, flavan-3-ols, anthocyanidins, and isoflavones. Pecans chiefly contain flavan-3-ols and anthocyanidins, along with some simple phenols such as hydroxybenzoic acid and protocatechuic acid [84]. Also, minor amounts of caffeic acid, p-coumaric acid, resveratrol, cinnamic acid, quercetin, and kaempferol has also been found in pecans [96]. Pecans contain procyanidins and prodelphinidins [97]. These are major proanthocyanidins or condensed tannins (CT) are

formed from flavan-3-ol namely (+)-catechin and epigallocatechin, respectively, and are usually present in the combination of up to four units (tetramers) [91,98]. Apart from phenolics, there are other classes of phytochemicals which are strictly lipid-soluble viz. carotenoids and phytosterols [99]. These lipophilic, plant-synthesized chemical compounds are known to impart health benefits to humans and act as an antioxidant agent in oil [100]. Senter [28] analyzed 10 cultivars for total carotene and xanthophylls (carotenoids). The values for total carotenoids in cultivars varied from 0.897 to 1.403 µg/g of oil. The author did not find any significant difference among cultivars for total carotenoid content. Senter and Horvat [17] reported the presence of sterols in pecan oil ranging from 0.1% to 0.29%. Derewiaka et al. [101] reported six phytosterols in pecans, namely, β-sitosterol (152 mg/100 g oil), avenasterol (22 mg/100 g oil), cycloaretneol (9.4 mg/100 g oil), campesterol (6.5 mg/100 g oil), stigmasterol (2.6 mg/100 g oil) and stigmastadienol (2.5 mg/100 g oil). There has been no study exploring the phytosterol content in different cultivars. Phytosterol content could be considered as one of the significant factors contributing to the storage life of pecans as researchers have previously reported about their contribution towards the antioxidant property of other tree-nut oils [102]. Various factors affecting the levels of above-mentioned phytochemicals have been discussed below:

Flavonoids:

Senter et al. [30] monitored anthocyanidin levels in Stuart and Schley for 16 weeks kept at 32°C and with 50% RH and found a strong correlation between the concentration of flavonoids and storage period. As the storage progressed, the leucoanthocyanidin

polymerized to form phlobaphenes, which led to discoloration in pecans. The total change in anthocyanidins was comparatively less in Stuart than in Schley. Additionally, the levels of total flavanols decreased in both varieties but the authors did not see a definite trend in total phenol change over time. The effect of irradiation (0–3.0 kGy) on the phytochemical profile and storage stability of pecans has been also studied [41b]. The irradiated pecans stored at kept 40°C and 55–60% RH for 134 days. The pecans showed a decrease in the concentration of condensed tannins (CT) and total phenols, though, the antioxidant capacity increased in both varieties during storage. The authors explained that the flavanols, like catechin and epicatechin, might have polymerized to form complex substances that are more potent than monomers. These complex compounds are also known as proanthocyanidins or CT. As the results showed the levels of CT diminished with storage, this does not sound like a plausible reason for the increase in antioxidant activity. Irradiation has been proved to favor the degradation of tannins, which lead to the formation of phenolic acids. The newly formed phenolic acids might have been responsible for contributing to an increase in antioxidant activity in pecans [103].

Simple Phenols:

Senter et al. [84] studied the effect of storage on simple phenols in Stuart variety stored at 21°C and 65% RH for 12 weeks. The authors noted a significant decrease in the concentration of phenolic acids during storage viz. gentisic acid, gallic acid, protocatechuic acid, and vanillic acid along with sensory scores. The quantity of p-hydroxybenzoic acid decreased but the change was not significant. The results showed a strong positive

correlation between sensory acceptance and phenolic content. Microwave and conventional roasting also lead to decrease in phenolic content of pecans [96].

Lipo-soluble compounds:

The tocopherols are one of the very potent antioxidant compounds present in the oil. γ-tocopherol is the most active form of tocopherols and is found in abundant in pecan oil [99]. Other forms of tocopherols such as α-, β – and δ-tocopherol also present in pecans in minute quantity. However, these are reported not to possess the free radical neutralizing ability and thus, do not contribute towards total antioxidant activity in pecans. It has been reported that the storage has a negative effect on levels of γ-tocopherol [81]; Rudolph et al. [104] reported a roughly 90% reduction in the γ-tocopherol content of pecan stored at 70°C for 9 day. Yao et al. [46] reported a significant decrease in γ-tocopherol in Stuart and Schley stored at 23.9°C and 60–70% RH for 12 months. Other lipid-soluble components such as carotenoids have long been known for their antioxidant activity in presence of lipophilic electrophiles [105]. However, no studies have been reported on the changes in levels of carotenoids in pecans with storage.

Packaging & Storage of Pecans

As previously discussed, extrinsic factors, namely temperature and RH, play a significant role in the storage stability of pecans. The effects of these external factors can be abated by the containment of the pecans in packaging materials [106]. To increase its effectiveness in preserving the pecan quality, several researchers have tried modifying the internal conditions of the package by altering the gas composition. Apart from these factors, the length of potential storage and the rate at which quality is lost, despite being packaged, is

known to be related to the rate of metabolic activity of pecans. The effects of these factors on the packaging and their impact on the stability of pecans during storage have been summarized below:

Type of Packaging Material:

Typically, product respiration rate is used as an index of general metabolic activity. The produce with a higher respiration rate tends to deteriorate much faster as compared to the product having a low respiration rate. Beaudry et al. [107] determined respiratory rates of nuts of 19 cultivars of pecan in-shell and shelled after harvesting (moisture > 8%) and drying (moisture – 3%). The presence of shell and moisture content had a profound impact on the respiration rate of pecan; it was observed that presence of shell diminishes the respiration rate by 15% to 40% whereas reducing the moisture content abated the respiration rate by 99% when the moisture content was reduced from 12% to 3%. The respiration rate has been proven to be variety dependent. The researchers have suggested considering both pecan moisture and genotype when selecting the appropriate packaging material for retail storage at ambient temperature. The most efficient barrier for pecan quality degradation is the shell itself. The in-shell pecans can be stored for at least 36 months at 0°C and 75% RH [34]. Shell is relatively more effective at preventing entry of air and moisture than most packaging materials. Even though retaining the shell is desirable for preserving the pecan quality, pecan handlers prefer to shell the nuts since in-shell would take more space during storage and incur higher cost for transportation. Hence, it is recommended to pack the pecans after shelling to mitigate the quality losses. The summary

of previous research pertaining to packaged and unpackaged pecans and their length of storage has been tabulated in (Table 2.4).

As previously discussed in this review, moisture, light, and presence of oxygen are a few of the major factors affecting the pecan kernel quality during storage [31,50]. So, the choice of packaging material should be based on physical attributes of packaging material such as water vapor transmission rate (WVTR), oxygen transmission rate (OTR), and transparency of packaging material. Polyethylene (PE) and low-density polyethylene (LDPE) are the most used package for pecans in retail sales as these are economic, easily available and permit the consumer to see the product before buying. Few disadvantages associated with using polyethylene-based packages are high WVTR, OTR, and transparency, which enables oxygen, light, and moisture to penetrate the package and affect pecan quality. Contemporary retail practices in the US for shelled raw pecans involve packing the pecan kernels in transparent LDPE or PE pouches. Since PE and LDPE do not have very good barrier properties, researchers experimented with different packaging materials and laminates to prolong the storage life of pecans. During a detailed investigation on the effect of various packaging material (LDPE, Polyethylene terephthalate + Polyethylene, Polyethylene Terephthalate-Silicon oxide + PE), it was observed that walnuts packaged with LDPE oxidized significantly faster than rest of the packaging materials [111]. Dull and Kays [112] studied the effects of various flexible packaging materials (nitrocellulose coated cellophane – NCCP, polyvinylidene chloride coated cellophane, ionomer film, and metalized ionomer film) and modified atmosphere (vacuum and nitrogen, only for polyvinylidene chloride coated cellophane) on quality (taste, color, and moisture) of Stuart under simulated retail market conditions (room

temperature and continuous lighting). The authors found that the pecans packaged in polyvinylidene chloride coated cellophane vacuum-maintained pecan nutmeat had better quality than other packaging materials and/or treatments tested.

Modified Atmosphere:

Since pecans respire and continue to have enzymatic activity throughout storage, unless deactivated using heat or irradiation, it is essential to maintain the packaging environment that can slow down the rate of deterioration. The pecans, without shell and any kind of packaging material, have been reported to last anywhere between 16 and 70 weeks (3–16 months), depending on the temperature and RH of the environment (Table 2.4). There are different treatments that have been investigated to delay rancidity in pecans at room temperature. The strategies have been focused on regulating the levels of oxygen around the stored pecans [31]. There are different methods to diminish the contact of oxygen with pecans, namely, by applying vacuum, nitrogen (N_2), carbon dioxide (CO_2), oxygen scavengers (such as baking soda, ascorbates, etc.), or edible coatings [9]. Raw and roasted pecans stored for 52 weeks at ambient temperature in CO_2 flushed pouches (a laminate of nylon and ethyl vinyl acetate) have been reported to have an equivalent change in quality as of pecans stored at 1.7°C for the same duration [109]. The CO_2 flushed pecans can last up to at least 134 weeks or 31 months at refrigeration temperature, depending on the type of packaging materials used and RH on the storage environment [34]. The extensive study by Wright [34] revealed that packing pecans under vacuum would be better than any other modified atmosphere in terms of delaying rancidity and prolonging shelf life. However, some researchers did not agree with outcomes and argued that the pecans placed in a low

oxygen concertation environment (less than 2%) will experience anaerobic conditions. The anaerobic conditions would be suitable for fermentation, which would impart acidic and fruity flavor to pecans [112,113]. Sacharow [114] recommended N_2 over CO_2 for modification of the internal atmosphere of the package for the storage of pecans as the latter could be absorbed by pecans and impart acidic flavor due to the formation of carbonic acid. It has been suggested that using the packaging materials with O2 transmission rates above 0.08 cm^3 O_2 100/cm/24 hr. would be beneficial to preserve the natural flavor(s) of pecans. Hao et al. [21] stored pecans in hermetically sealed metal cans at −20°C. The authors reported that pecans were edible even after 25 years of storage with very insignificant lipid oxidation and changes in color attributes of pecans. Harris [115] reported that pecans dried to 1.6% moisture and packaged in glass jars in vacuum were edible after 7 years in ambient storage.

Edible Coating:

In food industry, the flush packaging equipment is expensive [114]. Thus, the edible coatings can provide economic means for extending the storage life of pecans with barrier properties as of a package, thus eliminating the need of packing the pecans. Many experiments have been conducted to test various saccharide, protein, and lipid-based edible coatings on different nuts including walnut, almonds, pecans, hazelnuts, etc., with success in prolonging storage life. Godkin et al. [116] immersed pecan kernels in a 40% sucrose syrup and stored it at 45°C. The authors observed a delay of 6 weeks in the onset of rancidity in those pecan kernels when compared to the untreated pecans. Senter and Forbus Jr. [90] coated pecan kernels with acetylated monoglycerides and reported a stronger

significant effect of variety than lipid coating on the storage life of pecans. Some researchers also attempted to include antioxidant substances such as tocopherol, vitamin C, nordihydroguaiaretic acid and tenox in the edible coating to delay rancidity with little or no success [90,116,117]. Nevertheless, Baldwin and Woods [118] designed an experiment with a complex combination of edible coating and additives to see how it could affect pecan's storage stability. They studied the effects of hydroxypropyl cellulose (HPC) and carboxymethylcellulose (CMC) with various additives (surfactants, emulsifiers, and antioxidants). Out of the several polysaccharide-based edible coatings and food additive combinations, the instrumental and sensory analyses revealed that pecans dipped in distilled water containing 2% CMC, 0.2% lecithin, 3% propyl gallate and 0.5% α-tocopherol had a higher sensory preference, lower color darkening, and hexanal development during storage (20–25°C for 9 months).

Regression & Kinetic Models to Predict Quality Changes in Pecans

Regression is used for time series modeling, forecasting, and finding the causal effect relationship between the variables [119]. Regression analysis can be used for predicting the degree of impact of physical, chemical and biological factors on pecan quality. For instance, regression models have been used to predict the change in the color of hazelnut and soybean during storage. The regression equations for various quality parameters have been summarized in (Table 2.5). The equations reflect the impact of factors like moisture, storage time and lipid-oxidation products on color, flavor, texture and overall acceptability of pecans. Originally designed for biological systems, kinetic models could be used to predict food quality changes that occur during processing [120]. Kinetic parameters have

been widely used for the development of food preservation processes, analyzing the reduction of microbial population, and calculating empirical coefficients. The experiments are conducted to calculate fundamental kinetic parameters such as activation energy, entropy, and enthalpy. These parameters are used to analyze the quality changes in foods caused by thermal processing and aid in optimal designing of thermal processing conditions to diminish quality losses [121]. The general rate law for reaction kinetics to calculate changes in quality attribute of a food product [122] can be described as:

$$\frac{dP}{dt} = \pm kP^n$$

where k is the rate constant ($time^{-1}$), t is the time taken for a reaction to occur (min), n is reaction order and P is a quantitative value for a quality attribute. The core concept of kinetic studies on food quality changes is to study a quality attribute as a function of a factor affecting the quality of a food product e.g., temperature, time, relative humidity, etc. The kinetics of changes in food quality follows zero-, first-, or second-order reactions. More information on the kinetic models in thermal processing has been discussed in detail by Ling et al. [121]. For storage study, Lund [123] coined a concept called Q_{10}-value which describes the rate of quality changes with temperature. It can be used to interpolate the storage time at lower temperatures based on the data obtained by conducting shelf-life tests at higher temperatures.

There is no study reported on the kinetic modeling of pecan quality; nevertheless, there are some researchers who have explored the changes in physical and chemical attributes during processing and storage in other food products. Nelson [124] summarized the activation energy (E_a) for various food quality attributes; E_a for food quality loss ranged from 63 to 126 kJ/mole, 209 to 418 kJ/mole for microbial inactivation and 8 to 63 kJ/mole

for enzymatic reactions or oxidation reactions. Ling et al. [121] compiled a review on the kinetic modeling of various attributes of different food products. In this review, we have discussed studies related to the quality change in high fat-containing food (such as hazelnut and peanut) during processing and storage.

Özdemir and Devres [125] developed a kinetic model on change in color during hazelnut roasting for a temperature range of 100–160°C and roasting time up to 60 minutes. The rate of color changes was significantly affected by temperature and time over the experimental conditions. The color change during roasting of hazelnuts was seemed to follow third-degree polynomial with Arrhenius-type temperature dependence. The activation energy (E_a) for the lightness (L) was found to be 62.3 kJ/mol and reported equation of L and a-values as:

$$L = 83.5e^{-1.4/T} - 9.7 \times 10^{17} e^{-\frac{1.8305.7}{T}} t - 1.92 \times 10^{8} e^{\frac{9848.7}{T}} t^2 + 2.5 \times 10^{15} e^{-\frac{18826.1}{T}} t^3$$

$$a = 3.4 \times 10^{16} e^{-16653.8/T} - 0.0013 e^{-\frac{917.6}{T}} t + 1.2 \times 10^{6} e^{-\frac{7916.7}{T}} t^2 - 1.3 \times 10^{7} e^{-\frac{10884.1}{T}} t^3$$

Based on the model equations, the scatter plot of experimental and predicted value was a straight line, with less heteroskedasticity indicating that the distribution of the variance of the error was constant and symmetrically distributed across various levels roasting temperature. Similar statistical equations and kinetic models were developed by Kong et al. [126] while investigating quality changes in soybean during storage (22 to 40°C at 70% RH). The kinetic parameters were well described by zero-order kinetics and the temperature dependency of all obtained parameters followed the Arrhenius model. The resulting equations provided a simple method to monitor soybean quality and predict quality changes of soybeans during storage at various conditions. The activation energies

(E_a) for Hunter L and total color change in varying temperature conditions were 89.03–98.95 and 94.39–103.28 kJ/mole, respectively.

Future Studies

Pecans are subjected to varying environmental conditions during storage, transportation, and distribution. Most of the academic research has focused on the storage temperature range of 0°C to 30°C and 50 to 75% RH. However, pecan may experience a much wider range of temperatures and RH after harvest. Also, very few studies mentioned about and explained the impact of moisture on texture, the number of studies reporting the impact of varying RH condition on texture is limited.

Further research should be conducted on determining keeping time and shelf-life determination of pecans based on sensory evaluation. This approach can be used to find the actual length of storage when pecan is no longer acceptable by the consumer. The pecan cultivars vary in yield, size, disease resistance, and chemical composition. The studies available on the presence of phenolic and non-phenolic compounds is limited. The USDA nutritional database reports the general nutritional composition of pecan instead of the individual cultivar. Also, the studies are limited to the storage life of various cultivars. The studies regarding cultivar differences can help future breeding programs develop prolonged storage duration -stable pecans. The cultivar selection for pervious research has less to do with economic importance and more to do with the availability of pecan varieties. To ensure academic research is relevant to the pecan industry, the research should be focused on commercial cultivars as these are major share in total pecans grown in the US.

The kinetic model is a very useful, convenient, and reliable mathematical tool to study food quality loss. The researchers have worked on numerous food products to develop models explaining the change in food quality during processing and storage. Nevertheless, limited work has been done of developing a kinetic model for nuts including almonds, hazelnuts, etc. There is not any study reported, related to the mathematical model on pecan. Some factors such as the rate of lipid oxidation, color oxidation, etc., are known to be temperature-dependent, yet their kinetic parameters are unknown. With the help of these parameters, the researchers would be able to compare and understand the impact of environmental conditions on pecan quality among multiple studies.

Conclusion

Pecan has been historically important in terms of its production and business share in the nut market. This has created the need for a systematic scientific understanding of pecan handling which has to be based essentially on incessant research studies on pecan. Since it is a consumer-based commodity, consumed as such and as an inclusion in some food preparations, research going into pecan is both, promising and lucrative. The paper has attempted to promulgate the idea of consolidating the literature on pecan and has tried to highlight and address the gaps in the literature. With more research directed towards the commercially important cultivars, their phytochemical profile, and their storage stability, we will be in a position to handle pecans more efficiently to prolong their shelf life. Factors like temperature, RH and packaging methods play a cardinal role in deciding the quality and shelf life of pecans and must be controlled carefully at all stages of pecan storage. The role of mathematical models in predicting the quality and shelf life of pecans emerges to

be of direct interest to the pecan industry. Even though the existing literature has some models proposed already for other nuts, there is a need for a dynamic yet simple model for pecan to be made available to pecan handlers working at the different levels of the supply chain. With the kind of science and technology that surround us today, making such systems available for practice in the pecan industry is practically attainable.

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Tables

Table 2.1. Summary of variety, growing location, year, extraction method and fatty acid profile of pecan

Variety	**Location, year**	**Extraction method**	**Lipid content (%)**	**Palmitic acid % ($C_{16:0}$)**	**Stearic acid % ($C_{18:0}$)**	**Oleic acid % ($C_{18:1}$)**	**Linoleic acid % ($C_{18:2}$)**	**Linolenic acid % ($C_{18:3}$)**
Cheyenne[61,108]	Texas, 1974	Chloroform:Methanol (2:1)	75	4.45	1.63	36.41	25.69	1.26
	Texas (US), 2002-2007	Hexane	55.1	5.99	0.23	66.53	22.92	0.11
	Texas (US), 2002-2007	Hexane	55.9	6.23	0.24	70.99	19.03	0.08
Stuart[26,61,109]	Florida, 1958	Cold pressing	-	6.6	2.2	68.8	21	1.1
	Georgia (US), 1970-1972	Soxhlet (Diethyl ether)	75.1	6.28	2.08	65.24	24.62	1.46
	Texas, 1974	Chloroform:Methanol (2:1)	72	4.29	2	66.39	23.31	1.76
Desirable[34a,110]	Texas	Soxhlet (Petroleum ether)	66.18	5.9	2.24	66.66	23.68	1.24
	Texas, (US), 2004	Hexane	-	5	2	71	20	1
	Texas, (US), 2004	Hexane	-	6	2	59	31	1
	Texas (US), 2002-2007	Hexane	53.58	5.53	0.22	65.66	24.17	0.11
	Texas (US), 2002-2007	Hexane	61.43	5.22	0.25	72.53	17.53	0.1

Wichita[26,108]	Georgia (US), 1970-1972	Soxhlet (Diethyl ether)	76.7	6.2	2.47	73.09	16.97	1.13
	Texas (US), 2002-2007	Hexane	58.5	5.83	0.27	71.13	17.94	0.11
	Texas (US), 2002-2007	Hexane	64.33	5.47	0.27	60.82	18.83	0.12
Schley[25,26]	Georgia (US), 1970-1972	Soxhlet (Diethyl ether)	75.2	5.99	2.08	68.73	21.82	1.13
	Georgia, 1962	Goldfisch (petroleum ether)	76	6.65	1.6	61.88	29.13	0.84
Moneymaker[109]	Florida, 1958	Cold pressing	-	6.3	2.6	51	37.8	1.7
Curtis[109]	Florida, 1958	Cold pressing	-	6.1	3.1	71.8	18.1	0.8
Mahan[61]	Texas, 1974	Chloroform:Methanol (2:1)	74	4.13	1.15	36.05	23.47	1.87
Pawnee[34a]	Texas, (US), 2004	Centrifugation, hexane	-	6	3	66	23	1
Shawnee[34a]	Texas, (US), 2004	Centrifugation, hexane	-	6	2	75	15	1

Table 2.2. Summary of effects of factors on quality and chemical attributes (QCA) of pecan.

Factors → QCA↓	**Variety**	**Early Harvesting**	**Moisture**	**Roasting**	**Conditioning: Steam**	**Conditioning: Hot water**	**Conditioning: Dielectric heating**	**Irradiation**	**Freezing/ Refrigeration**	**Storage**
Color	Yes	Yes	-	Yes	Yes	Yes	No	No	No	Yes
Texture	Yes	Yes	Yes	Yes	No	No	No	No	Yes	Yes
Oil content	Yes	Yes	No	Yes	No	No	No	No	No	No
Free fatty acid	No	No	Yes	Yes	Yes	Yes	No	No	No	Yes
Primary oxidation	No	No	No	Yes	Yes	Yes	Yes	Yes	No	Yes
Secondary oxidation	No	No	Yes	Yes	No	No	No	No	No	Yes
Flavonoids	Yes	-	-	Yes	-	-	-	Yes	-	Yes
Tannins	Yes	-	-	-	Yes	Yes	No	Yes	-	Yes
Phenolic acids	Yes	-	No	Yes	-	-	-	Yes	No	Yes
Phytosterols	-	-	-	-	-	-	-	-	-	-
Tocopherols	Yes	-	-	Yes	-	-	-	Yes	No	-

Table 2.3: Quantification of minerals responsible for promoting oxidation in pecans

	Minerals (mg/100g)					
Genotypes	**Cu**	**Fe**	**Cr**	**Zn**	**Ca**	**Mg**
Chevenne	1.44	1.93	0.11	5.6	0	140
Western	1.22	2.52	0.15	8.21	5.3	130
Tejas	1.22	2.65	0.13	7.18	5.3	160
Cherokee	1.1	2.41	0.2	8.03	0	150
Schley x Barton	1.09	2.15	0.13	5.3	5.3	150
Shoshoni	1.06	2.28	0.16	6.26	5.2	160
Stuart	1.8	2.02	0.16	8.16	0	120
Schley x McCulley	0.9	2	0.15	5.65	10.5	120
Mahan	0.87	2.11	0	5.4	5.3	170
Desirable	0.82	1.93	0	10.4	21.2	170

Table 2.4: Summary of reported phytochemicals in different cultivars (next page).

Cultivars	Proanthocyanidin (CT) (mg/100g FW)	Total ORAC (µmol TE/100 g)	Total FRAP (µmol Fe^{2+}/100 g)	Total Phenols		γ-tocopherols (µg/g of oil)
				(mg EA/100g)	(mg CAE/100g)	
Cheyenne	563[111] 779[112]	21600[111]	16100[111]	2160[111]	-	300[38] 264.8[111]
Choctaw	779[112] 562[111]	20000[111]	17600[111]	2300[111]	-	- -
Desirable	742[112] 1050[34b] 795[34a] 420[111]	12810[34b] 12330[34b] 16300[111]	18600[111]	1950[111]	3120[34b] 1980[34a]	259[38] 211.98[111]
Elliott	491[111]	18100[111]	14000[111]	2000[111]	-	225.7[111]
Gracross	495[111]	18000[111]	17300[111]	2200[111]	-	221.9[111]
Kanza	1590[34b] 1410[34a]	15960[34b] 24510[34a]	-	-	3060[34b] 3180[34a]	97[34b]
Kiowa	845[112] 1080[34a] 425[111]	17040[34a] 16800[111]	17900[111]	2040[111]	2280[34a]	230.6[111]
Pawnee	690[34a] 400[111]	16860[34a] 17000[111]	15500[111]	2000[111]	2160[34a]	204.4[111]
Schley	789[112]	-	-	830[21]	-	247[38]
Shawnee	1140[34a] 995[112]	18690[34a]	-	-	2130[34a]	-
Stuart	736[112] 515[111]	18800[111]	18300[111]	1080[21] 1065[21] 2270[111]	-	237[38] 229.65[111]
Sumner	1007[112] 452[111]	18600[111]	15200[111]	1930[111]	-	241[38] 167.4[111]

Western	487[111]	12500[113] 17900[111]	17000[111]	2190[111]	-	277.3[111]
Wichita	1398[112] 583[111]	13721[113] 20100[111]	17300[111]	2440[111]	-	241.8[111]

ct-condensed tannin, fw-fresh weight, orac- oxygen radical absorbance capacity, te- trolox equivalents, frap- ferric reducing ability of plasma, ea-ellagic acid, gae-gallic acid equivalent, cae-chlorogenic acid equivalent

Table 2.5: Summary of various packaging material used in pecan storage study

Packaging material	**Temperature (°C)**	**RH (%)**	**Gas composition**	**Storage length (weeks)**	**Findings**
Without packaging[21,27,62,67,76]	30	55	Air	70	Rancid flavor developed in 5 months or less in shelled pecans stored at room temperature or above. Mold growth occurred in pecan stored at temperature > 10°C and RH 70%
	22	-	Air	34	
	24	64	Air	34	
	0	75	Air	43	
	10	75	Air	26	
	21	75	Air	21	
	32	50	Air	16	
PE (perforated)[34b,68,114]	21	65	Air	16	Pecans stored in PE bags. As compare to non-irradiated pecans, irradiated pecans experienced higher degradation of phytochemicals by the end of storage.
	21	65	Air	12	
	40	55-60	Air (Irradiated)	19	
PP bags[31,68]	21	65	Air	42	Better storage stability than pecans stored in direct air contact
	21	65	Air	12	
Cellophane[38]	0.6, 23.9	60-70	Air	52	No mold growth reported in any of the mentioned environmental conditions. Pecans stored 0.6°C experienced min. quality changes
CP-NC[115]	24	60	Air	24	Lower shelf life than pecans stored in PE because of high oxygen transmission rate. No mold growth reported

CP-PVdC[115]	24	60	Nitrogen and Vacuum	24	No significant effect of modified atmosphere and storage time on pecan quality.
Nylon and EVA laminate [93]	22	65%	CO_2 (91.8%) O_2 (8.1%)	52	No mold growth reported. The changes in pecan quality was not significantly different from pecans stored at refrigeration temperature without CO_2.
Metallized ionomer film[115]	24	60	Air	24	Best barrier properties. Adversely impacted flavor profile of pecans due to formation of undesirable flavoring compounds in anaerobic conditions
Glass jars[27,116]	0	75	Vacuum	134	Best packaging material for pecans. Impervious barrier properties granting longer storage stability than any other packaging material.
	0	75	CO_2	134	
	0	75	N_2	47	
	10	75	Vacuum	134	
	10	75	CO_2	56	
	10	75	N_2	40	
	21	75	Vacuum	43	
	21	75	CO_2	26	
	21	75	N_2	26	
	22	50	Air	52	
Hermetically sealed cans[25]	-20	-	Vacuum	1304	

PP-Polypropylene, PE-Polyethylene, LDPE- Low Density Polyethylene, CP-cellophane, NC-Nano Cellulose, PVdC- Polyvinylidene chloride, EVA- Ethylene-vinyl acetate

Table 2.6: Summary of various packaging material used in pecan storage study

Packaging material	**Temperature (°C)**	**RH (%)**	**Gas composition**	**Storage length (weeks)**	**Findings**
Without packaging[21,27,62,67,76]	30	55	Air	70	Rancid flavor developed in 5 months or less in shelled pecans stored at room temperature or above. Mold growth occurred in pecan stored at temperature > 10°C and RH 70%
	22	-	Air	34	
	24	64	Air	34	
	0	75	Air	43	
	10	75	Air	26	
	21	75	Air	21	
	32	50	Air	16	
PE (perforated)[34b,68,114]	21	65	Air	16	Pecans stored in PE bags. As compare to non-irradiated pecans, irradiated pecans experienced higher degradation of phytochemicals by the end of storage.
	21	65	Air	12	
	40	55-60	Air (Irradiated)	19	
PP bags[31,68]	21	65	Air	42	Better storage stability than pecans stored in direct air contact
	21	65	Air	12	
Cellophane[38]	0.6, 23.9	60-70	Air	52	No mold growth reported in any of the mentioned environmental conditions. Pecans stored 0.6°C experienced min. quality changes
CP-NC[115]	24	60	Air	24	Lower shelf life than pecans stored in PE because of high oxygen transmission rate. No mold growth reported

CP-PVdC[115]	24	60	Nitrogen and Vacuum	24	No significant effect of modified atmosphere and storage time on pecan quality.
Nylon and EVA laminate [93]	22	65%	CO_2 (91.8%) O_2 (8.1%)	52	No mold growth reported. The changes in pecan quality was not significantly different from pecans stored at refrigeration temperature without CO_2.
Metallized ionomer film[115]	24	60	Air	24	Best barrier properties. Adversely impacted flavor profile of pecans due to formation of undesirable flavoring compounds in anaerobic conditions
Glass jars[27,116]	0	75	Vacuum	134	Best packaging material for pecans. Impervious barrier properties granting longer storage stability than any other packaging material.
	0	75	CO_2	134	
	0	75	N_2	47	
	10	75	Vacuum	134	
	10	75	CO_2	56	
	10	75	N_2	40	
	21	75	Vacuum	43	
	21	75	CO_2	26	
	21	75	N_2	26	
	22	50	Air	52	
Hermetically sealed cans[25]	-20	-	Vacuum	1304	

PP-Polypropylene, PE-Polyethylene, LDPE- Low Density Polyethylene, CP-cellophane, NC-Nano Cellulose, PVdC- Polyvinylidene chloride, EVA- Ethylene-vinyl acetate

Table 2.7: Summary of regression equations, correlation and coefficient of determination of various parameters

Response	Temp (°C)	RH (%)	Regression Equation	r	COD
RESPIRATION					
Respiration rate in shelled nuts[90]*	-	-	(-1.571) +0.321*(% MC)	-	0.84
Respiration rate in in-shell nuts[90]*	-	-	(-1.45) +0.157*(% MC)	-	0.40
COLOR					
Lightness[68]	21	65	33.93-0.44*(STW)	-	0.88
a (green to red)[68]	21	65	7.79+0.06*(STW)	-	0.61
b (blue to yellow)[68]	21	65	15.47-0.23*(STW)	-	0.88
ΔE- Stuart[21]	32	50	$0.57+0.84*(STW)-0.021*(STW)^2$	0.97	-
ΔE- Schley[21]	32	50	$0.71+0.86*(STW)-0.011*(STW)^2$	0.99	-
TEXTURE					
Hardness (N)[58]	-	-	(-0.235) *(% MC) +12.21	-0.64	-
First compression Area[58]	-	-	(-0.464) *(% MC) +17.04	-0.8	-
Springiness[58]	-	-	1.197*(% MC) +1.014	0.8	-
Fracturability (TPA)[56]	-	-	19.06-1.13*(% MC) +0.00474*(TR)	-	0.21
Hardness (TPA)[56]	-	-	23.86-0.856*(% MC) +0.00541*(TR)	-	0.053
Springiness (TPA)[56]	-	-	0.57-0.0681*(% MC)-0.000026*(TR)	-	0.63
Chewiness (TPA)[56]	-	-	1.04-0.137*(% MC) +0.00019*(TR)	-	0.315
SENSORY & STORAGE TIME					
Crunchiness- Raw pecans[76]	24	55-65	63.307+0.0317*(TP)-771.568*(CD)	-	0.67
Hardness[56]	-	-	5.27+0.50*(% MC) + 0.000031*(TR)	-	0.49
Fracturability[56]	-	-	8.28-0.93*(% MC)-0.00141*(TR)	-	0.753
Crunchiness- Roasted pecans[76]	24	55-65	93.7-30.6*(CD)-19.7*(% MC) +2.49*(TBARS)	-	0.99
Cohesiveness[56]	-	-	(-0.69) +1.42*(% MC)-0.000078*(TR)	-	0.79

Denseness[56]	-	-	5,22+0.59(% MC)-0.000282(TR)	-	0.44
Flavor[68]	21	65	$4.96-0.46+0.02*(STW)^2$	-	0.95
Rancid flavor - Raw pecans[76]	24	55-65	(-57.042) +959.786*(CD)+16.436*(% MC)-0.001*(OFP)	-	0.82
Rancid flavor - Roasted pecans[76]	24	55-65	7.33+5.681*(% MC) +5.158*(TBARS)-0.002*(OFP)	-	0.998
Ranid aroma - Raw pecans[76]	24	55-65	6.821+1.355*(TBARS)+7.072*(PV)	-	0.88
Rancid aroma - Roasted pecans[76]	24	55-65	24.754+0.13*(PV)+11.864*(% MC)-0.051*(LC)	-	0.97
Storage time in days (pecan oil)[87]	70	-	28.25-0.5*(% linoleic acid)	-	0.8
Storage time in days (pecan oil)[87]	70	-	15.48+0.47*(% oleic acid)	-	0.79
PHENOLIC COMPOUNDS					
Concentration of phlobaphene (ABS)[21]	32	50	(-0.048) +0.01*(STW)	0.85	-
Concentration of anthocyanidin (ABS)[21]	32	50	0.0067+0.0036*(STW)	0.92	-
LIPID OXIDATION					
Total volatiles (log_{10})[68]	21	65	5.34+0.048*(STW)	-	0.89
Hexanal (log_{10})[68]	21	65	3.53+0.13*(STW)	-	0.78
Peroxide value-Stuart[21]	32	50	0.085+0.104*(STW)	0.68	-
Peroxide value-Schley[21]	32	50	(-0.052) +0.25*(STW)	0.96	-

*(Log mg CO2 kg-1 hr-1)

MC- moisture content, STW- storage time in weeks, CD- conjugated dienes, OFP- organic fluorescent pigments, PV- peroxide value, LC- lipid content, ABS- Absorbance, ΔE- Total color change, r- correlation, COD- coefficient of determination or R2, TR- thawing rate, TBARS- Thiobarbituric acid reactive substances

Figure

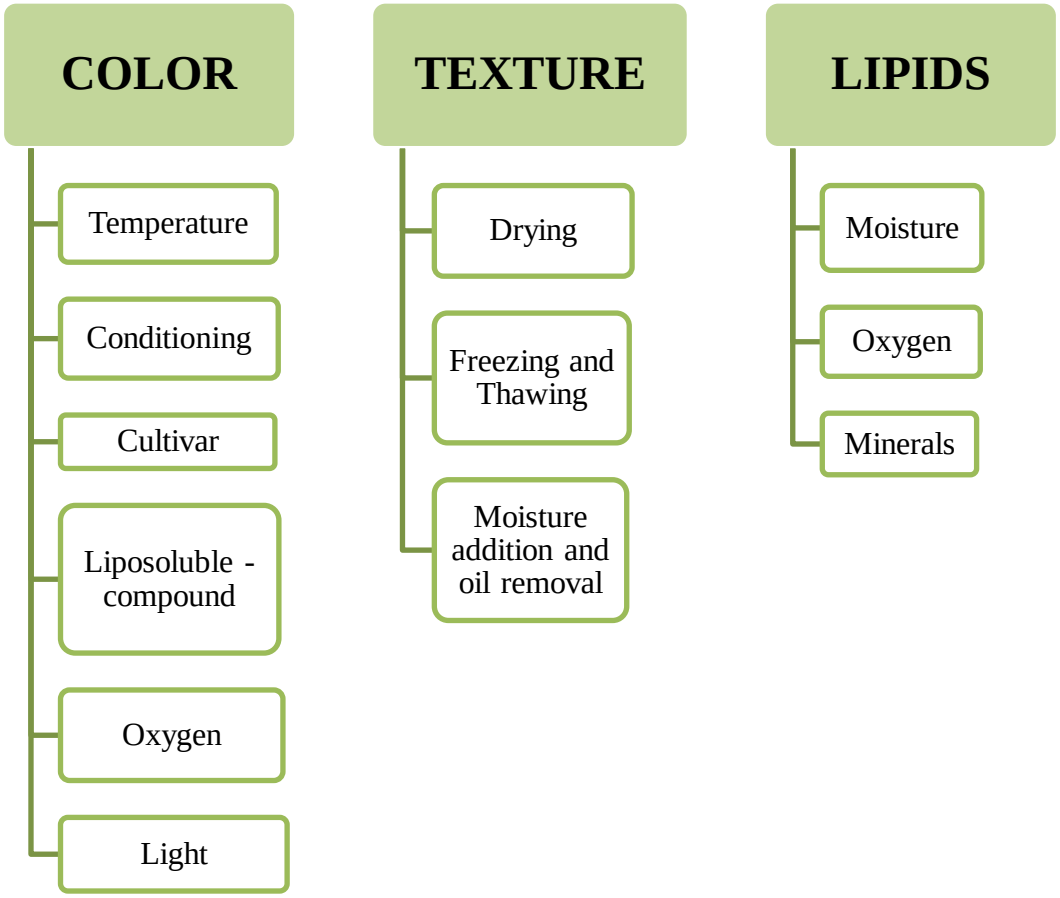

Fig. 2.1: Summary of factors affecting pe can quality attributes

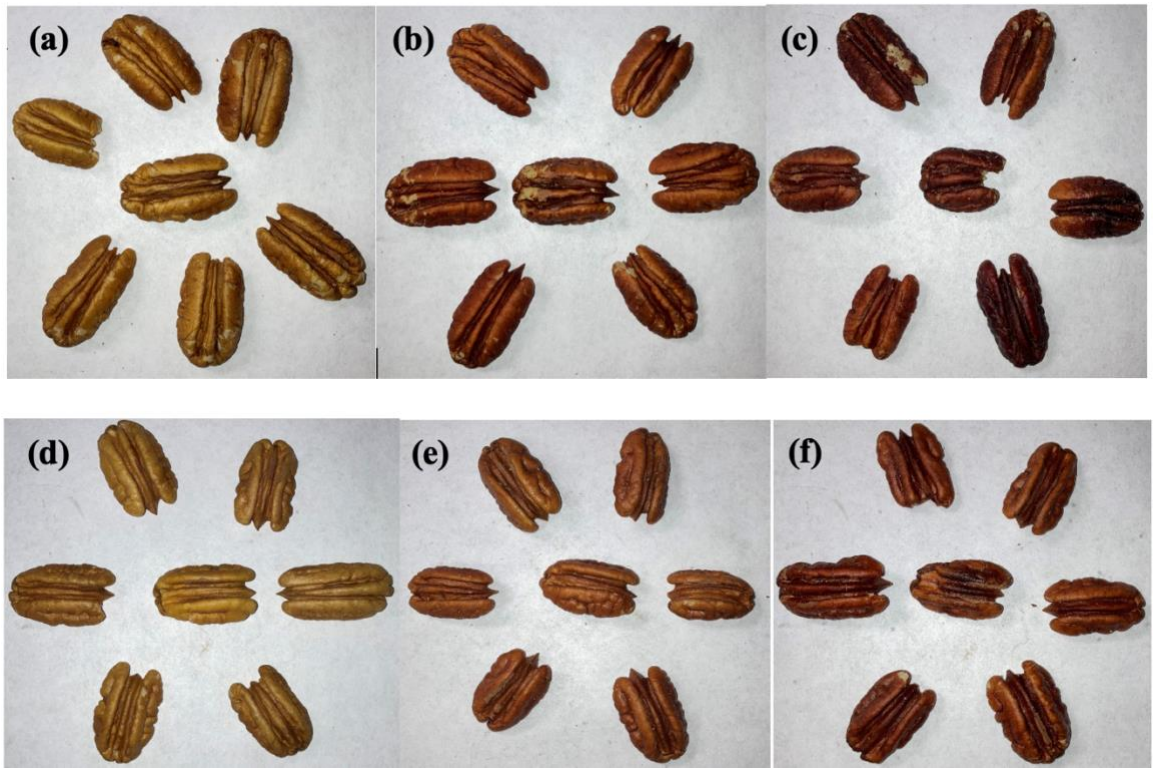

Fig. 2.2: Changes in different pecan varieties during storage under different environmental conditions: (a) to (c) – Desirable stored at 40°C and 50% RH for 0, 6 & 10 weeks, respectively (d) to (f) – Stuart stored at 30°C and 30% RH for 0, 7.5 & 12.5 months, respectively

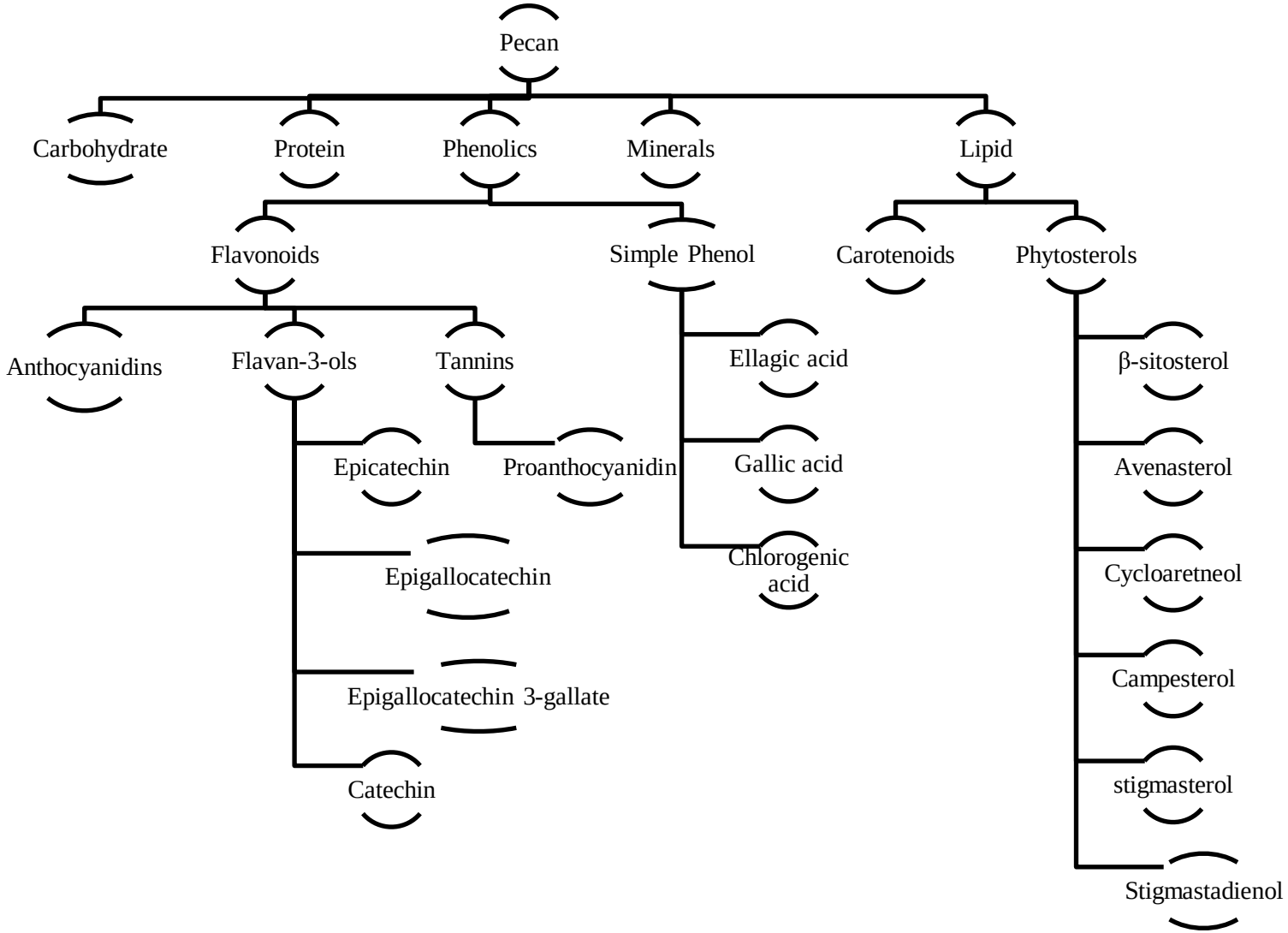

Fig. 2.3: Organization of macro- and micro-nutrients in pecan

CHAPTER 3

PECAN COLOR CHANGE DURING STORAGE: KINETICS AND MODELING OF THE PROCESSES[2]

[2] Prabhakar H., Bock C., Kerr W.L., Kong F. 2022. Current Research in Food Science. 5: 261-271. Reprinted here with permission of the publisher.

Abstract

Postharvest changes in pecan nutmeat color are affected by many factors, both internal and external. The temperature, relative humidity (RH) of the surrounding environment, and storage time are major factors contributing to color deterioration of the nutmeats. Kinetic models have long been employed to provide insights into the physical and chemical changes in food systems; however, no kinetic model has been developed describing the color changes of pecan nutmeats during storage. The objective of this research was to determine the effect of temperature, RH and storage time on pecan nutmeat color change. Pecan nutmeats of three commercially important cultivars (Stuart, Pawnee and Desirable) were subjected to different temperatures (20, 30 and 40 °C) and RH conditions (30, 50, 75% and 80%) for up to 450 days in simulated storage. The observed color changes of the pecan nutmeats were measured as lightness, chroma and hue (LCh). Additionally, the USDA pecan color rating scale was digitized to encourage its use among researchers. It was observed that the change in hue followed a zero-order decay whereas change in lightness and chroma followed a first-order decay. The value of the reaction constants ranged from 0.010 to 1.315 day^{-1}. An Arrhenius model was used to estimate the activation energy (Ea) corresponding to different storage conditions. The values revealed significant effects of temperature, RH and storage days on color degradation. The breakdown of flavonoids and reaction products from Maillard browning could be responsible for the formation of the reddish-brown color observed in degraded nutmeats. The kinetic parameters and models were used to develop a user-friendly online interface for predicting color change depending on selected parameters, with illustrations of the resulting pecan color (https://tinyurl.com/uspecans). The results of this study will aid pecan growers,

processors and researchers to predict and visualize changes in color of pecan nutmeats during storage under various conditions of temperature and RH, and duration of storage. Although the study used cultivars Stuart, Pawnee and Desirable, the results likely have more general applicability to other cultivars too.

Introduction

Carya illinoinensis (Wangenh.) K. Koch, commonly known as pecan, is a native North American tree species cultivated across the southern states of the U.S. from Georgia to California. The U.S. is a major producer of pecans and is responsible for 40–45% of the world's total pecan production (McEachern, 2014; NASS, 2020), making it a commercially important specialty crop in the U.S., with a market value of US$560 to 700 million (NASS, 2020). Worldwide, the U.S. has the largest per capita annual consumption of pecans (136–272 g) (Miaschi, 2018). Nonetheless, 45% of U.S. grown pecans are exported to other countries, with a value of more than US$470 million (ERS, 2021). Thus, the commodity is widely traded.

During domestic and international distribution and transportation, pecans may experience adverse environmental conditions which can cause quality losses. One of the chief quality losses to occur is color degradation. Indeed, a pecan nutmeat's color is used as an indicator of freshness and quality by wholesale distributors and retailers (Florkowski and Hubbard, 1994; Kays, 1979). Pale colors indicate freshness, while dark colors indicate advanced age and rancidity. Recently, the United States Department of Agriculture (USDA) updated the pecan color standard scale based on a study by Thompson et al. (1996). The study recommended a 6-color scale instead of 4-color scale to include a wider range of pecan color obtained after harvesting. The new scale, based on the Munsell system, embraces a wider range of pecan colors to represent that observed after harvesting. It comprises a 1 to 6 ordinal scale representing the colors light cream, cream, golden, light brown, reddish brown and dark reddish brown. The characteristic cream to golden color associated with fresh pecans is due to the presence of various phytochemicals including

carotenoids and flavonoids (Kays and Wilson, 1976). As noted, with time, pecan color changes from bright cream, yellow or golden to either brown or reddish brown. The reason(s) behind the change in color with nutmeat degradation is not fully explored (Prabhakar et al., 2020). But considering the importance of nutmeat color, developing a dynamic understanding of the effect of environmental conditions and time based on models to predict nutmeat color change will aid growers, processors and retailers to better plan storage and distribution of the commodity.

Pecan nutmeats contain various macro and micronutrients that play a significant role in quality changes. Pecan nutmeats are rich in poly unsaturated fatty acids (PUFA), making them susceptible to lipid degradation (Polmann et al., 2019; Zhang et al., 2018). Similarly, change in color may be due to various chemical reactions that occur in the nutmeats. The changes in color can be quantified using kinetic parameters including rate constants (k) and activation energies (E_a). Kinetic parameters and rate constants are important components of kinetic models which can be used to explore reasons for changes in food quality and shelf life of food products (Haefner, 2005). Kinetic modeling aids in understanding the quality changes at a molecular level (Van Boekel, 2008). It is an established and reliable technique that has been used to predict quality changes in various food products, including almonds (Ciftci and Ozilgen, 2019), walnuts (Vinson and Cai, 2012; Zhang, Zheng, Zhou, Huang and Wang, 2016), soybean (Kong and Chang, 2009), various fruit (Aamir et al., 2013; Lin and Tiejin, 2001; Pereira et al., 2006; W. Zhang, Luo, Wang, Gu and Lv, 2021), hazelnuts (Özdemir and Devres, 2000), and many other commodities (Ayustaningwarno et al., 2020; Song et al., 2019). No kinetic models have been developed for pecans, despite pecan nutmeats being perishable, and despite the fact

that they rank third among tree nuts in area under production in the U.S. – only almond and pistachio have larger production areas (NASS, 2017). During the postharvest process of storage, transport, redistribution, retail shelf time, and in some cases export, pecans experience a range of conditions in temperature and relative humidity (RH). Temperature may attain 50 °C and RH as high as 80%, respectively (Premtitikul, 2012), but most previous research has focused on storage temperatures ranging from 0 °C to 30 °C and an RH of 50–75%.

The overall objective of this study was to systematically investigate the effects of temperature (20, 30 and 40 °C), RH (30%, 50%, 75% and 80%), and storage time on pecan color change. The temperature based kinetic attributes, including the rate constants (k), activation energies (E_a), and the ratio of rate constants for temperature increase of 10° (Q_{10} coefficients), were determined for pecan nutmeat color change. The kinetic attributes were subsequently used to design a user-friendly online interface that allows input of temperature, RH and storage time parameters to determine the impact on pecan nutmeat color.

Material & Methods

Pecan Production and Source of Nutmeats:

Three cultivars of pecan (Stuart, Pawnee and Desirable) were harvested from orchards located at the USDA-Agriculture Research Service (ARS) Fruit and Tree Nut Research Laboratory, Byron, Georgia (U.S.A.), (+32.6650 N, + 83.7419 W, elevation of ≈156 m, 240 d freeze-free growing period, annual precipitation of 118 cm). Orchards received standard tree management practice for the state of Georgia (Wells et al., 2019). The experiment was performed twice, with pecans harvested in November 2018 and December

2019, respectively. In each season, the pecans were processed within 1 week of harvesting. The harvested pecans were conditioned prior to shelling by dipping in 85 °C water for 3 min, followed by drying at room temperature for 20–25 min and shelling via mechanical sheller (Modern Electronics, Mansfield, LA) (Forbus Jr and Senter, 1976). After shelling, pecans were dried at 20 °C and 45% RH overnight to a moisture content of 4–5% moisture content (AOAC, 2016) and stored at −20 °C in a commercial freezer until use in the experiments. Information on the different grades of pecans is provided (Table 3.1).

Experimental Plan and Design:

The desired RH was achieved by using 200 mL saturated salt solutions placed in a static humidity chamber (STC) which was a 1-L glass jar with a rubber gasket to seal the lid. The saturated salt solutions used to achieve the different RH were: magnesium chloride (30–32% RH), magnesium nitrate (50–52% RH), sodium chloride (75% RH) and ammonium sulfate (80–81% RH) (Certified ACS, Fisher Chemical, Waltham, MA). For the sake of simplicity, the RHs will be denoted as 30%, 50%, 75% and 80%, respectively, at each storage temperature. The STCs were placed in temperature-controlled chambers at 20, 30 and 40 °C. For each temperature × relative humidity treatment (replicates, n = 2), 50 g of whole pecans were placed in a nylon bag suspended above the saturated solutions on an aluminum mesh disc in the STC (Fig. 3.1). To simulate a real storage environment and corresponding air composition, the jars were opened periodically (every 1–2 weeks) for 30 s to allow fresh air into the container. The samples were drawn (n = 2) at predetermined intervals based on previous reports of pecan color change in the literature (Blackmon, 1932; Brison, 1945; Kays, 1979; Magnuson, Koppel, Reid, & IV, 2015; Mexis et al., 2009;

Senter and Wilson, 1983). A total of five samples of nutmeats were collected from the STCs for each temperature × RH condition treatment (+1 baseline sample). The STCs were stored in duplicates (n = 2) for each treatment combination. The storage time ranged from 15 to 450 days, depending on the treatment (Table 3.2). The fungal growth assessment was done visually.

The experimental design was a generalized randomized complete block design (GRCBD) with samples drawn on 5 occasions and 1 baseline or control sample (year and cultivar were treated as block effects). Storage time was unique to each RH condition at the different temperatures. Thus, storage time was nested within RH. A similar condition existed for cultivar and year with cultivar being nested within year. In the GRCBD, treatments (combinations of temperature, RH, and storage days) were replicated within each block (combination of year and cultivar). In an ordinary (un-replicated) randomized complete block design (RCBD), if there are insufficient degrees of freedom to fit block by treatment interaction terms it is necessary to assume that treatment effects do not differ across blocks (Shieh & Jan 2004). Such an assumption is often considered reasonable. In the current GRCBD, there is replication within each block, so block by treatment interactions could be included in the model and assessed. However, including such terms would make the model quite complex and cumbersome and the interpretation of the fitted model would become challenging. Thus, to simplify the analysis, the block by treatment interaction terms were omitted, as one would do for an ordinary, un-replicated RCBD.

Color Measurement:

A hand-held trismulus Minolta Chroma Meter (Minolta Corp., Ramsey, NJ) was used to measure the color characteristics of the pecan samples using the Hunter's L, C, and h scale, where L is lightness (0.00 = black to 100.00 = white), C is Chroma (0.00 = grey to 100.00 = bright or intense), and h is Hue (0–360°). Delta Hue (Δh), which is the difference in current hue and baseline hue, was also calculated as an alternative measure of hue. The observations were made under the International Commission on Illumination (CIE) standard illuminant D_{65}, representing average daylight and color temperature of 6500 K. The colorimeter was calibrated using a white standard plate with the following color coordinates for lightness (L) = 97.59, green to red (a) = 0.39, and blue to yellow (b) = 1.75) before the color measurements of the pecan samples were taken. For color measurement, a uniform bed of pecan kernels was dorsally exposed to colorimeter lens. The measurements were done by taking 50 g of kernels and dividing into 3 groups (n = 3, pseudo-replicates), each containing approximately 5–8 pecans.

Kinetic Analysis:

To study the impact of storage period and temperature on pecan nutmeat color, kinetic parameters associated with the measured change in color were calculated. Chemical reaction kinetics can be applied to quantify color attributes of a food in the form of the general rate law (Lado and Yousef, 2002; Van Boekel, 2001):

$$\frac{dP}{dt} = \pm kP^n \quad (1)$$

where k is the rate constant, t the reaction time, and n the reaction order. In general, P represents a quantitative value of L, C and/or h. According to Ling et al. (2015), the kinetics of food quality change follow zero (equation [2]) or first (equation [3]) order reactions:

$$P = P_0 - kt \quad (2)$$

$$P = P_0 e^{-kt} \quad (3)$$

An Arrhenius equation was used to investigate the effect of temperature (T) on the rate of color degradation (*k*):

$$k = k_0 e^{-\frac{E_a}{RT}} \quad (4)$$

where *k* is the rate constant, k_0 is a pre-exponential factor, R is the ideal gas constant (8.314 $J.mol^{-1}K^{-1}$), and T is the absolute temperature (K). E_a is the activation energy ($kJ.mol^{-1}$) and is defined as the minimum energy needed to start a chemical reaction (sometimes called the energy barrier). Equation 4 can be rewritten as;

$$\ln k = -\left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \ln k_0 \quad (5)$$

By plotting ln *k* with 1/T(K), slope (E_a/R) can be obtained which can be further solved to calculate E_a (kj/mol). Chemical reactions are sensitive to temperature, and the Q_{10} value of a reaction is often used for reporting the temperature dependence and effect on the reaction rate as the temperature increases or decreases by 10°C:

$$Q_{10} = \frac{k_2}{k_1} \quad (6)$$

Where k_1 is reaction constant at temperature T_1 and k_2 is the reaction constant at temperature T_2 (T_2=T_1+10°C). The equation 5 and equation 6 can be combined to calculate Q_{10} as:

$$Q_{10} = \frac{k_2}{k_1} = e^{(-\frac{E_a}{R})(\frac{1}{T_2}-\frac{1}{T_1})} \quad (7)$$

Q_{10} is a unitless value.

Development of a User Interface for Prediction of Pecan Nutmeat Color Based on Storage Conditions:

The models and parameters derived from kinetic analysis were incorporated into a web application to provide a user interface that can be used to predict nutmeat color. The online application was constructed using computer programming languages including Hyper Text Markup Language (HTML), JavaScript and Cascading Style Sheets (CSS). A similar program was constructed for Microsoft Excel which is downloadable and does not require internet access to operate. For Excel, inbuilt functions including IF, IFERROR, AND and OR were used to make a prediction statement from inputs provided by the user. The web application is compatible with most commonly available web browsers and devices.

Statistical Analysis:

Based on an inspection of the normal probability and quantile plots of the data and the observation that the variance was approximately constant throughout the distribution, it was concluded the data were amenable to parametric analyses. However, distribution of storage days was found to be right skewed. Thus, storage days were transformed by taking Log (storage days + 1). For instance, transformed storage day values of 0, 20, and 30 days were 0, 1.32, and 1.49 days, respectively.

First, a mixed model analysis was used to determine the effects of temperature, RH and storage time on color attributes (LCh). Storage days, temperature (°C), and RH (%) were considered fixed effects whereas crop year and cultivar (which was nested in crop year) were treated as random effects. The two-way interactions among fixed effects (temperature, RH and storage days) were studied, as were the two-way interactions

where storage days were nested within RH. A Tukey's HSD post hoc test (α = 95%) was performed to explore whether there were differences among means for the different treatments. The data recorded from any specific treatment or RH was independent of other treatments and was not affected by pecan sampling. The treatment results are presented as the mean± the standard deviation (SD). The effect of cultivars on color attributes was not studied due to limitations of experiment design, and the need for more data from a wider range of cultivars and years to draw firm conclusions (thus, cultivar data was pooled in the mixed model analysis).

Second, linear and exponential regression analyses were used to determine the rate constants (k) and activation energy (E_a). A linear regression analysis was used to determine k and Ea for hue (independent variable) and storage days (dependent variable, not transformed). An exponential model was used to calculate k and E_a for lightness and chroma (both independent variables) vs storage days (dependent variable, not transformed). The fit for both models were assessed based on the adjusted coefficient of determination (adj. R^2). All the statistical analyses were performed using JMP®, Version 15 Pro (SAS Institute Inc., Cary, NC).

Results

Pecan color changes during storage:

A digitized version of the USDA 6-point pecan nutmeat color scale was created (Fig. 3.2), and the color coordinates of the Thompson et al. (1996) pecan nutmeat color scale was tabulated (Table 3.3). The pecans harvested at the end of the 2018 and 2019 crop seasons (from all three cultivars) and used for storage experiment were of a cream color grade on the USDA pecan color scale (color grade 2) (Table 3.1). The summary of the mixed model

analysis of main effects, and two-way interactions affecting color attributes (L, C and h) showed that all main effects, including RH (a factor whose effect on pecan color has not been studied previously), and interactions were significant for each color attribute (Table 3.4). Based on Tukey's means separation, all color attribute values showed a decline with storage days at the various temperatures and RH combinations used in the experiment (Table 3.5-3.8).

The interaction between temperature and RH is shown in Fig. 3.3. At 20 °C, rate of color degradation was relatively less over the storage days. But as temperature increased, hue declined considerably. At a RH of 50% or less, the hue values indicated development of red color. In contrast, at 75% and 80% RH, change in hue was greater. Thus, color change was found to be dependent on varying temperature and RH conditions. According to the LCh color scale, hue values approaching zero corresponds to a red color and whereas high hue values (approx. 65°–60°) corresponds to a brown color. The interaction between temperature, RH and storage days shows a change in slope with storage days as storage conditions change. The slope becomes steeper as temperature and RH increase. The regression analyses of the individual color attributes, L, C and h, showed different patterns of decline over time, depending on temperature and RH (Fig. 3.4). The lightness and chroma presented an exponential decay during storage whereas hue followed a linear decay. The rate of color darkening increased at higher temperature; the slope for change in hue was steeper and decreased linearly with storage time. For each increase in temperature, the slope was steeper, indicating a zero-order decay. For lightness and chroma, the relationship was curvilinear, indicating that color attribute degradation became stagnant after an initial sharp decrease, indicating a first-order decay. The mean Δh (an

alternative measure of ΔE) at each time point, temperature and RH is presented and decreased in a constant manner regardless of cultivar (Table 3.8-3.9).

Kinetic Analysis of Color Degradation:

The rate constants (k) for lightness, chroma and hue increased with temperature for all three cultivars (Table 3.10), and the extent of variability in color attributes in the different harvesting seasons can be seen. All reported k values are negative, denoting declining slope. The activation energy, E_a was derived using an Arrhenius model, and the range in Ea values for hue (h), lightness (L) and chroma (C) were: 20.08–57.30 kJ/mol, 6.53–25.38 kJ/mol, and 7.63–28.05 kJ/mol, respectively. The k and regression parameters of all color attributes are also provided (Table 3.10). Decline in hue was more temperature sensitive compared to the decline in lightness or chroma. To examine the effect of RH on the rate of color degradation of pecan nutmeats, the activation energy (E_a) was calculated and compared to all color attributes (LCh) across the range of RH. RH had a significant effect on Ea for hue ($p < 0.05$). The pecan nutmeats stored below 75% RH had significantly lower Ea for hue than pecans stored above 70% RH. Contrary to this, there was no evidence that RH had any significant effect on the Ea for either the lightness or chroma color attributes. Our experiment data was variable as evidenced by the large standard deviations in E_a for lightness and chroma, which may have contributed to the challenge of detecting differences for the two attributes (Table 3.10). Q_{10} values pertaining to the different storage conditions are presented in Table 3.11 and can be used to determine the extent of color change in pecans under various environmental conditions.

Predicting Pecan Color Change during Storage using Kinetic Parameters:

One way to predict color change in pecan nutmeats is to identify the extent of color degradation represented by the rate constant (k). By checking the color grade of harvested pecans using the USDA pecan color scale (Fig. 3.2), the corresponding hue value can be determined (Table 3.3). For example, golden pecans (color grade no. 2) may have hue values ranging from 67° to 79° (Table 3.3). One approach is to take the average of these numbers, i.e. 73°. Assuming that the target pecan color grade is light brown (color grade no. 4), or a hue of 60°, the number of days it will take for the hue to change (under defined conditions) can be estimated. Albeit this is a rapid method to determine the initial hue value of pecan, and it is not as accurate as a colorimeter. A second approach is to determine color coordinates by taking RGB (Red Green Blue) coordinates. These coordinates can be acquired from a digital image of the pecan nutmeat by using commonly available computer software and online applications including MS Word and Google Sheets, respectively. The RGB coordinates can be further transformed to get lightness, chroma and hue values either using formulae or online color coordinate transformation web application(s). The hue value obtained from either of the abovementioned two methods can be used in Equation (7):

$$S = \frac{Initial\ hue - Final\ hue}{k_{T,RH}} \qquad (8)$$

where S is number of storage days required for the pecan nutmeats to reach a final hue value, hue is color attribute value and k corresponds to the rate constant at the specified temperature (T °C) and relative humidity (RH %) (Table 3.10 should be used for locating the appropriate rate constant for k under specific storage temperatures and RH). Note that the pecan color prediction was based on the hue (h) attribute alone as it was found to be a

reliable indicator for color change for most of the storage experiment conditions. The hue values obtained can be looked up on the Munsell color scale to obtain visual color.

A third method to determine color change is to use the E_a and Q_{10} values. The color prediction may be interpolated depending on the storage temperature by estimating rate constants (k), which can be derived from the activation energy (Ea). Referring to Equation (5), k_1 corresponds to the reaction rate for color degradation at the lower storage temperature (T_1) and k_2 corresponds to the reaction rate for color degradation at the higher storage temperature (T_2). The values can be obtained from Table 3.10. The new k values can be used to calculate S in equation (7). A fourth, and quick way of determining S is to use the Q_{10} values presented in Table 3.11. The Q_{10} value represents an increase or decrease in the rate of a reaction with every 10 °C change in temperature. By dividing S with the Q_{10} value at a specific temperature (T), the new S can be determined at T+10 °C.

$$S_{T+10°C} = \frac{S_T}{Q_{10(T+10°C)}} \quad (9)$$

For example, at 20 °C, 30% RH, and after 270 days in storage, pecan nutmeats developed a hue value of 60°. If the Q_{10} value for a temperature increase from 20 °C to 30 °C is 2.50, pecan nutmeats will develop a hue value of 60° in 108 days (i.e., 270 days/2.50) at 30 °C and 30% RH. These formulae were used to create the web-based application presented in the next section.

Web-based Application to Determine Pecan Nutmeat Color Change:

The rationale behind developing an online model to predict pecan color change under different storage conditions was to make the information accessible to a broad group,

including other researchers and non-scientific audiences. The equations, constants and kinetic parameters reported above were incorporated into an easy-to-use interface where an individual can ascertain the impact of storage period, temperature, and RH on pecan nutmeat color (Fig. 3.5). The link to the web application can be found here (https://tinyurl.com/uspecans). An individual can obtain information on the effects of storage time and the extent to which color change will occur along with illustrations. The user can make a selection by clicking the down arrow (highlighted in Fig. 3.5). The down arrow activates a drop-down menu where the user can select the options for cultivar, temperature and RH. The results of the selection will show the number of days the pecan nutmeats will take to degrade. The users can refer to the USDA pecan nutmeat color scale to determining the grade of the pecan at different points in time during storage. The baseline color grade for the pecans used in the experiment was cream (color grade no. 2). So, the results may vary if the initial pecan nutmeat color grade increases or decreases. The use of the online model is not limited to any device and does not require installation of any software.

Discussion

High temperature (>30°) storage conditions resulted in a more dramatic decline in hue values as compared to storage at 20 °C. After 120 and 30 days, visual fungal growth and decay precluded color assessment of pecans stored at RH 75% and 80% (20 and 30 °C), respectively. No visual fungal growth was observed in pecans stored at 40 °C (30%–80% RH) until the end of storage period. Please note that fungal growth was not assessed microbiologically and only visual observations were taken. The impact of change in

chroma during storage on pecan color was minimal, hence the discussion pertaining to this color attribute is limited. Previous studies indicated that decline in lightness (L) of pecan nutmeats followed a linear trend (Forbus Jr. et al., 1980; Senter and Wilson, 1983). But we observed that lightness (L) exhibited a first order or exponential decay during long term storage. The previous storage studies were conducted over a maximum of 15 weeks, which could be the reason for the reported trend as linear if only the initial steep decline in L was captured. The effect of RH on color of pecan nutmeats was reported for the first time, although the effect was conditioned by temperature. Increase in RH of storage environment escalated the rate of color degradation, evident from increase in rate of reaction (k) and activation energies (E_a).

These results are in agreement with those reported by Brison (1945), Kays and Wilson (1976) and Wright (1950). Development of the red and brown colors in pecan nutmeats with storage time is likely due to flavonoid degradation and the Maillard reaction (Senter et al., 1978). Flavonoids are one of the most common pigments in pecan nutmeats. Flavonoid molecules become very unstable if they come in contact with air and show affinity for polymerization when exposed to acidic conditions. Senter et al. (1978) conducted an extensive study identifying the flavonoids present in pecan nutmeats, namely leucoanthocyanidin and leucodelphinidin (flavan-3,4-diols). They exposed pecan nutmeats to 70 °C for 10 days and extracted the red colored condensed tannins (phlobaphenes and anthocyanidins). After extraction of the red colored pigments, the pecans were reported to be a light golden color, indicating the effect of a high concentration of the polymerized flavonoids on pecan nutmeat color. Rosenheim (1920) described the original unchanged flavonoid molecules as colorless. A study on discoloration of pears found that under similar

temperature conditions, leucoanthocyanidins, along with catechin, underwent oxidation and polymerized resulting in red-colored condensed tannins, namely phlobaphenes and anthocyanidins (Springob et al., 2003). Pecans also possess flavan-3-ols in the form of catechins (de la Rosa et al., 2019). Whether catechins are involved in the phlobaphene formation in pecan nutmeats has not been established. In addition, the mechanism behind conversion of leucodelphinidin to condensed tannins is unexplored. The transformation normally happens in the presence of heat and under acidic conditions. During pecan storage, especially at high temperature (>25 °C), synthesis of high levels of primary and secondary oxidation products have been noted. The products of oxidation contribute to the acidity in the pecan nutmeat matrix (Magnuson et al., 2015; Pyriadi and Mason, 1968; Rudolph et al., 1992). The hot, acidic conditions, along with presence of oxygen in storage environment, is likely sufficient to initiate the chemical reactions that result in formation of the red color in pecan nutmeats (Fig. 3.6) (Ribeiro et al., 2020).

The brown color development in pecan nutmeats may be due to the Maillard reaction. Pecan is known for its high fat content, but it also contains a significant amount of sugar and protein (USDA, 2019). Sugar and protein are primary reactants for the Maillard reaction; the reducing end of the carbohydrate reacts with the –NH2 group of amino acids to form a Schiff base which undergo an Amadori rearrangement and degradation to form Maillard reaction products. The increase in temperature accelerates formation of Maillard reaction products, evident from changes in the activation energy (Ea). In terms of food quality, Ea indicates the sensitivity of the reaction to changes in temperature. The range of reported Ea based on color change due to Maillard browning is 23–65 kJ/mol (Van Boekel, 2001). During the storage experiments, an increase in Ea was

observed as the RH increased (Table 3.10). According to Labuza (1980), water activity and excess moisture content in food systems affects the rate of the Maillard reaction. The water activity, aw, for stored pecans ranged from 0.43 (at RH of 30%) to 0.75 (at RH of 80%). Pecans stored at 20 °C and 70% or at higher RH (>70%) experienced rapid development of a brown coloration with all three cultivars. As temperature and RH increased to 40 °C and 80% RH, respectively, a reddish-brown color developed indicating the presence of reaction products of flavonoid polymerization and non-enzymatic or Maillard browning. Some reports suggest that the change in color of pecan nutmeats is due to lipid oxidation but it has not been experimentally established (Brison, 1945; Thewes et al., 2021). It could be argued that lipid oxidation indirectly affects the color development by providing suitable conditions for polymerization of flavonoids.

Conventionally, total color change (ΔE) has been used as a general parameter in foods to measure and understand overall change in color. However, it was observed that ΔE was not sensitive enough to describe changes in overall color of pecan nutmeats over the duration of the experiments. The lightness and chroma values decreased rapidly during the initial storage period and became stagnant afterwards. Contrary to this, hue values decreased steadily, which is why change in hue (denoted as Δh) could be employed to evaluate pecan nutmeat color change. The hue was found to be a good overall instrumental measurement parameter for pecan color but as RH increased (>75%), change in lightness became more prominent than change in hue. ΔL could be a reliable indicator of color change for pecan nutmeats stored at ≥75% RH. However, storing pecans at RH greater than 75% is not advisable as the pecans become susceptible to fungal growth and are thus rendered unsafe for human consumption.

Finally, a digitized version of the USDA 6-point pecan nutmeat color scale was created (Fig. 3.2). The USDA established the 6-point LCh pecan nutmeat color standard scale used by growers and processors to grade harvested pecans (Thompson et al., 1996), which is accessible to all researchers and pecan growers only through the USDA. Many researchers have relied on the Munsell Color or CIE systems to evaluate pecan nutmeat color (Kays and Wilson, 1977; Kays, 1979; Senter and Wilson, 1983; Von Wandruszka, Smith and Kays, 1980). Based on the results of Thompson et al. (1996), the digitized version of the USDA scale was created. Even though the USDA pecan nutmeat color scale was designed for grading pecans at the time of harvest, it is well suited to address the color changes in pecan during storage. Better accessibility and use of the color scale for reporting scientific data will bring greater uniformity and coherence in the narration of research reporting and other practical aspects of judging pecan nutmeat quality of U.S. grown pecans (the color coordinates given by Thompson et al. (1996) pecan nutmeat color scale has been tabulated in Table 3.3). For instance, it took approximately 270–300 days for pecan nutmeats to become light brown (color grade no. 4) at 20 °C and 30% RH. The pecan nutmeats attained color grade no. 4 more rapidly at higher temperature; the nutmeats took 124–157 days to turn light brown at 30 °C and 30% RH, but only 13–21 days to turn light brown at 40 °C and 30% RH, respectively. Ideally, perfectly ripened pecans possess a light cream color (color grade no. 1) but there may be anomalies. The baseline color grade for pecans used in this storage study was cream (color grade no. 2). It may take longer for pecan nutmeats of color grade no. 1 to degrade to color grade no. 6 of the USDA pecan nutmeat color scale. However, our model would be advantageous as it provides a conservative prediction on pecan nutmeat color.

The equations used for the online color prediction tool have some caveats. Even though the model predicts color change of pecan nutmeats, the current version can be used only for predicting the color of pecans stored under the range of experimental conditions in which the study was conducted (temperature, RH and storage time). Future studies that encompass additional factors and conditions (temperature, RH, packaging material, atmospheric composition etc.) will result in more information that can be integrated into the models to improve the usefulness, application, comprehensiveness, and accuracy of such online tool. Additionally, the kinetic parameters can be readily modified to suit various conditions including improving farming practices, changing soil composition and introduction of improved cultivars.

Conclusion

Pecan nutmeat color is widely used as an indicator of freshness and quality among wholesale distributors and retailers. The rate of color degradation depends on storage conditions, particularly temperature and relative humidity. Pecans maintained under low humidity conditions (<75%) and high temperature (>30 °C) resulted in more rapid development of a reddish-brown color, possibly due to breakdown of flavonoids and Maillard reaction products. The remining conditions tested (RH>75% and temperatures of 20–30 °C) resulted in only a brownish pigment being detected - likely a result of the Maillard reaction alone. The pecan nutmeats experienced least color degradation during low temperature (20 °C) and dry environment (30% and 50% RH) conditions. The overall quality degradation of pecans (texture and oil quality) under these conditions needs further investigation. The difference in rate of decay diminished as storage temperature increased.

The change in hue followed a zero-order reaction whereas lightness and chroma followed first-order decay. Kinetic parameters including rate constants, activation energy and Q10 values were calculated and incorporated in an online, easy-to-use interface where individuals can check the impact of storage, temperature and RH on pecan color (https://tinyurl.com/uspecans). Our experiments revealed that RH had a significant effect on activation energy (E_a); Ea increased with an increase in RH indicating that the rate of color degradation (k) was elevated at high RH. By incorporating the constants and equations behind a user-friendly interface, a coherent system was constructed that simplified use of the research outcomes for non-scientific readers, pecan growers, and processors, and other stakeholders. Thus, our work highlights the possibility of integration of computer programming tools in food science research to build intelligible and practical models to predict quality changes in food.

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Tables

Table 3.1 The classification system used to determine pecan quality of the pecans of the three cultivars used in the storage study based on the USDA pecan quality standard (USDA, 1969). The pecan color grade was determined using the USDA pecan color rating scale (Fig. 3.3).

Year	**Cultivar**	**Color grade**	**Nut Size (halves/kg)**
2018	Stuart	Cream, No.2	Mammoth (≲ 550)
	Pawnee	Cream, No.2	Jumbo (662-770)
	Desirable	Cream, No.2	Mammoth (≲ 550)
2019	Stuart	Cream, No.2	Jr. Mammoth (552-660)
	Pawnee	Cream, No.2	Mammoth (≲ 550)
	Desirable	Cream, No.2	Mammoth (≲ 550)

Table 3.2 Storage time in days for all environmental conditions used in the experiment (temperature and relative humidity). The storage matrix was the same for all cultivars (Stuart, Pawnee and Desirable) and crop years (2018 and 2019).

Temperature (°C)	**Relative humidity (%)**			
	30	**50**	**70**	**80**
20	450	380	225	40
30	380	230	150	25
40	300	150	100	15

Table 3.3 The color co-ordinates corresponding to the six grades of the USDA pecan color rating scale (Thompson et al., 1996; USDA, 1969)

Grades	Color coordinates[a]			
	HVC	**RGB**	**Lab**	**LCh**
Light cream	2.5Y,8,4	223,200,150	81,1,28	81,28,88°
Cream	10YR, 7,4	202,171,128	72,5,27	72,27,79°
Golden	7.5YR,6,4	179,142,110	62,9,22	62,24,67°
Light brown	5YR,5,4	154,115,89	52,12,21	52,24,60°
Reddish brown	2.5YR,4,4	130,87,69	41,16,18	41,24,49°
Dark reddish brown	10R,3,4	105,61,52	31,18,14	31,23,37°

[a]HVC- (Hue, Value, Chroma), RGB (Red, Green, Blue), Lab (lightness, red to green, blue to yellow), LCh (lightness, Chroma, Hue), Y (Yellow), YR (yellow-red), R (Red).

Table 3.4 Summary of fixed effects and interactions of the mixed model analysis for hue lightness and chroma for pecans stored at different temperatures, RH and storage days.

Source	F Ratio (Hue)	F Ratio (Lightness)	F Ratio (Chroma)	Prob > F
Temperature (T, °C)	133.72	320.96	180.96	<0.05
RH (%)	5.18	222.76	183.58	<0.05
Storage days [% RH]	213.84	1184.53	545.06	<0.05
T * RH	8.34	22.52	13.47	<0.05
T *Storage Days [% RH]	12.68	19.92	11.89	<0.05

Table 3.5 Least square mean values[a] of pecan nutmeat hue (h) under different storage conditions (n=3).

	Relative Humidity							
	30%		**50%**		**75%**		**80%**	
Temp (°C)	**Days**	**Hue**	**Days**	**Hue**	**Days**	**Hue**	**Days**	**Hue**
20	0	71.48±2.79 a	0	71.48±2.79 a	0	71.48±2.79 a	0	71.48±2.79 a
	90	66.14±3.64 ab	75	65.55±3.44 ab	37	66.57±2.99 ab	8	69.28±2.77 a
	180	63.01±2.30 bc	150	62.91±2.47 bc	74	65.18±4.59 bcd	24	68.72±2.51 ab
	270	60.39±2.75 cd	225	61.128±3.33 cd	111	64.74±2.21 bcd	16	68.52±2.83 ab
	360	58.63±2.83 d	300	59.35±3.96 cd	148	62.66±2.73 cd	32	67.73±2.48 ab
	450	52.50±4.06 e	375	57.77±2.93 e	185	61.10±3.96 d	40	65.84±2.86 b
	Mean	*64.24±1.94 B*	*Mean*	*64.73 ± 2.04 AB*	*Mean*	*65.64±2.38 AB*	*Mean*	*67.52±3.28 A*
30	0	71.48±2.79 a	0	71.48±2.79 a	0	71.48±2.79 a	0	71.48±2.79 a
	75	61.65±2.79 b	45	66.78±2.16 b	30	65.90±3.25 a	5	69.60±3.06 a
	150	54.78±2.98 c	90	58.93±3.91 c	60	57.40±6.45 b	10	69.24±2.37 a
	225	51.94±3.54 cd	135	56.36±2.31 d	90	57.11±4.01 b	15	67.68±2.05 a
	300	47.63±4.85 de	180	53.32±2.59 de	120	54.45±3.67 b	20	64.71±3.03 b
	375	46.75±4.60 e	225	52.99±2.64 e	150	52.72±3.55 b	25	63.17±2.32 b
	Mean	*59.07±2.08 DE*	*Mean*	*61.21±2.23 CD*	*Mean*	*60.15±2.36 D*	*Mean*	*64.25±3.39 ABC*
40	*0*	*71.48±2.79 a*	*0*	*71.48±2.79 a*	*0*	*71.48±2.79 a*	*0*	*71.48±2.79 a*
	30	61.33±5.58 ab	28	65.46±2.80 a	7	68.20±3.03 a	3	65.97±3.81 ab
	60	55.93±4.52 bc	56	58.81±5.91 b	14	65.27±2.34 b	6	62.44±2.37 bc
	90	51.70±5.14 cd	84	56.75±5.06 b	21	60.65±2.35 c	9	62.19±4.13 c
	120	49.44±2.85 d	112	55.33±3.31 bc	28	57.29±4.06 d	12	55.25±5.16 d
	150	46.82±5.73 d	140	50.50±5.05 c	35	54.76±2.95 e	15	54.32±3.49 d
	Mean	*56.91±2.34 EF*	*Mean*	*60.04±2.28 D*	*Mean*	*58.67±1.77 DE*	*Mean*	*52.96±3.56 F*

[a] The values are tabulated as mean ± standard deviation. The lowercase letters indicate differences between means at different storage times for each humidity × temperature interaction. The uppercase letters indicate difference in hue at the four humidity levels at all temperatures.

Table 3.6 Least square mean values[a] of pecan nutmeat lightness (L) under different storage conditions (n=3).

	Relative humidity							
	30%		**50%**		**75%**		**80%**	
Temp (°C)	**Days**	**Lightness**	**Days**	**Lightness**	**Days**	**Lightness**	**Days**	**Lightness**
20	0	72.09±4.10 a	0	72.09±4.10 a	0	72.09±4.10 a	0	72.09±4.10 a
	90	54.55±6.02 b	75	55.00±6.64 b	37	51.42±4.47 b	8	53.51±5.08 b
	180	48.83±5.61 bc	150	49.57±6.15 c	74	50.79±7.13 bc	16	50.17±4.40 bc
	270	45.99±3.68 cd	225	43.73±1.29 c	111	51.27±5.41 bc	24	50.88±3.97 bc
	360	45.07±3.25 cd	300	43.72±4.44 c	148	45.22±3.68 c	32	46.55±2.23 bc
	450	40.94±3.38 d	375	43.18±3.73 c	185	45.10±3.65 c	40	44.12±2.76 c
	Mean	*56.59±2.04 A*	*Mean*	*56.46±2.05 A*	*Mean*	*55.03±2.11 AB*	*Mean*	*48.05±2.02 D*
30	0	72.09±4.10 a	0	72.09±4.10 a	0	72.09±4.10 a	0	72.09±4.10 a
	75	48.65±5.78 b	45	50.11±5.51 b	30	49.79±5.32 b	5	52.84±3.70 b
	150	44.23±4.29 c	90	43.51±2.78 c	60	43.81±4.94 c	10	49.82±3.35 bc
	225	41.06±3.46 cd	135	41.64±2.01 cd	90	44.55±5.92 c	15	49.27±5.16 cd
	300	40.31±4.97 cd	180	39.93±1.98 d	120	41.05±3.98 c	20	46.91±5.94 de
	375	39.85±3.61 d	225	40.97±4.76 d	150	40.58±4.69 c	25	43.83±2.79 e
	Mean	*52.87±2.05 BC*	*Mean*	*50.70±2.09CD*	*Mean*	*50.08±2.12 D*	*Mean*	*41.99±2.06 E*
40	0	72.09±4.10 a	0	72.09±4.10 a	0	72.09±4.10 a	0	72.09±4.10 a
	60	45.52±3.85 b	28	50.69±4.34 b	7	54.63±6.28 b	3	49.19±4.80 b
	30	45.41±5.51 bc	56	44.55±3.04 c	14	50.96±2.97 c	6	43.03±3.14 c
	90	41.57±3.44 c	84	44.39±3.95 c	21	46.75±3.88 d	9	44.27±4.76 c
	120	39.63±2.95 c	112	41.89±4.09 cd	28	41.65±4.20 e	12	38.48±4.57 d
	150	38.75±3.64 c	140	40.16±2.96 d	35	39.84±2.91 e	15	37.40±3.41 d
	Mean	*49.63±2.12 D*		*Mean 49.93± D*	*Mean*	*42.70±2.02 E*	*Mean*	*28.10±2.36 F*

[*] The values are tabulated as mean ± standard deviation. Different letters indicate significant difference between means based on Tukey's HSD (α = 0.05). The lowercase letters indicate differences between means at different storage times for each humidity × temperature interaction. The uppercase letters indicate difference in lightness at the four humidity levels at all temperatures.

Table 3.7 Least square values[a] of pecan nutmeat chroma (C) under different storage conditions (n=3).

Temp (°C)	Relative humidity							
	30%		50%		75%		80%	
	Days	Chroma	Days	Chroma	Days	Chroma	Days	Chroma
20	0	49.14±2.30 a	0	49.14±2.30 a	0	49.14±2.30 a	0	49.14±2.30 a
	90	43.09±6.79 b	75	36.50±5.21 b	37	36.03±3.59 b	8	34.42±3.24 b
	180	37.41±7.28 bc	150	35.68±4.60 b	74	35.85±6.68 b	16	33.65±3.10 b
	270	35.87±5.53 bc	225	31.97±2.14 b	111	38.41±5.05 b	24	34.95±2.47 b
	360	34.15±2.87 c	300	34.81±4.62 b	148	32.59±4.47 b	32	34.41±2.17 b
	450	31.68±3.02 c	375	33.07±2.07 b	185	32.23±6.98 b	40	32.34±1.91 b
	Mean	*41.39±2.69 A*	*Mean*	*40.15±2.73 AB*	*Mean*	*39.11±2.89 AB*	*Mean*	*32.41±2.59 BC*
30	0	49.14±2.30 a	0	49.14±2.30 a	0	49.14±2.30 a	0	49.14±2.30 a
	75	36.14±6.13 b	45	36.33±3.83 b	30	35.57±3.56 b	5	34.99±3.27 b
	150	31.72±3.16 bc	90	31.32±3.41 c	60	31.09±4.32 b	10	33.84±2.63 b
	225	31.58±2.56 bc	135	30.36±1.84 c	90	34.14±6.02 b	15	34.83±4.33 b
	300	29.96±4.69 c	180	30.14±2.02 c	120	31.22±3.70 b	20	33.21±4.50 b
	375	30.10±3.99 c	225	29.93±2.72 c	150	30.11±5.49 b	25	31.20±1.89 bc
	Mean	*38.17±2.73 CD*	*Mean*	*36.56±2.85 CD*	*Mean*	*36.34±2.93 CD*	*Mean*	*29.55±2.41 D*
40	0	49.14±2.30 a	0	49.14±2.30 a	0	49.14±2.30 a	0	49.14±2.30 a
	60	31.22±2.57 bc	28	35.95±3.35 b	7	36.39±3.70 b	3	34.53±4.21 b
	30	34.63±4.42 b	56	32.90±3.29 c	14	35.92±2.53 b	6	28.34±2.55 cd
	90	31.07±2.99 bc	84	33.91±3.94 bc	21	35.00±2.16 b	9	30.98±3.25 c
	120	30.09±2.20 bc	112	32.66±3.08 cd	28	29.96±2.31 c	12	25.56±3.71 de
	150	29.06±5.29 c	140	30.51±3.08 d	35	30.16±2.37 c	15	25.32±2.77 d
	Mean	*35.46±2.93 E*	*Mean*	*36.28±2.94 E*	*Mean*	*31.03±2.52 E*	*Mean*	*18.97±2.47 F*

[a] The values are tabulated as mean ± standard deviation. Different letters indicate significant difference between means based on Tukey's HSD ($\alpha = 0.05$). The lowercase letters indicate differences between means at different storage times for each humidity × temperature interaction. The uppercase letters indicate difference in chroma at the four humidity levels at all temperatures.

Table 3.8 Summary of F ratio and adjusted coefficient of determination (R^2) for the linear and exponential regression solutions for the LCh of pecan nutmeats stored under different conditions of relative humidity (RH and temperature) over different numbers of days[a].

Temperature (°C)	RH (%)	Lightness		Chroma		Hue	
		F ratio	Adj. R^2	F ratio	Adj. R^2	F ratio	Adj. R^2
20	**30**	78.34	0.75	81.77	0.78	70.41	0.70
	50	70.52	0.71	80.60	0.80	80.75	0.77
	70	71.96	0.72	76.94	0.76	74.56	0.72
	80	71.82	0.78	90.47	0.80	5.57	0.18
30	**30**	123.23	0.79	56.61	0.62	133.07	0.80
	50	131.16	0.85	73.49	0.75	117.3	0.83
	70	94.06	0.74	46.84	0.57	61.36	0.64
	80	88.32	0.75	63.44	0.67	30.84	0.51
40	**30**	146.09	0.81	70.92	0.67	70.56	0.74
	50	130.30	0.81	47.24	0.60	66.39	0.71
	70	121.23	0.79	115.00	0.79	106.59	0.77
	80	166.75	0.82	128.28	0.76	72.71	0.65

[a]Data from the three cultivars Stuart, Desirable and Pawnee combined.

Table 3.9 The least square mean values[a] of change in hue (Δh) of pecan nutmeats with storage time in days (n=6) at different temperatures and RH.

Temp (°C)	Relative humidity (%)							
	30		50		75		80	
	Days	Δh	Days	Δh	Days	Δh	Days	Δh
20	0	0	0	0	0	0	0	0
	90	4.69±2.53a	75	4.05±1.84 a	37	2.36±2.46 a	8	3.24±3.13 a
	180	10.07±1.98b	150	8.45±1.22 b	74	3.49±1.46 a	24	3.06±3.73 a
	270	12.92±1.10c	225	10.35±4.08 c	111	6.50±1.65 b	16	3.72±3.02 a
	360	13.65±3.1d	300	13.59±5.11 d	148	9.49±1.77 c	32	3.86±3.53 a
	450	18.03±2.65e	375	15.02±1.55 e	185	9.58±2.74c	40	5.06±2.85 a
30	0	0	0	0	0	0	0	0
	75	9.94±0.89 a	45	5.00±1.90a	30	5.31±1.71 a	5	0.803±2.03 a
	150	15.14±2.08 b	90	13.07±4.06b	60	9.00±2.71 b	10	0.78±2.13 a
	225	19.67±1.69 c	135	14.53±1.06c	90	12.73±2.83 b	15	3.81±0.81 b
	300	24.06±1.32 d	180	17.67±1.89d	120	16.34±3.43bc	20	5.51±1.63 c
	375	26.28±2.11 e	225	18.14±2.84d	150	19.64±1.51 e	25	8.07±1.62 d
40	0	0	0	0	0	0	0	0
	30	7.40±3.94 a	28	5.38±1.52 a	7	4.33±1.63 a	3	3.81±1.63 a
	60	13.65±1.55 b	56	10.16±1.54 b	14	6.80±2.12 a	6	8.24±2.12 b
	90	18.01±4.18 bc	84	12.42±1.05bc	21	11.03±2.00bc	9	10.80±4.18 bc
	120	22.12±2.32 c	112	14.78±1.32c	28	14.59±1.52 c	12	17.25±4.36 c
	150	22.50±4.74 bc	140	18.67±2.09 d	35	16.69±0.55 d	15	17.73±3.36 c

[a]The values are tabulated as mean ± standard deviation (n=6). Different letters indicate significant difference between means based on Tukey's HSD (α = 0.05). Data from the three cultivars Stuart, Desirable and Pawnee combined.

Table *3*.10 Summary of the rate constants (k) and activation energy (E_a) for color attributes pertaining to pecan nutmeat color of three different cultivars (Desirable, Pawnee, and Stuart) stored at different temperatures and relative humidity (n=2).

Cultivars	Temp (°C)	RH (%)	Lightness			Hue			Chroma		
			k (day^{-1})	Adj. R^2	E_a (kJ/mol)	k (day^{-1})	Adj. R^2	E_a (kJ/mol)	k (day^{-1})	Adj. R^2	E_a (kJ/mol)
Desirable	**20**	**30**	0.006±0.001	0.85	15.10±13.52a	0.032±0.001	0.95	29.16±8.08b	0.001±0.003	0.68	23.83±14.89a
	30		0.012±0.008	0.98		0.066±0.001	0.87		0.011±0.006	0.91	
	40		0.019±0.023	0.89		0.157±0.037	0.91		0.025±0.034	0.85	
	20	**50**	0.013±0.003	0.94	11.33±16.02a	0.033±0.006	0.78	30.34±3.75b	0.018±0.013	0.8	16.23±22.95a
	30		0.021±0.001	0.98		0.082±0.012	0.93		0.017±0.012	0.99	
	40		0.040±0.009	0.94		0.178±0.019	0.77		0.047±0.007	0.9	
	20	**75**	0.041±0.001	0.94	12.64±6.65a	0.045±0.009	0.82	40.87±1.25ab	0.053±0.002	0.85	22.60±5.94a
	30		0.039±0.043	0.92		0.164±0.016	0.86		0.077±0.002	0.77	
	40		0.061±0.020	0.97		0.474±0.021	0.97		0.105±0.12	0,92	
	20	**80**	0.156±0.116	0.95	10.77±12.96a	0.050±0.017	0.52	57.30±7.78a	0.268±0.005	0.89	24.86±4.56a
	30		0.118±0.166	0.94		0.324±0.028	0.89		0.209±0.247	0.93	
	40		0.348±0.076	0.96		1.048±0.175	0.96		0.402±0.013	0.95	
Pawnee	**20**	**30**	0.010±0.003	0.89	22.10±0.19a	0.039±0.005	0.85	20.08±1.69b	0.008±0.009	0.63	23.32±8.24a
	30		0.014±0.006	0.93		0.052±0.006	0.76		0.016±0.021	0.81	
	40		0.017±0.010	0.88		0.140±0.021	0.83		0.040±0.011	0.86	
	20	**50**	0.006±0.006	0.97	15.27±6.76a	0.027±0.005	0.78	27.51±4.77ab	0.014±0.002	0.92	12.81±1.38a
	30		0.031±0.002	0.99		0.081±0.007	0.85		0.035±0.002	0.99	
	40		0.039±0.002	0.99		0.127±0.014	0.97		0.053±0.010	0.99	
	20	**75**	0.043±0.001	0.86	10.26±0.29a	0.054±0.007	0.92	37.61±0.92a	0.069±0.020	0.82	14.89±6.77a
	30		0.060±0.028	0.93		0.130±0.020	0.86		0.082±0.013	0.66	
	40		0.064±0.005	0.97		0.492±0.005	0.99		0.110±0.014	0.92	
	20	**80**	0.153±0.005	0.82	18.00±0.71a	0.171±0.018	0.97	37.44±3.83a	0.243±0.058	0.95	8.70±6.74a
	30		0.231±0.034	0.97		0.312±0.003	0.9		0.351±0.031	0.95	
	40		0.412±0.122	0.95		0.959±0.121	0.84		0.385±0.051	0.94	
Stuart	**20**	**30**	0.012±0.001	0.99	19.55±14.34a	0.043±0.006	0.99	26.19±3.75bc	0.010±0.005	0.88	26.08±26.57a

30		0.020±0.007	0.98		0.067±0.011	0.93		0.024±0.016	0.93	
40		0.029±0.025	0.95		0.166±0.016	0.92		0.042±0.036	0.95	
20	**50**	0.008±0.001	0.88	19.38±2.16a	0.039±0.005	0.88	22.28±4.90c	0.021±0.003	0.76	25.87±13.87a
30		0.023±0.008	0.96		0.087±0.014	0.87		0.024±0.012	0.92	
40		0.041±0.004	0.97		0.130±0.006	0.96		0.039±0.042	0.9	
20	**75**	0.013±0.013	0.89	25.38±20.41a	0.045±0.011	0.8	42.75±5.41ab	0.034±0.007	0.59	28.05±1.16a
30		0.037±0.007	0.97		0.122±0.001	0.86		0.042±0.046	0.87	
40		0.100±0.064	0.97		0.489±0.040	0.99		0.153±0.031	0.93	
20	**80**	0.182±0.018	0.91	6.53±3.14a	0.064±0.022	0.18	46.44±1.15a	0.386±0.006	0.95	7.63±1.40a
30		0.261±0.037	0.94		0.325±0.039	0.95		0.373±0.030	0.9	
40		0.287±0.036	0.97		1.315±0.103	0.95		0.431±0.025	0.94	

The values are tabulated as mean ± standard deviation (n=2). k (rate constant), E_a (Activation Energy). E_a's with different letters indicate significant difference between estimated values based on Tukey's HSD ($\alpha = 0.05$). Three parameter exponential model for lightness and chroma: predicted color attribute = a + b*exp (c*storage days). All *k* values are negative.

Table 3.11 Summary of Q_{10} values (hue) of pecan nutmeats exposed to different temperatures.

Temperature	RH	Q_{10} value[a]
20→30	30	1.65±0.37
	50	2.57±0.39
	75	2.92±0.64
	80	4.61±2.39
30→40	30	2.52±0.16
	50	1.74±0.37
	70	3.56±0.59
	80	3.45±0.52

The values are tabulated as mean ± standard deviation (n=2).

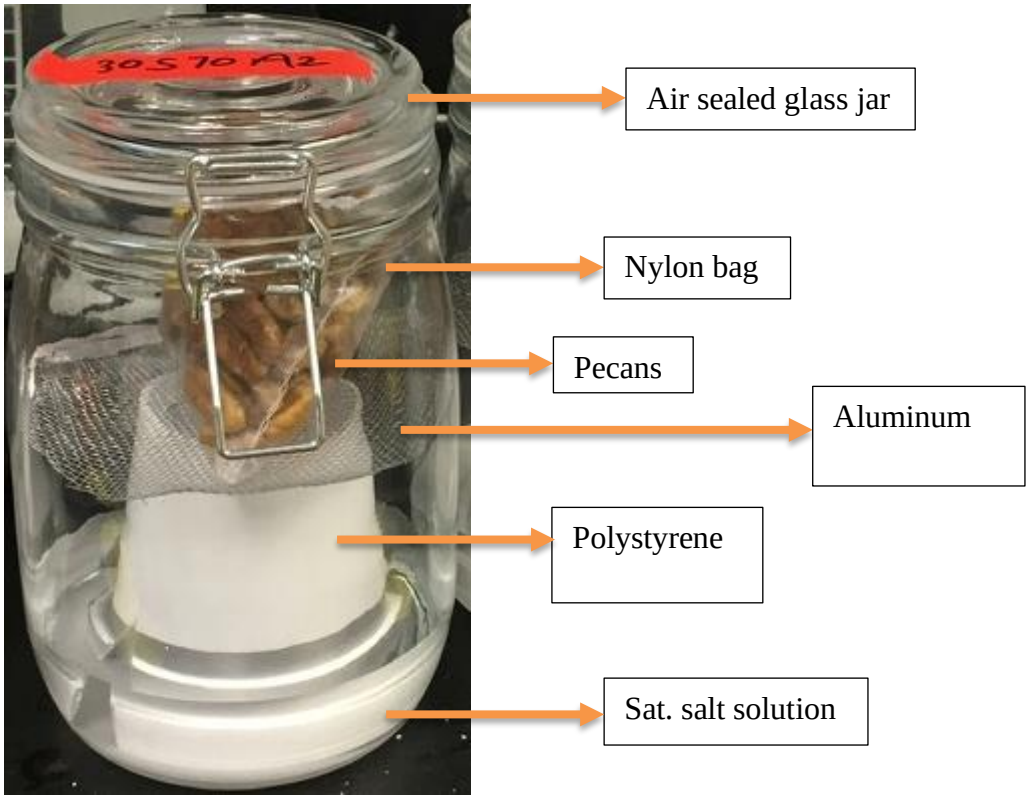

Figure 3.1. The static humidity chamber used in the pecan nutmeat storage experiments

1	2	3	4	5	6
Light Cream	**Cream**	**Golden**	**Light Brown**	**Reddish Brown**	**Dark Reddish Brown**

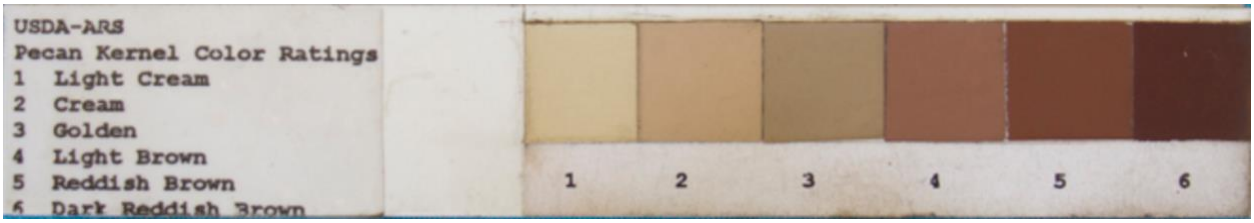

Figure 3.2 The digitized version of the pecan color scale and standards (A) adapted from the USDA pecan color rating scale (B) and results presented by Thompson, Grauke, and Young (1996). The digital version of the scale can be reproduced anywhere using the color coordinates provided in Table 3.

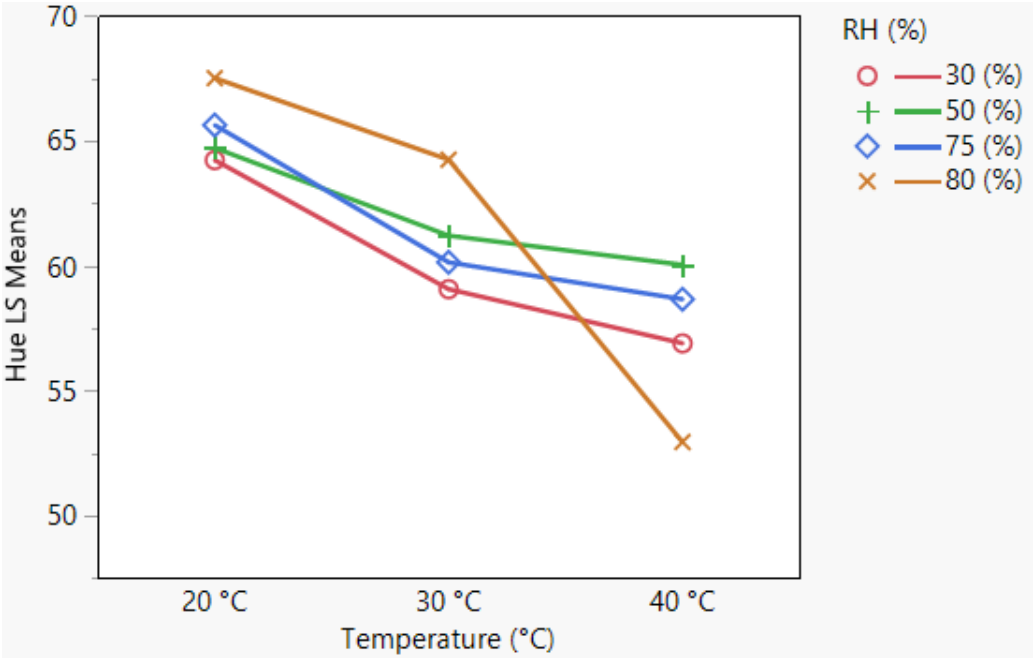

Figure 3.3. Interaction plot illustrating change in pecan hue with change in relative humidity (%) and temperature (°C). Note that hue values approaching zero indicates red color. (F-ratio = 8.34, p-value <0.05)

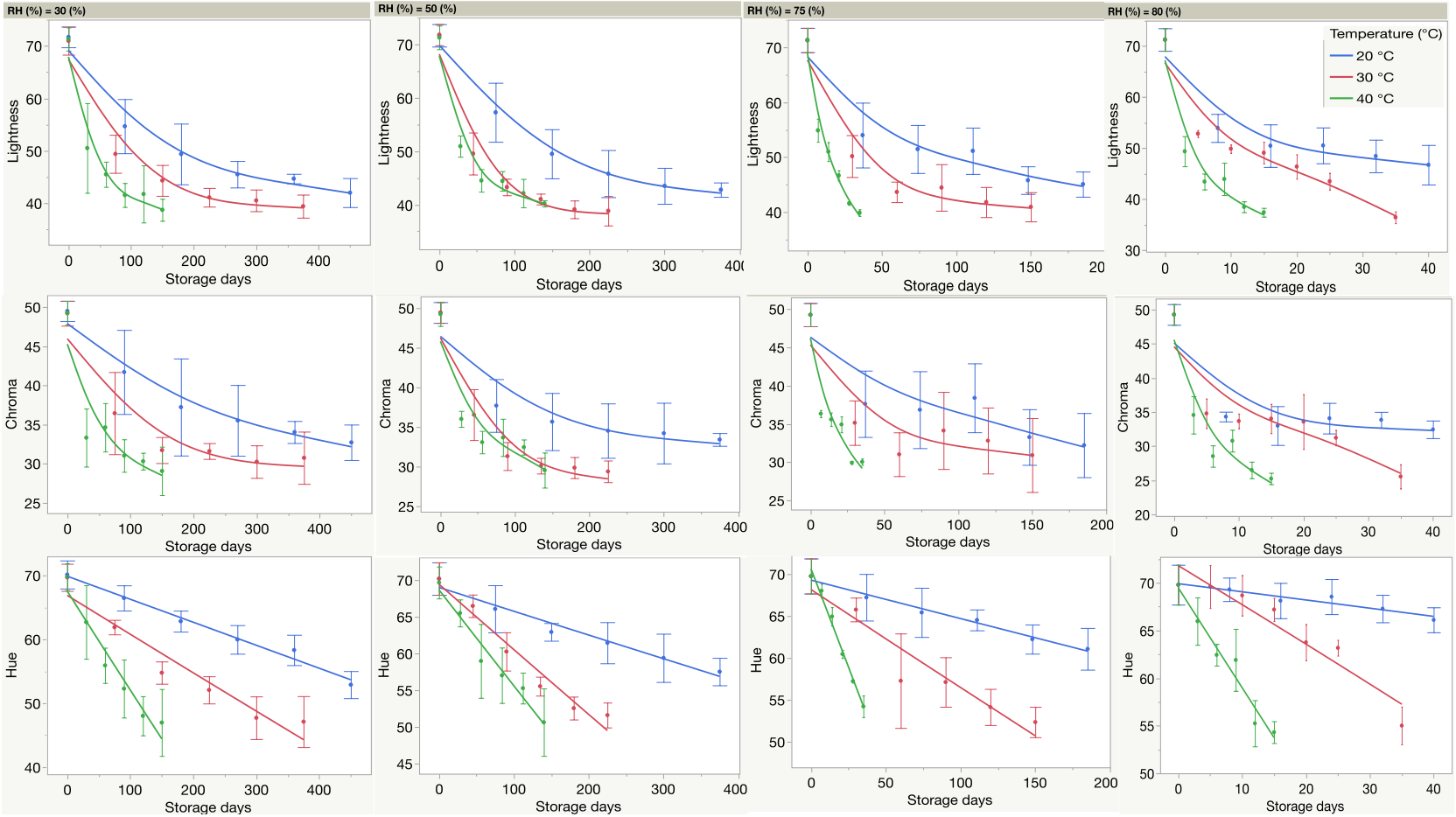

Figure 3.4. The change in color attributes of pecan nutmeats during storage periods of up to 450 days at different temperatures and RH (n=3)

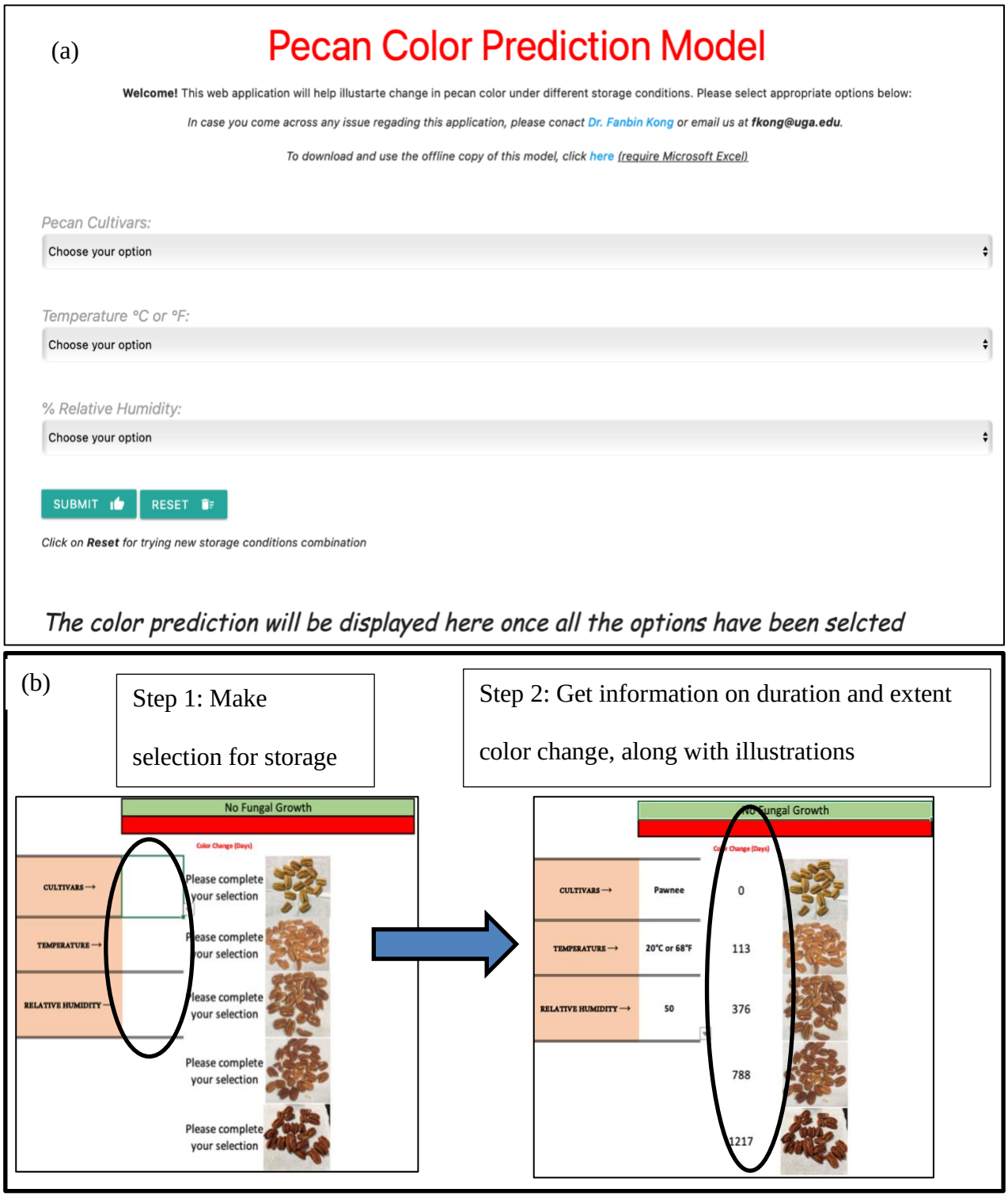

Figure 3.5. (a) Online web application for pecan color prediction - the user can select different storage condition combinations (cultivar, storage temperature and relative humidity) (b) the Microsoft Excel – version of the pecan color prediction model which can be downloaded to devices. The prediction from both these models will provide illustrations of pecan color change.

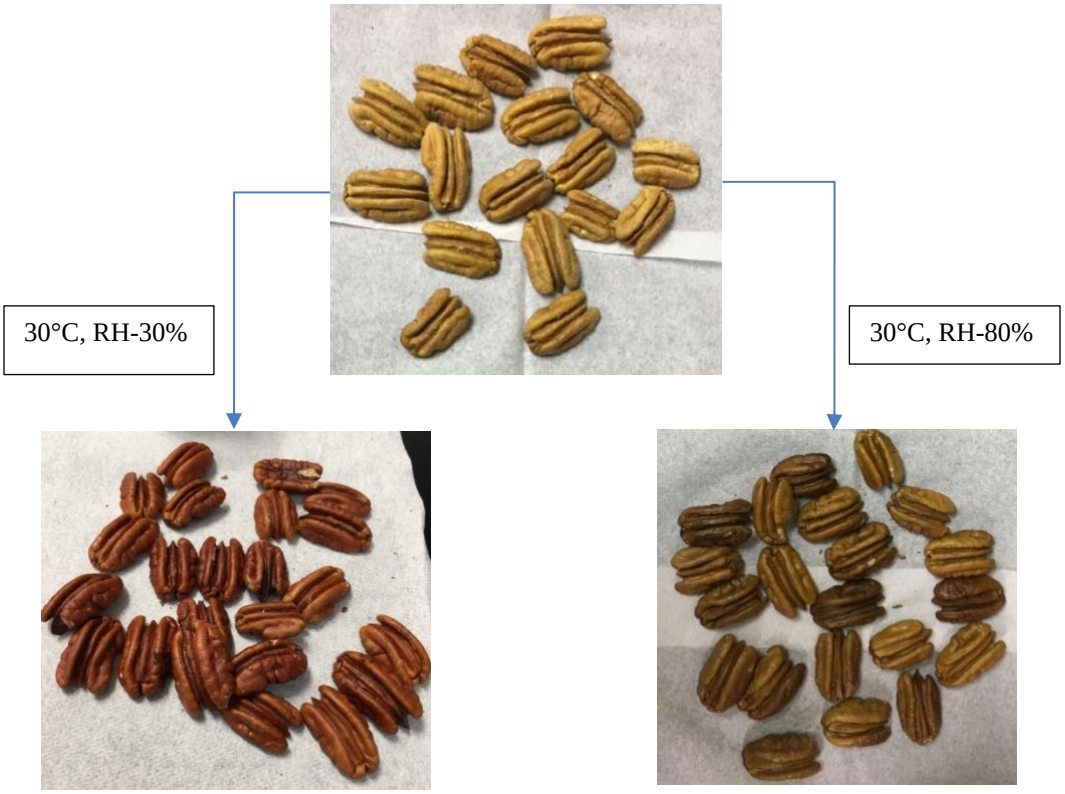

Figure 3.6. Color development in pecan nutmeats (cultivar Stuart) stored under different % relative humidity (30 and 80%) and at 30°C.

CHAPTER 4

EFFECT OF RELATIVE HUMIDITY, STORAGE DAYS AND PACKAGING ON PECAN KERNEL TEXTURE: ANALYSES AND MODELING[3]

[3] Prabhakar H., Kerr W.L., Bock C., Kong F. 2022. Submitted to Journal of Texture Studies.

Abstract

The studies expounding effects of storage conditions on texture changes are limited. The researchers have been proposing methods to measure pecan texture instrumentally. But current protocols and/or attribute fail to address huge variability during experimentation. Additionally, there are no predictive model to estimate changes in pecan texture during storage. This study addresses all the above concerns and investigate effects of different relative humidity (RH, 30 to 90%) and packaging material (PEN [polyethylene nylon], PP [polypropylene], LDPE [low density polyethylene] and ML [metallic laminates]) on pecan texture, introducing a rift ratio (F/H or fracturability to hardness ratio) to address variability in the data and predictive model to estimate changes in textural attribute of pecans during storage. The textural analysis was conducted on pecans cores and intact pecans to measure area under curve, fracturability, hardness, cohesiveness, chewiness, springiness, and rift ratio. It was observed that values for rift ratio obtained using intact pecan method had high R^2 (0.72) as compared to rest of textural attribute. A 3-parameter logistic model was employed to predict pecan texture during storage. The pecans stored at 75%, 80% and 90% lost half of initial fracturability at approx. 115, 3, and 0.15 days (~ 4 hours), respectively. The pecans stored in LDPE, PP and PEN packs at 80% lost half of initial fracturability at approx. 26, 57, and 78 days, respectively. The presence of any kind of package delayed the fracturability loss by at least 8 folds at 80% RH. The pecans stored in ML did not experience significant change in textural attributes.

Introduction

Pecan is among the few US native crops with an annual crop value of 560 to 700 million USD (NASS, 2020). The Pecan trees are alternate bearing and take anywhere between 5 to 10 years before producing nuts (R. Zhang, Peng, & Li, 2015). The yield of pecan trees is often diminished by factors such as excessive rain, drought, winds, sunlight exposure, or damage inflicted by insects, rodents, birds, or molds (Erickson, Santerre, & Malingre, 1994). One strategy used by pecan growers and processors is to store nuts for extended periods to ensure a buffer to meet production demand both within and outside the US (NASS, 2020). Along with Color and aroma (S. Kays, 1979; Prabhakar, Bock, Kerr, & Kong, 2022), pecan texture is an important indicator of pecan quality. Absence of crispiness and/or brittleness can discourage buyers from consuming pecans, and might a (Prabhakar, Sharma, & Kong, 2020) discourage them from purchasing future products. Several researchers have investigated the effects of different conditions encountered during harvesting, storage and transportation on texture of pecans including drying (Shult & Brusewitz, 1998), freezing, thawing, and freeze/thaw cycles (Anzaldúa-Morales, Brusewitz, & Junus, 1999; Surjadinata, Brusewitz, & Bellmer, 2001), oil removal (Shult & Brusewitz, 1998; C. Zhang, H. Brusewitz, O. Maness, & A. M. Gasem, 1995), and moisture restoration (Anzaldua-Morales, Brusewitz, & Maness, 1998).

Pecan kernels are non-uniform in size and have irregular surface structure which make it challenging to conduct instrumental measures of texture. The asymmetrical surface makes it difficult to attain a repeatable contact area between probe and nut, thus introducing variations that cause the test method to be inaccurate (Bourne, 2002). Thus, researchers have relied on sensory panelists for texture evaluation of (Ocòn, Anzaldúa-

Morales, Quintero, & Gastélum, 1995; Resurreccion & Heaton, 1987; Taipina, Lamardo, Rodas, & del Mastro, 2009). Resurreccion and Heaton (1987) developed an objective texture method to measure texture for distinguishing differences between early and traditionally harvested pecans. The authors conducted a puncture test and calculated the shear force required to cut the pecans halves using a blunt blade attachment. The proposed method did not reflect situations where pecans experience mechanical deformation during handling and storage. to address issues with sample non-the uniformity criteria, Ocòn et al. (1995) proposed a method where samples are prepared by driving a cork borer perpendicularly through the pecan kernel and taking out cylinders of uniform dimensions (Prabhakar et al., 2020). The core method is the most adopted textural analysis method for pecan texture (Anzaldúa-Morales, Brusewitz, & Anderson, 1999; Shult & Brusewitz, 1998; Surjadinata et al., 2001). However, these researchers found very low correlation between sensory and instrumental analysis for texture determination, indicating a need for more accurate ways to determine textural attributes.

There are many reports of the effect of processing methods (roasting, drying, dehydration, etc.) on texture of walnuts (Kita & Figiel, 2007), pistachio (Farahnaky & Kamali, 2015; Mohammadi Moghaddam, Razavi, Taghizadeh, & Sazgarnia, 2016), macadamia (Domı, Azuara, Vernon-Carter, & Beristain, 2007; Tu et al., 2021), pecans (J. Zhang et al., 2019) and pecan shells (Littlefield, Fasina, Shaw, Adhikari, & Via, 2011). However, there are few studies investigating the effects of moisture migration (from kernels to environment and vice versa) on pecan kernel texture and tree-nuts in general, with and/or without use of commonly available packaging materials such as PE, PP, cellophane, etc. (Prabhakar et al., 2020). Furthermore, ability to predict changes in texture

under a given set of conditions is valuable for the industry to maximize quality of kernels during storage, or to maximize shelf life once in a store for consumers. Probabilistic models can be used for to predict shelf life based on a specified set of conditions. However, there are no such model(s) available for predicting changes in pecan kernel texture with changing storage/distribution conditions.

The objectives of this research were to investigate changes in pecan kernel texture due to environmental conditions (RH and packaging type), and to develop a predictive model suitable to estimate change in texture of pecan kernels attributes as storage progressed under different environments.

Material and Methods

Pecan Production, Source of Nutmeat and Storage Experiment:

Three cultivars of pecan (Carya illinoinensis 'Stuart', 'Pawnee' and 'Desirable') were harvested from orchards located at the USDA-Agriculture Research Service (ARS) Fruit and Tree Nut Research Laboratory, Byron, Georgia (U.S.A.), (+32.6650 N, + 83.7419 W, elevation of ≈156 m, 240 d freeze-free growing period, annual precipitation of 118 cm). Orchards received standard tree management practice for the state of Georgia (Wells, Prostko, & Carter, 2019). The experiment was performed twice, with pecans harvested in November 2018 and December 2019, respectively. In each season, the pecans were processed within 1 week of harvesting. The harvested pecans were conditioned prior to shelling by immersing in 85 °C water for 3 min, followed by drying at room temperature for 20–25 min and shelling via mechanical sheller (Modern Electronics, Mansfield, LA) (Forbus Jr & Senter, 1976). After shelling, pecans were dried at 20 °C and 45% RH

overnight to a moisture content of 4–5% moisture content (AOAC, 2016) and stored at −20 °C in a commercial freezer until use in the experiments. Information on the different grades of pecans has been provided by Prabhakar et al. (2022).

Experiment Treatments:

The pecans were stored in different RH conditions. The desired RH was achieved by using 200 mL saturated salt solutions placed in a static humidity chamber (STC) consisting of a 1-L glass jar with a rubber gasket to seal the lid. More detailed information on construction of the STCs has been provided by Prabhakar et al. (2022). The saturated salt solutions included magnesium chloride (30–32% RH), magnesium nitrate (50–52% RH), sodium chloride (75% RH), ammonium sulfate (80–81% RH) and potassium nitrate (89-93% RH) (Certified ACS, Fisher Chemical, Waltham, MA) (Rockland, 1960). For the sake of simplicity, the RHs will be denoted as 30%, 50%, 75% 80%, and 90%, respectively. The STCs containing pecans from three cultivars were placed in temperature-controlled chambers at 20, 30 and 40 °C. For each temperature × humidity treatment (n = 2 jars for each combination), 50 g of whole pecans (25 to 40 pecan halves) were placed in a nylon bag suspended above the saturated solutions on an aluminum mesh disc in the STC. To simulate a real storage environment and corresponding air composition, the jars were opened periodically (every 1–2 weeks) for 30 s to allow fresh air into the container. In addition, some pecans were placed in packages available to pecan producers and packers viz. low-density polypropylene (LDPE, thickness:50-54 µm), polypropylene (PP, thickness:45-50 µm), polyethylene-nylon (PEN, thickness:105-110 µm) and metallic laminates (ML, thickness:105-110 µm). The packages were obtained from OpenTip.com

and sealed using American International Electric Heat Impulse sealer (City of Industry, CA) The packaged samples were stored at 58% and 80% RH at temperature range similar to the unpacked STC pecans. The kernel samples were drawn at predetermined intervals based on previous reports of pecan quality changes in the literature (Blackmon, 1932; Brison, 1945; S. J. Kays, 1979; Magnuson, Koppel, Reid, & Chambers IV, 2015; Mexis, Badeka, Riganakos, Karakostas, & Kontominas, 2009; Senter & Wilson, 1983). The storage time ranged from 15 to 450 days, depending on the treatment. The mold growth assessment was performed visually and samples with mold growth were discarded. Any mold growth was assessed visually and samples with mold growth were discarded.

Sample Preparation:

Pecan Core Method -

The samples were prepared according to method published by Ocòn et al. (1995). To obtain uniform samples for texture analysis, a cork borer was inserted perpendicularly through the pecan kernels to obtain cylindrical specimens 3 mm in diameter and 5 mm in length. The cored samples were analyzed using single compression method as the cores were not strong enough to sustain second compression. The textural attributes studied included first peak (hardness) and area under curve (AUC).

Intact Pecan-Halve Method -

The intact pecan kernels or halves were compressed under a flat probe for texture profile analysis (TPA, double compression). The textural attributes studied included fracturability, hardness, cohesiveness, springiness, and chewiness. In TPA, these textural attributes can

be defined as follow; fracturability is the first break in the curve force vs extension/time curve, hardness is the highest force on the first compression cycle (always followed by fracturability), cohesiveness is the ratio of (positive) first and second force areas, springiness is the recovery distance between the end of first and start of second compression, chewiness is product of hardness x cohesiveness x springiness and can be defined as force required to chew the food product . In addition to these textural attributes, fracturability/hardness ratio (F/H, referred to as rift ratio from this point onwards) was also studied.

The cored and intact pecan samples were compressed up to 50% of strain under a 55mm compression probe using a TA.XT2 texture analyzer (Texture Technologies Corporation, Scarsdale, New York/Stable Micro Systems, Haslemere, Surrey, UK). The test parameters were as follow: pre-test speed – 1mm/s, test speed – 5 mm/s, post-test speed – 5 mm/s. A total of 10 measurements were taken from unpacked and packed pecans. The packed pecans were only analyzed using intact pecan method.

Predictive Model -

A three-parameter logistic (3PL) model, a type of sigmoid model, was used to predict the changes in pecan textural attributes over time. The 3PL model is a type of logistic model prominently used in immunoassays research (Herman, Scherer, & Shan, 2008) such as ELISA, microbial growth prediction (Fujikawa, 2010), dose-response relationships (Andrade-Mogrovejo et al., 2022; Carøe, Ebbehøj, Bonde, Flachs, & Agner, 2018; ElHarouni et al., 2022), and geological phenomena (Chen et al., 2019; Joshuva, Deenadayalan, Sivakumar, Sathishkumar, & Vishnuvardhan, 2019). The parameters give

unique information such as maximum value to response achieved (asymptote), growth rate or slope, and the value of a predictor variable for median response (inflection point) (Fig. 4.1). The 3PL model equation can be denoted as:

$$\hat{y} = \frac{c}{1+exp^{(-ax+ab)}} \qquad (1)$$

Where a is the growth rate or slope, b is the inflection point, c is the asymptote and ŷ is the predicted response. The logistic model was built using a non-linear function in JMP®, Version 16 Pro (SAS Institute Inc., Cary, NC).

Experimental Design and Statistical Analyses -

The design of the experiment was a generalized randomized complete block design (GRCBD) where storage days and RH were experimental factors and cultivars were treated as a block. The whole experiment was repeated twice, indicating replication within each block. To avoid complexity and simplify the interpretation of the statistical output, interactions of block and treatment with other factors were omitted. The preliminary experiment indicated no significant effect of temperature on any of textural attribute of pecans ($p>0.05$). Thus, readings from all temperature conditions were pooled for the analysis. The outliers were determined and removed using the "jacknife distance" method.

$$J_i = \sqrt{\frac{(n-2)n^2}{(n-1)^3} \times \frac{{M_i}^2}{1-\frac{nM_i^2}{(n-1)^2}}} \qquad (2)$$

Where n = number of observations, p = number of variables and M_i = Mahalanobis distance for the i^{th} observation. The upper critical line (UCL) is the limit beyond which the Ji values are considered outliers and could be omitted from the analysis. Penny (1996) has provided a detailed account on calculating UCL for jacknife analysis. Subsequently, a mixed model

analysis was performed on refined data. The experiment data was normally distributed, and the model residual plots did not indicate heteroskedasticity. The model fixed effects were RH and storage days whereas cultivar was considered a random effect. The storage days were nested within RH. The dependent variables for core method were hardness and AUC and for intact pecan method were fracturability, hardness, F/H, cohesiveness, chewiness and springiness. The 3PL model parameters were statistically analyzed using One-way ANOVA. The main effects and their interactions (where applicable) were studied and their interactions with blocks were omitted. The fit for the statistical models (mixed (mixed model, ANOVA and 3PL) were assessed based on the adjusted coefficient of determination (adj. R^2). A Tukey's HSD post hoc test (confidence level, $\alpha = 95\%$) was performed to explore differences among means for the different treatments. Multivariate correlation analysis was conducted to understand relationship among multiple dependent factors (textural attributes). All statistical analyses were performed using JMP®, Version 16 Pro (SAS Institute Inc., Cary, NC).

Results

Pecan Core Method:

The change in AUC and hardness with storage time is illustrated in supplementary figure 4.2. The total work done significantly decreased with increase in RH and storage time (Table 4.1). The change in AUC during storage was small among pecans stored between 30 to 75% RH. The change in AUC was greatest for pecans kept at 80% RH. The hardness of the cored pecans was significantly affected by RH and storage time (Table 4.1). The hardness value increased with greater RH. At higher humidity conditions (≧75%), the

hardness increased as storage progressed. The pecans stored at and below 50% experienced a significant decrease in hardness with storage time (Fig. 4.3). Even though the goodness of fit for AUC and hardness was low (0.15 and 0.24, respectively), statistical significance of main effects and interactions do indicate that the independent variables were affected by the predictors. The detailed tabulation of change in AUC and hardness with respect to RH and storage days can be found in table 4.2 and 4.3.

Intact pecan-halve method:

Fracturability and Hardness -

The Fracturability of pecans was most significantly affected by RH as substantiated by goodness of fit (R^2 – 0.67). The fracturability could be defined as the first break point on TPA curve corresponding to a force value. Thus, lower force value corresponds to high fracturability as it signals early fracturability. For unpacked pecans, the increase in RH caused the fracturability value to increase indicating the pecans were losing brittleness (Table 4.1). The change in fracturability increased drastically as RH increased >50% (Fig. 4.4).

For pecans stored in different package materials, the fracturability significantly decreased with change in RH, storage period and packaging material (Table 4.4). The loss of fracturability was minimum in pecans stored in metallic laminates and maximum in pecans stored in LDPE packages. The loss in fracturability was intermediate in PEN and PP packages but the value was in proximity to that for samples in LDPE (Fig. 4.5A, Table 4.5). The overall fracturability of pecans stored in LDPE, PP and PEN at 58% RH was significantly lower than those stored at 80% RH. The impact of environment RH was

negligible for samples stored in metallic laminates. A detailed tabulation of changes in fracturability with RH conditions can be found in table 4.5. Unlike results measured using the core method, the TPA of packed and unpacked pecans did not reveal a definite pattern in terms of change in hardness across storage days and RH.

Rift ratio (F/H) -

There were significant effects of RH and storage duration on F/H (Table 4.1). F/H was greatest at 80% RH and least at 30% RH, and the coefficient of determination of mixed model analysis (R^2 = 0.72) further indicated a relationship between RH and storage duration on F/H. There were significant effects of packaging on F/H (Table 4.4). The LDPE experienced maximum increase in rift ratio followed by PE, PP, and metallic laminate (ML). The difference in rift ratio of LDPE, PE, PP and ML stored at 58% RH were not significant. This ratio was further explored for use in predictive modeling to estimate loss of brittleness during storage. The 3PL model was employed to predict the change in rift ratio with storage time. The growth rate (change in response units per day) indicates an increase in RIFT ratio with time, the inflection point is defined as the time taken to lose half of the fracturability value, and the asymptote refers to maximum rift ratio retained during storage. In addition, the time taken for pecan to lose all fracturability at constant RH condition can also be determined. During storage, it was observed that packaged and unpackaged pecans stored at 58% RH or below did not experience significant loss of fracturability. Thus, predictive model was made only for pecans stored at 75% or above.

Values of the logistic parameters for packaged and unpackaged pecans are tabulated in Tables 4.6 and 4.7. The growth rate and inflection point for unpackaged pecans significantly increased with increase in RH. From the rift point in Table 4.6, it was determined that unpackaged pecans stored at 75%, 80% and 90% lost half of the initial rift ratio at ~115 days, 3 days, and 0.15 days (~ 4 h), respectively. By multiplying the inflection point by 2, the time required at constant RH for complete loss of fracturability (rift ratio= 1.0) was calculated as 230 days for 75% RH, 6 days for 80% RH and 0.30 days (8 h) for 90% RH. The growth rate and inflection point for RH between 75% to 90% can be determined by following equations:

$$Growth\ rate(unpacked\ pecans) = -51.24 + 0.70 * RH \qquad (3)$$

$$Inflection\ point(unpacked\ pecans) = 2.72^{(36.16-0.43*RH)} \qquad (4)$$

Since no definite trend was observed for the asymptote, based on the value for nonpackaged pecans can be assumed to be 0.95 by taking average of asymptote. Table 4.7 contains the growth rate, inflection point and asymptote values for packaged pecans stored at 80% RH. The growth rate was highest in LDPE, followed by PP and PE, indicating a higher water absorption rate in the LDPE package. The pecans stored in LDPE, PP and PEN at 80% RH lost half of initial the fracturability at ~ 26 days, 57 days, and 78 days, respectively. The number of days to reach complete loss of fracturability at constant RH was calculated as: LDPE – 52 days, PP – 114 days, and PEN – 156 days. The rift ratio for packaged pecans stored in 58% RH remained unchanged during storage. Under extreme humidity conditions, the packages provided a decent barrier against moisture transfer, delaying loss

of fracturability as compared to pecans with no package, where the fracturability loss occurred in matter of hours. The following equation predicts the rift ratio at a specific storage day for pecans packaged in abovementioned materials:

$$F/H = 0.35 + PC + 0.0026 * Storage\ days \qquad (5)$$

Where PC is a 'package constant' with values as follows: LDPE =0.084, PEN = -0.042, PP = -0.041. The water vapor transmission rate corresponding to LDPE, PEN and PP are 1.30, 0.41, and 0.50 g.mL/24 hr.100 in^2 , respectively (38°C, 50 to 100% RH) (Tock, 1983).

Cohesiveness -

The cohesiveness of unpackaged and packaged pecan kernels was significantly affected by RH and storage duration, with adjusted R^2 of 0.12 and 0.17, respectively (Table 4.1). The cohesiveness of unpackaged pecans significantly increased with an increase in RH. The unpackaged pecans stored at 75% RH or above experienced a sharp increase in cohesiveness (Fig. 4.4). The pecans stored in metallic laminates had a minimum cohesiveness, however, and was not significantly different from PP and PEN (Table 4.4). LDPE packaged pecans experienced the greatest change in cohesiveness among all the packages (Figure 4.6).

Springiness -

The springiness of unpackaged pecans was significantly affected by RH and storage time (Table 4.1). The change in RH and packaging material had little to no impact on change in the springiness of packaged (< 58%) and unpackaged pecans (<50%) (Table 4.4, figure 4.6). The springiness increased significantly at RH levels higher than 75% (Figure 4.6).

Despite exhibiting significant effect, the adjusted R^2 for unpackaged and packed pecans were 0.27 and 0.11, respectively, indicating limited ability of predictor variables to estimate textural attributes.

Chewiness -

Unlike springiness, the chewiness of unpackaged and packaged pecans significantly increased with increase in RH. The unpackaged pecans stored at or below 50% was significantly less chewy as compared with pecans stored at 75% or higher (Figure 4.6). The packaging material had no significant impact on chewiness of pecans, indicating chewiness change was similar across packaged pecans (Table 4.1 and 4.4, Table 4.5). As with cohesiveness and springiness, chewiness had low adjusted R^2 of 0.17 and 0.14 for unpackaged and packaged pecans, respectively.

Discussion

The fracturing of pecans is Ocòn et al. (1995) the first sensation that a consumer comes across when ingesting pecans. Given their irregular structure, one should expect variations in observations of instrumental texture analysis. The shape and size of pecan kernel is influenced by a number of factors such as sunlight exposure, cultivar, or damage by insects and rodents (Sparks, 1993). To address this problem, Ocòn et al. (1995) suggested cutting cores out of pecans and cutting the ends of cores to form a cylinder with standardized dimensions. This sample preparation technique sacrifices important key textural attributes, specifically fracturability, due to removal of testa and absence of numerous fracture points. The role of pecan testa in fracturability of pecans will be explained in detail later in the

manuscript. Another issue we experienced is that the pecan kernels kept at low RH (≦50%) started crumbling as the cork borer was inserted, making it difficult to maintain intact samples. As Ocòn et al. (1995) acknowledged by this sample preparation technique is also time consuming, making it an inconvenient protocol to follow in an extensive storage study (Anzaldúa-Morales, Brusewitz, & Anderson, 1999; Surjadinata et al., 2001).

One issue with purely compressive tests is that each pecan has a unique overall size (within a range) and an undulating surface; thus, when a disk-shaped probe pushes through the sample it experiences differing forces based on both the material properties and the total cross-sectional area the probe is contacting. This influences both the maximum measured force as well as the force experienced at the first fracture point if it exists. The reality of non-uniform samples has long hampered the ability to make precise measurements of texture attributes. One way researches have addressed this problem is to normalize any force-time data by the sample volume or weight. In this work we tested the hypothesis that normalizing the "fracturability", that is the force at first break under compression, by the force experienced under full compression, often defined as the "hardness", would help mitigate issues with sample variability. By taking the ratio of fracturability and hardness (rift ratio), the onset of fracturing could be compared across multiple pecan kernels, with varying mass and size, since the ratio would take into accounts maximum force experienced by the kernel during the test. The minimum value of the ratio could be 0, indicating a very brittle/crisp product (such as potato chips) while a maximum value of 1 would indicate no fracturability at all (such as chewy products) (Fig. 4.7). It was statistically determined that moisture was primarily responsible for changes in texture of pecan kernels stored under different temperature and RH conditions. To better understand

the effect of moisture on textural attributes, the moisture migration from the environment to pecans (and vice versa) were tracked using % change in weight of pecan kernels. The multivariate analyses revealed that the rift ratio had a moderate positive correlation with change in weight of pecan kernels (Fig. 4.8). A sigmoid model could be used to predict F/H ratio with the change in % weight of pecans (Fig. 4.9). A sharp increase in F/H value can be detected as % weight of pecan kernels increases beyond 0.12%. The F/H ratio reaches 0.5 and 1.0 as change in weight reaches 0.25% and 0.50%, respectively. The logistic model parameter for F/H and % change in weight can be found in Table 4.8.

The migration of moisture occurs due to a difference in water vapor pressure and water activity between product and surroundings. The food products with higher water activity leads to moisture loss from product to environment increases and vice versa (Afolabi, 2014). At low moisture content, the plant cells become condensed and fragile, contributing to brittleness and easy fracturability (Capuano, Pellegrini, Ntone, & Nikiforidis, 2018; C. V. Nikiforidis, Kiosseoglou, & Scholten, 2013). Light micrographs revealed cells in the pecan testa are much more compacted than in cotyledon tissues (the white meat of the pecan kernel), contributing to brittleness of pecans (Fig. 4.10). In addition to that testa is present is the barrier between cotyledon and environment. Such an arrangement of cells makes pecan testa more susceptible to moisture absorption (Rábago-Panduro, Morales-de la Peña, Romero-Fabregat, Martín-Belloso, & Welti-Chanes, 2021). As moisture in the pecan increases, the compact cells start to swell and have greater cell wall flexibility, and increase in the intracellular distance, causing loss of fracturability. The increase in concentration of water molecules and presence of oleosomes (oil storage entities in pecans) contributes a cushioning effect against compressive forces and increases

springiness (Constantinos V. Nikiforidis, 2019). As the moisture increased during storage, the pecans became more cohesive, indicating resistance towards breakdown. In addition, the overall kernel mass increased, which contributed to cohesiveness due to new hydrogen bond formation (Blahovec, 2007). This would also indicate that the pecan with increased moisture levels required more work to chew, which was indeed indicated by an increase in chewiness.

For samples placed in any packaging, the fracturability loss was delayed by at least 8-fold (Table 4.6 and 4.7). For packaged pecans exposed to 80% RH, kernels stored in LDPE experienced greater gain in moisture than those in PP, PEN and laminate because of the greater water vapor transmission rate (Tock, 1983). That is, the WVTR for LDPE was 1.30 g.mL/24 hr.100 in^2 (38°C, 50 to 100% RH), compared to values of 0.50 and 0.41 g.mL/24 hr.100 in^2 for PP and PEN, respectively. Unlike LDPE, PEN and PP, the metal laminate package was essentially impervious to moisture migration. As moisture could not enter, the textural attributes of pecans did not change significantly in the laminate packages, making them suitable packaging material for pecan kernels being handled in high RH environment.

Conclusion

Pecan texture is one of the important quality attributes of pecans, along with color and flavor, that is affected by storage, handling, and distribution conditions. This study investigated the two different texture methods, viz. the core method by Ocòn et al. (1995) and compression of intact pecans, for their versatility for studying the texture of pecans in differing packages and environmental conditions. The intact pecan method was found to

be a reliable indicator of texture changes when analyzed using the rift ratio, that is by measuring the fracture force normalized by the maximum force experienced in compression. This helped reduce some of the variability of the data. Out of all the textural attributes, fracturability was found to be the most sensitive indicator in terms of reacting to environment moisture content. Pecans became less fracturable, and more cohesive, chewy and springy as moisture migrated from the environment into pecans. Fracturability was drastically reduced as the environment RH was >50% for unpackaged pecans and >58% for packaged pecans. It was found that the any kind of moisture barrier around pecans was able to deter texture change by at least 8 -fold. Pecans kept in LDPE experienced the greatest change in texture whereas pecans in metallic laminates did not change significantly during the storage. For the first time, a model and predictive equations were built to estimate changes in textural attributes of pecans along with meaningful model parameters such as growth rate and inflection point. Thus, our study explores the possibility of integration of stochastic models from other fields of STEM to food science research to build consequential models able to predict texture change in food.

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Tables

Table 4.4 Mixed model analysis and means for the effects of relative humidity (RH) and storage duration (SD, days) on textural attributes of nonpackaged pecans (cores or kernels). For the analysis SD was nested within RH (SD[RH]).

Method	Variable	Source	F Ratio	Prob > F	Adj. R^2 (Model)	% RH	Least Sq mean[a]		95% Confidence limits
Core method	**Total area under curve**	**SD[RH]**	2.88	0.02	0.14	**30**	18.87	A	16.97-18.64
		RH	8.66	<.0001		**50**	19.88	A	19.25-20.54
						75	17.74	B	17.17-18.30
						80	18.99	A	18.30-19.70
	Hardness (N^b)	**SD [RH]**	7.80	<.0001	0.24	**30**	15.81	C	15.21-16.41
		RH	10.06	<.0001		**50**	16.06	C	15.59-16.52
						70	17.15	B	16.75-17.55
						80	19.79	A	17.9-21.68
Intact Pecan-halve method	**Fracturability (N^b)**	**SD [RH]**	123.34	<.0001	0.67	**30**	33.51	C	26.94-40.09
		RH	349.88	<.0001		**50**	45.40	C	39.03-51.78
						70	167.92	B	160.98-174.85
						80	604.37	A	511.88-696.86
	Cohesiveness	**SD [RH]**	5.64	0.0002	0.12	**30**	0.25	B	0.24-0.26
		RH	27.94	<.0001		**50**	0.26	B	0.25-0.27
						70	0.30	A	0.29-0.31
						80	0.34	C	0.32-0.36
	Springiness	**SD [RH]**	22.20	<.0001	0.27	**30**	0.39	D	0.38-0.4
		RH	63.49	<.0001		**50**	0.41	C	0.4-0.42
						70	0.47	B	0.46-0.48
						80	0.73	A	0.6-0.85

Chewiness (N[b])	**SD [RH]**	11.64	<.0001	0.17	**30**	19.43	B	17.87-21
	RH	37.52	<.0001		**50**	21.18	B	19.67-22.7
					70	30.82	A	29.18-32.47
					80	35.62	C	33.65-37.59
F/H	**SD [RH]**	161.04	<.0001	0.72	**30**	0.18	D	0.15-0.21
	RH	471.98	<.0001		**50**	0.25	C	0.22-0.27
					70	0.80	B	0.78-0.83
					80	1.00	A	0.94-1.06

[a]Different letters for the means in each RH group indicate significant difference between the means based on Tukey's HSD ($\alpha = 0.05$).
[b]N-newton to indicate force.

Table 4.2 Total area under the curve (AUC) for work done to compress cores of nonpackaged pecan kernels subject to compression tests after being stored under different storage duration and relative humidity (RH) conditions

RH	Storage Days	LSmean (AUC) [a]		95% Confidence limits
30	0	20.39	ABC	18.83-21.96
	30	17.19	ABCD	15.13-19.24
	60	18.99	ABCD	17.27-20.72
	75	19.49	ABCD	17.79-21.18
	90	17.30	ABCD	15.91-18.68
	120	19.02	ABCD	17.26-20.78
	150	18.50	ABCD	17.06-19.94
	180	21.07	ABCD	18.49-23.66
	225	18.20	ABCD	15.03-21.37
50	0	19.45	ABCD	17.62-21.28
	14	22.16	A	20.04-24.27
	28	21.65	A	19.7-23.61
	42	21.72	A	19.61-23.84
	45	19.36	ABCD	17.25-21.47
	56	17.01	ABCD	14.84-19.19
	70	19.60	ABCD	17.54-21.66
	75	20.60	ABCD	18.54-22.66
	90	21.43	AB	19.32-23.55
	135	15.24	ABCD	12.4-18.07
	180	15.91	ABCD	12.92-18.9
	225	17.56	ABCD	15.5-19.62
	300	20.46	ABCD	16.45-24.47
75	0	19.45	ABCD	17.62-21.28
	7	18.74	ABCD	16.56-20.91
	14	17.61	ABCD	15.56-19.67
	21	18.37	ABCD	16.31-20.42
	28	18.60	ABCD	16.54-20.66
	30	16.95	ABCD	14.9-19.01
	35	15.50	BCD	13.44-17.56
	37	19.51	ABCD	17.46-21.57

	60	17.47	ABCD	15.46-19.48
	74	18.29	ABCD	16.28-20.29
	90	15.45	BCD	13.34-17.57
	111	19.28	ABCD	17.17-21.4
	120	19.69	ABCD	17.57-21.8
	148	17.83	ABCD	15.59-20.08
	150	16.99	ABCD	14.15-19.82
	185	15.21	ABCD	12.22-18.2
80	0	19.44	ABCD	17.43-21.44
	5	17.87	ABCD	15.87-19.88
	7	21.73	ABCD	18.74-24.72
	8	17.54	ABCD	14.55-20.53
	10	17.92	ABCD	15.81-20.03
	14	17.34	ABCD	15.33-19.34
	15	19.82	ABCD	17.81-21.82
	16	21.27	ABCD	18.28-24.26
	21	14.77	D	12.76-16.77
	24	19.72	ABCD	16.88-22.55
	25	17.87	ABCD	14.88-20.86
	28	15.22	CD	13.11-17.34
	32	19.37	ABCD	16.53-22.21
	35	17.51	ABCD	15.46-19.57
	40	24.90	A	20.89-28.91

[a] Different letters for the means in each RH group indicate significant difference between the means based on Tukey's HSD ($\alpha = 0.05$).

Table 4.3 Hardness of cores of nonpackaged pecan kernels subject to compression tests after being stored under different storage duration and relative humidity (RH) conditions.

RH	Storage Days	LSmean [a]		95% Confidence limits
30	0	18.52	ABCH	17.45-19.58
	30	14.72	DEFG	13.22-16.23
	60	16.00	BCDEFGH	14.81-17.19
	75	16.08	BCDEFGH	14.89-17.27
	90	14.68	E	13.71-15.66
	120	16.49	BCDEFGH	15.33-17.66
	150	15.77	BCDEFGH	14.71-16.84
	180	16.57	ABCDEFGH	14.86-18.28
	225	13.49	DEFGH	11.23-15.75
50	0	18.93	ABC	17.62-20.23
	14	17.45	ABCDEFGH	15.94-18.96
	28	16.91	ABCDEFGH	15.52-18.31
	42	16.12	BCDEFGH	14.61-17.62
	45	14.55	EFG	13.09-16.02
	56	14.61	EFG	13.15-16.08
	70	15.10	BCDEFGH	13.63-16.57
	75	16.06	BCDEFGH	14.55-17.57
	90	16.32	BCDEFGH	14.89-17.75
	135	13.52	EG	11.5-15.54
	180	13.80	CDEFGH	11.54-16.06
	225	14.24	E	12.81-15.67
	300	18.53	ABCDEFGH	15.67-21.39
75	0	18.93	ABC	17.62-20.23
	7	17.07	ABCDEFGH	15.47-18.67
	14	15.57	BCDEFGH	14.06-17.07
	21	16.30	BCDEFGH	14.87-17.73
	28	17.19	ABCDEFGH	15.76-18.62
	30	15.11	BCDEFGH	13.51-16.71
	35	17.05	ABCDEFGH	15.58-18.51
	37	17.76	ABCDEFGH	16.21-19.31
	60	15.35	BCDEFGH	13.84-16.86
	74	16.94	ABCDEFGH	15.51-18.37
	90	17.00	ABCDEFGH	15.5-18.51
	111	18.52	ABCDFGH	17.02-20.03

	120	19.29	ABC	17.83-20.76
	148	16.60	ABCDEFGH	15.1-18.11
	150	17.76	ABCDEFGH	15.74-19.78
	185	17.74	ABCDEFGH	15.72-19.76
	0	18.69	ABCDFH	17.29-20.08
	5	18.19	ABCDEFGH	16.76-19.61
	7	20.36	AB	18.23-22.49
	8	18.05	ABCDEFGH	16.03-20.07
	10	18.16	ABCDEFGH	16.56-19.76
	14	17.34	ABCDEFGH	15.91-18.77
	15	19.09	ABC	17.63-20.56
80	16	20.03	ABC	18-22.05
	21	17.14	ABCDEFGH	15.71-18.57
	24	18.39	ABCDEFGH	16.37-20.41
	25	18.84	ABCDEFGH	16.82-20.86
	28	18.57	ABCDFGH	17.1-20.03
	32	19.50	ABCDEFGH	17.37-21.63
	35	19.08	ABCDH	17.53-20.63
	40	23.66	A	20.46-26.85

[a] Different letters for the means in each RH group indicate significant difference between the means based on Tukey's HSD ($\alpha = 0.05$).

Table 4.4 Mixed model analysis and means for the effects of relative humidity (RH) and storage duration (SD, days) on textural attributes of pecan kernels in different types of packaging materials. The least mean square indicates the textural attribute for the pecan kernels stored in different packaging at 80% RH. For the analysis SD was nested within RH (SD[RH]).

Variable	Source	F Ratio	Prob > F	Adj. R^2 (Model)	Package[a]	Least sq mean[b]		95% Confidence limits
Fracturability (N^C)	**Package**	43.19	<0.01	0.70	**AL**	30.70	C	14.18-47.21
	SD[RH]	83.32	<0.01		**LDPE**	147.43	A	135.29-159.57
	RH	352.84	<0.01		**PEN**	119.49	B	108.28-130.71
	Package*RH	39.44	<0.01		**PP**	118.71	B	109.06-128.37
	SD*Package[RH]	8.01	<0.01					
Cohesiveness	**Package**	5.98	<0.01	0.17	**AL**	0.30	B	0.28-0.31
	SD[RH]	8.36	<0.01		**LDPE**	0.33	A	0.32-0.34
	RH	23.501	<0.01		**PEN**	0.31	B	0.3-0.32
	Package*RH	10.12	<0.01		**PP**	0.31	B	0.3-0.32
	SD*Package[RH]	2.03	0.06					
Springiness	**Package**	0.68	0.567	0.11	**AL**	0.46	A	0.44-0.49
	SD[RH]	9.92	<0.01		**LDPE**	0.45	A	0.44-0.47
	RH	9.15	<0.01		**PP**	0.47	A	0.45-0.48
	Package*RH	1.30	0.27		**PEN**	0.46	A	0.45-0.47
	SD*Package[RH]	0.63	0.71					
Chewiness (N^b)	**Package**	1.38	0.25	0.14	**AL**	31.83	A	28.03-35.64
	SD[RH]	3.61	0.03		**LDPE**	34.51	A	31.98-37.05
	RH	11.91	<0.01		**PEN**	31.99	A	29.52-34.47
	Package*RH	5.12	<0.01		**PP**	34.79	A	32.63-36.95

	SD*Package[RH]	1.15	0.33					
F/H	**Package**	41.98	<0.01	0.71	**AL**	0.13	C	0.07-0.2
	SD[RH]	82.78	<0.01		**LDPE**	0.60	A	0.55-0.65
	RH	347.54	<0.01		**PEN**	0.53	AB	0.48-0.57
	Package*RH	33.69	<0.01		**PP**	0.49	B	0.45-0.53
	SD*Package[RH]	8.03	<0.01					

[a] Packaging materials are LDPE = low density polypropylene, PE = polyethylene, PP = polypropylene, and ML = metal laminate.
[b]Different letters for the means in each packaging group indicate significant difference between the means based on Tukey's HSD ($\alpha = 0.05$).
[c]N-newton to indicate force.

Table 4.5 Summary of textural attributes of pecan kernels subject to compression tests after being stored in different packaging under different storage duration and relative humidity (RH) conditions.

Variable	Package[a]	% RH	LSmean[b]		95% Confidence limits
F/H	ML	58	0.13	C	0.04-0.23
		80	0.12	C	0.03-0.22
	LDPE	58	0.17	C	0.12-0.21
		80	1.02	A	0.94-1.11
	PEN	58	0.26	C	0.22-0.31
		80	0.79	B	0.71-0.87
	PP	58	0.20	C	0.15-0.25
		80	0.78	B	0.72-0.84
Fracturability (N)	ML	58	30.70	CD	7.34-54.05
		80	30.70	CD	7.34-54.05
	LDPE	58	36.28	D	25.33-47.23
		80	258.58	A	236.9-280.26
	PEN	58	61.57	C	50.26-72.88
		80	177.42	B	158.04-196.8
	PP	58	46.31	CD	33.93-58.7
		80	191.11	B	176.3-205.93
Cohesiveness	ML	58	0.30	BC	0.28-0.32
		80	0.30	BC	0.28-0.32
	LDPE	58	0.29	C	0.28-0.3
		80	0.37	A	0.35-0.39
	PEN	58	0.30	BC	0.29-0.31
		80	0.31	BC	0.29-0.33
	PP	58	0.30	C	0.29-0.31
		80	0.32	B	0.31-0.34
Springiness	ML	58	0.46	AB	0.43-0.49
		80	0.46	AB	0.43-0.49
	LDPE	58	0.44	B	0.42-0.45
		80	0.47	AB	0.44-0.49
	PEN	58	0.45	B	0.44-0.46
		80	0.47	AB	0.45-0.49

	PP	58	0.44	B	0.43-0.46
		80	0.49	A	0.47-0.51
Chewiness (N)	**ML**	58	31.83	AB	26.46-37.21
		80	31.83	AB	26.46-37.21
	LDPE	58	28.63	B	26.26-31
		80	40.40	A	35.91-44.89
	PEN	58	32.24	B	29.72-34.77
		80	31.74	AB	27.49-36
	PP	58	30.55	B	27.72-33.38
		80	39.04	A	35.77-42.3

[a] Packaging materials are LDPE = low density polypropylene, PEN = polyethylene nylon, PP = polypropylene, and ML = metallic laminate.
[b] Different letters for the means in each RH group indicate significant difference between the means based on Tukey's HSD ($\alpha = 0.05$).

Table 4.6 The parameters for three-parameter logistic model of the rift (fracturability/hardness) ratio for nonpackaged pecan kernels stored at 75,80 and 90% relative humidity (RH)

Parameter	**RH**	**Least sq mean**		**95% Confidence limits**	**R^2**
Growth rate (a)	75	1.23	C	0.34-2.12	0.90
	80	5.35	B	4.46-6.24	0.97
	90	11.89	A	11-12.78	0.63
Inflection point (b)	75	115.44	A	100.7-130.2	0.90
	80	3.17	B	1.60-4.74	0.97
	90	0.15	B	0.06-0.24	0.63
Asymptote (c)	75	0.99	A	0.88-1.09	0.90
	80	0.92	A	0.82-1.03	0.97
	90	0.95	A	0.85-1.05	0.63

[a]Different letters for each parameter group indicate significant difference between the means based on Tukey's HSD ($\alpha = 0.05$).

Table 4.7 The parameters for 3PL model for packed pecans stored in different packaging materials at 80% RH. Pecan stored below 80% RH did not experience significant change in texture. The same is true for pecans stored in ML.

Parameter	**Package[a]**	**Least Sq Mean**	**95% Confidence limits**	**R^2**
Growth rate (a)	LDPE	0.06	0.06-0.06	0.88
	PEN	0.02	0.02-0.02	0.98
	PP	0.03	0.03-0.03	0.98
Inflection point (b)	LDPE	26.25	26.23-26.28	0.88
	PEN	78.05	75.01-81.1	0.98
	PP	56.99	54.17-59.81	0.98
Asymptote (c)	LDPE	1.00	1-1	0.88
	PEN	1.01	1-1.03	0.98
	PP	1.01	0.99-1.02	0.98

[a]LDPE = low density polypropylene, PEN = polyethylene nylon, and PP= polypropylene.

Table 4.8 Summary of the parameters for the three-parameter logistic model of the rift (fracturability/hardness) ratio vs the % change in weight of unpacked pecan kernels (R^2 – 0.73)

Parameter	**Estimate**	**95% Confidence limits**
Growth Rate	6.52	3.89-9.15
Inflection Point	0.24	0.16-0.32
Asymptote	0.90	0.82-0.98

Figures

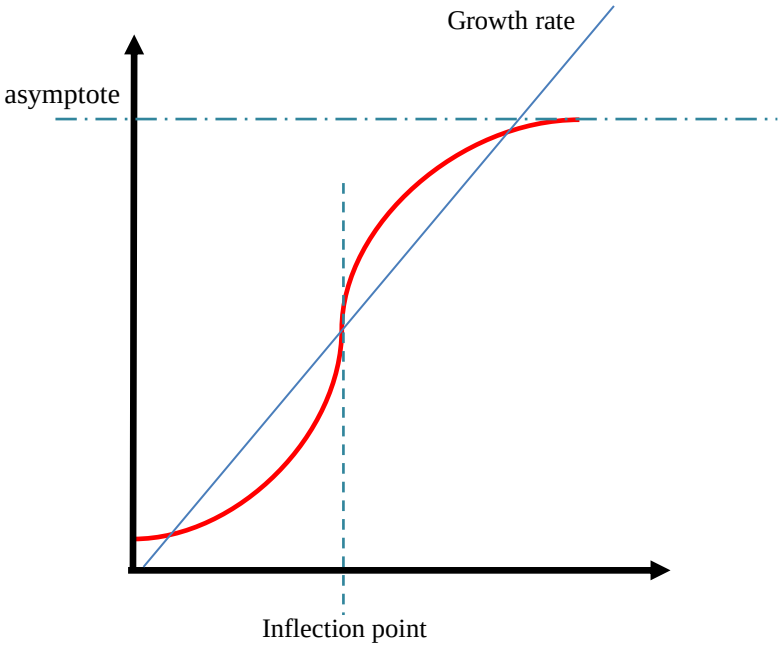

Figure 4.1 The three parameter logistic (3PL) model indicating the model parameters including the asymptote, inflection point and growth rate

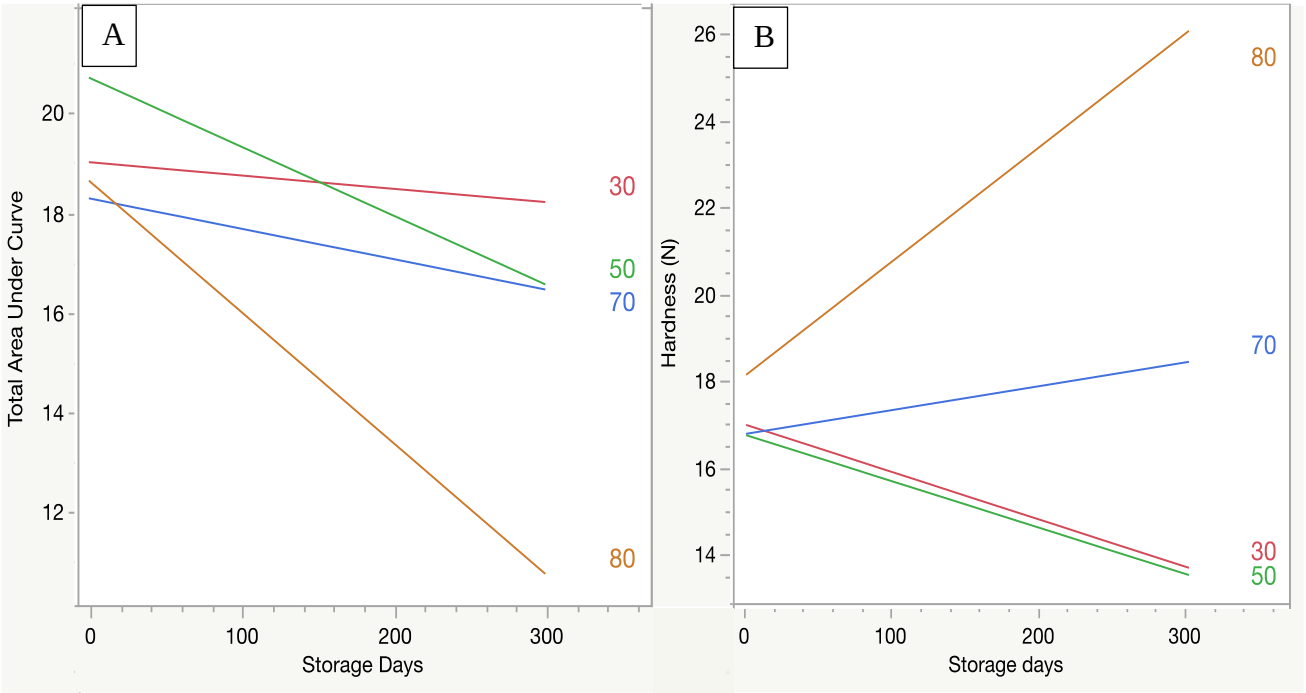

Figure 4.2 Interaction plots illustraing change in A. area under curve, and B. hardness of based on compresison tests of cores from nonpackaged pecan kernels stored under different RH conditions and storgae durations

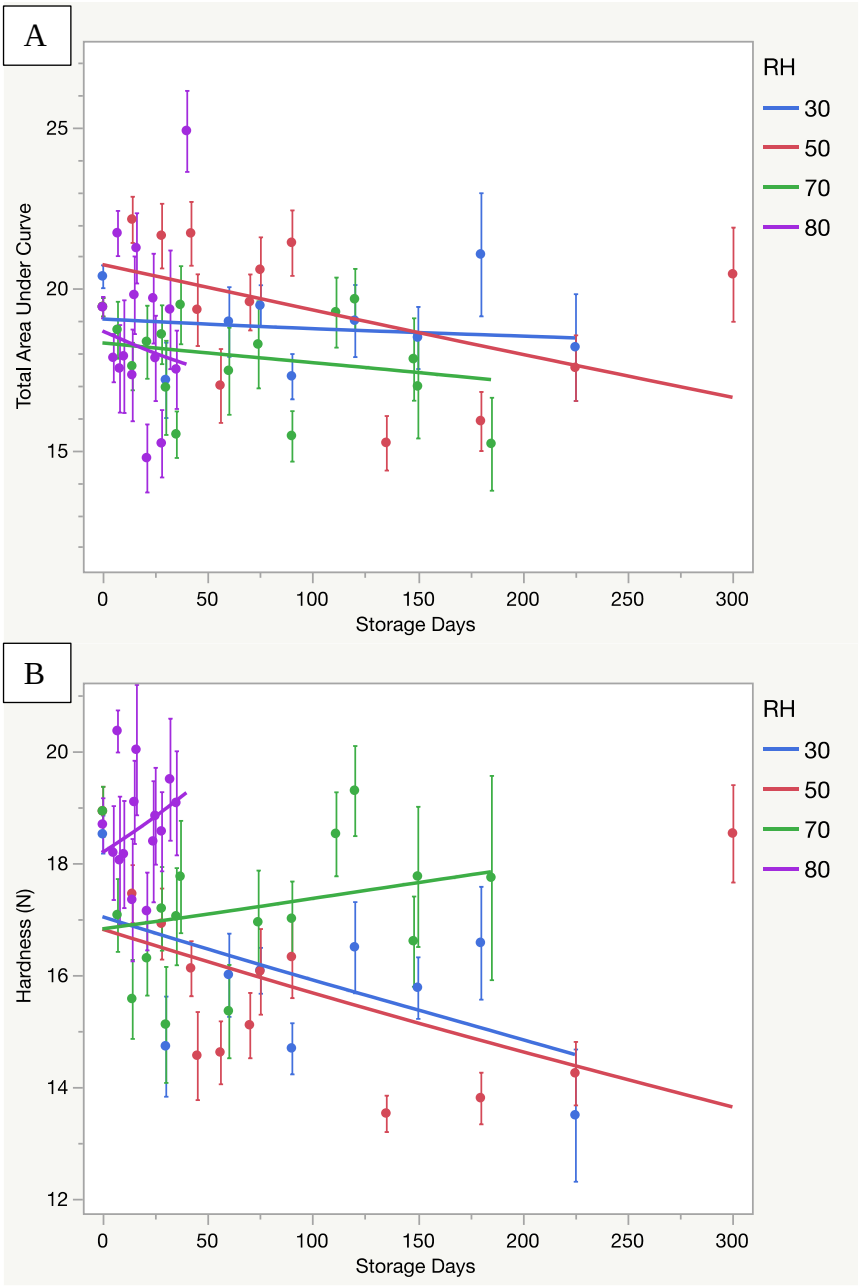

Figure 4.3 The change in area under curve (A), and hardness (B) of cores of unpackaged pecan kernels under different relative humidity conditions (RH) and storage durations.

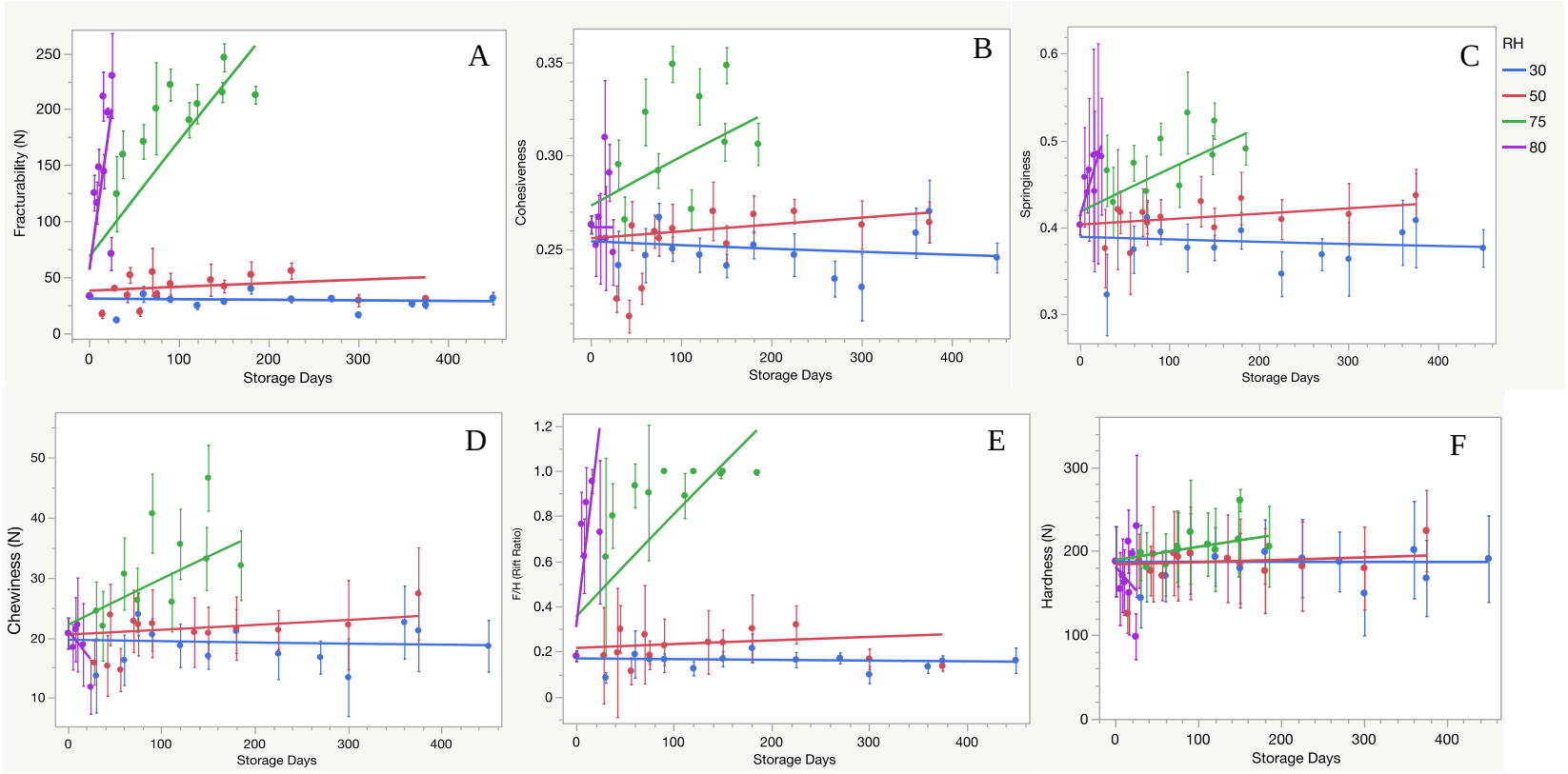

Figure 4.4 The change in textural attributes of nonpackaged pecan kernels under different relative humidities (RH) and storage duration.

A. Fracturability, B. Cohesiveness, C. Springiness, D. Chewiness (N), E. F/H (rift) ratio and F. Hardness (N)

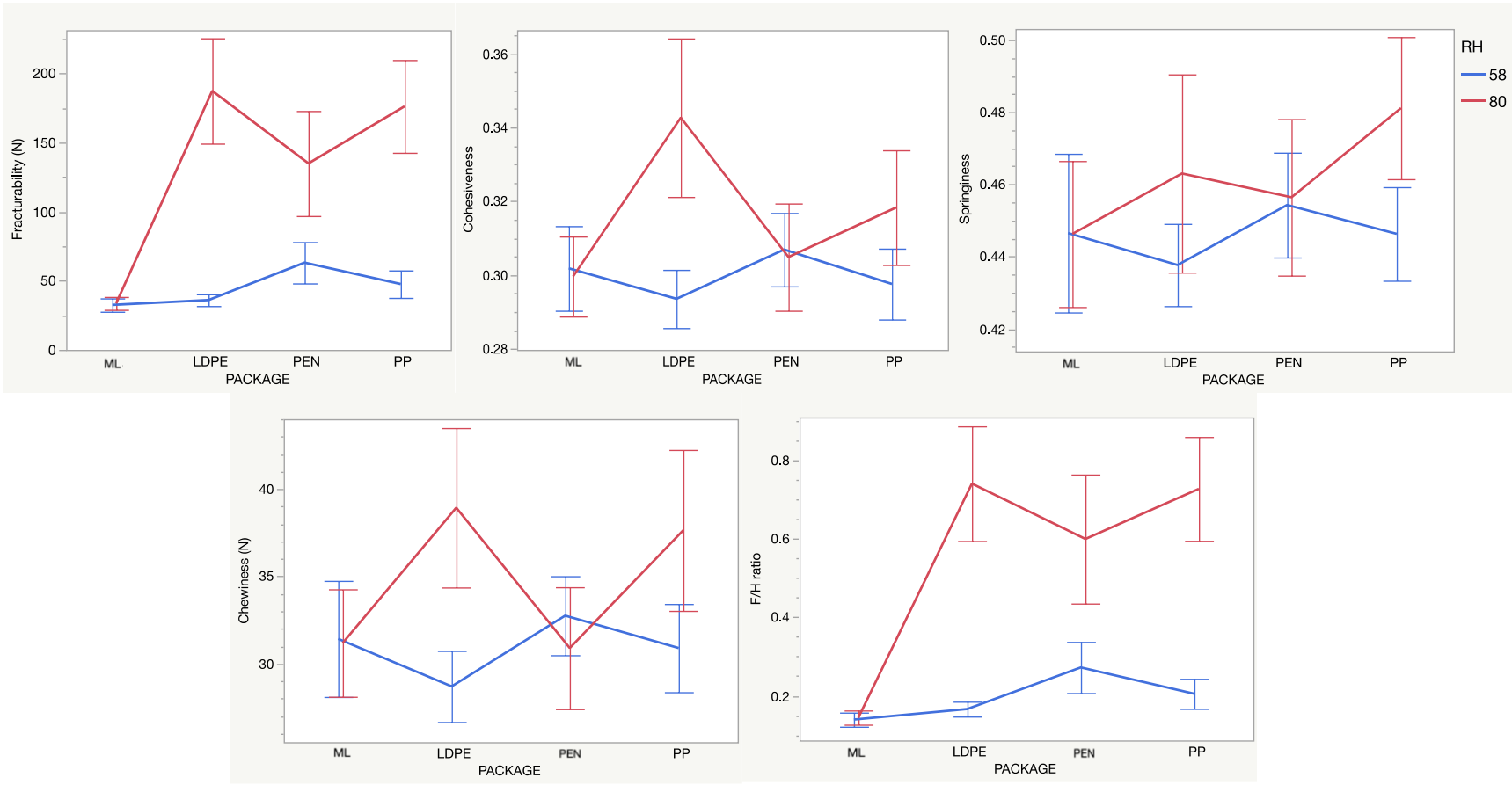

Figure 4.5 The interaction plots for change in textural attributes of pecan kernels packaged in different materials and under different relative humidities (RH) and storage durations. A. Fracturability, B. Cohesiveness, C. Springiness, D.Chewiness (N), and F. F/H (rift)

ratio . Packaging materials are LDPE = low density polypropylene, PEN = polyethylene nylon, PP = polypropylene, and ML = metal laminate.

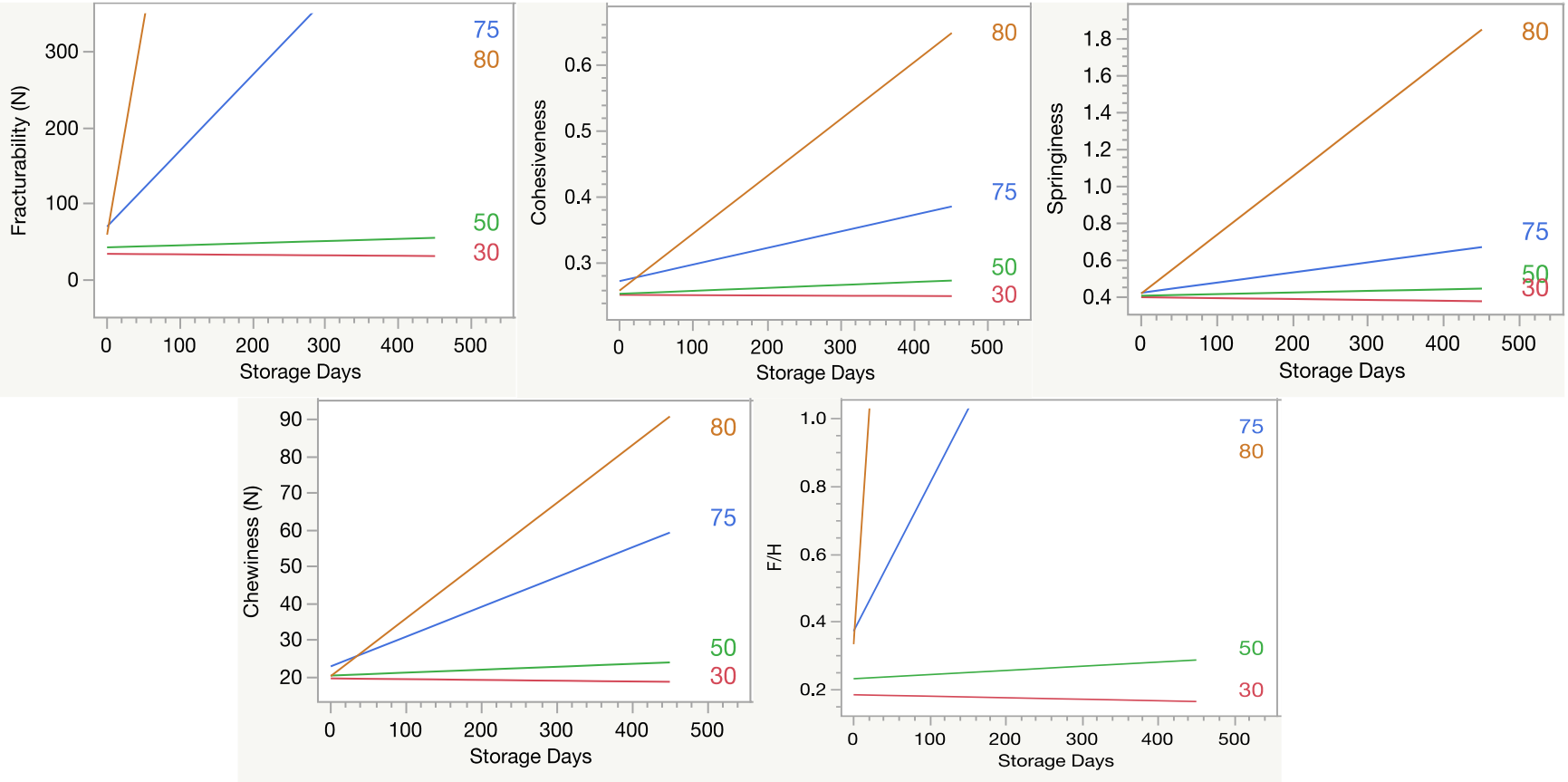

Figure 4.6 Interaction plots illustaring changes in the texture profile attributes of nonpackaged pecan kernels stored under different relative humidity conditions and storage durations. A. Fracturability, B. Cohesiveness, C. Springiness, D. Chewiness (N), and E. F/H (rift) ratio.

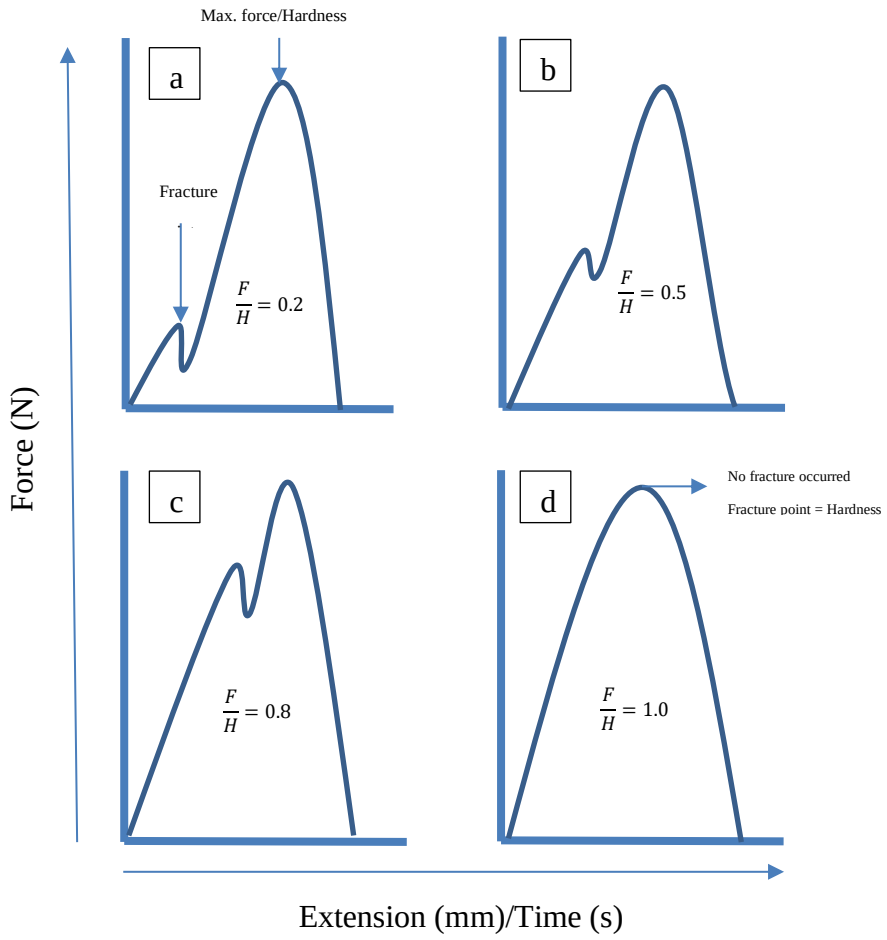

Figure 4.7 The change in the rift (F/H) ratio with constant hardness (N) during first compression. Graphs (a) to (d) represent with brittle/crisp texture to spongy/soft texture, respectively.

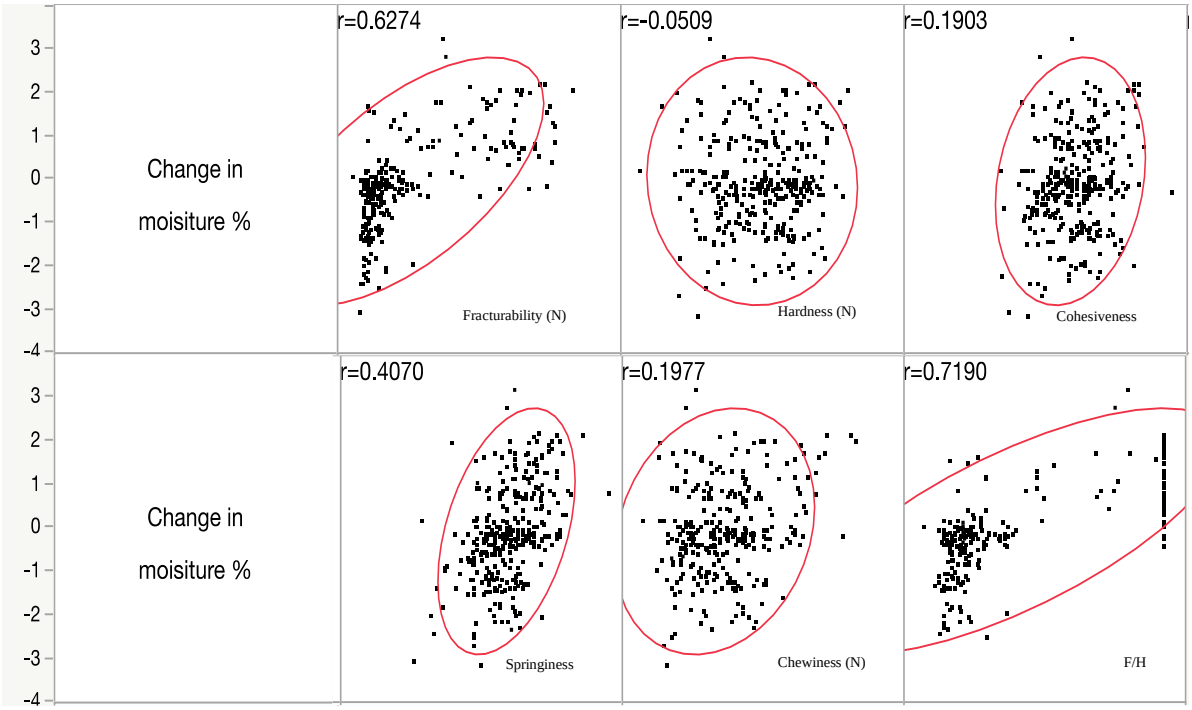

Figure 4.8 Correlation (r) between the percent change in weight and textural attributes of pecan kernels

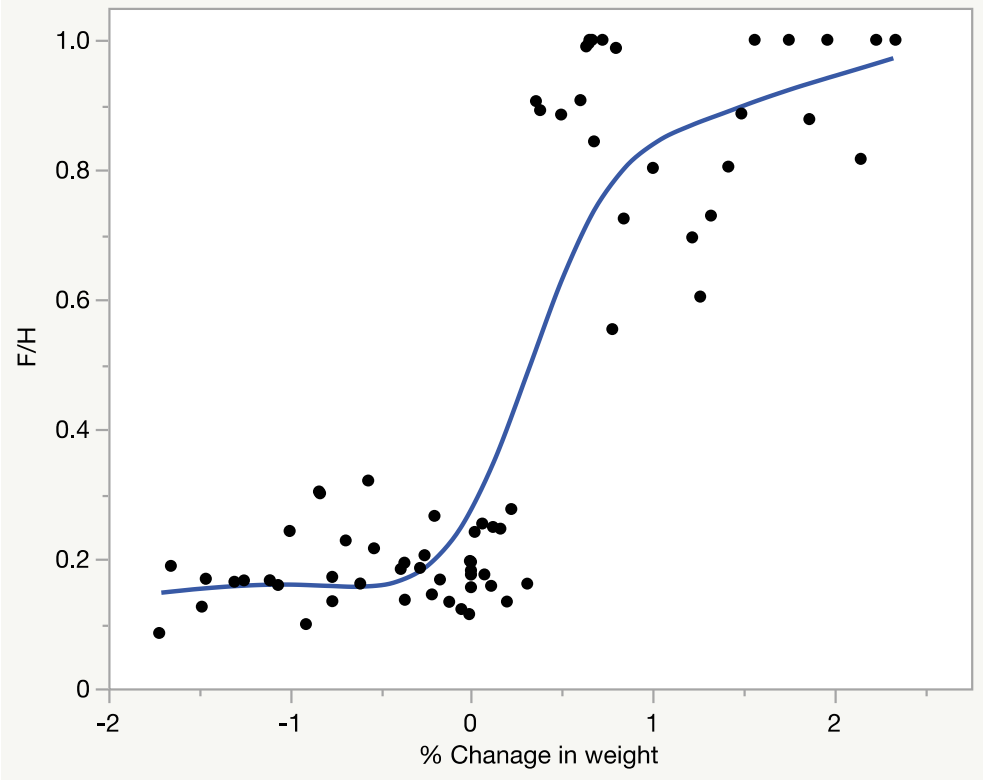

Figure 4.9 The sigmoid relationship between the rift (fracturability/hardness) ratio and the percent change in weight of unpacked pecan kernels stored under different RH (30 to 90%) primarily due to moisture (R^2 – 0.73)

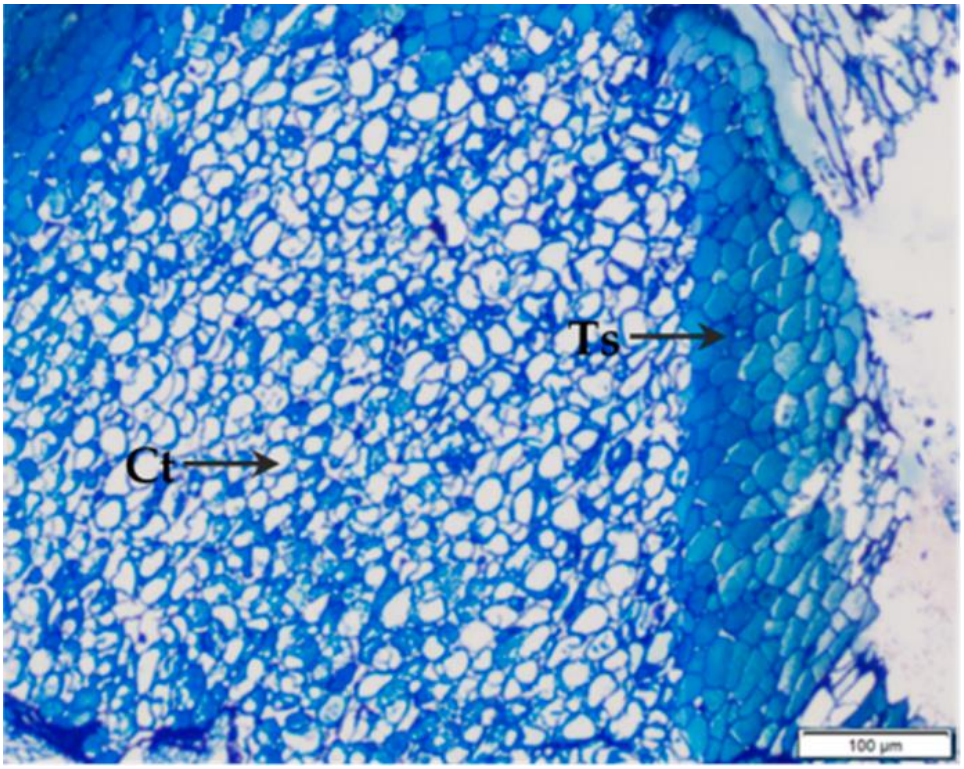

Figure 4.10 Light microscopy micrographs of the testa (Ts) and cotyledon tissue (Ct) of dry pecan nuts, adapted from Rábago-Panduro, Morales-de la Peña, Romero-Fabregat, Martín-Belloso, and Welti-Chanes (2021)

CHAPTER 5

CHANGES IN CHEMICAL CHARACTERSTICS AND MODELLING SENSORY PARAMETERS OF STORED PECAN NUTMEATS[4]

[4] Prabhakar H., Stoner-Harris T., Adhikari K., Mishra A., Bock C., Kong F. 2022. Submitted to Food Packaging and Shelf Life

Abstract

Pecan is a major specialty crops produced in the US. Sensory evaluation and chemical analyses of pecan nut meats are integral components of shelf life and have been employed to investigate changes during storage, but there remains a lack of knowledge regarding storage stability. Specifically, the association between of shelf life and chemical characteristics has not been investigated. We aimed to investigate the chemical changes in pecan nuts during a range of storage treatments (temperature, relative humidity, packaging material and modified atmosphere). The results of the chemical analyses were used to build a volatile compound based sensory prediction model. The work has utility as a rapid method to measure lipid oxidation in pecan, which is of value to the pecan industry. The research also determined a possible association between pecan nut volatile compounds and sensory attributes of pecans, and their perception by human subjects. Building a sensory based prediction model would reduce dependency on expensive and time-consuming sensory methods.

Introduction

Pecan, Carya illinoinensis (Wangenh.) K. Koch, is a native North American tree species. The US is a major producer of pecans in world, alongside Mexico, Australia and South Africa (McEachern, 2014). The US alone contributes 40–45% of the world's total pecan production (NASS, 2020). Pecans have been reported to be commercially cultivated in at least 15 US states (Prabhakar et al., 2022). Many European and Asian countries have established markets for imported US pecans and demand is increasing (ERS, 2021; Zhang et al., 2015). As pecans are stored, transported, and distributed for both domestic and international trade, the nut is exposed to a range of environmental conditions (Prabhakar et al., 2020). Since pecans are predominantly composed of unsaturated fats, they are prone to oxidation resulting in rancidity and a reduced shelf life. As oxidation progresses, undesirable volatile compounds are generated (USDA, 2019).

Numerous studies have been conducted to understand the impact of storage and processing on pecan nutmeat sensory perception. Research has explored the oxidative stability in raw and roasted pecan nutmeats via sensory evaluation using trained panelists alongside chemical analyses to determine the extent of lipid oxidation (Erickson et al., 1994; Murley et al., 2020). Descalzo et al. (2021) conducted a storage duration study on pecan nutmeats stored at 2 and 20°C and developed regression models to predict the change in chemical attributes of the pecan nutmeats. In addition, a few studies have investigated how consumer preference changes based on fresh pecan nutmeat appearance, texture, color, and taste (Descalzo et al., 2021; Resurreccion & Heaton, 1987). However, none of these studies provided a means to translate chemically quantified lipid oxidation status to sensory evaluation of the pecan nutmeats. Some of the researchers have conducted in depth

analyses of volatile compounds produced by raw and roasted pecans, and the perception of the volatiles by human subjects (Gong et al., 2018a; Wang & Odell, 1972). But only a few studies have evaluated the changes in concentration of volatiles and generation of new volatiles during storage (Thewes, Both, Thewes, Brackmann, Wagner, et al., 2021).

Furthermore, only limited work has been aimed at developing a sensory based prediction model for volatile compounds produced by pecan nutmeats during the storage period. Jiang et al. (2017) combined sensory and gas chromatographic analysis to build a decision based predictive tool (using a random forest network) to estimate changes in fatty acid profile of pecan nutmeats. But the study was based on a small sample size, limited storage treatments (shelled and unshelled pecans stored at 35°C for 20 days only) and did not examine the spectrum of volatile compounds responsible for the undesirable odors associated with oxidation that humans perceive.

The objective of our study was to investigate the extent of lipid oxidation in packaged and unpackaged pecan nutmeats stored in different temperature and relative humidity (RH) conditions using chemical profiling and sensory analysis. The information obtained from the analyses was used to build and validate an artificial neural network or ANN model for prediction of sensory attributes based on data from a trained sensory panel who rated nutmeat acceptability. We discuss the possible use of economic and rapid lipid oxidation determination methods, including free fatty acid measurement, use of peroxide values and anisidine values, for the pecan industry to gain insight to pecan nutmeat quality changes as affected by external factors during storage.

Material and Methods

Pecan Production and Storage:

Pecan nuts ('Pawnee') were harvested from an orchard located at the USDA-Agriculture Research Service (ARS) Fruit and Tree Nut Research Station, Byron, Georgia (U.S.A.) (+32.6650 N, + 83.7419 W, elevation of ≈156 m, 240 d freeze-free growing period, annual precipitation of 118 cm). The orchards received standard tree management practice for the state of Georgia (Wells et al., 2019). The nuts were harvested in December 2019 and the pecans were processed within 1 week of harvesting. The harvested pecan nuts were conditioned prior to shelling by immersing in 85 °C water for 3 min, followed by drying at room temperature for 20 to 25 min and shelling via a mechanical sheller (Modern Electronics, Mansfield, LA) (Forbus Jr & Senter, 1976). After shelling, pecans were dried at 20 °C and 45% RH overnight to a moisture content of 4–5% (AOAC, 2016) and stored at −20 °C in a commercial freezer until use in the experiments. Information on the different (color and size) grades of pecans has been provided by Prabhakar et al. (2022).

Storage Experiment:

The pecan nutmeats were stored in a static temperature-controlled humidity chamber (STC) consisting of a 1-L glass jar with a rubber gasket lid. More detailed information on construction of the STCs has been provided by Prabhakar et al. (2022). To obtain the desired RH, saturated salt solutions of magnesium chloride (28–32% RH), and ammonium nitrate (56–60% RH) were used (Certified ACS, Fisher Chemical, Waltham, MA) (Rockland, 1960). For the sake of simplicity, the RHs will be denoted as 30% and 58%. The STCs containing nutmeats were placed in temperature-controlled chambers at 20, 30

and 40 °C and 30% RH. For each temperature × humidity treatment (n = 2 jars for each combination), 50 g of nutmeats (25 to 40 pecan halves) were placed in a nylon bag suspended above the saturated solutions on an aluminum mesh disc in the STC. This treatment is indicated as 'No Pack-30', with the pecan nutmeats being stored without packaging material at 30% RH. To simulate a real storage environment and corresponding air composition, the jars were opened periodically (every 1 to 2 weeks) for 30 s to allow fresh air into the container. Depending on treatment, other pecan nutmeats were placed in packages available to pecan producers and packers. The internal atmosphere for some the packages were modified with N2 flushing. The packaging materials used were low-density polypropylene (LDPE, thickness: 50 to 54 µm, dimensions: 20 cm × 30 cm), polyethylene-nylon with vacuum packing (PEV, thickness:105 to 110 µm, dimension: 20 cm × 30 cm) and metallic laminates (ML, thickness:105 to 110 µm, dimensions: 20 cm × 30 cm). The packages were procured from OpenTip.com and sealed using an American International Electric Heat Impulse sealer (AIE, City of Industry, CA, USA). The vacuum packaging and N2 flushing were done using a Henkelman 600 Double Chamber Vacuum Packer (Original Henkelman Vacuum Systems, Hertogenbosch, Netherlands). The packaged samples were stored at 58% RH at the same temperature ranges as the unpackaged STC pecan nutmeats. Furthermore, additional pecan nutmeats (10 kg) were stored in 60 cm x 100 cm sacks (Jutemill LLC, Durham NC) and kept outside (without temperature and RH control) to observe quality degradation of pecans with intact shell. The change in temperature experienced at the location is presented (Supplementary Fig. F1 5.1). The kernel samples were drawn at predetermined intervals based on previous reports of pecan nutmeat quality changes in the literature (Blackmon, 1932; Brison, 1945; Kays, 1979;

Magnuson et al., 2015; Mexis et al., 2009; Senter & Wilson, 1983). The storage time ranged from 100 to 500 days, depending on the treatment. The mold growth assessment was performed visually and samples with mold growth were discarded.

Sample Preparation and Lipid Oxidation Analysis:

Oil Extraction –

Oil was expressed using a Carver Press Model 3853 (Carver Inc., Wabash, IN, USA). The 20 -30g of pecan halves were brought to 40°C to allow easy flow of oil and hand crushed into small pieces. The crushed pecans were placed in a 6.25 cm (2.5") test cylinder with filter pads (No. 2090). The test cylinder was pressed at up to 15,900 kg (35000 lbs.) of pressure. The pressed oil was collected, stored in amber colored vials and frozen at -20°C until further analysis.

Free Fatty Acid -

The free fatty acid content of the nutmeats was determined using a previously described method (Rukunudin et al. 1998). A 3 to 5 g sample of pecan oil was mixed with 95% ethanol (Thermo Fisher Scientific [Fisher Scientific International], Waltham, MA, US) and a few drops of phenolphthalein indicator (Sigma-Aldrich Inc., St. Louis, MO, US) was added. The mixture was titrated with 0.013N NaOH (Sigma-Aldrich Inc. [Millipore Sigma], St. Louis, MO, US). The free fatty acid was estimated as % oleic acid as follows:

$$\%\ FFA\ (as\ oleic\ acid) = \frac{Titrant\ volume\ (ml) \times normality\ of\ NaOH\ (N) \times 28.2}{sample\ weight\ (g)} \qquad (1)$$

Peroxide Value -

The peroxide value (PV) was determined using the American Oil Chemists Society (AOCS) Official Method Cd 8b-90. A 3 to 5 g sample of pecan oil was mixed with 50 mL of 3:2 acetic acid: isooctane solution (Sigma-Aldrich Inc. [Millipore Sigma], St. Louis, MO, USA). 1 mL of saturated potassium iodide was added, and the solution shaken periodically (3-5 times) for 1 minute. The reaction was stopped by adding 50 mL deionized water, followed by addition of 2 mL 1% starch solution (Spectrum Chemical Mfg. Corp., New Brunswick, NJ, USA). The resultant mixture was titrated with 0.1N sodium thiosulfate solution (Sigma-Aldrich Inc. [Millipore Sigma], St. Louis, MO, USA). The PV was calculated as follows:

$$PV\ (meq/kg\ of\ oil) = \frac{Titrant\ volume\ (ml) \times normality\ of\ Na_2S_4O_6\ (N) \times 1000}{sample\ weight\ (g)} \qquad (2)$$

Anisidine value -

The anisidine value (AV) was calculated using AOCS Official Method Cd 18-90. A 0.5 to 1.5 g of pecan oil was mixed with iso-octane (Sigma-Aldrich [Millipore Sigma], St. Louis, MO, USA) and filtered. The 0.25% p-anisidine solution (recrystallized p-anisidine [Sigma-Aldrich Inc., St. Louis, MO, USA] mixed with glacial acetic acid solution [Sigma-Aldrich Inc., St. Louis, MO, US]) was mixed with the filtrate and kept in dark for 10 minutes. The background (blank + samples with p-anisidine) and derivative absorbance values (blank + samples with p-anisidine) were measured at 350 nm. The following formula was used to calculate the AV:

$$AV\ (ppm) = \frac{25([1.2A_s] - A_b)}{sample\ weight\ (g)} \qquad (3)$$

Where A_s and A_b denote sample and background absorbance values, respectively.

HS-SPME-GC-MS Analysis -

Two grams of ground pecan nutmeat samples from each treatment were placed individually in a 20 mL screw-cap vial fitted with a screw cap containing a polytetrafluoroethylene/silicone septum. A 1960 µL aliquot of distilled water and 40 µL of 0.2 mg/mL 1,3-dichlorobezene (Sigma-Aldrich Inc., St. Louis, MO, US) solution (in methanol) were added to the vial. After equilibration for 20 minutes at 60°C, followed by spinning at 250 rpm in the autosampler (Model GC Sampler 80, Agilent Technologies, Santa Clara, California, USA), a 50/30 µm divinylbenzene/carboxen/polydimethylsiloxane solid phase microextraction (SPME) fiber was used to extract volatile compounds from the sample headspace for 20 minutes at 60°C. The SPME fiber was desorbed into the injection port of a GC/MS system (Model 7890A/5977A, Agilent Technologies, Santa Clara, California, USA) equipped with an HP-5MS column (30 m × 250 µm × 0.25 µm) to separate the analytes at 250 °C for 5 min in splitless mode. Helium was used as the carrier gas with a linear flow velocity of 1 mL/min. The initial temperature of the column was 35 °C for 2 min, programmed at 2 °C /min to 70 °C, and was increased at a rate of 6 °C /min to a final temperature of 230 °C. The MS detector scanned a mass range (m/z) from 50 to 500 m/z with a scan speed of 1.562 µ/s. Three replications of each sample were performed. Identification of volatile compounds was based on both the mass spectra database (NIST/EPA/NIH mass spectral library, Version 2.2, 2014) and the Linear Retention indices (LRI). The LRI were calculated based on the retention time of a series of n-alkanes (C7-C30) in hexane solution (in methanol) (Sigma-Aldrich Inc., St. Louis, MO, USA) and compared with previously reported values in the literature to validate the results. Semi-

quantification and relative concentrations for the identified compounds was reported based on the area under the curve of the internal standard, 1,3-dichlorobenzene.

Sensory Evaluation -

A descriptive method for sensory analysis was performed where a panel (n = 9) of assessors (age 22 to 35) was trained during multiple one-hour sessions to ensure they were acquainted with the pecan nutmeat attributes of interests, including freshness (the aroma of freshly deshelled pecans) and rancid/oxidized characteristics (the aroma pertaining to oxidation of oil). A total of 7 to 8 hours were devoted to training and orientation. The proposal for use of human subjects in research was reviewed and approved by the University of Georgia, Institutional Review Board (UGA-IRB). The panelists were not permitted to eat the treated pecan nutmeats at any point during the study and were only allowed to sniff the samples. The definitions and reference samples used for training the panelists have been tabulated (Table 5.1). A 15-point hedonic ordinal scale was used to collect sensory data. The references and their position on the scale was discussed among the panelists and the adjustments were done as per the consensus. Each of the nine sensory panelists evaluated the stored unpacked (No Pack-30), packed (LDPE-58, PEV-58, ML) and shelled pecans in triplicates (N=3). During all evaluations, the references (Table 5.1) for each attribute were provided but encouraged not to be used too often. To prevent modality saturation, panelists were trained to reset the olfactory senses by sniffing their own skin. Additionally, the numbers of samples were limited to 5 to 7 per session. The samples were assigned randomly to the panelists and labeled as 4-digit random code to reduce error related to order of presentation. The panelists were directed to take at least a

couple of brief breaks per session. With a total of 25 sessions conducted, the blind evaluations were conducted at every 4th session.

Predictive Modeling (Artificial Neural Network [ANN]) -

The data obtained from the experiment was utilized to develop an ANN model and derive predictive equations for pecan nutmeat freshness. The ANN consists of at least one hidden layer comprising one or more nodes/neurons. The nodes/neurons serve as nonlinear functions of the original inputs, known as activation functions. For this study, only the hyperbolic tangent function (*TanH*) was used which has an output range of [−1, 1] (Lin & Wang, 2008). The formula for *TanH* is as follow:

$$TanH = \frac{e^{2x}-1}{e^{2x}+1} \qquad (4)$$

Where x is the linear combination of the predictor variables. The model was validated using the K-Fold method with k = 5. A random seed of 222 was used which could be repeated to reproduce the obtained estimates. Freshness and rancid/oxidized aroma data from the sensory panel were used as independent variables. Various combinations of number of hidden layers, types of activation functions and number of nodes/neurons were tested. The ANN models with one hidden layer comprising 4 and 3 nodes/neurons for freshness and rancid/oxidized aroma, respectively, were found to have the best fit. The estimates were calculated for developing the prediction equations. The fit of the model for training and validation was determined using the coefficient of determination (R^2). The ANN model was built using JMP®, Version 16 Pro (SAS Institute Inc., Cary, NC, USA).

Statistical Analysis -

There were multiple designs of experiment (DOE) employed in the study. Experiments exploring the effects of temperature, RH, packaging material and storage days (SD) on extent of lipid oxidation and concentration of volatile compounds had a completely randomized design (CRD). The results were analyzed using 4-way ANOVA where storage days were nested within packaging material and temperature. The sensory study had a generalized randomized complete block design (GRCBD) where temperature, RH, packaging material and storage days (SD) were experimental factors, and sensory panelists were the block factor. As with the previous DOE, storage days were nested within packaging material and temperature. The results from the sensory experiment were analyzed using mixed model analysis where temperature, RH, packaging material and storage days were treated as fixed effects and participants were treated as a random effect. A Tukey's HSD post hoc test ($\alpha = 95\%$) was performed to explore differences among means for the different treatments in all the experiments. In addition to applying inferential statistics, exploratory statistical tools were employed for data mining; Principal Component Analysis (PCA) was performed on the sensory and lipid oxidation data, followed by cluster variable (CVA) analysis to examine associations between different responses (FFA, PV, AV, Freshness, degree of Rancidity/Oxidation, and the 33 volatile compounds identified). Correlation analysis was also performed to explore any associations among multiple chemical responses to storage. All statistical analyses were performed using JMP®.

Result and Discussion

Lipid Oxidation:

Free Fatty Acid (% FFA as Oleic Acid) –

Pecan oil consists primarily of triacyl glycerides (TAG) with fatty acids esterified to a glycerol backbone (Kochhar, 1996). There are a number of factors which could lead to hydrolysis of the TAG molecule and liberate fatty acids including water, enzyme activity and storage duration (Badings, 1984). The packaged and unpackaged pecan nutmeats exhibited an increase in % FFA content as storage progressed. Furthermore, the rate of free fatty acid formation drastically increased as RH increased >50% (Fig. 5.2). The % FFA content was significantly higher in pecans stored in LDPE-58 as compared PEV-58, and shell-var due to high moisture permeability (Table 5.2) (Badings, 1984). Overall, unpacked pecans exhibited less FFA formation due to presence of less moisture in environment.

Peroxide Value (PV, meq/kg of oil) -

The increase in FFA content also accelerates the overall oxidation of oil, especially unsaturated fatty acids (Labuza & Dugan Jr, 1971). The liberated FFA participates in an autoxidation reaction which could be triggered due to the presence of oxygen, metal ions, heat and light (Choe & Min, 2006). This phase of lipid oxidation is called initiation. During initiation, an initiator (metal ions, lipoxygenase, sensitizers etc.) cause abstraction of hydrogen from unsaturated fatty acid(s) that form alkyl radicals. In the presence of oxygen, the alkyl radicals react with oxygen to form peroxyl radicals. The peroxyl radicals thus formed can interacts with new fatty acid molecule to form lipid hydroperoxide which is a primary oxidation product and is a part of the propagation phase of the lipid oxidation

reaction (Shahidi & Wanasundara, 2002). The early stages of propagation, when the lipid hydroperoxide formation is minimal, is known as the induction period (Fig. 5.3). The increase in concertation of lipid hydroperoxides could indicate the onset of formation of undesirable volatile compounds which causes the rancid/oxidized aroma of unpalatable pecan nutmeats. It should be noted that the lipid hydroperoxides are non-volatile and odorless, and only indicate the probability of formation of secondary oxidation products (Yi et al., 2020). The induction periods and summary of PV for packed and unpacked pecans have been tabulated (Table 5.2 and Table 5.3). Both packaged and unpackaged pecans stored at lower temperature had a longer induction period. As the storage temperature increased, the induction period decreased, indicating early onset of oxidation/rancidity. The packaged pecans (in LDPE and PEV) stored at 58% RH had a much shorter induction period compared to the unpackaged pecans. The shorter induction period could be attributed to involvement of moisture in hydrolyzing FFA from the glycerol backbone and increasing the substate available for lipid hydroperoxides. The concept of the induction period was applied to data retrieved from the trained sensory panelists (Table 5.3). The days taken to perceive slight rancidity from the consumer perspective (a rancid/oxidized hedonic score of 5) was proximal to the induction period obtained using the peroxide value (meq/kg of oil). The hedonic score of 5 was chosen because the consumers were not as highly trained as a descriptive panel and may have a slightly higher threshold for detecting any rancid aromas. The longest induction period and lower value of perceived slight rancidity by the panelists was observed in pecan nutmeats packaged in ML (Table 5.3). It has been established that lipid hydroperoxides are good indicator of the onset of lipid oxidation (Espinosa-Andrews et al., 2022) but the application of this knowledge

has not been taken further. The chemical method to determine lipid hydroperoxides would be a potentially cost-effective way for the pecan industry to conduct in-house shelf-life studies and constructing quality control limits of oil and oil-based products.

Anisidine Value (AV, ppm) -

The lipid hydroperoxides further degrade to volatile and non-volatile secondary oxidation products consisting of aldehydes, ketones, furans, alcohols, short chain hydrocarbons, etc. (Kochhar, 1996; Min & Boff, 2002). The derivation and pathways involved in formation of these simpler compounds is discussed later (see section 3.2). One of the quickest ways to determine secondary oxidation products is using a colorimetric analysis AV. Being one of the most common methods employed in industry, it measures (primarily) saturated and branched aldehydes generated due to hydroperoxide decomposition which are known cause of rancid/oxidized flavors in food (Gordon, 2004; Xu et al., 2022; Yang & Boyle, 2016). We detected different 2-alkenal compounds during this investigation that were correlated with AV and is discussed later (see section 3.2.1.1). The pecan nutmeats stored in ML and inshell experienced the least secondary oxidation product formation throughout the storage study, followed by No Pack-30 and the PEV-58 treatments (Table 5.2). The vacuum-packaged pecans (PEV) experienced similar level of AV as the unpackaged pecans (No pack -30) even though packaged pecans were invariably vacuum packaged (an environment less conducive to formation of peroxyl radicals since oxygen availability is limited). The PEV packaging consists of layer of polyethylene, which allows water vapor and oxygen to pass through. The presence of a vacuum significantly slowed down the formation of secondary oxidation products as compared to the LDPE-58 treatment, which

had the highest formation of secondary oxidation products of all treatments (Table 5.2). The AV is traditionally employed as a quality measure of refined oil and that industry has established limits on fresh (<10 ppm) and fried oil (<20 ppm) (Manzoor et al., 2022; Naik et al., 2022; Tompkins & Perkins, 1999). A high AV indicates increases in the concentration of secondary oxidation products but unlike refined oils, there are no established limits of AV concentration for pecan nutmeats beyond which the product could be deemed unfit for consumption. The possibility of a limit for oil-in-pecans were explored in this study (Table 5.3). It is safe to assume that an AV ≧1.5 ppm could indicate the onset of volatile compound formation. However, there were anomalies. For instance, shelled pecans and the PEV-58 (30°C) treatment did not show development of even a slight rancid aroma at AVs of 6 ppm and 3.5 ppm, respectively.

The use of these types of chemical analysis methods for understanding degradation of the oil-in-food matrix is scarce but could be further explored to find threshold concentration for different types of (oil rich) food (Noor & Augustin, 1984; Tompkins & Perkins, 1999).

Volatile Compounds -

As lipid hydroperoxides increase in concentration, they start to degrade and form different volatile and non-volatile compounds, collectively called secondary oxidation products. This study focused on volatile compounds only. The FFAs give rise to different type of lipid hydroperoxides (*n*-ROOH) as illustrated (Fig. 5.4). The *n* represents the position of the -OOH on the hydrocarbon chain. For instance, experiments have revealed that action of oxygen on oleic acid leads to formation of numerous peroxide molecules including 8-

ROOH, 9-ROOH etc. As the storage progresses, different types of free radicals accumulate (e.g., H+ dissociated during the initiation step, OH- dissociated during the propagation step, presence of metal ions, etc.) and react with the lipid hydroperoxides, giving rise to alkoxy radicals. The long chain of alkoxy radicals could cleave at certain positions forming short chain hydrocarbons, also known as secondary oxidation products (Fig. 5.4). The process of cleaving is known as β-scission. A detailed account of the cleavage mechanism and resulting chemical compounds has been provided by Min and Boff (2002).

3.2.1 Identification of volatile compounds

During our investigation a total of 33 volatile compounds were identified from pecan nutmeats. The volatile compounds consisted of 7 alcohols, 12 aldehydes, 4 carboxylic acid (with 2 methyl esters), 1 furan, 5 ketones, 3 lactones and 1 terpene. A detailed summary and quantification of all volatiles compounds is presented (Table 5.4). Aldehydes, alcohol, and carboxylic acid were prominent classes of volatile compounds detected across all packaging types, RHs and temperatures. It has been reported that aldehydes and ketones are prominent secondary lipid oxidation products in vegetable oil (Seppanen & Csallany, 2001). The concentration of aldehyde, ketones, alcohol, and lactones increased with increases in temperature in LDPE, and PEV packaging (Fig. 5.5). The pecan nutmeats stored in ML experienced a significant change in aldehyde concentration only due to temperature. However, the concentration of aldehydes was less than in the other treatments (Fig. 5.5). Aldehydes constituted more than 50% of the total volatiles in pecan nutmeats stored at 20°C (across all treatments except No Pack-30). As the storage temperature increased, quantities of carboxylic acid, ketones and lactones were elevated, indicating

break down of unsaturated aldehydes and formation of termination reaction products (Fig. 5.5) (Min & Boff, 2002). For No Pack-30, the quantity of ketones was higher than aldehydes, but overall concentrations of these chemical classes were low. The pecan nutmeats stored in ML did not experience any major change in carboxylic acid, ketones and lactones content even at the higher storage temperatures. Thus, pecan nutmeats stored in barrier packaging (impervious to water and oxygen) and with a modified atmosphere experienced delayed onset of rancidity (Fig. 5.5). The possible mechanisms and pathways associated with production of the different volatile compounds are discussed individually in the following subsections.

Aldehydes -

Pecan oil is rich in unsaturated fats such as oleic and linoleic acids. The degradation of these fatty acids primarily leads to aldehyde production including hexanal, octanal, nonanal, 2-decenal, and 2-undecenal, which are derived from cleavage and peroxidation (Erten & Cadwallader, 2017; Javed et al., 2018; Xiao et al., 2014) as well as secondary oxidation processes (Bail et al., 2009; Ribeiro, Klein, et al., 2020). Nonanal, octanal and hexanal were major aldehyde compounds detected during storage of pecan nutmeats (Table 5.4). Octanal and Nonanal have been associated with rancid fat aroma (Soderhjelm & Eskelinen, 1985). These volatile compounds form due to cleavage of 9-OOH and 11-OOH oleate hydroperoxides, respectively (Fig. 5.4) (Morales et al., 1997; Shahidi, 2005). Hexanal is produced due to breakdown of 13-OOH linoleate hydroperoxide (Fig. 5.4) (García-Martínez et al., 2009; Morales et al., 1997; Shahidi, 2005; Shahidi & John, 2013). Nonanal has also been found at high concentrations in roasted nuts (Agila & Barringer,

2012; Vázquez-Araújo et al., 2008). 2-octenal and 2-decenal were also present to a considerable extent across all treatments (Table 5.4). There is extensive research supporting production of 2-Octenal and 2-Decenal from 11-OOH linoleate and 9-OOH oleate hydroperoxide, respectively, via scission (Fig. 5.4) (Badings, 1959; Badings, 1970; Schieberle & Grosch, 1981; Swoboda & Lea, 1965). 2-Heptenal is derived from the decomposition of 13-OOH linoleate and was present in minute quantities in all pecan nutmeat samples regardless of treatment (Fig. 5.4). It has been reported that 2-heptenal could form due to photooxidation of oil and formation of 12-OOH linoleate hydroperoxide (Frankel et al., 1979). Grebenteuch et al. (2021) reported possible formation of heptanal during the heat treatment of 2-nonenal. Heptanal has been reported to be present in oil containing linolenic acid (Nielsen et al., 2004). Pecan nutmeats have been reported to contain linolenic acid to some extent which might have contributed to formation of heptanal (Franco Estrada et al., 2022; Wu et al., 2022). Decanal and 2-undecenal were present in small quantities regardless of treatment (Table 5.4). Decanal and 2-Undecenal are formed during cleavage of 8-OOH oleate hydroperoxides (Fig. 5.4). Benzaldehyde and benzeneacetaldehyde have been reported to be present in pecan nutmeats as well and are reported to have an almond-like aroma (Gong et al., 2018b). Benzaldehyde and benzeneacetaldehyde degraded with increases in temperature and progression of the storage study (Table 5.4). So, perhaps benzaldehyde and benzeneacetaldehyde could be used to predict freshness of pecans as discussed in a later section (section 3.4.2). Benzaldehyde has been demonstrated to be a product of phenylalanine degradation (Hidalgo & Zamora, 2019). The pecan nutmeats stored in ML showed an increase in benzaldehyde and benzeneacetaldehyde content (Table 5.4). The sensory panelists reported

a desirable roasted aroma in pecans kept at 40°C throughout the storage period which could be attributed to these two compounds. The content of all branched alkenals had pronounced correlations with AV (Table 5.5). However, the branched aldehydes are not the only major volatiles produced from pecan nutmeats. Previously a positive correlation between lipid oxidation and hexanal was demonstrated for different types of products such as meat and meat products (Beltran et al., 2003; Shahidi & Pegg, 1994), soybean oil (Koelsch et al., 1991), rapeseed oil (Andersson & Lingnert, 1998), mayonnaise, and potato chips (Azarbad & Jeleń, 2015). During our investigation, the change in nonanal concentration was the most prominent among the aldehydes, followed by hexanal and octanal (Fig. 5.6). The volatile aldehydes were further explored for predicting the rancid/oxidized aroma of stored pecan nutmeats (see section 3.4).

Alcohol -

The alcohols 1-octanol, 1-hexanol, 1-pentanol and 1-heptanol were present at the highest content in unpackaged and packaged pecan nutmeats (except those packaged in ML) (Table 5.4). Studies conducted on oils with a similar lipid profile to pecan nutmeats (for instance, soybeans) reported that the formation of n-hexanol, n-pentanol and n-heptanol are the major causes of quality loss and might be generated as secondary lipid oxidation products (Arai et al., 1970; Gong et al., 2018a; Kato et al., 1981; Zhan et al., 2022). The alcohol 1-pentanol possess a characteristic raw pecan aroma (Burdock, 2016). However, higher concentrations could be perceived as oxidized oil (Kochhar, 1996). The concentration of 1-pentanol increased with an increase in temperature (Table 5.4). 1-Pentanol has been reported to be formed from 13-ROOH linoleate hydroperoxide (Fig. 5.4). Contrary to this,

1-octanol and 1- heptanol have been reported to be formed from the breakdown of 13-ROOH oleate hydroperoxides (Fig. 5.4). No definite pathway for production of 1-hexanol has been reported. The concertation of alcohol in pecan nutmeats was found to be comparatively lower in the low humidity environment (30%). Furthermore, the generation of alcohol was almost nonexistent in samples stored in ML packaging. This might indicate a role of moisture and oxygen in promoting formation of alcohols either directly or indirectly. The concentration of 1-heptanol, 1-hexanol and 1-octanol was relatively higher in the PEV-58 treatment than the LDPE-58 treatment (Fig. 5.4). However, panelists rated the PEV-58 treatment nutmeats as having significantly higher rancidity compared to those from the LDPE-58 treatment at all storage temperatures (Table 5.6). It is established that alcohol has a higher flavor threshold than those of aldehydes (Kochhar, 1996). So high levels of alcohol do not necessarily correspond to a rancid or oxidized aroma. Research has indicated possible pathways for alcohol generation, a prominent one being conversion of aldehyde to alcohol in the presence of alcohol dehydrogenase (ADH) (Morales et al., 1997; Thewes et al., 2022; Thewes, Both, Thewes, Brackmann, Schultz, et al., 2021; Thewes, Both, Thewes, Brackmann, Wagner, et al., 2021). But these studies misconstrued findings of original research done by Marquard et al. (1995) and Eriksson et al. (1977). The authors in the original work suggested ADH converted off-flavors caused by aldehydes to relatively less aromatically strong alcohols. The studies did not claim that pecan nutmeats contain ADH. ADH exists in pecans but only in pecan tree leaves. The alcohol formation has less to do with breakdown of secondary oxidation products (for instance aldehydes) and more to do with the propagation phase of lipid oxidation. The alkoxy radicals during the propagation phase are very unstable and react with nearby free fatty acids to liberate

alcohol and a free radical. The reaction increases with increases in temperature, which was observed in our study (Fig. 5.6, Table 5.4). The mechanism has been explained in detail by Min and Boff (2002). 1-Octen-3-ol and 3,5-Octadien-2-ol, both unsaturated alcohols, were also detected in pecan nutmeat samples, albeit in low quantities as compared to other alcohol compounds. It has been reported that 1-Octen-3-ol is responsible for imparting a mushroom flavor in milk and milk products and has been reported to form from scission of linoleate hydroperoxide (Hoffmann, 1962).

Ketones -

2-decanone, 2-nonanoe, 2-heptanone, and 3-nona-2-one were detected in stored pecan nutmeats (Fig. 5.6, Table 5.4). Ribeiro, Klein, et al. (2020) and Horvat and Senter (1980) reported presence of 2-heptanone in oxidized oil of different pecan cultivars. 2-Heptanone has been associated with a rancid coconut oil aroma (Kellard et al., 1985). 2-Octanone has been reported in roasted peanuts (Bett & Boylston, 1992), frying oil (Endo et al., 2001) and cooked chicken (Api et al., 2019). Authors have speculated that ketone generation might be due to fungal growth generated as one of the metabolites (Beier et al., 2014; Kinderlerer, 1993; Thewes, Both, Thewes, Brackmann, Schultz, et al., 2021; Thewes, Both, Thewes, Brackmann, Wagner, et al., 2021). The ketone compounds, such as 2-heptanone and 2-nonanone, have been found in mold-ripened cheeses (Moio et al., 2000; Yan et al., 2020). However, during our experiment, there was no (visible) fungal growth on any of the stored pecan nutmeats. In fact, none of the studies related to pecans that we cited above reported fungal growth during their investigations. It is established that ketones are formed at the end of the lipid oxidation process, also called the termination phase (Choe & Min, 2006;

Kochhar, 1996). As the hydroperoxide levels increases, concentration of free radicals and aldehydes increase as well. The concentration of free radicals further increases during scission and cleavage of lipid hydroperoxides. In a matrix where concentration of free radicals is high, these highly unstable molecules react with each other to form ketones. Thus, the ketone compounds indicate the progression and extent of lipid oxidation. The ketone formation was prominently observed in LDPE-58 and PEV-58 pecan nutmeats stored at 58% RH (Fig. 5.5). But shelled pecans did not produce much ketone at any time over the storage period. The results are in agreement with those from a study by Thewes, Both, Thewes, Brackmann, Wagner, et al. (2021) on shelled pecans. The unpackaged pecans did not show a change in ketone concentration (Fig. 5.5). As stated in section 3.1.1, presence of excess moisture might lead to hydrolytic cleavage of TAG molecules, increasing substate available for primary oxidation products (such as lipid hydroperoxides), which in turn increases concertation of secondary oxidation products (such as volatile compounds). As the lipid oxidation reactions reach the termination stage, ketone concentration increases. Based on this process, concentration of ketone compounds could be used to estimate the extent of lipid oxidation due to high moisture and temperature conditions. The exact reaction mechanisms for the formation of ketones have yet to be elucidated (Kochhar, 1996).

Acids -

The presence of moisture and lipolytic enzymes promotes cleavage of fatty acid from TAG molecules (Kochhar, 1996). The acids are further involved in formation of free radicals, aldehydes, alcohols and ketones (Choe & Min, 2006; Kellard et al., 1985). Octanoic acid

and Nonanoic acid were the major volatile fatty acids (FA) detected in packaged and unpackaged pecan nutmeats (Fig. 5.6, Table 5.4). Pecans stored at 30% RH had an overall lower volatile FA content than those stored at 58% RH regardless of storage temperature (Fig. 5.6, Table 5.4). Pecans stored in ML packaging had the least volatile FA generation due to the excellent barrier properties of the package type. Nonanoic acid and octanoic acid are associated with raw pecan nutmeat volatiles and contribute towards fatty and cheesy notes at low concentration (Gong et al., 2018b). They also reported an increase in concentration of nonanoic acid and octanoic acid during roasting. Similar trends were observed in our study (Fig. 5.6). The production of methyl esters of nonanoic acid and heptanoic acid was minimal and did not appear contribute meaningfully to the volatile profile.

Lactone, Terpenes and Furan -

The involvement of lactones in imparting stale off-flavors in modified and unmodified packaged foods has been discussed (Kinsella, 1969; Langler & Day, 1964). However, some research has been aimed at exploring the association of lactones with desirable aromas such as the cooked flavor (Jeon, 1996) or peach (Horvat et al., 1990). γ-Heptalactone, γ-octalactone and γ-ethyl-butyrolactone were detected in stored pecan nutmeats under varying environmental conditions. The concentration of lactones increased with increasing temperature (Fig. 5.6, Table 5.4) and have been reported to be associated with roasted pecans (Wang & Odell, 1972). The panelists noted development of a roasted aroma in pecan nutmeats stored at >30°C. However, none of the lactones were found in quantifiable concentrations in nutmeats from any of the treatments, negating their involvement in the

roasted aroma in pecans (Fig. 5.5). This further emphasizes the need for more research to clarify the role of lactones in the lipid oxidation process. However, D-limonene, a terpene, had a strong negative association with the oxidation/rancid aroma and a strong positive association with freshness of pecans (section 3.4.2). Research indicates that D-limonene has a citrus like aroma (John et al., 2017; Tice, 1996). Ribeiro, Klein, et al. (2020) reported D-limonene present in various pecans cultivars. D-limonene appears to be oxygen and temperature sensitive (Fig. 5.5). The quantity of D-limonene was relatively high in pecan nutmeats stored in ML packaging and inshell, and all the panelists detected a fresh aroma in the pecans from these treatments (Fig. 5.6). Pecans stored in PEV, and LDPE packaging had relatively low quantities of D-limonene (Table 5.4). Based on these observations, D-limonene could be used to predict freshness of pecan nutmeats. 2-pentlyfuran is another compound detected in stored pecan nutmeats. However, the concentration was very low regardless of treatment (Table 5.4). Furans are derived from oleate and linoleate hydroperoxides (Fan, 2015). Ribeiro, Ribeiro, et al. (2020) reported development of furan in pecans over long term storage at 20°C.

Sensory Analysis -

Pecan nutmeats stored in ML packaging had the highest freshness scores, followed by pecans stored inshell (Table 5.6). It should be noted that pecans stored in shell (or shelled pecan) were subject to more extreme temperature and RH changes yet still received a high freshness score (Fig. 5.1). The pecans stored in PEV packaging had comparatively a higher freshness score compared to those stored in LDPE packaging regardless of temperature (Table 5.6). The unpackaged pecan nutmeats kept at 30% RH were not perceived to change

much in overall freshness score compared to those pecan nutmeats stored at a high RH (Table 5.6). The freshness and rancid/oxidized aroma were significantly affected by temperature, package type and storage duration (Table 5.6). The order of change in overall pecan nutmeat freshness score from high to low for different treatments was ML>inshell>N Pack-30>PEV-58>LDPE-58. Pecan nutmeats stored in LDPE and PEV packaging received the highest rancidity/oxidation scores during storage (Table 5.6). The panelists perceived comparatively less oxidized/ rancid aroma from pecan nutmeats stored in ML packaging and inshell (regardless of temperature and RH conditions). The panelist rating in overall rancid/oxidized score for pecan nutmeats from high to low was LDPE>PEV>No Pack>ML>inshell. The possible associations of volatile compounds with sensory perception is discussed in the following sections.

Exploratory Statistics and Data Mining:

Hierarchical Cluster Analysis -

The hierarchical cluster analysis (HCA) was used to explore the groups or clusters within pecan nutmeat treatments, and sensory attributes. The dendrogram of clusters and a scatterplot matrix shows a total of 8 clusters were identified (Fig. 5.7). All the baseline observations were grouped together (cluster 1) and were rated as the fresher of the samples (Fig. 5.7). Pecan nutmeats stored at 20, 30 and 40°C, and for up to 60 days were as fresh as the baseline pecan nutmeats (day 0), indicating the effectiveness of a complete barrier or modified package in delaying generation of undesirable volatiles compounds. Shelled pecans were able to retain a fresh aroma and resist development of rancidity up to 90 days in storage, which was equivalent to the sensory scores of pecan nutmeats stored at 20, 30

and 40°C in ML packaging for 240, 180 and 120 days, respectively (cluster 2). Pecan nutmeats stored in high RH conditions (58%) experienced the highest rancidity score followed by those packaged in PEV (cluster 8) (Fig. 5.7). Pecan nutmeats stored at 40°C for 180 days was the only treatment in cluster 5 and had a rancidity score of 6 as well as freshness score of 4.78 at 180 days of storage.

Principal component analysis -

The correlation based PCA was performed on mean values of sensory attributes, which included freshness scores, rancid/oxidized aroma scores, with volatile data as supplementary variables. The PCA provided two principal components (PCs), explaining 87.1% and 12.9% of the variability in PC1 and PC2, respectively (Fig. 5.8). The loading plot revealed that associations of sensory attributes with different volatile compounds. Freshness was strongly associated with D-limonene, a terpene associated with citrus aroma. Freshness was also strongly negatively associated with decanal, 2-octenal and 1-heptanol (Fig. 5.8). Most ketones did not appear to be associated with freshness. But ketones appear to be strongly associated with a perceived oxidized/rancid aroma. As discussed (section 3.2.2.3), pecan nutmeats stored at high temperatures experienced rapid generation of ketones. However, there were numerous other volatiles which had higher PC1 scores including nonanal, γ-ethylbutyrolactone, 1-pentanol, hexanal, 1-nonanol and nonanoic acid (Fig. 5.8). Even though ketones appear to influence the oxidized/rancid aroma, further analysis is required to confirm their involvement. The cluster analysis was performed identify groups of volatiles which could explain most of the variability in the panelist sensory data. A summary of clusters formed is presented (Table 5.7). Linear regression

was applied to the identified clusters for predicting sensory attributes (Fig. 5.9). For the perceived oxidized/rancid aroma, cluster 1 and 2 explained more variability than cluster 6 (which contains mostly ketones). The loading plots indicate some alcohols, aldehydes, and lactones explain much more variability of PC1 (Fig. 5.8). Even though ketones played a greater role in PC2, the coefficient of determination was lower due to contributing less variability on that axis (12.9%) (Fig. 5.8 and 5.9). For perceived freshness of pecan nutmeats, volatiles in cluster 2 explained more variability than the remaining clusters (Fig. 5.9). Thus, volatile compounds in cluster 1 and 2 were used to develop a predictive neural model for determination of the freshness or oxidized/rancid aroma of stored pecan nutmeats, respectively.

Predictive model (Artificial Neural Network [ANN]) -

The most informative clusters for freshness and rancid/oxidized aroma were determined from the PCA (section 3.4.2, Table 5.7 and Fig. 5.9). The volatile compounds in cluster 2 were used as predictors to estimate freshness in pecan nutmeats. The cluster consisted of D-limonene, 3,5-octadien-2-ol, 2-octenal, octanoic acid, decanal, 2-decenal, and nonanoic acid (methyl esters). For the freshness prediction model, 1 hidden layer with 4 nodes or neurons were found to provide the best fit (Fig. 5.10). The training and validation of the predictive model for freshness had an R^2 value of 0.94 and 0.79, respectively. The volatile compounds in cluster 1 were used as predictor to estimate the rancid/oxidized aroma in pecan nutmeats (Table 5.7). The cluster consisted of 13 of the 33 volatile compounds including octanal, nonanal, 1-octanol heptanal, γ-octalactone, 1-octen-3-ol, γ-ethylbutyrolactone, 1-pentanol, hexanal, 2-heptenal, 2-nonenal, 1-nonanol, nonanoic acid,

1-hexanol, and γ-heptalactone. For the rancid/oxidized aroma prediction model, there was 1 hidden layer with 3 nodes or neurons that were selected and were found to provide the best fit (Fig. 5.10). The training and validation of the predictive model for the rancid/oxidized aroma had an R^2 value of 0.84 and 0.98, respectively. The estimates for the model predictor variables for both freshness and rancid/oxidized aromas are presented (Table 5.8). The estimates can be used to calculate the node/neuron (N) values to calculate the respective responses. For instance, assuming the aim is to predict freshness of pecan nutmeat samples exhibiting the following volatile concentration profile (ppm): D-limonene (30.17), 3,5-octadien-2-ol (10), 2-octenal (0.6), octanoic acid (10), decanal (100), 2-decenal (15), nonanoic acid methyl ester (0). Based on the estimates in Table 5.8, the following regression model is used to calculate node 1 (N_1):

$$Freshness, H_1 = Tan\,H(0.5\,[6.59 - 0.25\,(D - Limonene) + 0.0162\,(3{,}5 - Octadien - 2 - ol\,) - 0.00266\,(2 - Octenal) - 0.00051\,(Octanoic\ acid)\ + 0.001648\,(Decanal) + 0.001317\,(2 - Decenal)\ - 0.00209\,(Nonanoic\ acid, methyl\ ester)] \quad (5)$$

Where *TanH* represents the hyperbolic tangent function (eq. 4). The *TanH* function is commonly embedded in popular software (for instance, in Microsoft Excel the function is *TanH*). Following the same approach, all the nodes (N_1 to N_4 pertaining to freshness) can be calculated and used in the following linear regression model:

$$Freshness = 1.77 + 15.11N_1 + 12.57N_2 - 7.28N_3 - 9.23N_4 \quad (6)$$

Based on the assumed concentration of volatile compounds, a freshness score 4.52 was obtained for the above example. Similar procedures may be followed to calculate the nodes/neuron values for the rancid/oxidized aroma using the variables presented in

Supplementary Table T6. Based on this approach, a linear regression model can be developed using the estimates provided. It should be noted that the model will be treated as a function of the hyperbolic tangent formula i.e., the equation should follow the given format; *TanH* (0.5[*linear equation from Table 5.8*]). Thus, the equation to calculate the rancid/oxidized aroma using the nodes (N_1 to N_3) is:

$$Rancid/oxidized\ aroma = 6.43 - 1.93N_1 + 3.40N_2 + 5.91N_3 \quad (7)$$

Conclusion

The changes in chemical and sensory attributes of pecan nutmeats were estimated under a range of environmental conditions (temperature, package type, RH and a modified atmosphere). The treatment factors mimic typical pecan industry storage, handling, and distribution conditions. For the first time, the effect of storing pecans under different RH conditions were explored. The level of RH (30% and 58%) affected the rate of formation of free fatty acids. The studied also explored potential use of a quick lipid oxidation determination method (viz. PV and AV) to estimate the induction period and thus the palatability of stored pecans. The induction period for PV coincided with induction period for sensory scores which could help pecan industry to design in-house shelf-life storage study by using quick and economical chemical methods. At the AV value of less 2 ppm, descriptive scores for rancid/oxidized aroma stayed < 5 for pecans stored at 30% RH. However, for pecans stored RH 58% and in-shell, AV was found to be not reliable indicator of oxidized/rancid aroma. The study highlighted the involvement of volatile compounds, in addition to aldehydes, is generating the undesirable rancid aroma of old pecan nutmeats. It was found that ketones, alcohols and lactones were robust indicators of lipid oxidation

under high temperature conditions. For the first time, a predictive model was developed to estimate sensory score of attributes (pertaining to pecans) from the volatile compounds detected from pecan nutmeats. The predictive models and their equations (eq. 6 and 7) could be used to determine the state of freshness and rancidity/oxidization of pecan nutmeats. These trained models could be used to reduce reliance on sensory panel e.g., evaluating samples by combining analytical and predictive modeling technique as well as sensory analysis to tackle sensory fatigue in human subjects and evaluate large number of samples at once. This would reduce costs associated to run panel and will be time efficient. Furthermore, machine learning models such as ANN can be further trained and improved by adding more data to the existing database to achieve more accurate predictions regarding sensory attributes of pecan nutmeats.

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Tables

Table 5.1: Summary of sensory descriptors, their definitions, sample preparation and the respective rating on the hedonic ordinal scale.

Sensory descriptor	Definition	Reference sample	Intensity rating[a]
Freshness	The aroma associated with freshly de-shelled pecans	Pecan nutmeats stored at 25°C and 55% RH for two days	3
		Fresh shelled pecan nutmeats	12
Rancid/oxidized	The aroma associated with rancid fats and oils	Canola oil (Kroger) microwaved (1100W) for 3 minutes	3
		Pecan nutmeats stored at 40°C and 30% RH for 2 months	12

[a]Intensity rating of samples are based on a 0–15 hedonic ordinal scale.

Table 5.2: Summary of % free fatty acid (FFA, as oleic acid), peroxide value (PV) and anisidine value (AV) with respect to temperature, package, RH and storage time (mean ± standard error, n=3). Means with different letters or signs (upper case [ABC], lower case [abc], and *,**,***) indicate significant difference between estimated values (within the column) based on Tukey's HSD ($\alpha = 0.05$). The analysis model fit F ratio for FFA ($R^2 = 0.87$), PV ($R^2 = 0.93$) and AV ($R^2 = 0.78$) was 7.02, 12.91 and 3.67, respectively. All the responses were significantly affected by main effects and interactions of temperature (°C), package-RH x temperature (°C) and storage days x temperature (°C) x package-RH.

Temperature (°C)	Packaging-RH	Storage time (days)	% FFA (as oleic acid)			AV (ppm)			PV (meq/kg of oil)		
20	LDPE-58	0	0.141 ± 0.020	HIJ		0.610 ± 0.033	DEFGHI		0.232 ± 0.034	EF	
	LDPE-58	105	0.277 ± 0.057	GHIJ		0.512 ± 0.450	EFGHI		1.792 ± 0.597	CDEF	
	LDPE-58	210	0.281 ± 0.042	GHIJ		0.185 ± 0.085	I		1.501 ± 0.852	DEF	
	LDPE-58	315	0.309 ± 0.044	FGHIJ		0.582 ± 0.036	DEFGHI		0.789 ± 0.022	DEF	
	LDPE-58	420	0.435 ± 0.042	EFGHIJ		0.902 ± 0.391	BCDEFGHI		1.441 ± 0.481	DEF	
	LDPE-58	525	1.109 ± 0.309	BCDEFGHI		1.040 ± 0.075	BCDEFGHI		13.343 ± 2.177	ABCDEF	
	Mean		0.425 ± 0.104	cd		0.638 ± 0.112	de		3.183 ± 1.412	c	
	ML	0	0.141 ± 0.020	HIJ		0.610 ± 0.033	DEFGHI		0.232 ± 0.034	EF	
	ML	60	0.212 ± 0.001	GHIJ		0.150 ± 0.026	I		0.238 ± 0.074	EF	
	ML	120	0.279 ± 0.014	GHIJ		0.367 ± 0.212	FGHI		0.167 ± 0.046	EF	
	ML	180	0.352 ± 0.026	EFGHIJ		0.681 ± 0.035	CDEFGHI		0.644 ± 0.546	DEF	
	ML	240	0.380 ± 0.160	EFGHIJ		1.135 ± 0.095	BCDEFGHI		0.600 ± 0.112	DEF	
	ML	300	0.515 ± 0.045	CDEFGHIJ		0.985 ± 0.055	BCDEFGHI		2.810 ± 0.618	BCDEF	

	Mean		0.313	±	0.042	cd	0.654	±	0.106	de	0.781	±	0.297	c
	No pack - 30	0	0.141	±	0.020	HIJ	0.610	±	0.033	DEFGHI	0.232	±	0.034	EF
	No pack - 30	90	0.424	±	0.183	EFGHIJ	0.213	±	0.017	I	0.897	±	0.020	DEF
	No pack - 30	180	0.277	±	0.066	GHIJ	0.208	±	0.007	I	0.662	±	0.100	DEF
	No pack - 30	270	0.191	±	0.015	GHIJ	0.222	±	0.122	I	1.599	±	0.366	CDEF
	No pack - 30	360	0.498	±	0.021	DEFGHIJ	0.623	±	0.089	CDEFGHI	2.460	±	1.376	CDEF
	No pack - 30	450	0.249	±	0.022	GHIJ	0.895	±	0.103	BCDEFGHI	0.618	±	0.121	DEF
	Mean		0.296	±	0.045	d	0.462	±	0.083	e	1.078	±	0.285	c
	PEV-58	0	0.141	±	0.020	HIJ	0.610	±	0.033	DEFGHI	0.232	±	0.034	EF
	PEV-58	105	0.161	±	0.005	GHIJ	0.086	±	0.036	I	1.481	±	0.536	DEF
	PEV-58	210	0.531	±	0.337	CDEFGHIJ	0.265	±	0.225	GHI	1.089	±	0.147	DEF
	PEV-58	315	0.307	±	0.011	FGHIJ	0.191	±	0.142	I	1.652	±	0.802	CDEF
	PEV-58	420	0.529	±	0.047	CDEFGHIJ	2.705	±	0.067	BCDEFGHI	1.082	±	0.119	DEF
	PEV-58	525	0.545	±	0.176	EFGHIJ	1.270	±	0.549	BCDEFGHI	1.076	±	0.074	F
	Mean		0.382	±	0.072	cd	0.886	±	0.280	cde	1.100	±	0.168	c
	Grand average		0.355	±	0.035	***	0.665	±	0.086	**	1.527	±	0.377	***
	LDPE-58	0	0.141	±	0.020	HIJ	0.610	±	0.033	DEFGHI	0.232	±	0.034	EF
	LDPE-58	75	0.573	±	0.038	BCDEFGHIJ	0.130	±	0.080	I	2.621	±	0.249	BCDEF
	LDPE-58	150	0.461	±	0.033	EFGHIJ	0.607	±	0.397	DEFGHI	1.463	±	0.103	DEF
	LDPE-58	225	0.497	±	0.068	DEFGHIJ	1.419	±	0.941	BCDEFGHI	1.634	±	0.210	CDEF
	LDPE-58	300	1.139	±	0.603	BCDEFGH	3.883	±	0.898	BCDE	11.057	±	0.249	ABCDEF
	LDPE-58	375	0.972	±	0.172	BCDEFGHIJ	2.980	±	2.015	BCDEFGHI	16.592	±	1.072	ABCD
30	Mean		0.630	±	0.127	bc	1.605	±	0.510	cde	5.600	±	1.836	bc
	ML	0	0.141	±	0.020	HIJ	0.610	±	0.033	DEFGHI	0.232	±	0.034	EF
	ML	60	0.615	±	0.164	BCDEFGHIJ	1.886	±	0.356	BCDEFGHI	0.695	±	0.225	DEF
	ML	120	0.388	±	0.025	EFGHIJ	1.168	±	0.243	BCDEFGHI	0.506	±	0.031	DEF
	ML	180	0.263	±	0.051	GHIJ	0.379	±	0.041	FGHI	1.820	±	0.191	CDEF
	ML	240	0.414	±	0.028	EFGHIJ	1.404	±	0.211	BCDEFGHI	5.020	±	0.250	ABCDEF
	ML	300	0.563	±	0.047	CDEFGHIJ	3.941	±	0.159	BCD	6.559	±	0.440	ABCDEF

	Mean		0.397	±	0.054	cd	1.565	±	0.359	bcd	2.472	±	0.739	c
	No pack - 30	0	0.141	±	0.020	HIJ	0.610	±	0.033	DEFGHI	0.232	±	0.034	EF
	No pack - 30	75	0.353	±	0.018	EFGHIJ	0.948	±	0.273	BCDEFGHI	2.844	±	0.047	BCDEF
	No pack - 30	150	0.289	±	0.006	GHIJ	0.719	±	0.101	BCDEFGHI	1.658	±	0.624	CDEF
	No pack - 30	225	0.383	±	0.077	EFGHIJ	0.383	±	0.265	FGHI	3.333	±	0.335	BCDEF
	No pack - 30	300	0.393	±	0.126	EFGHIJ	1.455	±	0.465	BCDEFGHI	3.425	±	0.546	BCDEF
	Mean		0.312	±	0.038	cd	0.823	±	0.152	bcd	2.298	±	0.425	c
	PEV-58	0	0.141	±	0.020	HIJ	0.610	±	0.033	DEFGHI	0.232	±	0.034	EF
	PEV-58	75	0.799	±	0.344	BCDEFGHIJ	1.288	±	0.669	BCDEFGHI	6.308	±	2.632	ABCDEF
	PEV-58	150	0.942	±	0.516	BCDEFGHIJ	0.940	±	0.890	BCDEFGHI	6.939	±	6.197	ABCDEF
	PEV-58	225	1.486	±	0.627	BCD	4.074	±	1.427	B	20.955	±	16.006	A
	PEV-58	300	0.619	±	0.095	BCDEFGHIJ	3.646	±	0.267	BCDEFG	12.573	±	3.576	ABCDEF
	PEV-58	375	1.338	±	0.417	BCDE	3.999	±	0.280	BC	18.622	±	6.087	AB
	Mean		0.887	±	0.181	ab	2.426	±	0.506	cde	10.938	±	3.175	a
	Grand mean		0.567	±	0.067	**	1.638	±	0.221	*	5.459	±	1.084	*
	LDPE-58	0	0.141	±	0.020	HIJ	0.610	±	0.033	DEFGHI	0.232	±	0.034	EF
	LDPE-58	45	0.422	±	0.165	EFGHIJ	1.102	±	0.835	BCDEFGHI	2.616	±	2.169	BCDEF
	LDPE-58	135	0.752	±	0.141	BCDEFGHIJ	3.709	±	0.382	BCDEF	17.653	±	0.134	ABC
	LDPE-58	180	1.576	±	0.236	AB	7.961	±	0.733	A	12.817	±	6.835	ABCDEF
	LDPE-58	225	2.540	±	0.230	A	11.164	±	1.317	A	16.166	±	3.053	ABCDE
	Mean		1.086	±	0.297	a	4.909	±	1.382	a	9.897	±	2.646	ab
40	ML	0	0.141	±	0.012	J	0.544	±	0.068	HI	0.229	±	0.020	F
	ML	60	0.486	±	0.027	DEFGHIJ	0.217	±	0.116	I	0.077	±	0.020	EF
	ML	120	0.775	±	0.040	BCDEFGHIJ	0.220	±	0.133	I	0.143	±	0.004	EF
	ML	180	1.165	±	0.045	BCDEFG	0.093	±	0.015	I	0.461	±	0.056	EF
	ML	240	1.295	±	0.015	BCDEF	0.085	±	0.013	I	0.385	±	0.125	EF
	ML	300	1.512	±	0.079	BC	0.270	±	0.045	GHI	2.430	±	0.340	CDEF
	Mean		0.837	±	0.145	ab	0.262	±	0.054	e	0.590	±	0.233	c
	No pack - 30	0	0.141	±	0.020	HIJ	0.610	±	0.033	DEFGHI	0.232	±	0.034	EF

	No pack - 30	51	0.229	±	ND	EFGHIJ	0.171	±	ND	BCDEFGHI	7.538	±	ND	ABCDEF
	No pack - 30	102	0.525	±	0.026	CDEFGHIJ	0.455	±	0.242	FGHI	1.728	±	0.643	CDEF
	No pack - 30	153	0.407	±	0.008	EFGHIJ	1.645	±	0.923	BCDEFGHI	10.580	±	9.340	ABCDEF
	No pack - 30	204	0.532	±	0.147	CDEFGHIJ	1.390	±	0.323	BCDEFGHI	2.146	±	0.163	CDEF
	No pack - 30	255	0.697	±	ND	BCDEFGHIJ	2.154	±	ND	BCDEFGHI	4.400	±	ND	ABCDEF
	Mean		0.414	±	0.063	cd	1.052	±	0.259	cde	4.131	±	1.886	bc
	PEV-58	0	0.141	±	0.020	HIJ	0.610	±	0.033	DEFGHI	0.232	±	0.034	EF
	PEV-58	45	0.288	±	0.029	GHIJ	0.213	±	0.179	I	1.454	±	0.454	DEF
	PEV-58	90	0.472	±	0.044	EFGHIJ	0.113	±	0.007	I	1.395	±	0.377	DEF
	PEV-58	135	0.804	±	0.021	BCDEFGHIJ	0.914	±	0.143	BCDEFGHI	1.390	±	0.085	DEF
	PEV-58	180	0.732	±	0.053	BCDEFGHIJ	1.191	±	0.059	BCDEFGHI	2.501	±	0.050	CDEF
	PEV-58	225	0.893	±	0.080	BCDEFGHIJ	3.636	±	0.886	BCDEFGH	4.855	±	0.488	BCDEF
	Mean		0.555	±	0.084	cd	1.113	±	0.376	cde	1.971	±	0.447	c
	Grand mean		0.723	±	0.088	*	1.697	±	0.412	*	3.813	±	0.880	*,**
Variable	Shelled-Var	0	0.141	±	0.020	HIJ	0.610	±	0.033	DEFGHI	0.232	±	0.034	EF
	Shelled-Var	90	0.194	±	0.017	GHIJ	0.065	±	0.035	I	0.217	±	0.026	EF
	Shelled-Var	180	0.132	±	0.003	IJ	0.390	±	0.076	FGHI	1.087	±	0.133	DEF
	Shelled-Var	270	0.183	±	0.015	GHIJ	0.189	±	0.085	I	0.513	±	0.035	DEF
	Shelled-Var	360	0.304	±	0.014	FGHIJ	0.834	±	0.169	BCDEFGHI	1.984	±	0.508	CDEF
	Shelled-Var	450	0.585	±	0.015	BCDEFGHIJ	8.998	±	2.507	A	3.951	±	0.372	BCDEF
	Mean		0.256	±	0.048	d	1.847	±	1.016	bc	1.330	±	0.406	c
	Grand mean		0.256	±	0.048	***	1.847	±	1.016	*	1.330	±	0.406	**,***

ML: pecans stored in metallic laminates and flushed with nitrogen, **LDPE -58**: pecans stored at 58% RH and low-density polypropylene packaging with normal air, **PEV-58:** pecans stored at 58% RH and Polyethylene-nylon packaging under vacuum, **No Pack-30:** pecans stored at 30% RH without any packaging material, **Shelled-Var**: shelled pecan nutmeats stored outside without temperature and humidity control, **ND** response not determined because of damaged samples

Table 5.3: Summary of the peroxide value (PV) induction period and sensory induction period. Both responses followed a similar trend. Number of days for pecan nutmeats to develop a slightly rancid aroma was deduced, along with the corresponding anisidine value (AV, ppm). This information and technique could be applied in the pecan industry to conduct in-house storage studies and quality control tests and to monitor pecan nutmeat quality.

Packaging (%RH)	Temperature (°C)	PV -Induction period (days)	Sensory- Induction period (days)	Days to reach sensory score of 5 (slightly rancid)	Corresponding AV (ppm)
No Pack (30%)[a]	20	>450	>450	>450	<1
	30	>375	>375	250	<1
	40	150	100	120	1.75
LDPE (58%)[b]	20	360	>525	>525	<1
	30	225	225	250	<1
	40	40	30	75	2.5
PEV (58%)[c]	20	>450	425	>450	<1
	30	175	150	300	3.5
	40	35	45	140	1.5
Shelled[d]	Variable	315	360	450	6
ML (58%)[e]	20	>450	>500	>500	<1
	30	300	250	250	<1
	40	145	120	175	<1

a – No Pack-30**,** pecans stored at 30% RH without any packaging material

b- LDPE -58, pecans stored at 58% RH and low-density polypropylene packaging with normal air

c - PEV-58**,** pecans stored at 58% RH and Polyethylene-nylon packaging under vacuum

d - Shell, shelled pecan nutmeats stored outside without temperature and humidity control

e - ML, pecans stored in metallic laminates and flushed with nitrogen

Table 5.4: Summary of the 33 volatile compounds identified from stored pecan nutmeats with respect to temperature, package, RH and storage days (mean ± standard error, n=3). Different letters (upper case [ABC or WXYZ] or lower case [abc]) indicate significant difference between estimated values (within the column) based on Tukey's HSD ($\alpha = 0.05$). The analysis model fit F ratio for the 33 volatiles varied from 5 to 200 and the coefficient of variation (R^2) ranged from 0.51 to 0.92. All the responses were significantly affected by main effects and interactions of temperature (°C), package-RH x temperature (°C) and storage days x temperature (°C) x package-RH. (**ND** response not determined because of damaged samples). Click on the given link to open table https://tinyurl.com/pecantable54

Table 5.5: Summary of the correlations between anisidine value and the different 2-alkenals detected from pecan nutmeats (estimated by HS-SPME-GC-MS analysis) (p value <0.05).

Volatile compound	Correlation (r)	95% CI
Hexanal	0.69	0.44-0.83
Heptanal	0.70	0.47-0.84
2-Heptenal	0.72	0.5-0.85
Octanal	0.72	0.50-0.86
2-Octenal	0.68	0.43-0.83
Nonanal	0.70	0.46-0.84
2-Nonenal	0.81	0.64-0.90
Decanal	0.53	0.22-0.74
2-Decenal	0.68	0.44-0.83
2-Undecenal	0.56	0.25-0.76

Table 5.6: Summary of sensory (freshness and rancid/oxidized aromas) scores for samples of pecan nutmeats receiving different treatments (mean ± standard error, n=3). Different letters (upper case [ABC], lower case [abc], and asterisks [*, **, ***]) indicate significant difference between estimated values (within the column) based on Tukey's HSD ($\alpha = 0.05$). The F-ratios for the main effects and interactions (third order) for freshness and the rancid/oxidized aroma score ranged from 18 to 460. The coefficient of variation (R^2) for the model describing the freshness and rancid/oxidized aroma responses were 0.48 to 0.79, respectively. All the responses were significantly affected by the main effects and their interactions; [temperature (°C)], [package-RH x temperature (°C)], [storage days x temperature (°C) x package-RH]. (**ND** response not determined because of damaged samples)

Temperature (°C)	Packaging -RH	Storage days	Aroma score - freshness				Aroma score - rancidity/oxidization			
20	LDPE-58	0	6.25	±	3.99	ABCDEFGHI	1.25	±	1.16	IJKLMNOPQ
		105	4.39	±	1.33	ABCDEFGHIJKLMN	1.47	±	0.91	NOPQ
		210	4.74	±	1.68	ABCDEFGHIJM	1.83	±	1.22	MNOPQ
		315	3.31	±	1.83	IJKLNOPQRSTUVW	2.25	±	1.15	HIJKLMNOPQ
		420	2.42	±	1.39	PQRSTUVWXYZA1	2.83	±	1.53	GHIJKLMNOPQ
		525	2.39	±	1.51	QRSTUVWXYA1	3.32	±	1.83	FGHIJKLM
	Mean		3.91	±	2.06	cde	2.16	±	1.53	de
	ML-0	0	6.25	±	3.99	AB	1.25	±	1.16	IJKLMNOPQ
		60	6.22	±	1.39	A	0.83	±	0.61	MNOPQ
		120	5.22	±	2.11	ABCDEFGHIJM	0.67	±	0.43	MNOPQ
		180	5.50	±	1.50	ABCDEFGHI	0.67	±	0.43	MNOPQ
		240	4.78	±	1.39	ABCDEFGHIJKLMNO	0.56	±	0.50	MNOPQ
		300	3.89	±	1.17	ABCDEFGHIJKLMNOPQRSTW	0.44	±	0.50	MNOPQ

	Mean		5.32	±	2.16	a	0.74	±	0.67	f
	No pack - 30	0	6.25	±	3.99	ABCDEFG	1.25	±	1.16	IJKLMNOPQ
		90	4.43	±	1.49	ABCDEFGHIJKLMN	1.56	±	1.29	NOPQ
		180	4.42	±	1.67	ABCDEFGHIJKLMN	1.38	±	0.88	OPQ
		270	4.07	±	1.59	BCDEFGHIJKLMNOP	1.08	±	0.69	PQ
		360	ND				ND			
		450	3.23	±	1.13	JKLNOPQRSTUW	2.24	±	1.39	KLMNOPQ
	Mean		4.48	±	1.81	abc	1.51	±	1.17	ef
	PEV-58	0	6.25	±	3.99	A	1.25	±	1.16	IJKLMNOPQ
		105	4.38	±	1.65	ABCDEFGHIJKM	1.39	±	0.96	OPQ
		210	3.86	±	1.45	CDEFGHIJKLMNOP	1.43	±	1.00	OPQ
		315	3.40	±	1.15	IJKLNOPQRSW	1.88	±	0.98	KLMNOPQ
		420	2.72	±	1.91	KLNOPQRSTUVW	2.57	±	1.98	HIJKLMNOP
		525	2.40	±	1.68	PQRSTUVWX	4.07	±	2.36	FGHI
	Mean		3.84	±	1.95	cde	2.11	±	1.83	e
	Grand mean		4.38	±	2.03	*	1.62	±	1.57	****
30	LDPE-58	0	6.25	±	3.99	AB	1.25	±	1.16	IJKLMNOPQ
		75	2.79	±	1.75	KLNOPQRSTUVW	3.24	±	1.83	FGHIJKLMN
		150	2.25	±	1.10	QRSTUVWXYA1	3.61	±	1.61	FGHIJKL
		225	1.99	±	1.22	STUVWXYZA1	4.50	±	2.16	FG
		300	1.35	±	0.93	VXYZA1	6.58	±	2.49	E
		375	ND				ND			
	Mean		2.92	±	1.84	fgh	3.84	±	2.47	c
	ML-0	0	6.25	±	3.99	ABCDE	1.25	±	1.16	IJKLMNOPQ
		60	6.44	±	2.13	ABC	0.94	±	0.58	LMNOPQ
		120	4.72	±	2.08	ABCDEFGHIJKLMNOPQR	1.61	±	0.70	HIJKLMNOPQ
		180	5.33	±	1.92	ABCDEFGHIJKLM	1.06	±	0.30	KLMNOPQ
		240	3.89	±	1.76	ABCDEFGHIJKLMNOPQRSTUVW	2.22	±	0.83	GHIJKLMNOPQ
		300	2.67	±	1.22	JKLMNOPQRSTUVWXYZA1	3.22	±	1.86	FGHIJKLMNOPQ
	Mean		4.88	±	2.56	ab	1.72	±	1.27	ef

	No pack - 30	0	6.25	±	3.99	ABCD	1.25	±	1.16	IJKLMNOPQ
		75	3.81	±	1.54	DEFGHIJKLMNOPQ	1.86	±	1.29	KLMNOPQ
		150	3.49	±	1.65	HIJKLNOPQRSW	1.69	±	0.89	MNOPQ
		225	2.00	±	1.44	STUVWXYZA1	3.00	±	1.65	GHIJKLMNO
		300	2.26	±	1.33	QRSTUVWXYZA1	2.40	±	1.61	IJKLMNOPQ
		375	ND				ND			
	Mean		3.56	±	1.99	def	2.04	±	1.47	e
	PEV-58	0	6.25	±	3.99	ABCDEFG	1.25	±	1.16	IJKLMNOPQ
		75	3.47	±	1.34	EFGHIJKLMNOPQRSTUW	2.33	±	1.01	HIJKLMNOPQ
		150	2.56	±	1.26	NOPQRSTUVWXYZA1	3.36	±	1.39	FGHIJKLMNO
		225	3.25	±	1.56	GIJKLMNOPQRSTUVW	2.19	±	1.24	HIJKLMNOPQ
		300	2.18	±	1.27	STUVWXYZA1	4.54	±	2.63	FG
		375	2.08	±	1.46	PQRSTUVWXYZA1	4.00	±	1.75	FGHIJK
	Mean		3.30	±	1.94	efg	2.95	±	2.12	d
	Grand mean		3.67	±	2.13	**	2.64	±	2.21	**
	LDPE-58	0	6.25	±	3.99	A	1.25	±	1.16	IJKLMNOPQ
		45	2.90	±	1.26	KLNOPQRSTUVW	2.79	±	1.65	GHIJKLMNOP
		90	ND				ND			
		135	1.03	±	0.82	XYZA1	8.85	±	2.75	CD
		180	0.72	±	0.58	YZ	12.32	±	1.72	A
		225	0.61	±	0.43	Z	13.00	±	1.86	A
	Mean		2.31	±	1.85	h	7.64	±	4.77	a
40	ML-0	0	6.25	±	3.99	ABCDEFGHI	1.25	±	1.16	IJKLMNOPQ
		60	6.11	±	1.45	ABCDEFGHI	1.28	±	1.00	JKLMNOPQ
		120	5.33	±	1.41	ABCDEFGHIJKLMN	1.33	±	0.83	IJKLMNOPQ
		180	4.78	±	2.05	ABCDEFGHIJKLMNOPQRS	6.00	±	4.21	EF
		240	3.33	±	1.32	EFGHIJKLMNOPQRSTUVWXYZA1	8.67	±	2.55	BCDE
		300	1.44	±	0.73	TUVWXYZA1	11.11	±	2.09	ABC
	Mean		4.54	±	2.58	abc	4.99	±	4.55	b
	No pack - 30	0	6.25	±	3.99	A	1.25	±	1.16	IJKLMNOPQ

		51	3.06	±	1.48	JKLNOPQRSTUW	1.76	±	1.35	MNOPQ
		102	2.74	±	1.23	LNOPQRSTUVW	2.94	±	2.09	GHIJKLMNO
		153	1.51	±	0.94	UVXYZA1	6.85	±	2.26	E
		204	1.78	±	1.07	TUVXYZA1	7.53	±	2.74	DE
		255	2.15	±	1.54	RSTUVWXYZA1	9.72	±	2.65	BC
	Mean		2.91	±	1.76	fgh	5.01	±	3.76	b
	PEV-58	0	6.25	±	3.99	ABCDEFH	1.25	±	1.16	IJKLMNOPQ
		45	3.68	±	1.99	EFGHIJKLMNOPQRSW	1.58	±	1.23	MNOPQ
		90	2.21	±	1.32	STUVWXYZA1	4.03	±	1.79	FGHIJ
		135	2.49	±	1.31	PQRSTUVWXA1	4.53	±	2.23	FG
		180	1.04	±	0.64	XYZA1	9.39	±	2.58	C
		225	0.85	±	0.65	YZA1	11.42	±	2.53	AB
	Mean		2.75	±	1.97	gh	5.37	±	4.25	b
	Grand mean		3.13	±	2.08	***	5.74	±	4.49	*
Shelled		0	6.25	±	3.99	ABCDEF	1.25	±	1.16	IJKLMNOPQ
	Variable	90	5.15	±	2.13	ABCDEFGM	0.74	±	0.63	Q
		180	3.85	±	1.51	EFGHIJKLMNOPQR	1.32	±	0.85	OPQ
		270	3.57	±	1.75	FGHIJKLMNOPQRSW	2.96	±	2.62	GHIJKLMNO
		360	3.61	±	2.07	EFGHIJKLMNOPQRSW	2.22	±	1.27	KLMNOPQ
		450	2.54	±	1.91	OPQRSTUVWX	4.21	±	2.86	FGH
	Mean		4.16	±	2.20	bcd	2.12	±	2.21	e
	Grand mean		4.16	±	2.20	*	2.12	±	2.21	***

ML: pecans stored in metallic laminates and flushed with nitrogen, **LDPE -58**: pecans stored at 58% RH and low-density polypropylene packaging with normal air, **PEV-58:** pecans stored at 58% RH and Polyethylene-nylon packaging under vacuum, **No Pack-30:** pecans stored at 30% RH without any packaging material, **Shell**: shelled pecan nutmeats stored outside without temperature and humidity control, **ND** response not determined because of damaged samples

Table 5.7: Summary of the clusters of volatile compounds identified by the cluster variable analysis (CVA). The clusters are based on the association of the different volatile compounds with each other.

Cluster	Members	R^2 with own cluster	R^2 with next closest cluster	1-R^2 ratio
1	Octanal	0.974	0.778	0.117
	Nonanal	0.954	0.708	0.156
	1-Octanol	0.968	0.822	0.182
	Heptanal	0.976	0.867	0.183
	γ-Octalactone	0.971	0.871	0.225
	1-Octen-3-ol	0.942	0.75	0.231
	γ-Ethylbutyrolactone	0.909	0.644	0.256
	1-Pentanol	0.898	0.638	0.281
	Hexanal	0.888	0.619	0.294
	2-Heptenal	0.936	0.806	0.328
	2-Nonenal	0.876	0.644	0.347
	1-Nonanol	0.94	0.903	0.618
	Nonanoic acid	0.868	0.79	0.626
	1-Hexanol	0.649	0.48	0.674
	γ-Heptalactone	0.933	0.909	0.737
2	Decanal	0.698	0.157	0.358
	Nonanoic acid, methyl ester	0.707	0.226	0.378
	3,5-Octadien-2-ol	0.593	0.084	0.444
	Octanoic acid	0.75	0.48	0.48
	2-Decenal	0.806	0.659	0.569
	D-Limonene	0.55	0.247	0.598
	2-Octenal	0.764	0.631	0.638
	1-Heptanol	0.509	0.232	0.639

3	Benzaldehyde	0.67	0.053	0.348
	Benzeneacetaldehyde	0.67	0.083	0.36
4	Furan, 2-pentyl-	0.526	0.227	0.613
	2-Undecenal	0.526	0.282	0.66
5	Heptanoic acid, methyl ester	0.32	0.014	0.004
6	2-Nonanone	0.967	0.738	0.128
	2-Decanone	0.964	0.739	0.138
	3-Nonen-2-one	0.884	0.588	0.281
	2-Octanone	0.961	0.868	0.293
	2-Heptanone	0.94	0.91	0.663

Table 5.8: Summary of estimates of the predictor variables obtained from the neural network. The estimates can be used to calculate the freshness and or rancidity/oxidized score of ocean nutmeats as perceived by human modalities.

Aroma - freshness				
Volatiles	**Node 1 (N_1)**	**Node 2 (N_2)**	**Node 3 (N_3)**	**Node 4 (N_4)**
Intercept	6.59	-16.27	-20.91	13.95
D-Limonene (ppm)	-0.25283	0.500538	0.564373	-0.69396
3,5-Octadien-2-ol (ppm)	0.0162	0.028059	0.002805	-0.00123
2-Octenal (ppm)	-0.00266	-0.00026	0.001367	0.005283
Octanoic acid (ppm)	-0.00051	-0.00023	0.000115	0.001137
Decanal (ppm)	0.001648	-0.00723	0.00122	0.009298
2-Decenal (ppm)	0.001317	0.001379	0.001819	0.005087
Nonanoic acid, methyl ester (ppm)	-0.00209	-0.00619	0.014899	0.0071
Aroma - rancidity/Oxidization				
Intercept	-2.8375	-1.134	-2.423	
1-Pentanol (ppm)	0.000138	-0.00013	-0.0016	
Hexanal (ppm)	0.000297	0.000165	-0.00028	
1-Hexanol (ppm)	0.000802	0.000209	-0.00007	
Heptanal (ppm)	-0.0005	0.002933	0.000951	
1-Octen-3-ol (ppm)	0.003458	-0.00402	0.011244	
Octanal (ppm)	0.000121	0.001828	-0.00091	
γ-Ethylbutyrolactone (ppm)	0.003129	0.003702	0.002837	
2-Nonenal (ppm)	0.007173	-0.0005	-0.00908	
2-Heptenal (ppm)	0.003106	-0.00022	0.003298	
Nonanoic acid (ppm)	-5.16e-5	5.606E-06	0.000634	
1-Octanol (ppm)	0.000234	0.000376	-0.00039	
Nonanal (ppm)	-0.00018	-2.9e-5	-6.36e-6	
γ-Heptalactone (ppm)	0.006133	-0.00373	0.002032	
1-Nonanol (ppm)	0.002335	-0.00167	-0.00214	
γ-Octalactone (ppm)	0.000962	0.000107	0.000469	

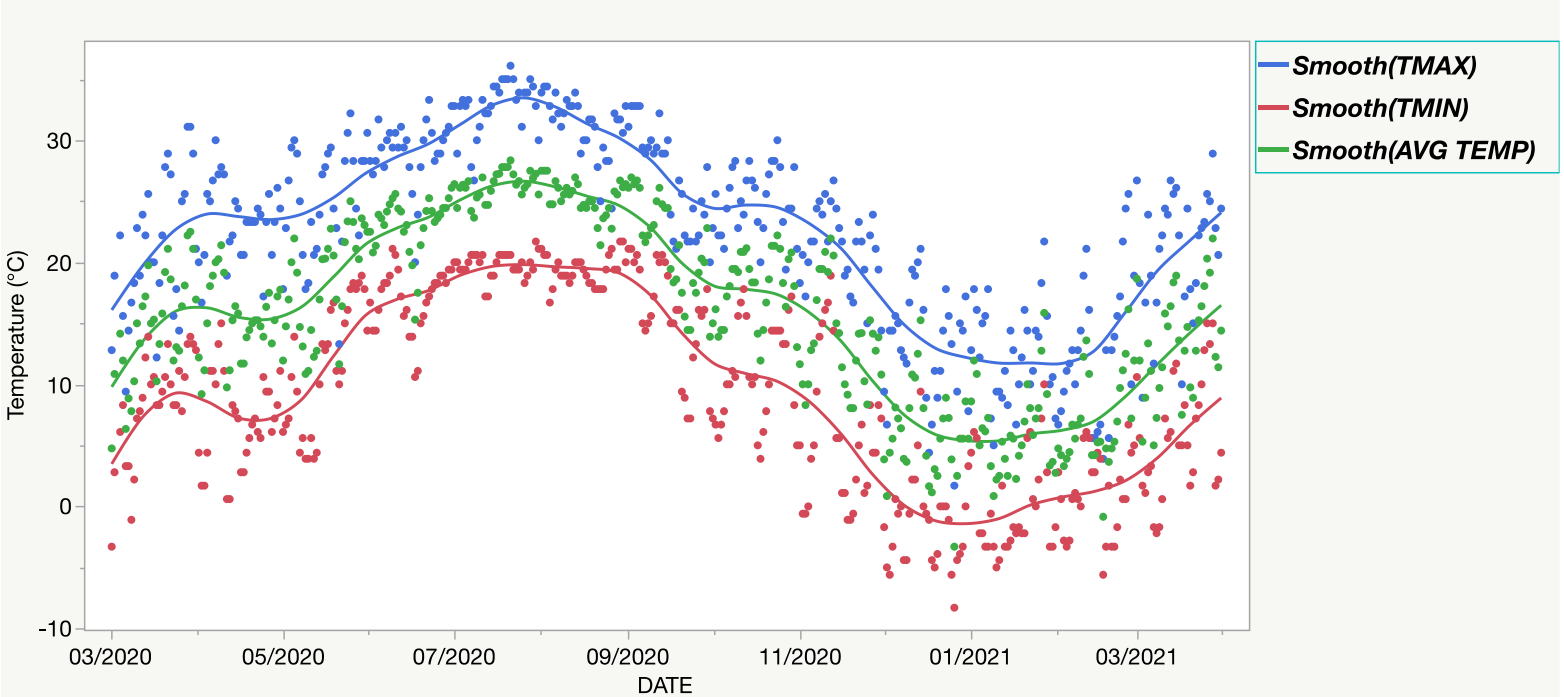

Figure 5.1: Historic weather data from the National Weather Service, National Oceanic and Atmospheric Agency from March 2020 to April 2021 (location – Watkinsville, GA, US) during the period when shelled pecan nutmeats were stored outside. The figure presents maximum, average and minimum temperature recorded for each day. During storage, the highest and lowest temperature recorded were 36.1°C and -8.3°C. The shelled pecan nutmeats experienced temperature >30°C for 75 days, >20°C but <30°C for 180 days, and <20°C for 140 days.

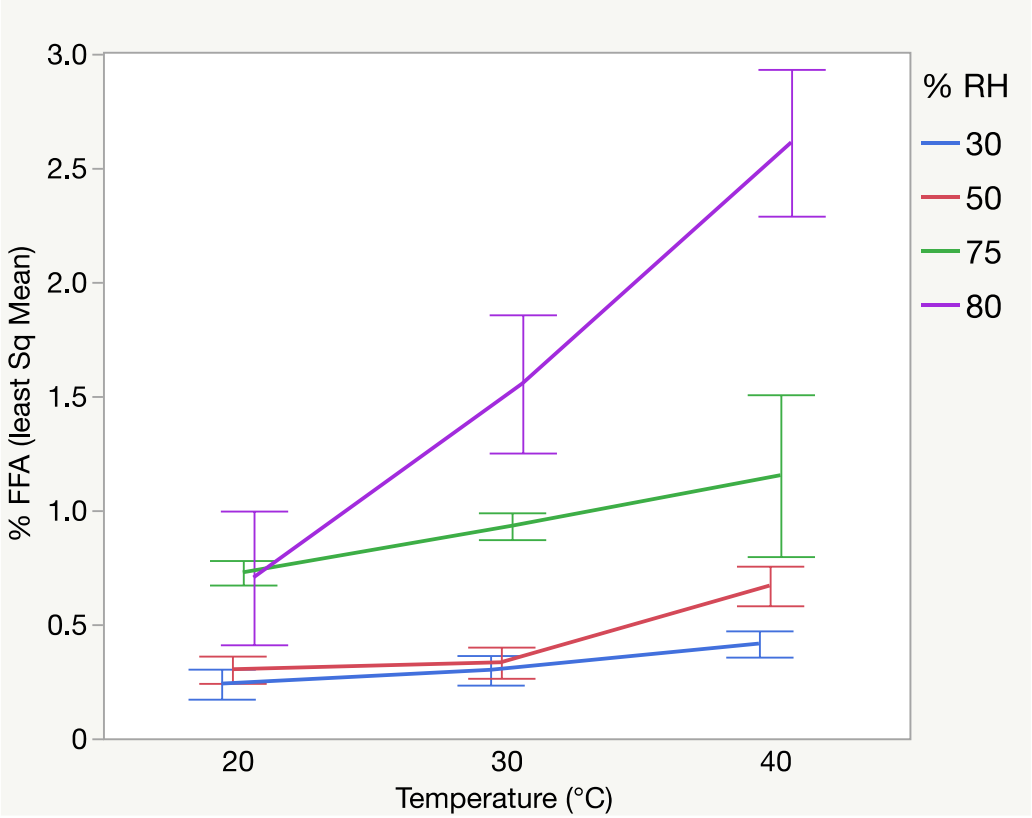

Figure 5.2: A two-way interaction plot of temperature and relative humidity effects on the % free fatty acid (FFA) in unpackaged pecan nutmeats . The % FFA content increased at RH>50%. The coefficient of determination (R^2) for the model was 0.51.

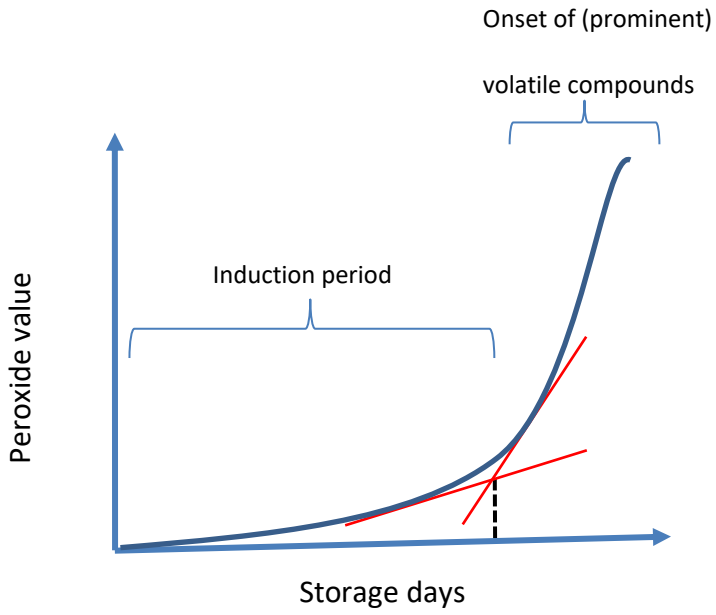

Figure 5.3: Illustration depicting typical change in peroxide value (PV) of oil as storage time progresses. The PV represents the concentration of peroxyl radicals. During early stages of the propagation reaction, the formation of peroxyl radical is minimal. The concertation of the peroxyl radicals subsequently increases dramatically, and the time it takes to reach the point of sudden increase is the induction period and marks the onset of formation of undesirable volatile compounds.

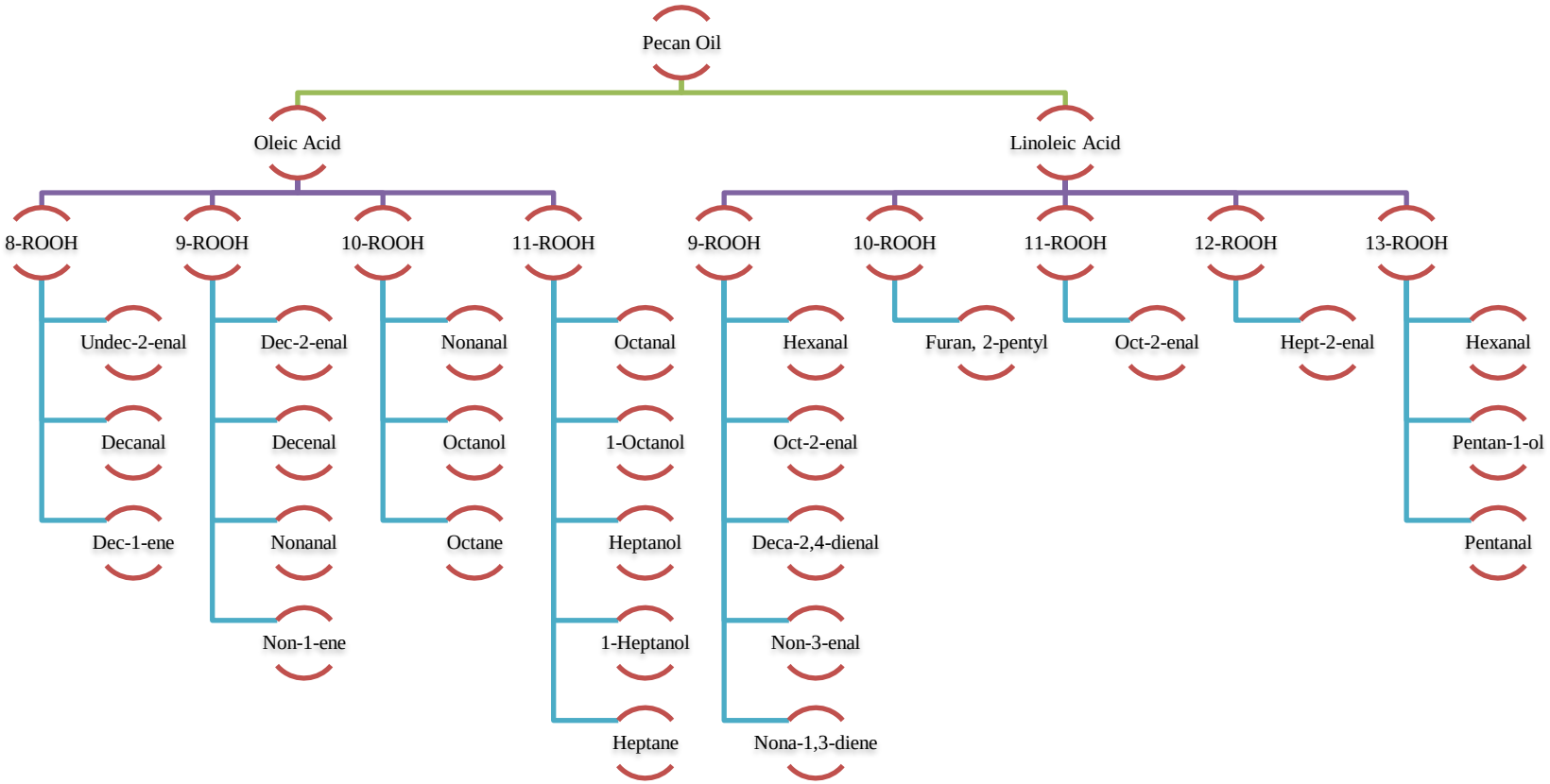
Pecan Oil
Oleic Acid
Linoleic Acid
8-ROOH
9-ROOH
10-ROOH
11-ROOH
9-ROOH
10-ROOH
11-ROOH
12-ROOH
13-ROOH
Undec-2-enal
Decanal
Dec-1-ene
Dec-2-enal
Decenal
Nonanal
Non-1-ene
Nonanal
Octanol
Octane
Octanal
1-Octanol
Heptanol
1-Heptanol
Heptane
Hexanal
Oct-2-enal
Deca-2,4-dienal
Non-3-enal
Nona-1,3-diene
Furan, 2-pentyl
Oct-2-enal
Hept-2-enal
Hexanal
Pentan-1-ol
Pentanal

Figure 5.4: A flow diagram of possible biochemical pathways for some of the most commonly reported volatile compounds produced during oxidation of pecan oil. Oleic and linoleic acid are prominent fatty acids in pecan nutmeats and are produced during auto-oxidation. Both fatty acids undergo chemical reaction with available free radicals and oxygen to form lipid hydroperoxides. The prefix number denotes the position of the -OOH group on the hydrocarbon chain (Badings, 1959; Frankel et al., 1979; Jeon, 1996; Kochhar, 1996; Min and Boff, 2002).

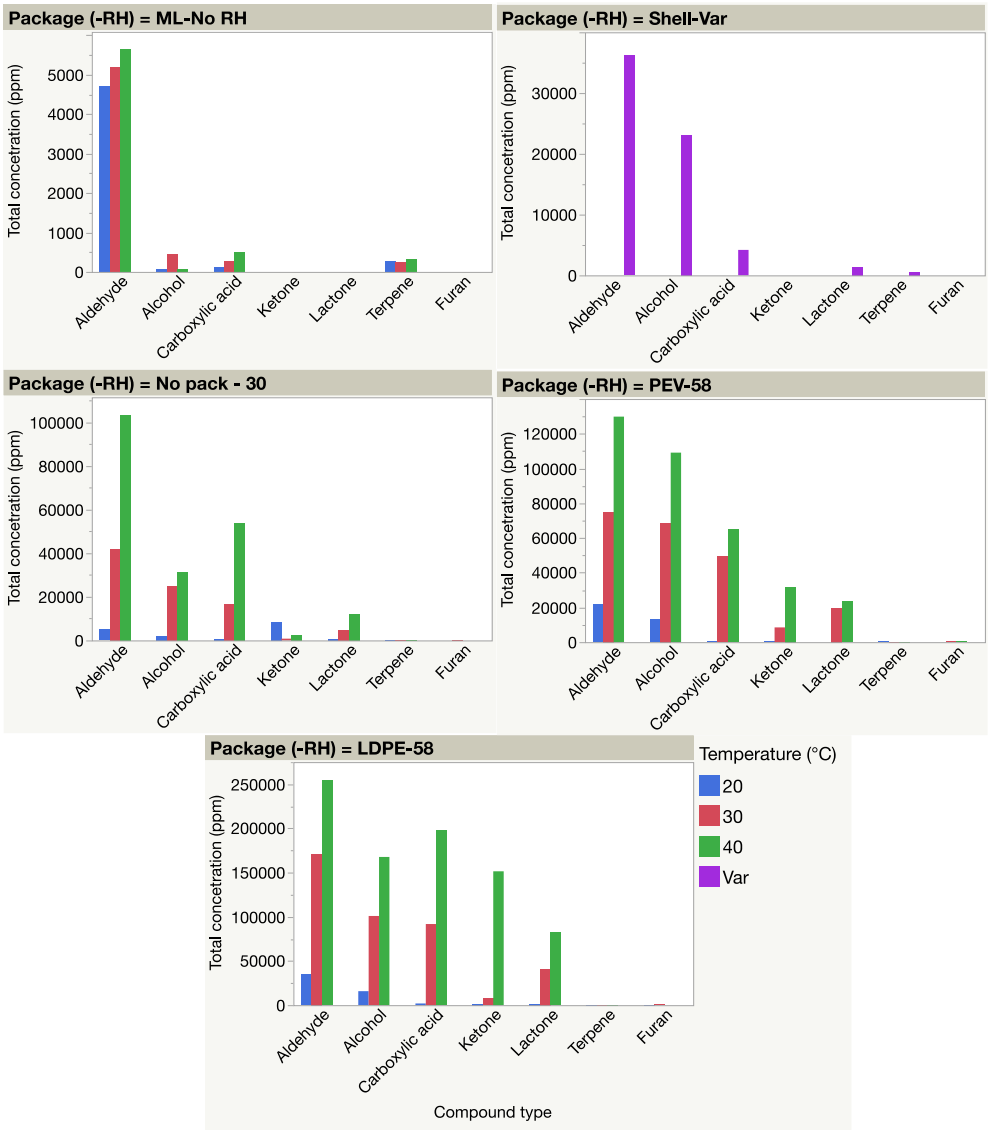
Package (-RH) = ML-No RH
Package (-RH) = Shell-Var
Package (-RH) = No pack - 30
Package (-RH) = PEV-58
Package (-RH) = LDPE-58
Total concetration (ppm)
Aldehyde
Alcohol
Carboxylic acid
Ketone
Lactone
Terpene
Furan
Compound type
Temperature (°C)
20
30
40
Var

Figure 5.5: The cumulative concentration of different chemical compounds in packaged and unpackaged pecan nutmeats stored at different temperatures (Var = pecan nut meats stored outside). ML: pecans stored in metallic laminates and flushed with nitrogen; No Pack-30: pecans stored at 30% RH without any packaging material; LDPE -58: pecans stored at 58% RH and low-density polypropylene packaging with normal air; Shell: shelled pecan nutmeats stored outside without temperature and humidity control; PEV-58: pecans stored at 58% RH and Polyethylene-nylon packaging under vacuum.

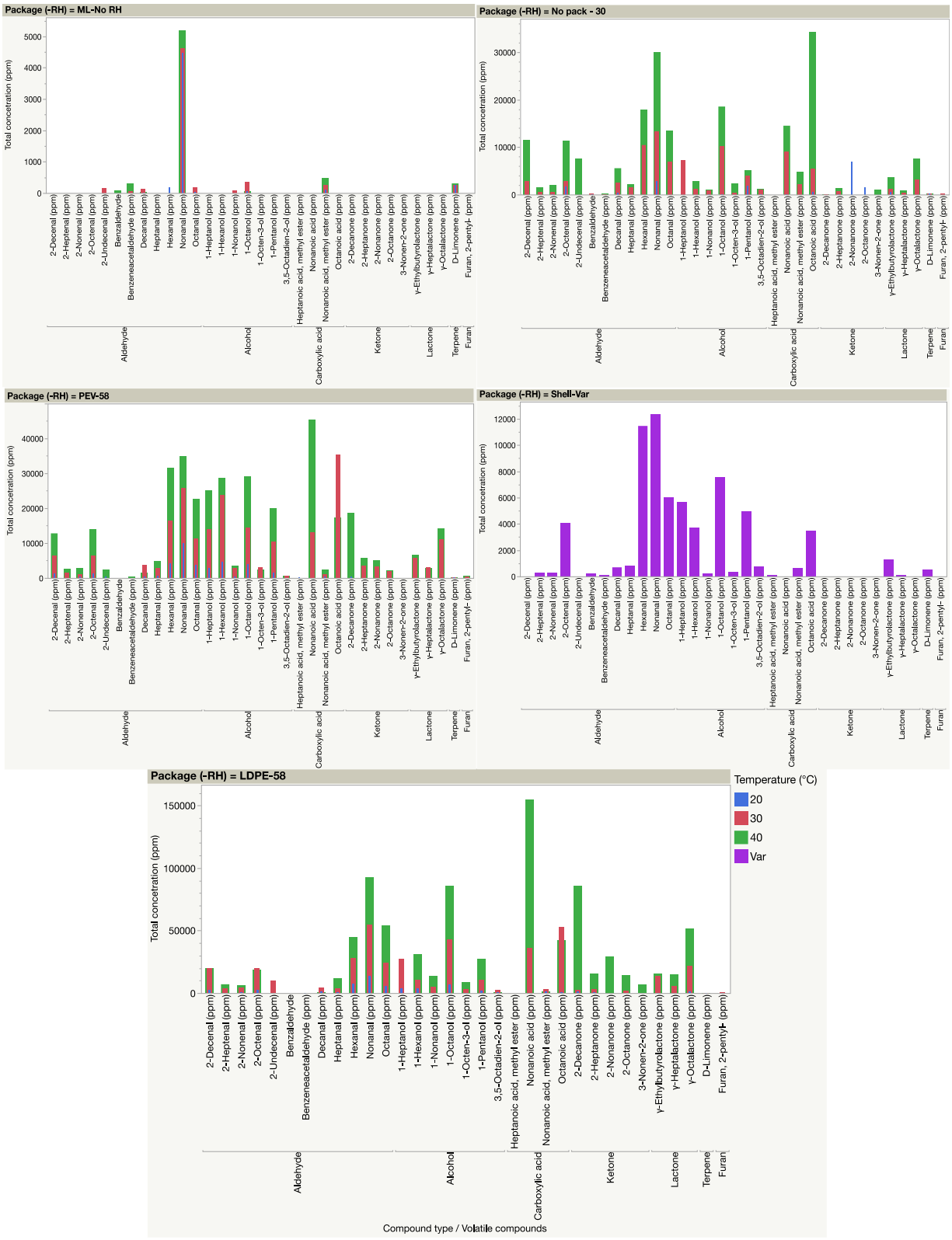
Package (-RH) = ML-No RH
Package (-RH) = No pack - 30
Package (-RH) = PEV-58
Package (-RH) = Shell-Var
Package (-RH) = LDPE-58
Total concetration (ppm)
Aldehyde
Alcohol
Carboxylic acid
Ketone
Lactone
Terpene
Furan
Temperature (°C)
20
30
40
Var
Compound type / Volatile compounds

Figure 5.6: Changes in total volatile concertation of pecan nutmeats due to temperature and package type treatments. **(a)** Metal laminate package (ML) – 0% relative humidity (RH, pecans stored in ML and flushed with nitrogen), **(b)** No Pack-30 (pecans stored loose at 30% RH without any packaging material), **(c)** Polyethylene-nylon with vacuum packing (PEV-58, pecans stored at 58% RH in PE-nylon packagesunder vacuum) **(d)** Shelled pecans (pecans stored outside without temperature and humidity control, and **(e)** Low-density polypropylene packaging (LDPE -58, pecan nutmeats stored at 58% RH and in LDPE packages with normal air).

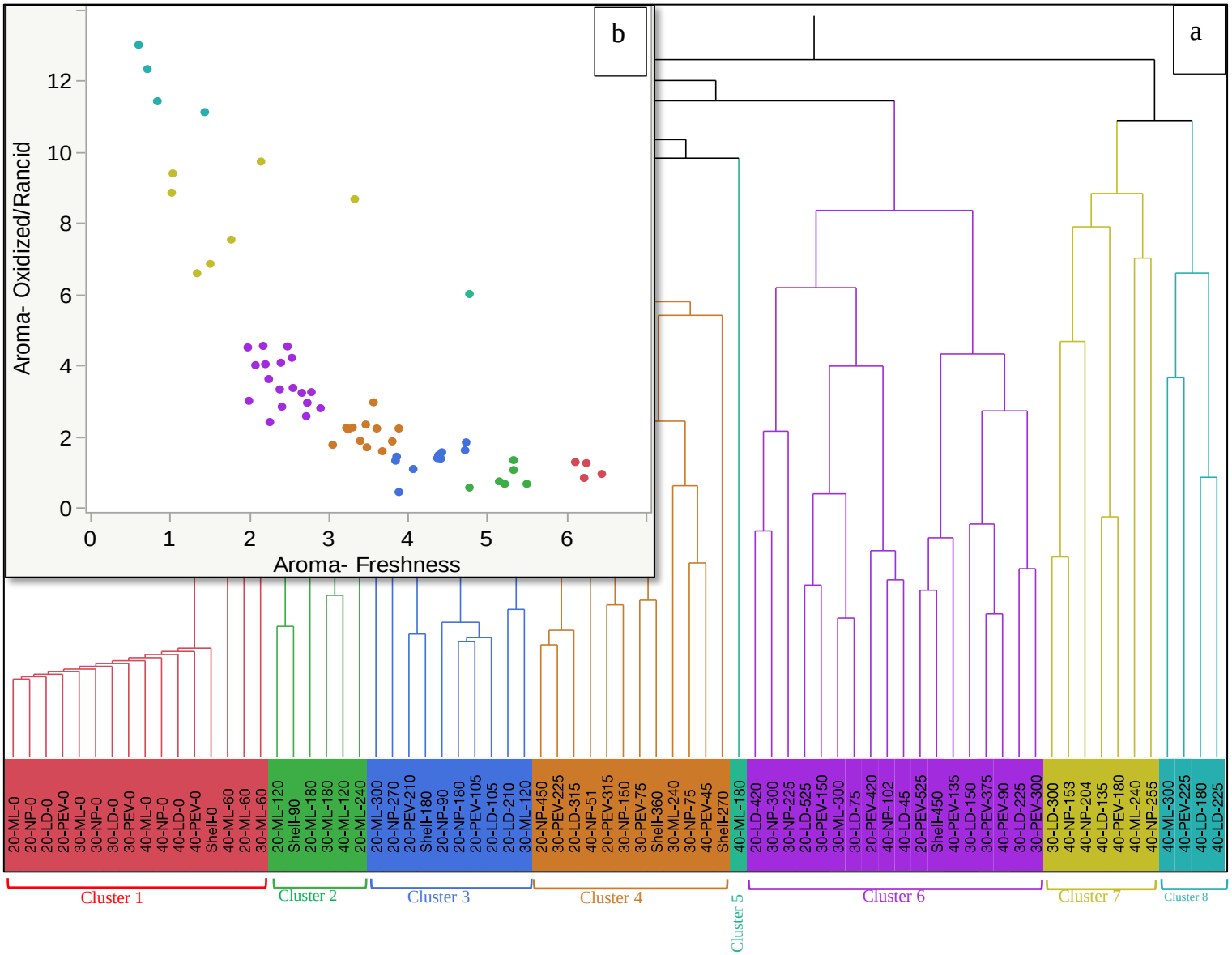
a
b
Aroma- Oxidized/Rancid
Aroma- Freshness
0
2
4
6
8
10
12
0
1
2
3
4
5
6
20-ML-0
20-NP-0
20-LD-0
20-PEV-0
30-ML-0
30-NP-0
30-LD-0
30-PEV-0
40-ML-0
40-NP-0
40-LD-0
40-PEV-0
Shell-0
40-ML-60
20-ML-60
30-ML-60
20-ML-120
Shell-90
20-ML-180
30-ML-180
40-ML-120
20-ML-240
20-ML-300
20-NP-270
20-PEV-210
Shell-180
20-NP-90
20-NP-180
20-PEV-105
20-LD-105
20-LD-210
30-ML-120
20-NP-450
30-PEV-225
20-LD-315
40-NP-51
20-PEV-315
30-NP-150
30-PEV-75
Shell-360
30-ML-240
30-NP-75
40-PEV-45
Shell-270
40-ML-180
20-LD-420
30-NP-300
30-NP-225
20-LD-525
30-PEV-150
30-ML-300
30-LD-75
20-PEV-420
40-NP-102
40-LD-45
20-PEV-525
Shell-450
40-PEV-135
30-LD-150
30-PEV-375
40-PEV-90
30-LD-225
30-PEV-300
30-LD-300
40-NP-153
40-NP-204
40-LD-135
40-PEV-180
40-ML-240
40-NP-255
40-ML-300
40-PEV-225
40-LD-180
40-LD-225
Cluster 1
Cluster 2
Cluster 3
Cluster 4
Cluster 5
Cluster 6
Cluster 7
Cluster 8

Figure 5.7: Hierarchical cluster analysis (HCA) of the different pecan nutmeat treatments and associated sensory attributes (the freshness and rancid/oxidized aroma score). **(a)** Dendrogram of the various clusters of the pecan nutmeat treatments, and their position on **(b)** a scatter plot of freshness and rancid/oxidized aroma scores. The treatments are coded as follow: 'temperature (°C)' - 'Package' - 'storage day'. For example, 20-ML-180 denotes pecan nutmeats stored at 20°C in metallic laminate packaging (N_2 flushed) for 180 days. The clusters are color coded to facilitate tracing on the scatter plot.

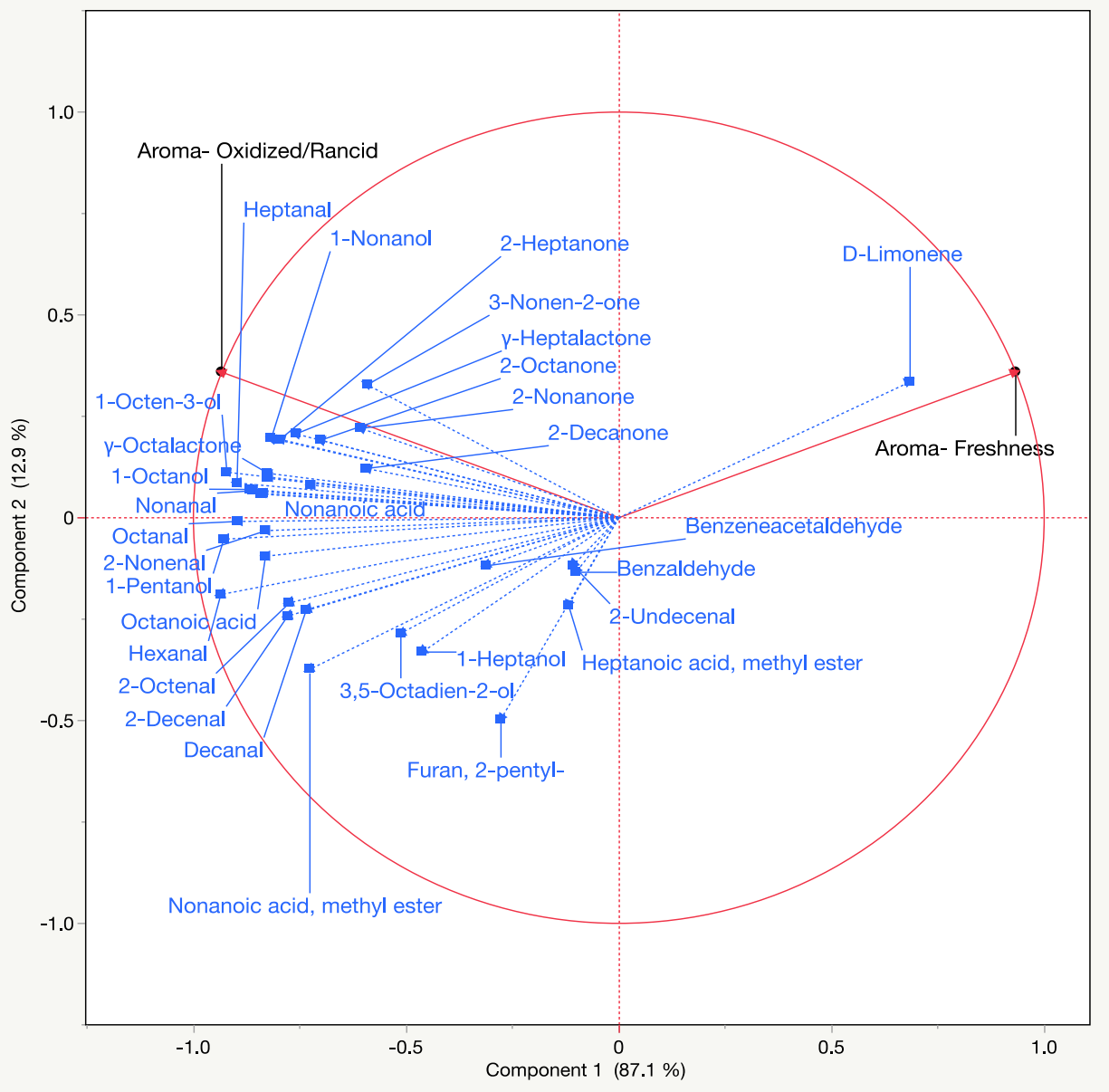

Figure 5.8: Principal components loading plot of freshness and rancidity/oxidization aroma based on panelist responses and the volatiles compounds (33) as the supplementary variables.

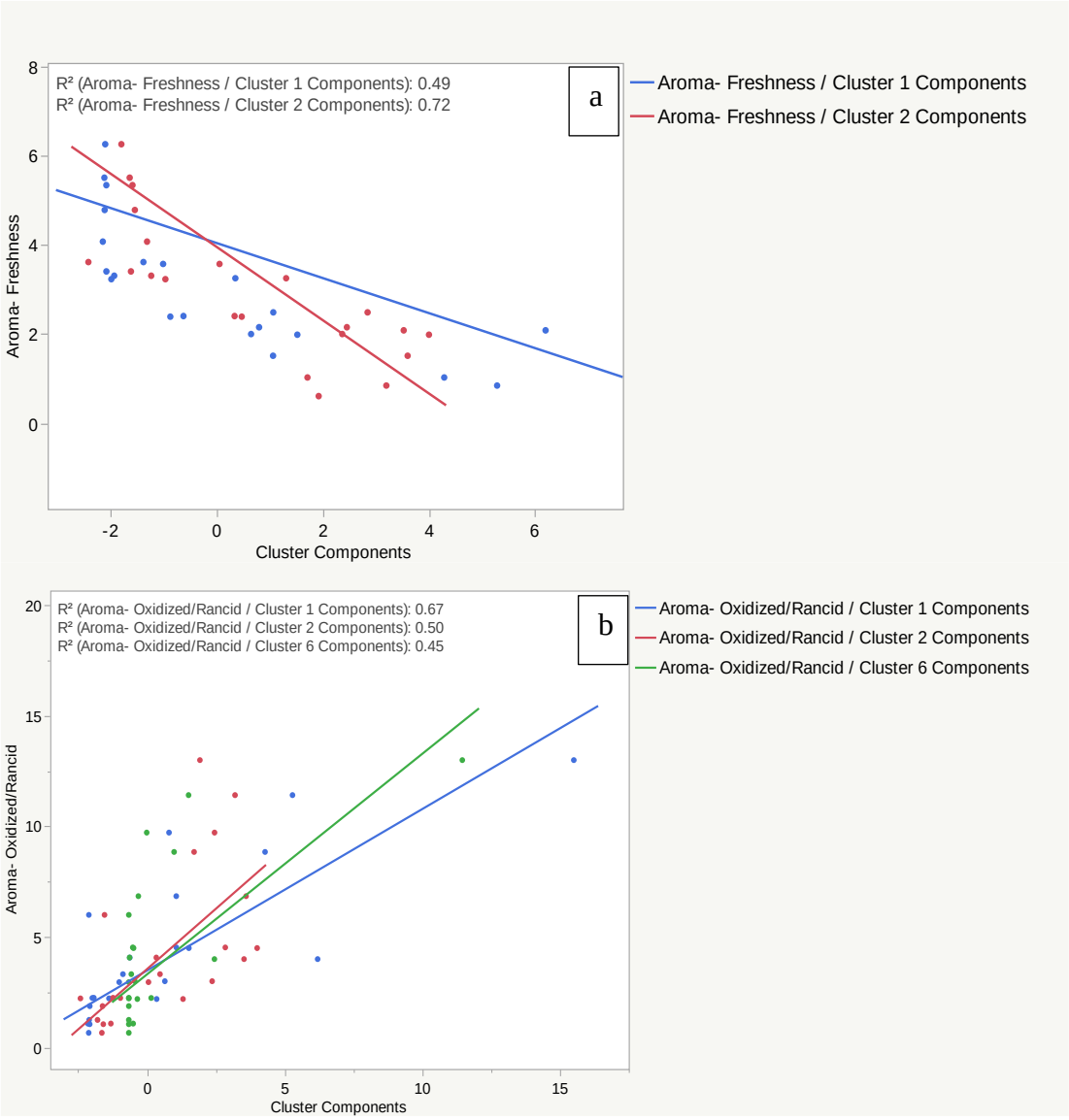

Figure 5.9: The linear association of clusters from the hierarchical cluster analysis with **(a)** freshness aroma score and **(b)** rancidity/oxidization aroma score of pecan nutmeats. Cluster 2 (R^2 = 0.72) and cluster 1 (R^2 = 0.67) had the highest coefficient of variation for freshness and rancidity/oxidization aroma scores, respectively. The volatile compounds in each cluster are presented in tabulated form in Supplementary Table T4.

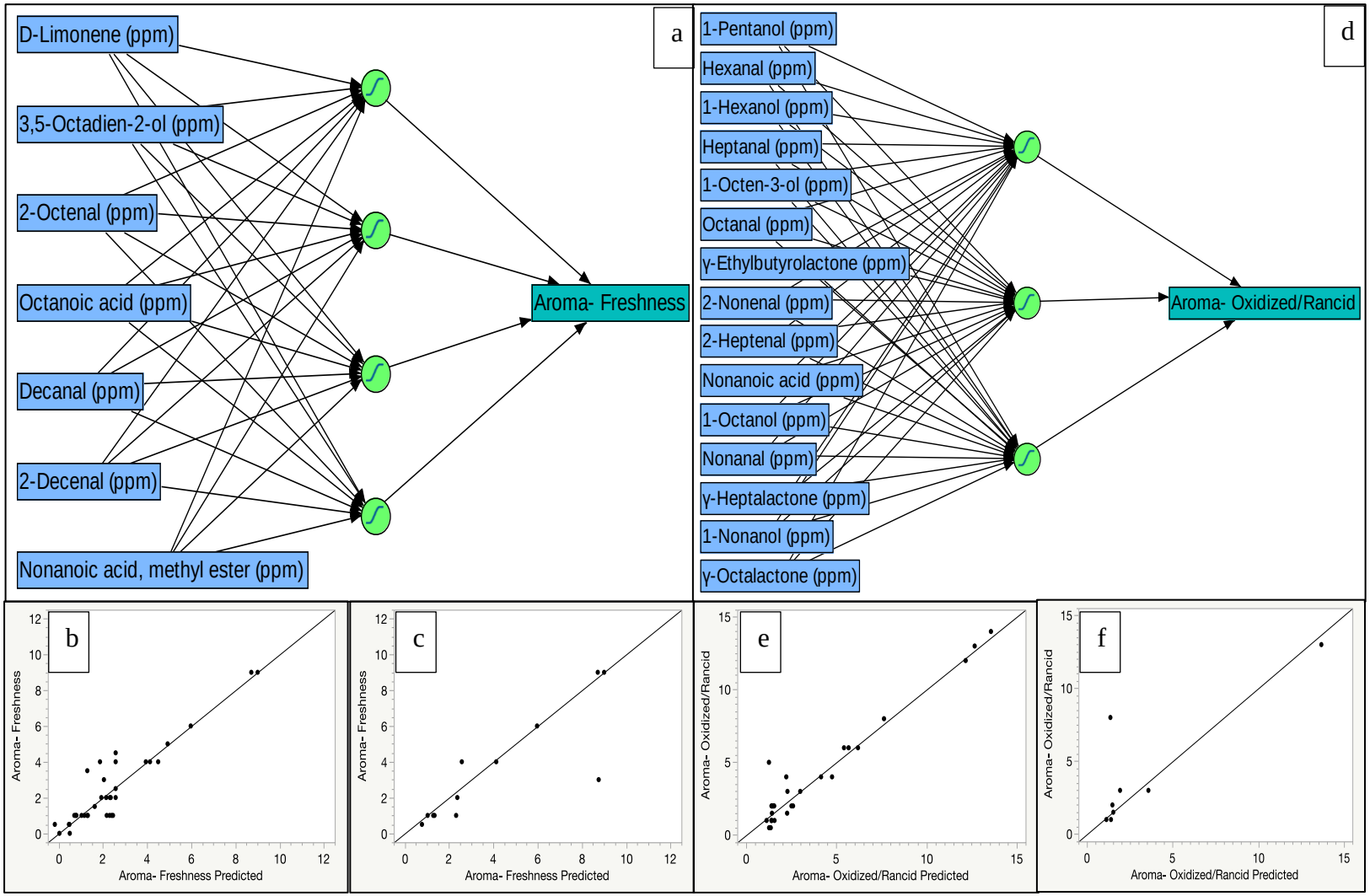
a
D-Limonene (ppm)
3,5-Octadien-2-ol (ppm)
2-Octenal (ppm)
Octanoic acid (ppm)
Decanal (ppm)
2-Decenal (ppm)
Nonanoic acid, methyl ester (ppm)
Aroma- Freshness
d
1-Pentanol (ppm)
Hexanal (ppm)
1-Hexanol (ppm)
Heptanal (ppm)
1-Octen-3-ol (ppm)
Octanal (ppm)
γ-Ethylbutyrolactone (ppm)
2-Nonenal (ppm)
2-Heptenal (ppm)
Nonanoic acid (ppm)
1-Octanol (ppm)
Nonanal (ppm)
γ-Heptalactone (ppm)
1-Nonanol (ppm)
γ-Octalactone (ppm)
Aroma- Oxidized/Rancid
b
Aroma- Freshness
Aroma- Freshness Predicted
c
Aroma- Freshness
Aroma- Freshness Predicted
e
Aroma- Oxidized/Rancid
Aroma- Oxidized/Rancid Predicted
f
Aroma- Oxidized/Rancid
Aroma- Oxidized/Rancid Predicted

Figure 5.10: Neural network diagram for **(a)** freshness and **(d)** rancidity/oxidization aroma of pecan nutmeats. The predictors (volatile compounds) for each sensory attribute (response) were determined based on a principal component analysis and hierarchical cluster analysis. The **(b)** training and **(c)** validation of the model for predicting freshness had a coefficient of variation (R^2) of 0.94 and 0.79, respectively. The **(e)** training and **(f)** validation of the model for predicting rancidity/oxidized aromas had a coefficient of variation (R^2) of 0.84 and 0.98, respectively.

CHAPTER 6

CONCLUSION

Pecan is one of the major tree nuts grown in the US. As covered in the detailed literature review in Chapter 2, researchers have introduced predictive models for other tree nuts like almonds, pistachios, walnuts etc. capable of estimating quality changes due to external and internal environment. The researchers have concluded that factors like temperature, packaging material, moisture and modified atmosphere play a crucial role in deciding the quality and shelf-life products. However, the studies investigating the effects of these factors on pecans are scarce. An extensive study to add to scientific understanding of changes in pecan quality during storage and distribution is desirable. Additionally, the role of mathematical and probabilistic models in predicting the quality and shelf life of pecans emerges to be of direct interest to the pecan industry.

In Chapter 3, the effects of temperature (20 to 40°C), storage days (up to 450 days) and RH (30 to 80%) were studied. Pecans stored <75% RH resulted in more rapid development of a reddish-brown color whereas pecans stored at >75% RH had brown color development. The intensity of red color was appear to be temperature dependent; it increased with increase in temperature. The pecan nutmeats experienced least color degradation during low temperature (20°C) and dry environment (30% and 50% RH) conditions. The investigation into the kinetic aspect revealed that change in hue followed a zero-order reaction whereas lightness and chroma followed first-order decay.

Furthermore, E_a increased with an increase in RH indicating that the rate of color degradation (*k*) was elevated at high RH.

Chapter 4 discussed development of instrumental texture measurement indicator i.e., rift ratio (F/H) as well as changes in pecan texture due to varying RH and packaging condition (30 to 90%). The idea of using intact pecans rather cores were used to collect better textural information from pecan kernels. This methodology, along with measuring rift ratio, helped reduce some of the variability of the data and give meaningful evaluation of loss of fracturability in pecans. The study also emphasized the effects of moisture in the environment on fracturability, cohesiveness, chewiness and springiness of pecans. It was found that the any kind of moisture barrier around pecans was able to deter texture change by at least 8 -fold. Pecans kept in LDPE experienced the greatest change in texture whereas pecans in metallic laminates did not change significantly during the storage.

The changes in chemical and sensory attributes of pecan nutmeats due to change temperature, package type, RH and a modified atmosphere was discussed in Chapter 5. The study explored the application quick lipid oxidation determination method (such as PV) to extract meaningful information pertaining to storage stability of pecans. The investigation also explored the generation of different volatile compounds (aldehydes, ketones, alcohols, acids, lactones, terpene, and furan) responsible for imparting undesirable rancid aroma of pecan nutmeats as well as sensory evaluations of stored pecans involving human subjects. In addition to this, the association of chemical and sensory evaluations were also studied which were further used to build a machine leaning predictive model i.e., Artificial Neural Network.

The study explored different mathematical and predictive models able to predict changes in color, texture, extent of lipid oxidation and sensory attributes of pecans stored varying environmental conditions. It was noted during investigation that pecan color change was temperature dependent reaction. Mathematical models such as Arrhenius and Q_{10} model were used to estimate kinetic parameters to estimate shelf life of pecans. It was also observed that change moisture in surrounding environment of pecans and type of packaging material changed the textural attributes of pecans, specifically fracturability. A sigmoid model (3-parameter logistic model) was employed to predict the change in textural attributes of pecans during storage. The excess moisture around pecans not only affect pecan texture but also chemical attributes and sensory properties of pecans. High RH, temperature conditions, and presence of oxygen lead to quick deterioration of pecans. A machine learning algorithm based predictive model, viz. neural network, was employed to estimate sensory attributes of pecans using concentration of volatile compounds generated under different storage treatments. This aspect of predictive model might work as a quick tool to get sensory scores from human perspective and reducing dependency on human panelists. These models could be further incorporated with computer programming languages such as JavaScript, python, etc. to build user interface capable of tapping into predictions without going in to complicated predictive equations. One of such as product built can be found in the link provided (https://tinyurl.com/uspecans). These easy-to-use web applications can be deployed online to use as tool to quickly look in to predicted changes in pecans stored under varying storage conditions including conditioning, packaging material, modified atmosphere, temperature and RH. Furthermore, machine learning algorithms makes it easy to build on these current databases by incorporating data

from other research pertaining to pecans to added and aid in improving predictions. This extensive study serves to help Georgia pecan growers (and eventually US) to increase the market share of their product globally. As United States pursue selling more pecans internationally, this research will aid in planning, improving, and maintaining the pecan quality during long time transportation and distribution, which is critical for US pecan to remain competitive in the international marketplace. This long-term objective could be further bolstered by following future work.

1. The effect of RH on the pecans could be further explored to learn the changes in chemical makeup as RH increases or decreases.
2. A multiple year study (3-10 years) could be employed to learn the effect of cultivars on pecan quality during storage.
3. The USDA has set grades for pecans based on their size and weight. Similar research work is required to establish critical limits for physical and chemical characteristics of pecans for commercial use as well.
4. A cumulative database could be built where researchers working on effects of multiple variables (temperature, package, rainfall, and daylight exposure, etc.) on pecans around the world can pool their experimental data. This database would aid in making a robust machine learning model capable of predicting both pre and post-harvest characteristics of pecans.
5. This study only explored some of mathematical and probabilistic models. More models could be explored to have a better prediction of pecan quality changes during storage.

6. Integration food science and computer science could be examined to make web applications suitable for non-scientific audiences and with interface that is readily available for use.