Almond Flavor, Sensory and Shelf-Life Preservation

December 8, 2016

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Almond Flavor, Sensory and Shelf-Life Preservation

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- Steve Lindsay, AQFS Committee Member (Moderator)
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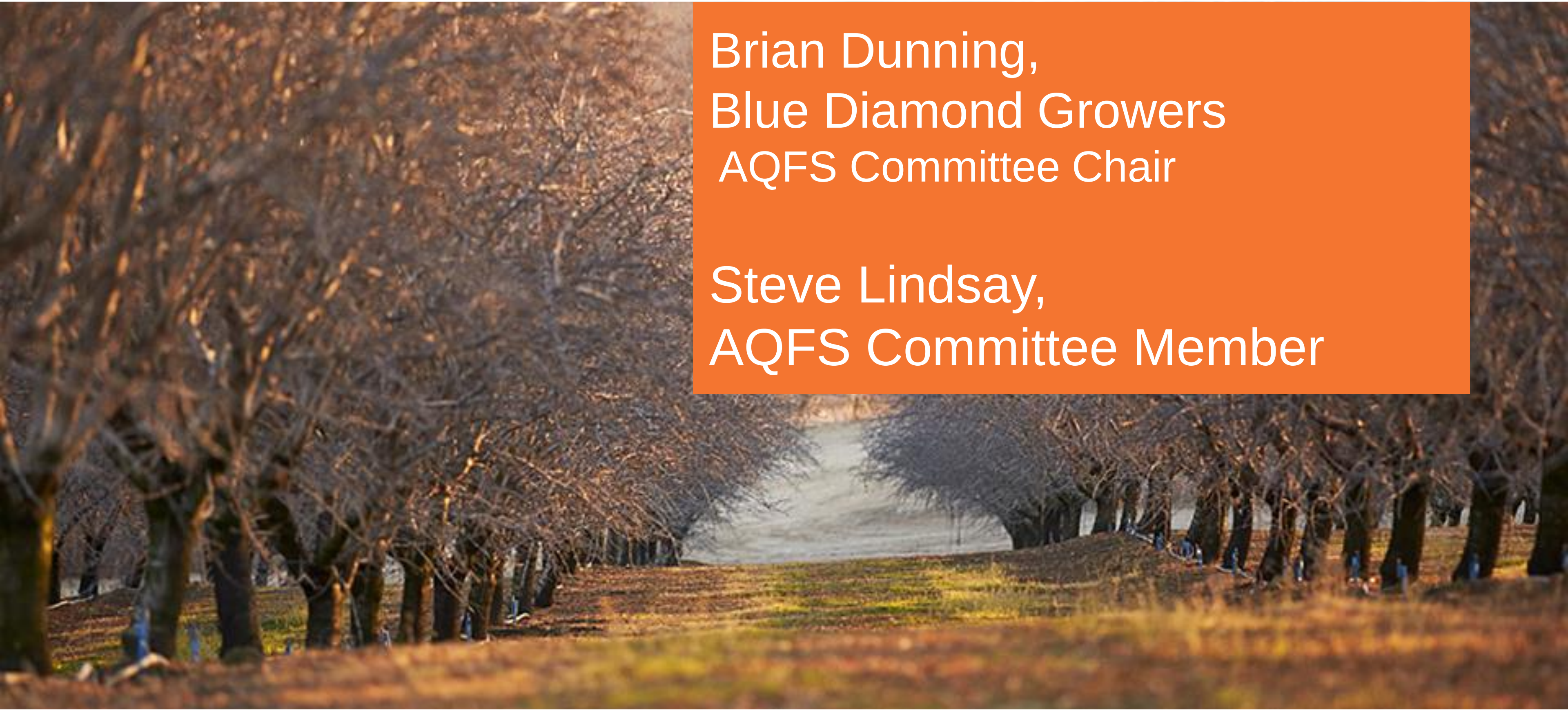

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Chemical Characterization of Oxidative Changes in Roast Almonds

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Dec 8, 2016

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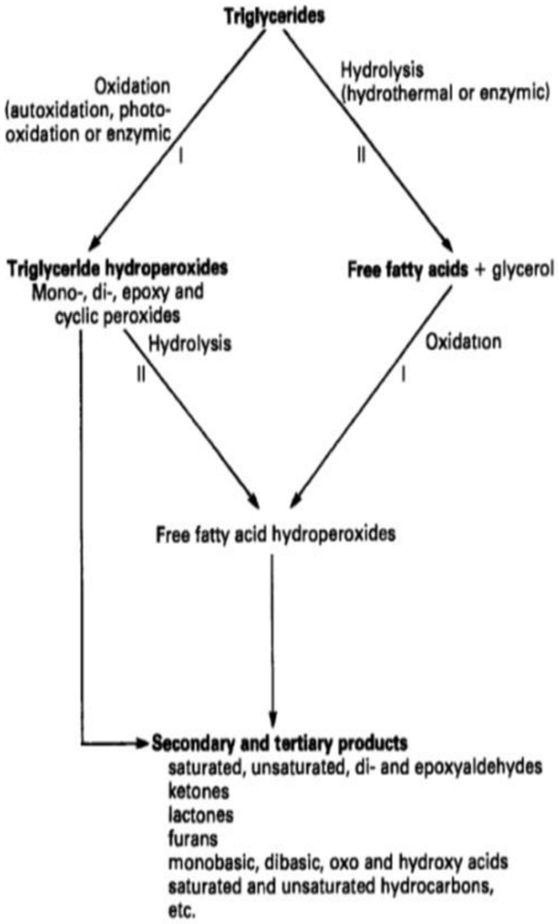
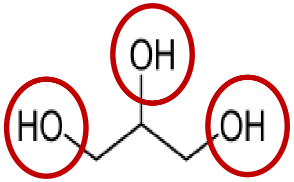
Almonds & Rancidity

- Rancidity is the unpalatable odor and flavor of deteriorating edible fats and oils in foods
- Occurs via two chemical reaction pathways in almonds:
- **Oxidation**
  - Oxidation of triglycerides
- **Hydrolysis**
  - Addition of *water* across triglycerides and release of fatty acids (FFAs)
  - oxidation



Al Closer Look at the Fats in Almonds

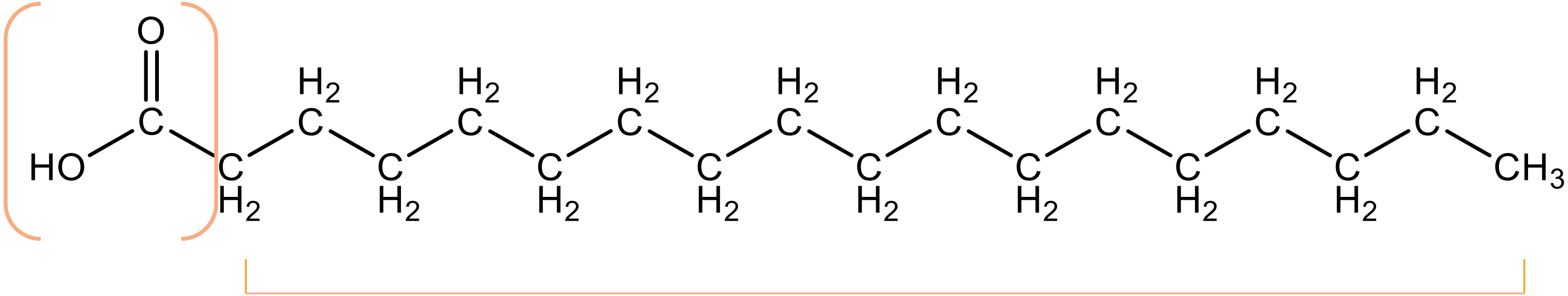
- By weight, almonds are roughly 50% fat
- These fats are composed of triglycerides
- A triglyceride is molecule that is composed of 3 fatty acids attached to glycerol



- Glycerol is a simple sugar alcohol
- Three *hydroxyl* groups that can react with fatty acids
- Backbone of all triglycerides

What is a Fatty Acid?

- A fatty acid is a long chain of carbon and hydrogen with an carboxylic acid group at the end of the chain

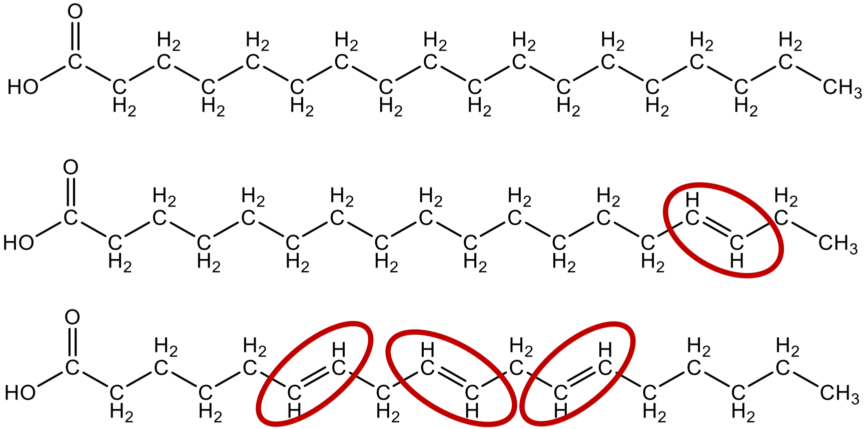


Acid

Long hydrocarbon chain – hydrophobic and fat like

A Closer Look at Fatty Acids

- Fatty acids can be saturated (no double bonds) or unsaturated (double bonds)
- Double bonds give fluidity (kinks) to fats and are the site of oxidation



Saturated fat

Monounsaturated fat (MUFA)

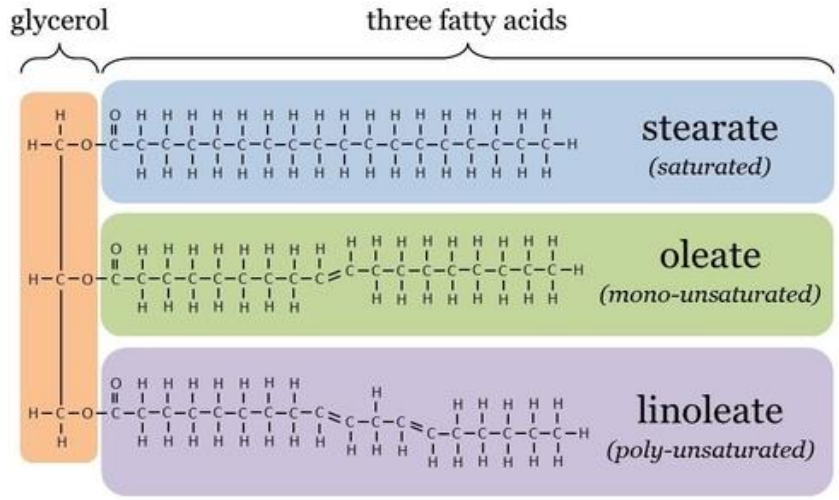
ω

Polyunsaturated fat (PUFA)

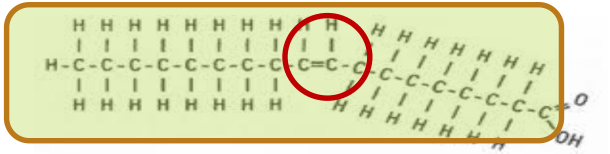
ω

The Fatty Acids in Almonds

- Oleic 60-75%; linoleic 19-30%; steric 1-3%; palmitic 0.5-8%

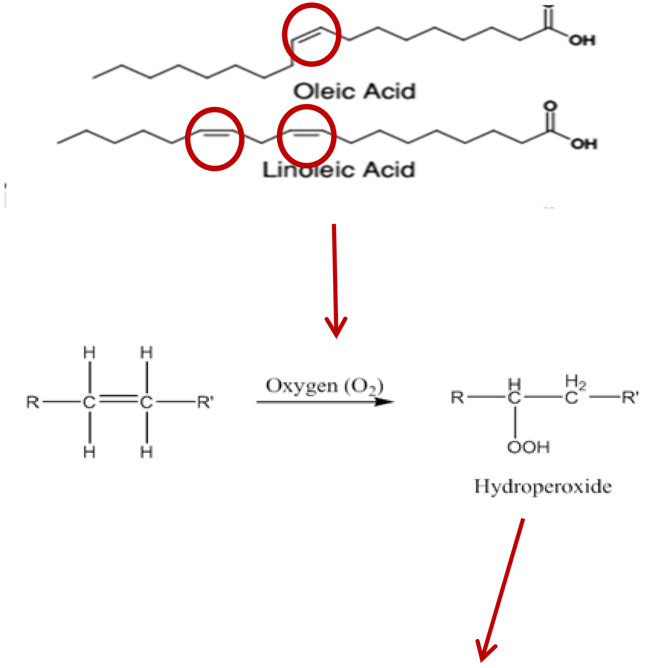


A "free" Fatty Acid



Rancidity in Almonds

- Rancidity occurs primarily via the oxidation of oleic [18:1] and linoleic [18:2] acids
  - Initiated by exposure to heat (e.g. pasteurization, blanching, roasting, etc.,), moisture and/or oxygen (e.g. during storage)
- When fatty acids are oxidized they form lipid hydroperoxides
- These break down into volatiles that can be detected by the nose



Measuring Rancidity

- Although rancidity is a real problem confronting processors, there is no completely objective chemical method for determining rancidity
  - Industry relies on several analytical methods for routine estimates of oxidation however, there is no uniform or standard method for detecting oxidative changes
- Challenges:
  - Lipid oxidation is a dynamic process and levels of chemical markers of lipid oxidation change throughout the lipid oxidation process
  - Little is known regarding correlations between chemical measures of rancidity and consumer acceptance/perception of almonds

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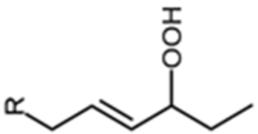
Chemical Measures

moving analytical targets



Lipid Peroxide

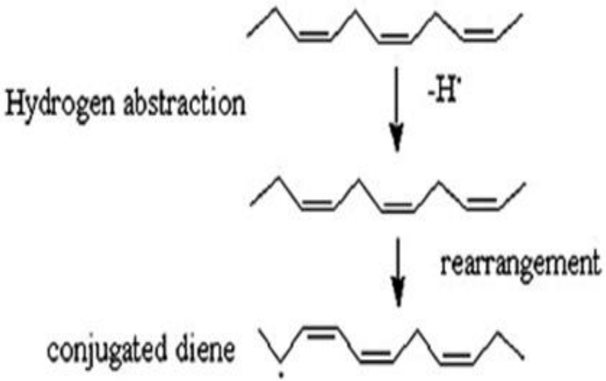
I. Oxidative Rancidity:

- Peroxide Value (PV)
  - Lipid peroxides are the first product of oxidation and are used as an indicator of the early oxidative changes
  - Measures initial stages of rancidity
  - Almonds PV < 5 meq/Kg is considered the benchmark
- However:
  - PV levels decrease as oxidation progresses and lipid peroxides break down
  - Low levels can be present when there is extensive lipid oxidation

Chemical Measures

moving analytical targets

- Conjugated Dienes (CDs)
  - Measures initial stages of rancidity
    - When linoleic acid is oxidized, it can rearrange to form a CD
    - CDs absorb UV light at 232–234 nm which can be measured
- However:
  - CD levels can decompose as oxidation progresses
  - No industry values for CDs for almonds

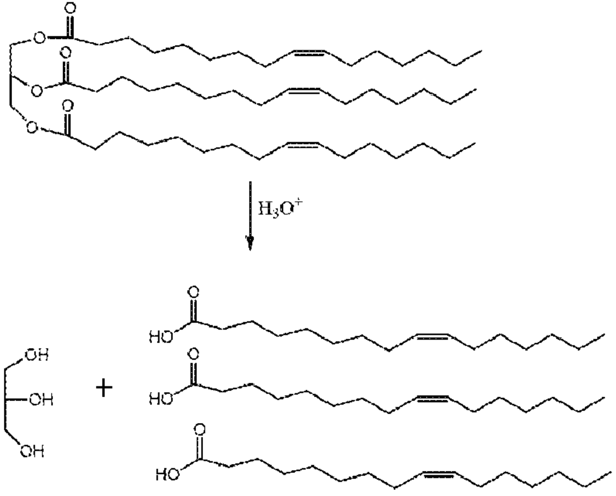


Chemical Measures

moving analytical targets

II. Hydrolytic Rancidity

- Free Fatty Acids (FFA):
  - Hydrolytic or enzymatic release of FFAs
    - More susceptible to oxidation
  - Industry standard is < 1.5% FFAs
- Found to correlate with sensory evaluation in butter
  - No studies in almonds



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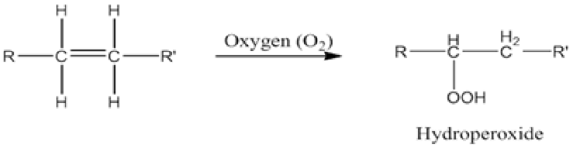
Chemical Measures

moving analytical targets

III. Head Space Volatiles

- Measures the later stages of oxidation
- Lipid peroxides breakdown to form volatile compounds
- Generated during roasting for flavor



- Hexanal
  - Most commonly measured
  - No industry standard for hexanal in almonds
  - A wide range of volatile compounds exist in raw, roasted, and stored almonds

Linking Rancidity with Consumer Linking

Study Design

- Objective 1:
- Monitor common markers of lipid oxidation and volatile aroma profiles in light and dark roasted almonds undergoing accelerated shelf-life conditions that promote rancidity development over 12 months

- Objective 2:
- Determine the consumer hedonic response (degree of liking) of light and dark roast almonds to determine how consumer liking correlates with the chemical measures during rancidity development during accelerated shelf-life storage

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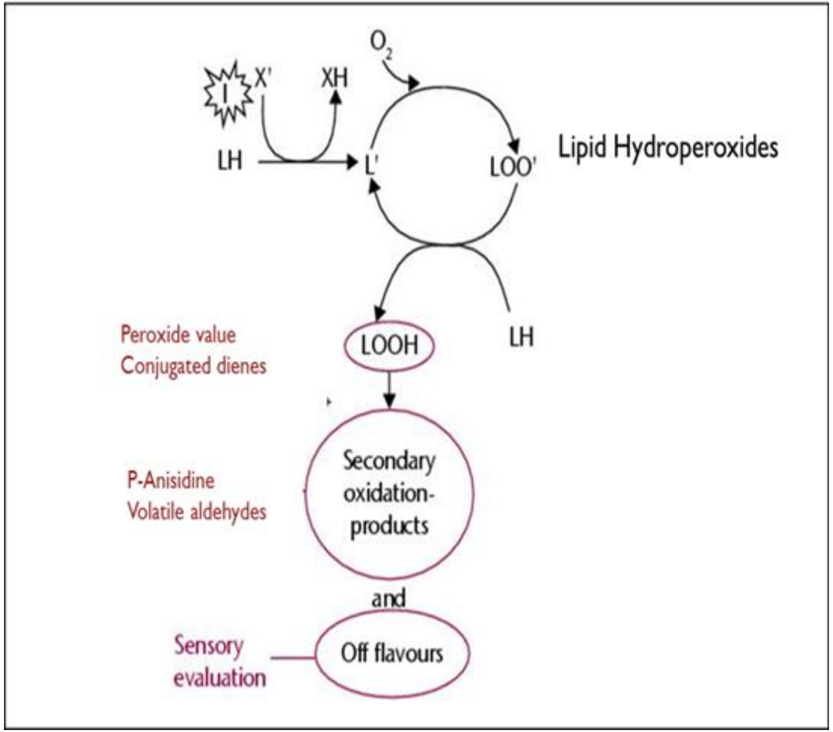
Samples

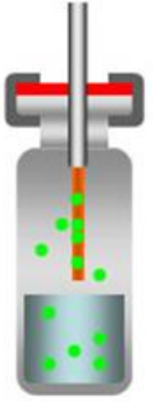
- De-hulled, raw Nonpareil almonds obtained from Blue Diamond Growers (Sacramento, CA)
- Almonds were dry roasted at 115 ± 6ºC for 60 min or 152 ± 6ºC for 15 min to achieve a ‘light’ or ‘dark’ degree of roast respectively
- Almonds were stored at 39 ±1ºC and RH of 15 ±1%
- Almonds were randomized and stored in open bags to maximize oxidation during storage

Analytical Measurements

- Primary Oxidation Products
  - Peroxide Value
  - Conjugated Dienes
- Hydrolytic Rancidity
  - Free Fatty Acids
- Vitamin E
  - Tocopherols (α, $\beta + \gamma$ and δ)
- Head Space Volatiles
- Sensory Measures
  - Consumer Hedonic Analysis



Volatiles by SPME-HS GC/MS



- Sample Preparation
  - A 50 g sample of almond was ground/ particle sized at 841 microns
  - 5 g of this sample was placed in a 20-mL SPME vial
  - Headspace was equilibrated for 4 hours at room temperature
- Sample Extraction
  - CTC Combi/PAL autosampler (Zwingen, Switzerland)
  - Samples were agitated at 500 rpm and pre-equilibrated at 40ºC for 45 min, after which they were extracted with a 1 cm 30/50um StableFlex DVB/CAR/PDMS fiber exposed for 45 mins at 250 RPM

Consumer Hedonic Analysis

- Untrained consumers (99) between the ages of 14 and 80 and who consumed almonds at least once a month, were recruited
- Consumers were served samples of 6-7 almonds at room temperature, with randomly generated 3-digit numbers as sample identifiers
- Consumers were asked to indicate their liking of samples by marking a 9-pt hedonic scale with accompanying phrases as anchors

DISLIKE EXTREMELY	DISLIKE VERY MUCH	DISLIKE MODERATELY	DISLIKE SLIGHTLY	NEITHER LIKE NOR DISLIKE	LIKE SLIGHTLY	LIKE MODERATELY	LIKE VERY MUCH	LIKE EXTREMELY
1	2	3	4	5	6	7	8	9

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Hedonic Ratings

- Significant differences in liking related to the storage time
  - Consumers had a significant difference in liking between samples aged 0, 2, 4, and 6 months, while there was no significant difference found between samples aged 6, 8, and 10 months
- No significant difference was found in liking related to roast level

	Storage Time					
Analysis	0 months	2 months	4 months	6 months	8 months	10 months
Light Roast	7.4 ± 1.4 a	6.6 ± 1.5 b	5.8 ± 1.55 c	4.9 ± 1.9 d	4.9 ± 2.0 d	4.7 ± 2.1 d
Dark Roast	7.2 ± 1.7 a	6.8 ± 1.4 b	5.8 ± 1.7 c	4.7 ± 2.0 d	4.5 ± 2.0 d	4.2 ± 2.0 d

*A rating of 5 indicates that the consumer is indifferent to the product and below this begins to dislike the product

Correlation with Measures of Lipid Oxidation

Light Roast Almonds

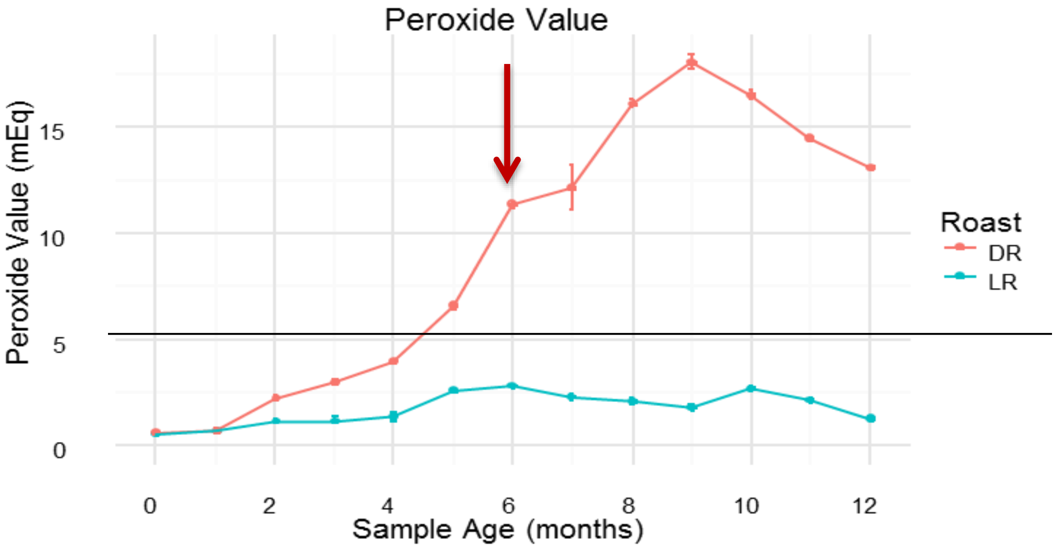
Analysis	Storage Time						
	0 months	2 months	4 months	**6 months**	8 months	10 months	12 months
Peroxide Value (mEq/g oil)	0.57 ± 0.04 e	1.13 ± 0.14 d	1.38 ± 0.20 d	**2.84 ± 0.02 b**	2.14 ± 0.18 c	2.70 ± 0.08 b	1.26 ± 0.08 d
Free Fatty Acid Value (% oleic)	0.21 ± 0.00 d	0.25 ± 0.00 cd	0.28 ± 0.00 bc	**0.31 ± 0.01 abc**	0.32 ± 0.02 ab	0.36 ± 0.03 a	0.36 ± 0.03 a
Conjugated Dienes (%)	0.213 ± 0.000 f	0.222 ± 0.00 f	0.255 ± 0.000 cd	**0.242 ± 0.003 e**	0.261 ± 0.008 bc	0.267 ± 0.002 b	0.302 ± 0.001 a
Alpha Tocopherol Conc. (mg/kg oil)	435 ± 4 a	424 ± 16 a	406 ± 1 abc	**387 ± 3 bcd**	362 ± 4 def	363 ± 32 def	334 ± 11 f
Beta + Gamma tocopherol Conc. (mg/kg)	34.3 ± 0.5 ab	34.0 ± 0.2 ab	34.1 ± 0.3 ab	**32.8 ± 0.5 ab**	31.9 ± 0.4 ab	33.5 ± 1.0 ab	31.7 ± 0.9 ab
Mean Consumer Hedonic Score	7.4 ± 1.4 a	6.6 ± 1.5 b	5.8 ± 1.55 c	**4.9 ± 1.9 d**	4.9 ± 2.0 d	4.7 ± 2.1 d	

Correlation with Measures of Lipid Oxidation

Dark Roast Almonds

	Storage Time						
Analysis	0 months	2 months	4 months	6 months	8 months	10 months	12 months
Peroxide Value (mEq/g oil)	0.61 ± 0.04 n	2.21 ± 0.12 m	3.96 ± 0.07 l	**11.36 ± 0.23 j**	16.07 ± 0.53 g	16.48 ± 0.18 g	13.00 ± 0.03 i
Free Fatty Acid Value (% oleic)	0.20 ± 0.03 j	0.18 ± 0.00 i	0.37 ± 0.01 g	**0.36 ± 0.01 e**	0.42 ± 0.04 c	0.54 ± 0.04 c	0.57 ± 0.04 a
Conjugated Dienes (%)	0.216 ± 0.001 j	0.238 ± 0.001 i	0.286 ± 0.002 g	**0.362 ± 0.001 e**	0.464 ± 0.003 c	0.464 ± 0.002 c	0.508 ± 0.001 a
Alpha Tocopherol Conc. (mg/kg oil)	444 ± 1 a	418 ± 7 ab	396 ± 2 bc	**358 ± 8 de**	328 ± 8 fg	277 ± 6 h	292 ± 9 h
Beta + Gamma tocopherol Conc. (mg/kg)	35.0 ± 0.1 a	34.0 ± 0.8 abcd	34.4 ± 0.5 ab	**32.3 ± 0.3 cdefg**	32.0 ± 0.6 efg	31.0 ± 0.1 g	31.2 ± 1.3 fg
Mean Consumer Hedonic Score	7.2 ± 1.7 a	6.8 ± 1.4 b	5.8 ± 1.7 c	**4.7 ± 2.0 d**	4.5 ± 2.0 d	4.2 ± 2.0 d	

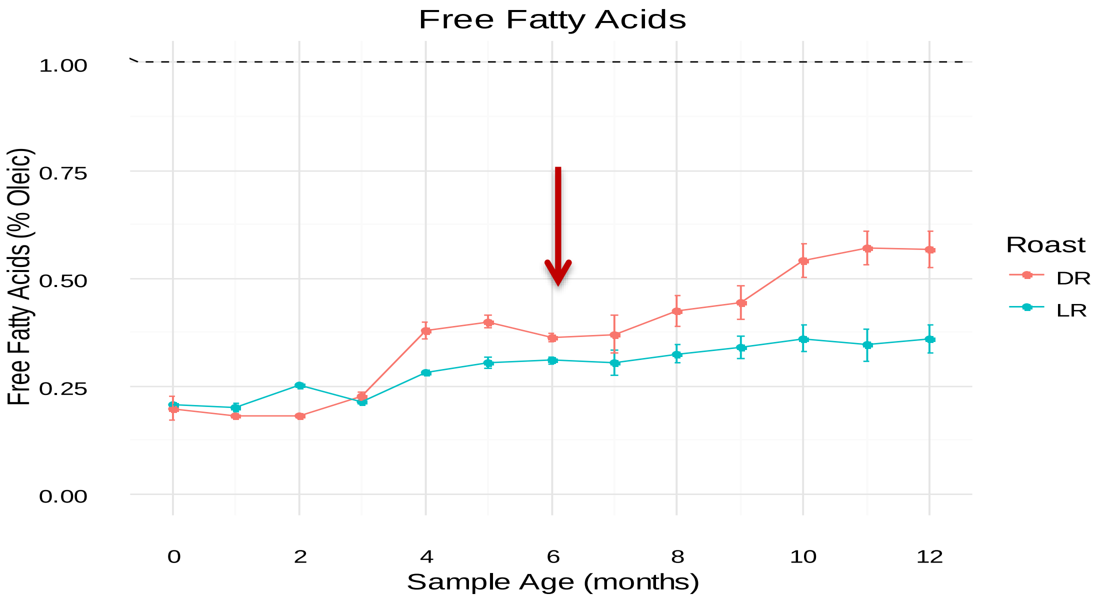
Peroxide Values



- PV measures early oxidation, and almonds are considered to not have undergone significant lipid oxidation if values are < 5 mEq/kg
- Doesn't correlate with consumer liking in light roast almonds

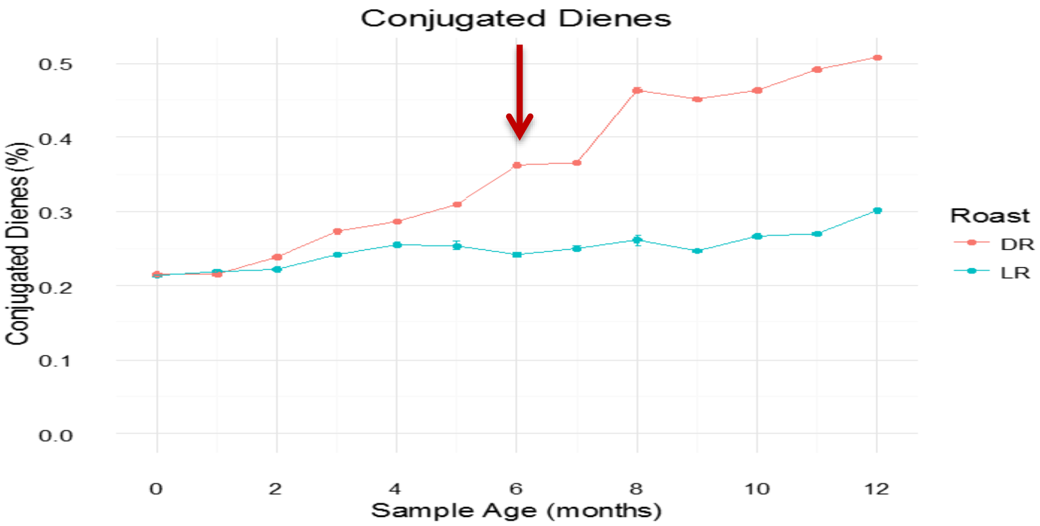
Free Fatty Acids

(% Oleic)



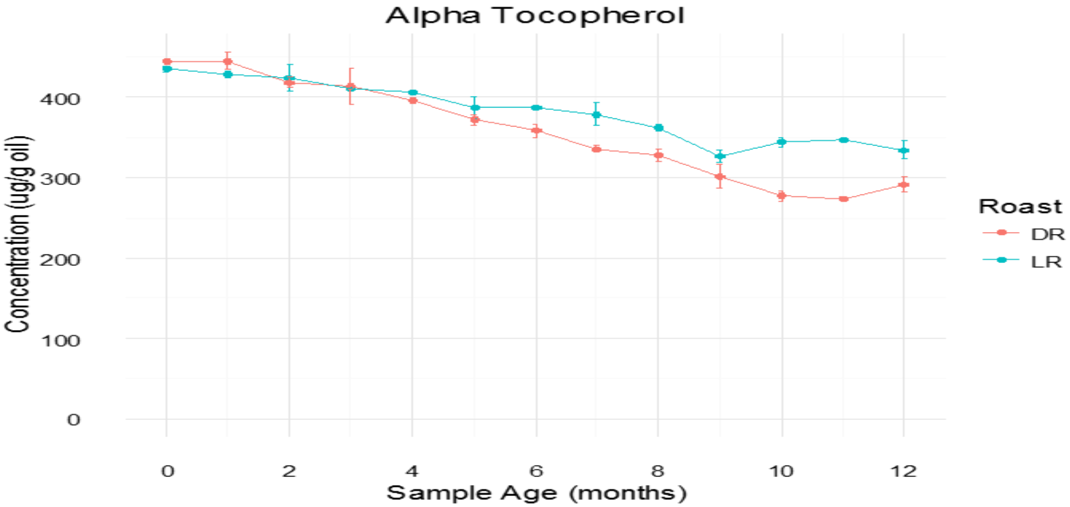
- FFAs indicate hydrolytic rancidity in almonds and the “recommended” maximum value is < 1.5 % oleic
- Never exceeded, however roasting would inactivate lipase enzymes

Conjugated Dienes



- Significant increases were observed at 2 months for the DR samples and at 3 months for LR samples
- Correlate with consumer liking however sensitivity is very low

Alpha Tocopherol

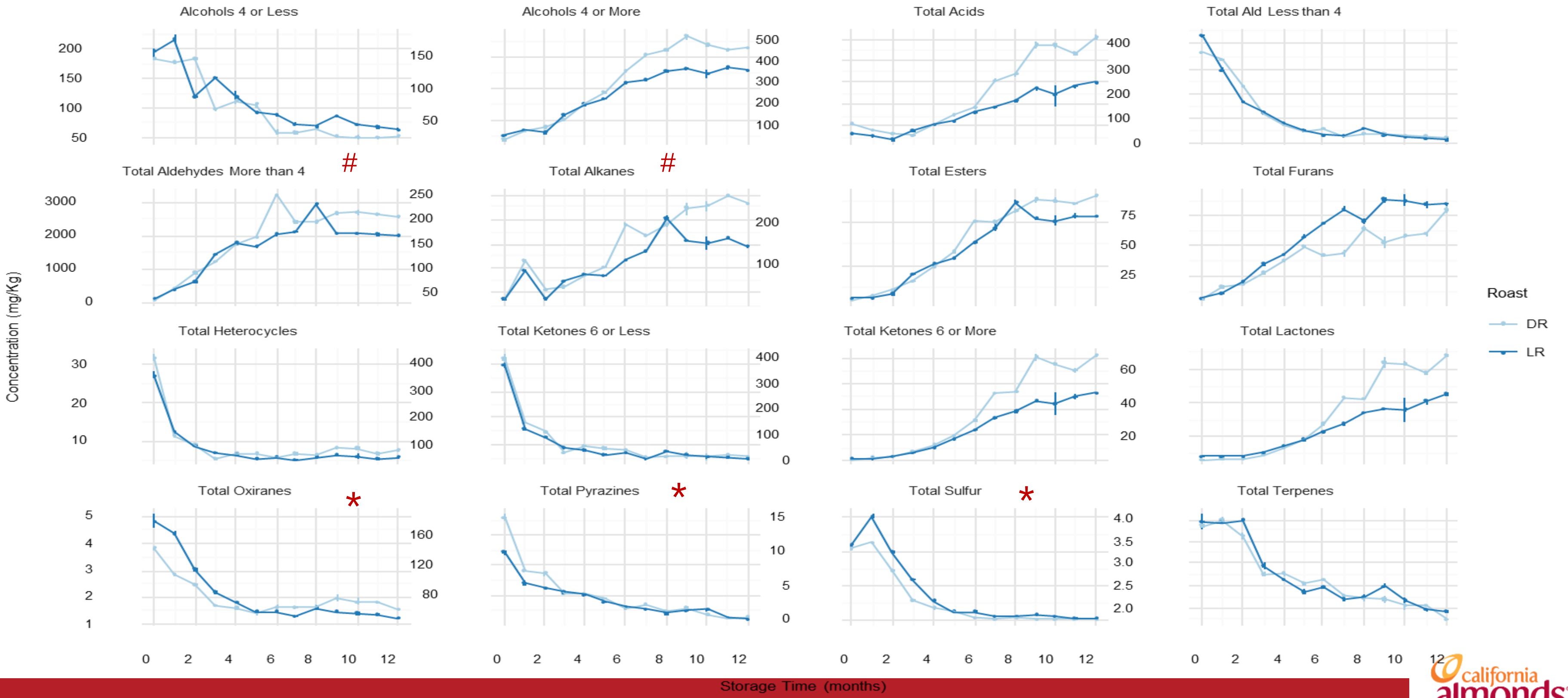


- All isomers were found also to correlate significantly with consumer liking at $p < 0.01$, though alpha tocopherol had the highest r^2 value at 0.814, whereas beta + gamma and delta tocopherol had a correlation r^2 values of 0.721 and 0.625 respectively

Volatile Compounds

- A total of 99 volatile compounds were identified in roasted almonds over the 12 months of storage
- Compounds include: 8 acids, 17 alcohols, 19 aldehydes, 5 alkanes, 4 esters, 11 ketones, 13 pyrazines, 3 terpenes and 20 other compounds
- Authentic standards were available to confirm identifies of 63 compounds
- Tentative identities of the remaining 33 compounds were made by comparing MS spectra with the NIST Library and calculated Kovat's retention indices (KI) with literature values of standards chromatographed under comparable conditions

Trends in Total Volatiles by Class



Changes from 0 to 2, 4 months of select compounds with significant correlation ($p < 0.01$) to consumer liking

Name	Correlation Value	Concentration in DR			Concentration in LR		
		0 Months	2 Months	4 months	0 Months	2 Months	4 months
Positive Correlations							
methoxymethyl oxirane	0.939	3.7 ± 0.0	2.27 ± 0.03	1.18 ± 0.04	4.73 ± 0.25	2.80 ± 0.05	1.33 ± 0.03
ethylpyrazine	0.921	5.56 ± 0.08	3.45 ± 0.09	2.79 ± 0.10	5.11 ± 0.15	3.28 ± 0.04	2.87 ± 0.05
2,3-dimethylpyrazine	0.918	3.67 ± 0.04	2.36 ± 0.11	1.77 ± 0.02	3.22 ± 0.04	2.05 ± 0.21	1.87 ± 0.08
2-ethyl-6-methylpyrazine	0.908	5.41 ± 0.10	3.59 ± 0.10	2.97 ± 0.13	4.24 ± 0.17	3.16 ± 0.06	2.93 ± 0.04
2,5-dimethylpyrazine	0.886	80.1 ± 1.4	49.2 ± 1.29	37.1 ± 1.17	60.6 ± 1.49	40.3 ± 0.43	36.6 ± 0.72
3-methylbutanal	0.886	92.9 ± 0.8	64.4 ± 0.89	19.6 ± 1.09	114 ± 1.19	46.4 ± 1.04	20.3 ± 0.63
2-methylbutanal	0.884	225 ± 3	146 ± 2.37	43.7 ± 0.691	260 ± 4.84	106 ± 1.82	47.9 ± 1.17
2,6-dimethylpyrazine	0.870	13.7 ± 0.31	8.45 ± 0.23	6.09 ± 0.13	8.7 ± 0.45	6.57 ± 0.36	6.1 ± 0.085
2-ethyl-5-methylpyrazine	0.861	2.11 ± 0.06	1.35 ± 0.03	1.12 ± 0.04	1.51 ± 0.03	1.18 ± 0.024	1.12 ± 0.01
methylpyrazine	0.855	44.6 ± 1.78	21.8 ± 0.48	15.8 ± 0.58	35.5 ± 0.57	17.4 ± 0.25	15.4 ± 0.20
pyrazine	0.842	2.49 ± 0.14	1.19 ± 0.04	0.917 ± 0.03	2.41 ± 0.04	0.984 ± 0.04	0.833 ± 0.01

Change from 0 to 2, 4 months of select compounds with significant correlation ($p < 0.01$) to consumer liking

		Concentration in DR			Concentration in LR		
Name	**Correlation Value**	**0 Months**	**2 Months**	**4 months**	**0 Months**	**2 Months**	**4 months**
Negative correlations							
hexanoic acid	-0.900	1.05 ± 0.06	14.7 ± 3.00	59.8 ± 2.11	1.96 ± 0.32	12.3 ± 0.15	56.3 ± 1.22
pentanal	-0.902	3.92 ± 0.04	62.8 ± 0.59	110 ± 1.26	5.5 ± 0.06	41.3 ± 0.84	111 ± 0.79
hexanal	-0.902	58 ± 0.34	716 ± 16.30	1360 ± 15.9	77.9 ± 1.8	492 ± 9.25	1390 ± 8.25
2-pentylfuran	-0.909	4.86 ± 0.14	13.9 ± 0.23	28.8 ± 0.58	6.48 ± 0.33	16.3 ± 0.42	32.4 ± 0.35
2-hexenal	-0.922	0.393 ± 0.01	2.93 ± 0.17	5.13 ± 0.27	1.23 ± 0.01	2.67 ± 0.02	5.28 ± 0.03
2-heptenal	-0.928	0.799 ± 0.03	6.51 ± 0.23	17.6 ± 0.32	1.1 ± 0.057	5.12 ± 0.07	19.2 ± 0.34
1-butanol	-0.931	0.542 ± 0.03	1.48 ± 0.03	2.78 ± 0.07	0.623 ± 0.01	1.05 ± 0.02	2.62 ± 0.02
3-octen-2-one	-0.934	0.465 ± 0.01	5.58 ± 0.15	17.2 ± 0.34	0.755 ± 0.05	5.6 ± 0.09	14 ± 0.35
styrene	-0.943	1.53 ± 0.02	3.85 ± 0.05	5.02 ± 0.17	1.79 ± 0.05	2.47 ± 0.05	5.28 ± 0.02
1-pentanol	-0.946	3.79 ± 0.06	16.8 ± 0.22	36.9 ± 0.81	6.31 ± 0.14	11.7 ± 0.13	34.6 ± 0.27

Compounds with significant correlation with consumer liking ($p < 0.05$) and an absolute regression slope of >2 µg/kg change in concentration per unit liking

Compound Name	Linear R^2 value	Slope of Conc. (µg/kg) vs. liking	Aroma Quality	Aroma Threshold (µg/kg)	DR 4 month	DR 6 month	LR 4 month	LR 6 month
heptanal	0.952	-82.55	fatty, oily, powerful, rancid, citrus, sharp	50[1,O]	**85.4 ± 2.0**	**187 ± 3**	**87.1 ± 0.9**	**137 ± 2**
octanal	0.885	-93.24	citrus-like, soapy, penetrating	55[1,O]	**69.5 ± 1.5**	**158 ± 5**	**69 ± 1**	**127 ± 3**
hexanal	0.814	-736.91	fatty, green, grassy	75[1,O]	**1360 ± 15.9**	**2380 ± 34.6**	**1390 ± 8.25**	**1480 ± 6.5**
1-octen-3-ol	0.753	-11.27	mushroom, earthy, green, oily, fungal	1[4,W]	**7.29 ± 0.237**	**14.9 ± 0.365**	**5.75 ± 0.158**	**10 ± 0.207**
benzaldehyde	0.586	-2.53	artificial almond, sweet, cherry	350[W]	8.79 ± 0.334	10.6 ± 0.568	9.1 ± 0.0877	8.71 ± 0.195
furfural	0.631	4.63	sweet, woody, almond, bread	3,000[4,W]	5.2 ± 0.219	3.95 ± 0.12	4.55 ± 0.0394	3.78 ± 0.0424
2-methylbutanal	0.781	83.19	fruity, dry, slightly green, chocolate, nut	10[5,O]	**43.7 ± 0.691**	**23.1 ± 1.8**	**47.9 ± 1.17**	**18.8 ± 0.159**
3-methylbutanal	0.785	35.66	musty, chocolate, nutty, malty	5.4[5,O]	**19.6 ± 1.09**	**11.2 ± 0.675**	**20.3 ± 0.63**	**8.28 ± 0.141**

Conclusions

- All chemical measures of rancidity behaved significantly different between LR and DR almonds
- PV does not relate to consumer liking and 5 mEq/kg is not a good measure of rancidity development in roasted almonds
- FFA remain below recommended 1.5% oleic indicating this is not a good measure of rancidity development in roasted almonds
- Consumer liking was not different based on roast level
  - Consumers changed liking significantly by 2 months, by 4-5 months consumers neither liked nor disliked the almonds
  - Consumers disliked almonds on average by 6 months for both LR and DR
- At 2 months, significantly decreases were observed in compounds related to roasted flavor (pyrazines) indicating that flavor fade occurs rapidly
- Headspace volatiles correlate better with consumer liking than PV, CD, and FFA, and at 6 months significant increases in aldhydes were observed with the strongest correlation with heptanal, followed by octanal and hexenal

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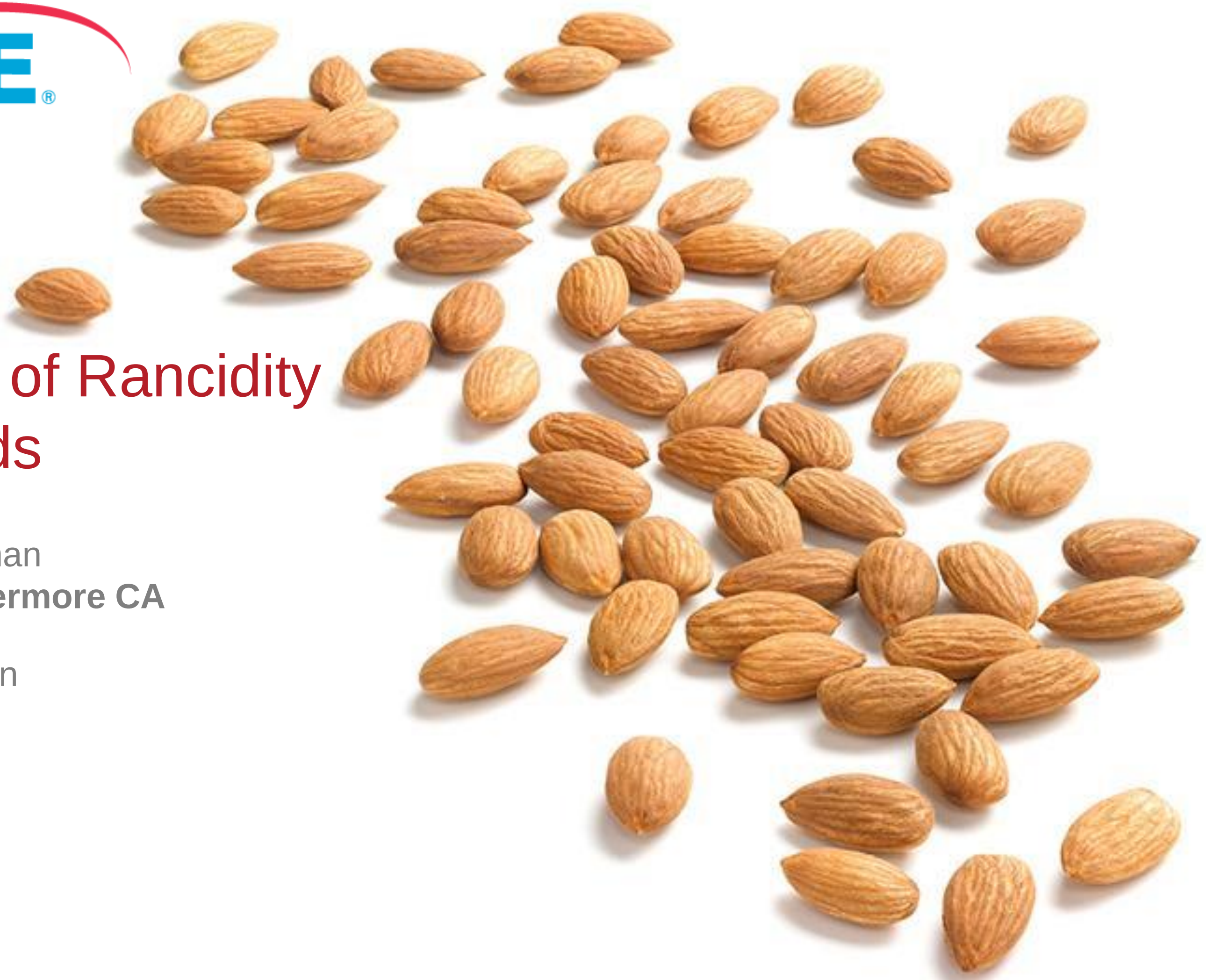

Sensory Evolution of Rancidity in Roasted Almonds

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growing ADVANTAGE
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Content

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About Covance

As of October 2015, we are part of the Covance portfolio of leading food solutions.

Heritage in food safety, process validation and commercialization. Providing services across the product development continuum: product & process development, food safety & quality, consumer & sensory

Foundation in product & process development and commercialization in the food, beverage & nutritionals industries

Product Design and Integrity

Solutions for the life cycle of your product

CONCEPT → DEVELOPMENT → LAUNCH → QUALITY PROGRAMS → BRAND PROTECTION

Product Design

- Idea Generation
- Culinary Services
- Product and Process Development
- Consumer Research
- Sensory Evaluation
- Regulatory Considerations
- Commercialization and Scale-Up

Product Integrity

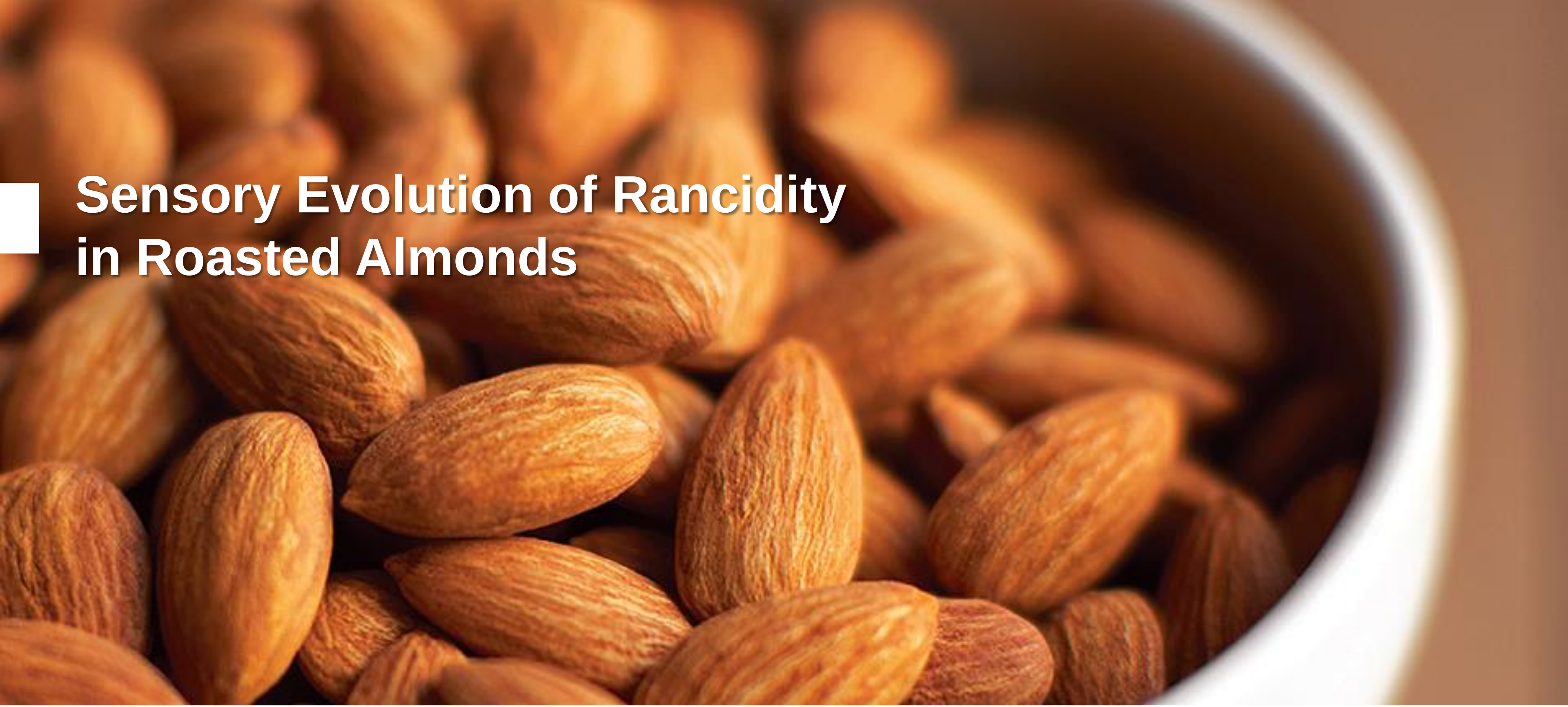
- Nutritional Chemistry Solutions
- Microbiology and Food Safety
- Adulterant and Non-Targeted Analyses
- Contaminants/Pesticides/Residues
- Risk Assessments
- Challenge Studies and Process Validations
- Shelf-Life and Stability Testing

Sensory Evaluation

Our Approach:

- Tap into our pool of 40 highly trained panelists with an average of 5+ years of experience.
  - These are not consumers and they do not provide their liking or opinions.
  - Skilled at describing sensory characteristics and intensity ratings of a wide variety of products.
  - Screened for olfactory & gustatory acuity and ability to describe flavor nuances.
  - Extensively screened and provided with 3+ months of training before qualification.
- Overseen by experienced panel leaders
  - Advanced degrees (Master’s or Ph.D. in Sensory Science)

Sensory Evolution of Rancidity in Roasted Almonds



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The Almond Conference

Roasting Changes Volatile Profile of Almonds

ROASTING

<u>Maillard Reaction</u>
(non-enzymatic browning)

- Ketones
- Aldehydes
- Pyrazines
- Alcohols
- Thiols
- Sulfides
- Furans
- Pyrroles

http://bulknuts.ca/products/raw-almonds
http://www.clipartpanda.com

Processing & Environment Changes Volatile Profile of Almonds

Sunlight

Heat

Ambient Humidity

Metal Ions (Iron)

O_2

Atmospheric Oxygen

O_2

Time

Lipid Oxidation

- Peroxides
- Conjugated Dienes

- Aldehydes (ie. hexanal)
- Ketones
- Alcohols (1-octen-3-ol)

RANCIDITY

http://bulknuts.ca/products/raw-almonds
http://www.clipartkid.com
http://followgreenliving.com
http://etc.usf.edu/clipart/
http://gizmodo.com
http://www.istockphoto.com
https://recycling.ncsu.edu

Background & Objectives

Background:

- As demand for almonds continues to grow, products may be shipped longer distances and stored over extended periods of time.
- It is important to monitor the flavor of almonds over time, to ensure the quality and value of exports and products are preserved.

Objectives:

- To identify changes in sensory profile throughout storage.
- To identify volatile compounds related to key sensory attributes, and assess which of these are most related to consumer liking.

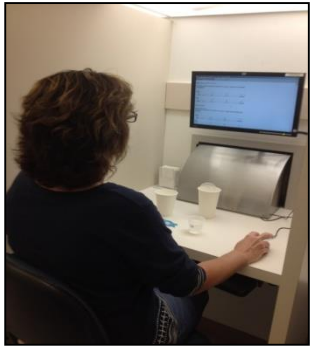
Product Descriptions

- Raw Non-pareil almonds with skin (2014 harvest).
- Dry roasted – 239 ± 6°F for 60 min => **LIGHT Roasted (LR)**

  – 305 ± 6°F for 15 min => **DARK Roasted (DR)**
- Samples were stored at 15% ± 1% relative humidity and 102 ± 1°F for intervals of 1 to 12 months.
  - 12 accelerated storage times + Control (13 samples total) at two roast levels.
    - All samples were analyzed using HS-SPME-GC-MS.
  - 6 samples (Control + 5 storage times) were assessed by trained panelists & consumers.

Storage time (months)	**0 (Control)**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
Descriptive Analysis & Consumer Testing	x		x		x		x		x		x		
HS-SPME-GC-MS	x	x	x	x	x	x	x	x	x	x	x	x	x

Methodology – Descriptive Analysis



- Descriptive testing was conducted by Covance using trained panelists.
- 10 panelists, 3 replications.
- Panelists participated in one 2-hour orientation session to discuss the samples and review the references.
- The light roast samples were assessed before the dark roast samples.
- The control sample in each roast level was used as a reference to rate the degree of difference and was anchored to the scoresheet.
- Samples were identified by 3-digit codes and were served in a randomized and balanced order within each roast level.
- Panelists rated attribute intensities on 15-point line scales.

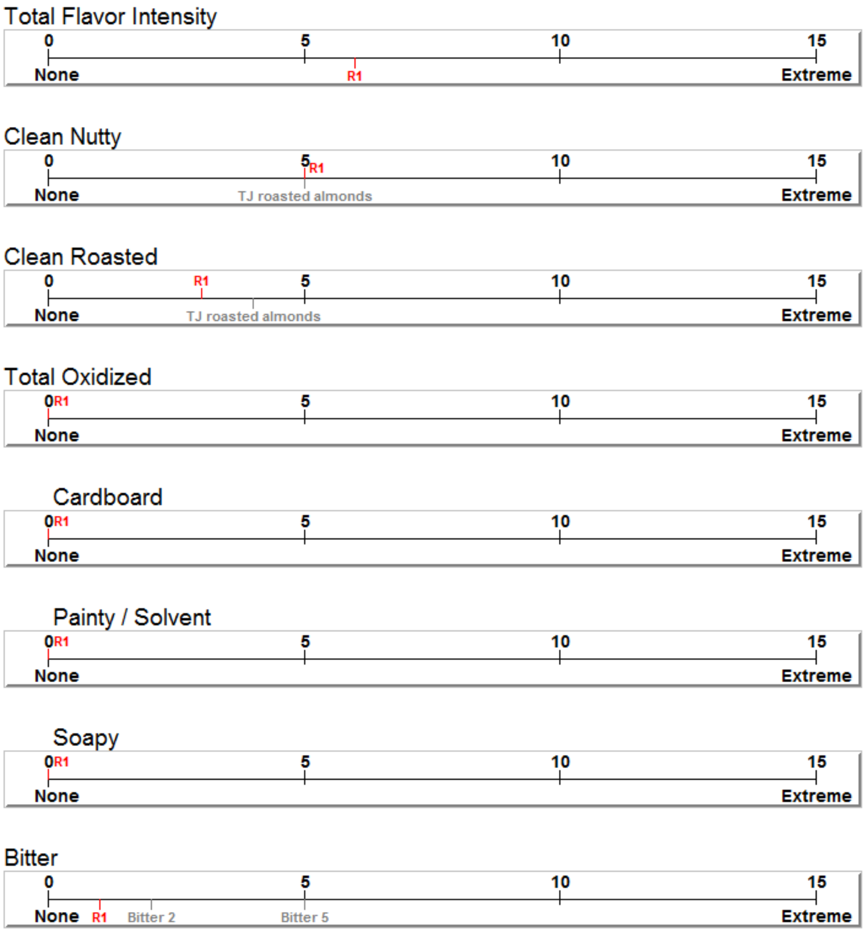
Methodology – Sensory Attributes

- **Overall Degree of Difference (vs. Control)**
- **Aroma and Flavor**
  - Total Aroma/Flavor Intensity
  - Clean Nutty
  - Clean Roasted
  - Total Oxidized
    - Cardboard *
    - Painty / Solvent *
    - Soapy *
  - Bitter *
- **Texture – Initial**
  - Hardness
- **Mouthfeel**
  - Pungent / Irritation / Burning
  - Astringent

R1 = Light Roast Control (LCON)

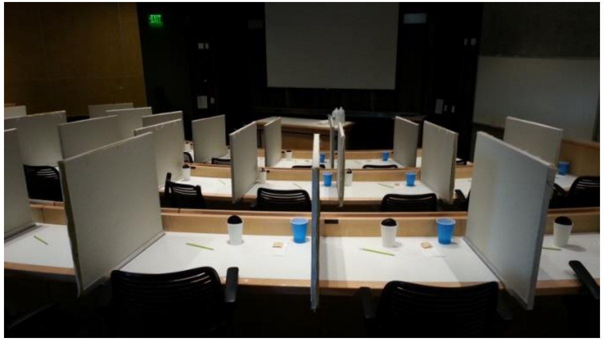
* Flavor only

FLAVOR:



Methodology – Consumer Test

- Central Location Testing was performed at UC Davis.
- 99 consumers, 1 replication.
- Consumers consumed almonds at least once a month, were not pregnant and aged 14-80 years.
- Consumers were instructed to taste at minimum of 3 almonds before making an assessment.
- Consumers evaluated 12 samples (6 samples for each roast level).
- Serving order of all 12 samples was randomized to control for position biases.
- All products were served unbranded.



How much do you like this sample overall?

☐	☐	☐	☐	☐	☐	☐	☐	☐
Dislike Extremely	Dislike Very Much	Dislike Moderately	Dislike Slightly	Neither Like Nor Dislike	Like Slightly	Like Moderately	Like Very Much	Like Extremely

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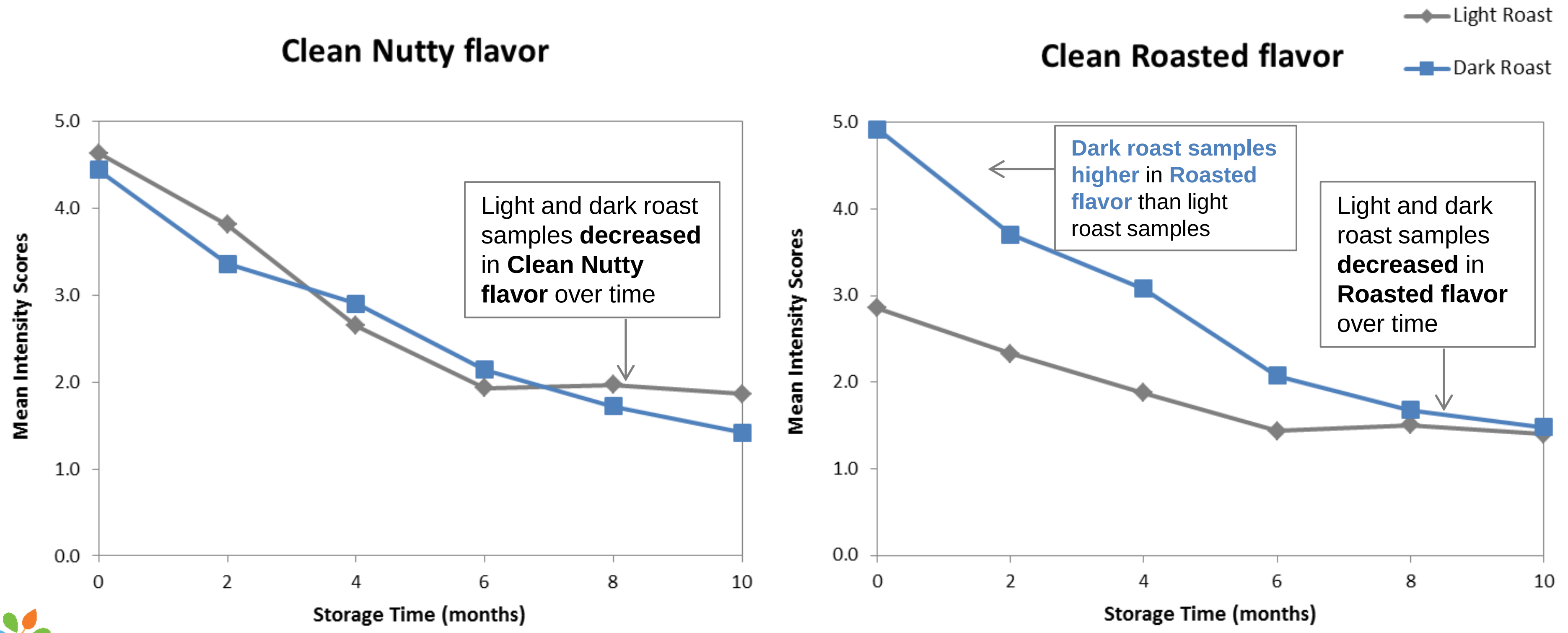
Methodology – HS-SPME-GC-MS

- Headspace Solid-Phase Microextraction Gas Chromatograpy/Mass-Spectrometry (HS-SPME-GC/MS)
  - Measured at UC Davis, 3 replicates
  - 98 volatile compounds, most confirmed with authentic standards
    - 8 acids
    - 17 alcohols
    - 19 aldehydes
    - 5 alkanes
    - 2 esters
    - 11 ketones
    - 13 pyrazines
    - 3 terpenes
    - 20 other compounds

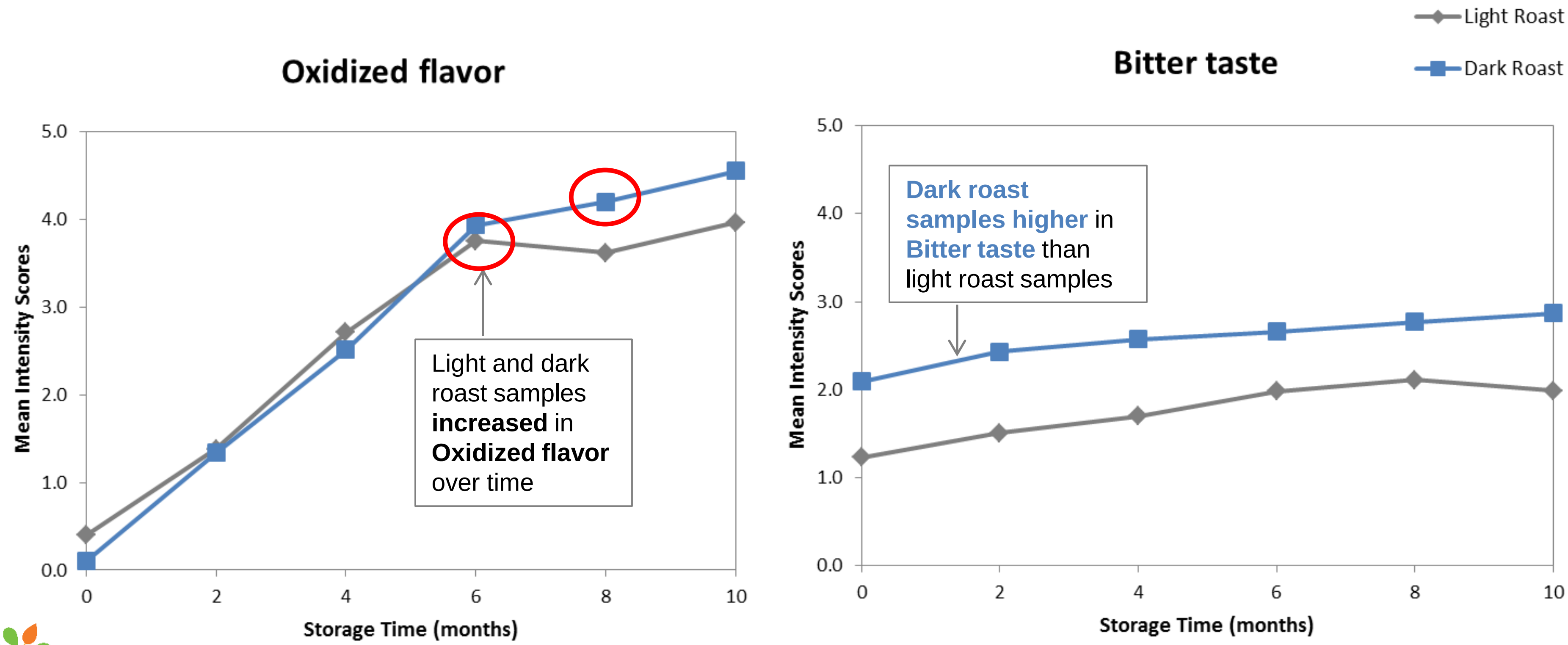
http://www.elcalabs.com/GCMS.html

Descriptive Analysis Results

Clean Nutty & Clean Roasted Flavors Decreased Over Time



Oxidized Flavor & Bitter Taste Increased Over Time



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Consumer Test Results

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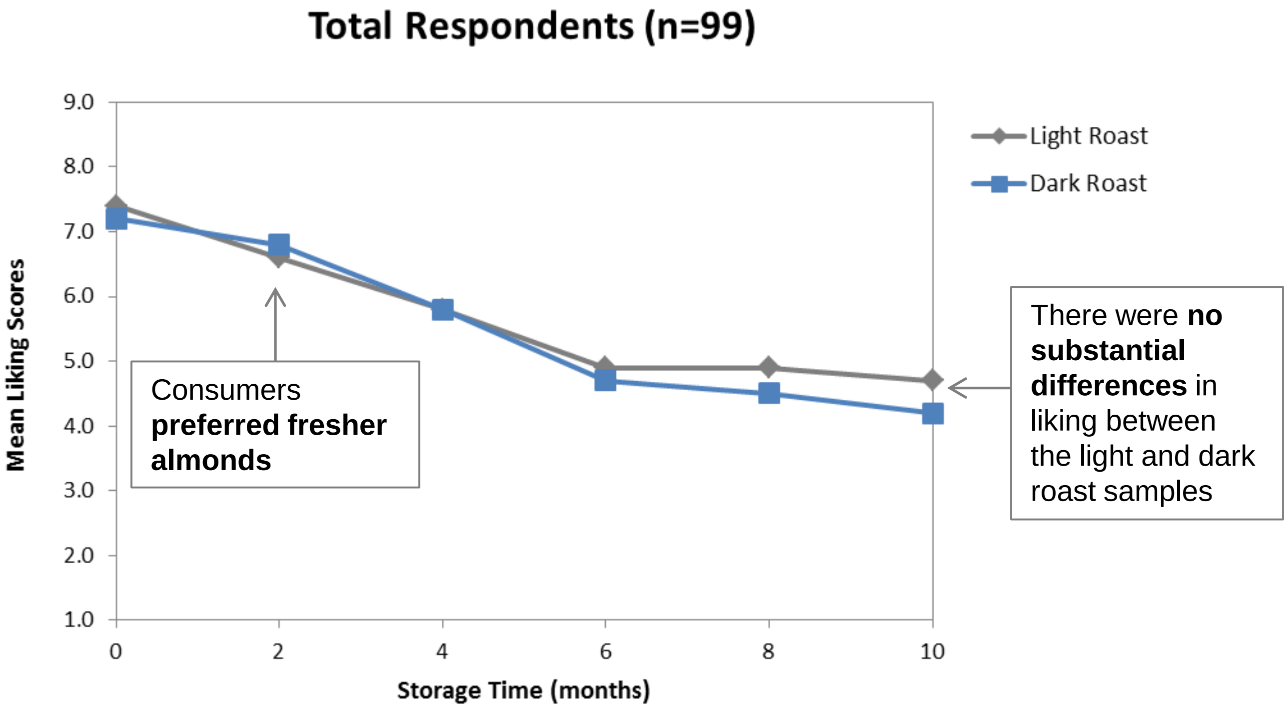
All Consumers Preferred Fresher Almonds

POSITIVE CORRELATIONS

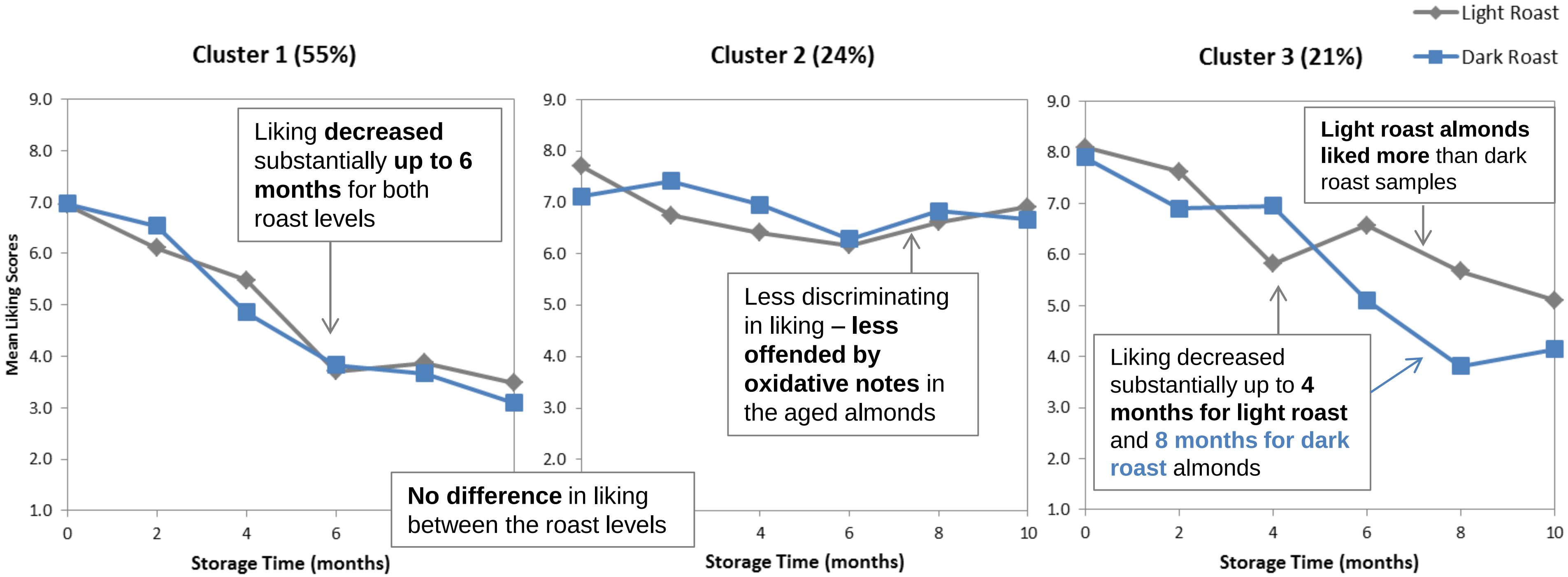
- Clean Nutty aroma and flavor
- Clean Roasted aroma and flavor

NEGATIVE CORRELATIONS

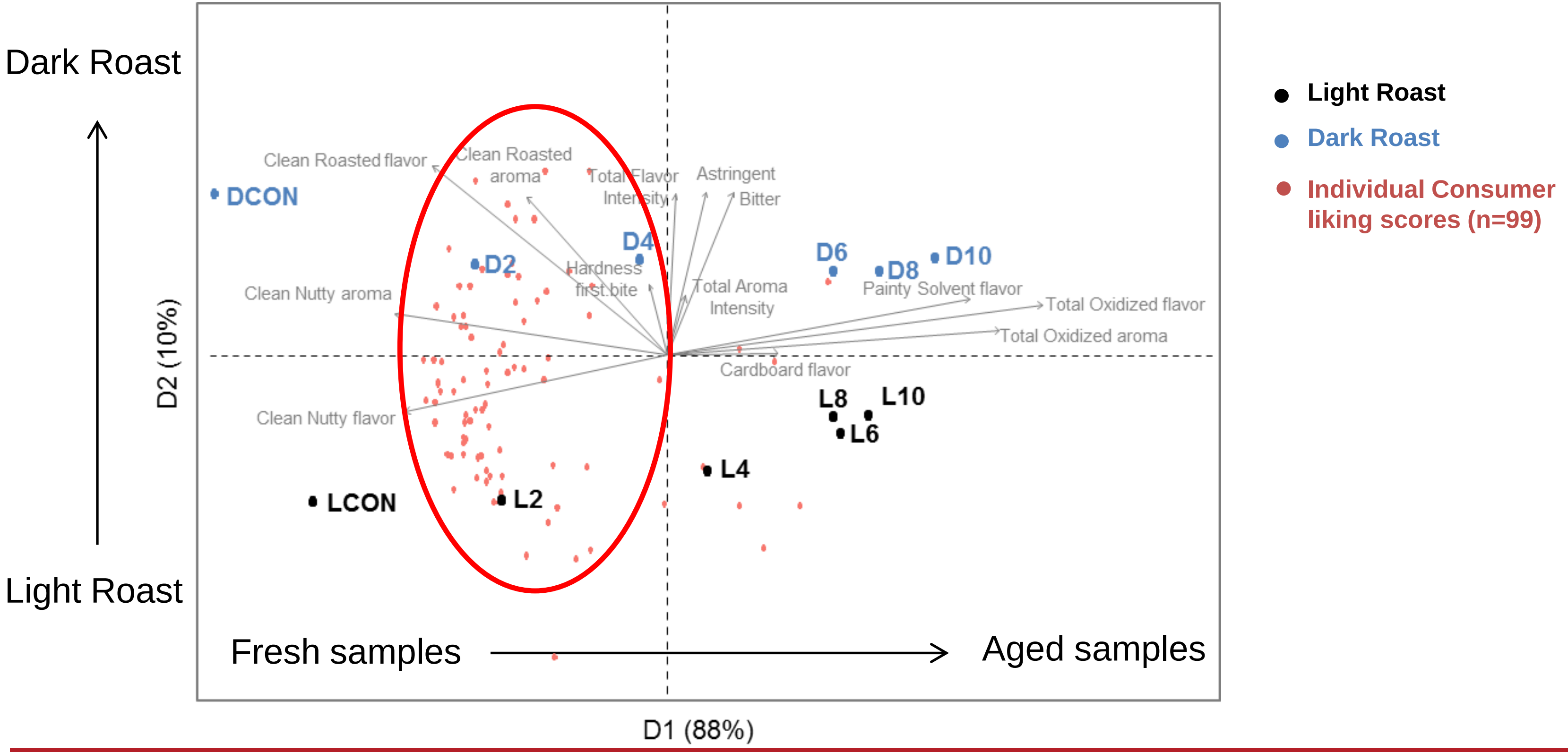
- Oxidized aroma and flavor
- Cardboard flavor
- Painty/Solvent flavor
- Soapy flavor
- Bitter taste
- Pungent/Irritation/Burning mouthfeel



Three Clusters of Consumers with Different Liking Patterns

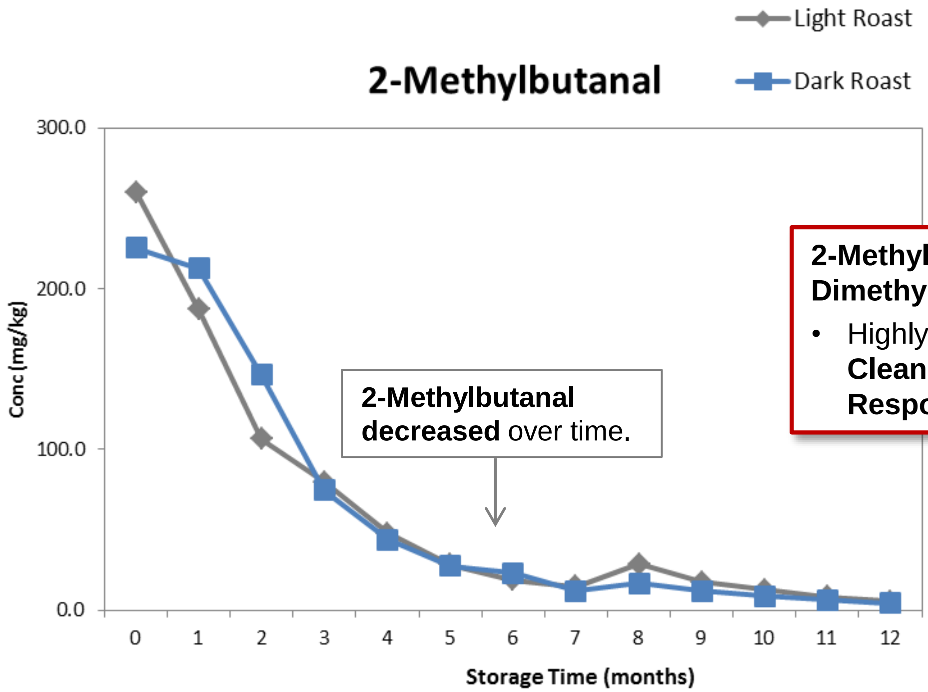


Relating Descriptive & Consumer Data



Analytical Results

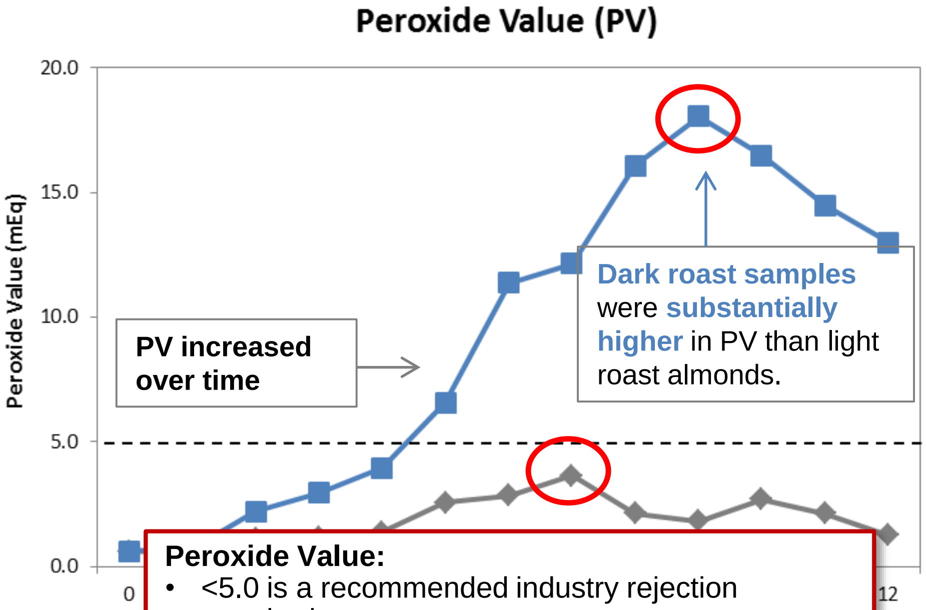
Analytical Measures – 2-Methylbutanal

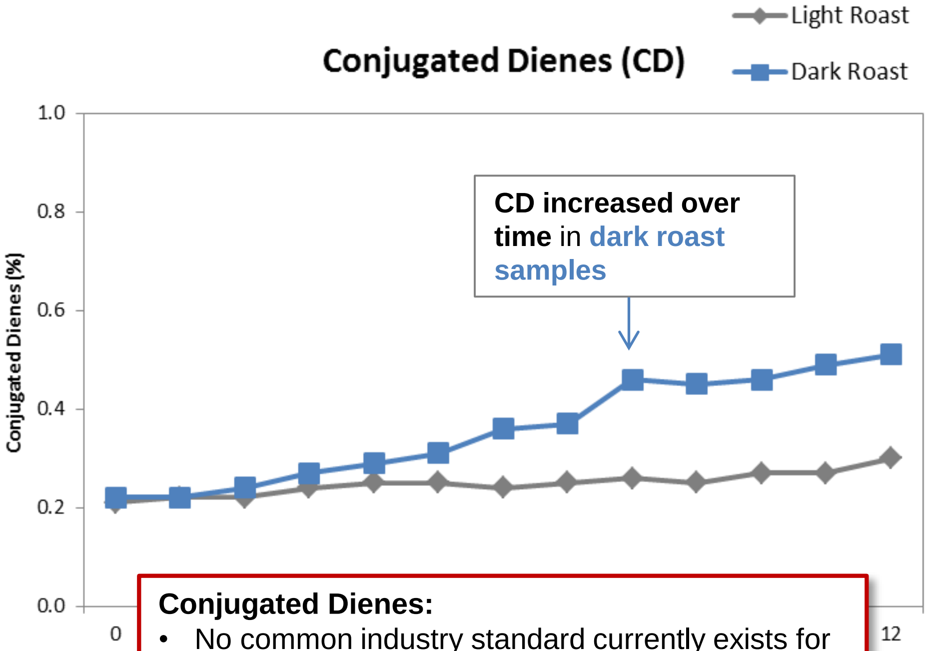


2-Methylbutanal, 3-Methylbutanal & **2,5-Dimethylpyrazine:**

- Highly **positively** correlated with **Clean Nutty** and **Clean Roasted flavors**, as well as liking of **Total Respondents**, and **Clusters 1** and **3**.

Analytical Measures – Lipid Oxidation Breakdown





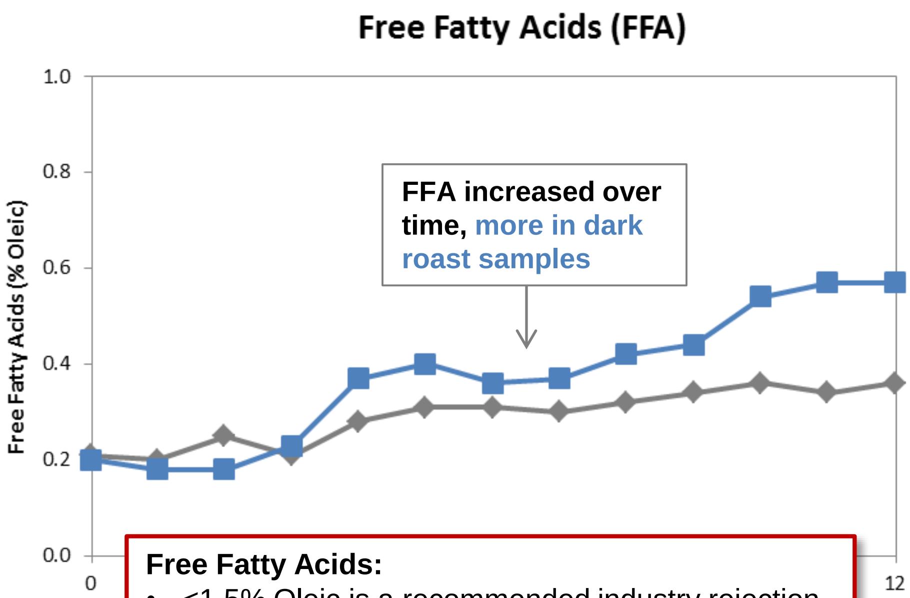
Peroxide Value:

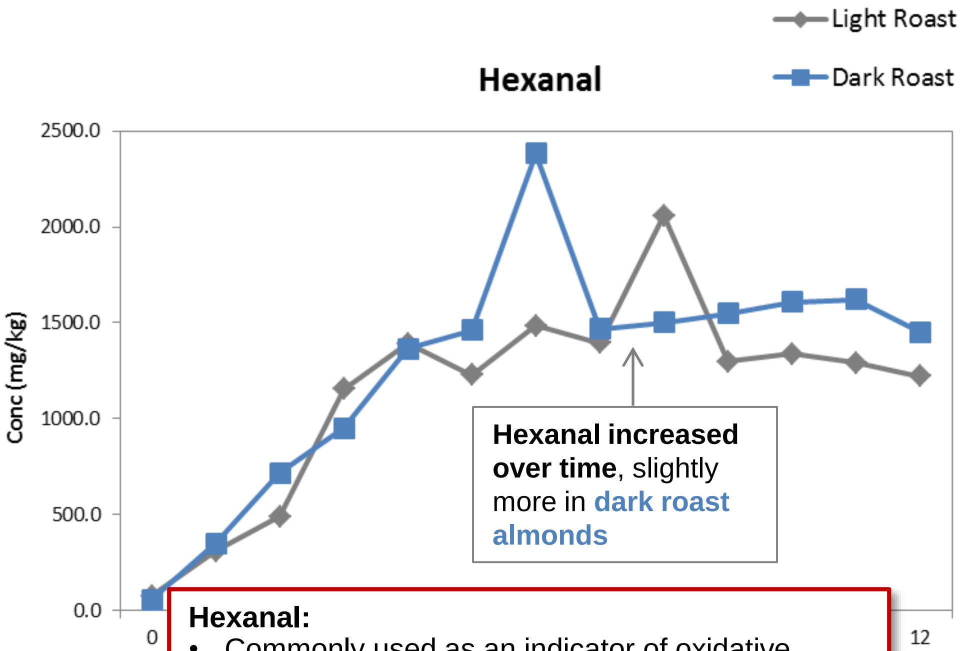
- <5.0 is a recommended industry rejection standard.
- None of the light roast samples were greater than 5.0, despite being perceived as rancid at the later time points.
- PV peaked at 9 months for dark roasted samples, while rancidity continued to increase.

Conjugated Dienes:

- No common industry standard currently exists for CD.
- There was very little change in light roast samples, despite being perceived as rancid at the later time points.

Analytical Measures – Lipid Oxidation Breakdown (Con't)





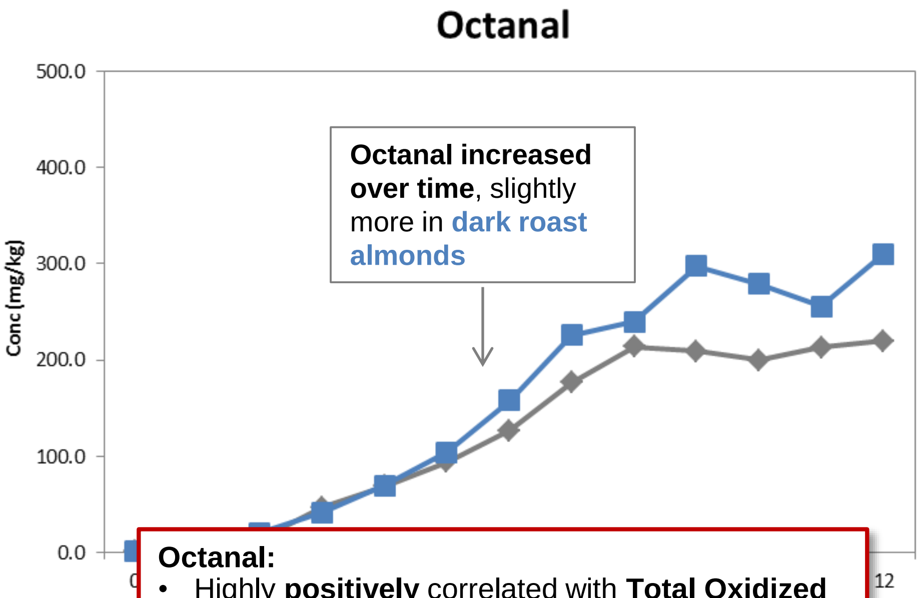
Free Fatty Acids:

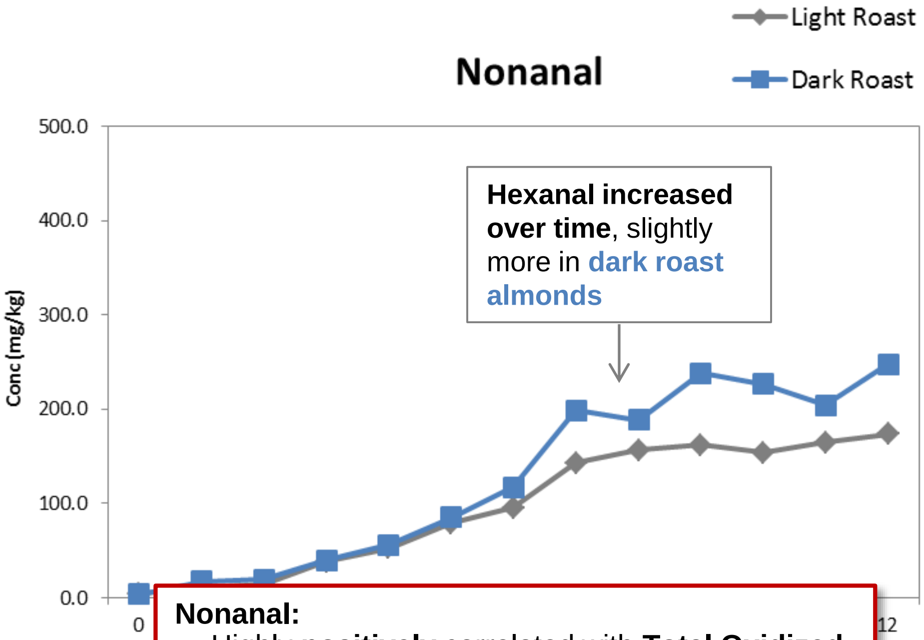
- <1.5% Oleic is a recommended industry rejection standard.
- No samples were greater than 1.5% Oleic, despite being perceived as rancid at the later time points.

Hexanal:

- Commonly used as an indicator of oxidative rancidity in industry (currently no standard).
- Highly **positively** correlated with **Total Oxidized flavor**.
- **Negatively** correlated with liking for **Total Respondents**, and **Clusters 1** and **3**.

Analytical Measures – Lipid Oxidation Breakdown (Con't)





Octanal:
- Highly **positively** correlated with **Total Oxidized flavor**.
- **Negatively** correlated with liking for **Total Respondents**, and **Clusters 1** and **3**.
- Not previously been reported as an oxidative indicator in nuts.

Nonanal:
- Highly **positively** correlated with **Total Oxidized flavor**.
- **Negatively** correlated with liking for **Total Respondents**, and **Clusters 1** and **3**.
- Not previously been reported as an oxidative indicator in nuts.

Key Findings – Analytical Measures

- Current **industry indicators of oxidation did not do a great job** at predicting sensory rancidity and consumer liking.
  - For light roast samples, Peroxide values were less than 5.0 mEq and Conjugated dienes had very little change, despite being perceived as rancid at the later time points.
  - All almond samples had Free Fatty Acid levels less than 1.5% Oleic, despite being perceived as rancid at the later time points.
- **Rancidity** attributes were related to the volatile compounds **hexanal, heptanal**, **octanal** and **nonanal.**
  - These compounds were negatively correlated to consumer liking.
  - Heptanal, octanal and nonanal have not previously been reported as an oxidative indicator in nuts.
- **Clean Nutty** and **Clean Roasted** attributes were related to **2-methylbutanal**, **3-methylbutanal** and **2,5-dimethylpyrazine**.
  - These compounds were positively correlated to consumer liking.

Key Findings – Descriptive & Consumer Testing

- **Storage time** had a **strong influence** on consumer liking, as well as almost all descriptive attributes and headspace compounds in both light and dark roasted almonds.
- In contrast, **degree of roasting did not affect** consumer liking and only influenced approximately half the descriptive attributes and ~75% of the headspace compounds significantly.
- Oxidative flavor changes tended to **peak after 6 months at 102°F** for **light roasted samples**, and **8 months at 102°F** for **dark roasted samples** and remained stable for up to 12 months of storage.
- Three clusters of consumers had different liking patterns, however they **all preferred the fresher almond samples**, regardless of roast level.
  - Total Respondents and Clusters 1 and 3 liking were negatively correlated with lipid oxidation by-products, however, Cluster 2 consumers were less offended by oxidative notes.
  - Cluster 3 consumers preferred light roast almonds more than dark roast samples, which may be due to a negative correlation with bitter taste.

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california almonds
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CHEMICAL DRIVERS FOR NUT QUALITY DETERIORATION

Ronald B. Pegg

Department of Food Science & Technology

December 8, 2016

UNIVERSITY OF GEORGIA

Susceptible to …

- Microbial spoilage … mold

- Oxidation

- Textural degradation

Solutions…

- Microbial spoilage … mold → Reduce moisture content to 4-6%
- Oxidation → Nitrogen flush, vacuum package
- Textural degradation → Protect against too high/too low RH

What is needed to achieve this?

$

Factors that Affect Shelf Life

- Almonds are relatively low-moisture, high-oil-containing nuts with a long shelf life when properly handled.
- Almond quality and shelf life can be influenced by three general factors: the *product characteristics*, the *environment* during distribution and storage, and the *package*.
- These factors interact in many ways to influence almond quality and to impact shelf life.
- Shelf life guidance for almonds must specify the product and the storage conditions.

Major Factors Influencing Almond Quality and Shelf Life (ABC 2014)		
Product characteristics	Environment	Package
Composition; Water activity; Form.	Temperature; Humidity; Oxygen; Processing conditions; Insects, pests, microorganisms.	Physical protection; Moisture barrier; Gas barrier.

ABC Recommendations – Storage Conditions and Handling Practices

- Storage for all almond forms in cool and dry conditions (<50°F/<10°C and <65% relative humidity) is recommended.
- The optimal goal of the recommended storage conditions is to maintain <6% MC, which helps preserve shelf life.
- A cool temperature of <50°F/<10°C is optimal, but a higher temperature that does not stimulate insect activity may work as well to control moisture migration (and also minimize lipid oxidation).
- Almonds are a shelf-stable nut that can have more than two years of shelf life when stored at the recommended conditions.

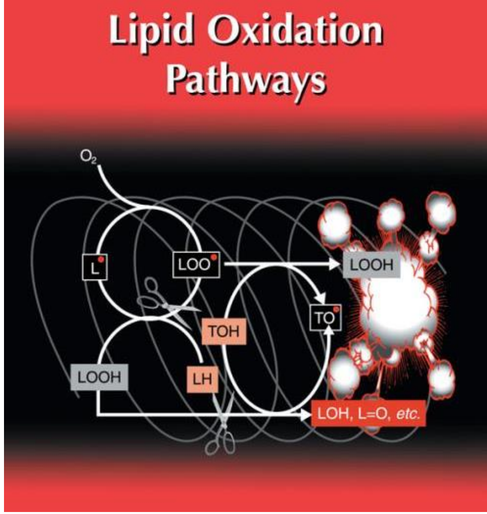
High Quality → Moisture <6%, a_w 0.25-0.35, Free fatty acids <1.5%, PV <5 meq/kg

- Rancidity is a general term for the unacceptable off-flavors and off-odors that eventually develop as fats breakdown through various reactions.
- Before, what we call, true rancid notes develop, we often sense cardboardy, painty or stale notes associated with the product … or sometimes desirable flavor notes are lost or are masked by developing secondary products of lipox.
- This is oxidative rancidity.
- Hydrolytic rancidity occurs when fatty acids are released from fat triglycerides (by naturally occurring enzymes) and are now considered free.
- Free fatty acids are more susceptible to oxidation than triglycerides. (*The presence of moisture enhances this type of rancidity*).

Expeller-pressed Oil

- Oil is recovered with a Carver press

Lipid Oxidation



- Lipid oxidation (lipox) is a complex series of undesirable reactions that cause the breakdown of fats and oils.

- In almonds, the oxidation reactions lead to a loss of quality as the nuts develop "rancid" flavors and odors.

- During lipox, O_2 reacts spontaneously with the fatty acids in fats to form primary breakdown products (e.g., peroxides, conjugated dienes) and, as oxidation progresses, secondary products (e.g., volatile aldehydes, ketones) are formed that give rise to off-flavors and off-odors.

- Oxidation can be measured by testing for the presence or accumulation of one or more of these primary and secondary products.

Initiation

$$LH \xrightarrow{\text{initiator}} L^{\bullet} + H^{\bullet}$$

Propagation

$$L^{\bullet} + O_2 \longrightarrow LO_2^{\bullet}$$

$$LO_2^{\bullet} + LH \longrightarrow LO_2H + L^{\bullet}$$

Termination

$$L^{\bullet} + L^{\bullet} \longrightarrow L{-}L$$

$$L^{\bullet} + LO_2^{\bullet} \longrightarrow LOOL$$

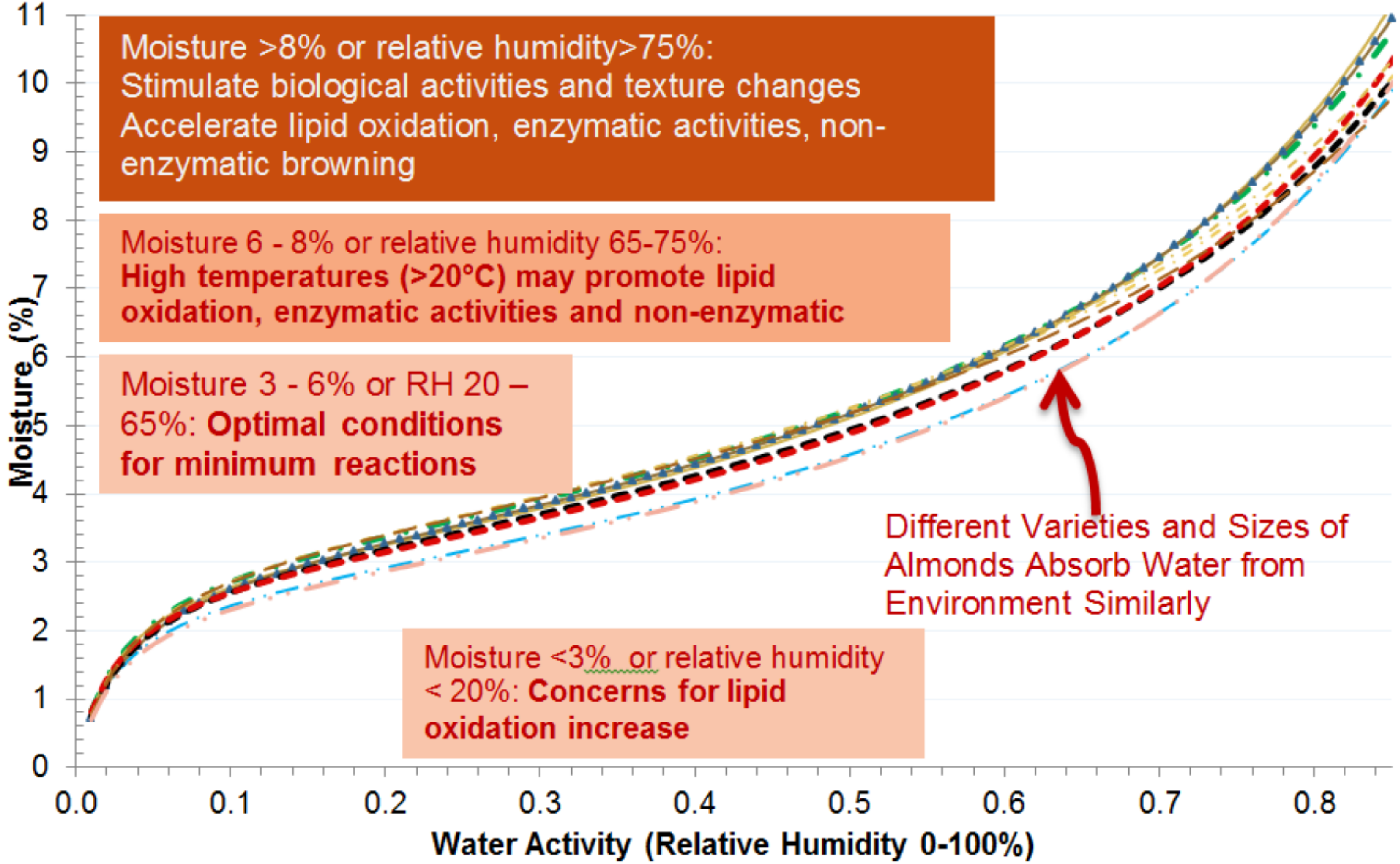
Hydroperoxide - unstable

LOOH → aldehydes, ketones, alcohols, hydrocarbons

- High storage temperatures, increased moisture, light, and some metal ions (e.g., iron) may promote lipid oxidation in almonds and reduce shelf life.

- Processing also makes almonds more susceptible to oxidation — blanching and cutting increase the surface area exposed to O_2, and roasting changes the almond microstructure which allows more oil within the cells to be exposed to O_2.

- Water activity (a_w) level affects lipid oxidation rates — lipid oxidation is typically lowest when almond aw is ~0.25 to 0.35 (~3–4% moisture content), and increases above or below that a_w range.


Moisture >8% or relative humidity>75%:
Stimulate biological activities and texture changes
Accelerate lipid oxidation, enzymatic activities, non-enzymatic browning
Moisture 6 - 8% or relative humidity 65-75%:
High temperatures (>20°C) may promote lipid oxidation, enzymatic activities and non-enzymatic
Moisture 3 - 6% or RH 20 – 65%: Optimal conditions for minimum reactions
Different Varieties and Sizes of Almonds Absorb Water from Environment Similarly
Moisture <3% or relative humidity < 20%: Concerns for lipid oxidation increase
Moisture (%)
Water Activity (Relative Humidity 0-100%)
0
1
2
3
4
5
6
7
8
9
10
11
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8

Peroxide value (PV)

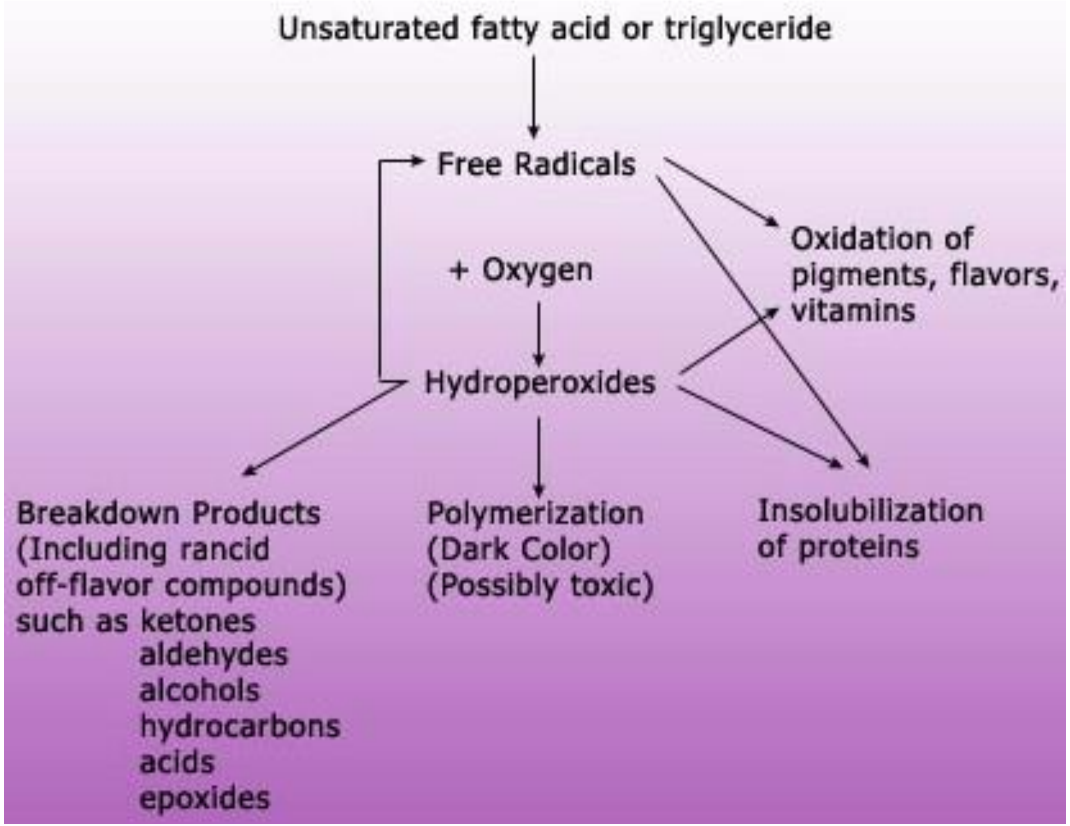
- Peroxides (LOOH) can be measured by techniques based on their capability to liberate iodine (I_2) from potassium iodide (KI). Their content is usually expressed in terms of milliequivalents of active O_2 per kilogram of fat.

- Although the PV is applicable for following LOOH formation at the early stages of oxidation, it is, nevertheless, highly empirical. The accuracy is questionable, the results vary with details of the procedure used, and the test is extremely sensitive to temperature changes.

- During the course of oxidation, peroxide values reach a peak and then decline.

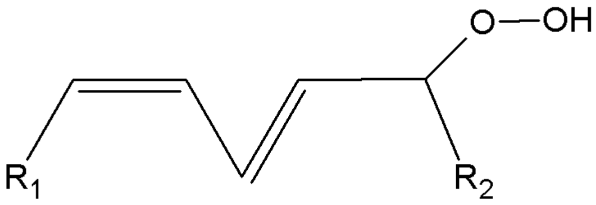
$$LOOH + 2H^+ + 2KI \rightarrow I_2 + LOH + H_2O + 2K^+$$

$$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI \text{ (starch indicator)}$$



As oxidation progresses, PV will peak and then decline as the peroxides quickly break down, so a low PV is not always a sign of freshness or good quality.

Conjugated Dienes (CDs)



- CDs are carbon compounds (with 2 double bonds separated by a single bond) produced when PUFAs break down during the initial stages of lipid oxidation.

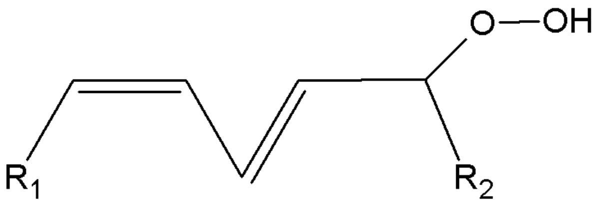
- They give rise to an absorption peak at ~233 nm in the UV region.

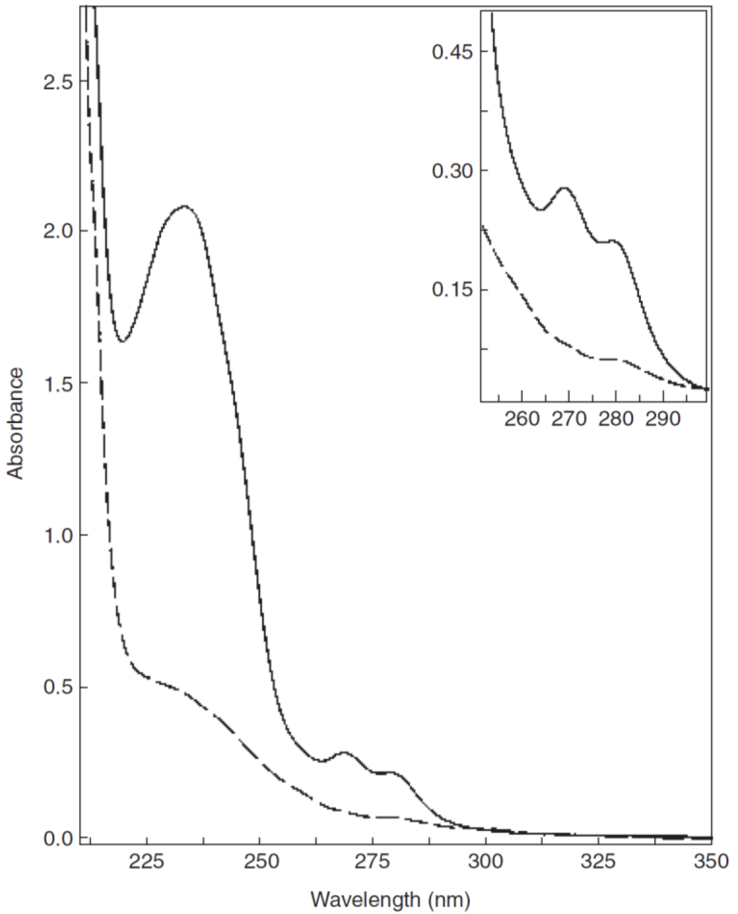
- In almonds they arise predominantly from rearrangement of the double bonds of linoleic acid.

- An increase in UV absorption reflects theoretically the formation of primary oxidation products in fats.

- Good correlations between CDs and PVs have been found in edible oils … BUT these tend to be oils rich in PUFAs.

- In almonds, CDs are generated as a result of oxidation of linoleic acid (~10-18%)
- PVs develop from all mono- and polyunsaturated fatty acids undergoing oxidation.

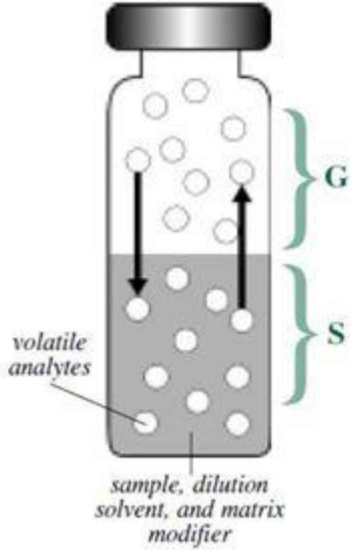




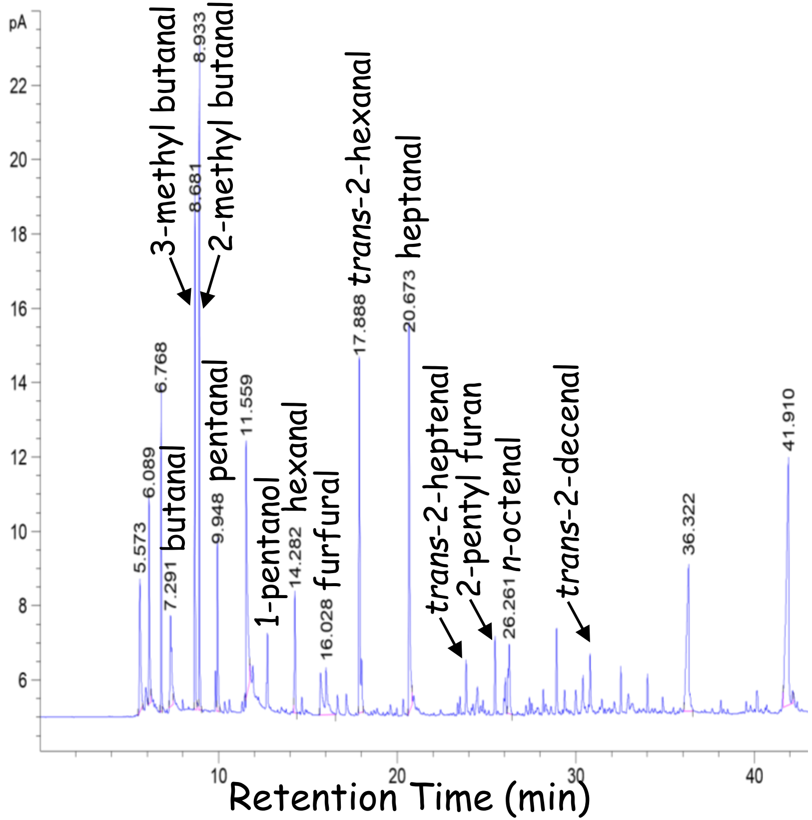
Volatiles Reaching our Nose

- Hexanal is an important secondary product of lipox of linoleic acid.
- It is a volatile aldehyde with a “fatty, green, grassy” note.
- It forms as almonds oxidize during storage; it can be measured and used as an indicator of oxidative rancidity.
- Other volatile compounds exist in raw, roasted, and stored almonds.
- Emerging research is showing that selected volatiles other than hexanal might be sensitive markers of early oxidation in almonds.

Headspace – Solid Phase Microextraction – Gas Chromatography – Mass Spectrometry Analysis



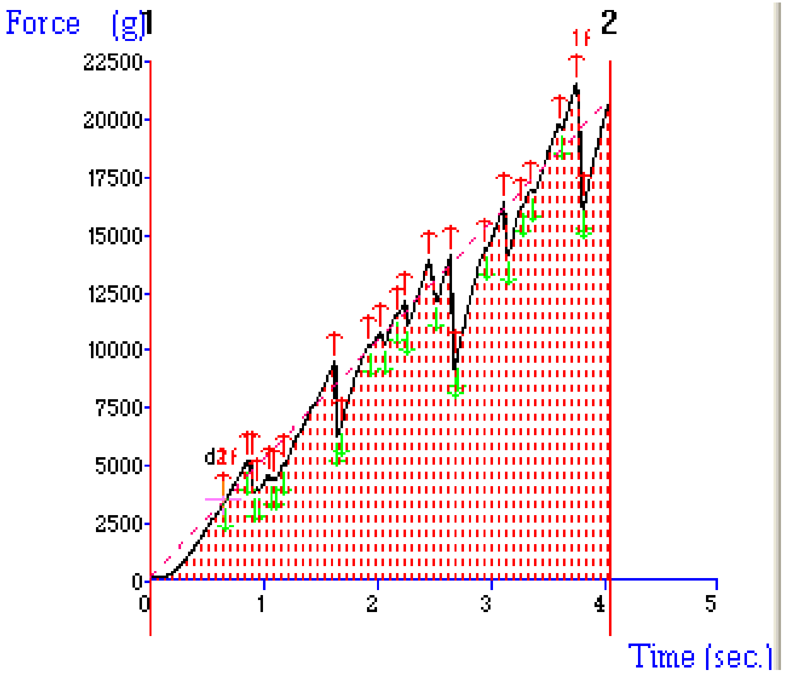
12 mo - Roasted Almond Sample in a PP Bag @35 °C/65% RH



Method for Texture & Sound Analysis

- Texture analysis can be performed using a Texture Technologies TA-XT2i texture analyzer.
- The fracturability of whole almonds can be evaluated using the texture analyzer with a compression disk.
- The audio can be recorded during texture analysis and analyzed to provide a more complete fracturability profile.

Description of textural factors extracted from the force/displacement curves



Parameter	Textural association
Number of force peaks (FP)	Crispness Brittleness
Average gradient (AG)	Chewiness
Average drop-off (AD)	Crispness Brittleness

Study Design

The effects of environmental storage conditions on roasted and raw almond quality characteristics were investigated with an incomplete factorial design (n = 25) over 16-mo and 24-mo, respectively.

Raw Only
UCs
T and %RH

- Ambient RH
  - 4 ^{o}C
- 50% RH
  - 15 ^{o}C
  - 25 ^{o}C
  - 35 ^{o}C
- 65% RH
  - 15 ^{o}C
  - 25 ^{o}C
  - 35 ^{o}C

Raw and Roasted
PPBs
T and %RH

- Ambient RH
  - 4 ^{o}C
- 50% RH
  - 15 ^{o}C
  - 25 ^{o}C
  - 35 ^{o}C
- 65% RH
  - 15 ^{o}C
  - 25 ^{o}C
  - 35 ^{o}C

Roasted only
HBBs
T (No %RH)

- 4 ^{o}C
- 15 ^{o}C
- 25 ^{o}C
- 35 ^{o}C

Samples were analyzed at 2-mo intervals until consumer rejection or conclusion of the study, and compared to baseline values.

Rejection timeline for raw and roasted almond samples

Rejection timeline (mo) for all samples

A (Raw PPB)				35/65			35/50		25/65	15/65
B (Raw UC)		35/65		35/50 4/90			25/65 15/65		25/50 15/50	
Mo	**0**	**2**	**4**	**6**	**8**	**10**	**12**	**14**	**16**	**>> 24**
C (Roast PPB)							35/65	35/50	25/65	
D (Roast HBB)									35	

Shelf-life:
HBB >> PPB > UC
At 35 °C, roasted > raw

Samples that <u>were not</u> rejected

Sample	Rejection Rate
A 25/50	22.5%
A 15/50	10.0%
A 4/90+	12.7%
C 25/50	18.6%
C 15/65	20.6%
C 15/50	8.9%
C 4/90	9.8%
D 25	2.9%
D 15	7.9%
D 4	5.9%

Summary

<u>Chemical</u>

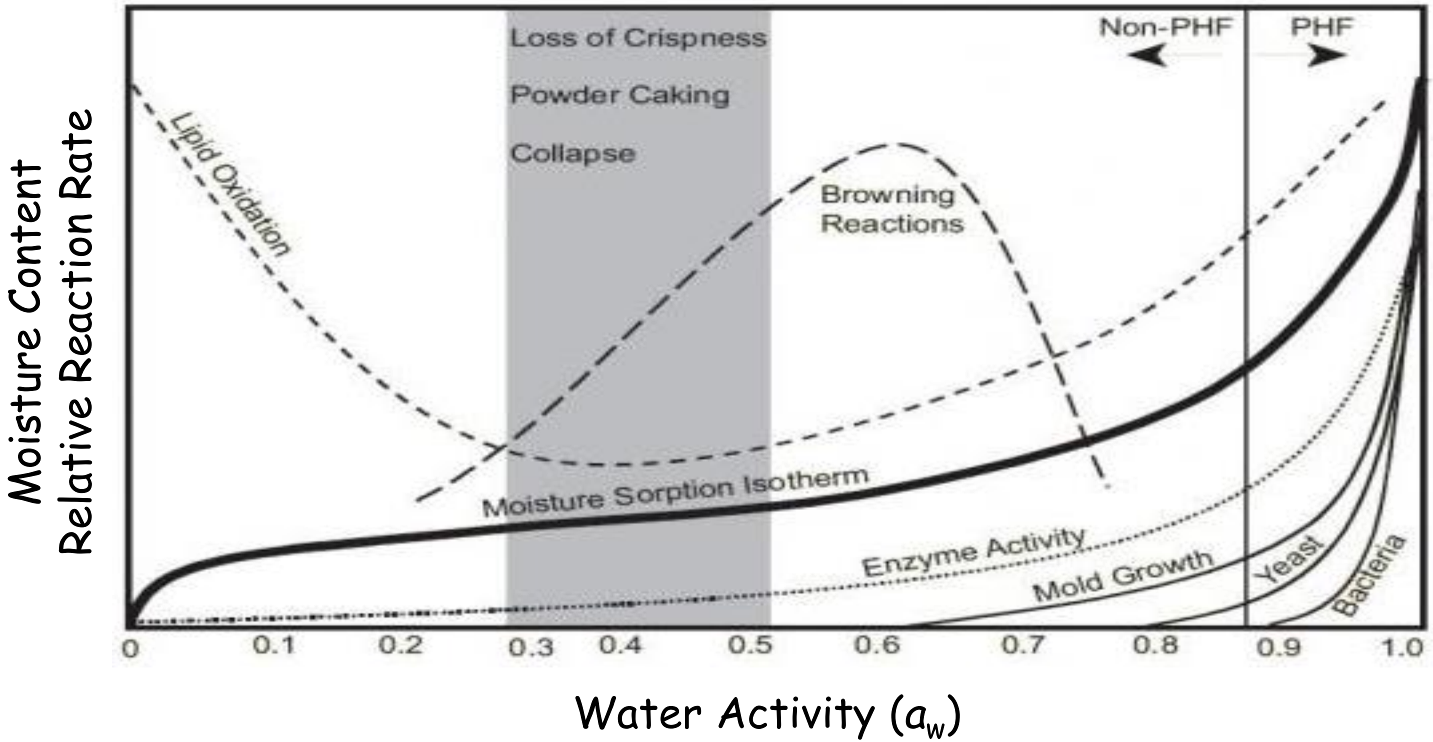
- ↑ values → ↓ overall acceptability and ↑ rejection rate
- Univariate analysis revealed …
  - Overall acceptability: a_w > FFAs > PVs
  - Rejection rate: FFAs > PVs

<u>Textural</u>

- ↑ FPs, ADs → ↑ overall acceptability and ↓ rejection rate
- ↑ AGs → ↓ overall acceptability and ↑ rejection rate
- Univariate analysis revealed …
  - FPs > ADs

Lipid oxidation is lowest at a_ws of ~0.2 to 0.4

Water Activity (a_w) – Stability Diagram



source: www.aqualab.com

Overall Study Conclusions

- For both raw and roasted almonds, an interaction of chemical and textural parameters predicted shelf life.
- Both temperature and humidity are important to regulate during storage …
  - Almonds stored at higher Ts degraded more rapidly than counterparts at lower Ts.
  - Almonds stored at higher %RH degraded more rapidly than counterparts at lower %RH
- Using univariate analysis, a_w and MC were determined to be the better predictors of overall acceptability and rejection rate.

Acknowledgments

Almond Board of California

Guangwei Huang

Karen Lapsley

William Kerr,
University of Georgia

The Role of Packaging and Storage Conditions on the Shelf-life of Almonds

William Kerr
Professor, Department of Food Science & Technology
Director, Food Product Research and Development Laboratory
University of Georgia, Athens GA

Why Packaging?

- Portion control
- Protect product from outside world
- Marketing
- Product information
- Ingredient, nutritional labeling, traceability
- **Protect from quality changes**

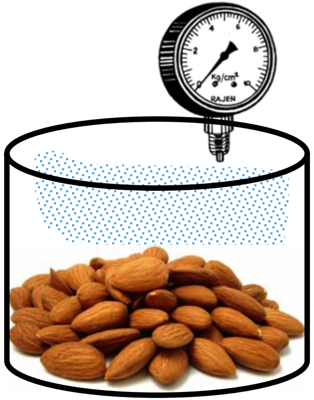
Almonds – What Can Go Wrong

- Many chemical changes can occur during storage
- Lipid oxidation
- Loss of aromatic compounds that contribute to flavor
- Loss of nutrients
- Changes in color
- Changes in texture

A Good Place to Start-The Role of Moisture

- The rate of chemical reactions in foods depends on temperature and moisture

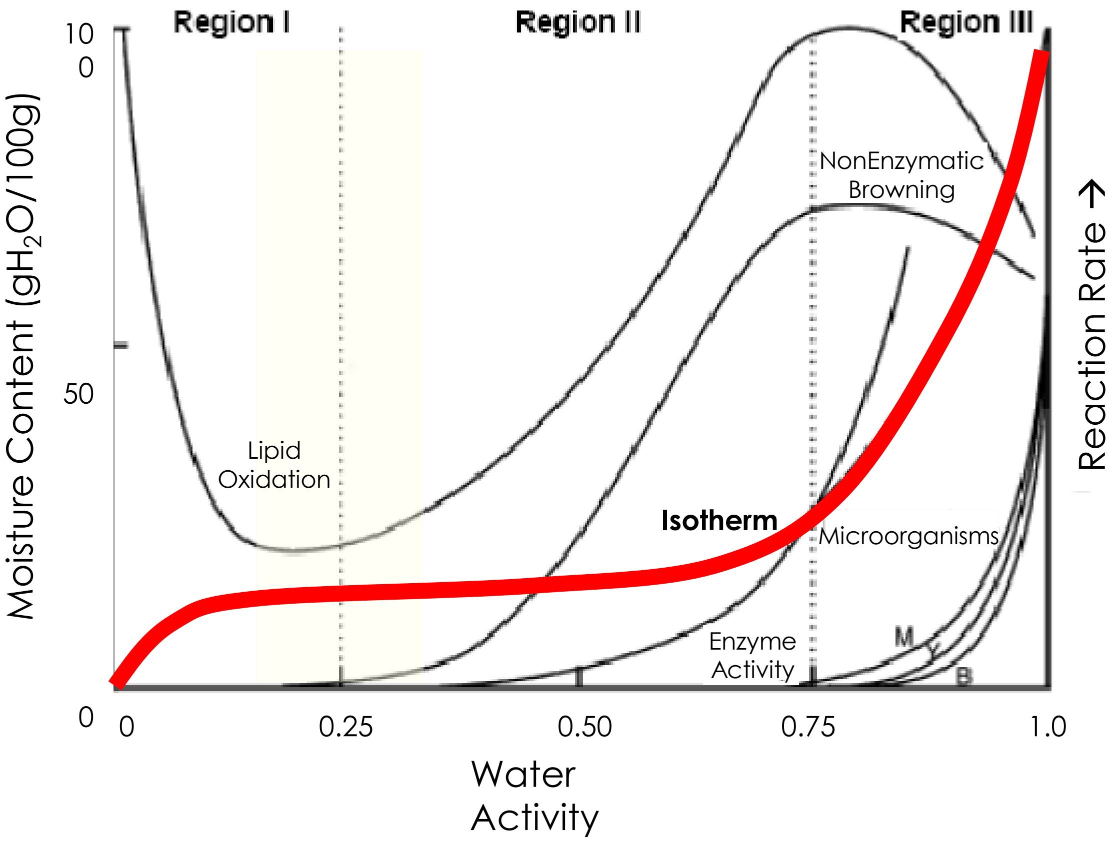
Moisture Content
Weight of water in food compared to total weight
Range: 0 to 100 $gH_2O/100g$



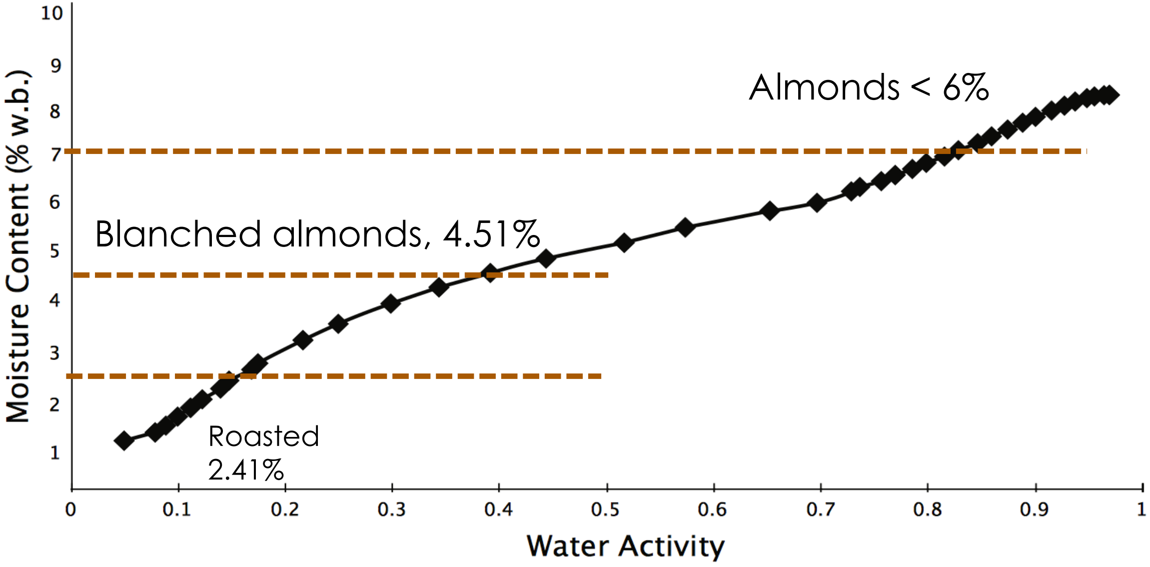
Water Activity
Related to number of water molecules
Measured by vapor pressure
Range: 0 to 1

- Many chemical reactions need water to proceed
  -Vitamin C loss, enzymatic browning, non-enzymatic browning
- Lipid oxidation is tricky. Sometimes too little water can be a problem.
- Water activity seems to be a better predictor for chemical reactions
- Water activity is the basis for several food regulations e.g.
- "*If the water activity of food is controlled to 0.85 or less in the finished product, it is not subject to the regulations of 21 CFR Parts 108, 113, and 114*."

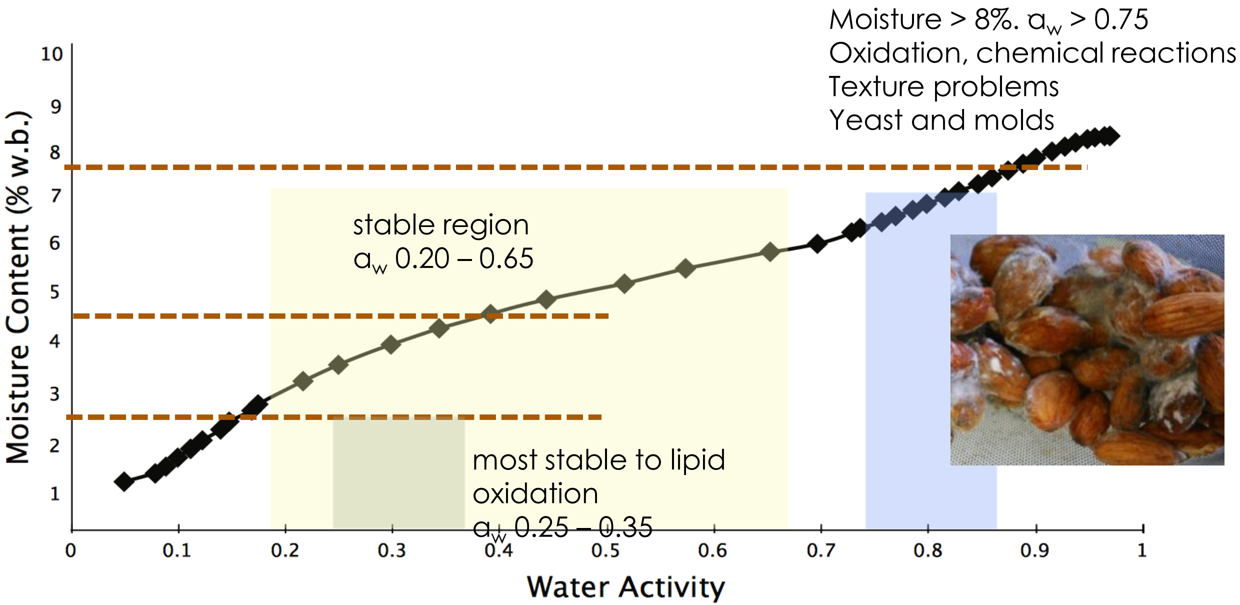
Food Stability Map



Moisture Isotherm – shows how moisture content varies with water activity

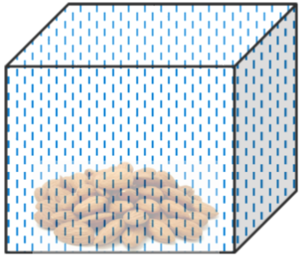


Moisture Isotherm – shows how moisture content varies with water activity

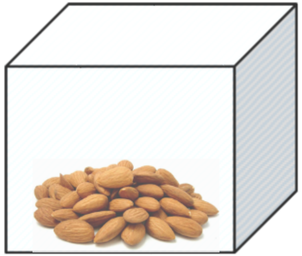


Storing at different relative humidity causes sample to lose or pick up moisture

Original Sample
a_w = 0.25

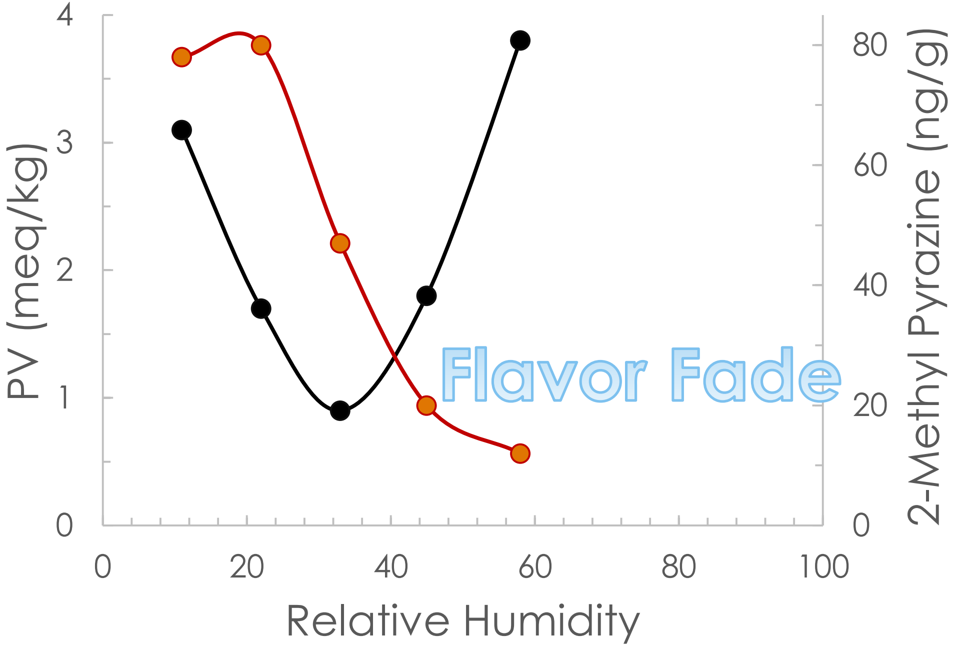


At 65% RH, sample picks up moisture until a_w = 0.65



At 15% RH, sample loses moisture until a_w = 0.15

Peroxide Values and 2-Methyl Pyrazine at 12 wks- Peanuts

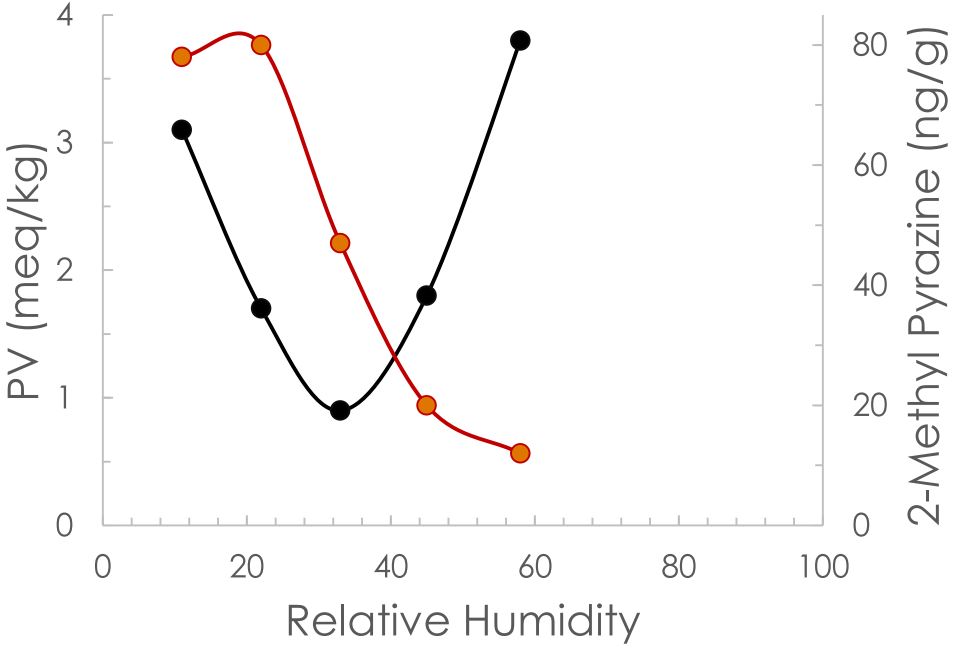


Abegaz, 2003. *Role of moisture and ingredients in peanut quality*.

Perception of oxidation may increase as roasted flavors decrease

a_w =	0.22	0.33	0.45
Poasted Peanut	42.9	37.5	27.1
Rancid	11.4	11.7	15
Cardboard	16.2	17.7	22

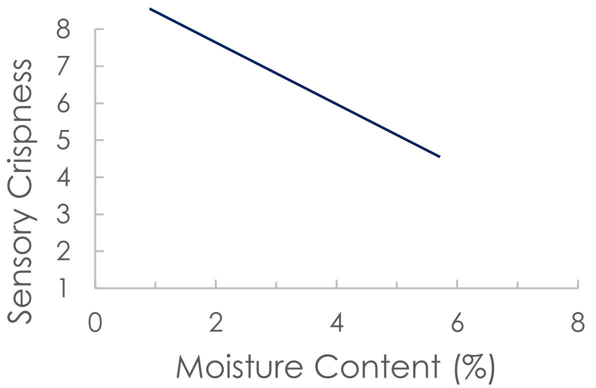
Descriptive Panelist Scores



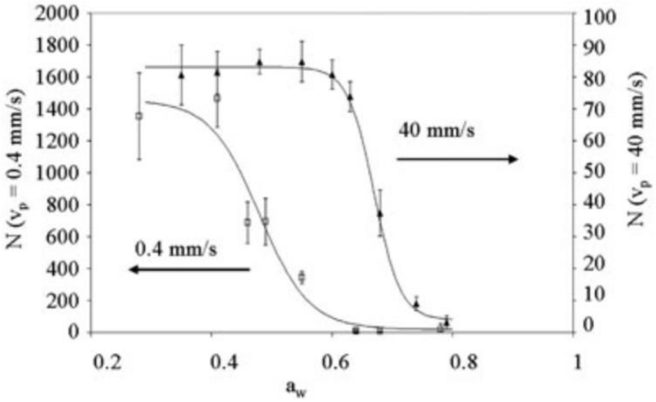
Abegaz, 2003. *Role of moisture and ingredients in peanut quality*.

Texture is Also Affected by Moisture

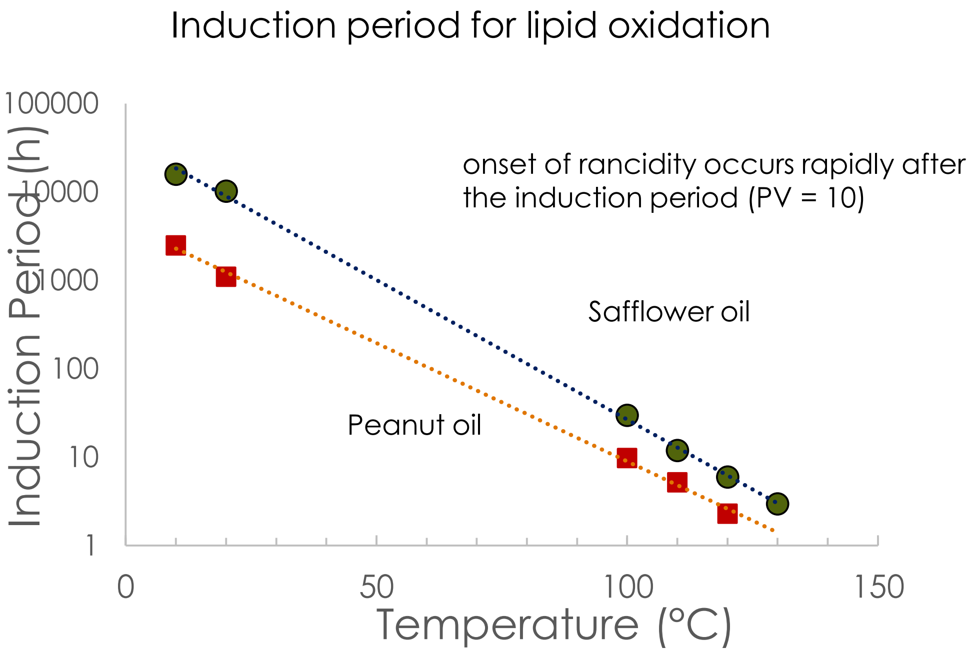
Peanuts: *Baker et al* 2002



Dry Biscuit: *Castro-Prada et al* 2008



Most chemical reactions are faster at higher temperatures



Min and Boff. 2002. *Lipid oxidation of edible oil*. Ch 11 in Food Lipids.

Q_{10} – How much faster a reaction occurs when temperature is increased by 10°C

	Q_{10} (5°C)	Q_{10} (20°C)	Q_{10} (40°C)
Enzymatic reactions	1.87	1.76	1.64
Lipid oxidation, nutrient loss	3.51	3.10	2.70
Nonenzymatic browning	6.58	5.47	4.45

After Taoukis et al. 2014. Reaction kinetics. *Food Engineering Handbook*.

Oxygen Also Matters

- Lipid oxidation (and some other reactions) need O_2 to proceed

Initiation: $RH \longrightarrow R\cdot$

Propagation: $R\cdot + O_2 \rightleftarrows ROO^\bullet$

$ROO^\bullet + RH \longrightarrow ROOH + R\cdot$

Termination: $R\cdot + R\cdot \longrightarrow RR$

$R\cdot + ROO\cdot \longrightarrow ROOR$

$ROO^\bullet + ROO\cdot \longrightarrow ROOR + O_2$

Tools at Hand

- Get the samples dry
- Control the storage humidity
- Control the temperature
- Limit oxygen
- Packaging

ABC Technical Information Kit

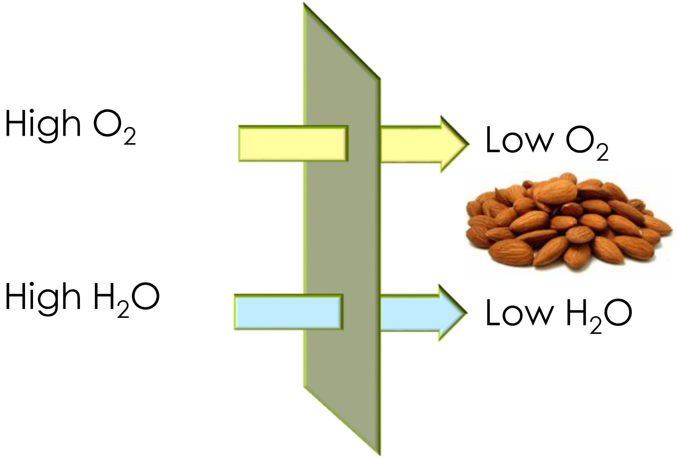
- Store under cool and dry conditions (<10°C/50°F and <65% relative humidity)
- Keep moisture at 6% or less
- Avoid exposure to strong odors. Protect from insects and pests
- Protect roasted products from oxygen. Nitrogen flushing and/or vacuum packaging are options.
- Whole natural almonds can be stored for about 2 years if kept at (<5°C/41°F and <65% RH)
- Rotate stock to optimize shelf life

COMMON PACKAGING FOR CONTAINER SHIPMENT		
PRODUCT	VOLUME	CONTAINER
Natural Almonds	25 lbs 50 lbs 2200 lbs	Cartons Fiber bulk bin
Cut Almonds	25 lbs 1000 lbs 1500 lbs	Cartons with plastic liner Fiber bulk bin with plastic liner
Roasted Almonds	25 lbs	Cartons with vacuum-packed foil bags
In-Shell Almonds	50 lbs	Sacks

Source: ABC Technical Kit

The Role of Packaging in Promoting Shelf Life

- Packaging can limit the uptake of moisture and oxygen



The rate of transfer depends on key package properties

- Water vapor transmission rate (WVTR)

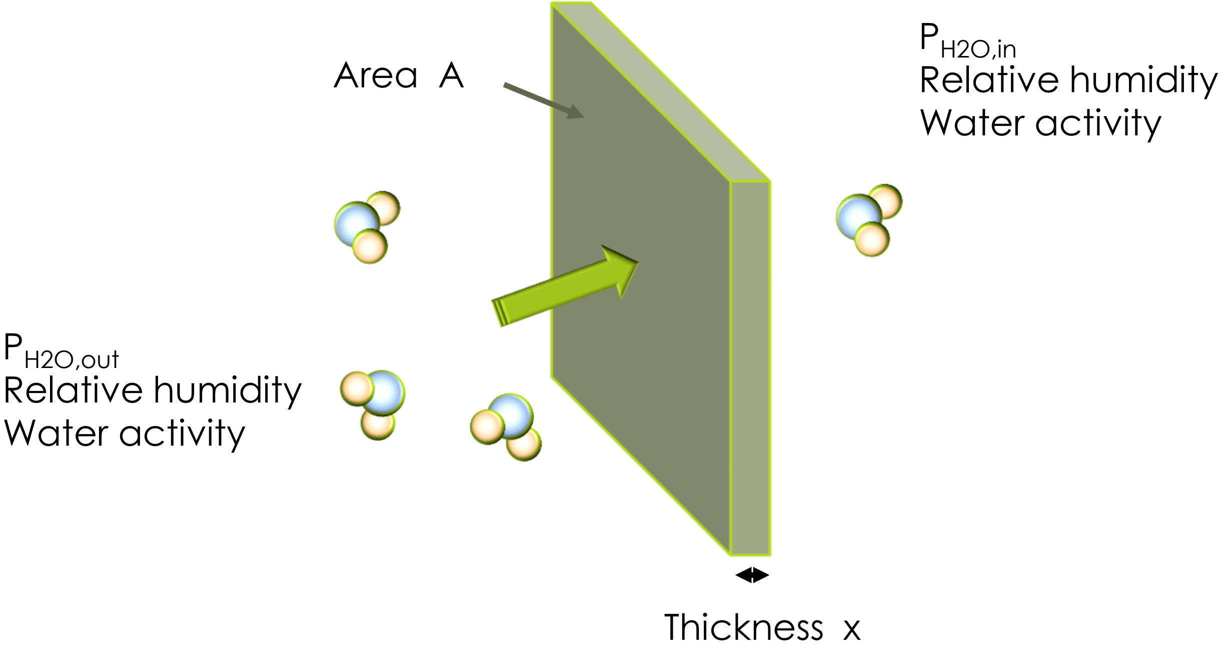
$$WVTR\left(\frac{gH_2O}{m^2day}\right) = \frac{kA(P_{H2O,out} - P_{H2O,in})}{x}$$

$$OTR\left(\frac{cc\ O_2}{m^2\ day\ atm}\right) = \frac{KA\ (P_{O_2,out} - P_{O_2,in})}{x}$$

- Oxygen transmission rate (OTR)

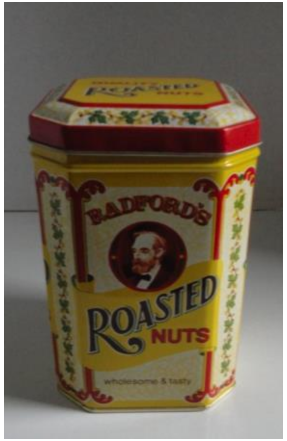
$$OTR\left(\frac{cc\ O_2}{m^2day\ atm}\right) = \frac{KA(P_{O2,out} - P_{O2,in})}{x}$$

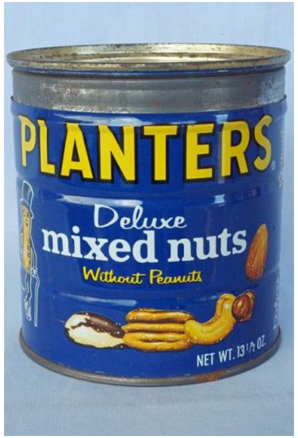
$$WVTR\left(\frac{gH_2O}{m^2day}\right) = \frac{kA(P_{H2O,out} - P_{H2O,in})}{x}$$



Some Possibilities

- ***Metal Cans***: made from tin or aluminum.
- May be coated with laquer.
- Excellent prevention of air, moisture and microorganisms
- Cost and weight can be issues





- ***Glass***: Excellent prevention of air, moisture and microorganisms
- Cost, added weight, breakability are issues

- ***Paper, board and foil***: relatively cheap, light packaging
- Board may be coated with polyethylene to limit interaction with contents
- Cardboard box may support plastic liner
- Foil lining can help limit H_2O and O_2

Flexible packaging

- ***Polythene***: low density for film wrapping. Some resistance to moisture transfer. High density PE for greater durability.
- ***Polypropylene***: can form clear bottles that can hold hot product
- ***Polyamide*** (nylon)**:** good oxygen barrier. Useful for vacuum packs.
- ***Polyethlene terephthalate*** (PET):can form rigid bottles with heat resistance (CPET)
- ***Polystyrene***: expanded polythene used for trays and insulated containers.
- ***Others***: butylated polypropylene (BOPP), ethylene vinyl alcohol copolymer

PE films

Woven PE

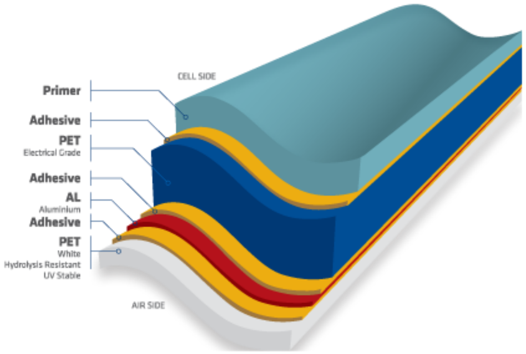
PS trays

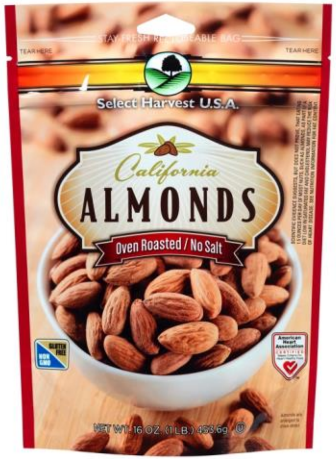
PP containers

Combinations of materials can be useful

8-mil PET Prima Exo-Shell/70-ga BOPP/ink/adhesive/Metallized BOPP/adhesive/BOPP

Laminates combine performance of different materials





- Plastic layers provide strength, flexibility, printability
- Foil layers limit transfer of H_2O and O_2

Material	WVTR (g/m^2 24 h)	OTR (cc/m^2 24 h)	Light Barrier
Metal can	0	0	100%
Glass jar	0	0	<5%
Foil	0	0	100%
Al laminate	<1	<1	100%
HDPE	145	53,000	<5%
LDPE	560	178,000	<5%
PP	260	81,000	<5%
PET	800	1500	<5%
Cellophane	137,000	4500	<5%

Some Studies at UGA

- Almonds stored in different packages at temperatures between 4 and 35°C
- Relative humidity between 50 and 65%

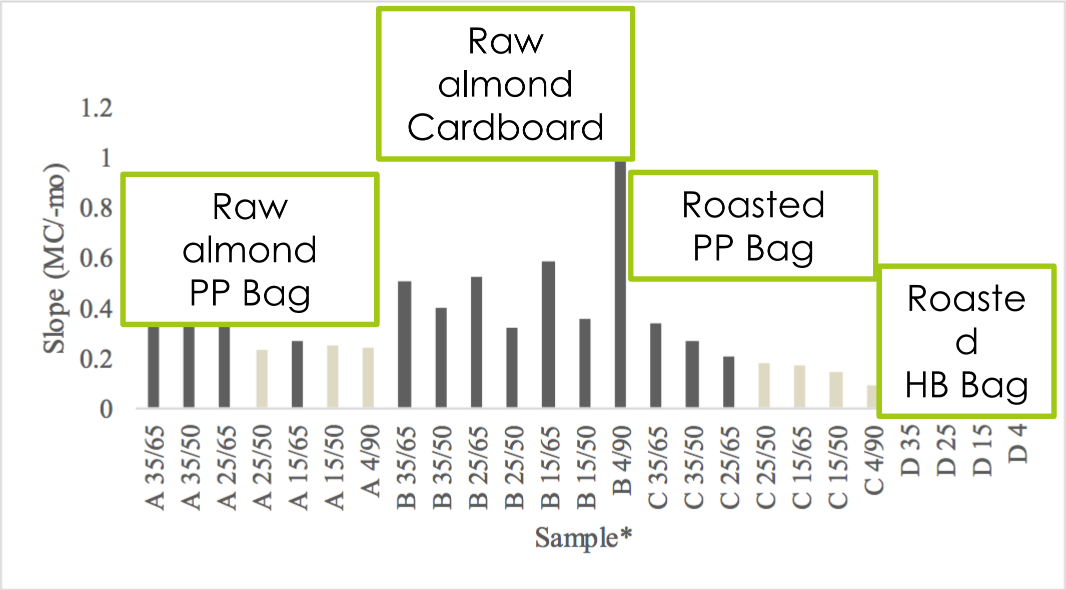
Table: Packaging of Nonpareil Raw and Roasted Almonds

	Raw	Roasted
Cardboard Box (600 ± 5 g)	X	
Polyethylene Bag (300 ± 5g)[a]	X	X
High Barrier Bag[b,c]		X

[a]Bags were flushed with food-grade N_2 and sealed. Initial O_2 level was < 0.5%.

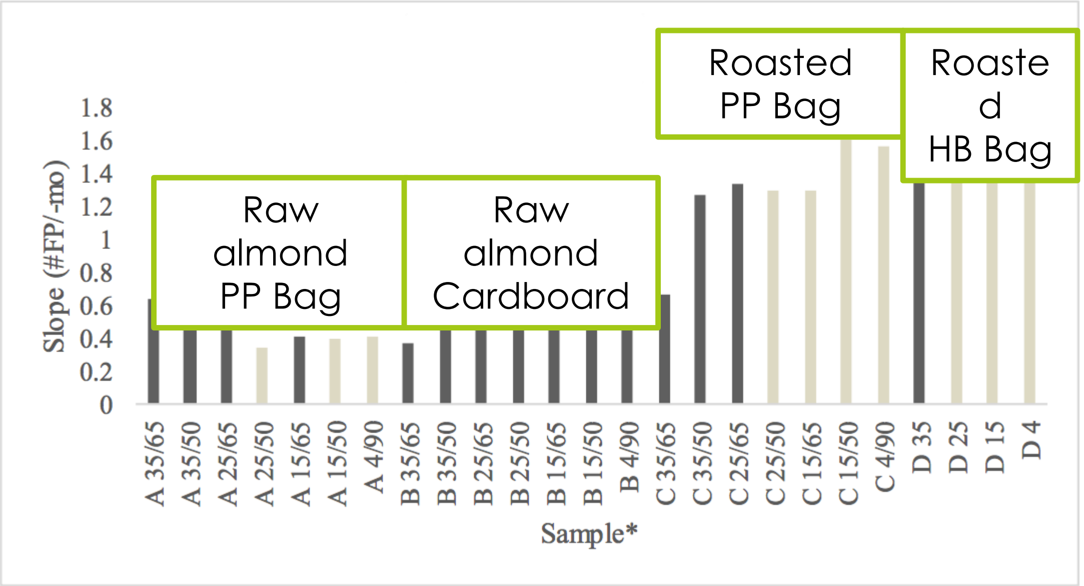

TEMPERATURE
24.8
25.0
HUMIDITY
50.4
65.0

Package makes a big difference in the rate of moisture pickup



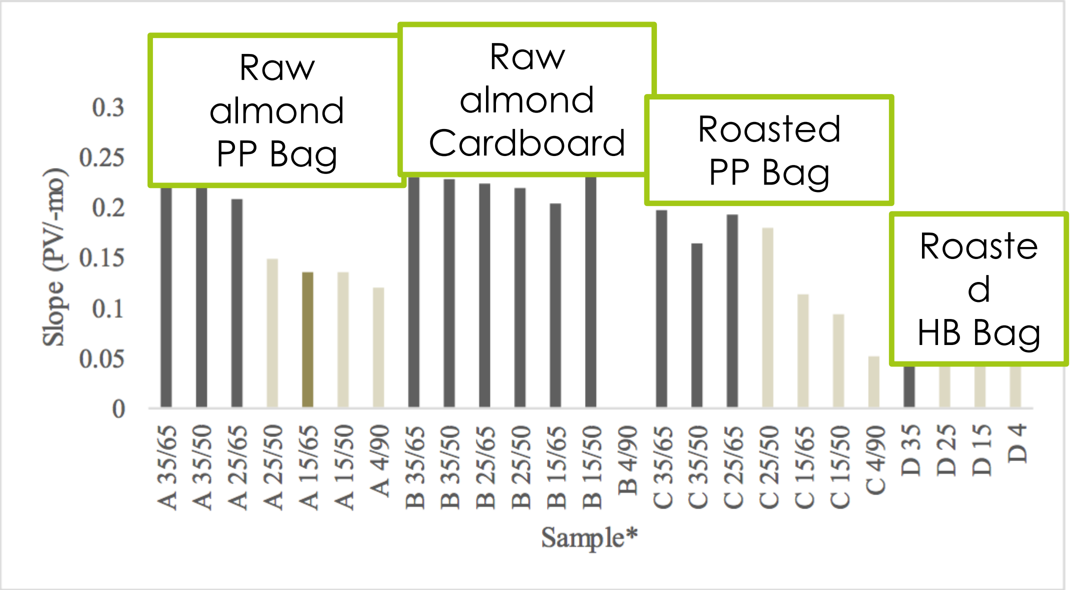
- Laminate pouch (HB) helps limit moisture pickup
- Cardboard box does not prevent moisture pickup. RH is important.
- PP provides limited protection.

Crunchiness as measured by number of fracture events



- Roasted are drier. Start with higher crunchiness.
- HB bags give most protection for roasted.
- PP bags okay if low temperature and humidity.

Peroxide values measure lipid oxidation



- Greatest lipid oxidation for raw samples in cardboard box. RH not important.
- HB bag helps protect against oxidation.
- PP bag provides some protection for roasted nuts.
- Oxidation high in raw nuts in PP bags and high temperature and humidity.

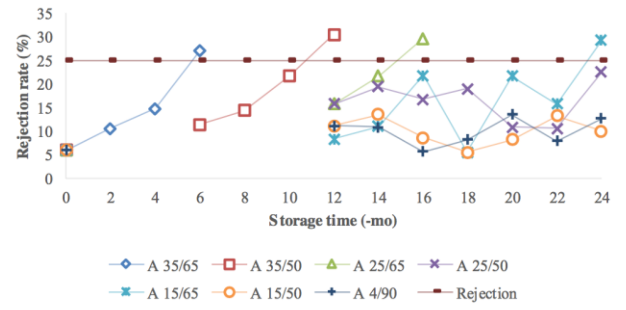
Sensory Tests

- Within 10 months, 4 samples had failed (>25% rejection)
  - Raw, 2 mo, cardboard box, 35°C/65% RH
  - Raw, 6 mo, cardboard box, 35°C/50% RH
  - Raw, 6 mo, cardboard box, 4°C
  - Raw, 6 mo, polyethylene bag, 35°C/65% RH
  - Roasted in PE bag, 35°C/65% RH (borderline)

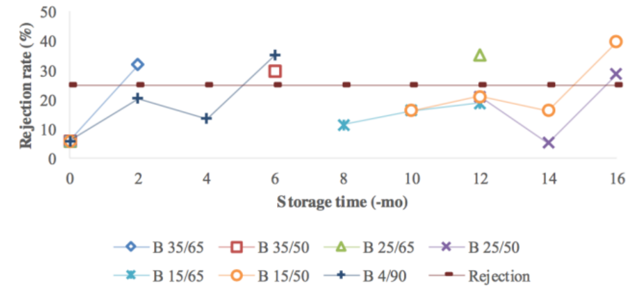
- Samples in boxes at high RH absorb water. Flavor volatiles decrease, oxidation begins. Loses texture of crunchy almond.

Sensory Tests: Consumer Rejection

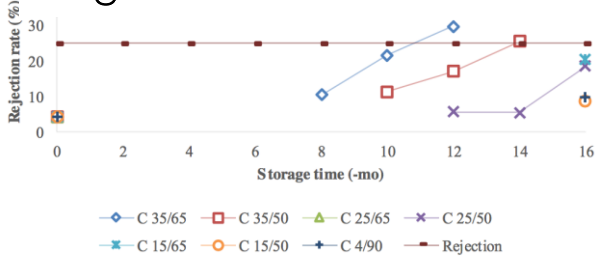
Raw almonds in PP bags



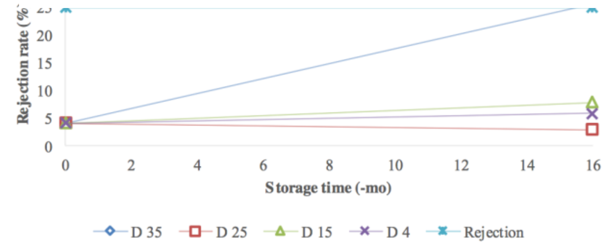
Raw almonds in Cardboard



Roasted almonds in PP bags



Roasted almonds in HB bags



Raw almonds: consumer rejection

- Samples at 35°C/65% RH in cardboard failed (>25% rejection) within 2 months. Samples at 4°C/90%RH failed within 6 months.
- Raw almonds in cardboard at 15 or 25°C and 50% RH failed after 16 months.
- In PP bags, samples at 35°C/65%RH failed after 6 months.
- Samples at 25°C/65%RH failed after 16 months. Those at 15°C/65%RH lasted until 24 months.

Roasted almonds: consumer rejection

- in PP bags, roasted almonds at 35°C/65%RH failed at 12 months; at 35°C/50%RH at 14 months; 25°C/65%RH at 16 months
- Samples fail for different reasons: odor, flavor, texture
- Only one sample (35°C,65%RH) failed in HB bag after 16 months

A few other studies . . .

Mexis et al. 2010. Effect of oxygen absorber, nitrogen flushing, packaging material oxygen transmission rate and storage conditions on quality retention of raw whole unpeeled almond kernels. *LWT*. 43: 1-11

-raw, unpeeled whole almonds

-PET/LDPE,   LDPE/EVOH/LDPE bags

-some had oxygen scavenger pouches ZPT-50 (zinc pyrithione)

-measured PVs and FFAs, some volatile compounds

-O_2 absorber useful for preserving shelf-life regardless of temperature and exposure to light

Lin etal. 2012. California Almond Shelf Life: Lipid Deterioration During Storage. *J Food Science* 77:C583-C593

-Whole almonds with and without PE package for 600 days. Also blanched and blanched/sliced

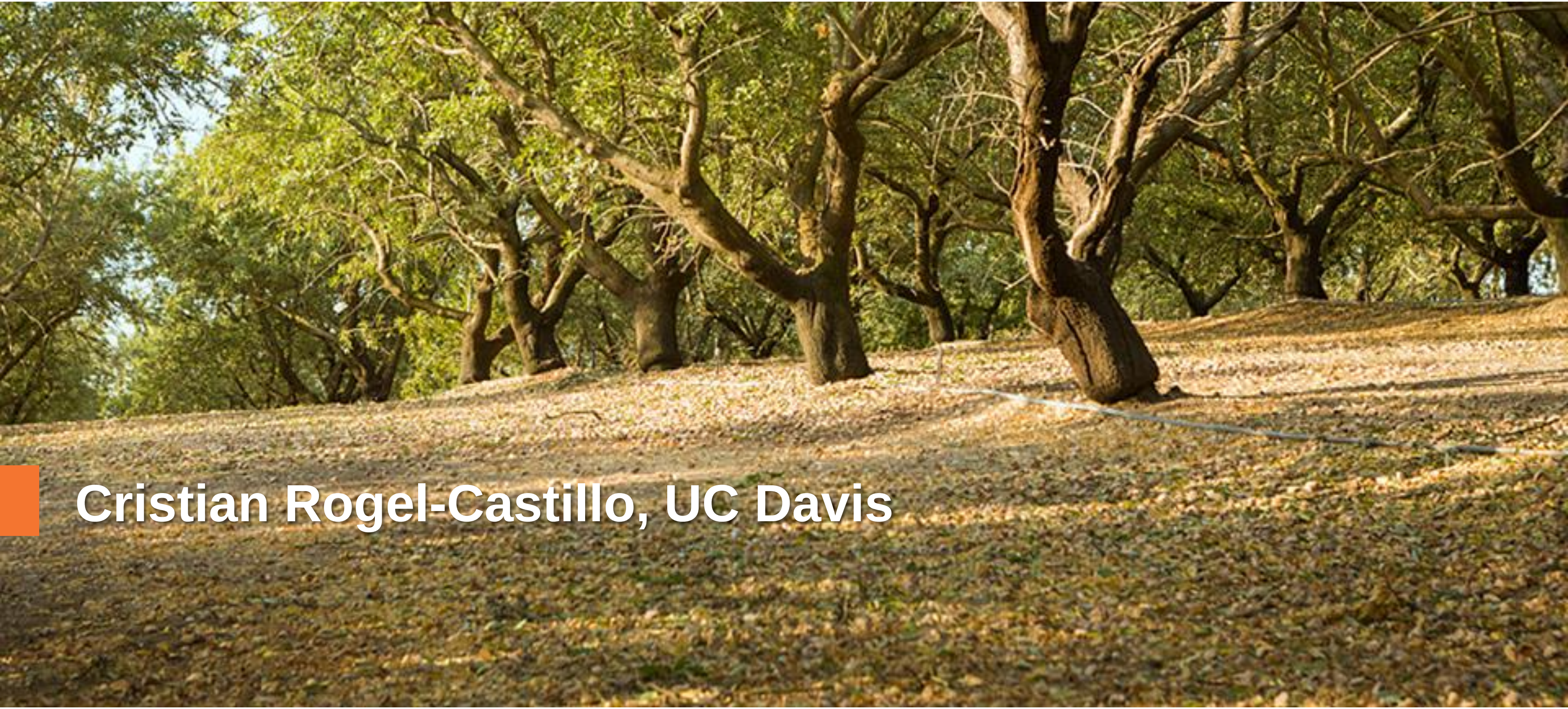
-Raw stored in sealed 1 lb PE bag or cartons. Blanched in PE bags.

-not much measured changes in PVs, IVs and FFAs for natural almonds

-more dramatic changes for blanched or blanched/sliced almonds. Skins may protect FFAs from further oxidation

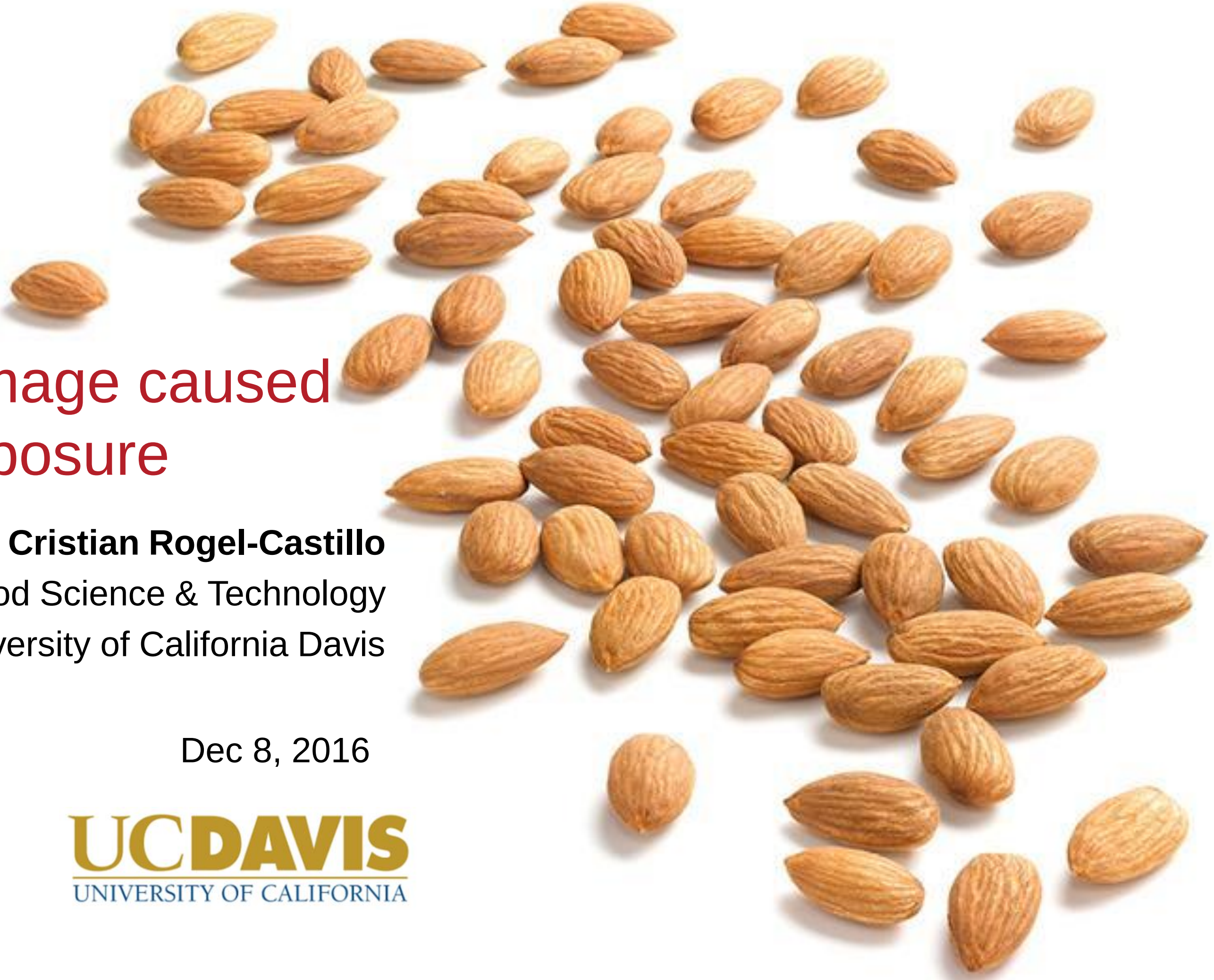
Conclusions

- Roasting helps lower initial moisture. Enhances crunchiness.
- Moisture, temperature and oxygen are all relevant.
- Storage of raw almonds can work if low temperature and humidity are maintained.
- Storage of raw almonds in sealed PP packages provide further protection
- Roasted nuts in PP can last ~12 months at 35°C/65%RH. Lower temperature and humidity provide better protection.
- Roasted nuts in high barrier bags have longest shelf-life. Up to 16-24 months.
- **Acknowledgements: Almond Board of California**



Cristian Rogel-Castillo, UC Davis

Concealed Damage caused by Moisture Exposure



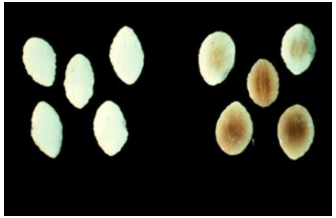
Cristian Rogel-Castillo
Food Science & Technology
University of California Davis

Dec 8, 2016

california almonds
Almond Board of California

UC DAVIS
UNIVERSITY OF CALIFORNIA

Concealed Damage



- Concealed damage (CD) results in a brown to black discoloration of almond nutmeat; especially after roasting
- To date, CD cannot be detected by screening methods, and little is known about the chemistry, and relationships between moisture and CD formation, and the mechanism by which color forms
  - Lower consumer acceptance, bitter flavors and possibly lower nutritional value due to degradation of amino acids and lipids
  - May be more susceptible to lipid oxidation and rancidity development which may influence shelf-life
- Our goal was to establish a chemical understanding of CD development in almonds and how it relates to temperature and moisture exposure

Research on Concealed Damage

1. **Effect of moisture and temperature in the development of CD**
2. Development of a screening method for the detection of almonds with CD before roasting
3. Effect of drying and storage in almonds with CD

How Moisture and Temperature may Influence CD in Almonds

Water (Rain)
Heat
(Windrows/Stockpiles)

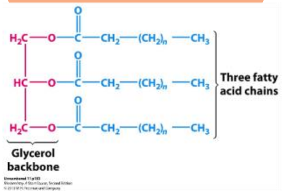
Lipids (Oil)
Proteins
Carbohydrates

→ Hydrolysis

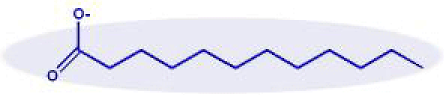
→ Free fatty acids
Free amino acids
Reducing sugars

→ Further reactions such oxidation

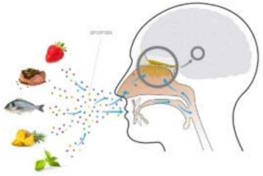
→ Volatiles



A "free" Fatty Acid



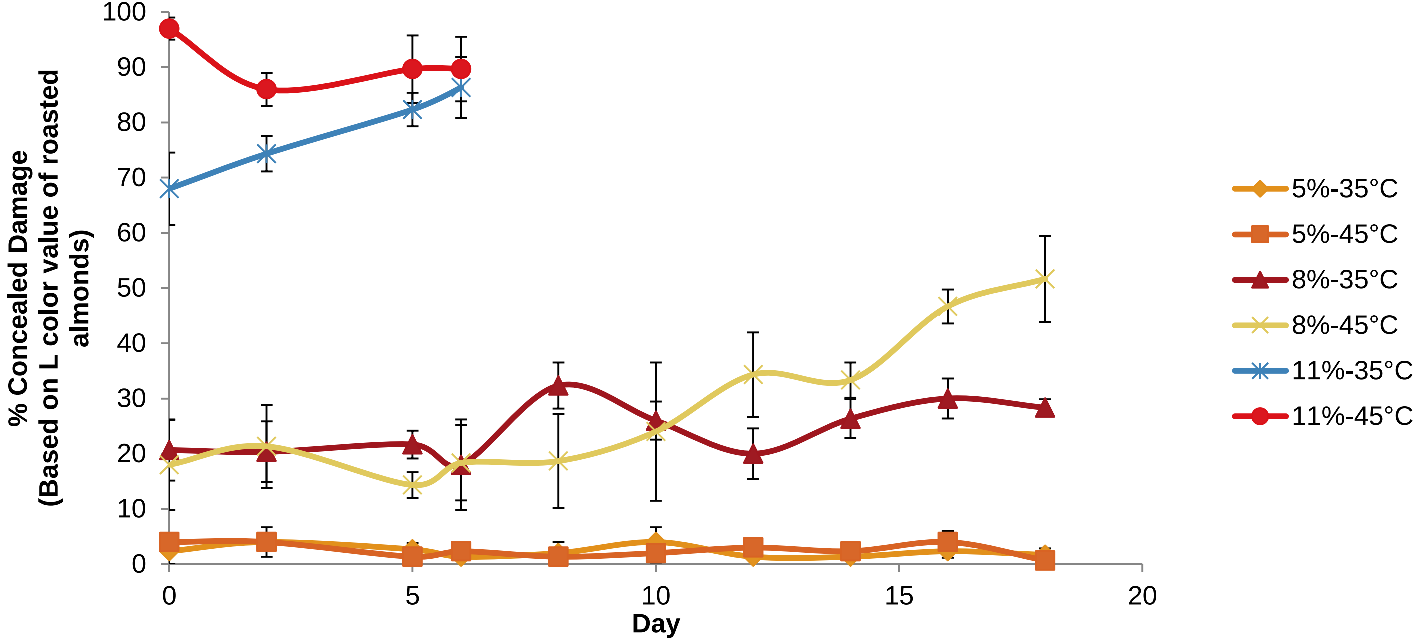
smell



Developing a Model for Evaluating CD in Raw Almonds

- Our first objective was to classify the almonds into two groups: No concealed damage (control) and those with concealed damage (CD)
- Raw almond kernels are cut in a half, numbered and placed into 2 identical racks
- One rack of is roasted [120°C/248°F for 90 min]; while, the other is not roasted
- Roasted almonds that develop color (have CD) are matched with the raw almonds
- Identify raw almonds that will develop CD

Percent CD in Raw Almonds Held at 5%, 8% and 11% Moisture at 35°C and 45°C over 18 Days



Color Development in Raw and Roasted Almonds (120°C/248°F for 90 min) Exposed to 5% (Control) and 11% Moisture (CD)

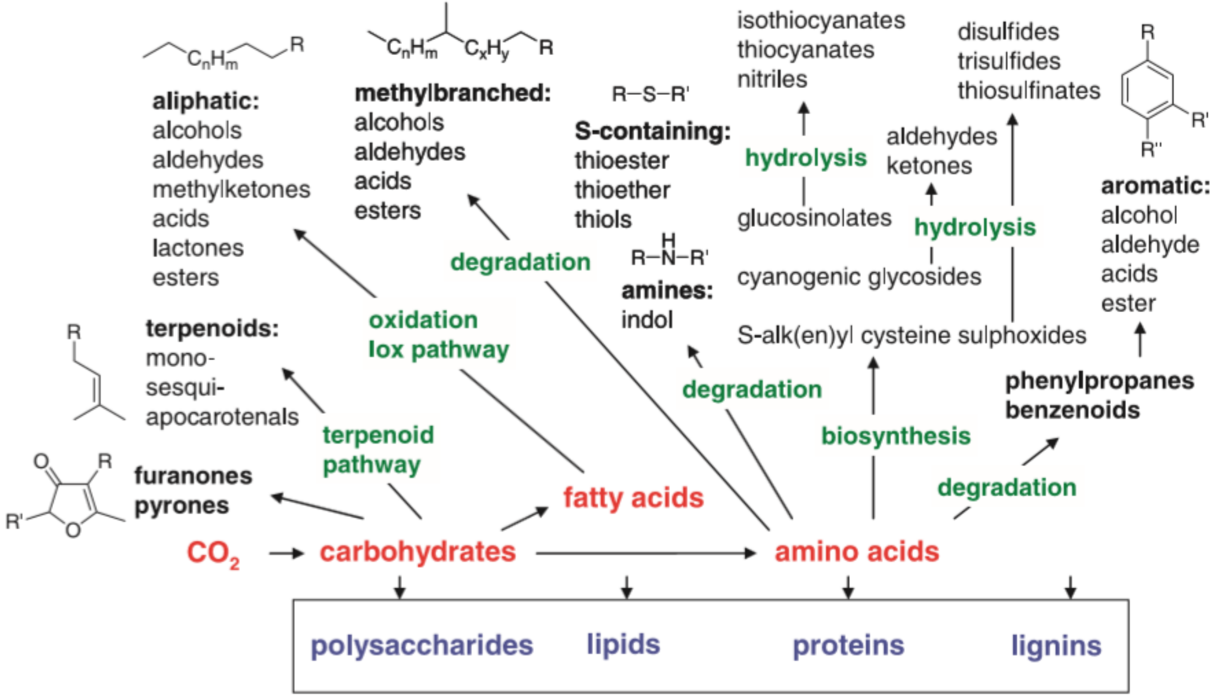
CD is a Challenge as it is a *Hidden Defect*

- Although CD is a hidden defect, the chemical changes that result in the brown pigmentation may come though the Maillard reaction
- Moisture produces precursors for the Maillard reaction through the degradation of lipids, carbohydrates and proteins
- Many of these compounds break down into volatiles

raw and roasted almonds exposed to 5% moisture (control)

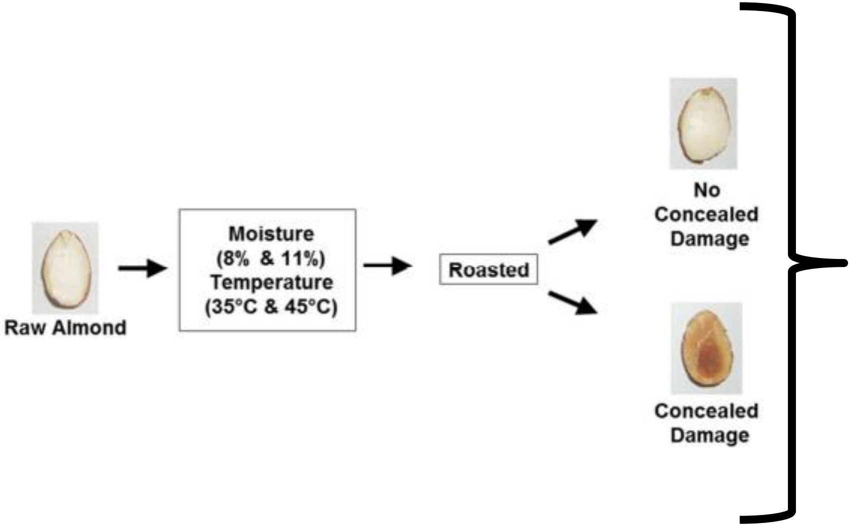
raw and roasted almonds exposed to 11% moisture.

Different Pathways for the Production of Volatile Compounds



(Schwab, W., et al. (2008). "Biosynthesis of plant-derived flavor compounds." The Plant Journal 54(4): 712-732.)

Identify Changes in Volatile Compounds in Almonds with CD



CD ➔ Increase in volatile related to:

1) Lipid oxidation
   - Acetic Acid
   - Hexanal
   - Nonanal
   - Alcohols

2) Amino acid metabolism
   - 3 – methyl – 1 – butanol

Our results suggest that **post-harvest moisture exposure** resulting in an internal kernel **moisture > 8%** is a key factor in the development of CD in raw almonds, and that CD is **accelerated by temperature.**

Rogel-Castillo et al. Journal of Agricultural and Food Chemistry **2015** *63* (37), 8234-8240

Research on Concealed Damage

1. Effect of moisture and temperature in the development of CD
2. **Development of a screening method for the detection of almonds with CD before roasting**
3. Effect of drying and storage in almonds with CD

Developed NIR Model for Identifying Raw Almond Kernels with CD before Roasting

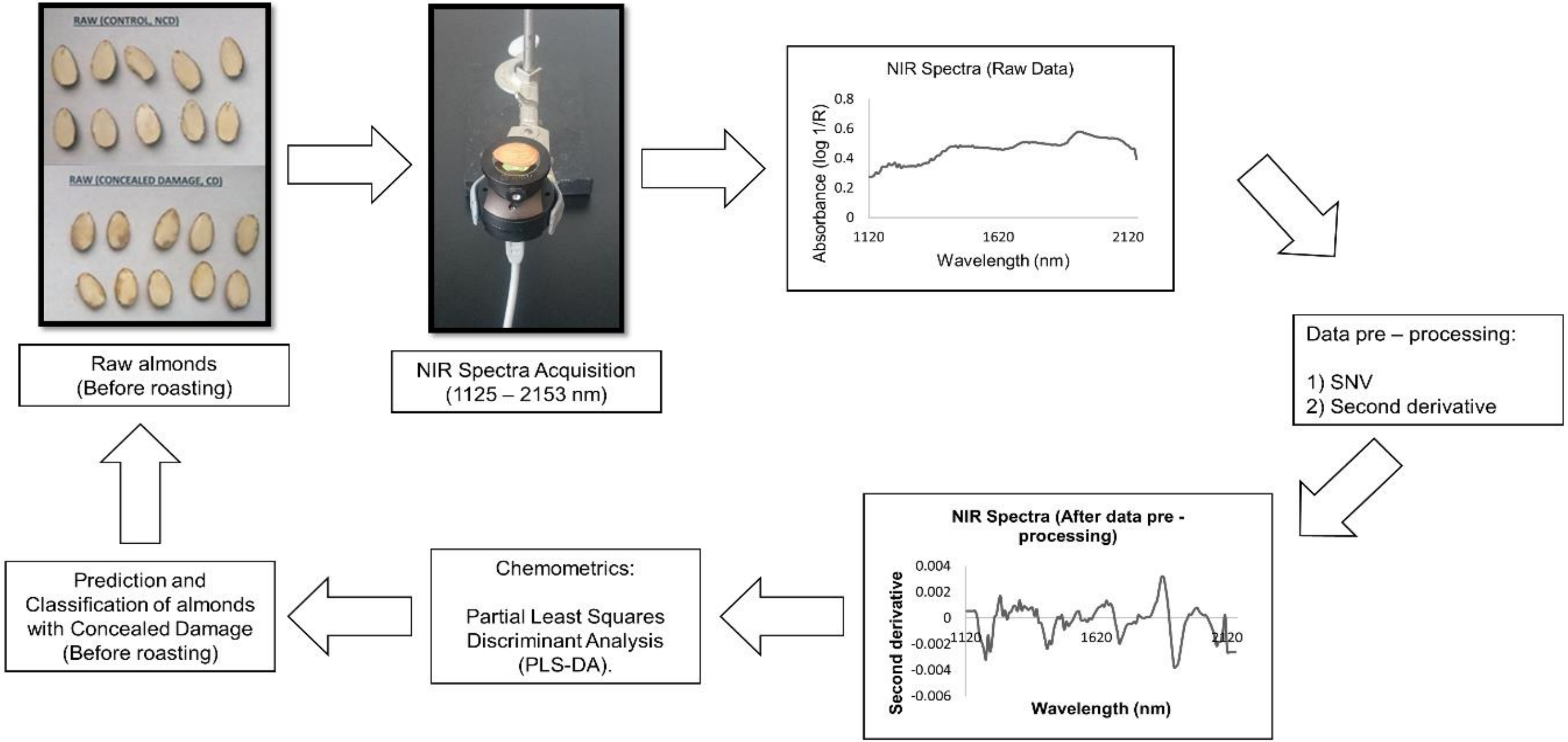
- To date, there are no rapid, robust methods for detecting CD in raw almonds
- Previous studies focused on the use of UV-Vis, pH and color measurements (LCh) to predict almonds with CD before roasting without positive results
- Our studies suggest that lipids, protein and carbohydrates degrade in almonds with CD

Rogel-Castillo, C., Boulton, R., Opastpongkarn, A., Huang, G., & Mitchell, A. E. (2016). ***Use of Near-Infrared Spectroscopy and Chemometrics for the Nondestructive Identification of Concealed Damage in Raw Almonds (Prunus dulcis).*** Journal of Agricultural and Food Chemistry, 64(29), 5958-5962.

How NIR Works

- Near Infrared (NIR) Spectroscopy was evaluated as a technique as it is a non-destructive method that can be used to measure lipids, carbohydrates and proteins in raw almonds
- This techniques may be suitable for in-line NIR sorting of raw almonds

NIR Spectroscopy as a Tool to Classify Almonds with CD before Roasting



A New NIR Spectroscopy Model

- Differences between “normal” almonds and “moisture damage” were in the region corresponding to lipid content as well as protein and carbohydrates.
- <u>**NIR model:**</u>

	Pearson, T.C (1998)	Nakariyakul, S. (2014)	Nakariyakul et al. (2011)	Rogel-Castillo*
Range (nm)	700 – 1400	700 – 1400*	700 –1400*	1125–2153*
% Error rate	12.4 – 27.5	5.8	8.8	8.2 – 9.2
% False positive	0.7 – 5.4	2.91 – 3.41	0.58 – 1.74	12.4 – 16.1
% False negative	11.1 – 23.8	14.81 – 62.96	31.48 – 53.70	10.6 – 17.2

*** Selected wavelengths**

Rogel-Castillo, C., Boulton, R., Opastpongkarn, A., Huang, G., & Mitchell, A. E. (2016). ***Use of Near-Infrared Spectroscopy and Chemometrics for the Nondestructive Identification of Concealed Damage in Raw Almonds (Prunus dulcis).*** Journal of Agricultural and Food Chemistry, 64(29), 5958-5962.

Research in Concealed Damage

1. Effect of moisture and temperature in the development of CD
2. Development of a screening method for the detection of almonds with CD before roasting
3. **Effect of drying and storage on almonds with CD**

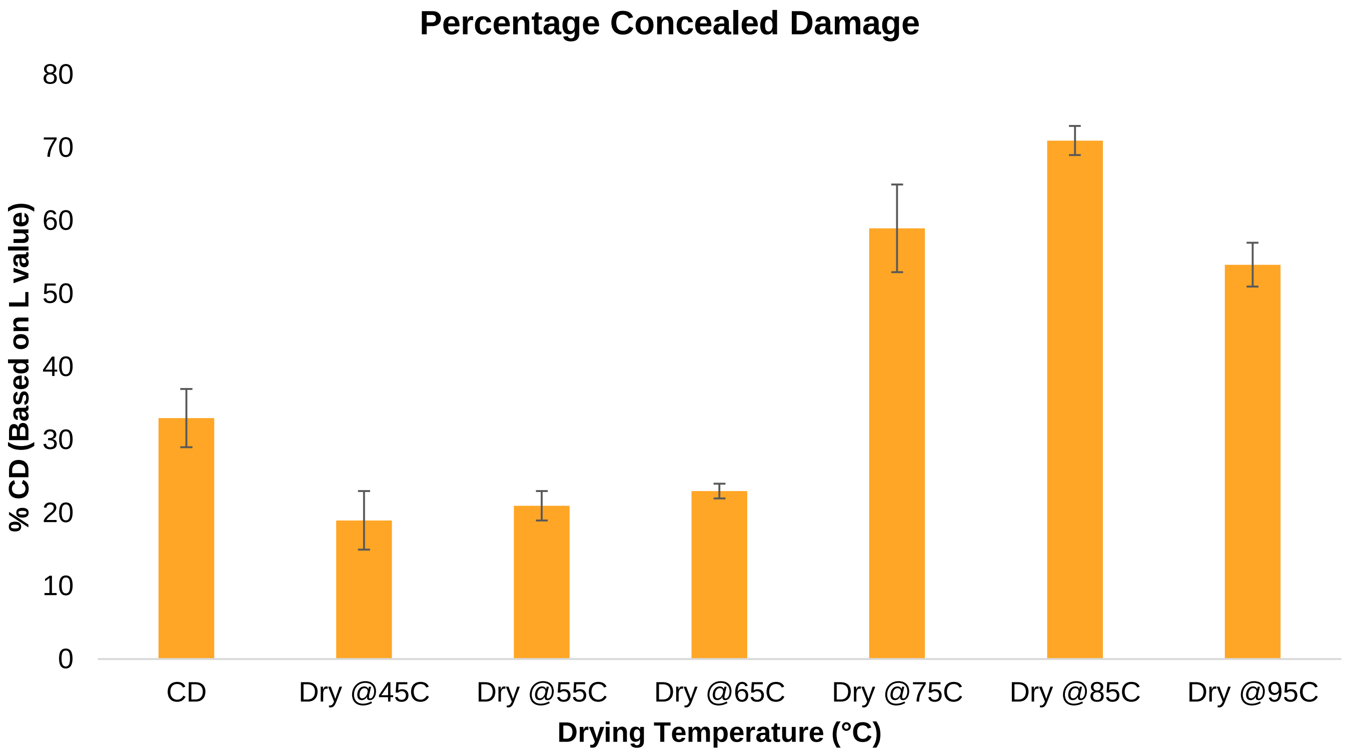
Moisture and Concealed Damage

- We demonstrated that post-harvest **internal kernel moisture ≥ 8%** is a critical factor in the development of CD in raw almonds and that CD development is accelerated with increasing temperature
- In typical commercial practices, almonds are left in the field to dry in windrows to a kernel moisture content of < 6%. Almonds are then stored in stockpiles until they can be processed
- However, during a rainy season, almonds may be exposed to extra moisture while in windrows and/or stockpiles
- Under these conditions, almonds are typically dried at the hulling/shelling facility back to ~6% moisture
  - However, almonds may experience prolonged moisture exposure do to drying limitations of processors

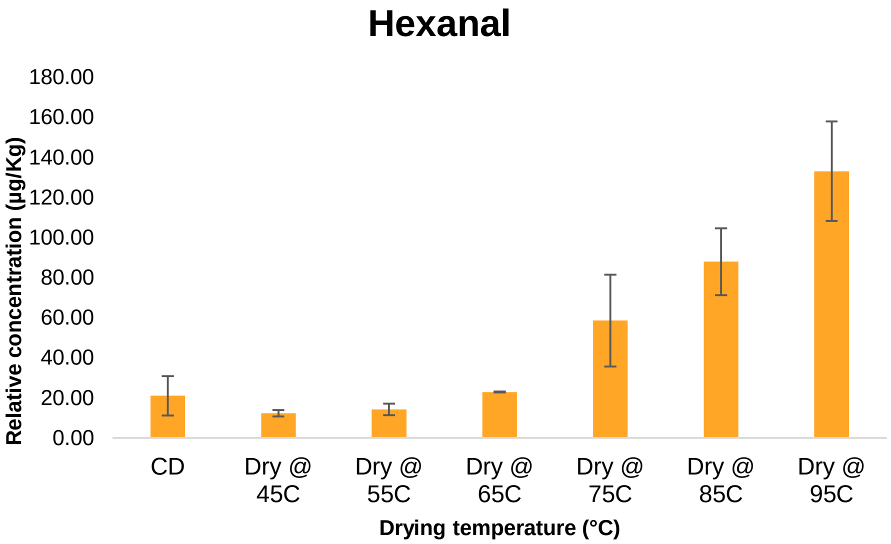
Moisture and Concealed Damage

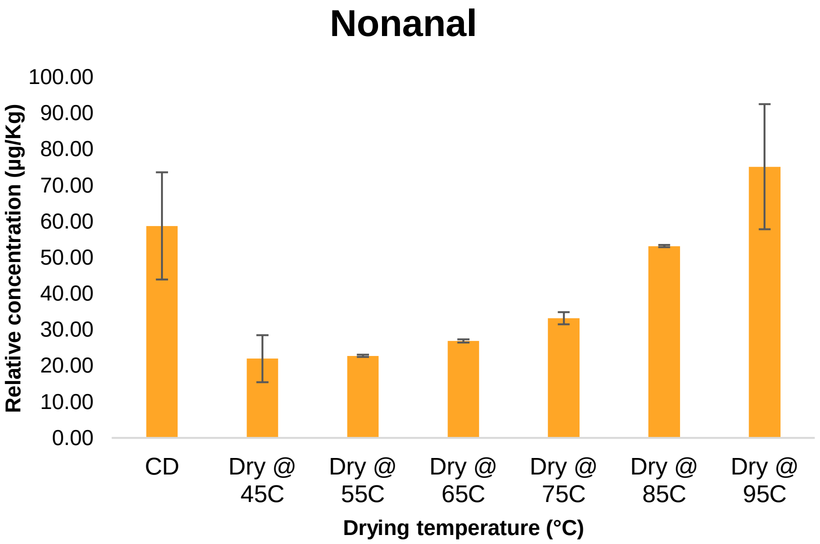
- Pearson (1998) was the first to recognize that drying wet almonds prior to roasting had the potential to reduce visible signs (pigments) associated with CD
  - Heat promotes the loss of water and facilitates the Maillard reaction leading to the formation of pigments
- However, the chemical changes related to lipid oxidation that occur in response to moisture exposure in almonds, don't go away with drying
  - We recognized that the lipid oxidation by-products formed during moisture exposure may promote early rancidity development and decreased shelf-life in moisture-exposed almonds
- Oxidation of oleic and linoleic acids will increase production of volatile compounds related to off-odors and rancidity including: aldehydes, ketones, acids, alcohols, hydrocarbons, lactones, and esters
  - Evaluate the influence of drying moisture-exposed almonds on volatile compounds and during accelerated storage

Effect of Drying on the Visual Color of Almonds with CD

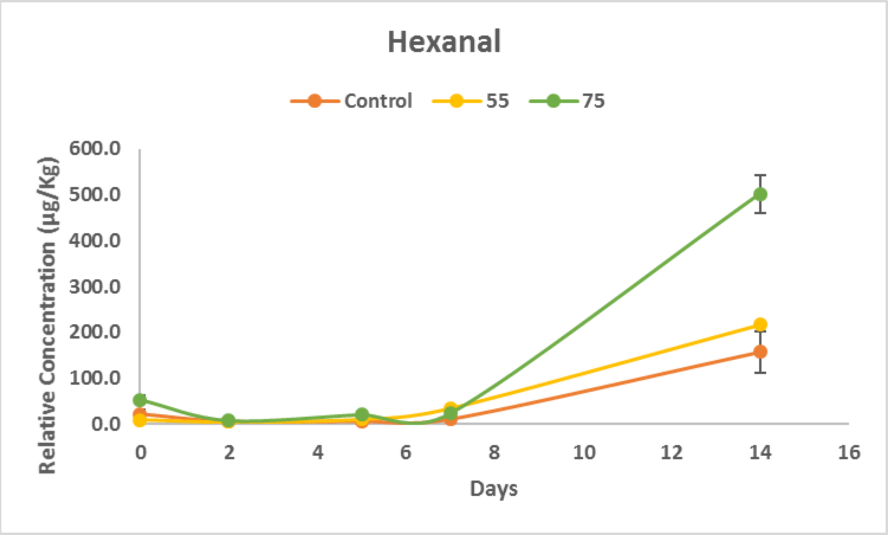


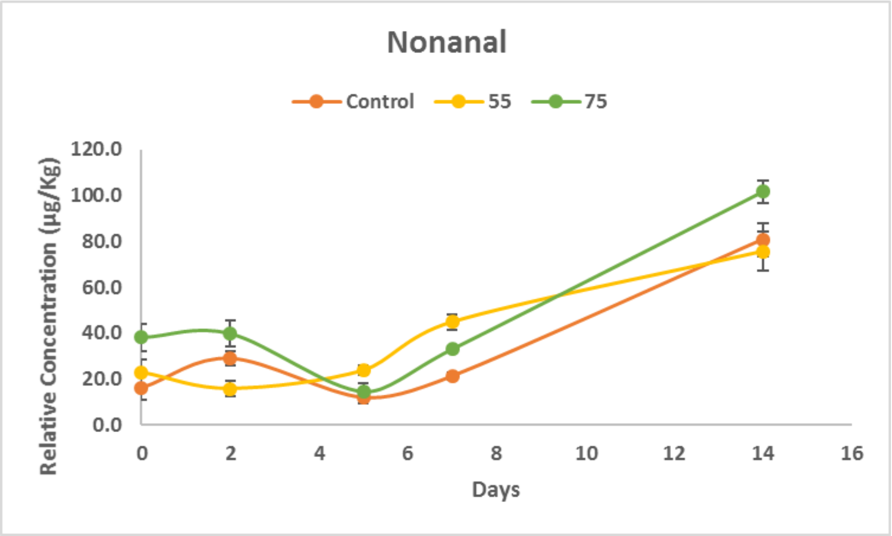
Effect of Drying Temperatures on Volatiles in Moisture Exposed Almonds





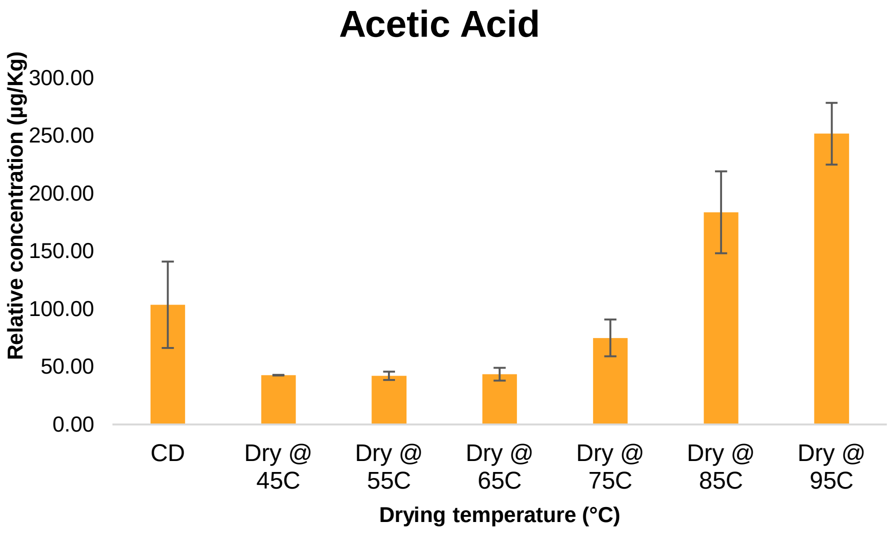
Effect of Accelerated Storage on Moisture Exposed and Dried Almonds

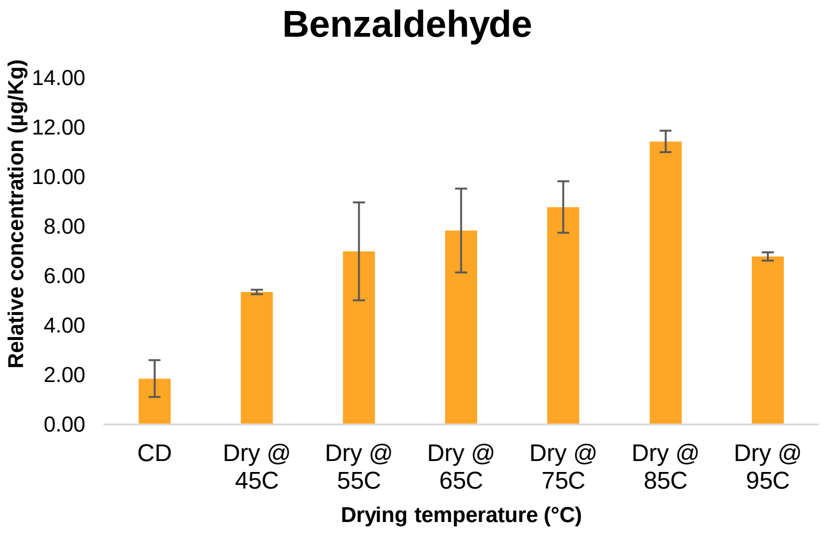




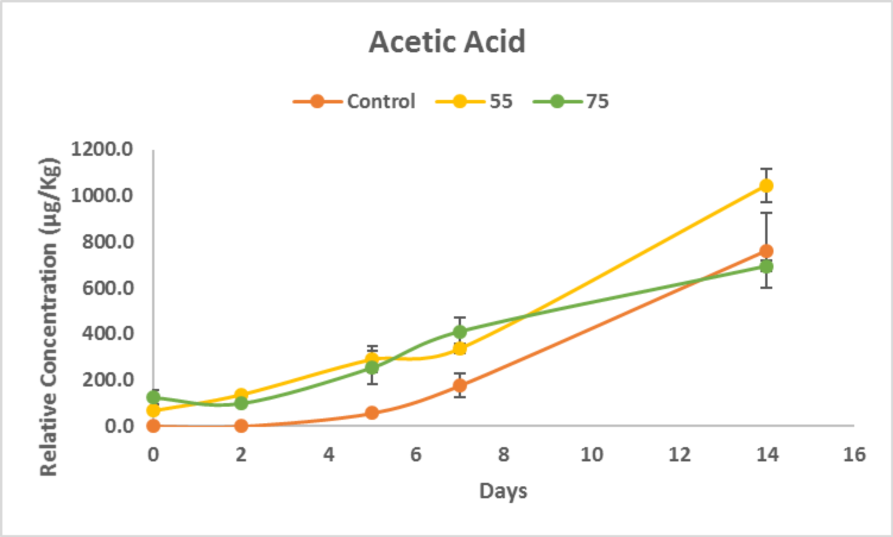
** Accelerated storage at (45°C/80% RH), 1 week = 1 month*

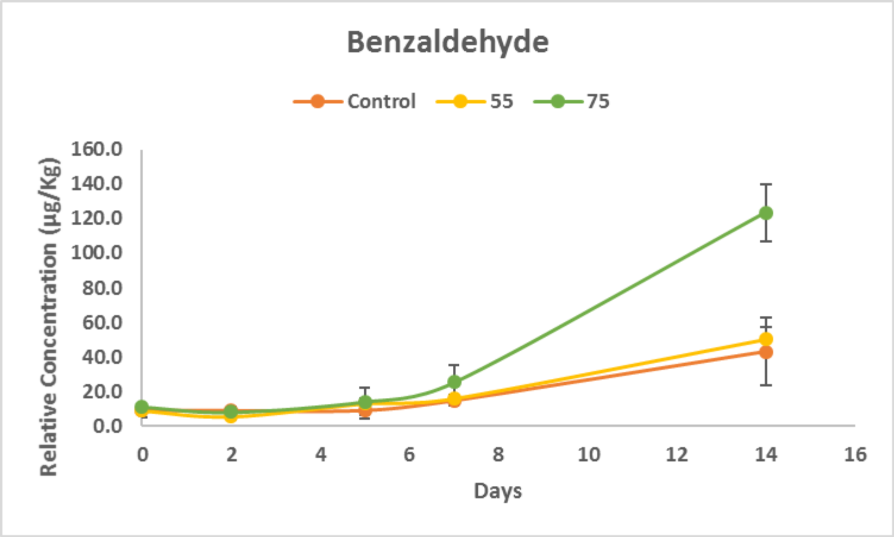
Effect of Drying Temperatures on Volatiles in Moisture Exposed Almonds





Effect of Accelerated Storage on Moisture Exposed and Dried Almonds





** Accelerated storage at (45°C/80% RH), 1 week = 1 month*

Maillard Reaction

Reducing groups

* Reducing sugars

* Lipid oxidation by-products (Aldehydes, ketones)

+

Free amino acids

=

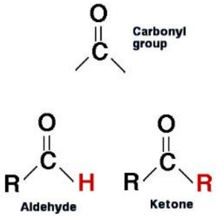
Early Maillard reaction / Amadori rearrangement

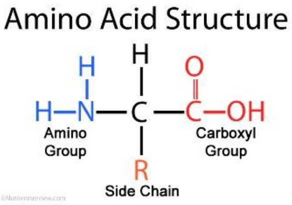
→

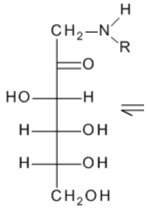
Advanced Maillard reaction

→

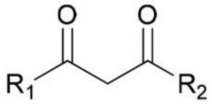
Melanoidins formation (brown pigments)



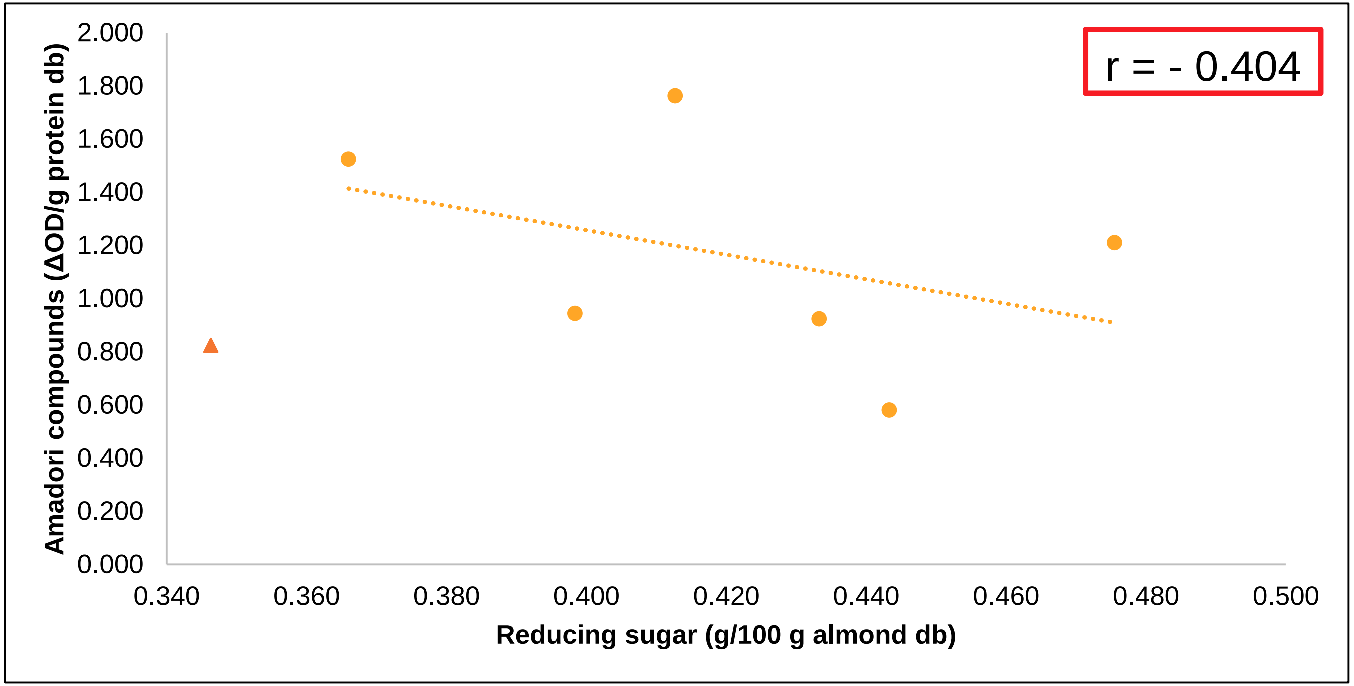




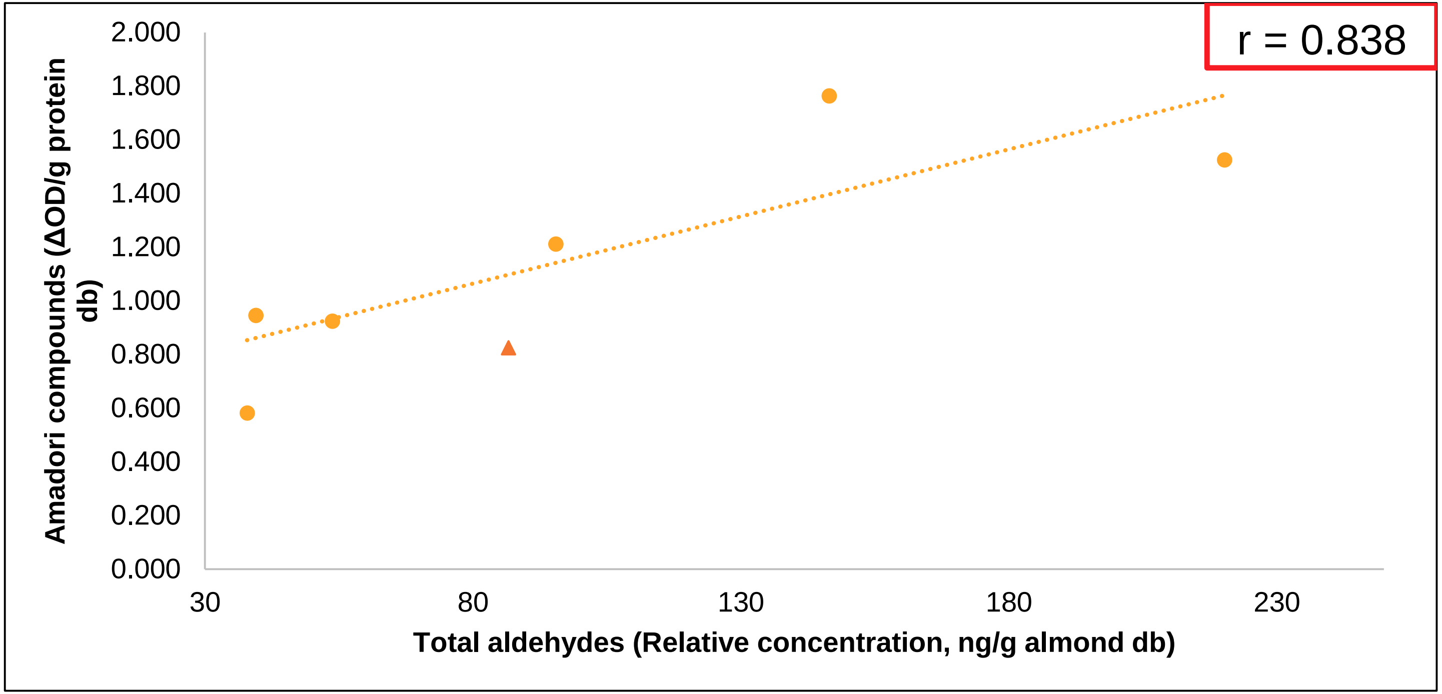
Amadori Product



Correlation between Reducing Sugar and Amadori Compounds in Almonds Dried between 45°C and 95°C (▲: CD)



Correlation between Total Aldehydes and Amadori Compounds in Almonds Dried between 45°C and 95°C (▲: CD)



Conclusions

- Results demonstrated that drying between 45°C - 55°C reduces the visible sign of CD (i.e. pigmentation) and decrease lipid oxidation
- Increased drying temperatures above 75°C promote lipid oxidation and the Maillard reaction (i.e. pigmentation)
- Furthermore, our results suggest that lipid oxidation by-products may participate in the browning reaction instead of reducing sugars
- In addition, it is known that some of the by-products of lipid oxidation are related with off-flavors (e.g. aldehydes, ketones, and organic acids) suggesting that almond with CD after drying may present defects in quality.
- Hence, further analysis (specially, sensory analysis) should be done to test the effect of drying in the quality of almonds with CD after drying in consumer acceptance (next research in our lab).
- Moreover, alternative drying protocols and technologies should be tested in the future to find the best drying condition (temperature and time) to control CD minimizing the effect in quality.

Thank You For Your Attention

california almonds®

Almond Board of California

Questions?