OXIDATION AND ITS CHALLENGES

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OUTLINE

• Introduction
• Challenge #1
• Challenge #2
• Challenge #3
• Challenge #4
• Conclusion
INTRODUCTION
BIOGRAPHY

• From Allen, OK

• Research and Career
  • Southeastern Oklahoma State University (1999-2003)
  • Texas A&M University (2003-2009)
  • The Samuel Roberts Noble Foundation (2009-2011)
  • Tyson Foods, Inc. (2011-CURRENT)
    • Food Safety and Research Laboratory/WBA Analytical Laboratory (2011-2017)
    • Ingredients & Specialty Products (2017-CURRENT)

• Johnny Bench is my cousin.

• Family
  • Wife – Lara, Two Kids – Madi and Katie
  • 3 Furry Kids – Tinker, Bears, Jaxson
GROUND RULES

• BE PRESENT AND PARTICIPATE.
• SOME TOPICS MAY MAKE YOU UNCOMFORTABLE AND CAUSE FEELINGS TO ARISE.
• DOCUMENT THOUGHTS AND PAIN POINTS TO CIRCLE BACK TO AT A LATER TIME.
• THESE ARE MY OPINIONS AFTER 10 MONTHS IN THIS BUSINESS SEGMENT.
• SIT BACK, RELAX, AND ENJOY THE TALK.
WHAT VARIABLES CONTRIBUTE TO OXIDATION?

Temperature
Time
Oxygen
Fat
Processing Time
Contact with Air
Antioxidant Effectiveness
Air Flow
Screens
Antioxidant Pressure
Trucking
Winter
Pro Oxidants
Moisture
Raw Material Quality
Age
Heat
Weather
Agitation
Transportation
Antioxidant Application
Antioxidant Application
Testing Methods
Lab Variation
Unsealed
Application
Sunlight
Surface Area
Storage
Presses
Temperature
Crystal Orientation
Surface Area
Stress
Blending
Unsealed
Travel Distance
CHALLENGE #1

UNDERSTANDING DEGRADATION

IT'S NOT CONFUSING

BUT I'M CONFUSED
I’VE GOT MY ION YOU

• **Oxidation**
  • To undergo or cause to undergo a chemical reaction with oxygen, as in formation of an oxide.
  • To lose or cause to lose hydrogen atoms.
  • To undergo or cause to undergo a decrease in the number of electrons.
  • To lose freshness after prolonged exposure to air and often to a darken in color.

• **Rancidification**
  • The process of becoming rancid; the oxidation of oils and fats which this involves.
  • Having a rank, unpleasant, stale smell or taste, as though decomposition, especially of fats and oils.

• **Degradation**
  • To lower in character or quality; debase.
  • Weaken or worsen; deteriorate.
  • The breakdown of an organic compound,

_________ ION IS A NIGHTMARE

PLAY A FUN GAME OF GUESS THE MOVIE
CHILDISH AND SIMPLE IN CONCEPT

- **Simplistic Overview of Lipid Oxidation**
- **Concept is Taught in Biology, Biochemistry, Food Science, and Chemistry Courses**

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CHILDISH AND SIMPLE IN CONCEPT
IN REALITY, IT’S A SLASHER WITH SEQUELS

- **Passive View of Fatty Acid Degradation**
- **Termination Leads to Secondary Volatile and Non-Volatile Compounds**

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Neda Mimica-Dukić, Nataša Simin, Emilija Svirčev, Dejan Orčić, Ivana Beara, Marija Lesjak and Biljana Božin (2012). The Effect of Plant Secondary Metabolites on Lipid Peroxidation and Eicosanoid Pathway, Lipid Peroxidation, Dr. Angel Catala (Ed.), InTech
IN REALITY, IT’S A SLASHER SEQUEL
• **The overall view of fatty acid oxidation is utter chaos.**

• **Notice the pattern of various reaction products and consider the possibilities of other unknown reactions taking place.**
NOW WE ARE RAISING HELL
TORTUOUS ON SO MANY LEVELS

- Enzymatic oxidase activities, ex. Xanthine
- Note the following:
  - Hydrogen peroxide
  - Metal oxidation/reduction reactions
  - Role of Vit E and C

TORTUROUS ON SO MANY LEVELS
ONE OF THE MANY MASKED REACTIONS

- Biogenic Amines are formed from the degradation of amino acids.
G.I. Mohammed, A.S. Bashammakh, A.A. Alsiabai, H. Alwael, M.S. El-Shahawi, A critical overview on the chemistry, clean-up and recent advances in analysis of biogenic amines in foodstuffs, TrAC Trends in Analytical Chemistry, Volume 78, 2016, Pages 84-94, ISSN 0165-9936
ONE OF THE MANY MASKED REACTIONS
JUST A BLOODY MESS

- *Fenton-like mechanism*
- *Myoglobin reactions that take place*
VS. DEGRADATION

1-2 DEGRADATION IS COMING FOR YOU
3-4 TITRATE PEROXIDES MORE
5-6 ADD ANTIOXIDANT QUICK
7-8 OFFAL TRUCKS RUNNING LATE
9-10 LOAD REJECTED AGAIN
CHALLENGE #2

UNDERSTANDING ANTIOXIDANTS

Hey

Ain't my fault this time
WHAT THE INDUSTRY IS TRULY DEALING WITH
WHAT THE INDUSTRY IS TRULY DEALING WITH
WHAT THE INDUSTRY IS TRULY DEALING WITH

• **Product Degradation** can also be compared to the fission reaction between a neutron and Uranium-235.

• **If an antioxidant was perfect, what kind of world would we live in?**

• **Is there truly a way to stop all potential reactions and control the rate of free radical production?**

• **Consider the fact that antioxidants cannot treat every free radical produced within the biological matrices the rendering industry produces.**

• **Are the free radicals that contribute to PV truly producing by-products that lead to sensory issues?**
CHALLENGE #3

LABORATORY TESTING AND UNDERSTANDING YOUR RESULTS

I'LL CHECK SOME DATA REAL QUICK, HE SAID

HAS BEEN MUMBLING "BUT THAT DOESN'T MAKE SENSE" FOR THE LAST 3 HOURS
LABORATORY FALLACIES

• ISO does not matter.
  • ISO 9001:2015
  • ISO 17025:2017

• Numerous methods exist to detect or quantify the exact same things.

• Methods from years ago are still applicable

• Methods are designed and used to test every matrix
  • There are no method limitations

• Method validations do not matter
  • Analytes
  • Matrices
  • Proficiency
TOTAL VOLATILE BASE NITROGEN

- Designed to detect trimethylamine and ammonia.
- Used as quality indicator for fish meal and fish meal raw material.
- Utilizes Kjeldahl Distillation
  - Extracted with perchloric acid
- Ion Selective Electrodes (ISE)
  - Converts the activity of a specific ion dissolved in a solution into an electrical potential.
  - Similar to pH probe.
## TOTAL VOLATILE BASE NITROGEN

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<th>Kjeldahl TVBN (mg/100g)</th>
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<td>113.2</td>
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TBARS

- 2-thiobarbituric acid reactive substances – acid distillation followed by 2-thiobarbituric acid derivatization.
- Defined as a measure of malondialdehyde (MDA) present in a sample.

\[
\begin{align*}
2 \text{H} \text{N} \text{C} \text{H} \text{H} \text{H} \text{S} \text{N} \text{H} & \quad \text{H} \text{H} \text{S} \text{N} \text{H} \\
\text{O} & \quad \text{O} \\
+ \text{H} \text{C} \text{O} \text{C} \text{H} & \quad \text{OH} \\
\rightarrow -2 \text{H}_2 \text{O} & \quad \text{OH} \\
\end{align*}
\]

- Measures everything, including all natural compound classes, not just malondialdehyde.
  - Aldehydes, aromatic aldehydes, ketones, ketosteroids, acids, esters, sugars, imides and amides, amino acids, oxidized proteins, pyridines, pyrimidines, vitamins, and organic or bio-organic acids.

BIOGENIC AMINES

- VARIOUS METHODS USING GAS AND LIQUID CHROMATOGRAPHY
- DERIVATIZATION IS COMMONLY UTILIZED

- VARIATION CAN BE SEEN ACROSS METHODS AND INSTRUMENTATION
  - SAMPLE VARIATION
  - COELUENTS
  - DETECTION LIMITS
  - NO CLUE WHY SIG. DIFF.

<table>
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<tr>
<th>Analyte</th>
<th>Mass Spec (ppm)</th>
<th>Derivatization HPLC (ppm)</th>
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<tbody>
<tr>
<td>Cadaverine</td>
<td>607.8</td>
<td>314</td>
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<tr>
<td>Histamine</td>
<td>&lt;1</td>
<td>16.9</td>
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<td>Phenylethylamine</td>
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<tr>
<td>Putrescine</td>
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<tr>
<td>Spermidine</td>
<td>6.5</td>
<td>55.3</td>
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<td>Spermine</td>
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<td>Tryptamine</td>
<td>&lt;1</td>
<td>nd</td>
</tr>
<tr>
<td>Tyramine</td>
<td>629.7</td>
<td>9.3</td>
</tr>
</tbody>
</table>

HTTP://WWW.CHROMEDIA.ORG/CHROMEDIA?WAXTRAPP=YFIQPHeSmBpmBLIEcCUvCK
PEROXIDE VALUES

- **COMMONLY USED TO DETERMINE THE RANCIDITY OF A SAMPLE CONTAINING FAT OR OIL SUBJECT TO OXIDATION.**

- **NUMEROUS METHODS USED TO DETECT PEROXIDES.**
  - **AOCS Cd-8-53 Titration**
    - \( R-O-O-R + 2I^- + 2H^+ \rightarrow 2ROH + I_2 \)
    - \( I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-} \)
  - **FOXII**
  - **SAFTest**
  - **CDR FoodLab**

- **MANY METHODS EMPLOYED TO EXTRACT FAT.**
  - **Petroleum Ether**
  - **Hexane**
  - **Chloroform**
  - **Isopropanol**
CHALLENGE #4
ME & YOU

CONGRATULATIONS
YOU'RE PART OF THE PROBLEM.
...megenerator.net
PEROXIDE VALUE FAT EXTRACTION VALIDATION

- **Tyson Foods** led initiative with the National Renderers Association to standardize fat extraction prior to determination of peroxides via AOCS titration or other means of analysis.

- **Method modification** is ISO:17025 accredited.

- **Goal** is to standardize a fat extraction method for rendered products.

**Players**

- **Renderers**
  - Six

- **3rd Party Laboratories**
  - Seven

- **Pet Food Companies**
  - Four

- **Universities**
  - Three
PEROXIDE VALUE TEST METHODS VALIDATION

• Attempt to validate each method side-by-side in one laboratory at one time over a period of days on various product matrices including fats and meals.
  • AOCS with ether fat extraction
  • FOXII
  • SafTest
  • CDR FoodLab
• Gain an understanding of the variation with each method.
• Identify if all methods are statistically equivalent
• Look at human variation
• Address any other industry concerns
PET FOOD ALLIANCE

Mission Statement for the CSU/FPRF Pet Food Alliance:

- Bring together members of the pet food and rendering industries together to collaboratively develop implementable solutions for industry challenges and identify opportunities for innovation, growth, and mutual success.

Key Pillars of the Pet Food Alliance:

- As the Pet Food Alliance moves forward beyond identification and discussion of industry challenges, these pillars remain pivotal to the future success of the Alliance:
  - Focus on uniting members of the pet food and rendering industries
  - Engage with and encourage widespread participation from additional industry members
  - Facilitate research guided by industry input to address real-world industry challenges
  - Establish multidisciplinary collaborations with academia and industry
  - Proactively engage in building industry sustainability, across all efforts
Posing two key questions to major pet food companies.

1. How was it determined that PV would be the test to use for freshness criteria?

2. How or why was 10 Meq/kg fat chosen as the maximum?

Leader: Jacob Swann – American Proteins, Inc.

Jacob.swann@amprot.com
WHAT VARIABLES CONTRIBUTE TO OXIDATION?

- Temperature
- Time
- Oxygen
- Fat
- Antioxidant
- Blend
- Antioxidant Application
- Raw Material
- Moisture
- Age
- Weather
- Agitation
- Transportation
- Handling
- Cooking Temperature
- Testing Methods
- Unsealed
- Crystal Orientation
- Sunlight
- Blending
- Surface Area
- Contact with Air
- Antioxidant Effectiveness
- Antioxidant Pressure
- Pro Oxidants
- Trucking
- Spring
- Screens
- Air
- Heat
- Air Flow
- Raw Material Quality
- Summer
- Presses
- Fall
- Lab Variation
- Travel Distance
- Chemical Reactions
- Antioxidant Blending
- Freshness
CONCLUSION

• Trying to understand product degradation is a challenge all in its own.
• We do not know what we are even dealing with that starts the free radical formation today.
• Detailed research studies are needed on rendered products to truly understand the culprits that are leading to potential issues along with palatability studies that support a real concern.
• Do not be afraid to challenge laboratory data.
• Collaborative activities are needed to truly solve industry problems.
  • When we all take ownership in the game, it will get fixed. —Brandon Lachner

Any follow-up questions, email me at bj.bench@tyson.com
ACKNOWLEDGEMENTS

• Lara Bench and My Kiddos
• Tyson Foods, Inc. Ingredients and Specialty Products FSQA Team
  • Roy Slaughter
  • Shane Parks
  • Robert Jones
  • Nancy Halstead
  • Ray Stout
  • Pam Parmer and Texarkana Laboratory Team
  • FSQA Supervisor Team
• Tyson Foods, Inc. Ingredients and Specialty Products Group
  • Madison Turner
• Tyson Foods, Inc Food Safety and Research Laboratory
• Numerous collaborators and many others along the way
QUESTIONS OR COMMENTS

bj.bench@tyson.com