Working Group #1

Mechanisms of Formation and Methods of Mitigation

2nd Acrylamide in Food Workshop
Chicago · April 13-15, 2004

A. Mechanisms of Formation

B. Food categories

C. Methods of Mitigation - Control / Intervention Points

A. Mechanisms of Formation

1. Carbonyls + Asparagine → acrylamide (AA)

Three potential pathways from the Schiff base

1.1 - Oxazolidin-5-one intermediate, decarboxylation, rearrangement to the Amadori and beta elimination to AA.

- Pathway marginal versus Amadori (1-5%).
- Rate limiting step beta elimination. General applicability of the beta elimination pathway to other amino acids shown (phenylalanine to styrene, asp to acrylic acid, other vinylogous compounds).
- So far no evidence for the oxazolidin-5-one nor azomethine ylide intermediate.
- Impact of pH ?

1.2 - Decarboxylation and 1 cleavage of the imine to AA

- Or via 3-APA.
- Rate limiting step is decarboxylation reaction. Gluc → 3-APA

A. Mechanisms of Formation

1. Carbonyls + Asparagine → acrylamide (AA)

   1.3 - 3APA so far identified and quantified in potatoes

   - Efficient yield of AA from 3APA (60%) in high moisture models (Prof. Schieberle, Munich).
   - Direct decarboxylation from free Asn also possible
   - Potential of this intermediate to be involved in formation of AA under pressure cooking conditions ?

A. Mechanisms of Formation

2. Aspartate + Sugar → acrylic acid + NH_3 → acrylamide

- Minor pathway, e.g., asparaginase conversion of Asn →Asp led to 97% ↓ AA in potato crisps
- Aspartic acid → β-alanine → acrylic acid
  - (C1 decarboxylation favored)
- β-alanine is more efficient than acrylic acid + NH_3 in generating AA

3. Triglycerides → → → acrolein → acrylamide

- Potential source of carbonyls (see Mechanism 1.)
- Certain "cold-pressed" oils can lead to AA upon heating (wheat germ)

A. Mechanisms of Formation

4. Other

- Meat systems: Carnosine → beta alanine → acrylic acid
- In the presence of creatine lead to N-methylacrylamide and N,N-dimethylacrylamide
- Acrylic acid + methylamine → N-methylacrylamide
- Serine and cysteine → acrylic acid (via pyruvic acid → lactic acid → acrylic acid)

5. Prevalence of each: ***Pathway 1 is the Major Route***.

B. Food categories

1. Contains acrylamide
2. Significant in diet
3. "Top Eight"

   French fries (FF), French fries (OB), breakfast cereals, potato chips, cookies, coffee, toasted bread, pies and cakes

Additional focus on infant foods - baby foods in jars, teething biscuits

Recognize uniquely high products, encourage research - gingerbread, coffee substitutes, etc.

C. Methods of Mitigation

Potato crisps

- Potato → potato flakes → potato crisp
- Moisture control: increase 0.5% gives mean 20% reduction
- Sugar control: ↓ 15% = ↓ 15% AA
- Acidity control: ↓ pH = ↓ AA and ↓ consumer acceptance
- Blanching: ↓ AA ≈80%
- Asparaginase (A. oryzae): ↓AA 97% in lab; color, flavor acceptable
  - Collaboration with Novozyme on enzyme standardization
- Challenges of scale up: AA reduction "lost" in variability (RSD 15%, 2-σ 28 %)
- Several years to commercialization

C. Methods of Mitigation

Almonds

- Lab test results are preliminary:
  - Temperature more critical than time
  - AA formation uses basically all sugars, only a portion of free Asn
  - AA formation correlates with free Asn, which varies greatly
  - AA may correlate with color (Hunter L)
- Process mitigation is complex due to multiple applications and customer requirements

C. Methods of Mitigation

Breakfast Cereals

- Test:
  - Product: rotary cooked, flaked wheat breakfast cereal
  - Intervention: process steps, not raw materials
- Earlier work showed AA formed mainly during the toasting step
- Pre-drying flakes:
  - Reduced AA but relationship non- linear
  - More fragile product broke more easily, higher manufacturing losses.
  - Negative impact on flavor
- No practical means to control flake moisture
- Great variability within and between lots
- No practical strategies that reduce AA and maintain key sensory attributes
- Future work: wheat varieties, levels of polyphenolics ?

C. Methods of Mitigation

Potato slices

- Objective: Prevention of formation, manipulation of the reaction
- Physical removal (steam distillation), chemical reaction
- Effects of pretreatments
  - Surface washing = ↓ 28% AA
  - Basil/rosemary/thyme = ↓35% AA
  - Blanching = no impact
- Competing amino acids, additive effects Glu/Asp = ↓ 43% AA
- Problem of scale up
- Future work: apply recent information on effects of Ca^{++} and phytate?

C. Methods of Mitigation

Effects of Consumer food preparation

- % AA exposure due to home preparation unknown
- AA increase with temp., frying time, color (browning)
- Toasted bread : AA increase with degree of darkness. 2/3 reduction by scraping off the surface !
- Home storage of potatoes: less AA at room temperature vs. cold
- French fries: soaking in water 15 min. (2/3 reduction)
- Consumer acceptability still to be studied
- Precision of home fryers, ovens a confounding variable in application of any consumer message.

Questions for all Working Groups

1. What have we accomplished so far?
   - Importance of free Asn, carbonyls from other sources
   - Major route identified, with three possible sub-routes
   - Role of other amino acids, e.g., carnosine in meat
   - Importance of ammonium compounds in baked wares
   - Good progress and data on potato chips and French fries
   - AA decline in stored coffee - potential mitigation mechanisms ?
   - Malted beverages, dark beers: no problem (low ppb levels)

Questions for all Working Groups

2. What gaps are remaining?

- Identification of the key intermediates
- Quantitation of precursors in foods
- Kinetics, rate limiting steps = identification of control points
- Yeast *vs.* chemical leavening in baked goods
- Understand AA formation in closed, high moisture systems, e.g., retorted baby foods, prune juice, black olives
- Raw commodity patterns: variation within and between cultivars, seasonal variation
- Formation of AA adducts with amino acids, proteins in foods, stability in storage, digestion

Questions for all Working Groups

3. What are the uncertainties?

- Consequences of “slowing down” Maillard reaction, lower quantities of “beneficial” compounds?
- Consequences of mitigation measures, potential creation of other problem compounds – *Question to WG Risk Characterization*
- How specific is asparaginase ?

Questions for all Working Groups

4. Are we covering all the territory? If not, is it covered by another Working Group? If so, is anything being duplicated in another Working group?

- EU HEATOX project will study formation mechanisms and kinetics of AA in different foods (potato, cereal/bread, coffee)
  - Recommend close communication/interaction with HEATOX team:
  - Feasibility, impact of proposed mitigation measures
  - Impact of mitigation on the formation of other “undesirable” compounds.
  - Will any JIFSAN Workshop measures cause concern for HEATOX?
- Effective communication of formation/mitigation learnings to:
  - Smaller producers, private label producers, co-packers
  - Restaurant/food service and retailers with in-store preparation

Questions for all Working Groups

5. What research is needed?

- See question *2. What gaps are remaining?* above
- Advanced glycation end products
- Role of water
  - Steam distillation of AA away from foods during processing
  - "Closed" processing situations, e.g., retorted or pasteurized products
- What mechanisms drive AA decline in stored roasted coffee? Guide for other products, processes?

WG1-Specific Questions

1. What is a realistic reduction?
   - Modest reductions have been achieved in Europe in certain food categories, potato products, crisp bread, baby biscuits. In others, considerable hurdles (breakfast cereals, coffee). Impact of seasonality not adequately studied
   - Process controls have had minor effects, no substantial further reduction without compromising quality or fundamental changes in raw materials, pretreatment or processing.

WG1-Specific Questions

2. Does this reduction significantly reduce the exposure to acrylamide from food?
   - What reduction is necessary to reduce the risk ? *(Question to WG Toxicology)*
   - Need concerted reduction for all foods, removal from one food product category will not impact overall average consumption (population)
   - Reduction in selected products could lower intake for certain individuals

WG1-Specific Questions

3. What is a realistic date(s) to achieve the target?
   - Several years to commercialize asparaginase treatment for selected potato products
   - Expect progress in "small steps"

4. Can we predict - based on the knowledge of the mechanisms - which other foods could be problematic ?
   - Apply established kinetic models (e.g. Bronek Wedzicha)
   - Measurement of intermediates (retorting, formation in certain foods under high moisture conditions)