The Maillard Reaction

Kinetics and applications

Ling 1908 work on beer
Brewing process browning
Color from sugar & protein

Maillard 1912 model system
1:4 glycine + glucose @ 37°C
color & carbon dioxide

Four pathways
- reducing sugar + amine
- high temperature carmelization (sugar oxidation)
- ascorbic acid (low pH juices)
- lipid peroxidation
The Maillard Reaction

> > 2000 types of confectioneries
> thousands of recipes
> non-chocolate products
  - main ingredient - sweeteners
  - most are reactive (sucrose, sorbitol)
  - most are heated to some boiling temperature
  - final moisture determines state (glass vs rubber)
  - caramels have added reaction products

T.P. Labuza

The Maillard Reaction Sequence

The Maillard Reaction Pathway
The Maillard Reaction

Undesirable Consequences
- darkening
- loss of solubility
- loss of protein biological value
- toxicity/mutagenicity (IQs)

Desirable Consequences
- desirable flavors - e.g. cereal (indication of loss of toxicity) beer, coffee, caramels, chocolate, tea
- increased palatability/nutrition - indicator of doneness
- brown colors - toasting, roasting, chocolate, coffee, beer
- generation of antioxidants/anticarcinogens
**The Maillard Reaction**

Substrates: free amino group plus aldehyde or ketose group

\[ \begin{align*}
[A] & \quad [R] \\
\text{amino acids} & \quad \text{reducing sugars} \\
\text{proteins-$\varepsilon$-lysine} & \quad \text{ascorbic acid} \\
\text{aspartame} & \quad \text{ketones} \\
\text{disodium guanylate} & \quad \text{aldheydes} \\
\text{MSG} & \quad \text{orthophenolics} \\
\text{sucrose (hydrolyzed)} & \quad \text{} \\
\end{align*} \]

**Sweetener Ingredients**

- relative sweetness
- solubility and crystallization
- hygroscopicity
- flavor development

**Sucrose hydrolysis**

- low pH
- high temperature
- yields glucose + fructose

**Major factors in color/flavor**

- time temperature sequence
- water content profile
- type of reactants
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\[
\frac{dA}{dt} = -\frac{dR}{dt} = k_1[A][R] - k_3[AR]
\]

Assume \( k_1 \gg k_3 \)

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Rate

\[
\frac{dR}{dt} = -k[A][R] = -k'[R]
\]

\[ R = R_0 e^{-k't} \]

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% Glucose Remaining

Baisier & Labuza JFS 40:707 (1992)

- 0.4 M glucose 37°C pH 7

- 0.05 M glycine
- 0.2 M glycine
- 0.4 M glycine

\( k_{0.05} = 1.62 \text{ hr}^{-1} \)
\( k_{0.2} = 3.62 \text{ hr}^{-1} \)
\( k_{0.4} = 7.78 \text{ h}^{-1} \)
\( k_1 = 22 \text{ hr}^{-1} \text{ M}^{-1} \)
The Maillard Reaction

pH Effects

\[ K_{eq} = \frac{[RNH_2][H^+]}{[RNH_3^+]} \]

\[ \log K_{eq} = \log[H^+] + \log[\text{base}] = -\text{pH} = -\text{pK}_a \]

\[ \% \text{ unprotinated} = \frac{(10^{-\text{pH}} - \text{pK}_a)100}{1 + 10^{-\text{pH} - \text{pK}_a}} \]

The Maillard Reaction

% Unprotinated

<table>
<thead>
<tr>
<th>pH</th>
<th>Glycine</th>
<th>Lysine</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$2.5 \times 10^{-7}$</td>
<td>$2.45 \times 10^{-6}$</td>
</tr>
<tr>
<td>3</td>
<td>$2.5 \times 10^{-6}$</td>
<td>$2.45 \times 10^{-4}$</td>
</tr>
<tr>
<td>5</td>
<td>$2.5 \times 10^{-3}$</td>
<td>$2.45 \times 10^{-2}$</td>
</tr>
<tr>
<td>7</td>
<td>0.25</td>
<td>2.45</td>
</tr>
<tr>
<td>8.9</td>
<td>17</td>
<td>50</td>
</tr>
<tr>
<td>9</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>9.6</td>
<td>50</td>
<td>84</td>
</tr>
<tr>
<td>11</td>
<td>96</td>
<td>~100</td>
</tr>
</tbody>
</table>
The Maillard Reaction

acid region

\[ \log (k_{\text{obs}}) = c + \log[H^+] = c - \text{pH} \]

slope = 1

10 fold decrease for 1 pH unit

basic region

\[ \log (k_{\text{obs}}) = c + pOH = c + \text{pH} \]

slope = 1

Pilkova et al. Die Nahrung 34:759 (1990)

\[ pK = 9.39 \]

\[ pK = 9.2 \]

problems with most studies

- single points in time
- high temperature changes with time
- pH not controlled → decreases rate
- amine - sugar ratio unknown and varies
- moisture - time profile unknown
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Sugar Type

Sugar Type

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Sugar: Hemoglobin (5:1) pH 7.3 @ 37°C


T.P. Labuza
The Maillard Reaction

Sugar: Hemoglobin (5:1)  pH 7.3  @ 37°C


R₁-NH₂ + R₂-CHO → Schiff Base
Schiff Base → AR
AR → Fluorescence
AR → Pigments

d[AR] = kₐ [R] - k₅ [AR]

[AR] = k₇/k₅ kₐ [R] e⁻ᵏ₅ᵗ - e⁻ᵏ₇ᵗ

determine k₃ from initial R loss rate
non-linear regression to solve for k₅
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Brown Pigment Formation Rate

\[ F = k_{k_f} \left[ \frac{e^{k_{a_f}}}{k_{a_f} - k_{a_f}} \right] \]

\[ + e^{k_{b_f}} \left[ \frac{e^{k_{a_f}}}{k_{a_f} - k_{a_f}} \right] \]
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\[ B = B_o + \left[ F \right] + k_{BB} \left[ B \right] \left[ F \right] = k_{BB} \]

or \[ B = B_{ind} + k_{BB} \left( t - t_{ind} \right) \]

Casein - glucose \( a_w = 0.7 \)
### The Maillard Reaction

Factors influencing browning ratio and type of AA and sugar:
- Sugar: amine ratio
- pH
- Solvent state
- Temperature

#### Baisier data (pH 7 @ 37°C with 0.1 M glycine)

<table>
<thead>
<tr>
<th>M</th>
<th>OD/h x 10^4</th>
<th>glucose ratio</th>
<th>OD/h x 10^4</th>
<th>browning ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>625</td>
<td>12.5</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>0.3</td>
<td>326</td>
<td>7.5</td>
<td>28.9</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>196</td>
<td>5.0</td>
<td>17.4</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>55</td>
<td>2.5</td>
<td>4.9</td>
<td></td>
</tr>
<tr>
<td>0.06</td>
<td>24</td>
<td>1.5</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>0.04</td>
<td>11</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

#### Baisier data (pH 7 @ 37°C with 0.4 M glucose)

<table>
<thead>
<tr>
<th>M</th>
<th>OD/h x 10^4</th>
<th>glucose ratio</th>
<th>OD/h x 10^4</th>
<th>browning ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>68</td>
<td>10</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>0.3</td>
<td>62</td>
<td>7.5</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>49</td>
<td>5.0</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>46</td>
<td>2.5</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>0.04</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>
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Wolfram et al. 1974 JAGFC 22:791

The Maillard Reaction


- model TPN solution @ 30°C and pH 6.5

<table>
<thead>
<tr>
<th>Amino Acid</th>
<th>OD/mole day</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lysine</td>
<td>0.008</td>
</tr>
<tr>
<td>Tryptophan</td>
<td>0.259</td>
</tr>
<tr>
<td>Cysteine</td>
<td>0.264</td>
</tr>
<tr>
<td>L+T+C</td>
<td>0.054</td>
</tr>
<tr>
<td>Commercial</td>
<td>0.019</td>
</tr>
</tbody>
</table>

Ashoor & Zent JFS 4:1206 1984

The Maillard Reaction

10 hr @ 120°C

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The Maillard Reaction

General Protein Browning

<table>
<thead>
<tr>
<th>pH</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td></td>
</tr>
</tbody>
</table>

The Maillard Reaction

Schnickles et al 1976  J Ag F Chem 24:901

<table>
<thead>
<tr>
<th>Protein</th>
<th>lysine (mg)</th>
<th>OD/g solids day</th>
<th>OD/mg lysine day</th>
</tr>
</thead>
<tbody>
<tr>
<td>gluten + 10% lys</td>
<td>33</td>
<td>34</td>
<td>1.1</td>
</tr>
<tr>
<td>casein</td>
<td>14</td>
<td>10</td>
<td>0.7</td>
</tr>
<tr>
<td>whey</td>
<td>8.6</td>
<td>8.5</td>
<td>1.0</td>
</tr>
<tr>
<td>soy</td>
<td>7.6</td>
<td>7.5</td>
<td>1.0</td>
</tr>
<tr>
<td>egg alb</td>
<td>3.6</td>
<td>4.9</td>
<td>1.4</td>
</tr>
</tbody>
</table>

The Maillard Reaction

Sugar  Gel Strength  Color (L)

<table>
<thead>
<tr>
<th>sugar</th>
<th>gel strength</th>
<th>color (L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sucrose</td>
<td>no gel</td>
<td>none</td>
</tr>
<tr>
<td>lactose</td>
<td>125</td>
<td>77.6</td>
</tr>
<tr>
<td>fructose</td>
<td>148</td>
<td>69.1</td>
</tr>
<tr>
<td>mannose</td>
<td>193</td>
<td>64.5</td>
</tr>
<tr>
<td>xylose</td>
<td>287</td>
<td>43.2</td>
</tr>
</tbody>
</table>

Mitchell  U Nottingham  - BSA + 3% sugar 60 min @ 121°C
The Maillard Reaction

Industrial Control of Browning

- Conditioning of potatoes for chips
- Glandless cottonseed - gossypoll
- De-sugaring of eggs for drying
- Processing temperature control

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Temperature Effect

<table>
<thead>
<tr>
<th>Item</th>
<th>aw</th>
<th>T°C</th>
<th>E_A (Kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry cabbage</td>
<td>0.1</td>
<td>25-40</td>
<td>40</td>
</tr>
<tr>
<td>Casein-glucose</td>
<td>0.5</td>
<td>25-45</td>
<td>33</td>
</tr>
<tr>
<td>Processed cheese</td>
<td>0.97</td>
<td>5-40</td>
<td>24</td>
</tr>
<tr>
<td>Glucose-Glycine</td>
<td>1</td>
<td>50-100</td>
<td>20</td>
</tr>
</tbody>
</table>
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**Nutritional Consequences**

<table>
<thead>
<tr>
<th>Product</th>
<th>% blocked lysine</th>
</tr>
</thead>
<tbody>
<tr>
<td>raw milk</td>
<td>0</td>
</tr>
<tr>
<td>freeze dried milk</td>
<td>0</td>
</tr>
<tr>
<td>pasteurized milk 74°C 40 sec</td>
<td>0</td>
</tr>
<tr>
<td>UHT pasteurized 140°C 3 sec</td>
<td>0-2</td>
</tr>
<tr>
<td>spray dried milk</td>
<td>0-3</td>
</tr>
<tr>
<td>sweetened condensed milk</td>
<td>5-12</td>
</tr>
<tr>
<td>roller dried (no preconcentration)</td>
<td>10-15</td>
</tr>
<tr>
<td>evaporated milk</td>
<td>15-20</td>
</tr>
<tr>
<td>drum dried</td>
<td>20-30</td>
</tr>
</tbody>
</table>

J. Mauron      Nestle Co.

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The Maillard Reaction

**Toxicological Consequences**

- decreased weight gain
- increased liver weight
- increased kidney weight
- increased ceacum
- increased heart weight
- increased serum GOT, AP
- accumulation of pigment in tissues
- presences of vacuolated hepatocytes
- increased Zinc loss in urine

*eg Lee et al. 1981, rats fed 10 months with browned casein 10% diet also with 5-10% MRP in diet*
The Maillard Reaction

Toxicological/Nutritional consequences to humans

MRPs ~ 1.5-2% of diet
?
protein bioavailability
pro/anti mutagenicity of MRPs (imidazo quinolines and furfural) especially heated foods
high fructose corn syrup in normal diet (1/3 into serum)

Medical Aspects

glycosylation inhibitors

- toxicity of sulfite - use in processing
- tea catechins
- drugs

Medical Aspects

diabetes control - glycated hemoglobin

- atherosclerosis initiation
- reduced elasticity of connective tissue
- nephropathy
- kidney function - basement membrane
- retinopathy eg corneal protein - cataracts

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Any Questions

University of Minnesota

T.P. Labuza