The Role of pH in Maillard-Type Reactions

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Outline of the presentation

Basic principles of pH/Maillard

- pH versus reactivity (nucleophilicity)
- pH versus buffer
- pH to control the Maillard reaction

Examples from flavour research

- O-heterocycles – caramel-like/sweet
- N-heterocycles – roasty/sweet
- S-heterocycles – roasty/savoury
The first scheme of the Maillard reaction

- Aroma
- Taste
- Colour
- Antioxidants
- Texture
- Nutritional value
- Contaminants
- Toxic compounds

(Hodge, 1953)
(Davidek et al., 2002)
Loss of Glc under boiling conditions:
- rapid loss at pH 10-12
- high loss at pH 8-12

Loss of Lys under boiling conditions:
- slower decrease at pH 10-12
- small loss at pH 4-9

(Ames, 1998)
pH decrease and browning as affected by the type of sugar

(van Boekel et al., 2000)
Colour and flavour formation *via* Maillard reactions depend very much on the pH

**Glucose + β-alanine**

<table>
<thead>
<tr>
<th>pH</th>
<th>Browning</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.3</td>
<td>□</td>
</tr>
<tr>
<td>6.4</td>
<td>▲</td>
</tr>
<tr>
<td>3.5</td>
<td>▓</td>
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</tbody>
</table>

(Hayashi & Namiki, 1986)

**Rhamnose + L-proline**

- Roasty
- Burnt sugar
- Furanone
- Propionyl
- Popcorn maltol
- Nutty
- Diacetyl
- Baked
- Furaneol
- Popcorn

(Shaw et al, 1990)
Major reaction pathways as affected by the pH

Glucose + RNH₂

Schiff base

1,2-Enaminol

1-deoxyosone route

C₁ + C₅

C₂ + C₄

Retro-aldol

C₁ + C₅

C₂ + C₄

C₃ + C₃

Retro-aldol

3-DO

3-deoxyosone route

1-DO

4-DO

2,3-Endinol

Amadori compound

pH < 5

pH > 7
Major steps of the early stage of the Maillard reaction

1. Glucose + R-NH₂ → R-CH=N-H-R (Schiff base)
2. R-CH=N-H-R → R-CH=N-R (Amadori compound)
3. N-Glucosylamine
4. 1,2-Enaminol
1,2-enolisation

\[
\begin{align*}
\text{1,2-Enaminol} & \quad \text{Glucosone} \\
\text{2,3-Enaminol} & \quad 5\text{-Hydroxymethylfurfural (HMF)} \\
\text{Amadori compound} & \quad \text{3-Deoxyosone} \\
\text{2,3-Endiol} & \quad \text{1-Deoxyosone} \\
\text{4-Deoxyosone} & \quad \text{Pyridaine derivative}
\end{align*}
\]
Formation of acetic acid (Phosphate buffer, 0.2 mol/L, 120°C)

From glucose/glycine

From Amadori compound

(Davidek et al., 2003)
Formation of some $C_2$ and $C_3$ degradation products by the Maillard reaction

Glycosone

$\text{HO} \quad \text{OH} \quad \text{O}$

$\text{R} \quad \text{H} \quad \text{O}$

$\text{HO} \quad \text{O}$

$\text{R} \quad \text{OH} \quad \text{CH}_3$

1-Deoxyosone

$\text{HO} \quad \text{O}$

$\text{R} \quad \text{H} \quad \text{O}$

$\text{HO} \quad \text{O}$

$\text{R} \quad \text{OH} \quad \text{CH}_3$

$\Delta$ pH 6.4

$\square$ pH 9.3

$\bigcirc$ pH 3.5

(Glucose/β-alanine)

(Hayashi & Namiki, 1986)
Role of buffer on pH control and reactivity in the Maillard reaction

(Xyl/β-Ala, pH 7.3)

Conclusion:
- Intramolecular proton abstraction with $\text{XO}_2^-$ → more efficient, catalytic effect
- Intermolecular proton abstraction with $\text{OH}^-$

Mechanism:
- Nucleophilic addition
- Proton abstraction from $\alpha$-position
- Enolisation: A, sugar isomerisation
- Dehydration: B, 3-deoxyosone formation

(Rizzi, 2004)
Formation of the Amadori compound in the Glc/Gly system

(D-glucose 0.1 M and glycine 0.1 M, H₂O or phosphate buffer 0.1 M, T = 90°C)

- pH 5
- pH 6
- pH 7

(Kervella et al., 2002)
Summary: pH effects on reactions occurring in the Maillard cascade

pH changes depend on:

- Formation of acid/base: HCOOH, HOAc, glycolic acid
- Consumption of acid/base: aminoketones $\rightarrow$ pyrazines
- Buffering capacity of Maillard/food system

Typical reactions in the ‘Maillard reaction’:

- Amino/carbonyl reactions: basicity of $\alpha$-NH$_2$, pK$_a$
- Aldol/retro-aldol reactions: ‘alkaline’ conditions
- Enolisation and elimination: ‘alkaline/acidic’ conditions
- Radical reactions: ‘alkaline conditions
- Oxidation and reduction
Impact aroma compounds with caramel/sweet character: \(O\)-Heterocycles

![Chemical structures with odour thresholds in water (\(\mu g/L\)).](image)

(Wild, 1988)
Formation of Furaneol (1 M aq. solution, no buffer, pH= const., T= 90°C)

From glucose and glycine

From Amadori compound

(Blank et al., 1997)
Formation of furaneol from Amadori compounds via acetylfuraneol

\[
\text{Amadori compound} \xrightarrow{a} \text{- Amino acid} \xrightarrow{b} \text{1-Deoxyosone} \xrightarrow{c} \text{Furaneol}
\]

(Blank et al., 1997)
Degradation of pentose sugars via the Maillard reaction

(Xyl/Gly, boiling, 2 h)

Pentose

1-DO  3-DO

Norfuraneol  2-Furfural

(Monti et al., 1998)
Formation of furylethylether indicating aging flavour of beer

2-furfuryl acetate

2-furanmethanol

2-furfural

Maillard reaction

reduction by yeast

FEE formation is correlated with
- high EtOH content,
- darker colour,
- lower pH.

(Vanderhaegen et al., 2003, 2004)
Impact aroma compounds with roasty/sweet character: \(N\)-Heterocycles

- 2-Acetyl-1-pyrroline (roasty, 0.02)
- 2-Acetyltetrahydropyridine (roasty, 0.06)
- 2-Acetyl-2-thiazoline (roasty, 0.05)
- 2-Acetylpyrazine (roasty, 0.4)

(Threshold values in ng/L air)
Formation of impact odorants from proline/sugar mixtures at pH 7

Reaction conditions:
Pro (4 mmol) + ‘sugar’ (2 or 0.1 mmol)
Phosphate buffer (pH 7.0, 0.1 mol/L)
Reflex, 2 h

(Schieberle et al., 1995, 1998, 2000)
Increased yields of roasty odorants: Reaction of secondary degradation products

Reaction conditions:
1-Pyrroline (10 µmol) + MG or HP (10 µmol)
Phosphate buffer (pH 7.0, 0.5 mol/L)
Reflux, 30 min

(Schieberle et al., 1995, 1998)
Increased yields of roasty odorants from key intermediates: ATHP from HOP

Reaction conditions:
HOP (1 µmol)
Phosphate buffer (pH 7.0, 0.5 mol/L)
Reflux, 30 min

(Schieberle et al., 1995, 1998)
Impact aroma compounds with roasty / savoury character: S-containing odorants

- **2-Methyl-3-furanthiol (MFT)**
  - Chemical structure: ![SH] ![O] ![H] ![H] ![H]
  - Description: Meat, coffee
  - Character: Sulfury, meaty
  - Ox: 0.007 µg/L H₂O

- **2-Furfurylthiol (FFT)**
  - Chemical structure: ![SH] ![O] ![H] ![H] ![H]
  - Description: Coffee, meat
  - Character: Sulfury, coffee-like
  - Ox: 0.01 µg/L H₂O

- **3-Methyl-2-buten-1-thiol**
  - Chemical structure: ![SH] ![O] ![H] ![H] ![H]
  - Description: Beer, coffee
  - Character: Sulfury, catty
  - Ox: 0.0003 µg/L H₂O

- **3-Mercapto-3-methylbutyl formate**
  - Chemical structure: ![SH] ![O] ![H]
  - Description: Coffee, beer
  - Character: Sulfury, catty
  - Ox: 0.003 µg/L H₂O

- **Potato, beer**
  - Chemical structure: ![S] ![O] ![H] ![H] ![H]
  - Description: Cooked potato-like
  - Character: Sulfury, cabbage-like
  - Ox: 0.2 µg/L H₂O

- **Methional**
  - Chemical structure: ![S] ![O] ![S] ![S] ![S]
  - Description: Cabbage, beer
  - Character: Sulfury, cabbage-like
  - Ox: 0.006 µg/L H₂O

- **Dimethyltrisulfide (DMTS)**
  - Chemical structure: ![S] ![S] ![S]
  - Description: Potato, beer
  - Character: Cooked potato-like
  - Ox: 0.2 µg/L H₂O
Cysteine and pentose sugars are important precursors for thiols

Ribose

Cysteine

Norfuraneol

2-Methyl-3-furanthiol

2-Furfural

2-Furfurylthiol

(Münch et al., 1997)
Formation of 2-furfurylthiol (FFT) from 2-furfural in the presence of H₂S

\[
\begin{align*}
\text{H}_2\text{S} + \text{FFT} & \rightarrow \text{H}_2\text{O} + \text{FFT} \\
\text{H}_2\text{S} + \text{Cys} & \rightarrow \text{H}_2\text{O} + \text{S} + \text{H}^+ \\
\end{align*}
\]

(1 mmol each) Thiosemicetal

First-order kinetics of H₂S release from cysteine

Conditions:
0.1 M Cys, buffer, 100 °C
Detection:
Sulfide/silver ion selective electrode

(Münch et al., 1997)

(Zheng & Ho, 1994)
Formation of 2-furfurylthiol (FFT) from sugar fragments and H₂S

(Münch et al., 1997)
**Reaction conditions:**
Precursors (each 1 mmol)
Phosphate buffer (50 mL, 0.5 mol/L)
Autoclave (145 °C, 20 min)

**Mechanism:**
Aldol-type condensation
Cyclisation, dehydration

(Hofmann & Schieberle, 1998)
Formation of S-containing odorants from alcohols under acidic conditions

Reaction conditions:
Alcohol, acetate buffer, pH 4.0, 100 °C

Mechanism:
Acid-catalysed alkylation of amino acid S-atom via cationic intermediates.
Unsaturated alcohols form electrophilic species in acidic media reacting with ambient nucleophilic sites.
(R, R': H, Me)

Sunstruck off-flavour in beer:
Light-induced radical reaction of isohumulone and an SH-source (riboflavin-photosensitized reaction)

(Sakuma et al., 1991)
Formation of methional and DMTS during accelerated aging of beer

**Reaction conditions:**
Storage for 5 days at 40 °C

**Mechanism:**
Strecker degradation of methionine to form methional.
Formation of sulfite/aldehyde adducts trapping methional.
→ Higher DMTS amounts at lower pH via disproportionation of DMDS

(Gijs et al, 2002)
The role of pH in the Maillard reaction: Conclusions

• Many steps in the Maillard cascade are affected by the pH

• pH effect can be different, favouring reactions under acidic or alkaline conditions

• Buffer may have various tasks: i.e. constant pH (reaction control), catalytic effect (increasing reaction rate)

• Neutral pH (6-7) is often the best compromise for flavour formation

• Final amounts depend on formation & degradation, both of them are influenced by pH and may lead to off-notes

Thanks for your attention
Back-up slides
Formation of sotolon from 4-hydroxy-L-isoleucine (HIL) and its lactone

\[
\begin{align*}
\text{HIL} & \quad \text{Sotolon} & \quad \text{HIL-Lactone} \\
\text{OH} & \quad \text{NH}_2 & \quad \text{O} \\
\text{OH} & \quad \text{O} & \quad \text{NH}_2 \\
\end{align*}
\]

<table>
<thead>
<tr>
<th>Carbonyl compound</th>
<th>Sotolon yield (mol%) (from HIL-Lactone)</th>
<th>Sotolon yield (mol%) (from HIL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylglyoxal</td>
<td>35.9</td>
<td>7.4</td>
</tr>
<tr>
<td>2,3-Butanedione</td>
<td>0.3</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>

(Blank et al., 1996)
Lactonisation of 4-hydroxy-L-isoleucine (HIL) is favoured under acidic conditions

Reaction conditions: 100°C, 1 h, phosphate buffer
Analytical technique: FAB-MS

(Blank et al., 1997)
Formation of sotolon from hydroxyisoleucine (HIL) and its lactone: Influence of the pH

![Graph showing the yield of methylglyoxal + HIL-lactone and methylglyoxal + HIL as a function of pH.]

- **Methylglyoxal + HIL-Lactone**
- **Methylglyoxal + HIL**

→ **Optimum: pH 5-6**
Sotolon formed from 4-hydroxy-L-isoleucine by thermally induced oxidative deamination

(Blank et al., 1997)
Formation of secondary degradation products: 1-Pyrroline and methylglyoxal

Retro-aldol reaction

Strecker reaction