Understanding Maillard-type reactions in food processing

Case study: Extrusion

Nancy, September 17, 2012

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Goal: Better control of the Maillard reaction cascade under food processing conditions

Food processing: Extrusion

Holistic approach

Food chemistry: Flavour formation

Targeted approach
Extrusion is an integrated process in which raw materials rich in starch and protein are plastified and structure-modified in a cylinder under pressure and shear at elevated temperatures followed by expansion of the die at the end of the extruder.

Flour Mix (~10% H₂O)

Water, Oil, ...

110–180°C
80–170 bars

Steam

Moisture: 10%

Expansion

~15–20%

~5-10%

Average residence time: 20–30 seconds
Parameters affecting product quality

Recipe
→ Ingredients
→ Specific precursors
→ Concentration, ratio
→ Catalyst
→ pH
→ ...

Extrusion
→ Heat load (T, t)
→ Screw speed, SME
→ Moisture
→ Number of barrels
→ Slurry vs. dry addition
→ ...

- Study the effect of extrusion parameters and recipe composition on furaneol formation from rhamnose and lysine

- Identify recipe and processing conditions during extrusion of rice flour favouring the formation of caramel flavour while considering physico-chemical properties of the final product
**Experimental design:** Key product attributes are affected by both recipe and extrusion parameters

**Recipe parameters**
- pH
- Ratio Rha/Lys
- Phosphate

**Extrusion parameters**
- Moisture levels
- Screw speed
- Temperature
- Residence time
- Slurry vs. dry

<table>
<thead>
<tr>
<th>pH</th>
<th>6.4</th>
<th>7.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rha:Lys</td>
<td>3:0</td>
<td>3:1</td>
</tr>
<tr>
<td>PO4 (mol/kg)</td>
<td>0.035</td>
<td>0.134</td>
</tr>
<tr>
<td>Moisture (%)</td>
<td>17</td>
<td>20</td>
</tr>
<tr>
<td>Screw speed (rpm)</td>
<td>300</td>
<td>400</td>
</tr>
<tr>
<td>Temp. (°C)</td>
<td>120</td>
<td>135</td>
</tr>
<tr>
<td>Barrel length</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>Addition</td>
<td>Dry</td>
<td>Slurry</td>
</tr>
</tbody>
</table>

**Product characterisation**
- Texture
- Crispness
- Colour
- Flavour
- Acrylamide
- Starch degradation
- Granulometry
- Viscosity
- Sensory

**Fractional factorial design:**
- 32 instead of 576 trials
- Determining all main effects and two-factor interactions of 3 recipe and 5 process parameters

**Holistic product characterisation:**
- Chemical, physical, sensorial
- Using 16 methods
Sensory assessment
Reconstituted products from experimental design

- Trained panel (14 panelists)
- Product
  - Extruded powder (85%)
  - Sugar (15%)
- Reconstitution
  - 12.4g product
  - 100mL milk at 70°C
- 32 Products evaluated vs. reference

<table>
<thead>
<tr>
<th>Parameters</th>
<th>units</th>
<th>Low</th>
<th>Medium</th>
<th>High</th>
</tr>
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<td>Screw speed</td>
<td>rpm</td>
<td>300</td>
<td>400</td>
<td>500</td>
</tr>
<tr>
<td>T</td>
<td>°C</td>
<td>120</td>
<td>135</td>
<td>150</td>
</tr>
<tr>
<td>length barrel</td>
<td></td>
<td>short</td>
<td>long</td>
<td></td>
</tr>
<tr>
<td>Addition</td>
<td></td>
<td>dry</td>
<td>slurry</td>
<td></td>
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</table>

- Identification of statistically relevant trends
Colour development
Modulation of colour in product through recipe

**Key parameters**
- pH 6
- pH 7
- Rha/Lys 3:0
- Rha/Lys 3:1
- Phosphate low
- Phosphate high
- 17% H2O
- 20% H2O
- 23% H2O
- 300rpm
- 400rpm
- 500rpm
- 120° C
- 120° C
- 135° C
- 150° C
- Dry Slurry

**Sensory impact**
- Light
- Dark

**Range covered by A01-A32 (vs. REF)**
- tEasySwallow
- aLump
- tSmooth
- Burnt
- Nutty
- aDark
- Caramel
- Toasted
- Processy
- Off
- Overall acid
- WholeGrain
- Mushroom
- astringent
- bitter
- aftertaste
- t1Thick
- tThick
- tFluffy
- t1Wettability
- tSemolina
- Cooked
- Milky
- Rice
- Vanilla
- sweet

11th International Congress on the Maillard reaction
Furaneol formation
Free amino acids, moisture, T and phosphate are most critical

Conversion of rhamnose to furaneol can be modulated through
1. changes of extrusion and/or
2. recipe parameters
Acrylamide
Temperature is most critical

Mitigation options

- pH 6.4
- pH 7.7
- Rha:Lys 3:0
- Rha:Lys 3:1
- Phosphate 0.035 mol/kg
- Phosphate 0.134 mol/kg
- 17% H2O
- 20% H2O
- 23% H2O
- 300 1/min
- 400 1/min
- 500 1/min
- 120 °C-Long
- 120 °C
- 135 °C
- 150 °C
- Dry
- Slurry

11th International Congress on the Maillard reaction
Structure and Texture
Moisture and temperature are most critical

Structure = f (SME)
Texture = f (SME)

Cell walls / µm

Visco5min / mPas ViscoMax / mPas

pH 6.4 pH 7.7
Rha:Lys 3:0 Rha:Lys 3:1
Phosphate 0.035 mol/kg Phosphate 0.134 mol/kg
17% H2O 20% H2O 23% H2O
300 1/min 400 1/min 500 1/min
120 °C-Long 120 °C 135 °C 150 °C
Dry Slurry

Semolina Crispy

11th International Congress on the Maillard reaction
Starch degradation

$MW = f(SME)$

<table>
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<tbody>
<tr>
<td>Moisture</td>
<td>%</td>
</tr>
<tr>
<td>Starch</td>
<td>%d.b.</td>
</tr>
<tr>
<td>Total fibers</td>
<td>%d.b.</td>
</tr>
<tr>
<td>Proteins</td>
<td>%d.b.</td>
</tr>
<tr>
<td>Fat</td>
<td>%d.b.</td>
</tr>
<tr>
<td>Ash</td>
<td>%d.b.</td>
</tr>
</tbody>
</table>

Structure of amyllopectin, a branched starch

Viscosity $= f(MW)$

Viscosity $= f(MW)$

Rice Flour
- Moisture: 8-13%
- Starch: 88-92% dry basis
- Total fibers: 0.3-1%
- Proteins: 6-9%
- Fat: 0.5-1%
- Ash: 0.3-1%

Viscosity vs. Time

SME 92 → SME 35

Carbohydrates (g/100g)
- Low $H_2O$, Low $T$
- High $H_2O$, High $T$
Effect of recipe/extrusion parameters
Options for flavour optimization

- Free amino acid and phosphate affect furaneol, but not SME
- Temperature affects both furaneol and SME
  \[150°C \rightarrow \text{more viscous}\]
- Moisture affects both furaneol and SME
  \[17% \rightarrow \text{less viscous}\]

Next step:
Full factorial design in a smaller space for final product optimisation
Goal: Better control of the Maillard reaction cascade under food process conditions

Food processing: Extrusion
Holistic approach

Food chemistry: Flavour formation
Targeted approach - CAMOLA

0.15 mmol $[^{12}\text{C}_6]$-glucose
0.15 mmol $[^{13}\text{C}_6]$-glucose
0.1 mmol glycine or proline
1 mL 0.5 M phosphate buffer pH 5, 7 or 9

Heating: 135° C/20min
Glucose + Proline → Furaneol

Major pathways

- Aqueous systems: Intact skeleton at pH 5; recombination of C3+C3 at pH 7 and 9
- Dry systems: Intact skeleton (>84%)
- Rice: Intact skeleton (>80%), some recombination of sugar fragments at pH 7 and 9
**Glucose + Glycine → Furaneol**

**Major pathways**
- **Aqueous systems:** Intact skeleton at pH 5; less relevant with increasing pH
- **Dry systems:** Intact skeleton independent of pH
- **Rice models:** Intact skeleton independent of pH, only little by sugar fragmentation

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Glucose + Glycine $\rightarrow$ Furaneol (pH 7)

- **Aqueous system**: Intact skeleton (major) and C3+C3 recombination (minor)
- **Dry system**: Intact skeleton (almost exclusive)
- **Rice model**: Intact skeleton (almost exclusive)
- **Extrusion**: Intact skeleton (almost exclusive), about 8% from inherent precursors
Formation of Furaneol

Model systems:
- Furaneol is mainly formed from intact glucose skeleton
- Except in aqueous systems at weak basic pH where fragmentation is dominating

Food system & extrusion:
- Furaneol is almost exclusively formed from the intact glucose skeleton

(Schieberle et al., 2003; Schieberle, 2005)
Conclusions & Outlook

Ensuring product quality by extrusion

- Flavour generation can be modulated and optimised with respect to other food product attributes (colour, texture, …)
- The holistic approach based on experimental design and a global product characterisation allows rapid optimisation of recipe and extrusion parameters
- This requires an integrated approach of various scientific and engineering disciplines

Future focus

- Better understanding of chemical reactions taking place and their interactions during food processing (targeted experiments, CAMOLA, …)
- Better understanding of material properties and transformation in Maillard systems
- Better integration of food physics & engineering (e.g. physical state, Tg, heat load) in our Maillard world to achieve better control
Thanks to…

- Hélène Chanvrier, PTC Orbe, Structure, texture
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