Der ganzheitliche Ansatz in der Produktentwicklung

Bildung von Karamell-Flavour durch Extrusion

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Nestle PTC Orbe
Flavour is one of the major drivers of consumer preference

However, there are many other factors of similar importance:
- Colour, shape, texture,
- Nutritive value, safety,
- Convenience, packaging, …

Flavouring can be achieved by:
- Adding finished flavours,
- Generating flavours upon food processing, e.g. extrusion

Louis-Leopold Boilly, Les Cinq Sens (The Five Senses), 1823.
Flavour generation upon extrusion

**Recipe**
- Ingredients
- Specific precursors
- Concentration, ratio
- Catalyst
- pH
- ...

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

Highly complex system
Manifold interactions & variability

Effects difficult to predict

Product characterisation

1. Model product
2. Target product

Systematic approach
Experimental design

Sensory evaluation
Volatile/non-volatiles analyses
Chemical/physical measurements
Objective:

- Identify conditions favouring the transformation of rhamnose into furaneol - a caramel-like smelling compound

Extruded product: Effect of extrusion parameters and recipe composition on furaneol formation from rhamnose and lysine

Optimised recipe and processing conditions favouring the formation of caramel flavour upon extrusion of rice flour
Target compound: Furaneol  
(4-Hydroxy-2,5-dimethyl-3(2H)furanone)

- Key flavour: • **Fruits** ➔ strawberry and pineapple  
  • **Roasted products** ➔ coffee, almonds, cereals

- Odour and taste: • fruity, caramelized, sweet
- Odour threshold: • depending on pH  
  • 21-158 µg/kg water
- Formation: • degradation of 6-deoxy-sugars  
  in the presence of amino acids
- Properties: • white to yellow powder  
  • sensitive to oxidation
Thermally induced formation of furaneol from sugars & derivatives

Amadori compounds

Sugar fragments

C_{3} + C_{3}

6-Deoxyhexose

Hexose phosphates

Strecker-assisted chain elongation

Hexose sugars
Experimental setup: Key product attributes affected by recipe and extrusion parameters

Recipe parameters
- pH
- Ratio Rha/Lys
- Phosphate

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

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

Fractional factorial design:
- 32 instead of 576 trials
Modelling furaneol yield & rhamnose degradation by estimating
- all main effects and
- two-factor interactions
of 3 recipe & 5 process parameters
Holistic approach: Analytical characterisation of samples from experimental design

Flavour ⇔ Recipe/process parameters ⇔ Other key product attributes

**List of analysis:**

- Residual rhamnose (HPLC/DAD)
- Furaneol (GC/MS)
- Acrylamide (HPLC/MS)
- Chemical composition (NIR)
- Moisture (MNR)
- Molecular weight profile of starch (GFAS = Gel Filtration Analysis of Starch)
- Molecular weight profile of debranched starch (SEC = Size Exclusion Chromatography)
- Molecular weight profile of proteins (HPSEC = High Performance Size Exclusion Chromatography)
- Colour
- Viscosity (rheometer, RVA profile)
- Granulometry (laser diffraction)
- Texture (X-ray tomography)
  - Porosity (cells size & cell walls distributions, degree of anisotropy)
  - Crispiness (average drop off, force Max)
- Sensory evaluation
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

- Identification of statistically relevant trends

Normalization parameters

<table>
<thead>
<tr>
<th>Parameters</th>
<th>units</th>
<th>Low</th>
<th>Medium</th>
<th>High</th>
</tr>
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<tbody>
<tr>
<td>pH</td>
<td></td>
<td>6.4</td>
<td>7.7</td>
<td></td>
</tr>
<tr>
<td>Rha:Lys</td>
<td></td>
<td>3.0</td>
<td>3:1</td>
<td></td>
</tr>
<tr>
<td>Phosphate</td>
<td>mol/kg</td>
<td>0.035</td>
<td>0.134</td>
<td></td>
</tr>
<tr>
<td>Moisture</td>
<td>%</td>
<td>17</td>
<td>20</td>
<td>23</td>
</tr>
<tr>
<td>Screw speed T</td>
<td>rpm</td>
<td>300</td>
<td>400</td>
<td>500</td>
</tr>
<tr>
<td>T length barrel</td>
<td></td>
<td>120</td>
<td>135</td>
<td>150</td>
</tr>
<tr>
<td>Addition</td>
<td></td>
<td>dry</td>
<td>short</td>
<td>long</td>
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Range covered by A01-A32 (vs. REF)

- Flavor
- Texture & Appearance

Wide diversity of sensory perception

Range of sensory attributes
Correlation matrix
No correlation between furaneol level and SME
Correlation matrix
Furaneol vs SME

Furaneol is positively correlated with the degradation of rhamnose and colour development.

SME is negatively correlated with viscosity.
Sensory evaluation
Link between sensory data and SME or Furaneol

Furaneol is related to odour, flavour, and taste attributes

High ➔ caramel, bitter/astringent, strong overall/aftertaste, burnt/nutty/toasted and dark color

Low ➔ mild notes, sweet, vanilla, milky, cooked, rice

SME is related to texture and appearance

High ➔ smooth, easy to swallow

Low ➔ thick, semolina, wetability
Furaneol formation
Free AA, moisture, T and phosphate are most critical

Conversion of rhamnose to furaneol can be modulated through changes of extrusion and/or recipe parameters

Enhanced with furaneol

Reduced with furaneol

Flavor

Sensory impact

Range covered by A01-A32 (vs. REF)

Enhanced with furaneol

Reduced with furaneol
The diagram illustrates the effect of various factors on Furaneol and SME. Temperature affects both Furaneol and SME. Free amino acid and phosphate affect Furaneol, but not SME. Moisture affects both Furaneol and SME.
Colour development through extrusion
Modulate colour in product through recipe

### Key parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>pH</td>
<td>6, 7</td>
</tr>
<tr>
<td>Rha/Lys</td>
<td>3:0, 3:1</td>
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<tr>
<td>Phosphate</td>
<td>low, high</td>
</tr>
<tr>
<td>H2O</td>
<td>17%, 20%, 23%</td>
</tr>
<tr>
<td>RPM</td>
<td>300, 400, 500</td>
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<tr>
<td>Temp</td>
<td>120°C, 135°C, 150°C, Long</td>
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### Sensory impact

<table>
<thead>
<tr>
<th>Sensory attribute</th>
<th>Sensory score</th>
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</thead>
<tbody>
<tr>
<td>Easy Swallow</td>
<td></td>
</tr>
<tr>
<td>Lump</td>
<td></td>
</tr>
<tr>
<td>Smooth</td>
<td></td>
</tr>
<tr>
<td>Burnt</td>
<td></td>
</tr>
<tr>
<td>Nutty</td>
<td></td>
</tr>
<tr>
<td>Dark</td>
<td></td>
</tr>
<tr>
<td>Caramel</td>
<td></td>
</tr>
<tr>
<td>Toasted</td>
<td></td>
</tr>
<tr>
<td>Processy</td>
<td></td>
</tr>
<tr>
<td>Off</td>
<td></td>
</tr>
<tr>
<td>Overall acid</td>
<td></td>
</tr>
<tr>
<td>Whole Grain</td>
<td></td>
</tr>
<tr>
<td>Mushroom</td>
<td></td>
</tr>
<tr>
<td>Astringent</td>
<td></td>
</tr>
<tr>
<td>Bitter</td>
<td></td>
</tr>
<tr>
<td>Aftertaste</td>
<td></td>
</tr>
<tr>
<td>Thick</td>
<td></td>
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<tr>
<td>Fluffy</td>
<td></td>
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<tr>
<td>Wettability</td>
<td></td>
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<tr>
<td>Semolina</td>
<td></td>
</tr>
<tr>
<td>Cooked</td>
<td></td>
</tr>
<tr>
<td>Milky</td>
<td></td>
</tr>
<tr>
<td>Rice</td>
<td></td>
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<tr>
<td>Vanilla</td>
<td></td>
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<tr>
<td>Sweet</td>
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### Colour generation

<table>
<thead>
<tr>
<th>Colour range</th>
<th>pH 6 Rha/Lys 3:0</th>
<th>pH 7 Rha/Lys 3:1</th>
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</thead>
<tbody>
<tr>
<td>Light</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dark</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Range covered by A01-A32 (vs. REF)**

-6 -5 -4 -3 -2 -1 0 1 2 3 4 5 6
Acrylamide
Temperature is most critical

Acrylamide
-75 -50 -25 0 25 50 75
-6 -4 -2 0 2 4 6

Furaneol ext / mol%  Furaneol dry / mol%

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

17-235 ppb
SME measured / Wh/kg  SME calculated / Wh/kg

-15 -10 -5 0 5 10 15

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

No effect of recipe parameters on SME

Higher SME is achieved with low moisture, high screw speed, low temperature and long extruder.
Structure and Texture
Moisture and temperature are most critical

Structure = f(SME)
Texture = f(SME)
Structure
Wide variety of structures obtained

- Graph showing mean cell size (μm) and porosity (%) with various data points and circles.
- Data points include:
  - Porosity: 70, 75, 80, 85, 90
  - Mean cell size: 12 mm
  - Temperatures: 120°C, 135°C, 150°C
  - Rha:Lys: 1:0, 3:1
  - PO4: 0.035 mol/kg, 0.134 mol/kg
  - H2O: 17%, 20%, 23%
  - Flow rates: 300 L/min, 400 L/min, 500 L/min
Texture: Starch degradation
Depolymerisation of amylopectin increases with SME

<table>
<thead>
<tr>
<th>Rice Flour</th>
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<tbody>
<tr>
<td><strong>Moisture</strong></td>
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<tr>
<td><strong>Starch</strong></td>
</tr>
<tr>
<td>Total fibers</td>
</tr>
<tr>
<td>Proteins</td>
</tr>
<tr>
<td>Fat</td>
</tr>
<tr>
<td>Ash</td>
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Long Chain DP~50
Short Chain DP~25

Structure of amylopectin, a branched starch

SME 92 ← SME 35

Amylopectin, high MW Intermediate depolymerized
High MW
Low MW

SME Intermediate generated, amylose constant

Texture: Starch degradation
Depolymerisation of amylopectin increases with SME
Starch degradation

MW = f (SME)

Viscosity = f (MW)

SME 92 → SME 35

Low MW Intermediate generated, amylose constant

High H2O High T

Amylopectin

Low H2O Low T

Amylose
Conclusions

Critical parameters for generation of furaneol from rhamnose during extrusion:

- Furaneol generation is affected both by recipe parameters (Lys, PO$_4$) and extrusion parameters (T, moisture)
- Recipe parameters permit furaneol modulation w/o impact on texture
- Lower pH will limit colour and acrylamide development w/o affecting furaneol formation
- Addition of amino acid will enhance furaneol while limiting acrylamide formation
- Temperature and moisture affect both furaneol formation and texture (→ SME)

Full factorial design
### Thanks to...

<table>
<thead>
<tr>
<th>Name</th>
<th>Affiliation</th>
<th>Field</th>
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<tbody>
<tr>
<td>Hélène Chanvrier</td>
<td>PTC Orbe</td>
<td>Structure, texture</td>
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<td>Tomas Davidek</td>
<td>PTC Orbe</td>
<td>Flavour, acrylamide</td>
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<tr>
<td>Valérie Leloup</td>
<td>PTC Orbe</td>
<td>Macromolecular chemistry</td>
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<td>Werner Pfaller</td>
<td>PTC Orbe</td>
<td>Extrusion</td>
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<td>Andreas Rytz</td>
<td>NRC Lausanne</td>
<td>Experimental design</td>
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<tr>
<td>Silke Illmann</td>
<td>Univ. Karlsruhe</td>
<td>Diploma work</td>
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<tr>
<td>Claudia Leeb</td>
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<tr>
<td>Heike Schuchmann</td>
<td>Univ. Karlsruhe</td>
<td>Extrusion</td>
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... and to you for your kind attention!