Optimization of caramel flavour generation upon extrusion cooking

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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, structure, texture,
- Nutritive value, safety,
- Convenience, packaging, …

Flavouring can be achieved by

- adding compounded and/or reaction flavours
- generating flavours upon food processing, e.g. extrusion

Louis-Leopold Boilly, Les Cinq Sens (The Five Senses), 1823.
Extrusion with direct expansion
Product structure created by extrusion

Flour Mix (~10% H$_2$O)

Water, Oil, ...

Moisture: 10%

110–180°C
80–170 bars

~15–20%

Average residence time: 20–30 seconds

~5-10%

Steam

Expansion

The cereal is expanded to its final size at the extruder outlet

Downstream processing

80–170 bars

110–180°C

~15–20%
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
→ ...

Manifold interactions, Effects difficult to predict
Systematic & multidisciplinary approach, Experimental design

4-Hydroxy-2,5-dimethyl-3(2H)-furanone (Furaneol®) as a target compound generated from sugars

Favourable conditions
• low moisture
• high pH
• T > 120 °C
Objective

- 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

 Optimised recipe and processing conditions
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

<table>
<thead>
<tr>
<th>pH</th>
<th>6.4</th>
<th>7.7</th>
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</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
- 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)
- Texture: Spoon test
- Sensory evaluation
- 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

Wide diversity of sensory perception

Range of sensory attributes

<table>
<thead>
<tr>
<th>Parameters</th>
<th>units</th>
<th>Low</th>
<th>Medium</th>
<th>High</th>
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<tbody>
<tr>
<td>pH</td>
<td></td>
<td>6.4</td>
<td>7.7</td>
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</tr>
<tr>
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<td></td>
<td>3:1</td>
<td>3:1</td>
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<td>mol/kg</td>
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<tr>
<td>Moisture</td>
<td>%</td>
<td>17</td>
<td>20</td>
<td>23</td>
</tr>
<tr>
<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>
</tr>
</tbody>
</table>

Range covered by A01-A32 (vs. REF)

Texture & Appearance

Flavor

- Burnt
- Nutty
- aDark
- Caramel
- Toasted
- Processy
- Off
- Overall
- acid
- WholeGrain
- Mushroom
- astringent
- bitter
- aftertaste
- t1Thick
- tThick
- tFluffy
- tWettability
- tSemolina
- Cooked
- Milky
- Rice
- Vanilla
- sweet
Correlation matrix
No correlation between Furaneol level and SME

32 samples produced in experimental design
Resulting in products with sufficiently different properties
Correlation matrix
Furaneol vs SME

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

SME is negatively correlated with viscosity.
Conversion of rhamnose to furaneol can be modulated through changes of extrusion and/or recipe parameters.
Acrylamide
Temperature is most critical

Furaneol ext / mol%  Furaneol dry / mol%

Acrylamide

-6 -4 -2 0 2 4 6

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% 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
Colour development
Modulate colour in product through recipe

**Colour generation**

**Browning reactions**

*pH 6*  
Rha/Lys 3:0

*pH 7*  
Rha/Lys 3:1

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**Key parameters**

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

**Sensory impact**

- tEasySwallow
- aLump
- tSmooth
- Burnt
- aDark
- Caramel
- Toasted
- Processy
- Off
- Overall acid
- WholeGrain
- Mushroom
- astringent
- bitter
- aftertaste
- t1Thick
- tThick
- tFluffy
- t1Wettability
- tSemolina
- Cooked
- Milky
- Rice
- Vanilla
- sweet

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**Colour range**

- Range covered by A01-A32 (vs. REF)
SME
Temperature, moisture, screw speed are most critical

No effect of recipe parameters on SME

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

Structure = \( f (\text{SME}) \)

Texture = \( f (\text{SME}) \)

Visco5min / mPas  ViscoMax / mPas

-1500 -1000 -500 0 500 1000 1500

pH 6.4  pH 7.7

Rha:Lys 3:0  Rha:Lys 3:1

Phosphate 0.035 mol/kg  Phosphate 0.134 mol/kg

Cell walls / µm

-15 -10 -5 0 5 10 15

Process

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
Structure
Wide variety of structures obtained

- Rha:Lys 1:0
- Rha:Lys 3:1
- 0.035 mol/kg PO4
- 0.134 mol/kg PO4
- 17% H2O
- 20% H2O

Cell walls (um)
- 600
- 800
- 1000
- 1200

Mean cell size (um)

Porosity (%)
- 75
- 80
- 85

Dry
Slurry

Main effect
- 0
- 200
- 400
- 600
### Rice Flour

<table>
<thead>
<tr>
<th>Component</th>
<th>%</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>%</td>
<td>8-13</td>
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<tr>
<td>Starch %d.b.</td>
<td></td>
<td>88-92</td>
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<tr>
<td>Total fibers</td>
<td>%</td>
<td>0.3-1</td>
</tr>
<tr>
<td>Proteins %d.b.</td>
<td></td>
<td>6-9</td>
</tr>
<tr>
<td>Fat %d.b.</td>
<td></td>
<td>0.5-1</td>
</tr>
<tr>
<td>Ash %d.b.</td>
<td></td>
<td>0.3-1</td>
</tr>
</tbody>
</table>

Texture: Starch degradation

Depolymerisation of amylopectin increases with SME.

![Structure of amylopectin, a branched starch](image)

**Low MW Intermediate generated, amylose constant**

**Amylopectin, high MW Intermediate depolymerized**

### Carbohydrates

<table>
<thead>
<tr>
<th>Component</th>
<th>%</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amylopectin</td>
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<td></td>
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<tr>
<td>Intermediate 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intermediate 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amylose</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Molecular weight

- **High MW**
- **Low MW**
Starch degradation

MW = f (SME)

Amylopectin, high MW Intermediate depolymerized
Low MW Intermediate generated, amylose constant

Starch degradation

Viscosity = f (MW)

SME 92 → SME 35
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 → more viscous

Moisture affects both furaneol and SME
17% → less viscous
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)
- Temperature and moisture affect both furaneol formation and texture (→ SME)
- 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