Starch technology
in: Food Technology and Biotechnology I

Evžen Šárka; evzen.sarka@vscht.cz;
History

- Egypt (3500 BC) – wheat, dusting of wounds, cosmetics (powdered), papyrus production, glowing
- “amylum“ = fine flour
- Cato described the production of starch (234-139 BC)
Marcus Cato the Elder

• /was a Roman statesman, commonly referred to as Censorius (the Censor)/
• His regulations against luxury were very stringent. He imposed a heavy tax upon dress and personal adornment, especially of women.
• His personal motto became: „Ceterum (autem) censeo Carthaginem esse delendam“ - Carthage must be destroyed.
• Cato is famous not only as statesman or soldier, but also as author. His manual on running a farm (De Agri Cultura or "On Farming") is his only work that survives completely.
• Probably Cato's most important work, Origines, in seven books, related the history of the Italian towns, with special attention to Rome, from their legendary or historical foundation to his own day.
Starch production in USA

corn wet-process grindings

mil. t of starch

years
History of starch in the Czech Republic

- The first (potato) starch factory of Bedřich Krupička here was established in 1810; before World War I: 186 farm starch manufactories (90% of Austria-Hungary); 70% of starch was exported
- Market outlets loss during the both world wars.
- After 1948 (nationalization): a significant fall, there were 15 starch firms in Bohemia and Moravia in 1975, and 8 firms (with 29 small starch factories) in 1981, starch factories were built in Slovakia as well.
Starch production in Europe

• about 9 mil. t starch per year (60-65 mil. t starch per year in the world)

• 46 % corn starch, 16 % potato starch (quota), 38 % wheat starch (data from 2009)

• Czech Republic: only potato starch (19 000 t/year) and wheat starch (18 000 t/year) 😊
EU & starch derivatives

Starch factories in the Czech Republic

**Potato starch factories:**
- AMYLEX Radešínská Svratka s.r.o. (Žďár nad Sázavou) → Novidon s.r.o. Hodíškov (2012)
- Škrobárny Pelhřimov a.s. about 13000 t/year
- Lyckeby Amylex a.s. Horažďovice about 18000 t/year

**Wheat starch factories:**
- Amylon a.s. Havlíčkův Brod about 7000 t/year
- Krnovská škrobárna s.r.o. about 7000 t/year
Starch is comprised of two polysaccharides, amylose and amylopectin. The monosaccharide units are linked by 1,4'-alpha-glycoside bonds in amylose like those in maltose. Amylopectin contains 1,4'-alpha-glycoside bonds and 1,6'-alpha-glycoside bonds as well.

- **Amylose**
Structure of starch

• amylopectin

Amylose accounts for about 20-25% by weight of starch and consists of 1000-6000 glucose molecules. Amylopectin consists of 50,000-1,000,000 glucose units.
• Creation of hydrogen bridges
Structure of starch

- amylose: (dis)continuous helix with 6 molecules of glucose per turn; the cavity having iodine affinity – blue color
Amylopectin

- Some of chains form double helixes

http://glycopedea.eu/Introduction-64

Structure of starch
**Starch and Starch Derivatives in Commercial Use**

**Native Starches**

<table>
<thead>
<tr>
<th>Amylose</th>
<th>Amylopectin</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 - 25%</td>
<td>75 - 80%</td>
</tr>
</tbody>
</table>

Genetically modified cultivars

<table>
<thead>
<tr>
<th>Starches</th>
<th>Amylose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waxy maize</td>
<td>5%</td>
</tr>
<tr>
<td>Amylo maize</td>
<td>60 - 70%</td>
</tr>
<tr>
<td>Waxy sorghum</td>
<td></td>
</tr>
<tr>
<td>Waxy rice</td>
<td></td>
</tr>
</tbody>
</table>

Chemically modified esters, ethers, cross-linked, cationic, oxidised

<table>
<thead>
<tr>
<th>Starches</th>
<th>Derivatives</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monophosphates</td>
<td></td>
</tr>
<tr>
<td>Acetates</td>
<td></td>
</tr>
<tr>
<td>Hydroxypropyl adipates</td>
<td></td>
</tr>
<tr>
<td>Diphosphates</td>
<td></td>
</tr>
</tbody>
</table>

Hydrolysed starches - acid, enzyme

<table>
<thead>
<tr>
<th>Starches</th>
<th>Derivatives</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corn syrups</td>
<td></td>
</tr>
<tr>
<td>Maltodextrins</td>
<td></td>
</tr>
<tr>
<td>Glucose</td>
<td></td>
</tr>
</tbody>
</table>

Dextrins - low moisture, heat, acid treatments

<table>
<thead>
<tr>
<th>Starches</th>
<th>Derivatives</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yellow gums</td>
<td></td>
</tr>
<tr>
<td>White gums</td>
<td></td>
</tr>
<tr>
<td>British gums</td>
<td></td>
</tr>
</tbody>
</table>
Uses of Starch and Derivatives

Food Uses
sauces
soups
dressings
baked goods
dairy products
meat products
drinks
ice cream
refrigerated
depth-frozen
dry mix
tropical storage - liquids (30°)
ambient (temperate)

Industrial Uses
paper and board
textiles
plastics
rubber
oil
pharmaceuticals
medicine
 cosmetics
 adhesives
 sewage and water treatment
 alcohol

thickening
gelling
stabilising
sweetening
 bulking
 texturising
fat replacement

sizing
coating
texturising
viscosity control
flocculation
ion exchange
adhesive
dusting
fuel
Size of starch granules:

- (a) potato 10-80 μm
- (b) wheat 2-10 μm, 10-40 μm
- (c) corn (hollow) 5 – 25 μm
- rice 3-8 μm (granule conglomerate), multi-cornered
Properties of starch:

• hygroscopic matter
  (equilibrium moisture: potato starch 21 %, wheat starch 14 %)

• insoluble in cold water
Properties of starch and starch disperses:

- **swelling** of the granules (reversible)
- **gelatinisation** at about 60 °C (irreversible) → starch gel

When the starch granules are heated in water, amylose is leached progressively as the temperature is raised.
Properties of starch and starch disperses:

- **starch gel** $\rightarrow$ **solid starch gel**: (cooling)

- **retrogradation**

  post-gelatinization changes accompanying the restoration of molecular order in starch

Rheology

- Rheology is a part of physics dealing with forces and deformations (change of body dimensions), their relationships and their interrelationships with time.
- It deals with procedures, instruments and material properties.
**Newtonian liquids**

- For Newtonian liquids the shear stress is proportional to velocity gradient:
  \[ \tau = \eta \cdot \gamma , \]

- The shear stress \( \tau \) [Pa] can be defined from the shear force \( F_x \) as \( \tau = dF_x/dA \), where \( A \) is the parallel area.

- The deformation can be expressed as the velocity gradient or shear rate \( \gamma = -du_x/dy \).

- The proportionality constant \( \eta \) [Pa.s] is called viscosity coefficient or (dynamic) viscosity [Pa.s].
Rheology of concentrated dispersion systems

1 – Newtonian liquid
2 – shear thinning (pseudoplastic)
3 – shear thickening (dilatant: when increase in viscosity is accompanied by volume expansion)
4’ – Bingham plastic fluid
4 – non-Bingham plastic fluid

• A viscoplastic material that behaves as a rigid body at low stresses but flows as a viscous fluid at high stress

\[ \tau \] – shear stress [Pa]
\[ \gamma \] – velocity gradient (shear rate) [s\(^{-1}\)]
Rheology of concentrated dispersion system

\[ \tau \] – shear stress [Pa]

\[ \gamma \] – velocity gradient (shear rate) [s^{-1}]

\[ \eta_2 \] – apparent viscosity [Pa.s]

1. Newtonian
2. \( \eta_2 \) – shear thinning
3. \( \eta_2 \) – shear thickening
4. Non-Bingham plastic fluid
Rheology of concentrated dispersion systems

- Fluids that exhibit decreasing shear stress and apparent viscosity with respect to time at a fixed rate are called thixotropic fluids (shear thinning with time).

- Thixotropy is important e.g. in painting – the paint shall be flowing only during the painting process.

- The reverse phenomenon is called rheopexy.
A Brabender viscoamylograph provides information on gelatinization as well as on the properties of the cooled paste. This instrument records the torque needed to counteract the viscosity that develops when a starch suspension is subjected to heating and cooling regimes. Viscosity is measured in arbitrary units (Brabender units) that reflect paste consistency; for this reason, Brabender results are described in terms of paste properties and pasting temperatures at specific times.

»1 – wheat starch, 2 – potato starch, 3 – maize starch
Potato starch processing
## Potato starch processing

### Composition of the potato:

<table>
<thead>
<tr>
<th>Component</th>
<th>(%)</th>
<th>scope (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>75,0</td>
<td>63 – 87</td>
</tr>
<tr>
<td>Starch</td>
<td>19,0</td>
<td>8 - 30</td>
</tr>
<tr>
<td>Proteins</td>
<td>3,0</td>
<td>0,7 – 4,7</td>
</tr>
<tr>
<td>Fibre</td>
<td>1,5</td>
<td>0,9 – 2,5</td>
</tr>
<tr>
<td>Ash</td>
<td>1,3</td>
<td></td>
</tr>
<tr>
<td>Soluble carbohydrates</td>
<td>1,1</td>
<td></td>
</tr>
<tr>
<td>Fat</td>
<td>0,2</td>
<td></td>
</tr>
</tbody>
</table>
Potato starch processing

1. Storing
2. Stones and dirt catchers
3. Washing
4. Rotary saw blade
5. Centrifuges
6. Washing centrifuges
7. Press
8. Purification
9. Vacuum rotary filter
10. Hot air dryer
11. Sieving

Potatoes → stones, tops → water → stones, tops, tops → dirt separation → washing → water → washed potatoes → grinding → mashed product → centrifuges → potato fruit water → purified water → raw starch slurry → vacuum rotary filter → hot air dryer → sieving → starch
Potato starch processing

- after grinding dilution with water (10 – 200 %)
- SO$_2$ addition (0,02 – 0,04 %)
- fruit water separation (decanter centrifuge); there is a worm rotating at different speed inside, the difference is 200 – 400 min$^{-1}$ (inner 1500 min$^{-1}$, outer 1200 min$^{-1}$)
- smaller quantities of waste water - feeding, fertilizing, event. source of protein
Starch extraction

- Conical centrifugal sieves

Screening separates starch from pulp. The pulp can be reground and a second extraction performed to obtain a total starch yield of 12-19%, based on raw potatoes.
Hydrocyclone 10 mm

Cylonette 10A (long model)

Cylonette 10B (short model)

Vortex finder
Removal water from starch 😊

- = filtration on rotating vacuum drum filters
- output water content 38 – 40 %
Drying

- pneumatic ring dryer, air 140 – 160 °C (t < 175 °C - chemical changes of starch), output temperature 46 – 49 °C
- output water content 17 – 18 %
Principle of cyclone
Finishing

• sowing machines: separation of agglomerates and lumps
• storing – bulk silos, packing in bags or big bags
Wheat starch processing
Advantages

• wheat flour has a high starch content, low water content (consequences - lower microbial contamination ⇒ better storability, less waste water)
• vital gluten is produced as a by-product (better marketability than starch)
• year-round production
• cheaper raw material
Disadvantages

• starch granules must be separated in two fractions A and B (10 μm)
• higher protein content in starch – Maillard reaction, celiatics
• smaller porosity of starch granules (more compact) \(\Rightarrow\) difficult processing to produce modified starches
Martin (dough ball) process

wheat flour

continuous dough mixer

extractor

Starch slurry from the dough washer is screened to remove any remaining gluten and then fine screened to remove bran.

rotary screen

washing tank

centrifuges

vacuum rotary filter

hot air dryer

sieving

packaging

bran

NaOH

sedimentation tank

The residual gluten is partially dried by roller compression and then flash dried.
Dough preparation

- bakery continuous kneaders, time delay about 70 s, appropriate maturing 10-20 min (swelling of gluten)

Wheat flour and water (2 : 1) are blended and the dough is allowed to rest, hydrate, and strengthen the gluten matrix.
Dough washing

- ribbon blenders

The dough is kneaded while washing with water to remove the starch.
Refining centrifuges

• (Conical centrifugal sieves)

Centrifugal separation of the starch slurry separates the large starch granules (type A starch) from the small granules (type B starch).
Drying

- pneumatic ring dryer, air 140 – 160 °C (t < 175 °C - chemical changes of starch), output temperature 46 – 49 °C

Type A starch is essentially pure and may be dewatered and flash dried to 10 – 12 % moisture.
Dextrins
Pyrodextrin discovery

- It was the partial burning of starch stored in a textile factory in Dublin in September 1821.
Dextrins

• are made by dry-roasting starch alone or in the presence of a catalyst (an acid or a salt)
• temperatures up to 130 °C – starch loses capillary and bound water; decomposition of amylopectin aggregates, glycoside bonds are broken up - at first (1-6) later (1-4) ⇒ reduction in degree of polymerization
Dextrins

- temperatures over 130 °C
  - irreversible removal of water molecules from the terminal of starch to form glucose anhydride, creation of new branched macromolecules due to reversion (reaction reducing terminal group with another OH group), recombination (new branching) and transglycosidation (1-6 to 1-4, and conversely)
Dextrin manufacture

1. Starch
2. Acidification
3. Mixing
4. Redrying
5. Converting
6. Cooling
7. Water addition
8. Mixing
9. Sieving
10. Packaging

Dextrin grit

Dextrin
Application - adhesives

- white dextrins (gums): glue for offices
- yellow dextrins (gums): gummed sheets and labels
- tube winding, bag-seam pastes, laminating and sealing of paperboard, books, cigarette seam adhesives

- (adhesive ability = resistance to breakage) corn dextrin < potato dextrin < alum dextrin
- Amylon Havlíčkův Brod: a big factory
Other applications

- textile industry – finishing; gluing leather
- thickening dyes (water solutions)
- production of matches (heads); in the ignition lines; pencils
- metal industry: in foundry molds - as an auxiliary binder of bentonite sand mixtures to improve plasticity and ability for tamping down and to increase abrasion resistance of molds

- in the production of heat resistant ceramics, grinding (abrasive) wheels
- in food (coated products, additives for bakeries, in frozen foods, in fillings - fat replacement)
Modified starches

- chemically modified starch
- enzymatically modified starch (maltodextrins)
- physically modified starch

- oxidation, degradation substitution
- pregelatinized starch
- extruded starch
Pregelatinized starch

- Pelhřimov, Polná; Krnov
- converting starch to hydrated (gelatinized) state by heating it in an aqueous slurry to a temperature above the gelatinization temperature and then the water is quickly removed (no hydrogen bonds between the OH groups are created)
Pregelatinized starch

- manufacture:
  - on hot rolls (starch slurry, starch gel):
    1. The starch slurry is drawn downward between the nip of the hot rolls to form a thin film. The film dries as the rolls turn and is scraped off and ground to produce a fine powder.
    2. The starch slurry is heated in an autoclave or in an heater above the gelatinization temperature and is then drawn downward between the nip of the hot rolls to form a thin film (energy savings, higher quality)
  - spray drying a gelatinized starch paste
Functional properties

• Pregelatinized starch quickly rehydrates in cold water. (Pregelatinized starch is an essential component in foods in which cooking is not employed, such as in instant puddings).

• Combination of properties: pregelatinized starch is prepared after oxidation, acetylation etc.
Starch extrusion – extruded starches

- starch gel originates by mechanical and thermal treatment, initial water content in the range from 15 to 30%
- spontaneous expansion and evaporation of water \(\Rightarrow\) fast drying
Application of extruded starches

- foundry industry: in foundry molds - as a binder
- components of chipboards
- paper and textile industry
Starch oxidation

The oxidations by specific or non-specific oxidants in water may proceed in four different ways, producing distinct products with aldehyde, ketone or carboxyl groups on C-2, C-3 or C-6 carbons. Increasing number of carbonyl and carboxyl groups into the starch molecules cause changes in the chemical and physical properties.
Starch oxidation

- **selective oxidation** (nitric acid – C6 forming galacturonic acid, 50 % of groups oxidized; periodic acid – C2 a C3 za forming starch dialdehyde)

- **nonselective oxidation**:
  - **acidic** medium (chromic acid, KMnO$_4$, H$_2$O$_2$, Cl$_2$, oxyhalogenic acids, peracids, ozone)
  - **alkaline** medium (sodium hypochlorite, chlorinated lime, alkaline peroxides, alkaline permanganate, ammonium persulphate, electrolysis of alkaline starch slurry in NaCl solution)

reverse regeneration of iodates to periodates electrolytically

prepared directly in paper factories
Oxidized starch production

1 – reaction tank, 2 – tank for starch slurry, 3 - tank for lye, 4 – tank for NaClO, 5 – tank for sodium sulphite, 6 – tank for HCl, 7 – accumulating refinery tank, 8 – refinery separators, 9 – diffusion tanks, 10 – vacuum filter, 11 – dryer, 12 – sieving
Impact on viscosity

Heated aqueous dispersions of oxidized starches have lower viscosities (when cooking) which depend on the extent of oxidation than native starches. On the other hand, they have high viscosity after cooling.

COOH \( \eta \)  

- Depolymerization
- Lower gelatinization temperature
- Temperature depends on pH
Application of oxidized starch
E 1404

• Moramyl OXB = potato – paper industry – 80-85 % of uses
• Moramyl OXP = wheat – for gypsum-board walls
• Další použití: thickener, stabilizer, kitchen spice, jelly in confectionery, ice creams, improves the water holding capacity of dough, breading batters for deep fried foods (fish, meat), excipient in pharmacy, textile manufacture (warp sizes, in finishing and printing), starching of linen, it improves the mechanical properties of the leather, insulation
Substitution of starch

- ethers
- esters
- cross-linked starch

The following properties can be changed:
- hydration ability (solubility)
- dispersion stability (retrogradation)
- rheological properties
- chemical properties
Starch derivatives

• degree of substitution DS: the number of substituted groups per a glucose unit of starch, in practice mostly used in the range 0.01 to 0.5, the maximum value of about 1 (theoret. max 3)
Starch derivatives

• reaction in heterogeneous system
• max. 60 °C
• sufficiently long reaction time 5-6 h (diffusion in starch granule + reaction)
• (Mono)esters
E 1420 Acetylated starch

• reaction with acetic anhydride (according to PREY):

\[
\text{starch-OH} + \text{NaOH} + (\text{CH}_3\text{CO})_2\text{O} \rightarrow \\
\text{starch-O-CO-CH}_3 + \text{CH}_3\text{COONa} + \text{H}_2\text{O}
\]

(pH 8-8.5; 35-38 °C, 3-4 h; 3% NaOH, side reaction: decomposition of the acetate anhydride to acetate; yield 50 %)

• reaction with vinylacetate:

\[
\text{starch-OH} + \text{CH}_2=\text{CH-O-CO-CH}_3 \rightarrow \text{starch-O-CO-CH}_3 + \\
\text{CH}_3\text{CHO}
\]

(pH 9-10; 35 – 38 °C; higher yield 60 – 70 %; side reactions)

Low DS (degree of substitution) starch acetates have major use in foods where they provide thickness, body, and texture.
E 1410 Monoester phosphate starch (Monophosphate)

- Soluble at normal temperature
- Moramyl E = wheat
  - high water linkage, can industry, ketchups, spreads etc.
- Moramyl EB = potato
  - ice cream, ketchups, mayonnaise, dressings

Cooked aqueous dispersions of starch phosphate compared to natural starch have increased gel clarity, increased viscosity, a more cohesive texture, and gels that are stable to retrogradation.
E 1410 Monoester phosphate starch (Monophosphate)

\[ \text{starch} - \text{OH} \ + \ \text{NaO} \]

\[ \text{NaO} \]

\[ \text{O} = \text{P} \quad \text{O} - \text{starch} \]

\[ \text{HO} \]

\[ \text{OH} \]

\[ \rightarrow + \text{H}_2\text{O} \]
E 1450 Sodium octenylsuccinate starch

- thickener, stabilizer

• **TRECOMEX TWELVE, TRECOMEX TWELVE 02:**
  - better consistency of meat spreads, meat cans and meat mixtures
  - higher fat binding in a product
  - better production economy
  (yolks displacement)

• **OPASET 2070:**
  - pancakes, pasta

• - dough elasticity
  - dry surface

octenyl succinic acid
• Ethers
Starch ethers

- common characteristic is the nature of the ether bond of a substituent in a starch molecule
- opening of oxirane circles; nucleophilic substitution, alkylation (Williamson synthesis); addition to unsaturated compounds (Michael synthesis)
E 1440 Starch hydroxypropylether

- thickener, stabilizer

*Hydroxypropyl derivatives* are typically produced by reaction of propylene oxide with starch under alkaline conditions. At low degree of substitution the physical properties of these ethers are similar to those of low DS starch acetates. In *textiles*, low DS starch ethers are employed as warp sizing. In *foods*, starch ethers provide thickness and texture and the ability to hold water at low temperature.
• Cross-linked starches
Cross-linked starches

- Cross-linking of starch reinforces the intermolecular binding by introducing covalent bonds to supplement natural intermolecular or intramolecular hydrogen bonds.
- Cross-linked grid

(starch)-O-R-O-(starch)

is created by esterification or etherification reactions.

Cross-linking restricts granule swelling, increases peak viscosity on cooking, and increases the stability of the gelatinized granule.
Cross-linked starches

- The influence on physical properties has the number of crosslinks, the character of substituent is not so important.
- Most cross-linked starches are quite lightly derivatized, containing ca. one cross-link for every 100 to 3000 anhydro-D-glucosyl units (degree of substitution, DS 0.0003 – 0.01).
- At low degree of substitution an increase in peak viscosity is observed when measured by a Brabender amylograph.
E 1412 Diester phosphate starch (Diphosphate)

- Thickener, stabilizer
  - Moramyl ZB = potato – soluble at normal temperature – meat cans, meat spreads, meat mixtures, mayonnaise, fillings
  - Moramyl ZBH = potato – soluble at increased temperature - jam, dressings, meat industry
E 1412 Diester phosphate starch (Diphosphate)

2 starch – OH +

\[
\text{NaO} \quad \text{O} \\
\text{O} \quad \text{P} \\
\text{O} \quad \text{starch} \\
\text{starch} - \text{O}
\]

\[
\rightarrow
\]

\[
\text{NaO} \quad \text{O} \\
\text{O} \quad \text{P} \quad \text{O} \\
\text{P} \quad \text{ONa} \\
\text{NaO} \quad \text{O} \\
\text{Na}_2\text{H}_2\text{P}_2\text{O}_7
\]
Diethers  Cross-linked starches

\[
2 (\text{škrob}) \cdot C + \text{Cl} - \text{CH}_2 - \begin{tikzpicture}
    
    
    
    \node at (0,0) (a) {O};
    \node at (0,-0.5) (b) {CH};
    \node at (1,-0.5) (c) {CH}_2;
    \draw (a) -- (b);
    \draw (b) -- (c);
    \end{tikzpicture} \xrightarrow{\text{NaOH}} \text{epichlorohydrin}
\]

\[
(\text{škrob}) \cdot \text{O-CH}_2\cdot \text{CH-CH}_2\cdot \text{O-(škrob)} + \text{NaCl} + \text{H}_2\text{O} \downarrow \text{OH}
\]
Food producers use *acetylated distarch adipate* (ADA) for many purposes, including as a stabilizer, a thickener, a firming agent, a solvent agent, a carrier agent, an encapsulating agent, a moisture control agent, a flavour modifier, a texturizer and an anti-stick agent. Stabilisation prevents syneresis, meaning that, compared with native starches, ADA is suitable for use in yoghurts and in chilled sauces, e.g. Bechamel. ADA is used as a fat-replacer in mayonnaise, yoghurt, dressing and cooking margarine. It is also applied in ketchup, cocoa syrups, fruit preparation, fruit pies and fillings, relishes, pickles and baby food.
E 1442 Hydroxypropyl starch diphosphate (hydroxypropylether of cross-linked starch phosphate)

- thickener, stabilizer

- **TRECOMEX AET4:**
  - meat spreads, meat cans or for meat mixtures
  - no liberation of meat souses in products
  - higher stability and compactness of pancakes, meat spreads, meat cans and meat mixtures
  - no gelatinous blocks
  - better production economy

- **pancakes, pasta**
  - smooth texture
  - better texture of pancakes and pasta
  - dry surface
E 1442 Hydroxypropyl starch diphosphate (hydroxypropylether of cross-linked starch phosphate)

- thickener, stabilizer
- SWELY GEL 790:
  - full taste of instant products
  - soluble by normal temperature
  - smooth texture
  - resistant to mechanical strain
Cationic starch ethers

- The process has two steps, the first one is a reaction of epichlorohydrin to prepare cationic substituent.
Cationic starch ethers

- cationic substituent then reacts with starch (pH 10.5 - 12; 25 - 35 °C, about 7 hours):

\[
\text{starch} - \text{OH} + \text{Cl} - \text{H}_2\text{C} - \text{CH} - \text{CH}_2 - N^\oplus_{R_1 R_2 R_3} \rightarrow
\]

\[
\text{starch} - \text{O} - \text{H}_2\text{C} - \text{CH} - \text{CH}_2 - N^\oplus_{R_1 R_2 R_3} + \text{HCl}
\]
Cationic starch ethers

- Batelov, Horažďovice
- Zeta potential measurements show that these cationic starch derivatives have a positive charge at pH of between 4 and 9,
- Cationic starch dispersions increase stability and clarity compared to dispersions of native starches
- Paper industry - wet-end additives and sizings (linkage with cellulose – higher strength of the paper, cleaner waste water, higher yield, lower cost production)
- Temperature 25 - 35 °C, pH 10.5 - 12, about 7 hours
Hydrolysed starches:

- syrups
- powdered syrups
- crystalline glucose or maltose
Glucose syrups

- are purified concentrated water solutions of glucose produced by acid or enzymatic starch hydrolysis; depending on the degree of hydrolysis, glucose syrup may contain, in addition to glucose, maltose and higher saccharides.
- The level of hydrolysis is described by dextrose equivalent (DE). By total hydrolysis DE = 100.
- Usually DE 38 - 48 %.
Acid hydrolysis of starch

• breaking both $\alpha$-D-(1$\rightarrow$4) and $\alpha$-D-(1$\rightarrow$6) linkages
• linkages $\alpha$-D-(1$\rightarrow$6) are hydrolyzed 4 times faster
• a bimolecular reaction in an excess of water – first-order reaction
• the result of hydrolysis is a mixture of carbohydrates with different degree of polymerization
Acid hydrolysis of starch

- undesirable chemical reactions: reverse of glucose (back polymerization), formation of hydroxymethylfurfural

\[
\text{starch} \rightarrow \text{HO-CH-CH-OH} \rightarrow \text{HOCH}_2-\text{CH} \rightarrow \text{CH-CH}=\text{O} \rightarrow \text{H}^+ \rightarrow -3 \text{H}_2\text{O} \rightarrow \text{HOCH}_2-\text{CH} \rightarrow 5\text{-hydroxymethylfurfural}
\]

- follow-up decomposition of HMF in acid solution \(\Rightarrow\) dark polymers, or levulinic acid

\[H_2C-\text{CO}-\text{CH}_2-\text{CH}_2-\text{COOH}\]
Acid hydrolysis production

1. Starch
2. Acid
3. Soda
4. Steam
5. Active carbon + kieselguhr
6. Vacuum
7. Sirup
8. Vacuum
9. Vacuum
10. Vacuum
11. Vacuum
12. Vacuum
13. Vacuum
Maltose syrups

- production using enzymes
- the prevailing component in dry substance is maltose
Enzymatic hydrolysis production (Havlíčkův Brod)

used enzymes are:

- $\alpha$-amylase
- $\beta$-amylase
- glucoamylase
- pollulanase and isomaltase
α-amylase

• breaks α-D-(1→4) linkages, endo-acting enzyme (attacking the starch chain in the interior part)
• the resulted product: mixture of oligosaccharides + maltose + glucose; on the branching: isomaltose and panose ⇒ viscosity fall; content of reducing matters increases slowly
\(\beta\)-amylase

- breaks \(\alpha\)-D-(1\(\rightarrow\)4) linkages as well, exo-acting enzyme – it acts on the non-reducing ends of starch polymer chains and produces maltose, it stops on the branching \(\alpha\)-D-(1\(\rightarrow\)6) – formation of limit dextrins
- viscosity falls slowly, DE increases very fast
• breaks $\alpha$-D-(1→4) and $\alpha$-D-(1→6) linkages, the linkage $\alpha$-D-(1→6) is split more slowly
• exo-acting enzyme $\Rightarrow$ it acts on the non-reducing ends of starch polymer chains and produces maltose
• DE increases
Pollulanase a isomaltase

- break $\alpha$-D-(1→6) linkages in amylopectin,
- linear chains of amylose remain in solution after hydrolysis
HFCS (High Fructose Corn Sirup) or HFS:

– produced from glucose syrups, by catalytic activity of glucose isomerase, part of glucose molecules is isomerised to fructose.
– completing the name by number – fructose content in dry matter HFS 42, HFS 55 etc.
– production of HFCS is quoted in EU
Enzyme hydrolysis + isomerisation

Starch slurry

Dry substance 30-35 % (17-22 Bé)

Liquifaction

pH adjustment

Enzymes

Saccharification

Precoat filtration

Carbon treatment

Enzymes

Isomerisation

Further filtration

Ion exchangers

Evaporation

Glucose/maltose syrup

Dry substance 30-35 % → 70-83 %

High fructose syrup

(90 °C, 10-90 min, DE 10-12 (output))

Termostable α-amylase, t = 110 °C

60 °C; previous inactivation of α-amylase (temp.), 6-96 h (β-amylase), or glucoamylase; followed by pasteurization

Direct input of steam
Application possibilities of glucose and syrups

- Energy source for human body (food, sweets, drinks, syrups – competition with sugar, medicine)
- Crystalline glucose can be as a part of instant products
- Ice cream with solid glucose are solider; glucose prevents of crystal formation; when using starch syrups (glucose or HFS) syrups for iced fruit – better form, lower freezing point and lower price
- Bakery - better conditions for fermentation, gold-brown rind, uniform porosity and good taste of products
- Viscosity – adhesives, paints
- Air-drying slowing down – concrete
- Fermentation production
- Chemical production (e.g. sorbitol)