in cooperation with

Max Rubner-Institute
Institute of Safety and Quality of Cereal

66th Starch Convention

April 15th – 16th 2015

Detmold, Germany

Program
Evening Program
Exhibition
Participants
Summaries
Wednesday, April 15th 2015

1330 Opening Remarks by the President of the Association of Cereal Research, Götz Kröner, Ibbenbüren (Germany)

1. Starch Biosynthesis and Structure

1.1. Robert G ('Bob') Gilbert, Cheng Li, Alex C. Wu and Ian D Godwin, Brisbane (Australia)
Creating plants with improved starch properties by theory-driven biotechnology

1.2. Luisa Trindade, Xing-Feng Huang and Richard G. F. Visser, AJ Wageningen (The Netherlands)
Expression of an amylosucrase gene in potato results in larger starch granules with novel properties

1.3. Bart Goderis, Joke A. Putseys, Geertrui M. Bosmans and Jan A. Delcour, Leuven (Belgium), Cédric J. Gommes and P. Van Puyvelde Liege (Belgium)
Structure-Property Relations in Amylose-Lipid Complexes

1.4. Robert G ('Bob') Gilbert, Kai Wang and Robert Henry, Brisbane (Australia)
The influence of amylose fine structure on starch digestibility

1530 Coffee Break

2. Sweeteners

2.1. Michael Radeloff, Berlin (Germany)
Starch hydrolysis – nutritive syrups and powders

2.2. Frank Lipnizki, Mattias Nilsson and Aurelie Dupuy, Søborg (Denmark)
New Membrane Concepts for the Starch and starch-based Sweetener Industry

3. Modification

3.1. Kommer Brunt and Laura Mout, HV Haren (The Netherlands)
Dutch view on “ISO/TC 93 Starch (including derivatives and by-products)”: in the past, present and future

1730 Exhibitor’s Forum - short term presentations

To be continued on page before last
Evening Program

Wednesday, April 15th 2015
After the Exhibitor’s Forum “Bread and Wine”-Get-together in the “Haus des Brotes” (Exhibition Hall).

Wine

Baden
2011er Kirchberghof, Weingut Dr. Benz
Spätburgunder Rotwein, trocken

Franconia
2012er Weingut Roth
Domina Qualitätswein, trocken

Palatinate
2012er Dürkheimer Riesling
Qualitätswein, trocken

Rhinehessen
2012er Rivaner Kabinett
Prädikatswein, trocken

Wuerttemberg
2012er Schlossgut Hohenbeilstein
Lemberger, rosé, trocken

Rhinehessen
2014er Weingut Knobloch
Dornfelder, Qualitätswein

Bread

Pretzels
savoury Snacks
Mediterranean baguette
Small wheat rolls

20:00 Social gathering at Strates Brauhaus, Lange Straße 35, Detmold

Please make your reservation until 4pm, if possible.

Thank you!
This year we have reorganized our Lunch. Please sign in at the convention office. You will get a receipt and a special bracelet you have to wear during lunch.

The menu:

**Wednesday, April 15th 2015**
Lasagne "Italian Style"
Bruschetta with tomatoes
Mixed green salad

for the costs of 10,-€ including beverages

**Thursday, April 16th 2015**
Cream of potatoe soup
with bacon (separately)
Baguette slices
with creme of leek or egg salad
Mini-Wraps filled
with roasted turkey or bacon
Chicken stick "Sweet Pepper" and
Grilled medaillon of pork with SALSA-Dip

for the costs of 10,-€ including beverages

**Beverages:**
Mineral water
Coca-Cola
Orangejuice
Apple Spritzer

Bon appétit
and interesting conversations!
Exhibitor’s Forum – Short Presentations
(Wednesday, April 15th, approx. 5.30 p.m.)

1. Frank Spalek, MMW Technologie GmbH
   News from Lutherstadt Wittenberg

2. Erwin Weber, NETZSCH Pumpen & Systeme GmbH
   Starch and starch related products are perfectly handled with
   NETZSCH pumps

3. Willi Witt, Cemsan DIS TIC. A.S.
   Cemsan leader in grain processing, equipment manufacturing,
   automation and R&D

4. Dirk-Michael Fleck, Bühler AG
   From Ethanol to Biorefinery

5. André Zillmann, Bilfinger Water Technologies
   Wedge Wire Technology in the Starch Industry

6. Moritz Buck, ANDRITZ AG, Pumps
   Centrifugal Pumps in Starch Processing - Air-Degassing Pumps for
   Fibrous- and Foaming-Slurries
Exhibition Hall Association of Cereal Research
Stand allocation

11th Bioethanol and Bioconversion Technology Meeting and 66th Starch Convention from April 14th – 16th 2015
Exhibition

Andritz Feed & Biofuel Div., Muncy (USA)

Andritz Gouda BV, PD Waddinxveen (Netherland)

ANDRITZ AG, Pumps, Graz (Österreich)

AVA- Huep GmbH & Co. KG, Herrsching (Germany)

Behn & Bates Maschinenfabrik GmbH & Co. KG, Muenster (Germany)

Bilfinger Water Technologies GmbH, Aarbergen (Germany)

Brabender GmbH & Co.KG, Duisburg (Germany)

Bühler GmbH, Braunschweig (Germany)

Cemsan DIS TIC. A.S., Arifiye, Sakarya (Turkey)

GEA Westfalia Separator Group GmbH, Oelde (Germany)

GIG Karasek GmbH, Gloggnitz-Stuppach (Austria)

HEIN, LEHMANN GmbH, Krefeld (Germany)

Krettek Filtrationstechnik GmbH, Viersen (Germany)

Gebr. Lödige Maschinenbau GmbH, Paderborn (Germany)

MMW Technologie GmbH, Lutherstadt Wittenberg (Germany)

NETZSCH Pumpen & Systeme GmbH, Waldkraiburg (Germany)

Ponndorf Anlagenbau GmbH, Kassel (Germany)

Sigma Process Technologies, Atasehir/Istanbul (Turkey)

VetterTec GmbH, Kassel (Germany)

W. Kunz dryTec AG, SWISS COMBI, Dintikon (Schweiz)
Effective April 08th 2015, 4 p.m.

Abdelrahim, Ahmed
AlMonairy for Corn Products, Cairo (Egypt)

Abeele, van den, Theo
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GEA Wiegand GmbH, Ettlingen

Abeln, Dieter
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1. Starch Biosynthesis and Structure

1.1. **Robert G ('Bob') Gilbert, Cheng Li, Alex C. Wu and Ian D Godwin**, Brisbane (Australia)

Creating plants with improved starch properties by theory-driven biotechnology

Many of the functional properties of starch are influenced by the chain-length distribution (CLD): for example, the rate and location of digestion in humans (which is very important for nutrition-related diseases such as obesity and diabetes, and the viscosity of starch solutions (important in food additives). Attempts to produce plants yielding desirable CLDs (e.g. with the longer chains that result in slow digestion) have met with limited success. Based on fundamental theory [1,2], it is predicted that changing a single residue in the active site of starch branching enzyme (SBE) would lead to a slight change in the minimum chain-length requirements for SBE to operate, which in turn would lead to a moderate but significant change in the CLD. Extensive atomistic molecular dynamics simulations have been performed to suggest which residues to change. Changes were implemented [3] by site-directed mutagenesis: creating plasmids with the desired sequence, and expressing these in E. coli. In vitro tests [4] show that the resulting mutant mSBEIIa enzymes have different activities and suggest that the length of the transferred chain can be varied by mutation, and verifies the predictive capability of the molecular dynamics simulations. However, testing by using these mutants in leaf callus shows that the starch produced therein has qualitatively different size distributions from that in the grain, so this cannot be used as a quick in vivo test [5]. The work shows analysis of the molecular weight distribution can yield information regarding the enzyme branching sites useful for development of plants yielding starch with improved functionality.


**Professor Robert ('Bob') G Gilbert** is author of more than 400 papers. He now divides his time between the University of Queensland (Australia) and the Huazhong University of Science and Technology (China, under the Chinese 1000-Talents program). In starch, his team works on the relations between its biosynthesis, the complex multi-level molecular structure and functional properties.
1.2. Luisa Trindade, Xing-Feng Huang and Richard G. F. Visser, AJ Wageningen (The Netherlands)

Expression of an amyllosucrase gene in potato results in larger starch granules with novel properties

In planta modification of starch by genetic engineering has significant economic and environmental benefits as it makes the chemical or physical post-harvest modification obsolete. An amyllosucrase from Neisseria polysaccharea fused to a starch binding domain (SBD) was introduced in two potato genetic backgrounds to synthesize starch granules with altered composition, and thereby to broaden starch applications. Expression of SBD-amylosucrase fusion protein in the amylose-containing potato resulted in starch granules with altered morphology and altered physico-chemical properties including improved freeze-thaw stability, higher end viscosity, and better enzymatic digestibility. This novel starch has advantages in many food applications such as frozen food.

Luisa Trindade, born 21 April 1971 in Algés (Lisbon)
1989-1995 Instituto Superior de Agronomia, Universidade Técnica de Lisboa, Portugal
Engineer of Agronomy (equivalent to a Master of Science).
Specialisation: Plant Breeding

Master of Science in “Microbial Molecular Genetics” graduated with cum laude.

2013 – now Group Leader Biobased Economy and Associate Professor
Wageningen University
Wageningen UR - Plant Breeding
Size of the group: >20 people

1.3. Bart Goderis, Joke A. Putseys, Geertrui M. Bosmans and Jan A. Delcour, Leuven (Belgium), Cédric J. Gommes and P. Van Puyvelde Liege (Belgium)

Structure-Property Relations in Amylose-Lipid Complexes

This paper discusses a case study on amylose–glycerol monostearate (GMS) complexes made from rather short amylose chains. Three different crystalline complexes with increasing thermal stability can be distinguished: type I, type IIA, and type IIB. All complexes consist of GMS-loaded amylose helices that pack hexagonally into lamellar habits. The complex melting points are proportional to the thickness of the lamellae and depend on the amount of water in the system. For type I complexes, Small Angle X-ray Scattering (SAXS) experiments reveal folded amylose chains and a lamellar thickness governed by the presence of two stretched lipid molecules per amylose helix. In the conversion from type I to type IIA complexes, the short amylose chains unfold and assume a stretched conformation, which increases the number of aligned lipid molecules within the helices to four. In type IIB complexes, another pair of lipid molecules is added. A quantitative relation between crystal layer thickness, water content and melting point for amylose–GMS complexes is derived, based on thermodynamic principles. This relation also predicts the melting points of other amylose–monoacyl glycerol complexes.

Interestingly, the gelation of aqueous starch suspensions is enhanced in the presence of type I amylose-GMS complexes as, during heating, short amylose fragments are liberated from these complexes that, upon cooling, promote amylose aggregation and
thus gel formation. Rheometry in combination with in situ SAXS reveals that the gel is composed of interconnected, cylindrically aggregated amylose double helices. The gel stiffness is proportional to the total volume occupied by these aggregates.

**Bart Goderis** is the head of the Laboratory for Macromolecular and Structural Chemistry (MSC) at the Chemistry Department of the KU Leuven. The research is focused on biobased polymers in food and non-food context, nano-engineered polymer materials and the principles of polymer crystallization. Special attention goes to investigating how the properties of soft matter relate to molecular and morphological features.

### 1.4. Robert G (‘Bob’) Gilbert, Kai Wang and Robert Henry, Brisbane (Australia)

The influence of amylose fine structure on starch digestibility

Amylose, one of the two starch types, is a glucose polymer comprising a small number (typically 3–11) long branches. It is well known that amylose content is a major influence on starch functional properties. However, it has recently been realized [1,2] that there is also a significant influence of amylose fine structure (i.e. the chain-length distribution, CLD, of individual branches) on some properties. It has been found [1-4] that the amylose CLD shows several distinct components, indicating different sets of enzymatic processes. These influence properties. Thus, for example, foods containing starches with more shorter amylose chains are slower to digest, while those containing a large number of long amylose chains tend to be unpalatable. In a study on a number of carefully selected rice varieties, differing in single nucleotide polymorphisms (SNPs) in GBSSI and SSIIa genes, it was found that the amounts of both long and short amylose branches changed with the same trend as amylose content, and affected starch gelatinization. This suggests selection strategies to produce rice varieties with improved qualities.


**Professor Robert (‘Bob’) G Gilbert** is author of more than 400 papers. He now divides his time between the University of Queensland (Australia) and the Huazhong University of Science and Technology (China, under the Chinese 1000-Talents program). In starch, his team works on the relations between its biosynthesis, the complex multi-level molecular structure and functional properties.

### 2. Sweeteners

#### 2.1. Michael Radeloff, Berlin (Germany)

**Starch hydrolysis – nutritive syrups and powders**

Using advanced enzymatic starch conversion technologies followed by modern separation and purification processes and blending practices provide today a manifold of nutritive syrups and powders offering a wide range of carbohydrate functionalities. High fructose syrups and glucose syrups comprising high dextrose and high maltose
syrups, available also in their dried or pure crystalline forms, cover a wide range of food, pharmaceutical and technical applications. Beyond controlled sweetness starch saccharification products provide a diversity of physical properties such as viscosity, reducing sugar content, osmotic pressure, crystallisation retardation, gloss, humectancy, consistency and many others.

Dr. Michael Radeloff is an internationally experienced carbohydrate chemist from Hamburg University specialised in the field of industrial business-to-business markets. His focus extends from addressing client product development strategies, analysing market opportunities through to a practical, detailed technical product application assessment.

As a well-established consultant he works across the full spectrum of renewable agricultural raw materials and the production of derivatives in a broad range of different application areas. He also creates in house training programmes meeting customer requirements for regulatory, quality assurance and sustainability issues working with a proven global network of experts in the field.

Based in Berlin Michael Radeloff actively works with clients across Europe, Asia and North America on both short and long-term projects.

2.2. Frank Lipnizki, Mattias Nilsson and Aurelie Dupuy, Søborg (Denmark)
New Membrane Concepts for the Starch and starch-based Sweetener Industry

1. Introduction
Both the development of nowadays membrane technology and nutritive sweeteners started in the middle of the 20th century. The development of the asymmetric membranes using phase inversion was pioneered by Loeb and Sourirajan in the 1960-ies, while the discovery of glucose isomerase was a milestone in the commercialisation of high fructose corn syrup in the beginning of the 1970-ies. The use of membranes in the sweetener industry started in the 1980-ies with DDS Filtration, now Alfa Laval Business Centre Membranes, as one of the pioneering companies. The aim of this presentation is to give an update on recent developed membrane concepts for the starch and starch-based sweetener industry and it will focus on three novel concepts: (1) water recovery from the 3-phase starch decanter by reverse osmosis in the wheat starch production to improve the overall water balance, (2) demudding of starch-based sweeteners with a decanter-ultrafiltration process replacing rotatory vacuum filters and improving product quality and (3) the use of a membrane bioreactor (MBR) in the wastewater treatment plant of starch factories.

2. Water recovery from 3-phase starch decanter using ultrafiltration
The first focus application is related to the wheat starch extraction. In the process, the wheat flour is mixed with water and then separated by a 3-phase decanter resulting in an A-starch fraction, a gluten and B-starch fraction, and a fraction consisting of solubles and pentosanes. In order to optimise the water consumption it is possible to apply UF for concentrating the solubles and pentosanes and recovering water for recycling in the process i.e. dough preparation. Applying this concept reduces the water consumption by approx. 20% resulting in reduction of water from 2.4 m3 water/ton flour to 2 m3 water/ton flour for a wheat starch line and from 1.7 m3 water/ton flour to 1.3 m3 water/ton flour for a wheat gluten line. It should be noted that this concept does not only improve the overall water balance for the starch extraction but reduces also the energy required for the concentration of the soluble/pentosane fraction by evaporation. An
application study for the treatment of 56 m3/h soluble/pentosane fraction from a wheat starch decanter will be presented.

3. Demudding of starch-based sweeteners by a decanter – ultrafiltration synergy process
After the after liquification and saccarification of the starch the resulting starch-based sweeteners needs to be polished. This demudding step is conventionally done with rotary vacuum filters using kieselguhr as filter aid. Alternatively, a decanter – ultrafiltration synergy process has been developed. This closed process avoids potentially hazardous filter aids, limits the exposure of the sweeteners to the outer atmosphere and achieves higher product qualities than the conventional approach. A case study of a low DE 42 – 50 line and a high DE95 line for the demudding of corn-based sweeteners will be shown.

4. Membrane bioreactor for wastewater treatment in starch factories
Despite efforts to reduce the water consumption in the starch and starch-based sweetener industry and close the water loop as much as possible often some effluents streams are generated which have to be removed from the process and discharged. In the last 20 years, membrane bioreactors (MBRs) combining activated sludge treatment with a filtration through an MF/UF membrane, either submerged in the biology or in a side-stream, have established themselves in a wide range of industries and it can be foreseen that MBRs will also establish themselves in the area of the starch and starch-based sweetener industry. In particular combining MBRs with NF/RO polishing could result in water stream suitable direct recycling or blending with in-take water streams. A case study related to the wastewater treatment plant of a modified potato starch producer using Alfa Laval’s hollow sheets MBR modules will be used to highlight the potential of this emerging technology.

5. Conclusions and outlook
Overall, membrane processes have their potential in the starch and starch-based sweetener as highly selective and energy-saving separation processes and these new applications will support this trend. R&D efforts are currently focusing on the optimisation of these new applications and on the increased further integration of membrane technologies in the starch and starch-based sweetener production plus starch-based biorefineries aiming at the optimal utilisation of the starch containing crops.

Frank Lipnizki

His main research interests are the integration and optimisation of membrane process for the food, biotech and process industry. Frank Lipnizki has authored over 25 publications in reviewed journal and books and gave more than 40 presentations at international conferences on membrane technology.
3. Modification

3.1. Kommer Brunt and Laura Mout, HV Haren (The Netherlands)
Dutch view on “ISO/TC 93 Starch (including derivatives and by-products)”: in the past, present and future

The International Organization for Standardization (ISO) is an independent, non-governmental organization made up of members from the national standards bodies of 163 countries. ISO standards are developed by groups of experts organized within Technical Committees (TC’s). TC’s are made up of representatives of industry, NGO’s, governments and other stakeholders, who are put forward by ISO’s members. Each TC deals with a specific subject.

The ISO Technical Committee for “Starch (including derivatives and by-products)”, ISO/TC 93 started its activities in 1958 and has developed in total 25 different ISO standards for the characterization of starch, starch derivatives and by-products. ISO 11543:2000 dealing with the determination of the hydroxypropyl content in modified starch by a NMR method is the most recent published method. In addition, methods were published as ISO standards for the determination of various heavy metals (As, Hg, Pb and Cd) in starch and starch derived products. In modified starches, ISO standards were published for the determination of the acetyl, carboxyl, adipic acid, carboxymethyl and hydroxypropyl content. And of course also ISO standards were developed for the determination of moisture and impurities in starches as fat, protein and ash. An overview of the 25 developed ISO standards is shown in the table below.

For the last approximate fifteen years, no new ISO standards for the characterization of starch and its derivatives have been developed. The last meeting of the Technical Committee was in December 2011. Nowadays just 11 different countries join as an active “Participating-member” ISO/TC 93 being Barbados, China, Cuba, Hungary, Iran, Ireland, Jamaica (chair), Republic of Korea, The Netherlands, Russia and Santa Lucia. Unfortunately, at the moment ISO/TC 93 is more or less in a stand-by mode.

From a Dutch view, starch and starch products are important agricultural products which “deserve” an active ISO/TC 93. New work items can be proposed and new member countries are very welcome in the Technical Committee. Presumably some of the previously developed ISO standards should be updated applying modern techniques. For example, ICP-MS is nowadays the state of the art for the determination of heavy metals and maybe a guidance document for the characterization of the viscosities of the different starches and starch products should be developed. The application of new instrumentation as amongst others the Brabender Viscograph-E and the Rapid Vicso Analyzer have not yet been described in an ISO standard. Another possible new work item can be the development of a standard protocol for the colour measurement for (glucose)syrups.

Interested organizations (in possible new work of ISO/TC 93) are invited to contact NEN, the Dutch member body of ISO (laura.mout@nen.nl), to discuss options for participation.

Developed ISO standards by ISO/TC 93 Starch (including derivatives and by-products)

<table>
<thead>
<tr>
<th>ISO standard</th>
<th>Title</th>
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<tbody>
<tr>
<td>ISO 1666:1996</td>
<td>Starch - Determination of moisture content - Oven-drying method</td>
</tr>
<tr>
<td>ISO 1741:1980</td>
<td>Dextrose - Determination of loss in mass on drying - Vacuum oven method</td>
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<td>ISO Number</td>
<td>Standard Title</td>
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<tr>
<td>ISO 1742:1980</td>
<td>Glucose syrups - Determination of dry matter - Vacuum oven method</td>
</tr>
<tr>
<td>ISO 1743:1982</td>
<td>Glucose syrup - Determination of dry matter content - Refractive index method</td>
</tr>
<tr>
<td>ISO 3188:1978</td>
<td>Starches and derived products - Determination of nitrogen content by the Kjeldahl method - Titrimetric method</td>
</tr>
<tr>
<td>ISO 3593:1981</td>
<td>Starch - Determination of ash</td>
</tr>
<tr>
<td>ISO 3946:1982</td>
<td>Starches and derived products - Determination of total phosphorus content - Spectrophotometric method</td>
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<td>ISO 3947:1977</td>
<td>Starches, native or modified - Determination of total fat content</td>
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<td>ISO 5377:1981</td>
<td>Starch hydrolysis products - Determination of reducing power and dextrose equivalent - Lane and Eynon constant titre method</td>
</tr>
<tr>
<td>ISO 5378:1978</td>
<td>Starches and derived products - Determination of nitrogen content by the Kjeldahl method - Spectrophotometric method</td>
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<td>ISO 5379:2013</td>
<td>Starches and derived products - Determination of sulfur dioxide content - Acidimetric method and nephelometric method</td>
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<td>ISO 5381:1983</td>
<td>Starch hydrolysis products - Determination of water content - Modified Karl Fischer method</td>
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<td>ISO 5809:1982</td>
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<td>ISO 5810:1982</td>
<td>Starches and derived products - Determination of chloride content - Potentiometric method</td>
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<td>ISO 11212-1:1997</td>
<td>Starch and derived products - Heavy metals content - Part 1: Determination of arsenic content by atomic absorption spectrometry</td>
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<td>ISO 11212-2:1997</td>
<td>Starch and derived products - Heavy metals content - Part 2: Determination of mercury content by atomic absorption spectrometry</td>
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<tr>
<td>ISO 11212-3:1997</td>
<td>Starch and derived products - Heavy metals content - Part 3: Determination of lead content by atomic absorption spectrometry with electrothermal atomization</td>
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<tr>
<td>ISO 11212-4:1997</td>
<td>Starch and derived products - Heavy metals content - Part 4: Determination of cadmium content by atomic absorption spectrometry with electrothermal atomization (including Cor 1:1997)</td>
</tr>
<tr>
<td>ISO 11213:1995</td>
<td>Modified starch - Determination of acetyl content - Enzymatic method</td>
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<td>ISO 11214:1996</td>
<td>Modified starch - Determination of carboxyl group content of oxidized starch</td>
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<td>Modified starch - Determination of adipic acid content of acetylated di-starch adipates - Gas chromatographic method</td>
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<td>ISO 11216:1998</td>
<td>Modified starch - Determination of content of carboxymethyl groups in carboxymethyl starch</td>
</tr>
<tr>
<td>ISO 11543:2000</td>
<td>Modified starch - Determination of hydroxypropyl content - Method using proton nuclear magnetic resonance (NMR) spectrometry</td>
</tr>
</tbody>
</table>
Kommer Brunt (1950) is educated in The Netherlands at Utrecht University, at the Agricultural University Wageningen and at Groningen University (PhD in 1980).

Scientific career:
1979 – 1985 Analytical Chemist at the Potato Processing Research Institute TNO.
1985 – 1998 Head of the Department Analytical Chemistry and Raw Materials of the Netherlands Institute for Carbohydrate Research TNO.
1998 – 2006 Product manager and project leader carbohydrate analyses at the TNO Nutrition and Food Research Institute.
2013 - Director of Rotating Disc B.V. for training and advice in carbohydrates and dietary fibre in food and feed.

Author and/or co-author of over 70 scientific papers published in national and international scientific journals

3.2. Dorien M. Dries, Sara V. Gomand, Jan A. Delcour and Bart Goderis, Leuven (Belgium)
Insights in the Conversion of Native Starches into Their Granular Cold-Water Swelling Counterparts

Native starch’s inability to swell in water at room temperature has evoked the development of starches of enhanced cold-water swelling capacity, making it possible to extend starch functionality to instant and convenience foods. Granular cold-water swelling starch (GCWSS) can be produced by an aqueous alcohol treatment at elevated temperature. Provided treatment temperature and ethanol concentration are correctly balanced, the native double helical order of crystalline amylopectin is lost and single helical crystals are created. We here report on the mechanism of conversion of native starches of different botanical origin into their GCWSS counterparts. At a treatment temperature of 95 °C, decreasing ethanol concentrations led to a changeover from granules with a Maltese cross pattern to granules with only hazy birefringence, as demonstrated by polarized optical microscopy. A gradual decrease in native crystallinity and increase in V-type crystallinity were demonstrated by wide-angle X-ray diffraction. These observations went hand in hand with a gradual decrease in post-treatment gelatinization enthalpy and increase in swelling power. By including a waxy starch in this study, it was shown for the first time that the linear amylose fraction is the main responsible for V-type crystal formation in GCWSS. We also demonstrated how amylose chain lengths influence the amount and perfection of created V-type crystals. Finally, beyond state-of-the-art in situ collected X-ray and calorimetric measurements provided new insights in the structural transitions taking place.

Dorien Dries was born on the 28th of February 1989 in Turnhout, Belgium and currently lives in Leuven, Belgium. In 2010, she obtained a Bachelor’s degree at the faculty of Bio-engineering at the KU Leuven. She finished her Master in Food Technology in 2012 at the same faculty, with her MSc Dissertation titled: “The role of wheat endogenous lipids in dough making”. She currently works as a PhD student at the Laboratory of Food Chemistry and Biochemistry (KU Leuven), under the supervision of Prof. Jan Delcour, in close collaboration with the KU Leuven Polymer Chemistry and Materials Laboratory, under the supervision of Prof. Bart Goderis. Earlier collaboration between the two aforementioned research units has led to the elucidation of the relationship between starch structure on different levels and starch physical properties. Her research topic comprises the complex structure, functionality and modification of cereal starches and starches from other botanical origins.
3.3. **Maurice Essers, Johan Timmermans and Ricardo Nagtegaal**, AJ Zeist (The Netherlands)

The role of water in starch modifications

Modified starches have been developed for a very long time and its applications in food and non-food industry are obvious. Modification of starch is carried out to tune the structure of starches in order to improve the positive characteristics and to reduce the adverse effects of the native starch. This can be done via enzymatic, chemical and physical treatment. All these techniques tend to alter the conformation of the starch polymer with changed physicochemical properties and modified structural features of high technological value. Most enzymatic and chemical modifications are carried out in slurry, in which water acts as a reaction medium between the starch and the reagent. On the contrary, physical and physical-chemical modification of starch is mainly done under semi-dry or dry conditions. Examples of physical modification methods are pregelatinization, hydrothermal treatment, annealing, alkaline roasting and dextrination. Physically and physical-chemical modified starches have a growing interest due to the fact that they can be produced without the use of additional chemicals; they offer the potential to make clean label functional carbohydrates. Physical modification solely uses temperature, pressure and water to alter the starch granular structure in order to induce pre-gelatinisation, re-crystallisation etc. Physical-chemical treatment is conducted under the same conditions but with the addition of an acid or base catalyst in order to alter the chemical structure of the starch. Although it is considered to be a simple and inexpensive modification technique it turns out that these processes are difficult to scale up and to get control of the final product quality. For example thermally inhibition is a process for making visco-stable starches. The process is described via heat treatment of a dehydrated (anhydrous) alkaline starch. In the practical situation, it turns out that it is difficult to obtain the desired viscosity characteristics. Pyrodextrination is another physical-chemical modification technique, in which under acid conditions in combination with heat and moisture, the starch is hydrolyzed, re-polymerized and re-arranged (transglucosidation). In this process, water is actively involved in the mechanism of modifying the starch structure. It is used for making resistant starches. A disadvantage of this process is the side reactions that lower the yield significantly.

In order to improve these processes it is therefore essential to get a better insight how to control the prime reaction parameters. In general, temperature and pressure are easily to adjust but water is a different story. Its physical state and its related role in the reaction mechanism are affected by the other reaction parameters. In the last couple of years, TNO has put a lot of effort to get more insight in how to control this. For example the influence of the method of dehydration prior to performing alkaline roasting is hardly described in literature. In this presentation we will show the results of a study in which we demonstrate the effect of the method of dehydration on the total inhibition reaction and how this determines the final product properties, e.g. viscosity properties. For the pyrodextrination process we will show a method for reduction of side components, e.g. color reduction. Also in this case control of the water activity turns out to be the key. Finally we will describe the usage of Super Heated Steam (SHS) as an efficient and mild tool to modify starch.

The results of these studies will be used to generate novel starches which includes new functional and value added properties as demanded by the industry.

**Maurice Essers**

*Born in Maastricht (the Netherlands), I attended the Joan of Arc gymnasium and studied chemistry at the RWTH Aachen. From 1996-2008 industrial career in Paper, sugar and starch industry:*

*More specific:*
The Focus in my research (present job) is:
- Development clean green and healthy carbohydrates
- Development industrial starches

3.4. Markus Schirmer, Uzwil (Switzerland)
A novel approach for structural analysis of high viscous starch based products during heating

Analytical instruments and applications are important tools to characterize and improve raw materials used in food production. This knowledge is fundamental for the process optimization and serves as a useful instrument for product development. For cereal based foods many standardized analytical systems are known. Those systems are well described in many publications especially concerning the raw materials, however without correlation to end product characteristics. The main aim of this thesis is to obtain a global view of the desired components with connections to production parameters applied in food industry. In order to achieve this objective allowing to observe complex food systems exemplary on bread, new innovative methods were combined with well-known microscopic techniques.

As starch is the main component of wheat based product such as bread it was chosen for further investigation. The study of analytical methods to investigate structural changes of starch during heating revealed that they are all working with water in excess. Considering that wheat dough is a complex food system with limited water content no in situ analysis of starch gelatinization under actual condition is possible until now. The newly developed method enabling micrographic analyses for numerous structural features is based on confocal laser scanning microscopy (CLSM) combined with image analyzing techniques. Structural and morphological changes can be quantified and discussed in detail. The relationship between heat treatment and structural features was first proven with different starch suspensions by common thermo physical analytical techniques such as differential scanning calorimetry (DSC).

The new method was used to investigate the onset of starch gelatinization by using threshold values, which are based on the first derivatives, where values of CLSM and DSC showed the highest correlation. The gelatinization temperature that is in micrographs obtained through the shape and size analysis of starch granules is highly depending on the water content.

In summary, a visual online detection system to investigate changes in starch granules on a microstructural scale during heating was developed. This in situ system monitors the structural changes of starch granules such as starch gelatinization with the advantage of being unaffected by secondary factors.

Dr. Markus Schirmer is the manager of the Bakery Innovation Center at Bühler headquarters in Uzwil. His professional background has helped him function as a link between technology and baking production. As a master baker, Mr. Schirmer also completed an engineering degree and then did a doctorate in grain process engineering at the Technical University of Munich.
4. Enzymes

4.1. **Mads Weibye, Chee-Leong Soong and Paolo Ronchi**, Bagsvaerd (Denmark) Novozymes Secura® - The most robust beta amylase
Go straight to maltose syrup with the lowest risk of infection and lowest cost of conversion.

Innovation in starch processing: A new microbial beta-amylase enables you to make maltose syrups at pH 4.8 or even lower. Secura® works perfectly with Novozymes' low-pH alpha amylase LpHera® (presented last year at Detmold), letting you run low pH all the way from liquefaction to saccharification, reducing chemical costs.

Secura® is more heat-stable, allowing production to run at higher temperatures. This reduces the risk of infection and saves energy costs. Secura® is Chometz-free Kosher and Halal-certified, thanks to microbial technology.

To assist our customers in optimal use of Secura®, either alone and in combination with Novozymes' pullulanase Promozyme® D6, a simulation model has been created based on 126 laboratory trials. This model is available for Novozymes customers. Contact your Novozymes Account Manager or Technical Services Representative to learn more.

**Mads Weibye**, born in Copenhagen (Denmark) Academy Profession graduate in Chemical and Biotechnical Science 1990
Employed at Novozymes (Novo Nordisk) 1990, Working area (application R and D) 1990-2007 Joined Novozymes Technical Service (Grain processing) 1/5 2007

Working areas has included: Detergent Enzyme Chemistry, Leather Industry, Protein Hydrolyses, Starch Degrading Enzyme, Other polymers: Hyalouronic acid
Analytical experience, with special knowledge’s with in HPLC / GPC- multi angle laser light scattering

4.2. **Jan Delcour, Christophe M. Courtin, Kristin Verbeke** and **Willem F. Broekaert**, Leuven (Belgium)
From Wheat Bran to Arabinoyxlan Oligosaccharides: From Scientific Concept to a Spinout Dealing with Production, Demonstration of Prebiotics Effects, Regulatory and Intellectual Property Aspects and Product Applications

Prebiotics are selectively fermented ingredients that allow specific changes, both in the composition and/or activity of the gastrointestinal microflora, that confer benefits upon host well-being and health. The most studied prebiotics are the fructans inulin and fructo-oligosaccharides. Over the past years, we used a multidisciplinary approach – in part funded by Healthgrain - to study the properties of arabinoxylan oligosaccharides (AXOS) as novel prebiotics. We here report on a pilot scale process for extracting AXOS from wheat bran, and on studies of their prebiotic effects in chickens and rats as well as in humans. We also demonstrate the feasibility of in situ production of AXOS in breadmaking by using appropriate enzyme technologies and deal with their regulatory status in view of the most recent definitions of dietary fibre and the views on health effects of prebiotics.

**Jan A. Delcour** is a full professor at KU Leuven in Leuven, Belgium. His research focuses on generating basic insights into the constituents of cereals, as well as on plant and microbial enzyme systems converting them. The team also focuses on applying such insights in cereal based biotechnological processes to develop and optimize processes, develop
health promoting constituents, and contribute to product organoleptic properties. Dr. Delcour is W.K. Kellogg Chair in Cereal Science and Nutrition at KU Leuven and the author of more than 500 peer reviewed publications which have been cited over 11,250 times. He is (co-)inventor of 22 patent families. His Hirsch index is 54. He is co-founder of the spinout Fugeia, co-author of the third edition of "Principles in Cereal Science and Technology", and co-editor of "Advances in Enzymes in Grain Processing", and "Fibre-rich and wholegrain foods: improving quality". He is an ISI highly cited author and received multiple awards including the Osborne Medal from AACC International, the Bertebos Prize of the Royal Swedish Academy of Agriculture and Forestry and the Harald Perten Award from the Perten Foundation. He is a Fellow of the ICC Academy, Past-President of AACC International, Senior editor of Cereal Chemistry, and Chairman of LFoRCe, the Leuven Food Science and Nutrition Research Centre.

5. Green Chemistry

5.1. Agnes Rolland-Sabate, Lorena Sciarini, Sophie Guilois, Denis Lourdin, Eric Leroy and Patricia Lebail, Nantes (France)
Starch destructuration by ionic liquids

The creative design and application of innovative technology for the optimization of renewable resources is a research topic raising a huge interest. Among all polysaccharides investigated as potential alternatives to conventional oil based plastics, starch has attracted a large amount of attention. Starch is one of the most abundant biopolymers in nature, and considering its low cost, renewability, biocompatibility and biodegradability, it can be considered as a raw material for the elaboration of biologically degradable materials. Given its granular structure, starch shows low solubility in any conventional solvent in spite of being highly hydrophilic. However, when suspended and heated in excess water, starch undergoes an order-disorder transition called gelatinization. During gelatinization starch granules swell and amylose progressively leaches out of the granule, and the semi-crystalline structure is disrupted. Although some starch molecules are readily solubilized in water, some granule remnants may still be present even after gelatinization has occurred. Thus, starch insolubility represents a problem when trying to obtain homogeneous amorphous materials.

In the last decade, the performance of ionic liquids (ILs) as solvents for biopolymers has generated lots of interest. ILs are room-temperature molten salts: they present high thermal stability and are not volatile. Then they offer an alternative to common organic solvents. They have been classified as green solvents as they are also easily recyclable and some of them are biodegradable. One of ILs major advantages is that they offer the possibility of being tailored by modifying the chemical structure of the cation and anion moieties. The present work focuses on the influence of the cation by comparing the thermal destructuration of starch in mixtures with water and two acetate based ionic liquids: EMIM and Cholinium Acetate (EMIMAc and CholAc). This latter presents the advantage of a very low toxicity, choline being an essential nutrient and thus biocompatible. The destructuration of native maize starch in mixtures of water and ILs containing acetate anions was studied in dynamic heating conditions, combining calorimetry, rheology, microscopy and chromatographic techniques. A phase diagram of starch in water/IL solutions was established. EMIMAc and CholAc have shown to be appropriate solvents for starch destructuration when mixed with the correct amount of water (30% water for EMIMAc and 20% water for CholAc). Two different phenomena take place when starch is heated in EMIMAc and CholAc solutions: at low concentration of both ILs, gelatinization is the dominating phenomenon, whereas at higher concentration, depolymerization and dissolution of starch take place. This results in an optimum destructuration temperature as low as 40-50 °C for an IL/water ratio close to
0.7. In addition, specific macromolecular chain breakings appear to take place, depending on the nature of the IL cation, resulting in different macromolecular structures of recovered starch. These results open the possibility of solvent media design for a controlled modification of starch macromolecular characteristics.

Agnes Rolland-Sabate

I studied physical chemistry and food-processing in France. I have worked at INRA (National Institute of Agronomic Research) in Nantes since 1999 in the field of starch and by-products characterization, for applications in food, biomedicals and biomaterials. My current activities are in elucidation of structure-property-function relationships, method development for the structural and the macromolecular characterization, and enzymatic catalysis in heterogeneous phase.

5.2. Eric Leroy, Saint-Nazaire (France)

Ionic liquids as processing aids and functional additives for starch based materials

The development of efficient biobased thermoplastic starch materials requires exploring new paths. The path studied in this work is comprised of using ionic liquids as a new family of plasticizers that can modify the transformation of starch during extrusion and the final properties of the resulting material. Unlike classic plasticizers ionic liquids potentially grant a large variety of properties by tuning the structure of their consisting anion and cation. On the other hand, it is well known that the characterization and the comprehension of the influence of regular starch plasticizers, glycerol for one, was done through a long process, and many questions have yet to be answered.

That’s why we chose to proceed with a screening approach: Various ionic liquids were synthesized by combining the biocompatible cholinium cation with biodegradable anions. A screening of their plasticizing properties on starch was then conducted using a twin screw microcompounder to simulate extrusion on a 10 grams scale. A more detailed study was then performed on the impact of the selected ionic liquids on the thermoplasticization mechanism, rheology in the molten state and the properties of the plasticized starch. It is shown that the cholinium based ionic liquids synthetized are less efficient as starch plasticizers than commercial imidazolium ionic liquids, and induce a higher starch depolymerisation during melt processing due to higher viscosity levels.

Dr. Eric Leroy joined CNRS at the GEPEA (Process Engineering for Environment and Food) research unit in Nantes/Saint Nazaire in 2008. Since then his research is focused on natural polymers processing and particularly on the use of ionic liquids as processing aids. Co-author of 40 peer reviewed papers and 2 patents, he received the CNRS Bronze medal in 2013.

6. Application

6.1. Chi-Wah Yeung and Hubert Rein, Bonn (Germany)

Starches as excipient in the pharmaceutical technology

As popular compounds, starches are not only used in food engineering, but are also well accepted in the pharmaceutical industry. A certain number of starches (corn, potato, pea, wheat, and rice) are mentioned in the European Pharmacopoeia (Ph. Eur.). Pfeilwurz (eng. maranta) can be found in the Deutsches Arzneibuch (DAB 6, Erg.-
Band). Moreover, tapioca starch is registered in the United States Pharmacopoeia (USP). In the field of pharmacy, starches are used in versatile domains. They are primarily used as excipients in oral solid-dosage formulations such as tablets, but also in unguents and liquids.

In tablets, starches are used as fillers, which disintegrate once taken due to their swelling pressure. Application of starches as binding agents in wet granulation processes is also observed. Further starch applications include solubility improvement and coazervation.

Three parameters (temperature, pressure and water content) determine the application of starches. Additionally, exposure of starches to higher or lower levels of thermal energy leads to the induction of new properties, rendering them appropriate for their various roles such as disintegrant, binding agent, matrix formulation, complexing agent and microencapsulation (Fig. 1).

![Fig. 1 Reactions of water and starch at different temperatures /pressures](image)

Swelling: Starch as disintegrant
Gelatinization: Starch as binding agent or excipient in unguents
Amorphous starch: Starch as matrix formulation
Solution: Starch as complexing agent
Retrogradation: Starch as microencapsulation (coazervation)

**Chi-Wah Yeung** studied pharmacy at the University of Bonn, Germany. In 2011, he began his PhD study in the working group of PD Dr. Hubert Rein. He is working on hot-melt extrusion of different polymers like starches. Furthermore, he investigates the surface tension of APIs and excipients.

6.2. **Marilyn Rayner**, Lund (Sweden)

Starch Pickering Emulsions – formulation opportunities

This conference contribution showcases some of our recent work in the area of starch granule stabilized Pickering emulsions. We have demonstrated the application of quinoa starch granules in a variety of formulations ranging from topical creams [1], to dried oil filled powders [3] and double emulsions with high encapsulation stability [4]. Quinoa starch granules stabilized emulsions have been shown to be highly stable during freeze-thawing and extended frozen storage. Through the careful application of heat the interfacial layer of starch can be partially gelatinized *in situ* enhancing barrier properties.
This starch barrier has also been quantified by in vitro lipolysis of the encapsulated oil, as well as by release studies. This versatile technology platform has practical applications in a variety of food, cosmetic and pharmaceutical formulations.

**Pickering Emulsions:** Particle-stabilized emulsions, so-called Pickering emulsions, are known to possess many beneficial properties, including being extremely stable. Emulsions are a mixture of two immiscible phases (i.e. oil and water) where one is dispersed into the other in the form of small droplets, which need to be stabilized to prevent them from re-coalescing. Emulsion droplet stabilization is often achieved by the addition of surfactants or emulsifiers, which act by decreasing the interfacial tension between the phases, increase the steric hindrances and/or electrostatic repulsion between the droplets, and thereby increase the stability of the emulsion. Pickering emulsions on the other hand are stabilized by solid particles adsorbed at the interface between the two immiscible phases (see figure 1B). The particle stabilization of emulsion droplets is achieved when spontaneous accumulation of particles at the oil-water interface occurs. The fundamental science of Pickering emulsions in the context of food is described in some recent reviews [2, 5, 6]. Emulsions stabilized by solid particles are usually more stable against coalescence and Ostwald ripening compared to systems stabilized by surfactants[7]. The reason the stability observed in Pickering type emulsions is that particles prevent interfacial interaction by volume exclusion, i.e. the particles create a physical barrier preventing contact between droplets. Once the particles absorbs to the oil-water interface they are effectively trapped there. This phenomenon is ascribed to the fact that if the particles have favorable wetting conditions and are >10 nm in size their adsorption at the oil water interface is effectively irreversible.

There are many types of particles reported in the literature for use in Pickering type emulsions. Much of the initial and fundamental work has used synthetic or inorganic particles including silica, latex, and clays. More recently there has been a large interest in using biomass based edible particles such as protein particles and microgels, cellulose and chitin nano crystals, and starch based particles [2, 5, 6]. Starch granules, as opposed to many other particles used to generate Pickering emulsions, are edible, abundant, derived from a natural source, and are approved as food ingredients and pharmaceutical excipients.

**Starch granules as Pickering agents:** Starch granules isolated from several different botanical sources have been studied with respect to their capacity to stabilize emulsions. In this respect, two critical properties of the starch granules have been found: the size of the starch granules and their hydrophobicity[8]. The particles primarily used in our work are intact starch granules isolated from quinoa (*Chenopodium quinoa* Willd.) with various hydrophobic modification. Quinoa starch granules were chosen as Pickering agents for several reasons; among them that quinoa does not contain gluten, and the granules are small (0.5 to 3 µm in diameter) with a unimodal size distribution (figure 1A). Small size is of interest as it reduces the amount required (mg of starch per ml of oil) to stabilize a given emulsion droplet interface. Other small starch granules of interest are rice (5 µm)[9, 10] and amaranth (1 µm)[11] with varying amylose/amylopectin rations. It should also be pointed out that even smaller starch particles can be generated from native starch by acid hydrolysis (nano-crystals) [12] or by dissolution and precipitation methods (nano-spheres) [13] but they do necessarily not retain the special physicochemical properties of intact starch granules, specifically the ability to gelatinize in the presence of water and heat (discussed below).
In general, the emulsifying capacities of native starch granules have been observed to be low, however, the hydrophobicity can be increased by chemical or physical modification. Starch granules can be chemically modified by treatment with different alkenyl succinyl anhydrides, for example octenyl succinic anhydride (OSA). OSA modified starch (E1450) is approved in food applications with a degree of modification up to 3% based on the dry weight of starch. Another way to increase the hydrophobicity of starch is by dry heating, which causes the proteins associated at the starch granule surface to become more hydrophobic. In this case thermal modification has the advantage that no specific labeling is required in food applications. The emulsifying capacity of hydrophobically modified starches by OSA or dry heating have been studied with respect to different types of starch granules, granules with varying levels of amylose content (ranging 1.9-27%) and different degrees of OSA modification, or dry heating at various treatment times and temperatures [8-10, 14, 15].

Encapsulation and barrier properties: Core-shell microcapsules is a type of encapsulation technique that is composed of a solid shell surrounding a core-forming space available to permanently or temporarily entrapped substances. Encapsulation and controlled release has a wide application potential in a range of products: from oxidation sensitive oils, flavours and fragrances to pharmaceuticals, bio-actives, and probiotics. In this context we have used starch granules to create a layer (few µm) at the oil-water interface thereby encapsulating oil droplets. In addition to encapsulating an oil phase, double water-in-oil-in-water emulsions (W₁/O/W₂) have also been prepared entrapping hydrophilic substances in the inner aqueous droplets (W₁) located inside larger oil drops stabilized by OSA-modified quinoa starch granules and dispersed in an external continuous aqueous phase (W₂). In a study reported by Matos et al. the initial encapsulation efficiency of a hydrophilic tracer in a quinoa starch granules stabilized W₁/O/W₂ emulsion system was found to be over 98.5% immediately after emulsification.
production, remaining the encapsulation stability during storage over 90% after 21 days [16]. To put these figures in perspective, it may be considered that a double emulsion has a good stability when the initial encapsulation efficiency is around 95% and after a few weeks of storage it is still around 70-80%. It is believed that the large desorption energy and low mobility of the starch granules at the oil water interface aids in retaining the internal aqueous droplets dispersed in the emulsified oil.

In addition to creating highly stable emulsions typical of Pickering emulsions, one of starches’ special physicochemical properties, specifically its ability to gelatinize when heated in the presence of water can be utilized in a novel way. Through the careful application of heat treatment starch granules adsorbed at the oil water interface can be partially gelatinized in situ creating cohesive layer around the oil drops [15, 17]. A non-heated quinoa starch granules stabilized emulsion is shown in figure 1B and in the inset of figure 1D. Here distinct, individual granules are observed covering the oil droplets with some spacing between them. In contrast an emulsion drop after heat treatment is shown in figure 1D, (right) during which swelling and leached starch molecules causes the boundary between the individual granules to become diffuse, yet the granules still remain as particles at the oil interface to a certain degree. This was verified by observation of drops under polarized light where the internal structure of swollen granules was indicated by remaining birefringence at the oil interface. This was interpreted as a fraction of granules still remained or that there is some persisting crystalline structure at the oil interface. Heat treatment thus can achieve a cohesive outer layer into the aqueous phase that gives rise to the enhanced barrier properties observed in heat treated starch stabilized emulsions.

This technique for creating oil-core starch-shell microcapsules has many potential uses, for example heat treatment of starch granule Pickering emulsions have also been used as an effective pre-treatment before drying emulsions into oil filled powders and dried double emulsions [3, 18], and in the case of liquid oils heat treatment to seal the starch layer was necessary to prevent emulsion collapse upon drying.

The barrier properties of the partially gelled starch layer at the oil-water interface have been quantified via the decrease in the rate of lipolysis, under the premise that tightly covered oil-water interface by starch granules will reduce the capacity of lipase to digest the lipids within the oil droplets [2, 15, 17]. In a study by Timgren et al. 2011, the pH-stat method was used as a way to quantify the barrier effect of the starch-shell. Here, by comparing the rate of lipolysis of heat treated emulsions to that of an unheated emulsion control, the relative barrier effect was found, where 0% is the control (maximum lipolysis rate) and 100% would indicate no lipolysis at all (complete barrier to lipase). In figure 1D the relative barrier effect is plotted as a function of heat treatment temperature (1 min treatment time) for both fresh and stored emulsions. The relative barrier effect increases when the emulsions are heat treated above the gelatinization temperature of OSA modified quinoa starch (i.e. gelatinization temperatures: onset (To) at 46.1°C, peak (Tp) at 60.0°C and conclusion (Tc) at 70.4°C respectively) and some improvement is also after 4 weeks of refrigerated storage allowing for retrogradation to occur.

**Freeze thaw stability of particle stabilized emulsions**: Starch granule stabilized emulsions have also been observed to have increased resistance to coalescence induced by the partial crystallization of the oil phase during frozen storage. Model mayonnaise emulsions with oil contents ranging from 5 to 67% were stabilized using OSA modified quinoa starch granules and subsequently exposed to environmental stresses consisting of heat abuse, centrifugation, freezing, and thawing after varying lengths of storage at -20°C. It was found that the starch granule stabilized emulsions were more resistant to various destabilization processes compared to conventional emulsions. Particularly, the freeze-thaw stability improved remarkably for the starch granule-stabilized emulsions which were stable to crystal induced phase separation with no increase in droplet size over a period of 70 days compared to the conventionally
stabilized (whole egg yolk) emulsions, that separated after 7 days but before 42 days [2]. It is believed that the large physical size of the particles prevent intra droplet penetration of crystalized oil during storage, thus preventing coalescence upon thawing.

**Conclusions and outlook:** Starch Pickering emulsions possess a variety of useful properties beyond that of simply stabilizing emulsions droplets, which are also creating new formulation opportunities, including:

- The possibility to create emulsions with moderately large droplet sizes that exhibit outstanding long-term coalescence stability, without the use of surfactants.
- The capacity to encapsulate ingredients by creating dense interfacial layers creating oil-core, starch-shell microcapsules.
- The ability to modulate the rate and extent of lipid digestion via barrier properties at the oil-water interface.
- The capability to affect the release of substances from the emulsion matrix.
- The improvement of process stability towards freezing and drying.

These opportunities arise from the exceptionally high energy of detachment of starch granules from the oil-water interface, the physical size of the starch granules, as well as the possibility to change granule properties in-situ to enhance barrier properties at the oil-water interface. The resulting encapsulating ability of starch based Pickering emulsions has many potential applications in food products including taste masking (i.e. hiding the flavour of health promoting but ill tasting ingredients) as well as protecting sensitive compounds from various types of degradation (i.e. oxidation, or reactions with other ingredients) during processing and storage. This together with the fact that starch granule based particles are per definition generated from renewable resources and are bio-degradable, sets starch granules in an ideal position to not only receive continued academic research interest in the area, but also see wider industrial use in the near future.

**References:**


**Marilyn Rayner** graduated with a B.Sc. in biological engineering, from the University of Guelph, Canada in 1999 and earned her PhD in Food Engineering from Lund University 2005 on modelling droplet formation in membrane emulsification. Currently she is an Associate Professor in Food Engineering at Lund University working in the areas of multi-physics modelling, interfacial phenomena, and particle stabilized emulsions.

6.3. **Andreas Becker**, Krefeld (Germany)

Starch Products for the Paper Industry – Opportunities & Challenges

During the last couple of years the paper industry in Europe has seen a variety of challenges and changes. Starting with a higher degree of consolidation coupled with overcapacity in the graphic sector as a result of new media and IT, the industry nowadays is focusing on cost optimization at maintained quality.

As a supplier to the paper industry it is important to understand the impact of such trends and changes to review the current situation, products and offerings in the different paper grades and applications therein.

Thus challenges in the market can be turned into opportunities which may lead to new developments, products and solutions, possibly opening up new markets as well.

Within the classical paper applications examples are given for trends and demands in the wet-end, surface sizing and coating applications.

Developments of Cargill to meet these customers’ demands are presented and discussed.

C☆iBond for Wet-end applications to fulfil customer expectations with regard to cost, availability and performance not only due to potato regime changes.

C☆iFilm and C☆iCoat to meet customer demands in paper coating in a challenging environment driven by a very high cost focus due to overcapacity and mills closures.

Due to the industry changes mentioned the paper industry is not only looking for new solutions within the classical paper production and starch application areas but also into new markets and products based on fibers.

Here also the starch supplier may play an important role especially with regard to environmental aspects replacing fossil based materials.

**Dr. Andreas Becker** studied Chemistry and since 1991 he is employed by Cargill (Cerestar until 2002). During his career - working in the Application and Development Centre in Krefeld, Germany - Andreas Becker has taken several positions focusing on the development and application of starches for the paper industry. Since 2011 he is leading the research and development as well as the application technology within Cargill Starches and Sweeteners Europe for the paper area and since 2015 also for industrial.
Thursday, April 16th 2015

3. Modification

3.2. **Dorien M. Dries, Sara V. Gomand, Jan A. Delcour** and **Bart Goderis**, Leuven (Belgium)
   Insights in the Conversion of Native Starches into Their Granular Cold-Water Swelling Counterparts

3.3. **Maurice Essers, J. Timmermans** and **R. Nagtegaal**, AJ Zeist (The Netherlands)
   The role of water in starch modifications

3.4. **Markus Schirmer**, Uzwil (Switzerland)
   A novel approach for structural analysis of high viscouse starch based products during heating

10:00 Coffee Break

4. Enzymes

4.1. **Mads Weibye, Chee-Leong Soong** and **Paolo Ronchi**, Bagsvaerd (Denmark)
   Novozymes Secura® - The most robust beta amylase
   Go straight to maltose syrup with the lowest risk of infection and lowest cost of conversion.

4.2. **Jan Delcour, Christophe M. Courtin, Kristin Verbeke** and **Willem F. Broekaert**, Leuven (Belgium)
   From Wheat Bran to Arabinoxylan Oligosaccharides: From Scientific Concept to a Spinout Dealing with Production, Demonstration of Prebiotics Effects, Regulatory and Intellectual Property Aspects and Product Applications

12:00 – 13:00 Lunch Break

5. Green Chemistry

5.1. **Agnes Rolland-Sabate, Lorena Sciarini, Sophie Guilois, Denis Lourdin, Eric Leroy** and **Patricia Lebail**, Nantes (France)
   Starch destructuration by ionic liquids

5.2. **Eric Leroy**, Saint-Nazaire (France)
   Ionic liquids as processing aids and functional additives for starch based materials

6. Application

6.1. **Chi-Wah Yeung** and **Hubert Rein**, Bonn (Germany)
   Starches as excipient in the pharmaceutical technology

15:00 Coffee Break

6.2. **Marilyn Rayner**, Lund (Sweden)
   Starch Pickering Emulsions – formulation opportunities

6.3. **Andreas Becker**, Krefeld (Germany)
   Starch Products for the Paper Industry – Opportunities & Challenges

17:00 Closing remarks by the Chairman of the Starch Experts Group, **Willi Witt**, Oelde (Germany)
Quality controls for cereal cultivation

- Cereal analyses
- Flour analyses

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