67th Starch Convention

April 13th – 14th 2016
in Detmold

Program
Evening Program
Exhibition
Participants
Summaries
Wednesday, April 13th 2016

from 8:00  Registration

13:30  Opening Remarks by the President of the Association of Cereal Research, Götz Kröner, Ibbenbüren (Germany)

1. Market

13:30  1.1. Michael vom Dorp, Krefeld (Germany)
Termination of sugar regime 2017 – Opportunities and Challenges

14:00  1.2. Sara Girardello, Oxford (United Kingdom)
Recent developments in the EU and US starch markets

14:30  Coffee Break

2. Starch Basics: Biosynthesis
(Session in parallel – venue: Seminar room in basement)

15:00  2.1. Samuel Zeeman, Zurich (Switzerland)
Developing a yeast-based system for reconstruction the starch biosynthesis pathway

15:30  2.2. Samuel Zeeman, Zurich (Switzerland)
Proteins that are important for amylose synthesis

2. Modification (Session in parallel – venue: lecture hall)

15:00  2.1. Christina Gabriel, Hendrik Wetzel, Sylvia Radosta and Waltraud Vorweg, Potsdam (Germany)
Modified starch as potential water-based binder system for interior coatings

15:30  2.2. Marco Ulbrich and Eckard Flöter, Berlin (Germany)
Acid-thinned corn starch – Impact of modification parameters on molecular characteristics and functional properties

16:00  Coffee Break

16:30  2.3. Michael A. Radeloff, Berlin (Germany)
Physically modified starches

17:00  2.4. Vitaly Kocherbitov, Malmö (Sweden)
Understanding Starch Gelatinization: The Phase Diagram Approach

17:30  Exhibitor’s Forum – short term presentations

Continued on the penultimate page
Lunch will be served in the exhibition hall:

The menu:

**Wednesday, April 13th 2016**
- Asparagus cream soup
- Canapés with ham paté
- Canapés with herb cream cheese
- Canapes with trout filet
- Canapés with Camembert

Dessert: Panna Cotta

**Thursday, April 14th 2016**
- Tomato mozzarella basil skewers
- Mini meatballs
- Small pork escalope
- Small chicken escalope
- Caesar wraps

Dessert: Vanilla mousse

**Beverages:**
- Mineral water
- Coca-Cola
- Orange juice
- Apple Spritzer

Bon appétit and interesting conversations!
Wednesday, April 13th 2016

20:00  **Social gathering** at the restaurant “Gastronomie am Hermannsdenkmal”, Grotenburg 50, Detmold (Teutoburg Forest)

**Buffet**

Starters:
- Rösti potatoes with pieces of cured ham,
- Sheep’s cheese wrapped in bacon,
- Tomato-mozzarella skewers
- Bruschetta fungi-toasted bread with mushrooms in an onion vinaigrette
- Salad buffet

Main dishes:
- Filet of pork on a creamy mushroom sauce
- Chicken breast fillet with tomatoes, olives an sheep’s cheese

Accompaniments
- Basmati rice
- Potato croquettes
- Potato gratin

Dessert:
- Mousse of white & dark chocolate
- Tiramisu

**Bus transfer**

A bus transfer is organized for you.

19:05 h  **Bus stop 1**  **Train station Detmold** (Elisabethhotel)

19:15 h  **Bus stop 2**  **Sparada Bank - Willi-Brandt-Platz/Paulinenstrasse**
  (For the Hotels Lippischer Hof, Detmolder Hof and Best Western Residenz, Altstadt Hotel)

19:30 h  Meeting at parking place at Hermanns Denkmal, Grotenburg 50, Detmold and short walk to the Hermanns Denkmal

**Departure:**  from 22:00 h

**Thank you!**
Exhibition Hall Association of Cereal Research
Stand allocation

12th Bioethanol and Bioconversion Technology Meeting and 67th Starch Convention from April 12th – 14th 2016

Stand sizes:
- Stands 1 – 6, 10, 11, 13: 20 m²
- Stands 7 a/b, 8 a/b, 9 a/b, 12 a/b, 14 a/b, 16 – 18: 10 m²
- Stand 15: 12 m²
- Stands 18 – 22: 15 m²
- Stand 23: 10 m²
Exhibition

Andritz Gouda BV, PD Waddinxveen (Netherland)

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

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

Brabender GmbH & Co. KG, Duisburg (Germany)

Bühler GmbH, Braunschweig (Germany)

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

GEA Group AG, Oelde (Germany)

Hein. Lehmann GmbH, Krefeld (Germany)

Gebr. Lödige Maschinenbau GmbH, Paderborn (Germany)

MMW Technologie GmbH, Lutherstadt Wittenberg (Germany)

Myande Group Co. Ltd., Yangzhou, Jiangsu (China)

PIERALISI Northern Europe B.V., Eibelstadt (Germany)

Terrace International Inc., Bolingbrook (USA)

TUMMERS, Simon Dryers Technology, Nottingham (United Kingdom)

VetterTec GmbH, Kassel (Germany)

WeissBioTech GmbH, Ascheberg (Germany)

W. Kunz dryTec AG, SWISS COMBI, Dintikon (Switzerland)
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Effective April 7th, 2016

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<td>Matthäus, Bertrand, Dr.</td>
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Summaries

1. Market

1.1. **Michael vom Dorp**, Krefeld (Germany)
Termination of sugar regime 2017 – Opportunities and Challenges

![Summary of the opportunity post Sugar Regime](image)

**Michael vom Dorp**, Cargill Deutschland, Since 1990 Application Engineer and then Technical Service Manager at Maizena, Cerestar and at last Cargill in Krefeld with the main focus on dairy industry / ice cream / fruit processing. Coordinator and later on Advisor in the Application Centre EMEA Dairy & Frozen Desserts, Currently Technical Service Manager for Specialty Sweeteners as Stevia, Erythrit and Trehalose for Cargill Starches and Sweeteners in EMEA, Member of the ZDS’s ice cream committee since 1990 and chairman of the advisory board since 2001; Chairman of INTER-ICE organization committee since 2007.

1.2. **Sara Girardello**, Oxford (United Kingdom)
Recent developments in the EU and US starch markets

The global native and modified starch market stands at over 38 million, compared to 35.5 million tonnes in 2010. Niche starches such as pea starch, rice starch and sago starch have grown the fastest in recent years, followed by native cassava starch. Africa is the market that exhibited the fastest growth. However, its share of global demand is quite small. Growth in Asia has slowed down in recent years but the region remains the driver of growth accounting for over 65% of global demand.
In the EU, maize starch dominates the native starch market; output is estimated at over one million tonnes. The largest volumes are for modified starches and dextrin at just below 1.6 million tonnes. Most of the EU starch output is consumed within the region, with the exception of native potato starch. Of this, around 45% is exported. Asia is the largest outlet, with China alone accounting for over 50% of shipments to this region. Potato starch has important applications in Asian cuisine and there is no substitute for it. The EU cassava starch market is very small; however, the recent 30,000 tonne duty-free quota granted to Vietnam has the potential to expand use of this product. This is likely to be at the expense of domestic potato starch.

In the US, maize starch is the main product. Around two million tonnes of native maize starch are produced annually; similar volumes of modified maize starch are also manufactured each year. Native starch output from other raw materials, including potato, is very small. Most native maize starch is used domestically, while exports of modified starch are bigger at 15-20% of output. Recent investment has been directed at increasing capacity for specialty starches, such as pea and potato starch.

*Sara Girardello* heads the Starch and Sweeteners Research Team of LMC International Ltd. Sara gained an MSc in Applied Statistics from the University of Oxford, UK and an MA (Hons) in Economics from the University of Verona, Italy, before joining LMC in 2004. In 2009, she completed an MSc in Horticulture (with Distinction) at the University of Reading, UK.

2. Starch Basics: Biosynthesis
(Session in parallel – venue: Seminar room in basement)

2.1. **Samuel Zeeman**, Zurich (Switzerland)

   Developing a yeast-based system for reconstruction the starch biosynthesis pathway

Starch, as the major nutritional component of our staple crops and a feedstock for industry, is a vital plant product for mankind. Starch is composed of glucose polymers that form massive, semi-crystalline granules. The precise structure and composition of starch determines its functionality and thus its suitability for industrial applications. However, there is currently no versatile model system that allows the detailed investigation of the relationships between the biosynthetic apparatus, the structure of the glucans and their functional properties.

To address this, we decided to develop a heterologous system that simulates starch synthesis. We expressed the core Arabidopsis starch biosynthesis pathway in the yeast *Saccharomyces cerevisiae* purged of its endogenous glycogen-metabolic enzymes. We obtained insoluble starch-like granules with a characteristic semi-crystalline organization, showing that this system indeed simulates starch biosynthesis. By creating a library of yeast strains in which we systematically varied the complement of biosynthetic enzymes, we could investigate how each enzyme influences alpha-glucan structure and solubility.

This yeast system has the potential to accelerate starch research and help create a holistic understanding of starch granule biosynthesis, providing a basis for the targeted biotechnological improvement of crops.
2.2. **Samuel Zeeman, Zurich (Switzerland)**
Proteins that are important for amylose synthesis

Starch is composed of two glucose polymers; branched (amylopectin) and near-linear (amylose). Although amylopectin is the major component, responsible for the semi-crystalline nature of starch, the amount of amylose strongly influences the physico-chemical behaviour of starchy foods during cooking and of starch mixtures in non-food manufacturing processes. The GRANULE-BOUND STARCH SYNTHASE (GBSS) is the glucosyltransferase specifically responsible for elongating amylose polymers. It is the most abundant protein found associated with starch granules and is the only protein known to be required for its biosynthesis.

Recently, we discovered that a second protein that we designated PROTEIN TARGETING TO STARCH (PTST) is also specifically required for amylose synthesis in the model plant Arabidopsis. PTST is a plastidial protein possessing two domains; an N-terminal coiled coil domain, typically associated with protein-protein interactions, and a C-terminal carbohydrate binding module (CBM) that enables it to bind to starch. Arabidopsis mutants lacking the PTST protein synthesise amylose-free starch and are phenotypically similar to mutants lacking GBSS. Analysis of granule-bound proteins showed a dramatic reduction of GBSS protein in the ptst mutant’s starch granules.

Using a combination of biochemical methods, we showed that GBSS and PTST physically interact via a coiled-coil-based interaction. Furthermore, we provide direct evidence that GBSS requires PTST to localise to starch granules and that the CBM domain of PTST is required for this localisation. Our conclusion is that PTST fulfils a previously unknown non-enzymatic function in targeting GBSS to starch and propose that PTST represents a promising new gene target for the biotechnological modification of starch composition; it is widely conserved in starch crops and, from our data, appears to be exclusively involved in amylose synthesis.

**Samuel C. Zeeman** studied Natural Sciences at Gonville and Caius College, University of Cambridge, followed by a PhD with Tom ap Rees in Plant Biochemistry in 1996. He moved from Cambridge to the John Innes Centre (Norwich, UK) and worked as a post-doc with Alison M. Smith and Cathie Martin until early 2002. He then took up an independent position at the University of Bern. In April 2005 he took up his current position as Professor of Plant Biochemistry at the ETH Zurich, receiving tenure in 2010. Professor Zeeman’s research focuses on carbohydrate metabolism in plants, aiming to understand how plants make and then use the primary products of photosynthesis, sugars and starch. His work has centred on the use of the model plant species Arabidopsis thaliana, combining classical and reverse genetics with biochemistry. His contributions include defining previously uncharacterised steps in the pathway of starch degradation and exploring the complexity of starch biosynthesis.

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2. Modificatob (Session in parallel – venue: lecture hall)

2.1. **Christina Gabriel, Hendrik Wetzel, Sylvia Radosta und Waltraud Vorwerg, Potsdam (Germany)**
Modified starch as potential water-based binder system for interior coatings

Our work aimed at the chemical modification of degraded starch for the application in the coating sector as binder, with the focus on paints and varnishes. For this purpose, cold-water dispersible hydrophobized starch esters and ethers with high solid contents (≥ 30 % (w/w)) and viscosities between 100 and 1000 mPa·s should be synthesized. Additionally they should form continuous films and show adhesion to different substrates.

As starting product a degraded potato starch (Emox TSD) with a molar mass of 1.18·10^5 g/mol (SEC-MALLS) was used and modified by esterification and etherification reactions. The short chain esters (C_2-C_4) were esterified by carboxylic acid anhydrides and the starch hexanoates...
(C₃) by carboxylic acid vinyl esters. Epoxy alkane derivatives were used for the synthesis of hydroxyalkyl starch ethers (C₂-C₄, C₆). Beside the type of substituent and the chain length, also the degrees of substitution (DS) and molar substitutions (MS) were varied from 0.05 to 1.1.

The DS / MS-values were determined by the methods ¹H-NMR spectroscopy (starch ether and ester (C₆)) and saponification with subsequent acid-base titration (starch ester). Water and a co-solvent were used for the dispersibility tests. The rheological measurements were done on an oscillation rheometer with a cone-plate geometry. Amplitude and frequency sweeps were performed, as well as viscosity measurements. Films were casted based on the starch dispersions by using a doctor blade with a gap size of 0.1 mm on glass plates. The wet and dry layer thicknesses were determined from the resulting films by a wet film thickness gauge and a profilometer. Additionally cross cut tests were performed by a cross cut tester to evaluate the adhesion on the used glass plates. The last two mentioned methods were only performed with the samples which formed continuous films.

The first tests to the compatibility of commercial binders (Acronal A 754, Acronal S559, AQA Gloss) and our functionalized starches were done by mixture them and film casting afterwards.

Tests on aluminium plates were done with selected starch ester dispersions and added additives and isocyanate hardener. A doctor blade with a gap size of 0.20 or 0.25 mm was used for the film casting. Based on these films cross cut tests and short-time corrosion stability tests (STCST) were performed. The coatings on the aluminium plates were subjected to internal stress by thermal cycling for the STCST. A quantitative evaluation of the loss of protection was obtained by electrochemical impedance spectroscopy (EIS).

The modification led to cold water-soluble or dispersible products with applicable concentrations between 30 and 45 % (w/w) and viscosities in the range of 10²-10³ mPa·s (100 s⁻¹). The most samples had a newtonian flow behaviour and showed viscoelastic properties with higher values for the loss modulus (G'″) in the frequency sweep. Continuous films were observed with starch esters in the DS range of 0.13-0.81 and in the case of the starch ethers with MS values of 0.77-0.91. Wet and dry layer thicknesses of 50 µm and 7-12 µm were obtained. In the cross cut test the esters had clearly better results with values of 0 and 1, in contrast to the ethers with values of 4.

The compatibility tests with the 3 commercial binders showed that the Acronal binders showed compatibility with the modified starches, while the AQA Gloss was not compatible. 42 % of the synthetic binder could be mixed with the functionalized starches.

On aluminium plates the esters showed good adhesion (0-1). The tested ether could be classified in the worst class (5). In the short-time stability tests the barrier properties corresponded to the hydrophobicity of the starch ethers and esters and the starch butyrate with a DS of 0.65 had the best performance.

The investigations showed that the synthesized starch esters possessed better film forming properties compared to the starch ethers. According our experiments and especially based on the results of the film formation, the cross cut test and the STCST the starch esters and not the ethers could be the preferred class for an application in the coating sector. Additionally the results showed that the starch esters could be an alternative to petroleum-based polymers as binder in paints and varnishes in the future potentially.

Christina Gabriel was born in 1988 in Kassel (Germany) and studied at the University of Ulm (2007-2010, 2011-2013). She spent one semester abroad in Málaga (Spain) 2012/13. Her Master thesis was completed at the Fraunhofer Institute for Applied Polymer Research IAP (Germany). Thereafter, she continues her work as a PhD student at the Fraunhofer Institute in cooperation with the University of Potsdam.
2.2. **Marco Ulbrich und Eckard Flöter**, Berlin (Germany)

Acid-thinned corn starch – Impact of modification parameters on molecular characteristics and functional properties

Since the restricted applicability of native starches for gelification, acid-thinned starches are of great interest in the food sector, e. g. in gelled sweets. However, the acid modification process of the starch is often based on trial-and-error because modification parameters such as hydrolysis time, temperature, and acid concentration cannot be presently related to the molecular degradation of the starch polymers and resulting product functionality.

The impact of two process parameters on the molecular structure of the starch and in particular the amylose fraction, and functional properties (gelation temperature, gel strength) was investigated. Therefore acid-thinned corn starches were prepared systematically using the slurry process at 40 °C by varying the parameters acid concentration (0.09-0.72 M HCl) and hydrolysis time (4 and 24 hours) while the basic granular structure was preserved.

The characterization using SEC-MALS-DRI proved molecular degradation mostly of the amyllopectin progressively with increasing acid concentration after short hydrolysis (4 hours). However, an additionally extensive degradation of the amylose fraction was found when hydrolyzed for a long time (24 hours). Decreasing sol-to-gel-transition temperature was found with decreasing $M_w$ of both, the acid-thinned starch sample as well as the corresponding amylose fraction. The correlation between molecular properties and gel strength gave evidence of an optimum degree of hydrolysis. Acid-thinning of the starch to $M_w$ of about $12 \times 10^6 – 8 \times 10^6$ g/mol and $3 \times 10^5 – 2.5 \times 10^5$ g/mol for the amylose fraction, respectively, resulted in the highest gel strength within the present study. With respect to high firmness of the starch gel, a gentle hydrolysis is preferable, which is ensured applying a low acid concentration (0.09-0.36 M HCl) for 4 hours. However, long hydrolysis with high acid concentration (0.18-0.72 M HCl) causes strong molecular degradation of the amylose fraction and therefore prevents the formation of a stable amylose gel network structure.


2.3. **Michael A. Radeloff**, Berlin (Germany)

Physically modified starches

Modern starch milling technologies not only produce the common native starches from corn, wheat, potato and cassava but also can extend the range of commercially available starches by native starch specialities such as waxy and high amylose varieties of corn, potato, pea and rice starch.

The functionality of these native starches in form of swelling and gelling behaviour is defined by botanical characteristics such as granule size, amylose-, phosphate and lipids content. The diversity of these native starch functionalities can be extended by physical starch modification techniques.

Pregelatinized starches are obtained by drum and roll drying, extrusion or spray cooking often complemented by agglomeration. Heat moisture treatment and annealing result in cold water swelling granular starches and resistant starch, respectively. This extended range of clean label...
functional native starches is successively replacing E-number coded chemically modified food starch additives from the ingredient list of modern convenience and processed foods.

**Dr Michael Radeloff** is a carbohydrate chemist from Hamburg University. He held several international management positions in the starch industry in R&D, Product Development and Marketing. Michael is the owner of Thales-Consult Berlin, a long established consultancy specialised in renewable agricultural raw materials, their derivatives and applications. The consultancy services are addressing client product development strategies, are analysing market opportunities, provide technical product application assessments and develop in-house customer training programmes.

2.4. **Vitaly Kocherbitov**, Malmö (Sweden)

Understanding Starch Gelatinization: The Phase Diagram Approach

Temperature and hydration induced transitions in starch – water systems has been known for centuries but not understood on fundamental thermodynamic level. To investigate them we used a combination of optical microscopy, synchrotron radiation X-ray scattering (SAXS), sorption calorimetry and DSC. For the first time, we established thermodynamically consistent phase diagrams of three starch - water systems. Transitions in native potato starch, acid-hydrolyzed starch and cross-linked starch microspheres were investigated. Gelatinization, glass transition, sub-Tg transition and melting of freezable water were systematically analyzed.

By constructing a phase diagram for the native potato starch-water system, we show that gelatinization can be interpreted in analogy with a eutectic transition. The phase rule explains why the temperature of the gelatinization transition is independent on water content. Furthermore, the melting endotherm observed in DSC represents a liquidus line; the temperature for this event increases with increasing starch concentration. Moreover, at room temperature both the lamellar spacing and the inter-helix distance were observed to decrease with increasing starch content for starch concentrations above 65 wt%. We also showed that SAXS can be used to analyze the fractal dimension of starch particles surfaces and characterize properties of starch - water interface.

In sorption calorimetric experiments, acid-hydrolyzed starch and in cross-linked starch microspheres exhibit very clear isothermal glass transitions. In the former case the glass transition was followed by spontaneous crystallization, while in the latter case the cross links prevented crystallization.

**References:**

**Vitaly Kocherbitov** graduated from Saint-Petersburg University in 1993 where he defended his PhD thesis on the topic of thermodynamic stability and vapor-liquid equilibria in 1997. In 2000 - 2003 he worked in Lund University (Sweden) studying hydration of surfactants. Currently he is as an Associate Professor in Malmö University (Sweden). Among his research interests are hydration of biopolymers, water sorption, calorimetry, phase and glass transitions, liquid crystals and molecular modeling.
3. Starch Basics: Starch Structure
(Session in parallel – venue: Seminar room in basement)

3.1. Paul Nommensen, Foxhal (The Netherlands)
Powder reology review

In most cases starch is dried after it is refined. It turns then into a powder. It stays in this state until it is resuspended just before it is introduced in application. A lot of handling is involved in between. During the handling the powder has to flow. Unfortunately serious problems are experienced from time to time. This justifies the study of powder flow. And because powders behave in a complex manner this study is often referred to as “powder rheology”.

In contrast with rheology of fluids, powder rheology is still very ill-understood. In this presentation some aspects are highlighted like the difference between fluid and powders. Also the effect is examined that botanical origin of the starch has on powder flow. Properties of the starch granules are considered in order to explain the observed differences.

Dr.ir. P.A. Nommensen works for Avebe in the Innovation Centre. He obtained a master of science in applied physics at the University of Technology Delft. He graduated at the University Twente with research on rheology of suspensions.

3.2. Evzen Sárka, Prague (Czech Republic)
Waxy Starch – New trends in research (review)

Elongation and branching of amylopectin during its biosynthesis is a complex process and requires an array of enzymes viz., starch synthases, starch branching enzymes and debranching enzymes. Synthesis of amylose, however, is brought about solely by the enzyme granule-bound starch synthase I or waxy protein.

Molar size and branch-chain length of amylopectin affect the gelatinization behavior of waxy starches and rheological properties of their pastes and gels. Amylose retrogrades in gels of normal starches within a day of aging and involves a crystallization process. On the other hand, amylopectin forms very weak gels at relatively high concentrations that also break down on shear.

Digestibility of waxy starch is influenced by interplay of various factors including granule size, granule porosity, amylopectin chain length distribution, and degree of crystallinity. Crystallization of normal starchy materials into resistant starch (RS3) is a result of re-association of amylose chains in the form of double helices that are loosely arranged into a partially crystalline system that resists the diffusion and binding of hydrolytic enzymes.

Annealing and heat moisture treatment (HMT) are often used to modify the physicochemical properties and digestibility of starch granules. Amylose molecules play an important role in starch annealing therefore for waxy maize starch, the annealing effect on starch structure and functionality is less compared to amylose-containing starch. An HMT (25% moisture, 100 °C, 16 h) was performed on waxy maize starch by Jiranuntakul et al. (2011), resistant starch content increased from 27% to 40.3%.

Starch can be debranched at α-1, 6 linkages by debranching enzymes (e.g. isoamylase and pullulanase) under specific conditions. For waxy starches, only short linear chains are released when starch is debranched, and therefore these chains have a relatively narrower MW distribution.
The low-amylose rice starch is more susceptible to acetylation using acetic anhydride compared to the medium- and high-amylose rice starches. The findings indicate possible use of acetylated waxy starch in food models that are required to withstand fair amount of heat and where gelling is required at a higher temperature.

The amylose-amylopectin ratio of starch affects its properties and uses. Until recently, scientific books cited only applications of waxy *maize* starch but in recent time the interest of industry increases in processing and use of other high amylopectin starches. The survey of new uses of waxy maize, rice, wheat, barley and potato will be presented. Ones of modified products are starch-based nanoparticles which may be used as fillers and reinforcing agents in polymer composites, carriers for drug delivery, barrier coating materials and stabilizers in oil-in-water emulsions.

*This research was supported by the “Wheat with specific starch composition and features for food and non-food purposes” QJ1310219 research grant of the Ministry of Agriculture.*

**Evzen Sárka**, born in Prague, Czech Republic, 2 July.1953. Education: University of Chemistry and Technology (UCT Prague), Faculty of Food and Biochemical Technology, PhD graduated in 1976. Associate Professor at the same university since 2012, head of a starch laboratory at the Department of Carbohydrates and Cereals. Research interest: sugar and starch technology, juice purification, measuring of particle size using image analysis; modeling processes in carbohydrate technologies; digestibility of starch, extrusion, biodegradable plastics. Prof. Sárka is a member of ICUMSA (International Commission for Uniform Methods of Sugar Analysis) and of ESST (European Society of Sugar Technologists), and of the Scientific Committee of the International Conference on Polysaccharides-Glycoscience held every year in Prague.

### 3. Modification (Session in parallel – venue: lecture hall)

#### 3.1. Jeroen J.G. van Soest und Kommer Brunt, Heerenveen (The Netherlands)
Starch based dietary fibres, analytical characterization and health effects

Dietary fibres are important components of food products. Starch based dietary fibres are amongst others different categories of resistant starches (RS1, RS2, RS3 and RS4), high amylose starches and resistant maltodextrins. High amylose maize starches and pulse starches as pea starches contain high quantities of natural resistant starch. Resistant maltodextrins are starch based manufactured products. Well-known brand names are for example Fibersol and Nutriose.

Dietary health effects can be subdivided in small intestinal and large intestinal effects. Small intestinal effects have to do mostly with satiety, obesity, glycemic index and diabetes. And the large intestine effects deals amongst others with stool and constipation, blood cholesterol levels and coronary heart diseases and possibly colon cancer.

However in 2011, the EFSA has rejected the dietary fibre health claims of resistant maltodextrins (reduction of post-prandial glycaemic responses, maintenance of normal blood LDL cholesterol concentrations, maintenance of normal (fasting) blood concentrations of triglycerides, and changes in bowl function).

Dietary Fibres are important for nutritional labeling of products. There are dedicated analytical methods available for the determination of resistant starch (e.g. AOAC 2002.02), resistant maltodextrins (e.g. AOAC 2001.03). Also in the most recent AOAC dietary fibre protocols (AOAC 2009.01 and 2011.25) resistant starch and resistant maltodextrins are quantified as dietary fibre.
Dr. Jeroen van Soest studied Chemistry at University of Utrecht and has a PhD in starch based plastics. He has over 80 publications and patents and over 100 presentations at international conferences. He is winner of several scientific development prizes (amongst which the Prix Cerealier). He is expert in the field of analytical chemistry and biopolymer, amongst which starch or carbohydrate, product developments (products like FlourBond, Paragon, Solanyl). He has experience in new product- and market development from ideation to commercialization. Specialties: working with customers, communication, innovation, product development, management. Technical background: Carbohydrates, Polysaccharides (Starch, Gums), Proteins, Biopolymers - Food, Feed and Non-Food products, Analytical chemistry, Quality Control. Currently he is BU manager of the Carbohydrates Competence Center CCC of Eurofins Food NL. He has been working for various renowned companies like Rodenburg Biopolymers, CPKelco, Meneba.

3.2. Stylianos N. Raphaelides, Thessaloniki (Greece)

A process designed for the continuous production of starch inclusion complexes on an industrial scale

The process described in this work aimed at exploring the possibility to produce starch inclusion complexes as effectively as possible concerning their yield, in processing conditions which will affect the physical state of the guest molecules as little as possible using conventional processing equipment already available in the market.

The main processing steps of this process are the gelatinization of native starch in a double drum drier and the subsequent extrusion of the starch with added fatty acid aqueous soap solution at temperatures as low as 80°C for extrusion times of 30-40 s.

The complexes were formed in a twin screw cooker extruder operated at 80 or 100°C and screw speeds of 80, 100, 145 or 204 rpm. The physicochemical characteristics of the extrudates were studied and the structural modifications taken place in the starch matrix, during extrusion, were investigated using XRD analysis. The results from extrudate samples produced under various processing conditions indicated that amylose inclusion complexes with the fatty acids, in all cases were effectively formed and they were suitable for utilization. The processing conditions employed were fairly mild ensuring that complexes, produced using thermally sensitive guest molecules, would not be degraded when the process will be operated in an industrial environment. The process could be ideal for the effective protection of sensitive and unstable bioactive compounds as well as of nutraceuticals against adverse environmental conditions and for their controlled release in the human gastrointestinal tract.

The same process was employed for the formation of thermoplastic starch suitable as a raw material for the production of fully biodegradable materials. In this case apart from pregelatinized maize starch and fatty acids, glycerol was added as well. The processing conditions employed were: heating at 80 or 100°C in all heated sections of the extruder and rotational screw speeds 80 or 115 or 145 or 210 rpm. The examination of physicochemical properties of the extrudates indicated that the addition of fatty acids affected the functionality of starch-glycerol systems.

Structural studies carried out using X-ray diffraction analysis, revealed that the combined effect of fatty acid and glycerol addition to gelatinized maize starch systems during extrusion cooking caused significant changes in the structural characteristics of the extrudates which mainly influenced their mechanical properties. It appears that glycerol molecules were more uniformly distributed in the starch system which did not contain added lipids whereas in the case of the lipids added to the system there was a different structural organization possibly with patches rich in glycerol and others mainly occupied by the amylose - fatty acid crystallites formed. These changes could lead to products with tailor made functional properties suitable to be potentially utilized as biodegradable materials e.g. in packaging applications.
4. Application

4.1. Penelope A. Patton, Hoffmann Estates (USA)
Optimising performance of thickening starches in foods using texture maps

Starches are commonly used thickening agents for foods, but the complexities of their swelling behaviour-concentration relationship and how these impact the rheological behaviour and textural properties of foods are not well understood. A comprehensive model has been developed that predicts such textural properties as cohesiveness, adhesion, shape retention, cling, slipperiness, cuttability and mouth clearing from the swelling volume and concentration of the starch.

It is revealed that even small changes in starch concentration or processing conditions can lead to surprisingly large changes in product texture. It also reveals that two food products of equivalent viscosity can differ dramatically in textural attributes, a function solely of the swelling power of the starch. The powerful insights provided by these texture maps are illustrated in this talk for the case of a simple gravy, but are equally applicable to such diverse applications as retorted soups, yogurts, puddings, and salad dressings. The use of these maps allows the starch producer to develop structure/function-optimized starch ingredients, and the food formulator to intelligently design food products and tightly control production quality.

Penelope Patton is a Research Fellow in Innovation and Commercial Development at Tate & Lyle. She has worked in product development for Tate & Lyle, formally A.E. Staley, for 29 years, in the areas of starch chemical and physical modification, characterizations, fermentation, purification, and process optimization, resulting in 13 patents and patent applications. She has developed carbohydrate-based products for use in foods and beverage applications, pharmaceuticals, adhesives, coatings, industrial thickeners and binders, and most recently was a key contributor to the development of CLARIA® clean-label functional food starches. Penelope has a PhD in Polymer Science and Engineering from the University of Massachusetts at Amherst, with specialization in polymer physical chemistry.

4.2. Judith K. Whaley, Hoffmann Estates (USA)
Designing starches for use in multi-phase food applications

Intelligent design of starch-based ingredients and effective formulation of such ingredients remains a challenge for scientists in the field. While extensive empirical knowledge has been acquired and used to build a multi-billion dollar global industry, research into the underlying physics of such systems has been sparse and a consistent framework for examining how the structure and function of such starches is exploited in multi-phase foods systems is elusive. In this research, we begin by outlining key structural features of widely used starches; we then relate those structural features to observed physical properties, including rheology, interfacial properties, swelling behaviour, and related properties.
In parallel, we review key considerations that are critical to understanding performance in multi-phase foods, including how to define specific foods in terms of their underlying phases and how to predict the impact of starch on each phase. From the underlying structural and functional properties, we develop maps to predict performance in multi-phase foods, including yogurt, salad dressing, and fabricated potato chips. Finally, we show that many of the seemingly complex properties of these foods, including the sensory properties and related consumer appeal, can be anticipated on the basis of these texture maps.

Judith Whaley is the Vice President for New Product Development at Tate & Lyle. Judith has launched 6 new starch products over the past 3 years, including the CLARIA® line of starches, PULPIZ®, and TENDER-JEL®. She also initiated development work on functional sugars, resulting in the launch of DOLCIA PRIMA™ Allulose syrup and has been highly involved with the development and launch of natural high potency sweeteners, including a range of monk fruit derived sweeteners under the PUREFRUIT® brand and a stevia-based sweetener under the TASTEVA® brand. Previously, Judith lead the development of ingredient systems and helped shape the technology strategies for National Starch Food Innovation where she held management roles and oversaw research in materials science, high-throughput experimentation, sensory & consumer insights, and high moisture food applications. During her 15 years with the company, Judy was closely involved with the development and launch of 15 new products. Judith has a B.S. in chemical engineering from Stanford University and a Ph.D. in chemical engineering from the University of Massachusetts at Amherst.

4.3. Denbigh R.J. Lloyd, London (United Kingdom)
Developing the essential food ingredients for the future: What are the implications for the starch industry?

The food ingredients industry in the 21st century continue to face new dynamics ranging from ever increasingly sophisticated consumer demands, health concerns and a more detailed regulatory environment; through to greater market competitiveness, price sensitivity, industry consolidation, raw material availability and global demand.

The responses of the different elements of the ingredients industry to these issues demonstrate the diversity of approach needed to both survive and to grow in this environment. Meeting these challenges have shaped and continue to refocus their business models as well as encouraging them to reach out to different markets and novel product and service developments. What can we learn from this and what are the implications for the starch industry?

D.R.J.Lloyd, based outside London, Denbigh Lloyd is a Business Development, Marketing & Training Specialist, advising on both strategy and implementation of corporate, product marketing, branding and business development programmes in major international Business To Business companies; particularly in the Food and Agro-industrial product markets. Over 30 years international food ingredients industry experience includes flavours, dairy and starch as well as active trade organisation representation at European and international level. He also works in close project collaboration with Harper Adams University and the Department of Food Science and Agri-Food Supply Chain Management in the UK.
4.4. **Natalie Russ** and **Thomas Vilgis,** Mainz (Germany)

New perspectives in cold-soluble, physically modified starches

The presentation shows two different ways to achieve physically modified tapioca starch and the influence on mechanical properties of an aqueous starch paste is investigated. A completely cold soluble tapioca starch powder is produced by spray drying a previously gelatinized starch paste. Rehydrating the received white powder forms a viscous paste with significant loss in elasticity. Heating of a native tapioca starch suspension in contrast yields highly viscous paste with dominating elastic behavior.

The combination of the spray dried tapioca starch with nongelling food hydrocolloids, such as xanthan gum, λ-carrageenan, and guar gum restores the mechanical properties and creates new starch based thickening agents with stable structure. Rheological measurements of a gelatinized native tapioca starch paste compared to a rehydrated paste made from the spray dried starch show significant differences in viscosity and viscoelastic properties, which depend on temperature, amplitude, frequency, or shear rate.

Further rheological, optical, and scattering investigations indicate weakening of the amylose network structure generated by the harsh shear and heat conditions during the spray drying process. The addition of water soluble hydrocolloids stabilizes the degraded gel structure by different mixing behaviors. According to the molecular nature of the added hydrocolloids, such as chain flexibility or charge distribution, different phase behavior in the starch based composite system is induced. Thus, the stepwise replacement of starch by hydrocolloids influences the mechanical properties to various extents.

The mixtures of spray dried tapioca starch and hydrocolloids have hydrocolloid dominated functional properties, and mixing the cold soluble tapioca starch with xanthan gum, λ-carrageenan, or guar gum on dry basis, a thickening effect with a weak gel character can be easily produced by hydration without heating. Depending on the desired application, the mechanical properties and texture can be controlled and tuned by the choice of hydrocolloid and by varying the mixture composition. Amylose and λ-carrageenan molecules are thermodynamically compatible, and a stable and well-mixed phase is formed.

The mixture with xanthan gum and guar gum results in a phase separation where the hydrocolloid molecules separate into local domains. Phase separation is induced by thermodynamic incompatibility and mutual exclusion effects between amylose and xanthan or guaran molecules. The different phase behavior in the mixed systems is supported by confocal laser scanning microscopy and by covalent labeling of the hydrocolloids with specific fluorescence dyes.

5. Sweetener

5.1. **Mads Weibye**, Copenhagen (Denmark)

An unmateched Gluco-amylase blend – drawing a better line, Novozymes new Extenda product range

Target for developing a new gluco-amylase blend has from Novozymes been, to give syrup producers new process possibilities without the need of investment in OPEX, this way the product fits very well in line with Novozyme new alpha-amylase: LpHera®, new Beta-amylase: Secura®

One of the limitations that is limiting the max DX when producing high dextrose syrups is the generation of iso-maltose, iso-maltose is generated due to the D-glucose condensation reaction, commonly called reversion. Novozymes new series of gluco-amylase, Extenda®, will reduce the amount of iso-maltose generated during saccharification,

This will enable the starch producers to increase the DX level and/or increase your DS level in saccharification, Extenda® will enable syrups producers to one or a combination of the following: less raw material costs, energy costs and water costs.

Using Novozymes new saccharification product range - Extenda, enables you to rethink your plant capacity and removing current limitations.

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5.2. **Tom Kleinhout**, Leiden (The Netherlands)

Modeling specialty syrup production

Since 1831 starch is being used to produce sweeteners for the food industry. Next to maltodextrins, sugar syrups are important starch derived ingredients for this market. Generally sugar syrups are categorised based on composition, e.g. the percentage of glucose and maltose but also dextrose equivalent. This means that there are three main groups: 1) dextrose or glucose syrups, 2) maltose syrups and 3) specialty syrups. For this latter group there is not one particular sugar composition, but a whole range as it depends on the desired application. Many of these special syrups are then either made non-enzymatically or by blending syrups with standard characteristics to match the required specifications.

Would it be possible to produce these specialty syrups in a one-step enzymatic saccharification process? Approaching this challenge is like trying to solve a Rubik’s cube: there are many possible combinations of enzymes and processing conditions and only one set of specifications that needs to be matched. It requires either a lot of luck or a lot of work to find the right combination of parameters. At DuPont we decided to go for the second option: to build a large library or model of saccharification data which includes different enzymes and processing conditions.
In total more than 12,000 saccharifications were performed with a high throughput method especially developed for this model. The model was designed with the help of statistical software as well as expert knowledge. Validation experiments have been initiated and have helped to understand how the model can be applied. It can be seen as a two-step process:

- First a large library or model was generated which included all possible enzymes and the whole range of processing conditions. This model, because of the amount of parameters, is not a perfect one, however it is an invaluable tool for identifying particular ranges of enzymes and conditions that will likely result in a syrup matching the specifications.

- The second step allows for a much simpler set of experiments to be performed on larger scale with a relevant liquefact. This validation step will double click on the suggested ranges and in this way the recommendations coming from the ‘big model’ are fine tuned.

The Specialty Syrup Model can be employed to find more cost-effective ways to produce current syrups, to identify novel syrups or to change production of specialty syrups altogether.

Tom Kleinhout is an enthusiastic researcher who has been working for DuPont Industrial Biosciences for over five years now. His background is in Food Biotechnology in which he holds an MSc degree. In his current role as Application Associate in Grain Processing he is involved in innovation projects with a particular focus on enzymes for starch processing, saccharification and sweeteners.

5.3. Yong-Cheng Shi, Manhattan (USA)

Structure of waxy maize starch hydrolyzed by maltogenic α-Amylase in relation to its retrogradation

Maltogenic α-amylase is widely used as an antistaling agent in bakery foods. The objective of this study was to determine the degree of hydrolysis (DH) and starch structure after maltogenic amylase treatments in relation to its retrogradation. Waxy maize starch was cooked and hydrolyzed to different degrees by a maltogenic amylase.

High-performance anion-exchange chromatography and size exclusion chromatography were used to determine saccharides formed and the molecular weight (Mw) distributions of the residual starch structure, respectively. Chain length (CL) distributions of debranched starch samples were further related to amylopectin (AP) retrogradation. Differential scanning calorimetry (DSC) results showed the complete inhibition of retrogradation when starches were hydrolysed to ≥20% DH. Mw and CL distributions of residual AP structure indicated that with an increase in % DH, a higher proportion of unit chains with degree of polymerization (DP) ≤9 and a lower proportion of unit chains with DP ≥ 17 were formed.
A higher proportion of short outer AP chains that cannot participate in formation of double helices support the decrease in and eventual inhibition of retrogradation observed with increase in % DH. These results indicate that the maltogenic amylase plays a powerful role in inhibiting the staling of baked products even at limited starch hydrolysis.

Dr. Yong-Cheng Shi is a professor in the Department of Grain Science and Industry at Kansas State University (KSU). He received his Ph.D. in Grain Science with an emphasis in starch chemistry from KSU. Prior to becoming a faculty at KSU in 2006, he worked for National Starch Food Innovation (Bridgewater, New Jersey) from 1994 to 2005. His research areas include structure and function of cereal carbohydrates, physical, chemical, and enzymatic modifications of starches and flours, and developing technologies and products for food, nutrition, emulsion, encapsulation, and pharmaceutical applications. He has 15 granted US patents, numerous corresponding patents throughout the world, and more than 60 publications pertaining to starch and cereal carbohydrates. He co-edited a book with Dr. C. C. Maningat on Resistant Starch: Sources, Application and Health Benefits in 2013. He was an Associate Editor of Cereal Chemistry from 2006 to 2013 and currently sits on the Advisory Board of Starch and Food Digestion journals.

6. Technology

6.1. Maurice Essers, Ron van den Dool, Jerome Diaz and Ricardo Nagtegaal, Zeist (The Netherlands)
Binary starch systems for making novel resistant starch structures

The polymerization of monosaccharides under acidic conditions in vacuum is a well-known process and has been the subject of numerous publications and patents. One of the first publications on the polymerization of monosaccharides under acidic conditions in vacuum was published by Mora in the late 1950s. Mora’s group detailed the chemical synthesis of polysaccharides from glucose, maltose and several other sugars. The polymerization occurs via an acid catalyzed condensation reaction that occurs in the melting phase (above the melting point of glucose, 150°C), resulting in the formation of new glycosidic bonds between two hydroxyl groups and releasing water. The latter is during the process removed by applying vacuum conditions.

The random nature of the polymerization-condensation (polycondensation) reaction results in polymerized products containing a variety of glycosidic linkages and a mixture of anomeric conformations. Structurally, polydextrose (aka polyglucose) is reported to have an average of about 30% branching, depending on course on the polycondensation conditions that have been applied. The predominant sugar linkage in polydextrose is α 1-6. Polydextrose is a water soluble polysaccharide that is also considered as a dietary fiber.

Another well-known phenomenon is that many synthetic polymers dissolve in their corresponding monomer. The melting behavior of starch in glucose has hardly been studied. In this presentation we will show the results of a study in which this has been explored. It turns out that pre-gelatinized starch can be dissolved into a glucose melt up to 50 mass percentages. Surprisingly, this has not been reported in literature so far. Consequently, the polycondensation reaction of this binary starch-glucose system has not been explored as well. It may be envisioned that if starch is able to participate in a polycondensation process with glucose, glucosylation of the starch occurs resulting in a branched starch structure with an increased resistance or attenuated hydrolysis during digestion. It may also be possible to use this process for the production of novel starch based-prebiotics.

In this oral presentation we will discuss the reaction conditions and the results of the corresponding structural analyses. Furthermore we will show the results of an in vitro digestibility study.
Maurice Essers, after finishing high school (Joan of Arc lyceum in the Netherlands), I studied chemistry on the technical university in Aachen (RWTH). My professional career started at the South African Paper and Pulp industry (SAPPI) at R&D Maastricht. Then I joined Cargill and was assigned in Bergen op Zoom, Cedar Rapids (USA) and Krefeld (Germany). The main focus in my research was about that time modification of starches for industrial applications. Then I moved to Syral, formerly Tate and Lyle (R&D Aalst, Belgium), were I worked on the development of food and industrial starches. Since 2008, I'm employed by TNO and working in the carbohydrate group in Zeist. Since then the focus in my work is, clean label modification of starches, healthy carbohydrates, development green processes for making industrial starches, analytics and project management.

6.2. Willi Witt, Arifiye-Sakarya (Turkey)
The challenge of by-products and their conversion in starch processing

Starch out of corn, wheat, potato, tapioca and different others crops is one of the most important renewable resources. Worldwide up to 80 millions tons of starch and more than 10 million tons in the EU 214 and their related products are processed every year.

The co-products are amounting to approximately 75% of the processed starch, which means about 6,6 million tons based on dry matter of co-products. It is obviously that the co-products playing an important role in relation to the feasibility of the starch plant.

In a wheat starch process nearly 100 % of the final starch or 3,5 million tons per year are co-products. Nearly 20 % of the starch production is vital wheat gluten as the main co-product.

The feasibility of a wheat starch plant is not given under the circumstances only to produce native wheat starch, vital wheat gluten and wheat gluten feed as one of the quantity-based co-products in wheat processing.

Especially in a wheat starch process it is possible to process an considerable amount of the co-product, the so-called B-Starch, which are a mixture of small granule starches like B-starch granules, some part of non starch carbohydrates like pentosans or hemicellulose, soluble like minerals and sugar as well fat.

During the last 20 years huge starch plants were established in which the so-called B-starch was processed to bio-ethanol and the resulting stillage was concentrated and dried to a protein rich animal feed product. Another possibility is to produce methane out of the stillage.

It is also possible to ferment the B-starch to other fermentable products like lysine. Because of the big amount of non-starch components in this fermentation raw material it is only possible to produce an impure amino acid for the animal feed application.

Many trials and developments were done to use the B-starch as a raw material for the bakers yeast production. That is in general possible but not applicable like molasses because of the missing amount of nitrogen and some trace elements, which are parts of the molasses.

In this presentation a possibility is shown how to improve the feasibility of a wheat starch plant to recover and upgrading the quantity and quality of the B-starch granules, so that the total starch yield could be improved by approximately 19%. That would lead into a total starch yield up to 55% based on commercial basis. This additional amount of starch can increase the feasibility much better than the conversion to ethanol of this part.

The remaining C-starch together with the bran can be converted stepwise into glucose, cellulose, hemicellulose, lignin and bio-methane. In a first step the remaining starch will be converted into glucose. After separating the de-starched brans a low temperature alkali process
can be introduced to convert the brans into lignin, cellulose and arabinoxylan. The advantage of this more gentle disintegration will lead into a lignin fraction that has a much higher molecular weight and therefore a thermoplastic characteristic in comparison to other methods.

This configuration will improve the feasibility of a starch plant enormous because the glucose yield out of the wheat will be much increased and the additional high value added co-products like lignin, cellulose and arabinoxylan are also playing an important role.

Using a considerable part of the straw, which is harvested with the grain, the production of lignin, cellulose and arabinoxylan and therefore the feasibility can be further extended.

Thursday, April 14th 2016

3. Starch Basics: Starch Structure
(Session in parallel – venue: Seminar room in basement)

0830  3.1. **Paul Nommensen**, Foxhal (The Netherlands)
       Powder reology review

0900  3.2. **Evzen Sárka**, Prague (Czech Republic)
       Waxy Starch – New trends in research (review)

3. Modification (Session in parallel – venue: lecture hall)

0830  3.1. **Jeroen J.G. van Soest** und **Kommer Brunt**, Heerlen (The Netherlands)
       Starch based dietary fibres, analytical characterization and health effects

0900  3.2. **Stylianos N. Raphaelides**, Thessaloniki (Greece)
       A process designed for the continuous production of starch inclusion complexes on an
       industrial scale

0930  **Coffee Break**

4. Application

1000  4.1. **Penelope A. Patton**, Hoffmann Estates (USA)
       Optimising performance of thickening starches in foods using texture maps

1030  4.2. **Judith K. Whaley**, Hoffmann Estates (USA)
       Designing starches for use in multi-phase food applications

1100  4.3. **Denbigh R.J. Lloyd**, London (United Kingdom)
       Developing the essential food ingredients for the future: What are the implications for
       the starch industry?

1130  4.4. **Thomas Vilgis** und **Natalie Russ**, Mainz (Germany)
       New perspectives in cold-soluble, physically modified starches

1200  **Lunch Break**

5. Sweetener

1300  5.1. **Mads Weibye**, Copenhagen (Denmark)
       An unmatedhec Gluco-amylase blend – drawing a better line, Novozymes new
       Extenda product range

1330  5.2. **Tom Kleinhout**, Leiden (The Netherlands)
       Modeling specialty syrup production

1400  **Coffee Break**

1430  5.3. **Yong-Cheng Shi**, Manhattan (USA)
       Structure of waxy maize starch hydrolyzed by maltogenic α-Amylase in relation to its
       retrogradation

6. Technology

1500  6.1. **Maurice Essers**, Ron van den Dool, Jerome Diaz and **Ricardo Nagtegaal**,
       Zeist (The Netherlands)
       Binary starch systems for making novel resistant starch structures

1530  6.2. **Willi Witt**, Arifiye-Sakarya (Turkey)
       The challenge of by-products and their conversion in starch processing

1600  **Closing remarks** by the Chairman of the Starch Experts Group, **Willi Witt**,
       Tecklenburg (Germany)
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Getreide- und Fettanalytik GmbH
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The Association of Cereal Research

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