

Review and Summaries

61. Starch Convention 2010

From the 21. till 22. of April, 2010 the Association of Cereal Research organized the 60. Starch Convention in Detmold. 175 participants from Austria, Belgium, Brasil, Denmark, France, Great Britain, Sweden, Switzerland, Taiwan, Thailand, The Netherlands, Uganda, USA and Germany visited this international well known congress. Lecturers from scientific and economic areas presented different interesting papers. During the Starch Convention. The visit of the Bioethanol Meeting was highly affected due to the Island volcano because air traffic in Europe was impossible.

1. Fundamentals

1.1. **Agnès Rolland-Sabaté, Sophie Guilois and Paul Colonna**, Nantes (France) Molecular and Structural Characterization of Undegraded Starches in Aqueous Systems

Functional properties of starches are determined by their macromolecular characteristics and the conformation in solution of both constitutive polymers. The need to investigate the biological variability is reinforced by the recent opportunity to create easily new genotypes using results from genomic studies. In this context, the characterization of starch macromolecules is of considerable importance for their structural assessment. Different methods have been described to study amylopectin branching characteristics; most of them are based upon a sequential approach using enzymatic hydrolysis of the macromolecule followed by characterization of the hydrolysed fragments. These experimental approaches are long and tedious, and rather unsuited to the characterization of large series of samples generated by post-genomic research or industrial processing. To characterize starch polysaccharides, the method usually used is high-performance size exclusion chromatography (HPSEC) combined with multi-angle laser light scattering (MALLS).



Agnès Rolland-Sabaté
(INRA)

The limitation of HPSEC columns is their low exclusion limit regarding amylopectin size. Further technical improvements are necessary to gain fractionation systems effective on the entire distribution of amylopectin to achieve its complete structural characterization. The present work analysed the structural properties of starches with different amylose content and from different botanical sources using a combination of A4F (Asymmetrical Flow FFF) and HPSEC with MALLS, on-line quasi elastic light scattering (QELS) - which provides the RH distributions - and DRI (differential refractometric index) techniques. The procedure, involving a dimethylsulfoxide (DMSO) pre-treatment and then a solubilisation in water, provides a representative injection sample without alteration of the degree of polymerisation. The originality of this approach was the determination of structural parameters for each slice of the elugrams and data analysis using the theory of hyperbranched polymers. Amylopectin M_w and RG were around $1.05-3.78 \times 10^8 \text{ g}\cdot\text{mol}^{-1}$ and 163-255 nm, respectively. HPSEC and A4F data are matchable but A4F allows a better separation of amylopectins and thus an enhanced structural characterisation of starches. One advantage of this experimental approach is to get both, distributions as function of molar masses and hydrodynamic radii as well. *De novo* synthetic amyloses, strictly linear, were used as a linear basis for the calculations. The hyperbranched polymers theory, based upon the tri-functional polycondensation ABC model, has led to underestimate the branching degree of amylopectins compared to results obtained with selective enzymatic hydrolysis. However, a quantitative agreement was found with literature data in the number of branching point calculations, for amylopectins using the ABC model modified by the introduction of a multiplying factor. The latter was determined from amylopectin structures previously described. This method, which takes 2-3 h, enables the characterization of native amylopectins while avoiding lengthy and successive degradation steps. Here, applied to amylopectins from different botanical sources, it allowed to point out differences according to the botanical origins.

1.2. **Sylvia Radosta, Waltraud Vorwerg and Henrik Petersen**, Golm (Germany) Molecular Characteristics of Starch Products

Developments by target-oriented plant breeding or genetic modification open the question to identify changes in molecular characteristics of the new starches in comparison to commercial starches. One structural feature of starch is the molar mass distribution, which is not sufficient to describe different structures because of the high polydispersity and the mixture of the main components amylopectin and amylose. According to the work of Hizukuri et al. a methodical combination is proposed to get more information about molecular structure of starch components. Based on the molar mass distribution determined by size exclusion chromatography with multi angle laser light scattering (SEC-MALLS) the fractionation of potato and maize starch according to structure and molar mass by preparative chromatography was applied as the first method. The characterisation of the fractions was performed by measurement of the molar mass distribution by analytical SEC-MALLS, iodine staining, debranching with Pullulanase and determination of the branch-chain length distribution. The second method includes the enrichment of amylopectin and amylose by complexation with thymol and cyclohexanol. These enriched starch fractions have been the basis for additional solution fractionation on preparative scale size exclusion columns. The properties of these sub fractions were compared with fractions from the parent starch.



Dr. **Sylvia Radosta** (Fraunhofer Institut für Angewandte Polymerforschung)

The fractionation of potato and maize starch solution by preparative SEC with iodine staining of the fractions showed that there was a broad overlap region of amylopectin and amylose in the chromatogram. The reason for this is the different solution structure between the highly branched amylopectin and the linear amylose. For the same hydrodynamic volume the molar mass of the compact densely branched amylopectin is much higher than that of the linear amylose. The investigation of molar mass fractions from the preparative SEC with analytical SEC-MALLS showed that small amounts of other structural components influenced the SEC-MALLS calibration curve even in the region where mainly the amylose was eluted. Therefore the SEC-MALLS investigation of total starches gives the molar mass of the amylopectin component primarily. The molar mass of amylopectin fractions was determined in the region 10^7 to 10^8 g·mol⁻¹. To get the real molar mass of the amylose, the amylopectin has to be separated. Debranching investigations of maize amylopectin with Pullulanase revealed that the side chain distribution changed only marginally with the quantity of debranching. The comparison of debranched amylopectin fractions confirmed former results that the side chains in potato amylopectin were longer than those in maize amylopectin. There was no dependence of the side chain length on amylopectin molar mass of both starch varieties. The debranching of amylose fractions offered a higher degree of branching for the higher molar mass fractions of the amylose. SEC-MALLS calibration curves showed the strong difference in amylose structure before and after debranching. Amylose molar mass after debranching was lower than 10^6 g·mol⁻¹. It was assumed that the molar mass of maize amylose is lower than that from potato. The results of the methodical combination showed a high reproducibility.

2. Technology

2.1. **Ronny Vercauteren**, Vilvoorde (Belgium) Production and Properties of Isomalto-oligosaccharides

This lecture will focus on oligosaccharides that are commonly called "isomalto-oligosaccharides". This terminology covers mixtures of carbohydrates like isomaltose, isomaltotriose, panose and higher branched oligosaccharides. These substances are already known for several decades and are formed during the enzymatic or acidic hydrolysis of starch molecules into glucose syrups. Some 25 years ago, new technologies emerged to produce the isomalto-oligosaccharides on larger scale. The first research studies in Japan indicated that these products were potential prebiotics and further research was conducted to explore this field in depth. Today prebiotics



Ronny Vercauteren
(Cargill Vilvoorde R&D Center)

are an established group of products in Western society and are known for their health improving properties. As such, also the isomalto-oligosaccharides are receiving more attention in Europe and North-America with regard to their potential health promoting functions. The lecture will describe the history of the production of isomalto-oligosaccharides and their functional benefits in food applications. Attention will be paid towards the different modes of analysis. Also coverage will be given of their physiological effects.

2.2. **Eugen Müller**, Darmstadt (Germany) New Developments in Enzymatic Starch-Gluten Separation

Separation processes after milling of cereals to obtain the maximum quantity of native starch are known since decades. For many years enzymes are applied in this processes in order to increase the efficiency of the mechanical separation. The targets for the enzymes are complex non-starch polysaccharides from the plant cell walls. Specifically pentosans (arabinoxylans) and β -glucans belong to this fraction. Consequently the predominant enzymes applied are fungal hemicellulases (pentosanases/xylanases/ β -glucanases) from different microorganisms. The hemicellulose fraction represents about 3-5% of the flour, but binds about 5 to 10 times the amount of water when water is added to the process. The water binding capacity is responsible for higher viscosity and consequently poorer separation efficiency and finally lower starch yields. The currently used enzymes do not always represent the optimal enzyme activity spectrum to address the distribution of different hemicelluloses; therefore the target of this investigation was to identify an optimal blend of the different enzymes. Another target was to optimize the fit of the pH and temperature profiles to the requirements of the process. It could be shown, that an optimized enzyme blend can increase the starch yield by 1-2%, confirmed by a higher amount of filtrate and a lower fraction of the gluten-water phase.



2.3. **Thomas Roick**, Hamm (Germany) Complex Processing of Wheat Starch Factory Process Water and Recovery of Water Soluble Arabinoxylans as Concentrates

The objective of this work is the production of dietetic effective soluble fibre (water-soluble arabinoxylan) from the process water of the wheat starch industry and the complex processing as well as economic utilization of all material streams and products resulting from the process. The target of the first step of the process is the highest possible mechanical separation in the centrifugal fields of separators or decanters of the contents in the flour. The process water, clarified by separators, is boiled up with a jet digester after addition of α -amylase. Afterwards it is separated centrifugally. The thermally treated and clarified process water is saccharified with glucoamylase. The saccharified process water is centrifuged with a self-desludging centrifuge in order to separate the Protein-Lipid components which are coagulated and flocculated during the saccharification step. More than 90% of existing lipids and approx. 50% of proteins will be removed from the process water. The ultrafiltration of the clarified process water was done with industrial membrane filters from polyethersulfon with a cut-off point at 100.000 Dalton. The addition of protease during ultrafiltration increases the filtration speed and reduces the protein content of the final product. The retentate is pasteurized and concentrated up to 25-30% TS by evaporation. The glucose-rich permeate is evaporated likewise (>50% TS).



The permeate concentrate fulfills the requirements of the fermentation substrate for the yeast industry. The vapor condensates of the retentate and permeate concentration can be fed back into the process of starch production. The retentate concentrate contains the water-soluble arabinoxylans. These arabinoxylans can be precipitated with ethanol. This precipitated arabinoxylan filtered out, dried and ground with an Ultrarotor to a dietetic water soluble fibre. The ethanol in the exhausted air of the arabinoxylan drying process can be recovered with an accordingly equipped Ultrarotor system. The wheat arabinoxylan concentrate, with a brand name

“NAXUS”, is an important functional ingredient in baked products affecting water binding, starch retrogradation and product volume. NAXUS is stable under acid and extruding conditions. It can be used without restrictions in soups and in drinks such as fruit juice.

NAXUS is an ideal stabilizer and flavor enhancer. Moreover, its viscous properties make it suitable as partial fat replacer in foods like yoghurt. NAXUS has clinically proven positive effects for the prevention of Type II diabetes. Clinical trials by the German Institute of Human Nutrition with both healthy and pre-diabetic volunteers confirm that NAXUS improves the glucose metabolism in the body and optimizes the insulin response. Due to its specific structure, NAXUS can only be degraded by specific bacteria. In a direct comparison with inuline, NAXUS showed 5 times more potent prebiotic properties than inuline after 3 week dosage. This is shown by the prebiotic index, related to selective stimulation of beneficial bacteria. NAXUS was shown to have potent activity with regard to the maintenance and improvement of metabolic homeostasis, i.e. the maintenance of the normal substrate and energy balance in the human body. In a study with mice fed with normal (CT), high fat (HF) or high fat + NAXUS (HF+NX), the latter group gained significantly less body weight, although caloric intake was identical. This showed that NAXUS provides important effects on body weight management. The view of the economy of the process shows that a technical realization of the procedure requires further optimizations regarding yield increase, in particular, within the range of the main product in order to make good economic sense. The implementation of this extraction process is a valuable objective as one third of the assigned fresh water remains in the starch factory.

3. Basics in Starch Technology - Protein Separation

3.1. **Willi Witt**, Oelde (Germany)

Comparison of Generally Applied Processes for Protein Separation with Common Starch Containing Raw Materials

The production of proteins based on different starch containing raw materials like corn, wheat and potato is commonly applied. Within these processes starch is the main product and besides some



Dr. Willi Witt
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other products the protein fraction is one of the most valuable by-products. For example, the wheat starch production is only feasible under recovering the wheat protein, the so-called wheat gluten, as the very high valuable product for use in food, feed and technical applications. Using other raw materials for starch production becomes a very important issue. These new raw materials like pea, barley, oat, rye and rice are also associated with the production of proteins and fibers. But in these cases the protein could be a main product, especially in case of processing peas. Starch and protein processing out of corn, wheat and potato requires very different and special process steps.

Recovering starch and protein from corn is a so-called wet process, including steeping the corn kernels to soften the corn structure, wet grinding, extraction and separation of the starch from the protein and soluble. Using wheat as raw material dry milling is required to

separate the bran from the flour; otherwise it's impossible to recover the native protein as so-called gluten in its required quality, with the special physical-chemical characteristic. In the wet process the gluten-protein is recovered out of the flour by means of preparing slurry and separating the gluten from the starch milk with centrifugal equipment and screens. Potatoes contain nearly 75 % water. In order to open the cell structure and to recover the starch granules and the protein containing fruit water, the potatoes are cleaned and ground in a special mill, the so-called rasp. The protein containing fruit water is separated from starch and fibers with different techniques to recover the protein after a pH adjustment and precipitation at high temperature. After that step the coagulated protein is separated, dewatered and dried.

Protein recovery from other raw materials like pea, barley, oat, rye, rice and others requires different process steps in comparison to corn, wheat and potato. In the front-end process a polishing and dry milling step to separate the bran and fiber from the endosperm is necessary, before the protein is separated from the carbohydrates like starch, hemicelluloses and fine fibers.

The opening of the cell structure can be applied by milling the endosperm into fine particles and dissolving the proteins with solvents like water under caustic conditions. These process steps are well known from the production of soy protein and fiber out of soy flakes or soy flours. In case of soy the flakes have to be steeped under caustic conditions and wet grinded to open the cell structure and to dissolve the protein, which is precipitated at the isoelectric point and a moderate temperature. It can also be used a flour to open the cell structure and to reduce the required steeping time. There can be many small differences in the processing procedure of these different raw materials.

An alternative to separate proteins from carbohydrates is air separation. This technique is very well known for different materials and also well known for the separation of wheat flour into a protein and a starch enriched fraction. The air separation has the advantage that on the one hand no water is required and on the other hand no waste water is caused. This technique is also used as pre-conditioning of the flour before protein extraction. Membrane filtration is also applied as a special process step to pre-concentrate a protein containing liquid for a more efficient protein precipitation step or separate proteins into different fractions. A new raw material for the protein recovery is stillage from ethanol processes using different raw materials. After separating the course fibers, the proteins are separated and concentrated by means of mechanical separating equipment like nozzle-disc-separators and/or decanters.

4. Basics in Starch Technology -Thermal Modification

4.1. Jeroen Poldervaart, Waddixveen (The Netherlands) Pre-gel Starch Production with Drum Dryers

Drum drying has many applications. One of the most common, but also one of the toughest is drying of starch for both food and technical applications. Drum drying of starch requires a robust, heavy-duty machine. Royal GMF-Gouda is the leading drum dryer manufacturer and its drum dryers are in use at all major starch producing companies world-wide, as well as at many smaller companies active in this field.



Starch is widely present in nature and is the most important source of nutrition. However, starch in its native form is not optimal for use and digestibility, which is the reason why high starch containing products are being heat treated. The unique characteristic of native starch to produce a viscous paste when heat treated, provides the ability for use in a wide range of applications, both in food and for technical use. Therefore, starches are modified into forms with specific properties for the required application. A common modification is drum drying of starch slurries. Due to fast evaporation of water, cold soluble starch with a long shelf life is acquired. Drum drying is a

thermal (physical) modification, often done in the final stage of a starch modification process, in which, for example, chemical modifications or fermentation are done before drying.

When a slurry of native starch is brought onto the hot surface of a drum, it will start to gelatinize (swell) almost immediately. The starch granules absorb water and their volume expands dramatically. The individual starch molecules are still held together in a greatly swollen reticulated network. However, the water will also start to evaporate at the same time, resulting in an open structure of the starch granules. When drum dried starch is being dissolved in cold water, the granules will start to swell without the solution being heated; the so-called cold swelling properties.

The gelatinizing starch slurry on the drying drum becomes very viscous and sticky. It strongly adheres to the drum surface when passing the narrow gaps between the applicator rolls and the drying drum, by which a thin film is formed from which the remaining moisture can easily be evaporated before being scraped from the drum. The narrow gaps are required for the best possible product quality, but also cause high shear forces. The shear forces vary when changing the gap distances. After a single rotation of the drying drum the product film is scraped off by a knife, which is fixed in a heavy-duty knife holder. The knife holder needs to be a very rigid construction to ensure that the strong adhering product film will be removed over the entire length

of the drum. The characteristics of starch while being dried requires a very robust mechanical design of the drum dryer. In the presentation the design will be discussed step by step. Both single and double drum dryers are used to dry starch. However, the highest production output related to surface area is achieved on single drum dryers, which are capable of handling slurries with a high dry solid content. Furthermore, the end product from a single drum dryer differs from a product made on a double drum dryer. The reason hereof, as well as optimal machine and process settings, will be discussed along the above mentioned machine design. When a range of products is dried, it is best to find one single setting for the machine in terms of steam pressure and gap settings to avoid constant resetting of the machine. These settings can be determined in the GMF-Gouda pilot plant in the Netherlands, before transferring them to industrial sized machines. Furthermore, in cooperation with NIZO Food research, there is the possibility for toll manufacturing and producing marketing batches in a food grade environment.

4.2. **Jesper Oldrup**, Soeborg (Denmark) Advances in Starch Pregelatinization



Jesper Oldrup
(Royal GMF-Gouda)

In the presentation is given an overview of the work done by GEA Niro in developing a Spray Cooking Nozzle for pregelatinization of starch. GEA Niro is manufacturing spray and freeze dryers, and has been in the market for 75 years. The development of the Spray Cooking Nozzle has been done to investigate the marked need for this type of process equipment in conjunction with spray dryers. Search in expired patents has been used in the development of the pilot scale nozzle. The design is made versatile as holding time, steam consumption, nozzle pressure and cooking temperature can be changed independently. Pictures of the Spray Cooking Nozzle and the FSD Spray Dryer are shown and general limitations to spray drier capacity are discussed. Analytical data of the obtained spray cooked starch powder shows it is comparable to a commercial available pregelatinized starch, regarding agglomerate shape and size as well as viscosity in cold solution.

4.3. **Thomas Brümmer**, St. Gallen (Switzerland) Principles of Extrusion Cooking for the Modification of Starches

Starches are widely used in food, feed, pharmaceutical and industrial applications. They are used in their native form, but also as enzymatic, thermal and/or mechanically modified products or as derivatives. Extruders and especially twin screw cooking extruders are used since longer times for the thermal/mechanical modification as well as reactor for the chemical derivatization of starches. The thermal/mechanical modification by extrusion cooking looks in particular on the change of viscous characteristics of starches like the hot- and cold paste viscosity for various applications as additive. This lecture will present several aspects of the extrusion of starch. It will start with a basic introduction into extrusion technology, with a focus on starch processing. The system-analytical model, which is the basis for understanding extrusion processes, will be presented and explained. Some results from earlier research projects, regarding the understanding of the influences of extrusion parameters on starch structure and behaviour, will be shown. Also some practical examples will be discussed, how to run an extrusion process to influence the starch characteristics like solubility and viscosity in a defined way. This lecture wants to show that extruders do not have to be a black box anymore.



Dr. Thomas Brümmer
(Brümmer Extrusion
Consulting)

5. Modification

5.1. **Katrin Schwikal, Katrin Petzold-Welcke**, Rudolstadt, **Thomas Heinze**, Jena and **Bodo Saake**, Hamburg (Germany) Chemical Modification of Non-cellulosic Polysaccharides

Recently, functional polymers from biopolymer sources gain an increasing influence in scientific and practical work. Biopolymers like polysaccharides can not only be found in high quantities. Additionally, nature had been done an excellent advance synthesis performance. By the use of these polymers a great variety of functional polymers can be obtained with a so called polymer analogous chemical modification. By this way a great variety of different functional groups can be covalently bound on the polymer and different functional polymers, which can be used in many applications, are achievable. But the main advantage of such a modification is the possibility of a simple adjustment of the properties by adjusting the content of the functional group. In addition, it is possible to adjust the substituent distribution along the polymer chain and inside the repetition unit, which has been shown for a long time ago in cellulose chemistry.



Katrin Schwikal (Thüringisches Institut für Textil- und Kunststoff-Forschung e.V.)

In recent years, other polysaccharides such as starch and hemicelluloses became more and more important for the purpose of a holistic use of biomass. Especially the hemicellulose xylan belongs to those biopolymers that are most abundant in wood and other plants such as grasses, cereals, and herbs and it is an interesting widely unused polymer in starch production, too. By reason of their different molecular structures, the properties of the resulting functional polymers and the synthesis path ways may differ compared to that for cellulose derivatives. In the lecture principles of the chemical modification focused on starch and xylan will be discussed. A special attention will be paid to potential ways of the adjustment of properties comparable to the synthesis path routes in the non-cellulose polysaccharide chemistry.

5.2. **Henky Muljana, Francesco Picchioni, Leon P.B.M. Janssen** and **Eric Heeres**, Groningen (The Netherlands) Acetylation of Starch in Supercritical Carbon Dioxide

Acetylated starch derivatives are important commercial products. A well established synthetic methodology involves the reaction of starch with acetic anhydride (AAH) in water with basic salts like sodium acetate (NaOAc) as the catalyst. Drawbacks of the use of water are the undesired side reaction of AAH to form acetic acid and the high costs of water removal in the work-up/drying section of the process. To improve the selectivity, organic solvents such as pyridine and DMSO can be used. However, these solvents have a much higher environmental impact than water and are also difficult to separate from the product due to their relatively low volatility. Supercritical CO₂ (scCO₂) could be a very promising alternative. It is not toxic, relatively inert and is known to have a positive effect on reaction rates and selectivities. In addition, solvent removal is easily performed by a depressurization step.

We report here our research activities on the acetylation of potato starch with AAH and a number of base catalysts in a batch reactor set. The reactions were studied in a broad pressure range (6-25 MPa) and acetylated potato starch with a range of degrees of substitution (DS) were obtained. Other important reaction parameters such as the anhydride conversion (X_{AAH}), and the selectivity of the reaction (S_{SA}) were also determined. The highest DS (0.29) at 90°C was found near the critical point of the mixture (15 MPa). The latter value was determined by parallel experiments using a high pressure view cell. Furthermore, additional experiments with a range of starch particles sizes showed a clear relation between the DS and the particle size, indicating that mass transfer inside the particle is limiting the



Prof. Dr. **Eric Heeres**
(University of Groningen)

overall conversion rates and is more important than intrinsic kinetic effects. The effects of process conditions and particularly pressure were quantified using non-linear multivariable regression. In addition, important product properties of the products prepared in $s\text{CO}_2$ (viscosity in water and relevant thermal properties) were determined and compared with the typical products prepared in water. The results show remarkable differences both in thermal stability and viscosity profiles.

5.3. **Jianwei Zhao, Henk A. Schols, Zhenhong Chen, Zhengyu Jin and Harry Gruppen**, Wageningen (The Netherlands)
Chemical Fine Structure of Cross-linked Hydroxypropyl Potato and Sweet Potato Starches

Starch is often modified in order to obtain special products with desired properties for certain applications. Cross-linking and hydroxypropylation are two important modifications used in the starch industry. Cross-linked starches offer acid, heat and shear stability when compared to their parent native starches. Hydroxypropylation improved clarity of starch paste, greater viscosity, reduced syneresis and freeze-thaw stability. Combination of cross-linking and hydroxypropylation resulted in improved properties of such starches.



Sweet potato starch is an important ingredient used in the Asian food industry. The aim of this study was to investigate the distribution of cross-linkage and hydroxypropyl groups in such starches by chemical and enzymatic methods. Sweet potato starch and potato starch were cross-linked with sodium trimetaphosphate (STMP) and hydroxypropylated with propylene oxide, respectively and jointly. We studied the level of cross-linking and hydroxypropylation of the modified starches by using scaled down colour assays enabling us to

deal with small sample amounts. The degree of substitution (DS) of cross-linking ranged from 0.97×10^{-4} to 5.18×10^{-4} , and the molar substitution (MS) of hydroxypropylation ranged from 0.151 to 0.176. The modification level of sweet potato starch is slightly higher than the corresponding modified potato starch using the same modification conditions, probably due to the different granule structure.

In order to locate the positions of the modifying groups of cross-linked and hydroxy-propylated starch, the modified starches were analyzed by enzymatic method comparing with corresponding native starch. The starch samples were gelatinized and hydrolyzed by pullulanase, β -amylase, α -amylase and a combination of pullulanase, α -amylase and amyloglucosidase, and the hydrolysates were analyzed by HPSEC, HPAEC and MALDI-TOF mass spectrometry. It has been found that the cross-linking demonstrated only a slight resistance to the starch degrading enzyme due to the low DS of cross-linking. The hydroxypropylation hindered the enzymatic hydrolysis evidently. Further cross-linking combined with hydroxypropylation of starch had only a limited additional effect on enzymatic degradation. The results suggested that the hydroxypropyl substituents predominantly distribute in the amorphous regions and peripheral of clusters of starch granules, the hydroxypropyl groups unevenly distribute within these regions. The substitution of hydroxypropyl on sweet potato starch presents the similar tendency compared to potato starch.

5.4. **Ronald K. Terpstra**, Veendam, **Albert J.J. Woortman**, Zeist and **Johan C.P. Hopman**, Veendam (The Netherlands)
Yellow Dextrins: Evaluating Changes in Structure and Colour During Processing

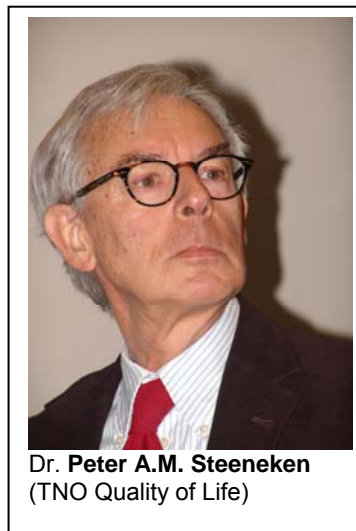
Yellow dextrins are made by pyrodextrination, a starch derivatization which is mainly controlled by moisture, acidity and the amount of heat the material is exposed to. The starch molecules are modified by depolymerization, transglycosylation and the formation of conjugated double bonds. Despite the fact that it is one of the oldest starch modifications, it can still produce products with peculiar and fascinating behaviour. A size exclusion chromatography system (SEC) equipped with four detectors (4D: Light scattering, Viscosity, UV and RI) was used to elucidate structural changes during the preparation of a yellow dextrin. The chromatograms of a certain measurement with this system



are shown. The four detectors used were not only able to capture the ordinary behaviour in the early stage of the process, but also reveal interesting information about the structural changes in the final stage of the dextrination. The obtained information points to a final product which has a small fraction of intensely coloured and physically linked small starch fragments. A conversion of the 400 nm absorbance into a yellow-index parameter (YI) was helpful in finding a plausible cause of the observed phenomena.

6. Application Food/Non-food

- 6.1. **Peter A.M. Steeneken, Albert J.J. Woortman, Zeist and Lizette A.A.C.M. Oudhuis, Veendam (The Netherlands)**
Processing Stability of Cross-linked Starches in Acid Sauce Application and Identification of Some of the Molecular Factors Involved



The thickening functionality of four acetylated di-starch adipates with variations in starch source and amylose and adipate contents was evaluated in a simplified small-scale model sauce system at fourteen processing conditions with variations in temperature, shear, and pH. A processing stability factor for a given starch was defined as a normalised standard deviation of model sauce viscosities calculated over all fourteen treatments. Adipate and acetate substituents were stable at all processing conditions. The processing stability of modified starches was found to decrease in the order waxy maize > amylopectin potato > normal potato. The release of solubles increased in that order and the solubles from the normal potato starches were enriched in amylose. Molar mass determinations of the soluble fraction before and after saponification of the cross-links revealed that processing at high temperature caused much more molecular degradation than at high shear and that in all cases the soluble fraction was only scarcely cross-linked. These results

suggest that the negative effect of amylose on processing stability is due to its ineffective cross-linking in the intact starch. Distinct morphological changes were induced by processing: generally, swollen cross-linked starches respond to processing by the common swelling and leaching pattern, but amylopectin-starch granules subjected to high shear are disintegrated into tiny particles. Presumably, these morphological responses are related to the effectiveness of cross-linking in the processed starch granules.

- 6.2. **Maurice Essers, Rachel M van der Kaaij, Peter Sanders, Willem C. Drost, Ricardo M.A. Nagtegaal, Mario T.R. Van Wandelen, Maurits J.M. Burgering and Jan-Willem van der Kamp, Zeist (The Netherlands)**
A Novel Method for the All-in-one Measurement of Dietary Fibre in Food Products, Including Resistant Starch

The term “dietary fibre” was first introduced by Hipsley in 1953, as the non-digestible carbohydrates and lignin that are intrinsic and intact in plants, added in food products. Research, carried out by H.C.Trowell in the seventies of the last century, indicated a relationship between dietary fibre and its beneficial health effects in humans, e.g. preventative towards colon cancer, coronary heart diseases etc. Since then, many years of debate and discussion about the definition of dietary fibre, its beneficial impact on health and development of analytical methods, took place.

In 2008/2009, the CODEX Alimentarius Commission, setting standards for WHO/FAO, and the European Union adopted similar definitions of dietary fibre. Both definitions include all carbohydrate polymers which are neither digested nor absorbed in the human small intestine. Codex and EU also agreed on claims of dietary fibres in food; at least 3 g of fibre per 100 g is needed in order to claim a certain food product to be “source of fibre”. Since the seventies, numerous *in vitro* digestion methods have been developed



in order to simulate the small intestinal transit. Till recent, AOAC Official Method 985.29 (Lee & Prosky, 1981) was generally accepted to be the standard method for measuring dietary fibre. However, this gravimetric analysis only measures resistant starches partially and non-digestible oligosaccharides, like resistant maltodextrines, in a minor extent. In 2007, the EFSA (European Food Safety Authority) recommended from that point of view the following:

For practical purposes, it would be advisable that analytical methods could actually correspond better to the physiologically resistant starch present in foods and that a single assay could be used to quantify all components of dietary fibre. This challenged TNO to develop an alternative method for the measurement of total DF in food products, which includes resistant starch and non-digestible oligosaccharides. The new method, which we nicknamed “as eaten”, is largely based on the physiologically relevant steps in food digestion. It includes a mimic of chewing, stomach transit and small intestinal enzymatic degradation. Recently, the AOAC adapted a new method for measuring dietary fibre (AOAC Official Method. 2009.01, McCleary). Although similarities between the new adapted method and the TNO “as eaten” method exist (e.g. usage of pancreatic enzymes), the main difference is that the TNO method “as eaten” includes food pre-treatment steps (cooking/boiling etc.) as well. In this presentation we will demonstrate the impact on measuring the total dietary fibre in several food products (bread, spaghetti and beans) when TNO’s method “as eaten” is applied instead of the AOAC method 985.29. Significant differences in dietary fibre content were observed for Dutch white bread, which according to this method may be addressed as a “*source of fibre*”.

6.3. **Thomas Kipping and Hubert Rein, Bonn (Germany)** Lozenges Based on Extruded Starch

During the past four decades there has been intensive research on modified- and controlled-release drug delivery systems. The most common way to produce controlled-release tablets is by applying wet granulation or direct compression techniques. Both techniques produce high costs. Hot-melt extrusion shows many benefits compared to conventional manufacturing techniques. The continuous mode of operation and the potential to save production costs are the main advantages. The aim of this work is the development of lozenges for buccal use. An important aspect was to characterize the suitability of different starches for extrusion. Extrudates made of five different types of starch (corn starch, Eurylon[®]5, pea starch, potato starch and Waxilys[®]200) were produced by using a Brabender single screw extruder (type 811201) fitted with a slit die (length: 3 mm, width: 8 mm, height: 2,5 mm). A cork borer (diameter: 8 mm) was used for shaping biplanar lozenges. Three different batches were compared: Placebo- menthol- and clove oil-lozenges.



Thomas Kipping
(Universität Bonn)

All samples were stored in a climatic exposure test cabinet (climatic zone 2 according to ICH Q1F Guideline). Glass transition temperatures were determined by differential scanning calorimetry. Water contents of the extrudates were measured by thermogravimetry. It could be shown, that an increase of moisture content leads to a decrease of glass transition temperature. For investigating the hardness of the extrudates a tablet hardness distribution tester was used. Hardness of the extrudates rapidly increased during the first two weeks of storage time, then remained constant. The degree of hardness could be linked to the type of starch used for extrusion. Crystallinity of the extrudates was determined by X-ray diffractometry. According to the X-ray data, for nearly all samples extrusion led to a complete amorphisation of the starch. Scanning electron microscopy proofed the results of the X-ray diffractometry. Organoleptic features of the lozenges were evaluated by questionnaires. Sufficient dissolving times in mouth of more than 30 minutes could be observed. Drug release rates could be related to the ratio of amylopectin and amylose of the used starch. Waxylis[®]200 showed strongest cooling intensities, whereas lowest cooling intensities were obtained for Eurylon[®]5. According to the fact that Waxylis[®]200 is a nearly amylose-free starch, the formation of inclusion complexes of flavour compounds with amylose is nearly impossible. This obviously leads to an initially faster release of menthol, resulting in higher flavour intensities. According to the obtained data, hot-melt extrusion and following die-cut of the extrudates is an interesting way for developing lozenges, providing a controlled-release of an active agent.

6.4. **Sarah Veelaert, Johan Peremans and Johan Steyls**, Vilvoorde (Belgium)
Use of Starch as a Carrier Material for Liquid Ingredients

In many industries ingredients in a dry powder are preferred over a liquid form. This is especially the case for flavours. In addition, certain flavours are being encapsulated to be protected against oxidation or evaporation. Two traditional processes used in the flavour industry are spray-drying and plating. Both processes will be described with their specific disadvantages and advantages. We recently developed Starrier R, a new starch based carrier. Starrier R can be used as carrier for liquid ingredients, and is having clear benefits in the encapsulation of flavours, in particular. Starrier R is a pregelatinized starch with an excellent absorption capacity for all liquids thanks to its unique flake shape and particle size. It can be used to convert liquids and oils into free flowing powders by a simple blending operation. The liquids are entrapped inside the porous structure of the carrier by an absorption mechanism. The new technology making use of Starrier R is compared with a conventional spray-drying process and with plating on traditional carriers like maltodextrin. Advantages of the Starrier R technology are a significant cost saving, a high loading (up to 60%), no formation of off-flavours, no loss of volatile flavour notes during manufacturing and a controlled release of the flavour.



Sarah Veelaert (Cargill
Vilvoorde R&D Center)

6.5. **André Lehmann und Bert Volkert**, Potsdam-Golm, (Germany)
Novel Synthesis Pathways to Thermoplastic Starch Esters

Starch as low cost biomaterial becomes more and more important in the field of bioplastics. Starch itself can be processed by thermal treatment using a plasticizer to give e.g. several kinds of packaging material. However the high water uptake of such materials combined with relative low values for tensile strength or tensile modulus is a disadvantage. These problems can be avoided by chemical modification of starch. Starch esters are the most promising material to reach properties which are comparable to PP and PE. This presentation will show a comparison of different possibilities to synthesize thermoplastic starch esters and will show the effect of the synthesis pathway on the mechanical properties of resulting starch esters. Further on a novel and simple as well a fast synthesis pathway of starch mixed esters will be described. This synthesis stands for a toolbox to create different starch mixed esters with a variety of mechanical properties. A plasticized starch acetate propionate laurate can already reach the mechanical properties like PP without any fibers or nano clays. The characterization of all products is accomplished by ^{13}C -NMR, SEM and mechanical tests.



André Lehmann
(Fraunhofer Institut für
Angewandte)

6.6. **Detlev Glittenberg, Peter Leonhardt and Andreas Voigt**, Krefeld (Germany)
Cost-optimized Top-Coating Formulations and Energy Savings by the Introduction of a New Cold-soluble Polymer



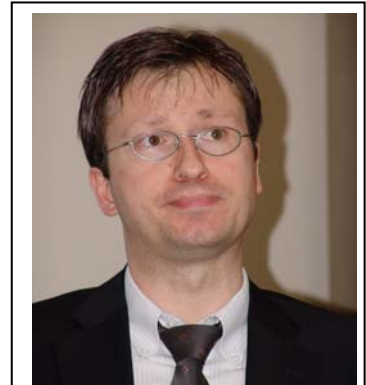
Dr. Detlev Glittenberg
(Cargill Deutschland GmbH)

Starting from industrially pre-coated paper, double-coated wood free papers are produced on our pilot coater at 1400 m/min. It is demonstrated how much latex can be replaced in a glossy top-coating formulation by a new cold soluble biopolymer. Besides the synthetic binder, the amount of thickener is also reduced, without compromising the appearance and printability of the double-coated papers. As the biopolymer contains only 8% water, the solids of the formulation can be increased by dry addition of the new co-binder - the more latex replaced, the higher the solids. Due to the favourable visco-elastic properties and water binding of the new co-binder, such formulations can be smoothly run in bent blade mode despite the very high solids. Each percent of higher solids leads to significant savings of drying energy, which again improves the given cost

efficiency of the new binder system. The implemented solids levels of above 70% should allow creation of glossy sheets without the necessity of high aspect ratio pigments. Via total replacement of kaolin by carbonates, the 74% solids level we already achieved for pre-coatings should come into reach also for topcoating formulations. Thus, in the second part of our pilot study, the conventional top-coating formulations are replaced by pure carbonate-based types in order to produce even whiter papers and create further opportunities for improved economics at maintained gloss and printability.

6.7. **Marco Ulbrich**, Berlin, **Sylvia Radosta** and **Waltraud Vorwerg**, Golm (Germany)
Starch Products with Different Amylose/Amylopectin Ratio – Interaction with a Paper Pulp and Relation to Paper Strength

Starch products are important additives in the industrial paper making process improving the paper quality. In Germany the demand is about 620.000 t and in Europe even 2.2 M t annually (2008, vdp). About 20 % thereof are used in the wet end application particularly to enhance the paper dry strength but also to improve the retention. The cationic modified starch product must be dissolved completely to enable the electrostatic interaction with the anionic charged paper pulp and binding of the starch polysaccharides to the fiber before sheet forming. A consequence of the closed water cycle in paper mills is that solute substances concentrate resulting in a high electrolyte load in the process water. That leads to screening effects on the polyelectrolyte and on the pulp charges and affects the starch adsorption and the paper strength dramatically. In addition to impacts like e. g. degree of substitution (DS) or electrolyte environments the amylose-amylopectin-ratio of the starch product is supposed to influence the starch adsorption and especially resulting paper strength properties.



Dr. **Marco Ulbrich** (Technische Universität Berlin)

The adsorption of starch products with 1 % amylose (waxy potato starch, WPS), with 21 % amylose (conventional potato starch, PS) and with 82 % amylose (high amylose potato starch, HAPS) each with DS 0.03 was investigated under laboratory conditions. The characterization of the adsorbed starch was carried out by a method based on size exclusion chromatography with multi angle laser light scattering (SEC-MALLS) giving information about adsorbed amount and molecular composition. The adsorption was carried out in water with different electrolyte contents at four different initial starch concentrations between 1...6 % related to pulp. The determination of the distribution of the substituents by means of starch fractionation (semi preparative SEC) and subsequent polyelectrolyte titration (PET) helped to explain the molecular composition of the adsorbed starch. Hand sheets were produced using a WPS and a PS each with three graded DS values between 0...0,13 in water qualities according to the adsorption experiments. Tensile strength and bursting strength of hand sheets were determined. The experimental design was evaluated statistically with Statgraphics Plus 4.1 software.

Independent of the amylose-amylopectin-ratio the adsorption of the starch derivatives with DS 0,03 generally decreased with increasing electrolyte content. At the same time the tensile strength generally decreased. The paper strength of hand sheets made with starch derivatives having conventional amylose-amylopectin-ratio of 21/79 (PS) was significantly higher compared to those made with genotypes of higher (WPS) or lower (HAPS) amylose content in all cases. Even in deionised water (DW) HAPS adsorbed to a very high amount on the pulp, but this was not reflected in accordance with paper strength. Especially for starch derivatives with high DS 0,13 both, breaking length and bursting resistance of the hand sheets, were not affected by the amylose-amylopectin-ratio of the starch source. To sum up, a good correlation between starch adsorption and resulting paper strength was found. However, the wet end application of genotype starches with increased amylose content (HAPS) or exclusively amylopectin (WPS) did not generate better adsorption and paper strength compared to conventional PS.

Some pictures from the Convention

