

Perspectives of Starch in Food Science

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Abstract: Starch is amongst the most abundant plant products and is a mixture of two polymers, amylose and amylopectin. During food processing starch is transformed by hydrothermal treatments. The structural features of starch in food cover a size range of more than six orders of magnitude and encompass the macromolecules, crystalline domains, phase separated amylose and amylopectin structures, starch granules and extensive starch networks. The structure of starch is also influenced by specific and non-specific interactions with other food constituents and ingredients. Starch, particularly amylose, is able to specifically interact with small ligands and form helical inclusion complexes that influence the colloidal properties of aqueous food systems. Furthermore, the nutritional properties of starch, for instance the amount of resistant starch, which is not digested in the upper human gastrointestinal tract, but fermented by the colonic microflora, are determined by food composition and processing conditions. An in-depth understanding of the relationships between processing and structure of starch taking into account the different structural levels will allow the prediction and control of bulk properties of food including textural, sensory and nutritional properties.

Keywords: Amylose inclusion complex · Food · Resistant starch · Starch digestibility · Structure

1. Introduction

Starch is synthesised in plants in the form of partly crystalline granules and is composed of two polymers, the linear amylose and the branched amylopectin, the monomer being α -D-glucopyranose in both cases. The biological function of starch is storage of carbon and energy. In food, on the other hand, starch acts as a structuring agent owing to transformations during processing. From the nutritional point of view, processing improves the accessibility of starch-degrading enzymes to starch and increases its digestion rate. At the Laboratory of Food Chemistry and Technology of the Institute of Food Science at ETH Zurich research on starch has a strong tradition which goes back to 1960 and was initiated by Professors Hans Neukom and Jürg Solms. Today investigations on structural and nutritional properties of starch in food present the focal point of research of

which three aspects will be reviewed in the following. The first part concentrates on the structure of starch at different levels of hierarchy from the macromolecule to the bulk, as influenced by processing conditions. A further topic is the specific interaction between starch, in particular amylose, and small ligands that are able to induce the formation of helical inclusion complexes. Finally, the nutritional properties of starch that is digestibility and fermentability as assessed by *in vitro* experiments are discussed. Only native and physically modified starches from different botanical origin are considered. However, many of the described properties apply just as well to chemically modified starch.

2. Structural Features of Starch in Food

In food starch is either a component of the processed plant material such as tubers or cereals, or it is added as stabiliser and texture agent. During food processing, starch is generally exposed to a thermal treatment in presence of a certain amount of water. The latter is a good plasticiser for starch since it depresses the glass transition temperature T_g by relieving the polymer–polymer interaction through hydrogen bonding [1]. Further-

more, water depresses the melting temperature of starch crystals T_m although it is a rather poor solvent for starch. The extent of starch transformation depends on the temperature-time-moisture conditions and the deformation rate during processing. But also the interaction with other food components such as proteins, non-starch polysaccharides and lipids determine the structure of starch and, thus, the bulk properties of the product.

An overview of the structural features of starch in food ranging from nanoscale to macroscale is presented in Fig. 1. Amylose and amylopectin macromolecules represent the molecular level (Fig. 1a). The starch polymers may be degraded to a certain extent. During bread processing, for instance, endogenous wheat enzymes (amylases, glucoamylases) degrade starch, the degradation products serving as substrate for yeast. Starch degrading enzymes may also be added to bread dough to retard staling of bread [2][3]. High thermo-mechanical energy input as it occurs during cooking-extrusion also promotes cleavage of the starch polymers [4]. The next level of structure is formed by ordered starch polymers, *i.e.* crystallites (Fig. 1b). In native starch the side chains of amylopectin in double helical configuration form crystallites. Food processing may promote an increase of order at the double helical and crystalline

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level without altering the long-range order of starch if processing occurs at temperatures between T_g and T_m . These conditions are met during high-temperature drying of pasta and, as a result of physical starch modification, the textural quality of pasta is improved [5]. In most cases food processing involves melting of starch crystals, but cooling and ageing of amorphous starch in presence of water promotes its recrystallisation. Both starch polymers tend to recrystallise although at different rates [6]. The recrystallisation of amylopectin and amylose is also referred to as retrogradation. In bread the recrystallisation of starch as assessed by wide-angle X-ray diffraction, differential scanning calorimetry (DSC) and polarised microscopy contributes to the firming of bread crumb [2]. At a lower level of organisation starch systems are characterised by phase separation in the micrometer range (Fig. 1c). During processing amylose and amylopectin tend to form separate phases due to their thermodynamic immiscibility. In food, starch is generally present in combination with other polymeric ingredients, such as proteins and non-starch polysaccharides which form further separate phases [7]. Investigations on mixtures of starch and non-starch hydrocolloids showed that the morphology of the amylose phase is largely influenced by the type of admixed hydrocolloid and by processing conditions which, in turn, determine the rheological properties of the dispersions [8]. One of the most important structural features of starch in food are the starch granules at different stages of swelling and disintegration (Fig. 1d). As detailed in Fig. 2, the increase of viscosity of starch dispersions is closely related to starch granule swelling and solubilisation also referred to as gelatinisation. Swelling of starch contributes to phase separation of amylopectin and amylose which, in turn, promotes the leaching of amylose into the intergranular space [9]. It should be added that large differences in the swelling and solubilisation behaviour of starch are found depending on the botanical origin of starch. Furthermore, lipids and other polymeric food ingredients tend to restrict granule swelling and amylose leaching [10]. A complete disintegration of the granular structure requires rather severe processing conditions, that is high thermal and mechanical energy input as it occurs during drum-drying of starch for the production of pregelatinised starch. Finally, a starch network structure may extend to the macroscopic level and largely influence the rheological proper-

ties of food (Fig. 1d). For instance, the aggregation of amylose in the continuous phase as a consequence of the unfavourable interaction with water is the structural basis for the spontaneous gelation of starch. In plant-based food, the formation of interconnected networks may be hampered if starch is located within cells. In mashed potatoes the compartmentalisation of starch results in a product which

exhibits plastic flow rather than a solid material behaviour in spite of the high starch content [11]. Finally, it should be mentioned that all supramolecular structures are in a non-equilibrium state. The structures are prone to reorganisation towards lower free energy and influence the textural and nutritional properties of the product.

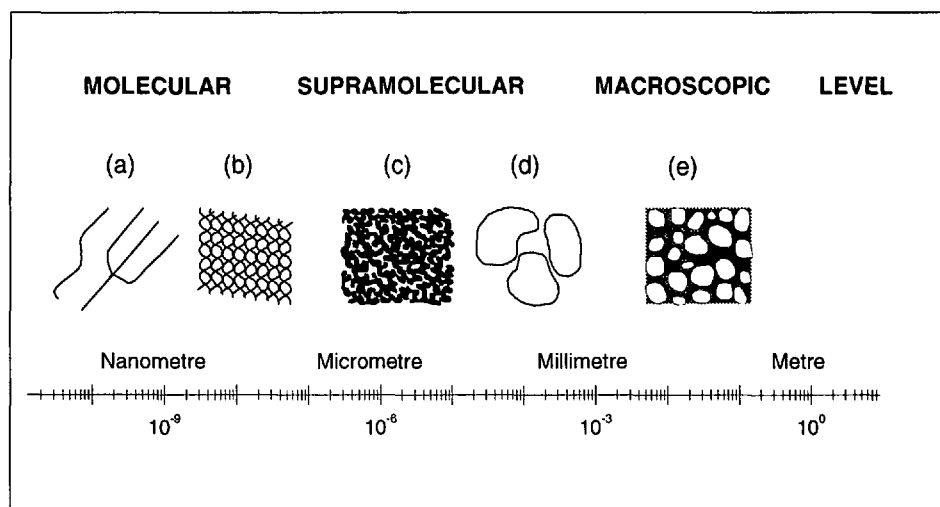


Fig. 1. Structural features of starch at different levels of hierarchy.

(a) Amylose and amylopectin macromolecules, (b) ordered double helices of starch forming crystallites, (c) phase separated amylose and amylopectin, (d) swollen starch granules, (e) starch network.

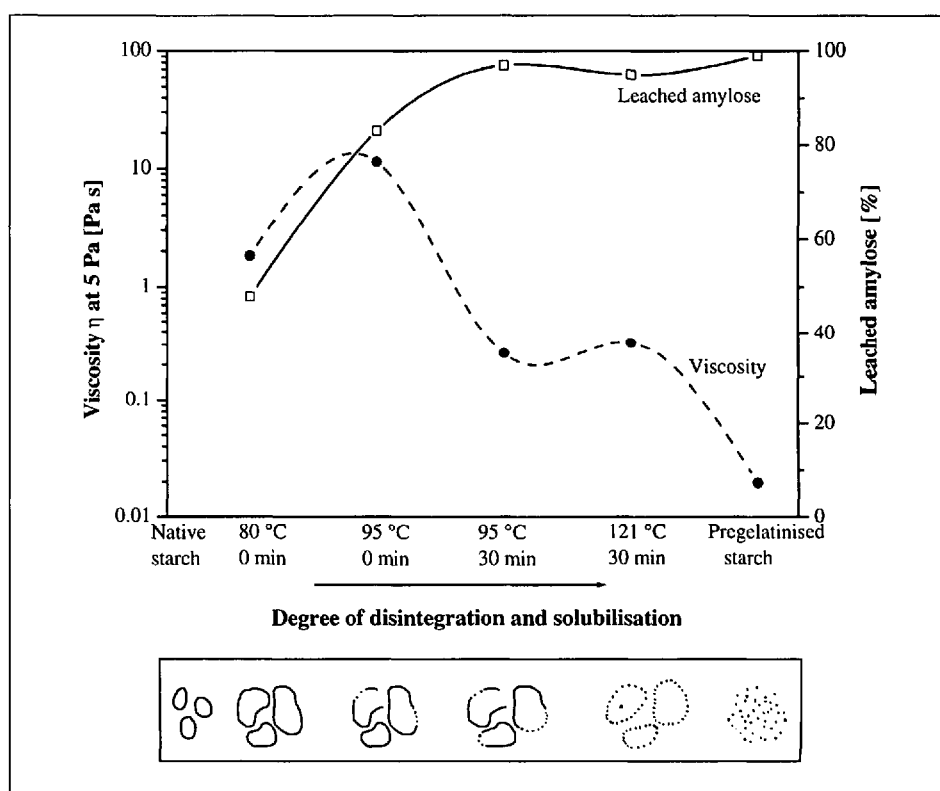


Fig. 2. Influence of starch swelling and amylose leaching as detected by amperometric iodine titration [9] on the viscosity of an aqueous starch dispersion at a concentration of 2 g dry starch/100 g dispersion.

3. Interaction of Starch with Small Ligands

Starch and especially the linear biopolymer amylose is known to interact specifically with small ligands such as fatty acids, monoglycerides, alcohols and flavour molecules. This specific interaction induces the formation of a left-handed single amylose helix in which the ligand can be hosted. Katz [12] described this so-called V amylose as well as the partly crystalline nature of starch already in the thirties while he was investigating the reasons for bread becoming stale. He falsely attributed the diffraction diagram of V amylose to gelatinised starch (V stands for Verkleisterung, *i.e.* gelatinisation). The formation of a single amylose helix is in contrast to retrograded amylose or amylopectin which crystallise in double helices and thus, yield different crystalline structures. Meanwhile, different types of crystalline structures of V amylose dependent on the ligand inducing the helix are known. The best documented V_h amylose is usually induced by linear molecules like fatty acids, and consists of a left-handed single amylose helix with 6_5 conformation and a pitch of 0.805 nm. The ligand is included in the hydrophobic cavity of the helix. Similarly, the complexation with naphthol leads to a eight-fold single amylose helix and a pitch of 0.79 nm [13]. Other ligands such as n-butanol or isopropanol, which are larger in cross-section compared to fatty acids for example, yield different crystalline structures. They were earlier attributed to a seven-fold helix. In more recent studies a six-fold helix is postulated in the crystalline state whereby the ligand might not be included in the helical cavity [12][14]. Many flavour compounds belong to this group.

Originally, the binding of flavour compounds to starch was investigated primarily in molecularly dispersed systems [15–17]. However, food systems are not homogeneous and more recently, research has focussed on starch systems, which are usually not fully disintegrated, as described earlier in this paper. It was of particular interest to investigate a possible influence of starch complexation on the rheological properties of these systems in presence of ligands. As a main result a complexation induced gelation of aqueous starch dispersions in presence of complexing emulsifiers was found [18]. Similar phenomena were observed with a variety of flavour molecules, whereby the formed gel was softer [19]. It is hypothesised that the water insoluble com-

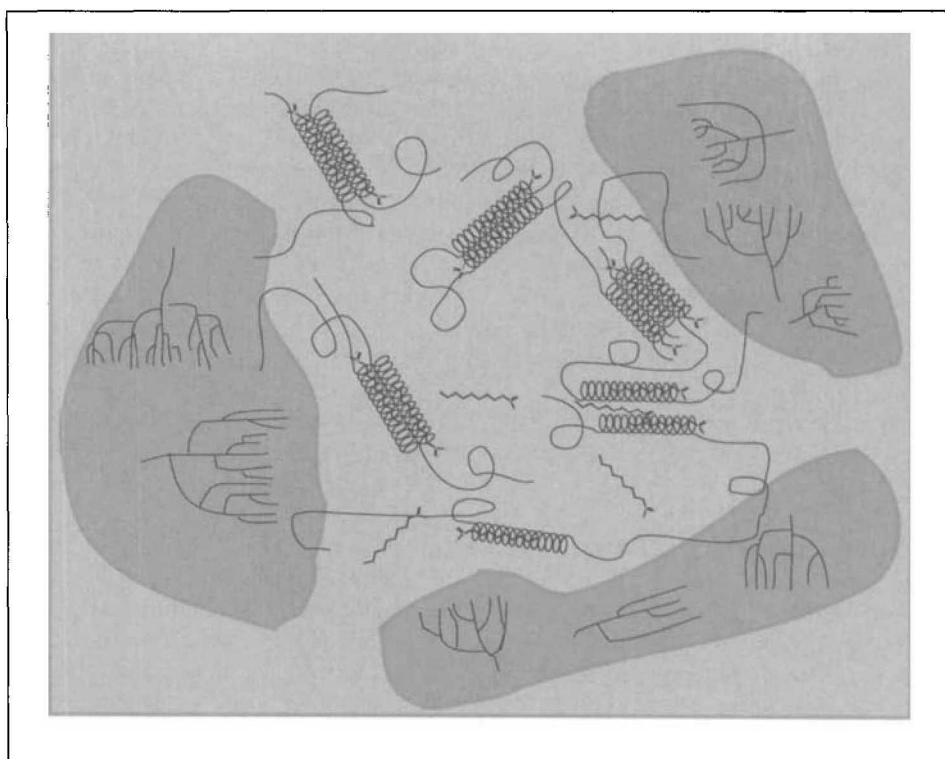


Fig. 3. Schematic presentation of a model for the complexation induced gelation in aqueous potato starch dispersion (2 g dry starch/100 g dispersion) with decanal as ligand.

plexes aggregate and are prevented from precipitation due to the presence of starch granule fragments in the starch dispersion and the formation of an intergranular network. A model of the complexation induced gelation with decanal as ligand is shown in Fig. 3.

The binding of single flavour compounds has also been studied using molecular modelling. This project was carried out in collaboration with Vinh Tran from the INRA, in Nantes, France. In a basic approach single helices were modelled first, and flavour compounds were introduced in a docking procedure using the MSI packages. From this study it was concluded that molecules inducing V amylose structures similar to V amylose complexed with isopropanol can be hosted in the helical cavity, as shown in Fig. 4 for menthone as ligand. However, after the docking procedure the helical structure lost partially its symmetry. It is therefore concluded that the ligands are included in the helical cavity only when the complexes are not highly crystalline.

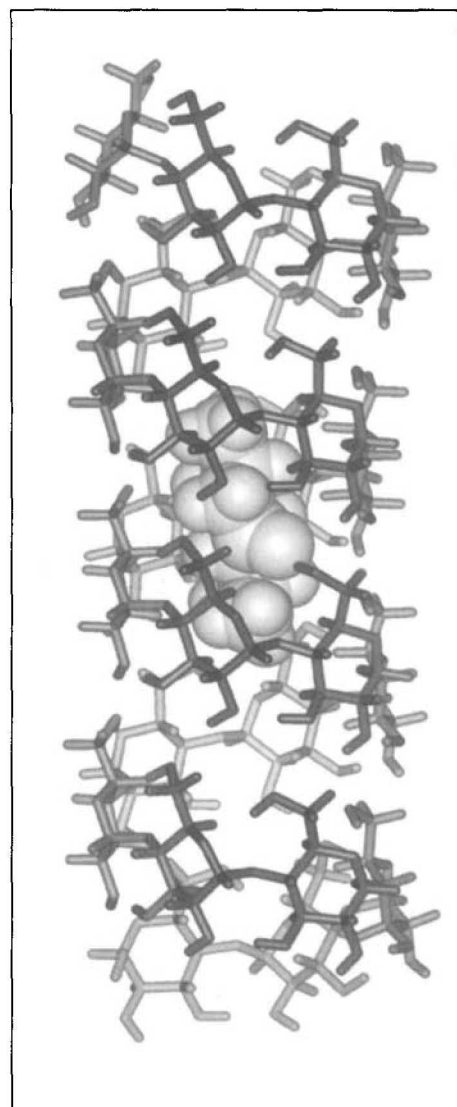


Fig. 4. Left-handed single amylose helix with 6 residues per turn complexed with menthone, modelled with the MSI packages (InsightII, Discover, Biopolymer) using the force field CFF91. Conformation of the primary hydroxyl groups is tg.

The addition of complexing molecules can also be used deliberately to improve product quality, for example to reduce stickiness of mashed potatoes during the potato flake process [20] or the stickiness of pasta [21].

The formation of inclusion complexes is limited to certain molecules. During food processes non-specific interactions between starch and small ligands can also occur. Extrusion cooking for example is suitable for physical entrapment of volatile compounds in a glassy matrix [22]. In this case, the retention of flavour molecules is only diffusion controlled.

4. Nutritional Aspects of Starch

Starch is the quantitatively most important energy source in the human diet. Until recently, it was regarded as being completely digested and absorbed in the small intestine, at least after cooking. This concept has been challenged by observations that parts of the starch reach the colon, where they are subject to bacterial fermentation. Today, these indigestible parts are generally recognised as part of the dietary fibre fraction.

4.1. The Fate of Starch in the Human Gastrointestinal Tract

The digestion of starch is initiated in the mouth by salivary α -amylase, which retains some activity when passing the stomach. However, most starch is digested in the small intestine by pancreatic α -amylase. The end products from amylose degradation are maltose and maltotriose, whereas amylopectin digestion additionally leads to α -limit dextrins, *i.e.* oligomers containing $\alpha(1\rightarrow6)$ linkages. The degradation products diffuse from the small intestine lumen to the brush border, where they are finally degraded to glucose by α -glucosidase and oligo- α -1,6-

glucosidase. The absorption of the monosaccharide is followed by an increase in blood glucose levels. Factors affecting starch digestibility include structural features of the starch (amylose/amylopectin ratio, degree of gelatinisation, retrogradation, complex formation), structural features of the food (*e.g.* extent of cellular integrity) and the presence of other components such as soluble dietary fibre [23]. Most of these factors may be influenced by food processing. Starch in freshly cooked potatoes, breakfast cereals or most types of bread is known to be rapidly digested and absorbed, whereas pasta, cereal products based on intact grains and legumes produce low responses in blood glucose. For the ranking of food items on the basis of their blood glucose response, the glycaemic index (GI) was introduced. It is characterised as the incremental blood glucose area after ingestion of a test product as a percentage of the corresponding area following an equicarbohydrate load of pure glucose or white bread as a reference product [24].

Resistant starch (RS) is defined as the sum of starch and starch degradation products not absorbed in the small intestine of healthy individuals [25]. RS is divided into four types (Table), which are differently affected by processing. On one hand, the RS I content may be reduced by processing due to a disintegration of cellular structures. Gelatinisation, which usually means complete loss of crystalline order in most starchy foods, leads to a disappearance of RS II. On the other hand, RS III is formed by retrogradation during processing, cooling and storage under moist conditions. Additionally, chemical modification to produce gelling agents and thickeners may result in RS IV. Not being digested, these fractions reach the colon, where they are used as substrates by the faecal microflora.

Short chain fatty acids (SCFA) as the main fermentation products are known to induce different physiological effects. The degradation of RS in the colon leads to high levels of butyrate, which is the most important energy source for colonocytes and has shown beneficial effects on some colonic pathologies [28].

4.2. In vitro Methods to Study Physiological Properties of Starch

In vivo experiments to study digestibility and fermentability of dietary polysaccharides are laborious and difficult to perform. Thus, *in vitro* methods have been developed at our laboratory to mimic the events taking place in the human gastrointestinal tract (Fig. 5). Carried out under standardised and accurately controlled conditions, they offer the possibility to screen a wide variety of substrates and thus restrict the design of human *in vivo* studies to the most promising substrates. Moreover, this system allows us to investigate influences of processing on physiological properties of food.

In vitro digestion experiments on differently processed wheat products showed that a high degree of gelatinisation led to an increase in starch digestibility, whereas a moderate increase in the fat content of a meal caused a decrease [29]. These observations were verified by *in vivo* studies by measuring blood parameters in healthy humans. Moreover, starch was found to be almost completely degradable in hot potato products [30]. During cooling, however, a considerable amount of retrograded amylopectin was formed. The extent of retrogradation was dependent on storage temperature and time. Additionally, RS formation was influenced by addition of emulsifiers during processing and crust formation during frying.

The amount of cereal RS present in fermentation substrates influenced *in vitro* fermentation patterns. Low amounts of fermentable starch decreased gas production and changed SCFA proportion [28]. In contrast, the fermentability of potato products was mainly influenced by structural changes caused by different processing techniques [29]. Additionally, structural aspects turned out to be the main determinant for fermentability of pure RS preparations [31]. The high molecular order of resistant starch granules (resembling RS II) made the substrate poorly susceptible to the human colonic microflora. In contrast, the degradation of retrograded amylose (RS III) led to high accumulation rates and considerable total amounts of fermentation products.

Table. *In vitro* nutritional classification of starch modified from Englyst *et al.* [26], extended by Baghurst *et al.* [27]

type of starch	example of occurrence	digestibility
• rapidly digestible starch	freshly cooked starchy food	rapid
• slowly digestible starch	most raw cereals	slow but complete
• resistant starch		
type I physically inaccessible starch	partly milled grains, seeds	resistant
type II resistant starch granules	raw potato and banana	resistant
type III retrograded starch	cooked and cooled potato, bread and corn flakes	resistant
type IV chemically modified starch		resistant

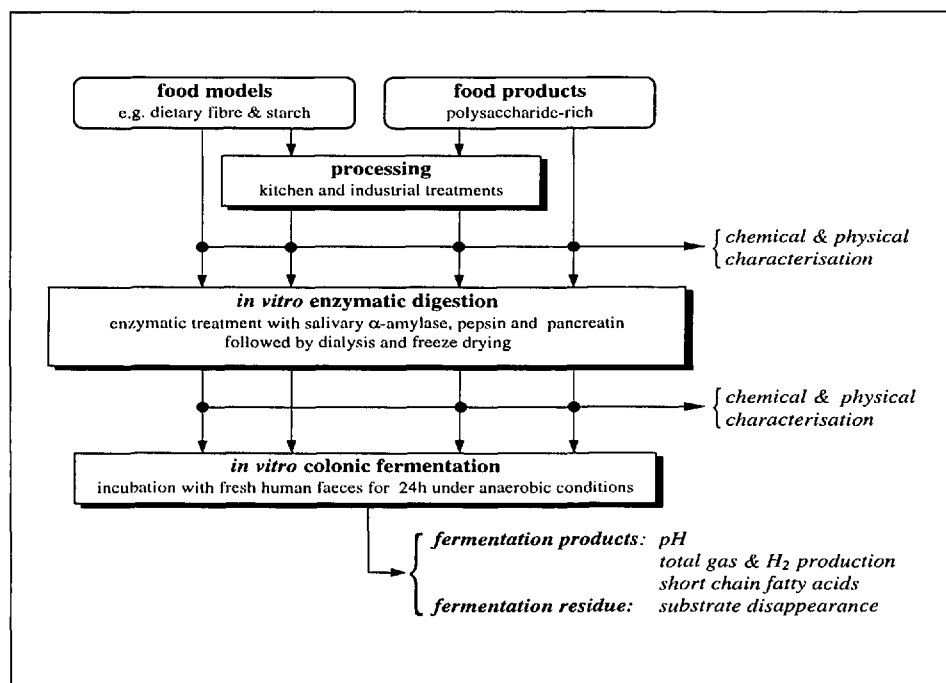


Fig. 5. *In vitro* system to investigate the influence of processing on digestibility and fermentability of polysaccharide-rich food products.

5. Conclusions

Starch plays a key role in food as it presents the main carbohydrate and thus energy source in the human diet and at the same time exhibits broad technological functionality. Processing conditions and the interaction with other food components determine the structure of starch in food and of all properties related to structural organisation such as texture, flavour release and digestibility. A comprehensive description of starch in food requires the combination of chemical, physical and physiological characterisation methods. Our integrated approach to understanding the processing-structure-property relationships of starch in multi-component and multiphase systems may provide a new route for optimising the overall quality of food.

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