Carbohydrates in food occur as natural constituents or are added as ingredients or additives. The most important endogenous carbohydrates in food are starch, depolymerized starch, sucrose, lactose, glucose, fructose and sorbitol (digestible) and carbohydrates such as raffinose, stachyose, resistant starch, pectin, cellulose, hemicelluloses including pentosans, fructans, chitin, and seaweed polysaccharides (indigestible). Carbohydrates added to food are often derived from raw materials, e.g. sucrose, polyols, lactose, oligosaccharides, starch and pectins or they appear in plants not usually consumed as food like exudate gums, seed gums or algal polysaccharides. Many are conversion products: chemical like carboxymethylcellulose, polydextrose, lactulose, enzymatic like modified starches and starch syrups or microbial like xanthan and gellan gum.

Carbohydrates are added to foods because they have many technological functions: anticaking, bulking, emulsifying, gelling, humectant, stabilizer, sweetener, thickener (Codex Alimentarius). Functions not listed by Codex Alimentarius include: chelator, cryoprotectant, drying aid, fat replacer, flavour carrier, flavour and colour precursor through Maillard reactions, substrate in fermentations. The physiological functions of carbohydrates, i.e. as source of energy with various dietetic functions, and as source of fermentation substrate in the large intestine, is discussed in different ITG papers [1]. In the last decade, a number of novel dietary carbohydrates have been introduced for food applications. One important group is non-digestible oligosaccharides (NDOs) like inulin or sucrose-derived fructo-oligosaccharides, soy-derived galactosyl-sucroses and galacto-oligosaccharides derived from lactose, xylo-oligosaccharides and lactulose, which are increasingly being added to foods, particularly in some European countries and Japan [2]. Other groups are formed by a range of new carbohydrate-based fat replacers and by new dietary fibre preparations (e.g. resistant starch).

Non-digestible carbohydrates

Carbohydrates are usually classified according to their molecular size (degree of polymerization) into sugars, oligosaccharides and polysaccharides, with subgroups identified by the nature of the constituent monosaccharides. Such a chemical classification, however, needs to be supplemented according to physiological effects (Table 1) [3].

A most important classification from the point of view of physiology is according to digestibility in the small intestine [4]. There are three main types of carbohydrates that are undigestible in the human small intestine: Non-starch polysaccharides (NSP), resistant starch (RS) and NDOs.

Dietary carbohydrates that have escaped digestion in the upper gastro-intestinal tract are principal substrates for bacterial growth in the colon next to mucus [5, 6]. About 10–60 g/day has been estimated to reach the colon [7] and it is estimated that 8–40 g/day of resistant starch contributes to the major part of the fermentable substrate available, followed by 8–18 g/day non-starch polysaccharides, 2–10 g unabsorbed sugars and 2–8 g of oligosaccharides [7]. However, in a recent survey based on determination of resistant starch in major foods, the calculated average intake in European countries was around 4 g/day [8].

Several beneficial effects are claimed on the consumption of non-digestible oligosaccharides (NDOs) and since their average daily ingestion is lower than the level considered as safe (not over 15 g/day [9]), supplementation of NDOs could be beneficial. Tomomatsu [10] mentions effective daily doses of NDOs in pure
form of 3 g of fructo-oligosaccharides, 2–2.5 g of galacto-oligosaccharides, 2 g of soybean oligosaccharides, and 0.7 g of xylo-oligosaccharides. During the past decade various novel types of NDOs have been introduced as new ingredients for food manufacture, particularly in Japan where they are already one of the most popular functional food components. Although these oligosaccharides may contribute to the flavour and physicochemical characteristics of foods, their anticipated and increasingly documented beneficial effect on health is the main reason for their rapidly increasing use.

They are classified as prebiotics because they are not hydrolysed nor absorbed in the upper part of the gastrointestinal tract, are claimed to beneficially affect the host by selectively stimulating the growth and/or activity of one or a limited number of bacterial species already resident in the colon and in addition may repress pathogen colonization, growth or virulence and induce systemic effects which can be beneficial to health [9–14]. NDOs have also been shown to inhibit development of pathogens in the intestines by inhibiting the attachment of bacterial pathogens to mucosal surfaces. NDOs may act as receptor analogues which interfere in the specific interaction between surface adhesins or lectins of bacterial pathogens and the oligosaccharide component of glycoconjugate receptors present on the brush border [15].

Another steadily growing class of dietary carbohydrates is formed by carbohydrate-based fat and sugar replacers. They contribute to lower energy intake. High fat intake is associated with increased risk for certain types of cancers, saturated fat intake is associated with high blood cholesterol and coronary heart disease.

Resistant starch is a relatively new class of dietary carbohydrates which attract increased interest of food manufacturers due to beneficial effects they might have for human health. Their fermentation in the colon causes a lowering of the pH, formation of short chain fatty acids and, for various types of resistant starch, a high proportion of butyrate (for review see, e.g. Refs. [8, 16]). They further increase faecal bulk, protect against colonic cancer, improve glucose tolerance and lower blood lipid levels [1, 16]. Many of these properties they have in common with other dietary fibres. The nutritional significance of this latter group of non-digested carbohydrates has already been recognised for many years, the range of dietary fibre preparations is still growing [17].

**Definitions**

According to the IUB-IUPAC nomenclature, oligosaccharides are defined as saccharides containing between three and 10 sugar moieties. Other authorities classify saccharides including anything from three to 19 monosaccharide units in this group. There is not a rational physiological or chemical reason for setting these limits. Dietary carbohydrates form a continuum of molecular sizes from simple sugars to complex polymers and there is no simple, straightforward methodology to separate oligosaccharides from polysaccharides [3, 18]. From a dietary point of view, many disaccharides possess properties similar to the larger sugars and are often major components of oligosaccharide products. Hence, disaccharides such as lactulose or xylitolose are included as oligosaccharides [9].

In general, food-grade oligosaccharides are not pure products, but are mixtures containing oligosaccharides with different degrees of polymerization, the parent polysaccharide or disaccharide and monomeric sugars. Often they are available in several grades of purity. Fat replacers are of a lipid, protein or carbohydrate nature. They are categorized into three groups: low-calorie fats, fat substitutes and fat mimetics. Low-calorie fats are outside the scope of this paper. Fat substitutes are lipid- or fat-based macromolecules that physically and chemically resemble triglycerides (e.g. sucrose esters or alkyl glycoside polyesters). Fat mimetics are protein- or carbohydrate-based substances that imitate organoleptic or physical properties of triglycerides and are common food constituents like starch, cellulose, pectin, inulin or the synthetic polydextrose, a randomly bonded polymer of glucose, sorbitol, and citric or phosphoric acid. Fat substitutes are stable at cooking and frying temperatures, fat mimetics are not because they bind excess water [19].

Resistant starch is starch that escapes digestion and absorption in the small intestine of humans and reaches the large bowel. The most important forms of resistant starch in the diet are: botanically encapsulated starch present in ‘intact foods’ (type I), starches with a B-type crystalline structure present in unheated foods (type II, e.g. tubers, banana, high amylose corn and rice varieties), starch retrograded as a result of full gelatinization and dispersion by processing (type III), and thermally
modified starch as a result of dry-heat treatments and chemically modified starches. Amylose rich starches retrograde to form a more rigid product than amylopectin rich starches. Retrograded starches characteristically form the B-type pattern [8, 16, 20].

Non-starch polysaccharides, being the main class of carbohydrates constituting dietary fibre, has been the subject of numerous studies on both physiological and technological functionality. Recently the EU-concerted action PROFIBRE was finished and reported [21]. The necessity of a common platform for technology and nutrition, based on the physico-chemical properties of the dietary fibre constituents was strongly recognised in that project. The present review, however, will be confined mainly to oligosaccharides.

Physicochemical properties of functional food-related novel carbohydrates relevant to foods and food production

Physical properties

Oligosaccharides

Oligosaccharides are water soluble and typically 0.3–0.6 times as sweet as sucrose. The sweetness depends on chemical structure, the degree of polymerization of the oligosaccharides present and the levels of mono- and disaccharides in the mixture. The low sweetness makes them suitable as bulking agents and as flavour enhancers. The higher their molecular weight, the more viscosity they provide leading to improved body and mouthfeel. They also have humectant properties, alter the freezing temperature of frozen foods and may effect the glass-transition temperature of foods. Oligosaccharides do not bind minerals and are easy to incorporate into processed foods. Many of them have also been shown to be strong inhibitors of starch retrogradation [9].

Fat replacers

Fat contributes key sensory and physiological benefits to foods, it contributes to the combined perception of mouthfeel, taste and aroma/odour. Fat also contributes to creaminess, appearance, palatability, texture, lubrication properties of foods and increases the feeling of satiety during meals. It also can carry lipophilic flavour compounds, can act as a precursor for flavour development and stabilize flavour. A very important characteristic of fat is its use for frying [19].

Carbohydrate-based fat substitutes physically and chemically resemble fats and oils, they are also stable at cooking and frying temperatures. Carbohydrate-based fat mimetics differ strongly from fats and oils. Generally they adsorb a substantial amount of water and are therefore not suitable for frying. However, many of them are suitable for baking and retorting. Since they can only carry water-soluble flavours but not lipid-soluble flavours they are less flavourful than fats and oils [19]. In addition, lowering the fat content of a food by replacing fat with a fat substitute also affects the vapour pressure of the food which is directly related to flavour intensity. The functionality of the carbohydrate-based fat substitutes is based on their ability to increase viscosity, to form gels, provide mouthfeel and texture, and to increase water-holding capacity. Polydextrose, a carbohydrate-based sugar (bulking agent) and fat replacer, is soluble up to 80% giving viscous solutions which behave Newtonian. Because of its high Tg (glass transition temperature, ~110°C), it contributes to more stable foods. Polydextrose also functions as a cryoprotectant, freezing point depressor and gives an over-all cooling effect to the food [22].

Chemical and microbial stability

Oligosaccharides

Most oligosaccharides have a moderate reducing power by which they are still liable to Maillard reactions when used in food to be heat processed. Fructo-oligosaccharides of the GFn type (composed of fructofuranosyl residues and one terminal, non-reducing glucosyl residue), lactosucrose and glycosylsucrose have no reducing power. At pH < 4 and treatments at elevated temperatures or prolonged storage at ambient conditions oligosaccharides present in a food can be hydrolysed resulting in loss of nutritional and physicochemical properties. For fructo-oligosaccharides it is reported that in a 10% solution of pH 3.5 less than 10% is hydrolysed after heat treatments of 10 s at 145°C, 5 min at 45°C, or 60 min at 70°C. After two days at 30°C, less than 5% is hydrolysed. The stability can greatly differ for the various classes of oligosaccharides depending from the sugar residues present, their ring form and anomic configuration and linkage types. Generally β-linkages are stronger than α-linkages, hexoses are more strongly linked than pentoses and deoxysugars, pyranoses are more strongly linked than furanoses. Because they are not utilized by mouth microflora to form acid or polyglucans, they can also be used as low-cariogenic sugar substitutes in products like confectionery (in combination with bulking agents), chewing gums, yoghurts and drinks. NDOs still remain substrates for micro-organisms and will be metabolised in fermentation processes.

Fat replacers

Carbohydrate-based fat substitutes are mixtures of sucrose esters formed by chemical transesterification or interesterification of sucrose with one to eight fatty acids, the class with six to eight fatty acids are called sucrose fatty acids polyesters, the class with one to three fatty acids are called sucrose fatty acid esters (SFE). Unlike sucrose fatty esters polyesters the SFEs are easily
hydrolysed and absorbed by digestive lipases and are, thus, caloric. SFEs containing five to seven free hydroxyl groups with one to three fatty acid esters results in hydrophilic and lipophilic properties and, thus, gives them excellent emulsifying and surface active properties. In addition they are effective lubricants, anticaking agents, thinning agents and antimicrobials [19]. Other carbohydrates modified to fatty acid esters are sorbitol, trehalose, raffinose and stachyose. The functionality and potential application of the sucrose fatty acid polyesters is governed by the type of fatty esters used in the manufacture.

The chemical stability of carbohydrate-based fat mimetics is comparable with the stability of NDOs and depends upon the type of constituent sugar residues, ring form and anomeric configuration, type of linkages and degree of branching. It also depends upon their solubility. At low and high pHs and high temperature they are liable to degradation. Since they are polysaccharides their participation in Maillard reactions is negligible. Polydextrose, being a mixture of molecules ranging in degree of polymerization of 1 to 100 with a molecular weight average of 10, shows Maillard reactions unless they have been reduced [22]. For use as a fat mimic polydextrose is coated with fat. Polydextrose is only partially fermented by intestinal microorganisms producing short chain fatty acids.

Sources
Naturally occurring

Oligosaccharides
NDOs occur naturally in food raw materials and food products. The most prominent example are fructans (e.g. inulin) which are common to edible parts of a variety of plants like onion, Jerusalem artichoke, chicory, leek, garlic, artichoke, banana, rye, barley, yacon and salsify. For most of these sources, concentrations range between 0.3 and 6% of fresh weight; for chicory and salsify these values are between 5 and 10% while in Jerusalem artichoke and yacon they can go up to 20%. Based on the average consumption of these natural sources, an average daily consumption of fructooligosaccharides in Maillard reactions of 806 mg/day has been estimated [11, 23]. Other carbohydrates modified to fatty acid esters are sorbitol, trehalose, raffinose and stachyose. The availability of well-defined enzymes allows the specific production of NDOs. Enzymatic hydrolysis of inulin is a process which is already commercially used for the production of fructooligosaccharides containing the F type (composed of only fructofuranosyl residues) and the G type (composed of fructofuranosyl residues and one terminal, non-reducing glucosyl residue).

A new source of NDOs are plant cell wall polysaccharides. Similar enzymatic hydrolysis processes could also be applied for the production of a whole array of oligosaccharides from this source. Such plant polysaccharides are often present in large amounts in fibre-rich by-products and wastes (e.g. cereal bran, fruit pomace, sugar-beet pulp, potato fibre and press cakes of oleaginous seeds or pulses). The availability of well-defined enzymes or enzyme combinations for the tailored production of NDOs from these substrates is a prerequisite. More and more they are becoming available. Figure 1 schematically shows the potential production of oligosaccharides from different plant cell wall polysaccharides.

Oligosaccharides are also being produced starting out from small carbohydrates such as disaccharides using enzyme catalysed transglycosylation reactions. Current examples are listed in Table 2. Crittenden and Playne [9] showed schematic pathways of how these oligosaccharides can be manufactured starting from lactose, sucrose, inulin and starch and listed commercial available oligosaccharides [2].

Sucrose fatty acid polyester and sucrose fatty acid esters are mixtures of synthetic sucrose esters obtained by transesterification or interesterification of sucrose with fatty acids. The first step of the process involves hydrolysing and methylating fatty acids to form fatty acid methyl esters. The esters are added to sucrose for transesterification or to sucrose octaacetate for ester interchange using catalyst, under anhydrous conditions. The resulting crude product is purified by washing, bleaching and deodorizing to remove free fatty acids and odours, followed by distillation to remove unreacted fatty acid methyl esters and sucrose esters with low degrees of fatty acid substitution [19].
Most carbohydrate-based sugar and fat replacers are extracted from by-products rich in cell wall polysaccharides, from seaweed, seeds, chicory roots, purified from plant exudates or produced by food-grade microorganisms. Resistant starch is obtained from amylose-rich corn starch, gelatinized by autoclaving and cooled under conditions promoting retrogradation (at 4°C and a hydration level of more than 70%). Resistant starch can also be formed in the food by promoting starch degradation during cooking process and post-cooking treatment.

Polydextrose is obtained by vacuum thermal polymerization of glucose, using citric acid as catalyst and sorbitol as plasticizer. Without further refinement crude polydextroses are acidic, bitter and astringent and are able to react with amine groups [22]. By further processing the undesirable characteristics can be removed (e.g. removal of citrate esters, neutralization and reduction).

![Production of oligosaccharides by enzymatic hydrolysis of plant polysaccharides](image)

**Fig. 1.** Production of oligosaccharides by enzymatic hydrolysis of plant polysaccharides [29].

<table>
<thead>
<tr>
<th>Starting saccharides</th>
<th>Enzyme used</th>
<th>NDOs formed</th>
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</thead>
<tbody>
<tr>
<td>Lactose</td>
<td>β-Galactosidase</td>
<td>β-Galacto-oligosaccharides</td>
</tr>
<tr>
<td>Lactose and sucrose</td>
<td>Levanucrase</td>
<td>Lactosucrose</td>
</tr>
<tr>
<td>Maltose and sucrose</td>
<td>Cyclomaltodextrinulcanotransferase</td>
<td>Glucosylsucrose</td>
</tr>
<tr>
<td>Sucrose</td>
<td>Fructosyltransferase</td>
<td>Fructo-oligos, GFn type</td>
</tr>
<tr>
<td>Starch &gt; &gt; &gt; maltose</td>
<td>α-Glucosidase</td>
<td>Isomaltooligosaccharides</td>
</tr>
<tr>
<td>Starch &gt; maltodextrins</td>
<td>β-Glucosidase</td>
<td>Gentio-oligosaccharides</td>
</tr>
<tr>
<td>Sucrose</td>
<td>Sucrose-6-glucosylmutase</td>
<td>Palatinose</td>
</tr>
<tr>
<td>Palatinose</td>
<td>Intermolecular condensation</td>
<td>Palatinose oligosaccharides</td>
</tr>
<tr>
<td>Lactose</td>
<td>Isomerization by alkali</td>
<td>Lactulose</td>
</tr>
</tbody>
</table>

![Table 2. NDOs obtained by transglycosylation reactions](image)
Uses of functional food related carbohydrates

Typical products in which NDOs are applied are listed in Table 3.

Carbohydrate-based sugar and fat replacers have found uses in many products (e.g. baked goods, salad dressing, beverages, frozen deserts, margarine, shortening, spreads and butter, confectionery, processed meat products, dairy products, soups, sauces, gravies and snack products).

Process monitoring for function

Process monitoring for function must deal with dosages, composition (homogeneity) of dietary carbohydrate preparations and elucidation of chemical structures, reactivity through reducing groups (Maillard reaction), loss through hydrolysis, the relationship between chemical structure (DP, type of monosaccharides, type of glycosidic linkages, degree of branching) and functionality. Van Laere et al. [25] showed in vitro that the oligosaccharides present in an arabinoxyloligosaccharide preparation or transgalacto-oligosaccharides were not selectively fermented by bifidobacteria. They can be fermented by various species. Their presence was found to give the fermentation a more saccharolytic character.

An accurate determination of the amount of dietary carbohydrates in food including differentiation to various types is therefore often a prerequisite. However, analysis is rather complex. For instance in food a wide variety of different NDOs exists, frequently accompanied by high concentrations of digestible monomeric sugars like glucose and fructose, dimeric sugars like sucrose, maltose and lactose or by maltodextrins. The determination of oligosaccharides is hampered by the need to differentiate between the various classes of NDOs and within a class between structural variations, since the physiological effects of these groups might be different. High-performance Anion-Exchange Chromatography (HPAEC) is useful in the analysis of most of the individual oligosaccharides present in foodstuffs. Sample pre-treatment is of ultimate importance in this process. Size-exclusion chromatography is an essential part of this. A drawback of HPAEC analysis is that this technique can only be efficiently used in combination with Pulsed Amperometric Detection (PAD). PAD detectors lack a uniform response towards the same functional groups of carbohydrates. When reference compounds are available for each and every oligosaccharide, this is not a problem but this is not often the case. A promising alternative is detection based on a post column reaction [26]. An important step forward in the identification of unknown structures is the on-line combination of mass spectrometry with HPAEC using a suitable interface [27]. For absolute structure elucidation NMR-spectroscopy is essential.

For the analysis of fructans and fructo-oligosaccharides, a method has recently been validated in a collaborative study based on extraction, removal of starch and malto-dextrins by amyloglucosidase treatment, followed by degradation of the fructans and fructo-oligosaccharides to fructose with an inulinase and the fructose determined by HPAEC-PAD. The concentration of fructans and fructo-oligosaccharides is calculated from the fructose value with correction for sucrose present [28].

Methods of analysis of dietary fibre can be divided into two groups:

- Gravimetric methods in which the fibre is isolated and weighed. It includes non-starch polysaccharides (NSP) and lignin and possibly includes part of inulin and resistant starch. The type of NSP cannot be identified.
- Component analysis methods in which dietary fibre constituents are determined more or less specifically. Lignin and resistant starch are not included, inulin might possibly be partially included [18].

Several methods to analyse resistant starch have been published. In principle, the methods mimic the hydrolysis of the starch in the upper part of the digestive tract.

<table>
<thead>
<tr>
<th>Table 3. Typical products in which NDOs are applied</th>
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<tbody>
<tr>
<td><strong>Milk products</strong></td>
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<tr>
<td>Fermented milk</td>
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<td>Instant powders</td>
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<td>Powdered milk</td>
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<tr>
<td>Ice cream</td>
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<td></td>
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<tr>
<td><strong>Confectionery</strong></td>
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<td>Candy</td>
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<td>Cookies</td>
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<td>Biscuits</td>
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<td>Chocolate</td>
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<td>Sweets</td>
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<tr>
<td><strong>Fruits</strong></td>
</tr>
<tr>
<td>Jam</td>
</tr>
<tr>
<td>Preserves</td>
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<td>Marmalade</td>
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</table>

by endogenous enzymes. Quantification of resistant starch can then be made by direct analysis of the residual starch after the hydrolysis or by subtracting the amount of starch that had been digested from the total starch content of the sample. None of the methods presently available are able to analyse resistant starch as defined because they only quantify enzyme resistant starch, whereas potentially digestible starch reaches the end of the small intestines. In samples collected at the end of the small intestine of humans three more or less distinct fractions could be recognized: oligosaccharides, crystallites (linear chains of α-glucans) and long chains or damaged starch granules [20].

Future development and research needs

It is obvious that we lack knowledge on the dynamics of the fermentation of oligosaccharides in the large intestine. We need to know more about the relationship between the chemical structure of individual oligosaccharides and of groups of structurally related oligosaccharides and their fermentability by important intestinal bacteria beneficial to health: the rate at which oligosaccharides are fermented depending on DP, sugar and glycosidic linkage and degree of branching, synergy between bacteria during fermentation, relationship between substrate, bacteria and fermentation products, nature of the fermentations and saccharolytic capacity. This knowledge is required to optimise oligosaccharide preparations. Are the present oligosaccharides fermented too fast, only in the proximal part of the colon and should future NDOs be targeted more for the distal part? How should the ideal NDOs look and how can they be tailored? To answer these questions our analytical potentials need to be improved and should enable us to monitor the conversion of individual oligosaccharides in the large intestines. Improvements in our understanding of the role of carbohydrates in normal cell processes and diseases is likely to lead to the development of new dietary oligosaccharide products for the prevention or treatment of pathogen colonization of the gastrointestinal tract. With this larger knowledge base we will be able to tailor-make novel dietary carbohydrates (e.g. NDOs, fat replacers, fibre preparations) by improving extraction and fractionation procedures and modification by controlled enzymatic, chemical or physical treatments to induce desired physiological and nutritional properties. Also new process designs can be developed to generate and optimize novel carbohydrates with desired nutritional and physiological properties from polysaccharides indigenous to the raw materials (e.g. formation of resistant starch by physical treatments, change proportions of soluble and insoluble dietary fibre, affect the digestibility of starch and colon fermentability of dietary fibre rich foods, binding of water, bile salts, multivalent cations, etc., and the porosity and micro-structure of the cell wall matrix.

References


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