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Review

Production of Oligosaccharides from Agrofood Wastes

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Abstract: The development of biorefinery processes to platform chemicals for most lignocellulosic substrates, results in side processes to intermediates such as oligosaccharides. Agrofood wastes are most amenable to produce such intermediates, in particular, cellooligo-saccharides (COS), pectooligosaccharides (POS), xylooligosaccharides (XOS) and other less abundant oligomers containing mannose, arabinose, galactose and several sugar acids. These compounds show a remarkable bioactivity as prebiotics, elicitors in plants, food complements, healthy coadyuvants in certain therapies and more. They are medium to high added-value compounds with an increasing impact in the pharmaceutical, nutraceutical, cosmetic and food industries. This review is focused on the main production processes: autohydrolysis, acid and basic catalysis and enzymatic saccharification. Autohydrolysis of food residues at 160–190 °C leads to oligomer yields in the 0.06–0.3 g/g dry solid range, while acid hydrolysis of pectin (80–120 °C) or cellulose (45–180 °C) yields up to 0.7 g/g dry polymer. Enzymatic hydrolysis at 40–50 °C of pure polysaccharides results in 0.06–0.35 g/g dry solid (DS), with values in the range 0.08–0.2 g/g DS for original food residues.

Keywords: biorefinery; food waste; oligosaccharides; saccharification; (bio)catalysts; prebiotics

1. Introduction

When considering abiotic resources, including all mineral and fossil resources, there is a progressive perception that, while new extraction technologies and their careful and efficient use will lead to a long-term availability with an increasing price per ton, their use will be ultimately restricted to the higher value-added applications as their depletion progresses, according to the Hubbert peak theory [1]. Thus, in terms of sustainability, the need of renewable resources to turn linear feedstock processing and use to a circular one, seems evident to integrate human activities within natural cycles with the lowest impact possible [2]. In this aspect, Circular Integration emerges as a mixture between Circular Economy, Industrial Ecology and Process Integration as a strategy to optimize the use of material and energy resources and maximize the cyclic nature of resource use [2]. To this end, renewables resources of solar origin, including water and air convective movements for energy and biomass for energy, food, feed, chemicals and materials should play a progressively important role in facing human needs while avoiding resource depletion and irreversible impacts to the Planet [2,3]. Plants and algae are able to turn solar energy and simple chemical compounds into organic matter by means of photosynthesis, and their productivity in this sense can be intensified by genetic, chemical, agro and

forestall engineering approaches, to name a few. Lignocellulosic biomass, of any origin is, therefore, a most promising raw material for biorefineries, considering such facilities as integrated refineries turning biomass into fuels, platform chemicals, food, feed and materials using integrated processes with an optimized used of resources [4]. This vision can be extended to resources of aquatic origin (seaweed, seagrass and microalgae) as well as residues from livestock [5,6]. In general, apart from forestall and energy crops biomass, most of it depends on the production of biomass and, in particular, food wastes [7,8]. While more than 100,000 M tons of biomass wastes are yearly produced [7], wastes strictly considered as food wastes (foods not consumed from any part of the food supply chain or any part of the food that is non edible and, therefore, becomes a residue) account for more than 1300 M tons each year [8]. The valorization of biomass wastes into a plethora of useful energy vectors, chemical compounds and ingredients receives a notable amount of interest from all stakeholders, including researchers and entrepreneurs. They are a source to several value-added products, such as monosaccharides (glucose, xylose, mannose, fructose, arabinose and more), oligosaccharides (fructo- or FOS, xylo- or XOS, galacto- or GOS, galacturonic- or GALOS, lactosucrose, etc.), biofuels (ethanol, butanol, dimethylether –DME-, biodiesel, hydrogen), bioactive compounds (flavonoids, phenolic acids, terpenes, terpenoids, carotenoids), nanocellulose (bacterial, wood-related), lignin and its derivatives (a source of aromatics from biomass and prospective substitute of the aromatic or BTEX fraction produced in oil refineries) [8]. Oligomers from cellulose, hemicellulose, lignin, pectin and other biomass-related polymers, as chitin, compose a class of value-added compounds with an enormous potential. As indicated by Bhatia et al. [9], their bioactivity turn them into useful ingredients for cosmetics, foods and drugs, and they can be applied, prospectively, to almost countless applications in health improvement and new therapeutic approaches (gut health, immune system boosting, cancer treatment, anti-adhesive action, to name some applications in this area). They can be obtained from several wastes related to food and agriculture, such as, for example, vine shoots [10], banana peels [11], sugar beet residues [12] and wheat chaff [13]. Agrofood related waste is a rich source of mannooligosaccharides [14], while oligomers such as those from alginate, agarose and κ-carrageenan, can be derived from macroalgae [15].

Lignin oligomers are notorious for their rich variability and number of functional groups, rendering them valuable platform chemicals for their application in commodity and advance materials and coatings [16]. Nevertheless, lignin depolymerization is nowadays complex to control, while lignin itself is relatively inert as a material ingredient, an aspect that hinders its inclusion into novel materials. Effective lysis to polyols, with their importance in polyurethane formulation, seems a promising application of the abundant lignin (accounting for 15–40% dry weight of lignocellulosic biomass). To render it more reactive, lignin can be turned into lower molecular weight fractions by an assortment of catalytic routes (acid, basic, with metal oxides, ionic liquids and enzymes) and in sub- and supercritical conditions using several solvents. However, up to now, these processes should be enhanced notably both from the technical perspective, facing catalysts deactivation and lignin repolymerization, and from the economical viewpoint, as harsh pressure and temperature conditions turn these operations unfeasible [16].

In later years, there is an increasing evidence of cellooligomers (COS) utility in the formulation of food complements for calves in the preweaning period, when they are developing their ability to digest cellulose and the intake of cellooligosaccharides can help them to develop a better rumen environment [17]. COS could be used together with isoflavones as a valuable food complement to reduce bone fragility when estrogen concentrations are low, i.e., during menopause and afterwards [18]. COS are less studied than other oligosaccharides, due to the refractory nature of cellulose itself, a very high molecular weight biopolymer. It can present up to 90%–95% crystallinity and is organized into tightly bonded bundles named microfibrils, which conforms higher-order bundles or macrofibrils. They are obtained from lignocellulosic sources by depolymerization, either by hydrolysis or by oxidative routes. Hydrolysis of residual cellulose can be achieved using endo- and exoglucanases with a reduce activity of β-glucosidases [19] or modified carbon catalysts [20]. Enzyme-driven lytic oxidation is performed with polysaccharide monooxygenases (LPMOs) [21], enzymes that are present nowadays

in most up-to-date cellulolytic enzyme industrial preparations. β-glucosidases not only hydrolyze cellobiose but they can catalyzed the reverse reaction (transglycosilation) to render C2, C3, C4 and C5 COS (cellobiose, cellotriose and higher molecular weight oligosaccharides) in the presence of relatively low concentrations of water [22].

The hemicellulose fraction in lignocellulosic biomass is a rich source of xylooligosaccharides and mannooligosaccharides. Hemicellulose can reach up to 35% in corncob and 25% in nutshell, with similar values for straws, corn stover, sugarcane bagasse and other food-related wastes [9–11,23]. Hemicelluloses are linear-ramified heteropolysaccharides with a relatively low molecular weight (circa 15 kDa) very rich in xylose, galactose, fructose, glucose and mannose. One of the main polymer fractions in hemicelluloses is xylan, a polymer of xylose linked by β-1,4-xylosidic bonds that can be depolymerized by acid, enzymatic, mechanical and thermal operations (and some of their combinations) to xylooligosaccharides (xylobiose, xylotriose, up to xylodecaose) or XOS. In particular, acetic acid pretreatment enhances endoxylosidase action, reducing the associated costs [24]. XOS have a recognized potential as prebiotics, being a common ingredient of food complements [9,10]. They are also present in cosmetics, used as gelling agent and for the treatment of diabetes [9,25]. They are also active as immunomodulators and immunostimulators, and their antioxidant activity can be notable too [9]. However, their cost is a major concern to exploit all their potential, with prices in the 40–80 USD/kg range [9]. Mannooligosaccharides can be derived from mannans (both α- and β-mannans, from yeasts and plants, respectively), glucomanans, galactomanans and glucogalactomannans, that can be degraded by an assortment of enzymes acting on the β-1,4-linkages between the glycosidic moieties: β-mannanases, β-mannosidases, β-glucosidases and some auxiliary enzymes (α-galactosidases and acetyl mannan esterases). Antitumor and antimetastatic action of mannans and glucans is well-studied [26]. This property is also present in their oligomers, which also show a prebiotic activity that controls microbiota population in the gastrointestinal tract [9,26].

A well-known heteropolysaccharide in vegetable and fruit peels is pectin. Its composition and structure are notably more complex than the ones of the other polysaccharides typically encountered in lignocellulosic biomass [27]. Linear regions conformed only by α-1,4 linked galacturonic acid are known as homogalacturonans, while there are other parts of pectin rich in rhamnose that are branched or hairy regions. Rhamnogalacturonan I contains a main chain of rhamnose and galacturonic acid with lateral chains of galactose and arabinose, with several types of bonds. Rhamnogalacturonan II can contain, apart from all those monomers previously mentioned, other rare ones as apiose and aceric acid [27]. Though pectin is a typical food ingredient for jellies, marmalades and jams, its slow degradation in the intestine permits its use with calcium salts to treat diarrhea, it can ameliorate diverse colon cancer, promoting gut health by controlling microbiota populations (a prebiotic effect) [27,28]. Oligosaccharides derived from pectin potentially maintain and even increased pectin bounties in gut health, and can be produced from a diversity of peels and pulps from beet, citrus species, apple pomace and other fruit waste [9,12,28].

2. Autohydrolysis Processes

2.1. Definition and Main Process Variables

Autohydrolysis is a hydrothermal pretreatment based on the use of pressurized water. When water is above 120 °C, ionization processes are promoted so that the H_3O^+ concentration increases. According to [29], hydronium ions concentration at 250 °C is 23.3 higher than the one at 25 °C. As consequence, hemicelluloses and pectin (depending on the biomass) are subjected to depolymerization. Once this happens, acetic acid and uronic acids are released, which enhances the depolymerization process. In fact, the contribution of these acids to H_3O^+ formation is much higher than the water dissociation contribution [29]. Autohydrolysis can be a process that renders a high yield of oligosaccharides, as it allows minimizing the monomers and degradation products by adjusting the principal variables involved: time and temperature [30,31].

Although this method was firstly developed for the fractionation of lignocellulosic biomass by dissolving the hemicellulose fraction, it was successfully used for pectin depolymerization [32].

The hydrolysis mechanism includes the following steps [33]: i) migration of the protons to the solid surface, ii) chemisorption, iii) reaction between the proton and the polysaccharide in the surface, iv) cleavage and desorption of oligosaccharides and v) diffusion of the oligomers to the bulk liquor. Usually, the chemical reaction step is the rate-controlling one [33]. The main process variables are:

(1): Particle size: a small particle size increases surface area, porosity and improves flow properties. A big size leads the surface to overreact whereas the inside part would be incompletely hydrolyzed. However, it is important to take into account that the energy demand associated to milling is high so a compromise should be reached [34].

(2): Liquid-solid ratio (LSR): This value can vary from 2 to 40 g water/g dry material but it is usually between 8–10 g/g [35]. A low LSR increases acetic and uronic acids concentration, improving autohydrolysis efficiency. Furthermore, energy requirements during the reaction and purification processes can be reduced, resulting in lower operating costs and wastewater generation [36]. However, it is important to select a LSR value taking into account that a good impregnation of the material is necessary. The value also depends on the water retention capacity of the biomass [37].

(3): Temperature/time: these factors affect significantly the process and are usually grouped in one parameter: the severity factor [37]. It will be described below.

(4): pH: controlling and monitoring the pH during the process improves the selectivity to oligomers and minimizes a further reaction of this compounds to monomers and degradation products. Maintaining the pH above 4.0 limits the hydrolysis of polysaccharides and the formation of degradation products [38,39].

As commented above, in order to compare experiments in different conditions, severity factor is commonly used. It was firstly proposed by [40] for pulping processes, assuming that the overall kinetics follow a first-law concentration dependence and the rate constant has an Arrhenius type dependence on temperature. In addition, there are slight modifications of this general model in order to include different operational conditions such as non-isothermal temperature profiles [41] or low pH levels [42,43] in a combined severity factor.

According to the temperature profile, the treatment can be isothermal or non-isothermal. In the first case, once the target temperature is reached, it is maintained during the reaction time and then, the reactor is cooled down [44]. In the second case, once the target temperature is reached, the reactor is cooled down [45]. It is accepted that higher temperatures and shorter reaction times lead to higher pentoses yield and minor degradation products formation [37]. Furthermore, molecular weight distribution of oligosaccharides depends on time and temperature [46]. For a given temperature, an increasing reaction time lead to the accumulation of low molecular weight oligosaccharides.

Regarding to the reaction system, there are several reactor configurations that can be used in order to carry out the autohydrolysis process: batch reactor, semi-continuous reactor or continuous reactor [34]. The most commonly used is batch operation [37]. Finally, it has been reported that this process has several advantages over other treatments [47,48]:

(1): Reduced chemicals consumption. Acetyl groups naturally present in biomass are liberated, leading to an increase in acetic acid concentration, which catalyzes the process.

(2): Solubilization of hemicelluloses and pectic fractions as oligosaccharides and monosaccharides with limited generation of degradation products.

(3): Both solid and liquid resulting from the process are valuable products. The liquid is rich in oligosaccharides and the solid is an adequate substrate for further fractionation (by enzymatic hydrolysis, for example).

(4): Low capital cost due to low corrosion potential.

2.2. Application to Lignocellulosic Waste Residues

Autohydrolysis, which is a hydrothermal treatment, was at first used for the fractionation of woody biomass. Between 1970 and 1980, this process was employed in the delignification of different woods [49]. During the next decade, it was used as a pretreatment in order to maximize the accessibility to cellulose, which can be hydrolyzed (chemical or enzymatic treatment) to simple sugars and use them to produce biofuels or other chemicals [50–52].

In the 1990 decade, several studies showed the health properties of xylooligosaccharides [53,54], so the autohydrolysis started to gain attention not only as a method to enhance cellulose hydrolysis but a method to produce this kind of oligosaccharides selectively [55]. In 1999, it was the first time the autohydrolysis was used focusing attention into oligosaccharides production. Degradation kinetics of this fraction was studied, taking into account the xylan depolymerization into xylooligosaccharides and xylose. Xylose degradation products were also studied [30]. This study sets the bases for a new environmentally friendly method for hemicelluloses valorization.

From that moment on, several studies came up trying to apply this technology on different materials such as woods, agroindustrial and food wastes. Food wastes are especially interesting since they are produced in huge quantities, as commented in the introduction. They can be grouped in two categories: those generated within the raw material conditioning (Table 1) and those generated within the raw material processing or consumption (Table 2).

The food wastes in the first group contain a high xylan content so that the liquors obtained by autohydrolysis are rich in xylooligosaccharides.

Arabinan, which is usually present in these lignocellulosic residues, is more susceptible to hydrolysis than xylan, so the optimum conditions for XOS production (Table 1) are not the same as the ones for AROS production (190 °C, 36 min heating) [45,56,57]. In these studies, a similar conversion from xylan to XOS in similar conditions has been reported (65.6% for corncob, 64.3% for rice husks and 67% for barley husks). However, the degree of polymerization of these compounds is not mentioned.

When almond shells are treated, an increase in the severity of the process lead to xylooligosaccharides with a low degree of polymerization (xylobiose and xylotriose) [58]. However, due to the low concentration of these XOS (3.3 g/100 g dry solid—DS), enzymatic hydrolysis (leading to a yield of 8.2 g/100 g DS) and purification steps of the liquors were added.

In some cases, in addition to XOS, small amounts of galactooligosaccharides and glucooligosaccharides are obtained [44]. Maximum concentration of these compounds (10.1 g/L XOS, 0.7 g/L GAOS, 0.11 g/L GOS) were found at severity factors between 3.7–3.8. Below these severity factors, polysaccharides solubilization is low and, above these values, concentrations of monosaccharides and degradation products increase. Additionally, less than 30% of the produced xylooligosaccharides (0.025 g/g DS) have a degree of polymerization (DP) lower than 6 in the indicated conditions. However, the percentage can improve up to 37% (0.04 g/g DS) with a severity factor of 4.02. In this case, a lower concentration of total XOS (9 g/L instead of 10 g/L) is obtained. It shows that temperature and holding time should be adjusted precisely to obtain XOS with the desired DP.

By comparing references [46] and [59], we can appreciate that the optimum severity factor for the production of XOS from brewer's spent grains is 3.64 and that arabinan degradation is faster than xylan degradation, as commented above. The novelties in the last reference mentioned are the previous extraction of starch from the grains, which affects the prebiotic potential of the mixture obtained, the study of the main substituents (uronic acids and acetyl groups) in the XOS produced, and the partial enzymatic hydrolysis step (using endoxylanases) added to reduce the average molecular weight of the oligosaccharides produced.

Gullón et al. reported that, at relatively low severity factors (2.7), the solubilization of polysaccharides is higher in chestnut shells (24.5%) [60] than in other residues such as hazelnut shells (12.3%) [16]. In optimum conditions (180 °C, severity factor = 3.08), 7.1 g/L XOS and 6.8 g/L GOS were obtained. Arabinooligosaccharides and galacturonicoligosaccharides are more reactive its concentration was very low. The use of less severe conditions compared to other materials permits to

obtain substantial quantities of antioxidant compounds. In the work of Rico et al. [61], for example, a severity factor of 4.09 was needed to obtain 7.6 g/L of XOS, which lead to low concentrations of GOS, AROS (0.45 and 1 g/L) and antioxidant compounds.

Vine shoots could be an adequate feedstock for XOS and GOS production obtaining 12.2 g/L and 8.64 g/L, respectively, with a severity factor of 4.01 [62]. Other oligosaccharides were observed in small quantities (AROS, GALOS, MANOS). A further observation showed that the polydispersity of the hemicellulosic fraction decreased with higher severity, which indicates that the molecular weight distribution become narrower.

Table 1. Main results in autohydrolysis studies on wastes from raw material conditioning.

Year	Residue	Treatment	Conditions	Reactor	Product (g/g DS)	Ref.
2002	Corncob	Autohydrolysis non-isothermal	202 °C 39 min (heating) LSR = 8	Stainless steel Parr reactor V= 3.75. 2 Rushton turbines. Heating with external fabric mantles and cooled by internal stainless steel loops. PID-controlled Temp.	XOS (0.20 g/g) AROS (0.016 g/g)	[44]
2004	Rice husks	Autohydrolysis non-isothermal	212 °C 45 min (heating) LSR = 8	Parr reactor	XOS (0.10 g/g) GOS (0.027 g/g)	[56]
2004	Barley husks	Autohydrolysis non-isothermal	202 °C 39 min (heating) LSR = 8	Stainless steel Parr reactor	XOS (0.18 g/g)	[57]
2016	Vine shoots	Autohydrolysis non-isothermal	200 °C LSR = 8 H = 4.01	1.5 L stainless steel 5100 Parr reactor. PID-controlled Temp.	XOS (0.10 g/g) GOS (0.069 g/g)	[62]
2017	Hazelnut shells	Autohydrolysis isothermal	190 °C 5 min (heating) 5 min (holding) LSR = 10 N = 300 r.p.m. H = 3.92	High-pressure reactor (BR-300) 0.6 L stainless steel tank with heating block. Paddle agitator. Tap water cooling through internal coil.	XOS (0.10 g/g)	[44]
2018	Chestnut shells	Autohydrolysis non-isothermal	180 °C LSR = 8 H = 3.08	1.5 L stainless steel reactor using a Parr PID controller to control temperature	XOS (0.057 g/g) GOS (0.054 g/g)	[60]
2018	Peanut shells	Autohydrolysis non-isothermal	210 °C LSR = 8 H = 4.09	0.6 L stainless steel reactor (Parr 4842)	XOS (0.061 g/g)	[59]
2019	Almond shells	Autohydrolysis isothermal	200 °C 20 min (heating) 5 min (holding) LSR = 10 H = 3.94	1 L stainless steel 316 pressure reactor with provision for water circulation. PID-controlled Temp.	High DP XOS (0.077 g/g) Low DP XOS (0.033 g/g)	[58]

Note: H is the severity factor (Log (R0)).

The second group of wastes, whose autohydrolysis results are shown in Table 2, is characterized for being rich in other polysaccharides different from xylan, such as pectin or arabinan, which make them softer and more susceptible to hydrolysis. Residues with high content in pectin are orange peels, lemon peels, sugar beet pulp, apple pomace, passion fruit peels and olive by-products. Sugarcane bagasse and coconut meal are rich in xylan and mannan, respectively.

Optimum conditions for orange peels [63], lemon peels [64] and sugar beet pulp [65] autohydrolysis are very similar (160 °C, severity factor = 2.5), for the same LSR. Liquors from sugar beet pulp contain a high concentration of arabinooligosaccharides (13 g/L), whether the ones from orange and lemon peel are rich in pectooligosaccharides (17 g/L and 21 g/L respectively). The overall amount of

oligosaccharides obtained is higher for sugar beet pulp (31.2 g/100 g oven-dry biomass). Furthermore, evidence in all experiments indicates that acetyl substituents in oligosaccharides decrease drastically at temperatures higher than 160 °C, resulting in high monosaccharides and degradation products concentration. The conditions of sugar beet pulp autohydrolysis were optimized for the production of feruloylated arabinooligosaccharides [65]. The operation in a continuous flow reactor is also studied for scaling-up, which leads to similar results in terms of AROS production, but achieving a considerable reduction in the residence time.

Pectin extraction from apple pomace and citrus wastes has also been studied [66]. Although the aim of this study is to assess the properties of the pectin extracted, it can be extrapolated that autohydrolysis is suitable for pectin extraction and further depolymerization (as seen in [63] and [64] for orange and lemon peels). For apple pomace, the highest yield of pectin (40.13% *w/w*) was obtained at 150 °C, maintaining this temperature during 5 minutes. The pectin extracted had lower molecular weight than the one extracted by conventional methods, establishing the suitability of autohydrolysis for pectin depolymerization. This apple pomace pectin has more galactose and less arabinose than citrus pectin. This study set a basis for further investigations in pectic oligosaccharides production from apple pomace.

Another common peel residue, fruit peel passion peels, which are composed mainly of pectin and cellulose, were subjected to autohydrolysis. The results obtained were similar to those for orange peels [67]. The best conditions for oligosaccharides production were achieved at a similar severity factor (2.21), being the yield to total oligosaccharides 0.21 g/g DS, from which 0.14 g corresponded to POS and 0.05 g to GOS. Therefore, most glucan may come from the hydrolysis of starch and not from cellulose. In addition, hemicelluloses were more difficult to hydrolyze than pectin.

As a very common agricultural subproduct, with more than 46 Mtons/year production, sugarcane bagasse autohydrolysis was also studied aiming to higher yields of low DP XOS, which were maximized at 200 °C with a reaction time of 10 min [68]. Then, 11.63 g/L of xylooligosaccharides were produced, of which 98% had a degree of polymerization between 2 and 5. The effect of acetyl groups in the biomass was also studied by adding a 35% of white birch (similar composition to sugarcane bagasse but higher content in acetyl groups) to the mixture. The total amount of XOS obtained at 160 °C and a reaction time of 100 min was almost the same as that produced at 200 °C and 10 min without white birch, which indicates that the addition of acetyl groups increases the total amount of XOS and reduces the average DP.

A common residue from olive oil production, alperujo, has also been treated by autohydrolysis under a special configuration based on steam processing [69]. It was possible to obtain different fractions of oligosaccharides (POS, XOS and GOS) with specific range of molecular weight by fractionation through chemical hydrolysis (HCl, 70 °C, 2h), ultrafiltration and enzymatic hydrolysis (endo- and exo-polygalacturonases, pectinesterases and pectinliases, 40 °C, 72h) after the mild steam processing. As seen in other studies, a mild autohydrolysis process makes it possible to obtain high molecular weight oligosaccharides.

Autohydrolysis of coconut meal is interesting due to its high content in mannan polymers [70]. Under the optimum conditions (severity factor of 4.5), 0.23 grams total oligosaccharides per gram dry coconut meal were obtained, from which 90.5% had a DP between 2 and 6. The type of oligosaccharides was not studied but, according to coconut meal composition, the majority should be mannooligosaccharides. Liquid solid ratio was also studied (5–100), concluding that if the target products are monosaccharides, a low liquid solid ratio should be used, whereas if oligosaccharides are the target product, a high liquid solid ratio could give a better yield.

It should be noted that in the majority of the studies mentioned, the autohydrolysis liquors are subjected to purification and concentration and the spent solid can be used for further fractionation of cellulose and lignin. As seen, there are two approaches: try to optimize operational conditions to maximize oligosaccharides production with the desired DP in one step or carry out a fractionation process, extracting high DP oligosaccharides and processing them selectively through chemical or enzymatic methods. In both cases, a purification step (usually based on membranes) is needed.

Table 2. Main results in autohydrolysis studies on wastes from processing or consumption stages.

Year	Residue	Treatment	Conditions	Reactor	Product (g/g DS)	Ref.
2004	Brewery's spent grains	Autohydrolysis isothermal	190 °C 44 min (heating) 5 min (holding) LSR = 8 N = 150 r.p.m.	2 L stainless steel Parr reactor 4532 M. 2 Rushton turbines. Electric heating. Cooling by water through coil. PID-controlled Temp.	XOS (0.13 g/g)	[46]
2009	Sugar beet pulp	Autohydrolysis non-isothermal	160 °C LSR = 12 H = 2.46	3.75 L stainless steel Parr reactor	AROS (0.17 g/g) POS (0.15 g/g) GALOS (0.036 g/g)	[65]
2010	Orange peel	Autohydrolysisnon -isothermal	160 °C LSR = 12 H = 2.46 N = 150 r.p.m.	3.75 stainless steel Parr reactor fitted with two four-blade turbine impellers. Electric heating. Cooling through internal loop.	POS (0.20 g/g) AROS (0.076 g/g) GALOS (0.066 g/g)	[63]
2012	Alperujo	Steam processing, isothermal	170 °C 15 min, saturated steam	100 L stainless steel reactor	POS, XOS, GOS (no quantitative info on yield)	[69]
2013	Lemon peel	Autohydrolysisnon-isothermal	160 °C LSR = 12 H = 2.51 N = 150 r.p.m.	3.75 L stainless steel Parr reactor	POS (0.25 g/g) AROS (0.068 g/g) GALOS (0.026 g/g)	[64]
2013	Beet fiber (beet pulp)	Autohydrolysis isothermal	160 °C 5 min (heating) 2 min (holding) 3 min (cooling) LSR = 8	0.05 L reactor vessel made of SUS316. Reactor heated in a molten salt bath. Reactor cooled in a water batch to 50 °C in less than 3 min.	AROS (0.15 g/g)	[71]
2014	Citrus peel, Apple pomace	Autohydrolysis isothermal	150 °C, 5 min (holding) LSR = 30	Autoclave 0.5 L working volume. Thermocouple and pressure gauge to assay temperature and pressure inside the reactor.	POS (0.17 g/g)	[66]
2014	Coconut meal	Autohydrolysisnon-isothermal	275 °C, 14.5 min (heating + cooling) LSR = 10 H = 4.52	0.12 L stainless steel vessel. Heated by an aluminum block heater controlled by a PID. Vessel cooled with running tap water	MANOS (0.23 g/g)	[70]
2015	Brewery's spent grains	Autohydrolysisnon-isothermal	195 °C LSR = 8 H = 3.65	Stainless steel Parr reactor	XOS (0.12 g/g) GOS (0.040 g/g) AROS (0.032 g/g)	[59]
2017	Fruit passion peel	Autohydrolysisnon-isothermal	175 °C 5,5 min (heating) LSR = 16 H = 2.21	0.125 L stainless steel vessel heated by aluminum block heater and cooled by running tap water	POS (0.14 g/g) GOS (0.051 g/g)	[67]
2018	Sugarcane bagasse	Autohydrolysis isothermal	200 °C 10 min (holding) LSR = 10	0.6 L stainless steel reactor. Stirring with two four-blade turbine impellers. Electric heating. Water cooling by internal loop.	Low DP-XOS (0.12 g/g)	[68]

Note: H is the severity factor (Log (R0)).

Regarding to polymers susceptibility to autohydrolysis, it seems that the following order applies (from higher to lower susceptibility): POS < GALOS, AROS < XOS < MANNOS.

In the commented studies, some operational variables, such as particle size or agitation speed, have not been examined. These variables that are critical to understand the effect mass transfer in dynamic processes. The predominant type of operation is batch: in general, all the experiments were carried out on batch reactors optimizing the time and temperature.

Moreover, it is worthy to mention that autohydrolysis is not only suitable for the production of oligosaccharides but it is also useful for the production of a solid feedstock appropriate for further fractionation. It makes cellulose more accessible to enzymes and the sugars obtained by enzymatic hydrolysis can be upgraded to valuable products by catalysis and bioprocessing [41,47].

3. Acid Hydrolysis

Partial acid hydrolysis of polysaccharides is the oldest and was the most common technique to obtain different kinds of oligosaccharides. In this review, we focus on those oligosaccharides that can be obtained from food and agro-waste and the most important polysaccharides in this field are pectin and cellulose/hemicellulose. The acid treatments used for these polymers are very varied because of their completely different structure [72]. Diluted acids and high temperatures are standard conditions for pectin degradation. In contrast, cellulose can be very hard to hydrolyze due to its rigid crystalline structure that difficult the acid to penetrate the dense network [73]. In this case, hydrolysis is driven by concentrated or supported acids.

3.1. Pectin

Acid treatments to perform pectin depolymerization are scarce because of the advantages of autohydrolysis and enzymatic hydrolysis. Depending of the nature and concentration of the acid used, a variety of POS can be obtained, as pectin is composed by neutral and acidic sugars that are linked in different ways. In 1993, Thibault et al. used 0.1M HCl at 80 °C to depolymerized beet, apple and citrus pectin and they found that the linkage between GalA-GalA is more stable than GalA-Rha, and much more stable than neutral sugar-neutral sugar linkage. Therefore, they obtained mostly homogalacturonans (HG) and rhamnogalacturonans (RG) while the arabinans and arabinogalactans (AG) were hydrolyzed to low molecular weight oligomers [74].

HCl is the most common acid used for this purpose. In a recent publication, La Cava et al. treated the peels of four cultivars of pink/red and white grapefruits with 2M HCl at 110 °C for only 2 h to obtain a hydrolysate and use it as culture and encapsulating medium for *Lactobacillus plantarum* [75]. Pectin polymers and complexes from the pericarp of unripe tomato were hydrolyzed with 0.1M HCl at 80 °C for different reaction times to visualize and characterize the poly- and oligosaccharides by atomic force microscopy (AFM). They found that, when using these mild acid conditions, changes in intrinsic viscosity of the sample were observed due to the different rates of depolymerization of RGI and HG [76]. Coenen et al. also used 0.1M HCl at 80 °C but followed by a second hydrolysis with trifluoroacetic acid (TFA). The hydrolysate contained HG, xylogalacturonan XGA and RGI oligosaccharides. They applied the reaction to apple pectin modified hairy region to investigate the inter linkages between the different pectin structural elements. They demonstrated at oligomer level the position of the covalent linkage between HG or XGA to RGI by MS and MS/MS [77].

TFA is also frequently used as hydrolytic agent in pectins. Recently, Zhang et al. treated citrus pectin with 1.2 and 2M TFA at 85 °C to obtain fractions of POS and evaluated them as prebiotics. They also degraded this pectin with H_2O_2 in alkaline conditions and the POS fraction obtained with this method was the most promising prebiotic candidate for *Bafidobactorium bifidum* [78]. Manderson et al. obtained other POS but using the peel by-product of orange juice manufacturing. They produced prebiotic pectic oligosaccharides directly from orange peel albedo in large scale performing a pasteurizer extraction with HNO_3 at pH 1.5. The fraction obtained was treated by nanofiltration to remove excess of nitrates, and it contained not fully characterized POS and monosaccharides [79].

A different technique was used by Burana-osot et al. [80]. They performed a photochemical reaction to partially depolymerized citrus pectin using ultraviolet light in the presence of titanium dioxide catalyst at pH 4 (HCl) and pH 7 (NH_4OH). Using this technique, they can control the molecular size of the oligomers obtained by the exposure time to the UV light. To obtain good fractionated POS, 6 h of UV light exposure and pH 7 were the optimal conditions. They obtained POS of DP 2–18 and they also confirmed the presence of methyl ester groups of galacturonic acid after the photolytic reaction [80]. The main conditions and products can be found in Table 3.

3.2. Cellulose

Acid hydrolysis has been mainly used as a pre-treatment of lignocellulose before enzymatic degradation to monosaccharides and related derivatives. Exclusively chemical degradation in acidic conditions has been, in general, conducted in order to obtain, among others, glucose, xylose, furan derivatives or levulinic acid. Only in the few following examples, the objective was to perform the (in general acid) hydrolysis in a controlled process leading to oligosaccharides, collected in Table 4.

Bouchard et al. [81] studied the conditions allowing to improve the surface properties of cellulose nanocrystals (CNC) preparation from bleached kraft pulp. When performed at 45 °C for 25 min, the hydrolysis in 64% sulfuric acid led to oligosaccharides of degree of polymerization (DP) between 7 and 20. The precipitation of these soluble oligosaccharides onto CNC was achieved by dilution of the acid. At higher temperatures, the DP of the oligosaccharide decreased, and they remain very soluble at 65 °C. Reference compounds were prepared by 85% phosphoric acid hydrolysis of microcrystalline cellulose, followed by filtration and precipitation of the oligosaccharide mixtures.

Table 3. Acid hydrolysis of different kinds of pectins.

Pectin	Conditions	Product	Yield (g/g Dry Solid)	Ref.
Beet, Apple and Citrus	0.1 M HCl 80 °C, 72 h	HG, RG, arabinans and AG	Not given	[74]
Grapefruits	2 M HCl 110 °C, 2 h	POS and monosaccharides from hemicellulose and cellulose	Not given	[75]
Green tomato	0.1 M HCl 80 °C, 1, 8, 24 and 72 h	Polysaccharides, HG, RG	0.13–0.61	[76]
Apple MHR	0.1M HCl, 80 °C, 48 h followed by 0.05 M TFA 100 °C, 6 h	HG, XGA, RGI	Not given	[77]
Citrus peel	1.2–2 M TFA, 85 °C, 2.5 h 88.24 mM-66.18 mM H_2O_2 pH 10 90 °C, 4 h	POS 3628 and 2673 KDa (TFA) POS 3543, 2661 and 1283 KDa (H_2O_2)	Not given	[78]
Orange albedo	HNO_3, pH 1.5, 120 °C, 30 min	POS and monosaccharides	0.16	[79]
Citrus	1 g/L anatase TiO_2, pH = 7, UV λ = 220–340 nm, 6h	POS and pectic polysaccharides of lower Mw	0.88	[80]

Oligosaccharides with DP 3–11 in gram quantities were obtained by treating microcrystalline cellulose at room temperature (22 °C) using a 4:1 mixture of concentrated hydrochloric acid and concentrated sulfuric acid for 4–6 h [82]. The soluble oligosaccharides were precipitated with acetone, and purified by ion exchange column chromatography.

Cellulose of different sources (cotton linters, fibrous microcrystalline cellulose and their derivatives after alkaline treatment) were heated in 1 M HCl t 105 °C for 3 h [83]. The DPs of the resulting

oligosaccharides were estimated by size exclusion chromatography combined with a multiangle light scattering detector (SEC-MALS). The samples showed a bimodal elution pattern consisting of a major high molecular component of DP 35–101, and a minor low molecular component of DP 18–24.

A solid catalyst carrying acidic sulfonic groups was synthesized by carbonization of cellulose and sulfonation [84]. The prepared catalyst was shown to contain sulfonic, carboxylate and phenolic groups on a graphene matrix, and was used for the hydrolysis of crystalline cellulose. After 6 h at 100 °C, all the polysaccharide gave water soluble oligosaccharides, and the catalyst could be recovered by decantation. The soluble oligosaccharides mixture was analyzed after 3 h of reaction by matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS), showing an oligosaccharide mixture of DP 2 to 10.

Recently, another solid catalyst was recently prepared by oxidation of activated carbon under air at high temperature (425 °C) for 10 h [20]. Cellulose was hydrolyzed in the presence of this microporous catalyst in a semi-flow reactor by mix-milling for 1 h at 180 °C at a space velocity of 70 h^{-1}. These semi-flow conditions afforded oligosaccharides in 71% yield. By MALDI-TOF MS analysis, oligosaccharides of DP 2 to 13 were observed. The authors suggested that the adsorption of cellulose on the catalyst's surface prevents further degradation.

Table 4. Acid hydrolysis of cellulose.

Residue	Conditions	OGs	Yield (g/g Dry Solid)	Ref.
Bleached kraft pulp	64% H_2SO_4, 45 °C, 25 min	DP 7–20	Not given	[81]
Cellulose	HCl(c)/H_2SO_4 (c) 4:1, 22 °C, 4–6h	DP 3–11	0.02	[82]
cotton linters, fibrous microcrystalline cellulose	1 M HCl, 105 °C, 3 h	DP 35–101 DP 18–24	0.5–0.8	[83]
Crystalline cellulose	Sulfonated carbon solid catalyst, water, 100 °C, 6 h	DP 2–10	0.68	[84]
Cellulose	Oxidized microporous carbon, 180 °C, 1 h, mix-milling	DP 2–13	0.70	[20]
Cellulose	Sulfonated hydrothermal treated carbon, 165 °C, 6.5 h, ball-milling	DP 1–9	0.22–0.47	[85]

A recyclable acid solid catalyst was recently prepared by sulfonation of carbonized cellulose followed by hydrothermal treatment and it was used for the hydrolysis of cellulose by ball-milling [85]. The authors suggested a crucial role of strong Brønsted acid sites of the catalyst in the mechanocatalytic depolymerization process, though some contribution of auto-hydrolysis and homogeneous catalysis due to leaching of acidic groups cannot be excluded. The soluble fraction was analyzed by liquid chromatography coupled to a mass spectrometer (LC-MS) showing the presence of oligosaccharides with a DP of up to 9. The formation of larger oligosaccharides is also possible during ball-milling, but they were difficult to detect because of their lower solubility.

4. Enzymatic Processes

The enzymatic breakdown of the food waste biomass matrix consists of the depolymerization of its structural more relevant polysaccharides: cellulose, hemicellulose and pectin. These processes take place due to the simultaneous work of different enzymes, mainly catalyzed by hydrolases and to a lesser extent by lyases. These enzymes cleave ether and ester bonds, releasing oligosaccharides and monosaccharides. It is essential to take into account that the conditions employed in these processes

are gentler than those used in autohydrolysis and acid hydrolysis operations. However, there are some shared parameters in all the processes with a very similar influence in the results. We will comment on these parameters in the following subsections.

4.1. Process Variables

4.1.1. Pretreatment of Biomass

The food waste biomass is very recalcitrant, mainly because of the structure of its principal component, cellulose. This polymer presents different degrees of crystallinity polymorphisms [86] and take part of a complex network constituted by cellulose- hemicellulose-pectin, which causes an important problem of accessibility of the different enzymes employed. A simple mechanical pretreatment, milling, can increase the specific area of the substrate and reduce the length of cellulose fibers [87]. More complex physicochemical, hydrothermal and chemical pretreatments, such as acid [88], alkaline [89] and/or oxidative pretreatments [90], are also employed in order to favor the accessibility to the most recalcitrant structural polysaccharides and their reactivity. They can remove hemicellulose, pectin, proteins and extracts, on one side, reduce the length of cellulose fibers and its crystallinity, and increase the specific area, the porosity.

4.1.2. Temperature and pH

When enzymes are employed, the temperature is a very important parameter because proteins can suffer structural disorders and subsequent inactivation, while, with temperatures below optimal conditions, reaction rates can be too low. Therefore, an agreed temperature around 45 and 50 °C is recommended on average for the different enzymes mixtures. It is essential to consider that every single enzyme has its own optimal temperature, which usually tends to be superior to their maximum stability temperature. Thus, it is necessary to find a consensus between both values [91,92]. Another important aspect of this enzymatic reaction is the pH, whose operational value ranges from 3 to 5 [93]. The requirement of maintaining an adequate pH value needs pH control or buffer usage. Most common buffers are acetate [94] and citrate [95].

4.1.3. Particle Size and Solid Loading

The pretreatment of food waste biomass generally produces a size distribution that should be considered as an influential factor over enzymatic hydrolysis. Substrate particle size affects the overall rate of the hydrolysis process [96], given that this size impacts upon the efficiency of the substrate access of the enzymatic mixture, introducing mass transfer limitations in bigger particles. In addition, high solid presence in the reaction medium, an industrial tendency, increases viscosity and also affects the external and the internal mass transfer rate [97,98].

4.1.4. Side Products Formation

The use of mild temperatures and pH around neutrality reduce the degradation of biomass and side compound formation such as furfural and 5-hydroxymethylfurfural (HMF) (by dehydration of glucose and other hexoses) and corrosion problems. The reduction of aldehyde compounds formation is positive to avoid the inhibition of enzymes and of microorganisms in subsequent bioprocesses, apart from reducing cost in purification operations downstream the reaction section [99].

4.1.5. Source of Enzymes

Main natural source of cell wall degrading enzymes are members of phylo *Ascomycota* [100] and *Basidiomycota* [101]. Within *Ascomycota* phylum, *Aspergillus*, *Trichoderma* and *Neurospora* have important industrial applications as enzyme producers. However, in *Basidiomycota*, there are two of the most efficient lignocellulose biomass degraders: white and brown rot fungus.

4.2. Oligosaccharides from Agricultural Wastes Production by Enzymatic Hydrolysis

Oligosaccharides are intermediates of depolymerization reaction of lignocellulosic materials. In the 50s decade of twentieth century, the enzymatic hydrolysis of different substrates from lignocellulose was studied. Hydrolysis of isolated cellulose [102], xylan [103] (main component of hemicellulose) and pectin [104], generated some products of glucidic nature with a higher molecular weight than the one of monosaccharides (150–180 Da). This observation led to the verification of oligosaccharides formation during enzyme hydrolysis of biomass.

4.2.1. Cellulose

In the decade of the 70s, new studies about the use of enzyme for the production of single sugars for use as microorganism carbon source appeared. Wilke and Miltra studied enzymatic saccharification for process development of a specific source of cellulose that participate before in research for the production of cellulolytic enzymes: newsprint paper [105,106]. The knowledge about the huge amounts of lignocellulosic materials produced as residues in agriculture, opened a new variety of raw material that could be subjected to enzyme saccharification [107]. Cellulases is a group of enzymes that effect its lytic activity over cellulose, having a synergistic effect amidst all different enzymes activities. These enzymes and their main activities are collected in Table 5.

Production of β-glucans or gluco-oligosaccharides is a less studied subject in comparison to the production of glucose because of its importance as carbon source for bioprocesses and, lately, as promising C6 platform chemical within the biorefinery concept. It should be taken into account that β-glucosidase is an impediment of cellooligosaccharides (COS) accumulation, since this kind of enzymes hydrolyses glycosidic bond within cellobiose, yielding high amounts of β-D-glucose. Cellobiose is the product released by exo-glucanases that can be considered as a DP2 oligosaccharide.

Table 5. Principal enzymatic activities involved in cellulose degradation.

Enzyme Name	Enzyme Commission Number	Activity	Product
Endo-cellulase (endoglucanase)	3.2.1.4	Endohydrolysis of (1→4)-β-D-glycosidic linkages in cellulose	Cellodextrins
Cellulose 1,4-β-cellobiohydrolase (reducing end)	3.2.1.176	Hydrolysis of (1→4)-β-D-glycosidic linkages of reducing end of polymer	Cellobiose
Cellulose 1,4-β-cellobiohydrolase (non-reducing end)	3.2.1.91	Hydrolysis of (1→4)-β-D-glycosidic linkages from non-reducing end of polymer	Cellobiose
β-glucosidase	3.2.1.21	Hydrolysis of (1→ > 4)-β-D-glycosidic linkages in cellobiose	β-D-glucose

Removing one or some enzymes, or reducing their activities in the enzyme cocktail, allows obtaining oligosaccharides with a higher DP degree. That is the reason why some procedures are focused on the adsorption of these enzymes on its natural substrate. When the cellulase mixture gets in contact with cellulose, endo-cellulases and exo-cellulases bind specifically to it, due to the presence of a cellulose-binding domain (CBD) in their structure. Cellulolytic enzymes have specific domains that allows them to interact with cellulose [108]. Chu et al. demonstrated that the selective removing of β-glucosidase activity in a corncob residue manages to double cellooligosaccharide production in a subsequent enzymatic hydrolysis, leading to an increase in COS yield (from 0.15 g/g to 0.25 g/g, corresponding at final concentration of 7.6 g/L and 12.6 g/L, respectively) and selectivity (from 30 to 60%) [109]. Birhade et al., on the other side, discovered that these differential adsorption

processes are deeply influenced by the accessibility of cellulose. When phosphoric acid-swollen cellulose (PASC), ammonia-treated wheat straw (AWS), sodium hydroxide-treated wheat straw (NWS) and nitric acid-treated maize bran (NMB) were used as substrates in pre-enzymatic adsorption step with the following conditions: 20 FPU/g cellulose, pH 4.8, 20 min and 4 °C, 34% (PASC), 27.97% (NWS), 25.11% (NMB) and 8.11% (AWS) of endo-glucanase activity was retained. AWS waste showed a low interaction with β-glucosidase (next to 0.1%), and low endoglucanase retention, which makes this material the best option to selectively remove exo-glucanase activity. Adsorption with AWS followed by separation step and hydrolysis leaded to a different result. If the cellulose and exo-cellulose mixture was employed, cellobiose was the main product. However, if the supernatant of the adsorption step was used, the products were a mixture of cello-oligosaccharides with a DP > 6 (0.11 g/g), DP 2–6 (0.10 g/g) and monosaccharides (0.11 g/g) when AWS was employed [110].

4.2.2. Hemicellulose

Hemicellulose is a hetero-polysaccharide that constitutes an important part of the cell wall. This complex polysaccharide is the most abundant after cellulose [111]. Due to its composition and structure, to ensure its complete enzymatic hydrolysis, several enzyme activities should work together in a synergistic way, being the most important collected in Table 6. The principal component in most hemicelluloses is xylan, whose structure is a chain of β-D-xylose bonded through β(1→4) linkages [112].

Just as in the case of the enzymatic hydrolysis of cellulose, enzymatic commercial mixtures contain different enzyme activities. The analysis and determination of these activities is fundamental in order to estimate what kind of oligosaccharide mixtures can be achieved (their composition and molecular weight). Hespell et al. evaluated that corn fiber biomass subjected to a pretreatment of ammonia-explosion contains around 30% hemicellulose. Testing the xylanase activity of different enzymatic mixtures with colorimetric methods on this substrate, certain mixtures that were enriched in a single enzyme (e.g., β-glucosidase), presented hemicellulose activity, when apparently they should not. The reaction took place for 72 h with a 5% *w/w* DS at pH 4.8. After this reaction time, between 30%-40% of the hydrolysis products could be oligosaccharides [113]. The evaluation of xylanolytic activity is only a part of the hemicellulase activity because in hemicellulose breakdown numerous enzymes (collected in Table 5) are involved.

Mazlan et al. studied the most important operational factors that may affect the production of xylooligosaccharides from oil palm frond bagasse [114]. The optimal conditions resulting from the experimental design were a substrate loading of 1% (*w/w*) and a 50 U/mL of xylanase activity from a commercial mixture (Cellic Htec2®). Enzymatic activity was measured via 3,5-dinitrosalycilic acid assay using birchwood xylan as substrate. Under these conditions, a yield of 0.175 g of xylooligosaccharides (XOS) per gram of dry substrate was obtained. Jagtap et al. evaluated the use of wheat husk as substrate employing solid substrate loading ranging from 1% to 5% *w/w* DS, a certain value favored the production of XOS (1 g/L to 3.5 g/L, respectively). After hydrolysis optimization of enzymatic doses and time of reaction, maximum of XOS (10.8 g/L) was reached. Nevertheless, the increasing of substrate concentration to 10% *w/w* DS did not cause an improvement in XOS production, maybe due to the higher viscosity of the reaction liquid [115].

Another important factor is the source of xylanolytic enzymes. If the XOS recovery of commercial xylanase action is compared that due to microbial extracts, different results come forth when hydrolyzing the same substrate. In the work of Azevedo et al., different behaviors are appreciated when comparing the action of various microbial extracts that contain enzymes with xylanase activity and commercial preparations employing the same conditions (50 °C, pH 5, 1–96 h and hemicellulose from sugar cane bagasse) [116]. The concentrations reached with commercial enzymes are lower (0.50 g/L) than those obtained from the best microbial extract from *Aspergillus fumigatus* M51 (1.04 g/L). Microbial extract generated mostly xylobiose and xylotriose (0.59 g/L and 0.45 g/L, respectively) and a lower amount of high degree polymerization oligosaccharides (0.01 g/L). Optimization process employing *Aspergillus fumigatus* M51 xylanase reach a yield of 0.38 g/g after 72 h of reaction time. In the case of

commercial enzymes, similar amounts of xylobiose but only a small amount of xylotriose are obtained (0.51 g/L and 0.08 g/L, respectively). These results could be explained because microbial xylanase is an endo-xylanase, while commercial preparations could contain more xylanolytic enzymes optimized for xylan saccharification.

In Table 7, some other examples processes for XOS production are given. Residues that contain high amounts of hemicellulose, mainly as xylans, are wastes from stalks, stems and shell of crops. Pretreatment of these wastes are important for the isolation of hemicellulose, favoring XOS production. Temperature conditions are 40–50 °C—sometimes, slightly higher—, while solid dry loadings do not exceed 10% *w/w* in all cases.

Hemicellulose is built by a xylan backbone with some lateral substituents that constitute other kind of oligomeric sugar structure, being one of this side chains manooligosaccharides (MOS). Nguyen et al. observed that some wastes such as spent coffee ground contain high levels of mannose derived from hemicellulose. When this residue was pretreated by delignification and defatting and submitted afterwards to an enzymatic hydrolysis with a 10% *w/w* dry substrate loading at 45 °C and pH 4.8, a maximum oligosaccharides production yield is obtained between 4 h and 6 h after hydrolysis started. The highest yields were observed using a non-commercial pectinase, at 4.1 mg enzyme/g dry biomass, obtaining 38.2 g/L of DP62 MOS and 24.9 g/L of DP6 MOS (total yield 0.63 g/g DS) [117]. Rungruangsaphakun et al., on the other side, produced MOS using 16.52 U/mL of mannanase, with a solid loading of 15% of defatted copra meal, 50 °C and pH 6. After 12 h, these authors achieved a mean of 14.41 g/L MOS (0.095 g/g DS) and, after increasing scale by two orders of magnitude, 16.89 g/L MOS (0.11 g/g DS) [118].

Table 6. Principal enzymatic activities involved in hemicellulose depolymerization.

Enzyme Name	Enzyme Commission Number	Reaction	Product
Endo-1,4-β-xylanase (Endo-xylanase)	3.2.1.8	Random endohydrolysis of (1→4)-β-D-glycosidic bond	Xylan oligomers
Xylan 1,4-β-xylosidase	3.2.1.37	Hydrolysis of (1→4)-β-D-xylans from their non-reducing end	β-D-xylose
α-L-arabino-furanosidase	3.2.1.55	Hydrolysis of terminal non reducing α-D-arabinose of arabinan oligomers	α-D-arabinose
α-D-galactosidase	3.2.1.22	Hydrolysis of terminal non reducing α-D-galactose of galactan oligomers	α-D-galactose
Acetyl esterase	3.1.1.6	Release acetate by removing acetyl ester groups	Deacetylated xylan
Feruloyl esterase	3.1.1.73	Hydrolysis of ester bond between monosaccharides and ferulic acid	Ferulic acid and polysaccharide

Table 7. Examples of enzymatic hydrolysis of agricultural wastes to xylooligosaccharides (XOS).

Residue	Pretreatment	Enzymes and Offered Activity	Conditions	Products	Ref.
Almond shell	Autohydrolysis (LSR 10 g water/g dry solid, 180–220 °C isothermal, holding different times).	Endoxylanase from *Thermomyces lanuginosus* (Endoxylanase activity, 5, 10 and 15 U/mL)	50 °C, 4–48h 70 r.p.m. 1% *w/w* solid	XOS (DP: 2 and 3, Mw< 250 Da)	[58]
Brazilian syrah grape pomace flour	Dry and milling	Viscozyme L®and *Aspergillus niger* 3T5B8 (xylanase activity, 10–100 IU/g dry substrate)	40 °C, 6 h 200 r.p.m. 5% *w/w* solid	XOS (DP: 2 to 5) Viscozyme L (0.084 g/g DS, 100 IU/g) *Aspergillus niger* 3T5B8 (0.081 g/g DS, 100 IU/g)	[119]
Corn straw	Organic acid pretreatment (13.33% of solids and different lactic acid concentrations) and deep eutectic solvents pretreatment (5% of solids, 120 °C from 2–6 h),	Cellulase mixture provided by Genencor (China) (Cellulase activity, 10 FPU/g dry substrate)	50 °C, 72 h 2% *w/w* solid	XOS (DP: 2 to 4)	[120]
Corncob	Diluted acid pretreatment (1% of solid, 0.1 sulfuric acid, 60 °C and 12 h) filtering and autoclaved 1 h 120 °C.	Xylanase from *Bacillus aerophilus* KGJ2 (xylanase, 20 UI)	70 °C, 48 h 10% *w/w* solid	XOS (DP: 2 to 4)	[121]
Plantago major L.	Extraction with boiling water (1:25) 2 h stirring. Filtering and precipitation with ethanol (95%) and dry	Manannase (manannase activity, 0.2–4 U/mL) and hemicellulase (50–250 U/mL).	45 °C, 40 h 1% *w/w* solid	XOS and AROS (DP: 2 and 3)	[122]
Almonds shells	Dry almond shells alkaline extraction with NaOH (1–2 M) 121 °C 1h.	Endoxylanase from *Thermomyces lanuginosus* (5, 10 and 15 U/mL)	50 °C, 2–48 h and 2–6% *w/w* solid	XOS (DP: 2 (0.35 g/g) 3 (0.09 g/g) to 4 (0.01 g/g xylan))	[123,124]
Reed pulp	Alkaline (0.25–0.75%) and acid (0.55–1.65%) extraction of hemicellulose 150–160 °C, 30 min.	Xilanase activity 66 UI/g dry substrate and cellulose activity 10 FPU/g dry substrate	50 °C, 8 h, 40 h 5% *w/w* solid	XOS (0.144 g/g DS)	[125]

4.2.3. Pectin

Pectin is, in a great percentage, composed by homogalacturonan [126]. Consequently, pectinolytic activity of the enzymes employed in pectin depolymerization processes is tested mainly employing polygalacturonic acid as substrate. Despite the pectinolytic activity test, and due to the number of enzymes involved in the pectin breakdown (Table 8), the use of same activity units for different enzymatic mixtures of diverse origin can be misleading [127].

Table 8. Main enzymatic activities involved in pectin depolymerization.

Enzyme	Enzyme Commission Number	Reaction	Product
Endo-polygalacturonase	3.2.1.15	Random hydrolysis of galacturonic acid backbone in pectin	Oligomers of 1,4-α-D-galacturonoside
Exo-polygalacturonase	3.2.1.67	Hydrolysis of the first α(1→4) bond from non-reducing end of polygalacturonic acid	α-D-Galacturonic acid
Exo-poly-α-digalacturonosidase	3.2.1.82	Second α(1→4) bond from non-reducing end of polygalacturonic acid	Digalacturonate
Pectate lyase	4.2.2.2	Eliminate α(1→4) bond in galacturonic acid backbone	4-deoxy-α-D-galact-4-enuronosyl groups
Rhamnogalacturonan hydrolase	3.2.1.171	Hydrolyse α-D-galacturonic acid-(1→2)-α-L-rhamnose bond	Oligosaccharides with β-D-galacturonic acid at the reducing end
Rhamnogalacturonan endolyase	4.2.2.23	Eliminate α-D-galacturonic acid-(1→2)-α-L-rhamnose bond	4-deoxy-4,5-unsaturated D-galactopyranosyl uronic acid

According to the pectin source, the composition of its side sugar chains varies, as in the case of potato peel wastes that contain 75% of rhamnogalacturonan structure (constituted regions of galacturonic acid and rhamnose units). Rhamnogalacturonan chains can have galactose and arabinose oligosaccharides as side substituents. The balance of hydrolytic activities about these regions, presented in the different enzymatic preparations, allows getting specific oligomers of its sugars. Khodaei and Karboune isolated pectin from potato peel using a concentration of 0.5% *w/w* dry substrate, adding 0.2 U/mg of Depol 670L ® [128]. After 4 h, the oligosaccharides yield production was 0.94 g/g and, from the oligosaccharides obtained, 89.7% has a DP between 2 and 12, which indicates that the arabinanase to galactananase ratio of Depol 670L ®permits the specific release of arabinanan and galactanan oligosaccharides [129].

Citrus peel wastes, such as lemon peel, are a huge source of pectin. Gomez et al. studied the enzymatic hydrolysis after a washing step, in order to remove free sugars from the lemon peel. The conditions of the enzymatic reaction were 37 °C, pH 5, 5% *w/w* of dry solid loading and 5 U/mL of pectinase activity of different enzyme preparations that have different lytic activities towards arabinanan, arabinogalactan and galactan regions [130]. This study demonstrated that the use of enzyme mixtures with different activities changes the product distribution. The highest yield obtained under selected optimal conditions was 0.19 g/g. [128].

In recent years, there are some examples of processes to obtain pectinoligosaccharides (POS). All studies contained in Table 9 include a previous step of biomass pretreatment whose aim is the fractionation of raw materials. The reaction conditions in all cases are very similar, ranging from 45 °C to 50 °C at a low solid loading. When products were analyzed, the polymerization degree was determined, being possible to determine its size and weight.

Table 9. Examples of enzymatic hydrolysis of agricultural wastes to obtain POS.

Residue	Pretreatment	Enzymes and Offered Acti4vity	Conditions	Product	Ref.
Orange Peel Wastes	Water washing (4%, 6h, 30 °C, 170 r.p.m. rotational stirring) oven dry 65 °C 48 h	Fungal enzyme cocktail: xilanase (50 U/mL), pectinase(48,3 U/mL) cellulase (0,2 U/mL) and endo-celulase(2,8 U/mL)	4% of solid, 45 °C, 6 h and 170 r.p.m.	POS (DP 6 (0.06 g/g), 9 (0.28 g/g), 19 (0.04 g/g extracted DS))	[130]
Onion skins	50 g/L of dry and grinded biomass extracted with sodium hexametaphosphate (2%) 95 °C, 0.5 h	Viscozyme L®(endo-polygalacturonidase activity, 82.7 U/mL, 41.4 U/mL and 20.7 U/mL)	45 °C, 15–30 min, 200 r.p.m., 2.5–5% *w/w* dry solid(membrane reactor)	POS (DP 2 to 8) 22.0 g/(L·h)	[131]
Sugar beet	Acid hydrolysis with HCl (pH1.5), 80 °C, 1h. Cooling, filtering and adjusted at pH 3.5 with KOH. Finally, etanolic precipitation and demethoxylation step.	Endo-polygalacturonidase-M2 (Endopolygalacturonidase activity, 9.55 U/mL) and Rapidase Smart ®(Pectinmethylesterase activity, 0.52 U/mL)	50 °C, 2–15 min 0.5% *w/w* solid	POS (DP 2 to 9; MW 400–2000 Da)	[132]
Novel artichoke	Pectin extraction enzymatically assisted (Celluclast 1.5 L) at 50 °C. Filtering and ethanolic precipitation	Pectinex®Ultra-Olio (pectinase activity, 6.75 U/mL), Glucanex ®200G (pectinase activity, 0.63 U/mL) and Pentopan®Mono-BG (pectinase activity, 0.54 U/mL)	50 °C, 0.5–4 h, 750 r.p.m. 2% *w/w* solid	POS (DP 2 (0.023 g/g),3 (0.047 g/g), >3 (0.225 g/g pectin); MW 78–3500 Da)	[133, 134]
Hardy kiwi (*Actinidia arguta*)	Biomass was homogenate and defatted. Filtering deproteinization (Sevag method) and ethanolic precipitation	Endopolygalacturonidase from *Rhizopus* sp. (endo-pectinase activity, 0.2 U/mL)	50 °C, 3 h 2% *w/w* solid	POS (MW < 700 Da (0.12–0.20 g/g), 700 > MW > 3000 (0.66–0.68 g/g) and MW > 3000 (0.10–0.06 g/g pectin)	[135, 136]
Onion skins	1 g of onion skins extracted with 2% sodium hexametaphosphate 95 °C 0.5 h. Centrifugation and supernatant collection	Viscozyme L ®, Pectinase from Sigma Aldrich and endo-polygalacturonase M2 (endo-polygalacturonidase activity, 82.7 U/mL, 52.2 U/mL and 5.2 U/mL)	45 °C, 2h, 150 r.p.m. 10% *w/w* solid	POS (DP 2 (0.03 g/g DS), 3 (0.06 g/g DS), 4 (0.06 g/g DS) to 5)	[137]

5. Conclusions and Future Prospects

In the last years, with the progressive definition and development of biorefineries, biomass is becoming again a material resource of utmost importance. Its being intimately included in the Earth's element cycles turns it into the ideal renewable resource to obtain foods, feed, chemicals, materials and even fuels.

On its side, food, as a key vertex of the food-water-energy triangle, is clearly defined as a main human need, with an increasing importance as human population grows. The need for reducing food and food-related waste comes in hand with the need to valorize the unavoidable masses from the food production chain. In particular, polysaccharide related wastes are an evident source of bioactive compounds, having oligosaccharides a great potential for the development of food-related new products with elicitor, prebiotic, drug, prodrug and other bioactivities.

Oligosaccharides from cellulose, hemicellulose and pectin can be considered intermediates in the production of the main biorefinery platform chemicals of the C5 (pentoses) and C6 (hexoses) type. Though biorefinery upstream processes are mainly focused on the production of such platform chemicals, the development of new acid, basic, thermal and physicochemical biomass pretreatments have permitted the observation of operational conditions adequate for oligosaccharide production from pectin and hemicellulose, more prone to depolymerization than cellulose. Moreover, the advent of new enzymes, as LPMOs, and the more in-depth study of hydrolytic processes with classical hydrolytic enzymes and with supported acids have created new opportunities to obtain these bioactive oligomers, even acting on the more recalcitrant cellulose. While pectin and hemicellulose need of a careful tuning of operational conditions to avoid excessive hydrolysis, cellulose needs of harsher conditions to get cellooligosaccharides. In this last case, the use of enzymes reduces the risk of dehydration to aldehydes, but fine-tuning of acidity and temperature is needed to obtain the same result with hemicelluloses, using weak acids such as acetic and gluconic acids [138,139].

Finally, controlled process intensification with ultrasounds, microwave heating, hydraulic cavitation and pulsed electric fields should turn oligomer production into a more productive and less polluting activity, optimizing food waste valorization. To enhance the oligomer activity, chemical modifications such as acylations, esterifications, sulfonations, etc. as well as *de novo* synthesis of analogs can create more products or enhance the bioactivity of those now in place [140,141].

As a brief graphical abstract, Figure 1 shows some of the procedures and oligomers available from agrofood waste transformation via acid, supported acid, hydrothermal or autocatalytic and enzymatic routes.

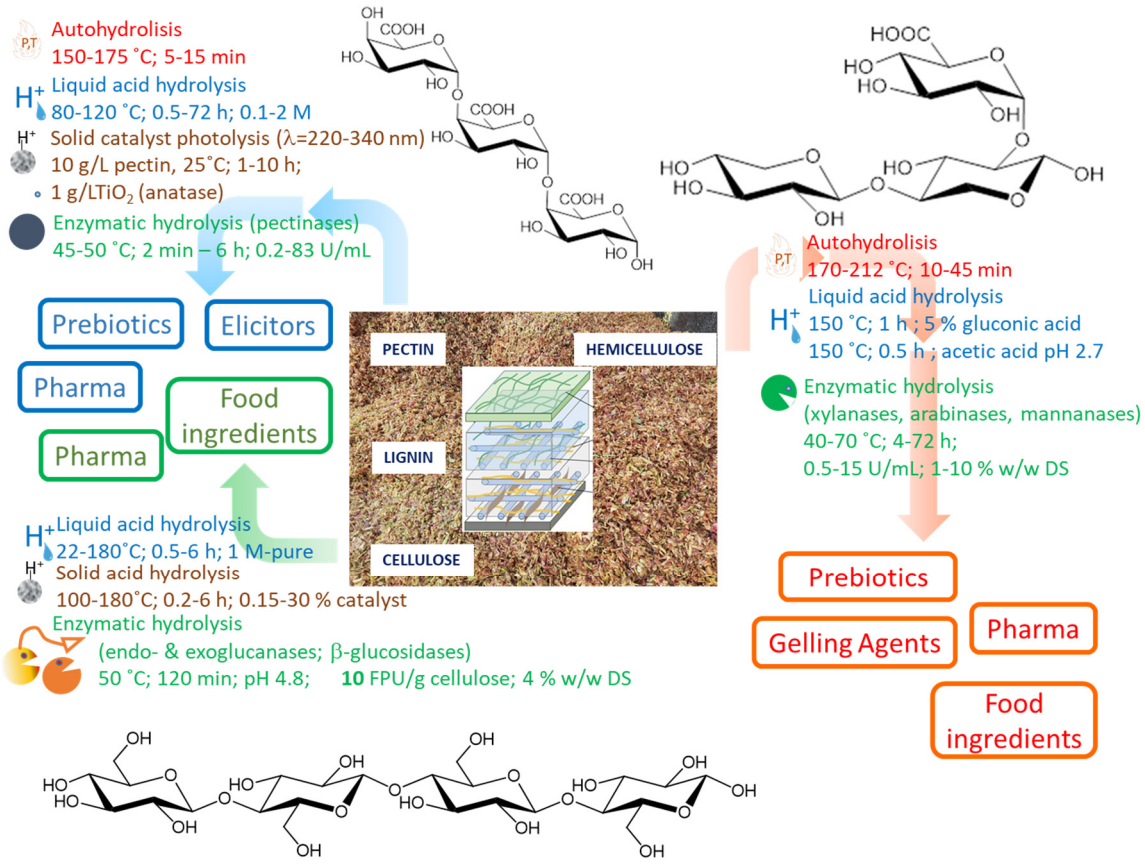

Figure 1. Valorization routes from agro-food wastes to oligomers, oligomer-based products and present/possible applications. The figure indicates the main operational variables, with their most typical values, for each type of processes and target oligosaccharides.

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