Obtaining Oligo- and Monosaccharides from Agroindustrial and Agricultural Residues Using Hydrothermal Treatments

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Abstract Agricultural and agroindustrial residues are major sources of cellulose, hemicellulose, and starch that can be converted into bioactive compounds, such as oligosaccharides and monosaccharides, using various chemical and biological methods. These bioactive compounds can be used as raw materials by food, cosmetic and pharmaceutical industries, as well as in the production of intermediate products and the development of biomaterials by chemical industries. In Brazil, the major industrial residues, which are corn residues, soybean residues, sugarcane bagasse, palm and coconut fibers, and grape and tomato seeds, among others, are produced at a rate of approximately of 600 million tons per year. Thus, the utilization of these residues using sustainable technology is of great interest. Hydrothermal treatment is a green technology that includes autohydrolysis as well as subcritical and supercritical hydrolysis, in which water is used at high pressures and temperatures to recover polysaccharides from complex vegetal matrices. The hydrolytic mechanisms can be improved by changing the ionic product or the polarity and electrical conductivity of water in subcritical and supercritical states. These properties promote the selective dissolution of the starch, hemicellulose and cellulose in the residues. The conversion of starch and hemicellulose into oligosaccharides and monosaccharides is preferentially performed at temperatures of less than 200°C. In contrast, the conversion of cellulose into oligosaccharides is promoted at temperatures greater than 200°C, with the highest amount oligosaccharide formation occurring at close to the critical point. In this article, the main biomass components, the properties of water under subcritical and supercritical conditions, and the latest studies of polysaccharide conversion in biomasses using hydrothermal treatments are reviewed.

Keywords Monosaccharides, Oligosaccharides, Biomass, Subcritical water, Supercritical water, Hydrothermal treatment

1. Introduction

The continuous population increase and the rapid consumption of non-renewable resources in the world have promoted extensive research of sustainable alternatives that could help to preserve the ecosystem for future generations [1]. A lignocellulosic biomass is a complex vegetal matrix composed mainly of cellulose, hemicellulose, starch and lignin. It is one of the most abundant raw materials in earth and it can be converted into marketable products without competition with the food supply chain. Recently, studies of biomass transformation have focused on the recovery of carbohydrates from starch, hemicellulose and cellulose to produce oligosaccharides, monosaccharides and ethanol [2]. The depolymerization of hemicellulose and cellulose into oligosaccharides, monosaccharides and their degradation products using conventional techniques, such as acid hydrolysis, alkaline hydrolysis and enzymatic hydrolysis, has been extensively studied [3]. However, these techniques present disadvantages in processing operations such as equipment corrosion, necessary neutralization steps and long reaction periods. In addition, the development of new economically feasible technologies for the production of target compounds with high yield and less pollution is required. Hydrothermal technologies are green technologies that are suitable for the recovery of valuable compounds from biomass in which water is used at high temperatures and pressures without the addition of catalysts. Among these technologies, autohydrolysis, subcritical hydrolysis and supercritical hydrolysis are the most studied techniques. Water at a high temperature and pressure acts as a reaction medium for chemical processing of biomass because of the change in its physicochemical properties compared to water under normal conditions. This change of properties includes a reduced dielectric constant which increases the solubility

of organic compounds, an increased ionic product which promote acid-base reactions and a greater density which improves solubility. These conditions led water to be considered as a suitable solvent and reaction medium for the decomposition of biomass. Several studies using model compounds composed of starch, hemicellulose and cellulose have shown that the use of water at mild temperature conditions (less than 200°C) led to the complete degradation of starch and hemicellulose into oligosaccharides, whereas supercritical water promoted the complete depolymerization of cellulose during short residence periods.

In this paper, a review of the state of the art of hydrolysis of the cellulose, hemicellulose and starch present in agricultural and agroindustrial biomasses is presented, aimed at a better understanding of the operational conditions that promote the formation of oligosaccharides and monosaccharides.

2. Biomasses

The production of plant biomasses, which are typically the non-food parts of plants, is based on the photosynthetic process, during which polymeric carbohydrates with a ratio of $[CH_{1.4}O_{0.6}]_n$ are generated. The chemical components of biomass are cellulose, hemicellulose, starch, lignin, ash and small amounts of extractable compounds, such as lipids and proteins. The main sources of lignocellulosic biomass can be classified as follows: forest residues; agricultural and agro-industrial residues; energy crops; municipal solid waste and organic industrial waste [3]. Cellulose, hemicellulose and starch are macromolecules composed of different types of sugars, whereas lignin is an aromatic polymer synthesized from phenylpropanoid precursors. Additionally, these components, including oligosaccharides, pectins, gums and waxes, are elements of dietary fiber, which is recognized for its health benefits and is included in the processing of fiber-rich products by food industry [4]. Table 1 shows the relative amounts of cellulose, hemicellulose, starch and lignin in various agricultural and agro-industrial lignocellulosic residues.

2.1. Major Polysaccharide Components of Biomasses

2.1.1. Cellulose

Cellulose is the most abundant biopolymer in nature. It is a linear homopolymer of β-(1→4)-D-glucopyranose with a high degree of polymerization (DP), of between 200 and 12,000. These DP values depend on the origin of the cellulose and the pretreatment of the biomass and affect its properties. Cellobiose is the basic structural unit of cellulose, consisting of two units of 4-O-β-D-glucopyranosyl -β-D-glucopyranose. Figure 1 shows the chemical structure of cellulose in a chair conformation (the most common conformation for cellulose). The C-2, C-3 and C-6 of each glucopyranose unit are linked to hydroxyl groups that undergo the characteristic reactions of primary and secondary alcohols. Moreover, the hydroxyl groups that are linked to C-1 and C-4 at the end of cellulose chain are the most reactive groups for intra- and intermolecular iterations and degradative reactions because they have reducing and non-reducing properties, respectively [5].

Cellulose constitutes up to 30% of the primary cell wall and 40 to 90% of the secondary cell wall [6], [7]. The basic units of cellulose are linked by intermolecular hydrogen bonds to form microfibrils with a diameter of between 3-25 nm [8], [9]. The strong hydrogen bonding between the cellulose units is mainly due to the close interaction between the hydroxyl groups in the equatorial orientation and hydrogen atom in the axial orientation, which results in high crystallinity and low solubility in aqueous media (8-14% solubility in water under normal conditions). Moreover, the microfibrils represent amorphous regions (15-20%) that are more vulnerable to chemical and enzymatic attack than are the crystalline regions [10]. Cellulose is not digested by human gastrointestinal enzymes and it has been used as a bulking additive in food manufacturing due to its water-absorbing ability and low solubility [4], [11], [12].
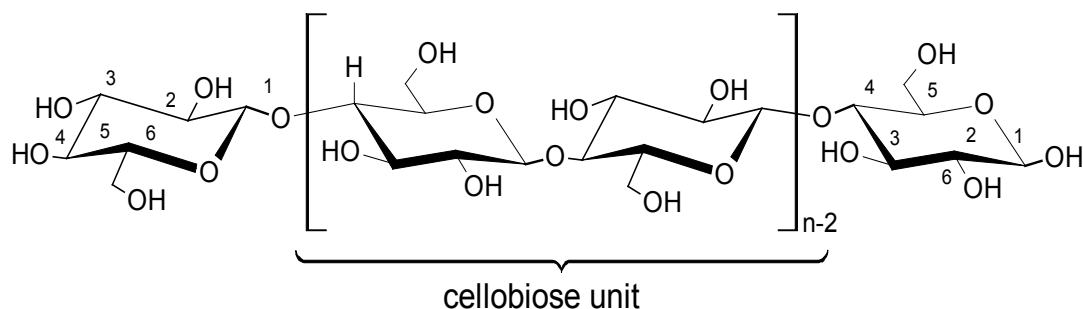

Figure 1.   Molecular structure of cellulose (adapted from Klemm *et al.* [5])
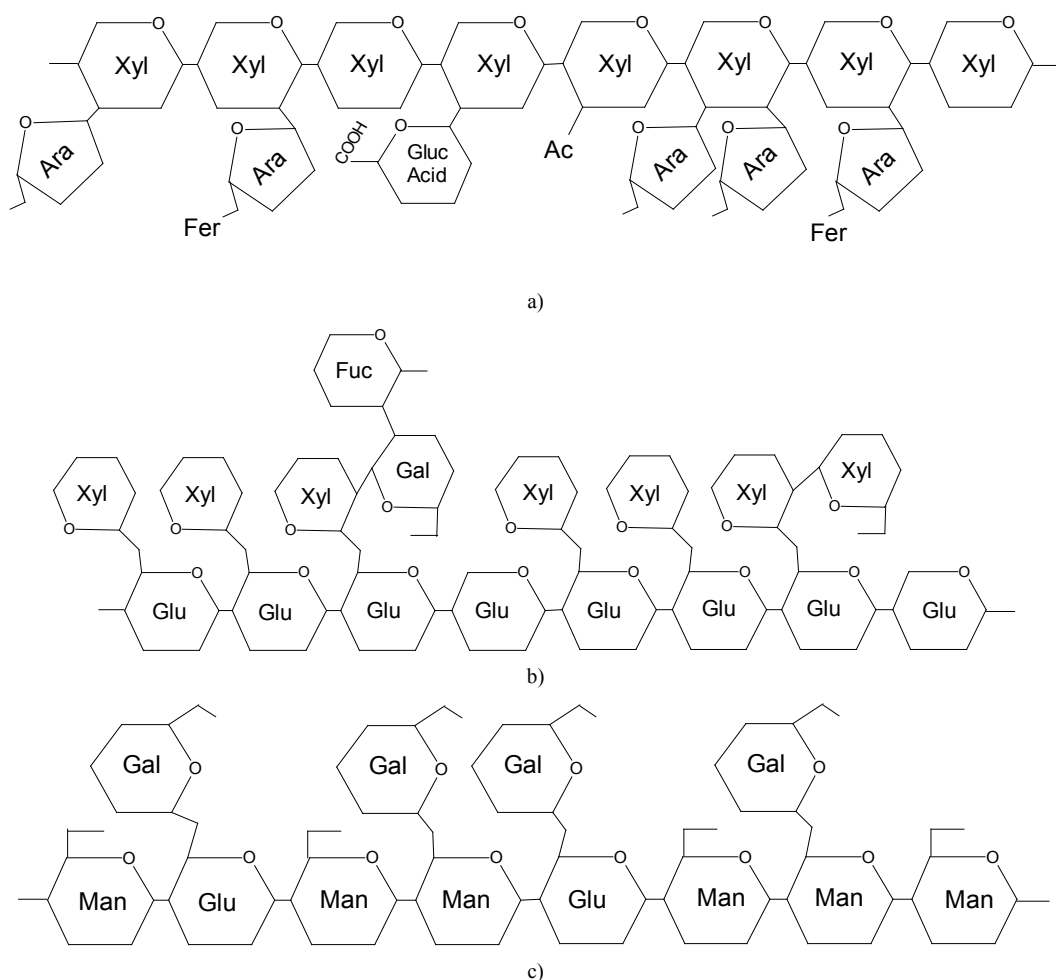
Figure 2. Schematic representation of the main types of hemicellulose in plants: a) glucuronoarabinoxylan, b) xyloglucan and c) galactoglucomannan (adapted from Scheller and Ulvskov [13]

2.1.2. Hemicellulose

Hemicellulose is a heterogeneous branched polymer with a backbone composed of glucose, mannose and xylose joined by β-(1→4) linkages in an equatorial configuration, and in some cases, linkages with uronic acid. Hemicellulose has structural and physic-chemical properties that are different from those of cellulose, pectin and starch. There are several classes of hemicelluloses, such as xylans, xyloglucans, mannans, glucomannans, arabinoxylans, glucoroarabinoxylans, 4-O-methyl-glucuronoxylans and β-(1→3,1→4)-glucans, as shown in Figure 2. In general, their structures resemble a long rod with branches and side chains linked by hydrogen bonds, and they have lower molecular weights than cellulose. In addition, hemicelluloses comprise a soluble fraction and an insoluble fraction, which can be degraded by intestinal microflora [13].

Hemicelluloses have many applications in the food industry, for example, seeds such as guar gum (galactomannans) and tamarind gum (xyloglucan) are used directly in products as bulking agents. β-(1→3,1→4)-glucans, a major component of barley and oat cells, contributes to the reduction of serum cholesterol concentrations. This compound is used in cereal products as soluble dietary fiber, and a daily intake of this hemicellulose has been recommended by the Food and Drug Administration [11], [13], [46], [47].

The hydrolysis of xylan to yield xylooligosaccharides (non-digestible oligosaccharides) using acid and enzymatic hydrolysis has been proposed to produce new prebiotics and soluble fibers. Xylooligosaccharides are used as dietary sweeteners and for food for diabetics [48].

2.1.3. Starch

Starch is one of the most abundant carbohydrates that is synthetized by plants and it can be found in roots, cereals and fruits. The most important sources of commercial starch are corn, potatoes, wheat, rice, cassava (tapioca) and sorghum, which provide the major energy sources in human and animal diets. Additionally, starch is the second major component of biomass, after cellulose. Starch is mainly composed of two homopolymers of glucose: amylose and amylopectin. Generally, normal starch (cereal starches) consists of 25% amylose and 75% amylopectin, waxy starches (maize, rice, and sorghum) consist of 0-8% amylose and high-amylose starches (maize and barley) consist of

40-70% amylose [11], [49], [50]. Furthermore, in nutritional terms, starch can be divided into the three following categories: rapidly digestible starch (RDS), slowly digestible starch (SDS) and RS (resistant starch). RDS is starch that is rapidly and completely digested in the small intestine, tends to be rapidly degraded to glucose and has a high glycemic index. SDS is starch that is digested in the small intestine at a lower rate than RDS. RS is the starch that is fermented in the large intestine by the gut microflora. This classification helps to predict the glycemic response to foods. Numerous physiological effects have been attributed to resistant starch, leading to its use as a dietary fiber and as a prebiotic ingredient, and include its contribution to preventing colon cancer and its hypoglycemic effect [51-53].

Table 1. Composition of agricultural and agroindustrial residues (% dry basis)

Biomass	Country	Cellulose	Hemi-cellulose	Starch	Pectin	Carbo-hydrate	Soluble sugars	Lignin	Protein	Ash	Ref.
Silver bird *Betula pendula*	Finland	43.1[a]	20.9[b]	-	-	-	2.6	8.2	-	-	[14]
Hardwood pine chips	United States	40.0[a]	17.0[b]	-	-	-	-	31.0	-	2	[15]
Japanese beech *Fagus crenata*	Japan	45.0	29.0	-	-	-	-	26.7	-	-	[16]
Sugi wood *Cryptomeria japonica*	Japan	43.0	23.0	-	-	-	-	32.0	-	-	[17]
Fern fronds *Pteris vittatal*	France	34.0	34.0	-	-	-	-	35.0	-	-	[18]
Switchgrass (*Panicum virgatum*)	United States	42.9[a]	23.5[b]	-	-	-	-	21.8	-	2.4	[19]
Beech wood	Turkey	45.1	31.5	-	-	-	-	22.3			[20]
Eucalyptus globulus wood	Spain	46.3	20.7	-	-	-	-	22.9	-	-	[21]
Rapeseed straw	Poland	49.2	14.6	-	-	-	-	21.6	-	-	[22]
Corn stalks	China	17.7	30.7	-	-	-	29.0	8.5	-	5.1	[23]
Corn stalks	China	22.8	43.0	-	-	-	-	15.6	-	-	[24]
Corn cobs	Spain	36.8	30	-	-	-	-	23.1	-	1.0	[25]
Corn cobs	Spain	34.3	31.1	-	-	-	-	18.8	3.3	1.3	[26]
Corn stover	United States	34.5	27.7	-	-	-	-	17.8	-	5.6	[27]
Rice husks	Spain	34.0[a]	15.9[b]	-	-	-	-	23.3	2.5	11.2	[28]
Rice husks	China	25.4	49.6	-	-	-	-	22.8	-	17.0	[29]
Defatted rice bran	Japan	-	-	-	-	54.6	-	11.1	19.3	13.6	[30]
Maize straw	China	25.5	30.3	-	-	-	-	18.3	-	3.6	[29]
Rye straw	Germany	43.6[a]	20.0[b]	-	-	-	-	22.0	-	-	[31]
Wheat straw	China	23.5	12.6	-	-	-	-	36.1	-	9.9	[23]
Wheat bran	China	38.6	21.5	-	-	-	-	23.8	-	4.1	[29]
Wheat husks	India	36.0	18.0	-	-	-	-	16.0	-	-	[32]
Babassu flour	Brazil	13.5	8.0	60.1	-	-	-	15.8	3.0	-	[33]
Sugarcane bagasse	Japan	36.4	37.2	-	-	-	-	16.8	-	-	[34]
Water lettuce biomass	China	53.0	15.0	-	-	-	-	6.0	14.0	2.3	[35]
Ginger bagasse after CO_2 extraction	Brazil	-	-	56.5	-	-	6.1	-	12.0	5	[36]
Citrus junos peels after CO_2 extraction	Japan	29.0	11.7	-	32.2	-	-	-	-	-	[37]
Cassava flour waste	Thailand	16.0	5.0	60.0	-	-	-	19.0	-	-	[38]
Cassava pulp	Indonesia	-	-	79.5	-	-	-	-	5.4	0.7	[39]
Brewer's spent grain	Portugal	-	-	-	-	50	-	-	30	5	[40]
Almond shells	Spain	26.8	32.5	-	-	-	-	27.4	-	2.8	[41]
Oil palm fronds	Malaysia	44	30	-	-	-	-	15.4	-	3.2	[42]
Empty fruit bunches	Korea	28.7	27.4	-	-	-	-	26.5	-	3.1	[43]
Oil palm shells	Malaysia	39.7	21.8	-	-	-	-	32.5	-	-	[44]
Pressed palm fibers	Brazil	-	-	-	-	48.6	-	32.1	6.3	3.1	[45]

Reported as: [a] glucose, [b] xylose, [c] nitrogen-free soluble substance, [d] crude fiber

Figure 3 shows schematic representations of amylose and amylopectin. Amylose is defined as a linear polymer of between 500 and 6000 units of α-(1,4)-D-glucopyranose with minor branches of a few molecules via α-(1,6) linkages [54]. The α-(1,4)-glycosidic bonds confer a random helical conformation of the molecule, in which the hydroxyl and hydrocarbon groups of anhydroglucose units are joined to form helices with parallel or antiparallel orientations. Analysis of the structure of amylose using X-ray diffraction revealed the presence of starch types A and B. These types are based on the hexagonal and antiparallel orientation of helical molecules, where in which type A is a helical molecule with eight molecules of water in the central region and type B has 36 water molecules in the central region. Amylopectin is a branched polymer with chains of α-(1,4)-D-glucopyranose connected by α-(1,6)-D-glucopyranose linkages. Amylopectin has a higher molecular weight than amylose and consists of between hundreds of thousands to tens of millions of anhydroglucose units. Chains of 15 to 20 units of glucose between the branching points are arranged in clusters, and they are linked by longer chains into several clusters. This polymodal distribution results in a starch granule having crystalline and amorphous regions [52], [55-57].
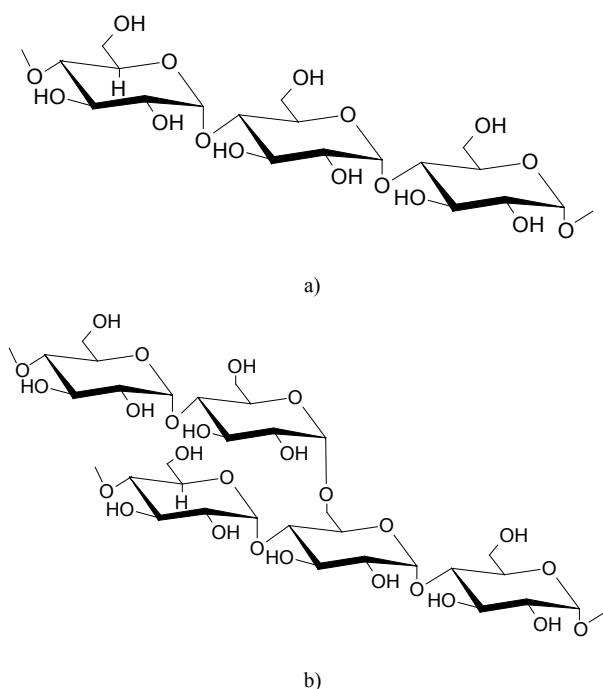

a)

b)

Figure 3. Schematic representation of the basic unit of a) amylose and b) amylopectin in starch (adapted from [57])

Acid hydrolysis of starch causes fragmentation of its chains, with the subsequent formation of oligosaccharides and monosaccharides of glucose. Due to its α-linkages, starch is easier to hydrolyze than are cellulose and hemicellulose [58]. Heating aqueous suspensions of starch granules causes them to swell, leading to disorganization of their structures, which is characterized by the loss of their birefringence, and the leaching of amylose and a portion of amylopectin, producing a viscous suspension (gelatinization). In addition, cooling this suspension promotes the realignment of linear chains of amylopectin in a process called retro gradation. Gelatinization improves the enzymatic hydrolysis of starch [11]. Commercial starches, mainly those from maize, tapioca, the potato and waxy maize, are chemically modified to improve their functional properties (viscosity, shelf stability, processing parameters, textures, appearance and emulsifiability). Enzymatic hydrolysis of starch produces non-digestible oligosaccharides, such as maltooligosaccharide, isomaltooligosaccharide, and cyclodextrin, which are used as low-calorie sweeteners by the food industry [59].

2.2. Biomasses in Brazil

Agricultural and agroindustrial residues are obtained mainly from industrial and commercial enterprises, and they are considered potential raw materials for the production of value-added chemicals. In Brazil, the soybean, corn, wheat, rice, cotton, cassava, citrus, coconut and forestry industries generate approximately 600 million tons of waste per year. Therefore, new solutions for their utilization must be proposed. Table 2 shows the current availability of the main agricultural and agroindustrial residues [60], [61].

Table 2. Availability of agricultural and agroindustrial residues in Brazil [60], [61]

Residue	1000 t_{DM}/year	Regional availability
Soybean waste (stalks, leaves)	118029	Midwest, Southeast
Corn waste (stalks, leaves)	31007	South, Southeast, Midwest
Rice straw	14102	South, Midwest
Forest residue	14511	North, South, Southeast
Corn cobs	10442	South, Southeast, Midwest
Citrus waste (bagasse, husks and seeds)	10384	n.s.
Cotton stalks	8561	Midwest
Sugarcane bagasse	6400	Southeast, Midwest, Northeast
Wheat straw	4966	South, Southeast, Midwest
Cassava bagasse	4214	n.s.
Sawdust	3950	Southeast, South
Sorghum leaves	1922	Southeast, Midwest
Rice husks	1772	South, Southeast
Coconut husks	452	North, Northeast, Southeast
Palm fibers	123	North, Northeast
Almond shells	71	Southeast, Midwest, Northeast
Sawdust	3950	Southeast, South

t_{DM}: ton of dry matter; n.s.: not specified

The residues obtained after sugarcane processing consist of leaves and immature plants, which are considered potential raw materials for second-generation ethanol production. In contrast, the residues of corn crops and those

generated by corn industries are mainly used as cattle feed. The residues generated by the palm-oil industry contain oils rich in alpha- and beta-carotenes, which are precursors of vitamin A, and have a high carbohydrate content. The extraction of palm fibers produces an oil rich in carotenoids, and the further conversion of its carbohydrate fraction into oligosaccharides and monosaccharides is a sustainable use of this residue [45], [62]. The residues generated by extracting antioxidant compounds from Brazilian ginseng roots contain high quantities of starch and cellulose. These residues can be used in hydrolytic reactions for saccharide production [63].

3. Chemical Conversion of Biomasses

Many technologies have been developed for the transformation of biomasses into valuable products for the food, pharmaceutical and chemical industries. In general, the chemical conversion of a biomass has been classified into three main categories, as follows: biochemical, mechanical and thermochemical conversion processes. The biochemical processes includes anaerobic digestion, saccharification and fermentation. Anaerobic digestion converts solid and liquid biomass into a mixture of methane and CO_2 in the absence of O_2. Saccharification and fermentation is a process that consists of the enzymatic hydrolysis of the cellulosic fraction into fermentable sugars under the mild conditions of 45-50°C and their subsequent fermentation by yeast at 37°C to yield ethanol. The mechanical processes are mechanical extractions of biomass seeds, such as canola, palm, sunflower and cotton seeds, to produce oil, which is further converted into biodiesel. Several sources have been employed to produce biodiesel, such as canola oil, palm oil, sunflower oil, soybean oil and recycled oil by mechanical processes. The thermochemical conversion processes include combustion, pyrolysis, gasification, liquefaction and chemical hydrolysis. Combustion processes are employed to produce electrical and thermal energy through burning the chemical energy stored in a biomass at temperatures of approximately 800-1000°C. Pyrolysis converts a biomass into liquid (bio-oil), coal and non-condensable gases by heating it at a temperature higher than 400°C and a pressure of between 0.1 and 0.5 MPa in the absence of air. Gasification is the partial oxidation of compounds at a high temperature, between 800 and 900°C that enhances the production of a combustible gas mixture of CO, H_2, CH_4, CO_2 and N_2. Liquefaction uses water temperatures of between 250 and 350°C and pressures of between 5 and 20 MPa to produce gases and aqueous and oily products. Chemical hydrolysis consists of the cleavage of the polymeric bonds of a biomass using acids, bases or water (hydrothermal treatment) to yield oligosaccharides with various degrees of polymerization, monosaccharides and platform molecules, such as lactic acid, glycerol and levulinic acid [64-68].

4. Hydrothermal Treatment of Cellulose, Hemicellulose and Starch in Biomasses

Hydrothermal treatment is a process in which water at a high temperature and pressure is used to catalyze hydrolytic reactions. Water is one of the most useful green solvents in the chemical industry due to its non-toxicity, non-flammability, and wide availability in nature. This type of process entails autohydrolysis, hydrothermolysis, aqueous liquefaction, liquid hot-water pretreatment, subcritical water hydrolysis and supercritical water hydrolysis. These processes use water at temperatures and pressures higher than 100°C and 0.1 MPa, respectively, which are classified as subcritical and supercritical water hydrolysis [15],[69-71]. In the hydrothermal conversion of polysaccharides, subcritical or supercritical water is used to produce insoluble oligosaccharides, oligosaccharides (DP < 10), monosaccharides, such as glucose, fructose and xylose, and polyols, such as xylitol and sorbitol. In addition, degradation products, such as phenolic and furan derivatives, which are toxic to humans and microorganisms, are formed [72]. Therefore, optimization of the hydrolytic process in terms of the monomers and oligomers yielded has been studied by several researchers for its use in the food and chemical industries [73]. In general, hydrolysis of a biomass using subcritical water (temperatures of 150°C < T < 374°C and pressures of P > Psat) for a few minutes causes the depolymerization of hemicellulose and starch, the partial depolymerization of cellulose and the improved susceptibility of the crystalline cellulose fraction to subsequent hydrolysis [36], [74]. Supercritical hydrolysis of a biomass (T > 374°C, P > 22.1 MPa) causes the depolymerization of the crystalline cellulose and the separation of the hydrolytic products of lignin [73]. Hydrothermal treatments have advantages over other conventional treatments, such as acidic and enzymatic hydrolysis, because the mild pH conditions result in fewer problems due to corrosion compared to acidic hydrolysis, the steps for the waste management and recycling acid are avoided, and the reaction conditions provide excellent selectivity with respect to the degradation of polysaccharides, resulting in a simpler procedure.

4.1. Physicochemical Properties of Water under Subcritical and Supercritical Conditions

Subcritical water, which is also called superheated water or pressurized hot water, is defined as water with a temperature of between 100°C and 374°C (critical temperature) and a pressure higher than that of its vapor saturate, up to 22.1 MPa, to maintain the water in its liquid state. Supercritical water is a fluid with a temperature and pressure higher than those at its critical point (374°C, 22.1 MPa) [75]. Figure 4 shows the subcritical and supercritical regions of water [76]. The physicochemical properties of subcritical and supercritical water, such as the density, viscosity, dielectric constant and ionic product, vary

considerably with the increase of temperature and pressure compared with the properties under normal conditions (Figure 5).
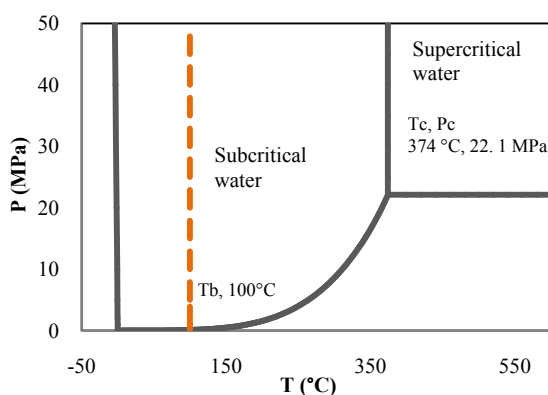

Figure 4. Pressure-temperature phase diagram of water: Tc = 374°C (critical temperature), Pc = 22.1 MPa (critical pressure), Tb = 100°C (boiling point). (data extracted from [76])

The physicochemical properties of water depend strongly upon its temperature; for example; ionization of hydrogen bonds at high temperatures causes a decrease in the dielectric constant from 35 at 200°C to 10 at the critical temperature of 374°C. This feature makes water in subcritical and supercritical states suitable for organic reactions and the miscibility of organic compounds increases with temperature. Moreover, the content of the ionic product ($K_w = [H^+][OH^-]$) of water is three orders of magnitude higher under these conditions than its value under normal conditions, so that it acts as acid-base catalyst. In addition, water's density decreases with the increase in temperature, from 1000 kg/m^3 at 25°C to 820 kg/m^3 at 250°C and 25 MPa. The combination of these phenomena causes the dependence of solvation power on temperature, in which high temperatures, near the supercritical point, lead to a high level of water dissociation and reduced density. These variations affect the kinetics of chemical reactions and the selectivity of a reaction within a network of reactions, and in many cases are considered catalytic [77], [78].

4.2. Hydrothermal Treatment of Lignocellulosic Biomasses

Different types of lignocellulosic biomasses were proposed as raw materials for the recovery of value-added compounds. This selection was based mainly on their abundance in the geographic region of study and their availability for conversion into value-added products. Treating a biomass with subcritical water at mild temperatures simultaneously catalyzes a number of chemical reactions, such as the progressive degradation of polysaccharides into xylooligomers, xylose monomers and degradation compounds (such as acetic acid and organic acids that decrease the pH of the medium). Higher temperatures and reaction periods promote the fragmentation of oligomers into monomers until a maximal monomer

concentration is reached, and the formation of dehydration products such as furfural. The acidic medium promotes the partial solubilization of the soluble lignin without considerable modification of the insoluble cellulose and lignin. The depolymerization behavior of hemicellulose at temperatures below 200°C has allowed investigation into separating it from the other structural components of the biomass, such as cellulose and lignin [28]. Tables 3 and 4 show the results of experimental studies of subcritical and supercritical hydrolysis of model compounds (cellulose, hemicellulose, and starch) and agricultural and agricultural residues, respectively.
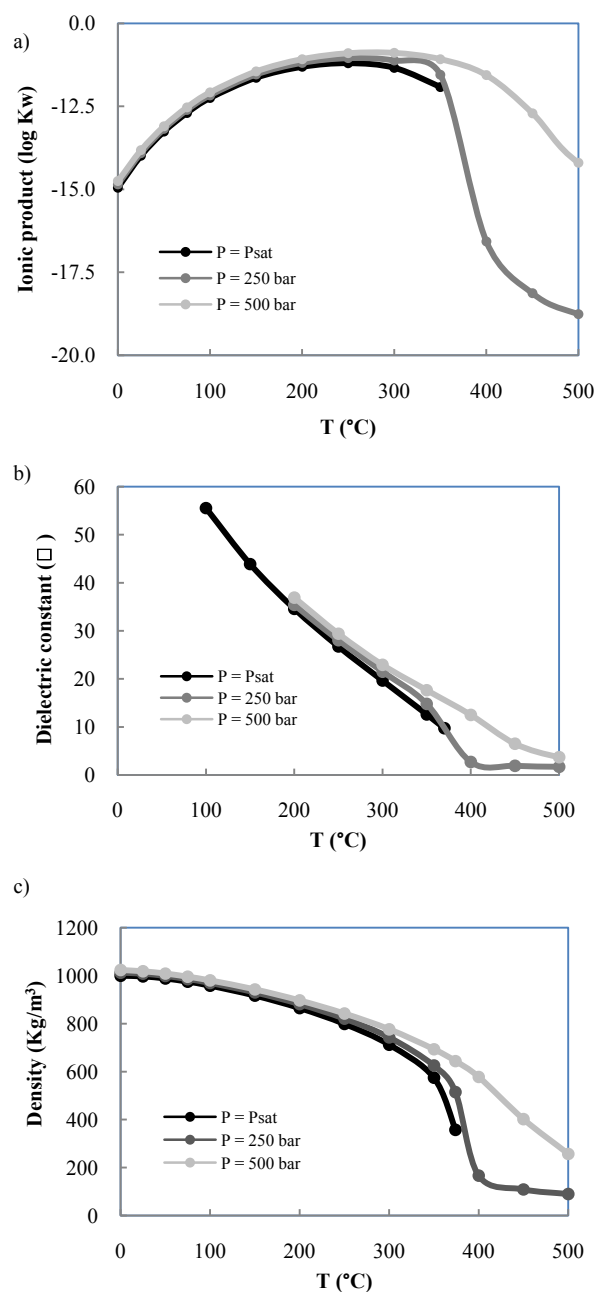

Figure 5. Physicochemical properties of water under subcritical and supercritical conditions (data extracted from [76],[79],[80])

Table 3. Subcritical hydrolysis of model polysaccharide compounds in a biomass

Compound	Size	Temp. (°C)	Pressure (MPa)	Cata-lyst	τ	S/F	Flow rate	System	Reactor dimension	Optimal conditions	Ref.
Cellulose	20-100 μm	320-400	25	None	0.05-10 s	2% w/w	10 mL/min	Continuous	Tubular reactor, 316 SS	OS: 72.2% (400°C, 0.01 s) MS: 42.6% (400°C, 0.15 s) 25.3% (350°C, 3.5 s)	[92]
Cellulose	40-100 μm	200-400	25	None	2 min	120 mg/5.7 mL	10 mL/min	Semi-continuous	5.7 mL, 0.85 cm i.d. x 10 cm length, 316 SS	MS: 18% (300°C, 340 s)	[93]
Cellobiose	n.s.	225-275	10	None	0-263 s	0.003 M	n.s.	Continuous	Tube reactor of various L/D, 316 SS	MS: Glucose: 31% (225°C, 263 s) DP: 5-HMF: 18%, Glycolaldehyde: 9% (275°C, 263 s)	[94]
Cellulose	n.s.	380 → 280-360	22→10	None	16 s → 15-50 s	60 mg/2.5 mL	-	Batch	5 mL, 7 x 2.5mm i.d., 13 cm length. 316 SS	OS: 28.1% (380°C, 16 s) MS: 39.5% (280°C, 44 s) OS: 25% (380°C, 0.25 s)	[95]
Cellulose	n.s.	250-380	25	None	0.25-0.75 s	2.5% w/w	Re: 1904-5500	Continuous	390 μL, high-alloy stainless steel (SAE designation type 4744)	MS: Glucose: 18% (360°C, 0.50 s) Fructose: 4% (360°C, 0.50 s) DP: 5-HMF: 5% Furfural: 2% (360°C, 0.75 s)	[81]
Cellulose	75-106 μm	280-380	10	None	0-60 min	n.s.	10-40 mL/min	Semicontinuous	n.s.	OS: Oligomers with DP of 28 (270°C)	[82]
Xylan	n.s.	180-300	> Psat	None	0-30 min	2 g/100 mL water	-	Batch	250 mL, 316 SS, 65 mm i.d. x 70 mm	MS: 20% (220 °C, 2 min)	[96]
Xylan	n.s.	200	> Psat	With and without CO_2	15 min	0.03 g/3 g acid solution	-	Batch	3.6 mL, 316 SS	MS: 5% (without CO_2) 15% (with CO_2)	[97]
Starch	n.s.	200	> Psat	With and without CO_2	15 min	0.03 g/3 g acid solution	-	Batch	3.6 mL, 316 SS	OS 90.5% (without CO_2) 34% (with CO_2) MS: 4.2% (without CO_2) 54% (with CO_2)	[97]

OS: oligosaccharide, MS: monosaccharide, DP: degradation product (dehydration and decomposition)   n.s.: not specified

Table 4. Subcritical hydrolysis of agricultural and agroindustrial residues

Biomass	Size	Temp. (°C)	Pressure (MPa)	Catalyst	τ	S/F	System	Reactor dimension	Optimal conditions	Ref.
Bean dregs	< 140 mesh	220-300	5.4-9.4	CO_2	2-10 min	1 g /200 mL	Batch	200 mL reactor, 316 SS	OS and MS 50% cellulose (without CO_2) 65% cellulose (with CO_2) (300°C, 360 s)	[98]
Rice husks	n.s.	180	> Psat	None	15-40 min	1 kg/8 kg water	Batch	n.s.	OS: 70% xylan (30 min) MS: 9% xylan (30 min)	[28]
Corn stalks (pre-washed)	< 40 mesh	384 → 280	> Psat	None	16-24	40 mg / 2.5 mL water	Batch	5 mL (i.d. 7 x 2.5 mm, length = 130 mm)	SupW OS: 17.2% d.b. MS: 23.24% d.b. (384°C, 17 s) SubW OS: 11.41% d.b. MS: 27.4% d.b. (280°C, 27 s)	[23]
Wheat straw (pre-washed)	< 40 mesh	384 → 280	> Psat	None	16-21	20 mg / 2.5 mL water	Batch	5 mL (i.d. 7 x 2.5 mm, length = 130 mm)	SupW OS: 10.37% d.b. MS: 1.60% d.b. (384°C, 19 s) SubW OS: 3.02% d.b. MS: 6.67% d.b. (280°C, 54 s)	[23]
Barley husks	> 1 mm	190-220	> Psat	None	0.55-0.88 h	1 kg/10 kg water	Batch	3.8 L 316 SS	OS: Xylo-OS: 18% d.b. Ara-OS: 2.2% d.b. (200°C, 0.7 h) MS: 4.5% d.b. (220°C, 0.7 h)	[99]
Sugarcane bagasse	> 40 mesh	200	> Psat	None	0-20 min	0.5-10 g/100 g water.	Batch	9 mL	OS: 86% xylan MS: 13% xylan (S/F: 0.5, t: 10 min)	[100]
Empty fruit bunches	> 50 mesh	160-180	> Psat		0-40 min	1 g / 8 mL	Batch	9 mL, 316 SS	MS: Xylose: 18 g/L (180°C, 10 min) Glucose: 0.8 g/L (180°C, 10 min)	[43]
Eucalyptus globulus wood	> 8 mm	180-220	> Psat	None	0-1 h	n.s.	Batch	0.6 and 3.8 L, 316 SS	OS: 62% xylan (212°C, 0.3 h for 0.6 L, 0.9 h for 3.8 L) MS: 8% xylan (212°C, 0.3 h for 0.6 L and 0.9 h for 3.8 L)	[21]
Corn cobs	> 0.3 mm	179	> Psat	None	23 min	625 g/5 L	Batch	10 L, Material: ANSI 304 and SS 316	OS: 64% initial xylan, 11% initial cellulose MS: 9% initial xylan, 5% initial cellulose	[41]
Almond shell	> 300 μm	179	> Psat	None	23 min	833 g/5 L	Batch	10 L, Material: ANSI 304 and SS 316	OS: 56% initial xylan, 3% initial cellulose MS: 10% initial xylan, 2% initial cellulose	[41]

OS: oligosaccharide, MS: monosaccharide

Table 4.   Subcritical hydrolysis of agricultural and agroindustrial residues (Cont.)

Biomass	Size	Temp. (°C)	Pressure (MPa)	Catalyst	τ	S/F	System	Reactor dimension	Optimal conditions	Ref.
Almond shell	> 300 μm	179	> Psat	None	23 min	833 g/5 L	Batch	10 L, Material: ANSI 304 and SS 316	<u>OS</u>: 56% initial xylan, 3% initial cellulose <u>MS</u>: 10% initial xylan, 2% initial cellulose	[41]
Rice husk	> 300 μm	179	> Psat	None	23 min	833 g/5 L	Batch	10 L, Material: ANSI 304 and SS 316	<u>OS</u>: 30% initial xylan 12% initial cellulose <u>MS</u>: 6% initial xylan, 1% initial cellulose	[41]
Ginger bagasse after CO₂ supercritical extraction	n.s.	176-200	15	CO₂	0-15 min	3 g/7 g of water	Batch	5 mL	<u>OS</u>: 10000 – 100000 Da: 30-40% hydrolyzate (176°C) 160 – 8400 Da: 60-75% hydrolyzate (188°C) <u>MS</u>: 18% starch (200°C, 11 min)	[36]
Beet fiber	n.s.	160-180	> Psat	None	5-15 min	3.8 g/35 g of water	Batch	50 mL	<u>OS</u> 84% d.b. (160°C, 12 min)	[101]

OS: oligosaccharide, MS: monosaccharide

4.2.1. Hydrothermal Treatment of Cellulose

Several studies of the depolymerization of cellulose in subcritical and supercritical water have been performed at temperatures above 200°C and pressures above its saturated pressure, and particularly in near-critical water, with the objective of providing a suitable reaction environment for the breakdown of its glycosidic bonds, which are highly resistant to chemical attack [15], [16], [81-95]. Hydrolysis of cellulose results in oligomers with various degrees of polymerization, including insoluble oligomers (DP < 200) and soluble oligomers (DP < 6).

Short residence times promoted the formation of oligosaccharides [81], [92]. These oligosaccharides are further converted into a monosaccharide, glucose, which is epimerized to form fructose. Glucose is further degraded to form several compounds, such as 5-HMF, erythrose, glycolaldehyde and acidic organic compounds. Insoluble residues of cellulose with predominantly aromatic carbon structures are also formed [73], [85], [102]. The scheme of the reaction pathways is shown in Figure 6.

Moeller *et al.* [85] studied the effect of the degree of cellulose crystallinity (38% to 74% crystallinity index) on its conversion and the saccharide yield at 205°C. A high level of conversion (approximately 40%) was obtained using cellulose with low crystallinity values (33% and 42% crystallinity index) due to the presence of larger amorphous regions. Moreover, no effect of the crystallinity on glucose and 5-HMF formation was found.

Tolonen *et al.* [81] studied the degradation of cellulose using water in sub- and supercritical media (280-380°C). The decrease of the dielectric constant of water as well as those of the polar solvents and the increase in the ionic product of water with values higher than those under normal conditions increased the solvation of hydrophobic compounds. The products obtained were insoluble oligosaccharides, water-soluble oligosaccharides, fructose, glucose, 5-HMF and furfural. The highest level of oligosaccharide formation (25% oligosaccharides) was attained at the highest temperature and the shortest reaction period (380°C, 0.25 s). Additionally, other researchers have reported that cellulose dissolution occurred at temperatures greater than 250°C [73], [91-93], [103].

A comparative study of the hydrolysis of cellulose under subcritical conditions (280°C, 40 MPa), supercritical conditions (400°C, 40 MPa), and using a combined treatment was performed to evaluate the variation in the reaction rate behaviors. Hydrolysis in supercritical media produced the highest yield of hydrolyzate compounds (47%, < 1 min), the rate of formation of oligomers was higher than the rates at which monomers and fragmentation products of cellulose, such as erythrose and glycolaldehyde, were formed. Subcritical hydrolysis resulted in the lowest yield (22.4%, 4 min), and the rate of formation of monomers was higher than

the rates at which oligomers and dehydration products, such as furfural, 5-hydroxymethylfurfural and levoglucosan (14.7%) were formed. The yield of monosaccharides in the subcritical medium was greater than that in the supercritical medium, indicating that the reaction mechanisms were different. The combined hydrolysis of cellulose using supercritical and subcritical media resulted in high yields of monosaccharides and oligosaccharides (66.8%) and low levels of fragmentation and dehydration products, such as furfural, 5-hydroxymethylfurfural (10.7%), erythrose and glycolaldehyde (9.7%) [65].

The use of an integral process of supercritical hydrolysis (384°C, 22 MPa) followed by subcritical hydrolysis (280°C, 22 MPa) was studied by Zhao *et al.* with the aim of maximizing the monosaccharide yield from the cellulose in corn stalks because the reaction rate of oligosaccharides is higher than the reaction rate of monosaccharides under supercritical conditions close to the critical point [23], [95], [102], [104], [105]. The maximum production achieved in the supercritical medium was 17.2% for oligosaccharides and 23.1% for monosaccharides in the short period of 17 s. The subsequent treatment at 280°C in the subcritical medium increased the production of monosaccharides from 23.2 to 27.4%. No xylose groups from hemicellulose were detected, indicating that they had been degraded in the supercritical medium.

The use of CO_2 as a "green" catalyst for hydrolysis in subcritical and supercritical media has been considered due to the formation of carbonic acid, which accelerates the reaction process. Investigations using CO_2 showed that the rate of monomer formation increased and the monomer yields were higher than those obtained using only water. An advantage of using CO_2 is that it can be easily separated from the product and can be recycled for use in the process [72], [97], [106], [107].

4.2.2. Hydrothermal Treatment of Hemicellulose

Like cellulose, hemicellulose contains a fraction that is susceptible to chemical attack, which is responsible for the formation of hydrolyzed products. The hydrolysis of hemicellulose using hydrolytic processes produces xylooligosaccharides with various structures and compositions. The variability depends primarily on the hemicellulose source and the hydrolytic process used. Hydrothermal treatment at temperatures of approximately 200°C produces a slightly acidic medium due to the partial cleavage of the acetyl groups of hemicellulose, yielding xylooligosaccharides of high molecular weight with a significant content of acetyl and uronic groups, which confer high solubility in water. Additionally, there is a partial depolymerization of cellulose and lignin, which can be separated for subsequent processing [108], [109]. In general, hemicellulose is hydrolyzed into high molecular weight oligomers, low molecular weight oligomer, xylose, furfural and degradation products, as shown in Figure 7 [96], [97].
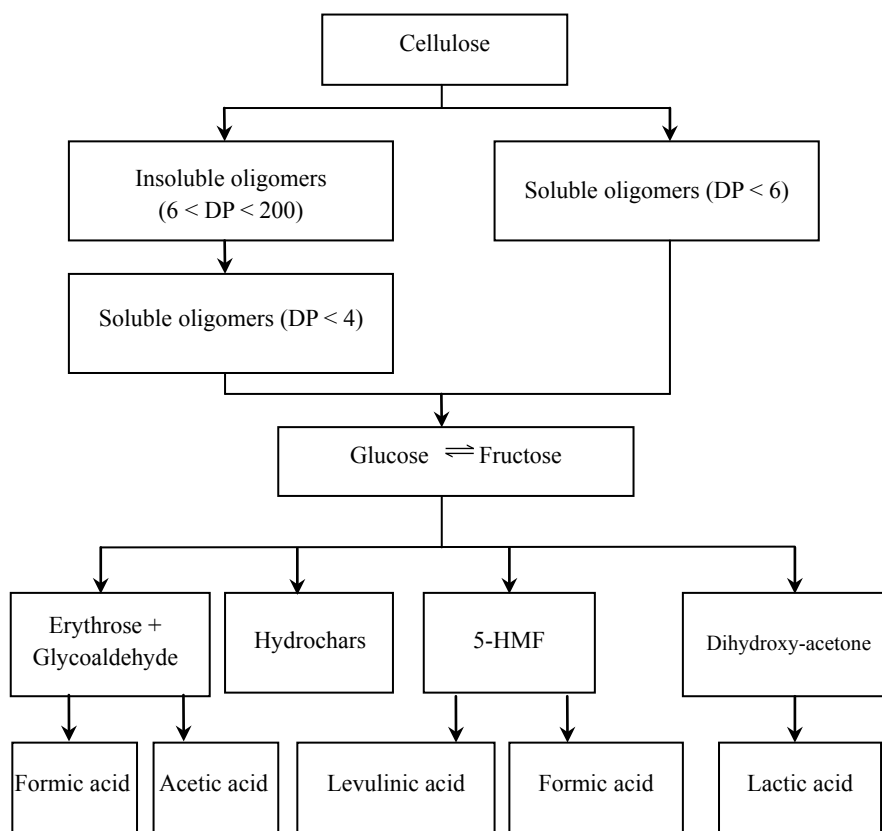

Figure 6. Main reaction pathways of cellulose hydrolysis (adapted from [73], [85], [102])
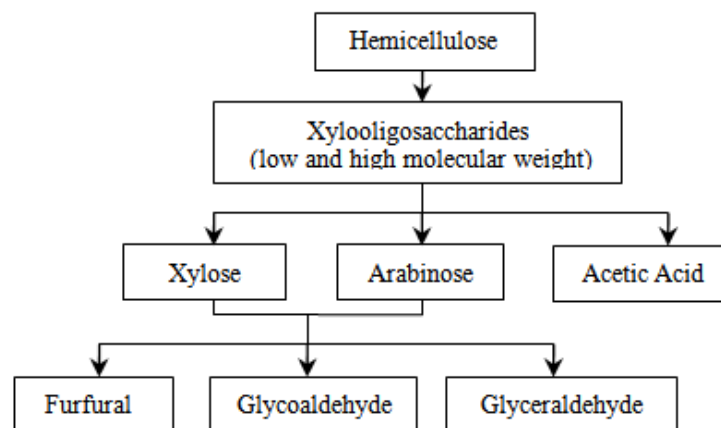
Figure 7.   Main reaction pathway of hemicellulose hydrolysis (adapted from [96])

Nabarlatz *et. al*. [41] studied the hemicellulose hydrolysis of six different lignocellulosic materials: corn cob, almond shell, olive stone, rice husk, wheat straw and barley straw and they found that xylooligomers formed were mainly 4-O-methylgucuronoxylan with different degrees of substitution of acetyl groups. Additionally, each raw material presented different yield of xylooligosaccharides and it was proportional with the quantity of acetic acid formed from acetyl groups and initial xylan content resulting in highest yield for corn cob (60% initial xylan) and lowest yield for rice husk (30% initial xylan) due to its lowest acetyl content. It was found that substrate with high lignin content as olive stone and almond shell resulted in low formation of oligossacharides from cellulose and polymerization of lignin. So, substrates with high lignin content and high acetyl groups in hemicelluloses lead on highest yield of xylooligosaccharides.

Garrote *et. al.* [99] studied the autohydrolysis of hemicellulose in barley husks at a temperature range between 190 and 220°C. The breakdown of hemicelluloses chains conducted at temperatures up to 200°C resulted on the highest concentrations of xylooligosaccharides (18% d.b.) and arabinosaccharides (2.2% d.b.), and the cleavage of substituents such as acetyl groups and uronic acid groups. The dissolution of these groups promoted an increment of hydrogen ions which led the hydrolytic degradation of polymer chains into oligosaccharide (xylo- and arabinooligosaccharides), monosaccharides (xylose, arabinose and glucose), furfural and non-saccharides compounds. The maximum concentration of xylose and arabinose were 3% d.b. and 2.2% d.b, respectively at 220°C. These results showed that temperatures up to 200°C favored the formation of oligosaccharides. Furthermore, the amount of degradation products of furfural, and non-saccharide compounds comprised 18% d.b. Among these non-saccharides compounds, hexanoic acid, octadecanoic acid, oleic acid, tetradecanoic acid and dehydroabietic acid were identified and they can be used as surfactants in cosmetics. Additionally, phenolic compounds such as vanillin, 3,4-dihydroxybenzaldehyde, 3-methoxy-4-hydroxybenzoic acid, and cinnamic acid can be used as food antioxidants. A purification of these non-saccharide compounds can increase the food grade of the oligosaccharides.

Jacobsen *et al.* [100] studied the dissolution of the hemicelluloses to 200°C and various S/F ratios from 0.5 to 10 in a batch system of 9 mL. It was generally observed that the initial pH decreased from 7 to 4.5, and continuously decreased with increasing reaction time. Additionally, high pH values were obtained at high ratios of S/F due to the increment in amount of acetic acids and uronic acids which promotes the reaction rate of hemicellulose hydrolysis. As obtained in other researches at this temperature, hydrolysate products consisted mainly of oligosaccharides and monosaccharides, being oligosaccharides concentration higher than monosaccharides concentration. Additionally, the lowest S/F ratio of 0.5 resulted in highest concentration of total sugars (86% of initial xylan) compared to S/F ratio of 10 (75% of initial xylan) showing that not only the effect of pH affects hydrolytic dissolution of the hemicellulose.

The non-isothermal hydrolysis of hemicellulose fraction of wood chips from 180 to 220°C in two reactors of 0.6 and 3.8 L showed a maximum yield of xylooligosaccharides (62% of initial xylan) at 212°C. Additionally, there was a continuous increment of xylose concentration with reaction time. Furthermore, saccharides yield presented similar behavior for both reactor capacities as its kinetic constants were close for both processes. In addition, there was a negligible depolymerization of cellulose and lignin showing selectivity for hemicellulose hydrolysis [21].

Vegas *et al.* [28] have studied the subcritical hydrolysis of rice husks at 180°C and different residence times using severity coefficient (3.5-4.0) as a measurement of treatment. It was observed an initial formation and further decomposition of xylooligosaccharides during reaction course. The maximum xylooligosaccharide concentration was obtained with severity coefficient (Ro) of 3.9. Relating to the xylose constituents, arabinosyl and acetyl substituents were less resistant than uronic substituent due to hydrolytic cleavage. Additionally, it was found that oligomers with DP < 25 constituted 90-94% of total xylooligosaccharides even at low severities.

4.2.3. Hydrothermal Treatment of Starch

Few applications of subcritical hydrolysis of starch have been founded in literature. From the obtained information, the main products of starch hydrolysis in subcritical medium are maltodextrins, dextrins and glucose; which have application in cosmetics, pharmaceutical and food industry. The subcritical hydrolysis of ginger bagasse at 200°C and 15 MPa resulted in highest degree of hydrolysis of 97.1% at a time of 15 min and the highest yield of reducing sugars of 18.1% at a time of 11 minutes. Different mixtures of oligosaccharides with different molecular weight distribution were obtained depending on reaction time [36]. Another application is the subcritical hydrolysis of potato starch and cassava starch for production of indigestible dextrin (ID). The highest ID for potato starch was obtained at 190°C and 2 min (14 %), and highest ID for cassava starch was obtained at 200 C and 2 min (6%) [110].

5. Conclusions

Hydrothermal treatment of agricultural and agricultural residues produces value-added products that have numerous applications, either as intermediates for chemical industry or as raw materials for food, cosmetic and pharmaceutical industry. One of the most interesting applications in the food industry is the formation of oligosaccharides that can be used as dietary fiber in food products or monosaccharides that can then be transformed into polyols. The conversion of cellulose, hemicellulose and starch using water in subcritical and supercritical states takes advantage of the changing properties of water at temperatures and pressures above normal conditions. Thus, depending on the polysaccharide type certain conditions promote highest oligosaccharides and monosaccharides formation. Based on hydrolysis studies of model compounds and lignocellulosic materials, starch and hemicellulose components are preferred to be converted at temperature less than 200°C, while cellulose is most suitable to be converted at temperature higher than 200°C for recovery of oligosaccharides and monosaccharides.

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