

Hydrothermal Treatments Applied to Agro- and Forest-Industrial Waste to Produce High Added-Value Compounds

María E. Vallejos,* Fernando E. Felissia, and María C. Area

Agro- and forest-industrial wastes are abundant and low cost sources of carbohydrates and phenolic compounds, which can be converted into biofuels, biomaterials, and high added-value compounds by different pathways in small and large biorefineries. The development of technologies based on hydrothermal treatments could improve the utilization of lignocellulosic wastes through the separation of its components (cellulose, hemicellulose, lignin, and extractives) in sequential processes. The adopted technologies for the separation and conversion of these lignocellulosic wastes into synthesis intermediates or products of high added value represent an important part of the total production cost. Low liquid to solid ratios and mild temperatures in the pre-treatment are interesting ways of reducing energy costs, subsequently economizing both steam and electricity. This work focuses on the advantages of using low liquid to solid ratios in the hydrothermal treatment of different agro- and forest-industrial wastes, paying particular attention to the performance of separation, purification, and conversion of hemicelluloses.

Keywords: Biorefinery; Agro- industrial wastes; Forest-industrial wastes; Sugarcane bagasse; Sawdust; Pine; Eucalyptus; Pre-treatment; Hemicelluloses; Liquid to solid ratio; Economics

Contact information: Programa de Celulosa y Papel - Instituto de Materiales de Misiones (CONICET-UNaM), Facultad de Ciencias Exactas Químicas y Naturales, 1552 Félix de Azara St. (3300), Misiones, Argentina; *Corresponding author: mariaxvallejos@gmail.com

AGRO- AND FOREST-INDUSTRIAL WASTE AS RAW MATERIAL FOR A BIOREFINERY

Relevance of Agro- and Forest-Industrial Waste

Biorefineries are analogous to petroleum refineries, which produce multiple fuels and products from petroleum, but instead use biomass as raw materials. Biorefinery technology is an alternative to the petroleum-based industry for energy, chemical, and material production from unconventional raw material. Given its renewable nature and low associated pollution, lignocellulosic biomass can be regarded as an important and sustainable source of carbohydrate (cellulose and hemicelluloses) fuel, cellulosic pulp, biomaterials, and a variety of chemicals.

Lignocellulosic residues generated by the agro-industry are available in large quantities at low cost. The chemical, thermochemical, and biological conversions of this waste into its main components allow the production of chemical intermediates for the manufacture of various products. The use of forest and agricultural lignocellulosic residues as raw materials to generate high value added products is important because of their renewable nature and high availability (Area and Vallejos 2012).

These raw materials are suitable for the installation of small biorefineries. Small biorefineries are not capital intensive and have lower transportation cost, lesser movements of liquid and solid streams, and lower heat transfer problems than large ones (Clauser *et al.* 2016).

Agricultural crop residues such as the straws of wheat, barley, rice, maize, oats, rye, cotton, sugarcane bagasse, and others represent an enormous underutilized resource that has great potential as raw material for chemicals and other technical products. Straw, the aboveground part of the cereal plant, comprises about half the total dry weight of the crop. Straw is the most useful by-product of cereal production, and it has been used for feeding livestock, bedding, growing mushrooms, *etc.* Straw is generally burned or directly ploughed into the field as a fertilizer. Straw and other fibrous cereal by-products amount to approximately 3000 million tons per year. Because of its enormous quantity, the utilization of straw to the utmost extent is now demanding attention in the major cereal-growing areas of the world (Yuan and Sun 2010).

Because of their high silica content, stationality of growing, and other issues, some problems related to the use of non-wood fibers include collection, transportation, storage, and handling. The main problem of agricultural wastes is their availability (limited to a time of year), which creates a need for proper storage to avoid deterioration. Sugarcane bagasse (*Saccharum officinarum*) is the lignocellulosic waste from the sugar industry. Its grow time is short, with a 1-year rotation. Wheat straw (*Triticum aestivum*), corn stalks (*Zea mays*), cotton stalks (*Gossypium*), and rice straw (*Oryza sativa*) are also monocots of short grow time with a 1-year rotation. Fibers are wastes of cereal harvesting (Area and Popa 2014).

Sugarcane bagasse is an abundant and renewable raw material, ideal for implementing the concept of biorefinery because it is possible to obtain multiple products from the diverse processes. While its capabilities are being intensively studied, there are still many potential products to be investigated and several processes to be optimized (Area *et al.* 2012).

Sugarcane bagasse is an important agro-industrial byproduct in Brazil, India, China, and Thailand. These four countries account for approximately 70% of the global sugarcane production (FAOSTAT 2016). Sugarcane bagasse is an important lignocellulosic waste in South America, where it accounts for approximately 50% of the global sugarcane production (~ 0.8 billion tons in 2012) (FAOSTAT 2016). Brazil, the world's largest producer of sugarcane, produced approximately 700 million tons during the 2010 to 2011 harvest (260 to 290 kg bagasse/ton sugarcane at 50% moisture) (CONAB 2011; Rocha *et al.* 2012). It is usually burned in sugar and ethanol mills to produce heat and electricity. In Brazil, the ethanol yield per hectare of sugarcane is actually 6000 L/ha, but it could reach 10,000 L/ha if 50% of the generated bagasse was converted to "cellulosic ethanol" (Rocha *et al.* 2012).

The use of industrial wood waste for power generation is difficult when sawmills are geographically dispersed. Therefore, prices are low enough that it is typical to burn them in open air, generating environmental and social problems. Sawdust is one of the most important products of the primary processing of wood. The application of chemical conversion treatments for the fractionation of sawdust's main components could lead to the better use of raw materials and the creation of high value products to complement commodities. One of the advantages of working with sawdust is that it does not need mechanical pre-treatments due to its fine particle character. However, it is difficult to

establish exactly the species and age of the raw material, as sawmills typically work with wood from different origins, generating a mixture of sawdust (Stoffel *et al.* 2014).

Eucalyptus is one of the main species cultivated in South America for pulp and timber. Although eucalyptus plantations for pulp are harvested under the age of 10 years, sawmills use older trees to obtain wood of high volume and strength. The forest industry is a predominantly productive entity in northeast Argentina and generates large amounts of waste such as sawdust, bark, and other wood residues. About 50% of industrially processed wood ends as waste, which generates 1.5 million dry tons of wood wastes per year, which are not properly exploited (Uasuf and Hilber 2012).

Due to their higher content of acetyl groups to provide an increase in catalyst concentration in the reaction medium, hardwoods and grasses are more favorable than conifers for hydrothermal processing (Ruiz *et al.* 2013; Vallejos *et al.* 2015a, 2015b). Most reports about hydrothermal treatments of eucalyptus refer to *Eucalyptus globulus*, a species used in Europe for pulping and now studied for bioethanol production (Mendes *et al.* 2009; Romani *et al.* 2010; Romani *et al.* 2011; Vila *et al.* 2011; Romani *et al.* 2012; Vila *et al.* 2013; Sun *et al.* 2014).

Chemical and Anatomical Characteristics of Agro- and Forest-Industrial Waste

The structural complexity of lignocellulosic materials hinders enzymatic hydrolysis because their conversion to bioethanol requires a pre-treatment step. The tree log is composed histologically of three parts: xylem or wood, cambium, and bark. In xylem, fibers are arranged in a typical concentric structure. In contrast, grasses have stems with numerous vascular bundles scattered in a ground tissue of parenchyma storing cells, which is surrounded by a strong and dense epidermis (Area and Popa 2014).

Cellulose distribution in cell walls has a regular pattern. Cellulose content increases from the outer layer to the inner layer. The cellulose content is highest in the secondary wall, especially in S2 and S3. The middle part of S2 possesses a lower concentration of hemicelluloses than the inner and outer parts of the secondary wall. The S1 and S2 boundary is highest in xylans and mannan content. Lignin is generally distributed with hemicelluloses in the spaces of intercellulose microfibrils in primary and secondary walls, and in middle lamella as a cementing component to connect cells and harden the cell walls of xylem tissues. About 60 to 80% of the total lignin is located within the secondary wall (Xu 2010).

The outer cell walls of the epidermis on the aerial parts of all herbaceous plants are coated with a multi-layered structure known as a cuticle. It is composed of a top coating of wax, a thick middle layer containing cutin embedded in wax, and a lower layer formed of cutin and wax blended with the cell wall substances pectin, cellulose, and other carbohydrates (the cuticular layer). Cutin is a polymer consisting of many long-chain fatty acids that are attached to one another by ester linkages, which creates a rigid three-dimensional network. Waxes are complex mixtures of long-chain acyl lipids that are extremely hydrophobic (Taiz *et al.* 2015).

Cellulose, hemicelluloses, and lignin are the main components of fibers. Lignin is an amorphous, aromatic, water insoluble, heterogeneous, three-dimensional, and cross-linked polymer. Hemicelluloses are a mixed group of both linear and branched heteropolymers mainly comprising five monomeric sugars. These sugars are D-glucose, D-mannose, D-galactose, D-xylose, and L-arabinose.

The degree of polymerization (DP) of hemicelluloses is 100 to 200, which is much lower than that of cellulose. The major hemicelluloses of hardwoods and gramineous plants are glucuronoxylan and glucomannan, followed by galactoglucomannans, arabinoxylans, and glucuronoarabinoxylans. Cellulose is a polymer consisting of linear β (1-4) D-glucopyranosyl units. The cellulose chains have a strong tendency to aggregate into highly ordered structural entities. This is due to the uniformity of their chemical constitution and spatial conformation. The DP of cellulose is often stated to be 5000 to 10000 glucopyranose units. The smallest cellulosic strand, with an average width of 3.5 nm in the mature cell wall, is the elementary fibril. These fibrils are organized into strands known as microfibrils (5 to 30 nm wide), which are visible under an electron microscope. The diameter of microfibrils depends on the source of cellulose and the positions of the microfibrils within the cell wall. Microfibrils are combined to form greater fibrils and lamellae and are embedded in a hemicelluloses-lignin matrix within the cell wall in wood fibers (Area and Popa 2014).

Sugarcane bagasse is composed of 32 to 45% cellulose, 19 to 24% lignin, 27 to 32% hemicelluloses (mainly xylans), and minor amounts of extractives and inorganic compounds (Area *et al.* 2009; Novo *et al.* 2011; Rocha *et al.* 2012; Vallejos *et al.* 2012). The wide compositional variation in cellulose and lignin content reported in the literature for sugarcane bagasse could be attributed to the complexity and variability of the lignocellulosic material by itself, but also to the presence of experimental errors in the analytical methods. The detailed chemical composition (as a percentage by weight on oven-dry bagasse, % o.d.b.) includes 43.1% glucans, 23.8% xylans, 1.7% arabans, 1.7% acetyl groups, 21.3% lignin, 2.1% extractives in alcohol-benzene, 2.7% extractives in hot water, and 1.5% of ash components (Vallejos *et al.* 2015a).

Xylans from xylan rich agro-industrial waste are the most abundant hemicellulosic polymers and have enormous potential for industrial applications. Freeze-dried xylo-oligosaccharides and hydrolysates containing high xylose contents from xylans rich agro-industrial waste can be used in a wide range of applications, including their conversion to xylose, xylitol, furfural, succinic acid, additives in papermaking, ethanol, hydrogels, films, and bio-based polymers (Garrote *et al.* 1999; Carvalheiro *et al.* 2004; Sedlmeyer 2011; Huang *et al.* 2016; Vargas *et al.* 2016).

The deepening of knowledge about water prehydrolysis has a broad range of applicability to present agro- and forest- waste utilization and is of fundamental interest to the development of new processes.

HYDROTHERMAL TREATMENTS AS FEATURED PRE-TREATMENT

As a first step, biorefinery needs the lignocellulosic waste to be fractionated into its major components (Yang and Wyman 2008; Zheng *et al.* 2009; Aditiya *et al.* 2016; Rabemanolontsoa and Saka 2016). A promising avenue as first step is autohydrolysis, which produces the dissolution of hemicelluloses to oligosaccharides and monosaccharides (Garrote *et al.* 2003; Sasaki *et al.* 2003; Gullón *et al.* 2012; Shulga and Vitolina 2012; Ek *et al.* 2014; Sun *et al.* 2014). A schematic diagram of the hydrothermal pretreatment is presented in Fig. 1.

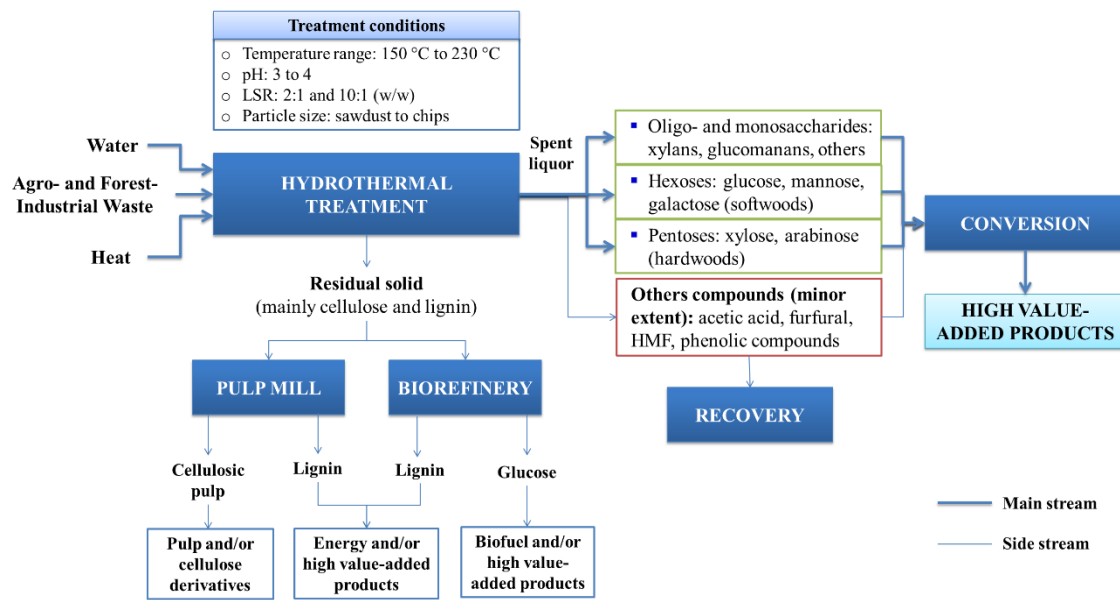


Fig. 1. Schematic diagram of hydrothermal pre-treatment

This approach, which involves mixing plant biomass with water and then heating the slurry under pressure, has been described as liquid hot water, hydrothermal, autohydrolysis, hydrothermolysis, aqueous-controlled pH, or combinations and variations of these terms. The best applications of neutral-pH aqueous pre-treatment are where low severities are required to achieve effective pre-treatment, such as with herbaceous plant biomass. However, it is less efficient in highly lignified feedstock such as softwoods because more intense treatments are necessary to achieve effective cellulose pre-treatment. Unfortunately, autohydrolysis does not achieve high hemicellulose sugar yields as when using strong diluted acids (Pu *et al.* 2013; Stoffel *et al.* 2014).

Autohydrolysis has a wide range of applications. For example, hot water extraction has been used prior to the production of kraft dissolving pulps, as well as steam explosion as a defibration process for fiberboard and hardboard products (Conner *et al.* 1985). It has also been tested as a green and economical wood pre-treatment method to increase solubility in ionic liquids (Deb *et al.* 2016).

In a comprehensive review, Lehto and Alén (2014) discussed the application of hot-water extraction as a chemical pretreatment of wood chips prior to alkaline pulping. Hot water treatment is suitable for producing hemicellulose-lean pulps and recovering xylan-derived products from the water extract (Borrega *et al.* 2011b). In this regard, it is a promising, economic, and environmentally friendly tool for recovering carbohydrate-rich materials prior to kraft or soda-AQ pulping (Vena *et al.* 2013a, 2013b). Prehydrolyzed chip cooking is significantly faster than unhydrolyzed chip cooking, requiring approximately 40% shorter cooking times to obtain similar kappa numbers at the same temperature (Kautto *et al.* 2010). However, prehydrolysis decreases the overall pulp yield and influences the papermaking properties of kraft pulps (Saukkonen *et al.* 2012). Additionally, it affects many aspects of the fiber line, requiring the pulp mill to incorporate modifications to meet the requirements for the overall process performance. Therefore, the economic balance is the decisive factor. The integration of pulp and paper technology with bioethanol production using an initial hot water treatment has also been studied (Phillips *et al.* 2013).

Hot water treatment has also been extensively studied as a pre-treatment for organosolv pulping with ethanol of different conventional and non-conventional raw materials (Garrote *et al.* 2003; Caparros *et al.* 2008; Alfaro *et al.* 2009; Romaní *et al.* 2011; Amendola *et al.* 2012; Vallejos *et al.* 2015b).

PHYSICOCHEMICAL ASPECTS OF HYDROTHERMAL PROCESSES

The hydrothermal process consists of treating the lignocellulosic material in aqueous medium at elevated temperature in a pressurized reactor. The combined effect of temperature and moisture softens the middle lamella, which is mostly composed of lignin. Hot water has a plasticizing action, which reduces the softening temperatures of hemicelluloses and lignin to less than or equal to 100 °C, which produces disaggregation of lignin-carbohydrate complexes as a function of the severity of the treatment (Chornet and Overend 1988). The structure of treated fibers becomes less ordered and more accessible because of the alteration in their physical properties (Belkacemi *et al.* 1991).

The generation of protons by the dissociation of water molecules and acetic acid is a key in hydrothermal treatments. In the above-mentioned conditions, water autoionization generates protons that act as catalysts during the hydrolysis of hemicelluloses, causing the cleavage of acetyl groups present in the form of esters of hemicelluloses heteropolymers, which are then released as acetic acid. Simultaneously, full or partial dissolution of hemicelluloses and their conversion to oligosaccharides and monosaccharides is achieved.

Protons have to overcome physical and chemical obstacles to penetrate the fibers. Lignin-carbohydrates association and cellulose crystallinity act as chemical barriers distributed throughout fiber walls. In the fractionation or pulping processes, hemicelluloses are selectively removed towards cellulose degradation and splitting of the α and β aryl ether bonds of lignin (Liu 2010). For this reason, the linkages between lignin and polysaccharides may play an important role in limiting the extraction of hemicelluloses (Tunc *et al.* 2010).

Xylan removal from hardwood species can be modeled kinetically as the sum of two parallel first-order reactions, one fast and one slow, which can be attributed to xylan accessibility. The slow rate may be due to a portion of the xylan being embedded within or attached to the lignin *via* lignin-carbohydrate bonds (Conner *et al.* 1985). Issues such as the depolymerization of cell walls catalyzed by the self-ionization of water, the further depolymerization of by products from the hydrolysis, and the mechanisms of aqueous pre-treatment are detailed in works from Wyman (2013).

Moreover, lignocellulosic fiber walls act as physical barriers for the extraction of hemicelluloses, which are in larger proportion in S2 layer of the secondary wall of fibers. The mechanisms necessary to extract hemicelluloses involve first the fragmentation of the hemicellulosic polymer by hydrolysis (this stage is crucial). The hemicellulosic fragments are then solubilized in hot water and finally they should diffuse through the microcapillaries to the outside of the fiber wall. Protons have to enter through the pores by diffusion. The fiber wall structure is interrupted by pits, whose size and form greatly differ according to species, growth, and location of fibers in the structure of the lignocellulosic material. The cell wall of treated fibers also exhibits molecular scale dimension porosity, which is due to the partial filling of spaces between cellulose microfibrils by lignin, hemicelluloses, and extractives. These spaces are generally referred to as microvoids. Pits and microvoids provide the major pathway for the interfiber conduction of liquids. Fiber

wall porosity is highly altered by the different processes to which the material is subjected. For example, delignified fibers present microvoids in the range of 2 to 5 nm (Stone and Scallan 1965; Sawabe *et al.* 1973).

Lignocellulosic materials have a porous structure, which allows water to access the fiber spaces in lumens, pits, and pores of fiber walls. Fibers immersed in water get soaked on the surface. Penetration continues to the interfiber spaces, capillaries, and lumens. The sorption of water into the fiber is a complex process that involves vapor phase diffusion into pores, surface diffusion along the fibers, and bulk diffusion through the cellulose material.

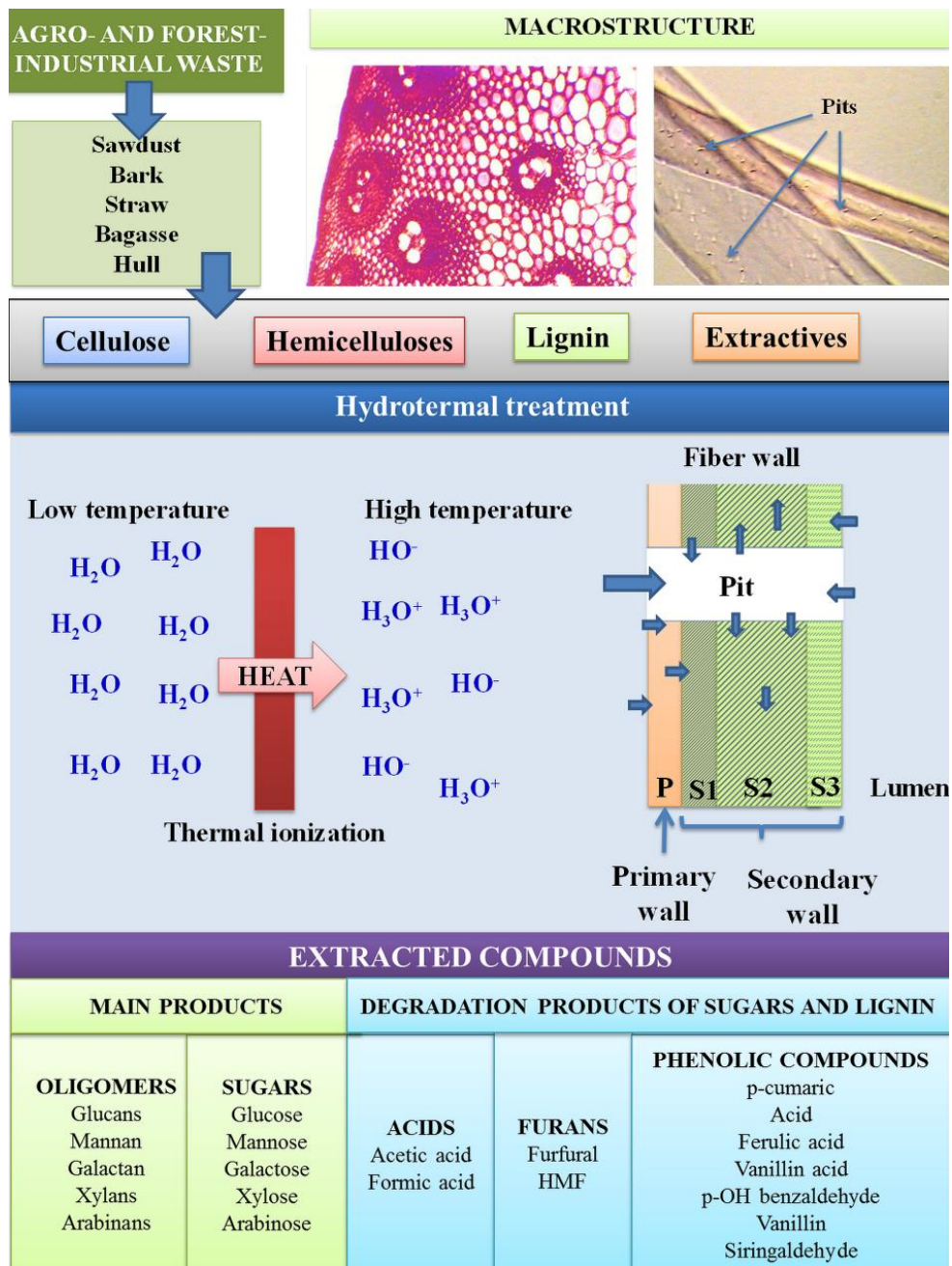


Fig. 2. Protonated water penetration into the fibers walls, extracted compounds, and formed degradation products

During wetting and penetration, water gets into interfiber spaces and the amorphous regions of the cell wall. As in papermaking pulps, water diffuses into the amorphous regions of the cellulose matrix and breaks inter-molecular hydrogen bonds between cellulose surfaces. Swelling is associated with the rapid increase in volume, while the surface area does not expand (Botková *et al.* 2013). For lignocellulosic material to swell, water must enter the fiber wall. Penetration by mass flow followed by diffusion into the fiber wall is a much more rapid process than vapor-phase or bound-water diffusion. This swelling effect increases the inter-molecular distance of the cellulose chains (Rowell 2016). Swelling of the lignocellulosic material also facilitates the diffusion of sugars and oligomers of hemicelluloses to the aqueous medium.

During autohydrolysis, lignin is also degraded through the cleavage of aryl-ether bonds, which results in a significant molecular weight reduction, a drastic increase of phenolic hydroxyl group content, and a reduction of aliphatic hydroxyl groups content. In addition, condensation reactions change the substitution pattern of the aromatic ring (Leschinsky *et al.* 2009b). A scheme including protonated water penetration into the fibers walls, extracted compounds, and formed degradation products is shown in Fig. 2.

PROCESS VARIABLES IN HYDROTHERMAL TREATMENTS

Beyond raw materials, the most studied variables in autohydrolysis treatment are temperature, time, particle size, liquid to solid ratio (LSR), and pH.

Temperature and Time

Liquid hot water treatment usually is carried out at temperatures between 150 °C and 230 °C. Below 100 °C there is no hydrolytic effect on material, and above 220 °C some cellulose is degraded. Between 240 °C and 250 °C, pyrolysis reactions become important (Liu *et al.* 2012). Hot water treatments at these high temperatures have also been used to extract lignin. Thermal hydrolysis at 200 °C, 30 bar, and a rye straw liquid to biomass ratio of 10:1 (w/w), referred to as the Aquasolve process, produces Aquasolve liquefied lignin (AL lignin). The liquid hot water (LHW) process is a two stage hydrothermal treatment with temperatures up to 260 °C at 80 bar with a liquid to biomass ratio of 10:1 followed by the Aquasolve process (Wörmeyer *et al.* 2011).

Hot-water extraction removes extractives and hemicellulose fractions from biomass. Higher temperature and longer residence time lead to higher mass removal. While high temperatures (greater than 200 °C) can lead to nearly total dissolution, the amount of sugars present in the extraction liquor decreases rapidly with temperature. A short reaction time is preferred for the hydrolysis of hot-water wood extracts (Liu *et al.* 2012).

Time is also important with respect to the decomposition of oligomers in liquors. Working with spruce at 170 °C, Krogell *et al.* (2013) found that the optimal extracted mass was 30%. Average molar masses of the extracted hemicelluloses decreased rapidly during the first 10 min of extraction. Working with birch coarse sawdust at temperatures between 180 and 240 °C, Borrega *et al.* (2011a) found that the complete degradation of xylans was accomplished at an expense of about 15% loss in cellulose yield at temperatures above 180 °C. The relationship between time and temperature can be set based on the objectives of the extraction. Rangel *et al.* (2016) studied hydrothermal process applied to *Eucalyptus rostrata*, *grandis*, and *saligna* industrial sawdust at temperatures from 120 to 190 °C and times from 20 to 40 min (P-factor from 4 to 1717). The extractives could be removed at

120 °C for 20 min; the highest extraction of hemicelluloses (mainly as sugars) took place at 190 °C for 20 min, and the maximum extraction of carbohydrates as oligomers was obtained at approximately 170 °C for 40 min.

The usual reported conditions of hydrothermal processing for hemicelluloses extraction from sugarcane bagasse and other agro waste are temperatures between 160 °C and 190 °C for 10 min, times from 20 to 90 min, and LSR from 1:6 to 1:10 (Ligero *et al.* 2011; Silva *et al.* 2011; Sukhbaatar *et al.* 2014; Vallejos *et al.* 2015a). Some older works tested higher temperatures such as 200 to 230 °C for 2 to 10 min, which produced important degradation (Laser *et al.* 2002; Vila *et al.* 2002). For example, autohydrolysis of corncob at temperatures up to 216 °C removed up to 94% of xylan and produced partial delignification with up to 26% lignin removal (Garrote *et al.* 2002).

Kinetic models and severity parameters are different mathematical methods that have been used to model hemicellulose hydrolysis. Severity parameters have been applied to compare different pre-treatment strategies, while kinetic models describe the changes of hemicelluloses by hydrolysis as a function of treatment conditions (Sixta *et al.* 2006). The effect of temperature and time is sometimes reported as the prehydrolysis factor (P-factor) and is based on the Arrhenius equation, which describes the intensity of the hot water treatment (Table 1) (Tunc and van Heiningen 2009; Vallejos *et al.* 2015a). This factor, similar to the H-factor used in the pulp and paper industry, expresses the hydrolysis time and temperature as a single variable in batch reactors. Due to its simplicity and ease of implementation, the P-factor is often utilized to compare hot water treatments performed at different temperatures, to control the extent of the prehydrolysis process, and to predict the solubilization of hemicellulosic components during acid treatments (Heitz *et al.* 1987).

Severity factor is another parameter usually used to characterize hydrothermal treatments that also combine temperature and time (Overend *et al.* 1987). Extractives and inorganics are removed at low severities, whereas fiber destructuration at the fibrillar level takes place when a severity increases. Depolymerization and solubilization of hemicelluloses begin at severity values lower than 2.5. A fast decrease in the cellulose degree of polymerization occurs at severity values of up to 3.8.

Particle Size

From an industrial perspective, agro-and forest wastes can be processed in a disk refiner before the hydrothermal pre-treatment to obtain fibers, whereas the hammer mill produces finer bundles. Chippers reduce the size of the woody feedstock to the range 10 to 30 mm. Milling can reduce the particle size to 0.2 to 2 mm. The fine grinding of the feedstocks to achieve a maximal reactivity of lignocellulosic materials is uneconomical from the viewpoint of energy consumption (Lomovsky *et al.* 2016).

The particle size of the reported raw materials varies from industrial-size chips to fine wood meal. Due to mass and heat transfer limitations, the larger the particle size, the lower the yield of extracted products (Song *et al.* 2008; Krogell *et al.* 2013; Deb *et al.* 2016).

Some authors choose to work with milled wood because particles size passing an 8 mm screen has shown no diffusional limitations (Garrote *et al.* 1999; Mittal *et al.* 2009). The time for a given temperature depends greatly on particle size, so that reaction time can vary from seconds to hours. In this regard, agro and forest industrial waste are excellent candidates for the application of these processes (Fig. 3).



Fig. 3. Comparative particle size of sawdust (left), industrial chips (center), and sugarcane bagasse (right)

For example, when treating aspen chips, 4.5 h at 150 °C is necessary to promote maximum extraction of xylans with minimal formation of furfural (Al-Dajani and Tschirner 2010). For sugar maple wood chips, an optimal mass of 23% was extracted at 160 °C for 2 h (Amidon and Liu 2009), whereas the optimum extraction of oligomeric carbohydrates by autohydrolysis of an extractives-free southern hardwoods mixture (SHM) of chips was obtained at 130 to 140 °C for 100 min and an LSR of 3.7:1 (Tunc and van Heiningen 2011). In contrast, times are reduced to minutes when working with sawdust or ground wood (Rangel *et al.* 2016).

Like straws and bagasse, agro waste and agro industrial waste have an ideal particle size to facilitate hot water impregnation. However, the density of the substrate plays a major role in the process. For example, almond shells and olive stones that have very lignified and dense cell wall structures. Such structures prevent the liberation of degraded lignin and the formation of gluco-oligosaccharides during autohydrolysis (Nabarlatz *et al.* 2007).

pH

pH is also a significant part of this process. For example, when working with loblolly pine chips at temperatures from 160 to 190 °C, Yoon *et al.* (2008) found that the optimal extracted mass was 24% at 190 °C and pH 3.5, whereas below this value the extraction yield rapidly decreased. High acid concentration produced more xylose monomer and resulted in the production of degradation compounds that inhibited subsequent hydrolysis and fermentations steps (Benkö *et al.* 2007; Feria *et al.* 2012; Lau *et al.* 2014). For this reason, adding alkali to neutralize the acids released during the pre-treatment process has been tried, and proved that the degradation of cellulose was reduced and the high molecular weight of hemicellulose was obtained from the extracts (Benkö *et al.* 2007; Yao *et al.* 2015).

Liquid-Solid Ratio

The effect of the liquid to solid ratio (LSR) on the dissolution of hemicelluloses is one of the least studied operational conditions, and its effect on the hydrothermal treatment is controversial. The liquid to solid ratio can vary between 2:1 and 100:1 (w/w) depending on the raw material, although most usual values are around 10:1. The extraction efficiency depends on the LSR because of the solubility limitations of xylans, lignin, and total dissolved wood (Chen *et al.* 2010). Saska and Ozer (1995) studied the aqueous extraction of sugarcane bagasse hemicelluloses and xylose syrup production using liquid to solid ratios of 5:1 and 10:1 to reduce the amount of water and to save considerable energy in the ulterior recovery of the extracted sugars. They found no significant differences in sugar yields between both liquid to solid ratios.

The influence of particle size is not significant for high LSR. However, for low LSR, increased particle size leads to a decrease in biomass solubilization, most likely due to a deficient lignocellulosic material impregnation (Carvalho *et al.* 2008). In the case of eucalyptus sawdust, the solid to liquid ratio was not significant in the extraction of hemicelluloses in the range 5:1 to 15:1 (Rangel *et al.* 2016). The impact of the liquid to solid ratio also vanished when working at high temperatures. Bagasse pre-treated at high solids concentration performed similarly to that pre-treated at low solids concentration, provided the pre-treatment temperature is maintained at 220 °C (van Walsum *et al.* 1996). Trials with bagasse at 200 °C for 10 min using an LSR of 0.5:1, 1.0:1, 3.0:1, 7.0:1, and 10.0:1 showed a significant decrease in yields only between 0.5 and 10 wt.% (Jacobsen and Wyman 2002). The combined yield of monomers and oligomers of xylose was higher at 0.5% solids concentration, about 86% in 10 to 12 min. However, at 10% solids concentration this yield was about 77% in 12 min. Yields were generally higher at lower solids concentrations.

The autohydrolysis treatment of corncobs at a liquid to solid ratio of 8:1 or 10:1 was slightly affected by the liquid to solid ratio, even if improved xylo-oligosaccharide percentage was extracted at the highest liquid to solid ratio tested. Little effects of the liquid to solid ratio on pre-exponential factors and activation energies were observed (Garrote *et al.* 2001b).

However, low liquid to solid ratios can be used to obtain high xylo-oligosaccharide concentrations in spent liquors; for example, the hot water pre-treatment of sugarcane bagasse at 170 °C for 60 min and LSR of 3:1 produced the maximum concentration of xylose and xylans (13.76 and 36.18 g L⁻¹, respectively) (Vallejos *et al.* 2012).

Rangel *et al.* (2016) applied a 23 factorial design to verify the influence of time, temperature, and liquid to solid ratio (5:1, 10:1, and 15:1) on the hydrothermal treatment of eucalyptus sawdust. They showed that the effect of liquid to solid ratio on the extraction of hemicelluloses in the studied range was not significant. These experiments demonstrated that the most influential factor was temperature, followed by time, and then temperature to time interaction.

Low liquid to solid ratio produces an increase of acetic acid concentration (catalyst) in the reaction medium promoting the further release of acetyl groups, which favors the autohydrolysis of lignocellulosic material. Hence, the use of low liquid to solid ratios and mild pre-treatment temperatures is an interesting way of reducing energy costs and thus economizing both steam and electricity (Vallejos *et al.* 2012). Moreover, autohydrolysis at mild temperatures produces high molecular weight xylo-oligosaccharides without substantially modifying cellulose and lignin, which enables their recovery for further

processing. Therefore, highly concentrated syrups with high xylo-oligosaccharides content can be obtained from lignocellulosic materials in these conditions.

Table 1 shows some examples of extraction yields and removed xylans by hot water treatment of various raw materials in different conditions of time, temperature, and liquid to solid ratios.

Table 1. Extraction Yields and Removed Xylans by Hot Water Treatment of Various Raw Materials in Different Conditions

LCM	P-factor	T (°C)	t (min)	LSR (w/w)	Yield* (%)	Removed Xylans* (%)	Reference
Eucalyptus ^a		181	37.5	6:1	84.6	58.4	1
Eucalyptus ^a		196	50.6	8:1	76	75.3	2
Eucalyptus ^b		150	113	5:1	79	54.4	3
Eucalyptus ^b		170	60	5:1	72.8	73.8	3
Eucalyptus ^a		175	60	6:1	74.6	75.6	4
Eucalyptus ^a		175	60	8:1	72.6	76.0	4
Eucalyptus ^a		175	60	10:1	72.7	75.7	4
Eucalyptus ^b	4-1717	120-190	20-60	8:1	5-15	0.70-94.6	5
Eucalyptus ^b	300-600-1500	170		5:1		83	6
Birch ^a		150	197	4:1	71.3	44	7
Birch ^a		150	197	8:1	77.1	50.1	7
Birch ^a		170	97	4:1	73	70.3	7
Birch ^a		170	97	8:1	65.3	73.8	7
Birch ^a	300-1000	150-170		4:1		50-61.4	8
Mixed hardwoods ^c		150	100	3.7:1	83.2	40	9
Sugarcane bagasse		143-177	20-70	1:1-11:1	76.7-95.3	39.0-94.6	10
Sugarcane bagasse		160-190	2.5-90	10:1	50-95	5-95	11
Brewery's spent grain		150	120	8:1	60.6	73.3	12
Brewery's spent grain		170	60	8:1	52.3	78.6	12
Wheat Straw ^d		188	40	10:1		43.6	13
Wheat Straw ^d		180	30	10:1		45.0	14

^aWood chips, ^bsawdust, ^c wood meal, ^dmilled.

* Some values of extraction yields and removed xylans were estimated from the results obtained by the authors. 1 (Garrote *et al.* 2003); 2 (Garrote *et al.* 2001a); 3 (Gütsch *et al.* 2012); 4 (Garrote *et al.* 1999); 5 (Rangel *et al.* 2016); 6 (Leschinsky *et al.* 2009a); 7 (Testova *et al.* 2009); 8 (Testova *et al.* 2011); 9 (Tunc and van Heiningen 2008); 10 (Vallejos *et al.* 2012); 11 (Santucci *et al.* 2015); 12 (Carvalho *et al.* 2004); 13 (Pérez *et al.* 2008); 14 (Ruiz *et al.* 2011).

TECHNICAL AND ECONOMIC ASPECTS OF LOW LSR

Liquid hydrothermal treatment produces higher amounts of solubilized compounds but in lower concentrations than those generated by steam explosion. This makes the hot water treatment not economically feasible on a large scale because of its high water consumption and high-energy requirement for hemicellulose recovery (Bobleter 1994). To

overcome this restraint, the use of low liquid to solid ratio treatment and liquid recirculation were proposed.

High LSR favors the extraction of hemicelluloses because it enhances the diffusion of reactants (water and generated acetic acid) within the lignocellulosic material and the extraction of hydrolyzed hemicelluloses (mainly xylans and xylose in hardwoods, canes, and grasses). However, technology based on low LSR results in more efficient water usage in the system, lower capital, and lower water handling operating costs. Consequently, operating costs reduction related with less water removal downstream, lower usage of fresh water and steam, and smaller storage tanks and pumping systems for the same amounts of feedstock is achieved. In contrast to these economic advantages, low LSR results in partial diffusion and transfer of the dissolved hemicelluloses outside the fiber walls.

Different products can be obtained from the autohydrolysis of sugarcane bagasse in a small-scale biorefinery. Xylose syrup, furfural, and xylitol can be produced from hemicelluloses present in spent liquors. Medium-density fiberboard (MDF) and energy can be produced from the residual solid (Clauser *et al.* 2016). In xylitol production, when liquid to solid ratio in the hydrothermal treatment is reduced from 7:1 to 5.5:1, the consumed energy decreases by 23% and IRR slightly improves (Clauser *et al.* n.d.).

Recirculation is another energy-saving strategy, which consists of the reintroduction of the spent liquor extracted from the hydrothermal treatment as fresh liquor of the next treatment. This is done until the desired concentration of hemicelluloses-derived products is reached. This approach reduces the operational costs and increases efficiency because it reduces the need for fresh water (Bobleter 1994). However, the effect of exposing this liquid containing oligomers, sugars, and degradation products on the kinetics of hydrolysis and degradation of hemicelluloses is not well known. There is a lack of information about this technology in the literature, so it requires further study.

At the same temperature (220 °C), typical steam explosion treatment requires 1.4 kg of steam per kg of lignocellulosic material (at 40% dry solids by weight in the solid-liquid system), whereas hot water treatment quadruples the steam demand, requiring 5.6 kg steam per kg of lignocellulosic material at 8% dry solids. When solids proportion in hot water treatment is increased to 12%, steam needs is reduced to 3.6 kg, so energy demand is still 2.7 times higher than that of the steam explosion (Kazi *et al.* 1998).

Because lignocellulosic wastes are abundant and have a low cost, they have been intensively studied as feedstock for bioethanol production for fuel. Pre-treatments affect the lignocellulosic material structure, which influences the enzymatic hydrolysis and fermentation processes for an effective fermentation and conversion of cellulose and hemicelluloses into bioethanol. Some important parameters such as catalyst loading, water content, reactor temperature, and residence time, could decrease the ethanol concentration in the fermentation broth, which would significantly increase its subsequent recovery and dehydration costs (da Silva *et al.* 2016).

Da Silva *et al.* (2016) studied different pre-treatment scenarios as diluted acid, liquid hot water, and ammonia fiber explosion for lignocellulosic bioethanol production processes on an industrial scale. Temperature, catalyst concentration, water, and solids loading in the enzymatic hydrolysis reactor were evaluated in order to observe their effects on energy consumption and bioethanol concentration. They reported that the total energy consumption decreased for liquid hot water treatment, increased for dilute acid treatment, and showed a minimum increase for the ammonia fiber explosion treatment. The explanation given by the authors was that the hydrolysis temperature decreased the amount of process water added to achieve the desired solids loading in the hydrolysis reactor.

Therefore, the behavior of total consumed energy differed partially due to the dilution of solids loading of the biomass stream. They found that the minimum selling price of bioethanol corresponds to liquid hot water treatment (\$1.78 per liter) at 190 °C, 81 wt.% of water content in the pre-treatment, and 23 wt.% of the solids loading in the enzymatic hydrolysis reactor (da Silva *et al.* 2016).

Archambault-Léger *et al.* (2015) showed that hot water flow-through treatment of cellulosic biomass for bioethanol production offers advantages over other methods. The selling price of cellulosic ethanol that included this pre-treatment technology (\$0.82 per liter) was lower than that using dilute acid (\$1.01 to 1.19 per liter), typical hot water (\$1.13 to 1.27 per liter), and steam explosion (\$0.86 to 1.18 per liter). The energy sensitivity analysis involved the effect of the variation of treatment parameters on energy consumption and the economics of the process, which included the liquid to solid ratios (4.5:1, 6:1, and 7.5:1). The studied parameters had an effect of less than 5% on the amount of trash to be burned or the amount of feedstock, as well as the high heating values leftover to sell as electricity credits.

The hot water flow-through treatment reactor is complex because it must include four screw feeders, a system of screens, piping, and valves. A continuous bagasse reactor is more expensive than a wood, corn stover, or grass reactor because the flowability characteristic of bagasse makes it necessary to use auger in the reactor to ensure stable continuous flow without plugging. The flow-through treatment reactor also needs to be larger, because solids concentration must be lower (140 kg/m³) than those of liquid hot water (17%) and steam explosion (50%) (Archambault-Léger *et al.* 2015).

Co-current, countercurrent, and flow-through reactor configurations based on the direction of the water flow and lignocellulosic feedstock into the reactor can be used in liquid hot water pretreatment. In flow-through reactor, the hot water passes over a stationary bed of lignocellulosic material. It is an effective configuration for removing hemicelluloses and lignin with the same severity (Bajpai 2016). In co-current configuration, water and lignocellulosic material are heated to the process temperature for the required residence time. In the countercurrent configuration, water and lignocellulosic material flow in opposite directions (Hu 2014). Flow-through reactor results in higher removal yield of hemicelluloses and lignin with respect to batch reactors. In a semi-continuous reactor, solid pumping and great milling are avoided, which considerably reduces the costs. A semi-continuous reactor can be the best technology for pre-treatment of biomass at industrial scale. Fixed bed reactors allow the operation in semi-continuous mode. Solid residence times between 20 and 40 min inside a fixed bed reactor were reported for hydrothermal treatment at 185 °C of hardwood small pellets (Rogalinski *et al.* 2008; Gallina *et al.* 2016). Liquid residence times below 2.00 min through the bed avoid the formation of degradation products. At 135 °C, flow effect is not perceived. At higher temperatures, removal yields increase together with the formation of degradation products.

The main drawback of hot water treatments in batch reactors is the significantly lower xylans yields compared to other reactor types due to the undesired degradation reactions of hemicellulosic sugars (Rogalinski *et al.* 2008; Ingram *et al.* 2009). Hot water pretreatments also produce a migration of lignin and lignin-carbohydrate complexes out of the wall cells, which form spherical droplets in the surface. In batch reactors, these droplets harden after the cooling, creating a barrier for enzymatic digestibility of the remaining solid. This effect is less evident in semi-continuous reactors because the water flow carries them constantly out of the system, being an important advantage of semi-continuous reactor (Gallina *et al.* 2016).

CONCLUSIONS

Forest and agro lignocellulosic residues (sawdust, bark, bagasse, straw, hulls, and others) are suitable raw materials for the installation of small-sized biorefineries, with the possibility of high value-added product generation. Pre-treatments of this waste are one of the most expensive stages in their conversion to bio-based products. Liquid hydrothermal treatment produces higher amounts of solubilized compounds but in lower concentrations than those generated by steam explosion. This makes the hot water treatment not economically feasible on a large scale because of its high water consumption and high-energy requirement for hemicellulose recovery. The use of low liquid to solid ratio in this treatment and liquid recirculation can overcome this restraint. Low liquid to solid ratio in hydrothermal treatment provides a simple and environmentally friendly means to produce high-content xylo-oligosaccharides spent liquors with enormous potential for industrial applications. The challenge is to find a suitable technology to solve the problems associated with the manipulation of agro and forest waste at high solids concentration.

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