### **1** Pretreatment Processes of Biomass for Biorefineries: Current Status

### and Prospective

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- 15 Shortened Title: Making Biorefinery happen

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#### 36 Abstract

- 37 This manuscript seeks to be a handy document for the academy and the industry to get quickly
- 38 up to speed on the current status and perspectives of biomass pretreatment for Biorefineries.
- 39 This review was divided into 2 biomass sources: vegetal and animal. Vegetal biomass is meant
- 40 to be the material produced by plants on land, or water (algae), consuming sunlight, CO<sub>2</sub>, water
- 41 and soil nutrients. This includes residues or main products from, for example: intensive grass
- 42 crops, forestry, and industrial and agricultural activities. Animal biomass is meant to be the
- 43 residual biomass generated from the production of food from animals (manure, whey, etc.).
- 44 This review does not mean to include every technology in the area, but it does include the
- 45 evaluation of Physical Pretreatments, Microwave Assisted Extraction and Water Treatments for
- 46 vegetal biomass. For animal biomass, a general review is given, based in physical, chemical and
- 47 biological pretreatments.
- 48 Keywords: Circular Economy, Clean Solvents, Process Intensification, Sustainability

### 49 Introduction

The concept of biorefinery could be evaluated as an analogous to the conventional 50 51 concept of oil refinery. That is an industrial plant where, through various processes, the 52 biomass is transformed into energy – heat, electricity, or biofuels – and a broad spectrum of bioproducts - materials, chemicals, food and feed. Achieving this wide range of products 53 54 requires the integration of different processes and technologies in, ideally, a single facility. 55 The processes taking place in a biorefinery can be classified as: physical – including mechanical processes – thermochemical processes, chemical and biotechnological processes. 56 57 These processes are not substantially different to the processes used in the petrochemical industry, except for the following three main aspects. 1) Biomass is commonly a solid, so, the 58 59 pretreatment processes are different. The biorefinery pretreatments are usually close to agrofood industries transformations. 2) The second difference lies in the products, biorefinery 60 61 products are usually solid nonvolatile products. Thus, distillation does not play the important role as in the petrochemical industry. In biorefinery processes, the membranes technology is a 62 typical downstream refining process. 3) The third main difference is the production of building 63 64 blocks. Petrochemical industry produces simple molecules such as ethylene, which are 65 transformed into chemicals by catalytic chemical reactions. Now, biorefinery industry produces 66 different platforms such as vegetable oils and lipids, lignin, sugars, proteins, biogas and synthesis gas. Organic chemistry, therefore, has to develop a new organization for chemical 67 production of these biomass platforms. 68

Recent reviews present a background of Biorefineries development. Chandel at al. have
 published bottlenecks, solutions, and perspective on lignocellulose biorefineries

71	commercialization. They claim that lignocellulosic biorefinery offers clear value proposition,
72	however, the success of commercial production of renewable chemicals and fuels at industrial
73	levels has not been achieved yet. They point as main stoppers the high capital and operating
74	costs, irregularities in biomass supply chain, technical process immaturity, and scale up
75	challenges (1). Zandi-Atashbar et al. give a comprehensive overview focused on optimization,
76	modelling issues and solution approaches in biomass supply chains (2). Cocero et al. reviewed
77	the subcritical and supercritical water fundamentals of fractionation processes to improve the
78	selectivity (3). Philp focused his review in the bioeconomy policy makers. He concluded that the
79	future is complex and multi-faceted, and the most difficult challenge is to quantify what is going
80	to be like. However, one of the visions for bioeconomy is the installation of distributed
81	integrated biorefineries plants of small/medium scale as opposed to the current reality of
82	massive fossil fuel and petrochemical economies of scale (4).
83	Biorefinery pretreatment processes are selected taking into account biomass
84	characteristics. The more conventional pretreatment processes are centrifugation, drying,
85	grinding, sieving, densification, pressing, cell breakage, explosion with steam, ammonia, or $CO_2$ .
86	Unbounded components are separated by extraction, which is improved by ultrasonic and
87	microwave treatments. Bounded components are separated by biological or chemical processes
88	such as enzymatic and chemical hydrolysis, depolymerization and other chemical
89	transformations processes. Hassans at al. reviewed the application of selected emerging
90	technologies such as ionizing and non-ionizing radiation, pulsed electrical field, ultrasound and
91	high pressure as promising technologies in the valorization of lignocellulosic biomass (5).

92	In addition to these conventional pretreatment processes, innovative technologies have been
93	developed as niche solutions for selective biomass fractionation – such as the ultrafast
94	supercritical water hydrolysis (3). This technology has been developed on an industrial scale by
95	the company Renmatix (6).
96	This review is focused on the status of research in pretreatment processes in
97	biorefineries. It is organized considering the biomass origin and innovative or broadly used
98	pretreatment processes applied to biomass. Experts in their areas have been asked to give an
99	opinion on the current state of the physical, microwave assisted and water based
100	pretreatments of vegetal biomass and the physical, chemical and biological pretreatments of
101	animal biomass.

### 102 Vegetal Biomass

#### 103 • Physical pretreatment

104 The aim of physical pre-treatment of biomass is to increase the surface area of the 105 material to improve enzymatic hydrolysis of cellulose or hydrolysis kinetics. This can be 106 achieved by reducing the particle size, increasing porosity or disrupting their structural 107 regularity. Different types of physical processes, such as mechanical processing, ultrasonic fields, electric fields and irradiation have been extensively studied (7, 8). Ultrasounds, electric 108 109 fields and irradiations are also considered as non-conventional energy sources (9). 110 Particle size reduction is normally the first step after harvesting the biomass to facilitate 111 transportation and storage, as it homogenize and increase bulk density (8, 10). It also improves

112 its processing since mass and heat transfer limitations are reduced as well as its ease to handle

113 and move it (11). The increase in surface area is not only due to the particle size reduction, but 114 also to the reduction in crystallinity and degree of polymerization. These latter effects are 115 mainly achieved due to the high shear forces generated in grinding and milling processes (7, 10, 116 12). Fractions of different sizes are generated during comminution operations, and it has been 117 demonstrated that structural molecules (lignin, cellulose and hemicelluloses) are accumulated 118 in the largest particles (> 1-2mm), while fines (< 0.4 mm) tend to concentrate the extractives 119 and inorganic compounds (13). The physical, structural and shearing properties of biomass have 120 to be considered, together with the aimed final particle size, to select the appropriate mill 121 equipment and operating conditions to optimal performance with lowest specific energy 122 requirements (8, 11). Hammer mills are the most commonly used. However, agricultural 123 biomass such as straw and grass, is processed using knife mill due to its lengthy morphology. In many cases, further densification up to 600-800 kg/m<sup>3</sup> is needed for non-woody materials 124 125 like: energy grasses, agricultural residues and food-industry residues. Two main approaches are 126 used: pressure agglomeration alone or with the addition of external binders (14) to produce briquettes and pellets. 127

Ultrasounds pretreatment affect the structure of the lignocellulosic materials due to mechanistic and chemical effects. Firstly, perforations are produced ("pitting") on the biomass (after long processing time, 5 h). This increases the porosity and improves the yield for enzymatic hydrolysis, although not as much as diluted ammonia pretreatment (15). Ultrasound pretreatment is particularly effective in the removal of amorphous components such as hemicelluloses and lignin, improving the accessibility to cellulose. For this purpose, a variety of solvents can be used: organic solvents, alkali, lime, hydrogen peroxide and surfactants (16).

135	Further, specific hemicelluloses such as $\beta$ -glucan from cereals, that produces high viscous
136	solutions, can be extracted using water as solvent with short processing time (30min) and high
137	molecular weight (17). The effects on the reduction of cellulose crystallinity are not so clear.
138	Some authors have shown an increase in crystallinity of the material after a combined
139	ultrasound-alkaline pretreatment and have attributed it to the removal of hemicelluloses, lignin
140	and amorphous cellulose (18). Others have observed its reduction due breakdown of hydrogen
141	bonds in cellulosic structure (19). Nevertheless, the improvement in sugar enzymatic yield was
142	only increased when ultrasounds were combined with sodium percabonate that promoted the
143	delignification.
144	Broadly, two types of radiation can be considered: ionizing and non-ionizing (see
145	microwave technology described in section "Microwave treatment and extraction"). The former
146	is represented by gamma ray (GR), as electromagnetic radiation, and electron beam irradiation
147	(EBI). Both are able to produce ionization of the macromolecules of the materials due to the
148	localized energy absorption. Their major effect is the increase in surface area of the biomass as
149	well as the reduction in molecular weight and crystallinity cellulose due to chain scission (8).
150	Several examples can be found for GR applied to wheat straw (20) and poplar bark (21). EBI has
151	also been applied to range of lignocellulosic biomasses from corn stover to paper mill sludge
152	(22). Efficiency of both processes is commonly increased by the subsequent application of
153	chemical pre-treatments or hydrothermal processing (7). The high-energy consumption and
154	absence of scale-up knowledge, limit their application as pretreatment (10).
155	Biomass, most of the times, is composed not only by cellulose, hemicellulose and lignin
156	but also by "extractives". Depending on the nature of the biomass, the extractives can account

157 from 5% up to 50%. These are usually lipids and phytochemicals (polyphenols, essential oils and 158 alkaloids), proteins, lipids or other polysaccharides such as pectin or starch (3, 23, 24). 159 The recovery of lipids (oils, fats and waxes) is often proposed (25, 26) since removing 160 the layer of waxy lipids covering the plant surface facilitates the access of solvents to the inner 161 part of the matrix, improving the going-on processing and subsequent fermentation. Further, 162 waxes are said to be critical inhibitors of fermentation (25). But, waxes are also a material with 163 important industrial applications (25). The extraction of lipids is industrially carried out by 164 mechanical pressing, for materials with relatively high content of oil and for high quality food 165 products or with highly non-polar organic solvents, namely hexane (25). Supercritical carbon dioxide is also a green solvent alternative to the extraction of lipophilic materials. However, its 166 167 broad industrial application is limited as its cost (initial investment) is perceived as high. It can 168 efficiently dissolved lipids and lipophilic molecules at mild pressure and temperature (i.e. 30-40 169 MPa and 40-50°C), leaving no residue in a dry solid matrix after depressurization (25). Recently, 170 it has been pointed also out as effective treatment to extract waxes and resin acids from 171 sawdust and wood pellets (25). 172 Phytochemicals like essential oils, polyphenols, alkaloids and tocopherols can be also

173 found in biomass. Essential oils are a mixture of volatile organic compounds, mainly terpenes,

174 that can be recovered by hydro or steam distillation (SD). The extraction of polyphenols,

175 commonly carried out with hydro-alcoholic mixtures, can be further improved with the use of176 ultrasounds and microwaves (27).

177 Regarding polysaccharides, pectin is one of the components in cell wall. Although they 178 are a source of fermentable sugars in their own, their previous extraction owes to the fact that

179	pectin might limit the exposure of cellulose and/or hemicellulose to degradative enzymes (28).
180	Further, pectin has important applications in its native or modified form in the food industry
181	and pharmaceutical (28, 29). Pectin is conventionally extracted by hot (90°C) acidify water (pH
182	1-2). Similarly to polyphenols, extraction rate and yield is greatly increased by the non-
183	conventional technologies being MAE more efficient that USAE (29). On the other hand,
184	conventional extraction processes for starch involve a mechanical grinding with water at mild
185	temperature (wet milling). Starch can also be co-extracted by mild hydrothermal process
186	(120°C, 5 MPa under $N_2$ ) (24). In other occasions, it is enzymatically hydrolysed as pretreatment
187	in the recovery of arabino-xylans (26). In this case, starch is recovered as dextrin.
188	Lignocellulosic materials such as agro-food residues (i.e. cereal bran and sugar beet
189	pulp) and herbaceous energy crops can be also used as sources of protein, peptides or amino
190	acids, which are mainly enclosed by cell wall polysaccharides. In the case of fresh green crops
191	proteins are precipitated at acid pH (4-5) or by heat coagulation from pressed juice, the global
192	yield normally accounts for the 40-60% and it has been shown that it can be improved with
193	pretreatment with pulsed electric fields as pretreatment (30). In fact, there is already a
194	demonstration green biorefinery plant in Germany (31). From dried raw materials, conventional
195	extraction involves alkaline pH (9-12) at temperatures from 40 - 90°C to avoid protein
196	denaturation with lower yields around 20%-30% (30). The use of non-conventional energies
197	(microwaves and ultrasounds) in the extraction can also improve the yield (32, 33).
198	Overall, the extraction of the valuables extractives from biomass can increase the cellulose,
199	hemicellulose and lignin content, and the formation of degradation products would be reduced
200	(3).

#### • Microwave treatment and extraction

As it is observed in Figure 1 (34), microwave technology exploration has increased in the last years. This expansion of the research is owed (in our opinion) to the new possibilities that microwaves can provide to improve both the energy use and the structural characteristics of the biomass. Therefore, there have been recent reviews on the subject (35–38). In the following, we will summarize what are, from our point of view, the most interesting facts related with this technology and we will propose the way forward towards scalable processes.

The interesting fact of the use of microwaves during biomass pretreatment is the possibility to apply fast, volumetric and selective heating (39, 40). This, in the end, result in less heat losses and more compact and flexible processes when compared with the conventional ones. Consequently, the material is selectively heated from inside out as opposed to conventional heating.

For every pretreatment process, it is especially important that cellulose can be effectively retrieved. For the particular case of microwaves, the localized and fast heating damages the structure of the biomass resulting in more porosity and surface area. This damage is the consequence of the cleavage of the lignocellulosic composite that in turn helps to split hemicellulose, lignin and cellulose. The result is the increased availability of hemicellulose and cellulose for further transformation (41, 42).

The breakup of vegetable cells have been reported in the literature related to the application of microwaves both as process factor or as pretreatment (43, 44). Figure 2 shows examples of such effects.

The damage and change on the biomass structure have been explained by two main hypotheses (35, 36). The first one addresses the direct interaction of the microwaves with the hydroxyl groups and hydrogen bonds of the lignocellulosic biomass (45). The second hypothesis involves the overheating and over pressure owed to the rapid heating of water trapped on the inside the structure of the plants (46).

227 Microwave based pretreatment have been used following primarily the same concepts 228 for conventional pretreatment such: organosolv (47), acid (48), alkali (49), ionic liquid (50). In 229 addition, novel concepts such steam explosion, ball milling, ultrasound and ozone pretreatment 230 have been applied together with microwaves (36, 38). It has also been used in conjunction with 231 microbial and enzymatic processing of the biomass.

The fast transmission of microwaves directly into the material helps to create potential for higher yields of treated matter and consequently helps the economy of the process (51). This opens the possibility for the economical use of biomass using a distributed production perspective. More compact, continuous processing equipment is thus possible.

Nevertheless, as with any other technological option, microwave pretreatment of biomass has got drawbacks. The main one is the lack of the phenomenological understanding necessary in order to be able to design and optimize the microwave enhanced pretreatment of biomass. Therefore, proposed future tasks as a way of suggestion are:

240 - "There's Plenty of Room at the Bottom". There is a huge gap of knowledge on the actual

interaction and kinetic effects of the microwaves and the lignocellulosic composites. Here,

242 physicochemical studies are essential to understand the molecular changes taking place.

243 Tools such infrared spectroscopy or microscopy can be applied. These studies have to be

244 performed for every main component of the biomass under study. In the case of

- 245 vegetables, this could include cellulose, lignin and hemicellulose in their representative
- crystallinities. Ash or inert matter (to the microwaves) can also be taken into account.

247 "Microwave Scale". To be able to predict the thermal behavior of the process and avoid 248 phenomena such "hot spots" (localized overheating), dielectric properties have to be 249 known. Such knowledge allows the prediction of the thermal dynamics and temperature 250 distribution in the sample (52). Mono-modal cavities need to be developed to be able to have strict control of parameters such as electromagnetic field distribution, frequency, 251 252 temperature (e.g. fiber optic sensors or MRI (53)), moisture content and packing density (or 253 bed porosity). With this data, it is possible to correlate the content and distribution of the 254 components of the biomass with the dielectric properties (54).

"Application Scale". In the personal view of the authors, the one-size-fits-all approach for
microwave so commonly found is tremendously detrimental for future applications. The
effective dielectric properties and electromagnetic fields found in a household microwave
cannot be simply extrapolated in a scaled-up version. Therefore, intensive mathematical
modelling efforts have to complement the work in order to be able to predict the process
evolution. Novel process configurations can be then proposed that allow to design the
equipment for each application with precise control of the material properties and yield.

- Water treatments
- **263** 1. From 150 to 225°C
- The use of water at mild temperatures has been greatly successful in the extraction and
  hydrolysis of less recalcitrant biomass components, like hemicellulose. In general,
  hemicelluloses can be extracted considering two different approaches: fractionation of
- 267 lignocellulosic materials into chemicals, and pre-extraction of hemicelluloses from
- 268 lignocellulose for further pulp production.
- 269 Fractionation

The fractionation is a pretreatment required to make cellulose more accessible for enzymatic hydrolysis. These pretreatments remove hemicelluloses together with lignin. There are numerous reviews in literature summarizing these treatments (55–58). The most studied treatments are catalyzed and uncatalyzed steam explosion, dilute-acid hydrolysis and liquid hot water. Alkaline hydrolysis has been studied to a lesser extent.

275 Steam Explosion refers to a pretreatment technique in which lignocellulosic biomass is 276 heated rapidly by high-pressure steam. The biomass/steam mixture is held for a period of time 277 to promote hemicellulose hydrolysis, and terminated by an explosive decompression. Steam 278 explosion is typically initiated at a temperature of 160-260°C for several seconds to a few minutes before the material is exposed to atmospheric pressure (56). Steam explosion involves 279 280 chemical effects where acetic acid is generated from hydrolysis of acetyl groups associated with 281 the hemicellulose and it may further catalyze hydrolysis but also xylose or glucose degradation (57). The process can also cause lignin transformation due to high temperature and acidity. In 282 283 many respects, the effects of the process on the lignin fraction are similar to those obtained

284	with acidolysis and ethanolysis (59). Fractionation of lignocellulosic materials can be reached by
285	coupling steam explosion with further extraction steps. Hemicelluloses can be removed by
286	water extraction and lignin by using alkali, aqueous acetic acid, or aqueous ethanol (60, 61).
287	Addition of acids, $H_2SO_4$ , $SO_2$ or $CO_2$ , in steam explosion can improve enzymatic
288	hydrolysis, decrease the production of inhibitory compounds, and lead to more complete
289	removal of hemicelluloses (55, 62–64). The optimal conditions of steam explosion pretreatment
290	of sugarcane bagasse have been found to be as following: 220 °C; 30 s residence time; water to
291	solid ratio, 2; and 1% $H_2SO_4$ (64). Wayman et al. (63) reported removal of hemicelluloses up to
292	89% of theory using up to 2.6% SO $_2$ on wood as catalyst. Puri and Mamers (65) investigated
293	lignocellulosic material subjected to the action of steam and high-pressure $CO_2$ . Examination of
294	the exploded furnishes indicated the pretreatment had substantially solubilized the
295	hemicellulose fraction of Eucalyptus regnans, giving a liquor rich in xylose (70% monomers).
296	Liquid Hot Water pretreatments use pressure to maintain the water in the liquid state
297	at elevated temperatures. This type of pretreatment has been termed hydro-thermolysis,
298	aqueous or steam/aqueous fractionation, uncatalyzed solvolysis, and aquasolv (66). Up to 60%
299	of biomass under hot water pretreatment at temperatures between 200-230°C for up to 15 min
300	can be dissolved. At these conditions, all of the hemicellulose, 4-22% of the cellulose, and 35-
301	60% of the lignin can be removed. Liquid hot water pretreatments are both helped and
302	hindered by the cleavage of O-acetyl and uronic acid substitutions from hemicellulose to
303	generate acetic and other organic acids. The release of these acids helps to catalyze formation
304	and removal of oligosaccharides. However, the polysaccharides and especially hemicellulose,
305	may be further hydrolyzed to monomeric sugars which are subsequently partially degraded to

306	aldehydes if acid is used. These compounds, principally furfural from pentoses and 5-
307	hydroxymethyl furfural from hexoses, are inhibitory to microbial fermentation (67).
308	Fractionation of lignocellulosic materials using autohydrolysis has been deeply
309	investigated (68–70). Chemical composition of the non-saccharide compounds in the
310	autohydrolysis liquors has been studied for commercial value (68). Liquors obtained by non-
311	isothermal autohydrolysis of Eucalyptus globulus wood and corncobs under a variety of
312	operational conditions were extracted with ethyl acetate in order to remove those compounds
313	and determine the specific antioxidant activity of different isolated fractions. Complete
314	chemical characterization, kinetic models and optimal operational conditions can be found in
315	literature (69, 70).
316 317	Pre-Extraction The interest of transforming pulp mills into an Integrated Forest Biorefinery (IFBR) is
318	increasing due to global and local concerns (71). The aim of this new concept is the removal and
319	commercialization of material that does not contribute to the paper product. Two research
320	topics have been investigated: pre-hydrolysis of wood chips with hot water (autohydrolysis),
321	and alkaline extraction of hemicelluloses from wood chips.
322	The concept of pre-hydrolyzing wood chips before conventional pulping is not new (72).
323	Generally, these papers reported research intended for the production of low-hemicellulose-
324	content dissolving pulps. Casebier et al. (73) investigated the chemistry and mechanism of
325	water pre-hydrolysis on both softwood and hardwood. The highest extraction yield for
326	softwood was near to 16% for softwood for a range of temperatures between 100-170 °C. For
327	hardwood in a range of temperatures of 170-180 °C, the highest weight loss was 18% in 45

328 minutes. It was found that lignin degradation and dissolution occur increasingly as reaction 329

conditions become more severe.

330 Garrote et al. (74) studied the deacetylation and hemicellulose (xylan) hydrolysis during 331 hydrothermal treatments based on the work done for Abatzoglou et al. (75). Several 332 lignocellulosic raw materials were treated to evaluate the severity factor. An average value of 130 kJ mol<sup>-1</sup> was obtained for the activation energy of xylan degradation. Autohydrolysis of 333 334 Eucalyptus *globulus* wood chips has been investigated reporting that 90.4% of the initial xylan 335 was removed in treatments, which also caused some delignification (up to 13.8% of the initial 336 lignin was removed) (76). Cellulose was almost quantitatively retained in solid phase. It is proposed that the solid phase can then be used for pulp and paper production. 337 338 Another severity approach to describe this process is the H-factor (77). A maximum of 339 about 12% of the wood (softwood in this example) mass was extracted as wood sugars at an H-340 factor of about 1,500 hours. When kraft cooking is applied after the water treatment, 40 to 60% 341 of the lignin can be removed, which is higher than corresponding kraft control cooks. Vila et al. (78) studied the recovery of hemicellulose before kraft pulping on Eucalyptus globulus wood 342 343 chips. Cooking conditions were found to give a good quality kraft pulp with a good balance 344 between kappa number (11.3) and intrinsic viscosity (1217 mL/g) when compared to a 345 commercial pulp used as a reference. 346 Hot-water extraction, or pre-hydrolysis, has been also used commercially for dissolving

pulp production by the pre-hydrolysis-kraft process. Here wood chips are subjected to harsh 347 conditions using steam at 160-180 °C for 30-120 min (72). The pre-hydrolysate formed is 348 349 displaced by black liquor and white liquor. In principle, it would be possible to recover the pre-

hydrolysate by drainage and water displacement; unfortunately, lignin precipitates generated
at high temperature and acidic conditions (79, 80) lead to large operational problems (81). A
formic acid (FA) reinforced aqueous pre-hydrolysis process is proposed to reduce the amount of
lignin precipitates (82). The molecular weight, Mw, and polydispersity, Mw/Mn, of the
precipitated lignin decreased from about 2600 g/mol and 3.0 at autohydrolysis conditions to
about 1100 g/mol and 2.0 at 20 g/L FA pre-hydrolysis, respectively.

356 The chemical mechanism of the removal of wood components from wood by hot water 357 extraction is presently still incomplete. However, some researchers have provided insight about 358 the possible mechanism of the removal of hemicellulose from lignocellulose with hot water. Conner (83) proposed the existence of two types of xylan, both of them modeled through first 359 360 order kinetics in a batch reactor. One fraction could be removed quickly and a second one was 361 removed at a much slower removal rate due to an association with lignin. The xylan removal 362 rate was affected by flow rate in flow-through reactor systems, which is inconsistent with 363 intrinsic homogeneous kinetics meaning there are other factors affecting xylan removal (84). In a recent study Chen et al. (85) identified the presence of lignin-carbohydrate complexes (LCC). 364 365 Chen also identified two types of xylan and proposed two different mechanisms for the removal 366 of each of them. At the early stage of extraction lignin-free xylan is removed and its dissolution 367 is controlled by the hydrolysis of this xylan until fragments are small enough that so that they 368 become soluble in water. After most of the relatively easy to remove xylan (i.e. lignin-free 369 xylan) is dissolved, the xylan dissolution rate is subsequently determined by the slower rate of 370 cleavage of lignin to which xylan is attached, producing soluble LCC xylan. Song et al. (86) 371 investigated the effect of particle size on the extraction of hemicelluloses from ground spruce

wood by hot-water extraction. They found that the strongest effect was on the initial stage of
the extraction and that the process is limited mainly by the diffusion in the fiber wall; mass
transfer limitations were observed on coarse wood shives. Monosaccharides and acetic acid will
diffuse out much faster than hemicelluloses.

**376** 2. From 225 to 350°C

377 Hydrothermal processes can be classified into four main processes: carbonization (HTC), 378 aqueous phase reforming (APR), liquefaction (HTL), and gasification (HTG). In these processes, 379 water can work as a solvent, a reactant, and or a catalyst. The main advantage of hydrothermal 380 processes over conventional methods is the possibility of using wet biomass without prior dewatering. The operational conditions of each process enable production of versatile 381 382 chemicals and fuels in solid, liquid, or gaseous state (87). Hydrothermal carbonization (HTC) can be described as a thermochemical process for 383 384 converting an organic feedstock into carbon-rich products. Typical conditions for HTC are 385 moderate temperatures (180-250 °C), high pressure (2-10 MPa) and presence of liquid water (88). The carbohydrates pass through hydrolysis and re-polymerize subsequently to a solid 386 387 product called hydro-char (a distinct denomination from the bio-chars produced by pyrolysis). 388 The hydro-char exhibits high hydrophobic and friable properties, and hence, is easily separated 389 from the liquid product. The hydro-char demonstrates superior performance relative to the raw 390 biomass in terms of higher mass and energy density, better dewaterability, and improved

391 combustion performance as a solid fuel (89).

Hydro-char yield and properties could depend on feedstock, process temperature and
 residence time. Wiedner and co-workers (90) studied the carbonization of poplar wood, olive

394 residues and wheat straw, and found that chemical properties of hydro-chars varied as a 395 function of carbonization temperature and to a much lesser extent also to feedstock, especially 396 at lower carbonization temperature. According to their work, increasing temperature during 397 the hydrothermal carbonization procedure leads to decreasing polarity and increasing 398 aromaticity of hydro-chars. Biomass transformation at high temperature is associated with 399 decreasing lignin content, increasing degree of lignin oxidation as well as increasing amounts of 400 highly condensed black carbon moieties. In general, hydrothermal carbonization results in a 401 product which is less aromatic and much less condensed than biochar produced during 402 pyrolysis or fire. Feedstock characteristics influence the nature of hydro-char mainly for single 403 compounds and at low temperatures. Material properties were nearly independent from 404 feedstock at carbonization temperatures above 180 °C. Gao and co-authors (91) reported that 405 during the hydrothermal carbonization of eucalyptus bark, temperature played an important 406 role in the yield, physicochemical properties, and thermal behavior of hydro-char products. 407 Effect of residence time was marginal. Higher temperature enhanced the hydrothermal conversion of raw material, resulting in lower yield, higher fixed carbon content, higher fuel 408 409 ratio, higher heating value, lower oxygenated functional groups and a higher thermal stability 410 of hydro-char. Hrncic and co-workers (87), and Wang and co-workers (89) enlist various 411 feedstocks studied for HTC, ranging from model substances to actual feedstock including 412 cellulose, glucose, agricultural residue, animal manures, food waste, municipal solid waste, 413 sewage sludge, and aquaculture and algal residues. In general, all biomass sources for pyrolysis 414 biochar can also be used for HTC (92).

The potential applications of hydro-chars were reviewed by Fang and co-authors (93). 415 Hydro-chars could be used as soil additive in order to increase water and nutrients retention, 416 417 thanks to its high porosity. It is also mentioned the possible application as low cost adsorbent 418 and for capacitor applications. However, most of the studies point the use of hydro-char 419 directly as a solid fuel that can be burned. Most hydro-chars, particularly the ones derived from 420 plant biomass, are considered to be a good potential solid fuel due to their low ash content; the inorganic minerals in the biomass enter the processing liquid during the HTC process, while in 421 422 pyrolysis, the nutrients are retained in the biochar. Materials with lower ash content would 423 burn cleaner and more efficiently since the presence of inorganic minerals that are involved in reactions during biomass combustion causes toxic emissions as well as fouling, slagging, and 424 425 corrosion in combustors. The higher heat value (HHV) has been found to be comparable to that 426 of lignite coal. In a study on lipid extracted algae, hydro-chars converted through HTC not only 427 had sufficient fuel ratio/high heating value for fossil fuel replacement, but also stable combustion characteristics at a high temperature. In addition, the low sulfur and ash contents 428 of hydro-char can provide an option for clean energy source (94). It is proposed an integrated 429 430 energy recovery process, which combines algal biodiesel production and solid fuel production 431 from lipid extracted algae.

On the feasibility of hydro-char plants, Tradler and co-workers proposed a
decentralized, small-scale plant, processing restaurant food waste (95). They found that
feedstocks high in proteins and fat resulted in lower hydro-char yields than feedstocks high in
carbohydrates. Average food waste from restaurants seemed to have an optimal composition
of nutrients for HTC; the energy content was determined as 23,000 kJ/kg. The study pointed

437	that a small-scale HTC plant for restaurants (50 L volume capacity) would pay for itself within
438	eight years. In another work, by Hitzl and co-authors (96), a HTC pilot plant is operated with
439	garden pruning and monitored during two years. The plant capacity was 150 kg/h (dry basis). It
440	was found that the elemental composition of HTC carbon is relatively constant. A carbon
441	content of higher than 60% (based on dry, ash-free matter) is achieved. Fixed carbon content
442	and volatile matter show low variation being the volatile content quite high with 61% on
443	average. Dried in a post-process treatment and pressed into pellets or briquettes, the HTC
444	carbon can be used as solid biofuel fulfilling the European standard (EN 14961-6).
445	On the hydrothermal liquefaction (HTL), the main objective is to obtain the maximum
446	amount of a liquid product with the characteristics of a fuel. The process delivers a liquid phase
447	called bio oil containing water-insoluble components; an aqueous phase with soluble
448	compounds; and a gas phase. The oil usually needs further refining in order to be accepted as
449	fuel and the gaseous product can provide the energy needed for the HTL. The components of
450	the aqueous phase can be recovered and considered as valuable products (97). The HTL bio oil
451	presents high viscosity and high heating value (98). In contrast to pyrolysis, HTL produce no
452	solids at optimized conditions, and the lower process temperatures cause no further
453	degradation on the oil (99). Typical temperatures for HTL process lay between 250 and 370 °C,
454	and pressure sufficient to keep water in liquid state (100). The heating value of the HTL bio oil
455	(30-36 MJ/kg) is higher than pyrolysis oil (20-25 MJ/kg). This is due to the fact that pyrolysis oil
456	retains several polar compounds (acids, alcohols, aldehydes, sugars) and water which are
457	formed during the process and are still present at the oil after cooling. In HTL, polar compounds

with oxygen are dissolved by the aqueous phase and only compounds with low oxygen content(phenols) are present at the oil phase (99).

460	HTL reactions has been conducted on various biomass, e.g., agricultural and forest
461	residues (101), algae (102), food processing residues (103), as well as sewage sludge (104), with
462	aim to optimize operation conditions and improve product yield. These reported results
463	indicate that the effect of the contents of cellulose, hemicellulose, and lignin on hydrothermal
464	bio-oil and biochar yields is uncertain. Apart from the synergistic effect of the three
465	components and feedstock species, the extracts such as terpenoid, pigment, fat, resin, pectin,
466	protein, alkaloid may also affect the yields of bio-oil and hydro-char in biomass hydrothermal
467	conversion (101). Several results were reported for bio-oil yield (wt %) with respect to
468	temperature, showing various trends of bio-oil synthesis. Most of the research reported the rise
469	of bio-oil with increase in temperature, however, there was a specific temperature at which
470	yield is maximum whereas increasing temperature beyond that temperature causes reduction
471	in bio-oil production (105).
472	A particular field of HTL is the decomposition of lignin (106), where the main objective is
473	to get phenols, e.g. for the production of resins. Lignin is less reactive than lignocellulosic
474	biomass and requires therefore higher temperature and maybe the support of a catalyst.

**475** 3. From 350 to 400 °C

This subsection explores the processes and technologies developed to make the
biomass a suitable feedstock for Biorefineries employing near and supercritical water (SCW).
For many applications, the pretreatment of biomass will mean the hydrolysis of polymeric
saccharides or phenolic into oligomers and monomers (107). The saccharide monomers would

480	be source of industrial sugars for fuels, chemicals and materials production. For other
481	applications, the pretreatment of biomass will mean the fractionation of the biomass into its
482	constitutive polymers. Those polymeric fractions would be focused in the production of a whole
483	range of biomaterials.
484	For reference, supercritical water is "just" water, at temperature and pressure
485	conditions above its critical point (Tc=374°C; Pc=22.1 MPa). Arbitrarily, near critical water will
486	be called to water at temperature between $350^\circ$ C and $374^\circ$ C and at the pressure above the
487	liquid vapor equilibrium. The use of SCW for pretreating biomass have been explored for more
488	than half century (108), but only few technologies could make it at pilot or industrial scale. Few
489	concepts are evaluated in the coming paragraphs, from SCW introduction, some successful
490	examples to remaining challenges.
491	The required temperature and pressure (enthalpy) to achieve the critical point of water
492	can be taken as quite high. However, bringing water up to this state is accompanied by some
493	outstanding physical properties that make water a very attractive solvent. To mention a couple,
494	the dielectric constant of water is drastically lower at supercritical conditions than at room
495	temperature (109). To give a strong example of what this means, water-oil systems could be
496	miscible if water is at its supercritical state. Another outstanding behavior is the change of the

ion product of water when moving from room temperature water to the supercritical state.

498 This property will make the reacting/extracting medium, a neutral or an ionic environment

depending the conditions that are chosen (110, 111). Only by mentioning those two properties,

500 one can conclude that near and supercritical water could be employed as a very powerful

solvent for Biorefineries. As it was mentioned at the beginning of the paragraph, the required

temperature could be considered as very high if compared to another biomass pretreatments.
This relatively high temperature (still lower than gasification or pyrolysis) also affects the kinetic
of the chemical reactions involved in the water medium. Following the Arrhenius behavior, a
higher temperate will be usually translated into higher reactions rates. This will represent a big
opportunity for process intensification and a big challenge for chemical reactions control. In
fact, the lack of precise control on temperature and reaction time is usually translated into
"burnt" biomass.

509 The physical and chemical behavior of SCW described in the previous paragraph have 510 motivated the application of this solvent to pretreat the more recalcitrant fractions of vegetal 511 biomass, like cellulose or lignin (107, 111-113). On the other side, the "easier" to 512 hydrolyze/extract polymers, like starch, pectin, proteins or hemicellulose are usually too overreacted in SCW. This is mainly because the reactions rates are increased so much that the 513 514 reaction time should be extremely low to be able to achieve some acceptable level of sugars 515 yields. Only few examples can be found in open literature about hemicellulose and starch hydrolysis/extraction in SCW. Those examples call for super low reaction times (114). 516 517 Cellulose hydrolysis in SCW has been extensively studied all around the globe. However, it 518 should be pointed that Dr. Sasaki and his team made a considerable big discovery when they 519 found that, at supercritical water conditions, the cellulose hydrolysis rate is increased more 520 than predicted by the Arrhenius Law at subcritical conditions (112, 115). That discovery has 521 inspired (and still does) many researchers around the globe to, for example: developed novel 522 reactors to effectively control reaction time and boost selectivity (116); produce 523 oligosaccharides and monosaccharides streams (117, 118); develop kinetic models and reacting

mechanisms (110, 119, 120); improve for cellulose hydrolysis equipment (121, 122) and;
develop cellulose hydrolysis from actual lignocellulosic feedstocks (114, 123). Unfortunately,
only few documents can be found in open literature about the hydrolysis of the cellulosic
fraction in SCW of actual vegetal biomass. Most of the advances have been done in pure
cellulose. This presents also an opportunity for researchers to increase the library of the
cellulosic fraction hydrolysis in SCW.

530 As evaluated above for the other biopolymers, the hydrolysis of lignin is also 531 challenging. Many researchers have tried to convert lignin into its constitutive monomers in 532 SCW. Differently to cellulose or hemicellulose, lignin is formed not only by one or a couple of monomers, but by many derivation of three base phenol alcohols: coumaryl, sinapyl and 533 534 coniferyl. Lignin hydrolysis in near and supercritical water presents a chemical reaction 535 challenge. Many parallel reactions have been demonstrated to happen when lignin is subjected 536 to SCW hydrolysis (124, 125). One group is the breakage of the polymer into oligomers and 537 monomers and other group is the re-bonding of the hydrolyzed molecules into a large molecular weight structures. Unfortunately, this re-bonding phenomenon is not taking place 538 539 recovering the native bond. Because of this, if the re-bonding effect is not well controlled, most 540 of the lignin based biomass can be converted into char-like materials. It is not yet unveiled what 541 would be the most promising approach to hydrolyze lignin into its monomers. Some authors 542 are inclined to maximized lignin hydrolysis in ionic mediums (124) (below the critical point of 543 water, affecting the ion product and others designed reactions where the monomers and 544 oligomers are re-bonded to external alcohols to stabilize the linkage (125)). Dr. Cocero and her 545 team have recently developed a technique to efficiently minimize the re-bonding effect while

still reacting at SCW conditions and without adding a secondary reagent alcohol. This technique
uses the Sudden Expansion Micro Reactor (116) to control reaction time efficiently at SCW
conditions and the reaction medium is dosed with sodium hydroxide to improve lignin
solubility. The scientists are still debating the nature of that process, being ionic-based actioned
by caustic doses (126) or free-radical-based (SCW nature) enhanced by caustic-aid solubility of
lignin.

### 552 Animal Biomass

553 Beside traditional agricultural crops and residues from agriculture and foresting, animal 554 manure is also one source of wet biomass (127). Animal manure contains a high concentration of carbon, nitrogen and phosphorus, whose natural decomposition emits two greenhouse gases 555 556 (GHGs): methane ( $CH_4$ ) and nitrous oxide ( $N_2O$ ), causing nutrient imbalance and pollution in the 557 environment (128, 129). Currently, the most common disposal technique of waste from farms 558 has been the direct land application where untreated derived wastes are used as a fertilizer 559 (130). In this context, there is a need to manage these wastes appropriately, seeking measures 560 for their use for energetic purposes (131, 132). Different techniques are reviewed in the 561 following subsections showing approaches to the conversion of animal waste to a more 562 valuable product. The types of pretreatment technologies reviewed in the coming subsections 563 can be classified as: physical, chemical and biological.

#### 564 Physical pretreatments

565 The physical pretreatment of manure is usually applied to convert the "raw" material 566 into a more efficient form in terms of storage, transport and capability of being employed in

567 further treatments. Among these methods, it can be mentioned: Solid-Liquid separation, Solar

568 Drying, Freeze Concentration and Compaction.

569 The **Solid-Liquid separation** processes (by gravity, mechanical, and chemical processes) 570 allows a redistribution of nutrients, facilitating their final management. The solid fraction is characterized by a higher concentration in organic matter (OM), organic nitrogen and 571 572 phosphorus, among others. In contrast, the liquid fraction is characterized by being less rich in some nutrients than the solid fraction, despite having still dissolved and suspended substances 573 574 in important quantities, such as ammoniacal nitrogen, potassium and other soluble salts. The 575 liquid fraction can be used for irrigation on near fields without elevating the soil test phosphorous levels (133). 576 Solar Drying processes aim to reduce the volume of water from the slurry and/or the 577 solid fraction of the slurry by drying with solar energy under controlled conditions (greenhouse 578 579 system) (134). In order to reduce ammonia emissions, before introducing the wastes into the greenhouse, the pH is modified and, if necessary, bio-filtration is applied to the generated gases 580 with the aim of minimizing gaseous emissions and odors. 581

Freeze Concentration is a technique defined as a method to remove water from solutions by freezing until the formation and separation of ice crystals occurs (135). The process involves the controlled reduction of the temperature of the solution of interest, below its freezing point, in order to avoid reaching the eutectic temperature in which all the components of the product would solidify at the same time. The efficiency of the process is determined by the purity of the ice formed (minimum retention of solutes) (135). FC allows a 50% reduction in the high humidity of solid residues derived from livestock waste.

589	Also, manure can be <b>compacted</b> at relatively high temperatures and pressures, then
590	compressed in a die to form pellets. Pelletizing converts fresh manure to a dry, pathogen-free,
591	easy to handle, finished product that can be used as a fertilizer, soil amendment, feed additive,
592	or energy fuel (136).
593 594	Chemical pretreatments Manure can be chemically treated to improve S-L separation, kill microorganisms,
595	eliminate odors, and limit the spread of diseases. Adding coagulating agents such as ferric
596	chloride, alum, lime, and organic polymers can greatly improve the dewatering characteristics
597	of manure. Coagulants bring manure solids together so they will settle more quickly. In addition
598	to the methods described here, several investigations about chemical treatment of manure
599	have been done using hydrothermal liquefaction to produce hydro-char, bio oils and gaseous
600	products. More details about these technologies can be found in the previous section: Water
601	treatments, From 225 to 350 °C.
602 603	Biological pretreatments Biological treatment uses naturally occurring microorganisms in manure to change the
604	properties of the waste, like: Nitrification-Denitrification, Anaerobic Digestion, Composting and
605	Bio-Drying.
606	Nitrification-Denitrification (NDN) from animal manure is a biological process whose
607	objective is the elimination of nitrogen from the liquid fraction of the slurry (Figure 3).
608	Nitrification is the aerobic oxidation of ammonia to nitrite and nitrate by autotrophic nitrifying
609	bacteria (i.e. $NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$ ). Denitrification is the anoxic reduction of nitrate to nitrite
610	and nitrogen gas by heterotrophic bacteria (i.e. $NO_3^- \rightarrow N_2$ ) (137). In relation to the composition
611	of the liquid fraction of purine, relative values between the chemical demand of oxygen and

612	nitrogen (COD/N ratio) of 6-8 are usually favorable for the NDN process. Under proper
613	operating conditions, maximum nitrogen removal efficiencies attainable are up to 70% (rest of
614	N will be separated in the solid fraction, assimilated by the biological sludge, or will remain in
615	the liquid effluent). If efficiency is evaluated on the liquid phase it may be more than 90% (138).
616	Another biological pretreatment is the Anaerobic Digestion (AD). In AD processes,
617	organic materials are degraded by bacteria converting it into a gas mixture, called biogas
618	(Figure 4). Biogas is generally composed of about 60% $CH_4$ and 40% $CO_2$ (139, 140). Four
619	successive biological processes are involved in the anaerobic degradation of OM including
620	hydrolysis, acidogenesis, acetogenesis and methanogenesis (141). The digestate from the
621	digester is a more stable product rich in ammonium and other nutrients that can be a good
622	source of fertilizer (139, 142). The microorganisms involved in this process are sensitive to
623	manure properties, including: pH, temperature and ammoniacal nitrogen (143). In general, the
624	recovery of biogas in the form of heat and electricity can be done in-situ, via combustion or
625	electric co-generation, taking advantage of a part of the thermal energy to heat the digester
626	(139).

627 **Composting** is a process of aerobic decomposition and stabilization of organic materials 628 in an operating regime that allows reaching thermophilic temperatures. With this process, a 629 stable and sanitized solid product is obtained, free of pathogens. To start the composting 630 process, it is recommended that the material to be composted has a moisture content between 631 50 and 60%, a carbon/nitrogen ratio (C/N ratio) between 25 and 30, and sufficient porosity to 632 favor circulation of air inside the stacked material, so often lignocellulose material is also added 633 that acts as a structuring agent (136). Compost, the resulting product of this pretreatment, is an

- odorless, low-moisture-content, fine-textured material that can be used in bulk as an organic
- 635 fertilizer or bagged and sold for use in nurseries and gardens and for potting media.
- 636 Composting can be completed within several weeks (136, 144).
- 637 **Bio-drying** is a technology that makes use of bioenergy from organic waste with high
- 638 water content to remove moisture and improve the utilization value and treatability of the
- 639 waste. The essential feature of bio-drying is the utilization of thermal energy, generated by
- 640 aeration degradation of OM in waste, to evaporate water, thus achieving self-drying (145). Bio-
- 641 drying technology is similar to that of composting. In this case, the main goal of bio-drying is to
- remove as much moisture as possible in the shortest time, by controlling process parameters
- 643 (different aeration and moisture content compared with composting) and the subsequent
- 644 product is utilized as refuse-derived fuel (RDF) (138, 145).

### 645 Research prospective

The biorefinery concept was proposed as early as the late 1980s (146), and nowadays is

- 647 not yet available due to the cost and complexity of processing biomass to generate practical
- 648 and usable chemicals and energy. Many research groups are involved in biomass valorization,
- 649 but efficient biomass fractionation is actually one of the major challenges posed to the
- 650 Biorefineries developments.
- 651 Another important challenge is the development of products close to the market. This is
- 652 illustrated by products supported in lignin or in aromatics from the lignin depolymerization.
- 653 There is already a market dedicated to produce biopolymers for aromatic monomers. Bio-based
- 654 conventional polymers' growth rates are at same level as global polymers: worldwide
- 655 production capacity is forecasted to increase from 6.6 million tons in 2016 to 8.5 million in

656	2021. In the absence of renewable aromatic building blocks, polymers are currently produced		
657	from a petrochemical aromatic molecule and a bio-based aliphatic molecule (147). Linked to		
658	lignin research, Ragauskas et al. have presented the next paradigm exposing reality: "although		
659	fundamental research has historically focused on converting lignin to chemicals materials, very		
660	little of this effort has been translated into commercial practice". So, what has changed to		
661	address this deadlock? (148).		
662	The vision for developed scale up processes considers the energy balance, and focuses		
663	research on the development of products close to market. This will redirect the research vision		
664	to address the deadlock.		
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1031 Figures and Captions

#### 1032 Figure 1



- 1034 Figure 1. Publication trends of the microwave pretreatment of biomass (34).
- 1035 Figure 2



1037 Figure 2. Transmission electron microscopy of the effects of microwave heating on vegetable

1038 cells (modified from (41)). Brassica napus rapeseed before microwave treatment (left). Brassica

- 1039 *napus* rapeseed after 5 minutes of microwave treatment. CW, cell wall; PB, protein bodies; MG,
- 1040 myrosin cells; OB, oil bodies.
- 1041



**Figure 4.** Schematic of basic process of anaerobic digestion.