1   # Pretreatment Processes of Biomass for Biorefineries: Current Status

2   # and Prospective

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15   **Shortened Title:** Making Biorefinery happen

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Abstract

36 This manuscript seeks to be a handy document for the academy and the industry to get quickly

37 up to speed on the current status and perspectives of biomass pretreatment for Biorefineries.

38

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_2, 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

50   The concept of biorefinery could be evaluated as an analogous to the conventional

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

53   bioproducts – materials, chemicals, food and feed. Achieving this wide range of products

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

56   mechanical processes – thermochemical processes, chemical and biotechnological processes.

57   These processes are not substantially different to the processes used in the petrochemical

58   industry, except for the following three main aspects. 1) Biomass is commonly a solid, so, the

59   pretreatment processes are different. The biorefinery pretreatments are usually close to agro-

60   food industries transformations. 2) The second difference lies in the products, biorefinery

61   products are usually solid nonvolatile products. Thus, distillation does not play the important

62   role as in the petrochemical industry. In biorefinery processes, the membranes technology is a

63   typical downstream refining process. 3) The third main difference is the production of building

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

67   synthesis gas. Organic chemistry, therefore, has to develop a new organization for chemical

68   production of these biomass platforms.

69   Recent reviews present a background of Biorefineries development. Chandel at al. have

70   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

108   fields, electric fields and irradiation have been extensively studied (7, 8). Ultrasounds, electric

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.

124   In many cases, further densification up to 600-800 kg/m^3 is needed for non-woody materials

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

127   briquettes and pellets.

128   Ultrasounds pretreatment affect the structure of the lignocellulosic materials due to

129   mechanistic and chemical effects. Firstly, perforations are produced ("pitting") on the biomass

130   (after long processing time, 5 h). This increases the porosity and improves the yield for

131   enzymatic hydrolysis, although not as much as diluted ammonia pretreatment (15). Ultrasound

132   pretreatment is particularly effective in the removal of amorphous components such as

133   hemicelluloses and lignin, improving the accessibility to cellulose. For this purpose, a variety of

134   solvents can be used: organic solvents, alkali, lime, hydrogen peroxide and surfactants (16).

135   Further, specific hemicelluloses such as β-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

166 dioxide is also a green solvent alternative to the extraction of lipophilic materials. However, its

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 of

176 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).

201   •   Microwave treatment and extraction

202   As it is observed in Figure 1 (34), microwave technology exploration has increased in the

203   last years. This expansion of the research is owed (in our opinion) to the new possibilities that

204   microwaves can provide to improve both the energy use and the structural characteristics of

205   the biomass. Therefore, there have been recent reviews on the subject (35–38). In the

206   following, we will summarize what are, from our point of view, the most interesting facts

207   related with this technology and we will propose the way forward towards scalable processes.

208   The interesting fact of the use of microwaves during biomass pretreatment is the

209   possibility to apply fast, volumetric and selective heating (39, 40). This, in the end, result in less

210   heat losses and more compact and flexible processes when compared with the conventional

211   ones. Consequently, the material is selectively heated from inside out as opposed to

212   conventional heating.

213   For every pretreatment process, it is especially important that cellulose can be

214   effectively retrieved. For the particular case of microwaves, the localized and fast heating

215   damages the structure of the biomass resulting in more porosity and surface area. This damage

216   is the consequence of the cleavage of the lignocellulosic composite that in turn helps to split

217   hemicellulose, lignin and cellulose. The result is the increased availability of hemicellulose and

218   cellulose for further transformation (41, 42).

219   The breakup of vegetable cells have been reported in the literature related to the

220   application of microwaves both as process factor or as pretreatment (43, 44). Figure 2 shows

221   examples of such effects.

222   The damage and change on the biomass structure have been explained by two main

223   hypotheses (35, 36). The first one addresses the direct interaction of the microwaves with the

224   hydroxyl groups and hydrogen bonds of the lignocellulosic biomass (45). The second hypothesis

225   involves the overheating and over pressure owed to the rapid heating of water trapped on the

226   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.

232   The fast transmission of microwaves directly into the material helps to create potential

233   for higher yields of treated matter and consequently helps the economy of the process (51).

234   This opens the possibility for the economical use of biomass using a distributed production

235   perspective. More compact, continuous processing equipment is thus possible.

236   Nevertheless, as with any other technological option, microwave pretreatment of biomass

237   has got drawbacks. The main one is the lack of the phenomenological understanding necessary

238   in order to be able to design and optimize the microwave enhanced pretreatment of biomass.

239   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

241   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

246   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

251   have strict control of parameters such as electromagnetic field distribution, frequency,

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).

255   -   "Application Scale". In the personal view of the authors, the one-size-fits-all approach for

256   microwave so commonly found is tremendously detrimental for future applications. The

257   effective dielectric properties and electromagnetic fields found in a household microwave

258   cannot be simply extrapolated in a scaled-up version. Therefore, intensive mathematical

259   modelling efforts have to complement the work in order to be able to predict the process

260   evolution. Novel process configurations can be then proposed that allow to design the

261   equipment for each application with precise control of the material properties and yield.

262 •   Water treatments

263   1.   From 150 to 225°C

264   The use of water at mild temperatures has been greatly successful in the extraction and

265 hydrolysis of less recalcitrant biomass components, like hemicellulose. In general,

266 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
270   The fractionation is a pretreatment required to make cellulose more accessible for

271 enzymatic hydrolysis. These pretreatments remove hemicelluloses together with lignin. There

272 are numerous reviews in literature summarizing these treatments (55–58). The most studied

273 treatments are catalyzed and uncatalyzed steam explosion, dilute-acid hydrolysis and liquid hot

274 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

279 minutes before the material is exposed to atmospheric pressure (56). Steam explosion involves

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

282 (57). The process can also cause lignin transformation due to high temperature and acidity. In

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   Pre-Extraction
317   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

333   130 kJ mol^{-1} was obtained for the activation energy of xylan degradation. Autohydrolysis of

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

337   proposed that the solid phase can then be used for pulp and paper production.

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.

342   (78) studied the recovery of hemicellulose before kraft pulping on Eucalyptus globulus wood

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

347   pulp production by the pre-hydrolysis-kraft process. Here wood chips are subjected to harsh

348   conditions using steam at 160-180 °C for 30-120 min (72). The pre-hydrolysate formed is

349   displaced by black liquor and white liquor. In principle, it would be possible to recover the pre-

350   hydrolysate by drainage and water displacement; unfortunately, lignin precipitates generated

351   at high temperature and acidic conditions (79, 80) lead to large operational problems (81). A

352   formic acid (FA) reinforced aqueous pre-hydrolysis process is proposed to reduce the amount of

353   lignin precipitates (82). The molecular weight, Mw, and polydispersity, Mw/Mn, of the

354   precipitated lignin decreased from about 2600 g/mol and 3.0 at autohydrolysis conditions to

355   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.

359   Conner (83) proposed the existence of two types of xylan, both of them modeled through first

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

364   a recent study Chen et al. (85) identified the presence of lignin-carbohydrate complexes (LCC).

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

372   wood by hot-water extraction. They found that the strongest effect was on the initial stage of

373   the extraction and that the process is limited mainly by the diffusion in the fiber wall; mass

374   transfer limitations were observed on coarse wood shives. Monosaccharides and acetic acid will

375   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

381   dewatering. The operational conditions of each process enable production of versatile

382   chemicals and fuels in solid, liquid, or gaseous state (87).

383   Hydrothermal carbonization (HTC) can be described as a thermochemical process for

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

386   (88). The carbohydrates pass through hydrolysis and re-polymerize subsequently to a solid

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).

392   Hydro-char yield and properties could depend on feedstock, process temperature and

393   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

408   conversion of raw material, resulting in lower yield, higher fixed carbon content, higher fuel

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).

415   The potential applications of hydro-chars were reviewed by Fang and co-authors (93).

416 Hydro-chars could be used as soil additive in order to increase water and nutrients retention,

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

421 inorganic minerals in the biomass enter the processing liquid during the HTC process, while in

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

424 reactions during biomass combustion causes toxic emissions as well as fouling, slagging, and

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

428 combustion characteristics at a high temperature. In addition, the low sulfur and ash contents

429 of hydro-char can provide an option for clean energy source (94). It is proposed an integrated

430 energy recovery process, which combines algal biodiesel production and solid fuel production

431 from lipid extracted algae.

432   On the feasibility of hydro-char plants, Tradler and co-workers proposed a

433 decentralized, small-scale plant, processing restaurant food waste (95). They found that

434 feedstocks high in proteins and fat resulted in lower hydro-char yields than feedstocks high in

435 carbohydrates. Average food waste from restaurants seemed to have an optimal composition

436 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

458   with oxygen are dissolved by the aqueous phase and only compounds with low oxygen content

459   (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

476   This subsection explores the processes and technologies developed to make the

477   biomass a suitable feedstock for Biorefineries employing near and supercritical water (SCW).

478   For many applications, the pretreatment of biomass will mean the hydrolysis of polymeric

479   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°C and 374°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

497   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

499   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

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

502   temperature could be considered as very high if compared to another biomass pretreatments.

503   This relatively high temperature (still lower than gasification or pyrolysis) also affects the kinetic

504   of the chemical reactions involved in the water medium. Following the Arrhenius behavior, a

505   higher temperate will be usually translated into higher reactions rates. This will represent a big

506   opportunity for process intensification and a big challenge for chemical reactions control. In

507   fact, the lack of precise control on temperature and reaction time is usually translated into

508   "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

513   overreacted in SCW. This is mainly because the reactions rates are increased so much that the

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

516   hydrolysis/extraction in SCW. Those examples call for super low reaction times (114).

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

524   mechanisms (110, 119, 120); improve for cellulose hydrolysis equipment (121, 122) and;

525   develop cellulose hydrolysis from actual lignocellulosic feedstocks (114, 123). Unfortunately,

526   only few documents can be found in open literature about the hydrolysis of the cellulosic

527   fraction in SCW of actual vegetal biomass. Most of the advances have been done in pure

528   cellulose. This presents also an opportunity for researchers to increase the library of the

529   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

533   monomers, but by many derivation of three base phenol alcohols: coumaryl, sinapyl and

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

538   molecular weight structures. Unfortunately, this re-bonding phenomenon is not taking place

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

546   still reacting at SCW conditions and without adding a secondary reagent alcohol. This technique

547   uses the Sudden Expansion Micro Reactor (116) to control reaction time efficiently at SCW

548   conditions and the reaction medium is dosed with sodium hydroxide to improve lignin

549   solubility. The scientists are still debating the nature of that process, being ionic-based actioned

550   by caustic doses (126) or free-radical-based (SCW nature) enhanced by caustic-aid solubility of

551   lignin.

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

555   of carbon, nitrogen and phosphorus, whose natural decomposition emits two greenhouse gases

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.

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

571   characterized by a higher concentration in organic matter (OM), organic nitrogen and

572   phosphorus, among others. In contrast, the liquid fraction is characterized by being less rich in

573   some nutrients than the solid fraction, despite having still dissolved and suspended substances

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

576   phosphorous levels (133).

577   **Solar Drying** processes aim to reduce the volume of water from the slurry and/or the

578   solid fraction of the slurry by drying with solar energy under controlled conditions (greenhouse

579   system) (134). In order to reduce ammonia emissions, before introducing the wastes into the

580   greenhouse, the pH is modified and, if necessary, bio-filtration is applied to the generated gases

581   with the aim of minimizing gaseous emissions and odors.

582   **Freeze Concentration** is a technique defined as a method to remove water from

583   solutions by freezing until the formation and separation of ice crystals occurs (135). The process

584   involves the controlled reduction of the temperature of the solution of interest, below its

585   freezing point, in order to avoid reaching the eutectic temperature in which all the components

586   of the product would solidify at the same time. The efficiency of the process is determined by

587   the purity of the ice formed (minimum retention of solutes) (135). FC allows a 50% reduction in

588   the high humidity of solid residues derived from livestock waste.

589   Also, manure can be **compacted** 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   Chemical pretreatments

594   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   Biological pretreatments

603   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

634   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

642   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

646   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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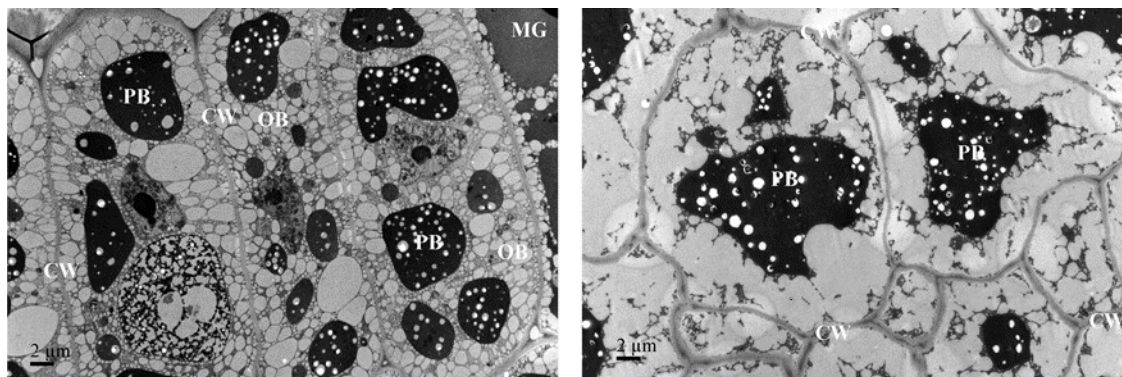1030

1031   Figures and Captions

1032   **Figure 1**
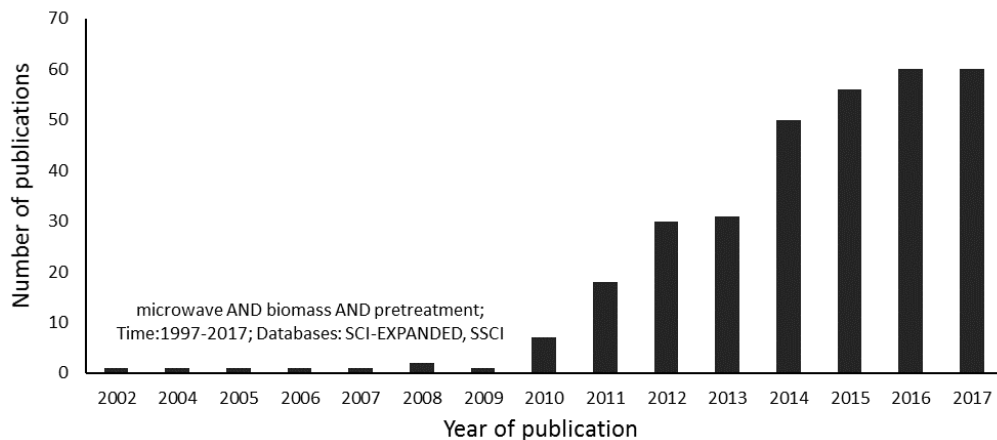
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1034   Figure 1. Publication trends of the microwave pretreatment of biomass (34).
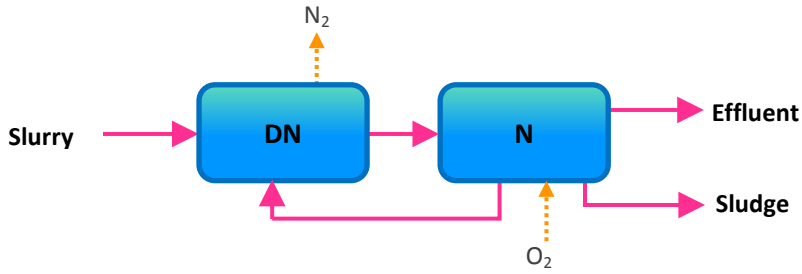
1035   **Figure 2**

1036

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,

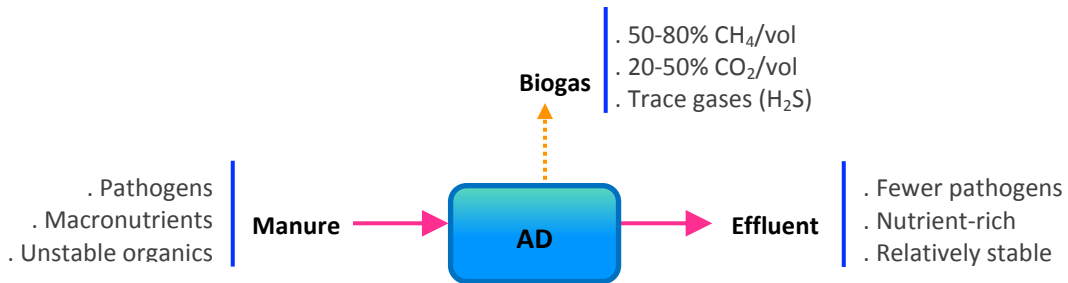1040   myrosin cells; OB, oil bodies.

1041

1042   **Figure 3**

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1044   **Figure 3.** Schematic of basic process of conventional nitrification-denitrification.

1045   **Figure 4**

1046

1047   **Figure 4.** Schematic of basic process of anaerobic digestion.