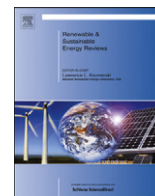Contents lists available at SciVerse ScienceDirect

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Hydrothermal processing, as an alternative for upgrading agriculture residues and marine biomass according to the biorefinery concept: A review

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ABSTRACT

The concept of a biorefinery that integrates processes and technologies for biomass conversion demands efficient utilization of all components. Hydrothermal processing is a potential clean technology to convert raw materials such as lignocellulosic materials and aquatic biomass into bioenergy and high added-value chemicals. In this technology, water at high temperatures and pressures is applied for hydrolysis, extraction and structural modification of materials. This review is focused on providing an updated overview on the fundamentals, modelling, separation and applications of the main components of lignocellulosic materials and conversion of aquatic biomass (macro- and micro- algae) into value-added products.

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Contents

1. Introduction

Considering the amount of biomass available, there is a clear opportunity to develop commercial processes that could generate products needed at very high volumes and low selling price. Most of

such products are now being made from non-renewable resources, mainly through oil refineries. These refineries, starting from a complex mixture (petroleum), use a wide range of unit operations to generate an impressive variety of products that are sold directly or transformed into value-added products such plastics and fibers. Approximately 17% of the volume of products derived from petroleum in the US is classified as chemicals [1]. If these chemicals could be obtained from renewable resources (e.g., biomass in a biorefinery), it would reduce petroleum dependence while also having a positive environmental impact. In recent years the use of different renewable

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raw materials (lignocellulose material (LCMs) and aquatic marine materials) has been a growing trend for different applications and products such as energy, fuels, chemical, cosmetics, medical applications, construction materials and high added-value products for food or feed. The term "biorefinery" borrows its origin from the classical petroleum refinery concept and refers to biomass conversion into fuels and chemicals with high added-value through the integration of clean processes [2,3]. Several technologies have been developed during the last decades that allow this conversion process to occur, the clear objective being now to make this process cost-competitive in today's markets. Hydrothermal processing is an alternative for the fractionation of these raw materials (LCMs and aquatic biomass). The fractionation refers to the conversion into its main constituent: LCMs (i.e., cellulose, hemicellulose and lignin); macroalgae (different polysaccharides depending of taxonomic groups); microalgae (oils, proteins, carbohydrates) [4–6]. Bobleter et al. [7] pioneered in using water for pretreatment to enhance the susceptibility of lignocellulosic material to enzymatic hydrolysis. The processes with liquid water under high temperature and pressure are also called autohydrolysis, hydrothermal treatment, hot compressed water (HCW), hydrothermolysis, liquid hot water (LHW), aquasolve process, aqueous processing and pressure-cooking in water [8–24]. The objective of this review is to present research progresses in hydrothermal processing of lignocellulosic materials and aquatic biomass for the fractionation of their main components. The fundamentals, mathematical modeling, effects of hydrothermal processing on cellulose, hemicellulose and lignin and their applications are reviewed. Additional information on the application of this technology to aquatic biomass (macro- and micro- algae) is also provided.

2. Hydrothermal processing of lignocellulosic material

Hydrothermal processing has been considered a cost-effective pretreatment [25] and in general, the major advantages that this process offers are: (1) the process does not require the addition and recovery of chemicals different from water, (2) limited equipment corrosion problems, (3) simple and economical operation [26–29]. For that reason, the hydrothermal processing can be considered an environmentally friendly fractionation process [30]. Lignocellulosic materials (LCMs) are the most abundant renewable biomass and its annual production was approximately estimated in 200 billion metric tons worldwide in 2007 [31]. LCMs are mainly composed of cellulose, hemicellulose and lignin and have great potential as cheap and renewable feedstock for different applications. In general, LCMs include agricultural residues, herbaceous, hardwood, softwood, cellulose wastes and industry co-products. Table 1 shows the composition of different lignocellulose materials. The fractionation of LCMs into products derived from their structural components is an attractive possibility leading to the biorefinery concept. However, the main problem of fractionation is the recalcitrant nature of these materials. Fractionation may be achieved through hydrothermal processing, whose first step is hemicellulose solubilization. Fig. 1 shows the scheme of a biorefinery using hydrothermal processing. This process has been mainly used as a pretreatment for bioethanol production; in recent researches, the use of a sequential process has been applied as an alternative of papermaking production, also as a technology for converting agro-food by-products into useful food ingredients [12, 65–71].

2.1. Fundamentals and operating conditions of hydrothermal processing

In hydrothermal processing LCMs are exposed to water in the liquid state, at elevated temperature and pressures, that penetrated cell's structures, hydrates cellulose, depolymerizes hemicellulose (to oligomers and monomers) being between 40% and 60% of the total biomass dissolved in the process (Fig. 2). In water at high temperatures (150–230 °C), the H-bonding starts weakening, allowing

Table 1
Composition of selected lignocellulosic materials (% dry matter).

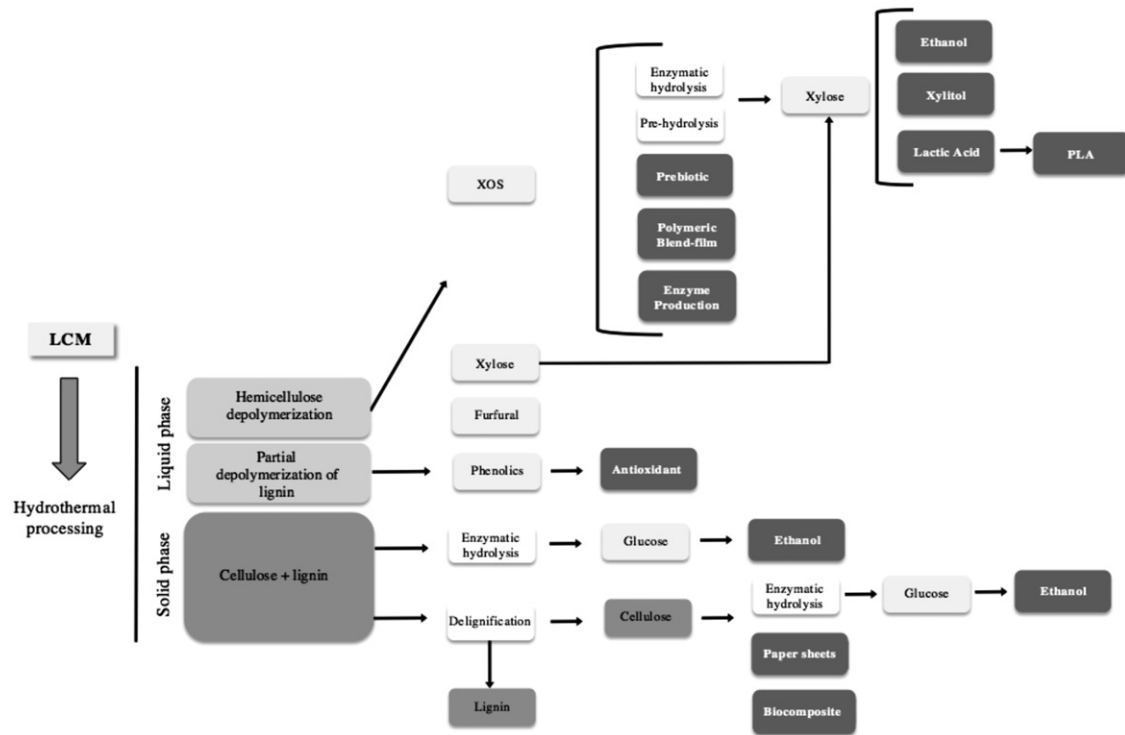| Raw material	Cellulose (%)	Hemicellulose (%)	Lignin (%)	References
Agricultural residues				
Corn cobs	38.8–44	33–36.4	13.1–18	Liu et al. [32]; Wang et al. [33]
Corn stover	34.32–36.5	20.11–31.3	11.9–13.55	Weiss et al. [34]; Liu and Cheng [35]
Wheat straw	33–40	20–33.8	15–26.8	Ruiz et al. [12]; Talebnia et al. [36]
Rice straw	35–36.6	16.1–22	12–14.9	Hsu et al. [37]; Yadav et al. [38]
Sugar cane bagasse	34.1–49	15.79–29.6	19.4–27.2	Mesa et al. [39]; Maeda et al. [40]
Barley straw	37.5	25.1–37.1	15.8–16.9	Sun et al. [41]; García-Aparicio et al. [42]
Rice husk	33.43	20.99	18.25	Garrote et al [43]; Abbas and Ansumali [44]
Rye straw	41.1–42.1	23.8–24.4	19.5–22.9	Ingram et al. [21]; Gullón et al. [45]
Rapessed straw	36.59–37	19.6–24.22	15.55–18	Díaz et al. [13]; Lu et al. [46]
Sunflower stalks	33.8	20.2–24.27	14.6–19.9	Ruiz et al. [47]; Caparrós et al. [48]
Sweet sorghum bagasse	41.33–45.3	22.01–26.3	15.2–16.47	Zhang et al. [49]; Goshadrou et al. [50]
Herbaceous				
Switchgrass	41.2–32.97	25.95–31.1	17.34–19.1	Keshwani and Cheng [51]; Hu et al. [52]
Alfalfa stems	24.7	14.7	14.9	Ai and Tschirner [53]
Coastal Bermuda grass	25.59	19.29	19.33	Wang et al. [54]
Hardwood				
Aspen	43.8	18	20.8	Tian et al. [55]
Hybrid Poplar	48.95	21.73	23.25	Pan et al. [56]
Eucalyptus	44.6	21.4	30.1	Gonzalez et al. [57]
Eucalyptus globulus	44.4	21.8	27.7	Romaní et al. [9]
Softwood				
Pinus radiata	45.3	22.5	26.8	Araque et al. [58]
Spruce	43.8	20.8	28.83	Shafiei et al. [59]
Cellulose wastes				
Newspapers	60.3	16.4	12.4	Lee et al. [60]
Recycled paper sludge	60.8	14.2	8.4	Peng and Chen [61]
Industry co-products				
Distiller's grains	12.63	16.9	–	Kim et al. [62]
Brewer's spent grain	18.8–20.97	15.18–32.8	21.7–25.62	Carvalheiro et al. [63]; Pires et al. [64]

Fig. 1. Scheme of a biorefinery using hydrothermal processing and LCMs as raw material.
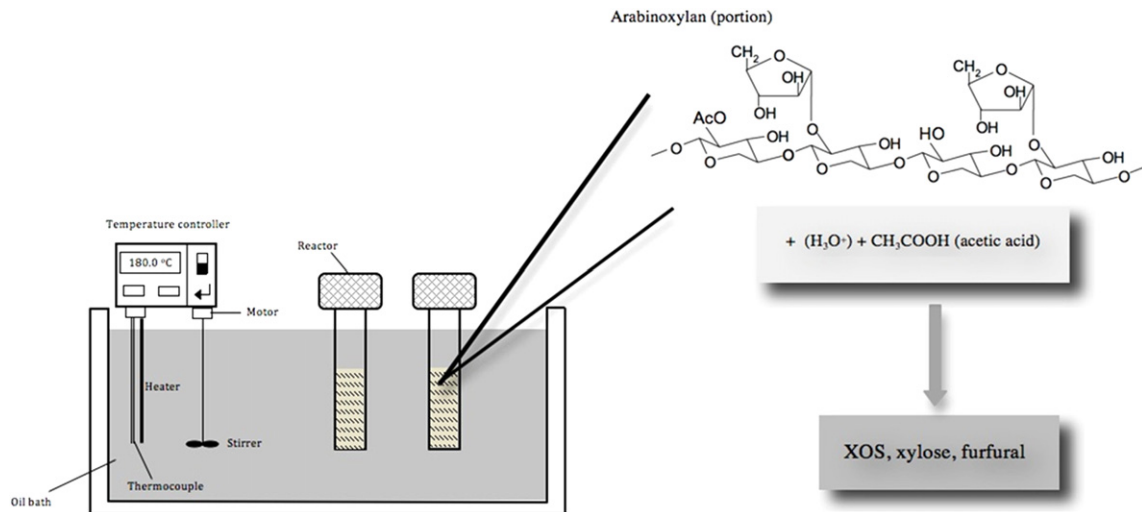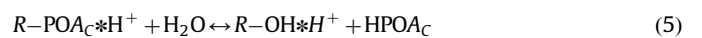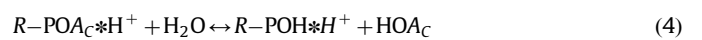

Fig. 2. Batch reactor systems for hemicellulose depolymerization in hydrothermal processing.

autoionization of water into acidic hydronium ions (H_3O^+) that act as catalysts and basic hydroxide ions (OH^-). In the subcritical region (100–374 °C) the ionization constant (K_w) of water increases with temperature. However, when exceeding its critical point (374 °C and 22.1 MPa), the values of dielectric constant, ionization constant (K_w) and ionic product of water drop drastically. Moreover, hydronium ions are generated from organic acids, mainly acetic acid from acetyl groups and uronic acid [28,72–75]. Acetyl groups are present in LCMs and as they are associated with hemicellulose, the hydration of the acetyl groups leads to the acidification of the liquor and thus, formation of hydrogen ions. A number of hypotheses have been suggested to explain this phenomenon. According to these considerations, in a recent work, Liu [76] presented the following model for

hemicellulose solubilization in hydrothermal processing.

$$H_2O \leftrightarrow H^+ + OH^- \tag{1}$$

$$H^+ + H_2O \leftrightarrow H_3O^+ \tag{2}$$

$$R{-}POA_C + H^+ \leftrightarrow R{-}POA_C{*}H^+ \tag{3}$$

$$R{-}POA_C{*}H^+ + H_2O \leftrightarrow R{-}POH{*}H^+ + HOA_C \tag{4}$$

$$R{-}POA_C{*}H^+ + H_2O \leftrightarrow R{-}OH{*}H^+ + HPOA_C \tag{5}$$

$$HOA_C \leftrightarrow H^+ + OA_C^- \tag{6}$$

$$R-POH*H^+ \leftrightarrow R-POH+H^+ \qquad (7)$$

$$R-OH*H^+ \leftrightarrow R-OH+H^+ \qquad (8)$$

Reaction steps to solubilize hemicellulose

$$R-X_nOH+H^+ \leftrightarrow R-X_nOH*H^+ \qquad (9)$$

$$R-X_nOH*H^+ + H_2O \leftrightarrow R-X_mOH*H^+ + HX_SOH \qquad (10)$$

Reaction steps to reduce the chain length inside the hydrothermal process liquor

$$HX_nOH+H^+ \leftrightarrow HX_nOH*H^+ \qquad (11)$$

$$HX_nOH*H^+ + H_2O \leftrightarrow HX_mOH*H^+ + HX_SOH \qquad (12)$$
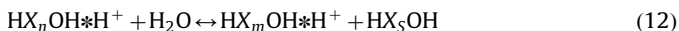
where X_n represents an n-xylooligomer middle group, $m+s=n$, R- denotes the cellulose or lignin bonded to LCMs, P represents a segment of hemicellulose, HX_nOH is an n-xylooligomer, HOA_C represents the acetic acid molecule and A_C is CH_3CO [76]. On the other hand, the most important operational variables of hydrothermal processing include temperature, residence time, particle size, moisture content (ratio liquid/solid) and pH influence on the fractionation of LCMs and must be taken into consideration to maximize the product yield (i.e., hemicellulose sugar production, accessible surface area for enzymatic saccharification, etc.). The relationship between temperature-time strongly influences the physical–chemical characteristics of LCMs in hydrothermal processing. Ballesteros et al. [77] reported an increase of hemicellulose-sugar degradation at higher temperatures and residence times, concluding that at more severe operational conditions there are more losses of hemicellulosic sugar. For this reason, a strict control is required for high temperature reactions due to thermal degradation. Several works showed that the products (pentose and oil yield) from hydrothermal processing are favored at lower reaction temperatures and longer residence times [78–80]. Normally, when larger particle sizes are used, heat transfer problems lead to overcooking of the exterior (with consequent formation of inhibitors) and incomplete autohydrolysis of the interior. This problem can be overcome by reducing particle size as the first pretreatment step. This size reduction process not only changes the particle size and shape, but also increases bulk density, improves flow properties, increases porosity, increases surface area and is usually required to make material handling easier before hydrothermal processing. The higher surface area increases the number of contact points for chemical reaction [12,81]. Mosier et al. [82] reported that size reduction is not needed since the lignocellulose particles break apart when cooked in water. Ballesteros et al. [83] showed that the utilization of very small chips of softwood in hydrothermal processing would not be desirable to optimize the effectiveness of the process and improve economy, due to the significant energy requirements of particle reduction process. However, in recent work, Hosseini and Shah [84] reported that it is possible to improve in 50% the energy efficiency of pretreatment by the optimization of particle size properties. According to Ruiz et al. [12], the use of blends with different particle size distributions has a selective influence over the sugar extraction: thus, the use of a blend with defined percentages of the various particle sizes is recommended before carrying out a hydrothermal processing. Moisture content and ratio liquid/solid may also greatly influence the ability of heat and chemicals (H_3O^+) to penetrate LCMs, causing an uneven treatment of material. An uneven treatment can potentially result in the selective degradation of the outer portion of the LCMs, while at the same time the interior is less affected by the treatment [81]. Cullis et al. [85] reported that the moisture content has a dramatic effect on the efficacy of the hydrothermal processing as a substantial decrease in the amount of hemicellulose-derived carbohydrates recovered in the water-soluble fraction was observed when increasing the starting moisture content from 12 to 30%, Rodríguez et al. [86] showed that it is possible to obtain high glucose, xylose, arabinose and acetic acid concentrations by combining high temperatures with a medium-low treatment time and liquid/solid ratio. On the other hand, the formation of hydronium ions from water and from organic acids is an important factor during hydrothermal processing, since the LCMs and water mixture will reach high temperatures and pressures during the process. These high temperatures and pressures will accelerate the acid-catalyzed hydrolysis of cellulose and hemicellulose as well as the acid-catalyzed degradation of glucose and xylose. Monitoring and control of the pH in hydrothermal processing will maximize the solubilization of the hemicellulose fraction as liquid soluble oligosaccharides while minimizing hydronium ions concentration and, more importantly, the degradation of these oligosaccharides and monosaccharides to degradation products [29,87]. Mosier et al. [88] pretreated corn fiber using pH controlled liquid hot water at 160 °C and a pH value above 4.0 and found that 50% of the fiber was dissolved in 20 min. The carbohydrates dissolved by the pretreatment were 80% soluble oligosaccharides and 20% monosaccharides with < 1% of the carbohydrates lost to degradation products. Cara et al. [89] reported a slight pH decrease of hydrothermal processing hydrolyzates, in the range of 3.8 to 3.3, and an increase of degradation product concentrations (furfural) from 0.4 to 1.7 g/L, respectively.

In hydrothermal processing there are different types of reactor configurations. (1) *Batch reactor:* LCMs solid particles are mixed with water in the reactor (Fig. 3A). The residence time of the reacting solid is long [8,16,90–92]. In a recent work, Gullón et al. [45] reported a conversion of 69.2% from initial xylan into xylooligosaccharides using a batch reactor configuration at 208 °C and rye straw as raw material; (2) *Semi-continuous reactor* of (flow-through partial flow-through): hot water is passed over a stationary bed of LCMs and dissolves lignocellulose components while the liquid products are rapidly swept out (Fig. 3B). The residence time of liquid products is short, compared to a batch reactor [16,82,93–98]. Liu and Wyman [99] reported that in this type of reactors the fluid velocity in flow through has a significant impact on hydrothermal processing. Increasing fluid velocity significantly accelerated solubilization of total mass, hemicellulose and lignin even at the similar liquid residence times; (3) *Continuous reactor* (co-current, counter-current): the LCMs are passed in one direction while water is passed in the same or opposite direction (Fig. 3C and D). A continuous reactor system is also typically required to operate at high temperatures and pressures to achieve a high conversion of the feedstock within a short residence time [16,82,100–102]. Makishima et al. [103] reported a 82% conversion of xylan in xylose and xylooligosaccharides using a continuous flow type reactor. Yu and Wu [16] suggested that the characteristics of liquid products are strongly influenced by the reactor configuration.

2.2. Modeling of hydrothermal processing

Modeling in hydrothermal processing provides a way to compare results from experiments carried out at different conditions. Table 2 shows the main mathematical models used in both isothermal or non-isothermal hydrothermal processing (Fig. 4A and B) [69,104]. An often used option to modeling the effects of the main operational variables by pseudo first order kinetics is the severity factor (R_0) proposed by Overend and Chornet [105] and Chornet and Overend [106]. This empirical model has been
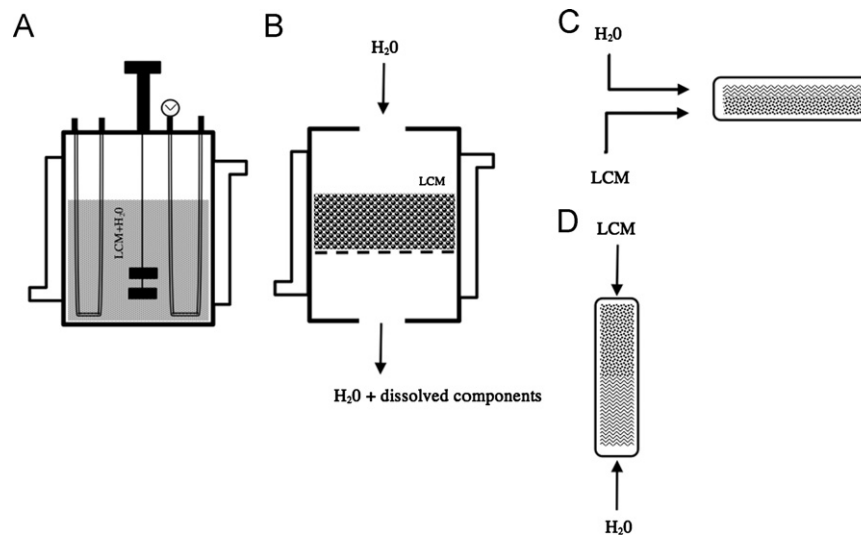
Fig. 3. Representation of different reactor configurations for hydrothermal processing. (A) batch; (B) semi-continuous (flow-through reactor); (C) continuous (co-current); (D) continuous (counter-current)(adapted from Mosier et al. [82]; Yu and Wu [16]).

Table 2
Models used in hydrothermal processing.

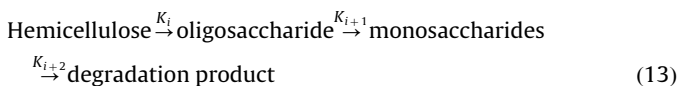| Effect	Model	Variables	Reference
Severity factor R_0, easy way for comparing results among experiments carried out under different conditions of temperature and time.	$R_0 = \int_0^t exp\left[\frac{T-100}{14.75}\right] dt$	t is the reaction time (min), T is temperature (°C), 100 is the temperature of reference and 14.74 is an empirical parameter related with activation energy, assuming pseudo first order kinetics. The results are usually represented as a function of log (R_0).	Overend and Chornet [105]; Chornet and Overend [106]
H-factor (HF), is a relationship between time and temperature, which is only an approximation of the reaction due to the fact that the proton concentration changes with time and activation energy. The concept of HF was development for Kraft/chemical pulping. However, also has been applied for hydrothermal processing Griebl et al. [64].	$HF = \int_0^t exp\left(43.186 - \frac{16115K}{T}\right) dt$	t is the time (min), T is the temperature in (°C) and the constants are related with the activation energy.	Liu et al. [76]
Severity factor R_0, in a non-isothermal hydrothermal processing, which includes the combination of temperature and reaction time along heating and cooling.	$logR_0 = log\left[R_{0\,Heating} + R_{0\,Cooling}\right]$ $logR_0 = \left[\int_0^{t_{MAX}} \frac{T(t)-100}{\omega} dt + \int_{t_{MAX}}^{t_F} \frac{T'(t)-100}{\omega} dt\right]$	t_{MAX} (min) is the time needed to achieve maximum autohydrolysis temperature, t_F (min) is the time needed for the whole heating-cooling period, $T(t)$ and $T'(t)$ stand for the temperature profiles in heating and cooling, respectively and ω is an empirical parameter.	Romaní et al. [9]
Model that explains the severity factor in function of chip size and processing time taking into account the diffusion of liquid into LCMs.	$R_0 = \frac{t}{\rho r^2((1-0.5\ln\,\varphi)/2M\varphi D\Delta C)} * e^{((T-100)/14.75)10^{-pH}}$	t is the time of reaction (min), T is the temperature (°C), D, is the diffusion coefficient, ρ is the density of the fluid, ϕ is thevoid fraction (porosity), r is the particle radius (mm), M is the molecular weight and ΔC is the concentration gradient.	Hosseini et al. [84]
Relationship between the severity factor and the viscosity of slurries made from sewage sludge during hydrothermal processing.	$\mu = 2.755 \times 10^5 \times R_0^{0.8250}$	μ is viscosity (Pa s/s) and R_0 is the severity parameter.	Yanagida et al. [107]
Model that explains the time needed for the chips to reach the desired temperature of wood with round or square cross section 1 and rectangular cross section 2 in hydrothermal processing.	(1) $t = a(T_{ht})^b(T_{ctr})^c(T_{init})^d D^e M^f G^g$ (2) $t = a(T_{ht})^b(T_{ctr})^c(T_{init})^d (TH)^d W^f M^g G^h$	t is the time estimated (min) for the center reach target temperature, T_{ht} is the heating temperature (°F), T_{ctr} is the target center temperature (°F), T_{init} is the initial wood temperature (°F), D is de diameter of round cross section (in), TH is the thickness of rectangular board (in), W is the width of rectangular board (in), M is the moisture content (%), G is the specific gravity, a–h are the regression coefficients.	Simpson [108]
Model for calculating the time needed for water diffusion into the LCMs as a function of the process and LCMs characteristics (assuming that LCMs have a porous structure) in hydrothermal process.	$t_w = \frac{\rho r^2(1-0.5\ln\,\varphi)}{2M\varphi D\Delta C}$	Where ρ is the density, r is the particle, ϕ is the porosity, D is the diffusion coefficient, M is the molecular weight and ΔC is the concentration gradient.	Hosseini et al. [109]
Model for calculating the temperature needed for different particle sizes. Temperature as a function of severity factor and radius in hydrothermal processing.	$T_2 = T_1 - 14.7\ln\left[\frac{R_2}{R_1}\left(\frac{r_1}{r_2}\right)^2\right]$	T_2 is the temperature (°C) needed for compensate the particle size increase, T_1 is the initial LCMs temperature which can be assumed as 20 °C r_1 and r_2 are the radius (cm), R_1 and R_2 are de severity factor.	Hosseini et al. [109]
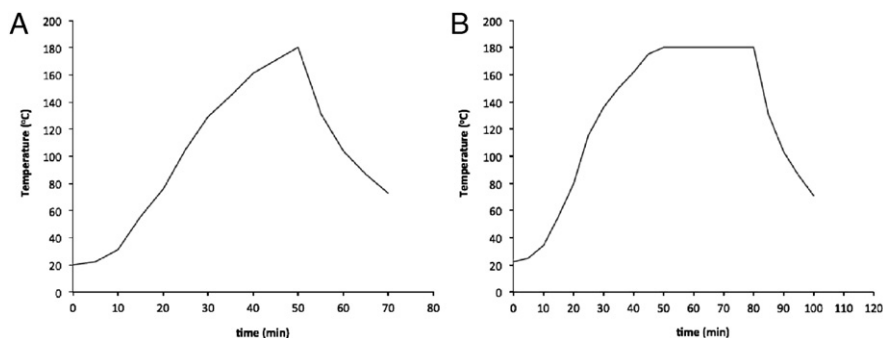
Fig. 4. Heating and cooling temperature profiles corresponding to: (A)non-isothermal and (B) isothermal regimen in hydrothermal processing(adapted from Romaní et al. [104]; Ruiz et al. [69]).

generally used to correlate the effects of operational conditions (i.e., temperature, residence time, particle size, pH) on hemicellulose solubilization. It was initially used to control the pulping process in the paper industry, but it was reintroduced for comparison of hydrothermal processing pretreatment severities on LCMs [110–112]. Hydrothermal processing is appropriate for hemicellulose depolymerization and, for a detailed understanding of the chemical reactions that occur during hydrothermal processing, the development of kinetic models enables a deeper insight on the several phenomena involved and provides mathematical equations suitable for simulation, optimization and design of operational strategies. Mathematical models based on pseudo-first order kinetics have been successfully employed for hydrolysis modeling. Garrote et al. [113] and Gullón et al. [45] suggested the kinetic reaction of hydrothermal processing using rye straw as raw material based on the following considerations: (1) a small part of the glucan fraction was degraded into glucooligosacharides, which were partially hydrolyzed to give glucose; (2) hemicelluloses were partially depolymerized along hydrothermal processing; (3) xylan was made up of two fractions (susceptible/non-susceptible to hydrothermal processing; the susceptible xylan fraction was hydrolyzed to give high molecular weight xylooligomers, which can be further decomposed into low molecular weight xylooligomers, subsequent xylose and promote dehydrated of xylose to furfural; (4) arabinosyl and acetyl groups hydrolysis are easily cleaved from xylan; (5) uronic acid fraction was made up of two fractions (susceptible/non-susceptible to hydrothermal processing). Similar considerations of xylan kinetic model were proposed by Garrote et al. [114] using corncob as raw material as follows:

$$\text{Hemicellulose} \overset{K_i}{\to} \text{oligosaccharide} \overset{K_{i+1}}{\to} \text{monosaccharides}$$
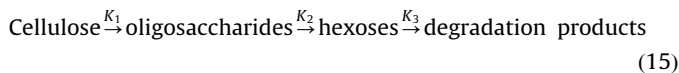$$\overset{K_{i+2}}{\to} \text{degradation product} \tag{13}$$

In order to provide a quantitative interpretation of xylan degradation under non-isothermal conditions Garrote et al. [115] proposed a modification, where some degradation of the slow-reacting fraction occurred at high temperatures. Nabarlatz et al. [116] developed a model for the kinetics of xylan depolymerization. The model assumes that the composition of each of the two xylan fractions in the LCMs does not change with the conversion, there is not direct formation of monomers (i.e., xylose, arabinose and acetic acid), the monomers are formed solely by depolymerization of the oligomers and the rates of monomer formation from oligomers are independent of the molar mass, structure and the oligomers. Carvalheiro et al. [63] proposed two models for xylan and arabinan degradation assuming that furfural was formed from both pentoses. Zhuang et al. [117] reported the kinetic modeling of xylan, measuring the oligosaccharides and monosaccharides as reducing sugar and the kinetic

model was thus adopted as:

$$\text{Xylan} \overset{K_1}{\to} \text{reducing sugars} \overset{K_2}{\to} \text{degradation products} \tag{14}$$

In a recent work Martinez et al. [118] proposed kinetic models for arabinan and acetyl groups based on sequential and parallel, irreversible and first-order reactions with Arrhenius-type temperature dependence and reported that the kinetic models provided a good prediction for the data of reaction liquors as function of the operational conditions. An overview about the kinetic modeling of cellulose hydrolysis can be found by Zhao et al. [119] and Rogalinski et al. [100] as follows:

$$\text{Cellulose} \overset{K_1}{\to} \text{oligosaccharides} \overset{K_2}{\to} \text{hexoses} \overset{K_3}{\to} \text{degradation products} \tag{15}$$

2.3. Effect of hydrothermal processing on cellulose

Cellulose is the most abundant biopolymer that can be obtained from numerous LCMs resources and there is a clear opportunity to develop commercial processes that could generate products that are needed at very high volumes and low selling price. One strategy to fractionation of LCMs is hydrothermal processing, since hemicelluloses are depolymerized into soluble products, whereas the solids from hydrothermal processing are enriched into cellulose and lignin. A variety of applications can be visualized for this phase from hydrothermal processing of LCMs. Currently, the most promising approach for using LCMs is enzymatic hydrolysis of the cellulose content after pretreatment for second generation bioethanol production (see Table 3). Pretreatment is required to alter the structure and chemical composition due to the robustness of LCMs. Hydrothermal processing as pretreatment caused re-localization of lignin on the surface of LCMs [127], thus enzyme accessibility to the LCMs structure in the pretreated material is favoured, increasing the potential of cellulose saccharification. Moreover, physical changes that improve enzymatic saccharification include an increase in pore size to enhance enzyme penetration and an increase in accessible area that has been shown to correlate well with the susceptibility of these substrates to enzyme saccharification using hydrothermal processing as pretreatment [27,95,128–134]. Table 4 shows the enzymatic saccharification yield using hydrothermal processing as pretreatment at different operational conditions and demonstrate the ability of this technology to make LCMs accessible to enzymes. Hydrothermal processing is a promising pretreatment for second generation bioethanol production, considering its great versatility and feasibility in the fractionation of LCMs, that it is a key in the development of biorefineries, but the large-scale commercial utilization of this pretreatment has still not been implemented. However, there are few companies that

Table 3
Production of bioethanol using hydrothermal processing as pretreatment under different operational conditions and raw materials.

Raw material	Temp. (°C)	Time (min)	Particle size	Ethanol Yield (%)	Reference
Wheat straw	195	6–12	–	89	Petersen et al. [14]
Rice Straw	180	30	250–420 μm	100	Yu et al. [25]
Switchgrass	210	15	–	72	Suryawati el at. [17]
Eucalyptus globulus	230	–	8 mm	86.4	Romaní et al. [26]
Wheat straw	214	2.7	0.5–2 mm	90.6	Pérez et al. [19]
Corn stover	195	10	–	61.2	Xu et al. [120]
Sugar cane bagasse	220	2	–	85	Walsum et al. [121]
Wheat straw	200	40	0.5–2 mm	96	Pérez et al. [122]
Poplar nigra	240	60	2–5 mm	60	Negro et al. [123]
Sweet sorghum bagasse	190	–	–	74	Rohowsky et al. [124]
T85 bermudagrass	230	2	500 μm	70	Brandon et al. [125]
Ulex europæus	230	–	8 mm	82	Ares-Peón [126]

Table 4
Enzymatic Saccharification of pretreated solids with hydrothermal processing as pretreatment.

Raw material	Temp. (°C)	Time (min)	Saccharification yield (%)	Reference
Prairie cord grass	210	10	94.53	Cybulska et al. [27]
Oil palm fronds	178	11.1	92.78	Goh et al. [135]
Coastal Bermuda grass	150	60	67.4	Lee et al. [136]
Corn stover	190	15	69.6	Zeng et al. [137]
Wheat straw	195	3	72	Thomsen et al. [138]
Switchgrass	200	10	74.4	Hu and Ragauskas [139]
Tamarix ramosissima	200	180	88	Xiao et al. [140]
Eucalyptus grandis	200	20	96.6	Yu et al. [141]
Barley husks	212	–	100	Ares-Peón et al. [142]
Eucalyptus globulus	230	–	97.9	Romaní et al. [104]
Wheat straw	180	30	90.88	Ruiz et al. [143]
Prairiecordgrass	190	1	81.28	Cybulska et al. [144]
Sugarcane bagasse	190	10	69.2	Silva et al. [145]

have operated as demo-scale plants. For example, Inbicon has been built a in Kalundborg Denmark using wheat straw as raw material under hydrothermal pretreatment conditions at 180–200 °C for 10–20 min with steam. This demo-scale plant is according to the Integrated Biomass Utilization System (IBUS)-concept that resulted in a continuous hydrothermal pretreatment [146–149]; moreover the Inbicon process has been recently reviewed by Larsen et al. [150]. In respect to the techno-economic study of hydrothermal process as pretreatment; only few analyses have been reported. Treasure et al. [151] reported an analysis of bioethanol and electricity production from hardwood and softwood as raw material and autohydrolysis as pretreatment, they concluded that the financial performance of autohydrolysis pretreatment appears to be most sensitive to ethanol yield, followed by capital investment and raw material cost. Recently Littlewood et al. [152] showed a minimum ethanol selling prices of £0.474/L ($2.85/gal) for hydrothermal pretreatment, also reported that the raw material (wheat straw) prices and the enzymes costs were the main contributors for the minimum ethanol selling prices in all scenarios studied and within the pretreatment area alone, the hydrothermal pretreatment was the lowest total area cost.

On the other hand, after hydrothermal processing the cellulose shows a little degradationat different temperatures > 230 °C. In a recent work, Romaní et al. [26] reported decreases of 5.29% and 19.55% of cellulose present in pretreated solids at 240 °C and 250 °C, respectively, defining the operational range where partial cellulose degradation began to take place. According to Sakaki et al. [153] cellulose started to degrade in hexoses and oligosaccharides above 230 °C and almost all cellulose was decomposed at 295 °C. Jin et al. [154] reported that cellulose hydrolyzes into glucose in 2 min at 300 °C, but that the glucose decomposes in 30 s under the same conditions. Other type of solid residues which contain mainly cellulose and lignin after hydrothermal processing are the raw material for pulp and paper marking [155]. Caparrós et al. [48] reported similar characteristics of paper sheets obtained from sequencing hydrothermal processing and ethanol pulping to those obtained by soda pulp. Vila et al. [68] showed the susceptibility of hydrothermally treated solids to kraft processing pulp which provided cellulose pulps with low kappa numbers, highly susceptible to alkaline oxygen bleaching. Romaní et al. [9] used the solids (cellulose+lignin) obtained after hydrothermal processing for delignification and improved the enzymatic saccharification of cellulose from Eucalyptus globulus. According to Alfaro et al. [156] the cellulose pulp with hydrothermal processing reduces kappa number, viscosity and decreases paper strength. Caparrós et al. [157] evaluated the solid phase obtained from hydrothermal processing using the organosolv process for produced paper sheets, analyzing the influence of operational variables on the viscosity, tensile index, burst index, tear index and brightness obtaining suitable characteristics of paper sheets.

2.4. Effect of hydrothermal processing on hemicellulose

The hemicellulose is the second most abundant polysaccharide in nature and is made up of amorphous heteropolysaccharides constituting 14–50% of the raw LCMs dry weight. Hemicellulose consists of various structural units, including five-carbon (xylose and arabinose) and six-carbon sugars (mannose, galactose, glucose), which can be substituted with phenolic, uronic or acetyl groups. The most abundant block of hemicellulose in hardwoods and many agricultural residues is xylan (made up mainly of xylose units) [43,158,159]. Hydrothermal processing is a suitable method for hemicellulose depolymerization, under selected operational conditions as hemicellulose can be almost totally removed from LCMs (see Fig. 2) [160], being decomposed into valuable soluble products such as oligosaccharides, monosaccharides, sugar-decomposition products (such as furfural or hydroxymethylfurfural) and acetic acid (from acetyl groups hydrolysis). Furthermore, when a xylan is subjected to hydrothermal processing under mild temperature, high-molar mass xylo-oligosaccharides

(XOS) and xylose are produced, being the major products derived from hemicellulose present in the liquor phase [22,45,161]. Under harsh operational conditions, xylose can be dehydrated to furfural, and furfural can be converted into degradation products [115]. Xylo-oligosaccharides are bioactive molecules with high-added value and have great prebiotic potential making them useful as ingredients for functional foods. From a nutritional point of view, XOS are usually considered to be nondigestible oligosaccharides [116,162–166]. Recently, solubilization studies of XOS from LCMs by hydrothermal processing have shown the efficiency of this technology to improve the yields of extraction. Gullón et al. [45] reported a yield of 69.2% of XOS with respect to the initial xylan at 208 °C, using rye straw as raw material. Nabarlatz et al. [167] reported 58.3% of crude XOS after hydrothermal processing at 179 °C for 23 min using ultra-filtration for the purification of XOS. Carvalheiro et al. [164] also reported a similar yield of 61% of XOS at 190 °C after 5 min, using brewery's spent grain. According to Garrote et al. [168], the hydrothermal processing in non-isothermal reaction conditions produced 23.2 g of oligosaccharides/100 g of oven-dried corncobs at 202 °C. Boussarsar et al. [92] showed that it is possible to obtain an acceptable xylose extraction yield and low degradation of sugar monomers for 2 h at 170 °C. Kabel et al. [165] and Carvalheiro et al. [164] in previous studies for the production of XOS by hydrothermal processing of brewery's spent grain reported that several oligosaccharide mixtures of different molecular weight distributions were obtained depending on temperature and reaction time (severity of reaction conditions). Longer reaction times led to a decreased amount of oligosaccharides and an increase of the concentration of monosaccharides, acetic acid and sugar decomposition products. Montané et al. [169] used active carbon as an alternative for the purification of XOS produced by hydrothermal processing. Vegas et al. [170] used ultra- and nano-filtration for the purification of oligosaccharides from rice husk hydrothermal processing liquors, reporting that it is possible to recover about 90% of the XOS present in hydrolysis liquors. Different reactor configurations have been used for improving the recovery of hemicellulose. According to Liu and Wyman [99], xylose yield improved from 60 to 82% with an increase in the fluid velocity from 2.8 to 10.7 cm/min on a flowthrough reactor using corn stover as raw material at 200 °C after 8 min residence time. Makishima et al. [103] found an effective recovery of hemicellulose using a tubular type reactor at 200 °C for 10 min, 82% of xylan fraction recovered as mixture of xylose, XOS and higher XOS with polymerization degree higher than 10. Garrote and Parajó [171] reported that more than 80% of the initial xylan can be removed from wood with a conversion in XOS up to 65% of the initial xylan in a batch reactor. Other important point is the deacetylation of hemicellulose during the hydrothermal processing; Garrote et al. [172] studied the time course of acetyl groups' hydrolysis from both xylan and xylan degradation products, and their relationship with the concentration of acetic acid. Xylitol, a pentitol derived from xylose by reduction has technological and biological properties, such as high sweetening power, anticariogenic properties and suitability for consumption by diabetics, that foster its utilization in the food industry. XOS produced in hydrothermal processing can be used as a source of xylose for the production of xylitol. However, these XOS cannot be directly metabolized by microorganisms. In order to prepare fermentation media for the production of xylitol from hydrothermal processing liquors, XOS must be first converted into monosaccharides by either acid or enzyme catalyzed reactions, this process providing a way to obtain xylose solutions. Rivas et al. [173] used the sequence (hydrothermal processing-posthydrolysis) with corncob hydrolysate and observed an increase in the productivity and yield of xylitol in comparison with the results obtained in a fermentation media made by the conventional acid hydrolysis pretreatment. Duarte et al. [174] produced xylitol and arabitol from brewery's spent grain hydrolysate using the sequence (hydrothermal

processing-posthydrolysis) by *Debaryomyces hansenii* without any detoxification treatment. Garrote et al. [175,176] used corncobs and *Eucalyptus globulus* as raw material in hydrothermal processing and concluded that generation of xylose solution to be used as fermentation media through sequential stages of hydrothermal processing-posthydrolysis, shows favorable features in terms of substrate conversion, reaction, selectivity and low inhibitor concentration.

Vázquez et al. [177] reported a concentration of 24 g xylose/L, using the sequence (hydrothermal processing-enzymatic posthydrolysis) using corncobs as raw material at 175 °C for 20 min, the advantage being that the hydrolysate after this sequence is free of sugar degradation products and the acetic acid concentration could be reduced, thus improving their potential fermentability. XOS can also be synthesized and used as thermoplastic compounds for biodegradable plastics, water-soluble films, coatings and capsules [178]. Glasser et al. [179] produced a thermoplastic from the chemical modification of pentose-rich oligosaccharides such as xylose. Lindblad et al. [180] produced hydrogels from hemicellulosic oligosaccharides and 2-hydroxyethylmethacrylate. In a recent work, Ruiz et al. [71] reported the viability of the application of the hemicellulosic liquid phase, recovery after hydrothermal process, in the production of polymeric blend films. The need to replace traditional plastics due the negative environmental impact caused, has increased the interest on the development of biodegradable polymers. Polylactic acid (PLA) is a biodegradable polymer with thermoplastic character, produced by polymerization of lactic acid (which can be obtained by fermentation of sugars derived from LCMs), that finds applications in such fields as packaging, disposable goods or textile fibres. Vila et al. [181] evaluated rice husks and *Eucalyptus globulus* in hydrothermal processing for the production of xylose-based culture media for lactic acid production and the application of the fiber contained in the pretreated solids for making PLA-based biodegradable composites. In a recent work González et al. [182] produced biodegradable biocomposites from *Citysus scoparius* using hydrothermal processing, obtaining a maximum concentration of oligomers (71% of the initial xylan) at 215 °C and a solid phase (cellulose+lignin) suitable as a reinforcement for PLA-based composites, the composites showing better stiffness compared with pure PLA. Other important application of hemicellulosic liquid phase after hydrothermal pretreatment is the production of xylanases [70].

2.5. Effect of hydrothermal processing on lignin

Lignin is the most abundant aromatic heterogeneous polymer formed by phenolic compounds and their precursors are three aromatic alcohols namely, (1) *p*-coumaryl, (2) coniferyl and (3) sinapyl alcohols, which are bonded together with over two-third being ether bonds (C–O–C) and the rest being C–C bonds. The respective aromatic constituents in the polymer are called *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S), the structure of lignin suggesting that it can be a valuable source of chemicals, particularly phenolics [8,183–186]. Lignin is always associated with hemicelluloses, not only as physical admixtures, but also through covalent bonds. During the hydrothermal processing lignin and lignin–hemicellulose linkages can undergo degradation, partial depolymerization and profound re-localization. Moreover, the fraction of solubilized lignin depends on the operation conditions (severity of reactions conditions) and on the raw material (LCMs) [28,66,127]. Lora and Wyman (1978) and Bobleter and Concin (1979) cited by Garrote et al. [28] and Zhang et al. [187] suggested a two-phase mechanism for lignin reaction: (1) a very fast reaction where lignin fragments with low molecular weight and high reactivity are solubilized by breaking lignin–carbohydrate bonds into soluble fragments; (2) a slower

reaction where the soluble fragments react with one another by recondensantion and lignin repolimerization, which also occurs in the presence of the organic acids liberated in the hydrothermal processing. Soluble lignin being aromatic and possessing many chromophoric structural units strongly absorbs ultraviolet (UV) light and the absorbance at either 205 or 280 nm is the basis of several techniques for the quantitative determination of soluble lignin [188,189]. The partial depolymerization of lignin and breaking of lignin–hemicellulose linkages produced part of the phenolics present in the hydrothermal processing liquors [66,190]. Using hardwood as raw material, Marchessault et al. [191] reported that the ether linkages of lignin are cleaved during hydrothermal processing causing a decrease in molecular weight and an increase in phenolic content. These phenolics, considered as the byproducts of LCMs hydrothermal processing are an attractive source for natural antioxidants and might have potential applications as food additives [183,192]. The extracts and compounds derived from soluble lignin can be selectively extracted from hydrothermal processing liquors with ethyl acetate. This phenolic-rich extract contains a variety of potentially valuable compounds with antioxidant, antimicrobial and biological activities comparable to that of synthetic antioxidants [193–195]. Several lignin-derived products have been identified. Garrote et al. [22] reported benzoic, gallic and cinnamic acids in the liquor after hydrothermal processing at 216 °C using barley husk as raw material. Conde et al. [196] found that hydroxytyrosol, homovanillyl alcohol, oleuropein, syringaldehyde, tyrosol, 3,4-dihydroxybenzaldehyde were the major phenolic compounds in the soluble fraction from the hydrolyzates of barley husks obtained by hydrothermal processing. In a recent work, Tsubaki et al. [197] used microwave as an alternative heating source for tea residues autohydrolysis and reported that vanillin, vanillic acid, dihydroconiferyl alcohol and guaiacol are degradation compounds originated from guaiacyl (G) units of lignin. In a similar way, syringaldehyde, syringic acid and sinapaldehyde were considered to be originated from syringyl (S) units of lignin. Conde et al. [198] reported that gallic acid, 3,4-dihydroxybenzaldehyde, vanillic acid, syringic acid, vanillin and p-coumaric acid were the major low molecular weight phenolics present in the refined media using barley husks as raw material. According to Castro et al. [195], the major compounds founded in lignin-derived fractions were syringaldehyde, vanillin, 4-formyl benzoic acid methyl ester, desaspidinol, syringol, guaiacol, homosyringic acid and methoxyeugenol using Olea europea wood as raw material. Pourali et al. [199] used subcritical water conditions and reported the production of eleven phenolic compounds (caffeic, ferulic, gallic, gentisic, p-coumaric, p-hydroxybenzoic, protocatechuic, sinapic, syringic, vanillic acids and vanillin) and concluded that the content of phenolic compounds increased with the temperature. Many beneficial effects on human health have been attributed to simple phenolics: oleuropein, hydroxytyrosol, caffeic acids (prevention of cardiovascular diseases); hydroxytyrosol, tyrosol, vanillin, vanillic acid, caffeic acids (prevention of tumoral diseases); p-coumaric acid, caffeic acid, ferulic acid (protection against LDL lipoprotein oxidation); gallic acid (skin protective ability); vanillin, (anti-inflammatory) [66,183,200–203]. In regard to antioxidant activity, Tsubaki et al. [204] reported the production of polyphenols above 200 °C, obtaining strong antioxidant activity using tea residues as raw material and microwave heating. Conde et al. [198] reported that the hydrothermal-extraction process was suitable for obtaining antioxidants, but the limited mass fraction of phenolics and the values determined for antioxidant activity, suggest that further purification would result in products of improved quality. Akpinar et al. [205] used ultra-filtration as an alternative to ethyl acetate extraction and reported that sunflower stalk liquors had higher antioxidant

activity than wheat straw, the hydrothermal processing being carried out at 160 °C for 1 h. Tsubaki et al. [206] also studied the extraction of phenolic compounds and reported that antioxidant activity increased in good correlation with the increase in the concentration of phenolic compounds in the extracted hydrothermal processing liquor. Garrote et al. [30] reported that the antioxidant activity of ethyl acetate extracts isolated from Eucalyptus globulus and corncob hydrothermal processing liquors showed a strong dependence on the hydrothermal conditions. Moreover, Pourali et al. [199] found that phenolic compounds could be selectively produced by temperature variations. Conde et al. [192] studied the in vitro antioxidant capacities of the ethyl acetate extract from hydrothermal processing using different LCMs and reported that the antioxidant capacities were comparable or higher than the ones of synthetic compounds, similar results being obtained by Castro et al. [195] using Olea europea wood at temperatures in the range of 190–240 °C. On the other hand, Li and Gellerstedt [207] reported that the solid residues obtained after hydrothermal processing showed improved susceptibility towards delignification with organic solvents. According to Hongzhang and Liying [208] the sequential application of hydrothermal processing-organosolv pretreatment is an effective process for the extraction of lignin (delignification) with reasonable yields and purity. Ruiz et al. [8] evaluated delignification using the sequence hydrothermal processing-organosolv process and concluded that the temperature and time as well as chemical structure were variables that showed a strong influence on lignin precipitation. Romaní et al. [9] used the sequence hydrothermal processing-organosolv process for delignification, resulting in an improved enzymatic saccharification.

3. Hydrothermal processing of aquatic biomass

Recently, aquatic biomass including macro- and micro-algae is gaining wide attention as an alternative renewable source of biomass, mainly because of their content of functional components such as oils, proteins and carbohydrates. Similarly to LCMs, it is necessary to find an alternative that allows the fractionation of their main components. The hydrothermal processing of aquatic biomass is of considerable interest as this technology is ideally suited to high moisture content feedstocks such as macro and microalgae biomass. Presently, there are few literature reports on hydrothermal processing of aquatic biomass. The subsequent sections will deal with the main applications of hydrothermal processing using macro- and micro-algae as raw material.

3.1. Hydrothermal processing of macroalgae

Macroalgae have a large potential as raw material for energy production and chemicals for food and medical industries. However, so far, most of the research has been concentrated on converting terrestrial biomass. A relatively new concept includes the utilization of marine biomass, and demands an assessment of how this marine biomass can contribute to the total biomass resources [209]. Oceans and seas cover over 70% of the Earth's surface, offering the possibility of sustainable cultivation of a vast potential biomass feedstock. The use of macro-algae or seaweeds biomass has several advantages including: (a) in the future, low fluctuations in biomass demand are expected due to overpopulation; (b) feasibility of fast growing rate in the open ocean; (c) higher photosynthetic activity (6–8%) than terrestrial biomass (1.8–2.2%); (d) no limitation by water and to a lesser extent temperature; and e) low costs of collection and null environmental damage [210–212]. The production of seaweeds and other aquatic plants reached 16.0 million tons in 2007, of which

aquaculture produced 14.9 million tons with a value of USD 7.5 billion [213], making annual primary production rates (grams/ $(m^2 \cdot year)$) higher for the major marine macroalgae than for most terrestrial biomass. Macroalgae can be subdivided into blue algae (*Cyanophyta*), green algae (*Chlorophyta*), brown algae (*Phaeophyta*) and red algae (*Rhodophyta*), the main regions for cultivation on a mass scale being the Far East, and on a smaller scale, Europe [211]. Nowadays, seaweeds applications are focused on human foods, cosmetics and fertilizers and for the extraction of many useful industrial chemicals such as phycocolloids (e.g., alginates), being also a potential source of long- and short-chain chemicals with medicinal and industrial application as biofuels [213,214]. Moreover, conversion of macroalgae into biofuel has been focused on the production of biogas by anaerobic digestion, but no thermochemical treatment was carried out over the raw material before the fermentation processes [215]. Recent studies have also been focused on the utilization of the sugars present in seaweeds (mannitol and laminarin for brown algae) for the production of bioethanol by fermentation [216–219]. However, research on the application of hydrothermal processing to macroalgae is limited [220,221]. The excellent solvent properties of water as a reaction medium and the usually high moisture content of macroalgae make hydrothermal treatment a promising processing technology for the direct use of macroalgae in the production of biofuels and high added-value compounds [222–227]. Hot water is used at temperatures from 100 to 374 °C, under high pressure, usually from 10 to 60 bar, corresponding to conditions below the water critical point. In the case of macroalgae, hydrothermal processing involves the reaction of marine biomass and water at elevated temperatures and pressures and its application has been demonstrated with and without the presence of catalysts for a wide range of biomass origins. Under these conditions biomass is decomposed to form new products, including a bio-crude fraction, a char fraction, a water fraction and a gaseous fraction [224]. Looking for alternatives to seaweeds application, mostly used in food and cosmetic area, preliminary experiments using the green macroalgae *Chaetomorpha linum* for biodiesel production were described by Aresta et al. [228]. Two techniques were compared: supercritical carbon dioxide (sc-CO_2) and hydrothermal processing and it was verified that hydrothermal processing was more efficient with a higher amount of oil extracted at plateau temperatures of 350–395 °C. Hydrothermal processing to bio-oil production was also carried out with the green seaweed *Enteromorpha prolifera* in a batch reactor evaluating the effects of the temperature, reaction time and Na_2CO_3 catalyst. A maximum bio-crude yield of 23 wt% with a Higher Heating Value (HHV) of 29.89 MJ/kg was obtained at 300 °C and 30 min with 5 wt% Na_2CO_3. The obtained bio-oil was a complex mixture of ketones, aldehydes, phenols, alkenes, fatty acids, esters, aromatics, and nitrogen containing heterocyclic compounds [225]. Anastasaki and Ross [212] evaluated the hydrothermal processing of *Laminaria saccharina* brown seaweed with and without the addition of catalyst (KOH) in order to maximize the bio-crude yield. A maximum bio-crude yield of 19.3 wt% was obtained with a 1:10 biomass:water ratio at 350 °C and a residence time of 15 min without the presence of the catalyst; the most important variables were considered to be temperature and reactor loading. The obtained bio-crude showed a HHV of 36.5 MJ/kg, a slightly lower value than the reported for crude petroleum (42.7 MJ/kg) [224,226]. Furthermore, analysis of the aqueous phase indicates that mannitol and laminarin present in brown seaweed are dissolved, suggesting a further utilization of the high sugar aqueous stream in a fermentative process to produce bioethanol. It was also established that the addition of the catalyst caused a reduction of sugars presence in this stage. Marine algae biomass conversion into ethanol is an option to be

considered since some algae hydrolysates contain more total carbohydrates and hexose sugars than some terrestrial LCMs. However, only few studies on this matter have been reported. Kim et al. [229] evaluated ethanol production from several macroalgae using *Escherichia coli* KO11 and *Saccharomyces cerevisiae* strains for sugar fermentation. Hydrothermal processing for the preparation of algal hydrolyzates was carried at 121 °C for 15 min in the presence of acid catalyst (H_2SO_4). Under the evaluated conditions *Laminaria japonica* hydrolysate contained a high amount of mannitol (30.54%) making it a cost-effective substrate for microbial ethanol production. *Escherichia coli* KO11 ethanol yield was 0.4 g ethanol/g of sugars, while the yeast strain was unable to ferment mannitol, this being attributed to catalyst application in hydrothermal processing.

As an alternative to subcritical hydrothermal processing, there is the possibility of applying supercritical extraction. A supercritical fluid is obtained when a fluid is forced to a pressure and temperature above its critical point (for water about to 374 °C)—its density is similar to a liquid, its viscosity is similar to a gas and its diffusivity is intermediate between the two states. Thus, the supercritical state is defined as a condition in which liquid and gas are indistinguishable from each other [227]. Schumacher et al. [223] studied the supercritical hydrothermal processing conversion in several seaweed species based in the principle that water gasification appears to be a useful technology for biomass with a high humidity content (up to 90%). Thus, biomass feedstock was gasified with supercritical water at 500 °C for 1 h. Even though the coke yields were significantly lower than those obtained with lignocellulosic and protein wastes, the total gas yields were higher than the reported for these materials, because algae polysaccharides and proteins are decomposed at 200 to 400 °C. The gaseous species detected were mainly hydrogen, methane and carbon dioxide where the highest values for H_2 and CH_4 were 16 and 104 g/g of seaweed, respectively. Additionally, the aqueous phase contained glycolic, formic and acetic acids and phenols. Microwaves as an alternative-heating source have been successfully applied for extraction of numerous biologically active compounds from a wide variety of natural resources, because it is characterized as a selective, efficient and environmental friendly process. This technique consists in a rapid delivery of energy to the total volume and subsequent rapid heating into the material structure accelerating the solubilization of compounds [230,231]. Polar solvents have permanent dipole moment and can absorb microwave radiation and water as a polar compound can absorb the microwave energy and transfer it to the sample, having as advantages over the organic solvents being a secure and ecologic reagent. Microwave-assisted hydrothermal processing is a technique that should be considered for the extraction of seaweeds' polysaccharides since the main sugars present in macro-algae (laminarin and fucoidans) are the water-soluble compounds [232]. Chen et al. [233] reported the use of microwave-assisted method to obtain polysaccharides from *solanum nigrum*. Navarro et al. [234] produced 3,6-anhydrogalactose units from galactose 6-sulfated residues of red seaweed galactans utilizing microwave irradiation to carry out the alkaline modification. The experiments were carried out in a domestic microwave oven heating the samples for 1 min at 1200 W using Teflon closed-vessels. Furthermore, Yang et al. [235] and Rodriguez-Jasso et al. [231], respectively evaluated the hydrothermal extraction of sulfated polysaccharides of *Undaria pinnatifida* and *Fucus vesiculosus* using a digestion microwave oven with a maximum delivered power of 630 W (at 172 °C). Results showed that microwave heating around 30–60 s was more effective in improving polymer dissolution without a noticeable structural degradation. A preliminary development of a microwave prototype at industrial scale was reported by Uy et al. [236]. Carrageenan

extraction of *Eucheumacottonii* and *Eucheumaspinosum* was carried out using an industrial single-mode cavity continuous microwave, at 38% of full power (800 W) and with a residence time of 30 min. Since these hydrocolloids are not water soluble, hydrothermal processing extraction was tested with aqueous mixtures of organic solvents. The extracted carrageenans showed high purity, without the need for further purification procedures. González-López et al. [237], produced compounds with antioxidant activity using non-isothermal autohydrolysis process and *Sargassum muticum* as raw material. In a recent works, Anastyuk et al. [238,239] used autohydrolysis as an alternative strategy for fucoidan depolymerization from brown algae *Silvetia babingtonii* and *Fucus evanescens*. The term autohydrolysis is referred to the acid polysaccharide hydrolysis under very mild conditions using –SO₃H groups as source of catalyst in substrate reaction. Rodrí-guez-Jasso et al. [240] reported the extraction of sulfated polysaccharides by autohydrolysis from *Fucus vesiculosus*. The results showed that the pH decrease in the reaction media at high temperatures and times, possibly due to the polysaccharides hydrolysis using the "*in situ*" –SO₃H groups as source of catalyst.

3.2. Hydrothermal processing in microalgae

Microalgae are an especially promising feedstock for advanced biofuels production for a number of compelling reasons, including high photosynthetic efficiency, higher area-specific yield, possibility of a frequent harvest because of their rapid growth rate and possibility of integration with fossil-fuel-fired power plants to recycle CO_2, via photosynthesis. They can also be cultivated in different climates, in saline/brackish water and on non-arable land so there is no competition with conventional cropland. Its cultivation can be coupled with wastewater bioremediation since they can also remove nitrogen, phosphorus and heavy metals [241]. The conventional approach for making biodiesel from microalgae involves the extraction of triglycerides from the microalgal biomass and its subsequent conversion (e.g., via transesterification) into biodiesel fuel. This approach requires dewatering of the microalgae, drying of the dewatered biomass paste, and then solvent extraction of the triglycerides from the

dried biomass, all these steps representing up to 90% of the energy needed to synthesize biodiesel from microalgae [242]. Microalgae biomass usually has a high moisture content (80–90%), so the drying process requires a large amount of heating energy. The hydrothermal processing is an alternative technology that significantly improves the overall thermal efficiency of the process [243], as the energy consumption required by hydrothermal processing is very low compared to other processes [244]. Hydrothermal processing offers the advantage that lipids can be extracted while wet and upgraded to produce a crude oil-like product. Another potential advantage is that the conventional lipid extraction methods only produce oil from the lipid fraction while hydrothermal processing can produce oil also from the carbohydrate and protein fraction (see Fig. 5). This is significant as some microalgae grow faster with lower lipid content and contain significant amounts of carbohydrates and proteins [245]. With higher plants, the chemistry of the process derives primarily from lignin, cellulose and hemicellulose components. In contrast, microalgae are not lignocellulosic in composition, and the chemistry is entirely different, involving proteins, lipids and carbohydrates (generally not cellulose) [246]. Hydrothermal processing of microalgae was first reported by Dote et al. [247] for high lipid forming from *Botryococcus braunii*. Those authors successfully used hydrothermal processing, catalyzed by sodium carbonate (Na_2CO_3), at 300 °C and a pressure of 10 MPa achieving a maximum yield of 64 wt% of oil with a HHV of 45.9 MJ/kg and a positive energy balance for the process (output/input ratio of 6.67: (1). The hydrothermal processing of *Botryococcus braunii* cells (moisture content of 92%) was also performed by Sawayama et al. [248] at 200, 300 and 340 °C with 5 wt% or without Na_2CO_3. The maximum yield of oil obtained was 64 wt% (dry basis) at 300 °C with Na_2CO_3 as catalyst. The produced gas consisted mainly of methane and carbon dioxide. Hydrothermal processing of the same microalgae was also studied by Banerjee el al. [249], who obtained oil in a yield of 57–64 wt% at 300 °C. The oil was equivalent in quality to petroleum oil. Minowa et al. [250] reported an oil yield of about 37% on organic basis by direct hydrothermal processing at around 300 °C, 60 min and 10 MPa from the low lipid containing microalgae *Dunaliella tertiolecta*
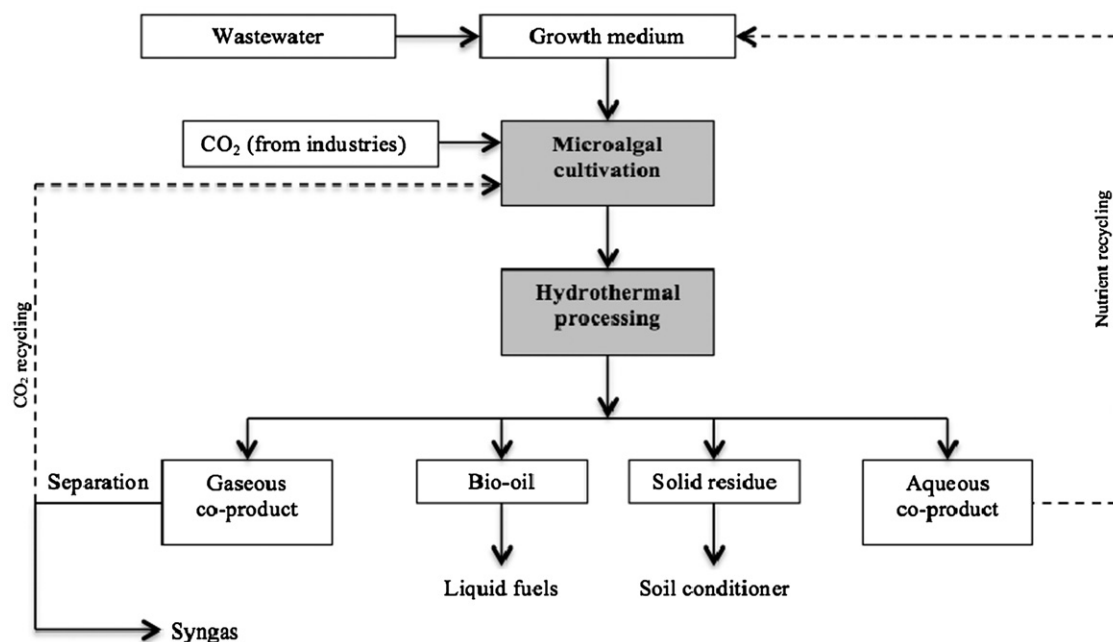
Fig. 5. Conceptual model for microalgal fuel production with hydrothermal processing of biomass conversion into bio-oil.

(lipid content 20 wt%). The oil had HHV of 36 MJ/kg, comparable to those of fuel oil and the process had a positive energy balance of 2.94:1. Other lower lipid containing microalgae such as *Spirulina* have been liquefied at 350 °C, 60 min, 5 MPa without catalyst by Matsui et al. [251]. Surprisingly high oil yields were reported (78.3 wt%) despite the low lipid content, however the oil showed high oxygen content. The most important factors in the hydrothermal processing of microalgae as raw material are temperature, residence time and catalyst dosage. To investigate the influences of these factors on oil yield, Shuping et al. [244] performed the hydrothermal processing of *Dunaliella tertiolecta* under various temperatures (280–380 °C), residence times (10–90 min), and catalyst dosages (0–10%). A maximum bio-oil yield of 25.8% was obtained at a reaction temperature of 360 °C and a holding time of 50 min using 5% Na_2CO_3 as a catalyst. The results showed that the decomposition of *Dunaliella tertiolecta* started at a reaction temperature lower than 280 °C, and both conversion and bio-oil yield were strongly dependent on the temperature between 280 and 380 °C. In relation to the residence time, the bio-oil yield appeared to present an initial sharp increase, remaining approximately constant with increasing reaction time beyond 50 min. Also, Yang et al. [252] performed the hydrothermal processing of *Microcystis viridis* under different conditions of temperature (300 and 340 °C), residence time (30 and 60 min) and catalyst dosage (0 and 5% of Na_2CO_3). The initial operational pressure was 3 MPa and the maximum pressure of the autoclave was 10–20 MPa. The maximum oil yield was 33% at the 30 min holding time, the reaction temperature of 340 °C and the alkali catalyst dosage of 5 wt%. The HHV of the oil was determined as 28–30 MJ/kg. Brown et al. [253] converted the microalga *Nannochloropsis sp.* into a crude bio-oil product via hydrothermal processing at different temperatures and a batch holding time of 60 min. A temperature of 350 °C led to the highest bio-oil yield of 43 wt%. The HHV of the bio-oil was 39 MJ/kg, which is comparable to that of crude petroleum. Alba et al. [254] conducted a study of hydrothermal treatment using the freshwater microalgae *Desmodesmus sp.*, in which a wide range of temperatures (175–450 °C) and reaction times (up to 60 min), was tested, using a batch reactor system. The maximum oil yield (49 wt%) was obtained at 375 °C and 5 min reaction time, recovering 75% of the algal calorific value into the oil and an energy densification from 22 to 36 MJ/kg. As presented previously the use of catalyst is one of the factors that should be taken into account in hydrothermal processing of microalgae. Several studies on hydrothermal processing of microalgae were carried out using different catalysts, mainly Na_2CO_3 (208, 209, 210, 213). Ross et al. [224] studied the influence of the catalyst type in hydrothermal processing using *Chlorella vulgaris* and *Spirulina* as raw material. Catalysts employed include the alkalis, potassium hydroxide and sodium carbonate and the organic acids acetic acid and formic acid. The yields of bio-crude were higher in the presence of organic acids compared to alkali catalysts. Biller et al. [245] investigated three catalysts: an alumina-supported Co/Mo catalyst, an alumina-supported Ni catalyst and an alumina supported Pt catalyst. The results indicate that the bio-crude yields from the hydrothermal processing of *Chlorella vulgaris* and *Nannochloropsis occulta* were increased slightly with the use of heterogeneous catalysts but the HHV and the level of de-oxygenation increased up to 10%. Duan and Savage [255] produced crude bio-oils from the microalga *Nannochloropsis sp.* via reactions in liquid water at 350 °C and 60 min in the presence of six different heterogeneous catalysts (Pd/C, Pt/C, Ru/C, $Ni/SiO_2–Al_2O_3$, $CoMo/\gamma-Al_2O_3$ (sulfided), and zeolite). Jena et al. [256] used NiO to assist in the hydrothermal processing of both single (*Spirulina*) and mixed algae (from open ponds with wastewater) cultures at 350 °C. Interestingly, the added NiO decreased oil yields. Duan and

Savage [255] refer that the use of a catalyst in hydrothermal processing may be a way to produce a crude hydrocarbon bio-oil directly from wet microalgae in a single processing step. Yeh et al. [257] present an overview of catalysts used in hydrothermal processing of algae and model compounds. Microalgae generally consist of carbohydrates, proteins and lipids. In order to understand the influence of biochemical content of microalgae on hydrothermal processing yields and product distribution, Biller and Ross [226] performed hydrothermal processing on four different microalgae species (*Chlorella vulgaris, Nannochloropsis occulata, Porphyridium cruentum* and *Spirulina*) and model biochemical compounds at 350 °C, 20 MPa and 60 min. The yields and product distribution obtained for each model compound have been used to predict the behavior of microalgae with different biochemical composition. Model validation using microalgae showed a broad agreement between predicted yields (using Eq. (16)) and actual yields for the different microalgae.

$$
\begin{aligned}
\text{Bio-crude yield \%} = \ & (\text{protein yield \%} * \text{protein content \%}) \\
& + (\text{carbohydrate yield \%} * \text{carbohydrate content \%}) \\
& + (\text{lipid yield \%} * \text{lipid content \%}) \qquad (16)
\end{aligned}
$$

The results showed that yields of bio-crude were 5–25 wt% higher than the lipid content of the algae depending upon biochemical composition. The yields of bio-crude follow the trend lipids > proteins > carbohydrates. Both proteins and lipids were more efficiently converted to oil without the use of catalysts while carbohydrates were better processed using Na_2CO_3. In water, the carbohydrate fraction of microalgae was converted to bio-crude oil with an efficiency of 5–10% only, and for the proteins the efficiency was around 20% [226]. The higher the amounts of lipids in the substrate, the higher the biomass yields. This was explained by the high thermal stability of fatty acids. Also, in Sawayama et al. [258] the energy balance of hydrothermal liquefaction of *Botryococcus braunii* and *Dunaliella tertiolecta* suggests that the higher lipid content microalgae *Botryococcus braunii* performed more favorably than the lower lipid microalgae *Dunaliella tertiolecta*. The hydrothermal processing of 100 g of dry microalgae results in approximately, 40% oil and 429.80% of an aqueous co-product [256]. The water phase resulting from the process concentrates trace mineral matter and nitrogen, phosphorus, potassium (NPK) and may represent a route for recycling of nutrients [224]. Based on this information, Jena et al. [256] evaluated its potential as a nutrient source for cultivation of microalgae *Chlorella minutissima*. Microalgal growth medium developed by using this aqueous co-product as a nutrient additive to deionized water at 0.2% v/v concentration resulted in the best growth (0.52 g/L) for *Chlorella minutissima*. This study established the proof of concept for combining microalgae cultivation with hydrothermal processing for nutrient recycling. Apart from studies conducted with the purpose of producing biodiesel, there are few studies on the application of hydrothermal processing in microalgae. One of the exceptions is the application of hydrothermal processing in microalgae to create a char product. Employing relatively moderate conditions of temperature (203 °C), residence time (2 h) and pressure (1.65 MPa), Heilmann et al. [246] converted *Chlamydomonas reinhardtii* in an energy efficient manner into an algal char product of unique composition and with energy contents in the bituminous coal range. Potential uses for the product include creation of synthesis gas and conversion into industrial chemicals and gasoline, application as a soil nutrient amendment and as a carbon neutral supplement to natural coal for generation of electrical power. No catalytic agents were identified by Heilmann et al. [246] that significantly accelerated carbonization and/or enhanced yield with algal substrates. Shen et al. [259] used *Spirulina* for the production of acetic acid under hydrothermal processing conditions at 300 °C, 17 MPa for

80 s with H_2O_2 oxidant. Results showed that acetic acid was obtained with a good yield of 14.9% on a carbon base proving that it is possible to develop a process for conversion of microalgae biomass into acetic acid.

4. Conclusions

The conversion of biomass into chemicals and energy is essential in order to sustain our present and future. In general, hydrothermal processing used in LCMs is the most promising technology that can be conceived as a first step to the fractionation and obtention of products with high added-value according to the biorefinery concept. Depending on the operational conditions (temperature, residence time, particle size, moisture and reactor configuration), hydrothermal processing can cause several effects including hemicellulose depolymerization (oligomers, monomers), alteration/degradation of lignin (phenolic compounds) and increased availability of cellulose. Owing to these effects, the products obtained are a valuable source of materials for the chemical, pharmaceutical, food and energy industries. Moreover, the use of hydrothermal processing in aquatic biomass (macro- and micro-algae) has been shown to be an interesting technology for the production of bio-crude oil and extraction of polysaccharides for different applications and hydrolysis into sugars for a further utilization in processes such as fermentation.

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