Microwave heating processing as alternative of pretreatment in second-generation biorefinery: An overview

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Article info
Article history:
Received 7 October 2016
Received in revised form 27 December 2016
Accepted 3 January 2017

Keywords:
Biorefinery
Pretreatment
Lignocellulosic material
Microwave heating
Bioethanol
Biofuels

Abstract
The development of a feasible biorefinery is in need of alternative technologies to improve lignocellulosic biomass conversion by the suitable use of energy. Microwave heating processing (MHP) is emerging as promising unconventional pretreatment of lignocellulosic materials (LCMs). MHP applied as pretreatment induces LCMs breakdown through the molecular collision caused by the dielectric polarization. Polar particles movement generates a quick heating consequently the temperatures and times of process are lower. In this way, MHP has positioned as green technology in comparison with other types of heating. Microwave technology represents an excellent option to obtain susceptible substrates to enzymatic saccharification and subsequently in the production of bioethanol and high-added compounds. However, it is still necessary to study the dielectric properties of materials, and conduct economic studies to achieve development in pilot and industrial scale. This work aims to provide an overview of recent progress and alternative configurations for combining the application of microwave technology on the pretreatment of LCMs in terms of biorefinery.

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1. Introduction

The biofuels obtained from LCMs also known as second-generation biofuels (2G) have been proposed as an alternative to reduce the dependence on fossil fuels [1,2]. Furthermore, 2G biofuels are obtained from renewable sources that are available in enough amount for a large scale production, their price is low and they have geographical diversity of supply [3]. The main steps involved in 2G bioethanol or lignocellulosic ethanol production are: (1) particle size reduction of LCMs, (2) pretreatment of LCM, (3) enzymatic hydrolysis of cellulose, (4) fermentation and (5) rectification-distillation (composed by a separation and ethanol purification) [4,5].

In this sense, LCMs pretreatment plays an important role to achieve a feasible bioethanol conversion, since it is necessary to break down the LCMs complex structure [6]. Pretreatment enables the modification of crystalline structures of cellulose, solubilization and depolymerization of hemicellulose and in some cases the lignin can be removed depending on the type of pretreatment used [7]. This important step allows an easier access for enzyme towards cellulose to obtain fermentable sugars [8].

On other hand, pretreatment is considered one of the most expensive stages in 2G bioethanol production taking up to 20–48% of the total operational cost [9], besides is the step where more energy is consumed [10,11]. In this context, many researchers are focused on the development of suitable pretreatments. The main challenge in the development of pretreatments is the following: (1) low operational cost, (2) application in a wide range of LCMs (3) easy recovery of the products in the liquid and solid phase, (4) low energy consumption, (5) robust for continuous operation and high loading material [12–15].

In general terms, the authors have classified the pretreatments as: (1) physical: milling, extrusion, freeze and microwave heating; (2) chemical: alkaline acid, dilute acid, ionic liquids, organosolv and ozonolysis; (3) physicochemical: steam explosion, fiber explosion ammonium, CO₂ explosion, liquid hot water, wet oxidation and (4) biological pretreatment: fungus [14,16]. It is important to mention that the combination of these pretreatments is necessary in some cases, depending on the compound to produce and in terms of a biorefinery.

Recently, microwave processing has attracted attention since it satisfies many requirements of green chemistry [17]. MHP avoids the use of solvents, separation agents, or other auxiliary chemicals and smokes and wastes are not generated. Moreover, time of process is reduced by 10 times less in comparison with other heating systems, which decreases the energy consumption [18]. The MHP has fast heat transfer [11], consequently, this technology allows redefining a lot of reactions where the thermal factor plays an essential role in the process. Also, this technology is considered as an alternative method to conventional heating and has been widely used in several areas due to its efficacy and it is easy to operate [19].

This review deals the fundamentals of microwave heating processing and provides an overview of its application as pretreatment (main reactions and its effect on lignocellulosic fractionation).

2. Fundamentals of microwave heating processing

In 1949 the engineer Percy L. Spencer discovered that electromagnetic frequency radiation could heat dielectric materials. After, some companies (such as General Electric and Raytheon) patented various systems focused on industrial heating and domestic appliances. Likewise Spencer’s patent was the first to propose the use of microwaves for heating and food applications [20]. Later in 1954, Von Hippel proposed a theory to understand the macroscopic interactions of microwave with the matter [21]. Interactions between electromagnetic waves and matters are expressed as conductive losses, dielectric losses, magnetic losses, etc. These mechanisms originate dielectric heating (microwave heating) that it is dependent on the electromagnetic field characteristics and the properties of the material [22]. His theory explained dissipated power, electric field intensity and propagation constant concepts.

Microwaves are a kind of electromagnetic radiation that is shaped like energy propagating in a vacuum in the absence of any material in motion. Microwaves can be observed as light and can be used as waves. They are non-ionizing waves, similar to low frequency waves used in cell phones and infrared [23]. Furthermore, microwaves are originated by the reversing of the dipole (separation of two charges positive and negative of equal magnitude which are separated by a fixed distance). Consequently, the positive charge goes to the bottom and the negative charge at the opposite side [21]. This fact also causes the reverse field, generating the inversion of the force that acting on it. This phenomenon does not occur immediately when the dipole is changed there is a very short time to propagate the change at this point. The continued investment of the dipole is called oscillation [21,24]. The oscillation generates the electric field, but also exist oscillation for the propagation and the formation of a magnetic field, these two oscillating fields produce an electromagnetic radiation, which are measured as frequencies. These frequencies are the number of complete oscillations of a particle performed in a unit of time, usually in one second (s⁻¹ or Hertz). The space between the oscillations is called wavelength [23]. Microwaves have a frequency in a range from 300 MHz to 300 GHz and a wavelength from 1 m to 1 mm [25,26]. In this way, the alignment of polar molecules caused by microwave irradiation forces the molecule dipoles to align in the radiation field (polarized). The realignment of polar molecules produces a displacement inside of the material which generates heat [21,27].

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MHP is generated through the friction from the rotational forces of the polar molecules present, these molecules attempt to direct by themselves in the direction of the oscillating microwave field as it is shown in Fig. 1 [29]. The band from 2.4 to 2.4853 GHz is usually used to produce microwaves [20]. This level of frequencies allows a homogeneous and efficient heating. Nevertheless, in some industrial applications, frequencies of 9.15 GHz are used. These frequencies show more uniform heating in bulk, besides provides an efficiency of energy transformation of about 85% whereas with 2.4 GHz only 80% [30].

MHP is produced directly from inside the material, leading to better heat transfer, and substantially it has a higher energy yield comparing to conventional ovens which transmit heat by conduction-convection [31]. Microwaves have low energy in their photons (0.03 kcal/mol). Therefore, microwaves do not affect directly the molecular structures, since the chemical bonds have an energy ranging from 20 to 50 kcal/mol. For this reason, it is considered a non-ionizing radiation. The arousal effect of the molecules by microwaves application only increases kinetic energy [32].

Heat propagation is carried up into two mechanisms (Fig. 1): (1) Ionic conduction is carried out where there are free ions or ionic species and the molecules are oriented by themselves by ionic motion generated in the electric field, thereby causing quick heating. If the solution is denser, there are more shocks and therefore more kinetic energy is converted. (2) Bipolar rotation referring to an interaction where polar molecules try to align themselves as fast as does the electric field. The movement causes friction...
of this type of heating, mainly the non-uniform heating [25,33]. Such models are based on predicting patterns of temperature and electromagnetic energy distribution in the heated material [40]. Maxwell’s equations are applied in MHP modeling the heat source description. Maxwell equations lead to determination of the spatial distribution of electromagnetic field, when heat transfer rate is faster the modeling is based on Maxwell’s equations, as well as the Lambert’s law assumes an exponential decay of the microwave power in the heated material. These models give only an approximate to the exact solution obtained with Maxwell’s equations. Although, the computation based on the Lambert’s law gives good results in case of thick wide or when the sample depth is smaller than the penetration depth [40–43].

Most of mathematical models are based on description of solids heating. Moreover, the microwaves are used to heat water flow systems and there is little research about liquid layer. Liquids heating with microwaves have uneven heating distribution in the water flowing due to non-uniform electric field patterns. Uniformity in liquid layer heating can be solved by utilizing a focused system and taking in account factors which influence the heating patterns like dielectric properties, ionic concentration, volume, and product shape [37,44].

The MHP mathematical models of liquids are more demanding than the models for solids, due to the combination of three phenomena: the electromagnetism, heat transfer and fluid dynamics, compared with models of solid that only consider the first two [43]. Pretreatments generally are carried out in a mix of LCMs and aqueous phase that can be water, acids, alkali or ionic liquids. The mixture forms an emulsion, which finally is submitted to pretreatment, but in this sense, there is little information on mathematical models for mixtures of solids with liquids.

3. Microwave heating processing: advantages and disadvantages

MHP offers many advantages over conduction and convection heating, for example: (1) faster heat transfer and shorter reaction times [45]; (2) the heating is dielectric, volumetric (around all material) and selective due to the heating is specific on molecules with dipole [46]; (3) the MHP offers an energy-efficient route of heating and therefore cost-effective [47]; (4) the heating is carried out directly within the mixture, there is not direct contact with the heat source, in this way surfaces overheating is prevented [48]; (5) MHP allows to obtain high products yields [49], (5) the equipment has good compactness, this characteristic allows equipment place repositioning, besides the turn on and turn off is instantaneous [48], (6) the non-conductor vessel used for heating avoids heat loss, because the microwaves pass through the vessel wall without heating it [50], (7) MHP can be considered friendly environment process [51]; (9) low degradation or formation of side products due to the short reaction times [52], (10) MHP allows the material overheating, because the maximum temperature achieved is not limited by the boiling point [32], (11) MHP improves moisture
reduction, this point can be considered as an advantage or disadvantage depending on the type of process \[33\].

On the other hand, MHP has some disadvantages. The main drawback is the distribution of microwave power around of material due to non-homogeneous material (composition, geometry, and ranges of size). MHP is non-uniform, the electromagnetic waves reflection resulting in formation of the standing waves. This phenomenon is called as resonance and it leads to local overheating, also known as heat spot \[22,53\]. However, the hot spots in materials may be controlled with the distributed microwave incidence in a closed system, besides controlling the proper thickness \[53\]. Other disadvantages in MHP are the low penetration of radiation in bulk products. Some materials have low energy absorption due to the dielectric properties possessed and in some materials mainly in foods, the dielectric properties strongly change with the temperature, (i.e. defrost) and therefore also its microwave absorption \[54\].

4. Dielectric properties

Dielectric constant \((\varepsilon')\) is the ability of molecules to be polarized by an electric field and thereby to store electric energy; this part is called the real part of the dielectric properties. Dielectric constant can be affected by the molecular weight, molecule shape and direction of their links \[55\].

Dielectric loss \((\varepsilon'')\) is the amount of energy lost in the material to be dissipated into heat when it contacts the microwaves. Dielectric loss can be determined as the ability to convert electrical energy into heat and it is caused by free electron conductivity. It is considered the imaginary part of the dielectric properties, and as lower as its value, the material has less ability to absorb microwaves \[56,57\]. Dielectric losses decrease when temperature increases, therefore, they are partially self-controllable \[58\].

The relation between the two parameters is known like dielectric loss tangent or dissipation factor \((\tan \delta = \varepsilon''/\varepsilon')\). This parameter is used to describe the material capacity to be heated by microwaves. It is a dimensionless parameter that reflects the energy losses in a dielectric material, in the case that \(\varepsilon'\) is zero the loss tangent is also overridden \[35\].

Additionally, the materials can be classified according to the dielectric loss tangent present as conductive materials, non-conductors and dielectric materials. (i) Dielectric materials cannot penetrate by microwaves, they have \(\tan \delta < 0\), for example the metal; (ii) Non-conductor materials are transparent to microwaves and have low or null dielectric loss, they have a level of \(\tan \delta\) from 0.1 to 0.5, some examples are teflon, glass, quartz and air. Non-conductors materials are the main materials used to manufacture vessels or reactors to heat with MHP; (iii) Dielectric materials: these absorb microwaves, having high levels of \(\tan \delta > 0.5\), they are ideal materials to heat by MHP, for example water \[21,59\].

In this sense, in the most of pretreatments, water is the main solvent for LCMs mixtures, therefore, the presence of \(\text{H}^+\) ion improves the dielectric loss factor due to ionic conduction mechanism and water is the main responsible for the electrical polarization \[60\]. Salts and carbohydrates dissolved in water reduce the relative permittivity. In a mixture with lower salt content, the dielectric properties are mainly conducted by water at higher frequencies and sugars have a weak effect on polarization or dielectric loss \[61\]. The permittivity drop of mixtures with water is the result of two mechanisms: (1) binding of free water molecules and (2) water volume replacement with a substance that contains a lower permittivity \[62\]. According to these facts, LCMs mixtures are good microwaves drivers due to its polarity compounds (cellulose, hemicellulose and lignin) and water presence.

Other important parameter is the penetration depth \((D_p)\); this parameter is affected by the modification of the dielectric properties and layer thickness. \(D_p\) defines the depth that can dissipate microwaves inside of the material \[63\]. Dielectric constant and dielectric loss are related because both determine the amount of energy absorbed in the material and the \(D_p\) \[64\]. Besides of dielectric properties, there are other parameters that influence the absorption and transfer of microwaves to achieve uniform heating as: chemical composition, thermal diffusivity, thermal conductivity, specific heat, particle size and density \[59,65\].

4.1. Biomass dielectric properties and pretreatments

Currently many researchers have used the microwave as heating source during pretreatment in 2G biofuels production but in most of the works where MHP has been used the dielectric properties of the LCMs were not studied. However, it is necessary to know the dielectric properties to understand the material interactions with the electromagnetic energy, as well as the estimation of the penetration depth. Dielectric properties help to determine the optimal conditions to heat LCMs by MHP. In this sense, when a material is more dipolar, the process present more dielectric losses and therefore more heat is generated inside. A high loss factor indicates that the material is susceptible to being treated with microwaves while a factor of low loss indicates otherwise. In Table 1 are shown some dielectric properties for some types of LCMs that have been studied. As it mentioned previously, the material composition is an important characteristic in the MHP. LCMs content hydroxyl groups strongly polarized with high hydrophilic properties and the presence of non-polar lignocellulosic fibers and polar groups lead in the dipole formation. Therefore the dielectric constant increases with a high load of fibers at all frequencies \[66\].

On the other hand, inside of LCMs the electric current flows in a higher amount by the crystalline region (cellulose), whereas in the amorphous region the current flow follows due to the presence of moisture \[73,74\]. In literature it is possible to find the development of pretreatments using some catalysts in combination with MHP. However, it is necessary consider that the addition of acids or alkalis in the pretreatments could decrease the orientation of the polarization in the material during the heating. A stronger pretreatment can reduce the hydrophobicity of the fibers, generating unlocked hydrogen bonds making them more reactive. This fact decrease the orientation of the polarization and dielectric constant \[73\]. Also, the electrolytic presence increases the dielectric loss in a frequency less than 2.45 GHz \[75\]. Significant changes were observed when was applied MHP with acid, whereby many sizes of pores and channels were formed after perform a combined pretreatment in water hyacinth biomass \[76\]. NaOH, metal complexes and halide ions have sensitizer effects that decrease the temperature, reaction time and energy requirement in biomass pretreatment with MHP \[77,78\]. Verma et al. \[79\] used MHP with ammonium ions pretreatments, they showed that ammonium molybdate is transformed to peroxometal complex when reacting with \(\text{H}_2\text{O}_2\) this complex acts as a microwave sensitizer that absorbs microwave energy to accelerate the catalysis.

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MHP in combination with water takes place in autohydrolysis pretreatment \[19\]. In autohydrolysis pretreatment with MHP, the presence of hemicellulose fraction improves the current flow, due to its ability to absorb moisture, resulting in a higher dissipation associated with the amorphous phase relaxations \[73\]. When autohydrolysis is performed, a controlled hydrolytic solubilization and
depolymerization of hemicelluloses occurs. Reaction is catalyzed by the hydronium ions from water autoionization. Subsequently, hydronium ions coming from organic acids (acetic acid) generated in situ from hemicellulosic fraction, they are formed when the temperature increase [4,80–82]. High temperatures trigger the ions increase, allowing the solubilization of less polar substances as the hemicellulose [24]. Moreover, aqueous environments help to increase the penetration depth and uniform heating [83].

5. Fundament of lignocellulosic material depolymerization with microwave heating

In the cellulose crystalline region, the electron transport is possible by the neat hydrogen chain [84]. Moreover in the cellulose amorphous region, the electrical conductivity increases above the glass transition temperature besides between 150 and 180 °C the ionic current arises and polarization is possible. Thus LCMs can be presented as alternative conductor with ionic regions (crystalline) and non-ionic regions (amorphous) [74]. Also, cellulose molecular chains have polar structure which are oriented when are subjected to an electric field [77]. In LCMs–solvent system, the polar molecules are the most important. When the microwave energy vibrates, these molecules are strongly heating resulting in hot spots formation [85]. High heat and vibrational motion could result in the rupture or explosion from some LCMs components, causing the crystalline cellulose relocation (Fig. 2).

Heat transfer by conduction-convection occurs when LCMs is placed on heated plates where heat is generated through the coil being transferred into the material. In contrast, microwave radiation causes LCMs breakdown, via molecular collision due to dielectric polarization [86]. Firstly, increase the temperature selectively in the more polar parts, causing non-homogeneous heating. Therefore, some hot spots are created within the material, and their explosion is generated due to the heat increase. The blast effect created between the particles by microwave heating improves the crystalline structures relocation [87]. Hot spots formation starts when the temperature uniformity is lost and their location depends on the heating period and water evaporation. This fact modifies the maximum energy point and then hot spots can relocate in the regions where there is still some moisture content [88].

A second theory to explain the changes in the material structure is due to the fast generation of pressure within of components during MHP, resulting in their fast expansion [29]. The O–H bonds of

**Table 1**

<table>
<thead>
<tr>
<th>Materials</th>
<th>Frequency</th>
<th>Dielectric constant</th>
<th>Loss factor</th>
<th>Tangent loss</th>
<th>Penetration depth (cm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil palm fiber</td>
<td>2.45 GHz at 500 °C</td>
<td>1.99</td>
<td>0.16</td>
<td>0.08</td>
<td>24.8</td>
<td>[67]</td>
</tr>
<tr>
<td>Oil palm Shell</td>
<td>2.45 GHz at 500 °C</td>
<td>2.76</td>
<td>0.35</td>
<td>0.12</td>
<td>13.4</td>
<td></td>
</tr>
<tr>
<td>Oil palm Shell char</td>
<td>2.45 GHz at 500 °C</td>
<td>2.83</td>
<td>0.23</td>
<td>0.08</td>
<td>20.6</td>
<td>[68]</td>
</tr>
<tr>
<td>Empty fruit bunch (18 wt% moisture)</td>
<td>2.45 GHz at 27 °C</td>
<td>6.4</td>
<td>1.9</td>
<td>0.3</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>EFB sample (64 wt% moisture)</td>
<td>2.45 GHz at 27 °C</td>
<td>57.4</td>
<td>18.6</td>
<td>0.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wood</td>
<td>2.3</td>
<td>0.11</td>
<td></td>
<td></td>
<td></td>
<td>[69]</td>
</tr>
<tr>
<td>Fir plywood</td>
<td>≈1.5</td>
<td>0.01–0.05</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particle board</td>
<td>≈2.5</td>
<td>0.1–1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bark (aspen)</td>
<td>≈9.4</td>
<td>0.22</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bark (pine)</td>
<td>≈4.4</td>
<td>0.18</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Switchgrass</td>
<td>0.15 GHz at 150 °C</td>
<td>2.2</td>
<td>0.09</td>
<td>0.039</td>
<td>30 m</td>
<td>[57]</td>
</tr>
<tr>
<td>2.45 GHz at 150 °C</td>
<td>2.2</td>
<td>0.09</td>
<td>0.041</td>
<td>10 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Switchgrass</td>
<td>0.15 GHz at 689 °C</td>
<td>20</td>
<td>65</td>
<td>3.2</td>
<td>0.5 cm</td>
<td></td>
</tr>
<tr>
<td>2.45 GHz at 689 °C</td>
<td>8</td>
<td>28</td>
<td>3.1</td>
<td>0.3 cm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 kHz at 180 °C</td>
<td>0.09</td>
<td>0.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Switchgrass char</td>
<td>8.2 GHz to 12.4 GHz</td>
<td>2.080</td>
<td>0.1849</td>
<td>0.09540</td>
<td></td>
<td>[70]</td>
</tr>
<tr>
<td>Ayous Wood</td>
<td>1.285</td>
<td>0.1055</td>
<td>0.07229</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bubinga Wood</td>
<td>1.685</td>
<td>0.1055</td>
<td>0.07229</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mbay wood</td>
<td>1.845</td>
<td>–0.125</td>
<td>0.059</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dibetou wood</td>
<td>1 kHz</td>
<td>137</td>
<td>26</td>
<td>59</td>
<td></td>
<td>[71]</td>
</tr>
<tr>
<td>Banana Fiber with polyurethane at 10%</td>
<td>2.45 GHz</td>
<td>2.7</td>
<td>0.53</td>
<td>0.06</td>
<td>3.1 cm</td>
<td></td>
</tr>
<tr>
<td>Pine wood</td>
<td>2.45 GHz</td>
<td>13.4</td>
<td>0.08</td>
<td>0.006</td>
<td>0.2</td>
<td>[72]</td>
</tr>
<tr>
<td>Arabica coffee</td>
<td>26.8</td>
<td>3.14</td>
<td>0.117</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 2.** Mechanism of MHP effects in lignocellulose pretreatment.
the biopolymers absorb the microwaves efficiently, which might lead the heating acceleration and pressure increase [89]. However, components with not enough hydration or less polar fails to keep pace with granule expansion, and the resultant stress causes the structures collapse and in some cases their rupture [29]. Therefore, the temperature distribution and the heat transfer in all LCMs fractions play an important role to carry out this reaction with uniform heat and enough pressure. In this way, to apply a pretreatment, it is necessary to control the reaction in order to know the precise microwave irradiation influence. Water loss by evaporation, and microwave power level should be controlled. These facts provide a constant pressure and temperature control during the reaction to ensure accurate data on their effect [85].

5.1. Microwave heating as pretreatment of lignocellulosic materials

The earliest works that applied MHP to improve the enzymatic susceptibility of LCMs were reported by Ooshima et al. [90] and Azuma et al. [91]. In the last work, hardwoods (eucalypt, poplar and shirakanba) were pretreated by microwave-assisted autohydrolysis. The pretreated solids showed enzymatic susceptibility yields of 88–93% and the furfural production was low at high temperatures.

More recently, Gabhane et al. [92] studied acid pretreatment on banana wastes by 3 different power sources (autoclaving, MHP and ultrasonication) and their effect on reducing sugars production after enzymatic hydrolysis. The highest sugar yield (36.84%) was obtained using acid-microwave pretreatment. Likewise, alkali pretreatment heated with microwaves has been the most studied combination. Zhu et al. [93] used acid and alkali pretreatment with MHP during 7 min and was observed that both pretreatments degrade hemicellulose and remove lignin in comparison with conventional pretreatment. Besides, MHP improved the lignin and hemicellulose solubilization and depolymerization, consequently decreases the crystallization degree of cellulose. Akhtar et al. [94] used microwave-alkali-acid pretreated during 3 min at 850 W and 150 °C on rice straw, they reported a cellulose increase up to 60.07%, reduction of 14.90% of hemicelluloses and 4.52% of lignin and reduction of crystallinity index (8.97% in comparison with native biomass). Singh et al. [95] also reported the increase of crystallinity index (54.55%) of cellulose on rice straw pretreated by NaOH assisted with MHP. The presence of aqueous NaOH increased intermolecular saponification of ester bonds cross-linking lignin and hemicellulose improving the enzymatic saccharification. Lai et al. [96] observed an increment of 41.55% of cellulose content and a decrease of 6.99% of crystalline structure using microwave-alkali pretreated oil palm trunks at 1:20 solid/liquid ratio. Table 2 summarizes the MHP in combination with other pretreatments to enhance the fractionation of LCM depolymerization.

In alkali pretreatments the microwaves can penetrate the material and directly vibrate the molecules. The molecules oscillation causes a fast heating and an eventually rupture of encrusted lignocellulose structure. The oscillations disrupt both molecular hydrogen bonds which were incorporated within the structure. Similar behavior was reported by Hamzah et al. [114] using oil palm empty fruit bunch pretreated with microwave-alkali method and Wang et al. [115] using Apocynum venetum fibers.

On the other hand, in Table 3 are shown some works where MHP was combined with different pretreatments to improve enzymatic saccharification for subsequent fermentation for bioethanol production.

The pretreatment process plays an important role in the biorefinery concept, this stage allows the fractionation of the main components of the lignocellulosic material. Additionally, the biorefinery concept could use the combination of technologies and integration of biomass conversion processes to produce a range of biofuels, chemicals, and materials (high added-value compounds). Conceptually, a biorefinery would apply hybrid technologies from different fields including chemistry agriculture and bioengineering. This way the implementation of microwave technology as heating source during biomass pretreatment allows the development of systems that attempt to render the term “waste” in add-value products. Also, a biorefinery approach involves multi-step processes within pretreatment, for this reason microwave heating processing is positioned as an attractive technology due to the reduction of the number of chemical processes during pretreatment. Moreover, the problems related process as mass and heat transfer in the pretreatment process can be eliminated by the synergism between several technologies as MHP and ultrasound, while the reaction efficiency and overall process economics is improved significantly [124].

Bussemaker et al. [125] studied the combination of MHP and ultrasound process with oxidative media on wheat straw. The combination of ultrasonic with MHP increased the delignification up to 3.6% more than using only MHP, the effect was attributed to lignin condensation and the reduction of additional hemicellulose and inorganic material resulting in an increase of residues purity. Mai et al. [126] and Darji et al. [127] tested MHP in combination with ionic liquid, the highly ionic and polar nature of the medium causes an effective dissolution of LCM compounds. The collision frequency between anions and cations of ionic liquid and biomass macromolecules intensified the breakage of hydrogen bonds within structural matrix. Karunanithy et al. [52] studied the sequential pretreatment method of extrusion-microwave using switchgrass and big bluestem as raw material. Operations were combined sequentially, first the material was milled and wetted, and then it was placed in an extruder process, where through a moving conveyor the MHP was applied. Extrusion-microwave pretreatment was carried up at 450 W for 2.5 min and 25% moisture, as a result the process did not show formation of HMF (hydroxymethylfurfural), furfural and formic acid, only acid acetic in low concentrations 0.12 g/L using switchgrass and 0.11 g/L with big bluestem were detected.

On the other hand, MHP was tested to improve the enzymatic saccharification process. Nomnabhay et al. [128] applied microwave irradiation to observe the influence of microwave and its non-thermal effects on the saccharification yield of oil palm empty fruit bunch fiber. Pretreatment was carried out at 100 W during 4 h with 1 break minute after every 10 min. The results showed an increase of 5.8 fold in the saccharification yield and the use of 15 FPU/g of enzyme less. This behavior can be explained by the modification of active site on the enzyme due to molecular rotation and acceleration. Therefore there is more opportunity for the substrate to adjust to the enzyme per unit time [129]. MHP would be more efficient at short times, since more significant changes are registered for the variable of temperature [130,131]. It should be noted that heating is not the only factor causing effects on the structure, because the electromagnetic field applied creates non-thermal effects that accelerate the destruction of the crystalline structures, disruption of silicified waxy surface and breakdown of the lignin-hemicellulose matrix to release sugars [94]. However, it has been difficult to distinguish the role of thermal and non-thermal factors. Also, it should be consider factors that can affect enzymatic reactions, such as enzyme thermal stability and the media (aqueous or non-aqueous) where the reaction is carried out [132]. Enzymatic saccharification of LCMs using MHP for fermentable sugar production is summarized in Table 4.

Some works where combined pretreatments with MHP were used to produce high added-value products in terms of biorefinery are mentioned: Rorke et al. [139] obtained 21 volatile compounds from waste sorghum leaves pretreated with microwave assisted with 2.5% HCl pretreatment. They found aliphatic acids,
<table>
<thead>
<tr>
<th>Pretreatment used in combination with MHP</th>
<th>Pretreatment best conditions reported</th>
<th>MHP conditions</th>
<th>Feedstock and particle size used</th>
<th>Raw material composition (%)</th>
<th>Material composition after pretreatment (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkali</td>
<td>20 g of biomass, 160 ml of 1% NaOH aqueous solution</td>
<td>700 W power for 30 min</td>
<td>Rice straw (1–2 cm length)</td>
<td>Cellulose (C): 38.6; lignin (L):13.6; hemicellulose (H): 19.7</td>
<td>C: 69.2; L: 4.9; H: 10.2</td>
<td>[97]</td>
</tr>
<tr>
<td>Alkali</td>
<td>20 g of biomass 160 ml of 1% NaOH aqueous solution</td>
<td>700 W for 25 min</td>
<td>Wheat straw (1–2 cm lengths)</td>
<td>C: 41.2; L: 21.3; H: 29.8</td>
<td>C: 79.6; L: 5.7; H: 7.8</td>
<td>[98]</td>
</tr>
<tr>
<td>Alkali</td>
<td>50 g/L of biomass load, 0.1 g/g of alkali loading</td>
<td>1000 W at 190 °C for 30 min</td>
<td>Switchgrass (425 μm)</td>
<td>Glucan (Gn):33.6; Xylan (Xn):19.3; L:21.4</td>
<td>*Removed: L:82; Xn: 11.8; Gn:1.8</td>
<td>[99]</td>
</tr>
<tr>
<td>Alkali</td>
<td>4 wt% NaOH solution, 2.5:1 liquid/solid ratio</td>
<td>40 °C for 24 h followed by MH 450 W for 3 min</td>
<td>Rice hulls (1–2 mm)</td>
<td>Gn: 37.49; Xn: 15.68; L: 23.11</td>
<td>C: 69.2, A: 1.43</td>
<td>[56]</td>
</tr>
<tr>
<td>Alkali</td>
<td>3.5 g of biomass in 31.5 g NaOH at 5%</td>
<td>140 °C for 10 min</td>
<td>Wheat straw (2 mm)</td>
<td>C: 41.2; C: 79.6; L: 21.3; L: 5.7; H: 25.8</td>
<td>Gn: 49.77; Xn: 22.93; L:20.76</td>
<td>[100]</td>
</tr>
<tr>
<td>Alkali</td>
<td>Alkali at 0.05% with a soak time in alkali 24 h, and 30% biomass loading</td>
<td>300 W at 180 °C for 6 min</td>
<td>Cotton plant (1 mm)</td>
<td>C: 38.26; H: 13.7; L: 29.95</td>
<td>C: 42.37; H: 2.81; L: 2.12</td>
<td>[101]</td>
</tr>
<tr>
<td>Dilute Acid</td>
<td>500 mg of biomass, 50 ml of H₂SO₄ at 5% (v/v)</td>
<td>700 W at 200 °C for 5 min</td>
<td>Garden biomass (1 mm)</td>
<td>C: 39.57; H:26.55; L:24.46</td>
<td>C: 67.31; H: 0.8.; L: 15.67</td>
<td>[86]</td>
</tr>
<tr>
<td>Dilute Acid</td>
<td>10 g of biomass with 200 ml of dilute sulfuric acid solution at 0.2 M</td>
<td>190 °C for 5 min, at less than 900 W</td>
<td>Sugarcane bagasse (0.42 mm)</td>
<td>C: 52.45; H: 25.97; L: 12.72</td>
<td>C: 59.66; H: 3.84; L: 23.72</td>
<td>[102]</td>
</tr>
<tr>
<td>Dilute Acid</td>
<td>10 g of biomass with 100 ml dilute sulfuric acid solution at 0.005 M</td>
<td>900 W at 180 °C for 30 min</td>
<td>Sugarcane bagasse (0.42 mm)</td>
<td>C: 48.45; H: 29.92; L: 17.12</td>
<td>C: 35.2; Xn: 20.6; L: 22.6</td>
<td>[103]</td>
</tr>
<tr>
<td>Diluid Acide</td>
<td>1% sulfuric acid</td>
<td>26 W at 140 °C for 20 min</td>
<td>Corn stover (quarter inch)</td>
<td>Gn: 35.2; Xn: 20.6; L: 22.6</td>
<td>C: 41; H: 20; L: 17.8</td>
<td>[85]</td>
</tr>
<tr>
<td>Organic Acid</td>
<td>25% acetic acid, 1:15 solid/liquid ratio</td>
<td>230 W for 5 min</td>
<td>Rice Straw (0.2 mm aperture size)</td>
<td>C: 47.10; H: 17.8; L: 31.0</td>
<td>*Removed L: 46.1</td>
<td>[104]</td>
</tr>
<tr>
<td>Organosolv with acid catalysts</td>
<td>25% propionic acid, 1:15 solid/liquid ratio</td>
<td>Batch reactor at 180 °C for 6 min</td>
<td>Softwood (2–6 mm long, 2–4 mm wide and 1–3 mm thick)</td>
<td>C: 47.8; H:20.3; L: 31.0</td>
<td>*Removed L: 51.54</td>
<td>[105]</td>
</tr>
<tr>
<td>Ammonium molybdate activated by H₂O₂</td>
<td>1 mM of ammonium molybdate, 0.88 M H₂O₂</td>
<td>400 W at 140 °C for 30 min with constant stirring at 900 rpm</td>
<td>Beech wood (0.425–0.6 mm)</td>
<td>C: 49.9; H: 33.4; L: 23.</td>
<td>C: 41.8; H: 6.9; L: 17.1; Ga: 32.7; Xn: 3.6</td>
<td>[79]</td>
</tr>
<tr>
<td>Autohydrolysis</td>
<td>75 g/L of substrate loading</td>
<td>680 W for 24 min</td>
<td>Rice straw (450 μm)</td>
<td>C: 36.9; H: 17.8; L: 19.5</td>
<td>C: 36.9; H: 17.8; L: 19.5</td>
<td>[106]</td>
</tr>
<tr>
<td>Autohydrolysis</td>
<td>5% solids load in 10 ml of water</td>
<td>75 W at 180 °C for 20 min</td>
<td>Corn stover (0.635)</td>
<td>C: 35.2; Xn: 20.6; L: 22.6</td>
<td>C: 36.9; H: 17.8; L: 19.5</td>
<td>[85]</td>
</tr>
<tr>
<td>Lime</td>
<td>0.1 g lime, 10:1 L/S ratio</td>
<td>1000 W for 4 min</td>
<td>Sweet sorghum bagasse (1–2 mm)</td>
<td>C: 36.9; H: 17.8; L: 19.5</td>
<td>C: 36.9; H: 17.8; L: 19.5</td>
<td>[107]</td>
</tr>
<tr>
<td>Steam Explosion</td>
<td>100 g of material with 15 L saturated steam</td>
<td>540 W for 5 min</td>
<td>Corn stover (6–20 mm)</td>
<td>C: 57; Xn: 9.9; L: 25.8</td>
<td>C: 30.3; Xn: 13.3; L: 17.2</td>
<td>[108]</td>
</tr>
<tr>
<td>Steam Explosion</td>
<td>100 g of material with 15 L saturated steam at 1.45 MPa pressure of saturated steam</td>
<td>540 W for 5 min at 200 °C</td>
<td>Corn stover (6–20 mm)</td>
<td>C: 57; Xn: 9.9; L: 25.8</td>
<td>C: 23.8; Xn: 3.2; L: 10.1</td>
<td>[109]</td>
</tr>
<tr>
<td>Immersion with CaCl₂</td>
<td>10% solid (w/v) with 300 mL of CaCl₂ solution</td>
<td>800 W for 12 min at 162 °C</td>
<td>Corn stover (2 mm)</td>
<td>C: 23.93; L: 11.5; H: 65.6</td>
<td>C: 47.10;</td>
<td>[85]</td>
</tr>
<tr>
<td>Pretreatment used in combination with MHP</td>
<td>Pretreatment best conditions reported</td>
<td>Material composition after pretreatment (%)</td>
<td>Material composition (%)</td>
<td>Raw material composition (%)</td>
<td>Feedstock and particle size used</td>
<td>Reference</td>
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</tr>
<tr>
<td>Alkali</td>
<td>15% ratio of 5.1 NaOH at 10%, 150 °C, 4–7 kg</td>
<td>X:16.33; L: 20.70; H: 5.59</td>
<td>L: 13.82; C: 30.41; H: 20.70; L: 13.82</td>
<td>Corn stalk (2 mm)</td>
<td>Oil palm empty fruit bunches (3 mm)</td>
<td>[110]</td>
</tr>
<tr>
<td>Acid</td>
<td>15% ratio of 40:1 in formic acid solution</td>
<td>1200 W for 10 min at −0.8 °C</td>
<td>C: 51.3; H: 28.6; L: 19.6</td>
<td>Beech wood (2 μm)</td>
<td>Beech wood (2 μm)</td>
<td>[111]</td>
</tr>
<tr>
<td>Alkali</td>
<td>15% ratio of 10:1 in NaOH</td>
<td>2004 W for 6 min at 0.8 °C</td>
<td>C: 49.6; H: 23.8; L: 26.6</td>
<td>Cotton straw (3.5 cm)</td>
<td>Corn stalk (1 mm)</td>
<td>[112]</td>
</tr>
<tr>
<td>Alkali</td>
<td>15% ratio of 10:1 in NaOH</td>
<td>200 W for 15 s of power followed by 15 s of without power for 45 min</td>
<td>C: 31.5; H: 25.0; L: 10.9</td>
<td>Corn stalk (1 mm)</td>
<td>Corn stalk (1 mm)</td>
<td>[113]</td>
</tr>
</tbody>
</table>

6. Energy consumption of microwave heating in pretreatments

The energy expenditure in the pretreatment raises considerably the total cost of bioethanol production, for this reason is a critical factor to consider in biorefinery processes. Best pretreatments promise to ensure a lower production cost on industrial scale. MHP could be a good equipment to reduce energy consumption because it has been described as a technology with energy efficiency [127]. The MHP has a better energy efficiency in the process of water removal it was reported 22.5 times higher than conventional heating [148]. Xia et al. [76] demonstrated that MHP dramatically reduces the pretreatment time by a factor of over 10. Energy input for microwave-acid pretreatment using 20 g/L of water hyacinth with 1% H2SO4 at 140 °C for 15 min was also calculated with energy waste of 11.8%. (Microwave input power starts up with 48.0 kJ and the energy output from bioethanol produced was 407.1 kJ). Therefore, they concluded that it is necessary to develop a continuous microwave system to reuse the waste heat and decrease energy input of pretreatment for large-scale application.

Wang et al. [89] reported an energy expenditure of 192 kJ using MHP in ionic liquids pretreatment for wood delignification. Their results were compared with oil bath heating that spent 560 kJ. Further, the lignin content in the wood pretreated by microwave was much lower than lignin from oil bath heating treatment.

Lu et al. [117] estimated the energy consumption in the pretreatment of rape straw using 10% of solid loading, for 3 and 6 min at 700 W and 10 min at 900 W, the energy consumption was 67.2, 153.9 and 169.2 kJ respectively to produce 1 g of glucose and 105.4, 230.7 and 235.2 kJ to produce 1 g of ethanol. The most energy consumed is used in the water evaporation. This phenomenon requires 2.5 kJ per gram of evaporated water at 25 °C, water evaporation resulted in energy expenditure of 92.8, 172.3 and 213.8 kJ respectively which represents from 48 to 64% of the total consumption of the process. Vani et al. [101] compared the energy consumption between alkaline pretreatment assisted with microwave heating processing and high pressure pretreatment using as substrate cotton plant residue. Microwave pretreatment was carried out with a loading of 17.5% w/v at 300 W for 6 min and high pressure pretreatment with load of 5% w/v at 180 °C and 100 rpm for 45 min. Results showed total energy consumption with MHP was 108 kJ whereas high pressure pretreatment consumption was 540 kJ, this means 5 times more energy.

Marx et al. [121] reported a lower power input (43.2 kJ/g of dry sweet sorghum bagasse) using acid pretreatment at 5% at 180 W
### Table 3
MHP in combination with others pretreatments for bioethanol production from LCMs.

<table>
<thead>
<tr>
<th>Pretreatment used in combination with MHP</th>
<th>Pretreatment conditions</th>
<th>Feedstock and particle size used</th>
<th>Untreated material composition (UMC) and composition material after pretreatment (TMC) (%)</th>
<th>Sugar yields (SY) in enzymatic hydrolysis</th>
<th>Ethanol yield (EY) and ethanol concentration (EC)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid 0.5% H$_2$SO$_4$</td>
<td>200 °C 5 min</td>
<td>Barley husk</td>
<td>UMC: Gn: 30.1; Xn: 28.7; A: 6.2 TMC: C: 85; H: 46; A: 52</td>
<td>85%</td>
<td>EY = 81%; EC = 15 g/L</td>
<td>[116]</td>
</tr>
<tr>
<td>Acid 10 g of straw, 90 g of 2% (v/v) H$_2$SO$_4$, solid loading of 30%</td>
<td>900 W 1 min</td>
<td>Rape straw (1 cm in length)</td>
<td>UMC: C: 37.0; H: 19.6; L: 18.0 TMC: C:42.3; H: 23.6; L:15.4</td>
<td>56.2%</td>
<td>EY = 65%; EC = 13.6 g/l</td>
<td>[117]</td>
</tr>
<tr>
<td>Biological-Hydrothermal</td>
<td>C. Subvermispora ATCC 90467 was incubed at 28 °C and 70% moisture for 8 weeks, followed by microwave hydrothermal pretreatment 0.6 g in 20 ml (solid/liquid)</td>
<td>Sugarcane bagasse (1–3 cm in length)</td>
<td>UMC: C: 42.2; H:70.4; L: 27.9 *Removed: L: 20.4; C: 5.5</td>
<td>89%</td>
<td>EY = 35.8%; EC = 15.4 g/l</td>
<td>[118]</td>
</tr>
<tr>
<td>Dilute ammonia 28% ammonium hydroxide solution (v/v) and water</td>
<td>130 °C for 1 h</td>
<td>Sweet sorghum bagasse (1–2 mm)</td>
<td>UMC: Gn: 45; Xn: 28; L: 22 TMC: C: 42; X:19; L: 12.37</td>
<td>4.2 g of glucose/10 g dry biomass</td>
<td>EY = 2.1 g/10 g dry biomass</td>
<td>[119]</td>
</tr>
<tr>
<td>Alkali 2.75% alkali concentration, 30 g/L substrate concentration, ratio 10:1 liquid/solid</td>
<td>800 W 100 °C 22.5 min</td>
<td>Rice husk (1 mm)</td>
<td>UMC: C: 35; H: 13; L: 15.2 TMC: C:46; H:20; L: 7.2</td>
<td>62.1%</td>
<td>EY = 82%; EC = 12.6 g/L</td>
<td>[120]</td>
</tr>
<tr>
<td>Alkali 0.05% sulphuric acid</td>
<td>180 W 20 min</td>
<td>Rice straw (1 mm)</td>
<td>UMC: C: 38; H: 26; L: 7 TMC: C:52; H:32; L: 3.5</td>
<td>74.1%</td>
<td>EY = 75.14%; EC = 19.2 g/L</td>
<td>[34]</td>
</tr>
<tr>
<td>Acid 28 °C for 10 min with a solution of 0.2 mol/l NaOH at L/S ratio of 10:3 (v/w)</td>
<td>600 W 15 min</td>
<td>Sweet sorghum (1.5 mm)</td>
<td>UMC: C: 36.60; H: 22.96; Acid lignin 5.90 TMC: NR</td>
<td>372 mg glucose/g glucan</td>
<td>EY = 93.9%; EC = 5.6 g/L</td>
<td>[121]</td>
</tr>
<tr>
<td>Alkali 1:10 ratio of 1% (w/w) NaOH after MHP biomass was neutralized and dried then was immersed in 1% (v/v) H$_2$SO$_4$ to achieve a liquid-to-solid ratio of 10:1 (v/w) for 1 h</td>
<td>850 W 150 °C 3 min</td>
<td>Cashew apple bagasse (20# mesh)</td>
<td>UMC: C: 19.21; H: 12.05; L: 38.11 TMC: NR</td>
<td>36.91</td>
<td>EY = 46.0%; EC = 16.2 g/L</td>
<td>[94]</td>
</tr>
<tr>
<td>Acid 3% (v/v) H$_2$SO$_4$ at L/S ratio of 4:1 (w/w)</td>
<td>1100 W for 3 s</td>
<td>Sago bark waste</td>
<td>UMC: C: 42.54; H: 14.9; L: 4.52 TMC: C:46.07 H:20; L: 7.2</td>
<td>62.6% maximum sugar yield</td>
<td>EY = 60.2%; EC = 30.67 g/l</td>
<td>[123]</td>
</tr>
</tbody>
</table>
Enzymatic saccharification of LCMs using MHP in combination with others pretreatments for fermentable sugars production.

- For 20 min to produce 82 g of reducing sugars/100 g of sorghum bagasse were obtained after enzymatic hydrolysis.

- Besides, it was observed that a large amount of energy consumed occurs during heating to reach the required temperature. Maximum energy yield was reported at 130°C with expenditure of 15–18 kJ, where grinding energy consumption of smaller particle sizes is rewarded with increased ethanol yield, also the amount of water in the pretreatment could be reduced, accordingly it would reduce energy consumption. Limayem and Ricke [149] considered the pretreatment energy efficiency as total sugar recovery (kg)/total energy consumption (MJ), they showed steam explosion consumed the highest level of energy and therefore the efficiency ratio is the lowest (0.26 kg sugar/MJ) when compared to organosolv that presents 0.31–0.40 kg sugar/MJ) and sulfite pretreatment (SPORL) 0.35–0.43 kg sugar/MJ. In this sense MHP energy efficiency can be calculated and obtain a comparison pattern.

- Biomass reactor loading is a major factor in the reduction energy consumptions. High solids loading is an operational strategy that allows higher yields of products with lower operating costs. Nevertheless, it is necessary suitable pretreatment conditions due to agitation problems with high loading substrate [150,151]. According to Vani et al. [101] for a cost-effective process the biomass loading in the microwave reactor should be more than 20%. Kannan et al. [123] reported the lowest energy consumption using 40% (w/w) of biomass loading and energy input of 33 kJ (1100 W for 30 s). In this process 12.7 kg were required to produce 1 g of sugar after enzymatic hydrolysis and 1.76 kg for 1 g ethanol after fermentation. They concluded that MHP in bioethanol production succeeded in 80% energy savings compared to rape straw by microwave pretreatment previously reported.

- On the other hand, Pang et al. [109] performed an economic analysis of steam explosion assisted with MHP pretreatment using corn stover, they considered the pretreatment time in the analysis. The cost of produced sugars was reported in 0.093 US dill/kg of sugars and the pretreatment resulted economically viable.

Although, microwave pretreatment has a higher investment, its operation cost is lower compared with conventional heating; this fact allows fast recovery of capital investment [101]. Furthermore, maintenance costs are lower and there is a commercial scale process improvement. The microwave pretreatment is economic and it has energy efficiency. Thus, this can be considered as viable technology with a promising future.

### 7. Microwave heating reactors

Microwave equipment consists in four basic parts: (i) Generator that provides electromagnetic energy to the samples; the most used is the magnetron. Magnetron is a cylinder, which contains an anode and a cathode; it is heated by high voltage with a strong magnetic field; (ii) Cavities have function as electrical oscillator in an anode and a cathode; it is heated by high voltage with a strong magnetic field; (iii) Waveguide is the medium where the waves are conveyed traveling from the generator to the channel which is responsible for transporting the waves from the generator to the applicator; (iv) Applicator is a system designed to ensure that the energy is transferred from the magnetron until it reaches the sample. It does not have specific dimensions; they depend on the frequency of transported waves. Currently, there are equipment with multimode and single-mode applicators [152]; (v) Resonator or cavity is workplace where the materials are exposed to microwaves, there are variations of cavities in the reactors these depend on the manufacturer and their application. The newest equipment has a control monitoring system of power, temperature and pressure [153].

Multimode microwave reactors (Fig. 3) possess a larger cavity in relation with the wave length and samples [154]. Microwaves coming into the cavity are reflected on the walls and repeatedly bounce before passing into the product, this phenomenon usually happening over thousand times in a domestic oven, increasing a...
reflection mode that avoids the wave’s orientation into the sample. Today two magnetrons are used in the reactors to maximize the homogeneity [155,156]. Multimode reactors have several advantages due to the possibility to homogenize the electromagnetic field with rotating devices (i.e. mode stirrers). They have the possibility of installing multiple microwave inlet ports, are cheaper than monomode reactor. It has large dimensions equipment that allows working with higher volumes. As a disadvantage these reactors do not present an analytical solution with the Maxwell equations due to solution of the Maxwell equations describing the electromagnetic field in the case of partially loaded applicators and the need for thermal insulation over large areas. Maxwell’s equations provide an exact solution for the propagation of microwave radiation within the samples [27].

Monomode microwave reactors or focused (Fig. 4) targeted the microwaves through a waveguide to reach the sample; this has a width as required by the wavelength, increasing the effectiveness of radiation, with the advantage of directing the wave to the material. Focused reactors have the possibility for constant power and temperature control, the energy has an uniform distribution of radiation since is more homogeneous throughout the cavity and then more reproducible results are generated. Monomode reactors are easier to design and present availability of analytical solutions. However, they have small dimensions and have a high production cost per load volume [43,157]. In Table 5 various types of microwave reactors available in market are shown.

On the other hand, the business perspective and scalability of microwave technology has been little studied, it would be convenient to study more to get a scale microwave continuous reactor. Filly et al. [162] developed oils extraction with microwave reactor. Results showed that this process maintains good product yields and the oils extraction can be comparable with the lab scale experiments. Peng et al. [164] developed the first reactor for LCM pretreatment in a pilot-scale continuous microwave irradiation. The reactor has a size of 3 m length $\times$ 0.760 m width $\times$ 1.750 m height; the maximum work temperature is 300 $^\circ$C with a maximum pretreatment capacity of 5 kg/h. Optimal pretreatment conditions using corn stover were obtained with 4.50 kW, 30 min, and 3.5% NaOH (w/v), the glucose and ethanol production were 63.22 and 31.29 g/100 g of pretreated dry material.

Likewise, Périsio et al. [165] reported the pilot-scale process for polyphenols extraction with MHP on lettuce using a MAC-75 multimode microwave reactor equipped with 4 magnetrons (4 1500 W, 2450 MHz) with a maximum power of 6000 W its capacity is of 150 L and contains a removable, rotating PTFE drum that allows up to 75 L of plant material to be loaded.

8. Future perspectives

Biofuels production from renewable sources such as 2G bioethanol is present as possible solution to substitution of fossil fuels that could to assure the energy supply of the planet. Therefore the identification of suitable pretreatment processing is a field with challenges and wide necessity research on development of integrated biorefineries. Recently, the numbers of publications, patents, applications and researches in the use of MHP have grown. This fact is due to MHP can be considered as a handy and environmentally friendly technology. Moreover, MHP has potentially improvements over conventional heating reactions that have led to high yields and process time reductions. Currently there are studies about the drying and extraction systems in scaling pilot using MHP. Nevertheless, there are few studies on the use of microwave reactors for LCMs pretreatments to pilot or industrial scale being necessary to devote efforts in this area.

In this way, it is necessary the development of systems and microwave reactors to operate at high loads and high pressures,
likewise, a homogeneous heat transfer to prevent hot spots formation which lead to the formation of degradation compounds.

The increasing use of MHP in the food industry, pharmaceutical and materials synthesis is demanding the development of industrial in-line process. Nevertheless for the development of this type of reactors it is necessary to deepen design of applicators (traveling wave, multimode, and monomode cavities), which enable high-power densities and faster heating rates. The development of electromagnetic models for the applicators would increase our understanding of MHP and enable an easier design to optimized microwave devices.

This technology has been applied to improve biological reactions such as enzymatic saccharification; however its use has been controversial because the non-thermal effect of microwaves in these reactions has not been specified completely. This fact would allow developing operational strategies to achieve higher fermentable sugars yields and the use of lower enzyme loading. Moreover, the use of microwave heating processing to decrease the recalcitrance of the LCM is a technology that is just beginning to be developed and can be regarded as a technique that is not well established due to the few types of biomass which it has studied. Also is necessary to extend the knowledge of the best conditions for pretreatment optimization.

Thus, it is recommendable to study dielectric properties of LCMs in order to select the more convenient materials to MHP or to facilitate the searching of best pretreatment's conditions.

9. Conclusion

MHP is based on electromagnetic radiation and it is generated through the friction from the rotational forces on the polar molecules present, this technology is selective and volumetric. Materials heating depend on their dielectric, electrical and magnetic properties as well as on composition and shape. Heat generation occurs limited thus increasing energy efficiency, reducing processing times, avoiding the generation of degradation products and avoiding superficial overheating. This work showed an overview of the use of MHP applied in different kind of LCMs pretreatment. MHP as pretreatment is the result of analysis combination and techniques to deliver a sustainable, economic and versatile process. Therefore it can be recommended as a technological option in the production of 2G biofuels. However, there is a little knowledge of dielectric properties and non-thermal effect. Indeed, a detailed knowledge of microwave engineering is required to develop efficiently microwave-heating equipment to a pilot or industrial scale.

Acknowledgements

Financial support is gratefully acknowledged from the Energy Sustainability Fund 2014-05 (CONACYT-SENER), Mexican Centre for Innovation in Bioenergy (Cemie-Bio), Cluster of Bioalcohols (Ref. 249564). This study was supported by the Secretary of Public Education of Mexico PROMEP project/103.5/13/6595 – UACOAH-PTC-292 and PROMEP project/D/103.5/14/10442 – UACOAH-PTC-312. We gratefully acknowledge support for this research by the Mexican Science and Technology Council (CONACYT, Mexico) for the infrastructure project - INFR201601 (Ref. 269461) and CB-2015-01 (Ref. 254808). The author A. Aguilar-Reynosa thanks to Mexican Science and Technology Council (CONACYT, Mexico) for master fellowship support.

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