



Review

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



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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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Contents

1. Introduction	51
2. Fundamentals of microwave heating processing	51
2.1. Microwave heating modeling	52
3. Microwave heating processing: advantages and disadvantages	52
4. Dielectric properties	53
4.1. Biomass dielectric properties and pretreatments	53
5. Fundament of lignocellulosic material depolymerization with microwave heating	54
5.1. Microwave heating as pretreatment of lignocellulosic materials	55
6. Energy consumption of microwave heating in pretreatments	57
7. Microwave heating reactors	59
8. Future perspectives	60
9. Conclusion	61
Acknowledgements	61
References	61

Abbreviations: LCMs, lignocellulosic materials; MHP, microwave heating processing; MHz, megahertz; GHz, gigahertz; ϵ' , dielectric constant; ϵ'' , dielectric loss; $\tan \delta$, loss tangent; Dp, depth penetration; 2G, second generation; C, cellulose; L, lignin; H, hemicellulose; Gn, glucan; Xn, xylan; HMF, hydroxymethylfurfural; Wt, weight; FPU, filter paper activity was expressed as filter paper units (FPU) per milliliter of enzymatic mixture; FPU/g, filter paper activity per gram of raw material; BGL, β -glucosidase; NR, not reported.

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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

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