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Microwave and microwave-chemical pretreatment application for agricultural waste

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ABSTRACT

This study aimed to investigate the effect of microwave (MW) and microwave–chemical (MWC) pretreatment on barley straw and to identify the acidic, basic, or oxidative chemicals that provide the highest sugar conversion for subsequent enzymatic hydrolysis. The MW and MWC processes were applied as a pretreatment step before fermentation. MW radiation at 200 and 300 W and MW radiation plus a chemical (H_2SO_4 or NaOH or H_2O_2) as catalyst were applied, and total sugar, total phenol, and Klason and acid-soluble lignin were measured. Although the MWC pretreatment produced a higher total sugar concentration than the MW pretreatment, the addition of an NaOH solution produced the best results in terms of all parameters. Fourier transform infrared analysis was also performed to observe the deterioration of molecular structures after the application of MW and MWC.

Keywords: Agricultural waste; Barley straw; Lignocellulosic materials; Microwave radiation; Pretreatment

1. Introduction

The increased energy requirement of the developing world has led researchers to search for new energy sources. Due to their recyclable and continual properties, renewable energy sources are always preferred to other new energy sources. Bioethanol is gaining attention in the fuel market. It is produced mainly using sugar- and starch-based materials, such as sugarcane and corn [1]. These materials are not only cost-effective, but also food for humans and animals. Therefore, agricultural and garden waste as well as natural forestry residue, which are all low cost and abundant forms of lignocellulosic biomass, are suitable as energy sources [2,3].

Cellulose, hemicellulose, carbohydrate polymers, lignin, and pectin make up almost 90% of dry plants and have complex structures in lignocellulosic biomasses [4]. Carbohydrate polymers need to be destroyed and released as simple sugars before fermentation for ethanol production. Lignin holds together cellulose and hemicellulose, and it protects them from attacks from living organisms and environmental conditions. In other words, lignin forms a protective barrier against plant destruction by fungi and bacteria to allow fuel conversion. This is a critical point for the fuel conversion of biomass because energy is produced by the fermentation process in

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which micro-organisms actively convert simple sugars released from the cellulose and hemicellulose of plants to ethanol. In this context, pretreatment is an important and practical way of disrupting the resistant carbohydrate–lignin shield that limits the accessibility of chemicals or micro-organisms and enzymes to cellulose and hemicellulose [5].

Microwave (MW) irradiation is an energy-efficient, environmentally friendly, and very effective pretreatment method in the hydrolysis of biomass [6–8]. The main advantages of MW irradiation are its rapid heating, high efficiency, and lack of a temperature gradient. Thus, it has a shorter pretreatment time, which in many cases represents a reduction in energy consumption as well [9,10]. Some MW pretreatment studies with or without chemicals have been conducted on the application of different lignocellulosic materials, such as rape straw, triticale straw, cornmeal, switchgrass, rice straw, barley straw, etc. [11–15].

MW heating has advantages compared to conventional heating [10]. MW heating together with a chemical that could be acid, alkaline, or oxidative can be used as catalyst for accelerating the reactions and increasing cellulose digestibility. Sulfuric acid and hydrochloric acid are the most commonly used inorganic acids, as powerful agents for cellulose hydrolysis. These acids are generally used in concentrations below 4% wt because concentrated acid usage has disadvantages of high acid and energy consumption, equipment corrosion, longer reaction time, and others [16]. Sodium, potassium, calcium, and ammonium hydroxides, which are all alkaline chemicals, and sodium hydroxide are most commonly used in MW heating [2–4,11,16,17]. Combination of MW heating and NaOH has effects such as increasing the internal surface of cellulose, decreasing the degree of polymerization and crystallinity, swelling of material, and disruption of the lignin structure [18]. Hydrogen peroxide is most commonly employed for oxidizing compounds and used for delignification of lignocellulose. Hydroxyl radicals are generated by hydrolysis of hydrogen peroxide, and the radicals can support degradation of lignin and produce low molecular weight products [19].

The energy requirement of Turkey, a developing country with limited fossil energy sources, is rising day by day. Thus, investigations focusing on new energy sources are vital for Turkey. Taking into consideration Turkey's agricultural potential, the possible usages of agricultural products like straw as an energy source was desired in this study. Barley straw was selected as the agricultural waste product from barley production because it is the most common grain in Turkey after wheat [20] and a readily available lignocellulosic feedstock that contains relatively high amounts of five-carbon (C5) sugars [21]. The average annual production of barley in Europe and Turkey is about 95 million and 9 million tons per year, respectively [22]. The annual barley straw production is estimated to be more than 1.2 times that of barley production based on the residue-to-crop ratio. In Europe, a rough count gives a total annual production of barley straw of 114 million tons, equivalent to 511 TWh, assuming a lower heating value (LHV) of 16.3 MJ/kg dry matter [21].

In this present work, combination with MW irradiation and chemicals that are acidic, basic, and oxidative was employed to pretreat the barley straw in order to enhance total released sugar concentration before enzymatic hydrolysis.

2. Materials and methods

2.1. Raw material-barley straw

The raw barley straw was obtained from the Central Anatolia Region. It was removed from weed, broken into pieces, and classified according to size. The raw barley straw was characterized as having a moisture content of 8.34% (w/w), ash content of 3.84% (w/w), Klason lignin content of 83.59%, and total sugar concentration of 140.98 mg/L [15].

2.2. Mechanical size reduction

Samples were crushed with a high-speed (5,000 rpm) blender for 15 min. The crushed material was sieved to obtain three different particle sizes: 0.6–1.0, 0.4–0.6, and <0.4 mm. Ground material was stored in a tightly closed glass jar at room temperature until use.

2.3. Irradiation pretreatment processes

Into a 100-mL beaker was placed 1 g of barley straw and 30-mL deionized water (DIW) or 30-mL chemical solution (3%). The beaker was subjected to the MW treatment in a laboratory MW oven (Milestone Microwave Laboratory System Model: Ethos 1600) at a frequency of 2,450 MHz for the irradiation process. To remove excess chemicals, the residual biomass was washed with 200 mL of DIW after the MW process. Samples were stored at 4°C in a fridge until measurement. Experiments were repeated at least twice, and average values were used.

2.4. Analytic measurements

The total sugar concentrations were measured using the phenol-acid method. UV absorbance was measured with a DR 5000 spectrophotometer (Hach-Lange, 254 nm, 1-cm quartz cell) at 490-nm wavelengths. Total phenolic concentrations were determined according to the Folin–Ciocalteu method, and the results were expressed as grams of gallic acid per liter. In accordance with the TAPPI standard, acid-insoluble lignin and acid-soluble lignin were determined [23,24].

Fourier transform infrared (FTIR) analyses were carried out at room temperature. Samples were measured directly on a Golden Gate Attenuated Total Reflection [25] accessory (Specac) housed in a Perkin-Elmer Spectrum 100 FTIR Spectrometer. The apparatus was operated with Perkin-Elmer Spectrum software (2006). The scan range was 4,000–6501/cm with a scan number of 64, a resolution of 41/cm, and a scan speed of 0.5 cm/s.

3. Results

MW irradiation can change and disorder the structure of lignocellulose and can be effective for the pretreatment of lignocellulosic biomass for sugar production. This study focused on the MW pretreatment method in which some factors were considered (irradiation power and time) and some chemicals (acidic, basic, and oxidative) and size reductions were examined for their effect on sugar release before enzymatic hydrolysis or the fermentation process for barley straw.

3.1. Irradiation power effect with chemicals

Firstly, 200 W–10 min and then 300 W–2.5 min (irradiation power–time) were applied as experimental conditions to 0.4-mm barley straw with three different chemicals. These chemicals had basic, acidic, and oxidative characteristics and weight/volume ratios (w/v) of 3% NaOH, 3% H_2SO_4, and 2.5% H_2O_2, respectively. The irradiation procedure was carried out with or without chemicals for 10 and 2.5 min. Total released sugar concentration was measured as shown in Fig. 1. There were significant increases in total sugar concentration when the irradiation power was increased from 200 to 300 W and when the irradiation time was decreased from 10 to 2.5 min. A comparison of the results showed that the best result was obtained with the addition of 417.5 mg/L 3% NaOH at 300 W power and 2.5-min application time. The 3% NaOH and 2.5% H_2O_2 chemical addition

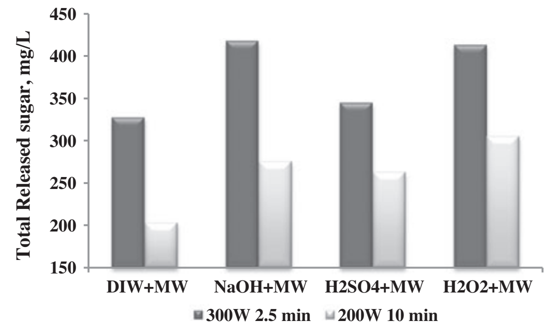

Fig. 1. Total released sugar concentration changes according to MW and MWC effect (200 and 300 W and grain size <4.0 mm).

results were quite similar: 300 W–2.5 min (417.5 and 275.0 mg/L) and 200 W–10 min (412.9 and 305.2 mg/L), respectively.

Hydrogen peroxide can convert lignin to acids and high yields of reducing sugars. On the other hand, these acids can inhibit the fermentation process and, thus, must be removed prior to enzymatic hydrolysis [26]. Alkali chemicals are an effective catalyst in MW pretreatment method for increasing the enzymatic hydrolysis of lignocellulosic biomass because it disintegrates the lignocellulosic structure better than the others do. NaOH with MW heating can disrupt the ester bonds between lignin and carbohydrates in the straw and results in the dissolution of the lignin and hemicellulose [9,11,27].

3.2. Irradiation time effect with chemicals

Fig. 2 shows the effect of NaOH and H_2O_2 on the percentage increase of released sugar at less than 200-W irradiation power during different irradiation times from 0.5 to 20 min. The total sugar concentration

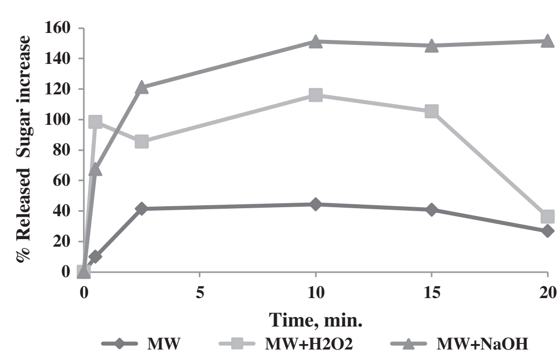

Fig. 2. Percentage increase of released total sugar concentration on MW and MWC (200 W and grain size <4.0 mm).

of the raw material that was not subjected to the MW pretreatment was 140.98 ± 1.94 mg/L. The calculations of the increases in total released sugar are based on this number. As seen in Fig. 2, at 10-min and 200-W irradiation power without any chemical addition, the released sugar increased 44.3% from 141.0 to 203.5 mg/L, which is the maximum. After that time, irradiation time had no improvement effect. At the same irradiation power, the effect of the addition of H_2O_2 and NaOH can be seen in Fig. 2. We observed that NaOH and H_2O_2 had significant effects on released sugar concentration over time. After 15 min, time generally had a negative effect on all sugar concentration increments (0.5 and 2.5 min for the MW irradiation with 279.68 mg/L H_2O_2 and 311.90 mg/L NaOH, respectively). However, the best results were obtained with 304.5 and 354.1 mg/L for H_2O_2 and NaOH, respectively. Released sugar amounts did not increase linearly according to increased time. More energy-efficient technology is important in applications; therefore, a short time is desirable. If the time increased in the MW pretreatment process, water will evaporate, much energy will be lost, and MW effects will be reduced [12].

3.3. Chemical effects on phenol and lignin

Fig. 3 shows the total released sugar and phenol concentration with/without chemical addition MW pretreatment in the signified conditions. The total sugar concentration of raw barley straw was 140 mg/L. It was observed that the maximum total sugar-releasing potential from barley straw was obtained using 300-W MW power with a 3% NaOH solution (w/v, 1:30) for 2.5 min. It can be said that the application of an alkaline solution to lignocellulosic material removes the lignin fibers of lignocelluloses effectively [11] and, thus, enhances the sugar yield [10]. The addition of H_2O_2 produced a similar impact to that of NaOH. The addition of H_2SO_4 was not as effective as the other chemicals, but it produced the same level with the addition of DIW.

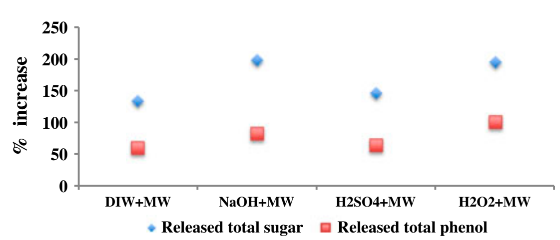

Fig. 3. Percentage increase of released total sugar and total phenol concentration on MW and MWC pretreatment (300 W and 2.5 min and grain size <4.0 mm).

It is accepted that radiation initiates chemical reactions in the macromolecules of cellulose materials. The reactions lead to the breaking up of chemical bonds and the production of free radicals. Some bonds of the macromolecules of cellulose materials are more capable of absorbing certain wavelengths of the radiation and are easily ruptured, and the molecules produce long- and short-lived radicals. The breaking up of chemical bonds and production of new radicals depend on the radiation dose and molecular structure [28]. On the other hand, increasing the reaction effect and efficiency using less energy is desired from an economic point of view. The addition of chemicals to the process may help.

Agricultural waste is a biomaterial composed of cellulose, hemicellulose, and lignin. Cellulose and hemicellulose contain sugar, and lignin is mainly composed of phenolic units. MW irradiation increases total released phenol with or without chemicals, as seen in Fig. 3. In addition, there is a correlation between phenolic compound concentrations in terms of total phenol and total sugar concentration. The degradation initiates at phenolic hydroxyl groups, beta-carbons adjacent to alpha-carbonyl groups, and any conjugated double bound [29].

The pretreated barley straw was filtered and processed to determine its Klason lignin content. Fig. 4 shows that the highest content of acid-insoluble lignin was obtained with the addition of NaOH. This result confirmed the formation of total sugar concentration, meaning increased lignin deterioration caused increased sugar release.

3.4. Size-reduction effect

Barley straw was irradiated at three different size ranges using 200-W power with 3% NaOH or without any chemicals. The sugar yield increased when the particle size decreased from 0.4 to 1.0 mm at two different irradiation times, 2.5 and 10 min, as seen in Fig. 5. Interference together with crushing to produce

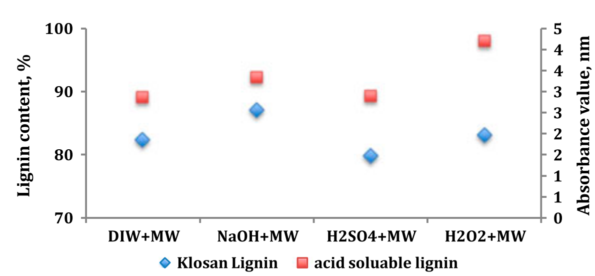

Fig. 4. Klason and acid-soluble lignin after MW and MWC pretreatment (300 W, 2.5 min and grain size <4.0 mm).

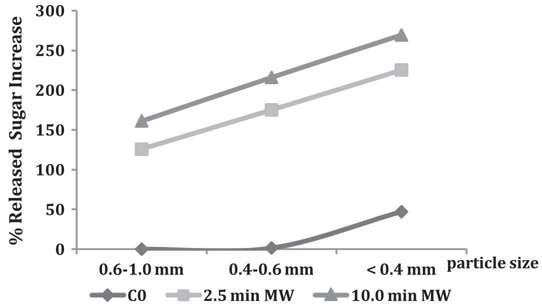

Fig. 5. Percentage increase of released total sugar concentration with/without 200-W MW at different grain sizes and irradiation time with 3.0% NaOH addition.

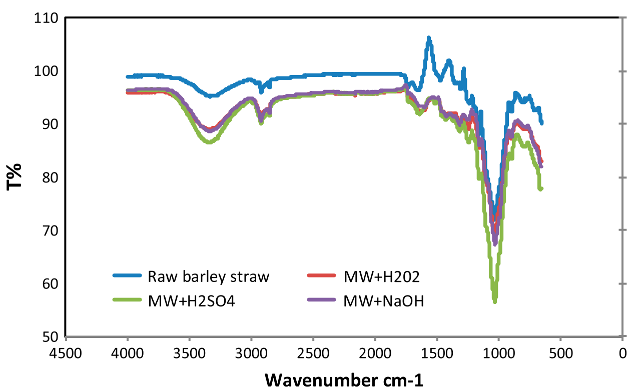

Fig. 6. IR spectroscopy of raw and pretreated barley straw at 300-W power and 2.5-min irradiation time.

Table 1
Raw and MWC-pretreated lignocellulosic material wavelength and chemical groups

Wave number (cm^{-1})	Chemical compounds or groups
833	p-hydroxyphenyl propane
980	C–O–H elongation of primary and secondary alcohols
1,100	C–O–C stretching of glycosidic linkages
1,050–1,170 cm	Vibration of the ring C–O–C
1,170	Arabinosyl side chains
1,374	Syringyl group
1,510	Aromatic ring
1,600	Aromatic ring
1,635	Aromatic ring
1,728 cm	Carbonyl group
3,440 and 2,906	Stretching of the hydroxyl groups present in cellulose, hemicellulose and lignin, and the axial deformation of C–H

the smaller size at these irradiation times may have increased the sugar release. When we compared three different particle sizes—0.6–1.0, 0.4–0.6, and <0.4 mm—the smallest particle size under every condition produced the highest sugar release. Crushing the hemicellulosic biomaterial may have increased the accessible surface area and decreased the degree of cellulose crystallinity [28,30]. Only size reduction increased the amount of sugar released by almost 50% compared to the raw material without any MW irradiation or chemical addition. Using both MW irradiation and 3% NaOH addition together improved sugar release by almost four and five times at 2.5 and 10 min irradiation time, respectively, at the smallest particle size (0.4 mm).

3.5. FTIR analysis

The chemical differences between untreated barley straw and that treated with MW irradiation and chemicals were observed by FTIR, as seen in Fig. 6. FTIR spectroscopy measures how well a sample absorbs light at each wavelength and helps to identify molecular structures originating from the information obtained and the possibility of assigning certain absorption bands to their functional groups. Table 1 shows the wavelengths of raw and microwave chemical (MWC)-pretreated lignocellulosic material and the affected chemical groups. Moretti et al.'s work (2014) related to the pretreatment of sugarcane bagasse with MW irradiation was adapted to the barley straw pretreatment application [31].

4. Conclusion

There are mainly two processes for energy (bioethanol) conversion from ligno-material: the hydrolysis of the cellulose in the lignocellulosic agricultural waste to produce reducing sugars and then the fermentation of the sugars to ethanol. For the first step, pretreatment of lignocellulosic materials is necessary for efficient conversions, as it removes lignin and hemicellulose and significantly enhances the hydrolysis of cellulose. MW irradiation was applied as a pretreatment method to barley straw, a form of agricultural waste, which increased released sugar concentration significantly. Furthermore, MW irradiation with chemicals yielded more encouraging results for the application of structural deterioration before enzymatic hydrolysis or fermentation for bioethanol production. When compared to the raw material without any MW irradiation or chemical addition, 300 W–2.5 min MW irradiation with the 3.0% NaOH, 3.0% H_2SO_4, and 2.5% H_2O_2 chemicals increased the released reducing sugar content by 2.1 times, 1.7 times, and 2.1 times, respectively. By MW power reducing from 300 to 200 W and irradiation time increasing from 2.5 to 10 min, the released reducing sugar content is improved by 1.4 times, 1.3 times, and 1.5 times, respectively. The best result was obtained with the addition of 417.5 mg/L 3% NaOH at 300-W power and 2.5- min application time. Only size reduction increased the amount of sugar released by almost 50%.

According to the FTIR analysis, NaOH and H_2O_2 caused similar structural deformations, but H_2SO_4 produced better results.

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