

Application of Microwave Heating in Biomass Hydrolysis and Pretreatment for Ethanol Production

Euis Hermiati^{1*}, Djumali Mangunwidjaja², Titi C. Sunarti², Ono Suparno², and Bambang Prasetya³

¹Research and Development Unit for Biomaterials, Indonesian Institute of Sciences (LIPI), Indonesia

²Department of Agroindustrial Technology, Faculty of Agricultural Engineering and Technology, Bogor Agricultural University, Indonesia

³Research Center for Biotechnology, Indonesian Institute of Sciences (LIPI), Indonesia

Abstract

Recently, due to depletion of fossil derived energy stock in the world, there are growing interests in utilizing biomass as sources of bioethanol. There are basically two types of biomass that are usually used or converted to ethanol, starchy and lignocellulosic biomass. The conversion of starchy and lignocellulosic materials are widely explored, however, there are still some drawbacks, such as high enzyme cost and intensive energy needed. Therefore, lower cost as well as energy and time efficient process technology in biomass conversion to ethanol is important in enhancing the use of biomass to substitute fossil fuel. Microwave heating offers some advantages to overcome these drawbacks, especially due to its quick heat transfer and its heating selectivity. In conventional heating the heat was transferred through conduction or convection process which took longer time. Thus, by using microwave, degradation of starchy and lignocellulosic biomass could be completed in shorter time than by using conventional heating method. The roles of microwave heating in the degradation of biomass, especially starchy and lignocellulosic biomass and its relation to the hydrolysis and pretreatment of that particular biomass for ethanol production are reviewed and discussed.

Keywords: biomass, pretreatment, ethanol, microwave

*Corresponding author

Jl. Raya Bogor Km. 46, Cibinong 16911, Indonesia

Tel. +62-21-87914511, Fax. +62-21-87914510

E-mail: euis.hermiati@lipi.go.id

Introduction

Biomass is usually defined as organic matter derived from plants, which is generated through photosynthesis. Biomass has important roles in human lives, because it provides food, fibers, medicines, construction materials, and energy. Biomass can be considered as solar energy stored in the form of chemical bonds of the organic materials. The use of biomass as energy resources has been known since older ages, however, it became not popular since the invention of energy from fossils, such as oil and coals. Recently, due to depletion of fossil derived energy stock in the world, there are growing interests in utilizing biomass as sources of energy, either through thermochemical processes (combustion, gasification, and

pyrolysis) or biochemical processes (fermentation and anaerobic digestion).

There are basically two types of biomass that are usually used or converted to ethanol, starchy and lignocellulosic biomass. Starchy materials such as corn, sorghum, and cassava, as well as lignocellulosic materials, such as wood, sugarcane bagasse, and switchgrass, are widely explored to be used for bioethanol production. The conversion of this biomass, especially lignocellulosics, still faces some drawbacks, such as high enzyme cost and intensive energy needed. Therefore, lower cost as well as energy and time efficient process technology in biomass conversion to ethanol is important in enhancing the use of biomass to substitute fossil fuel.

Microwave is electromagnetic waves between 300 MHz (wavelength 1 m) and 300

GHz (wavelength 1 mm). This range of spectrum lies between infrared and radiofrequency radiation. Microwaves are used in radar, microwave communication, UHF TV, and domestic heating oven in household kitchens. Microwave heating is also used in synthetic chemistry, preparations of samples for chemical analyses, and processing of other industrial materials. As electromagnetic waves, microwave can be transmitted without medium. Thus, heating process using microwave follows different mechanism from that of using conventional convection or conduction heating process, which needs medium to transfer the heat. Microwave heating is usually called dielectric heating since in microwave electric field, dipole molecules such as water or other dielectric materials, rotate vigorously to orient in the field. In the gas and liquid phases the molecules rotate so rapidly that they are normally able to respond to field reverses occurring at 10^6 times a second or higher, but in the solid state the molecular rotations are generally restricted and therefore reorientation in an electric field does not generally contribute to the dielectric constant (Gabriel *et al.*, 1998).

Recently, microwave heating have been used for hydrolysis of starch (Khan *et al.*, 1979; Yu *et al.*, 1996; Kunlan *et al.*, 2001; Nicolich *et al.*, 2008; Matsumoto *et al.*, 2008) and pretreatment as well as hydrolysis of lignocellulosic biomass (Azuma *et al.*, 1984; Ooshima *et al.*, 1984; Magara *et al.*, 1989; Kitchaiya *et al.*, 2003; Zhu *et al.*, 2005, 2006a, 2006b, 2006c; Hu & Wen, 2008; Keshwani, 2009; Robinson, 2010). Microwave heating is useful in hydrolysis of starchy or cellulosic biomass, because the process could be completed in shorter time, at lower acid concentration and without the use of expensive enzymes. Microwave heating is also useful in pretreatment of lignocellulosic biomass since the treatment could increase the susceptibility of hydrolytic enzymes and increase the extent of saccharification compared to conventional heating.

This review would explain and discuss existing literatures on the roles of microwave heating in the degradation of biomass, especially starchy and lignocellulosic biomass and its relation to the hydrolysis and pretreatment of that particular biomass to

produce sugars, which will be further fermented to ethanol.

Microwave heating

Operation mechanism of microwave system

A microwave heating system consists of a DC power supply that provides power to generate microwave energy, a magnetron that converts supplied power into microwave energy, an applicator and handling equipment that applies microwave energy to the work piece, and control panels that control electronics, instrumentation and automation of the system (Center for Materials Fabrication, 1993). Magnetrons generate microwave power up to 60 kW at 915 MHz and up to 6 kW at 2450 MHz. Applicators direct the microwave energy at the material. The most common applicator is the multimode cavity, essentially a rectangle box that provides a reasonably uniform field. The microwave energy is directly transferred to the molecules of the material. These molecules become stimulated and rotate millions of times a second in response to the electromagnetic field. This rotation quickly generates heat within the material in a manner similar to friction. An illustration diagram of a microwave oven is presented in Figure 1.

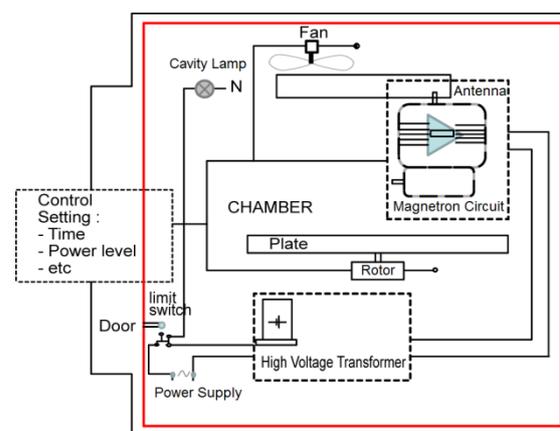


Figure 1. Illustrative diagram of a microwave oven.

As mentioned above, the heat that builds up inside a material in a microwave system is due to rotation of molecules in the material heated, and this relates to dielectric properties of the material. A dielectric material contains either permanent or induced dipoles which when placed between two electrodes acts as a

capacitor, *ie* the materials allow charge to be stored and no DC conductivity is observed between the plates (Gabriel *et al.*, 1998). The polarization of dielectrics arises from the finite displacement of charges of rotation of dipoles in an electric field. At the molecular level polarization involves the physical rotation of molecular dipoles.

Dielectric property of a material is usually described by its dielectric constant and dielectric loss factor (Motwani *et al.*, 2007). Dielectric constant is indicative of the ability of the material to store energy and polarized when subjected to an electric field, while the dielectric loss factor is associated with loss of dielectric field energy in the material which is dissipated as heat. Materials with loss factors between 0.01 and 1 generally heat adequately at microwave frequencies (Center for Materials Fabrication, 1993). However, these values are only guidelines, since the loss factor as well as dielectric constant is dependent on temperature, frequency and moisture content. Table 1 shows dielectric constant of some solvents as described by Gabriel *et al* (1998). It can be seen that dielectric constant of water (80.4) was much higher than that of the other solvents (organic solvents). This means that water would have better effects as a medium in microwave heating than the other solvents.

Table 2 shows dielectric constant and dielectric loss factor of some agricultural products as described by Tambunan *et al* (2000). The table shows that wheat and sorghum have higher dielectric constant and dielectric loss factor values than soybean. Table 3 shows those of different kinds of starches at 2450 MHz as described by Ndife *et*

al (1998). From the table, it can be inferred that corn or corn starch (waxy-maize) probably would be easier to be hydrolyzed under microwave heating than rice, tapioca, and amylomaize, because the formers have higher dielectric constant and dielectric loss factor values than the latters. Dielectric properties of corn starch slurries were reported by Ndife *et al* (1998), Motwani *et al* (2007) and that of α -D-glucose solutions by Liao *et al* (2003). Their studies confirmed that dielectric property is dependent on temperature, frequency and moisture content or concentration of the substances in water as the solvent.

Table 1. Dielectric constant of some solvents (Gabriel *et al.*, 1998).

Solvents	Dielectric Constant
Benzene	2.3
Carbon tetrachloride	2.2
Chloroform	4.8
Acetone	21.4
Ethanol	25.7
Metahnol	33.7
Water	80.4

Table 3. Dielectric properties of dry granular starches at 30°C. Ndife *et al.*, 1998).

Starch Type	Dielectric Constant	Loss Factor
Corn	2.74	0.14
Rice	1.25	0.00
Tapioca	2.25	0.08
Wheat	2.42	0.05
Waxy maize	2.81	0.43
Amylomaize	2.42	0.37

Table 2. Dielectric constant and dielectric loss factor of some agricultural products at different frequencies (Tambunan *et al.*, 2000).

Frequency (MHz)	Dielectric Constant			Dielectric Loss Factor		
	Wheat	Sorghum	Soybean	Wheat	Sorghum	Soybean
1.33	4.45	4.71	4.14	0.62	0.62	0.30
1.35	5.48	4.88	4.38	0.81	0.95	0.53
1.40	5.34	5.21	4.77	1.06	0.95	0.52
1.45	3.26	4.46	4.85	1.32	0.98	0.65
1.50	2.78	2.88	2.64	1.54	1.09	0.84
1.55	2.72	3.01	2.70	1.66	1.37	0.65
1.60	2.65	2.61	3.00	2.39	1.24	0.43

Effects of microwave irradiation (thermal and non thermal)

Even though it is still debatable, microwave radiation is considered to produce

thermal and athermal (non thermal) effects. Jacob *et al* (1995) reported that the properties of the irradiated material may not be similar to the conventionally treated material. Some

reports supported that both effects are occurred, while some others observed that the research did not detect any athermal effects of the microwave radiation. Pagnotta *et al* (1993) found that there was a mutarotation of α -D-glucose in ethanol-water mixture, and Porcellia *et al* (1997) reported that microwaves induced protein structural rearrangements. Banik *et al* (2003) described that microwave radiation affects biological systems, from microbial cells to animals as well as the human system. Further, they concluded that microwave could athermally induce different physiological effects, and act as promoting agents in inducing genetic changes in biosystems. Recently, Huang *et al* (2009) validated the existence of non thermal effects of microwave by doing experiments in electrolyte aqueous solutions. On the other hand, Welt *et al* (1993) could not find any non thermal effects of microwave during thiamine degradations, Meissner & Erbesdobler (1996) could not detect non thermal effects of microwave in the early formation of Maillard reaction, and Gedye (1997) also did not detect any non thermal effect in a series of organic reactions. Similarly, after conducting a research with good temperature control using five systems, including the Maillard reaction, protein denaturation, mutagenesis of bacteria, glucose mutarotation, and saturation solubility of sodium chloride, Shazman *et al* (2007) stated that their findings could not support the hypothesis of athermal effects induced by microwave radiation, since they could not detect any athermal effect in any of the tested systems.

In conclusion, the athermal or non thermal effects of microwave might be detected or not detected in some experiments. Thus, the effects of microwave heating with regard to all properties of the materials heated are still need to be verified.

Advantages of microwave heating

Microwave heating offers some advantages over conventional heating, especially for heating materials that have low heat conductivity. Among these advantages are as follows (Center for Materials Fabrication, 1993).

- Quick heat penetration. Microwave energy can penetrate into materials heated, so that it is able to directly and uniformly heat the materials.

- Selective heating. Different materials absorb microwave energy at different rates, so that a product with many components can be heated selectively.
- Amenable to automation. Microwave heating is electronics, so that it can be easily integrated with computers or other devices for automation.
- Improvement of product quality. Microwave heating avoids degradation of product strength and surface properties caused by excessive and long heating.
- Increased flexibility. Microwave energy can heat materials with complex shapes more uniformly, and the system can be switched on and off instantly.
- Combination with conventional methods. Microwave energy can be applied before, after, or inside conventional heating or drying units to decrease processing times by as much as 75%.
- High energy efficiency. Overall microwave energy efficiency is around 50%, while that of conventional fuel-fired heating processes is generally 10 to 30%.
- Space savings. Microwave heating equipment occupies only 20 to 35% of the floor space of conventional heating units.

Roles of microwave heating in starch degradation

There are some reports regarding the use of microwave heating in the degradation of starch from different kinds of starchy materials, such as wheat, rice, potato, and corn, in water or dilute acid solutions as mentioned above (Khan *et al.*, 1979; Yu *et al.*, 1996; Kunlan *et al.*, 2001; Nicolich *et al.*, 2008; Matsumoto *et al.*, 2008). Most of studies reported, 2450MHz microwave oven could be use for starch degradation. Concentration of starch suspension varies from 1% up to 50%, but a 10% of starch suspension was mostly used (Yu *et al.*, 1996; Kunlan *et al.*, 2001). Study on lower starch suspension (1-8%) was conducted by Palav & Seetharaman (2006), while that on higher concentration was carried out by Khan *et al* (1979) (10-30%), Palav & Seetharaman (2007) (33-50%), and Nicolich *et al* (2008) (33%). Some studies indicated the temperatures used in the process (Yu *et al.*, 1996; Azuma *et al.*, 1984; Ooshima *et al.*, 1984; Magara *et al.*, 1989; Hu & Wen, 2008;

Robinson, 2010). However, the others just reported the degree of power used, either in the term of percentage or wattage (Kunlan *et al.*, 2001; Pinkrova *et al.*, 2003; Palav & Seetharaman, 2007; Nolic *et al.*, 2008). According to Tsubaki *et al.* (2009), gelatinization of potato starch started at 120°C at 25% (w/w) of starch concentration. Further, they stated that solubilization of starch was significantly improved above this temperature, and most of the starch was solubilized at around 200 to 220°C accompanied by colored secondary decomposed materials. The longest time use for starch treatment or degradation using microwave heating that has been reported was 10 minutes. Most processes are reported could be completely finished in less than 10 minutes. Treatment or degradation of starch using microwave heating can use water or dilute acid, such as hydrochloric acid and sulfuric acid as media. Kunlan *et al.* (2001) reported that addition of anorganic salts containing Cl⁻ and SO₄²⁻ ions could enhance hydrolysis of starch. However, Cl⁻ ion gave better results.

The effects of microwave heating on degradation of starch are different from that of conventional heating which uses conduction method. Yu *et al.* (1996) suggested that microwave irradiation was probably not only increased the rate of energy transfer to enhance the reaction, but also changed the structures or conformations of the reactans. A study carried out by Palav & Seetharaman (2006) showed that gelatinization of starch during microwave heating was not the same as that which used conduction heating. This could be observed in the loss of birefringent properties and in the swelling of the starch granules. Further research showed that there were also significant differences in gel and starch molecule properties between materials resulted from microwave heating and those from conduction heating (Palav & Seetharaman, 2007). Luo *et al.* (2006) conducted a study to investigate changes in crystallinity, swelling power and solubility, gelatinization parameters, retrogradation characteristics and pasting properties of normal maize, waxy maize and amylomaize V starches at 30% moisture after subjected to microwave heating at 1W/g microwave energy for 20 minutes. From their research they concluded that microwave treatment resulted in changes in granular surface, swelling power

and solubility, X-ray diffraction intensities, gelatinization transition temperature, syneresis and pasting properties. Microwave treatment induced the rearrangement of molecules in sections of starch that are part of the crystalline region, and the irradiation had greater effects on amylose than on amylopectin. Thus, the extent of changes caused by microwave treatment depends not only on the crystal structure of starch, but also on its amylose content.

Microwave heating could convert starch directly to glucose in relatively short time. Compared with conventional heating, the reaction rate of starch hydrolysis to glucose was accelerated 100 times under microwave irradiation (Kunlan *et al.*, 2001). Yu *et al.* (1996) stated that 10% starch suspension in 0.5 M HCl could be completely converted to glucose only in 5 minutes without the formation of colored by-products, while that heated using conventional method was not hydrolyzed. Tsubaki *et al.* (2009) reported that 67% of glucose was produced from potato starch hydrolyzed using a batch system of microwave at 220°C. Based on molecular weight distribution analysis of the solubilized materials by size exclusion chromatography (SEC), it was revealed that there was a generation of maltooligosaccharides and glucose when heating temperature was increased. Tsubaki *et al.* (2009) also reported that 72.4% of reducing sugars was attained from corn starch heated using microwave between 210 and 217°C. Maximum sugar yield (111 wt%) could be achieved if halide metals, such as LiCl, BaCl₂ and FeCl₃ were added to the starch suspension, and the process was completed in around 120-180 seconds (Kunlan *et al.*, 2001). Nevertheless, this halide metals might inhibit the work of *Saccharomyces cerevisiae* if the sugar would be further converted to ethanol.

There might be some secondary decomposition materials produced after microwave heating of starch suspension, especially when the medium used is acid or the temperature used is quite high with a quite long heating time. Matsumoto *et al.* (2008) offered the use of activated carbon powder, which was added in starch suspension, then, it was subjected to microwave heating (220 to 240°C) at the same time. This was done especially to recover maltooligosaccharides.

The oligosaccharides were adsorbed on activated carbon, so that they were prevented from secondary decomposition, such as decomposition of sugars to hydroxymethyl furfural or some acids. These secondary products might inhibit fermentation of sugars to ethanol, so that their removal or their prevention of formation is very important.

Role of microwave heating in lignocellulosic degradation

One of the important steps for the utilization of cellulose contained in lignocellulosic materials is pretreatment. This step is still considered to be the rate limiting step in an economically feasible process for enzymatic hydrolysis of cellulose. The aims of pretreatment are mainly to degrade or reduce lignin content, to reduce cellulose crystallinity, and to increase porosity and surface area of the materials. Microwave irradiation is one of the pretreatment method for degradation of lignocellulosic materials. Early reports on this pretreatment were provided by Azuma *et al* (1984), Ooshima *et al* (1984), Azuma *et al* (1986), and Magara & Azuma (1989). A patent concerning apparatus and method of microwave pretreatment for cellulosic waste products was compiled by Cullingford *et al* (1993).

There are different kinds of lignocellulosic materials used for microwave pretreatment studies. Azuma *et al* (1984) used three types of woody materials, a softwood (akamatsu), a hardwood (buna), and a bamboo (mosochiku) to be pretreated with microwave irradiation. Other lignocellulosics studied are wheat straw (Ooshima *et al.*, 1984; Zhu *et al.*, 2006b; 2006c), rice straw (Ooshima *et al.*, 1984; Magara & Azuma, 1989; Zhu *et al.*, 2005; 2006a), rice hulls (Magara & Azuma, 1989), sugarcane bagasse (Ooshima *et al.*, 1984; Magara & Azuma, 1989; Kitchaiya *et al.*, 2003), switchgrass (Hu & Wen, 2008; Keshwani, 2009), and Bermuda grass (Keshwani, 2009). These lignocellulosics were subjected to microwave pretreatment of 2450 MHz in the range of 250 to 1000 W using batch system, except of Magara & Azuma (1989) that used 165-225°C. Some materials were put in closed systems or vials, some others were in open systems or vials. The temperature of heating ranged from 70°C up to around

230°C, while heating time ranged from 5 minutes up to two hours, even though it seems that there was not any significant change of glucose yield after 25-30 minutes of microwave pretreatment. The above studies showed that microwave treated lignocellulosic biomass was more susceptible to enzymes during saccharification process than without microwave pretreatment. For examples, the result of enzymatic hydrolysis of rice straw increased 1.6 times after microwave pretreatment at 170°C for 5 minutes, and that of sugarcane bagasse increased 3.2 times after microwave pretreatment at 200°C for 5 minutes (Ooshima *et al.*, 1984).

Temperature and time of heating treatment affects weight loss and the loss of chemical component from the lignocellulosics. Azuma *et al* (1984) noted that weight loss still increased above 230°C. However, higher microwave power with short pretreatment and the low microwave power with long pretreatment had almost the same effect on the weight loss and chemical composition of rice straw and wheat straw at the same energy consumption (Zhu *et al.*, 2005; 2006b). The temperature reached during microwave pretreatment affects enzyme susceptibility, and thus, sugars yields in hydrolysis of lignocellulosics. Azuma *et al* (1984) noted that the microwave irradiation above 180°C could markedly enhance the enzymatic susceptibility of woody plants. They also reported that reducing sugar production increased with the increasing of temperature, and reached a maximum at temperature 223-229°C.

In order to increase the effects of microwave heating pretreatment, some studies combined the treatment with alkaline treatment. Some used alkaline solution, such as NaOH, during microwave heating treatment (Zhu *et al.*, 2005; 2006a; 2006b; 2006c; Keshwani, 2009) and some used the alkaline solution before the lignocellulosic materials was subjected to microwave pretreatment (Zhu *et al.*, 2006a; Hu & Wen, 2008). According to Zhu *et al* (2006a), pretreatment of rice straw by combining microwave irradiation with alkaline solution could increase the initial hydrolysis rate but the hydrolysis yield remained almost unchanged. Hu & Wen (2008) found that switchgrass soaked in NaOH solution (0.1 g alkali/g biomass) before treated with microwave heating (190°C, 50 g/L solid

for 30 minutes) could produce 99% of potential sugars. Keshwani (2009) reported that optimum microwave heating pretreatment for switchgrass was using 2% of NaOH for 10 minutes, which resulted in 82% of glucose and 63% of xylose yield. Using the same microwave power treatment (250 W, temperature 80-85°C), optimum treatment condition for Bermuda grass was 1% NaOH for 10 minutes, which yielded 87% of glucose and 59% of xylose. Kitchaiya *et al* (2003) used glycerine to increase the effects of microwave heating pretreatment on sugar yield. The reason for this was that glycerine has a high dielectric constant, so that it might help absorb microwave energy better, and this might enhance microwave heating treatment in atmospheric pressure. Unfortunately, they did not conduct the experiment that uses only water as the medium, so that the effects of glycerine could not be compared. However, their results showed that samples with more water in glycerine dispersion produce almost the same yield of reducing sugars as that with less water. This was not surprising since the dielectric constant of glycerine at 20°C (41.1) is lower than that of water (80.4). Thus, for microwave heating water is the better solvent compared to glycerine.

The use of microwave heating in hydrolysis of cellulosic and lignocellulosic biomass was patented by Robinson (2010). He used metal salts, such as, NaCl, ZnCl₂, ZnSO₄, CuCl₂, CuSO₄ and some acids such as, sulfuric acid, hydrochloric acid, phosphoric acid, and acetic acid and heating time of 1-30 minutes at temperatures of 150-250°C. Cellulose conversion can reach up to 80%. Finally, a complete summary of the effects of microwave heating on major chemical components of lignocellulosic biomass (lignin, cellulose and hemicellulose), was provided by Tsubaki *et al* (2009), who stated that the required heating temperature for degradation of either lignin or cellulose corresponded with the glass transition (T_g) of the components. Therefore, microwave heating for lignin or cellulose degradation should be above T_g of lignin (180-190°C) or T_g of cellulose (230-250°C). The yield of reducing sugars from hemicellulose increased at 150°C, reaching maximum value at 204°C (64%), but further heating above 225°C decrease the yield due to

secondary decomposition of sugars (Tsubaki *et al.*, 2009).

Conclusion

Microwave heating is advantageous due to direct, rapid, and uniform heating. The use of microwave irradiation to generate heat is very promising to be applied in the pretreatment of lignocellulosic biomass and hydrolysis of starch as well as cellulose for ethanol production, so that some recalcitrants in the process of biomass conversion to ethanol, such as the high cost of pretreatment and hydrolytic enzymes, especially cellulose, could be reduced. Temperature applied in the process should consider the physicochemical properties of the biomass components, especially lignin, hemicellulose, cellulose, and starch. For examples, the glass transition of cellulose is much higher than that of lignin or starch, so that hydrolysis of cellulose should be conducted at higher temperature than degradation of lignin during pretreatment or hydrolysis of starch.

Heating time and energy consumption in microwave heating operation are low. A low heating time also reduces the formation of unwanted secondary decomposition products. Dielectric properties of materials that will be treated using microwave irradiation are important to be considered in order to achieve a better thermal effects of the energy. However, only a few, if it is not any of the reports correlate these properties with the result of microwave heating of biomass. Addition of some compounds that have high dielectric constants might help increase the effectiveness of microwave heating. Nevertheless, since sugars produced from starchy or cellulosic biomass would be further converted to ethanol, the addition of those compounds should consider the effects of those compounds on microorganisms, such as *Saccharomyces cerevisiae*, that will convert the sugar to ethanol. The compounds should not have inhibition or detrimental influence to the work of that microorganism.

As it was in conventional heating, the addition of some acid or alkaline solution in microwave assisted hydrolysis or pretreatment gave positive effects. However, the use of microwave heating still offers more advantages over conventional heating due to

shorter time, less acid or alkaline concentration; thus less energy and less acid and alkaline solution used.

References

- Azuma J, Tanaka F, & Koshijima T. 1984. Microwave irradiation of lignocellulosic materials I. Enzymatic susceptibility of microwave-irradiated woody plants. *Mokuzai Gakkaishi* 30: 501-509.
- Azuma J, Katayama T, & Koshijima T. 1986. Microwave irradiation of lignocellulosic materials VIII. Microwave irradiation of the neutral fraction (C-I-M) of Pine Bjorkman LCC. *Wood Research* 72: 1-11
- Bank S, Bandyopadhyay S, & Ganguly S. 2003. Bioeffects of microwave – a brief review. *Bioresource Technology* 87: 155-159.
- Center for Materials Fabrication. 1993. Industrial Microwave heating applications. *Techcommentary* 4(3): 3-6.
- Cullingford HS, George CE, & Lightsey GR. 1993. Apparatus and method for cellulose processing using microwave pretreatment. US Patent No. 5, 196, 069.
- Gabriel C, Gabriel S, Grant EH, Halstead BSJ, & Mingos PM. 1998. Dielectric parameters relevant to microwave dielectric heating. *Chemical Society Reviews* 27: 213–223.
- Gedye RN. 1997. The question of non-thermal effects in the rate enhancement of organic reactions by microwaves. *Microwaves: Theory and Application in Materials Processing* 4: 165-172.
- Huang K, Yang Y, Hua G, & Yang L. 2009. Experimental evidence of a microwave non-thermal effect in electrolyte aqueous solutions. *New Journal of Chemistry* 33: 1486-1489.
- Hu Z & Wen Z. 2008. Enhancing enzymatic digestibility of switchgrass by microwave-assisted alkali pretreatment. *Biochemical Engineering Journal* 38: 369-378.
- Jacob J, Chia LHL, & Boey FYC. 1995. Review: Thermal and non-thermal interaction of microwave radiation with materials. *Journal of Materials Science* 30: 5321-5327.
- Keshwani DR. 2009. Microwave pretreatment of switchgrass for bioethanol production. *Dissertation*. Graduate Faculty of North Carolina State University, Raleigh, North Carolina.
- Khan AR, Johnson JA, & Robinson RJ. 1979. Degradation of starch polymers by microwave energy. *Cereal Chemistry* 56: 303–304.
- Kitchaiya P, Intanakul P, & Krairiksh M. 2003. Enhancement of enzymatic hydrolysis of lignocellulosic wastes by microwave pretreatment under atmospheric pressure. *Journal of Wood Chemistry and Technology* 23: 217-225.
- Kunlan L, Lixin X, Jun L, Jun P, Guaying C, & Zuwei X. 2001. Salt-assisted hydrolysis of starch to D-glucose under microwave irradiation. *Carbohydrate Research* 331: 9–12.
- Liao X, Raghavan GSV, Dai J, & Yaylayan VA. 2003. Dielectric properties of α -D-glucose aqueous solutions at 2450 MHz. *Food Research International* 36: 485-490.
- Luo Z, He X, Fu X, Luo F, & Gao Q. 2006. Effect of microwave radiation on the physicochemical properties of normal maize, waxy maize and amylo maize V starches. *Starch/Starke* 58: 468-474.
- Magara K & Azuma J. 1989. Microwave-irradiation of lignocellulosic materials X: Conversion of microwave-irradiated agricultural wastes into ethanol. *Wood Research* 76: 1–9.
- Matsumoto A, Tsubaki S, Sakamoto M, & Azuma J. 2008. Oligosaccharides adsorbed on activated charcoal powder escaped from hydrolysis by microwave heating in water. *Proceedings of Global Congress on Microwave Energy Applications*. August 4-8, 2008, Otsu, Japan p. 785-788.
- Meissner K & Erbersdobler HF. 1996. Maillard reaction in microwave cooking: Comparison of early Maillard products in conventionally and microwave-heated milk. *Journal of the Science of Food and Agriculture* 70 (3): 307-310.
- Motwani T, Seetharaman K, & Anantheswaran RC. 2007. Dielectric properties of starch slurries as influenced by starch concentration and gelatinization. *Carbohydrate Polymers* 67: 73-79.
- Ndife MK, Sumnu G, & Bayindirli L. 1998. Dielectric properties of six different starches at 2450 MHz. *Food Research International* 31: 43-52.
- Nikolic S, Mojovic L, Rakin M, Pejin D, & Savic D. 2008. A microwave-assisted liquefaction as a pretreatment for bioethanol production by the simultaneous saccharification and fermentation of corn meal. *Chemical Industry and Chemical Engineering Quarterly* 14: 231-234.
- Ooshima H, Aso K, Harano Y, & Yamamoto T. 1984. Microwave treatment of cellulosic materials for their enzymatic hydrolysis. *Biotechnology Letters* 6: 289-294.
- Pagnotta M, Pooley CLF, Gurland B, & Choi M. 1993. Microwave activation of the mutarotation of α -D-glucose: An example of an interinsic microwave effect. *Physical Organic Chemistry* 6: 407-411.
- Palav T & Seetharaman K. 2006. Mechanism of starch gelatinization and polymer leaching during microwave heating. *Carbohydrate Polymers* 65: 364-370.

- Palav T & Seetharaman K. 2007. Impact of microwave heating on the physico-chemical properties of a starch-water model system. *Carbohydrate Polymers* 67: 596–604.
- Pinkrova, J, Hubackova B, Kadlec P, Prihoda J, & Bubnik Z. 2003. Changes of starch during microwave treatment of rice. *Czech Journal of Food Science* 21: 176–184.
- Porcellia M, Cacciapuotia G, Fuscoa S, Massab R, d'Ambrosiob G, Bertoldoa C, Rossa MD, & Zappiaac V. 1997. Non-thermal effects of microwaves on proteins: thermophilic enzymes as model system. *FEBS Letters* 402: 102-106.
- Robinson JM. 2010. Method of digesting cellulose to glucose using salts and microwave (muwave) energy. US Patent No. US2010/0044210 A1.
- Shazman A, Mizzrahi S, Cogan U, & Shimoni E. 2007. Examining for possible non-thermal effects during heating in a microwave oven. *Food Chemistry* 103: 444-453.
- Tambunan AH, Suyanto NA, & Harmen. 2000. Desain dan uji teknis alat pengukur nilai dielektrik berdasarkan metoda Q-meter. Design and performance test of measuring apparatus of dielectric properties using Q-meter method (in Indonesian). *Buletin Keteknikaan Pertanian* 4: 108-117.
- Tsubaki S, Sakamoto M, & Azuma J. 2009. Application of microwave heating for utilization of agricultural biomass. *Research Advances in Agricultural and Food Chemistry* 1:1-12.
- Welt BA, Steet JA, Tong CA, & Rossen JL. 1993. Utilization of microwave in the study of reaction kinetics in liquid and semisolid media. *Biotechnology Progress* 9: 481-487.
- Yu HM, Chen ST, Suree P, Nuansri R, & Wang KT. 1996. Effect of microwave irradiation on acid-catalyzed hydrolysis of starch. *Journal of Organic Chemistry* 26: 9608-9609.
- Zhu SD, Wu YX, Yu ZN, Liao JT, & Zhang Y. 2005. Pretreatment by microwave/alkali of rice straw and its enzymic hydrolysis. *Process Biochemistry* 40: 3082-3086.
- Zhu S, Wu Y, Yu Z, Zhang X, Li H, & Gao M. 2006a. The effect of microwave irradiation on enzymatic hydrolysis of rice straw. *Bioresource Technology* 97: 1964-1968.
- Zhu S, Wu Y, Yu Z, Chen Q, Wu G, Yu F, Wang C, & Jin S. 2006b. Microwave-assisted alkali pretreatment of wheat straw and its enzymatic hydrolysis. *Biosystems Engineering* 94: 437-442.
- Zhu S, Wu Y, Yu Z, Zhang X, Wang C, Yu F, & Jin S. 2006c. Production of ethanol from microwave-assisted alkali pretreated wheat straw. *Process Biochemistry* 41: 869-873.