

THE INTERNATIONAL JOURNAL OF SCIENCE & TECHNOLEDGE

Microwave-Assisted Per Acetic Acid to Pretreat Beech Biomass for Subsequent Thermal Conversion

Md. Suruzzaman

Department of Environment, Tsinghua University, Beijing, China

Abstract:

Microwave-assisted per acetic acid (PAA, 15% v/v) pretreatment effectively destroyed the structure of beech wood, and increased its cellulose crystallinity. The FTIR peaks originated from lignin decreased or disappeared, indicating that the pretreatment was effective at removing lignin. According to the TG analysis, the peak of hemicellulose disappeared for the pretreated biomass, indicating the removal of hemicellulose by the microwave-assisted pretreatment. Besides, the char yield of pretreated beech wood was only 10.1 %, which was much lower than raw beech wood. Therefore, the pretreatment can decrease catalyst deactivation by coke deposition, which a major obstacle for thermal conversion.

Keywords: Pretreatment, biomass, microwave, per acetic acid, lignin

1. Introduction

Due to continuous consumption of petroleum resource, it is necessary to find an alternative sustainable and renewable energy sources[1]. The demand of petroleum has increased firmly 57×10^6 barrels per day in 1973 to 82×10^6 barrels per day in 2004. It has reported that by 2025 total demand for liquid fuels will have increased by approximately 50 %. Lignocellulosic biomass can be the alternative and sustainable energy source.

Biomass is natural materials from living or recently dead plants, trees and animals which can be used as fuel and in industrial production[2]. It includes crops, forestry, marine products as well as organic waste such as municipal solid waste, sewage and pulp derived black liquor. It's naturally available, carbon-neutral and approximately $1.1 - 10^{11}$ tons is produced per year globally [3]. Obtaining biofuels from biomass has a promising future, however in most cases, biomass is unused because of lacking of a proper way to make it more efficient for example rice straw is a huge resource for lignocellulosic biomass which burned all over the world[4]. Currently biomass plays a vital role and makes up about 12 % of the world's energy [5].

Due to availability of lignocellulosic biomass and a number of technological advantages it attracts considerable attention as a platform for renewable energy production [6]. A number of advantages have also been recognized for lignocellulosic biomass such as increasing cost of petroleum oil where lignocellulosic biomass very cheap and available, economic instability and the problem of anthropogenic climate change where lignocellulosic biomass does not have a heavy impact on the environment. Furthermore, wood represents a carbon-neutral renewable resource for bioenergy and biomaterials production or can even help to sequester carbon dioxide. Lignocellulosic biomass reduces the emission of greenhouse gases. These feedstocks do not contribute to the world's food supply and using them avoids the food vs. fuel debate.

Recently microwave irradiation is one of the promising technology which has been showed quick process because of fastest & efficient heating & increased reactions rate. Microwave irradiation induces heat at the molecular level by direct conversion of the electromagnetic heat into their energy [7]. The reaction rate can be accelerated by this heating mechanism which also offers good yield, uniform as well as selective heating and achieve greater reproducibility of reactions [7]. Not only process energy requirement can be decreased but also has the power to start and stop the process instantaneously [8]. Indeed, It has been adopted by industry and widely used in different areas like chemical synthesis [9], solvent extraction [10], and solid state reactions [11]. Biomass structure in both mechanically & thermally can be changed in contact with the microwave and lignocellulosic biomass. It takes just few minutes while oil bath requires long time to pretreat biomass. Using of acids and microwave combindly can be another promising source to pretreat lignocellulosic materials.

Per acetic acid is an organic compound with $\text{CH}_3\text{CO}_2\text{H}$ chemical formula. It is a strong oxidant which has been mentioned as a selective delignification agent. Compare to alkaline or other chemical pretreatment PAA significantly plays vital role to increase the enzymatic saccharification [12]. Here, PAA has been used with microwave to lignify for fast pyrolysis process. PAA can converts lignin to soluble fragments by two ways. Firstly, it less the lignin molecular weight by cleaving b-aryl ether bonds and both carbon-carbon and carbon-oxygen bonds linked to the aromatic rings. Secondly, PAA increases the lignin water solubility by other reactions such as dealkylation of O-methyl groups, introduction of OH- group to aromatic rings into muconic acids [13]. These reactions increase the polarity of lignin and make water soluble lignin that easily wash away from the lignocellulosic biomass. 15 % PAA has been used in experiment and recognize it has significant impact to remove lignin as well as a partial amount of hemicellulose.

2. Material and Methodology

2.1. Sample

Beech (*Fagus crenata Blume*) wood was collected in Beijing, China and ground with a Wiley mill to 0.125 mm. The wood powder was air dried to approximately 10 % moisture content and used throughout this study.

2.2. Microwave-assisted per acetic acid for pretreatment

Microwave-PAA pretreatment was conducted in 15 % (v/v) PAA solution at 800 W and 1200 W under atmospheric pressure. The microwave oven used was a focused single-mode microwave synthesis system (2.45 GHz, NJL2-1, China), which was equipped with a stirring system. The maximum power of the microwave source was 2000 W and the power was controlled by the power controller. The temperature was measured using thermocouple-type thermometer.

Cut beech (2 g) together with 20 mL of formic acid were prone to microwave pretreatment. The samples were treated in the microwave oven under 800 W and 1200 W for various times (5 and 10 min). After cooking, the mixtures were decanted through a tared glass filter crucible. In a run, the solid residue (cellulosic pulp) was washed thoroughly with deionized water till the pH up to 7.

2.3. Component analysis and structural characterization

Regarding the particle characteristics of the raw bagasse and pretreated materials, such as appearance, particle size, crystalline structure, surface porosity and thermal degradation, they were explored by means of a number of instruments. These instruments included a scanning electron microscope (SEM, JEOL, JSM-6301F), an X-ray diffractometer (XRD, (Rigaku, D/MAX 2500 V), a Fourier transform infrared spectrometry (FTIR, Thermo Nicolet Nexus) and a thermogravimetry (TG, Mettler-Toledo).

3. Results and Discussion

3.1. Biomass sample characterization

The weight loss and regenerated biomass of beech showed in (Table 1) where microwave had a significant role. The regenerated biomass rate dropped markedly (from 100 % to 43.61 % by 800 W 10 min) when the microwave power increased. Obviously, a longer period of time led to more wood dissolved.

Power (W)	Time (min)	Wood Dissolved= $\left(\frac{M_{ow} - M_{reg}}{M_{ow}} \times 100\right) \%$	Regenerated Biomass= $\left(\frac{M_{reg}}{M_{ow}} \times 100\right) \%$
800	5	51.62	48.38
800	10	56.39	43.61
1200	5	53.71	46.29
1200	10	55.53	44.47

Table 1: Analysis of pretreated and untreated biomass

3.2. SEM Analyses

Scanning electron microscope (SEM) images of the beech and the pretreated beech at the different microwave power and pretreatment time demonstrated in Fig 1. For the raw beech, a complete and compact lignocellulosic structure clearly observed Fig 1a. After undergoing the pretreatment with the microwave power of 800 W, the structure of beech had been damaged to a certain extent so that some cracks were seen on the beech surface Fig 1c. When the microwave power of 1200 W, the disruption of the lignocellulosic structure became more pronounced Fig 1d, with the pretreatment time of 10 min, some tiny holes exhibited on the surface Fig 1e. For the heating time of 10 min, the fragmentation of the lignocellulosic structure due to the impact of microwave irradiation was more obvious than that with the pretreatment time of 5 min.

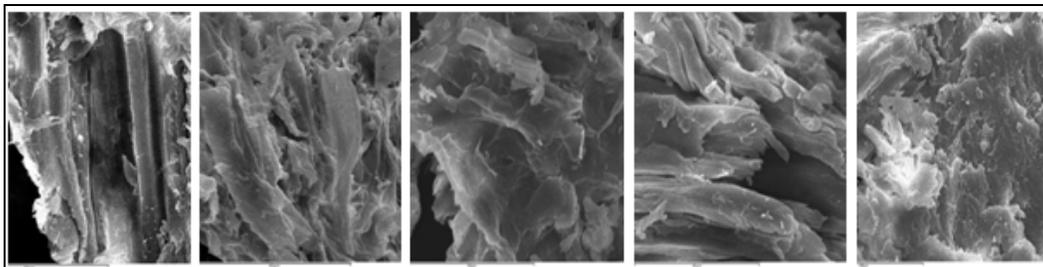


Figure 1: SEM images of (a) Beech wood, and pretreated samples with (b) 800 W 5 min, (c) 800 W 10 min, (d) 1200 W 5 min, and (e) 1200 W 10 min

3.3. XRD Analyses

To proceed further into the recognition of the cellulose structure, the XRD patterns of the raw beech and the pretreated materials sketched in Fig 2. It was reported that [14] a major diffraction peak of the cellulose crystallographic planes had been identified for 2θ ranging between 22° and 23° . For the beech, the crystalline structure was not notable, probably due to the coverage of cellulose by hemicellulose and lignin. For the pretreatment with the microwave power of 800 W and 1200 W, and the pretreatment time of 5 min and 10 min, the crystalline cellulose of the pretreated materials was clearly exhibited. The patterns also reflected that the crystalline structure of cellulose was hardly destroyed by the pretreatments, even though the microwave power is as high as 1200 W along with the pretreatment time of 10 min.

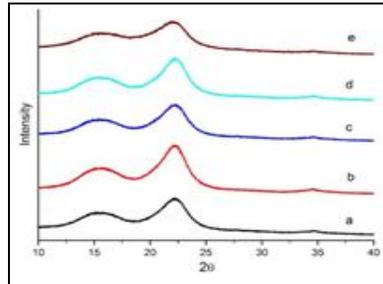


Figure 2: XRD patterns of (a) Beech wood, and pretreated samples with (b) 800 W 5 min, (c) 800 W 10 min, (d) 1200 W 5 min, and (e) 1200 W 10 min

The crystallinity index (CrI) of cellulose was strongly influenced by biomass composition, and increased proportionally with the crystalline cellulose content [15]. The diffraction patterns showed that the CrI of beech increased quickly from 35.94 % to 58.82 %, due to removal of most of the lignin and hemicellulose.

Sample	CrI/%
Beech	35.94
800 W 5 min	52.46
1200 W 5 min	58.82
800 W 10 min	53.30
1200 W 10 min	58.45

Table 2: CrI of raw beech and pretreated samples at various microwave power with the pretreatment times of 5 and 10 min

3.4. FTIR Analyses

In Fig 3 showed the FTIR spectra of the raw beech and the pretreated samples undergoing various operating conditions. Aromatic skeletal vibrations in the lignin fraction were assigned at 1597 cm^{-1} , 1508 cm^{-1} and 1408 cm^{-1} wave lengths [16]; the band at 885 cm^{-1} was from C–H out of plane bending of syringyl content in lignin. In the spectra of the treated residues, the decrease or disappearance in these peaks was directly related to delignification. The disappearance of the 1597 cm^{-1} band attributed to the characteristic of the aromatic ring vibrations of the phenylpropane groups of lignin [17], indicated that hemicellulose had been largely removed during per acetic acid pulping. Cellulose a homopolysaccharide composed of β -D-glucopyranose units linked together by (1 \rightarrow 4) - glycosidic bonds [16, 18]. And a sharp band 896 cm^{-1} in the spectrum of cellulose attributed to β -glycosidic linkages between the sugar units [19]. When the raw beech was examined, the band of 885 cm^{-1} is not notable, probably due to the coverage of cellulose by hemicellulose and lignin. However, when the beech was pretreated with the microwave power of 800 W and 1200 W by 5 min and 10 min, the band of 896 cm^{-1} is even not clearly exhibited, revealing the disruption and removal of hemicellulose and lignin by the pretreatment.

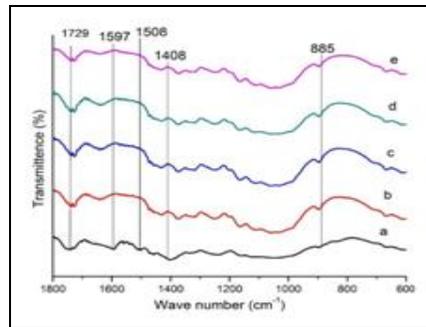


Figure 3: FTIR spectra of raw beech and pretreated samples at various microwave power

With the pretreatment times of 5 and 10 min, (a) beech, (b) 800 W 5 min, (c) 800 W 10 min, (d) 1200 W 5 min, (e) 1200 W 10 min

From the spectrum of beech, the major influence of the microwave-PAA pretreatment was to disrupt and removed hemicellulose and lignin from beech where 1200 W 10 min had more significant impact.

3.5. TG Analyses

The Arrhenius equation and the Coats and Redfern's integral method used to evaluate kinetic parameters from the data of TG and DTG curves range 200-400 °C with maximal weight loss was considered to be the range of basic destruction.

From the TGA distributions, it can be seen that the difference among the pretreated materials is slight, whereas there was a pronounced difference between the beech and the pretreated samples. It indicated that the pretreatment has a significant influence on the samples.

Three stages of decomposition can be clearly identified in the TG curves for the samples (beech, 1200 W 10 min, 1200 W 5 min, 800 W 10 min and 800 W 5 min). In the first stage, temperature below 220 °C, the weight loss of the samples is corresponds to the evaporation of light volatiles (mainly water). The second stage of decomposition, occurring between 220 and 380 °C, corresponds to a remarkable dropped in weight of samples due to liberation of volatile hydrocarbon from rapid thermal decomposition of hemicellulose, cellulose and some part of lignin. The third stage, after 380 °C, the weight loss is less important than the second period due to the steady decomposition of the more heavy components mainly from lignin.

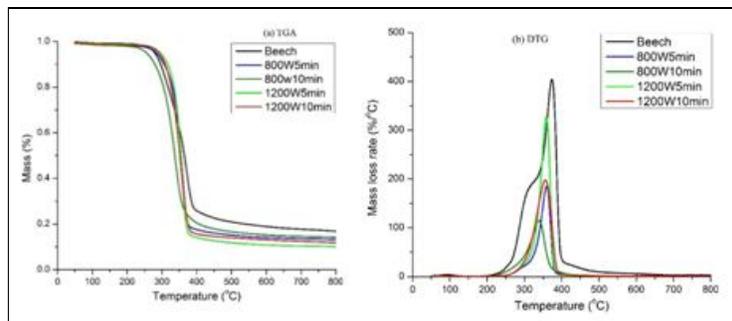


Figure 4: TGA and DTG distributions of raw beech and pretreated samples

At various microwave power with the pretreatment times of 5 and 10 min

Derivative thermogravimetric (DTG) analyses demonstrated in Fig 4-4b. In the DTG distribution of the beech, the peaks of hemicellulose and cellulose had been identified at 320 °C and 357 °C, respectively. The distribution of the beech and pretreated 5 min samples were characterized by a double-peak distribution. The first and the second peaks, developing at 320 °C and 357 °C represented the thermal degradations of hemicellulose and cellulose in the samples. After undergoing the pretreatments of 5 min, only the peak of cellulose exhibited which revealed that hemicellulose consumed dramatically. It could be seen that the peak of cellulose enhanced with the increasing of microwave power and pretreatment time. It showed that the pretreatments also had a pronounced impact on cellulose.

4. Conclusion

The aim of this research was to remove the lignin from beech biomass for subsequent thermal conversion and also to evaluate the effectiveness of microwave-per acetic acid pretreatment which used for the first time for beech biomass.

Microwave-PAA pretreatment changed the structure of raw biomass, removed lignin and a partial amount of hemicellulose, and make surface porosity according to FTIR and SEM. After the pretreatment some parts of hemicellulose removed which caused the DTG peak overlapped with DTG peak originated from cellulose. As the raw materials peaks were much higher than the others that showed high rated weight loss. Thermal degradation, char formation, hemicellulose and lignin removal noticed according to TG and DTG curves range 200-400 °C. The pretreatment time of 10 min and 1200 W had more impact compared to other pretreatment times and powers. Furthermore, thermal conversion process such as pyrolysis will require to observe the yield of aromatic components.

5. References

1. Farrell, A.E., Ethanol can contribute to energy and environmental goals (vol 311, pg 506, 2006). *Science*, 2006. 312(5781): p. 1748-1748.
2. Kadam, K.L., L.H. Forrest, and W.A. Jacobson, Rice straw as a lignocellulosic resource: collection, processing, transportation, and environmental aspects. *Biomass & Bioenergy*, 2000. 18(5): p. 369-389.
3. Tadesse, H. and R. Luque, Advances on biomass pretreatment using ionic liquids: An overview, in *Energy & Environmental Science*. 2011. p. 3913-3929.
4. Demirbas, A., Mechanisms of liquefaction and pyrolysis reactions of biomass. *Energy Conversion and Management*, 2000. 41(6): p. 633-646.
5. H. L. Chum, M.M.B., *Reviews*. ACS Monograph 183, American Chemical Society, Washington DC, 1985.
6. R.D., P., Biomass as feedstock for a bioenergy and bioproducts industry: the technical feasibility of a billion-ton annual supply. National Technical Information Information Service, Springfield, Virginia, USA., 2005.
7. Oliver, K.C., *Microwaves in organic and medicinal chemistry*. Wiley-VCH, 2005. Weinheim 45: p. 1677-1678.
8. Gabriel, C., et al., Dielectric parameters relevant to microwave dielectric heating. *Chemical Society Reviews*, 1998. 27(3): p. 213-223.
9. Bajia, S., R. Sharma, and B. Bajia, Solid-State Microwave Synthesis of Melamine-Formaldehyde Resin. *E-Journal of Chemistry*, 2009. 6(1): p. 120-124.
10. Mattina, M.J.I., W.A.I. Berger, and C.L. Denson, Microwave-assisted extraction of taxanes from *Taxus* biomass. *Journal of Agricultural and Food Chemistry*, 1997. 45(12): p. 4691-4696.
11. Caddick, S., Microwave assisted organic reactions. *Tetrahedron*, 1995. 51(38): p. 10403-10432.
12. Zhao, X., K. Cheng, and D. Liu, Organosolv pretreatment of lignocellulosic biomass for enzymatic hydrolysis. *Applied Microbiology and Biotechnology*, 2009. 82(5): p. 815-827.
13. Lawrence, W., McKelvey, R.D., Johnson, D.C., The peroxyacetic acid oxidation of a lignin-related b-aryl ether 1980. 83: p. 11-18.
14. Chen, W.-H., Y.-J. Tu, and H.-K. Sheen, Impact of dilute acid pretreatment on the structure of bagasse for bioethanol production. *International Journal of Energy Research*, 2010. 34(3): p. 265-274.
15. Kim, T.H., et al., Pretreatment of corn stover by aqueous ammonia. *Bioresource Technology*, 2003. 90(1): p. 39-47.
16. Sun, J.X., et al., Physico-chemical and thermal characterization of cellulose from barley straw. *Polymer Degradation and Stability*, 2005. 88(3): p. 521-531.
17. Chundawat, S.P.S., B. Venkatesh, and B.E. Dale, Effect of particle size based separation of milled corn stover on AFEX pretreatment and enzymatic digestibility. *Biotechnology and Bioengineering*, 2007. 96(2): p. 219-231.
18. Yu, J., et al., Combinations of mild physical or chemical pretreatment with biological pretreatment for enzymatic hydrolysis of rice hull. *Bioresource Technology*, 2009. 100(2): p. 903-908.
19. d'Almeida, A.L.F.S., et al., Thermal analysis of less common lignocellulose fibers. *Journal of Thermal Analysis and Calorimetry*, 2008. 91(2): p. 405-408