

<http://www.ejournalofscience.org>

# An Alkaline Pretreatment of Biomass for Subsequent Pyrolysis

Md. Suruzzaman

School of Environment, Tsinghua University, China

[shohel.rana43@gmail.com](mailto:shohel.rana43@gmail.com)

## ABSTRACT

Two stage acids (PAA+NaOH) combination and water bath-assisted pretreatment broke the structure of beech wood, and increased its crystallinity largely. The FTIR peaks originated from both hemicellulose and lignin were diminished indicating the two components were effectively removed by the pretreatment. TG analysis further confirmed that not only thermal degradation occurred but also hemicellulose and lignin were removed from the biomass. The char yield was decreased to 12.1 % for the pretreated beech wood sample. The results indicated that microwave-assisted acid pretreatment effectively improved the conversion efficiency of biomass in thermal conversion.

**Keywords:** Biomass, acid, NaOH, lignin, pyrolysis

## 1. INTRODUCTION

Energy is the basis of a national economy. Development and rational use of energy is a major issue in today's world. The demand for global energy is increasing while the reserves decreasing day by day. It has certainly paid attention to get renewable and sustainable energy [1] while second generation bio-fuels from lignocellulosic material stands for the alternative way to get energy because of its high calorific value, clean, non-polluting and renewable characteristics. With the continuous development of biomass technology, the use of lignocellulosic biomass is also under scrutiny

Biomass can easily obtain from living or recently dead plants, trees and animals which can be used as fuel and in industrial production [2]. Agricultural residue, forestry, marine products as well as organic wastes under biomass. It's naturally available, carbon-neutral and approximately 1.1 - 10<sup>11</sup> tons is produced per year globally [3]. Obtaining biofuels from biomass has a optimizing and promising future although till now it's not being used properly lacking of enough research.

Because of availability of lignocellulosic biomass and a number of technological benefits it attracts considerable attention as a platform for renewable energy production [4]. 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. It reduces the emission of greenhouse gases. These feedstocks never compete with fuel vs food debate.

Per acetic acid (PAA) is an organic compound with CH<sub>3</sub>CO<sub>2</sub>H chemical formula. It is also familiar as a selective delignification agent. It has significant role for enzymatic saccharification rather than other acids pretreatments [5]. Here, PAA has been used with NaOH for subsequent pyrolysis. PAA can convert lignin to soluble fragments by two ways. Firstly, it less the lignin molecular weight by cleaving β-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 [6]. 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.

Sodium hydroxide is an organic compound with chemical formula NaOH. It has been widely used in different sectors including the manufacturing of pulp and paper, drinking water, detergents and drain cleaner. According to chemical process which induce alkaline pretreatment where different kind of acids use to pretreat lignocellulosic biomass. Sodium hydroxide one of the important acids which pretreats lignocellulosic biomass and removes lignin for the enzymatic saccharification. Here, 1 % NaOH has been used with different times.

## 2. 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 Two Stage Acids (PAA and Sodium Hydroxide) Combination Pretreatment

15 % (v/v) PAA and 1 % (w/w) NaOH have been conducted in two stage. In first stage, cut beech (4 g) together with 40 mL of 15 % (v/v) PAA were prone to water bath. Raw materials have been pretreated with different times (1 h and 2 h) but constant temperature (80 °C). After pretreatment with PAA the sample washed thoroughly with deionized water until it reached pH 7 and dried (60 °C) in oven overnight. The same procedure had been followed by 1 % (w/w) NaOH for next stage and kept pretreated sample for further experiments. Indeed, only per acetic acid used to see the consequences of pretreatment.

### 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 diffract meter (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

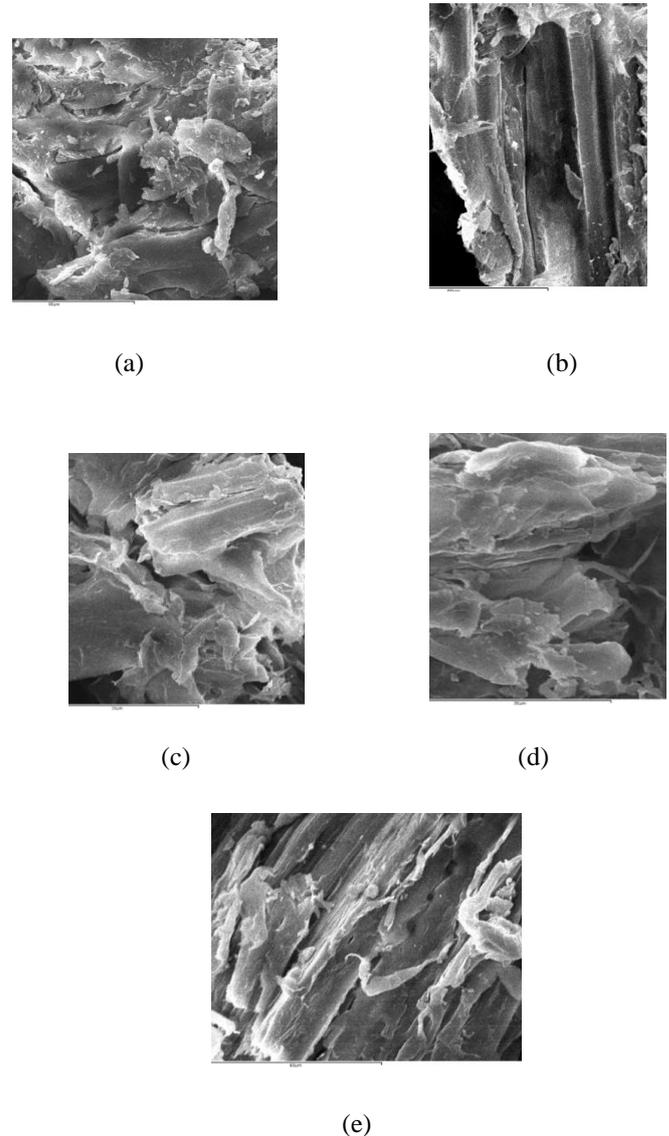
The weight loss and regenerated biomass rate of beech showed in (Table 1) where two stage acids have significant influence in pretreatment step. The regenerated biomass rate dropped to (from 100 % to 48.12 % by 2 h PAA) according to pretreatment times. Obviously, a longer period of time (2 h PAA) led to more wood dissolve.

**Table 1:** Analysis of pretreated and untreated biomass

Temperature (°C)	Time (h)		Wood Dissolved= $\left( \frac{M_{ow} - M_{reg}}{M_{ow}} \times 100 \right) \%$	Regenerated Biomass= $\left( \frac{M_{reg}}{M_{ow}} \times 100 \right) \%$
	PAA	NaOH		
80	2	0	51.88	48.12
80	1	1	49.79	50.21
80	2	1	51.16	48.84
80	1	2	46.59	53.41

### 3.2 SEM Analyses

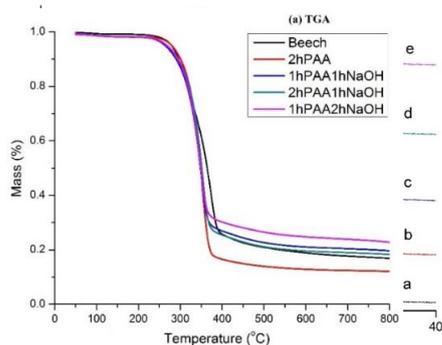
Scanning electron microscope (SEM) images of the beech and the pretreated beech at the different times demonstrated in (Fig 1). After undergoing the pretreatment with PAA the structure of beech had been damaged to a certain extent so that some cracks could be seen on the beech surface (Fig 1b-1e). When the pretreatment time is 2 h PAA the disruption of the lignocellulosic structure became more pronounced (Fig 1b) compared to other pretreatment times and some tiny holes were hardly exhibited on the surface (Fig 1b). Indeed, the impact for making surface more porous was less than microwave-acids pretreatment.



**Fig 1:** SEM images of (a) Beech wood, and pretreated samples with (b) 2 h PAA, (c) 1 h PAA+1 h NaOH, (d) 2 h PAA+1 h NaOH, and (e) 1 h PAA+2 h NaOH

### 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). In the past studies[7] it was reported that a major diffraction peak of the cellulose crystallographic planes had been identified for  $2\theta$  ranging between  $22^\circ$  and  $23^\circ$ . For the beech, the crystalline structure is not notable, probably due to the coverage of cellulose by hemicellulose and lignin. For the pretreatment with two stage acids combination, the crystalline cellulose of the pretreated materials was hardly appeared.

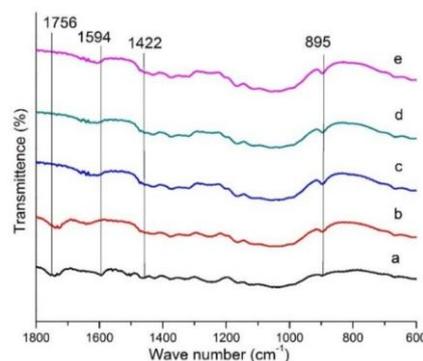


**Fig 2:** XRD patterns of (a) Beech wood, and pretreated samples with (b) 2 h PAA, (c) 1 h PAA+1 h NaOH, (d) 2 h PAA+1 h NaOH, and (e) 1 h PAA+2 h NaOH

The crystallinity index (CrI) of cellulose was strongly influenced by biomass composition, and increased proportionally with the crystalline cellulose content [8]. The diffraction patterns showed that the CrI of beech increased quickly from 35.94 % to 57.85 %, due to removal of most of the lignin and hemicellulose.

### 3.4 FTIR Analyses

In Figure 3, showed the FTIR spectra of the raw beech and the pretreated samples undergoing various operating conditions. The wave number  $1756\text{ cm}^{-1}$  deals with uronic ester groups which was hemicellulose or hemicellulose-lignin complexes. Aromatic skeletal vibrations in the lignin fraction were assigned at  $1594\text{ cm}^{-1}$ , and  $1422\text{ cm}^{-1}$  bands [9]. In the spectra of the treated samples the decrement or disappearance in these peaks was directly related to delignification. The disappearance of the  $1594\text{ cm}^{-1}$  band attributed to the characteristic of the aromatic ring vibrations of the phenyl propane groups of lignin [10], indicated that hemicellulose had been slightly removed during PAA and NaOH pulping. Cellulose a homopolysaccharide composed of  $\beta$ -D-glucopyranose units linked together by (1 $\rightarrow$ 4) -glycosidic bonds [9, 11, 12]. And a sharp band  $895\text{ cm}^{-1}$  in the spectrum of cellulose attributed to  $\beta$ -glycosidic linkages between the sugar units [13, 14]. When the raw beech examined the band of  $895\text{ cm}^{-1}$  was not notable, probably due to the coverage of cellulose by hemicellulose and lignin. However, when the beech was pretreated with PAA and NaOH the band of  $895\text{ cm}^{-1}$  was even not clearly exhibited, revealing the disruption and removal of hemicellulose and lignin by the pretreatment. From the spectrum of beech, the major influence of the two stage acids combination was to disrupt and remove partially hemicellulose and lignin from beech.



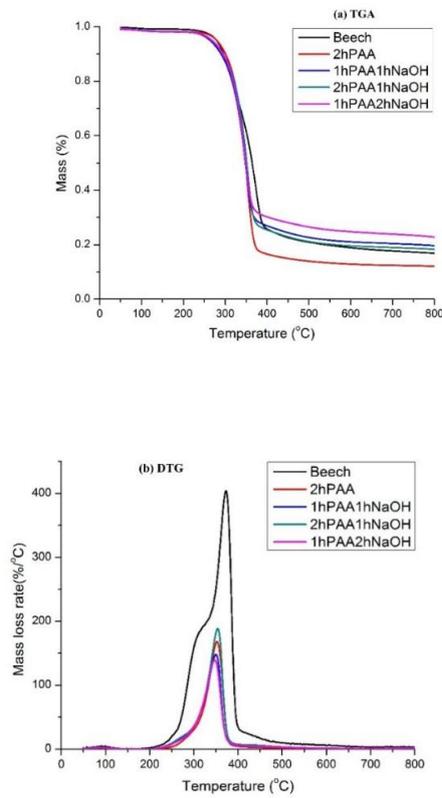
**Fig 3:** FTIR spectra of raw beech and pretreated samples at various microwave power with the pretreatment times, (a) beech, (b) 2 h PAA, (c) 1 h PAA+1 h NaOH, (d) 2 h PAA+1 h NaOH, (e) 1 h PAA+2 h NaOH

### 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 had been noticed that the difference among the pretreated materials was slight, whereas there was a pronounced difference between the beech and the pretreated samples. It obviously indicated that the pretreatment had a significant influence on the samples.

Three stages of decomposition clearly identified in the TG curves for the samples (beech, 2 h PAA, 1 h PAA+1 h NaOH, 2 h PAA+1 h NaOH and 1 h PAA+2 h NaOH). In the first stage, temperature below 220 °C, the weight loss of the samples was corresponds to the evaporation of light volatiles (mainly water). The second stage of decomposition, occurring between 220 °C 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 was less important than the second period due to the steady decomposition of the more heavy components mainly from lignin.



**Fig 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 thermo gravimetric (DTG) analyses demonstrated in (Fig 4). In the DTG distribution of the beech, the peaks of hemicellulose and cellulose identified at 320 °C and 357 °C. The distribution of the beech and pretreated 2 h PAA 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 2 h PAA, only the peak of cellulose exhibited which revealed that hemicellulose was consumed dramatically. It also had been seen that the peak of cellulose enhanced with the increasing of 2 h PAA. This reflected that the pretreatments had a pronounced impact on cellulose.

#### 4. CONCLUSIONS

The aim of this research was to evaluate the effectiveness of two stage acids (PAA+NaOH, used for the first time) combination pretreatment of beech biomass for subsequent pyrolysis.

Two stage acids combination NaOH and PAA found that it had the capability to dissolve lignin and a partial amount of hemicellulose. Especially, 2 h pretreatment dissolved more lignin and a partial amount of hemicellulose compare to other combination

pretreatment (NaOH and PAA with different times: 1 h and 2 h but same temperature 80 °C. After SEM analyses, less surface porosity was observed in 2 h PAA pretreatment compared to microwave-acids pretreatment. Reduction of char formation observed according to TG analyses by 2 h PAA where other pretreatments had less impact. Furthermore, partial amount of hemicellulose disappeared and DTG peak overlapped with the DTG peak originated from cellulose. A significant weight loss occurred by pretreatment in accordance with peak difference among raw materials and other pretreated samples.

Further research for example pyrolysis either fast pyrolysis or catalytic fast pyrolysis will require to investigate the yield of final products bio-oil or aromatic components such as LG, acetic acid, phenols etc.

#### REFERENCES

- [1] A.E. Farrell, Ethanol can contribute to energy and environmental goals (vol 311, pg 506, 2006), *Science*, 312 (2006) 1748-1748.
- [2] K.L. Kadam, L.H. Forrest, W.A. Jacobson, Rice straw as a lignocellulosic resource: collection, processing, transportation, and environmental aspects, *Biomass & Bioenergy*, 18 (2000) 369-389.
- [3] H. Tadesse, R. Luque, Advances on biomass pretreatment using ionic liquids: An overview, in: *Energy & Environmental Science*, 2011, pp. 3913-3929.
- [4] P. R.D., 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).
- [5] X. Zhao, K. Cheng, D. Liu, Organosolv pretreatment of lignocellulosic biomass for enzymatic hydrolysis, *Applied Microbiology and Biotechnology*, 82 (2009) 815-827.
- [6] W. Lawrence, McKelvey, R.D., Johnson, D.C., The peroxyacetic acid oxidation of a lignin-related b-aryl ether 83 (1980) 11-18.
- [7] W.-H. Chen, Y.-J. Tu, H.-K. Sheen, Impact of dilute acid pretreatment on the structure of bagasse for bioethanol production, *International Journal of Energy Research*, 34 (2010) 265-274.
- [8] T.H. Kim, J.S. Kim, C. Sunwoo, Y.Y. Lee, Pretreatment of corn stover by aqueous ammonia, *Bioresource Technology*, 90 (2003) 39-47.
- [9] X.F. Sun, F. Xu, R.C. Sun, P. Fowler, M.S. Baird, Characteristics of degraded cellulose obtained from steam-exploded wheat straw, *Carbohydrate Research*, 340 (2005) 97-106.

---

<http://www.ejournalofscience.org>

- [10] S.P.S. Chundawat, B. Venkatesh, B.E. Dale, Effect of particle size based separation of milled corn stover on AFEX pretreatment and enzymatic digestibility, *Biotechnology and Bioengineering*, 96 (2007) 219-231.
- [11] J. Yu, J. Zhang, J. He, Z. Liu, Z. Yu, Combinations of mild physical or chemical pretreatment with biological pretreatment for enzymatic hydrolysis of rice hull, *Bioresource Technology*, 100 (2009) 903-908.
- [12] J.X. Sun, F. Xu, X.F. Sun, B. Xiao, R.C. Sun, Physico-chemical and thermal characterization of cellulose from barley straw, *Polymer Degradation and Stability*, 88 (2005) 521-531.
- [13] A.L.F.S. d'Almeida, D.W. Barreto, V. Calado, J.R.M. d'Almeida, Thermal analysis of less common lignocellulose fibers, *Journal of Thermal Analysis and Calorimetry*, 91 (2008) 405-408.
- [14] J.X. Sun, X.F. Sun, R.C. Sun, P. Fowler, M.S. Baird, Inhomogeneities in the chemical structure of sugarcane bagasse lignin, *Journal of Agricultural and Food Chemistry*, 51 (2003) 6719-6725.