Thermo-chemical pretreatment of wood biomass from giant sensitive plant (*Mimosa pigra* L.)

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Abstract

Wood biomass is one of the abundant renewable resources, which consists mainly of cellulose, hemicellulose and lignin. Cellulose, a major component, is used as substrate for several industrial applications including energy and chemicals.In order to obtain cellulose from wood biomass, pretreatment process is an important step to remove lignin and hemicellulose. The aim of this study is to investigate the feasibility of thermo-chemical pretreatment (microwave-assisted chemical and autoclave-assisted chemical pretreatment) of wood biomassfrom a woody tropical weed, giant sensitive plant (*Mimosa pigra* L.). The wood biomass of giant sensitive plant was pretreated via 2 stages. The first stage, wood biomass was pretreated by using microwave (at 300 W for 10 min) or autoclave (at 121 ºC for 1 h), combined with 5%, 10%, 15% NaOH(w/v) or 0.5%, 1%, 1.5% H_2SO_4(w/v). The second stage, the pretreated wood biomass was bleached with 2%H_2O_2 at 70 ºC for 2 h. The results revealed that the best condition for microwave pretreatment was at 10% NaOH by increasing cellulose content of biomass around 33%, while bleaching ofpretreated wood biomass could increase cellulose content of biomass around 37%. When using autoclave pretreatment, the best condition was at 1% H_2SO_4 by increasing cellulose content of biomass around 40%, while bleaching of pretreated wood biomass could increase cellulose content of biomass around 43%.

Keywords: giant sensitive plant, *Mimosa pigra,* wood biomass, cellulose, pretreatment

Introduction

Lignocellulosic biomass including wood, agricultural crop are the most abundant and lowest cost feedstock in the world, which consist mainly of cellulose, hemicellulose and lignin (Cao et al., 2012). Cellulose is a polysaccharide that consists of D-glucose bound in chains by β-(1,4)-glycosidic bonds. It is used as substrate for production of energy and chemicals (Menon and Rao, 2012). Giant sensitive plant or *Mimosa pigra* L. is a woody tropical weed that was introduced from Indonesia for using as a green manure and cover crop in tobacco plantations. However, due to its rapid growth and spreading to many areas, it can lead to ecological and economic problem (Pramual et al., 2011). So far, this plant has never been utilized as a source of industrial commodities. Therefore, it can probably be the potential substrate for energy and chemicals production. In order to use cellulose from wood biomass as substrate for production of energy and valuable chemicals, it is necessary remove other components in wood biomass by using pretreatment process. Pretreatment is an important stepresulting in the separation of cellulose from lignocellulosic biomass, because this process is capable of removing lignin and hemicellulose. In addition, it can reduce the crystallinity of cellulose, and increase the porosity of the lignocellulosic biomass to improve the cellulose accessibility in cellulose hydrolysis process (Kumar et al., 2009). Various techniques were employed in the pretreatment process including physical, chemical, physicochemical and biological pretreatment (Kumar et al., 2009; Menon and Rao, 2012). Moreover, the combination of two pretreatment methods may be more effective than only single method(Nikzad et al., 2012). Thermo-chemical pretreatment is a kind of physicochemical pretreatment, which has been well known for pretreatment of lignocellulosic biomass because it could effectively remove lignin and hemicellulose, and improve the digestibility of lignocellulosic biomass. This process usually requires energy combined with a chemical such as microwave, stream explosion, liquid hot water, ammonia fiber explosion etc. (Galbe and Zacchi, 2007).

This study aims to investigate the feasibility of thermo-chemical pretreatment (microwave-assisted chemical and autoclave-assisted chemical pretreatment) of wood biomass from a woody tropical weed, giant sensitive plant (*Mimosa pigra* L.).

Methodology

Raw material

Wood biomass from giant sensitive plant (stem and branch) was collected from Hunka district, Chainat province. It was dried at 60 ºC for 5-7 days and milled to a size less than 1 mm (20 meshes) for the pretreatment experiments (Salehian et al., 2012).

Pretreatment method

Three grams of dry wood biomass from giant sensitive plant was mixed with 60 grams of chemical solution including 5%, 10%, 15% NaOH (w/v) or 0.5%, 1.0%, 1.5% H_2SO_4 (w/v). The mixtures were treated by microwave at 300 W for 10 minor autoclave at 121 ºC, 15 psi for 1 h.The residues were washed with distilled water until neutral pH and dried at 60 ºC. The pretreated wood biomass was them bleached with 2%H_2O_2 at 70 ºC in water bath for 2 h. The residues were washed with distilled water until neutral pH and dried at 60 ºC. Each pretreatment as performed in triplicate (Azzam, 1989; Binod et al., 2012; Cao et al., 2012).

Analytical method

Composition of cellulose, hemicellulose, lignin and ash in the samples was determined by forage fiber analysis (Goering and Van Soest, 1970). A scanning electron microscope (SEM) was used to detect the microscopic structure of pretreated wood biomass (Binod et al., 2012).

Statistical analysis

Data were analyzed for statistical significance by a one-way analysis of variance (ANOVA). Duncan's multiple range tests at the level of 5% were used to analyze the significances of different pretreatment methods(Cao et al., 2012).

Results

The wood biomass from giant sensitive plant used in this study mainly contained cellulose at 47.56%, hemicellulose at 20.90%, and lignin at 21.16% (w/w).The chemical compositions of pretreated wood biomass were analyzed and the results were present in Table1 and 2.

The microwave-assisted distilled water pretreatment could increase cellulose content from 47.56% to 48.14% or 1.22% of increased cellulose. When combine with chemicals including 5%, 10%, 15% NaOH (w/v) or 0.5%, 1.0%, 1.5% H_2SO_4 (w/v), the result revealed that the best condition was at 10% NaOH which could increase cellulose content up to 63.27% or 33.03% of increased cellulose. In addition, bleaching of pretreated wood biomass with 2% H_2O_2 could increase cellulose content up to 65.37% or 37.45% of increased cellulose. (Table 1)

The autoclave-assisted distilled water pretreatment could increase cellulose content from 47.56% to 48.08% or 1.09% of increasedcellulose. When combine with chemicals, the best condition was found at 1% H_2SO_4 which could increase cellulose content up to 66.69% or 40.22% of increased cellulose.In addition, bleaching of pretreated wood biomass could increase cellulose content up to 68.24% or 43.48%of increased cellulose. (Table 2)

SEM images of the untreated, microwave-assisted NaOH and autoclave-assisted H_2SO_4 pretreated wood biomass were illustrated in Fig 1. The untreated wood biomass hadsmooth and continuous surface, while microwave-assisted NaOH and autoclave-assisted H_2SO_4 pretreated wood biomass showed several pores on the wood surface.

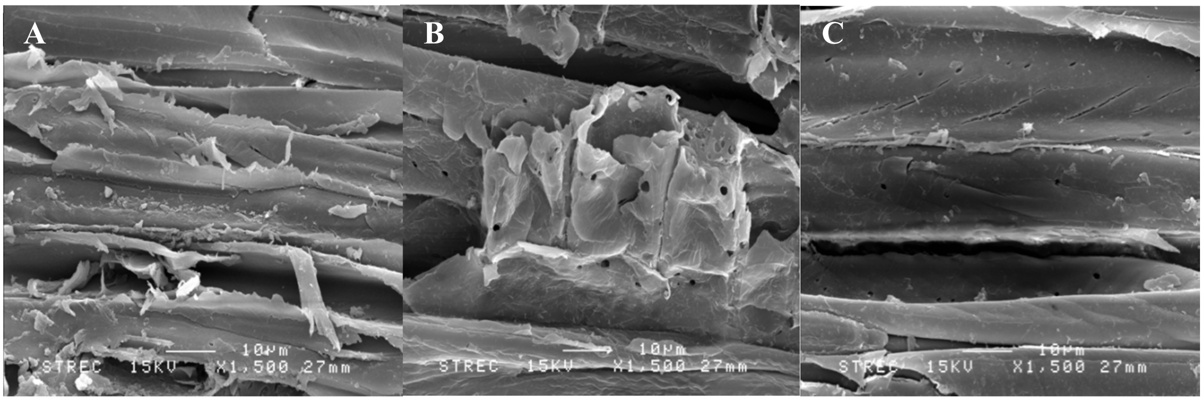

Fig 1: Scanning electron microscopic images of wood biomass from giant sensitive plant**.**A: Untreated; B: Microwave-assisted 10%NaOH and 2% H_2O_2 bleaching pretreatment;C: Autoclave-assisted 1% H_2SO_4 and 2% H_2O_2 bleaching pretreatment**.**

Table 1: Effect of the microwave-assisted chemical pretreatment on chemical compositions of wood biomass from giant sensitive plant.

Condition	Cellulose content (%)*	Hemicellulose content (%)*	Lignin content (%)*	Biomass yield(%)
Untreated	47.56 ± 0.31^{a}	20.90 ± 1.00^{g}	21.16 ± 0.41^{cdef}	100
Microwave at 300 W, 10 min				
H_2O	48.14 ± 0.85^{a}	21.03 ± 0.80^{g}	21.05 ± 0.43^{cdef}	96.67 ± 0.33
5% NaOH	61.81 ± 1.16^{de}	12.94 ± 0.42^{d}	19.09 ± 0.69^{abc}	70.66 ± 1.15
10% NaOH	63.27 ± 1.51^{e}	10.57 ± 0.66^{abc}	18.84 ± 0.32^{ab}	66.78 ± 0.19
15% NaOH	60.99 ± 1.38^{d}	12.13 ± 0.50^{cd}	19.23 ± 0.35^{abc}	63.78 ± 0.19
0.5% H_2SO_4	54.02 ± 0.14^{b}	20.25 ± 0.92^{g}	21.02 ± 1.39^{bcdef}	83.89 ± 0.51
1% H_2SO_4	54.82 ± 0.96^{bc}	19.10 ± 2.19^{efg}	21.54 ± 2.38^{def}	82.00 ± 1.73
1.5% H_2SO_4	55.18 ± 1.02^{bc}	17.53 ± 1.50^{e}	22.86 ± 1.52^{f}	81.33 ± 0.88
Microwave at 300 W, 10 min and followed bleaching with 2%H_2O_2 at 70 °C, 2 h				
5% NaOH + 2% H_2O_2	61.90 ± 1.72^{de}	10.81 ± 0.97^{bc}	20.03 ± 1.03^{abcde}	66.44 ± 1.02
10% NaOH + 2% H_2O_2	65.37 ± 0.22^{f}	8.87 ± 1.59^{a}	18.77 ± 1.61^{a}	62.89 ± 0.38
15% NaOH + 2% H_2O_2	62.18 ± 0.40^{de}	9.72 ± 0.16^{ab}	19.60 ± 0.41^{abcd}	59.78 ± 0.19
0.5% H_2SO_4 + 2% H_2O_2	54.87 ± 0.48^{bc}	19.56 ± 1.21^{fg}	20.84 ± 1.33^{abcdef}	80.56 ± 1.64
1% H_2SO_4 + 2% H_2O_2	55.88 ± 0.33^{c}	17.99 ± 0.54^{ef}	21.74 ± 1.04^{def}	80.67 ± 0.67
1.5% H_2SO_4 + 2% H_2O_2	56.26 ± 0.87^{c}	17.64 ± 0.33^{ef}	21.95 ± 0.86^{ef}	79.22 ± 0.69

* Mean ± one standard deviation derived from three replicates (N = 3). Different superscript letter (a,b,c) in the same column indicated the values were significantly different (ANOVA and DMRT, $P < 0.05$).

Table 2: Effect of the autoclave-assisted chemical pretreatment on chemical compositions of wood biomass from giant sensitive plant.

Condition	Cellulose content (%)*	Hemicellulose content (%)*	Lignin content (%)*	Biomass yield(%)
Untreated	47.56 ± 0.31^{a}	20.90 ± 1.00^{e}	21.16 ± 0.41^{c}	100
Autoclave at 121 °C , 1 h				
H_2O	48.08 ± 0.27^{a}	21.14 ± 0.91^{e}	19.24 ± 1.22^{ab}	88.00 ± 0.00
5% NaOH	62.30 ± 0.80^{c}	8.05 ± 0.81^{cd}	19.07 ± 1.03^{ab}	52.67 ± 0.67
10% NaOH	63.08 ± 1.62^{cd}	8.62 ± 0.39^{cd}	18.80 ± 0.87^{a}	50.11 ± 0.77
15% NaOH	62.96 ± 1.45^{cd}	9.14 ± 1.92^{d}	19.98 ± 0.76^{abc}	48.56 ± 0.97
0.5% H_2SO_4	60.07 ± 0.96^{b}	6.68 ± 0.70^{bc}	24.93 ± 0.78^{de}	68.22 ± 0.19
1% H_2SO_4	66.69 ± 0.11^{fg}	1.86 ± 0.92^{a}	25.25 ± 0.43^{de}	61.33 ± 0.67
1.5% H_2SO_4	66.65 ± 0.95^{fg}	1.98 ± 0.53^{a}	26.29 ± 0.78^{ef}	61.33 ± 0.33
Autoclave at 121 °C, 1 h and followed bleaching with 2% H_2O_2 at 70 °C, 2 h				
5% NaOH + 2% H_2O_2	64.42 ± 1.58^{de}	9.25 ± 1.99^{d}	19.33 ± 0.89^{ab}	50.22 ± 0.84
10% NaOH + 2% H_2O_2	65.84 ± 1.12^{ef}	8.46 ± 1.87^{cd}	19.45 ± 0.52^{ab}	46.11 ± 0.38
15% NaOH + 2% H_2O_2	62.32 ± 0.75^{c}	10.14 ± 1.70^{d}	20.63 ± 0.85^{bc}	44.66 ± 1.15
0.5% H_2SO_4 + 2% H_2O_2	62.72 ± 0.44^{cd}	5.50 ± 0.19^{b}	24.41 ± 0.46^{d}	61.33 ± 1.15
1% H_2SO_4 + 2% H_2O_2	68.24 ± 0.17^{g}	1.95 ± 0.70^{a}	24.37 ± 1.52^{d}	57.78 ± 0.19
1.5% H_2SO_4 + 2% H_2O_2	65.58 ± 1.02^{ef}	2.37 ± 0.18^{a}	27.09 ± 0.92^{f}	56.89 ± 0.38

* Mean ± one standard deviation derived from three replicates (N = 3). Different superscript letter (a,b,c) in the same column indicated the values were significantly different (ANOVA and DMRT, $P < 0.05$)

Discussion

Wood biomass from giant sensitive plant could be considered as a potential substrate for industrial commodity production since it contained high cellulose content of 48% (w/w)and is considered as a weed which need to be eradicated. However, in order to obtain cellulose from giant sensitive plant biomass, suitable pretreatment should be concerned. The selection of pretreatment method is an important step for pretreated lignocellulosic biomass because each method showed different effect on lignocellulosic biomass (Binod et al., 2012; Kumar et al., 2009). Several studies had indicated that thermo-chemical pretreatment is one of the most effectivemethods used to removing lignin and hemicellulose and also helped increasing the surface area and porosity of the lignocellulosic biomass (Galbe and Zacchi, 2007).

For microwave-assisted chemical pretreatment, the pretreated wood biomass by using 10% NaOH gave the highest cellulose content by increasing cellulose content around 33%. The effect of NaOH has been found to cause swelling, leading to an increase in internal surface area and disruption of the lignin structure (Cao et al., 2012). In addition, microwave can improve the alkaline pretreatment including the increase of delignification efficiency and decrease of pretreatment time (Keshwani and Cheng, 2011). Zhu et al. (2005) reported that using microwave-assisted 1% NaOH for pretreatment of rice straw could increase cellulose content around 80%. Moreover, bleaching of pretreated wood biomass with 2% H_2O_2 could increase cellulose content around 37% because bleaching with hydrogen peroxide after the pretreatment process could remove the remaining lignin. So, it can be deduced that hydrogen peroxide will improve the effectiveness of lignin removal and cellulose retaining (Cao et al., 2012). When using autoclave-assisted chemical pretreatment, the best condition was found at 1% H_2SO_4, which could increase cellulose content around 40% and removal of 91% hemicellulose was noted. Pretreatment of biomass with dilute H_2SO_4 could effectively removing hemicellulose, lead to the increasing of cellulose content (Nikzad et al., 2012).Nikzad et al. (2012) reported that using autoclave-assisted 1% H_2SO_4 for pretreatment rice husk could increase cellulose content around 37% and remove 73% hemicellulose. Moreover, in this case, bleaching of pretreated wood biomass with 2% H_2O_2 could help increasing cellulose content around 43% as well.

SEM images of untreated and pretreated wood biomass exhibited the physical changes in the wood biomass after pretreatment. The pretreated wood biomass had a more porous surface compare to that of untreated biomass. A similar structural change was also reported for corncobs pretreated with dilute sulfuric acid and sugar cane bagasse pretreated with microwave-assisted alkaline pretreatment (Binod et al., 2012; Nantapipat et al., 2013). This indicates that the pretreatment removed external fibers which can increase surface area and porosity of wood biomass (Binod et al., 2012).

Conclusion

Thermo-chemical process was found to be effective for pretreatment of wood biomass from giant sensitive plant. For microwave-assisted chemical pretreatment, the pretreated wood biomass using 10% NaOH gave the highest cellulose content at 65.37%, while autoclave-assisted chemical pretreatment using 1% H_2SO_4 gave the highest cellulose content at 68.24%.The SEM images revealed that the surface of wood biomass was changed after thermo-chemical pretreatment was applied.

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