

## Research Article

## Characterization of Diluted-acid Pretreatment of Water Hyacinth

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### Abstract

Water hyacinth (WH) is an abundant renewable lignocellulosic biomass. The renewable resources are widely studied to produce bioenergy and high value added products. The obstacle of converting the lignocellulosic biomass to products due to its recalcitrant structure, required disruption to enhance the chemical or enzyme accessibility. The aim of this study is to investigate the possibility of WH pretreatment with dilute sulfuric acid (DSA). The addition of sulfuric acid in pretreatment process was varied concentration at 1, 2, 3, and 4% (v/v). The chemical component was analyzed to optimize the pretreatment condition. The results showed that the 2% sulfuric acid had effect on cellulose recovery. The morphological changes of WH due to pretreatment were determined by Scanning Electron Microscopy (SEM). The images showed the destructive surface of all treated samples. The intact surface of native WH was destroyed after pretreatment process while the increment of acid concentration increased the rough surfaces. The Fourier Transform Infrared Spectrometer (FTIR) and X-ray diffraction (XRD) were used for analyzing functional groups and crystallinity, respectively. The FTIR patterns of DSA treated WH were slightly different due to the remained components in samples. The results showed the highest crystallinity index was 55% which was obtained from pretreated WH with 2% sulfuric acid, 80°C, 60 min. In the present study, it was found that DSA pretreatment is possible to modify the chemical structure of WH for developing economical processes.

**Keywords:** Sulfuric acid, Water hyacinth, Lignocellulosic biomass, Pretreatment, Crystallinity

### 1 Introduction

Water hyacinth (WH) is aquatic weed originated from the state of Amazon, Brazil [1]. It is a widespread to

rivers and canals in many regions of Thailand. Their spreading is becoming major problems in an aquatic ecosystem due to its rapid growth rate and barrier in water migration, transportation and irrigation channels [2].



The covering of WH blocks the passage of sunlight underwater that effects on growth of other aquatic organism and depletes nutrients and oxygen from water bodies adversely affecting the growth of aquatic species [3]–[5]. WH has been considered as raw materials in many applications such as phytoremediation [6], vermicompost [7], biofertilizer [8], absorbent polymer [9], biofuel as biodiesel [10], [11], biogas [12], bioethanol [13] or etc. WH contains high carbohydrate and low lignin content [14], especially high content of hemicellulose (35–55% of dry weight) [15]. The components are linked together with different covalent and noncovalent bindings to form a complex structure, strong and difficult to break into small molecules under raw condition [16], [17]. The recalcitrant structure of lignocellulosic biomass hinders the hydrolysis and blocks the accessibility of enzymes. Pretreatment is a crucial step to facilitate the separation of hemicellulose, cellulose and lignin and enhances the enzymatic saccharification [18], [5]. The physical structure of biomass can be modified by mechanical pretreatment for size reduction such as grinding, milling and comminution. Nevertheless, the chemical components are still remaining in the biomass, then the combination between chemical and mechanical pretreatment methods is considered to improve the process efficiency [19].

Many pretreatment technologies have been studied on a variety of biomass for efficient, cost-effective and environmentally friendly. To overcome the physicochemical barrier of biomass, pretreatment methods have been studied to reduce the operating costs based on different types of lignocellulosic biomass [20], [21]. The chemical pretreatments using acid and alkaline reagents have been widely studied because of their simplicity and efficient performance [22]. The acid pretreatment methods have advantages compared to other pretreatment methods in term of lignocellulose matrix disruption and amorphous cellulose conversion [23]. The acid pretreatments process is intensively studied in both inorganic and organic acids. However, the organic acid is less attractive due to an unclear mechanism in the pretreatment process [24]. The comparative study on the effect of organic and inorganic acid pretreatment for sugar conversion, reported that the achieved hydrolysis step was not only the acid concentration, temperature, and treatment time, but also the type of acid, differed in the mechanism in pretreatment process [24], [25]. However, the

hypothetical mechanism of organic acid pretreatment has been proposed on the modification of chemical bonding between lignin and carbohydrate, and disintegration of cellulose-hemicellulose fibrils [26]. The new group of organic salts is ionic liquids (ILs) that have been used in various lignocellulosic biomasses such as rice straw [27], water hyacinth [28], sawdusts [29], or sugarcane bagasses [30]. IL has potential in disruption the recalcitrant structure while preserving the cellulose fraction [31] and altering the crystalline to amorphous structure [32].

Due to high hemicellulose and low lignin contents in WH, acid pretreatment is especially suitable for hemicellulose removal from lignocellulosic components [33]–[35]. The loosening matrix of lignocellulosic structure can increase the porosity and improve enzymatic hydrolysis [36]. Dilute sulfuric acid pretreatment is generally referred to hydrolyze cellulose and hemicellulose by using acid as catalyst [35], to increase the solubility of hemicellulose and, to disrupt the chemical bonding between lignocellulosic components [37], [38]. The uses of dilute sulfuric acid have been reported in different lignocellulosic biomasses under high temperature, such as extracted olive oil (170, 190, and 210°C) [39], switchgrass (150 and 160°C) [40], rice straw (169–190°C) [41], cassava (160–200°C) [42], rapeseed straw (180°C) [43]. Releasing sugars of hemicellulose under high temperature lead to degrade to furfural and hydroxymethyl furfural, regarding as strong inhibitors to microbial fermentation [44], [45]. Therefore, the effectiveness of pretreatments depends on the physical structure and chemical composition of the biomass [46].

The aims of this study were to study the native, and DSA treated WH in compositional analysis, characterization of physicochemical changes in different sulfuric acid ( $H_2SO_4$ ) concentration, reaction time, and temperatures by using scanning electron microscopy (SEM), Fourier transform infrared (FTIR) and X-ray diffraction (XRD). As a result, we expected the characteristic changes of DSA treated WH under moderate temperature and low sulfuric acid concentration, leads to optimize the pretreatment process for further value added products.

## 2 Materials and Methods

### 2.1 Sample preparation

Fresh WH was obtained from Chee river, located

near Mahasarakham University, Sub-district of Ta Khon Yang, district of Kantarawichai, Maha Sarakham province, Thailand. In this study, we used the stem and leaf of WH which washed thoroughly with tap water after removing roots. The WH was cut into 0.5 to 1.0 cm and dried in oven at 60°C until weight constant. Then, the dried sample was ground and screened through 20 wire-mesh sieve. The sample was stored in an airtight container at room temperature until used.

## 2.2 Sulfuric acid pretreatment

Pretreatment was performed at different four concentrations of H<sub>2</sub>SO<sub>4</sub> (1, 2, 3, and 4% (v/v)) in Erlenmeyer flasks (250 ml) by mixing WH dried powder and H<sub>2</sub>SO<sub>4</sub> solution with the ratio 1:10 (w/v). The experiment was studied at different temperatures (60, 80, and 100°C) and incubated reaction in the water bath for 30 and 60 min. After pretreatment, the solid residue was removed by filtration, followed by washing with distilled water and air dried at room temperature. All data were expressed as average (performed as) of duplication experiments.

## 2.3 Compositional analysis of WH

The composition of cellulose, hemicellulose, and lignin of WH was measured according to Van Soest *et al.* [47]. The biomass recovery rate of the WH samples was calculated according to Equation (1)

$$\text{Biomass recovery rate (\%)} = \frac{[W_{bef}(\text{g}) - W_{aft}(\text{g})] / W_{bef}(\text{g}) \times 100}{(1)}$$

where,  $W_{bef}$  and  $W_{aft}$  were weight of sample before and after pretreatment, respectively.

## 2.4 Characterization of native and pretreated WH

### 2.4.1 Scanning Electron Microscope (SEM)

Surface morphology of samples was observed by SEM (JEOL JSM-6460LV) at an accelerated voltage of 15–20 kV after gold coating by sputtering device (SPI-MODULE, sputter Coater). The samples were coated and mounted on a conductive tape. The morphology of surfaces and pore was monitored and compared with magnification of 1500X.

### 2.4.2 Fourier-transform infrared spectroscopy (FTIR)

FTIR (PERKIN ELMER) spectroscopy was employed to identify the chemical changes before and after pretreatment. The spectrum was recorded in wave number between 4000 and 400 cm<sup>-1</sup> with detector at 4 cm<sup>-1</sup> resolution and 25 scan per sample. Samples were prepared by mixing 3 mg of dried sample with 300 mg of KBr (Spectroscopic grade) and subsequently pressed into disks for 3 min at 10 Mpa.

### 2.4.3 X-ray powder diffraction (XRD)

Crystallinity index of untreated and DSA treated WH was analyzed by XRD diffractometer (Bruker, D-8 Advance). The X-ray diffractograms were recorded in grade range between 10 to 30° (degree) of diffraction angle ( $2\theta$ ) at a scanning speed of 5°/min. The radiation was Cu K $\alpha$  ( $\lambda=1.54 \text{ \AA}$ ) with a step size of 0.03°, 40 KV, 30 mA.

Crystallinity of cellulose was calculated according to the empirical method proposed by Segal's equation [Equation (2)] [48].

$$\text{CrI (\%)} = [(I_c - I_{am})/I_c] \times 100 \quad (2)$$

where,  $I_c$  and  $I_{am}$  were crystalline and amorphous region, respectively.  $I_c$  was measured at  $2\theta = 22.6^\circ$ . Meanwhile,  $I_{am}$  was determined at  $2\theta = 18.0^\circ$ .

## 3 Results and Discussion

### 3.1 Compositional analysis of native WH and DSA treated WH

The chemical composition of native or untreated WH is presented in Table 1. and compared with previous reports. The native WH in this study consisted of 22.05% cellulose, 32.60% hemicellulose, and 4.53% lignin. Comparison to the previous reports, the untreated WH had differed contents due to where it originated from [49]. The chemical composition of DSA treated WH is shown in Table 2. These results revealed that the DSA treated WH promoted the hemicellulose releasing and altered the cellulose and lignin contents. The increment of H<sub>2</sub>SO<sub>4</sub> concentration above 2% (v/v), the results obtained the lower cellulose and hemicellulose contents. The higher temperature and reaction time caused the

loss of cellulose and hemicellulose contents (data not shown). Singh and Bishnoi [50] and Rezania *et al.* [51] reported a reduction in the hemicellulose and lignin contents and an increase in the cellulose content of pretreated WH with sulfuric acid. The higher cellulose content caused by disrupting the WH structure by acid [51] while high acid concentration resulted in the loss of polysaccharides [52].

**Table 1:** The composition of water hyacinth (% w/w)

Cellulose	Hemicellulose	Lignin	References
18.40	49.20	3.55	[55]
19.20	32.69	4.37	[58]
31.67	27.33	3.93	[59]
38.01	24.00	9.50	[22]
32.84	24.70	8.10	[53]
16.40	32.00	5.70	[51]
24.80	30.00	5.60	[60]
22.05	32.60	4.53	This study

**Table 2:** The composition of water hyacinth (% w/w) after DSA pretreatment

Treatment	Cellulose	Hemicellulose	Lignin
Native	22.05±0.1	32.60±0.3	4.53±0.3
2% H <sub>2</sub> SO <sub>4</sub> 60°C, 30 min	24.01±0.4	29.45±0.4	4.41±0.3
2% H <sub>2</sub> SO <sub>4</sub> 60°C, 60 min	24.65±0.2	27.70±0.6	4.13±0.2
2% H <sub>2</sub> SO <sub>4</sub> 80°C, 30 min	25.85±0.5	25.10±0.1	4.03±0.2
2% H <sub>2</sub> SO <sub>4</sub> 80°C, 60 min	26.45±0.5	24.60±0.2	4.01±0.4
2% H <sub>2</sub> SO <sub>4</sub> 100°C, 30 min	26.95±0.3	23.45±0.3	3.55±0.3
2% H <sub>2</sub> SO <sub>4</sub> 100°C, 60 min	28.45±0.4	22.60±0.2	3.23±0.5

The compositional changes of DSA treated and native WH residues were investigated the effect of temperature and time. The results showed that increasing the temperature had a tendency to increase the cellulose content while the hemicellulose and lignin content slightly decrease. These results agree with previous study that hemicellulose was solubilised by DSA and increase cellulose accessibility without removing much of the lignin from biomass [40]. The compositional analysis revealed that DSA pretreatment at high temperature and long reaction time lead to slightly

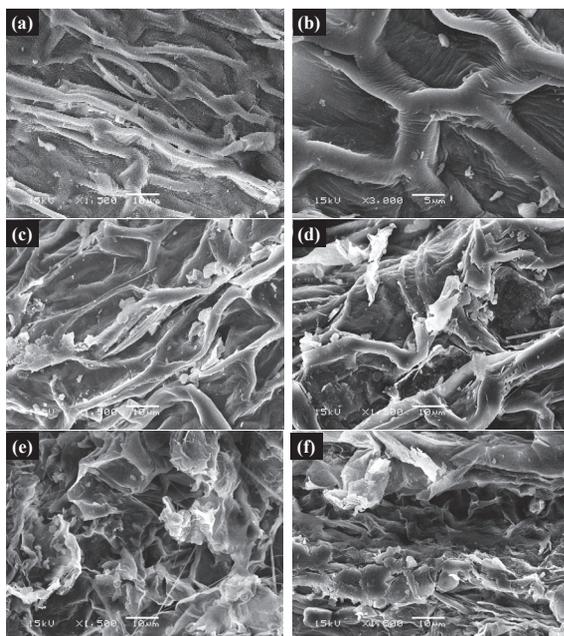
higher cellulose recovery than milder conditions.

The DSA pretreatments performed in hot water bath, which facilitated the heat through the materials without losing power. In hot water bath, heat transfer occurs through convection and followed by conduction. The water is the medium of heat transfer that hot water is indirectly contacted with the base of the glassware containing substrate [53]. During thermal pretreatment, lignin is eradicated merely up to a certain limit. However the dissolution and depolymerisation/repolymerisation of lignin reaction creates the redistribution on the fibre surfaces again [54], [55]. Moreover, the quantity of lignin solubilisation is related to its degradation during pretreatment process [56].

The biomass recovery after DSA treated WH at 80°C for 60 min, was observed and found that the recovery percentage was 68, 67, 63, and 62% (w/w) when applying 1, 2, 3, and 4% (v/v) H<sub>2</sub>SO<sub>4</sub>, respectively. Contrasting to Rezania *et al.* [51], the recovery percentage was 50, 62, 65, and 58% (w/w) when using 4, 5, 6, and 7% H<sub>2</sub>SO<sub>4</sub>, respectively. The higher recovery percentage obtained from our study caused by mild-pretreated condition with lower temperature and acid concentration. Xia *et al.* [57] reported the reaction time of pretreatment affected the weight percentage as increasing time from 5 to 45 min caused residual biomass decrease to 22%.

### 3.2 SEM analysis

The morphological changes in untreated and DSA treated WH were investigated by electron microscopy. The morphology of untreated WH had a well-shaped fibril and smooth intact with a rigid lignin compact structure (Figure 1). Similarly, the previous studies reported a firm and highly organized structure in untreated WH [51], [61]. The observation changes were found in DSA treated WH that the structural surface was rough scaly destructed cellulose matrix and cracked with a few hollows (as shown in Figure 1). The DSA treated WH showed the splitting surface which revealed the loss of matrix and chemical bonding. The comparison of untreated and DSA treated WH found that treated samples were more destroyed with higher acid concentrations. These results confirmed that the acid tended to interact with the cellulose component rather than the lignin in the specific WH structure [51] and loss of the structural integrity [49].



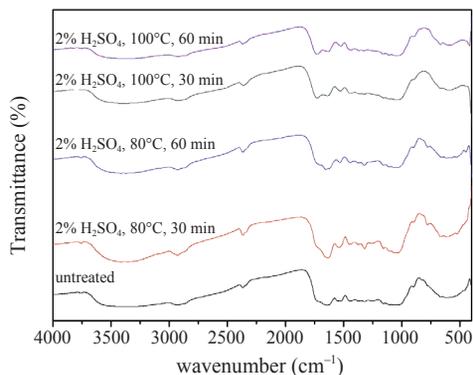
**Figure 1:** Electron microscope images of WH (a) untreated (1,500X), (b) untreated (3,000X), (c) 1%  $\text{H}_2\text{SO}_4$ , (d) 2%  $\text{H}_2\text{SO}_4$ , (e) 3%  $\text{H}_2\text{SO}_4$ , (f) 4%  $\text{H}_2\text{SO}_4$ ; all treated WH is 1,500X (pretreatment at 80°C, for 60 min).

The DSA treated WH shows more effect on the surface due to its retained moisture, and dilute acid penetrates through the substrate to disrupt the finer structure [51]. Thi *et al.* [61] reported that  $\text{H}_2\text{SO}_4$  pretreatment of WH caused compression of the carbohydrate content with a major collapse of cellulose fibers. Therefore, pretreatment induced physical changes in biomass by removing the external fibers and increasing the surface area [62].

At the same acid concentration, increasing the temperature and reaction time, increased rough and broken surface. The optimum DSA pretreatment condition was chosen by the high cellulose content obtained from compositional analysis. Our results showed the optimum condition at 2%  $\text{H}_2\text{SO}_4$  (80°C, 60 min). Then, SEM images were compared in various sulfuric acid concentrations at 80°C, 60 min. However, more broken surfaces indicated the higher cellulose and hemicellulose released.

### 3.3 FTIR analysis

The FTIR analysis was carried out to examine the



**Figure 2:** FTIR spectra of untreated WH and different DSA pretreatments.

changes in chemical composition and structure by comparing the FTIR spectra of WH before and after pretreatment (Figure 2). The FTIR profiles in all samples showed the similar patterns with a small changes of intensity. The intensity of FTIR spectra changing refers to the transformation in the sample composition while the broadening peak indicates the occurrence of weaker intra- and intermolecular hydrogen bonding and lower crystallinity [63].

The comparison of FTIR spectra in native WH and DSA treated WH, the intensity of peaks at  $1728\text{ cm}^{-1}$  was slightly decreased that revealed the deformation of  $\text{C}=\text{O}$  (stretching) in hemicellulose [64]. With an increase in reaction time and temperature, the peak intensities decreased which were observed in DSA treated WH samples and implied to deplete in hemicellulose content. The hemicellulose reduction was caused by deformation of hemicellulose into small molecules. The earlier reports, FTIR spectra at  $1043$ ,  $1162$ , and  $1720\text{ cm}^{-1}$  were attributed to the  $\text{C}-\text{O}$ ,  $\text{C}-\text{C}$  (stretching) or  $\text{C}-\text{OH}$  (bending),  $\text{C}-\text{O}-\text{C}$  vibration in hemicellulose, and carbonyl stretching of glycosidic linkage and hydroxyl groups of hemicellulose, respectively [65]–[67]. The FTIR spectra at  $1441$ ,  $1388$ ,  $1321$ ,  $1169$ ,  $1056$ ,  $1049$ , and  $897\text{ cm}^{-1}$  are associated with the cellulose [66], while spectrum around  $2900\text{ cm}^{-1}$  is reported to  $\text{C}-\text{H}$  stretching vibration band of cellulose component [68]. The FTIR spectra at  $1105\text{ cm}^{-1}$  is typically related to crystalline cellulose [69]. The lower peak intensity indicated to less crystalline cellulose structure. Moreover, The DSA treated WH samples showed the lower intensity of FTIR spectra-related cellulose than untreated WH because of sulfuric

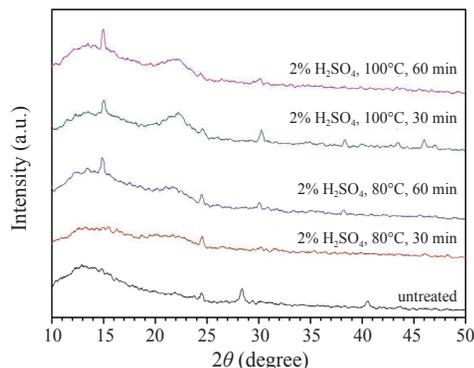
acid hydrolysis [70]. The FTIR spectra at  $1740\text{ cm}^{-1}$  corresponds to both ionic and acetyl ester bonds of ferric and *p*-coumaric acids of lignin [71]. The DSA treated WH samples had similar patterns because of clearly unchanged in lignin content.

The FTIR analysis revealed the consistent results with compositional analysis (shown in Table 2) that the intensity of FTIR spectra-related hemicellulose was decreased in DSA treated WH while the hemicellulose content was reduced by solubilization during DSA pretreatment. The FTIR spectra-related lignin showed similar patterns in all WH residuals, as almost no lignin was removed from the DSA treated WH. The cellulose content in DSA treated WH was increased due to the hemicellulose removal by pretreatment. Then, the remaining cellulose fraction in DSA treated WH was higher than untreated WH.

### 3.4 XRD analysis

X-ray-based measurements of crystallinity index (CrI) were used for analysis the DSA treated and untreated WH samples. The crystallinity index values can be analyzed by XRD and NMR with more accurate [72]. Figure 3. shows the XRD curve of all samples. Peaks appear at  $2\theta=18.0^\circ$  and  $22.6^\circ$ , suggesting the characteristic of amorphous and crystalline regions, respectively [48]. The CrI denotes the amount of crystalline cellulose present in the lignocellulosic biomass and its value depends on the chemical composition of biomass. The CrI of untreated WH was approximately 46% which was lower than DSA treated WH. These results occur when non-crystalline components is removed [73]. The different intensity of peaks between untreated and treated samples indicates in the different CrI [74].

The results showed that DSA pretreatment could increase the CrI of WH. The CrI in DSA treated WH samples was 48, 51, 55, and 49% when treated with 2%  $\text{H}_2\text{SO}_4$  at  $80^\circ\text{C}/30\text{ min}$ ,  $100^\circ\text{C}/30\text{ min}$ ,  $80^\circ\text{C}/60\text{ min}$ , and  $100^\circ\text{C}/60\text{ min}$ , respectively. There was an increment in both crystalline and amorphous regions of cellulose when increased temperature and reaction time. These results were agreed with the previous study that the increment of crystallinity index in dilute acid pretreated materials caused by the breaking down of the amorphous cellulose region [75]. The acid pretreatment process leads to hydrolyze hemicellulose resulting in the xylose releasing and loss of hemicellulose content. Moreover,



**Figure 3:** XRD patterns of untreated WH and different DSA pretreatments.

the dilute sulfuric acid pretreated WH at moderate temperature has been reported to be used to remove hemicellulose and recover the maximum xylose while cellulosic fraction remained in unhydrolyzed form [75].

Furthermore, thermochemical pretreatments can change the crystalline region of cellulose by disrupting inter/intra hydrogen bonding of cellulose chains [18]. The slight changes of CrI among DSA treated WH samples occurred because DSA was not effectively diffused through the entire particle. Similarly, cellulose microfibril is less effect in enzymatic accessibility due to recalcitrant structure to be immersed [40]. Contrasting to the previous report, the thermal pretreatment could reduce the cellulose crystallinity of WH [53]. Besides that, the reduction of cellulose content and CrI is owing to the complex forms breaking down into ordinary forms [75]. According to the remaining components after DSA treatments, higher cellulose and lower hemicellulose contents were owing to less solubilize cellulose than hemicellulose during acid pretreatment, while both crystalline and amorphous cellulose structures still remained in DSA treated WH residuals. The CrI of DSA treated WH depended on the amount of the crystalline region remaining in WH residual. As XRD results, the harsh pretreatment condition can disrupt the crystalline region, and loss CrI when increase the temperature (80 to  $100^\circ\text{C}$ ) and reaction time (30 to 60 min).

## 4 Conclusions

This study performed the DSA pretreatment of WH at moderate temperature which is considered to be a mild

pretreatment process compared to high concentrated acid in the thermal pretreatment process. The potential advantages of this study are to reduce amount of chemical usage and waste releasing. Our strategy tests obtain the changes of structure and surface in WH samples that benefits to remove the undesired components and enhance the further hydrolysis process. The DSA pretreatment of WH was effective in uses of 2% H<sub>2</sub>SO<sub>4</sub>, at 80°C for 60 min. In this study, the DSA pretreatment of WH has been studied and proven to be a practicable suggestion in structural changes. Due to its fraction, it must be continued with further studies on the bioconversion of sugars, compounds releasing, and value added products. The optimum pretreatment process is promising to develop for further research, to improve efficiency, and make the process economically viable.

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#### References

- [1] L. Gao and B. Li, “The study of a specious invasive plant, water hyacinth (*Eichhornia crassipes*): Achievements and challenges,” *Acta-Phytoecologica-Sinica*, vol. 28, pp. 735–752, 2004.
- [2] D. C. Schmitz, J. D. Schardt, A. G. Leslie, F. A. Dray, J. A. Osborne, and B.V. Nelson, “The ecological impact and management history of three invasive alien aquatic plants in Florida,” in *Biological Pollution the Control and Impact of Invasive Exotic Species*. Indiana: Indiana Academy of Science, 1993, pp. 261.
- [3] S. Dandelot, C. Robles, N. Pech, A. Cazaubon, and R. Verlaque, “Allelopathic potential of two invasive alien *Ludwigia* spp,” *Aquatic Botany*, vol. 88, pp. 311–316, 2008.
- [4] A. K. Forrest, J. Hernandez, and M. T. Holtzapple, “Effects of temperature and pretreatment conditions on mixed acid fermentation of water hyacinth using a mixed culture of thermophilic microorganisms,” *Bioresource Technology*, vol. 10, pp. 7510–7515, 2010.
- [5] R. Sindhu, P. Binod, A. Pandey, A. Madhavan, J. A. Alphonsa, N. Vivek, E. Gnansounou, E. Castro, and V. Faraco, “Water hyacinth a potential source for value addition: An overview,” *Bioresource Technology*, vol. 230, pp. 152–162, 2017.
- [6] P. Bathla, “Phytoremediation of metals contaminated distillery effluent using water hyacinth (*Eichhornia crassipes*),” *International Journal of Latest Technology in Engineering, Management & Applied Science*, vol. 4, pp. 283–290, 2016.
- [7] K. Blessy and M. L. Prabha, “Application of water hyacinth vermicompost on the growth of *Capsicum annum*,” *International Journal of Pharmaceutical Sciences and Research*, vol. 5, pp. 198–203, 2014.
- [8] S. Vidya and L. Girish, “Water hyacinth as a green manure for organic farming,” *International Journal of Research in Applied, Natural and Social Sciences*, vol. 2, no. 6, pp. 65–72, 2014.
- [9] A. B. Pitaloka, H. S. Asep, and N. Mohammad, “Water hyacinth for superabsorbent polymer material,” *World Applied Sciences Journal*, vol. 22, no. 5, pp. 747–754, 2013.
- [10] K. Alagu, H. Venu, J. Jayaraman, V. D. Raju, L. Subramani, P. Appavu, and S. Dhanasekar, “Novel water hyacinth biodiesel as a potential alternative fuel for existing unmodified diesel engine: Performance, combustion and emission characteristics,” *Energy*, vol. 179, pp. 295–305, 2019.
- [11] H. Venu, D. Venkataraman, P. Purushothaman, and D. R. Vallapudi, “*Eichhornia crassipes* biodiesel as a renewable green fuel for diesel engine applications: Performance, combustion, and emission characteristics,” *Environmental Science and Pollution Research*, pp. 1–14, 2019.
- [12] V. B. Barua and A. S. Kalamdhad, “Biogas production from water hyacinth in a novel anaerobic digester: A continuous study,” *Process Safety and Environmental Protection*, vol. 127, pp. 82–89, 2019.
- [13] I. Sunwoo, J. E. Kwon, T. H. Nguyen, G. T. Jeong, and S. K. Kim, “Ethanol production from water hyacinth (*Eichhornia crassipes*) hydrolysate by hyper-thermal acid hydrolysis, enzymatic saccharification and yeasts adapted to high concentration of xylose,” *Bioprocess and*

- Biosystems Engineering*, pp. 1–8, 2019.
- [14] S. Rezania, M. F. M. Din, S. F. Kamaruddin, S. M. Taib, L. Singh, E. L. Yong, and F. A. Dahalan, “Evaluation of water hyacinth (*Eichhornia crassipes*) as a potential raw material source for briquette production,” *Energy*, vol. 111, pp. 768–773, 2016.
- [15] A. Kumar, L. K. Singh, and S. Ghosh, “Bioconversion of lignocellulosic fraction of water hyacinth (*Eichhornia crassipes*) hemicellulose acid hydrolysate to ethanol by *Pichia stipitis*,” *Bioresour Technology*, vol. 100, pp. 3293–3297, 2009.
- [16] A. M. Boudet, S. Kajita, J. Grima-Pettenati, and D. Goffner, “Lignins and lignocellulosics: A better control of synthesis for new and improved uses,” *Trends in Plant Science*, vol. 8, no. 12, pp. 576–581, 2003.
- [17] A. D. Moreno, E. Tomás-Pejó, M. Ballesteros, and M. J. Negro, “Pretreatment technologies for lignocellulosic biomass deconstruction within a biorefinery perspective,” in *Biofuels: Alternative Feedstocks and Conversion Processes for the Production of Liquid and Gaseous Biofuels*. Massachusetts: Academic Press, 2019, pp. 379–399.
- [18] N. Mosier, C. Wyman, B. Dale, R. Elander, Y. Y. Lee, M. Holtzapple, and M. Ladisch, “Features of promising technologies for pretreatment of lignocellulosic biomass,” *Bioresour Technology*, vol. 96, no. 6, pp. 673–686, 2005.
- [19] W. Rodiahwati and M. Sriariyanun, “Lignocellulosic biomass to biofuel production: Integration of chemical and extrusion (screw press) pretreatment,” *KMUTNB Int J Appl Sci Technol*, vol. 9, no. 4, pp. 289–298, 2016.
- [20] E. Tomás-Pejó, P. Alvira, M. Ballesteros, and M. J. Negro, “Pretreatment technologies for lignocellulose-to-bioethanol conversion,” in *Biofuels*. Massachusetts: Academic press, 2011, pp. 149–176.
- [21] N. Srivastava, R. Rawat, H. Singh Oberoi, and P. W. Ramteke, “A review on fuel ethanol production from lignocellulosic biomass,” *International Journal of Green Energy*, vol. 12, no. 9, pp. 949–960, 2015.
- [22] M. Narra, J. Divecha, D. Shah, V. Balasubramanian, B. Vyas, M. Harijan, and K. Macwan, “Cellulase production, simultaneous saccharification and fermentation in a single vessel: A new approach for production of bio-ethanol from mild alkali pretreated water hyacinth,” *Journal of Environmental Chemical Engineering*, vol. 5, no. 3, pp. 2176–2181, 2017.
- [23] S. Y. Yoon, B. R. Kim, S. H. Han, and S. J. Shin, “Different response between woody core and bark of goat willow (*Salix caprea* L.) to concentrated phosphoric acid pretreatment followed by enzymatic saccharification,” *Energy*, vol. 81, pp. 21–26, 2015.
- [24] P. Amnuaycheewa, R. Hengaroonprasan, K. Rattanaporn, S. Kirdponpattara, K. Cheenkachorn, and M. Sriariyanun, “Enhancing enzymatic hydrolysis and biogas production from rice straw by pretreatment with organic acids,” *Industrial Crops and Products*, vol. 87, pp. 247–254, 2016.
- [25] P. Amnuaycheewa, W. Rodiahwati, P. Sanvarinda, K. Cheenkachorn, A. Tawai, and M. Sriariyanun, “Effect of organic acid pretreatment on Napier grass (*Pennisetum purpureum*) straw biomass conversion,” *KMUTNB Int J Appl Sci Technol*, vol. 10, no. 2, pp. 107–117, 2017.
- [26] K. Rattanaporn, P. Tantayotai, T. Phusantisampan, P. Pornwongthong, and M. Sriariyanun, “Organic acid pretreatment of oil palm trunk: Effect on enzymatic saccharification and ethanol production,” *Bioprocess and Biosystems Engineering*, vol. 41, no. 4, pp. 467–477, 2018.
- [27] N. Junniengkul, M. Sriariyanun, T. Douzou, P. Yasurin, and S. Asavasanti, “Optimization of alkyl imidazolium chloride pretreatment on rice straw biomass conversion,” *KMUTNB Int J Appl Sci Technol*, vol. 11, no. 3, pp. 199–207, 2018.
- [28] J. Gao, L. Chen, Z. Yan, and L. Wang, “Effect of ionic liquid pretreatment on the composition, structure and biogas production of water hyacinth (*Eichhornia crassipes*),” *Bioresour Technology*, vol. 132, pp. 361–364, 2013.
- [29] R. Alayoubi, N. Mehmood, E. Husson, A. Kouzayha, M. Tabcheh, L. Chaveriat, and I. Gosselin, “Low temperature ionic liquid pretreatment of lignocellulosic biomass to enhance bioethanol yield,” *Renewable Energy*, vol. 145, pp. 1808–1816, 2020.
- [30] Z. Zhang, I. M. O’Hara, and W. O. Doherty, “Pretreatment of sugarcane bagasse by acid-

- catalysed process in aqueous ionic liquid solutions,” *Bioresource Technology*, vol. 120, pp. 149–156, 2012.
- [31] P. Engel, R. Mladenov, H. Wulfhorst, G. Jäger, and A. C. Spiess, “Point by point analysis: How ionic liquid affects the enzymatic hydrolysis of native and modified cellulose,” *Green Chemistry*, vol. 12, no. 11, pp. 1959–1966, 2010.
- [32] R. Akkharasinphonrat, T. Douzou, and M. Sriariyanun, “Development of ionic liquid utilization in biorefinery process of lignocellulosic biomass,” *KMUTNB Int J Appl Sci Technol*, vol. 10, no. 2, pp. 89–96, 2017.
- [33] P. F. H. Harmsen, W. Huijgen, L. Bermudez, and R. Bakker, “Literature review of physical and chemical pretreatment processes for lignocellulosic biomass,” Wageningen UR-Food & Biobased Research, Wageningen, Nederland, Rep. 1184, Sep. 2010.
- [34] Y. H. Jung and K. H. Kim, “Acidic pretreatment.” in *Pretreatment of Biomass*. Amsterdam, Nederland: Elsevier, 2015, pp. 27–50.
- [35] J. C. Solarte-Toro, J. M. Romero-García, J. C. Martínez-Patiño, E. Ruiz-Ramos, E. Castro-Galiano, and C. A. Cardona-Alzate, “Acid pretreatment of lignocellulosic biomass for energy vectors production: A review focused on operational conditions and techno-economic assessment for bioethanol production,” *Renewable and Sustainable Energy Reviews*, vol. 107, pp. 587–601, 2019.
- [36] Y. Chen, R. R. Sharma-Shivappa, D. Keshwani, and C. Chen, “Potential of agricultural residues and hay for bioethanol production,” *Applied Biochemistry and Biotechnology*, vol. 142, no. 3, pp. 276–290, 2007.
- [37] C. Li, B. Knierim, C. Manisseri, R. Arora, H. V. Scheller, M. Auer, K. P. Vogel, B. A. Simmons, and S. Singh, “Comparison of dilute acid and ionic liquid pretreatment of switchgrass: Biomass recalcitrance, delignification and enzymatic saccharification,” *Bioresource Technology*, vol. 101, no.13, pp. 4900–4906, 2010.
- [38] A. Duque, P. Manzanares, I. Ballesteros, and M. Ballesteros, “Steam explosion as lignocellulosic biomass pretreatment,” in *Biomass Fractionation Technologies for a Lignocellulosic Feedstock Based Biorefinery*. Amsterdam, Nederland: Elsevier, 2016.
- [39] P. Manzanares, I. Ballesteros, M. J. Negro, A. González, J. M. Oliva, and M. Ballesteros, “Processing of extracted olive oil pomace residue by hydrothermal or dilute acid pretreatment and enzymatic hydrolysis in a biorefinery context.” *Renewable Energy*, vol. 145, pp. 1235–1245, 2020.
- [40] A. S. Patri, L. McAlister, C. M. Cai, R. Kumar, and C. E. Wyman, “CELf significantly reduces milling requirements and improves soaking effectiveness for maximum sugar recovery of Alamo switchgrass over dilute sulfuric acid pretreatment,” *Biotechnology for Biofuels*, vol. 12, no. 1, pp. 1–11, 2019.
- [41] T. C. Hsu, G. L. Guo, W. H. Chen, and W. S. Hwang, “Effect of dilute acid pretreatment of rice straw on structural properties and enzymatic hydrolysis,” *Bioresource Technology*, vol. 101, no. 13, pp. 4907–4913, 2010.
- [42] Z. Yu, Y. Du, X. Shang, Y. Zheng, and J. Zhou, “Enhancing fermentable sugar yield from cassava residue using a two-step dilute ultra-low acid pretreatment process,” *Industrial Crops and Products*, vol. 124, pp. 555–562, 2018.
- [43] M. Kuglarz, M. Alvarado-Morales, K. Dąbkowska, and I. Angelidaki, “Integrated production of cellulosic bioethanol and succinic acid from rapeseed straw after dilute-acid pretreatment,” *Bioresource Technology*, vol. 265, pp. 191–199, 2018.
- [44] H. B. Klinke, A. B. Thomsen, and B. K. Ahring, “Inhibition of ethanol-producing yeast and bacteria by degradation products produced during pre-treatment of biomass,” *Applied Microbiology and Biotechnology*, vol. 66, no. 1, pp. 10–26, 2004.
- [45] M. Cantarella, L. Cantarella, A. Gallifuoco, A. Spera, and F. Alfani, “Effect of inhibitors released during steam-explosion treatment of poplar wood on subsequent enzymatic hydrolysis and SSF,” *Biotechnology Progress*, vol. 20, no. 1, pp. 200–206, 2004.
- [46] S. Sarto, R. Hildayati, and I. Syaichurrozi, “Effect of chemical pretreatment using sulfuric acid on biogas production from water hyacinth and kinetics,” *Renewable Energy*, vol. 132, pp. 335–350, 2019.
- [47] P. J. Van Soest, J. B. Robertson, and B. A. Lewis,

- “Methods for dietary fiber, neutral detergent fiber, and nonstarch polysaccharides in relation to animal nutrition,” *Journal of Dairy Science*, vol. 74, no. 10, pp. 3583–3597, 1991.
- [48] L. Segal, J. J. Greely, A. E. J. Martin, and L. M. Conrad, “An empirical method for estimating the degree of crystallinity of native cellulose using X-ray diffractometer,” *Textile Research Journal*, vol. 29, pp. 780–794, 1959.
- [49] S. Rezania, M. F. Md Din, S. M. Taib, J. Sohaili, S. Chelliapan, H. Kamyab, and B. B. Saha, “Review on fermentative biohydrogen production from water hyacinth, wheat straw and rice straw with focus on recent perspectives,” *International Journal of Hydrogen Energy*, vol. 42, no. 33, pp. 20955–20969, 2017.
- [50] A. Singh and N. R. Bishnoi, “Comparative study of various pretreatment techniques for ethanol production from water hyacinth,” *Industrial Crops and Products*, vol. 44, pp. 283–289, 2013.
- [51] S. Rezania, H. Alizadeh, J. Cho, N. Darajeh, J. Park, B. Hashemi, M. F. M. Din, S. Krishnan, K. K. Yadav, N. Gupta, and S. Kumar, “Changes in composition and structure of water hyacinth based on various pretreatment methods,” *BioResources*, vol. 14, no. 3, pp. 6088–6099, 2019.
- [52] A. Singh, N. Singh, and N. R. Bishnoi, “Enzymatic hydrolysis of chemically pretreated rice straw by two indigenous fungal strains: A comparative study,” *Journal of Scientific and Industrial Research*, vol. 69, pp. 232–237, 2010.
- [53] V. B. Barua and A. S. Kalamdhad, “Effect of various types of thermal pretreatment techniques on the hydrolysis, compositional analysis and characterization of water hyacinth,” *Bioresource Technology*, vol. 227, pp. 147–154, 2017.
- [54] J. Li, G. Henriksson, and G. Gellerstedt, “Lignin depolymerization/ repolymerization and its critical role for delignification of aspen wood by steam explosion,” *Bioresource Technology*, vol. 98, pp. 3061–3068, 2007.
- [55] R. Kumar, G. Mago, V. Balan, and C. E. Wyman, “Physical and chemical characterizations of corn stover and poplar solids resulting from leading pretreatment technologies,” *Bioresource Technology*, vol. 100, no. 17, pp. 3948–3962, 2009.
- [56] I. Kamdem, N. Jacquet, F. M. Tiappi, S. Hiligsmann, C. Vanderghem, A. Richel, P. Jacques, and P. Thonart, “Comparative biochemical analysis after steam pretreatment of lignocellulosic agricultural waste biomass from Williams Cavendish banana plant (Triploid *Musa* AAA group),” *Waste Management and Research*, vol. 33, no. 11, pp. 1022–1032, 2015.
- [57] A. Xia, J. Cheng, R. Lin, J. Liu, J. Zhou, and K. Cen, “Sequential generation of hydrogen and methane from glutamic acid through combined photofermentation and methanogenesis,” *Bioresource Technology*, vol. 131, pp. 146–151, 2013.
- [58] B. Sornvoraweat and J. Kongkiattikajorn, “Separated hydrolysis and fermentation of water hyacinth leaves for ethanol production,” *Asia-Pacific Journal of Science and Technology*, vol. 15, no. 9, pp. 794–802, 2010.
- [59] J. G. Reales-Alfaro, L. T. Trujillo-Daza, G. Arzuaga-Lindado, H. I. Castaño-Peláez, and Á. D. Polo-Córdoba, “Acid hydrolysis of water hyacinth to obtain fermentable sugars,” *CT&F-Ciencia Tecnológica y Futuro*, vol. 5, no. 2, pp. 101–111, 2013.
- [60] S. Kumari and D. Das, “Biohythane production from sugarcane bagasse and water hyacinth: A way towards promising green energy production,” *Journal of cleaner production*, vol. 207, pp. 689–701, 2019.
- [61] B. T. N. Thi, L. K. Ong, D. T. N. Thi, and Y.-H. Ju, “Effect of subcritical water pretreatment on cellulose recovery of water hyacinth (*Eichhornia crassipes*),” *Journal of the Taiwan Institute of Chemical Engineers*, vol. 71, pp. 55–61, 2017.
- [62] K. Satyanagalakshmi, R. Sindhu, P. Binod, K. U. Janu, R. K. Sukumaran, and A. Pandey, “Bioethanol production from acid pretreated water hyacinth by separate hydrolysis and fermentation,” *Journal of Scientific & Industrial Research*, vol. 70, pp. 156–161, 2011.
- [63] A. Goshadrou, K. Karimi, and M. J. Taherzadeh, “Improvement of sweet sorghum bagasse hydrolysis by alkali and acidic pretreatments,” *Bioenergy Technology*, pp. 374–380, 2011.
- [64] D. Fu, G. Mazza, and Y. Tamaki, “Lignin extraction from straw by ionic liquids and enzymatic hydrolysis of the cellulosic residues,” *Journal of Agricultural and Food Chemistry*, vol. 58, pp. 2915–2922,

- 2010.
- [65] M. Kačuráková, A. Ebringerova, J. Hirsch, and Z. Hromadkova, “Infrared study of arabinoxylans,” *Journal of the Science of Food and Agriculture*, vol. 66, no. 3, pp. 423–427, 1994.
- [66] R. C. Sun, J. Tomkinson, P. L. Ma, and S. F. Liang, “Comparative study of hemicelluloses from rice straw by alkali and hydrogen peroxide treatments,” *Carbohydrate Polymers*, vol. 42, no. 2, pp. 111–122, 2000.
- [67] R. C. Sun and J. Tomkinson, “Characterization of hemicelluloses obtained by classical and ultrasonically assisted extractions from wheat straw,” *Carbohydrate Polymers*, vol. 50, no. 3, pp. 263–271, 2002.
- [68] G. N. Juárez-Luna, E. Favela-Torres, I. R. Quevedo, and N. Batina, “Enzymatically assisted isolation of high-quality cellulose nanoparticles from water hyacinth stems,” *Carbohydrate Polymers*, vol. 220, pp. 110–117, 2019.
- [69] C. Li, B. Knierim, C. Manisseri, R. Arora, H. V. Scheller, M. Auer, K. P. Vogel, B. A. Simmon, and S. Singh, “Comparison of dilute acid and ionic liquid pretreatment of switchgrass: Biomass recalcitrance, delignification and enzymatic saccharification,” *Bioresource Technology*, vol. 101, no. 13, pp. 4900–4906, 2010.
- [70] I. Ballesteros, M. Ballesteros, P. Manzanares, M. J. Negro, J. M. Oliva, and F. Sáez, “Dilute sulfuric acid pretreatment of cardoon for ethanol production,” *Biochemical Engineering Journal*, vol. 42, no. 1, pp. 84–91, 2008.
- [71] M. T. Sundari and A. Ramesh, “Isolation and characterization of cellulose nanofibers from the aquatic weed water hyacinth - *Eichhornia crassipes*,” *Carbohydrate Polymers*, vol. 87, no. 2, pp. 1701–1705, 2012.
- [72] K. Karimi and M. J. Taherzadeh, “A critical review of analytical methods in pretreatment of lignocelluloses: Composition, imaging, and crystallinity,” *Bioresource Technology*, vol. 200, pp. 1008–1018, 2016.
- [73] E. Abraham, B. Deepa, L. A. Pothan, M. Jacob, S. Thomas, and U. Cvelbar, and R. Anandjiwala, “Extraction of nanocellulose fibrils from lignocellulosic fibres: A novel approach,” *Carbohydrate Polymers*, vol. 86, pp. 1468–1475, 2011.
- [74] F. Fahma, S. Iwamoto, N. Hori, T. Iwata, and A. Takemura, “Effect of pre-acid-hydrolysis treatment on morphology and properties of cellulose nanowhiskers from coconut husk,” *Cellulose*, vol. 18, pp. 443–450, 2011.
- [75] R. Kumar, G. Mago, V. Balan, and C. E. Wyman, “Physical and chemical characterizations of corn stover and poplar solids resulting from leading pretreatment technologies,” *Bioresource Technology*, vol. 100, no. 17, pp. 3948–3962, 2009.