Journal of the Taiwan Institute of Chemical Engineers 000 (2017) 1–7

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

Effect of subcritical water pretreatment on cellulose recovery of water hyacinth (*Eichhornia crassipe)*

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A R T I C L E I N F O

Article history:
Received 3 September 2016
Revised 14 December 2016
Accepted 18 December 2016
Available online xxx

Key words:
Water hyacinth
Subcritical water treatment
Cellulose recovery

A B S T R A C T

The effect of subcritical water (SCW) pretreatment on cellulose recovery of water hyacinth was investigated in this study. Before SCW treatment, cellulose and hemicellulose contents of dried water hyacinth sample were 25.0% and 11.0%, respectively. After being treated at 165 °C and 50 bar for 30 min with a water to dried sample ratio of 10:1 (ml/g), cellulose content in the treated sample was 68.2% which is 131.5% of the untreated sample. Pretreatment using H_2SO_4 was also carried out in order to understand the effect of the chemical on lignocellulose degradation and compare it with that of SCW pretreatment. The results revealed that SCW treatment was an environmentally friendly method to recovery cellulose and remove lignin from water hyacinth which is promising for bioethanol production. The effects of SCW treatment on the composition and structure of water hyacinth were studied by TGA, FTIR and SEM.

1. Introduction

Water hyacinth is a widespread aquatic weed in tropical and subtropical areas. The growth rate of water hyacinth is 220 kg/ha/day. Its growth causes deteriorated native ecosystems, clogs up lakes and rivers [1–3]. However, biomass of water hyacinth has high cellulose and hemicellulose contents (Table 1.) which can provide sugars for bioconversion to fuel ethanol [2–11].

Among conversion steps to ethanol, pretreatment is a major challenge because of structural linkages in lignocellulose, which are difficult to break at initial conditions [3]. Among pretreatments, SCW also known as technology leads to a liquid phase rich in hemicellulose sugars and a solid residue rich in cellulose [12,13]. SCW treatment can reduce lignin content by breaking ether and ester bonds of lignin and hemicellulose [12] leading to improved sugar yield. In our understanding, optimal conditions of SCW treatment have not been studied for water hyacinth. Therefore, this study aimed at optimizing SCW pretreatment conditions to obtain maximum cellulose yield of water hyacinth and determining its suitability for ethanol production. Effects of temperature, time, water to solid ratio and pressure on cellulose recovery were studied. Thermogravimetric analysis (TGA), Fourier transform infrared (FTIR) analysis and scanning electron microscopy (SEM) analysis of SCW treated water hyacinth were carried out to investigate the effect of the treatment on sample's structure.

2. Materials and methods

2.1. Chemicals and materials

Glucose (anhydrous, ≥99.5%) and 3,5-dinitro-2-hydroxybenzoic acid were purchased from Sigma Aldrich (St. Louis, USA). Fresh water hyacinth used in this study was harvested from Hau River, Viet Nam. The plants (without roots) were cleaned, chopped to about 5 cm in length and sun dried for two days, then oven dried for two days at 70 °C. The dried sample was ground and screened through 0.7 mm wire-mesh sieve. The sample was stored in airtight plastic bags at 4 °C for further use.

2.2. SCW pretreatment

The equipment includes a reactor with heater, a thermocouple and a pressure gauge. The reactor is made of stainless steel with an inner volume of 200 ml that can tolerate pressure up to 100 MPa. For SCW pretreatment, nitrogen gas (99.9% purity) was used to maintain pressure in the reactor. One gram dried sample was mixed with 10 ml deionized water (DIW) and put in the reactor. The experiment was studied at different temperature (100 to 200 °C), time (15–90 min), DIW to solid ratio (7:1 to 20:1 ml/g) and pressure (0–150 bar). After pretreatment, the reactor was cooled to room temperature, the solid was removed by filtration, washed by DIW, then dried and its lignocellulosic content analyzed by TGA. Reducing sugars (RDS) content in the liquid hydrolysate was determined by DNS (3,5-dinitrosalicylic acid) method [14]. All data were expressed as average of duplicate experiments.

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http://dx.doi.org/10.1016/j.jtice.2016.12.028

Table 1
Lignocellulose contents of water hyacinth (% dry biomass).

Cellulose	Hemicellulose	Lignin	References	Treatment methods
23.3	22.1	not shown	[2]	Untreated
18.2	29.3	2.8	[11]	Untreated
18.3	23.3	17.7	[10]	Untreated
24.3	22.5	8.6	[10]	DMSO, 120 °C, 24 h
36		6.5	[3]	Untreated
49		not shown	[3]	Ultrasound, 20 min
25.0	11.0	2.5	this study	Untreated
68.2	0	0.9	this study	Subcritical water, 165 °C, 30 min, 50 bar

The yield of RDS and cellulose were calculated using Eqs. (1) and (2) as shown below:

$$\text{RDS yield (\%)} = \frac{\text{RDS (mg/g) obtained from DNS method}}{\text{theoretical RDS (mg/g)}} \quad (1)$$

Where theoretical RDS was obtained by the method of Xia et al. [2]

$$\text{Cellulose yield (\%)} = \frac{\text{Cellulose (\%) after treatment which based on remained solid}}{\text{Cellulose (\%) of untreated sample}} \quad (2)$$

Where cellulose (%) is obtained from TGA analysis.

2.3. Subcritical H_2SO_4 (SC H_2SO_4) pretreatment

Dried water hyacinth was treated by H_2SO_4 (0.25–5% w/v) under the following conditions: 165 °C, 30 min, 50 bar and a H_2SO_4 to dried biomass ratio of 10:1 ml/g.

2.4. Statistical analysis

T-test: two samples assuming equal variance was used for considering significant difference and insignificant difference of investigated points in this study.

2.5. Thermal analysis

Dried water hyacinth sample (5–7 mg) was pyrolyzed by TGA machine (Model: Perkin-Elmer) in the temperature range of 30–800 °C at an increasing rate of 10 °C/min. Thermogravimetry (TG) trials were carried out at a nitrogen flow rate of 40 ml/min [3].

2.6. SEM analysis

Surface morphology of samples were observed by SEM (JSM–6390LV, JEOL, Japan) at an accelerated voltage of 15–20 kV after gold or platinum coating by a JEOL JFC-1100 E sputtering device for 85 s prior to SEM observation.

2.7. FTIR analysis

A FTIR Bio-Rad FTS-3500 spectroscopy was employed in this study. The spectrum was obtained in the transmission mode in 4000–400 cm^{-1} at a resolution of 4 cm^{-1} with 40 scans per sample.

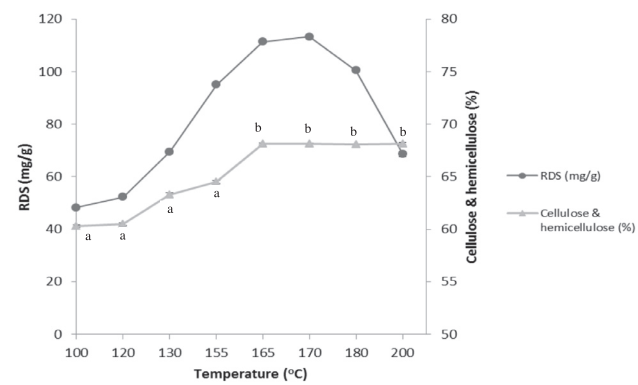

Fig. 1. Effect of temperature on lignocellulose and RDS content of water hyacinth. (a) cellulose & hemicellulose; (b) cellulose. Reaction conditions: 30 min, 50 bar, DIW to solid ratio = 10: 1 (ml/g).

3. Results and discussion

3.1. Effect of temperature on RDS and lignocellulose content

SCW is hot water between 100 and 374 °C using pressure to maintain water in liquid state. Fig. 1. shows that SCW temperature has strong effect on both liquid and solid compositions. RDS content increased from 48.2 mg/g to 111.3 mg/g as temperature was increased from 100 to 170 °C, then decreased to 100.4 mg/g and 68.6 mg/g as temperature was increased to 180 °C and 200 °C, respectively. These results are consistent with that of Xia et al. [2], Pronyk & Mazza [13] and Wei et al. [15] who reported that pretreatment at high temperature decreased sugars concentration due to degradation of sugars into smaller molecules such as furfural, acetic acid, 5-hydroxymethyl-2-furaldehyde (HMF) and formic acid.

In lignocellulosic materials, cellulose, hemicellulose and lignin are linked together in tight structure which is difficult to degrade at normal conditions. To release cellulose and hemicellulose, pretreatment is required to break links between cellulose, hemicellulose and lignin. Cellulose and hemicellulose content in the SCW treated water hyacinth in this study are shown in Fig. 1. Cellulose and hemicellulose content increased from 60.3% to 64.5% as temperature was raised from 100 to 155 °C. These results can be attributed to the role of SCW in the digestion of lignocellulosic component of water hyacinth. At 25 °C, the dielectric constant ε is 78.5. This value decreases to 55.43 at 100 °C/50 bar and 43.95 at 150 °C/50 bar because hydrogen bonding is weakened by increasing temperature. Hence polarity of water decreases with increasing temperature and water becomes more non-polar and a good solvent for organic compounds ($\varepsilon_{\text{dimethyl sulfoxide}}$ = 46.6 at 20 °C, $\varepsilon_{\text{methanol}}$ = 32.6 at 25 °C) [12]. In addition, as temperature increases water density decreases which leads to increase in diffusivity and hence to increase in degradation of cellulose, hemicellulose and lignin in the tight biomass matrix. It was observed