



## Nitrogen removal of ramie stalk treated by acid wastewater combined with *Clostridium thermocellum* and the kinetic study of pyrolysis

Buyun Wang, Ting Li, Ning Zhu, Bo Xiao\*

School of Environmental Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, PR China

### HIGHLIGHTS

- ▶ Straw may contain high nitrogen which should be removed before energy utilization.
- ▶ Acid combined with bacterium can remove nitrogen from biomass effectively.
- ▶ Wastewater from bioleaching is more suitable than H<sub>2</sub>SO<sub>4</sub> in the treatment.
- ▶ The treatment is fast, cheap, efficient and feasible.
- ▶ Pyrolysis kinetics shows the treated straws are suitable for gasification.

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### ABSTRACT

A pretreatment was developed to remove nitrogen from ramie residue and cotton stalk to eliminate potential nitrogen pollutants in biomass energy production. In the pretreatment, straw was treated with acid wastewater from bioleaching for 3 h followed by *Clostridium thermocellum* incubation for 2 h. Most nitrogen was removed from biomass waste and the major was that in protein. Pyrolysis process revealed most hemicellulose was removed and the kinetics fitted the first-order equation well. Apparent activation energy of ramie residue increased a little and mass loss became concentrated. Ultimate analysis and pyrolysis analysis revealed the treatment did not weaken the application value of biomass in energy production. Replacing acid wastewater with sulphuric acid, a higher nitrogen removal could be achieved; however, activation energy increased sharply.

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### 1. Introduction

Biomass energy has been thought to be an alternative to the traditional fossil fuel for a long time because there is no greenhouse gas CO<sub>2</sub> discharged in the whole cycle (Lim et al., 2012). In some countries such as Malaysia, biomass has been used to replace fossil fuel in electricity generation in large scale (Shafie et al., 2012). Biomass energy can be achieved from chemical methods such as direct combustion, pyrolysis or gasification (Lim et al., 2012) and the biological method especially fermentation for the production of ethanol, butanol microbial oil (biodiesel) (Huang et al., 2012; Lu et al., 2012) and etc. (Monlau et al., 2012).

Large amounts of low grade biomass such as agricultural and industrial residue is produced in the world. In China, more than 40,000,000 ton of cotton stalk and 400,000 ton of ramie residue is

produced as textile industry residue yearly which could be used to produce biomass energy. These residues are immature and contain high protein which might produce a great deal of nitrogen pollutant such as NH<sub>3</sub>, NO<sub>x</sub>, HCN and N<sub>2</sub>O in energy utilization such as pyrolysis and combustion (Hansson et al., 2004; Ren et al., 2011). Some techniques have been developed to deal with the nitrogen pollutants during the fuel utilization such as selective catalytic reduction, photocatalysis and acidreaction (Roy et al., 2009). However, large volume of catalyst is used in selective catalytic reduction and photocatalysis and the new catalyst developing is difficult. In acidreaction, large amount of wastewater is produced which may also endanger the environment. An available pretreatment may help to cut down the cost and waste production in the existing techniques by removing the nitrogen prior to the energy production. So far, the research of nitrogen removal from biomass is seldom reported. In Europe, nitrogen content is an important criterion to quality the biomass pellet fuel. It qualities many biomasses to be low grade biomass waste. China is also establishing similar standard.

\* Corresponding author. Tel./fax: +86 027 87557464.  
 E-mail address: xiaobo\_1977@126.com (B. Xiao).

The more, it has been proven that pretreatments can enhance the methane production during anaerobic digestion by improving the inner structure of stalks (Monlau et al., 2012). Pretreatment may also be helpful to upgrade the low grade biomass waste.

In this paper, an acid pretreatment followed by incubation of microorganism on ramie residue and cotton stalk is built to remove nitrogen. Pyrolysis kinetics is carried out to investigate the influence of pretreatment on pyrolysis process.

## 2. Methods

### 2.1. Materials

Ramie (*Bohesmeria nivea*) residue was the residual decorticated stem of ramie which was from farm in Xianning City, Hubei Province, China. Cotton (*Gossypium* spp.) stalk was the stem of cotton from farm around Wuhan City, Hubei Province, China. They were both the biomass residue of local textile industry. The samples were dried under the sun for 7 days to reduce the moisture content and then peeled by machine into stick 3 cm wide and around 20 cm long. In thermogravimetric analysis and pyrolysis, samples were crushed into particles of sizes of approximately 0.125 mm.

Sawdust was provided by furniture factory of Huazhong University of Science and Technology. It's a mixture of various kinds of wood. The sample was 0.125 mm in diameter.

Acid wastewater was the leachate of bioleaching of sewage sludge. The wastewater contained 184 mg/l COD, 0.9 mg/l nitrogen and 2.9 mg/l phosphorus. Its pH is 1.97.

PH of sulphuric acid solution is 2.01.

*Clostridium thermocellum* ATCC 27405 (bacterium) and *Trichoderma viride* Tr 3 (fungus) were stored in Huazhong University of Science and Technology.

Medium for microorganism contains 0.1% carbon source (see 3.1.2), 0.05% KH<sub>2</sub>PO<sub>4</sub>, 0.001% FeSO<sub>4</sub>·7H<sub>2</sub>O, 0.05%, K<sub>2</sub>HPO<sub>4</sub>, 0.1% yeast extract, 0.02% MgSO<sub>4</sub>·7H<sub>2</sub>O, 0.01% peptone, 0.5% CaCO<sub>3</sub> and 100% distilled water. PH of medium is 7.0.

### 2.2. Apparatus and procedures

Two consecutive steps were used to leach nitrogen out of biomass. In step 1, samples were treated with acid and further treatment by microorganism incubation was carried out in step 2. To be a control, treatment with only microorganism was also investigated.

Step 1: 10 g samples were treated with 100 ml acidified wastewater or sulphuric acid solution in flask for 2, 2.5, 3 and 3.5 h.

Step 2: The samples from step 1 were directly transferred into 100 ml distilled water and inoculated with 10 ml medium contained microorganism in log phase and then shaken at 300 rpm 30 °C. After treated for 2 h, the samples were cleaned with distilled water and dried under 80 °C for 6 h to reduce the moisture content and then the nitrogen removal efficiency was detected.

### 2.3. Analysis methods

Ultimate analysis of the samples was obtained with a CHN/O analyzer (Vario Micro cube, Elementar). Such analysis gave the weight percent of carbon, hydrogen, and nitrogen in the sample simultaneously, and the weight percent of oxygen was determined by standard analysis of the instrument. In order to investigate the variation in pyrolysis kinetics after treatment, thermogravimetric analysis of the samples was carried out by TA Instruments system (Diamond TG/DTA, PerkinElmer Instruments). A sample mass of 3.5 ± 1.0 mg was used for the thermogravimetric analysis in each

experiment. Nitrogen was used as a carrier gas. The heating rate was 10, 15 and 20 °C/min from 20 to 800 °C.

In order to study the nitrogen in the pyrolysis product, the pyrolysis experiment was conducted in a tube reactor (long 1000 mm, inner diameter 40 mm) with argon. Nitrogen compound in gas was measured by ISE. Solution is 0.1 mol/l H<sub>2</sub>SO<sub>4</sub> for NH<sub>3</sub> and 145 ml 0.1 mol/l NaOH with 5 ml 0.117 mol/l PbAcE·3H<sub>2</sub>O for HCN.

### 2.4. Kinetic modeling

Kinetic model was studied for samples pyrolysis to obtain the kinetic parameters including activation energy and pre-exponential factor. In this work, the isoconversional method was employed as a function of the extent of conversion and the differential method was used to obtain the pyrolysis kinetic parameters from the thermogravimetric data.

The results of thermogravimetric experiments were expressed as a function of conversion  $X$ , which was defined as

$$X = (W_0 - W_t)/(W_0 - W_f) \quad (1)$$

where  $W_0$  was the initial mass of sample;  $W_t$  was the mass of pyrolyzed sample and  $W_f$  was the final residual mass.

The rate of conversion,  $dX/dt$ , in thermal decomposition was expressed as

$$dX/dt = kf(X) \quad (2)$$

The reaction rate constant  $k$  was expressed by the Arrhenius equation

$$K = A \exp(-E/RT) \quad (3)$$

According to the  $n$ th-order reaction mechanism,  $f(X)$  was expressed as (Hu et al., 2007)

$$f(X) = (1 - X)^n \quad (4)$$

Substituting Eqs. (1), (3) and (4) into Eq. (2), the above equations yields

$$dX/dt = A \exp^{-E/RT} (1 - X)^n \quad (5)$$

Because heating rate ( $\phi$ ) is constant,  $\phi = dT/dt$

$$dX/dT = A \exp^{-E/RT} (1 - X)^n / \phi \quad (6)$$

If there is no secondary reaction in pyrolysis process,  $n = 1$  and integrate Eq. (6)

$$-\ln(1 - X) = kT/\phi \quad (7)$$

With a series of  $X$  and  $T$  sets, a series of  $ks$  can be calculated in Eq. (6). The  $ks$  and  $Ts$  are substituted into Eq. (3) and taking a natural logarithm

$$\ln k = -E/RT + \ln A \quad (8)$$

$A$  and  $E$  are the Arrhenius parameters, pre-exponential factor and activation energy, respectively;  $f(X)$  is the reaction model, that is a function of  $X$ ;  $n$  is reaction order.

Based on Eq. (8), activation energy  $E$  can be obtained from the slope of the straight line, which plotted based on  $\ln k$  versus  $1/T$ . The pre-exponential factor can be also obtained from the intercept.

## 3. Results and discussion

### 3.1. Nitrogen content

#### 3.1.1. Nitrogen content in samples treated by acid

It can be found in Fig. 1 that after treated by acid for 3 h, nitrogen content in straws will not decline more. Sulphuric acid can re-

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