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Thermal Degradation and Structural Characteristics of Corn Stover After Ferric Chloride Solution Pretreatment

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Thermal properties of the corn stover cellulose and these ingredients were examined by thermogravimetric analysis under dynamic conditions from ambient to 800 ºC, in order to predict the thermal behaviour of the corn stover cellulose after ferric chloride solution pretreatment. Thermogravimetric analyses were performed at heating rates of 10, 20 and 30 ºC/min^{-1} in nitrogen atmospheres. The parameters of the reaction kinetics were calculated following the Ozawa-Flynn-Wall (OFW) method and compared with untreated corn stover. Using non-isothermal conditions, average value of the reaction activation energy was determined to and 153.77 and 141.88 KJ/mol for the untreated and treated corn stover. Structure of corn stover was heavily damaged by ferric chloride solution pretreatment compared with untreated corn stover, as characterized by X-ray diffraction and scanning electron microscopy. Fourier transform infrared analysis indicated that ferric chloride solution pretreatment could easily remove the hemicelluloses.

Key Words: Ferric chloride solution pretreatment, Cellulose, Thermogravimetric, Structural.

INTRODUCTION

Biomass has recently attracted much public and industrial interest because of the increasing energy crisis and the environmental benefits[1-3]. Cellulose is one of the components of biomass, has attracted much attention for its biodegradability, mechanical properties, low density and price[4,5]. Thus, study on the relationship between the structure and chemical properties of cellulose is important, not only for scientific but also for chemical and fermentation industry. One of the most important properties of cellulose is its thermal stability[6,7].

Inorganic molten salts can be used as efficient solvents for biomass in a wide range of degrees of polymerization. Furthermore, it can also be applied as reaction medium for the derivatization of cellulose and the findings of the investigations suggested that molten salt hydrates are able to dissolve cellulose without pretreatment or activation[8-10]. Among these molten salt pretreatment, ferric chloride solution pretreatment could easily and effectively remove hemicelluloses and it can also significantly modify the structure of corn stover.

Ferric chloride solution pretreatment, which have been confirmed that could easily and effectively remove hemicelluloses and convert it to monomeric and oligomeric sugars[11,12], can be performed to pretreated biomass before pyrolysis. To date, however, there is still no comprehensive study on the ferric chloride solution pretreatment of corn stover pyrolysis. Thus, the primary goal of this work was to verify the thermal degradation characterization of corn stover pretreated by ferric chloride solution in order to determine its impacts on the pyrolysis of biomass. Thermal analysis was investigated by TG/DTG under dynamic conditions, the activation energy was calculated from the TGA data according to Ozawa-Flynn-Wall method. The structural characteristics of the pretreated corn stover were also analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) analysis.

EXPERIMENTAL

Corn stover was collected from Zhong Liang-shan, Chong Qing, China. The air-dried corn stover was milled to powder and screened to get furnish with an average sizes of 60-mesh. Then the powder was first extracted with toluene-ethanol (2:1, v/v) in a Soxhlet apparatus for 6 h. Samples free of wax were then dried in an oven at 60 ºC for 12 h. All chemicals used were of analytical grade.

Ferric chloride solution pretreatment: The dried corn stover was treated under the optimal condition, which was the findings of our previous study, that 100.0 g (by dry weight) of corn stover were immersed in 0.6 mol/L ferric chloride solution (1000 mL) and then treated at 170 ºC for 15 min. The treated sample was washed five times with de-ionized water. The solid residue was dried at 60 ºC before evaluate the effects of ferric chloride solution pretreatment and then character for structural features analyses.

Thermal degradation: The samples were subjected to thermal gravimetric analysis (TGA) studies using a STA449C thermal analysis system (NETZSCH). For these experiments, samples (10 ± 0.2 mg) were run from room temperature to 800 ºC at a rate of 10 ºC/min under nitrogen (50 mL/mim). Heating rates of 10, 20 and 30 ºC/min were used and continuous records of sample temperature, sample weight and heat flow were taken.

Kinetic parameters of the thermal degradation process were calculated from the TGA data according to the classical Ozawa-Flynn-Wall method (OFW)[13-15]. The formula is often given as:

$$\ln(\beta) = \ln\left[\frac{Af(\alpha)}{d\alpha/dt}\right] - \frac{E}{RT} \qquad (1)$$

In which, α is the degree of conversion, T is the temperature and $f(\alpha)$ is the conversion function (reaction model). Therefore, the activation energy is evaluated by the slope of the plot of ln β *versus* 1000/T.

Detection method: Scanning electron microscopy was performed to analyze the micro-structural changes and surface characteristics of untreated and treated corn stover. Samples were studied using a TESCAN VEGA || LMU scanning electron microscopy, where samples were coated with a thin layer of gold in an automatic sputter coater before observation. The representative images of untreated and treated by ferric chloride solution corn stover reported here were operated at 10 kV accelerating voltage. Fourier transform infrared (FT-IR) spectra were recorded between 4000 and 400 cm^{-1} obtained by using a Spectrum GX (Perkin Elmer, US). Discs were prepared by mixing 2 mg dried sample with 120 mg KBr then pressed in a standard device using a pressure of 16 MPa to produce 13 mm diameter pellets. The background spectrum of pure potassium bromide was subtracted from that of the sample spectrum. Crystalline structure of the treated and untreated sample was analyzed by X-ray diffraction using a Rigaku X-ray diffractometer (Rigaku D/MAX 2500PC Japan) with CuK_α radiation (k = 1.5406 Å) at 40 kV and 150 mA, respectively. The X-ray diffractograms were recorded range from 5-50º in steps of 4º/min with continuous scan. The corn stover crystallinity, as expressed by crystallinity index (Cr I), was determined from XRD data and calculated according to formula (1)[16]:

$$\text{Cr I} = \frac{(I_{002} - I_{am})}{I_{002}} \times 100 \qquad (2)$$

where I_{002} is the intensity for the crystalline portion of biomass (cellulose) at about $2\theta = 22.5$ and I_{am} is the peak for the amorphous portion (*i.e.*, cellulose, hemicelluloses and lignin) at *ca.* $2\theta = 18.7$.

RESULTS AND DISCUSSION

Pyrolysis kinetic analysis: The comparison of thermal degradation between the untreated and treated by ferric chloride solution were studied by determining their mass loss during heating at a rate of 10, 20 and 30 ºC/min, respectively. The mass loss curves of the samples are presented in Fig. 1. From the TGA curves it can be seen that the treated corn stover was more thermal degradation than the untreated. It was probably because more amorphous portion removed and the high crystalline of structural was increased. This revealed that amorphous portion and the crystalline order of cellulose played an important role in thermal degradation of the corn stover.

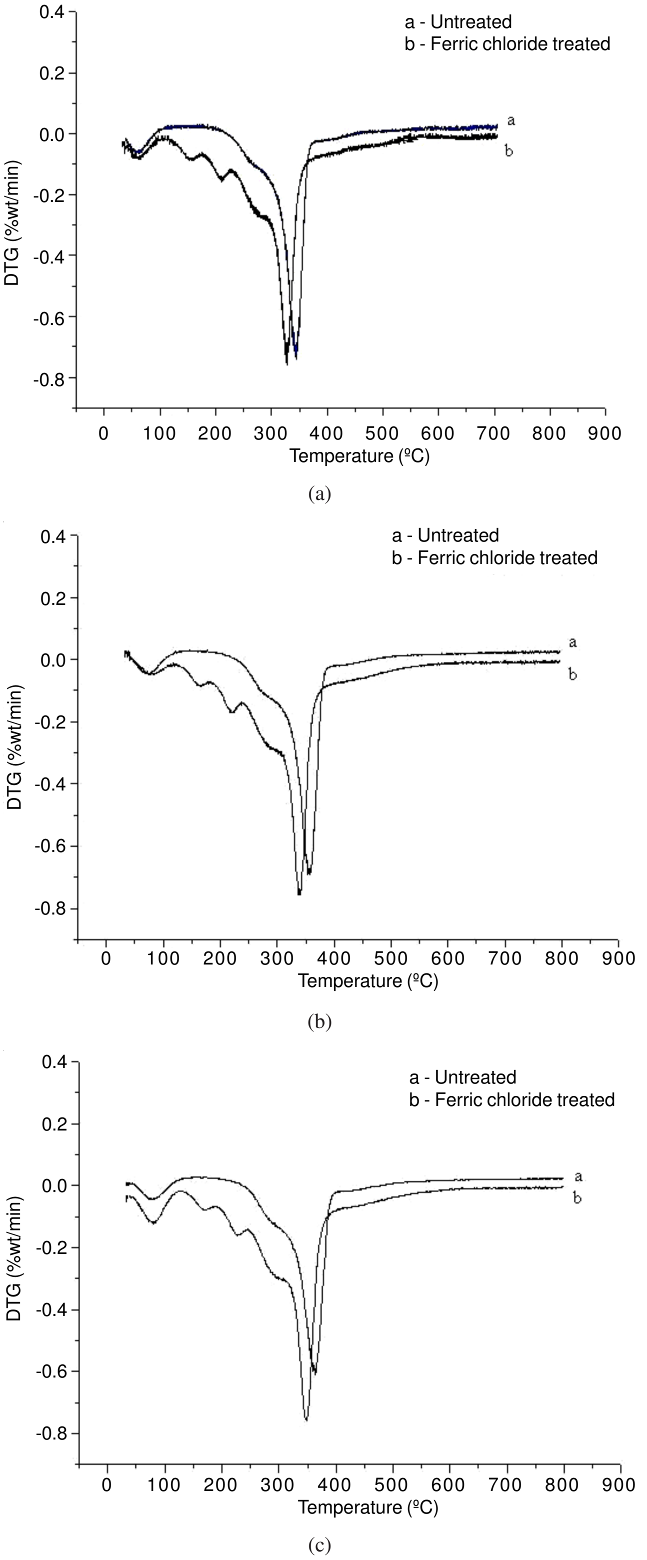
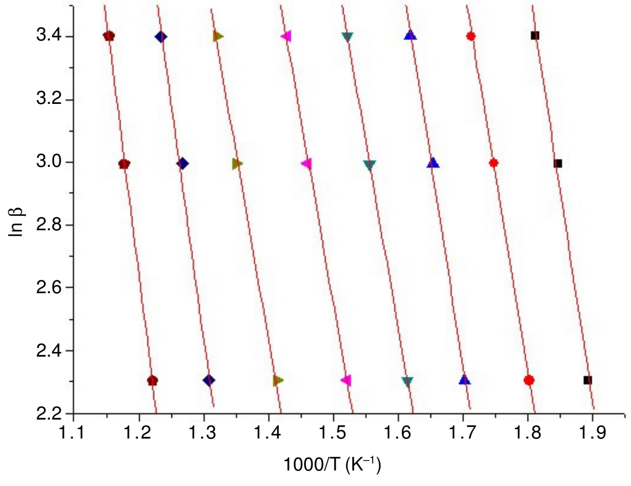
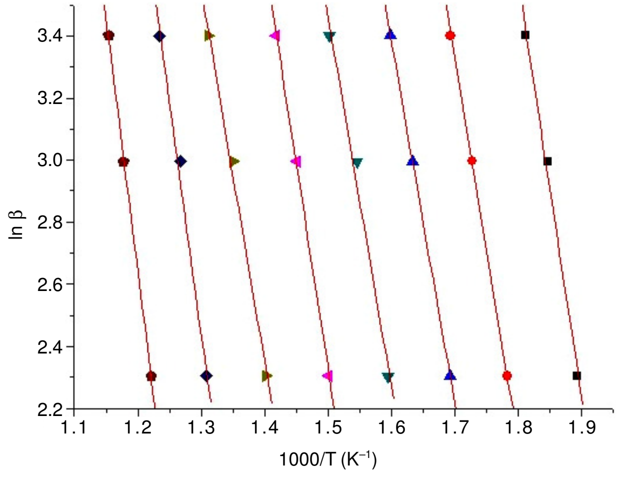


Fig. 1. Effect of ferric chloride solution pretreatment on thermal degradation rates of corn stover heated at (a) 10 min, (b) 20 min and (c) 30 min

In order to study the kinetic and thermal stability of untreated and treated by ferric chloride solution samples thoroughly, several heating rates of 10, 20 and 30 ºC/min were selected and evaluated by OFW method. The activation energy (E_a) not only directly obtained at diverse heating rates from TGA thermal curves, but also it has the advantage without need of previous knowledge of the reaction mechanism for solving the activation energy. The mass loss at different heating rates for untreated and treated was presented in Fig. 2. The OFW plots of log (heating rates) β *versus* 1000/T (temperature) for thermal degradation of samples was shown in Fig. 2. The straight lines fitting the data were nearly parallel, which indicated that the activation energies at different degrees of conversion were almost similar and suggested that this method can be well applied to study samples. The mean values of apparent activation energy were 153.77 and 141.88 KJ/mol, respectively. The E_a values, showed that the order of the thermo stability of two kinds of samples was untreated > treated, which was in accord with the results from thermal degradation temperature. It is suggested that, by ferric chloride solution pretreatment, the energies required for the thermal degradation was less than that of untreated sample.



(a)



(b)

Fig. 2. Arrhenius plots of logarithm of the heating rate *versus* the reciprocal temperature at difierent percentage conversions (a) untreated, (b) ferric chloride solution treated)

Crystallinity analysis: The crystallinity of the lignocelluloses is believed to be an important feature affecting enzymatic hydrolysis of cellulose[17,18]. The character of recycled corn stover after ferric chloride solution pretreatment was examined using powder X-ray diffraction and also compared to the corresponding untreated sample. As Fig. 3 shown, the untreated corn stover is highly crystalline (48.9 Cr I) and after ferric chloride solution pretreatment there is an observed increase in the crystalline index (69.0 Cr I). This increase in Cr I after ferric chloride solution prertreatment is consistent with the results reported by Liu *et al.*[19]. It is indicates that the recovered product is lowly amorphous and therefore has an increase in cellulose and would theoretically enable more crystallinity than untreated.

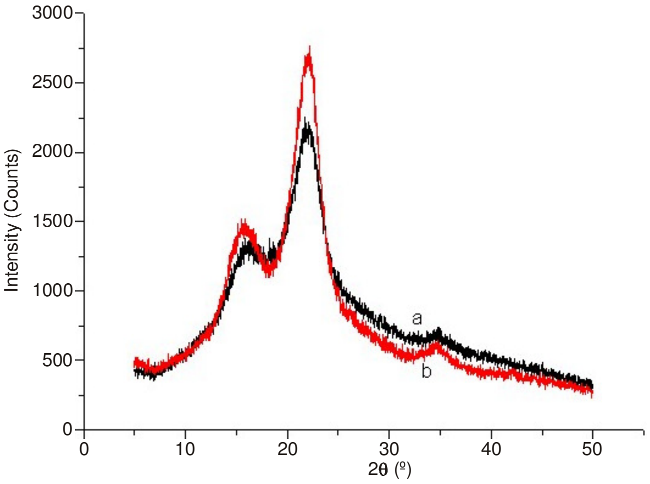
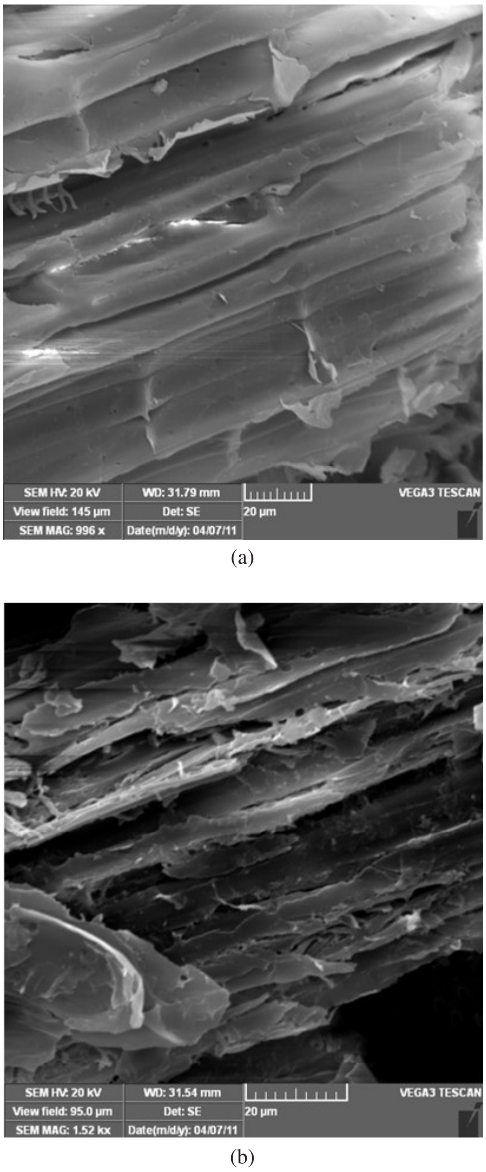


Fig. 3. X-Ray diffraction intensity curves of the samples (a) untreated, (b) ferric chloride solution treated

Morphological analysis of corn stover: The SEM micrographs of corn stover untreated and ferric chloride solution treated were taken at 1000 × magnification (Fig. 4). As can be seen, the surface of untreated corn stover is clear, flat and arranged compactly. In contrast, the surface was no longer smooth and covered with small fragments after the ferric chloride solution treated. The results show that ferric chloride solution pretreatment significantly alters the cellulose structure, reduce the particle size and more holes and length-wise grooves were seen on the surface.

FTIR spectra analysis: FTIR spectroscopy of the samples is shown in Fig. 5. Chemical finger printing of untreated and ferric chloride solution pretreated corn stover were measured by FTIR. For FTIR data, compared to the untreated corn stover spectrum, the bands at 1330 and 1120 cm^{-1} are decreasing for ferric chloride solution pretreatment, which is consistent with the XRD pattern, indicating the increase of cellulose crystallinity. The bands at 1370 and 1208 cm^{-1} decrease significantly for ferric chloride solution pretreated corn stover. In addition to that, Furthermore, significant decrease of bands intensity are observed at 1180 cm^{-1} (C-O stretch in cellulose and hemicellulose), 1330 cm^{-1} (C-O stretching in lignin and hemicellulose) and 1385 (C-H deformation in cellulose and hemicellulose) for the spectra obtained after ferric chloride solution pretreatment, which are likely due to the removal of major hemicelluloses.



(a)

(b)

Fig. 4. SEM of the cellulose rich fractions (a) untreated, (b) ferric chloride solution treated)

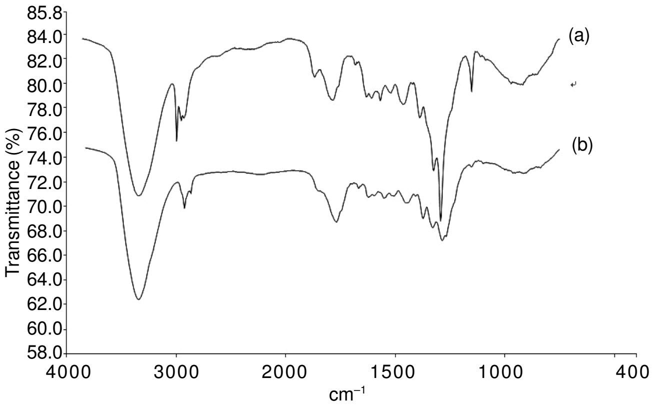


Fig. 5. FTIR of the cellulose rich fractions (a) untreated, (b) ferric chloride solution treated)

Conclusion

The pretreatment of corn stover by ferric chloride solution was conducted in this study. Results showed that pretreatment with ferric chloride solution can change the structure of biomass and increase the activation energy. The crystallinity and crystalline form of the cellulose may be changed by the treatment. The FTIR results indicated a change of amorphous components in the treated sample. SEM photos showed the scales on the corn stover surface were damaged and small holes were appeared after treated. Thermogravimetry revealed that thermal degradation of corn stover depend mainly on the cellulose structure and the content of amorphous components that were present in the corn stover. These changes are likely due to the hemicelluloses and other components in the corn stover removed and the relative content of cellulose increased.

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