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Influence of Chemical Treatment on Rice Straw Pyrolysis by TG-FTIR

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Abstract

The influence of treatment on pyrolysis characteristic and the products evolution performance of rice straw had been investigated by thermogravimetric analyzer coupled with Fourier transform infrared spectrometry(TG-FTIR). The results showed that after chemical treatment such as acid and alkali treatment, the initial pyrolysis temperature and the maximum weight loss temperature shifted to high temperature zone, the maximum weight loss rate increased, and the shoulder peaks of DTG went to fade. The ranges of E (activation energy), which was calculated through Flynn-Wall-Ozawa method, were 198~219kJ/mol, 184~216kJ/mol, 175~205kJ/mol, 184~216kJ/mol, and 205~230kJ/mol for raw-RS, H₂SO₄-RS, H₃PO₄-RS, HCl-RS, and NaOH-RS, respectively. The thermodynamic parameters of ΔH , ΔG , and ΔS were calculated at the DTG peak temperature. After chemical treatment, most of alkali metals were removed, and the absorbance intensities of CO₂ and CO decreased comparing to that of raw sample, while the evolution of pyrolysis products including C-H, C-O-H, and C-O-C functional groups were enhanced through acid. Particularly, C=O functional groups were decreased through acid, but increased through NaOH.

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1. Introduction

Agricultural residues is considered a renewable and alternative resource for renewable production. Rice straw is abundant in China and has great potential as a feedstock for the production of renewable fuels and commodity chemicals. Hence, efficient use of rice straw is of scientific importance and has application value. Many attempts have been made to utilize rice straw as raw material for preparation of value added products. Pretreatment before pyrolysis is one of the promising processes for transforming solid biomass mainly into liquid products, solid bio-char and combustible gases. The thermogravimetric coupled with Fourier-transformed infrared spectroscopy (TG-FTIR) technique has been proved to be a valuable tool to analyze the gas products during the pyrolysis of biomass. This paper aims to discuss the thermal and kinetic characteristics of pretreatments on rice straw, and FTIR can be used to determine the decomposition of samples and identify the volatile species(Xu et al.,2014).

2. Materials and Methods

2.1. Material and Treatment process

Rice straw(abbreviate for RS), collected from the countryside of Hangzhou, southeastern China, were crushed into particles with an average diameter of 100 mesh beads .Then the samples were impregnated with four different agents: H_2SO_4 , H_3PO_4 , HCl and NaOH, the acid and alkali agents which are analytically pure were diluted to 1,3,5,7,9 wt% solutions and 1,2,3 mol/L, respectively. After impregnation, all biomass samples were dried in an oven at 90 °C for 24 h, and then sealed in desiccator for analyzing.

2.2. Instruments and Methods

The TG-FTIR system consists of a thermogravimetric analyzer (TG 209 F3, Netzsch, Germany) coupled with a FTIR spectrometer (Tensor 27, Bruker, Germany). In each run the initial mass of the samples were between 10 and 12 mg, and nitrogen gas was used as carrier gas with purity over 99.99%. The flow rate of nitrogen gas was set at 40ml/min. Pyrolysis was conducted on the thermo-balance at heating rates of 10, 30, 50K/min from 30 to 700°C. The transfer line and FTIR gas cell were preheated separately to 230°C and 200°C to prevent condensation of volatiles. The spectrum scope was in the range of 650~4000 cm^{-1} and the resolution factor was 2.5 cm^{-1} .

3. Results and Discussion

3.1. Effect of chemical treatment on pyrolysis characteristic

The TG and derivative TG (DTG) curves for samples were shown in Fig. 1. It is observed that the TG curves moved to higher temperature after impregnation, DTG curves showed that the initial pyrolysis temperature T_i and the maximum weight loss temperature T_{max} shifted to higher values (Ji et al., 2013). Fig.2 presents the DTG curves of HCl- RS with different concentrations. Due to the different decomposition temperature ranges of hemicellulose and cellulose, the peaks were separated, which at higher temperatures was mainly due to the cellulose decomposition and the shoulder can be attributed to the hemicellulose decomposition at lower temperatures. With the increase of concentration, the shoulder went to fade, and the peaks overlapped. All discussions above indicated that impregnation with these agents tended to delay slightly pyrolysis process towards high temperature, this may be due to that some alkaline earth metallic inhaled in

rice straw acted as catalysts had been removed by agents, and the samples are more resistant to thermochemical decomposition. In addition, the NaOH-RS had a obscure change because of the Na cation , nevertheless, the acids made a greater influence on pyrolysis characteristic. Thus, comparing to physicochemical structure changes created by treatment process, the influence of removal of minerals played the dominant role in biomass pyrolysis.

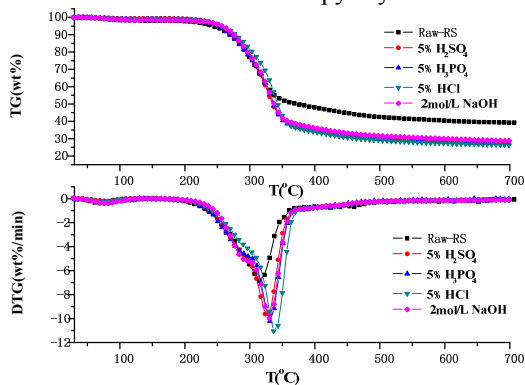


Fig.1. TG and DTG curves of rice straw pyrolysis with different agents(10K/min)

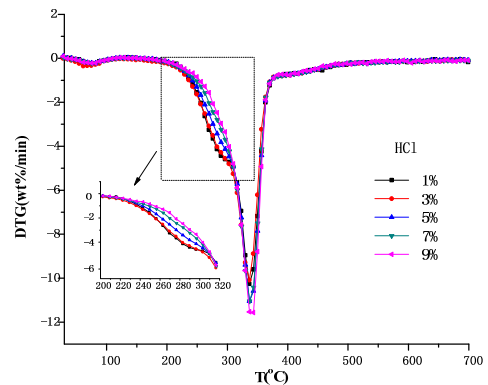


Fig.2 DTG curves of rice straw pretreated by HCl with different concentration(10K/min)

3.2. Kinetic analysis

The Flynn-Wall-Ozawa method was applied to calculate the pyrolysis kinetic parameters, and other thermodynamic parameters such as Enthalpies ΔH , Gibbs free energies ΔG , and entropies ΔS were calculated. The thermodynamic parameters at the maximum differential conversion were listed in Table.1. Activation energy E can be obtained from the slope. The ranges of E were 198~219kJ/mol, 184~216kJ/mol, 175~205kJ/mol, 184~216kJ/mol, and 205~230kJ/mol for Raw RS, H_2SO_4 -RS, H_3PO_4 -RS, HCl-RS, and NaOH-RS, respectively.

The thermodynamic parameters of thermal decomposition of Raw-RS, H_2SO_4 -RS, H_3PO_4 -RS, HCl-RS, and NaOH-RS were presented in Table 1. The A values of H_3PO_4 -RS was lower than that of Raw-RS, H_2SO_4 -RS, HCl-RS, and NaOH-RS, indicating the necessity for a lower rate of molecular collisions after treatment by H_3PO_4 . The changes of enthalpies revealed the energy difference between the reagent and the activated complex agreed with activation energies. Based on Table 1, more heat energies were required for NaOH-RS than other treatment in order to dissociate the bonds of reagents. The pyrolysis enthalpy of H_3PO_4 -RS was the minimum value. The change of the Gibbs free energy ΔG illustrated the total energy increase of the system at the approach of the reagents and the formation of the activated complex. Except the decomposition of H_3PO_4 -RS, all values of ΔS were positive, which illustrated that the activated complex were less organized structure compared to the initial substance (Xu et al., 2013).

Table 1 Thermodynamic parameters at the maximum differential conversion under the heating rate of 10 K/min.

sample	$A(s^{-1})$	$E(kJ/mol)$	$\Delta H(kJ/mol)$	$\Delta G(kJ/mol)$	$\Delta S(J/mol)$
Raw-RS	1.10E+16	200.8	195.9	167.7	48.3
1% H_2SO_4	2.63E+14	188.2	183.2	173.0	17.0
1% H_3PO_4	2.13E+13	177.2	172.2	174.5	-3.9
1%HCl	7.15E+14	197.2	192.1	176.7	25.2
1mol/L NaOH	5.66E+15	204.4	199.4	173.7	42.5

3.3. FTIR analysis of pyrolysis products

FTIR measurements were conducted with raw and treated samples to observe the influence of chemical treatment on rice straw (Long Jiang et al., 2013). The broad band at $3000\text{--}3800\text{ cm}^{-1}$ is attributed to O–H stretching vibrations of hydroxyl functional groups, and the band at $2800\text{--}3000\text{ cm}^{-1}$ is related to C–H stretching vibrations of CH_2 and CH_3 groups. The peak around 1734 cm^{-1} corresponding to the C=O stretching vibration is mainly caused by free carbonyl groups, therefore it is a typical hemicellulose marker. The spectra around 1200 cm^{-1} contain several bands in the C–O stretching region which were most probably cellulose-related absorptions, and these bands were sharpened by treatment. All the above variations might indicate some constituents had changed in cross linking reaction between the C–O–H, C–O–C and other functional groups. Except the NaOH-RS, the removal of some polysaccharides constituents could be verified from the decline of bands around 1730 cm^{-1} and the increase of the spectra around 1200 cm^{-1} after treatments.

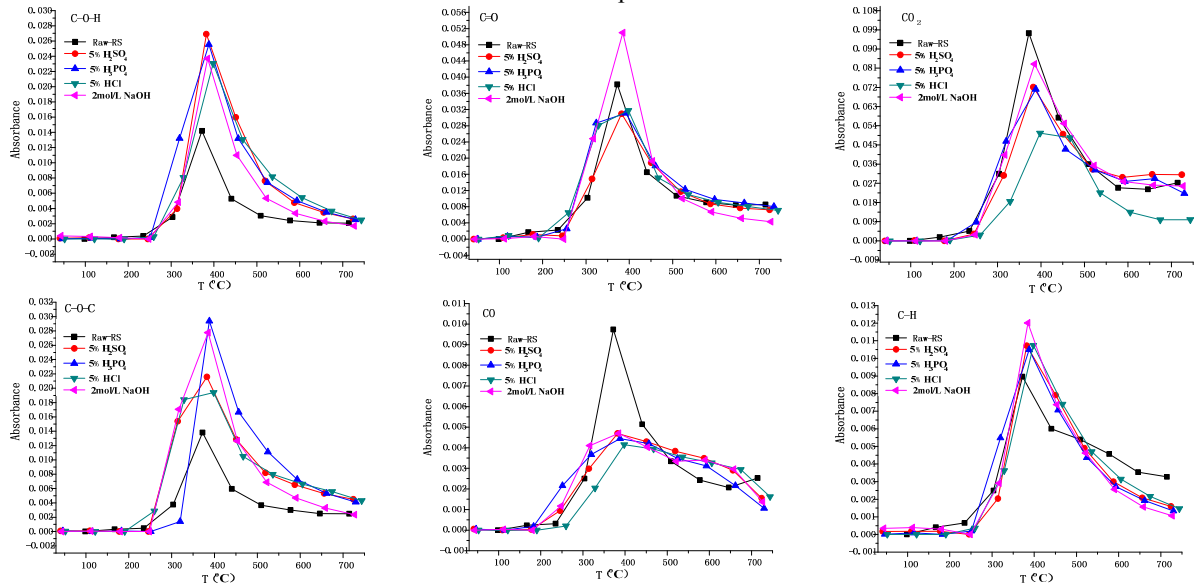


Fig.3. FTIR spectra of different functional groups for different agents (50 K/min)

According to Fig.3, the main releasing products of samples were CO_2 , CO, H_2O , C–H functional groups, C=O functional groups and C–O–C(H) functional groups. The specific wavenumbers of the spectra peak for each main volatile were listed as following: CO_2 : 2355 cm^{-1} ; H_2O : 3736 cm^{-1} ; CO: 2184 cm^{-1} ; C–H: 2978 cm^{-1} ; C=O: 1746 cm^{-1} ; C–O–C: 1170 cm^{-1} ; C–O–H: 1057 cm^{-1} . The volatile emission mainly focused at low temperature range of $200\text{--}400\text{ }^\circ\text{C}$, which corresponded well with the observation of DTG curves in Fig.1. Above $400\text{ }^\circ\text{C}$, the main releasing products of all samples decreased sharply. The emission of CO_2 displayed a highest peak around $350\text{--}400\text{ }^\circ\text{C}$, attributed to the cracking and abscission of C–C and C–O bonds associated with hemicellulose. The emission of CO released in the whole temperature range. The releasing of H_2O , C–H, C=O and C–O–C(H) functional groups mainly produced from decomposition of hemicellulose and cellulose. After treatment, most of alkali metals were removed, and the absorbance height of CO_2 and CO decreased comparing to raw sample, in particular, CO had a remarkable decline, which indicates the absence of alkali metals weakened the releasing of CO_2 and CO. However, the absorbance intensities of C–H, C–O–H and C–O–

C functional groups increased, which indicates the absence of alkali metals enhanced their releasing. It can be explained by the reason that the presence of alkali metals enhanced the demethanization reaction, and promoted secondary reaction of the primary unstable carbonyl/carboxyl groups to produce light gas such as CO₂ and CO.

4. Conclusions

After treatment, the T_i and T_{max} shifted to high temperature zone, the maximum weight loss rate increased, and with the increase of concentration, the shoulder peak of DTG disappeared. The ranges of E were 198~219kJ/mol, 184~216kJ/mol, 175~205kJ/mol, 184~216kJ/mol, and 205~230kJ/mol for Raw RS, H₂SO₄-RS, H₃PO₄-RS, HCl-RS, and NaOH-RS, respectively. Except the decomposition of H₃PO₄-RS, all values of ΔS were positive. The absorbance intensities of CO₂ and CO decreased comparing to raw sample, the absorbance intensities of C-H, C-O-H, and C-O-C functional groups increased. Particularly, C=O functional groups were decreased through acid treatment, but increased through NaOH treatment.

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