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TG-FTIR Study on Corn Straw Pyrolysis-influence of Minerals*

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In order to study the effect of minerals on biomass pyrolysis, experiments on pyrolysis of corn straw with different pretreatment methods were performed by using a thermogravimetric analyzer(TGA) coupled with a Fourier transform infrared(FTIR) spectrometer. The pretreatment methods included water washing and acid washing. The experimental results show that acid washing can remove almost all K^+ and 78% of Ca^{2+}, while water washing only removes most of K^+. The existence of K^+ and Ca^{2+} obviously favors the formation of compounds containing carbonyl groups and CO_2, but it will decrease the yields of compounds containing C—O—C groups. However, the formation of H_2O, CO and CH_4 are slightly affected by the removal of inorganic ions. With regard to the structure of the metal ions-adsorbed cellulose characterized by IR analysis, it can be considered that there is an "ion force" between metal ions and cellulosic biomass. The results of thermal kinetic analysis show that this force can make the reaction activation energy of the biomass pyrolysis decrease. A new mechanism is proposed for explaining the effect of inorganic ions on cellulose pyrolysis.

Keywords Biomass; TG-FTIR; Pretreatment; Minerals; Pyrolysis mechanism
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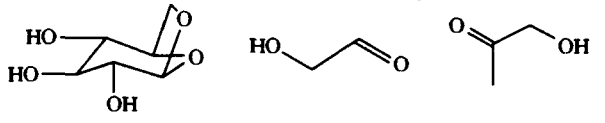
Introduction

Recently, concern about emission of greenhouse gases from combustion of fossil fuels has prompted a renewable interest in the combustion of biofuels due to their CO_2 neutrality[1,2]. Pyrolysis of biomass(cellulose and lignocellulose materials, *etc.*) is of great interest in the production of chemicals and fuels[3—6].

Biomass is comprised of hemicellulose, cellulose, lignin, a little of extract and ash. These components result in different pyrolysis products because of different mechanisms of thermal decomposition. The volatile products of cellulose pyrolysis are mainly comprised of levoglucosan, hydroxyacetaldehyde, acetol (Scheme 1), *etc.* Acetic acid and furfural are products of hemicellulose pyrolysis, and phenols of lignin pyrolysis[7].



Levoglucosan Hydroxyacetaldehyde Acetol

Scheme 1 Structures of levoglucosan, hydroxyacetaldehyde and acetol.

The pyrolysis behavior of lignocellulosic biomass and cellulose is significantly influenced by ash and existed inorganic ions[8—11]. Inorganic ions favor the formation of gas, char, and hydroxyacetaldehyde but they cause the total liquid yield to decrease and inhibit the formation of levoglucosan.

There have been many mechanisms proposed for the pyrolysis of cellulose or lignocellulosic biomass[9,12,13] to interpret the above phenomena, of which two are important. One is Shafizadeh's mechanism[7,12] in which levoglucosan is first produced in cellulose pyrolysis, yielding glucose, and then glucose undergoes a C_2—C_3 cleavage to form hydroxylacetaldehyde(Glycolaldehyde); the other is Richard's mechanism that the hydroxyacetaldehyde formation must involve the diversion of reaction channels prior to the formation of levoglucosan[13].

All the above researches aim at the pyrolysis of biomass, and the pyrolysis mechanisms focus on the

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formation paths of pyrolysis products, especially for those of levogancosan and hydroxylacetaldehyde. However, the mechanism of metal ions acting on biomass pyrolysis is not clear. Little information is available regarding the relationship between the formation of CO_2, H_2O and that of the primary pyrolytic products such as levoglucosan, hydroxyacetaldehyde and acids *etc.* in interpreting the pyrolytic mechanism of cellulose loaded with inorganic ions.

In order to clarify the relationship between the yield of pyrolysis liquid and the existence of inorganic ions, and to understand the mechanism of the effect of inorganic ions on biomass pyrolysis, we investigated the effect of pretreatment methods including water washing and acid washing on corn straw pyrolysis by using a thermogravimetric analyzer coupled with a Fourier transform infrared analyzer.

Experimental

1 Materials

Corn straw was pretreated by washing with room temperature water, 60 ℃ water and a 0.5% nitric acid solution. All the washing processes were performed by means of soaking and churning each sample of 1 g in the above washings (100 mL for each washing) for 12 h. After washing, the corn straw samples were filtered, and then dried at 105 ℃ for 10 h. The acid-washed corn straw sample was washed with distilled water until it was neutral, then filtered and dried at 105 ℃ for 10 h. Before the experiments, the pretreated corn straw samples were finely ground into powder(less than 100 meshes) in order to minimize the heat-transfer resis-tance and decrease the influence of vapor-solid and secondary reactions. The properties of the materials are listed in Tables 1 and 2.

Table 1 Chemical compositions and proximate analyses of the samples with different pretreatment methods

Corn straw sample	Component analysis(%, mass fraction)			Proximate analysis(%, mass fraction)		
	Homo-cellulose	Lignin	Extract*	Moisture	Volatile matter	Ash
Original	74.90	13.41	2.34	3.58	70.58	5.77
Room temperature water-washed	77.47	13.23	1.88	3.27	77.13	4.15
60 ℃ water-washed	77.43	14.01	1.72	3.03	78.28	3.81
0.5% HNO_3-washed	79.25	12.88	2.90	2.37	80.59	2.60

* Benzene-ethanol extractable(2:1, volume ratio).

Table 2 Ultimate and K, Ca analyses of the samples with different pretreatment methods

Corn straw sample	Ultimate analysis(%, mass fraction)				Metal elementary analysis(%, mass fraction)	
	C	H	N	O	K^+	Ca^{2+}
Original	45.8	5.3	0.6	42.3	0.63	0.70
Room temperature water-washed	44.6	5.2	0.6	45.3	0.01	0.57
60 ℃ Water-washed	45.1	5.4	0.4	45.2	0.03	0.70
0.5% HNO_3-washed	45.6	5.5	0.7	45.5	0.002	0.15

2 Carbon, Hydrogen and Nitrogen Contents

The contents of carbon, hydrogen and nitrogen in the air-dried samples were determined by using an EAI CE-440 elemental analyzer.

The oxygen content was calculated as the difference between the total content and the sum of carbon, hydrogen and nitrogen. The Ca and K contents were obtained by using a Dionex DX500 ICP ion chromatograph and a Perkin-Elmer Aanalyst 200 spectrometer.

3 FTIR Spectra of Solid Samples

The FTIR spectra of the samples were determined with a Bruker Equindx 55 Fourier transform infrared analyzer.

Each of the dried samples was mixed with IR grade KBr (Aldrich) and milled, respectively. The concentration of each of the samples was 1% (mass fraction) in the potassium bromide disk for IR analysis. The background spectrum of pure KBr was subtracted from the sample's spectra. The FTIR experiments were conducted in a region of 600—4000 cm^{-1}.

4 TG-FTIR Experimental Setup

The TG-FTIR system was a computer-controlled facility(shown in Fig. 1) consisting of a Netzsch STA 449C TG-DTA/DSC thermogravimetric analyzer coupled with a Bruker Equindx 55 FTIR spectrometer and

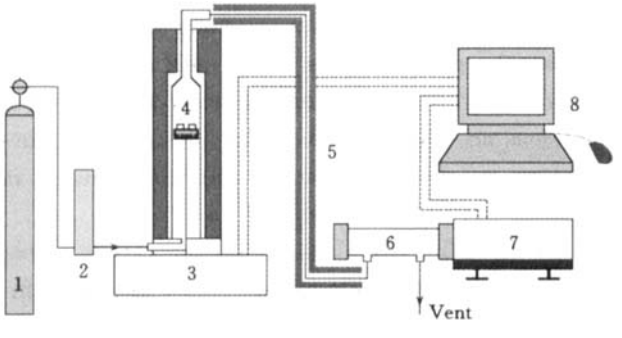

Fig. 1 TG-FTIR experimental system.

1. Helium cylinder; 2. mass flowmeter; 3. netzsch STA 449C thermogravimetric analyzer; 4. crucible and sample; 5. heat pipeline; 6. gas cell; 7. bruker equindx 55 FTIR spectrometer; 8. computer.