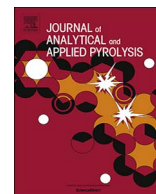




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## Pyrolysis and combustion characteristics of corncob hydrolysis residue

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## ABSTRACT

Corn cob hydrolysis residue (CHR) is a by-product of the furfural industry. In this paper, the thermal behavior of CHR was determined with the aim to promote its application as fuels or chemicals. Firstly, the pyrolysis and combustion of CHR in nitrogen and air, were respectively investigated by thermogravimetric analyzer coupled with Fourier transform infrared spectrometer (TG-FTIR). The TG and DTG (differential thermogravimetric) curves revealed that both the pyrolysis and combustion of CHR included three distinct stages. The main evolving gaseous products during pyrolysis were H<sub>2</sub>O, CH<sub>4</sub>, CO, CO<sub>2</sub> and oxygenated compounds, while combustion yielded considerable amounts of CO<sub>2</sub> in the temperature range of 345–500 °C. The presence of oxygen can increase the volatilization rate of organic matter in CHR and accelerate thermal decomposition of CHR. A total weight loss of 57.29 wt% and 77.53 wt% was observed for pyrolysis and combustion, respectively. The non-isothermal kinetic was used to analyze the activation energy (*E*) of combustion and pyrolysis processes. The *E* of CHR pyrolysis reaction is 135.45 kJ mol<sup>-1</sup> in temperature of 200–500 °C, while under the combustion process the value of *E* is 121.57 kJ mol<sup>-1</sup> and 135.45 kJ mol<sup>-1</sup> in 200–345 °C and 345–500 °C temperature ranges, respectively. In addition to it, the types of products and their proportions in pyrolysis process of CHR were studied by Py-GC/MS and the results indicated that the oxygenated compound produced from CHR pyrolysis mainly included acids, aldehyde, phenolics and anhydrides.

## 1. Introduction

Furfural is one of the most important chemicals in the world and is usually produced by dehydration of pentose which is present in the hemicellulose of agriculture residues, such as sugar cane bagasse, corncob, paper-pulp residues, grain hull, wheat and rice straw, rice and oat hulls, etc. China is the biggest producer and exporter of furfural production in the world. Commercially, sulfuric acid is used as homogeneous catalyst during furfural production from lignocellulose and this process is known as acid hydrolysis. A large amount of acid hydrolysis residues, which is mainly consisted of intractable cellulose condensation products and insoluble lignins, are generated from furfural industry [1]. It is necessary to treat and utilize these acid hydrolysis residues due to the tightening legislation and increasing environmental awareness. Up to now, the acid hydrolysis residues from furfural production have potential use as fertilizer, soil improver, activated carbon etc. [1,2].

More and more attentions have been put on thermal treatment of acid hydrolysis residue because of its compromise between energy recovery and material recovery. The preferred thermal conversion methods include pyrolysis and combustion. During pyrolysis or

combustion process, several factors such as feedstock composition, reactor type, reaction temperature, heating rate and gaseous environment have obvious influence on product characteristics and distributions [3,4]. Girisuta et al. [5] used catalytic pyrolysis to convert acid hydrolysis residues from miscanthus into liquid fuels. Li et al. [6] investigated the catalytic pyrolysis of corncob hydrolysis residue (CHR), and their study revealed that catalytic upgrading over HZSM-5 could improve the bio-oil quality and enhance the yield of mono-phenols in bio-oil. In order to obtain reusable products and control the thermal process, it is necessary to know the thermochemical properties of the feedstocks.

Thermal analysis and kinetic analysis of the sample are usually performed in thermogravimetric (TG) analyzer [7,8]. However, only TG analysis cannot detect the composition of evolved gas in each mass loss step. Therefore, more attention is paid on the direct on-line analysis of gas composition with a hyphenated technique. TG coupled with Fourier transform infrared spectrometry (TG-FTIR) is a useful tool in dynamic analysis because TG-FTIR not only can monitor the mass of the residue but also can detect the composition of the volatile products. TG-FTIR has already been utilized to study the thermal decomposition of oil

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sand, municipal solid waste (MSW), industrial lignins, pine sawdust and et al. [9–15]. Additionally, pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) is another hyphenated technique, and has been applied to evaluate the thermal degradation behavior and products of biomass and other materials successfully. For example, Wang et al. [16] applied Py-GC/MS to evaluate the influence of HZSM-5, HSAPO-34, and NaY on pyrolysis of corn straw fermentation residue. Liaw et al. [17] used Py-GC/MS to investigate the effect of material type and temperature on pyrolysis product distribution of Avicel, a-cellulose, Douglas Fir wood and Hybrid Polar wood. A number of studies have been reported in the literature on thermal characteristics of biomass with TG-FTIR and PY-GC/MS [9,18,19]. However, few articles show the degradation characteristics and product-evolution process of real corncob hydrolysis residue which is from a process of industrial furfural production. Since the components and structure of the corncob hydrolysis residue are different from that of common biomass, it is significantly to explore thermal characteristics of the corncob hydrolysis residue with different source and properties. Most of the current studies about biomass hydrolysis residue mainly focus on its pyrolytic behavior [5,6,20,21], however, detailed studies on distribution of specific products of pyrolysis integrated combustion for corncob hydrolysis residue with reaction temperature and time are relatively few.

In this paper, the combustion integrated pyrolysis characteristics, product-evolution process and kinetic analysis of CHR from industrial furfural production was systematically investigated with TG-FTIR and Py-GC/MS. Study on thermal behaviors of hydrolysis residue is of practical importance for better understanding of thermal behavior of it and promotes its applications as fuel and chemicals production.

## 2. Materials and methods

### 2.1. Feedstock

CHR was obtained from a local furfural manufactory in Tongliao in Inner Mongolia, China. The residue was dried at 105 °C in an oven and then was crushed to a particle size of < 0.25 mm. The ultimate, proximate and component analyses of corncob and its derived CHR are presented in Table 1. Ultimate analysis was performed on Eurovector EA3000 Elementar (Italy). Proximate analysis was tested according to Chinese National Standard Method of GBT212-2008. The chemical component analyses of corncob and CHR are carried out according to the procedure presented in Ref. [22]. From Table 1, it is observed that the CHR has lower oxygen content, higher lignin content and lower hemicellulose content compared with corncob.

### 2.2. Experimental apparatus and method

TG-FTIR instrument was coupled by a TG209F1 of NETZSCH

**Table 1**  
Ultimate, proximate, and component analysis of corncob and CHR.

	Corn cob	CHR
Ultimate analysis(wt%, daf)		
C	47.18	59.35
H	6.03	6.08
O	46.34	31.75
N	0.22	1.08
S	0.23	1.74
Proximate analysis (wt%, d)		
Volatiles	80.9	61.2
Fixed carbon	17.0	15.1
Ash	2.1	23.7
Component analysis (wt%,d)		
Hemicellulose	29.9	9.8
Cellulose	33.8	15.1
Lignin	30.7	42.7

(Germany) and a VERTEX70 FTIR spectrometer of BRUKER (Germany). About 5 mg sample was used and paved uniformly in an Al<sub>2</sub>O<sub>3</sub> ceramic crucible in each run. A thermocouple accurately detects the sample temperature through direct contact with the sample crucible. The final temperature of 700 °C and the heating rate of 10 °C/min were applied. N<sub>2</sub> was used as carrier gas in pyrolysis run while air was used as carrier gas in combustion run. The flow rate of carrier gas (N<sub>2</sub>/air) was maintained at 40 ml/min. The volatiles evolved from the sample during heating in TG were swept immediately to a gas cell through a stainless steel transfer line and then were detected by FTIR. To avoid the condensation of the volatiles, the stainless steel transfer line and gas cell were preheated to 220 °C. The resolution of 4 cm<sup>-1</sup>, spectrum scan frequency of 8 times per minute and the measurement range of 600–4000 cm<sup>-1</sup> were employed in FTIR test.

Py-GC/MS system consists of a PY-2020iD pyrolyzer of Frontier (Japan) and an Agilent 5890GC/5972MSD GC/MS (America). The temperature of the pyrolyzer was set at 550 °C. The chromatographic separation of the volatile products was performed using a Varian CP-Sil 24CB capillary quartz column (30 m × 0.25 mm, 0.25 μm). The column temperature program was set at 35 °C for 5 min, increased at a rate of 5 °C/min to 260 °C, and then kept at 260 °C for 15 min. He was used as carrier gas and its flow rate was maintained at 1.0 ml/min. The mass range of 40–550 *m/z* was chosen for the mass selective detector. The decomposition products were identified by means of the comparison between the experimental mass spectrum and the mass spectrum library attached to the Py-GC/MS apparatus. The identification of each volatile product can be confirmed if the qualification percentage reaches 85% and even higher.

## 3. Results and discussion

### 3.1. TG-FTIR analysis

#### 3.1.1. Pyrolysis of CHR

Fig. 1(a) shows the TG and DTG curve during pyrolysis of CHR at the heating rate of 10 °C/min. As presented in Fig. 1(a), three stages were observed in pyrolysis process of CHR. The first stage is from room temperature to about 200 °C. There are two visible DTG peaks in the first stage, the peak in the temperature range of 30–110 °C with a peak value at 57 °C and 1.79 wt% weight loss was due to the evaporation of absorbed water. The other peak is in the temperature range of 110–200 °C with a peak value at 157 °C and 2.44 wt% weight loss. Dehydration and decarboxylation occurs above 110 °C leading to the removal of oxygen as H<sub>2</sub>O and CO<sub>2</sub>. i.e., the break of lateral C–C bond produces CO<sub>2</sub>. At the same time, the cracking of aliphatic –OH groups in the lateral chains leads to the formation of H<sub>2</sub>O. The second stage in 200–500 °C, which belongs to fast thermal decomposition with 47.44 wt % total weight loss. A narrow and sharp DTG peak appeared in the temperature range of 200–500 °C, and the maximum weight loss rate reaches 8.5 wt%/min at 324 °C. The weight loss of the third stage, from 500 °C to about 700 °C, is 5.62 wt%, which is attributed to high temperature charring of the residue. Finally, CHR remains as a solid residue of about 42.16 wt% at 700 °C. These trends in mass loss are in good agreement with previous studies [9,19], suggesting that pyrolysis process of CHR, pine sawdust, dyestuff residue and etc. usually include three stages, namely moisture evaporation, thermal decomposition and charring of residue.

As a comparison, the TG and DTG curves of corncob pyrolysis are also presented in Fig. 1(b) which were performed on a Shimadzu DTG-60 (Japan). A noticeable difference is observed in the TG/DTG curves of corncob and its hydrolysis residue. The pyrolysis of corncob mainly occurs in 206–392 °C, and there are two distinct DTG peaks. These two distinct peaks centered at 301 °C and 335 °C can be attributed to the decomposition of hemicellulose and cellulose, respectively [23,24]. Lignin pyrolysis peak is not distinguishable, but the temperature interval of its decomposition occurs in a wide temperature range with a

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