Effect of Torrefaction Temperature on Biomass Pyrolysis Using TGA and Py-GC/MS

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Abstract—The effects of torrefaction on the pyrolysis of corn stalk were investigated using a thermogravimetric analyzer (TGA) and a pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). The results showed that with increasing torrefaction temperature, the volatile matter and oxygen content decreased, while the ash content and carbon content increased in torrefied corn stalk. The pyrolysis process of torrefied corn stalk can be divided into three stages. The first stage is from room temperature to 200°C, with little changes. The second stage occured between 200°C and 450°C. Because of the prior release of some volatile components by torrefaction, the total weight loss of torrefied corn stalk decreased with increasing torrefaction temperature. The third stage is the carbonization process above 450°C. With increased torrefaction temperature, the pyrolysis activation energy of corn stalk increases from 62.41 kJ/mol to 68.29 kJ/mol, and then decreases to 36.82 kJ/mol. Py-GC/MS analysis showed that the content of acetic acid in bio-oil reduced, while the content of many polycyclic aromatic compounds increased greatly, indicating that torrefaction could improve the quality of bio-oil.

Keywords-Biomass; Torrefaction; Bio-oil; Py-GC/MS; Pyrolysis

I. INTRODUCTION

Biomass utilization is getting increased attention. The low qualities of biomass, such as high oxygen content, high moisture content, strong hydrophilicity, low energy density, not easy to store, poor grinding, limited the further development of biomass technology [1-2]. As a result, biomass pretreatment is essential. As an effective method for biomass pretreatment, torrefaction is a thermochemical process conducted in the temperature range between 200 and 300°C under an inert atmosphere [3]. After torrefaction, and the moisture content and oxygen content of biomass are decreased [4]. Meanwhile, the energy density of biomass is improved, and the hydrophobicity is enhanced [5]. The fiber structure is damaged, and thus biomass becomes crispy [6]. Torrefaction of biomass has an important effect on the pyrolysis products of biomass [7-8]. Current research mainly focuses on the physicochemical properties of woody biomass. However, the reports of the torrefaction's effects on pyrolysis are limited. The third stage is the carbonization process above 450°C. Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) can rapidly and accurately distinguish the components of the pyrolysis products, which is an effective method for pyrolysis studying. The objectives of this paper were to study the effects of biomass stalk torrefaction on the pyrolysis using TGA and Py-GC/MS, and to provide basic data for biomass torrefaction.

II. EXPERIMENTAL

A. Materials

The corn stalk was screened into a particle size of 40–60 mesh, and then dried for 6 hours at 110°C. Proximate analysis of biomass was performed according to the D3172-07a standard. Ultimate analysis was carried out using an elemental analyzer (Vario macro cube, Elementar, Germany), and oxygen was estimated by the difference: O(%) =100% - C(%) - H(%) - N(%)- Ash(%). The heating value was measured in an adiabatic oxygen bomb calorimeter (XRY-1A, Changji Geological Instruments, China).

B. Torrefaction Methods

The torrefaction of biomass was performed using a fixed bed, as shown in Fig.1, which composed of a quartz tube, an electrical furnace, and an incondensable gas collection. The tube was pre-heated and stabilized at the required temperature (210, 240, 270 or 300 °C). Then the sample (5 g) was quickly placed in the center of the quartz tube. Pure N_2 (99.99%) was purged continuously to maintain an inert atmosphere. The torrefaction time was 30 min. After experiments, the solid products were collected for further analysis.

In this study, the corn stalk was denoted as CS. The torrefied corn stalk was denoted as TCS-X, with the "X" indicating the torrefaction temperature (in °C). For example, a run labelled TCS-270 corresponds to torrefaction of corn stalk carried out at 270 °C during 30 min.

The solid yield of the torrefied corn stalk is calculated from Equation 1.

$$Y_{mass} = \frac{M_{product}}{M_{feed}} \times 100\%$$

Where Y_{mass} is solid yield, and the subscripts "feed" and "product" stand for the raw corn stalk and torrefied corn stalk, respectively.

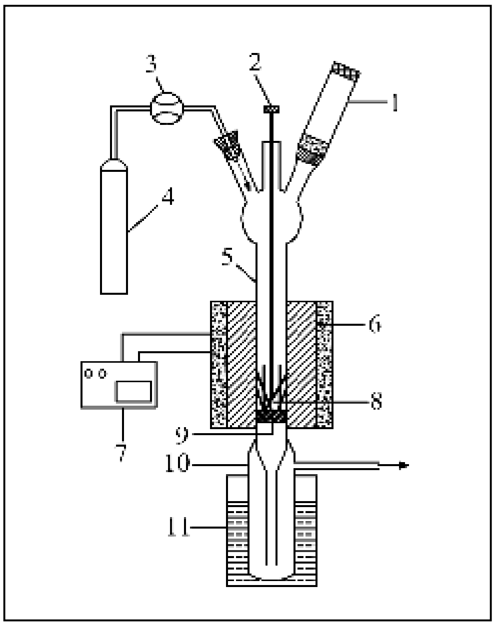


Figure 1. The lab-scale torrefaction device; (1) Feedstock container, (2) Thermocouple, (3) Flowmeter, (4) Nitrogen cylinder, (5) Quartz reactor, (6) Heating furnace, (7) Temperature controller, (8) Stainless wires, (9) Quartz wool, (10) Condenser, (11) Liquid nitrogen container

C. Py-GC/MS Analysis

A pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) system was used to separate and identify the volatile products of pyrolysis. This system is composed of a pyrolyzer (CDS 5250, Chemical Data Systems, USA) and a gas chromatography/mass spectrometer (Trace DSQ II, Thermo Scientific, USA).

The test parameters for pyrolyzer operation are as follows: sample mass, 0.5 mg; carrier gas, helium (99.999%) with a flow rate of 1 mL/min; pyrolysis temperature, 500°C; heating rate, 20°C/ms; holding time, 10 s. The parameters for GC/MS operation are as follows: injector temperature, 300°C; chromatographic separation, TR-5MS capillary column (30 m × 0.25 mm i.d., 0.25 µm film thickness); split ratio, 1:80; oven temperature, from 40°C (3 min) to 280°C (3 min), with a heating rate of 4°C/min; GC/MS interface temperature, 280°C; mass spectrometer, EI mode at 70 eV; mass spectra, from m/z 20 to 400 with a scan rate of 500 amu/s. Peak identification was carried out according to the NIST MS library and literature.

III. Results and Discussion

A. Effect of Torrefaction on Fuel Properties

The results of proximate analysis, ultimate analysis, and higher heating value (HHV) of dried and torrefied corn stalk are listed in Table 1 and Table 2. Torrefaction temperature has an important effect on the corn stalk. With increasing torrefaction temperature, the volatile matter gradually decreased. There is 74.34% of volatile in TCS-210, while there is 53.76% of volatile in TCS-290. After torrefaction, ash remained in the solid products, leading to an increase in the ash content of torrefied corn stalk. The fixed carbon content of torrefied corn stalk also increased with increasing torrefaction temperature. With increasing torrefaction temperature, the carbon content gradually increased, while the oxygen content considerably decreased. This was because moisture, CO_2, CO, and oxygen-containing carbohydrates were released during the torrefaction. The changes of carbon content and oxygen content leaded that heating value of corn stalk increased with increasing temperature.

TABLE I. PROXIMATE ANALYSIS AND HEATING VALUE OF CORN STALK

Sample	Proximate analysis (wt.%, db)			Heating value (MJ/kg)
	Volatiles	*Fixed carbon*	*Ash*	
CS	75.62	18.13	6.25	18.36
TCS-210	74.34	19.14	6.52	18.95
TCS-240	68.38	23.75	7.87	19.82
TCS-270	65.03	26.85	8.16	20.63
TCS-300	53.76	35.28	10.96	22.96

TABLE II. ULTIMATE ANALYSIS AND SOLID YIELDS OF CORN STALK

Sample	Ultimate analysis (wt.%, db)				Yields (wt.%)
	[C]	*[H]*	*[O]*	*[N]*	
CS	44.79	5.82	42.53	0.61	-
TCS-210	45.12	5.78	41.95	0.63	97.3
TCS-240	46.63	5.36	39.43	0.71	89.8
TCS-270	51.12	4.83	35.02	0.78	80.5
TCS-300	60.37	4.01	23.81	0.85	61.9

B. Thermogravimetric Analysis

The pyrolysis characteristics of dried and torrefied corn stalk at a heating rate of 10°C/min are shown in Fig. 2 and Fig. 3. It can be seen that the pyrolysis process can be divided into three stages. The first stage is from room temperature to 200°C, with little changes. The second stage occurs between 200°C and 450°C. Because of the prior release of some volatile components by torrefaction, the total weight loss of torrefied corn stalk decreases with increasing torrefaction temperature. Pyrolysis characteristics of TCS-300 are different from that of TCS-210, TCS-240, and TCS-270. The third stage is the carbonization process above 450°C.

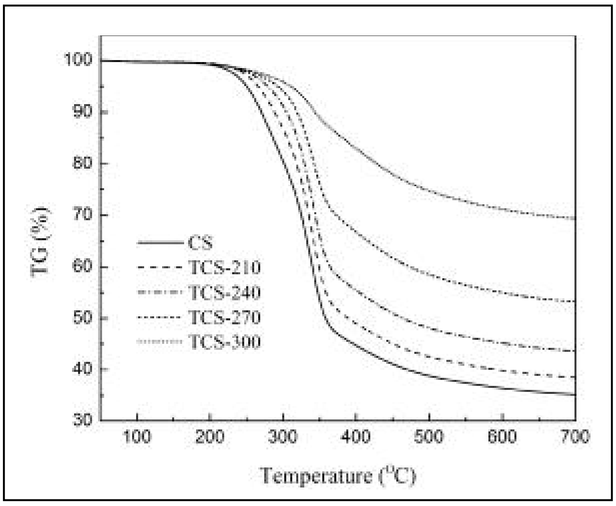
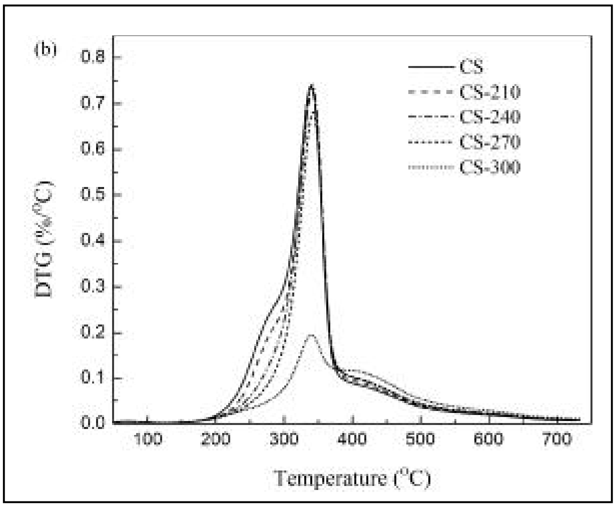


Figure 2. TG curves of corn stalk at the heating rate of 10 °C/min

Figure 3. DTG curves of corn stalk at the heating rate of 10 °C/min

C. Kinetics Analysis

The Coats–Redfern kinetic method is one of the most common models that used in kinetic analysis of biomass. The reaction equation of kinetics analysis can be described as:



$$\frac{\mathrm{d}a}{\mathrm{d}t} = A\exp(-\frac{E}{RT})(1-a)$$

where A is the pre-exponential factor, E is the activation energy, T is the temperature, and t is the time. a is the conversion rate of biomass, which can be calculated by

$$a = \frac{m_0 - m}{m_0 - m_\infty}$$

where m_0 is the initial mass of the sample, m is the sample mass at any time t, and m_∞ is the final mass after pyrolysis. According to the approximate expression of the Coats–Redfern method, Eq. (2) can be re-arranged and integrated as follows:

$$\ln\left[\frac{-\ln(1-a)}{T^2}\right] = \ln\left[\frac{AR}{bE}(1-\frac{2RT}{E})\right] - \frac{E}{RT}$$

where R is the universal gas constant and $\beta = \mathrm{d}T/\mathrm{d}t$ is the heating rate. For most temperature regions of biomass pyrolysis, $E/2RT >>1$, $(1\text{-}2RT/E) \approx 1$, so Eq. (4) can be simplified as:

$$\ln\left[\frac{-\ln(1-a)}{T^2}\right] = \ln\left[\frac{AR}{bE}\right] - \frac{E}{RT}$$

Thus, a plot of the left side of Eq. (5) versus $1/T$ should be a straight line with a slope $-E/R$ and an intercept of $\ln(AR/\beta E)$, from which E and A can be obtained.

Results of the kinetics analysis are listed in Table 3. With increased torrefaction temperature, the pyrolysis activation energy of corn stalk increases from 62.41 kJ/mol to 68.29 kJ/mol, and then decreases to 36.82 kJ/mol. The activation energy values of CS, TCS-210, TCS-240, TCS-270, and TCS-300 are similar. However, the activation energy value of TCS-300 is very low, which is unique compared to other materials. Figures 3 and 4 also show that the pyrolysis characteristics of TCS-300 are different from that of the other torrefied corn stalk samples. Previous studies have indicated that the thermal stability of the three components are lignin > cellulose > hemicelluloses [9-11]. The decomposition of biomass components directly lead to the pyrolysis property of biomass.

TABLE III. CALCULATION RESULTS OF COATS-REDFERN MODEL FOR CORN STALK

Sample	Heating rate/°C·min^{-1}	E/kJ·mol^{-1}	R^2
CS	10	62.41	0.9960
TCS-210	10	63.37	0.9943
TCS-240	10	68.29	0.9967
TCS-270	10	65.31	0.9912
TCS-300	10	36.82	0.9826

D. Effects of Torrefaction on Pyrolysis

The relative contents of typical compounds are shown in Table 4. The bio-oil has some acetic acid, furfural, hydroxy acetone, propionic acid, phenol substances. With increasing torrefaction temperature, the content of acetic acid in bio-oil gradually reduce, this is mainly because the hemicellulose were decomposed during torrefaction. It enhanced the corrosion resistance of bio-oil. With increasing torrefaction temperature, the furfural decrease first and then increased. For phenol substance, the content increases with the rise of temperature. This is mainly because the source of the phenol is lignin. The lignin breaks down slowly during torrefaction, leading its content increase in torrefied corn stalk.

TABLE IV. IDENTIFIED PYROLYTIC PRODUCTS FROM PYROLYSIS OF CORN STALK

No.	Compound	Yield, Percent of peak area (%)				
		CS	***TCS-210***	***TCS-240***	***TCS-270***	***TCS-300***
1	Acetic acid	39.82	35.27	30.41	25.65	13.19
2	Propanoic acid	5.63	4.85	4.01	3.26	1.53
3	2-Furanol, tetrahydro-	0.87	0.89	1.25	1.17	0.52
4	Furfural	5.23	6.96	3.82	2.97	1.34
5	2-Propanone, 1-hydroxy-	7.58	8.21	7.03	5.95	2.38
6	1-Hydroxy-2-butanone	0.36	0.41	1.35	1.26	0.29
7	Cyclopentanone	0.58	0.63	0.45	0.82	0.71
8	2-Propanone, 1-(acetyloxy)-	0.92	1.68	3.62	2.01	1.39
9	Phenol	2.63	2.89	3.34	4.05	6.28
10	Phenol, 2-methyl-	1.04	2.25	2.89	2.92	3.15
11	Phenol, 3-methyl-	2.12	2.03	2.23	0.65	0.27
12	Phenol, 2,4-dimethyl-	0.56	1.25	1.07	1.26	2.17
13	Phenol, 4-ethyl-	0.21	0.19	0.83	2.86	4.33
14	1,2-Benzenediol	5.26	6.21	4.05	5.63	7.29
15	1,2-Benzenediol, 4-methyl-	0.28	0.83	0.61	0.57	0.36

IV. CONCLUSIONS

Torrefaction has an important effect on pyrolysis of corn stalk. The results showed that with increasing torrefaction temperature, the volatile matter and oxygen content decreased, while the ash content and carbon content increased in torrefied corn stalk. The pyrolysis process of torrefied corn stalk can be divided into three stages. With increasing torrefaction temperature, the total weight loss of torrefied corn stalk decreases, which attributed to the prior release of some volatile components by torrefaction. With increased torrefaction temperature, the pyrolysis activation energy of corn stalk increases from 62.41 kJ/mol to 68.29 kJ/mol, and then decreases to 36.82 kJ/mol. Pyrolysis characteristics of TCS-300 are different from that of TCS-210, TCS-240, and TCS-270. The content of acetic acid in bio-oil reduced, while the content of many polycyclic aromatic compounds increases greatly.

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