The study of combustion characteristics of corn stalks and cobs via TGA-DTG-DSC analysis

X D Wang¹, J J Xue², Y J Zhu¹, C R Liu¹, X Y Hu², H Liang², and C Q Dong²,³

¹National energy biological power generation group corporation LTD, Beijing 100052, China
²National Engineering Laboratory for Biomass Power Generation Equipment, North China Electric Power University, Beijing 102206, China

Email: cqdong1@163.com

Abstract. To fully utilize the corn residuals, the combustion characteristics of corn stalks and corn cobs via TG-DTG-DSC (thermogravimetric-differential thermogravimetric-differential scanning calorimetry) were studied. The TGA, DTG and DSC curves are analysed and the combustible characteristics, burnout characteristics, comprehensive combustion characteristics are calculated to estimate the combustion characteristics of corn stalks and corn cobs. The results show the combustible ability of corn cobs is better than that of corn stalks. The ignition temperature of cobs is lower than that of stalks. The combustion rate of cobs is faster than that of stalks. However, the burnout characteristics of stalks are much better than that of cobs. The burnout temperature and time of stalks is higher and longer than that of cobs. The different combustion characteristic of stalks and cobs result from the difference of composition of stalks and cobs. The NIRS spectra also show the spectra of stalks and cobs are significantly different in the range of 1100-1300nm, where is the information of the C-H stretching vibration. In conclusion, it is better to co-combustion of corn stalks and cobs to improve the combustible and burnout characteristics, which will result in easier ignition and more stable combustion. The results of this study will provide guidance to the better utilization of biomass.

1. Introduction

Fully utilization of crop residual is one of the good way to solve crisis of energy and environment pollution. In China, about 2.73 hundred million tons of the corn residual are produced every year [1]. They are suitable for thermal utilization [2]. Usually, the corn stalks and cobs are gathered in different ways. The composition of stalks and cobs are different in the components content like semi-cellulose, ash and extractives [3-4].

Thermogravimetric analysis (TGA) was developed to determine the kinetic parameters from weight loss data and widely used to investigate the combustion and pyrolysis mechanisms of solid-phase decomposition reactions [5]. Differential scanning calorimetry (DSC) is a precious technique commonly used on fossil fuels undergoing combustion or pyrolysis, which records the temperature and heat flow associated with material transitions and gives quantitative and qualitative data on heating processes [6-7]. Near Infrared spectroscopy (NIRS) is a new way to analysis the corn residuals. It contains the composition information of the residuals, which has been a standard analysis method.
for International Organization for Standardization (ISO) and International Association of Analysts (AOAC) to analysis the residuals quantitative and qualitative [8-9].

In this study, the TGA, DTG and DSC curves of combustion of corn stalks and cobs were obtained. Afterward, the combustible characteristics, burnout characteristics, comprehensive combustion characteristics index were calculated for both of the corn stalks and cobs to estimate and compare the combustible ability of them.

2. Materials and methods

2.1. Samples

The whole corn residual is collected and dried in the nature. Then the corn stalks and cobs were divided into two parts. Then the stalks and cobs were grinded to be smaller enough to pass 80 mesh sieve, respectively. The powder sample will be put in the seal bag and put in the sample room.

2.2. TG

The PerkinElmer STA600 TGA (figure 1) was used in this study, which can record the TG, DTG and DSC curves of the combustion at the same time. Thermogravimetric analysis is a technology to measure the relationship between material mass and temperature under the control of temperature. The curve obtained by thermogravimetric analysis is called thermogravimetric curve (TG curve). Take the first derivative of TG curve with respect to temperature (or time) to get the rate curve of thermal weight loss (DTG curve). TG and DTG both describe mass change in the reaction process. However, both mass and energy change exist in the reaction. Specially, like crystal structure transformation and molten, some reaction only exist energy change. So the energy change also need to be examined to fully inspect a reaction process. Scanning calorimeter (DSC) curve can investigate the change of the sample in the process of reaction energy [10]. These three methods are commonly used in thermal analysis.

The air is the purge gas. The flow is 80 mL/min. The sample is heated from room temperature to 1073K at a heating rate of 10 K/min. The sample weight is about 10 mg.

Figure 1. PerkinElmer STA600 TGA

2.3. Collecting of NIRS spectra of corn stalks and cobs

The NIRS spectra of corn stalks and cobs were collected using the MicroNIR-1700 series by JDSU company. The spectra range is from 950 nm to 1650 nm. The sample window will be put on the surface of the sample when collecting the spectra.

2.4. Calculation of Combustible characteristics index
The combustible characteristics, burnout characteristics and comprehensive combustion characteristics of corn stalks and cobs are calculated as following.

2.4.1 Combustible characteristics. The combustible characteristics is considered as an enlarged reaction performance index, which mainly reflects the reaction ability of fuel in the early stage of combustion. The higher the combustible characteristics, the better the combustibility [11].

The combustible characteristics (Cr) index is calculated using function (1):

$$C_r = \frac{(dw/d\tau)_{\text{max}}}{T_i^2}$$

Where, \((dw/d\tau)_{\text{max}}\) is the maximum rate of combustion, \%/\text{min}; \(T_i\) is the ignition temperature, \text{K}; the ignition temperature is determined using the TG-DTG method [12-13].

2.4.2 Burnout characteristics

The ratio between the loss of weight corresponding to the ignition point and the combustible content on the TG curve is defined as the initial burnout rate \(f_1\), which reflects the influence of the relative volatile content on the ignition characteristics of the sample. The larger the \(f_1\), the better the combustibility of the sample. Sample of weightlessness from start to combustion 98\% combustible qualitative time defined as burnout time \(\tau_0\). At \(\tau_0\) moment, the sample weight loss and the ratio of combustible qualitative content in the sample is defined as the total burnout rate \(f\). The later burning rate of \(f_2 = f - f_1\), which reflects the burning performance of carbon in the samples that results from the amount and existence form of carbon in the sample. The greater \(f_2\), the better the burning performance of the sample.

The burnout characteristics is the index which take both ignition and combustion stability into consideration. The burnout characteristics is calculated using function (2):

$$C_b = \frac{f_1 \cdot f_2}{\tau_0}$$

Where \(f_1\) is the initial burnout rate, \%; \(f_2\) is the burn-off rate, \%; \(\tau_0\) is the burnout time, \text{min}. The detailed meaning of the parameters is shown in reference [12]. The bigger the \(C_b\), the better the burnout ability of the sample.

2.4.3 Comprehensive combustion characteristics

To describe the combustion characteristics of corn stalks and cobs comprehensively, the comprehensive combustion characteristic is used to reflex the ignition and burnout ability of the sample. For the slow heating combustion process, the initial combustion reaction can be considered as kinetic, that is, chemical kinetic factors control the reaction speed, and the combustion speed can be expressed by Arrhenius law approximately. After a series of transformations and arrangements, the comprehensive combustion characteristic is calculated using function (3):

$$S_N = \frac{(dw/d\tau)_{\text{mean}}(dw/d\tau)_{\text{mean}}}{T_i^2T_h}$$

Where \((dw/d\tau)_{\text{mean}}\) is the mean combustion rate, \%/\text{min}; \((dw/d\tau)_{\text{max}}\) is the max combustion rate, \%/\text{min}; \(\tau\) is the burnout time, \text{min}; \(T_i\) is the ignition temperature, \text{K}; \(T_h\) is the burn-out temperature, \text{K}; \((dw/d\tau)_{\text{mean}}/T_h\) is the ratio of average combustion velocity and burnout temperature of combustible substances. The higher its value is, the faster burnout is.

Combustion characteristic index \(S_N\) is a comprehensive characteristic index reflecting the ignition and burnout of biomass. The higher the value, the better the combustion characteristic.

3. Results and discussion

3.1. The NIRS spectra of corn stalks and cobs
The NIRS spectra of corn stalks and cobs are shown as figure 2. As figure 2 shown, the spectra of stalks and cobs are overlapped in the range of 1350-1650 nm, which is information of the stretching vibration of O-H and C-H of moisture, cellulose and starch molecular. It is the information of the same components of corn stalks and cobs [9].

The differences of the stalks and cobs are shown in the range of 1100-1300 nm, which is the information of stretching vibration of C-H and N-H. Stalks have significant peak in the range of 1100-1300 nm, while there is no peak in the range for the cobs. Stalks have more nitrogen [14]. Corn cobs have more hemicellulose and lignin [3, 15]. The cobs contains much less ashes [4].

![Figure 2. The yield and the heat value of bio-chars](image)

3.2. The mass loss and reaction rate of combustion of corn stalks and cobs

The TG and DTG curves of combustion of corn stalks and cobs were shown as figure 3. The detailed data of the combustion reaction are shown as table 1.

The combustion of corn stalks includes four stages. First, the TG curve drops slowly from room temperature till 250℃. Then the curve declines sharply till about 500℃. Meanwhile, several peaks appear in the DTG curve. Finally, the TG curve almost keeps stable from 500℃ till the end of the reaction (figure 3A). There are mainly three peaks in the DTG curve. The first peak is between 50-140 ℃, where the peak is at 78℃. It is the decomposition of the water and light volatile matter. The peak is small. The peak rate is only 0.45%/min, which means the content of water and light volatile matter is very low. The second peak is the main peak. It is in the range of 141-340℃ and the peak is at 306℃. It is mainly the decomposition and combustion of semi-cellulose. The peak rat is the maximum, which is 5.66 %/min. The third peak is much broader that other peaks, which is from 342℃ to 524℃. The peak is at 399℃. It is the decomposition and combustion of lignin. The peak rate is 1.64 %/min.

| Sample   | NO. | Beginning T/C | Ending T | Peak T | Peak rate |
|----------|-----|---------------|----------|--------|-----------|
| Corn Stalks | 1  | 50            | 140      | 78     | -0.45     |
|          | 2  | 141           | 340      | 306    | -5.66     |
|          | 3  | 341           | 524      | 399    | -1.64     |
|          | 4  | 525           | 800      |        |           |
Corn cobs

The combustion characteristics of corn cobs is different from that of stalks. The DTG curve of cobs have four peaks and the TG curves have five stages. In the first stage, the decomposition temperature is lower than that of stalks. But the peak rate is much higher. It suggests the content of light volatile matter is much more than that of stalks. For the decomposition of semi-cellulose and cellulose, there are three peaks for the cobs. The temperature range is narrower than that of stalks. It is because cobs contain more carbohydrate-based components. The last stage is the combustion of lignin [16-17]. Besides, the peak rates of cobs are all bigger than that of stalks.

3.3. The heat flow of corn stalks and cobs

The heat flow of corn stalks and cobs are shown as figure 4. For the stalks, there is only a broad Endo peak, which is consist with the combustion of semi-cellulose, cellulose and lignin. For the cobs, there are three Endo peaks. It is the similar shape as the DTG curve. It means the heat flow is from the combustion of the cobs. Interestingly, the second and third peak are almost the same high as the first one, which is different from the DTG curve. It means the components of the second and third peak produce more heat than the first one. Compared to stalks, the cobs produced much more heat. And the heat keeps stable from 250-500C. If co-combustion of stalks and cobs, the combustion will be more stable.
3.4. Combustible characteristics index

The combustible characteristics, burnout characteristics, comprehensive combustion characteristics are calculated using function 1-3 and shown as table 2.

From table 2, the combustible characteristics index of corn stalks is much bigger than that of cobs. It suggests the cobs is easy to be burned though the ignition temperature of them is without significant difference. The initial burnout rate (f1) means the mass loss ratio of the sample at the point of ignition point. The bigger the f1, the better the combustible characteristics of the sample. The f1 of cobs is bigger than that of stalks. The result of combustible characteristics index is consistent with f1.

The burn-off rate (f2) is the index of burnout ability of the carbon in the sample, which is related to the content and the existing form of the carbon. The bigger the burn-off rate, the better the burnout ability of the sample [12]. The f2 of the corn stalks is much bigger than that of cobs. Besides, the burnout time of corn stalks is also much longer than that of cobs. Similarly, the burnout time of corn stalks is much higher than that of cobs. However, the burnout characteristics (Cb) of corn stalks is smaller than that of cobs. It may result from the existing form of the carbon in the stalks and cobs are different from each other.

As a comprehensive index, the SN is used to estimate the fuel characteristics of the sample. Seen from table 2, the SN of cobs is much bigger than that of stalks. It is to say, for the corn residual, the cobs is better to be used as a fuel than stalks. The cobs are easy to be ignited. Both of the maximum and the average combustion reaction rate of cobs are bigger than that of stalks. But the combustion of cobs will end at a lower temperature. For the stable combustion, the stalks will help the cobs to continue with the combustion at higher temperature and hold for a long time.

**Table 2. Index of combustible characteristics, ignition characteristics and burnout characteristics**

| Sample       | Cr    | T_i/K | T_h/K | f1/% | f2/% |
|--------------|-------|-------|-------|------|------|
| Corn stalks  | 2.00E-07 | 533.14 | 887.85 | 12.13 | 85.87 |
| Corn cobs    | 3.12E-07 | 531.15 | 753.78 | 15.50 | 82.50 |

| Sample       | τ/min | Cb    | (dw/dt)_max | (dw/dt)_mean | SN     |
|--------------|-------|-------|--------------|--------------|--------|
| Corn stalks  | 28.29 | 3.68E-03 | 5.69         | 0.80         | 1.81E-12 |
| Corn cobs    | 22.38 | 5.72E-03 | 8.82         | 1.12         | 4.63E-12 |

**Figure 4. DSC curves of corn stalks and corn cobs**
4. Conclusion
The TGA, DTG and DSC curves are analysed and the combustible characteristics, burnout characteristics, comprehensive combustion characteristics are calculated to estimate the combustion characteristics of corn stalks and corn cobs. The results show the combustible ability of corn cobs is better than that of corn stalks. The ignition temperature of cobs is lower than that of stalks. The combustion rate of cobs is faster than that of stalks. However, the burnout characteristics of stalks are much better than that of cobs. The burnout temperature and time of stalks is higher and longer than that of cobs. The different combustion characteristic of stalks and cobs result from the difference of composition of stalks and cobs. The NIRS spectra also show the spectra of stalks and cobs are significantly different in the range of 1100-1300nm, where is the information of the C-H stretching vibration. In brief, it is better to co-combustion of corn stalks and cobs to improve the combustible and burnout characteristics, which will result in easier ignition and more stable combustion. Corn stalks and cobs are renewable, clean energy sources, which are cheap and have excellent fuel properties. Large-scale utilization of them can ensure energy supply and reduce carbon dioxide emissions at the same time. The parameters like ignition temperature and burnout temperature in this study provide basic reference data for the industrial operation process and equipment development of corn straw and corn cob. In addition, the combustible characteristics of corn straw and corn cob are good. Blending the corn straw and corn cob with coal can improve the ignition performance of coal and beneficial to the complete combustion of coal.

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