Study on pyrolysis and combustion characteristics of straw briquette fuel

Shuguang Liu 1,2, Jia Jiang 2, Xiaolong Chen 1, Bowen Xu 1 and Min Deng 1

1 School of Mechanical and Electrical Eng., Huangshan University, China;
2 Research and Development Center, Anhui Dorje Electric Co., Ltd., China
3 Email: Liushuguang@hsu.edu.cn

Abstract. Biomass is mainly composed of cellulose, hemicellulose and lignin. The content of each component has a great influence on the combustion of biomass. The combustion of biomass starts from its thermal decomposition. The main products of cellulose and hemicellulose are volatile components, while the main products of lignin are coke, and cellulose and hemicellulose are easier to decompose than lignin. Therefore, biomass combustion is a very complex process. In order to improve the quality of straw biomass fuels and pyrolysis with high efficiency, thermogravimetric-differential thermogravimetric (TG-DTG) technology was used to conduct thermogravimetric tests on agricultural straw fuels. The combustion characteristics, ignition characteristics, burnout characteristics and comprehensive combustion characteristics were investigated, and the combustion kinetics parameters were calculated.

1. Introduction

The crop straw occupies an extremely important position in China's agricultural and forestry biomass resources. Every year, the amount of straw collected in China is about 850 million tons, which is four times that of forest wood residues. Therefore, the crop straw is the most widely used biomass fuel in biomass combustion and power generation in China. However, low calorific value has always been an important reason for restricting the large-scale utilization of straw biomass. Especially when the carbon emission reduction capacity of biomass energy is analyzed according to the life cycle method, the energy consumption in the process of collection and transportation is larger than that of fossil fuels, and occupies a larger proportion in the whole life cycle utilization process. If not treated, the carbon emissions in this process cannot be ignored. In addition to improving the quality of biomass bulk fuel by means of physical and thermal conversion, [1] the utilization efficiency of biomass bulk fuel can be greatly improved by converting the abundant straw resources into straw briquette fuel. Straw briquette fuel is a biomass solid fuel with high density and high calorific value. It can also be used as biomass pyrolysis and gasification fuel to achieve efficient utilization of biomass fuels through crushing, drying, mechanical pressurization and other processes. [2] After extrusion, the density of straw raw material can reach 0.7~1.4g/cm³, and the energy density is equal to that of medium coal. The combustion performance of the formed fuel has also been greatly improved, and the combustion efficiency has increased from 10%~15% of straw direct combustion to 30%~40%. Our country also points out in the medium and long term plan of renewable energy that it plans to consume 500 million tons of biomass briquette fuel annually by 2020.[3]
Biomass pyrolysis is a process of transforming macromolecule organic matter into small molecule matter under the condition of isolating air, and it is one of the ways to utilize biomass energy efficiently. At present, a large number of studies on pyrolysis and gasification are focused on biomass monomers, such as straw, agricultural and forestry wastes, etc. There are few studies on briquette fuels. In order to promote biomass pyrolysis gasifier and improve the utilization of biomass resources, it is necessary to study the pyrolysis process and mechanism of biomass briquette fuel.

2. Materials and methods

2.1. Experimental materials
Rice Straw (RS) and Maize Straw (MS) were the most widely used biomass materials in rural areas. The coal samples were Fugu Coal (G) from Fugu, Shaanxi Province. The industrial analysis and elemental analysis of fuel are shown in Table 1.

| Sample | Ultimate analysis of fuels | Proximate analysis of fuels | HHV (MJ/kg) |
|--------|---------------------------|-----------------------------|-------------|
|        | M  | A   | V    | %    | C   | H   | O   | N   | S   |          |
| FG     | 7.29 | 17.64 | 58.65 | 4.91 | 23.14 | 46.34 | 25.61 | 63.94 | 2.97 | 3.64 | 0.85 | 0.55 | 24.26 |
| RS     | 6.56 | 7.49 | 69.15 | 4.91 | 23.14 | 46.34 | 25.61 | 63.94 | 2.97 | 3.64 | 0.85 | 0.55 | 14.11 |
| MS     | 6.56 | 7.49 | 69.15 | 4.91 | 23.14 | 46.34 | 25.61 | 63.94 | 2.97 | 3.64 | 0.85 | 0.55 | 16.26 |

2.2. Experimental equipment, sample preparation and test conditions
The STA409PC thermal analyzer of NETZSCH company was used in the experiment, which can carry out simultaneous thermal analysis of TG and DTG. The test samples were grinded by a coal mill and then separated by sieving. The test samples with particle size less than 200 mesh were obtained. The samples were then placed in a constant temperature drying box and dried at 105°C for 2 hours. The samples were taken out and cooled in a drying vessel and packed in a sealed bag for reserve.

Agricultural biomass combustion experiments were carried out with air atmosphere and gas flow rate of 80 mL/min. The heating rate was 20 K/min by non-isothermal method. The end temperature was 1173 K from room temperature. The mass of the test sample was about 10 mg.

2.3. Thermodynamic parameters of thermogravimetric analysis
The combustion process of different biomass is different. In order to compare the combustion characteristics of different samples more intuitively, the thermodynamic properties of biomass combustion can be characterized by a series of thermodynamic parameters. In order to facilitate comparative analysis, the abscissa of the TG/DTG curve is combustion temperature \( T \), and the longitudinal coordinate is the mass percentage of the actual weight \( W \) and initial mass \( m_0 \). The first derivative of the TG curve to the temperature is DTG curve, which is the weight loss rate of the sample in the unit of %/°C. The main thermodynamic characteristic parameters and their solutions are as follows: [4-5]

(1) Ignition temperature \( T_i \): Ignition temperature reflects the degree of difficulty of sample ignition. Generally speaking, the higher \( T_i \) is, the more difficult it is to ignite. It is an important characteristic point to measure the ignition characteristics of sample. Generally, the value \( T_i \) is determined by tangent method. As shown in Figure 1, the maximum weight loss rate \( \text{DTG}_{\text{max}} \) peak is perpendicular, and tangent is made at the intersection of the TG curve. The intersection of the tangent and the baseline is the corresponding ignition temperature.
(2) Maximum weightlessness rate $DTG_{\text{max}}$: The maximum weightlessness rate reflects the severity of sample reaction, which is the peak of severe weightlessness in $DTG$ curve. The larger the $DTG_{\text{max}}$ is, the more intense the reaction is. Generally, there are two weightlessness peaks in biomass combustion process. The first one is the combustion stage of sample volatile. Compared with coal, the volatile content in biomass is higher, corresponding to the fine $DTG_{\text{max}}$ peak. The second peak $DTG_{\text{max}}$ reflects the stage of fixed carbon combustion. The two maximum weightlessness rate peaks correspond to temperature $T_{1\text{max}}$ and $T_{2\text{max}}$, respectively.

(3) Burn-out temperature $T_h$: Burn-out temperature represents the temperature point at which the reaction of the sample is basically complete. As the temperature continues to rise, the sample no longer has significant weight loss change, and the $DTG$ curve is close to 0.

(4) Average weightlessness rate $DTG_{\text{mean}}$: represents the average weightlessness rate of the whole process from ignition to burnout. The more intense the whole combustion process, the greater the $DTG_{\text{mean}}$ value.

$$ DTG_{\text{mean}} = \frac{\alpha_{T_h} - \alpha_{T_i}}{T_h - T_i} $$

(1)

(5) Combustion characteristic index S: It reflects the ignition and burnout characteristics of the sample. It is an important parameter to indicate the combustion reaction. The larger the $S$ value, the more intense the combustion reaction is, and vice versa.

$$ S = \frac{DTG_{\text{max}} \times DTG_{\text{mean}}}{T_i^2 T_h} $$

(2)

3. Combustion dynamics analysis

3.1. Pyrolysis and combustion mechanism
The combustion mechanism of biomass requires the analysis of the thermal decomposition of volatile matter and the combustion of a small amount of porous coke formed by ignition combustion and volatilization analysis. The thermal decomposition of biomass is the first process that combustion must go through. Since biomass is mainly composed of cellulose, hemicellulose and lignin, the main components of hemicellulose and cellulose are volatile during pyrolysis, while the main products of lignin pyrolysis are carbon, a small amount of volatile matter and other substances, and the starting pyrolysis temperature of wood hemicellulose is $423 \sim 623K$, cellulose is $548 \sim 623K$, and lignin is $523 \sim 773K$ [6]. It can be seen that the ignition temperature range of volatile precipitation of each sample in this experiment is within the temperature range of hemicellulose and cellulose thermal decomposition indicated in literature [6]. The thermal decomposition process of biomass is a process...
of superposition and mixing. In the early stage of combustion, the main manifestation is the process of volatile matter precipitation ignition combustion, while in the later stage, the main manifestation is the process of coke formation and ignition combustion. Therefore, the analysis of biomass combustion mechanism needs to be carried out in stages.

At low temperatures, the volatile matter of biomass hemicellulose and cellulose will be ignited when the temperature and oxygen reach a certain level. The heat released from the combustion of volatile matter provides conditions for subsequent volatile matter to be released and ignited. At the same time, a small amount of porous coke will be formed after the volatile matter has been released. At this time, the temperature has not reached its ignition point. At the same time, the diffusion of oxygen to the coke surface is hindered by the volatilization analysis, so the primary manifestation is the precipitation of volatile matter and the fierce combustion reaction of ignition. At this stage, the ignition combustion occurs in the gas boundary layer around the porous particles formed after the volatilization analysis, which is the gas when the mixture of volatile matter and oxygen reaches a certain concentration and temperature. Phase ignition combustion, therefore, is a typical homogeneous ignition combustion model. The reaction rate is mainly determined by the rate and concentration of volatile matter. As the temperature continues to rise, the amount of coke produced by thermal decomposition of residual lignin is relatively small and spans a longer temperature range (time). The ash generated by combustion of a small amount of coke produced by thermal decomposition of cellulose in the preceding period wraps the residual lignin and hinders the contact between oxygen and coke. Although the temperature reaches the ignition point of coke, the burning rate is relatively low. The later stage of biomass combustion is mainly the slow combustion process of a small amount of coke. This stage is the multiphase reaction between solid coke and oxygen on the carbon surface. It belongs to the multiphase ignition combustion model [7]. The reaction speed mainly depends on the concentration of oxygen. Therefore, it is reasonable to study the kinetic parameters of biomass combustion process by stages.

3.2. Dynamic calculation method

The combustion process of straw is actually a pyrolysis reaction process. The simple heterogeneous pyrolysis reaction of solid fuel is generally expressed as:

$$A \text{ (solid)} \rightarrow B \text{ (solid)} + C \text{ (gas)}$$  \hspace{1cm} (3)

Where, $A$ is a solid reactant, which is decomposed into solid $B$ and volatile gas product $C$ by heating. Continuous introduction of weak air flow will bring the volatile gas products away in time, and the reaction is usually irreversible.

According to Arrhenius formula, the kinetic equation of matter is as follows: [8-9]

$$\frac{d\alpha}{dT} = K(T) f(\alpha) = A \frac{E}{R T} \alpha f(\alpha)$$  \hspace{1cm} (4)

Where, $\tau$ stands for time, min; $A$ is the pre-exponential factor, min$^{-1}$; $E$ is the activation energy, KJ/mol; $R$ is the general gas constant, 8.31J/(mol·K); $T$ is the absolute temperature, K; and $\alpha$ is the sample conversion rate, which is calculated as follows:

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty}$$  \hspace{1cm} (5)

$m_0$ is the initial mass of the sample, mg; $m$ is the mass of the sample at a certain time in the reaction process, mg; $m_\infty$ is the mass of the sample at the end of the reaction, mg. For non-homogeneous constant heating rate, the heating rate is constant, and equation (3) becomes

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \frac{E}{R T} \alpha f(\alpha)$$  \hspace{1cm} (6)

$f(\alpha)$ is a combustion kinetic model, which depends on the reaction type and mechanism. At present, the main methods of dynamic analysis are model-fitting method and model-free method. In this paper, the influence of forming pressure on combustion characteristics of biomass is mainly investigated. The
prefabricated model method is used to assume that $f(\alpha) = (1-\alpha)^n$ is the reaction model and $n$ is the reaction series. The $f(\alpha)$ is brought into the upper formula and the integral change of the upper formula is obtained by using the method.

$$G(\alpha) = \int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\beta} \int_0^\alpha e^{-\frac{E}{RT}d\alpha} = \frac{ART^2}{\beta E} \left(1 - \frac{2RE}{T}\right) e^{-\frac{ER}{T}}$$  \hspace{1cm} (7)

$G(\alpha)$ is an integral transformation function. Natural logarithms on both sides of the upper formula are obtained.

$$\ln \left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln \left[\frac{AR}{\beta E} \left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \hspace{1cm} (n = 1)$$  \hspace{1cm} (8)

$$\ln \left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \ln \left[\frac{AR}{\beta E} \left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \hspace{1cm} (n \neq 1)$$  \hspace{1cm} (9)

Normally, $\frac{E}{RT} \gg 1$, $1 - \frac{2RT}{E} \approx 1$, Eq. (8) and (9) are simplified as follows:

$$\ln \left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln \left[\frac{AR}{\beta E} - \frac{E}{RT}\right] \hspace{1cm} (n = 1)$$  \hspace{1cm} (10)

$$\ln \left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \ln \left[\frac{AR}{\beta E} - \frac{E}{RT}\right] \hspace{1cm} (n \neq 1)$$  \hspace{1cm} (11)

Let $y = \ln \left[\frac{-\ln(1-\alpha)}{T^2}\right] (n = 1)$ or $y = \ln \left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] (n \neq 1)$, $x = \frac{1}{T}$, $\alpha = -\frac{E}{RT}$, $b = \ln \left[\frac{AR}{\beta E}\right]$, then, the above formula can be converted to $y = ax + b$, and $y$ and $x$ can be linearly fitted by the values of thermogravimetric curves. The activation energy and pre-exponential factor can be calculated by slope $a$ and intercept $b$. In general, the kinetic calculation of biomass and coal combustion is $n=1$, but considering the diversity of biomass species, $n=0.33, 0.5, 0.67, 1, 1.25$ and 2, $[10, 11]$ the fitting range can be determined by linear correlation coefficient degree and optimal reaction series.

4. Analysis of combustion characteristics

The TG-DTG curves of the combustion of rice straw and corn straw briquette fuel prepared under different briquetting pressures are shown in Figure 2, and the heating rate is set at 20°C/min. It can be found from the figure that the combustion process of the two kinds of briquette fuels prepared under different pressure conditions is similar to that of powders, and there are two distinct weightlessness peaks. The main weightlessness temperature ranges from 200°C to 550°C, which are divided into four stages. The first stage corresponds to a slight drop in the TG curve near 100°C, which is due to the mass loss caused by the evaporation of most of the water in the briquette fuel and the overflow surface under the action of heat source, which is about 5%. The second stage corresponds to the first high and narrow mass loss peak in the temperature range of 200~400°C. It was found that severe combustion resulted in significant weightlessness. The third stage is the combustion of fixed carbon (400~550°C). Industrial analysis shows that the volatile content of biomass is much higher than that of fixed carbon, so the corresponding weight loss peak in this stage is shorter and wider than that in the first stage. The last stage is the burnout stage of briquette fuel, in which the fuel inner material is also basic. After burnout, the TG and DTG curves remained stable and almost unchanged. Although these four stages occur serially, there is no strict distinction between them in the whole combustion process, and the pyrolysis process of biomass usually lasts until the final stage of combustion because biomass itself contains a large amount of lignin which is difficult to pyrolysis.
To further compare the effects of forming pressure on the combustion characteristics of the two fuels, the combustion characteristics parameters obtained from the above thermodynamic analysis methods are listed in Table 2.

**Table 2.** Thermodynamic parameters of biomass combustion under different forming pressures.

| Sample | T_i(℃) | T_d(℃) | T_{1\text{max}}(℃) | DTG_{1\text{max}} (%/℃^-1) | T_{1\text{max}}(℃) | DTG_{1\text{max}} (%/℃^-1) | DTG_{mean} (%/℃^-1) | S \times 10^{-9} (/%2s^-1℃^-2) |
|--------|--------|--------|-----------------|---------------------|-----------------|---------------------|-----------------|------------------|
| MS     | 276    | 510    | 300             | -1.45               | 401             | -0.60               | 0.115           | 4.407            |
| MS-5MPa| 276    | 510    | 300             | -1.45               | 401             | -0.60               | 0.115           | 4.407            |
| MS-10MPa| 276  | 510    | 300             | -1.45               | 401             | -0.60               | 0.115           | 4.407            |
| MS-15MPa| 276  | 510    | 300             | -1.45               | 401             | -0.60               | 0.115           | 4.407            |
| RS     | 279    | 512    | 304             | -1.22               | 406             | -0.74               | 0.114           | 7.843            |
| RS-5MPa| 279    | 512    | 304             | -1.22               | 406             | -0.74               | 0.114           | 7.843            |
| RS-10MPa| 279  | 512    | 304             | -1.22               | 406             | -0.74               | 0.114           | 7.843            |
| RS-15MPa| 279  | 512    | 304             | -1.22               | 406             | -0.74               | 0.114           | 7.843            |
| RS-20MPa| 279  | 512    | 304             | -1.22               | 406             | -0.74               | 0.114           | 7.843            |

**Figure 2.** TG-DTG curves of corn stalk and cotton stalk combustion under different forming pressures.
Because the gradient of forming pressure is small, the variation range of characteristic parameters between the same raw materials with pressure is not obvious. However, in general, when the raw material is powder, it is easier to ignite. The higher the forming pressure and ignition temperature, the higher the maximum weight loss rate $DTG_{\text{max}}$ and the comprehensive combustion index $S$ are. The combustion mechanism of rice straw and maize straw after moulding belongs to static penetration diffusion combustion. Compared with powder, the combustion process has distinct inner and outer layers. Although the combustion process is similar in different stages, there are still differences in time and intensity. The initial volatilization rate slows down due to the tight structure, which increases the difficulty of ignition and the ignition point. This is also the main reason for the significant slowdown of the maximum combustion rate after moulding. After volatile combustion, the heat of fuel inner layer is transferred from the surface to the inside. With the increase of forming pressure, the remaining coke skeleton becomes more and more compact, which leads to the decrease of the intensity of fixed carbon combustion in this stage. Combining with the increase of ignition point in earlier stage, the comprehensive combustion characteristic index of briquette fuel decreases and the combustion performance deteriorates gradually. Compared with rice straw and maize straw, the comprehensive combustion characteristics of maize straw are better than rice straw, and the burnout rate is higher. The main reason is that the volatile content of corn stalk is higher than that of rice stalk and the ash content is lower.

According to Coats-Redfem method, the combustion weightlessness peak is fitted dynamically. According to the weightlessness characteristics of $DTG$ curve, the fitting results are shown in Figure 3. With the increase of forming pressure, the apparent activation energy of the second stage of combustion also shows an upward trend, that is, more heat is needed than powder to start combustion reaction, which shows that it has a higher ignition point after forming. As in the second stage, the energy required for fixed carbon combustion in the third stage increases with the increase of molding pressure. This is due to the heat transfer from outside to inside of the fuel inner layer after molding. The transfer rate is not as fast as that in the powder state, so more heat is needed to promote the fixed carbon combustion reaction in this stage.

![Figure 3. Fitting line of combustion dynamics under different forming pressure.](image)

By comparing the apparent activation energy of the two fuels, it was found that the corn stalk was lower than the rice stalk at each molding pressure, which was consistent with the thermogravimetric thermodynamic analysis results.

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