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Characteristics of Biomass Gasification in Flue Gas by Thermo–Gravimetry–Fourier Transform Infrared Spectrometer (TG –FTIR) Analysis

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Biomass renewable energy sources are widely applied to the process of power generation and heat production. In this paper, the effect of the different heating rate (20, 50, 70 °C/min) on the thermal weight loss process of peanut shell briquette is studied by TG-FTIR (Thermo–gravimetry–Fourier transform infrared spectrometer) method which the gasifying agent is selected by waste flue gas produced from pyrolysis gas combustion. The results show that the pre-pyrolysis water loss stage of peanut shell briquette is below 160 °C such thermal weight loss. The thermal oxidation reaction occurred at 160 - 750 °C for the pyrolysis stage. The coke gasification stage at 750 °C, the coke and CO_2 reduction reaction has CO precipitation under high temperature. The pyrolysis kinetics is investigated by Friedman method and DAEM (distributed activation energy model). When the conversion ratio is below 0.25, it is less than 170 kJ/mol of the activation energy. when the conversion ratio is 0.25 – 0.7, the activation energy ranges between 170 and 205 kJ/mol. The result is that the pyrolytic gaseous products are CO_2, CO, CH_4 and other low molecular hydrocarbons by FTIR method at real-time analysis. The CO_2 has the highest absorbance in pyrolytic gaseous products. At the same time, the absorption peak of CO occurred at 750 – 850 °C.

1. Introduction

At present, the one obstacle for sustainable development of the world is energy conservation. The carbon dioxide emission shows the growth of multiples with large utilization of fossil fuel (Cheng, 2009). The global greenhouse effect becomes more prominent, and the extreme weather and climate unbalance constantly happened in many areas. The environmental pollution and limited reserves of fossil energy, including oil and coal, are important problems. As the renewable energy, the biomass that be transformed into energy can reduce or even replace fossil energy (Purohit et al., 2006). The biomass can reduce and even replace the fossil energy. With the increasingly severe world energy crisis and enhanced awareness of energy conservation and environmental protection, biomass resources have drawn a lot of attention (Barontini et al., 2015).

As a kind of renewable resource, the biomass has the characteristics of low pollution and large storage capacity (Li et al., 2013). At present, the pyrolysis gasification technology is used in achieve the transformation and utilization of biomass energy. Chen et al. (2003) studied the factors affected biomass pyrolysis by small-sized test equipment. The smaller the heating rate is, the higher the pyrolysis temperature; the more the gas product is, the less the solid product. Minkova et al. (2000) investigated the pyrolysis and gasification of different biomass, including birch, sugarcane, straws and grass etcetera. The results showed that the volatilization of organic matter leads to more inorganic components of solid residue in the process of heat treatment. The pyrolysis products of three typical biomass crops (chaff, straw and corn cob) are analysed by Worasuwannamk et al. (2007). The result indicated that different content of cellulose, hemi-cellulose and xylogen in the biomass leads to a large difference in release rules of gaseous products during the pyrolysis process. Zhang et al. (2012) carried out a comparative analysis on pyrolysis characteristics of sawdust under N_2 and CO_2 and pointed out that the participant of CO_2 in the reaction is benefit to the gas emission in the pyrolysis products. At present, many scholars have carried out a large number of experiments and simulation

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studies on of biomass-pyrolysis gasification. Most of the studies were carried out using O_2, air, H_2O or O_2/H_2O mixture as gasifying agents. The results show that there are still some shortcomings in these studies, such as carbon residue high carbon content and low gasification efficiency.
In view of the above shortcomings, this paper proposed to make biomass pyrolysis gasification in the flue gas atmosphere (composed of N_2, CO_2, O_2 and other mixed gas). Using the waste flue gas and biomass undergoes pyrolysis gasification can improve the biomass pyrolysis conversion rate, which turn the biomass into high-quality clean energy or high value-added chemicals efficiently and reasonably. The application of TG-FTIR cannot only obtain the relationship between the weight loss and temperature of biomass thermal decomposition, but also used in detect the composition of gas products in real time. In recent years, TG - FTIR technology has been applied to the study of biomass pyrolysis gasification (Long et al., 2015). In this paper, the effect of the different heating rate (20, 50, 70 °C/min) on the thermal weight loss process of peanut shell is studied by TG-FTIR method.

2. Materials and experimental procedures

2.1 Samples

Select the common peanut shell briquette in North China as the experiment object, carry out corresponding pre-treatment such as smashing and drying, and then screen out 20 - 40 particles as the raw materials. Before the experiment, an analysis is carried out in the selected samples by using EA3000 organic element analyzer in accordance with the Method for Industrial Analysis on Solid Biofuel (GBT 28731-2012), and the analysis results are shown in Table 1.

Table 1: Proximate and ultimate analysis of feedstock

Ultimate analysis %					Proximate analysis %			
C_{daf}	H_{daf}	O_{daf}	N_{daf}	S_{daf}	M_{ad}	V_{ad}	A_{ad}	FC_{ad}
47.26	6.32	43.71	0.93	0.1	7.36	48.47	30.38	13.76

Daf = dry-ash-free; ad = air dried basis

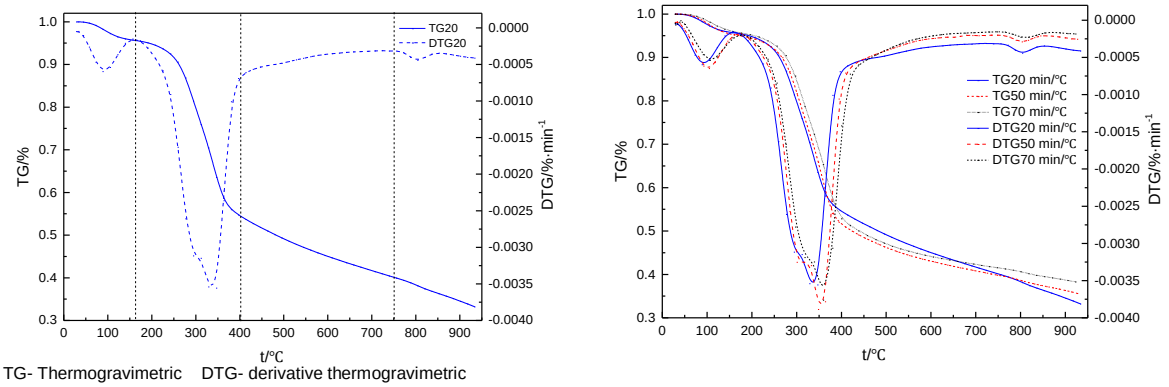
2.2 Experimental instrument and method

In this experiment, the low calorific value of gas produced by biomass pyrolysis gasification is used as the gasification agent. The simulation of flue gas composition is 80 % N_2, 15 %CO_2 and 5 % O_2. It is worth noting that due to there is difficult to provide water vapor under normal temperature during our experiment, so the small proportion of water vapor is incorporated into the proportion of CO_2.
The experiment carried out with a combined use of STA6000 simultaneous thermal analyzer manufactured by PerkinElmer and FTIR Spectrometer. In order to reduce the error arising from the experiment process and ensure accuracy of the experiment, each test takes samples of 6 to 7Mg into the alumina crucible. First, the gasifying agent can be into the experimental equipment ahead of time. So that it can avoid disturb of other factors in the equipment. The flow rate of carrier gas is set as 20.0 mL/min; keep the samples in the crucible for 1 min at a temperature of 30 °C. The samples are heated at the heating rate of 20, 50 and 75 °C/min, which the analysis temperature range is 30 – 900 °C. Blank test carried out during each experiment under the same conditions to eliminate the experimental error brought by equipment. During experiment, the gaseous product is connected with an infrared analyser through a thermal insulation pipeline (180 °C) to detect the component of gaseous product in real time.

3. Results and discussion

3.1 Gasification weight loss

The samples are divided into 4 stages according to temperature rise during the gasification and pyrolysis. For example, Figure 1(a) is the gasification and pyrolysis curve when the heating rate is 20 °C/min.
The first stage is below 160 °C, mainly for the evaporation of water. The second stage is between 160 °C and 400 °C, the cellulose, hemi-cellulose and a small amount of lignin in the straw briquette are decomposed under the heating condition, which is the main weight loss stage. The third stage is between 400 °C and 750 °C, which is the process of carbonization and the decomposition of lignin. During this stage, deep volatile components are diffused outwards slowly, the time of duration is longer and the residues include ash content and multirole fixed carbon. The fourth stage is the gasification process above 750 °C. Under high temperature, the oxygen and CO_2 in flue gas react with coke to produce CO. There is an obvious weight loss peak in the decreasing of sample content.



TG- Thermogravimetric DTG- derivative thermogravimetric

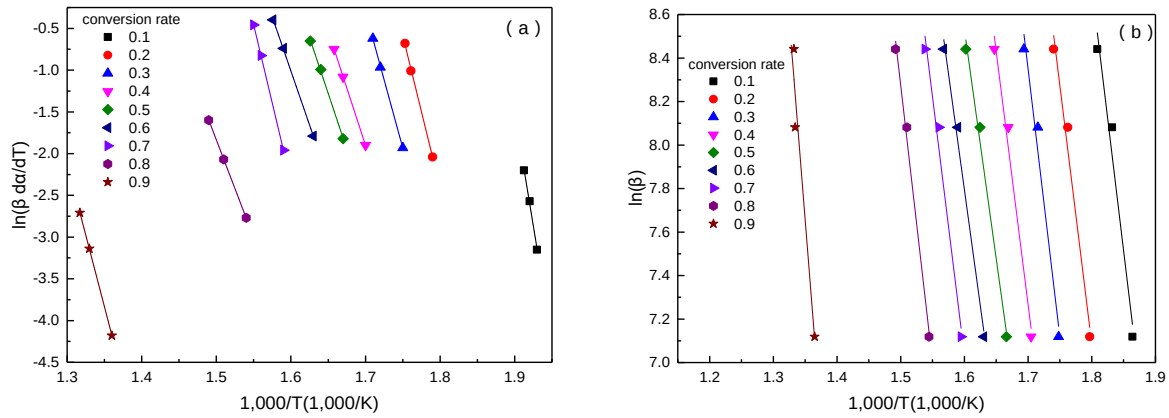
Figure 1: TG/DTG curves of straw: (a) Curves of Gasification Pyrolysis in 20 °C/min, (b) Weight loss Curves of Gasification Pyrolysis under Different Heating Rate

3.2 Effect of heating rate on gasification process

The heating rate has complex influence on the gasification and pyrolysis. Figure 1(b) is the TG-DTG curve of sample under 20 °C/min, 50 °C/min and 70 °C/min heating rate. The experimental results show that the influence of heating rate on the gasification and pyrolysis process is very evident. With the increase of heating rate, the reaction time required for pyrolysis of the sample particle becomes short, which is beneficial to the pyrolysis. The initial temperature of pyrolysis T_s and the temperature of weight loss peak T_{max} would be higher. However, the temperature difference between inside and outside of sample may be affected by the excess of heating rate, forming the temperature gradient and causing the thermal lag to affect the internal pyrolysis. In this experiment, the heating rate has evident influence on the percent of solid-state residue. The larger the heating rate, the higher the percent of solid-state residue. It mainly has great influence on the carbon content in residue. The heating transfer rate and diffusion rate of pyrolysis product of sample is relatively low.

3.3 Pyrolysis kinetic analysis

As can be seen from Figure 2, the linear regression line at the same conversion rate α is nearly parallel under different heating rate β. The following conclusions can be drawn from Figure 2. The average activation energy solved by Friedman method is 192.91 kJ/mol. The average activation energy solved by DAEM method is 183.67 kJ/mol. The difference among the results of these two methods is small. The linear correlation coefficient of Friedman method and DAEM method is very high. R^2 (Correlation coefficient) is above 0.99, which shows the reliability of method. The activation energy declines slowly with the reaction of pyrolysis after the conversion rate α reaches 0.7. The reason of this weak downward trend is that the rate of volatiles generation and escape is increasing with the increase of temperature, which makes the activation energy decreases. The activation energy increases rapidly after the conversion rates α reaches 0.8. At this time, the corresponding gasification and pyrolysis temperature is about 800 °C.



T-temperature K- Kelvin

Figure 2: The plots of methods according to (a) Friedman method, (b) DAEM

Biomass pyrolysis is a very complex thermal chemical reaction process (Bach and Chen, 2017). The advantage of simple one-order kinetic model lies in the simple calculation, so it is not necessary to calculate for temperature function. However, due to hypothesis reaction, the error of one-order reaction is increased (Nyakumaf et al., 2015). The multiple scanning rate method could avoid the influence of kinetic compensation effect in solving kinetics (Cai et al., 2007). The Friedman method and distributed activation energy model is used in this paper. According to the thermogravimetric curves in different heating rates (20 °C/min, 50 °C/min, 70 °C/min), the pyrolysis kinetic parameters of the samples were obtained under the atmosphere of flue gas.

3.4 Generation characteristic of pyrolysis gaseous product

Some small molecular products and some pyrolysis products with evident and particular functional groups are released in the pyrolysis process of raw materials. According to the changes of relative content of these pyrolysis products over time, the possible reaction in pyrolysis process could be predicted and the reaction mechanism of pyrolysis and co-pyrolysis process could be further understood. The infrared spectrum of these small modular gaseous products is relatively simple. The infrared spectra of these products can be obtained from infrared spectroscopy when these products exist individually. Some characteristic functional groups were selected to represent the product and then to analyze the infrared spectrum of the mixed components of the pyrolysis products.

Table 2: Activation energy results solved by Friedman method and DAEM

α	Friedman method		DAEM	
	E(kJ/mol)	R^2	E(kJ/mol)	R^2
0.05	186	0.98583	181	0.98967
0.10	188	0.98916	184	0.98912
0.20	207	0.99342	188	0.99017
0.30	204	0.99559	195	0.99239
0.40	170	0.99235	184	0.99452
0.50	175	0.99398	167	0.99624
0.60	189	0.98475	168	0.99667
0.70	225	0.98536	202	0.99605
0.80	183	0.98772	185	0.99329
0.90	275	0.98743	250	0.99030

Figure 3(a) is the three-dimensional infrared spectrum of pyrolysis product. It can be seen that the overall distribution of the main pyrolysis products and the general trend with time. The absorption peaks in the spectrum are numerous, which reflects the complexity of the product. The change regulation of characteristic peaks can be obtained through syncopating the three-dimensional infrared spectra of pyrolysis products. Then we can get the change trend of the corresponding pyrolysis product with the temperature increase. In the flue gas atmosphere, the change curve of the infrared absorption strength of sample gasification product over time has better corresponding relationship with DTG curve. The corresponding infrared spectrum is shown as Figure 4.

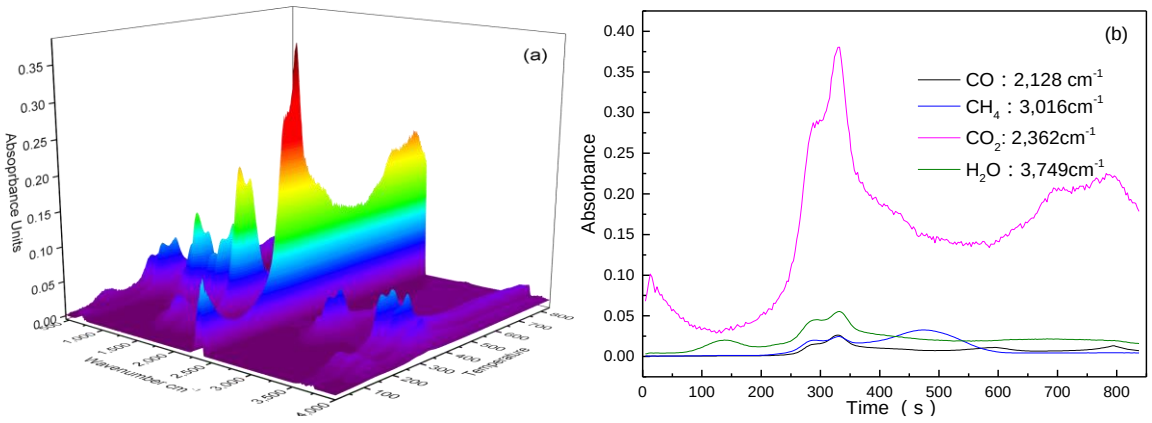


Figure 3: TG-FTIR analysis of evolved gases from the pyrolysis of straw at 70 °C/min (a) FTIR analysis of evolved gases (b) The evolved gases

According to Lambert-Beer's law, the absorbance is proportional to the concentration of the absorbing material and the thickness of the absorbing layer when a bunch of parallel monochromatic light passes through a uniform non-scattering light absorbing material vertically (Li, 2015). In the FTIR analysis, the product concentration is obtained by comparing the absorption intensity with the standard sample. However, the complexity of biomass pyrolysis product has great interference on the quantitative analysis. In our experiment we draw the concentration change curve of four main products H_2O, CO_2, CO, CH_4, see Figure 3(b). Hemi-cellulose pyrolysis occurred at around 314°C. Scission chain occurs for C-C and C-O. Cellulose degradation occurs at 366 °C, where C = O breaks. While at 803 °C, CO_2 is generated from the reaction of xylogen degradation with C and O at the same time. The concentration of CO_2 increases evidently, which corresponds to the CO_2 absorption concentration curve in Figure 3(b). CO_2 is significantly higher than the precipitation of other products at 404 °C precipitation content reached its maximum. CO is mainly generated from the pyrolysis of hemi-cellulose and second reaction of carbon dioxide. In Figure 6, the coke in the interval of rapid increase of concentration has redox reaction with the oxygen and CO_2 in atmosphere and generates CO, which requires that the reaction temperature reach above 800 °C. The weightlessness peak really corresponds to a particular pyrolysis reaction at around 800 °C. According to the variation of the concentration of products, it can be concluded that the product corresponding to the weightlessness peak is CO.

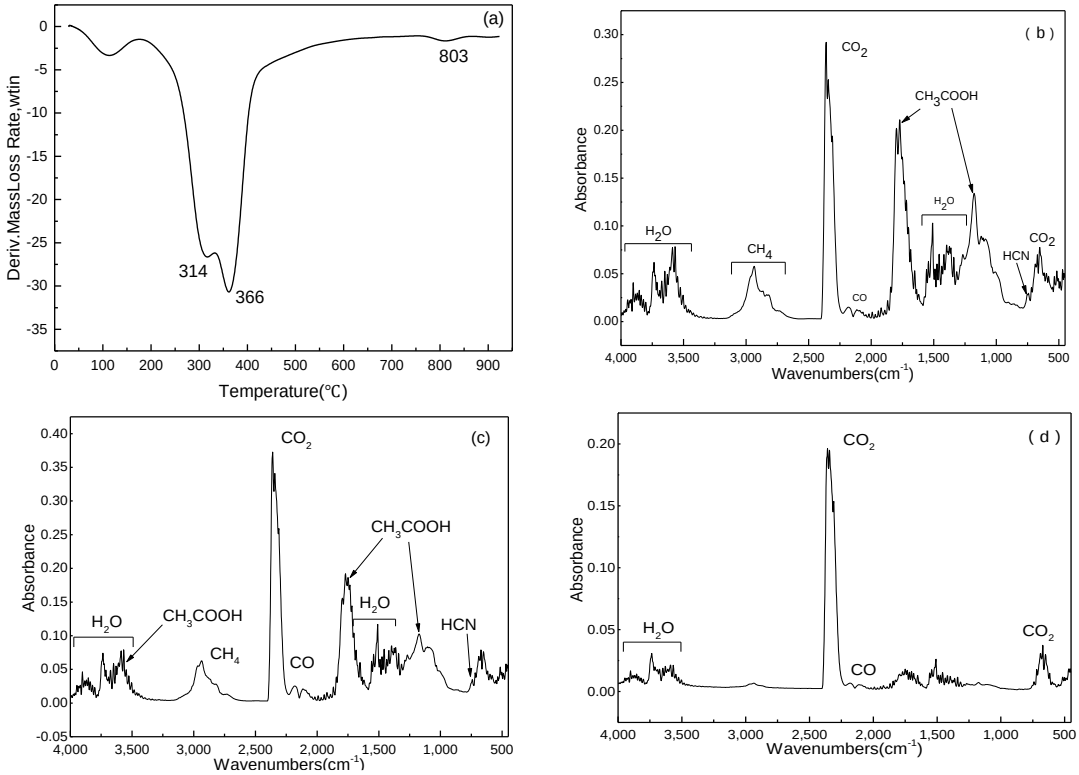


Figure 4: The FTIR spectra of straw pyrolysis: (a) DTG curve of straw at 70 °C/min, (b) IR spectra at 314 °C, (c) IR spectra at 366 °C, and (d) IR spectra at 803 °C

4. Conclusions

In view of the shortcomings of biomass-pyrolysis gasification technology, such as high tar content and low gasification efficiency, a new process is put forward. The gasification efficiency of the sample was improved by using the mixture of flue gas (N_2, CO_2 and O_2) as the carrier gas of pyrolysis. At the same time, the waste gas is recycled to achieve the effect of energy saving and emission reduction. The pyrolysis weight loss characteristic and product generation characteristic of peanut shell briquetting under flue gas atmosphere is studied by adopting TG-FTIR combination analysis method. The gasification peanut shell briquetting can be divided into four stages: dewatering stage below 160 °C, biomass pyrolysis volatilization stage between 160 °C and 400 °C and the carbonization stage between 440 °C and 750 °C as well as gasification reaction above 750 °C. The pyrolysis kinetics is studied by Friedman method and distributed activation energy model. When the conversion rate is lower than 0.25, the activation energy is lower than 170 kJ/mol. The pyrolysis

gasification characteristics of biomass were analyzed by TG-FTIR method in flue gas atmosphere, which provided a theoretical basis for biomass pyrolysis research.

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