Korean J. Chem. Eng., 35(2), 511-517 (2018)
DOI: 10.1007/s11814-017-0298-4

pISSN: 0256-1115
eISSN: 1975-7220

Characteristics and kinetics analyses of different genus biomass pyrolysis

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(*Received 2 June 2017 • accepted 18 October 2017*)

Abstract−Four kinds of biomass (Chinese silvergrass, corn stalk, rice husk and pine) in China were selected as experimental samples for this study. Pyrolysis process of these biomass was researched by thermogravimetric Fourier transform infrared spectroscopy at 10 K/min. The results show that the pyrolysis process of all samples can be divided into three stages, and the comprehensive characteristics of volatile release degree of Chinese silvergrass is the highest, followed by corn stalk and rice husk, the lowest is pine. FTIR spectra results indicate that the pyrolysis gaseous products are mainly CO_2, CO, CH_4 and H_2O. Kinetic parameters of the biomass were analyzed and determined by Coats-Redfern method, and the results show that corn stalk is the most susceptible to pyrolysis because the activation energy of Chinese silvergrass, corn stalk, rice husk and pine are 46.7, 29.3, 54.3 and 58.1 kJ/mol respectively.

Keywords: Pyrolysis, TG-FTIR, Biomass, Coats-redfern Method, Kinetic Analysis

INTRODUCTION

Biomass, which is just renewable energy that can be converted into three kinds of energy sources of gas, liquid and solid, has attracted worldwide attention. High efficient utilization of biomass energy has been placed in the important position of high technology research and development in the adjustment of national energy development strategy. Therefore, efficient utilization of biomass energy is an important subject of modern energy production and consumption [1]. There are abundant kinds of biomass resources in China. Biomass energy can be divided into the following four categories: agriculture, forestry, herbs and aquatic biomass [2]. Pyrolysis is not only one of the most efficient methods for converting biomass into valuable chemicals and fuels, but also the basis for thermochemical conversion processes.

Wang et al. [3] researched three kinds agricultural biomass of cotton stalk, corn stalk and corn cob by TG-FTIR, and the results showed that the thermal stability of the three kinds of experimental samples was in descending order. Deng et al. [4] studied the effect of heating rate on pyrolysis products of eucalyptus by TG-FTIR, and the research showed that the release of CO_2 and the concentration of C=O functional groups were concentrated in a high temperature zone when the heating rate was 30 °C/min. However, CO, H_2O and small molecular alkyl were hardly affected by heating rate [5]. For herbaceous biomass, Fu et al. [6] used thermogravimetry analysis to study Chinese silvergrass, reed and Chinese pennisetum, which were compared with the study results of rice husk. The results showed that the stability of Chinese silvergrass was the worst among them, and the stability of reed was the best. Chen et al. [7] studied pyrolysis characteristics and pyrolysis kinetics characteristics of five kinds of biomass (sawdust, fern stems, wheat stalk, sugar cane and jute), and found that pyrolysis of these biomasses can be divided into three pyrolysis stages: hemicellulose, cellulose and lignin pyrolysis; and the kinetic parameters calculated by DEAM model had good fitting quality and fast convergence speed. Wang et al. [8,9] and Zhao et al. [10,11] made thermogravimetric experiments on algae and terrestrial biomass, and their results showed that the apparent activation energy and thermal stability of algae were lower than that of terrestrial biomass; and the algae was easy to decompose, which may because algae contain a large number of extracts and little cellulose. Abdelouaned et al. [12] studied two kinds of biomass (beechwood and flax shives) and the volatile removal performance of their main components (cellulose, hemicellulose and lignin) in an inert atmosphere using thermogravimetric analyzer. Results showed that the Kissinger method was suitable for determining kinetic parameters of pure compounds. Bach et al. [13] studied the pyrolysis kinetics of microalgae biomass using seven reaction kinetics models. The results showed that the single-, two- and three-reaction models could not well adapt to the peaks and shoulders. The four-reaction models were satisfactory, but they could not accurately predict thermal degradation around the shoulder and small peaks. The seven-reaction models had high fitting accuracy when the thermal degradation of carbohydrates and proteins was divided into two stages.

The biomass pyrolysis characteristics and kinetics parameters have been widely studied by foreign [14-16,] and domestic scholars [17-19], but the comparative study of agricultural, forest and herbs biomass is scant. It is important to study the similarities and differences of pyrolysis mechanism of different genus biomass. The study results are useful to provide a theoretical basis and technical guidance for the development of herbaceous biomass utilization equipment by analyzing the existing corn stalk utilization equipment. We researched Chinese silvergrass of herbs, pine of forestry, corn stalk and rice husk of agriculture through TG-FTIR experiments. The pyrolysis characteristics of four samples and the release characteristics of the gas products were studied, and the kinetics of

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four kinds of samples were analyzed by Coats-Redfern method [20].

EXPERIMENTAL

1. Materials

Chinese silvergrass, corn stalk, rice husk and pine were selected to be researched in this study. These samples were dried and ground into powder with size less than a hole in 0.074 mm, so as to eliminate the influence of particle size on reaction. These samples were kept in airtight bins before the thermogravimetric testing. Proximate analysis and ultimate analysis of the samples are shown in Table 1.

2. TG-FTIR Experiment

NETZSCH STA449 thermal analyzer (TG) and Fourier transform infrared spectroscopy (FTIR) were used to study the pyrolysis process of the samples. The TG analyzer was connected with FTIR through an insulation pipe in the TG-FTIR experiment, so that the pyrolysis gas in TG could flow into FTIR where the gas product in the pyrolysis process could be measured.

The samples were placed in a dry oven and dried at 105 °C for 12 hours before the TG-FTIR experiment. About 10 mg samples were used in TG-FTIR experiment. Non-isothermal method was used in the experiment, and the experimental gas was high purity nitrogen with purity 99.999% and flow of 40 ml/min. The samples were heated from room temperature to 900 °C with a heating rate of 10 K/min, and then the samples were kept at the constant temperature of 900 °C for 10 minutes. The type of Fourier transform infrared spectroscopy was Nicolet iS10 analyzer produced by Thermo Scientific, and the analyzer had a scan number of 10 cm^{-1}, a resolution of 4 cm^{-1}, and a wave number range of 400-4,000 cm^{-1}.

Table 1. Proximate analysis and ultimate analysis of studied biomass samples (wt% on air dry basis)

		Chinese silvergrass	Corn stalk	Rice husk	Pine
Proximate analysis	Moisture	11.17	12.28	5.78	5.58
	Volatiles	64.78	65.97	65.89	63.85
	Fixed carbon	18.75	15.19	19.32	22.62
	Ashes	5.30	6.56	9.01	7.95
Ultimate analysis	C	42.11	41.60	47.51	40.62
	H	5.90	6.03	6.21	5.44
	O	34.37	31.17	28.76	39.43
	N	0.22	1.35	0.99	0.06
	S	0.09	0.16	0.91	0.10
HHVa (MJ/kg)		12.98	12.70	15.23	11.55

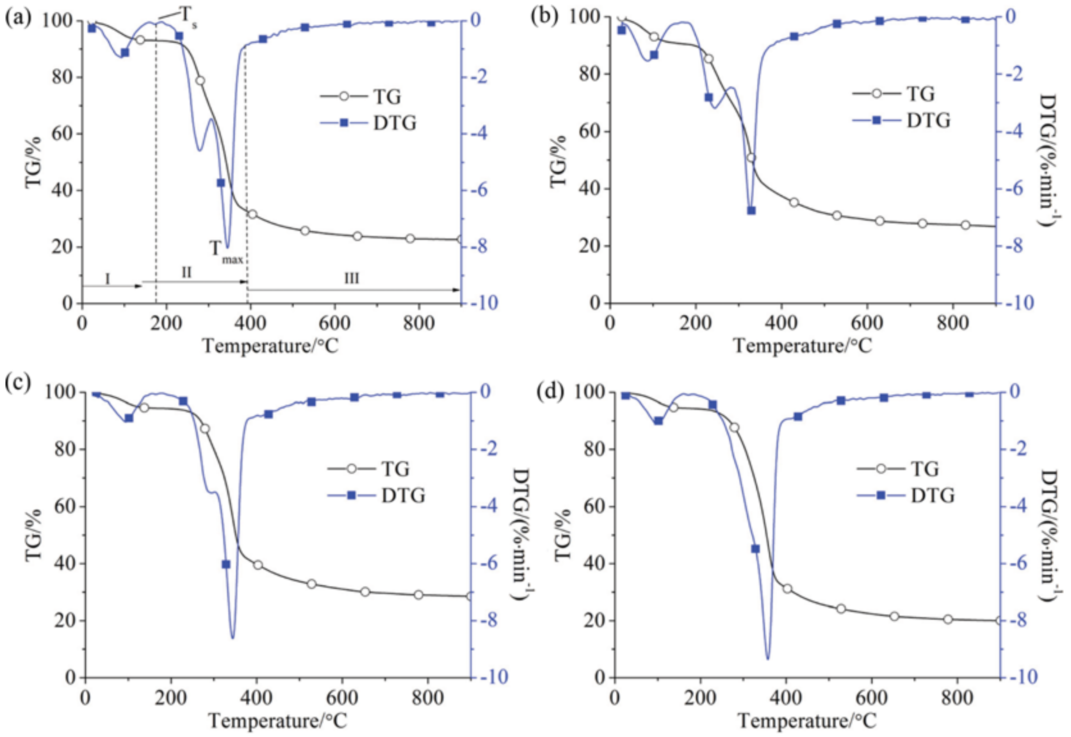

Fig. 1. TG and DTG curves of 4 samples at heating rate of 10 K/min. (a) Chinese silvergrass, (b) corn stalk, (c) rice husk, (d) pine.

All experiments were repeated three times to avoid errors.

RESULTS AND DISCUSSION

1. TG/DTG Analysis

The TG and DTG curves of the pyrolysis of four samples at the heating rate of 10 K/min are shown in Fig. 1. It can be seen that the pyrolysis process of four samples can be divided into three stages. The first stage (I) is the water loss drying stage (<158 °C), and only slight weight loss occurs at this stage. There is a small sample peak, the temperature of the weight loss peak is about 94 °C, which is due to the intrinsic combined water precipitation of the samples. The second stage (II) includes the volatile matter precipitation stage (158-410 °C) and the main pyrolysis stage. In the second stage, the maximum rate of weight loss reaches the maximum at 344 °C, which means that a large amount of volatile gas is produced due to the rapid decomposition of hemicellulose and cellulose components in the pyrolysis process. At the same time, the DTG curve shows a relatively smaller peak at about 275 °C except pine, which is due to the different pyrolysis rates of cellulose and hemicellulose. The research shows that the pyrolysis of the three components has two peaks in the curve of this stage in the pyrolysis process of Chinese silvergrass, corn stalk and rice husk, which is consistent with the results of Fu et al. [6]. The third stage (III) is the carbonization stage (410-900 °C), wherein carbon and ash are mainly produced. The curve in the third stage is gradually close to a straight line along with the process of reaction, and the weight loss rate is almost unchanged after 600 °C. Compared to cellulose and hemicellulose [18], lignin has a wider pyrolysis temperature range (generally from 150 to 900 °C). Therefore, the third stage is mainly pyrolysis process of lignin, which produces more coke, and the weight loss rate is gradually decreased in the third stage until the end of the reaction.

Fig. 1(a), 1(b) and 1(c) all have shoulder peaks; among them, the shoulder peak of Chinese silvergrass is obvious, mainly between 265-304 °C, the shoulder peaks of corn stalk and rice husk presenting slightly wavy, between 270-299 and 279-303 °C, respectively. But the DTG curve of pine shows fairly smooth, and it has no shoulder peaks; this may be due to an inconsistent distribution of the components of the four samples; the hemicellulose decomposition peak of pine is covered by the pyrolysis peak of cellulose [21]. Raveendran [22] found that hemicellulose is the easiest pyrolysis, followed by cellulose, lignin is the most difficult. Fu et al. [6] found in a study of several kinds of biomass pyrolysis, when the heating rate is low, the sample pyrolysis may appear two DTG peaks, and whether there is separation of the DTG peaks depends on the relative content of cellulose and hemicellulose in samples. The results [23] show that the greater the hemicellulose content of samples, the more significant the shoulder peak size; therefore, the hemicellulose content of Chinese silvergrass is higher. Table 2 is the pyrolysis parameters of four samples. This paper selects the index D of comprehensive characteristics of volatile release degree of biomass proposed in the literature [6,24,25]; it is defined as $D=\frac{(dw/dt)_{max}\cdot(dw/dt)_{mean}\cdot V_\infty}{T_S\cdot T_{max}\cdot\Delta T_{1/2}}$. The calculation shows that the lower the T_S, the much easier for the precipitate of the volatile matter, the greater the maximum weight loss rate of volatiles, the faster the speed to reach T_{max}, the lower the T_{max}, the sooner the peak released by volatile occurs, the more favorable for pyrolysis of biomass. As shown in Table 2, for agricultural and herbal biomass, the initial precipitation temperature of the volatiles of herbal biomass Chinese silvergrass is the highest, followed by corn stalks and the lowest is the rice husk, but the pyrolysis weight loss rate for the three samples in ascending order is Chinese silvergrass> corn stalks>rice husk; this is because of the higher hemicellulose content in Chinese silvergrass, so the volatiles release index of Chinese silvergrass is the highest, followed by corn stalk and rice husk. As the forestry biomass pine has a high content of lignin, and the pyrolysis range of lignin is broad, for 160-900 °C, so the DTG curve of pine is shifted to the high temperature zone, and the half width widened, resulting in the release of volatile pyrolysis characteristic index is low.

2. FTIR Analysis

2-1. Pyrolysis Characteristics of Biomass at Different Pyrolysis Stage

It is known from TG/DTG analysis that the pyrolysis process of biomass includes three stages, and the degree of reaction and reaction products is different along with the increase of temperature in each stage. Fig. 2 shows the FTIR spectra of different biomass in different pyrolysis stages; the infrared absorption peaks of the pyrolysis products of the four samples were analyzed by reference to the previous literature [26-28].

Fig. 2(a) indicates FTIR spectra of pyrolysis of four samples at their initial stages of pyrolysis. Fig. 2(a) shows that the precipitation of water in four samples at the initial pyrolysis stage is corresponding to wave number 3,950-3,500 cm^{-1} and 2,000-1,300 cm^{-1} [26]. Fig. 2(b) and 2(c) show the FTIR spectra of two main stages in the pyrolysis with different contents of cellulose and hemicellulose in different biomass, where the DTG curve appears double peak. The smaller peaks present before the other two components are pyrolyzed due to the poor stability of hemicellulose, so Fig. 2(b) is the FTIR spectrum of hemicellulose pyrolysis and Fig. 2(c) is the FTIR spectrum of cellulose pyrolysis. From Fig. 2(b) and 2(c), the wave number corresponding to the absorption peaks of 3,950-3,460 cm^{-1} and 1,600-1,300 cm^{-1} indicates the production of H_2O,

Table 2. Pyrolysis parameters of four samples

Sample	T_S/°C	T_{max}/°C	V_∞/%	$(dw/dt)_{max}$/%·min^{-1}	$(dw/dt)_{mean}$/%·min^{-1}	$\Delta T_{1/2}$/°C	D
Chinese silvergrass	172.2	344.6	77.3	8.22	0.800	22.3	3.8×10^{-4}
Corn stalk	165.8	324.7	73.2	6.88	0.758	19.7	3.6×10^{-4}
Rice husk	177.5	343.6	71.5	8.77	0.733	24.6	3.1×10^{-4}
Pine	183.8	357.4	81.6	9.30	0.836	43.7	2.2×10^{-4}

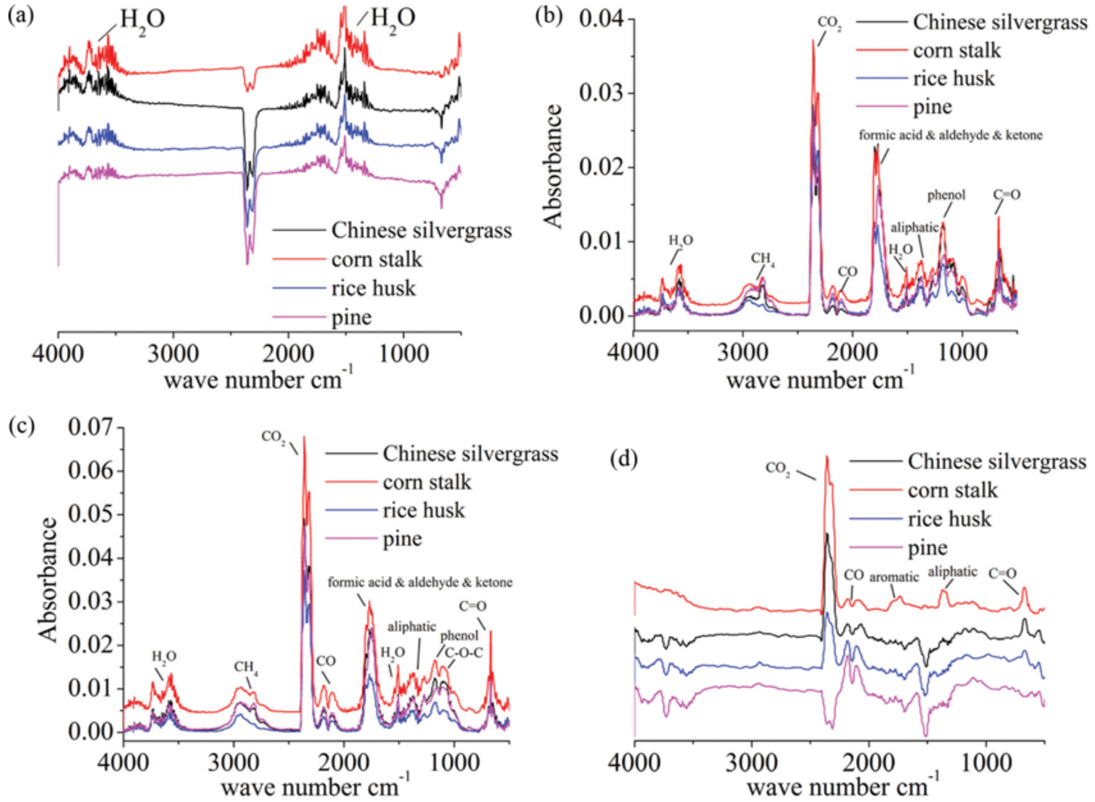

Fig. 2. FTIR spectra of different biomass in different pyrolysis stages. (a) Initial pyrolysis stage, (b) main pyrolysis stage 1, (c) main pyrolysis stage 2, (d) residual pyrolysis stage.

which indicates that hemicellulose and cellulose pyrolysis stage have hydroxyl dissociation to produce H_2O. The absorption peak near 2,941 cm^{-1} indicates that methane is produced in the pyrolysis process. The release of CH_4 is caused by the breakage of methoxy ($-OCH_3$); at the same time, it can be known from the literature [29], the release of CH_4, accompanied by aldehydes and acids, Fu et al. [30] determined aldehyde and acid also formed in this stage through spectral subtraction to eliminate 2,750-3,230 cm^{-1} interference peak. Characteristic peaks of 2,240-2,410 cm^{-1} and 2,190-2,100 cm^{-1} at this stage show the formation of CO_2 and CO. The release of CO_2 is mainly caused by the cleavage and reorganization of carbonyl group (C=O) and carboxyl (-COOH), and CO is mainly produced by the fracture of C=O and C-O-C [26]. In addition, the characteristic peaks at 1,890-1,600 cm^{-1} are mainly carbonyl (C=O) stretching vibrations, which correspond to the production of various oxygen containing organic compounds such as formic acid, aldehydes and ketones. The absorption peaks at 1,440-1,100 cm^{-1} are mainly phenol and aromatic compounds, or C-O-C stretching vibrations of aromatic ether or esters. The characteristic peak of 787-540 cm^{-1} is the stretching vibration of C=O [26].

When the temperature reaches 600 °C, the weight loss of the samples is more than 70%, the residual phase of pyrolysis is the process of slow weight loss. This stage is mainly the deep pyrolysis of the coke, especially the fracture of C-H bond and the C-O bond. Fig. 2(d) is the FTIR spectrum of different biomass in the residual pyrolysis stage. It can be concluded that the characteristic peaks of water absorbance are low, indicating that the carbonization stage hydroxyl (-OH) has been substantially completely removed, so, four samples all have C≡O contraction vibration of CO corresponding to 2,240-2,010 cm^{-1}. Other three kinds biomass except pine have C=O contraction vibration of CO_2 corresponding to 2,410-2,250 cm^{-1}; this is due to the high content of lignin in the pine, and the residual coke content of pine pyrolysis is higher; for the coke and the CO_2 produced by the aromatization of C=O and C-O a reduction reaction occurs, which produces a certain amount of CO. FTIR spectra of pyrolysis of rice husk at later stage are consistent with Chinese silvergrass, where all contain C-C, C-O and C-H contraction vibration corresponding to 1,500-900 cm^{-1} and C=O deformation vibration of CO_2 corresponding to 668 cm^{-1}. The FTIR spectrum of the later stage of pine pyrolysis is similar to rice husk. Corn stalk pyrolysis produces more products, wherein mainly products include carbon dioxide, O-H vibration of alcohol phenolic compounds corresponding to 1,367 cm^{-1} and C=O vibration of aldehydes and ketones corresponding to 1,736 cm^{-1} [26].

In summary, the pyrolysis of agricultural (corn stalk and rice husk) and herbal biomass (Chinese silvergrass) is similar, and forestry biomass (pine) is slightly different. The pyrolysis is divided into dry dehydration, volatile analysis and carbonization stage, which is consistent with the previous section of the thermogravimetric analysis. At the same time, the pyrolysis products of each sample are basically the same, namely, CO_2, CO, CH_4 and alcohol, acid, aldehydes, phenols and other compounds; the coupling of the various components of the composition, resulting in the absorbance and species of product are slightly different in the main pyrolysis

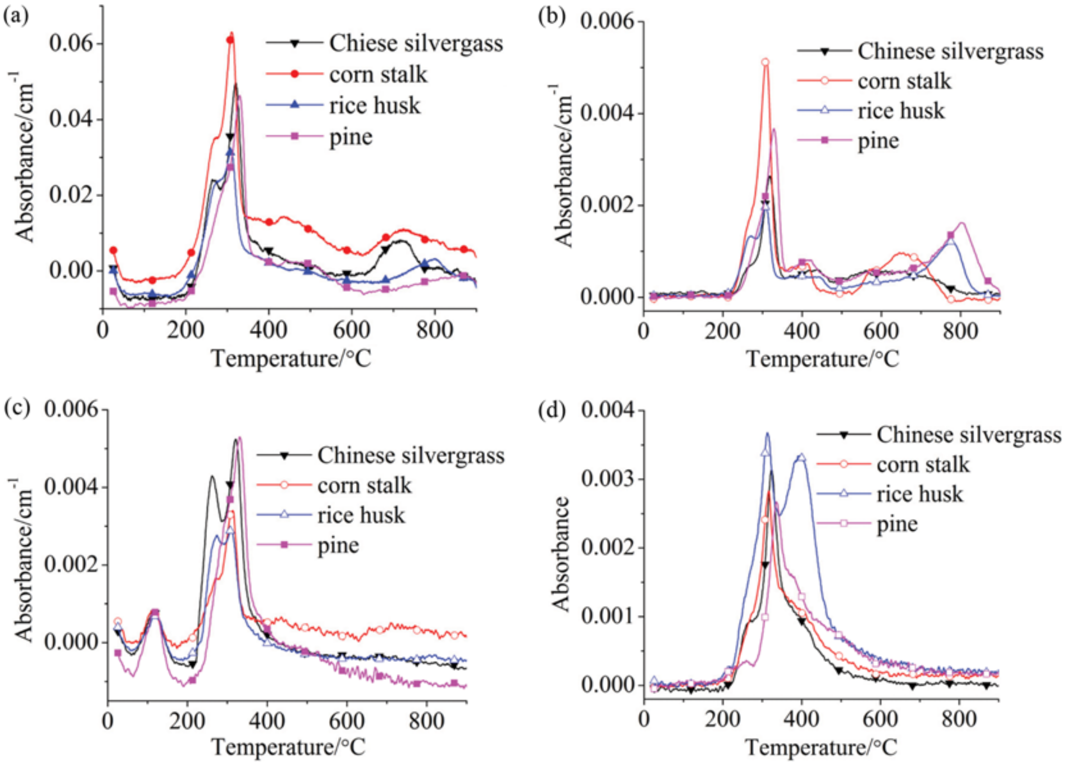

Fig. 3. Precipitation curves of main gaseous products from different biomass under heating rate of 10 K/min. (a) CO_2, (b) CO, (c) H_2O, (d) CH_4.

and carbonization stage.

2-2. Release Curves of Gaseous Products from Biomass Pyrolysis

To study the pyrolysis characteristics of different biomass, it is necessary to investigate the release characteristics of biomass during the pyrolysis process. Fig. 3 shows the release curves of gaseous products in the pyrolysis process of the four kinds of biomass at 10 K/min heating rate. Fig. 3 indicates that there is no other gas except water vapor when the pyrolysis temperature is below 200 °C, and the release of gas products H_2O, CO_2, CO and CH_4 mainly occurs in the temperature range of 200-400 °C, which is consistent with the TG curve in Fig. 1.

The release of CO_2 mainly occurs in the temperature range of 200-360 °C. When the pyrolysis temperature increases, the release of CO_2 increases gradually. For four samples except pine, the release of CO_2 gets a small peak when the temperature rises to 263 °C. This is due to the hemicellulose pyrolysis in the sample, resulting in the release of a large amount of CO_2. Fig. 1 shows that the content of hemicellulose in pine is less, the pyrolysis peak is covered by cellulose pyrolysis peak; therefore, for the CO_2 release curve of pine a small peak does not appear. Next, due to the pyrolysis of cellulose, the release amount of CO_2 increases rapidly, and reaches the peak near the temperature of 310-320 °C, then the release rate of CO_2 reduces gradually. When the temperature rises to 700 °C, Chinese silvergrass and corn stalk are subjected to secondary pyrolysis, which leads to a small peak and more release of CO_2, because the pyrolysis of C=O and C-O in some aromatic compounds incurs reorganization and other reactions. Fig. 3(b) shows that the release characteristics of CO and CO_2 are similar in the pyrolysis temperature range of 200-360 °C. The release of CO between 200 °C and 900 °C is mainly due to the pyrolysis of hemicellulose [28]. When the temperature is higher than 600 °C, the release of CO is mainly due to the pyrolysis of lignin, and the contribution of cellulose to the release of CO during the whole pyrolysis process is very small. For corn stalk and rice husk, the CO release curve near 270 °C shows a slight turn and then drastically increases. It can be seen from the literature [20], the peak is mainly because of the combined effect on pyrolysis of hemicellulose and cellulose. For the CO release from corn stalk a wide small peak appears at high temperature (>600 °C) near 650 °C, which is corresponding to the carbonization stage. For Chinese silvergrass, this small peak is not obvious, but there is still a certain amount of precipitation from 500-800 °C. However, rice husk and pine only show a small peak when the temperature rises to around 800 °C. This is most likely because the decomposition and condensation of lignin aromatic structure produce CO from the content of lignin in rice husk and pine at this point.

The release of water can be divided into two stages; the release of water increases at first and then decreases, and increases at last as the temperature increases. The first stage corresponds to the drying stage. With the increase of temperature, the precipitation rate gets faster and faster, and the maximum precipitation peak appears at about 118 °C. The second stage corresponds to the volatile matter precipitation stage. With the increase of pyrolysis temperature, the thermal decomposition reaction becomes more and more intense. The precipitation of water at this stage presents complex characteristics; the two water precipitation peaks formed in the

Table 3. Activation energy and correlation coefficient of biomass

Sample	Temperature (°C)	Correlation coefficient r	Frequency factor A (s^{-1})	Activation energy E ($kJ\cdot mol^{-1}$)
Chinese silvergrass	230.3-389.5	0.9907	2.2E+06	46.7
Corn stalk	196.9-369.4	0.9834	3.6E+07	29.2
Rice husk	239.2-373.3	0.9803	6.9E+05	54.3
Pine	249.4-378.2	0.9816	4.2E+05	58.1

temperature of 200-400 °C are due to the pyrolysis of hemicellulose and cellulose leading to a large amount of hydroxyl removal; when the temperature is higher than 400 °C, no water is produced, which is consistent with the previous FTIR analysis.

Compared with CO_2 and CO, the release of CH_4 is mainly in the higher temperature range 200-500 °C. For four samples, the maximum release peaks are all obtained near 325 °C, but there is an additional peak value at 400 °C for rice husk. It is because the pyrolysis of lignin begins to produce large amounts of phenol when the temperature rises to 400 °C [31], and the formation of phenol is due to the cracking of side chain methoxy group in lignin precipitates CH_4 [32], which makes the CH_4 release peak appear once again.

3. Kinetic Analysis

There are many methods for calculating the pyrolysis kinetics of biomass, such as Coats-Redfern method, Ozawa-Flynn-Wall method [33], KAS method [34] and DEAM method [35]. The biomass samples are analyzed using Coats-Redfern method in this study. The relationship between the reaction temperature, the reaction conversion rate and the other kinetic parameters of biomass gain mainly focuses on the dynamics of biomass pyrolysis. Biomass pyrolysis process can generally be expressed as follows [36].

$$\text{biomass}\rightarrow\text{char}+\text{volatiles} \tag{1}$$

The biomass thermal decomposition rate equation can be expressed as follow s [37]:

$$\frac{d\alpha}{dt}=kf(\alpha) \tag{2}$$

Generally speaking, $f(\alpha)$ can be replaced by $f(\alpha)=(1-\alpha)^n$, and the k of the Arrhenius equation can be expressed as $k=A\exp(-E/RT)$. Thus, Eq. (2) can be expressed as:

$$\frac{d\alpha}{dt}=kf(\alpha)=A\exp(-E/RT)(1-\alpha)^n \tag{3}$$

By putting the temperature rising rate constant $\beta=dT/dt$ into Eq. (3), we can obtain Eq. (4):

$$\frac{d\alpha}{dT}=\frac{A}{\beta}\exp(-E/RT)(1-\alpha)^n \tag{4}$$

Treating Eq. (4) by Coats-Redfern method, Eq. (5) and Eq. (6) can be obtained:

When n=1,

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right]=\ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right]-\frac{E}{RT} \tag{5}$$

When $n\neq 1$,

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right]=\ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right]-\frac{E}{RT} \tag{6}$$

In general reactions, 2RT/E is far less than 1, so the item $\ln[AR/RE(1-2RT/E)]$ in Eq. (5) and Eq. (6) can be approximated to $\ln(AR/\beta E)$. Therefore, when n=1, $\ln[-\ln(1-\alpha)/T^2]$ mapping of 1/T; when $n\neq1$, $\ln[1-(1-\alpha)^{1-n}/T^2(1-n)]$ is mapping of 1/T. If the selected n value is just right, an approximate straight line can be obtained. The activation energy E and the pre exponential factor A can be obtained, respectively, by the slope $-E/R$ and intercept $\ln(AR/\beta E)$ of the straight line.

Table 3 shows the pyrolysis kinetic parameters of four samples at the heating rate of 10 K/min for n=1 reaction order, and the fitting correlation coefficient is higher, which shows that the linear fitting can be carried out under the reaction order of n=1. The activation energy of Chinese silvergrass, corn stalk, rice husk, pine is about 46.7, 29.3, 54.3 and 58.1 kJ/mol, respectively, which shows that corn stalk compared to the other three samples is more susceptible to pyrolysis.

CONCLUSION

TG-FTIR and Coats-Redfern method were used to analyze the pyrolysis characteristics and pyrolysis kinetics of different kinds biomass. Results can be summarized as follows:

(1) The pyrolysis of agricultural, herbal and forestry biomass can be divided into three stages: water loss drying stage, volatile matter precipitation stage and carbonization stage. The volatiles release index of herbal biomass Chinese silvergrass is the highest, followed by corn stalk and rice husk, the lowest is pine.

(2) CO_2, CO, H_2O and CH_4 are the main gas products of the pyrolysis of four samples. Chinese silvergrass has a high similarity with corn stalk on the gas product release curves of CO_2, CO and CH_4. And Chinese silvergrass has some similarity to rice husk on the release curve of H_2O.

(3) Kinetic results show the activation energy of Chinese silvergrass, corn stalk, rice husk and pine is about 46.7, 29.3, 54.3 and 58.1 kJ/mol, respectively, which shows that corn stalk compared to the other three samples are more susceptible to pyrolysis.

ACKNOWLEDGEMENTS

The research described in this paper was financially supported by National Natural Sciences Foundation of China (51276023), Hunan Provincial Natural Science Foundation (2015JJ4005) and Hunan Province Department of Education Youth Project (16B001).

NOMENCLATURE

D : the comprehensive characteristics of volatile release degree of biomass

T_S : the initial volatile precipitation temperature [°C]

$(dw/dt)_{max}$: the maximum weight loss rate of volatile matter [$\%\cdot min^{-1}$]

V_∞ : the total weight loss rate [%]

T_{max} : the peak temperature corresponding to the $(dw/dt)_{max}$ [°C]

$(dw/dt)_{mean}$: the average volatile weight loss rate [$\%\cdot min^{-1}$]

$\Delta T_{1/2}$: the temperature range corresponding to $(dw/dt)/(dw/dt)_{max}=1/2$

β : heating rates [$K\cdot min^{-1}$]

α : conversion rate $\alpha=\frac{w_0-w_t}{w_0-w_f}$ [%]

t : time [s]

k : rate constant [s^{-1}]

n : reaction order

A : frequency factor [s^{-1}]

E : activation energy [$kJ\cdot mol^{-1}$]

R : gas constant [$8.314\ J\cdot mol^{-1}\cdot K$]

T : absolute temperature [K]

w_0 : sample initial weight [mg]

w_t : the weight of the sample at the time of t [mg]

w_f : residual solids weight at the end of reaction [mg]

REFERENCES

1. J. D. Yan, *Chemistry and Industry of Forest Products*, **34**, 151 (2014).
2. J. Xiao, J. C. Duan, H. Wang and X. G. Zhuang, *Safety and Environmental Engineering*, **10**, 11 (2003).
3. J. M. Wang, F. P. Cai, F. Q. Jin, B. Wang and B. Jiang, *Adv. Mater. Res.*, **512**, 468 (2012).
4. X. W. Yu, H. B. Ji, S. Z. Chen, X. G. Liu and Q. Z. Zeng, *Adv. Mater. Res.*, **806**, 260 (2013).
5. D. Z. Fu, Y. Tang, Z. H. Fu and W. Li, *Adv. Mater. Res.*, **884**, 148 (2014).
6. X. F. Fu, Z. P. Zhong, G. Xiao and R. Li, *Boiler Technol.*, **25**, 199 (2009).
7. Z. H. Chen, M. Hu, X. L. Zhu, D. Guo, S. Liu, Z. Q. Hu, B. Xiao, J. b. Wang and M. Laghari, *Bioresour. Technol.*, **192**, 441 (2015).
8. J. Wang, G. Wang, M. X. Zhang, M. Q. Chen, D. M. Li, F. f. Min, M. g. Chen, S. p. Zhang, Z. W. Ren and Y. J. Yan, *Process Biochemistry*, **41**, 1883 (2006).
9. J. Wang, M. X. Zhang, M. Q. Chen, F. F. Min, S. P. Zhang, Z. W. Ren and Y. J. Yan, *Thermochim. Acta*, **444**, 110 (2006).
10. H. Zhao, H. X. Yan, M. Liu, C. W. Zhang and S. Qin, *Chinese J. Oceanology and Limnology (English version)*, **29**, 996 (2011).
11. H. Zhao, H. X. Yan, M. Liu, C. W. Zhang and S. Qin, *Adv. Mater. Res.*, **113**, 170 (2010).
12. L. Abdelouaned, S. Leveneur, L. V. Hassimi, L. Balland and B. Taouk, *J. Thermal Anal. Calorimetry*, **129**, 1201 (2017).
13. Q. V. Bach and W. H. Chen, *Energy Convers. Manage.*, **131**, 109 (2017).
14. Y. M. Kim, T. U. Han, B. H. Wang, B. Lee, H. W. Lee, Y. K. Park and S. Kim, *Korean J. Chem. Eng.*, **33**, 1 (2016).
15. Y. Long, H. Zhou, A. Meng, Q. Li and Y. Zhang, *Korean J. Chem. Eng.*, **33**, 2638 (2016).
16. H. Haykiri-Acma and S. Yaman, *Fuel*, **86**, 373 (2007).
17. T. P. Wang, X. N. Ye, Q. Lu, Z. B. Zhang and C. Q. Dong, *Transactions of the Chinese Society of Agricultural Engineering*, **430**, 223 (201).
18. Y. Q. Huang, Z. G. Wei, X. L. Yin and C. Z. Wu, Transactions of the Chinese Society for Agricultural Machinery, **43**, 86 (2012).
19. S. Hu, L. S. Sun, J. Xiang, J. R. Qiu and M. H. Xu, *CIESC J.*, **58**, 2889 (2007).
20. F. Sevim, F. Demir, M. Bilen and H. Okur, *Korean J. Chem. Eng.*, **23**, 736 (2006).
21. S. R. Wang and Z. Y. Luo, *Pyrloysis of Biomass Components*, Science Press, Beijing (2013).
22. K. Raveendran, A. Ganesh and K. C. Khilar, *Fuel*, **75**, 987 (1996).
23. D. Vamvuka, E. Kakaras and E. Kastanaki, *Fuel*, **82**, 1949 (2003).
24. L. F. Gu, X. P. Chen and C. S. Zhao, *J. of Engineering for Thermal Energy and Power*, **18**, 561 (2003).
25. J. Xiao, L. H. Shen and M. Zheng, *Acta Energiae Solaris Sinica*, **28**, 972 (2007).
26. H. P. Yang, R. Yan, H. P. Chen, H. L. Dong and C. Zheng, *Fuel*, **86**, 1781 (2007).
27. D. Y. Che, W. Q. Jiang, *J. Chinese Agricultural Mechanization*, **37**, 241 (2016).
28. X. L. Gu, X. Ma and L. X. Li, *Acta Petrolei Sinica (Petroleum Processing Section)*, **29**, 174 (2013).
29. C. Liu, Y. Zhang and X. Huang, *Fuel Process. Technol.*, **123**, 159 (2014).
30. P. Fu, S. Hu, L. S. Sun, J. Xiang, Q. Q. Chen and T. Yang, *Proceedings of The Chinese Society for Electrical Engineering*, **29**, 113 (2009).
31. M. Brebu and C. Vasile, *Cellulose Chemistry Technol.*, **44**, 353 (2010).
32. D. L. Yao, B. L. Jin and H. Tao, *Energy Research Utilization*, **20**, 11 (2008).
33. Y. Xiang, Y. Xiang and L. Wang, *J. Environ. Chem. Eng.*, **4**, 3303 (2016).
34. A. Lim, B. Chin and Z. Jawad, *Procedia Eng.*, **148**, 1247 (2016).
35. J. Cai, F. He and W. Yi, *Chem. Eng. J.*, **124**, 15 (2006).
36. J. L. Liu, Chinese Academy of Forestry (2012).
37. A. Marini, V. Berbenni and G. Flor, *Zeitschrift Fur Naturforschung A*, **34**, 661 (1979).