Experimental and modeling studies on CO₂ gasification of biomass chars

Guangwei Wang^a, Jianliang Zhang^{a,*}, Jiugang Shao^b, Zhengjian Liu^a, Haiyang Wang^a, Xinyu Li^a, Pengcheng Zhang^c, Weiwei Geng^c, Guohua Zhang^{c,*}

^a *School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, China*

^b *Handan Steel Co.LTD, Handan, 056000, China.*

^c *State Key Laboratory of Advanced Metallurgy, University of Science and Technology Beijing, Beijing 100083, China*

*Correspondence authors. Tel.: +86 10 62332550; fax: +86 10 62332364.

E-mail addresses: zhang.jianliang@hotmail.com(J.Zhang); ghzhang_ustb@163.com(G.Zhang)

Abstract: The CO₂ gasification properties and kinetics of biomass chars including four kinds of herbaceous residues and two kinds of wooden residues have been studied by the method of isotherm-gravimetric analysis. In addition, the chemical components as well as physical structures of six chars were systematically tested. Results show that gasification reactivity of herbaceous residue char were better than that of wooden residue char. It was found that gasification reactivities of char were mostly determined by its carbonaceous structure. Four kinetic models were applied to describe the gasification behavior of biomass chars: the volumetric model (VM), the grain model (GM), the random pore model (RPM) and the modified random pore model (MRPM). It was found that the RPM and MRPM model were better for describing the reactivity of different chars. However, for the gasification process in which the peak gasification rate appears in high conversion range, the MRPM performs better. At the same time, a marked compensation effect was also presented between the activation energy and pre-exponential factor when the Arrhenius law was used to describe the temperature dependence of gasification rate of char.

Key words: Gravimetric analysis; Biomass char; CO₂ gasification; Physical structures; Kinetic models

1 Introduction

Fossil fuels (i.e., coal, natural gas, and petroleum, etc.) have played an important role in the past in transportation fuel supplies and will continue to do so. However, fossil fuels are not renewable and the declining reserves and the increasing demand for fossil fuels would cause great trouble in the future. The emissions of the greenhouse gases by burning fossil fuels have also brought a major environmental challenge [1]. Consequently, it is urgent to develop the alternative and sustainable energy technologies. Biomass is a kind of wide spread and renewable resource with high yield and carbon neutral property. In addition, during the utilization process, the emissions of sulfur oxide and nitrogen oxide are less than that of fossil fuel. All these properties make biomass resource have more advantages in environmental protection and social benefits. If biomass resource could be

utilized in industry circle, it would contribute to the energy conservation and emission reduction[2,3]. However, biomass resource also has some disadvantages like bad grindability, low density of energy and high content of moisture, which restrict its direct application in industrial field. Thereby, normally before utilization, the conversion process of biomass resource would be carried out, such as, combustion, gasification, carbonization, high temperature pyrolysis as well as alcoholic fermentation .etc. Among them, the gasification technology is the most promising one[4-6].

In general, biomass gasification process in the gasifier is very complex and includes water evaporation, volatiles pyrolysis, combustion, volatiles gasification and solid residue (char) with gasification agents. Generally, the rate of char gasification process is much lower than other processes, so it is usually considered as the rate-determining step in the overall conversion process [7]. Water has been widely used as gasification agent, but in recent years, due to the development of new energy technology, usage of water as gasification agent has reached its limit. However, as gasification agent, carbon dioxide has attracted more and more attention [8]. The advantage of using CO₂ as a gasifying agent is to recycle the CO₂ that is produced during the reduction processes and to convert it into a useful form of gas [9,10]. As a result, investigation on the reaction behavior and kinetic parameters of CO₂ gasification of biomass char under elevated temperature has an important impact on reactor design, control and efficiency [5,11,12].

CO₂ gasification behaviors of Biomass char have been widely investigated in the past. Zeineb et al. [3] studied that the influences of textural, structural and chemical properties of biomass chars on the CO₂ gasification rate. The results suggested that the gasification rate was shown to depend on the char external surface and the potassium content when the conversion was below 70%. At a higher conversion ratio, a satisfactory correlation between the Catalytic Index and the average gasification rate was identified. Okumura et al. [13] using Raman spectroscopy to investigate the influence of pyrolysis conditions on woody biomass char reactivity. It was shown that there was a correlation between the biomass char characteristics and the gasification rate. In particular, the relationship between the gasification reactivity and the carbonaceous uniformity structure have been noted. Wang et al. [14] studied the gasification reactivity of biomass chars and anthracite char with CO₂ through the TGA method and various kinetic models such as the volumetric model (VM) [15,16], the grain model (GM) [17,18] and the random pore mode (RPM) [19]. The results show that RPM and VM models were the best for describing the reactivity of biomass char and the gasification process of anthracite char, respectively. Seo et al. [20] studied the gasification of biomass chars with carbon dioxide at different temperatures. Compared with the calculated results by VM, GM and RPM models, it was found that the experimental data agreed well with the RPM model. Feroso et al. [21] studied the effect of the gasification temperature, pressure and CO₂ concentration during gasification of biomass chars. It was found that

among VM, GM and RPM models only the RPM model accurately predicted the conversion of different char except SPH14 which can be well fitted by the Langmuir-Hinshelwood model. Normally, RPM could well describe the gasification curve of char under CO₂ atmosphere, but when peak reaction rate appears at high conversion range over 0.393, the discrepancy between experiment data and model calculation is significant. Therefore, based on RPM, many further investigations were carried out. Zhang et al. [22] evaluated a semi-empirical kinetic model to reconcile with gasification reactivity profiles of biomass chars. It was found that the fitting parameters introduced in the modified random pore model well predicted the amount of the active potassium (K) in biomass char. Zhang et al. [23] have developed a modified random pore model (MRPM), which could be reduced to a traditional VM model, GM model, hybrid model and RPM model by varying the model parameters.

In the previous studies on biomass char gasification, the analyses about relation between microstructure and macroscopic property, as well as reaction rate appears in high conversion range are not sufficient. In this study, the char gasification properties and kinetic behaviors of peanut shell (PS), maize cob (MC), wheat straw (WS), rice lemma (RL), pine sawdust (PSD) and bamboo sawdust (BS) were investigated by using the method of isothermal thermogravimetric analysis (TGA). Various factors including elementary composition, alkali index, surface area and carbonaceous structure were also analyzed systematically. VM, GM, RPM and MRPM models were used to describe the kinetics of CO₂ gasification of biomass char at different temperatures.

2 Experiments

2.1 Samples

Four types of wooden raw materials including peanut shell (PS), maize cob (MC), wheat straw (WS), rice lemma (RL), as well as two herbaceous raw materials including pine sawdust (PSD) and bamboo sawdust (BS) were collected from Yuzhou city, Henan province, China. The samples were cut to the sizes of 0.5-1 mm. The char was prepared by devolatilizing the raw materials in a fixed bed reactor under a flowing nitrogen atmosphere (4L/min) at 1373 K for 90 min to ensure the pyrolysis process was fully completed. The experimental apparatus for the pyrolysis process of raw materials has been explained in the previous reports [14,24]. After devolatilization, the obtained chars were ground to fine powders using a mortar and pestle. Afterward, the particle sizes of samples were selected to that lower than 0.074 mm by using standard test sieve for experiments. The results of the proximate, ultimate analysis and high heating values (HHV) of samples are shown in Table 1. Table 2 shows the ash compositions of different chars. The morphology of raw materials was observed by using Scanning electron microscopy (SEM) (FEI Quanta-450) at the conditions of a 15 kV voltage and amplified 5000 times. The pore structures of samples were characterized by a N₂ adsorption technique at 77 K using a pore structure analyzer. Prior

to the analysis the samples were out-gassed overnight in vacuum at 573 K. Specific surface areas were obtained by the Brunauer-Emmett-Teller (BET) model. The BET specific surface areas was calculated from the linear plot in the relative pressure range of 0.05-0.25. The total pore volume of N₂ adsorbed was obtained at a relative pressure of 0.95. The pore size distributions were obtained by the density functional theory (DFT). Intrinsic carbon structures of char were investigated by a Raman spectrometer. Raman spectra of the samples were recorded with a LabRam HR Evolution, Jobin Yvon/Horiba spectrometer. Several char samples were sampled and deposited on a rectangular glass slide for the Raman analysis. Raman spectra were obtained in a backscattered configuration with an excitation laser at 532 nm. The Raman spectra at each position give average structural information of a large number of carbon micro-crystallites. The Raman spectra were recorded at 6 locations of the char samples.

2.2 Gasification tests

Thermogravimetric analysis (TGA) is one of the most commonly used techniques to investigate kinetics and mechanism during gasification and combustion of solid raw materials, such as biomass, petroleum coke, coal chars [25-28]. In this study, the tests were carried out on a thermogravimetric analyzer (HCT-3, Henven Scientific Instrument Factory, Beijing). At the beginning of each experiment, approximately 5 mg of char was placed in a crucible with height of 2mm and a diameter of 5 mm. According to results of the non-isothermal tests in the previous report [14], the temperatures for isothermal experiments were selected to be 1123 K, 1173 K, 1223 K and 1273 K, respectively. In each experimental run, the sample was heated at 20 K/min up to final gasification temperature in N₂ atmosphere. When the desired temperature was reached, N₂ was replaced by CO₂ with the flow rate of 60 ml/min. The final temperature was kept for gasification until no evident weight loss could be observed. Small amount of sample was used to avoid heat transfer limitation, which was important to ensure that the results had a good reproducibility. Each run was repeated at least for three times before a final result was ascertained.

The gasification conversion (X) (on ash-free basis) was calculated using the following equation:

$$X = \frac{(m_0 - m_t)}{(m_0 - m_\infty)} \quad (1)$$

where m_0 denotes the sample mass at the start of gasification; m_t is the sample mass at time t ; m_∞ is the mass of ash remaining in char after complete reaction.

2.3 Kinetic models

Combustion or gasification of char is a gas-solid non-catalytic heterogeneous reaction and the rate of conversion (reactivity or reaction rate) can be expressed as following:

$$\frac{dX}{dt} = k(T) f(X) \quad (2)$$

where k is the apparent gasification reaction rate constant, which is determined by temperature(T) and can be

expressed by the Arrhenius equation as:

$$k = k_0 e^{-E/RT} \quad (3)$$

where k_0 , E , and R are the pre-exponential factor, activation energy and universal gas constant, respectively.

The gasification of biomass char particles can be represented through a few models. In this study, three n th order kinetic models were applied in order to describe the reactivity of the char studied: the volumetric model (VM) [15,16]; the grain model (GM) [17,18] and the random pore model (RPM) [19]. These models give different formulations of the term $f(X)$. The VM model is the simplest model which does not consider the structure changes of the sample during reaction, but assumes that the gasifying agents react with the particles of char at all active sites, which are uniformly distributed on both the outside and inside the particle. The overall reaction rate is expressed by:

$$\frac{dX}{dt} = k_{VM} (1 - X) \quad (4)$$

The GM model or unreacted core model, proposed by Szekeley and Evans [18], assumes that a porous particle consists of an assembly of uniform nonporous spherical grains and the reaction initially occurs at the external surface of grains and gradually moves inside. The unreacted core behavior is applied to each of these grains during the reaction. As the reaction proceeds, only the ash layer remains. When the gasification reaction is controlled by the chemical reaction at the interface, the overall reaction is described as follows:

$$\frac{dX}{dt} = k_{GM} (1 - X)^{2/3} \quad (5)$$

The GM model predicts a monotonically decreasing reaction rate and surface area because the surface area of each grain is receding during the reaction. The RPM model considers the overlapping of pore surfaces, which reduces the interface area that is available for reaction. The reaction rate expression is then given by:

$$\frac{dX}{dt} = k_{RPM} (1 - X) \sqrt{1 - \psi \ln(1 - X)} \quad (6)$$

Because this model considers the effects of pore growth during the initial stages of gasification and destruction of pores owing to the coalescence of adjacent pores, it can simultaneously predict the maximum value of the reactivity as the reaction proceeds. The RPM employs two parameters, the apparent gasification reaction rate constant, k_{RPM} , and ψ which is utilized to represent the pore structure of the non-reacted sample.

In order to evaluate these models using the experimental results, Eqs.(4)-(6) were linearized as shown in Eqs.(7)-(9), respectively:

$$-\ln(1 - X) = k_{VM} t \quad (7)$$

$$3\left[1-(1-X)^{1/3}\right]=k_{\text{GM}}t \quad (8)$$

$$(2/\psi)\left[\left(1-\psi\ln(1-X)\right)^{1/2}-1\right]=k_{\text{RPM}}t \quad (9)$$

The experimental data obtained in the isothermal thermogravimetric runs was used to calculate the apparent gasification reaction rate constants (k_{VM} , k_{GM} and k_{RPM}) according to Eqs.(7)-(9). The Arrhenius plot ($\ln k$ vs. $1/T$) was then employed to calculate the activation energy, E , and the pre-exponential factor, k_0 , for each of the char samples and models according to Eq.(3).

The conversion-time relationships for the three models are:

$$X = 1 - \exp(-k_{\text{VM}}t) \quad (10)$$

$$X = 1 - \left(1 - k_{\text{GM}}t/3\right)^3 \quad (11)$$

$$X = 1 - \exp(-k_{\text{RPM}}t(1 + k_{\text{RPM}}t\psi/4)) \quad (12)$$

The k values were calculated by introducing the estimated E and k_0 values into Eq.(3). $X_{\text{calc},i}$ was obtained by introducing the k value, into Eqs.(10)-(12). The kinetic model can be tested and verified by comparing the experimental with calculated X values. The deviation (DEV) between the experimental and calculated curves was calculated using the following expression:

$$DEV(X)(\%) = 100 \times \frac{\left(\sum_{i=1}^N (X_{\text{exp},i} - X_{\text{calc},i})^2 / N\right)^{1/2}}{\max(X)_{\text{exp}}} \quad (13)$$

where $DEV(X)(\%)$ is relative error; $X_{\text{exp},i}$ is experiment data; $X_{\text{calc},i}$ is value calculated by model; $\max(X)_{\text{exp}}$ is the maximum conversion of experiment; N is the number of data points.

3 Results and discussion

To assess the validations of selected kinetic models and predict the kinetic behaviors of the studied samples, the experimental data were fitted by various models. By plotting $-\ln(1-X)$, $3\left[1-(1-X)^{1/3}\right]$, $(2/\psi)\left[\left(1-\psi\ln(1-X)\right)^{1/2}-1\right]$ as a function of time t , the slopes of curves at different reaction temperatures could be obtained to represent the reaction rate constants (k_{VM} , k_{GM} and k_{RPM}) of the biomass gasified reaction process corresponding to the models of VM, GM and RPM, respectively. In the RPM model, the value of ψ was obtained by optimum fitting and was a constant under different temperatures because ψ represented the original pore structure of the semi-char particle in the establishment of the RPM model. Fig. 1 shows the applications of the VM, GM and RPM models to the experimental results obtained from the gasification of six chars at different

temperatures. For these studies, a range of conversion from 0 to 0.9 was taken into account. Then, by using the reaction rate constants calculated at different temperature, the Arrhenius plot ($\ln k$ vs. $1/T$) was employed to calculate the activation energy (E) and the pre-exponential factor (k_0). Fig. 2 shows the Arrhenius plots for different chars using the reaction rate constants calculated with the VM, GM and RPM models. However, this method only be applied to the case under the chemical controlled regime. The change between the chemical and diffusional controlled regime can be detected from the change in the slop on the Arrhenius plot [29] . It can be seen in the Fig. 2 that there exists a good liner relation between the $\ln k$ and $1/T$ under different reaction temperatures of the semi-char gasified process, which further shows the interface chemical reaction is the controlling step during the biomass char gasified process under the present reaction temperature.

Fig.1 simultaneously shows that the liner correlation of the RPM, GM and VM. The BS-char gasified process was fitted well by RPM model, but the error was much larger than other semi-chars calculated by RPM model. As applying RPM model to the gasified reaction, it was shown that the gasified reaction rate increased firstly and then decreased with the increase of gasified conversation rate. In other words, there was a peak value of the conversation rate during the gasified reaction process. The RPM model considers a great deal of column shape of pores existed in the semi-char particles and the gasified reaction happened in the surface of the inner pores. With the proceeding of the reaction, both the increases of column bore diameter and reaction phase lead to the increase of gasification rate [17]. Finally, reaction progress brought about intersection of neighboring pores. Due to pore overlapping, the reaction surface area is lower and consequently, the reaction rate decrease. Conversely, the VM and GM models cannot describe the maximum value of reaction rate but predict a monotonous decrease of the reaction rate with conversion. Table 3 shows the pre-exponential factor, A , and activation energy, E , obtained by applications of different models. It can be seen in Table 3 that activation energies of the six kinds of biomass were distributed in the range of 140.8-183.6 kJ/mol, and the variations of the activation energies of different kinds of biomass char were slight. However, the pre-exponential factor varied greatly, for example, the pre-exponential factors of the BS and RL were 2.97 s^{-1} and $1.25\text{E}+05 \text{ s}^{-1}$, respectively. By comparing the gasified activation energy parameters of the six kinds of biomass chars in Table 3, the activation energies calculated by different models can be ranked from low to high as PS-char<PSD-char<MC-char<WS-char<BS-char<RL-char.

In order to compare the validation of each model, the experimental conversion was compared with the calculated values at the different temperatures. The results are shown in Fig. 3. In accordance with the previous results (Fig.1), the better the liner relation in Fig.1, the higher of the overlap ratio of the experimental and model calculation results in Fig.3 will be. In order to quantify the errors produced by the kinetic models, the deviation (DEV) between the experimental and predicted values was obtained using Eq.(13). The results obtained from the

three models for all char samples are summarized in Table 4. The lowest deviation was obtained using the RPM model, which means that the RPM model is the best model for describing the reactivity of the all char samples. But for RL char, VM model can be better to represent the gasified process. The reason for this maybe that ψ value is small and when this occurs, the RPM model predicts an almost monotonous decrease of reactivity with conversion, like the VM model.

Although RPM could fit well with the experimental results obtained from biomass char, this model was not suitable for the MC-char and BS-char in which the maximum gasification rate appears in high conversion range. Such trend is commonly observed in CO₂ activation of biomass chars with high alkali content [22]. Some researchers considered it to be resulted from the increase of specific area caused by pore collapse and development during gasification, while some researcher considers that the increase of active sites caused by alkalis is the reason. Huang and co-workers [30] believe that alkalis might be covered by some inert products during char preparation, and with the increase of conversion of char during gasification, this part of alkalis could be released and leads to the high gasification rates in high conversion ranges. To describe this condition, some modified Random Pore models have been developed [23,31]. One of them is the MRPM, which is semi-empirical model based on RPM by introducing a conversion term to RPM. It can be written as $\frac{dX}{dt} = k_{\text{MRPM}} (1-X)^n \sqrt{1-\psi \ln(1-X)}$ where n is a dimensionless power law constant. Fig.4 shows the applicability of the MRPM to the experimental results obtained from CO₂ gasification of biomass. The activation energy, pre-exponential factors for biomass chars are tabulated in Table 5. It can be found that better results can be obtained by MRPM than RPM. The activation energy calculated by MRPM model is 132.8-163.7 kJ/mol, and the calculated reaction order is 0.234-0.837 in the investigated temperature range. In the previous study [32], activation energy values for MC-char in CO₂ atmosphere was calculated by Gaur et al. to be in the range between 160 and 168 kJ/mol, as shown in Table 6. Zhou et al. [33,34] obtained activation energy values of 125.7-184 kJ/mol for WS-char under CO₂ atmosphere. Bhat et al. [35-37] obtained activation energy values between 197 kJ/mol and 238 kJ/mol for RL-char, and between 213 kJ/mol and 249 kJ/mol for PSD-char. The activation energy of BS-char was investigated by Sircar et al. [38] and found to be 125±30 kJ/mol. It shows that there exists a little difference for the values of activation energy in the references and this study, which may be resulted from the differences in coke-forming temperature, coke-forming time and the fuel properties themselves. But overall, the activation energies calculated in this paper are in accordance with that in the references.

Finally, in order to evaluate reactivity of different chars quantitatively, the reactivity index $R_{0.5}$, proposed by Takayuki et al. [39,40] is used in this paper.

$$R_{0.5} = \frac{0.5}{t_{0.5}} \quad (14)$$

where $t_{0.5}$ represents the time required to reach 0.5 carbon conversion. High reactivity index values are associated with high reactivity. The reactivity indexes for each char at different temperatures are summarized in Table 7. For each char, it is obvious that the reactivity index $R_{0.5}$ increased with the gasification temperature. It means that the gasification reactivity is dramatically influenced by gasification temperature. Furthermore, the reactivity indexes of PS-char, MC-char, WS-char, RL-char, PSD-char and BS-char at temperatures of 1123-1273 K were 0.58×10^3 - $5.81 \times 10^3 \text{ s}^{-1}$, 0.60×10^3 - $3.85 \times 10^3 \text{ s}^{-1}$, 0.52×10^3 - $4.31 \times 10^3 \text{ s}^{-1}$, 0.44×10^3 - $3.53 \times 10^3 \text{ s}^{-1}$, 0.31×10^3 - $1.84 \times 10^3 \text{ s}^{-1}$, and 0.32×10^3 - $2.72 \times 10^3 \text{ s}^{-1}$, respectively. Therefore, the detailed order of gasification reactivity sequence for various chars can be ranked as PSD-char < BS-char < RL-char < WS-char < MC-char < PS-char. In summary, the gasification reactivity of herbaceous residues are better than that of wooden residues.

The correlation between the gasification reactivity and raw material properties have been studied by previous investigations [40-42]. Through these studies, it was found that gasification reactivity were influenced by volatile content, content and composition of ash, particle size, specific surface area and microstructure. However, in this study the volatile matter may not be the main factor which affects the gasification reactivity, since most of the volatile matter (almost > 90 %) has been removed by the devolatilized process. As shown in Table 1. The main constituent of the sample is fixed carbon and ash. According to research of Zhang et al. [22], catalytic effect of K_2O is the strongest, Na_2O follows, CaO is weak, MgO has little effect and SiO_2 as well as Al_2O_3 could hinder reaction process. In order to denote the effects of mineral in ash on char gasification, the alkali index (AI value) was proposed [40,43], which is calculated by the following equation:

$$AI = Ash \times \frac{\text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O}}{\text{SiO}_2 + \text{Al}_2\text{O}_3} \quad (15)$$

As shown in Table 2, the order of the AI sequence for different biomass chars can be ranked as BS-char, MC-char, WS-char, PS-char, RL-char and PSD-char. The AI value for BS-char reaches to 535.45, which is obviously higher than the others, but the gasification reactivity of BS-char is much lower than the others. There was no good correlation between the reactivity and alkali index for different chars in this study. The particle size distributions for different semi-cokes are shown in Table 8, from which the particle size is concentrated between 10-50 μm . Among them, particle size of PS-char and MC-char are obviously larger than that of PSD-char and BS-char, but the gasification reactivities of PS-char and MC-char are obviously higher than that of PSD-char and BS-char, which is in discrepancy with the normal thinking that gasification reactivity is strengthened by lowering the particle size. It could be summarized that the characteristics of the raw material was not the main factor

affecting the gasification reactivity. Whereas, the structure or the carbon crystalline structure of the char may play a significant role in char gasification reactivity.

Morphological analysis was carried out on different samples. Fig.5 corresponds to the SEM photographs of different chars. After pyrolysis, different structures of cellulose, hemicelluloses and lignin in samples are broken to lead to the large differences of the surface of different samples. After pyrolysis and being crushed, for PS-char and MC-char, particle is cotton shaped with large porous structure; for WS-char and RL-char, particle is in strip shape with clear vertical texture and thick skeleton structure; for PSD-char, particles mainly exists in thin slice structure with smooth surface; for BS-char, columnar structure is kept with clear texture. It could be found from SEM that four kinds of chars from herbaceous residue are more porous than the two kinds of woody residue char. Accordingly gasification reactivities of herbaceous residue char are higher than that of woody residues char, which agree well with the conclusions from literature [8]. However specific surface of different samples can't be distinguished quantitatively from SEM pictures, so in order to further quantitatively investigate porous structure of different chars, N₂ adsorption (77 K) technique was used to test pore structure distribution and specific surface area.

Adsorption curves are shown in Fig.6, and they all present S shape belonging to II adsorption type according to IUPAC standard [44]. At the low relative pressure stage, the curve rises slowly with convex shape, which implies that adsorption process changes from monolayer to multilayer, meanwhile indicating more micropores exists in samples. At the high relative pressure stage, the curve rises quickly showing that medium and large pore structures exist. At the same time, the adsorption and desorption branches do not match at low relative pressure stage. The main reason is that there are large amount of very narrow slit pores or bottle shaped pores. The N₂ molecules at 77K are very slowly moving, so the adsorption in very narrow pores is kinetically limited. Different shapes of adsorption curves mean that distributions of pores are different for various samples. The textural properties of the different prepared chars are summarized in Table 9. For total surface area, PSD-char is the largest, and MC-char is the smallest. For average pore diameter, PSD-char is the largest and MC-char is the smallest. These indicate that though PSD-char has small amount of macropores, the micropore in it is abundant which contributes to mainly specific surface area. MC-char has many macropores, but the number of mesopores as well as micropores is small leading to low specific surface area. Normally the higher the specific surface area, the higher the gasification reactivity will be. However, for the studied samples in this paper, the similar tendency is not found. Similar result was also reported by Yuan et al. [36] who stated that the gasification reactivity of biomass chars is not controlled by the pore structure. Zhang et al. [12] also indicated that the pore structure obtained by the method of physical adsorption was not a clear index in predicting the gasification reactivity of different chars.

From above analyses, it could be summarized that volatile, ash, mineral type, particle size as well as specific

surface area are not critical factors affecting gasification reactivity. Large amount of literatures [13,36,40,45-47] show that gasification reactivities of different char had negative relation with carbonaceous structure. The Raman atlas of different samples are shown in Fig.7(a). Two main peaks appear in the range of the Raman shift between 900 and 1800 cm^{-1} . The peak appearing at a shift of 1300-1400 cm^{-1} is the D band, whose relative intensity increases with the number of amorphous carbon structures. The peak appearing at a shift of 1550-1600 cm^{-1} is the G band, which is attributed to a stretching vibration mode of graphite C=C bonds [48]. The intensities of D and G bands can be denoted by I_D and I_G , respectively. Generally, amorphous carbon structure could improve gasification reactivity of char, and accordingly the higher graphitization degree, the lower the gasification reactivity will be. However, as shown in Fig.7(a), I_D of different chars from high to low follows the sequence of RL-char, PSD-char, PS-char, WS-char, MC-char and BS-char. In addition, I_G has the same order as I_D , which means that gasification reactivity of different chars could not be ascertained only through I_D or I_G . It is known that the ratio of the intensities of the D band to the G band (I_D/I_G) is one of the most important Raman parameters to study the degree of organization of carbon materials [49]. The value of the Raman parameter I_D/I_G increases with the decrease in the uniformity of carbonaceous structure, or the increase in the degree of amorphousness. Fig.7(b) shows the dependence of parameter I_D/I_G of different chars, and it could be found that the order of I_D/I_G value sequence for various chars can be ranked as PSD-char<BS-char< RL-char<WS-char<MC-char<PS-char. This trend was identical with the trend of the gasification reactivity. Therefore, the I_D/I_G value might be developed to evaluate gasification reactivity of different chars. The relationship between gasification reactivity and Raman spectroscopy has been reported in literatures. Bar-ziv et al. [50,51] have developed the approach of applying Raman spectroscopy to characterize synthetic, coal and cellulose char. Doorn et al. [52] employed Raman spectroscopy to determine the degree of ordering in various carbonaceous materials including coals, activated carbon, soot, and correlated them with their oxidation reactivity measured by temperature-programmed oxidation. The linear relationship between the peak position of the G band and the maximum oxidation temperature has been found. In the previously study [14], the same phenomenon was also observed. In summary, the I_D/I_G can be regarded as an important factor to evaluate gasification reactivity of different chars.

Table 6 simultaneously shows that the activation energies for the six kinds of biomass chars and values of them can be ranked as PS-char<PSD-char<MC-char<WS-char<BS-char<RL-char. However, the order is different for activity of biomass char gasification. The main reason for this phenomenon is that the value of the gasification rate of the biomass chars is affected by both activation energy and pre-exponential factor. It is common sense that the lower the value of the activation energy and the higher the value of the pre-exponential factor, the faster the reaction rate will be. Comparing the activation energies and pre-exponential factors of the different kinds of

biomass chars, the pre-exponential factor increases with the increase of activation energy, which is referred as the kinetic compensation effect. In the present study, a marked compensation effect is also presented between the activation energies and the pre-exponential factors for the gasification reaction of different chars, as shown in Fig. 5. There is an obvious linear relation between E and $\ln k_0$. According to the study by Xie et al. [53,33], this may be due to the similar mechanisms of gasification reactions, especially for the oxygen-containing surface complexes C(O). For reactions with lower E values, it is more easy for the free active carbon site to connect with CO_2 to generate a C(O. However, in the meantime, the bond between C(O) becomes stronger and the char structure becomes more stable, limiting the movement of C(O) and leading to a lower k_0 value. From Fig. 8, It can be also seen that the BS-char deviates from the compensation curve. Table 2 shows the AI values of the 6 kinds of biomass chars. Except for 535.4 of BS-char, the other AI values are in the range of 1-60 without significant differences. Therefore, it could be preliminarily deduced that the content and composition of ash are the prime factors resulting in the deviation of the BS-char from compensation effect curve . Further study is needed to investigate the detailed mechanism.

4 Conclusions

In this work, six different biomass chars were gasified in a thermobalance at atmospheric pressure with CO_2 . It was established that the char gasification reactions were carried out under chemical reaction control at all the studied temperatures. The best model for describing the gasification reaction of biomass char was found to be the MRPM. The activation energies derived from the MRPM for the biomass chars lie in the range of 132.84-163.75 kJ/mol, and dynamics compensation effect during the gasification process is obviously existed. The reactivities of the different chars were compared using a reactive index. It was concluded that the gasification reactivities of herbaceous residues are better than that of wooden residues, and the increase of gasification temperature can obviously improve the gasification reactivity of biomass chars. The chemical components and physical structures of these chars were systematically tested. It is found that the carbonaceous structure is an important factor to evaluate gasification reactivity of different chars.

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Table 1

Proximate, ultimate analyses and high heating value of different chars

Sample	Proximate analysis (wt,%)				Ultimate analysis (wt,%)				HHV (MJ/kg)
	FC _d ^a	A _d	V _d	C _d	H _d	O _d ^a	N _d	S _d	
PS-char	68.67	29.97	1.36	69.05	0.32	0.21	0.52	0.32	23.58
MC-char	65.41	32.31	2.28	78.33	1.45	1.35	1.66	0.15	22.68
WS-char	61.81	36.63	1.56	65.74	0.93	3.17	1.06	0.65	21.05
RL-char	50.92	47.01	2.07	45.20	0.61	1.01	0.71	0.25	17.09
PSD-char	92.37	2.58	5.05	86.18	1.47	1.89	1.01	0.06	33.92
BS-char	78.69	20.35	0.96	69.54	1.02	2.08	0.73	0.13	27.25

^a Calculated by difference. FC, fixed carbon; A, ash; V, volatile matter; d, dry basis.

Table 2

Ash compositions of the different biomass chars (wt,%)

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	Na ₂ O	K ₂ O	MgO	<i>AI</i>
PS-char	33.09	8.11	5.55	35.41	1.34	7.22	2.85	38.10
MC-char	24.87	1.92	2.20	3.92	0.43	51.21	0.99	70.86
WS-char	31.85	0.78	0.89	15.10	0.32	29.63	4.56	56.69
RL-char	81.03	0.76	4.69	2.32	0.52	7.06	0.58	8.72
PSD-char	43.21	8.76	4.31	18.82	1.68	7.90	2.76	1.76
BS-char	1.70	1.12	0.31	46.66	1.41	13.18	12.64	535.45

Table 3Kinetic parameters of VM, GM and RPM models by fitting kinetic data of CO₂ gasification of different biomass chars

Sample	VM		GM		RPM		
	E (kJ/mol)	k_0 (s ⁻¹)	E (kJ/mol)	k_0 (s ⁻¹)	E (kJ/mol)	k_0 (s ⁻¹)	ψ
PS-char	128.4	1.21E+03	129.1	1.02E+03	129.8	5.45E+02	11.68
MC-char	144.4	6.63E+03	145.4	5.88E+03	146.4	1.22E+03	128.24
WS-char	163.5	4.22E+04	163.6	3.42E+04	163.3	7.26E+03	88.54
RL-char	183.5	1.25E+05	181.2	7.84E+04	180.3	4.05E+03	8.26
PSD-char	140.7	2.00E+05	141.2	1.69E+03	143.3	3.65E+02	149.37
BS-char	171.5	2.97	171.1	2.72	168.1	2.08	2.14E+03

Table 4

Deviation between experimental data and predicted values

Sample	<i>DEV X (%)</i>		
	VM	GM	RPM
PS-char	10.2	6.7	1.8
MC-char	14.0	10.9	3.4
WS-char	13.4	10.1	2.8
RL-char	9.3	5.2	2.1
PSD-char	13.8	10.6	2.5
BS-char	21.4	18.7	6.5

Table 5

Comparisons of the kinetic parameters of RPM and MRPM

Sample	RPM			MRPM			
	E (kJ/mol)	k_0 (s ⁻¹)	ψ	E (kJ/mol)	k_0 (s ⁻¹)	N	ψ
PS-char	129.8	5.45E+02	11.68	163.7	2.17E+04	0.807	8.33
MC-char	146.4	1.22E+03	128.24	132.8	6.85E+02	0.393	10.18
WS-char	163.3	7.26E+03	88.54	153.2	5.12E+03	0.604	11.38
RL-char	180.3	4.05E+03	8.26	149.5	4.07E+03	0.837	5.3
PSD-char	143.3	3.65E+02	149.37	144.7	7.88E+02	0.587	21.75
BS-char	168.1	2.08	2.14E+03	162.7	8.41E+02	0.234	1.87E+03

Table 6

Comparison of the activation energy values obtained in the present work and in literatures

Sample	E (kJ/mol)	Model	Reference
MC-char	160-168	Shrinking core model	Gaur et al(1992)[32]
WS-char	125.7	Random Pore model	Zhou (2014)[33]
WS-char	147-184	Modified Volume Reaction model	Li et al.(2009)[34]
RL-char	197	Volume Reaction model	Bhat et al.(2001) [35]
RL-char	203-238	Random Pore model	Yuan et al.(2011)[36]
PSD-char	232-249	Random Pore model	Yuan et al.(2011)[36]
PSD-char	213-222	Free-model	Dong et al.(2014)[37]
BS-char	125 $\pm$ 30	Random Pore model	Sircar et al(2014)[38]

Table 7The reactivity index ($R_{0.5}$) calculated for different chars

Temperature, K	$R_{0.5} \times 10^3 (\text{s}^{-1})$					
	PS-char	MC-char	WS-char	RL-char	PSD-char	BS-char
1123	0.58	0.60	0.52	0.44	0.31	0.32
1173	1.77	1.44	1.27	1.12	0.55	0.69
1223	3.33	2.66	2.51	2.34	1.03	1.60
1273	5.81	3.85	4.31	3.53	1.84	2.72

Table 8

Particles size distribution of different chars (%)

Particle size (μm)	PS-char	MC-char	WS-char	RL-char	PSD-char	BS-char
<10	1.86	1.73	0.2	12.18	13.09	21.42
10~30	32.14	40.42	24.02	82.43	40.27	60.26
30~50	34.04	36.02	36.27	4.34	30.43	17.01
>50	31.96	21.83	39.51	1.05	16.21	1.31

Table 9

Pore characteristic parameters of different chars

Sample	S_t (m ² /g)	V_t (cm ³ /g)	D_a (nm)
PS-char	22.56	0.0252	4.47
MC-char	4.31	0.0097	8.98
WS-char	29.56	0.0342	4.61
RL-char	9.62	0.0182	7.58
PSD-char	56.38	0.0485	2.16
BS-char	31.16	0.0241	3.10

Note: S_t , total surface area; V_t , total pore volume; D_a , average pore diameter.

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