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The effect of temperature and heating rate on char properties obtained from solar pyrolysis of beech wood

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H I G H L I G H T S

- Char was obtained during solar pyrolysis at various temperatures and heating rates.
- “Solar chars” up to 2000 °C and up to 450 °C/s have been produced.
- Temperature and heating rate jointly affected char yield, structure and reactivity.
- Reactivity evolution with temperature and heating rate were related to structure.

A B S T R A C T

Char samples were produced from pyrolysis in a lab-scale solar reactor. The pyrolysis of beech wood was carried out at temperatures ranging from 600 to 2000 °C, with heating rates from 5 to 450 °C/s. CHNS, scanning electron microscopy analysis, X-ray diffractometry, Brunauer–Emmett–Teller adsorption were employed to investigate the effect of temperature and heating rate on char composition and structure. The results indicated that char structure was more and more ordered with temperature increase and heating rate decrease (higher than 50 °C/s). The surface area and pore volume firstly increased with temperature and reached maximum at 1200 °C then reduced significantly at 2000 °C. Besides, they firstly increased with heating rate and then decreased slightly at heating rate of 450 °C/s when final temperature was no lower than 1200 °C. Char reactivity measured by TGA analysis was found to correlate with the evolution of char surface area and pore volume with temperature and heating rate.

Keywords:

Beech wood

Solar pyrolysis

Char structure

Reactivity

Combined effect

1. Introduction

Biomass is a renewable energy source that can partly relieve the energy crisis and environmental problems. Then the technology converting biomass effectively and efficiently into fuel and chemical stock receives more and more attention. Pyrolysis is one of the most attractive processes to convert biomass into economically renewable intermediates (Mettler et al., 2012). As pyrolysis is an endothermic thermochemical process, external heat is required. In standard pyrolysis, the heat is obtained by combustion of fossil fuel or of part of the initial biomass, which reduces the energy efficiency and increases the pollution discharge (Nzihou et al., 2012). For avoiding the disadvantage of standard pyrolysis, concentrated solar energy can be used to provide the heat for pyrolysis reactions. The biomass directly absorbs the heat from concentrated solar

energy thus resulting in fast or rapid pyrolysis, producing gases, tar and char.

The char is carbon-rich and can be further used as a fuel (gasification and combustion) or decontamination adsorbent. Firstly, it is necessary to understand the char reactivity for designing a high efficiency gasification or combustion reactor (Cetin et al., 2005). Secondly, the appropriate pore structure and surface area are important for preparing decontamination adsorbent (Demirbas et al., 2006). For making better use of char obtained from solar pyrolysis, the composition, surface area, pore structure and reactivity should be investigated in advance. Char reactivity and morphological structure are especially affected by the pyrolysis conditions (Blasi, 2009; Raveendran and Ganesh, 1998). The effects of pyrolysis conditions on the structure and reactivity of biomass chars have been investigated in several studies in relation to the following parameters: temperature (Fu et al., 2012a, 2011; Kim et al., 2012; Min et al., 2011; Bonelli et al., 2001), heating rate (Mermoud et al., 2006; Guerrero et al., 2005; Fushimi et al., 2003), residence time and pressure (Cetin et al., 2005, 2004).

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The char carbon content increases with temperature, which is the indication of increased structure ordering for lowering the reaction site concentration (Kumar and Gupta, 1994). The char surface area increases with temperature and then slightly decreases when the temperature is higher than 1173 K (Fu et al., 2012b). There is a significant diminution in char reactivity with the increase of temperature (above 1073 K) as previously reported (Guerrero et al., 2005; Chen et al., 1997). At lower temperature (below 1073 K), the release of volatile intensifies owing to the temperature increase enlarges the char surface area. However, there are more and more structural ordering and micropore coalescence for char when temperature keeps on increasing even higher than 1073 K.

The increase of heating rate causes a weak decrease in the carbon content and an increase in hydrogen and oxygen content of char. Moreover, the heating rate effect tends to disappear at high temperatures (Antal and Grønli, 2003). The presence of higher hydrogen and oxygen contents is related to the availability of active sites and thus to enhanced reactivity (Laurendeau, 2009). For slow heating rates (lower than 1 °C/s), no major change takes place in the particle morphology as volatile is released through the natural porosity (Della Rocca et al., 1999). For fast heating rates (higher than 10 °C/s), the original cellular structure is lost as a consequence of melting (Kurosaki et al., 2003). When the heating rate increases, the volatile release speeds up. Then large internal cavities and a more open structure of char is produced (Guerrero et al., 2005) owing to the fast volatile release producing internal overpressure and coalescence of the smaller pores, which leads to the increase of surface area and pore volume. So the char reactivity increases with heating rate can be explained by the higher surface area and pore volume (Cetin et al., 2005, 2004). Besides, heating rate rising shortens tar vapors residence time in pores and reduces the condensation reaction leading to char reactivity increase (Kurosaki et al., 2003). However, char obtained at high heating rate has lower surface area compared to that at low heating rate when temperature was 900 °C (Fu et al., 2012b). It is attributed to too high heating rate causing char interior higher temperature, a partial graphitization with formation of grapheme structure occurs, which does not contribute to the development of large surface area.

Almost all of the above conclusions have been deduced from univariable analysis. However, there is little information on the char prepared at different pyrolysis temperatures with different heating rates (Angin, 2013; Fu et al., 2012b). In this study, the bivariate analysis was used for investigating the combined effect of pyrolysis temperature and heating rate on char characteristics. Besides, there are two characteristics for the solar reactor that may affect char characteristics: (1) High temperature and heating rate can be achieved; (2) Two temperature zones exist as described in Ref. Hopkins et al. (1984) and modeled in Ref. Zeng et al. (2014a). Indeed, since only the sample is directly heated by solar radiation, the “hot” sample is surrounded by relatively “cold” gas. Then, most vapors issued from primary reactions are quenched as soon as they leave the sample. Then the evaluation of char obtained in two temperature zones reactor at high temperature (up to 2000 °C) and high heating rate (up to 450 °C/s) is investigated for the first time. The purpose of this paper was to: (i) characterize the structure and composition of chars generated under different pyrolysis conditions; (ii) study the reactivity of char prepared at different temperatures and heating rates; (iii) relate the characterization and reactivity for the char.

2. Experimental

2.1. Materials

Beech wood pellets were used for pyrolysis experiments. The initial sawdust particle size ranged from 0.35 to 0.80 mm. After sawdust compaction, the pellets were cylinders with 10 mm in diameter and 5 mm thick. The proximate analysis of beech wood is 85.3% volatile matter, 14.3% fixed carbon, 0.4% ash and 6% moisture. The ultimate analysis for beech wood is as follows: C = 50.8%, H = 5.9%, O = 42.9%, N = 0.3% and S = 0.02%.

2.2. Pyrolysis experiments

2.2.1. Solar reactor

As shown in Fig. 1, pyrolysis experiments were carried out under an argon flow in a transparent Pyrex balloon reactor (inside

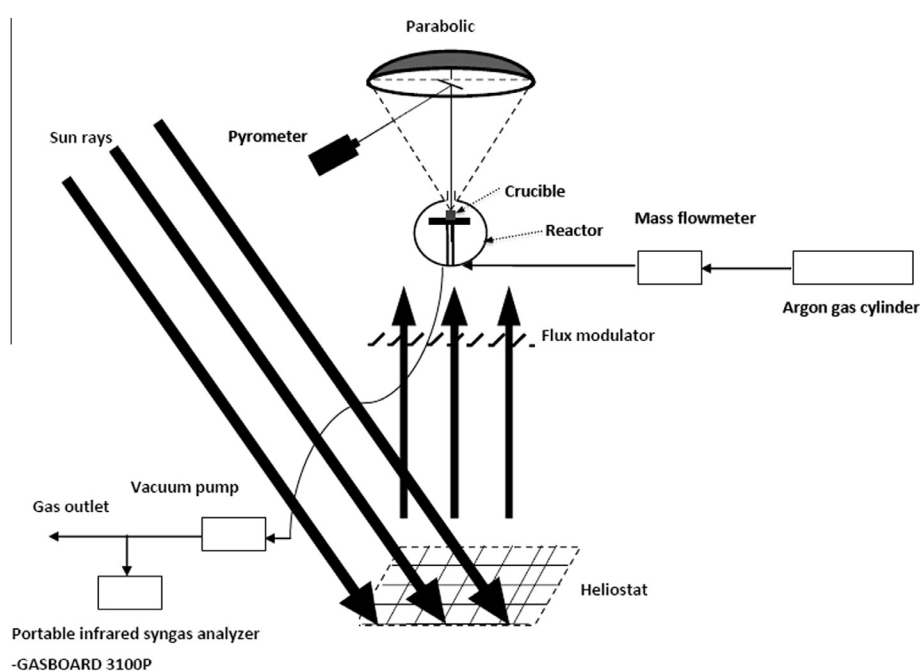


Fig. 1. Schematic of the solar pyrolysis experimental setup.

diameter 185 mm, volume 6 L). The pellet was placed in a graphite crucible insulated with black foam and located at the focus of a 1.5 kW vertical-axis solar furnace. The sample surface temperature was measured by a solar-blind optical pyrometer (KLEIBER monochromatic at 5.2 μm). A shutter controlled by a PID controller modulated the incident radiation and thus mastered the sample temperature, e.g. the heating rate and the final temperature. Gas products mixed with argon were taken out by a vacuum pump through the gas outlet located on reactor bottom.

2.2.2. Experimental procedure

Pyrolysis experiments were performed under argon flow rate of 6 NL/min. First, experiments were performed at four heating rates of 5, 50, 150 and 450 $^{\circ}\text{C}/\text{s}$ to the final temperatures of 800, 1200 and 2000 $^{\circ}\text{C}$. Afterwards, two other temperatures of 600 $^{\circ}\text{C}$ and 1600 $^{\circ}\text{C}$ with the heating rate of 50 $^{\circ}\text{C}/\text{s}$ were used for pyrolysis experiments. All experiments were maintained at pyrolysis temperature for 6 min. The temperature control results have been described in details in Ref. Zeng et al. (2014b). The real heating rates and final temperatures were approximated to the set values, which indicated that the temperature control system was accurate enough for experiments.

Each experiment was repeated at least 3 times to check the repeatability. After each pyrolysis experiment, the char residue was kept in the solar reactor until it cooled to the room temperature. After weighting for determining the yield, the char was stored in desiccator to prevent moisture absorption.

2.2.3. Char characterization

The elemental composition of char (CHNS) was determined by NA 2100 protein. Surface morphology was investigated by scanning electron microscopy (Philips XL30 FEG). XRD analysis was performed at room temperature using a PANalytical XPert Pro diffractometer (CuK radiation, $\lambda = 0.15418 \text{ nm}$, 40 kV–20 mA). The surface area and pore volume were observed by Brunauer–Emmett–Teller (BET Tristar II 3020 Micromeritics). The reactivity measurements were performed under isothermal conditions using thermogravimetric analyzer (TG-DSC 111 Setaram). In TGA experiments, 20 mL/min of nitrogen was used during the heating up period with the heating rate of 20 $^{\circ}\text{C}/\text{min}$ from room temperature to 800 $^{\circ}\text{C}$. After that, the sweeping gas was switched on to the air for starting the oxidation reaction. The total gas flow rate was 2 L/h with 20% oxygen ratio. The experiment was finished when the weight loss decreased close to zero.

3. Results and discussion

3.1. The effect of temperature and heating rate on char yield and composition

3.1.1. The effect on char yield

The yields of char prepared at different temperatures and heating rates are shown in Table 1. The char yields decreased with temperature and heating rate, which may be due to the primary or greater secondary decomposition of char (Şensöz and Angin, 2008). The char yield reduction rate with temperature was 0.004%/ $^{\circ}\text{C}$ (heating rate of 50 $^{\circ}\text{C}/\text{s}$). It increased to 0.011%/ $^{\circ}\text{C}$ (temperature of 1200 $^{\circ}\text{C}$). Then, the influence of heating rate on the char yield was more obvious than that of temperature. When the heating rate was high enough, there was no big difference of char yield produced at 150 and 450 $^{\circ}\text{C}/\text{s}$ at the same temperature. The char yield reduction rates with heating rate were 0.0090, 0.0112 and 0.0115%/ $^{\circ}\text{C}/\text{s}$, respectively for temperature: 800, 1200 and 2000 $^{\circ}\text{C}$. So the effect of heating rate on char yield was more significant at high temperature. With the low heating rate of 5 $^{\circ}\text{C}/\text{s}$, the

Table 1
Effect of pyrolysis temperature and heating rate on char yield.

| | Pyrolysis temperature ($^{\circ}\text{C}$) | | | | |
|--|--|----------------|----------------|---------------|----------------|
| | 600 | 800 | 1200 | 1600 | 2000 |
| Heating rate 5 $^{\circ}\text{C}/\text{s}$ | | | | | |
| Yield (wt.%) | – | 13.5 \pm 0.4 | 13.4 \pm 0.1 | – | 11.6 \pm 0.1 |
| Heating rate 50 $^{\circ}\text{C}/\text{s}$ | | | | | |
| Yield (wt.%) | 14.0 \pm 0.3 | 12.5 \pm 0.2 | 10.0 \pm 0.7 | 8.3 \pm 0.4 | 8.3 \pm 0.5 |
| Heating rate 150 $^{\circ}\text{C}/\text{s}$ | | | | | |
| Yield (wt.%) | – | 9.7 \pm 0.1 | 8.5 \pm 0.4 | – | 7.2 \pm 0.2 |
| Heating rate 450 $^{\circ}\text{C}/\text{s}$ | | | | | |
| Yield (wt.%) | – | 9.5 \pm 0.1 | 8.4 \pm 0.3 | – | 6.5 \pm 0.2 |

char yields were almost the same at 800 and 1200 $^{\circ}\text{C}$. The highest char yield was about 14%, which was obtained at 600 $^{\circ}\text{C}$ with the heating rate of 50 $^{\circ}\text{C}/\text{s}$. The lowest char yield was about 6.5% when the temperature and heating rate were 2000 $^{\circ}\text{C}$ and 450 $^{\circ}\text{C}/\text{s}$, respectively. This trend could be explained by the release of volatiles and intermediate size organics lower at 600 $^{\circ}\text{C}$ than at higher temperatures investigated.

3.1.2. The effect on char composition

Table 2 gives the composition of char generated at different temperatures and heating rates. The carbon, hydrogen, nitrogen and sulfur were directly determined while oxygen was calculated by difference. Char was mainly composed of carbon with mass content higher than 75%. When the temperature increased to 1600 $^{\circ}\text{C}$, there was rapid growth of carbon content while the hydrogen and oxygen contents declined sharply. The char was completely carbonized with almost 100% carbon content at temperature of 2000 $^{\circ}\text{C}$. The carbon content increase with temperature was assumed to come from the carbonaceous structure graphitization at high temperatures (Chen et al., 2012). Between 600 and 800 $^{\circ}\text{C}$, the decrease for hydrogen and oxygen contents was most obvious, owing to the char weak bonds cracking and cleavage (Demirbas, 2004). There was no obvious effect of heating rate on char composition when temperature was higher than 800 $^{\circ}\text{C}$, in accordance with what was mentioned before (Antal and Grønli, 2003).

3.2. The effect of temperature and heating rate on char morphology and structure

3.2.1. SEM analysis

Fig. S1 shows a comparison among SEM images of raw beech sawdust and its chars produced at different temperatures with the same heating rate of 50 $^{\circ}\text{C}/\text{s}$. As can be seen from Fig. S1a, the raw wood made of solid cells was bounded together and there was almost no cavity. There were many small pores appearing in the char caused by devolatilization when the pyrolysis temperature was 800 $^{\circ}\text{C}$ (Fig. S1b). However, the char was more and more twisted and rough with temperature rising, which meant that the deformation of char intensified with temperature increase up to 1200 $^{\circ}\text{C}$ (Fig. S1c). This trend could be explained by the release of volatiles and intermediate size organics increasing with temperature. The cracks and pores in the chars increased with temperature increase, as observed previously (Fu et al., 2012b). When the temperature increased to 2000 $^{\circ}\text{C}$, the macropores disappeared owing to melting as illustrated in Fig. S1d. Small grains appeared as agglomeration of spherules in the char surface (Fig. S1c). Furthermore, the char particles present more and more growth filament crystals (Fig. S1d). The grains and the crystals observed on char surfaces may be inorganic compounds that have migrated to the surface.

The SEM images of char produced at different heating rates and same temperature of 1200 $^{\circ}\text{C}$ are shown in Fig. S2. There was no

Table 2
Effect of pyrolysis temperature and heating rate on char composition.

| | Pyrolysis temperature (°C) | | | | |
|-----------------------|----------------------------|------------|------------|------------|------------|
| | 600 | 800 | 1200 | 1600 | 2000 |
| Heating rate 5 °C/s | | | | | |
| C (wt.%) | – | 82.7 ± 0.7 | 82.4 ± 3.9 | – | 99.8 ± 0.3 |
| H (wt.%) | – | 2.0 ± 0.2 | 1.4 ± 0.6 | – | 0 |
| N (wt.%) | – | 0.4 ± 0.4 | 0.2 ± 0.3 | – | 0 |
| O (wt.%) | – | 14.9 ± 0.5 | 16 ± 3.1 | – | 0.2 ± 0.3 |
| Heating rate 50 °C/s | | | | | |
| C (wt.%) | 76.4 ± 3.3 | 80.9 ± 0.4 | 82.3 ± 0.5 | 94.4 ± 1.7 | 99.8 ± 0.7 |
| H (wt.%) | 2.6 ± 0.2 | 1.4 ± 0.2 | 1.0 ± 0.2 | 0 | 0 |
| N (wt.%) | 0.3 ± 0.3 | 0.5 ± 0.1 | 0.6 ± 0.1 | 0 | 0 |
| O (wt.%) | 20.7 ± 1.2 | 17.2 ± 0.3 | 16.1 ± 0.3 | 5.6 ± 1.7 | 0.2 ± 0.7 |
| Heating rate 150 °C/s | | | | | |
| C (wt.%) | – | 82.4 ± 0.4 | 79.2 ± 1.3 | – | 99.7 ± 0.4 |
| H (wt.%) | – | 2.1 ± 0.2 | 0.8 ± 0.7 | – | 0 |
| N (wt.%) | – | 1.0 ± 0.6 | 0.8 ± 0.1 | – | 0 |
| O (wt.%) | – | 14.5 ± 0.5 | 19.2 ± 1.2 | – | 0.3 ± 0.4 |
| Heating rate 450 °C/s | | | | | |
| C (wt.%) | – | 82.5 ± 0.1 | 80.3 ± 0.9 | – | 99.8 ± 0.8 |
| H (wt.%) | – | 1.8 ± 0.2 | 1.1 ± 0.1 | – | 0 |
| N (wt.%) | – | 0.4 ± 0.4 | 0.7 ± 0.1 | – | 0 |
| O (wt.%) | – | 15.3 ± 0.3 | 17.9 ± 0.7 | – | 0.2 ± 0.8 |

major morphological change from raw wood except the rough surface observed for the char obtained at the heating rate of 5 °C/s (Fig. S2a). The char produced with the heating rate of 150 °C/s deformed a lot, with many open pores (Fig. S2c). However, char with few pores was observed when the heating rate increased to 450 °C/s (Fig. S2b). This may be due to high heating rate that resulted in plastic transformations and created smoother surfaces with spherical cavities (Cetin et al., 2004).

3.2.2. XRD analysis

The comparison of X-ray diffraction spectra of chars prepared at different heating rates and temperatures are shown in Fig. S3. The crystal plane indices C (002) and C (100) peak were present in the spectra, which correspond to 2θ values around 25° and 45°. The degree of azimuthal orientation and parallel of the aromatic lamellae is represented by C (002). And C (100) reflects the aromatic lamina size. To investigate the temperature influence on char crystallinity, the heating rate was constant as 50 °C/s. As the temperature increased from 800 to 1600 °C, the C (002) peak slightly sharpened. However, the C (002) peak greatly sharpened at temperature of 2000 °C. Then the degree of orientation of aromatic lamellae increased with temperature especially at 2000 °C owing to the sharper C (002) peak (Cui et al., 2006). The C (100) peak was sharper and sharper when the temperature rose from 800 to 1600 °C. The sharp trend was very clear at 2000 °C. And the higher the temperature, the higher the degree of condensation of the aromatic ring, as proved by the sharper C (100) peak (Cui et al., 2006). Two kinds of char obtained at different heating rates of 50 and 450 °C/s were compared to study the heating rate effect on crystallinity. It was found that the C (002) and C (100) peaks were sharper for char at 50 °C/s than those at 450 °C/s. This proved that the char prepared at high heating rate had low crystallinity owing to melting (Cetin et al., 2004). With temperature increase and heating rate decrease (higher than 50 °C/s), the crystallinity increased, which indicated that the char structure was more and more ordered and aromatic.

3.2.3. BET analysis

The surface area and porosity of char were measured by means of N₂ adsorption at –196 °C on the TriStar II 3020. Table 3 shows the effect of temperature and heating rate on char textural properties. As can be seen from Table 3, when the heating rate was 50 °C/s, the BET surface area increased from 70.2 m²/g to 110.2 m²/g with

temperature increased from 800 °C to 1200 °C then it decreased dramatically to 22.2 m²/g at 2000 °C. The pore volume increased about 17 times with increasing temperatures from 800 to 1600 °C, then there was a slight decrease at 2000 °C. The result was similar to that reported in literature, which showed that the total surface area firstly increases with rising temperature lower than 900 °C and then decreases when the temperature keeps increasing (Fu et al., 2012b). When the temperature increases from 800 to 2000 °C, there are two competing processes affecting the surface area: (1) Intensifying volatile release (Kim et al., 2012); (2) Thermal deactivation over 900 °C (Lu et al., 2002). The first process causes the increase of surface area and pore volume. The second process induces char melting, pore fuse and structure ordering leading to the decrease of surface area and pore volume. Based on these result, it was easily found that the first process defeated the second process and dominated with the temperature increase from 800 to 1200 °C. However, with temperature as high as 2000 °C, the second process seemed to be predominant causing the decrease of surface area and pore volume.

As depicted in Table 3, a gradual increase of the BET surface area and pore volume can be observed with heating rate peaking around 150 °C/s. This may be due to the higher heating rates resulting in char particles melting and creation of smoother surfaces and spherical cavities (Cetin et al., 2004, 2005; Mohanty et al., 2013). Then there was a slight decrease when the heating rate increased to 450 °C/s. It may be explained by char interior partial graphitization caused by inner high temperature at too high heating rates (Fu et al., 2012b). Between 5 °C/s and 50 °C/s, the BET surface area increased 14-fold while the pore volume increased about 6 times. After that, the change was not so obvious. It showed the significant effect of fast heating rate on surface area and pore volume. Once the heating rate was equal to the flash heating rate, the influence was not so obvious. In addition, the surface area and pore volume increased about 1.27 and 1.15 times when the heating rate increased from 50 °C/s to 150 °C/s, at temperature 1200 °C. However, they increased about 3 and 2.5 times at 2000 °C. As the heating rate kept increasing to 450 °C/s, they decreased about 1.1 and 1.2 times at 1200 °C. Then, they decreased about 2 and 1.6 times when the temperature was 2000 °C. By comparing with the heating rate effect at temperatures of 1200 °C and 2000 °C, it was easily found that the heating rate effect on char surface area and pore volume was more remarkable at higher temperatures.

Table 3
Effect of pyrolysis temperature and heating rate on char surface area and pore volume.

| | Pyrolysis temperature (°C) | | | |
|---|----------------------------|--------|--------|--------|
| | 800 | 1200 | 1600 | 2000 |
| Heating rate 5 °C/s | | | | |
| BET surface area (m ² /g) | – | 7.9 | – | – |
| BJH adsorption pore volume (cm ³ /g) | – | 0.0050 | – | – |
| Heating rate 50 °C/s | | | | |
| BET surface area (m ² /g) | 70.2 | 110.2 | 48.7 | 22.2 |
| BJH adsorption pore volume (cm ³ /g) | 0.0028 | 0.0470 | 0.0400 | 0.0323 |
| Heating rate 150 °C/s | | | | |
| BET surface area (m ² /g) | – | 140.8 | – | 60.3 |
| BJH adsorption pore volume (cm ³ /g) | – | 0.0540 | – | 0.0790 |
| Heating rate 450 °C/s | | | | |
| BET surface area (m ² /g) | – | 127.8 | – | 31.5 |
| BJH adsorption pore volume (cm ³ /g) | – | 0.0465 | – | 0.0524 |

3.3. The effect of temperature and heating rate on char reactivity

The reactivity often characterizes the oxidation or gasification rate, which refers to the evolution of carbonaceous solid mass loss at an instant with respect to its mass at this time, which can be calculated by using Eq. (1). The conversion degree expresses the degree of reaction advancement which can be written as Eq. (2).

$$R(t) = -\frac{1}{m(t)} \frac{dm(t)}{dt} = -\frac{m_2 - m_1}{(t_2 - t_1)m_1} \quad (1)$$

$$X = \frac{m_0 - m}{m_0} \quad (2)$$

where m is the instantaneous sample mass, m_0 the initial sample mass, $R(t)$ the reactivity at time t , m_1 the sample mass at t_1 time when weight measurement starts, m_2 the sample mass at t_2 time when the weight measurement ends. The conversion degree ($X = 20\% - 80\%$) was selected as a representative reactivity value for each experiment.

The apparent reactivity values, at heating rate of 50 °C/s, corresponding to air oxidation of chars generated at 800, 1200, 1600 and 2000 °C have been plotted in Fig. 2. As shown in Fig. 2, the reactivity of char generated at 1200 °C was the highest, whereas it was the lowest at 2000 °C. And the reactivity of char produced at 800 °C was higher than those obtained at 1600 °C. This may be due to the highest surface area and pore volume produced at 1200 °C. According to the CHNS results, the carbon and hydrogen contents increased and decreased respectively with temperature, which was the indication of increased structure ordering. The increased structure ordering was the indication for lowering the reaction site concentration (Lu et al., 2002). It seemed that the char reactivity reduced with temperature if we used the carbon and hydrogen concentration as indicator for reactivity. Indeed, the surface area and pore volume were more appropriate and accurate for reactivity evaluation. Besides, there was no big difference of reactivity for the chars at various high temperatures. For example, the reactivity of char obtained at 1200 °C was about 21% higher than that at 2000 °C. It was probably due to char structure ordering occurring at all these high temperatures.

The apparent reactivity values for chars prepared at temperatures of 1200 and 800 °C corresponding to different heating rates (5, 50, 150 and 450 °C/s) have been illustrated, respectively in Fig. 3 and Fig. 4. As can be seen from Fig. 3, the reactivity increased with heating from 5 to 150 °C/s. This could be due to the higher surface areas for char generated at higher heating rates (Cetin et al., 2005). And then it slightly decreased at the heating rate 450 °C/s when the temperature was 1200 °C. This may be due to the interior partial graphitization with too high heating rate (Fu et al., 2012b). Fig. 3 shows the reactivity of char obtained at heating

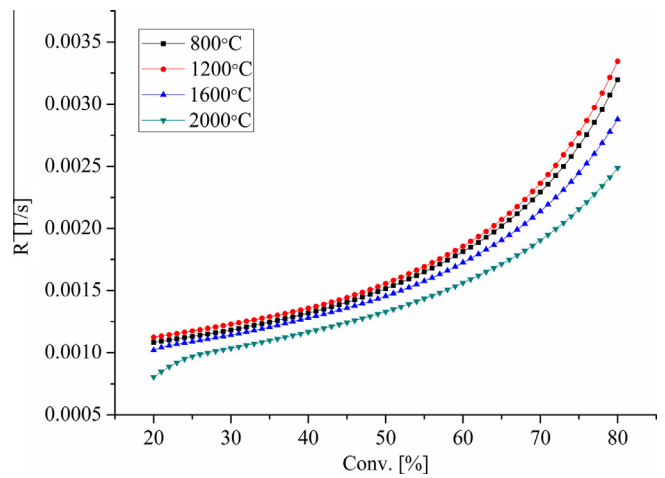


Fig. 2. Temperature effect on char reactivity, prepared at same heating rate (50 °C/s).

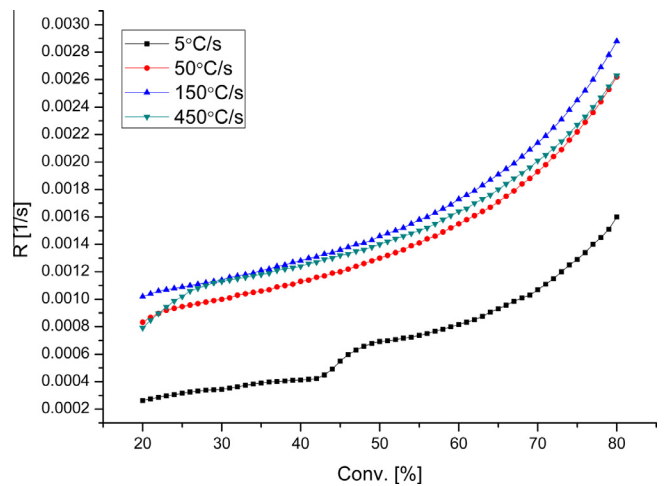


Fig. 3. Heating rate effect on char reactivity, prepared at 1200 °C.

rate 5 °C/s was much lower than those at higher heating rates. For example, chars generated at 150 °C/s had much higher reactivity (approx. 2.3 times) than those at 5 °C/s. However, the char reactivity kept on increasing with heating rate from 5 to 450 °C/s at temperature of 800 °C (Fig. 4). This was because the fast volatile release produces internal overpressure and coalescence of the smaller pores, leading to surface area and pore volume increase with heating rate (Guerrero et al., 2005). Another reason was that the tem-

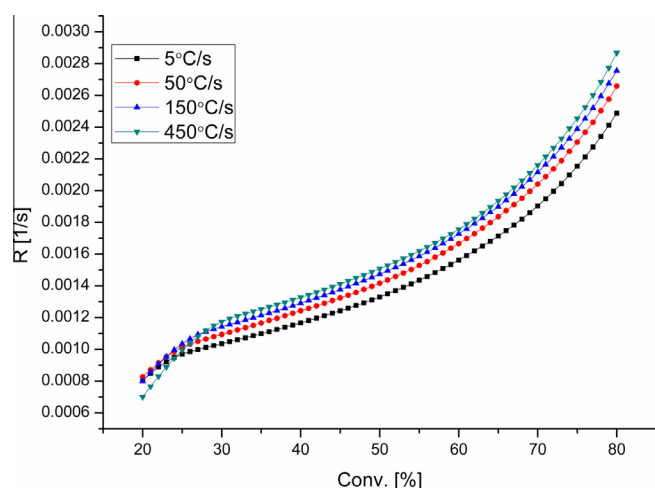


Fig. 4. Heating rate effect on char reactivity, prepared at 800 °C.

perature was not high enough (lower than 1200 °C) for char interior partial graphitization even with high heating rate as 450 °C/s. At first glance, the shape of char obtained at 5 °C/s was pellet, which had more compact structure with smaller surface area. Char produced at higher heating rates (50, 150 and 450 °C/s) were non-compact powder, which had bigger surface area and pore volume. Then the lower reactivity at lower heating rate can be attributed to the smaller surface area and pore volume with respect to the high heating rate (Cetin et al., 2004, 2005; Mohanty et al., 2013).

4. Conclusion

Char properties were influenced by solar pyrolysis temperature and heating rate. The char yield decreased with temperature and heating rate. Char carbonized degree increased with temperature increase and heating rate decrease (higher than 50 °C/s). The BET surface area and pore volume firstly increased with rising temperature from 800 to 1200 °C, then decreased at higher temperatures. They firstly increased with heating rate peak around 150 °C/s and then decreased at 450 °C/s when temperature was no lower than 1200 °C. The bigger the BET surface area and pore volume, the higher the char reactivity, which means that they are good indicators for char reactivity.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.biortech.2015.01.112>.

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