The structural characteristics of waste tire chars at different pyrolysis temperatures

Qiangqiang Ren 1, Limo He 1, Song Hu 1,2, *, Sheng Su 1,2, Yi Wang 1,2, Long Jiang 1,3, Jun Xiang 1,2

1 State Key Laboratory of Coal Combustion, School of Energy and Power Engineering, Huazhong University of Science and Technology, Wuhan 430074, China
2 China-EU Institute for Clean and Renewable Energy, Huazhong University of Science and Technology, Wuhan 430074, China
3 Department of New Energy Science and Engineering, School of Energy and Power Engineering, Huazhong University of Science and Technology, Wuhan 430074, China

E-mail address: husong@hust.edu.cn

Abstract. Pyrolysis was a promising technology to achieve waste tire (WT) dispose and utilization. However, large quantities of low quality waste tire chars (WTCs) would remain after pyrolysis and they could be employed to various applications. Further understanding the structural characteristics of WTCs at different pyrolysis temperatures would benefit to guide their utilizations. Herein, pyrolysis experiments were systematically conducted at 400 °C, 600 °C, 800 °C, and 1000 °C respectively to collect WTCs, whose structural characteristics were detailed analyzed. It was found that higher temperature can promote decrease of large and small aromatic ring systems, alkyl-aryl C-C bonds, defects with ordered arrangements of carbon skeleton structure. Pyrolysis can significantly promote pores formation, higher temperature would promote formation of micropores, while mesopores+macropores destroy before 600 °C and then gradually form. Higher temperature can promote decomposition of pyrrolic nitrogen and sulfur bridge with enrichment of oxidised nitrogen and sulphone bridge. Higher temperature would assist in generation of pyridinic nitrogen before 800 °C and quaternary nitrogen before 600 °C.

1. Introduction
Tire, has played a necessary role in transportation and its production capacity is sharply growing, even leading to an amazing predicted amount of 2.5 billion pieces in 2020 globally [1]. As a result, large quantities of WTs are generated for continuously upgrades of tires, which would cause massive pollutions to the environment because of their non-natural degradability. However, WTs are also regarded as a resource, which requires WTs should be reasonably disposed to achieve harmless treatment and reuse. Pyrolysis, one of the most promising technologies to treat WTs, can directly convert WTs to high valued oils [2, 3]. Unfortunately, there would be lots of low quality WTCs remaining after pyrolysis and their yields are commonly exceeding 40 wt% [4, 5], thus it is worth to be fully studied to achieve great economic improvement of WTs pyrolysis. Nowadays, WTCs can be upgraded to prepare carbon blacks [6], activated carbons [7], fuels [8], and electrode carbon materials [5]. As for any detailed application, WTCs are all reactants, whose structures would obviously affect the reaction process and products properties. However, as one of the most key parameters, pyrolysis temperature can directly and remarkably decide the pyrolysis reaction and structures of WTCs.
However, the effects of pyrolysis temperature on WTCs structures are not adequately studied. Further deeply investigating into char structures at different temperatures could make guidance to the high quality utilization of WTCs.

In this work, WT was pyrolyzed at different temperatures (400 °C, 600 °C, 800 °C, and 1000 °C) to collect WTCs respectively. Then, WTCs were deeply analyzed with element analyzer (EA), N2 adsorption-desorption analyzer, Raman spectroscopy (Raman) and X-ray photoelectron spectroscopy (XPS) respectively. Thus, the compositions, textural properties, and existence forms of element nitrogen/sulfur were determined to conclude the structural characteristics of WTCs at different pyrolysis temperatures.

2. Experiments and analysis methods

2.1. Preparation of WTCs

WT was bought from Sichuan Huayi Rubber Company and it was cut into about 40 mesh, its compositions were shown in our previous work [5]. Adequate amounts of WT (about 2 g) was paved in a quartz boat and placed into a horizontal furnace. Then heating WT to 400 °C, 600 °C, 800 °C, and 1000 °C respectively with a heating rate of 5 °C/min, then hold at the detailed temperatures for 1 hour to achieve completed pyrolysis of WT, the whole heat treatment operation was protected under continuous N2 flow of 0.5 L/min. Then the WTCs at different pyrolysis temperatures were collected and weighed to calculate the char yields as Eq. (1) respectively.

\[
\text{Yield (\%)} = \frac{M_{\text{WTC}}}{M_{\text{WT}}} \times 100\%
\]  

(1)

Where \(M_{\text{WTC}}\) was mass of WTCs and \(M_{\text{WT}}\) represented mass of WT. The pyrolytic chars from varied pyrolysis temperatures were named WTC400, WTC600, WTC800, and WTC1000 respectively.

2.2. Physical and chemical properties characterization

Element analysis of WTCs were determined by an element analyzer (Vario Micro Cube, Elementar) respectively. Textural properties of WTCs were performed in a N2-adsorption-desorption analyzer (BK100A, JWGB) at 77 K. The carbon skeleton structures of WTCs were studied by a Raman spectroscopy (DXR2, Thermo Fisher) with a laser excitation wavelength of 532 nm. The chemical states of element nitrogen and sulfur were revealed with an X-ray photoelectron spectroscopy (ESCALAB 250XI, Thermo Fisher).

3. Results and discussion

3.1. The yields and compositions

Table 1. The yields and compositions of WTCs at different pyrolysis temperatures

| Samples   | Yield (%)* | Element analysis (air dry basis, wt%) |
|-----------|------------|---------------------------------------|
|           |            | C     | H      | N      | S*     |
| WTC400    | 40.78      | 76.05 | 1.92   | 0.58   | 3.62   |
| WTC600    | 38.82      | 79.13 | 1.65   | 0.49   | 3.16   |
| WTC800    | 41.35      | 78.11 | 1.50   | 0.44   | 2.87   |
| WTC1000   | 41.45      | 85.28 | 1.25   | 0.37   | 2.55   |

*Data are from ref. [5].

The yields of WTCs are 40.78%, 38.82%, 41.35%, and 41.45% when pyrolysis temperatures are 400 °C, 600 °C, 800 °C, and 1000 °C respectively. Wholly, they take on a tendency of decreasing before 600 °C and increasing subsequently, while the variations are very small, suggesting retention time of 1 hour could guarantee sufficient pyrolysis of WT and the temperature can affect the char structures. In order to analyze the compositions of these chars, element analysis are chosen to be finished, whose results are listed in Table 1. As it can be clearly seen from the element analysis results, element carbon content generally increases from 76.05 wt% to 85.28 wt% with pyrolysis temperature rising from 400
to 1000 °C, which tells carbon skeleton can be promoted by higher temperature treatment. Besides, the corresponding element hydrogen, nitrogen, and sulfur contents are 1.92/0.58/3.62 wt%, 1.65/0.49/3.16 wt%, 1.50/0.44/2.87 wt%, and 1.25/0.37/2.55 wt% respectively. These three key elements contents all gradually decreases when the pyrolysis temperature is higher, illustrating defects in carbon skeletons decrease and carbon skeleton structures are more ordered.

3.2. The textural properties

| Samples  | SBET (m²/g) | S Micro | S Meso+Macro | V Total (cm³/g) | V Micro | V Meso+Macro | D Total (nm) |
|----------|-------------|---------|--------------|----------------|---------|--------------|--------------|
| WT       | 2.542       | NA      | 4.920        | 0.011          | NA      | 0.012        | 16.891       |
| WTC400   | 57.459      | NA      | 87.403       | 0.532          | NA      | 0.553        | 37.039       |
| WTC600   | 60.388      | 1.949   | 71.391       | 0.475          | 0.001   | 0.484        | 31.471       |
| WTC800   | 86.367      | 12.471  | 81.066       | 0.463          | 0.006   | 0.463        | 21.458       |
| WTC1000  | 70.943      | 88.339  | NA           | 0.518          | NA      | 0.531        | 29.230       |

SBET: by BET method, S Micro and V Micro: by t-plot method, S Meso+Macro and V Meso+Macro: by BJH method.

The textural properties can significantly reflect the physical structures, N₂ adsorption-desorption analysis of WTCs was finished, with BET, t-plot, and BJH methods being performed to know their textural properties detailedly. It is obvious that there will be many pores generating after pyrolysis since the surface area and pore volume both greatly increase, while the characteristics are different. When the pyrolysis temperature is 400 °C, there are large quantities of mesopores+macropores producing, because S Micro hardly changes and S Meso+Macro significantly improves from 4.920 m²/g to 87.403 m²/g compared with WT. However, S Micro and S Meso+Macro increase 1.949/-16.012 m²/g respectively as temperature rises from 400 °C to 600 °C, indicating some micropores form and mesopores+macropores destroy, resulting in a slight improvement of SBET. With the pyrolysis temperature further going to 800 °C, S Micro and S Meso+Macro increase 10.522/9.675 m²/g respectively, suggesting massive micropores and some mesopores+macropores appear, leading to SBET improves obviously. Besides, as the pyrolysis temperature increases to 1000 °C, S Micro and S Meso+Macro rise -12.471/7.273 m²/g respectively, telling lots of micropores destroy and some mesopores+macropores form, thus SBET is reduced from 86.367 m²/g to 70.943 m²/g. Therefore, it can be concluded that pyrolysis could significantly promote pores formation, the micropores appear firstly before 800 °C and subsequently are destroyed, and mesopores + macropores destroy before 600 °C and then gradually form, which brings out the phenomena that BET surface area increases and then decreases after 800 °C.

3.3. The carbon skeleton structures

The Raman spectroscopy could achieve excellent characterization of carbon skeleton structures, thus it was used to analyze the effects of pyrolysis temperature and their first-order Raman spectrums (800-1800 cm⁻¹) are shown in Figure 1 (a). It can be obviously seen that there are both two peaks at about 1350 cm⁻¹ and 1580 cm⁻¹, and their intensities are almost the same, indicating the chars are amorphous [9]. Thus, the first-order Raman spectrums are deconvoluted into 10 peaks like Figure 1 (b) based on the previous studies [5, 10] to deeply reveal the carbon skeleton structures: R band at 800-960 cm⁻¹, Sₐ band at 1060 cm⁻¹, S band at 1185 cm⁻¹, S_i band at 1230 cm⁻¹, D band at 1300 cm⁻¹, V_R band at 1380 cm⁻¹, V_L band at 1465 cm⁻¹, G_R band at 1540 cm⁻¹, G band at 1590 cm⁻¹, and G_L band at 1700 cm⁻¹.

With the assistance of the 10-peak method, three key band area ratios (A_D/A_G, A_D/(A_VR+VL+GR), and A_S/A_G) are acquired. It is obvious shown that A_D/A_G gradually and significantly decreases with pyrolysis temperature increasing from 400 °C to 1000 °C, signalling concentration of large aromatic ring systems (≥ 6 rings) would be reduced. Besides, A_D/(A_VR+VL+GR) almost keeps the same and only slightly increases, suggesting the ratio of large aromatic ring systems (≥ 6 rings) and small aromatic ring systems increasing, which indicates that small aromatic ring systems also decreases with higher pyrolysis temperature. Furthermore, A_S/A_G constantly decreases with the temperature rising, illustrating that alkyl-aryl C-C bonds would be decomposed by higher temperature treatment. The
phenomenon about decrease of large and small ring systems with alkyl-aryl C-C bonds indicates highly ordered arrangement of carbon skeleton structure.

3.4. The existence characteristics of nitrogen and sulfur

Element nitrogen and sulfur are special for WTCs because the requirements would be differentiated for various applications. For example, they need to be removed if the chars are used to prepare carbon blacks, while they are expected to be enriched when the chars are employed to produce electrode carbon materials [5, 6]. Besides, if WTCs are applied to be fuels, the release of nitrogen and sulfur would result in pollutant gases such as NOx and SO2. Thus the existence characteristics of nitrogen and sulfur in WTCs should be studied to determine the effects of pyrolysis temperature.

Usually, element nitrogen in chars exists in four chemical states based on XPS study [11]: pyridinic nitrogen (N-6, about 397.3 eV), pyrrolic nitrogen (N-5, about 399.0 eV), quaternary nitrogen (N-Q, about 401.5 eV), and pyridine nitrogen oxide (N-X, about 402.3 eV), whose relative contents (%) can be calculated by the area ratio of corresponding peak and all peaks. Taking WTC1000 for example, as shown in Figure 2 (a), the XPS spectrum of N 1s can be divided into four typical peaks. In addition, the element contents by EA are further combined, the contents for WTCs at different pyrolysis temperatures (absolute content, wt%) can be reasonably obtained and shown in Figure 2 (b). It tells that the element nitrogen exits in N-6, N-5, and N-Q where N-5 dominates, while the content of N-5 would gradually decrease and N-X constantly increases with the pyrolysis temperature rising from 400 °C to 1000 °C. Besides, N-6 and N-Q both take on a tendency of increasing firstly and then decreasing, but N-6 peaks at 800 °C and N-Q peaks at 600 °C. Therefore, it could be reasonably inferred that the effects of pyrolysis temperature on element nitrogen in WTCs are as below: higher pyrolysis temperature promotes decomposition of N-5 with enrichment of N-X as pyrolysis temperature rises.

Figure 1. Raman spectrums (a), analysis method schematic (b), and their corresponding band area ratios (c)
from 400 °C to 600 °C, while higher pyrolysis temperature promotes their enrichment firstly as for N-6 (before 800 °C) and N-Q (before 600 °C), and then leads to their decomposition.

Apart from element nitrogen, element sulfur is also key for WTCs because its content is extremely high commonly, which can also be understood from Table 1. Typically, taking WTC1000 for example whose XPS spectrum of S 2p is exhibited in Figure 3 (a), there are two sulfur pieces, they are sulfur bridge (S 2p3/2, -C-S-C-, about 164.0 eV and 165.3 eV) and sulphone bridge (S 2p5/2, -C-SOx-C- (x = 2-4), about 168.9 eV and 170.2 eV) [5, 12]. As for WTCs coming from different pyrolysis temperatures, their different XPS spectrums of S 2p illustrate element sulfur in WTCs exists in differentiated forms, whose contents are exhibited in Figure 3 (b). As for WTC400, element sulfur is mainly composed by S 2p3/2 whose content is high up to 3.51 wt%. However, when pyrolysis temperature rises from 400 °C to 1000 °C, the content of S 2p3/2 has been decreasing to 1.75 wt% and the corresponding S 2p5/2 increases from 0.11 wt% to 0.8 wt%. Therefore, it can be concluded that higher pyrolysis temperature would promote decomposition of S 2p3/2 with formation of S 2p5/2.

4. Conclusions
WT was pyrolyzed at 400 °C, 600 °C, 800 °C, and 1000 °C respectively to further study the structural characteristics of WTCs. The main conclusions were as following:
(i) The temperature between 400 °C and 1000 °C can assist WT to be fully pyrolyzed, higher temperatures can promote decrease of large and small aromatic ring systems with alkyl-aryl C-C bonds, thus carbon skeleton structure turns to be more ordered and defects decrease.

(ii) Pyrolysis could significantly promote pores formation in WTCs, higher pyrolysis temperature would promote formation of micropores, while mesopores+macropores destroy before 600 °C and then gradually form.

(iii) Higher pyrolysis temperature can promote decomposition of pyrrolic nitrogen and sulfur bridge with enrichment of oxidised nitrogen and sulphone bridge. Higher temperature would assist in generation of pyridinic nitrogen before 800 °C and quaternary nitrogen before 600 °C.

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