Co-pyrolysis Characteristics of Torrefied Coconut Shell and Coal

Zhilei Zheng¹, Xin Zhou¹, Siqiong Wang¹, Qingchun Li¹ and Yunfei Wang¹, ²*
¹College of Chemical Engineering, Ordos Institute of Technology, Ordos, Inner Mongolia, 017000, China
²Department of Solid Waste Treatment and Recycling, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, China
*Corresponding author’s e-mail: yunfeiwang111@126.com

Abstract. The co-pyrolysis of torrefied coconut shell (TCS) and Shenhua coal (SHC) was performed using a thermogravimetric analyzer (TGA). The pyrolysis and interaction characteristics of the raw feed materials (TCS and SHC) along with selected mass blend ratios were investigated. Compared to pyrolysis alone, the blend (Blend1-2 and Blend2-1) have one more maximum weight loss rate peaks. Initial decomposition temperature and maximum weight loss rate temperature gradually increase with increasing heating rate. There are two kinds of interaction was observed: physical and chemical interactions. Both the heating rate and the blending ratio have influence on the interaction. There is no chemical interaction at 3°C/min heating rate, and the physical dominates the interaction progress. At a heating rate of 3oC/min, both interactions exist, and the physical process dominates the progress of the interaction. The higher the mass ratio of TCS in the blend, the more significant the physical interaction.

1. Introduction
Biomass, which mainly derives from agricultural and partly is used as raw materials of organic fertilizer production, has achieved a lot of attention as a potential renewable energy resource[1-5]. However, all these studies remain in the laboratories, as the low energy density, storage, collection and transportation problems greatly limit the biomass energy sources as a large-scale industrial and chemical raw materials. Then the co-pyrolysis of biomass and coal gets the highlight and many studies have carried out, and have obtained remarkable results[6-8]. Among all these studies, co-pyrolysis of torrefied biomass, which has characteristics of lower moisture content, higher energy density and easier to grind, and coal is a promising way for biomass efficient utilization.

Without oxygen, heating at 200-300 ℃ is a low temperature process. It is considered that hemicellulose pyrolysis occurs at 200°C-300°C, cellulose pyrolysis at 240°C-350°C, and lignin pyrolysis at 280 °C-450 °C. In this process, biomass will lose moisture, releasing a large amount gas contains mainly CO and CO2, increasing the content of atomic carbon, decreasing that of atomic H and O, making biomass suitable for thermal conversion[9-12]. In this paper, we put concern on the co-pyrolysis of torrefied coconut shell and coal under different heating rate with different proportion, tending to reveal the influence of torrefied coconut shell on the coal during thermal process.
2. Experimental

2.1. Samples
The coconut shells which originate from Hainan province were bought online and were torrefied for 0.5h at 280°C in an air-isolated environment. After natural cooling, the samples were ground to 100-200 mesh and labeled as TCS. The coal sourced from Shenhua group, Inner Mongolia was also ground to 100-200 mesh and marked as SHC. TCS and SHC were blended in the mass ratio of 1:2 (labeled as Blend1-2) and 2:1 (labeled as Blend2-1).

2.2. Experimental equipment and conditions
The pyrolysis of TCS, SHC, Blend1-2 and Blend2-1 were studied by means of Hengjiu HTC-4 thermogravimetric analyser (TGA) from an ambient temperature up to 850°C. The heating rate were set to 3°C/min, 10°C/min and 30°C/min respectively. All experiments were conducted in nitrogen with the flow rate of 100 L/min (20°C, 1 atm).

2.3. Pyrolysis interaction study
A large number of co-pyrolysis experiments had carried out and have obtained the conclusion that there is an obvious interaction between biomass and coal[7,8,13,14].

In order to confirm whether the co-pyrolysis has a synergistic interaction in terms of the final pyrolysis product yield, the following formula is introduced in this experiment:

\[ \Delta W = W_{\text{experiment}} - W_{\text{calculation}} \]  

\[ W_{\text{calculation}} = W_{\text{SHC}} \times x_{\text{SHC}} + W_{\text{TCS}} \times x_{\text{TCS}} \]  

where \( W_{\text{experiment}} \) represents the experimental amount of the residual carbon. \( W_{\text{calculation}} \) is the theoretical amount of the residual carbon calculated by weighted ratio. \( W_{\text{SHC}} \) and \( W_{\text{TCS}} \) are the experimental amount of the residual carbon of SHC and TCS respectively. \( x_{\text{SHC}} \) and \( x_{\text{TCS}} \) are the mass ratio of SHC and TCS in the blend.

3. Results and discussion

3.1. TGA results
Figure 1 shows the TG and DTG curves of each sample with heating rate of 3°C/min, 10°C/min and 30°C/min. The pyrolysis characteristic parameters are shown in table 1. It can be seen from the curves in figure 1 that each sample has obvious weight loss during the pyrolysis process, and the weight loss is severe at a certain temperature range. The pyrolysis of coal which can be classified a macromolecular organic substance with relatively high C/H is generally considered to be divided into three stages, among which a large number of free radicals are generated between 300-500°C. These free radicals combine with each other to form tar, methane, etc., which finally escape in gaseous state out of the reaction system. The torrefaction of coconut shell at low temperature helps remove a large amount of oxygen-containing functional groups, and simplify the molecular
Figure 1. TG and DTG curves for SHC, TCH, Blend1-2 and Blend2-1: (a) 3 °C/min, (b) 10 °C/min, (c) 30 °C/min

structure. Even after removing some oxygen-containing functional groups, the remaining parts of coconut shell and other biomass materials, mainly consist of molecules with relatively low C/H such as cellulose, hemicellulose, and lignin, can still easily decompose in the form of volatile. Therefore, the pyrolysis weight loss process of TCS in figure 1 is more severe than that of SHC, and the initial decomposition temperature and maximum reaction rate temperature of TCS in table 1 are lower than SHC. Table 1 also shows that the initial decomposition temperature of Blend1-2 and Blend2-1 is somewhere between the former two samples. The possible reason is that the coals that are difficult to pyrolyze in the mixture do not start pyrolysis at this temperature, but instead play a negative role in hindering heat transfer, resulting in only a small part of TCS can reach the temperature required for pyrolysis. The higher the content of coal in the Blend, the more obvious this heat transfer hindering effect. In the pyrolysis process, when the heating rate is 3 °C/min and 10 °C/min, only one maximum weight loss rate peak appears when the coconut shell and coal are pyrolyzed separately, but the co-pyrolysis processes have two more obvious pyrolysis weight loss rate peaks. The position of these two peaks coincides with the peak of the maximum weight loss rate when TCS and SHC are pyrolyzed separately, so it can be explained that the two weight loss peaks in the co-pyrolysis process are the intense pyrolysis of TCS and SHC in the Blend. In addition, as the proportion of TCS increases, the intensity of these two pyrolysis weight loss peaks gradually increases.

As the heating rate increases, the temperature difference between the surface and the inside of the sample gradually increases. The temperature at which the sample begins to pyrolyze and the temperature at which the sample shows maximum weight loss rate gradually increases. But the heating rate does not have a significant effect on the yield of pyrolysis residue.
Table 1. Pyrolysis parameters of SCH, TCS, Blend1-2 and Blend2-1

| Heating rate (℃/min) | Samples | The initial decomposition temperature (℃) | Temperature of first peak (℃) | Temperature of second peak (℃) | Maximum reaction rate temperature (℃) | Residual mass (%) |
|-----------------------|---------|------------------------------------------|-----------------------------|-----------------------------|---------------------------------------|------------------|
| 3                     | SHC     | 346.1                                    | 429.4                       | -                           | 429.4                                 | 79.1             |
|                       | Blend1-2| 287.5                                    | 317.5                       | 429.3                       | 317.5                                 | 76.1             |
|                       | Blend2-1| 262.1                                    | 315.1                       | 419.6                       | 315.1                                 | 67.2             |
|                       | TCS     | 223.4                                    | 312.9                       | -                           | 312.9                                 | 55.4             |
|                       | SHC     | 343.4                                    | 452.1                       | -                           | 452.1                                 | 78.3             |
| 10                    | Blend1-2| 273.1                                    | 363.2                       | 444.8                       | 363.2                                 | 74.7             |
|                       | Blend2-1| 255.5                                    | 354.9                       | 416.2                       | 354.9                                 | 69.4             |
|                       | TCS     | 255.5                                    | 349.7                       | -                           | 349.7                                 | 67.4             |
|                       | SHC     | 348.5                                    | 532.3                       | -                           | 532.3                                 | 77.8             |
| 30                    | Blend1-2| 267.7                                    | 452.8                       | -                           | 452.8                                 | 66.6             |
|                       | Blend2-1| 269.8                                    | 440.1                       | -                           | 440.1                                 | 69.9             |
|                       | TCS     | 256.4                                    | 458.5                       | -                           | 458.5                                 | 51.9             |

3.2. Analysis of interaction

The relationship of $\Delta W_{Blend1-2}$ and $\Delta W_{Blend2-1}$ is shown in figure 2. It can be seen that $\Delta W_{Blend1-2}$ gradually decreases with the increase of pyrolysis temperature, and $\Delta W_{Blend2-1}$ shows a trend of decreasing first and then increasing. The main influencing factor of chemical interaction between the pyrolysis components during co-pyrolysis is that the severe weight loss temperature ranges coincide with each component during pyrolysis, especially in the free radical pyrolysis stage of coal. Only when the weight loss peaks, which are also called the stage of massive free radical generation (350-500℃), of DTG curve shows coincidence, the free radicals generated by the pyrolysis of single component can combine with each other and leave the reaction system in the form of tar or gas, resulting in obvious interactions, accordingly the final amount of pyrolysis residual carbon is reduced. In the higher temperature stage (>550℃), coal and biomass mainly undergo polycondensation reaction of their own molecular structure, with the main feature of H radicals generation and production of H2. At this stage, the entire pyrolysis system is rich in H radicals. Therefore, It can not produce more obvious chemical interaction.

It can be seen from figure 1 that, when heating rate was 3℃/min, SCH and TCS do not share the same temperature range, in which the DTG curves appear one peak. The $\Delta W$ that occurs at 3℃/min heating rate in figure 2 is greater than 0, which was not caused by the synergy of the TCS and SCH. The possible reason is that the TCS is rich in pores of various sizes, and after a preliminary pyrolysis the pores are more developed. The macromolecules produced by SCH pyrolysis are adsorbed in those pores, failing to escape from the reaction system, with the increase of pyrolysis temperature these macromolecules undergo self-polycondensation reaction, and are finally remained in the form of carbon residue, resulting in $\Delta W$ greater than 0. Therefore, the physical interaction caused by adsorption mainly occurs at this process. It can be seen from figure 1 that with the increase of the heating rate, the peak overlap of the DTG curves occurs gradually in pyrolysis of SCH and TCS, leading a possibility of chemical interaction between SCH and TCS. On the one hand, some of the macromolecules produced by SCH pyrolysis are adsorbed by the pores in the TCS, and as the temperature increases, they will eventually remain in the system in the form of residual carbon, resulting in an increase in the amount of pyrolytic carbon residue. On the other hand, the free radicals generated by TCS and SCH combine with each other, and eventually escape from the reaction system in gaseous form, resulting in a reduction in the amount of pyrolytic carbon residue. Therefore, there is a physical and chemical interaction in the pyrolysis system with a higher heating rate, and these two interactions will affect each other. For Blend1-2, due to the small ratio of TCS in the composition, the reaction system cannot provided sufficient pores during the pyrolysis process to adsorb various
macromolecules. Most of the molecules generated by co-pyrolysis escape the system in gaseous state, resulting in $\Delta W$ gradually decreases and eventually becomes less than zero. This also shows that as the heating rate increases, the chemical interaction between SHC and TCS gradually dominate the interaction process. For Blend2-1, because of the large ratio of TCS in the composition, sufficient pores can be provided during the pyrolysis process to adsorb various macromolecules, so the physical interaction dominates the interaction process at a higher heating rate and eventually lead to the situation appears in the figure2 where $\Delta W$ is significantly greater than 0 at a heating rate of 30°C/min.

![Figure 2. $\Delta W$ curves under various blending ratio](image)

4. Conclusions
TGA was used to investigate the thermochemical decomposition behavior of coconut shell (TCS), Shenhua coal (SHC), blend of TCS and SHC in mass ratios of 1:2 (Blend1-2) and 2:1 (Blend2-1). The TGA analysis shows that TCS and SHC have one maximum weight loss rate peak respectively and there blend (Blend1-2 and Blend2-1) have two maximum weight loss rate peaks. As the heating rate increases, the initial decomposition temperature and the maximum weight loss rate temperature show gradually increases. The heating rate does not have a significant effect on the yield of pyrolysis residue. Two interactions have been observed: physical and chemical interactions. Both the heating rate and the blending ratio have influence on the interaction. At low heating rate, there is no chemical interaction, and the physical dominates the interaction progress. At high heating rate, both the two kinds of interaction exist and the physical dominates the interaction progress. The higher the mass ratio of TCS in the blend, the physical interaction gets more significant.

Acknowledgments
This study was supported by the Science and Technology Plan Project with Applied Technology Research and Development of Ordos (2019501), Ordos Institute of Technology university-level college students innovation and entrepreneurship training program.

References
[1] Yao, D.D., Hu Q, Wang D.Q., Yang,H.P., Wu,C.F., Wang,X.H., et al. (2016) Hydrogen production from biomass gasification using biochar as a catalyst/support. Bioresour Technol, 216:159-64.
[2] Aboyade, A.O., Görgens, J.F., Carrier, M., Meyer, E.L., Knoetze,J.H. (2013) Thermogravimetric study of the pyrolysis characteristics and kinetics of coal blends with corn and sugarcane residues. Fuel Process Technol ,106:310-20
[3] Thengane,S.K., Gupta,A., Mahajani,S.M. (2019) Co-gasification of high ash biomass and high ash coal in downdraft gasifier. Bioresource Technology, 273:159-168.
[4] Gil, M.V., Casal, D., Pevida, C., Pis, J.J., Rubiera, F. (2010) Thermal behaviour and kinetics of coal/biomass blends during co-combustion. Bioresource Technology, 101:5601-5608.
[5] Xiao,X.B., Cao,J.P., Meng,X.L., Le,D.D., Li,L.Y., Yukioko,O., et al. (2013) Synthesis gas production from catalytic gasification of waste biomass using nickel-loaded brown coal char. Fuel, 103:135-140.
[6] Li,S.D., Chen,X.L., Liu,A.B., Wang,L., Yu,G.S. (2015) Co-pyrolysis characteristic of biomass
and bituminous coal. Bioresource Technology, 179:414-420.

[7] Wu,Z.Q., Li,Y.W., Xu,D.H., Meng,H.Y. (2019) Co-pyrolysis of lignocellulosic biomass with low-quality coal: Optimal design and synergistic effect from gaseous products distribution. Fuel, 236: 43-54.

[8] Wu,Z.Q., Li,Y.W., Zhang,B., Yang,W.C., Yang,B.L. (2019) Co-pyrolysis behavior of microalgae biomass and low-rank coal: Kinetic analysis of the main volatile products. Bioresource Technology, 271:202-209.

[9] Chen,D.Y., Zheng,Z.C., Fu,K.X., Zeng,Z., Wang,J.J., Lu,M.T. (2015) Torrefaction of biomass stalk and its effect on the yield and quality of pyrolysis products. Fuel, 159:27-32.

[10] Chen,D.Y., Yang,H.P., Yang,Q., Hao,H.M., Zhu,B., Chen,H.P. (2014) Torrefaction of agriculture straws and its application on biomass pyrolysis poly-generation. Bioresource Technology, 156:70-77.

[11] Ohliger,A., Föster,M., Kneer,R. (2013) Torrefaction of beechwood: a parametric study including heat of reaction and grindability. Fuel, 104:607-613.

[12] Chen,D.Y., Zhou,J.B., Zhang,Q.S., Zhu,X.F., Lu,Q. (2014) Upgrading of rice husk by torrefaction and its influence on the fuel properties. Bioresources Technology, 9:5893-5905.

[13] Lin,B.W., Zhou,J.S., Qin,Q.W., Song,X., Luo,Z.Y. (2019) Thermal behavior and gas evolution characteristics during co-pyrolysis of lignocellulosic biomass and coal: A TG-FTIR investigation. Journal of Analytical and Applied Pyrolysis, 144:104718.

[14] Jian,Y.M., Li,X., Zhu,X.Q., Ryuichi,A., Nakorn,W., Hu,Z.Z., et al. (2019) Interaction between low-rank coal and biomass during degradative solvent extraction. J Fuel Chem Technol, 47(1), 14-22.