Studies on biomass char gasification and dynamics

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Abstract. The gasification performances of two kinds of biomass char by experiment methods are studied, including conversion rate and gasification gas component with temperature and time. Experimental results show that gasification temperature has important effects on the conversion rate and gas component. In the range of experimental temperature, char conversion rates are no more than 30.0%. The apparent activation energies and apparent reaction frequency factors of two biomass chars are obtained through kinetic studies.

1. Introduction
Biomass energy is an important form of renewable energy. Biomass char is the solid component produced from raw biomass materials after chemical transformation which generally accounts for about 30% of input quality. Gasification technology is an effective way for biomass char utilization which can not only increase the gas output but also effectively dispose gasification solid products. However, comparing with coal and petroleum char, related researches on the gasification of biomass char is rather less [1]. The studies of related mechanism and influence factors are still in the initial stage [2, 3, and 4]. In this paper, the studies on the gasification of two typical biomass chars in rural areas of China are carried out in providing references for the treatments of solid products of the central gas supply systems.

2. Experimental researches
2.1. Preparation of biomass chars
The selected raw materials are corn straw and sawdust which are two typical biomass materials in the rural areas of China. The biomass chars are produced through pyrolysis in a laboratory-scale paralyzer. The pyrolysis conditions are as follows: heating rate being 10℃/min, N₂ flow rate being 2.0 l/min, pyrolysis temperature being 500℃ and duration being 1h in order for complete reaction. Then the biomass char is ground and screened with the size of 1.3~1.7mm [5].

2.2. Industrial and elemental analysis of biomass chars
The industrial and elemental analysis of biomass chars is shown in Table 1.
Table 1. Industrial and elemental analysis of biomass chars.

|                     | Corn straw char /% | Sawdust char /% | Corn straw char /% | Sawdust char /% |
|---------------------|--------------------|-----------------|--------------------|-----------------|
| Industrial analysis |                    |                 |                    |                 |
| Ma                  | 3.04               | 19.83           | 2.97               | 0.76            |
| Mad                 |                    |                 |                    |                 |
| Vad                 | 6.35               | 10.66           | 2.27               | 10.66           |
| Aad                 | 2.27               | 66.47           | 91.38              | 66.47           |
| FCad                | 91.38              | 66.47           | 91.38              | 66.47           |
| Low heating Value   | 24.67              | 26.39           | 5.76               | 8.90            |
| value /MJ·kg⁻¹      |                    |                 |                    |                 |

2.3. Experimental device
The schematic diagram of the experimental device is shown in Figure 1.

Figure 1. Schematic diagram of the experimental device. Nitrogen cylinder; 2. 14 Gas flow meter; 3. Pyrolysis reactor; 4. Thermocouple; 5. Electric heater; 6. Control device; 7. Peristaltic pump; 8. Steam generator; 9. Cooler; 10. Cooling water outlet; 11. Cooling water inlet; 12. Collecting liquid bottle; 13. Dryer; 15. Gas chromatograph; 16. Gas collecting device.

2.4. Experimental process
The experimental procedure can refer to [6]. Experimental temperature is 500 °C, 600 °C, 700 °C and 800 °C. N₂ flow rate is 1 l/s. S/C is 2.0 (S/C = the mole number of steam/the mole number of of carbon in biomass char). The reaction time is about 20 min. The rate of gasification can be determined by the changes of the quality of biomass chars before and after the reactions.

\[ X = \frac{G_0 - G_e}{G_0} \]  

Where \( X \) is the gasification rate of biomass chars; \( G_0 \) is the original quality of biomass chars, g; \( G_e \) is the residual quality of biomass chars at the end of the reaction.
3. Analysis of experimental results

3.1. Effects of temperature on gasification rate
Under the atmosphere of steam, when the gasification temperature is 500℃, 600℃, 700℃ and 800℃ respectively, the relationships between gasification rate and temperature are shown in Figure 2.

![Figure 2. Effects of temperature on the gasification rate.](image)

As can be seen from Figure 2, gasification rates increase with the increasing of temperature. For straw char, gasification rate increases from 12.8% at 500℃ to 23.3% at 800℃. For sawdust char, gasification rate increases from 7.2% at 500℃ to 28.1% at 800℃. The change tendency of gasification rate about sawdust char is more obvious than that of straw char, indicating that the reactivity of sawdust char is better than that of straw char, which is consistent with literature [7]. In the range of experiment temperature and time, the maximum gasification rate is not more than 30.0%.

3.2. Effects of temperature on gasification gas composition
Under the atmosphere of steam, when the temperature is 500℃, 600℃, 700℃ and 800℃ respectively, the relationships between gasification gas composition and temperature are shown in Figure 3.

![Figure 3. Effects of temperature on gasification gas composition.](image)
As can be seen from Figure 3, the variation trends of gas components are basically the same and the differences lie in the values. When the temperature is relatively low, biomass chars are less gasified and the gas components change slowly. With the increasing of temperature, the gasification reactions are accelerated and the gas components change greatly. When the temperature is low, the concentrations of H$_2$ are relatively high, both of which are over 40%, while the concentrations of CO and CO$_2$ are similar and relatively low. With the increasing of temperature, the concentrations of H$_2$ increase further, reaching up to the peak value of 58.0%. The concentrations of CO$_2$ significantly decrease while that of CO increase rapidly simultaneously. When the temperature reaches 800°C, the concentration ratio of CO and CO$_2$ is between 2 and 3. The concentrations of other gases in gasification gas of sawdust char are relatively high which may due to the complexity of volatilizations in it.

3.3. Effects of reaction time on gasification rate
Under the atmosphere of steam, when the temperature is 800°C and the duration is 5, 10, 15, 20 min respectively, the relationships between gasification rate with time are shown in Figure 4.

![Figure 4. Relationships between gasification rate with time.](image)

As can be seen from Fig 4, the gasification rates of two biomass chars increase with the increasing of time. The gasification rates increase quickly at the beginning phase and then slow down, which are because that the components which are difficult to gasify need more higher temperature and longer time than the gasification reactions of easy ones. The gasification rate curve variation trend of straw char is more gentle than that of sawdust char indicating that the reactivity of straw char is higher than that of sawdust char. At the end of the reaction, the gasification rate of straw carbon is 23.3% and that of sawdust carbon is 28.1%. Both of them are not more than 30%.

4. Kinetic studies
The reaction rate constant $k$ can be calculated according to unreacted shrinking core model[8]. The diagrams of ln$k$ and 1000/T are drawn and then linear fitted, so the Arrhenius curves can be obtained which are shown in Figure 5. The intercept values of the line are values of ln$k_0$ and the slope values are values of -E/R in Figure 5. The apparent activation energies E and apparent reaction frequency factors $k_0$ can be obtained by calculation which are shown in Table 2.
Figure 5. Arrhenius curves of gasification reactions.

Table 2. Kinetic parameters.

| Name of biomass char | Apparent activation energy $E$ (kJ/mol) | Apparent reaction frequency factor $k_0$ (1/min) |
|----------------------|----------------------------------------|---------------------------------|
| Straw char           | 57.80                                  | 79.58                           |
| Sawdust char         | 67.71                                  | 533.92                          |

5. Conclusion
Gasification temperature has important effects on gasification rates of biomass chars. With the increasing of gasification temperature, the gasification rates increase. In the experiment temperature and time range, the maximum gasification rates are not more than 30.0%. The reactivity of sawdust char is better than that of straw char. The gasification temperature also has great influences on gasification gas components. With the increasing of gasification temperature, the concentrations of H₂ and CO are significantly increase while the concentrations of CO₂ decrease significantly.
The reaction time has certain effects on the gasification rate of biomass chars. The gasification rates increase with the increasing of time in general and the variation trends are from fast to slow.
The apparent activation energies and apparent reaction frequency factors are obtained by using the unreacted shrinkage nuclear model which provide the basis for the establishing of dynamic equations.

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References
[1] H. Yanqin, Y. Xiuli, W. Chuangzhi et al, Study on CO₂ gasification reactivity of rice straw chars, Journal of Fuel Chemistry and Technology, 2009, 37(3):289-295.
[2] H. Haykiri-Acma, S. Yaman, S. Kucukbayrak, Gasification of biomass chars in steam-nitrogen mixture, Energy Conversion and Management, 2006, 47(7-8): 1004-1013.
[3] Y. Sekine, K. Ishikawa, E.Kikuchi, et al, Reactivity and structural change of coal char during steam gasification [J].Fuel, 2006, 85(2):122-126.
[4] Z. Yu, Z.Zhixiang, M. Fanfei, Experimental study of the reactivity of biomass char with CO₂ by the thermal analysis technique gasification reaction, Journal of China Coal Society, 2008,
33 (5) :579-582.

[5] Y. Zhanping, Y. Shijun, L. Xianli, et al, Experimental research on tar catalytic cracking over biomass char, Acta Energiae Solaris Sinica, 2011, 32(5):718-723.

[6] Y. Zhanping, H. Changsheng, J. Yonggang et al, Comparative study on pyrolysis and combustion characteristics of two kinds of antibiotics, Industrial Safety and Environmental Protection, 2016, 42(5):41-43.

[7] M. Tie, C. Hanping, T. Rujiang et al, Reactivity studies on biomass char in CO2 atmosphere, Acta Energiae Solaris Sinica, 2005, 26(6):766-781.

[8] Y. Zhanping, Study on Biomass Char Catalytic Reforming Technology Pyrolysis Tar, Tianjin University, 2010.