

The synergistic effecting mechanisms of biomass pyrolysis, biomass char gasification, and biomass ash on CO₂ co-gasification of biomass and high-sulfur petroleum

Huixia Xiao¹, Guangsuo Yu¹, Yifei Wang^{1*}

1 East China University of Science and Technology, Shanghai 200237, PR China;

**Corresponding author: wangyf@ecust.edu.cn*

Highlights

- Co-gasification of biomass and high-sulfur petroleum coke was proposed
- Reactivity, synergistic effects, and kinetic parameters were comprehensively compared
- The catalyst mechanism of PC gasification was related with ash compositions

1. Introduction

Recognized for its multi-ring aromatic structure, high carbon content (90-95%), and elevated heating value, petroleum coke (PC) also exhibits low ash and volatile matter. In the pursuit of enhancing the gasification reactivity of PC, researchers have extensively delved into the co-gasification of PC and biomass (B) [1-2]. On one front, researchers aim to exploit the rapid overflow characteristic of high volatile content in B to increase the pore volume of PC, thereby improving PC reaction activity [1-2]. There is a lack of systematic studies on the roles played by biomass pyrolysis, biomass char gasification, and biomass ash during the co-gasification process with PC. To thoroughly investigate the synergistic contributions of biomass pyrolysis, biomass char gasification, and biomass ash during the co-gasification of B and PC, five biomass waste materials (B, namely, pistachio nut shells (PNS), macadamia shells (MS), chestnut shells (CS), peanut shells (PS), and walnut shells (WS)), biomass char (C_B) and biomass low-temperature ash (A_B) were mixed with PC. The gasification reaction characteristics of B, PC, and their three mixtures were tested using a thermogravimetric analyzer. Comparisons of the experimental and theoretical TG/DTG curves and synergy factors ($SF_{0.9}$) revealed that PC:B exhibited inhibitory effects during the co-pyrolysis stage and synergistic effects during the co-gasification stage.

2. Methods

The high-sulfur petroleum coke (PC, from Quanzhou of China) and five types of biomass wastes (B, including Pistachio nut shell (PNS), Macadamia shell (MS), Chestnut shell (CS), Peanut shell (PS), and Walnut shell (WS)) were chosen as experimental raw materials. The mixed samples of B and PC, denoted as PC:B, were prepared in a mass ratio of 1:1. Based on the TG data for biomass, it was observed that biomass pyrolysis was essentially complete at 650°C. By isolating the biomass gasification sample at 650°C, biomass char (C_B) was obtained.

Gasification of all samples was conducted using a thermogravimetric analyzer (NETZSCH STA449-F3 Jupiter, Germany). The specific steps were as follows: 8 mg of the sample was weighed and placed in an alumina crucible with a diameter of $\text{Ø}6.7 \times 4$ mm. Initially, the sample was subjected to a high-purity nitrogen atmosphere with a flow rate of 120 ml/min. The temperature was ramped from room temperature to 105°C at a heating rate of 10°C/min, and the sample was held at 105°C for 5 min. Subsequently, the gas was switched to a CO₂ atmosphere, purged for 10 min to remove residual air in the reactor, and then the temperature was raised to 1500°C at a heating rate of 10 °C /min. The experiment concluded with a switch to high-purity nitrogen for cooling. To minimize experimental errors, each experiment was repeated 3-5 times, and the average values were calculated.

3. Results and discussion

Fig. 1 depicted the non-isothermal gasification TG/DTG curves for individual samples and mixed samples, respectively. Analyzing the TG/DTG curves of B and PC:B revealed a two-stage gasification process: the pyrolysis stage ($<650^{\circ}\text{C}$) and the coke gasification stage ($>650^{\circ}\text{C}$), abbreviated as S_P and S_G , respectively. Since PC was a black solid coke produced after cracking and coking of petroleum at 500°C , PC has a low volatile content and thus lacks the pyrolysis process. Based on the TG/DTG curves, the initial temperature (T_i), final temperature (T_f), maximum weight loss rate (DTG_{max}), and corresponding temperature for each reaction stage during the gasification process were determined. The T_i , T_f , and T_{max} of B and PC:B were close in S_P , and the temperature ranges were $50\text{-}217^{\circ}\text{C}$, $528\text{-}660^{\circ}\text{C}$, and $340\text{-}349^{\circ}\text{C}$, respectively. MS and CS exhibited the highest and lowest DTG_{max} values at 340°C , with values of $8.28\%/ \text{min}$ and $5.68\%/ \text{min}$, respectively. Similarly, PC:MS and PC:CS showed the highest and lowest DTG_{max} values at 334°C , with values of $4.35\%/ \text{min}$ and $3.01\%/ \text{min}$, respectively.

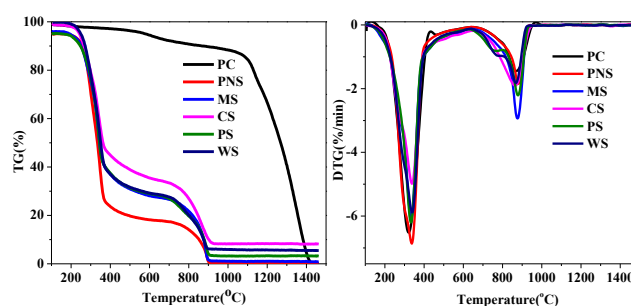


Figure 1. TG / DTG curves of single samples during non-isothermal gasification

Fig. 2 presented the theoretical and experimental TG/DTG curves of mixed sample co-gasification, and the corresponding reaction characteristic parameters are listed in Table 4. By comparing the characteristic parameters of the S_P , it could be seen that the T_i , T_f , and T_{max} measured by experiment and theoretical calculation were close to each other, and the DTG_{max} measured by experiment was slightly higher.

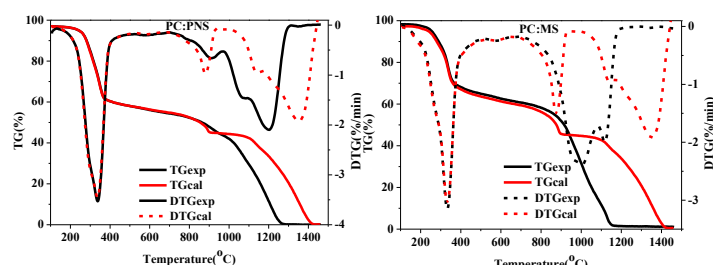


Figure 2. Comparison of TG / DTG curves between theoretical calculation and experiment

4. Conclusions

Comparisons of the experimental and theoretical TG/DTG curves revealed that the pyrolysis stage (S_P) and gasification stage (S_G) of PC:B exhibit antagonistic and synergistic interactions, respectively. The incorporation of B, C_B , and A_B significantly boosted the gasification reactivity of PC, and the first-order chemical reaction (Q1) proved more suitable for S_P , whereas the core-shrinkage model R2 was more applicable for S_G .

References

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Keywords

Biomass waste; High sulfur petroleum coke; Co-gasification; Gasification reactivity; Synergistic effects