Synergy mechanism analysis of petroleum coke and municipal solid waste (MSW)-derived hydrochar co-gasi
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HIGHLIGHTS

- Co-gasi
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frac
tion reactivity and synergy of petroleum coke and MSW hydrochar were studied.
- Overall synergistic effect was enhanced at lower temperature and higher hydrochar proportion.
- Synergistic effect was enhanced as conversion increased but weakened at mid-late co-gasi
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- Inhibition of active Ca/K transformation was first enhanced and then weakened as conversion increased.
- Active AAEM transformation during co-gasi
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 could well correlate synergy mechanism.

ARTICLE INFO

Keywords:
Petroleum coke
Hydrochar
Waste biomass
Co-gasi
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Reactivity
Synergy mechanism

ABSTRACT

In this work, the influences of the gasification temperatures (1000–1150 °C) and blended ratios (3:1, 1:1, 1:3) on the co-gasi
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 reactivity and synergy of petroleum coke (PC) and municipal solid waste (MSW)-derived hydrochar (HTC) were studied using a thermogravimetric analyzer (TGA). Chemical fractionation analysis (CFA) coupled with an inductively coupled plasma optical emission spectrometer (ICP-OES) was adopted for quantitatively investigating the active alkali/alkaline earth metal (AAEM) transformation (i.e., active AAEM content variation) during co-gasi
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 in order to correlate the synergy mechanism of co-gasi
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. The results indicated that the co-gasi
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 reactivity of the blended chars was enhanced with increasing gasi
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 temperatures and HTC char proportions. The variations of the synergy behaviour on co-gasi
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 reactivity at different conversions showed continuously enhanced synergistic effect at early co-gasi
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 stage and decreased synergistic effect with further co-gasi
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. Moreover, higher gasification temperatures and HTC char proportions were more favourable for the continuous enhancement of the synergistic effect as co-gasi
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 conversions increased. The overall synergistic effect on co-gasi
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 reactivity was more obvious at higher HTC char proportions and lower gasification temperatures. The relative transformation ratio (P) was proposed to characterize the active AAEM content variation during co-gasi
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. P was negative when more active AAEM remained in blended chars, meaning that there was inhibition effect on the active AAEM transformation. It was found that the inhibition effect on the active Ca/K transformation was first enhanced and then weakened whereas the promotion effect on the active Na transformation showed an opposite trend with increasing conversion of co-gasi
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, which well correlated the synergy behaviour variations during PC-HTC blended char co-gasi
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. This work not only revealed synergy mechanism of petroleum coke and MSW-based hydrochar co-gasi
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 but also provided reference data for the design and operation of industrial gasi
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 units consuming mixture of petroleum coke and waste biomasses.

1. Introduction

Petroleum coke is an important by-product derived from delayed coking of residual oil, and its production is rapidly increasing due to increasing requirement for crude oil densification and environmental protection. Gasification technology could effectively utilize petroleum coke, coal, biomass and other carbonaceous materials by converting them into raw coal gas, which provided (1) syngas for the production of
fertilizer, methanol, olefin, gasoline, diesel, natural gas and other chemicals [1–3]; (2) hydrogen for fuel cell production and refinery [4,5]; (3) fuel gas for integrated gasification combined cycle (IGGCC) power [6,7]; and (4) reducing gas for the iron industry [8]. Petroleum coke shows great advantages in terms of high carbon content, high heating value and little ash content. However, its gasification application is faced with some significant shortcomings, such as high graphitization degree, dense pore structure and tiny alkali/alkaline earth metal (AAEM) content [9,10], leading to longer reaction time, higher reaction temperature or catalyst additive required for high conversion.

Municipal solid waste (MSW) is a typical waste biomass and possesses large production and extensive source. Moreover, ample AAEM contained in MSW could avoid industrial catalyst addition, decrease catalyst cost, alleviate catalyst recovery problem and enhance reactivity in the petroleum coke gasification process [11]. This indicated that co-gasification of petroleum coke and MSW might be a technological option to handle abovementioned drawbacks of petroleum coke gasification. However, the direct application of MSW as a gasification material is restricted due to its high moisture content, low energy density and irregular particle shape [12,13]. Hydrothermal carbonization could transform MSW and other waste biomass into solid coke (noted as hydrochar) through dehydration and decarboxylation reaction. Compared with other pretreatment technologies, hydrothermal carbonization has attracted considerable attention from researchers and businesses due to its superiorities in little restriction of moisture content, high carbon fixation efficiency, mild reaction condition, abundant oxygen-containing functional groups in solid product and uniform particle morphology [14,15]. The industrial petroleum coke gasification system could reduce the cost of MSW hydrothermal carbonization by providing by-product pressurized steam. Furthermore, hydrochar could be directly used in petroleum coke gasifiers as a solid fuel, realizing efficient MSW conversion and avoiding resource waste and environmental pollution. Hence it is concluded that co-gasification of petroleum coke and MSW-derived hydrochar is beneficial to the comprehensive, clean and efficient usage of petroleum coke and MSW.

Gasification reactivity is a classical technical indicator to evaluate raw material applicability [16], and it would be seriously affected by synergy behaviour during co-gasification of carbonaceous materials. Thus, it is very necessary to deeply study the synergy behaviour on co-gasification reactivity. Recently, reports on the reactivity characteristic and synergy behaviour of petroleum coke and biomass co-gasification have gradually increased and the relative literatures were summarized in Table 1 [5,10,17–23]. Most previous studies were performed by TGA due to its dominant advantages of accurate, sufficient and real-time data recording [17,24], and stated that synergistic effect existed during the co-gasification of petroleum coke and biomass and was attributed to the AAEM in the biomass [5,10,17–23]. Furthermore, Edreis et al. indicated that more significant synergistic effect on petroleum coke and bagasse co-gasification existed when either the steam concentration or biomass proportion exceeded 50% [10]. Wang et al. noted that the synergistic effect on petroleum coke and corncob co-gasification was first enhanced and then weakened as the biomass ratio in the mixture increased [17]. Our previous study found the synergistic effect on petroleum coke and rice straw co-gasification was first stimulated and then diminished as the gasification temperature increased from 900 °C to 1100 °C [18]. Masnadi et al. also stated that the synergistic effect on the co-gasification of biomass and petroleum coke mixture existed when the K-to-Al molar ratios exceeded 1 [22].

Previous work has provided plenty of referential data. However, there was insufficient information on reactivity and synergy of petroleum coke and biomass co-gasification. From the viewpoint of raw materials used in co-gasification, hydrochar derived from hydrothermal carbonization of waste biomass was a kind of available gasification materials, but the co-gasification characteristics of petroleum coke and waste biomass after hydrothermal treatment have been rarely studied. From the viewpoint of assessment of the synergy behaviour during co-

<table>
<thead>
<tr>
<th>Researcher Feedstocks</th>
<th>Gasification reactor</th>
<th>Gasification condition</th>
<th>Gasification result</th>
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</thead>
<tbody>
<tr>
<td>Wang et al. [17]</td>
<td>Petroleum coke</td>
<td>TGA</td>
<td>Synergistic effect first increased and then decreased with increasing biomass proportion in blend.</td>
</tr>
<tr>
<td>Edreis et al. [10]</td>
<td>Petroleum coke</td>
<td>TGA</td>
<td>Significant interactions existed in co-gasification and became less significant when petroleum coke and biomass proportion and H2O concentration were 50%.</td>
</tr>
<tr>
<td>Wei et al. [18]</td>
<td>Petroleum coke</td>
<td>TGA</td>
<td>Catalytic/synergistic effect was observed in co-gasification process and mainly caused by alkali and alkaline earth metals in biomass ash.</td>
</tr>
<tr>
<td>Zhang et al. [19]</td>
<td>Petroleum coke</td>
<td>TGA</td>
<td>There was synergistic effect between petroleum coke and biomass in co-gasification due to biomass ash.</td>
</tr>
<tr>
<td>Nemanova et al. [20]</td>
<td>Petroleum coke</td>
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<td>There was synergistic effect on co-gasification of petroleum coke and biomass and was attributed to the AAEM in the biomass.</td>
</tr>
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<td>Habibi et al. [21]</td>
<td>Fluid coke</td>
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<td>Zhang et al. [5]</td>
<td>Petroleum coke</td>
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<td>Co-gasifying switchgrass char was conducive to enhancing gasification rate of fluid coke.</td>
</tr>
</tbody>
</table>

**Table 1** Literature review of reactivity and synergy of petroleum coke and biomass co-gasification.
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