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# Study on effects of ash on the evolution of physical and chemical structures of char during $CO_2$ gasification

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ABSTRACT

In this paper, the gasification reactivities of four types of Chinese coal were studied, each with different ash content and coal rank. Of the 4 coal types, 2 were HCl-washed and demineralized to investigate the effects of ash removal (for both dealkalization and demineralization) on coal gasification. The effects of ash on the evolution of physical and chemical structure were further studied using scanning electron microscopy equipped with energy dispersive X-ray analysis (SEM-EDX), $N_2$ absorption and FT-Raman techniques. The results show that the initial gasification rate of raw chars is twice as high as the HCl-washed and ash-free chars. The gasification rate of ash-free char significantly increases with the increase in carbon conversion and surpasses the gasification rate of raw char when carbon conversion is higher than 50%. Moreover, the specific surface area of ash-free char significantly increases with carbon conversion, resulting in the significant increase in the gasification rate. Whereas the specific surface areas of raw char and HCl-washed char both decrease during high-conversion stages. The FT-Raman analysis shows that the ash-free char band area ratios $A_{D3}/A_G$ and $A_{D4}/A_G$ are lower than those of raw char at the initial gasification stage; this results in the initial gasification rate decrease of ash-free chars. In addition, the ash-free char band area ratio $A_G/A_{all}$ is smaller than that of raw char in the high conversion stages.

## 1. Introduction

A clean and efficient technology, entrained-flow gasification technology, is widely applied in the coal-utilization industry [1]. Although the temperature in entrained-flow gasifiers can reach 1600 °C, the unreacted carbon content in the fine slag remains high (approximately 40 wt%) [2], which is attributed to the ash package [3,4]. Moreover, Chinese coal with ash content below 10 wt% only accounted for 20 wt% in the proven reserves, which suggests that the ash content in Chinese coals is generally high. So far, the effects of ash on coal gasification have been attracting increasing attention in the academic and industrial fields.

Coal ash has a significant effect on the physical and chemical structures of char. Some researchers claimed that alkali metals naturally presented in coals had catalytic effects on coal gasification [5–7]. Moulijn et al. [8] reported that the interaction of alkali carbonates with −COOH and −OH functional groups likely resulted in the formation of alkali–oxygen surface groups, which were considered as active sites. The formation of alkali–oxygen surface groups did not occur in the pyrolysis of demineralized char; this was due to the removal of alkali metals [9]. Xu et al. [10] found that alkali metals in ash also inhibited the progress of graphitization during pyrolysis, which resulted in the increase in gasification reactivity. Although most research focused on the effects of ash on chemical structure evolution during pyrolysis, less research had been conducted on the effects of ash on chemical structure evolution during gasification.

The coal ash not only presented a catalytic effect but also affected the development of the physical structure during gasification. Some researchers proposed that the molten ash wrapped the char and prevented the contact between unreacted carbon and gasification agents [11,12]. Other researchers also studied the development of the pore structure of char [12–14]. The specific surface area of char increased in the initial gasification stage, then significantly decreased in the later stages of conversion [13,14]. Li et al. [15] claimed that the decrease in specific surface area occurred at lower char conversions with higher ash content. Ding et al. [4] found that the specific surface area of demineralized char continued increasing during high conversion stages.

As mentioned above, coal ash has both positive and negative effects on char gasification. Thus, studying the effects of ash on char gasification in detail is an important goal. Although many studies have

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**Table 1**
Proximate and ultimate analysis and of coal samples.[a]

| Sample | Proximate analysis/d.% | | | Ultimate analysis/d.% | | | | |
|---|---|---|---|---|---|---|---|---|
| | VM | FC | Ash | C | H | N | S | O |
| NM | 49.22 | 40.33 | 10.45 | 74.65 | 3.32 | 1.20 | 0.58 | 9.80 |
| SF | 35.42 | 58.29 | 6.29 | 79.14 | 2.32 | 1.12 | 0.77 | 10.36 |
| ZJX | 30.19 | 51.58 | 18.23 | 70.23 | 4.28 | 1.19 | 0.34 | 5.73 |
| GZ | 8.45 | 73.76 | 17.79 | 74.52 | 2.00 | 1.05 | 4.07 | 0.57 |

[a] VM-Volatile matter, FC-Fixed carbon, d-Dry basis.

**Table 2**
Ash fusion temperature of samples.[a]

| Sample | Ash fusion temperature/°C | | | |
|---|---|---|---|---|
| | DT | ST | HT | FT |
| NM | 1086 | 1105 | 1121 | 1124 |
| SF | 1152 | 1167 | 1175 | 1179 |
| ZJX | 1458 | > 1500 | > 1500 | > 1500 |
| GZ | 1271 | 1345 | 1359 | 1373 |

[a] DT-Deformation temperature, ST-Soften temperature, HT-Hemispherical temperature, FT-Fluid temperature.

reported the effects of ash on the development of physico-chemical structures, reports that compare the different effects of dealkalization and demineralization on physico-chemical char structures during gasification are rare. In this paper, the effects of ash on coal gasification were studied via thermogravimetric analysis. The various evolution trends of the physical and chemical char structures for raw, HCl-washed and ash-free char were further compared via SEM-EDX, $N_2$ adsorption and FT-Raman techniques during gasification. The effect mechanism of coal ash on physical structures was also proposed during gasification.

## 2. Experimental

### 2.1. Sample preparation

Four types of Chinese coals with different ranks, such as Neimeng lignite coal (NM), Shenfu bituminous coal (SF), Zhujixi bituminous coal (ZJX) and Guizhou anthracitic coal (GZ), were chosen for the experiments. To diminish the effect of particle size distribution, the coal was crushed and filtered with a set of 20 μm and 40 μm mesh size filters. The volume average particle sizes were 36 μm, 41 μm, 37 μm and 40 μm for NM, SF, ZJX and GZ coal, respectively. The proximate and ultimate analyses of samples are summarized in Table 1. The ash fusion temperatures and ash compositions of samples are shown in Tables 2 and 3. Among four coal samples, SF coal has the lowest ash content; meanwhile, ZJX coal has the highest. During char preparation, all samples were heated at 25 °C/min to 800 °C and held for 30 min in a fixed bed under $N_2$ atmosphere.

To study the effects of ash on gasification processes, ZJX and GZ coals were demineralized with HCl and HF. The detailed steps of the acid-washing referred to the previous work [16]. The HCl-washed coals were referred to as ZJX-HCl and GZ-HCl coal, and the demineralized coals were referred to as ZJX-ashfree and GZ-ashfree coal. The proximate analysis of HCl-washed and ash-free coal is shown in Table 4.

### 2.2. Gasification experiments

$CO_2$ gasification experiments for coal samples were carried out with NETZSH STA4493F3 Thermogravimetric Analyzer (TGA). The gasification procedure is described by the following steps. Approximately 10 mg of sample particles were placed in a crucible and heated at 25 °C/min under a continuous $N_2$ flow of 80 mL/min. $N_2$ was replaced by $CO_2$ when temperature reached 1200 °C. The final temperature was maintained during gasification until no further weight loss was observed. The flow rate of $CO_2$ was set to 120 mL·min$^{-1}$. Gasification experiments were carried out in atmospheric pressure, and the external diffusion was avoided [17].

### 2.3. Property tests of samples

The surface morphology and element composition of samples were examined using a Hitachi SU-1510 scanning electron microscopy (SEM) equipped with an energy-dispersive X-ray spectroscopy (EDX). Multiple areas (approximately 50) were randomly selected for scanning, and average values were calculated to reduce error.

Pore structure parameters of samples were measured with an ASAP-2020 physisorption apparatus via the $N_2$ gas adsorption method. $N_2$ gas adsorption was operated at −196 °C, which could probe the pore range from 2 to 200 nm.

The Raman spectra of samples were recorded via Iuvia Reflerx Laser Raman spectra analysis. The laser beam (514 nm, 4 mW) focused on the particle surface, while the spectra, with a wavenumber range of 800–2000 cm$^{-1}$, were recorded to cover the first-order bands. Considering the heterogeneity of the char particles, twenty particles from each sample were randomly selected to test and determine the mean spectrum and average value.

### 2.4. Experimental data processing methods

The $CO_2$ gasification rates of samples were measured via TGA under $CO_2$ atmosphere. The carbon conversion x is expressed as

$$x = (w_0 - w_t)/(w_0 - w_{ash}) \quad (1)$$

where $w_0$ is the initial weight of char, $w_t$ is the weight at time t and $w_{ash}$ is the ash mass in the char. The gasification rate $r$ and instantaneous reactivity $R$ are defined as differential of carbon conversion with respect to gasification time:

$$r = -dx/dt \quad (2)$$

$$R = -dx/(w_t \cdot dt) \quad (3)$$

$R_{0.5}$ was defined by Takarada et al. as the comparison between gasification reactivities of different samples [12]. In this study, $R_{0.95}$ was proposed as the comparison between the gasification reactivities of different samples at high conversion stages. $R_{0.5}$ and $R_{0.95}$ are expressed by:

**Table 3**
Ash compositions of samples.

| Sample | Chemical composition of ashes (wt%) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | $SO_3$ | MgO | $Na_2O$ | $TiO_2$ | $K_2O$ | SrO |
| NM | 43.46 | 14.43 | 14.13 | 11.81 | 10.02 | 3.04 | 1.46 | 0.63 | 0.32 | 0.14 |
| SF | 44.20 | 18.19 | 11.28 | 15.58 | 5.63 | 1.12 | 1.89 | 0.60 | 0.95 | 0.41 |
| ZJX | 58.06 | 34.19 | 2.33 | 0.85 | 0.50 | 0.43 | 0.58 | 1.99 | 0.83 | 0.19 |
| GZ | 50.73 | 31.36 | 8.93 | 1.79 | 1.46 | 1.05 | 0.35 | 2.29 | 1.47 | 0.05 |