



Preliminary study on co-gasification behavior of deoiled asphalt with coal and biomass



Qian Zhang^{a,b}, Qingfeng Li^a, Linxian Zhang^a, Zhiqing Wang^a, Xuliang Jing^{a,b}, Zhongliang Yu^{a,b}, Shuangshuang Song^a, Yitian Fang^{a,*}

^aState Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China

^bUniversity of Chinese Academy of Sciences, Beijing 100049, China

HIGHLIGHTS

- Co-gasification of DOA with coal and biomass are proposed and studied.
- Pure DOA char shows low reactivity mainly for low surface area, high graphitization degree and low ash content.
- Co-gasification of coal and DOA does not show synergetic effect.
- Synergetic effect between biomass and DOA is observed.
- Potassium naturally in biomass can transfer to DOA and catalyzes the gasification of DOA.

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ABSTRACT

The co-gasification behavior of deoiled asphalt (DOA) with coal and biomass were investigated by a thermogravimetric analyzer (TGA). The gasification experiments were conducted under CO₂ atmosphere within an isothermal temperature range from 900 to 1100 °C. The physical properties of the samples were examined by X-ray diffraction (XRD), scanning electron microscopy–energy dispersive spectroscopy (SEM–EDS), N₂ and CO₂ adsorption and inductively coupled plasma–atomic emission spectrometry (ICP–AES). Compared with coal or biomass, the low surface area, high graphitization degree and the low ash content are the main reasons for the low reactivity of DOA. The co-gasification of coal and DOA does not show synergetic effect, while the combination of biomass and DOA shows higher gasification reactivity than that of being calculated. The synergetic effect is mainly caused by the alkali metals. Further study shows the transfer of the potassium from the surface of biomass to DOA greatly increases the active sites of the DOA, which leads to obvious improvement of the co-gasification reactions. Meanwhile, the gasification experiments of adding coal and biomass ashes to DOA also support the above explanations.

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1. Introduction

Upgrading of heavy petroleum has become increasingly important due to the rising demand for the light transportation fuels and the diminishing of light crudes [1,2]. A number of technologies [3,4] have been developed over these years, including thermal coking, fluid catalytic cracking, hydrocracking and solvent deasphalting. Among them, solvent deasphalting process has attracted more attention for which can remove asphaltenes and metal compounds effectively from heavy crudes and provides a better quality of deasphalted oil for further upgrading. However,

a large amount of deoiled asphalt (DOA) produced as byproduct, of which the utilization is closely associated with the economic benefits of the process. Therefore, more attention must be paid to optimize the utilization of DOA.

Gasification seems to be an ideal route for DOA utilization for which has efficiently and commercially converted different carbonaceous feedstocks into useful syngas (CO, H₂) with near zero pollution emissions [5,6]. However, two main problems need to be considered for the DOA's solid particles gasification process [7]: (1) the gasification temperature is higher than the DOA melting temperature. Thus, introducing the material into the gasifier is a main challenge, as the DOA particles might melt and possible plug the feeding system [8,9]. So the traditional feeding methods applied by coal or biomass are not suitable for DOA gasification [10]. (2) DOA char has a low gasification reactivity comparable to

* Corresponding author. Tel.: +86 351 2021137 801; fax: +86 351 2021137 802.
E-mail address: fyf@sxicc.ac.cn (Y. Fang).

petroleum char [7,11,12]. Therefore, a higher gasification temperature must be used for gasifying this kind of material, which will increase the energy consumption and the cost of gasification.

In order to solve these problems, two gasification processes have been proposed and tested in Institute of Coal Chemistry, Chinese Academy of Sciences (ICC, CAS): one is co-gasification of coal and DOA, the other is co-gasification of biomass and DOA. The reason for choosing the former method is as follows: coal gasification plants have been operated steadily for decades, while DOA is a potential feedstock for gasification. The mixture of coal and DOA can be partly entrained and pushed into the gasifier, which can solve the plugging problem and is helpful for the steady operation of the plant. Moreover, some researchers have reported that the alkali, calcium and magnesium species in coal could have some catalytic effect on coal gasification [13,14], which means co-gasification of coal and DOA might improve the reactivity of DOA. In fact, in 1980s, Cugini et al. [15] has studied the co-processing of coal/oil, although their purpose was to get more distillate products. And in recent years, the co-gasification of petroleum coke and coal slurries were studied [11,16], which is comparable to the co-gasification of coal and DOA.

The latter method, i.e. the co-gasification of biomass and DOA is considered by following reasons: the lower gasification reactivity of DOA results in a non-economical process for the higher gasification temperature condition. A moderate gasification condition can be realized by adding catalysts, and the most effective catalysts in carbon gasification are alkali metals (such as potassium) [17,18]. Compared to these expensive catalysts, using some other inexpensive alkaline-rich materials as substitutes is reasonable [11,17]. Biomass, especially the herbaceous plant, is usually rich in alkali compositions. Besides, biomass is an ideal renewable resource due to its abundance, lower sulfur content and CO₂ neutrality [19,20]. Recently, the co-utilization of coal and biomass has been studied and the possibility that use biomass as a catalyst in coal gasification has been reported [17,21,22]. However, few researches focused on the co-gasification of biomass and DOA [11,23].

In this study, the properties (such as ultimate and proximate analysis, surface area, and XRD) and CO₂ gasification behavior of DOA, coal and biomass chars were studied separately first. Then, the effects of temperature and blending ratio on co-gasification behavior of DOA with coal and biomass were investigated. The observed synergetic effect was discussed and explained. Finally, in order to confirm the catalytic effect, the alkali metals catalyst, coal ash and biomass ash were mixed with DOA, then the gasification behavior of the mixtures was evaluated.

2. Experimental section

2.1. Raw materials and sample preparation

Deoiled asphalt (DOA), shenmu bituminous coal (SM) and corn-cob (CC) were selected as raw materials. The DOA was a byproduct of “ten thousand ton industrial demonstration projects of heavy oil deep stage separation coupling raffinate residue granulation” [7]; SM (from Shaanxi, China) was the coal sample; and CC (a major agro-waste in North China) was chosen as the biomass sample. The proximate and ultimate analyses of these materials are shown in Table 1.

The chars used for gasification were prepared in a fixed-bed reactor as described elsewhere [24]. In brief, the raw sample was loaded in a crucible and maintained in the cooled zone of the reactor. When the reactor was heated to 900 °C under a flow of N₂ atmosphere (150 mL/min), the crucible was pushed to the constant temperature zone and held for 30 min. After that, the crucible was lifted to the cooled zone and maintained for 30 min. Finally, the

chars were taken out and ground with diameters less than 120 μm. The proximate and ultimate analyses of the chars are listed in Table 1 as well.

2.2. Blending method

The blending method must be firstly determined before studying co-gasification of DOA with coal and biomass. Two blending methods are available: raw materials are blended and then pyrolyzed; the other is the material is firstly pyrolyzed individually, and then the chars are mixed. The synergetic effects are not obvious during the co-pyrolysis of petroleum residue/coal/biomass [25,26]. Thus the latter way was selected to accurately evaluate the co-gasification effect. The DOA char was mechanically blended with CC char or SM char by weight ratios. The mixed samples contained 60 wt.% SM char and 40 wt.% DOA char are denoted as 60S40D. Likewise, the sample of 40C60D can be deduced by analogy.

2.3. Samples characterization

The proximate analyses were tested according to the Chinese standard of GB/T212-2001. The elemental analyses (C, H, N, S) were performed by an elemental analyzer (Elementar Analysensysteme GmbH, Germany), and the content of oxygen was calculated by difference. The crystalline structure of the samples were investigated by a RIGAKU D/max-rB X-ray diffractometer, which was operated with Cu K α radiation (40 kV, 100 mA, $K\alpha = 0.15408$ nm) and a scan rate of 4 degree/min. The morphology and elemental analyses were performed by SEM-EDS (JSM-7001F electron microscope equipped with a QX200 energy dispersive X-ray spectrometer). The micrographs, which were taken together with elemental maps of carbon, sulfur and potassium, provided useful information of the relationship between carbon topography and distribution of elements. Micrometrics Tristar 3000 and NOVA4200e were respectively used to perform N₂ and CO₂ adsorption to evaluate the micro and meso-macro pore structure of samples. The total surface areas of the samples were calculated by applying the Brunauer–Emmett–Teller (BET) equation for N₂ adsorption at 77 K and the Dubinin–Radushkevich (DR) equation for CO₂ adsorption at 273 K. The inorganic elements of the samples were determined by an inductively coupled plasma-atomic emission spectrometry (ICP-AES, iCAP 6300, Thermo Fisher Scientific). Besides, the ash fusion temperatures of the samples were performed according to the Chinese Standard GB/T 219-1996. The ashes were prepared by ashing samples in a muffle furnace. To avoid the possible volatilization of inorganic elements, the corn-cob and DOA were burned at 500 °C for 4 h, and the shenmu coal were burned at 700 °C for 4 h.

2.4. CO₂ gasification experiments

A Setaram SETSYS TGA was used to perform the CO₂ gasification experiments. In each run, about 5 mg of the char sample was used. First the sample was placed in a crucible (8 mm inner diameter and 5 mm height) and then heated up with heating rate of 30 K/min under N₂ atmosphere (99.999%, 120 mL/min). Once the desired temperature was reached, the gas was switched to CO₂ (99.8%, 120 mL/min) to conduct the isothermal gasification process.

The carbon conversion during gasification was defined and calculated by the following equation:

$$X = \frac{w_0 - w_t}{w_0 - w_\infty} \quad (1)$$

where w_0 , w_t and w_∞ represent the initial weight, the instantaneous weight at a gasification time t , and the left weight after the gasification is completed, respectively.

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