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Preparing coal water slurry from BDO tar to achieve resource utilization: gasification process of BDO tar-coal water slurry

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Abstract: 1,4-Butanediol (BDO) is an important organic and fine chemical raw material, but the waste liquid (BDO tar) discoal charged from the BDO production plant is complex in composition, contains salt, and is complicated to handle. In this study, BDO tar was treated by the method of waste-coal water slurry, and the gasification process of blending BDO tar was studied. The results show that as the BDO tar content increases, the organic component in the BDO tar causes the temperature point corresponding to the peak of the maximum reaction rate to migrate to the high temperature zone during the initial temperature to 150 ℃. In the temperature range of 200 ℃~300 ℃, the weight loss of BDO tar leads to a significant weight loss peak of TG curves. From 600 ℃ to the final reaction temperature range, the alkali metal Na enriches the surface of the coal char with more active "spot", and due to the alkali metal Na limits the graphitization of coal char, the active sites increase, which increases the coal char gasification reaction activity.

1 Introduction

1.1 BDO tar

BDO is an important commodity chemical that is widely used in industry for production of plastics, elastic fibers and pharmaceuticals [1]. BDO may also be converted to gamma-butyrolactone and tetrahydrofuran [2,3]. The main production processes of BDO are: Reppe method, n-butane/ maleic anhydride method, allyl alcohol method and butadiene method [4]. The main production process of BDO is the Reppe method. In the purification process of product BDO, BDO is refined by using a wiped film evaporator. A certain amount of viscous and difficult-to-volatile distillation substrate (BDO tar) is usually formed in the evaporator, and the substrate is dark brown and viscous, with high viscosity and complex composition. The method of handling BDO tar is complicated. At present, the factory uses incineration to treat it, which has a certain impact on the environment [5]. The waste coal-water slurry technology developed on the basis of traditional resources can effectively reduce the waste disposal problem and is a better way to protect the environment.

1.2 Previous study on waste-coal water slurry

The diversification of coal water slurry (CWS) can not only solve the pollution problem of some waste, but also realize their resource utilization, which is an inevitable trend of future development. Usually, waste-coal water slurry is prepared by mixing waste, coal, water and a bit of additive. Many scholars have studied adding black liquor [6], coking waste water [7], waste engine oil [8], petrdeum-coke-water [9], and obtained better modified CWS. A coal-wasteliquid slurry is proposed to dispose wasteliquids, which are used as a substitute for clean water in the preparation of a coal-based slurry fuel, and some environmental problems caused by wasteliquid discoal charge are resolved [10]. Many scholars have also studied the gasification performance of waste-coal water slurry. For example, black liquor could be an effective catalyst for petroleum coke gasification [11, 12]. Sodium and potassium ions in the oilfield wastewater are distributed in the surface and pores of the coal particles, which provide an active center and increase the gasification activity [13]. Cogasification in a CWS gasifier may be a viable alternative solution for biofermenting residue treatment [14]. In the research of scholars on waste-coal water slurry, there is no related research on blending BDO tar to make CWS. In order to better handle BDO tar and utilize BDO tar resources, it is of practical significance to study the blending of BDO tar to make CWS. This paper mainly studies the effect of blending BDO tar on the gasification performance of CWS and its mechanism.

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2 Material and Methods

2.1 Material

The coal sample is named ZK coal. The proximate and ultimate analysis of the coal samples is shown in *Table 1*. The BDO tar at the project site was provided by the Chinese chemical company. In the Reppe production process, high boiling impurities and some BDO are sent to the thin film evaporator for removal, and a certain amount of BDO tar is usually formed in the evaporator bottom [15]. The main components of BDO tar are shown in *Table 2*.

Table 1. Proximate and ultimate analysis of coal sample (ad, %*).

Sample	Proximate analysis				Ultimate analysis				
	M	A	V	FC	C	H	O	N	S
ZK	5.65	4.70	32.21	57.44	75.96	4.57	7.58	0.86	0.68

*Mass fraction

Table 2. Main components in BDO tar.

Sample	Main components	Relative percentage（%*）
Alcohol	1,4-butanediol（BDO）	30~40
	2-penten-1-methanol	<1
	Octanediol	5~10
	2-cyclohexen-1-methanol	5~10
	1,9-Nonanediol	15~20
	Terpene alcohol	20~25
Polymer	Polytetrahydrofuran	0~5
Inorganic matter	Sodium-containing inorganic salt	≈10
Other	/	<20

*Mass fraction

2.2 Methods

2.2.1 Thermal analysis and magnification experiment of gasification process

First, the experiment need to calculat the mass of BDO tar (0%, 1%, 2%, 5%, and 10%) which was proportion of mixed slurry, as well as deionized water and coal. Then the experiment obtained a mixed slurry which was approximately 60%, and five types of samples were obtained (i.e., ZB-n%, n=0, 1, 2, 5, and 10). Gasification of the slurry samples was conducted by using a thermogravimetric analyzer (NETZSCH STA 449F3, Germany). For each thermogravimetry (TG) measurement, a sample that weighed approximately 30 mg was weighted into an open alumina crucible. The temperature was set from 25 ℃ to 1400 ℃. The heating rate was 20 ℃/min. CO_2 with a flow rate of 100 mL/min was used as reaction gas.

2.2.2 Catalytic experiment of alkali metal on coal sample

To further illustrate the effect of blending BDO tar on the performance of coal water slurry gasification, the ZK coal was subjected to acid elution ash and loaded with alkali metal Na. The deashing coal is named DZK. The catalyst and coal mixtures were prepared by adding the appropriate amounts of Na_2CO_3 to ZK pulverized coal to obtain the following weight ratios of catalyst to dry ash free basis coal: DZK-Na^+. Under the isolation of air, DZK and DZK-Na^+ were heated to 920℃ in the tube furnace and kept for 1 h to obtain DZK char and DZK-Na^+ char[16]. 10 mg of DZK char and DZK-Na^+ char were placed in a thermal analysis instrument, and the reaction was carried out under the same conditions as in the previous thermal analysis.

2.2.3 Apparent morphology and graphitization of coal char

To further explain the influence mechanism of BDO tar on the gasification process of coal water slurry, the SEM-EDX (Tescan VEGA3 SBH-BRUKER XFlash 6|30, Germany) was used to analyze the apparent morphology and micro-chemical composition of the DZK char and DZK-Na^+ char. The graphitization of coal char was analyzed by XRD (LabX XRD-6000, Shimadzu, Japan).

3 Results

3.1 Analysis of gasification performance of samples

In the thermal analysis curves of gasification process, *Fig. 1* is the TG curves, *Fig. 2* is the DTG curves. In order to explain the variation of the thermal analysis curves of blended BDO tar, the BDO tar samples were subjected to the gasification experiment under the same conditions, and the result is shown in *Fig. 3*. It can be seen from *Fig. 1*, *Fig. 2* and *Fig. 3* that the slurry has three weight loss peaks in the gasification process, which are the process of water loss, volatile matter loss, coal char and CO_2 reaction. Around 150 ℃, the DTG curves migrates to the high temperature zone at the position of the weight loss peak with the increase of the BDO tar, which is caused by the volatilization of the low boiling point substance in the BDO tar sample; At the range of 200 ℃~300 ℃, the maximum weight loss rate increased with the increase of tar blending amount, which is mainly caused by the higher boiling point substance in the BDO tar sample. In the third stage, as the BDO tar blending amount increased, the TG curves migrate to the low temperature zone, indicating that the gasification reaction temperature of coal char and CO_2 began to decrease significantly, and BDO tar improves the gasification performance. Further observation of the thermal analysis curve of BDO tar shows that the TG curve tends to be gentle after 500 ℃. At this stage, the organic components are almost completely volatilized, mainly inorganic components acting on the gasification process.

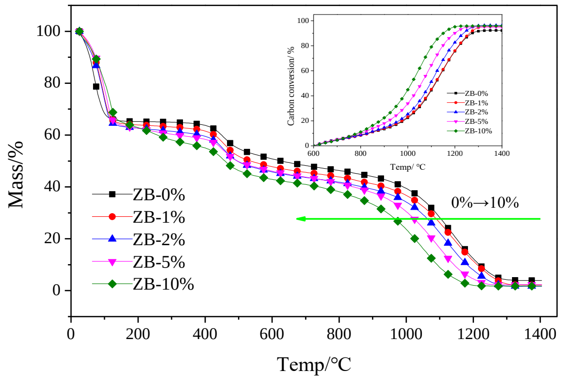

Figure 1. TG curves of different samples.

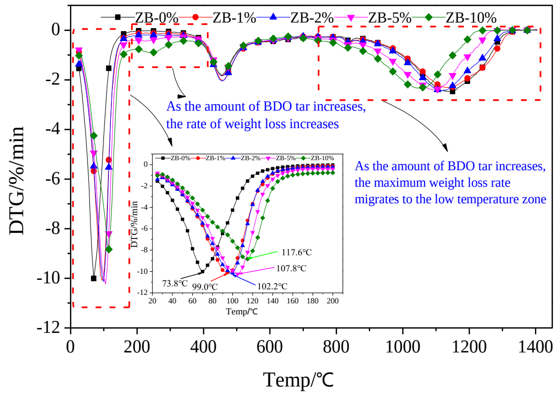

Figure 2. DTG curves of different samples.

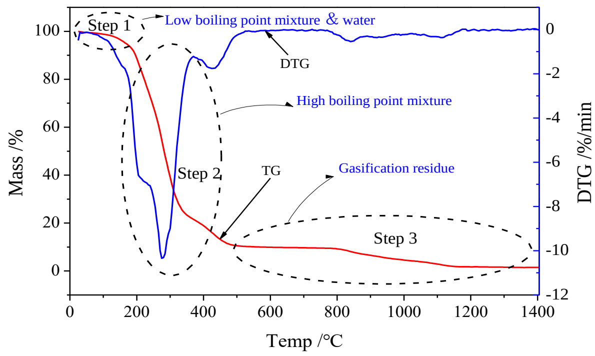

Figure 3. TG-DTG curves of gasification performance (BDO tar).

3.2 Mechanism of influence gasification performance

3.2.1 Catalytic action of alkali metal Na on dry ash free basis coal

At 500 ℃, the organic matter in the BDO tar has lost weight completely, and the catalytic effect still exists at the reaction temperature. Therefore, BDO residue (500 ℃) prepared by thermal analysis instrument was studied. It can be seen from the *Fig. 4* that the BDO tar residue is mainly crystalline minerals dominated by Na_2CO_3. Therefore, DZK char and DZK-Na^+ char are subjected to gasification thermal analysis experiments. The results are shown in *Fig. 5*, the gasification performance of DZK-Na^+ char is significantly better than that of DZK char. The alkali metal Na showed obvious catalytic effect during the gasification process.

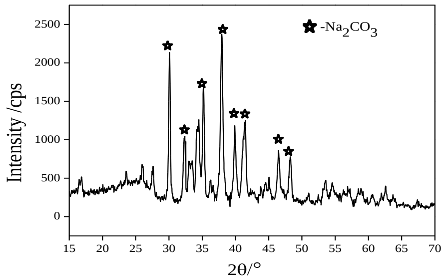

Figure 4. Crystal mineral gasification of BDO tar residue (500 ℃).

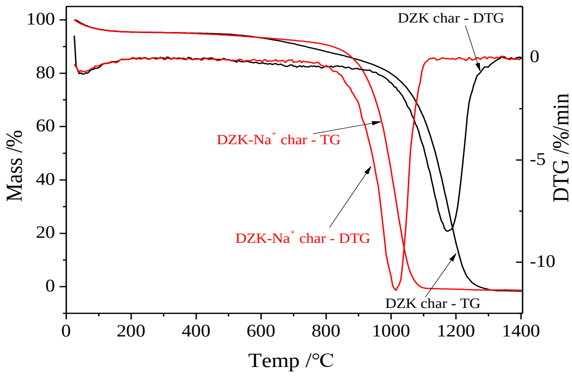

Figure 5. Effect of alkali metal Na on gasification thermal analysis curves of coal char.

3.2.2 Apparent morphology and graphitization of coal char

In order to further observe the effect of alkali metal Na on coal char, the two coal char samples were analyzed for apparent morphology and graphitization degree. The results are shown in *Fig. 6*, *Fig. 7*. It is shown in figure a that the surface of the DZK char is smoother. The "spot" which appears on surface of DZK-Na^+ char in the figure b. As shown in figure c, a large amount of fine "spot" is scattered on the surface of the coal char. So it is speculated that such "spot" become the active center, which shows more intense activity in this region, thereby catalyzing the process of coal char gasification. To further explain the mechanism of influence, the degree of graphitization of DZK char and DZK-Na^+ char by XRD. The XRD spectrum is shown in *Fig. 7*, where the

002 and 100 are respectively carbon diffraction peaks (002), carbon crystal diffraction peak (100). Then, the carbon crystallite structure parameters of the coal char are calculated by the Bragg equation and the Scherrer formula, namely the interfacial layer spacing (d_{002}), the stacking height (L_c) and the grain size (L_a). The diffraction peak (002) indicates the degree of orientation of the aromatic carbon network (layer) in the carbon crystal. The peak intensity is larger and the peak shape is narrower, the better the orientation of the aromatic carbon network. The diffraction peak (100) indicates the carbon crystal structure, the peak intensity is greater and the peak shape is narrower, the degree of condensation of the aromatic carbon network is higher[17, 18]. From *Fig. 7* and *Table 3*, it can be seen that due to the introduction of Na^+, the (002) carbon crystal surface diffraction peak of DZK-Na^+ char is gentler and lower than the DZK char. The values of the d_{002}, L_c, and L_a are all reduced. For DZK-Na^+ char, the growth of carbon basic lattice unit in the longitudinal direction and the growth of the crystallite size itself are relatively slow, indicating that the alkali metals hinders the carbon lattice growing of the coal char at high temperatures. The carbon crystal size and carbon matrix ordering degree decrease, the number of active sites on coal char surface increases, and the stability decreases, so that gasification reactivity of the DZK-Na^+ char is enhanced, so blending BDO tar improves the gasification process.

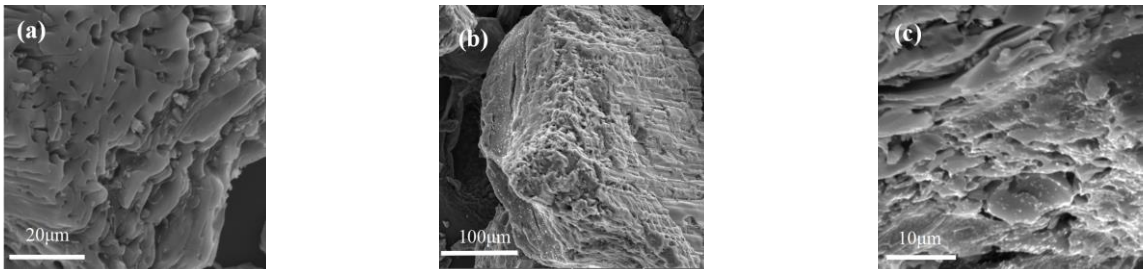

Figure 6. Apparent morphology analysis of different coal char (a: DZK char; b: DZK-Na^+ char; and c: DZK-Na^+ char).

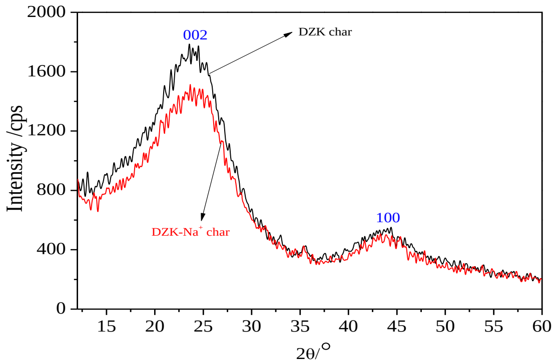

Figure 7. Analysis of graphitization of coal char

Table 3. Carbon crystallite structure parameters

Samples	$2\theta_{002}$	$2\theta_{100}$	d_{002}/nm	L_c/nm	L_a/nm
DZK char	24.105	43.960	3.6890	0.320	0.544
DZK-Na^+ char	23.940	43.678	3.7140	0.223	0.403

4 Conclusion

1) In the process of gasification, with the increase of BDO tar blending amount, during the initial temperature of gasification to 150 °C, the temperature point corresponding to the peak of the maximum reaction rate migrates to the high temperature zone, indicating that there is a the low-boiling components different with water of the tar in this stage; In the temperature range of 200 °C ~ 300 °C, the weight loss of the BDO tar causes the TG curves to shift downward; At the range of 600 °C to the final reaction temperature, because of the inorganic component in BDO tar, the TG curves migrates to the low temperature region, and the temperature required for the same carbon conversion rate is lower.

2) Since the alkali metal Na in the BDO tar enriches the surface of the DZK-Na^+ char with more "spot", the "spot" shows more intense activity, and due to the alkali metal Na limites the graphitization of coal char, hindering the stabilization of coal char, so the incorporation of BDO tar catalyzes the gasification process and improves the coal char gasification reaction activity.

Acknowledgements

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