Research Article

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Effect of direct coal liquefaction residue on the properties of fine blue-coke-based activated coke

Abstract: Activated coke was obtained by CO_2 activation with disused fine blue-coke serving as the main raw material and direct coal liquefaction residue (DCLR) as binder. The effect of the dosage and activation temperature of DCLR on the compressive strength of active coke and desulfurization were mainly investigated. The experimental results showed that the compressive strength of the activated coke increased first and then decreased with the increase in the amount of D-DCLR (DCLR after ash removal). When the amount of D-DCLR was 40%, the compressive strength of the activated coke was 492.55 N and the specific surface area was the highest (189.78 $m^2 \cdot g^{-1}$) among other samples. The results show that the activated coke has a high removal rate for low concentrations of sulfur dioxide. This work provides a way for efficient utilization of DCLR, which avoids waste of resources and environmental pollution. In addition, it is important for finding green and efficient blue-coke powder processing and utilization technology for the sustainable development of the blue-coke industry.

Keywords: fine blue-coke, direct coal liquefaction residue, activated coke, compressive strength, desulfurization

1 Introduction

Activated coke is a desulfurizer in the activated coke flue-gas desulfurization technology and is a key material for desulfurization performance and efficiency [1]. In the process of desulfurization, the activated coke will lose its activity and part of the carbon will be lost during regeneration. Therefore, new type of activated coke needs to be continuously supplemented. It is found that the consumption of activated coke accounts for 50–70% of the total cost of activated coke flue-gas desulfurization technology, which is the key factor affecting the economic performance of activated coke desulfurization technology [2]. At present, reducing the production cost of activated coke is critical to reduce the cost of flue-gas desulfurization technology of activated coke [3]. Therefore, it is imperative to develop cheap and efficient activated coke for flue gas desulfurization.

Blue-coke is a solid carbon product obtained by carbonizing highly volatile and weak/no caking coal at 650–700°C [4]. However, a large amount of waste fine blue-coke is produced during its production, transportation, and use. Statistics show that the Yulin area produces nearly 1 million ton of blue-coke powder every year, which seriously affects the sustainable development of the blue-coke industry [5]. This fine blue-coke is usually treated as low-grade fuel or discarded into rivers and fields, which not only wastes a lot of resources but also seriously pollutes the environment. Therefore, how to efficiently use fine blue-coke resources has become an urgent problem to be solved. Finding green and efficient blue-coke powder processing technology is important to the sustainable development of blue-coke industry.

Studies have shown that due to the high carbon, low ash, and other properties of fine blue coke, the preparation of carbon-based adsorbents using fine blue-coke as a raw material has broad prospects for development [6]. The key to prepare activated coke from fine blue-coke is the choice of binder. Researchers have done a lot of research, mainly adding high-temperature coal tar [7], coal tar pitch [8,9], and high-molecular polymers [10].

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Direct liquefaction of coal is a promising method for producing fuels for clean liquids.

Typically, the direct coal liquefaction residue (DCLR) is the main by-product, accounting for more than 30 wt% of the raw coal [11–14]. DCLR are usually discarded as waste, which leads to economic and environmental problems. Therefore, utilizing DCLR is important for the sustainable development of the materials. The main components of DCLRs are carbon-rich organic components with high utilization value [15,16]. As DCLR has low soften point and strong cohesiveness, it may be used in coal blending for coking as a binder. Large amounts of sticky melting metaplast provided by DCLR during the pyrolysis process can enhance coking properties of blending coals [17,18]. The traditional activated coke production has the problems of high cost and poor quality, therefore, new technology that uses fine blue-coke as raw material and DCLR as binder to prepare activated coke is put forward.

This study mainly researched the effect of the dosage and activation temperature of DCLR on the compressive strength of active coke and desulfurization. The research results in this article provide technical and theoretical support for the simple and high value-added utilization of fine blue-coke and D-DCLR, at the same time provide idea and method for the development of cheap and efficient activated coke for flue-gas desulfurization.

2 Materials and methods

2.1 Raw materials

The raw materials used in the experiment were fine blue-coke and DCLR. Fine blue-coke was taken from Shenmu blue-coke factory. DCLR was taken from a direct liquefaction plant. Since high ash content is not good for activated coke, ash will be removed from DCLR before the experiment [19]. Industrial analysis and elemental analysis of fine blue-coke, DCLR, and D-DCLR (DCLR after ash removal) are shown in Table 1.

2.2 Preparation of activated coke

Fine blue-coke and DCLR were crushed to less than 120 meshes. D-DCLR was mixed into the selected fine blue-coke in a certain proportion. Some water was added to the mixture and stirred fully. At 5 MPa, it was pressed to form a columnar strip (D7 mm × 10 mm) and then dried at room temperature.

The formed columnar strips were carbonized and activated at a heating rate of $10°C·min^{-1}$ in a tubular furnace. The carbonization temperature was 600°C and carbonization time was 60 min under the protection of N_2. When the carbonization process was completed, the temperature was further raised to the activation temperature of 900°C and activated gas CO_2 was introduced into the furnace at a rate of $100\,mL·min^{-1}$ for 30 min. The whole system was cooled to room temperature under N_2 protection to obtain activated coke. The main process flow is shown in Figure 1. Figure 2 is the diagram of carbonization or activation.

2.3 Characterization of activated coke

The scanning electron microscope (SEM) analysis of the activated coke was performed using a JSM-6390A scanning electron microscope, and the X-ray diffractometer (XRD) analysis was performed using a D8 ADVANCE type XRD (Brook, Germany). The infrared analysis was performed using an IR Prestige-21 type Fourier infrared spectrometer (Shimadzu, Japan). The Brunauer-Emmett-Teller (BET) analysis was measured by the JW-BK132F fully automatic physical sorbent instrument (Jingwei Gaobo, Beijing).

Table 1: Proximate analysis and elemental analysis of raw material

Sample	Industrial analysis (%)				Element analysis (%)				
	Mt	Aad	Vad	FCad	Cad	Oad	Had	Nad	St, ad
Fine blue-coke	2.15	16.77	12.07	69.01	72.88	24.58	1.06	0.88	0.6
DCLR	0.14	17.74	33.75	48.37	75.64	17.91	3.573	0.9	1.978
D-DCLR	0.26	10.62	33.19	55.93	78.24	15.4	3.733	0.96	1.667

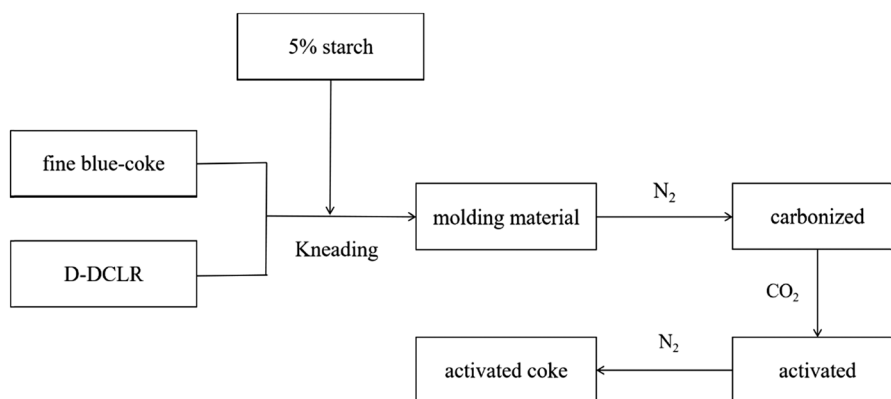FC – fixed carbon, M – moisture, A – ash, V – volatile component, ad – air drying.

Figure 1: Preparation process of a new type of activated coke.

2.4 Desulfurization performance determination

The desulfurization activity was evaluated using fixed-bed equipment at room temperature. The inlet sulfur dioxide concentration of the reactor is $2,000 \text{ mg} \cdot \text{m}^{-3}$, the rest is nitrogen, and the bed height is 12 cm. The desulfurization performance of the activated coke added with 40% direct liquefaction residue is compared with the commercial activated coke.
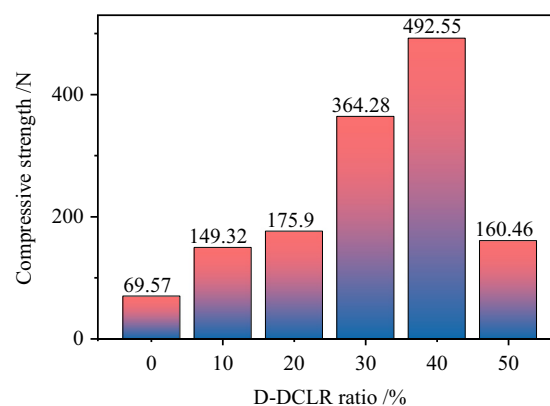

Figure 3: Effect of D-DCLR addition ratio on activated coke intensity.

3 Results and discussion

3.1 Effect of D-DCLR ratio on compressive strength of activated coke

The results are shown in Figure 3. It can be seen that the addition of D-DCLR has a significant effect on the compressive strength of the activated coke. With the increase in D-DCLR addition, the compressive strength of the activated coke appears to increase first and then decrease. In the 0–40% range, the compressive strength of the activated coke increased from the initial minimum to 492.55 N.
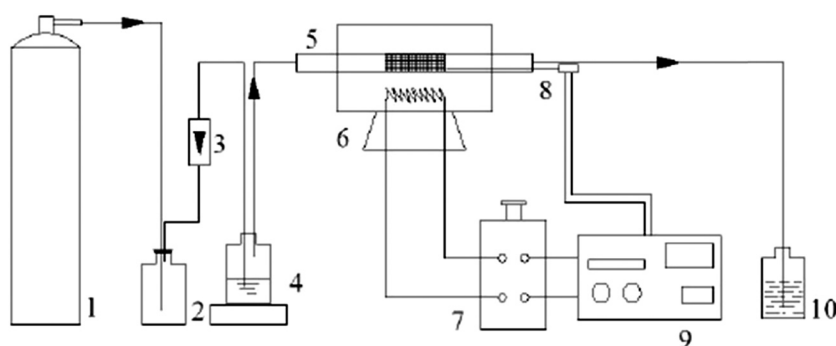

Figure 2: The diagram of carbonization or activation. (1) N_2 gas cylinder, (2) CO_2 gas cylinder, (3) flowmeter, (4) steam generator, (5) quartz reaction tube, (6) tube furnace, (7) pressure regulating transformer, (8) thermocouple, (9) temperature controller, and (10) gas washing bottle.

During the pyrolysis of D-DCLR, a large amount of colloid is produced. The colloids have good adhesion, can infiltrate the carbon particles, and make the dispersed particles tightly bound together. With the increase in the amount of D-DCLR added, more and more colloids were generated by pyrolysis, which makes the bond between the fine particles closer. On further increasing the proportion of D-DCLR addition, the intensity of the activated coke is reduced, because too much D-DCLR will produce a large number of colloids, while the colloid has poor fluidity at high temperatures [20]. Excessive colloidal body will hinder the escape of volatiles generated during pyrolysis, thereby forming pores of different sizes inside and outside the activated coke, and gradually reducing the intensity of the activated coke. Excessive colloids can hinder the escape of volatiles generated during the pyrolysis process.

As a result, pores of various sizes are formed inside and outside the activated coke, which gradually reduces the intensity of the activated coke [21,22]. On the other hand, with the increase in the amount of D-DCLR added, the carbon content and ash content have gradually increased. The liquefaction residue flowability study by Japanese scholars found that with the increase in carbon content and ash content, the cohesiveness of the residue is also improved.

3.2 SEM characterization of activated coke

When the ratio of D-DCLR addition is different, the prepared activated coke is characterized by SEM. The results are shown in Figure 4. It can be seen from Figure 4a that when the amount of D-DCLR added is 0, the activated coke has many small gaps, and the particles are loosely distributed, which is because the fine blue-coke is almost non-cohesive. As the pyrolysis temperature increases, coal pyrolysis generates a large amount of gas that escapes from the interior of the coke. As a result, a large number of gas passages are formed, and no cohesive colloidal body is produced in the pyrolysis process so that the fine blue-coke particles show a state of dispersion and non-adhesion.

From Figure 4b–e, it can be seen that as the proportion of D-DCLR is gradually increased, the fine blue-coke particles are gradually bonded together by the molten substances produced by the pyrolysis process. When the D-DCLR addition ratio is increased to 40%, the adhesion between the particles is tight, because as the D-DCLR addition ratio increases, D-DCLR pyrolysis process continuously

produces viscous and fluid colloids. These colloidal bodies continuously infiltrate the carbon particles and bond them to each other, and the strength of the activated coke is continuously increased.

However, as can be seen from Figure 4f, as the D-DCLR ratio is further increased, a porous honeycomb appears on the surface of the activated coke, and the particles are still bound together by many molten substances. This is because the ratio of D-DCLR is too high, and excessive colloidal bodies are generated during the pyrolysis process. Excessive colloidal bodies can block the escape passage of volatiles generated by pyrolysis of organic groups [23]. With the increase in the proportion of D-DCLR added, mineral content increases. Minerals have an inhibitory effect on the escape of volatile matter between coal particles [24], making excessive gas stay in the surface and interior of the activated coke, making a large number of holes on the surface and inside, thereby reducing the intensity of the activated coke.

3.3 XRD characterization of activated coke

Activated coke is prepared from fine blue-coke, and its fixed carbon content is high. Figure 5a shows the XRD pattern of activated coke prepared at different activation temperatures, and Figure 5b shows the XRD patterns of activated coke prepared at different D-DCLR ratios. From the figures, It can be seen that there are two strong characteristic peaks around $2\theta = 26°$ and $2\theta = 43°$, and the characteristic peak around 26° is obviously stronger than the characteristic peak around 43°, which belong to the (002) and (100) crystal face diffraction characteristic peak of carbon materials, respectively [25].

From Figure 5a, it can be seen that with the increase in the activation temperature, the burning loss rate of the activated coke increases, and the amorphous carbon arranged on the surface and internal crystallites in a random layer structure is reduced [26]. From Figure 5b, it can be seen that the addition ratio of D-DCLR has little effect on the crystal structure of the activated coke. In addition to the (002) and (100) characteristic peaks in the spectrum, there are other impurity peaks, such as the SiO_2 diffraction peak around $2\theta = 27°$ [27].

The SiO_2 diffraction peak at 900°C under the activation condition is stronger than the 850°C condition in Figure 5a. This is mainly due to the increase in the activation temperature, the increase in carbon loss, and the increase in the activated coke ash. In Figure 5b, the SiO_2 diffraction peak at 40% D-DCLR ratio is slightly
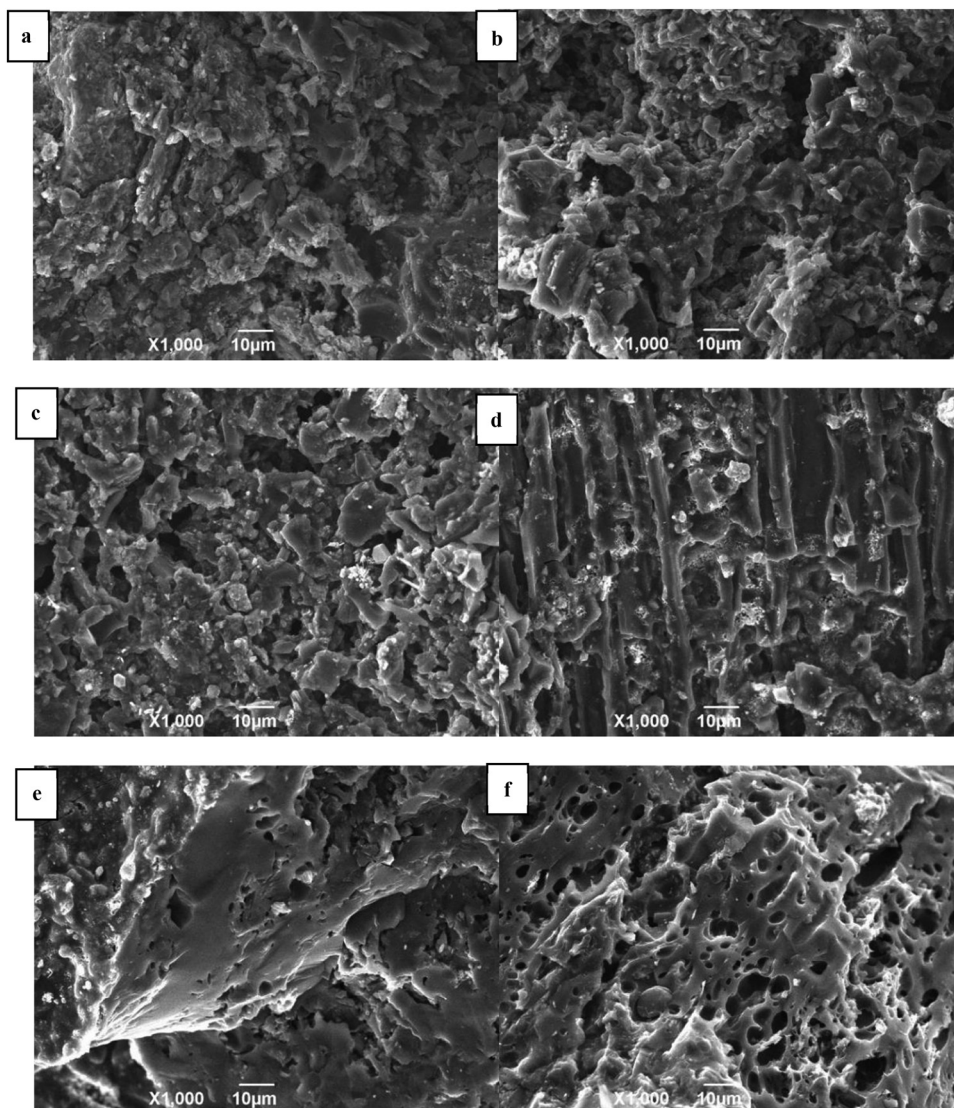
Figure 4: The SEM images of different D-DCLR additions on the properties of activated coke. (a) D-DCLR addition ratio = 0%; (b) D-DCLR addition ratio = 10%; (c) D-DCLR addition ratio = 20%; (d) D-DCLR addition ratio = 30%; (e) D-DCLR addition ratio = 40%; (f) D-DCLR addition ratio = 50%.

stronger than the diffraction peak at 30% addition ratio, this is because the more D-DCLR is added, the higher the ash content in the activated coke, and the impurity diffraction peak is higher [28].

3.4 Infrared spectrum analysis of activated coke

The infrared analysis results of the activated coke are shown in Figure 6, which are the activated coke infrared spectrums of 0% D-DCLR, 30% D-DCLR, and 40% D-DCLR,

respectively. It can be seen from Figure 6 that as the amount of D-DCLR added increases, the type of functional groups contained in the activated coke does not change, but the intensity of the absorption peaks changes. $3,600–3,200\,\mathrm{cm}^{-1}$ is the vibrational peak of hydroxyl function in alcohol, phenol, and water [29]. And the absorption peak increases with the increase in the D-DCLR addition amount, which may be due to the thermal decomposition of organic components such as asphaltenes and heavy oil in D-DCLR with the increase in the D-DCLR content. The characteristic peak near $1,700–1,500\,\mathrm{cm}^{-1}$ is the vibration peak of the carbon-oxygen double bond in the carbonyl group and the carbon-carbon double bond in the
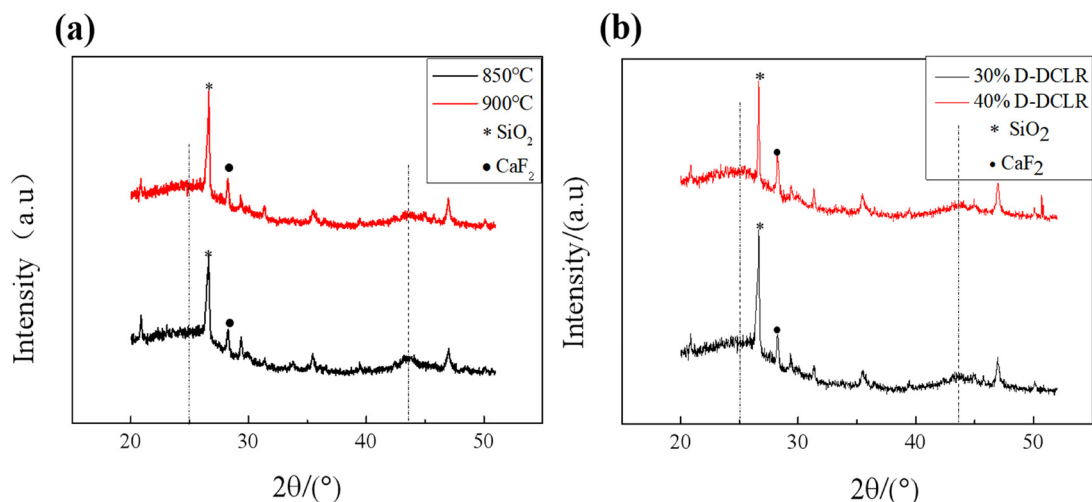
(a)

(b)

Figure 5: XRD patterns of (a) activated coke prepared at different activation temperatures and (b) activated coke prepared at different D-DCLR ratios.
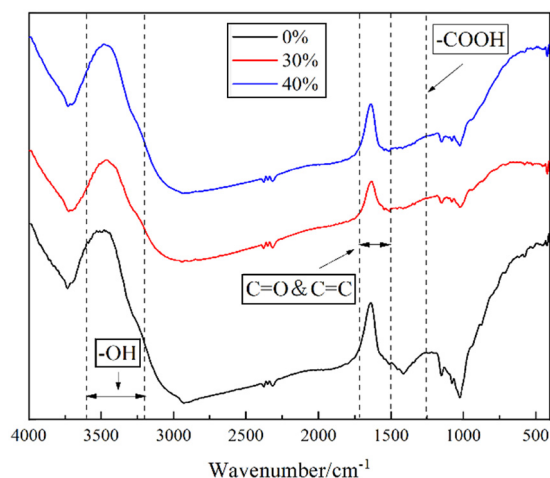

Figure 6: The IR spectra of activated coke.

benzene [30]. Near $1,255\,cm^{-1}$ is the vibrational peak of oxygen-containing functional groups in ether, epoxy compounds, and non-epoxy compounds. There is a relatively broad absorption peak around $604\,cm^{-1}$, and it increases with the increase in the D-DCLR content, it is the absorption peak of minerals, indicating that with the increase in D-DCLR addition, the ash in the activated coke constantly increases.

3.5 Pore structure analysis of activated coke

Figure 7a is the N_2 adsorption-desorption isotherm curve of different raw materials specific activated coke, Figure 7b is the pore size distribution curve of different raw materials

specific active coke. As can be seen from Figure 7a, according to the IU-PAC classification, the N_2 isotherm adsorption-desorption curve of the activated coke belongs to the type II curve, which shows that the activated coke is mainly composed of micropores and mesopores. The adsorption capacity of AC2 (D-DCLR addition ratio = 40%) activated coke is larger than that of AC1 (D-DCLR addition ratio = 30%) activated coke, and the adsorption increases rapidly, indicating that AC2 activated coke has better adsorption performance and pore structure than AC1 activated coke, and the specific surface area is increased by 39.36%.

Table 2 is the structure parameters of the activated coke. The specific surface area of AC1 is $136.18\,m^2{\cdot}g^{-1}$. Compared with AC1, various parameters of AC2 have been improved. Especially, the specific surface area has increased by 39.36% ($189.78\,m^2{\cdot}g^{-1}$). This may be because with the increase in the amount of DCLR added, the increase in volatile matter in the pyrolysis process is conducive to further pore formation. Moreover, the residual iron catalyst is contained in the DCLR, which is beneficial to the catalytic pore formation of the activated coke.

3.6 Desulfurization performance of activated coke

The desulfurization performance of the activated coke added with 40% DCLR is compared with the commercial activated coke. The desulfurization rate for the first 120 min is shown in Figure 8. As can be seen from Figure 6, the desulfurization rate of activated coke AC0 (D-DCLR addition
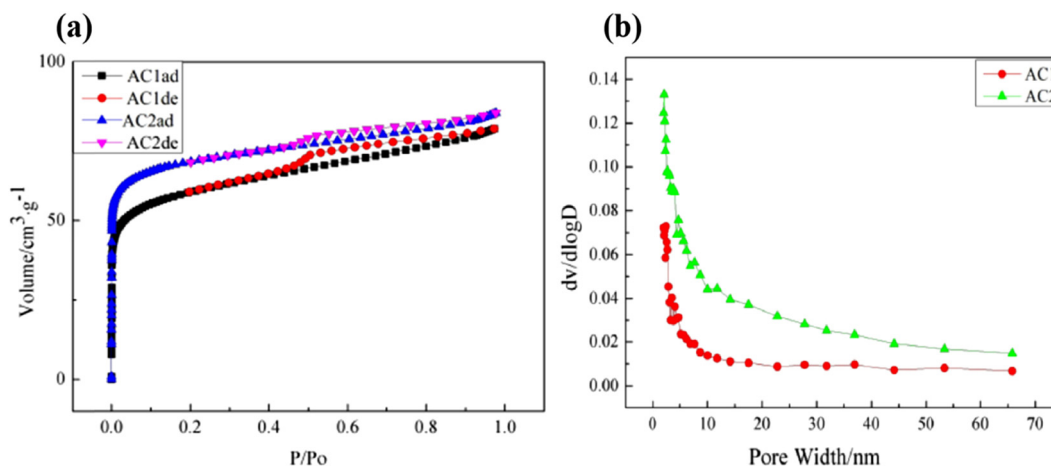
Figure 7: (a) N$_2$ adsorption-desorption isotherm curve of different ratios of activated coke; (b) pore size distribution curve of different proportions of activated coke.

Table 2: Structure parameters of activated coke

Material	S_{BET} (m$^2\cdot$g^{-1})	V (cm$^3\cdot$g^{-1})	V_{micro} (cm$^3\cdot$g^{-1})	$D_{average}$ (nm)
AC1	136.18	0.079	0.049	2.491
AC2	189.78	0.122	0.068	2.573

S_{BET} – specific surface area of activated coke, V – the total pore volume, V_{micro} – the micropore volume, D – the average pore diameter of the activated coke.

ratio = 0%) and activated coke AC2 (D-DCLR addition ratio = 40%) in the first 20 min are all about 95%, and then the desulfurization rate of AC2 has decreased but remains above 80%, but the two activated cokes in the whole desulfurization process show a consistent change law, indicating that the activated coke has a high removal rate for low concentrations of sulfur dioxide. The activated coke has a high removal rate for low concentrations of sulfur dioxide and
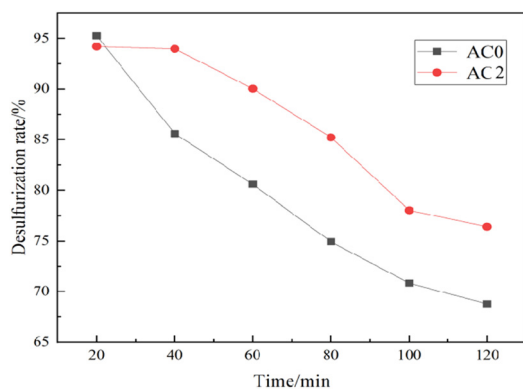
its desulfurization performance. Adding DCLR to prepare activated coke can lower the cost and realize comprehensive utilization of resources [30]. With the extension of desulfurization time, the main reason for the decrease in desulfurization rate is that activated sites on the activated coke surface are occupied by the adsorbed gas, resulting in a reduction in the active sites and a decrease in the desulfurization rate.

4 Conclusion

In summary, this study prepared a columnar activated coke with fine blue-coke as the main raw material and D-DCLR as the binder. The effects of different DCLR additions on the properties of the activated coke were investigated. Among them, when the ratio of D-DCLR was 40%, the activated coke strength is the highest (492.55 N), and the specific surface area is 189.78 m$^2\cdot$g^{-1}. The desulfurization performance of the activated coke added with 40% DCLR (AC2) and the commercial activated coke was researched. The results show that the activated coke has a high removal rate for low concentrations of sulfur dioxide. This work provides a way for efficient utilization of DCLR, which avoids waste of resources and environmental pollution. In addition, it is important for finding green and efficient blue-coke powder processing and utilization technology for the sustainable development of the blue-coke industry.

Figure 8: The desulfurization rate of activated coke vs time.

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