Filling of Nanocarbon Particles in the Pores of Unburned Carbon and Its Application in Gasification Ash Separation

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ABSTRACT: The nanocarbon particles and diesel are used as hydrophobic solid particles and the liquid phase to produce the mixture collector for the flotation separation of unburned carbon (UC) particles from gasification ash. Scanning electron microscopy/energy-dispersive spectrometry and mercury porosimeter measures were used to prove the filling of nanocarbon particles in the pores of UC particles. Mercury porosimeter results illustrate that the pores of the UC particles after the action of the mixture of nanocarbon particles and diesel are reduced compared with that after the action of diesel. The number of >4000 nm pore was significantly reduced, and the number of <250 nm pore nearly disappeared. The results of the flotation tests found that the use of the mixture of nanocarbon particles and diesel as a collector resulted in not only increasing the concentrate yield but also reducing the ash of the concentrate. Throughout this investigation, the filling of nanocarbon particles in the UC holes/pores plays an important role in the enhancement of flotation recovery of UC particles. The filled pores in the UC particle surface can increase the contact area between bubbles and UC particles, thereby increasing the adhesion of bubble–particles, reducing the probability of particle detachment, and ultimately improving the flotation recovery of UC.

1. INTRODUCTION
Coal gasification ash as an important proportion of fly ash and its comprehensive utilization become an important factor in achieving circular economy in the coal chemical project. Unburned carbon (UC) is one of the resources in the gasification ash. Most of the UC entrained in the syngas produced by the gasifier have high carbon content and strong water absorption. Matjie et al. studied the basic characteristics of gasification ash and its residual carbon, which found that the UC is porous and mostly has a sponge-like structure. If the gasification ash is directly blended into the boiler, the calorific value of the coal powder will greatly reduce. If it is directly used as cement or concrete and other materials, these UC particles will reduce the strength of concrete because of its strong water absorption. When preparing concrete products as aggregates or admixtures, the consistency of the slurry can be increased, the setting time is prolonged, and the strength is then lowered. Furthermore, the durability of concrete products is affected, if the gasification ash is effectively separated into two products: UC and ash particles. The UC can be directly blended into the boiler while the high ash particles can be used in the production of cement, concrete, and masonry. Therefore, the gasification ash needs separation to recover low ash carbon particles, which greatly improves the energy utilization efficiency and benefits the potential value of these secondary resources.

Froth flotation was invented in 1905 for mineral separation. Froth flotation is carried out on the basis of surface chemistry, and fine mineral particles are separated on the basis of their hydrophobicity difference. Recently, the candle soot has been found to be super-hydrophobic. They can be prepared through spraying of nanocarbon particles collected by incomplete combustion of the candle. At present, the preparation methods of nanocarbon particles mainly include arc discharge, synthesis, pyrolysis organic, laser ablation, ultrasonic-assisted, microwave-assisted, and microwave hydro-thermal-assisted method, and so forth. These methods were costly. In industrial production, carbon particles in the mixture collector can be prepared by collecting incomplete combustion products of waste incineration and coal power plants, carbonaceous waste generated by petrochemical plants, and cracking of natural gas and coalbed methane. This is also a way to recycle waste resources. Xia et al. enhanced the coal flotation by the mixture of nanocarbon particles and n-dodecane as an efficient flotation collector. They found that nanocarbon particles can adsorb on the coal surface and increase the surface roughness of coal particle. The nanocarbon particles can improve the hydrophobicity of coal surface and they can accelerate the rupture of liquid film during the attachment of bubbles and hydrophobic particles. The conventional flotation of UC from gasification ash is difficult because the pores of the UC particles may be filled with water causing the difficulty in the attachment of UC particles and bubbles.

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In this paper, nanocarbon particles with diesel create a kind of mixture collector for gasification ash flotation. The nanocarbon particles were filled in the pores of UC particles during the condition and flotation of gasification ash. In this paper, scanning electron microscopy (SEM) and mercury porosimeter measurement were used to illustrate why the mixture collector can improve UC flotation.

2. RESULTS AND DISCUSSION

2.1. Gasification Ash Flotation Results. The flotation results of gasification ash using different collectors are shown in Figure 1. The mixture of diesel and nanocarbon particles is used as the collector, and the yield of floated UC particles is significantly higher than that of diesel. However, the ash content of floated UC using diesel is higher than that using the mixture collector as the collector. This represents that the mixture collector of diesel and nanocarbon particles enhances the recovery of UC particles from gasification ash. The floated UC particles can be used as the pulverized coal because it only has about 18–21% ash content. In order to evaluate the flotation effect of two collectors on UC particles in gasification ash, the combustible recovery rate was calculated from the following equation.

\[
\text{Combustible recovery} = \frac{Y_c(100 - A_c)}{Y_f(100 - A_f)} \times 100
\]

where \(Y_c\) is the yield of the clean coal (%); \(Y_f\) is the yield of the feed (%); \(A_c\) is the ash content of the clean coal (%); and \(A_f\) is the ash content of the feed (%).

As is shown in Figure 2, regardless of the dosage of collector, the mixed collector has better recovery effect on UC (combustible) in the gasification ash than diesel.

2.2. Mechanism Analysis. 2.2.1. X-ray Photoelectron Spectroscopy Results. As is shown in Figure 3, Xia et al. found that the atomic content of C 1s is nearly 93% of the surface of nanocarbon particles through the fitting results of X-ray photoelectron spectroscopy (XPS) analysis. However, that of O 1s is nearly 7%.

For C 1s peaks, they found that the content of C≡C and C–C on the nanocarbon particle surface is nearly 82 and 13%, respectively. However, the proportion of C–O group on the surface of nanocarbon particles is about 6%. It means that the nanocarbon particles are very hydrophobic. In our previous study, the contact angle of nanocarbon particles is also very higher, nearly 136°.

Figure 4 shows the XPS wide energy spectrum and the fitting results of C 1s. The surface of fly ash is 83% C 1s and 17% O 1s. It is found that most of the elements on the surface of gasification ash are C and O by XPS wide energy spectroscopy. In addition, the XPS wide energy spectrum results of the gasification ash showed that the UC particle surface did not adsorb lots of harmful elements such as mercury and chloride and could be directly recovered as a fuel for the boiler.

For C 1s peaks, C–C/C–H, C–O, O=C–O, COOH, CO\(_3^{2-}\), and COO\(^-\) bonds correspond to the following binding energies 284.8, 285.5, 286.6, 287.8, 289.1, 290.7, and 292.0 eV, respectively. The content of C–C/C–H on the gasification ash surface is 65.22%, while the C–O is 8.39%, and the content of C≡O is 10.28%. The content of O=C–O is 3.75%. The COOH is 4.98%. However, the content of CO\(_3^{2-}\) is 4.08%. The content of COO\(^-\) is 3.29%. The C–C/C–H functional groups are hydrophilic while the functional groups of C–O, C≡O, O=C–O, COOH, CO\(_3^{2-}\), and COO\(^-\) are hydrophilic. The gasification ash surface is relatively much more hydrophilic than the nanocarbon particle surface. If the nanocarbon particles can adsorb on the UC particle surface, the floatability and hydrophobicity of the UC particles should be enhanced and hence its flotation recovery will also be increased. Further investigations are given through porosimeter analysis and SEM/energy-dispersive spectrometry (EDS) analysis.

2.2.2. Porosimeter Analysis. Figure 5 illustrates the porosity of the UC particles after the action of the diesel and mixture collector. The porosity of the UC particles by the mixture collector is generally reduced compared with that of the UC particles by the diesel, especially the micropores smaller than 250 nm are substantially disappeared, and the pores larger than 4000 nm are significantly reduced. Also, the reduction in these pores indicates that the nanocarbon particles can effectively fill in the pores of UC particles. Some chemical bonds of atoms on the solid surface are in an unsaturated state. This feature causes an adsorption field on the solid surface. Under the action of the adsorption field, the external molecules aggregate on the solid surface because the surface area of the pores is larger, and the surface residual energy is higher than the outside surface of the particles. Therefore, the nanocarbon particles are more easily adsorbed by the inner surface of the pores, thereby filling the pores.
2.2.3. SEM/EDS Analysis. Figure 6 is the scanning electron microscope results of the UC after the action of the diesel and mixture collector. Figure 7 is the EDS results of UC particle surface using the diesel and mixture collector. The particles adsorbed on the surface of UC particles using diesel are less than that using the mixture collector. In addition, the pores of UC particles using diesel have fewer filled particles than the UC particles using the mixture collector as shown in the rectangle in Figure 6. The large flocs of nanocarbon particles in the mixed collector filled the macropores in the UC particles and the small flocs filled the micropores, eventually leading to the pore reduction. As well known, nanocarbon particles adsorbed on the coal surface can accelerate the rupture of liquid film during the attachment of particles and bubbles.12 Furthermore, Chen et al. found that the coal surface hydrophobic gradually increased with the decrease of roughness.21

As shown in Figure 8, the surface of UC particles has pore filled by water during the flotation process. The filling of water in the UC particle pores forms the “water pocket”.12,23 However, the pores in hydrophobic surface usually entrap the air which forms the “air pocket”.16 The water pocket reduces the solid contact area for the bubble-particle adhesion. The UC particles after the filling of hydrophobic nanocarbon particles in pores can increase the hydrophobic solid area for the adhesion of bubble-coal surface. In addition, the adhesion
probability of particles and bubbles can be enhanced because the pores will be filled with the hydrophobic solid nanocarbon particles instead of the water. This ultimately leads to an increase in the attachment and decrease in the detachment because the contact area between coal surface and bubble is enlarged. Therefore, the yield of the floated UC particles is higher for the mixture collector than diesel.

3. CONCLUSIONS

The flotation recovery of UC particles from gasification ash with the diesel and nanocarbon particle mixture is better than that with diesel as the collector. The mixture collector not only increases the yield of floated UC particles significantly but also decreases its ash content. Nanocarbon particles can effectively fill in the pores of the UC particles, increasing the hydrophobic solid area for the adhesion of bubble–coal surface and enhance the adhesion probability of particles and bubbles. This ultimately leads to an increase in the attachment of UC particles onto the bubble surface and the decrease in the detachment of UC particles from bubbles. Therefore, the yield of the floated UC is higher for the mixture collector compared to the diesel.

4. EXPERIMENT AND METHODS

4.1. Gasification Ash Samples and Experiment Materials. The gasification ash comes from the Shell coal gasifier of Datong Coal Mine Group, Shanxi, China. The coal reacts with steam and oxygen in a gasifier to produce crude syngas and ash. The gasification ash entrained in the crude syngas contains partially UC. The UC forms gasification ash through the condensing purification system. The proximate analysis (on air dry basis) of gasification ash (<0.5 mm) is shown in Table 1. The ash content of this gasification ash sample is low, which means that the gasification ash samples contain amounts of combustible matter.

The gasification ash sample size composition (on dry basis) is listed in Table 2. In addition, the ash content and yield of <0.045 mm is more than those of other size fractions. Tap water was used in the flotation experiments. The properties of tap water are shown in Table 3.

4.2. Preparation of the Novel Flotation Collector. The recovery procedure of nanocarbon particles (candle soot) is similar to that of Qahtan et al. The experimental operation is displayed in Figure 9a. Place a 250 mL glass beaker upside down on top of four candle flames so that the incompletely burned area hits the inside of the beaker for some time. Finally, the nanocarbon particles are collected as in Figure 9b.

4.3. Flotation Experiments. In this paper, the 1.5 L cell of XFD flotation experimental machine was used for gasification ash flotation. The pulp concentration was 4%. The mixture of nanocarbon particles and diesel or diesel was used as the collector. Their dosages were 5000, 7000, 9000, and 11 000 g/t. The experimental operation is similar to that of Qahtan et al. The experimental operation is displayed in Figure 9a. Place a 250 mL glass beaker upside down on top of four candle flames so that the incompletely burned area hits the inside of the beaker for some time. Finally, the nanocarbon particles are collected as in Figure 9b.

4.4. XPS Tests. XPS tests of nanocarbon particles and UC particles were performed in an ultra-high vacuum system using the surface analysis system (ESCALAB 250 Xi, USA) at room temperature. XPS peak fitting software was used for data processing (peak fitting).

4.5. SEM/EDS Tests. The SEM test for nanocarbon particles and UC particles in the pores of UC particle. A layer of gold is sprayed on the surface of sample to increase conductivity before the SEM/EDS tests.

Table 1. Proximate Analysis of Gasification Ash (on Air-Dry Basis)

| moisture (%) | ash (%) | fixed carbon (%) | volatile (%) |
|--------------|---------|-----------------|-------------|
| 30.24        | 25.92   | 43.03           | 0.81        |

Table 2. Screen Results of Gasification Ash (on dry basis)

| size fraction (mm) | yield (%) | ash (%) |
|--------------------|-----------|---------|
| >0.500             | 3.31      | 18.19   |
| 0.050–0.250        | 19.02     | 22.65   |
| 0.250–0.125        | 19.05     | 18.14   |
| 0.125–0.074        | 13.53     | 27.81   |
| 0.074–0.045        | 7.90      | 43.70   |
| <0.045             | 37.19     | 59.20   |
| total              | 100.00    | 37.60   |

Table 3. Property Analysis of Tap Water

| ion content (mg/L) | K⁺ | Ca²⁺ | Mg²⁺ | Na⁺ | Cl⁻ | SO₄²⁻ |
|--------------------|----|------|------|-----|-----|-------|
| conductivity (μS/cm) |    |      |      |     |     |       |
| 155.70             | 9.17 | 72.01 | 24.35 | 42.53 | 74.23 | 75.88 |
4.6. Mercury Porosimeter Tests. Mercury porosimetry is a very useful pore size of material testing technique. The pore can be investigated between 500 μm and 3.5 nm. Mercury porosimetry can provide the pore size distribution, the porosity, and total pore volume. The mercury porosimeter tests for floated UC particles of the collector dosage are 9000 g/t. Using the Autopore IV 9500 high-performance automatic mercury intrusion instrument produced by Micromeritics in the United States, the filling of nano-carbon particles in UC particle pore was analyzed.

Figure 9. Nanocarbon particle recovery apparatus (a), nanocarbon particles (b) and mixture of diesel and nanocarbon particles (c).12

Figure 10. Dispersion state of nanocarbon particles in the mixture collector.

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Notes

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