Detachment Force of Air Bubbles Detached from Low-Rank Coal Surface in the Presence of Adsorbed Oleic Acid–Dodecane Collector Mixture

Yinfei Liao,* Hourui Ren, Maoyan An, Yijun Cao, Zhe Yang, Xiaodong Hao, and Xingwei Song

ABSTRACT: It is well known that mixed collectors can effectively strengthen the flotation of low-rank coal. However, less concern has been paid to the detachment of low-rank coal flotation using mixed collectors. In this study, the force of air bubble detachment from low-rank coal surface treated by oleic acid (OA), dodecane (D), and oleic acid–dodecane (OA–D) collector mixture was investigated using microforce balance. The results showed that the process of bubble detachment from the low-rank coal surface was divided into three stages: relaxation stage, stretching stage, and sliding stage. The equilibrium contact angle and critical contact angle were the transition points between different stages. The order of detachment force required for bubble detachment from the surface of low-rank coal was OA–D > OA > D, indicating a synergistic effect between OA and D. Based on the three parameters of equilibrium contact angle, critical contact angle, and contact line length, a theoretical model was proposed to calculate the detachment force. The calculated results were in agreement with the measured results.

1. INTRODUCTION

Flotation is one of the most effective and widely used separation methods for fine and very fine materials. According to the different surface properties of particles, flotation reagents are added to separate the particles efficiently.1 During the flotation process, bubbles are selectively adsorbed to hydrophobic particles.2 The interaction of bubbles and particles is divided into three stages: collision, attachment, and detachment. A turbulent environment is necessary for flotation, but the strong turbulent flow fields will also adversely affect the attachment between bubbles and particles.3 When the external force is greater than the adhesion force between particles and bubbles, the bubbles will detach from the particles, which will cause low recovery of the flotation concentrate.4,5 Therefore, it is of great significance to study the process of bubble–particle detachment in flotation.

As an important part of flotation, bubble–particle detachment has attracted wide attention in recent years. The study of bubble–particle detachment originated from the stress analysis of the aggregate.6 A great deal of work has been done on bubble–particle detachment using various devices and models. Nguyen et al.7,8 built a mechanical model based on the force analysis of particles attached to the plane fluid interface. As shown in Figure 1, the forces acting on the particles are capillary force, buoyancy force, pressure, and gravity. Wang et al.9 divided the forces acting on the bubbles into adsorption forces and detachment forces, and the capillary forces generated by the surface tension were considered to be the main forces stabilizing the bubble–particle aggregates. Based on the equilibrium force analysis of bubble–particle...
aggregates, Schulze\(^{10}\) proposed a new theory to study the stability of the agglomerates in the flotation process and calculated the maximum size of the flotation particles under given conditions. Xu et al.\(^{11}\) calculated the maximum detachment force based on the maximum amplitude of the particles detaching from the bubbles. The maximum separation force increased with the contact angle of particles and the viscosity of the suspension medium. Knüpfert et al.\(^{12}\) found that the capillary forces acting on the particles cause the particles to deform at the interface during the detachment process. They built a simple model based on the particle interface deformation and wettability. The collector has a considerable impact on the detachment of particles—bubbles\(^{13}\) that can change the surface hydrophobicity of particles. The hydrophobicity of particles strongly influences the bubble—particle separation force. The probability of particles separating from the bubbles is smaller if the particles are more hydrophobic.\(^{14}\) Fosu et al.\(^{15}\) reported that the collector can increase the hydrophobicity of the mineral surface, and the detachment force increased with the concentrations of SIPX and PAX. Similarly, Jańczuk et al.\(^{16}\) observed that the detachment force of bubbles from the surface of low-rank coal was related to the thickness of the \(n\)-alkane membrane and the type of \(n\)-alkane. Nonpolar collectors can increase the contact area between coal particles and bubbles, increasing the stability between bubbles and particles.\(^{17}\) Moreover, shale oil can enhance the absorption effect of bubble on oxidized coal particles and significantly increase the recovery of oxidized coal.\(^{18}\) Therefore, the collector played an important role in the bubble—particle detachment force.

China is rich in low-rank coal reserves, accounting for more than 40% of the explored coal resources.\(^{19}\) With the development of coal mining mechanization, the yield of fine low-rank coal is increasing. The efficient separation of coal and gangue is the key to make full use of low-rank coal. A common method for processing low-rank coal slime is flotation. Nonpolar oils such as diesel and kerosene are often used as collectors to enhance the fine low-rank coal particles’ hydrophobicity that makes the separation possible.\(^{20,21}\) However, low-rank coal has developed porosity and abundant oxygen-containing functional groups, which make coal particles hydrophilic and increase the difficulty of flotation.\(^{22}\) Many scholars have used mixed collectors to improve the separation performance of low-rank coal. Zhen et al.\(^{23}\) found that adding a certain amount of dodecyl trimethyl ammonium chloride (DTAC) can effectively enhance the hydrophobicity of low-rank coal and reduce the induction time between coal particles and bubbles. Similar researches indicated that the mixed collector of dodecane and \(n\)-pentanoic acid can also obtain shorter induction time and higher coal hydrophobicity.\(^{24}\) Jia et al.\(^{25}\) observed that when dodecane is mixed with a small amount of tetrahydrofurfuryl esters (THF) as a collector, the surface hydrophobicity of low-rank coal can be significantly improved. A higher recovery was obtained using the mixture of dodecyl trimethylammonium bromide and diesel as the collector in low-rank coal flotation.\(^{26}\) Recently, some scholars used molecular dynamics simulation methods to study the absorption behavior of mixed collectors on the low-rank coal surface. Liu et al.\(^{27}\) found that the mixed collector of dodecane and \(n\)-valeric acid had better flotation performance due to the co-adsorption that occurred on the low-rank coal surface. Furthermore, Zhang et al.\(^{28}\) indicated that the adsorption capacity was enhanced by the hydrogen bond and electrostatic attraction of C12EO4. The collector properties including the organic types, chain length, side chains, etc., will greatly affect the flotation\(^{29,30}\) and the detachment process in flotation. Although mixed collectors in low-rank coal flotation have been widely researched, their effect on the detachment of bubbles—particles is rarely investigated.

In this paper, mechanical properties of air bubble detachment from low-rank coal surface in the presence of dodecane (D), oleic acid (OA), and their mixture (OA–D) were investigated. The properties of samples were analyzed using XPS and SEM measurements. The force of the air bubble detaching from the low-rank coal surface treated by different collectors was measured by microforce balance. The effect of mixed collectors on the detachment process was discussed. A theoretical model was established to calculate the detachment force, and the measured force and calculated force were compared. The results of this study are expected to provide a new understanding of the enhancement of low-rank coal flotation with mixed collectors.

2. RESULTS AND DISCUSSION

During the detachment force test, in which the low-rank coal surface was treated with the mixed collector, representative pictures of the bubble deformation were obtained, as shown in Figure 2. The curve of the force measured by the microforce balance over time is shown in Figure 3.
equilibrium state, the force becomes zero, and the contact angle between the bubble and the low-rank coal surface is called the equilibrium contact angle. The process of the bubble from the compression state to the equilibrium state is defined as the relaxation stage.

(2) Stretch stage. As the bubble is stretched downward from the equilibrium state, the force becomes positive and gradually increases to the maximum value, and the maximum force is defined as the detachment force. At the same time, the contact angle between the bubble and coal surface increases gradually, and the maximum contact angle is called the critical contact angle. But the three-phase contact line length between the bubble and coal surface does not change, and the bubble is not detached from the coal surface.

(3) Sliding stage. As the bubble is further stretched downward, the radius of the three-phase contact line gradually shortens, indicating that the bubble gradually separates from the coal surface. Moreover, the detachment force and contact angle remain unchanged until the bubble completely separates from the coal surface, that is, the radius of the three-phase contact line is zero. Finally, the bubbles pull away from the coal surface, and the detachment force rapidly reduces to zero. The latter two stages, namely, the stretch stage and sliding stage, constitute the actual detachment process.

Figure 4 shows the photographs of bubble detachment from the low-rank coal surface treated by different collectors. It can be found that there are distinct differences in the contact angle, contact line radius, and bubble deformation during air bubble detachment from the low-rank coal surface. The contact line radius and bubble deformation are greater after the low-rank coal surface is treated by collectors. Moreover, the effect of OA–D on the contact line radius and bubble deformation is more significant compared to that of OA and D, indicating that the adhesion strength between the air bubble and low-rank coal surface after OA–D treatment is higher than that of OA and D. The higher the adhesion strength is, the stronger the stability of bubble particle aggregates. Therefore, the probability of particle desorption in the flotation process is reduced, which will be conducive to obtain higher flotation recovery.

Table 1 presents the detachment force and correlated parameters during bubble detaching from low-rank coal surface. The order of detachment force was OA–D > OA > D > coal, suggesting that the detachment force between the bubble and low-rank coal surface is enhanced by collector treatment. Compared to D or OA, the detachment force between the bubble and OA–D-treated low-rank coal is greater. It is indicated that the mixed use of OA and D is more conducive to increase the detachment force and improve the stability of bubble particle aggregates. This can well explain that the flotation recovery of OA–D was higher than that of OA and D in a previous work because the stability of bubble particle aggregates was enhanced and the detachment probability was reduced. Many studies have shown that the collector can enhance the stability of the bubble—particle aggregates by improving the hydrophobicity of particles. Thus, it can be inferred that the improvement effect of the three collectors on the surface hydrophobicity of low-rank coal is OA–D > OA > D. This deduction is consistent with the contact angle measurement and flotation results reported in previous studies. Low-rank coal surface is rich in oxygen functional groups. D is a nonpolar collector and can adsorb on the hydrophobic area. D has a proper length of 12 carbon atoms in the structure. For alkane, the long chain length may favor increasing the hydrophobicity of the coal surface but will also result in the loss of selectivity in the flotation process. D cannot effectively interact with these hydrophilic sites. OA, a polar collector, has a chain length of an 18-carbon structure that can interact with the hydrophilic sites on the coal surface through the carboxyl groups. The long hydrocarbon chains will enhance the surface hydrophobicity to a large extent. OA–D combines the advantages of D and OA, so it greatly improves the surface comprehensively. Moreover, it is interesting to note that the equilibrium contact angle, critical contact angle, and contact line radius all decrease in the order of OA–D > OA > D > coal. This means that the equilibrium contact angle, critical contact angle, and contact line length are positively correlated with the detachment force. The contact angle and contact line radius are closely related to the adhesion strength of bubbles on the low-rank coal surface, and the adhesion strength can be characterized by the detachment force. Therefore, there is an inevitable correlation between the detachment force and the three parameters, namely, equilibrium contact angle, critical contact angle, and contact line length, and the relationship between them will be modeled in the following section.

According to the theoretical model of Wark et al., the detachment force between the bubble and low-rank coal surface was analyzed. Figure 5 shows the geometry and force illustration of the bubble and low-rank coal surface in...
which the vertex of the bubble is the origin of the coordinate system and the vertically downward direction is positive.

The force causing the bubble to adsorb to the solid surface is the capillary force $F_c$ acting around the three-phase contact. Its vertical component is:

$$F_c = -2\pi r_{pc} \sigma \sin \theta$$  \hspace{1cm} (1)

where $r_{pc}$ is the contact line radius, $\sigma$ is the air–water interfacial tension, $\theta$ is the bubble–coal surface contact angle, and the negative sign indicates that the direction of the force is upward.

The buoyant force $F_b$ and gravity force $F_g$ acting on the bubbles can be expressed as follows:

$$F_b = -V \delta g \ P_b = V \delta g$$  \hspace{1cm} (2)

where $V$ is the bubble volume and $\delta g$ is the gas density.

The static pressure acting on the bubble is the pressure difference between air and water on the three-phase line, which can be expressed as:

$$F_p = -2\pi r_{pc} (P^a_B - P^w_B)$$  \hspace{1cm} (3)

where $P^a_B$ and $P^w_B$ are the pressure of air and water on the three-phase contact line, respectively. According to the curvature of the meniscus, $P^a_B > P^w_B$ can be judged, and the negative sign indicates that the direction of static pressure is upward.

The force measured by the microforce balance is $F_e$ and the direction is downward. In the process of the bubble detaching from the low-rank coal surface, the bubble is considered to be in the force balance state, so the mechanical relationship can be expressed as the following equation:

$$-2\pi r_{pc} \sigma \sin \theta - V \delta g - \pi r_{pc}^2 (P^a_B - P^w_B) + F = 0$$  \hspace{1cm} (4)

When the bubble–coal surface contact angle reaches the equilibrium contact angle $\theta_e$, the force $F_e$ measured by the microforce balance is 0. Meanwhile, when the bubble–coal surface contact angle reaches the critical contact angle $\theta_c$, the force $F_c$ measured by the microbalance reaches the maximum value. Both of the transition states can be expressed as the following equations:

$$-2\pi r_{pc} \sigma \sin \theta_e - V \delta g - \pi r_{pc}^2 (P^a_B - P^w_B) + F_e = 0$$

$$-2\pi r_{pc} \sigma \sin \theta_c - V \delta g - \pi r_{pc}^2 (P^a_B - P^w_B) + F_c = 0$$  \hspace{1cm} (5)

The above equations can be simplified into the following equation:

$$F_d = 1.84 \pi r_{pc} \sigma (\sin \theta_e - \sin \theta_c)$$  \hspace{1cm} (6)

The detachment force can be calculated using eq 6. Figure 6 shows the comparison of the calculated and measured detachment force. It can be seen that the calculated detachment force is generally larger than the measured value.

This mainly results from the fact that the bubble cannot keep a spherical shape during the detachment process, which makes the contact line radius used for the calculation slightly larger than the actual value. Moreover, the deviation between calculated and measured values becomes smaller as the detachment force increases, for example, when the low-rank coal is treated by collectors. To reduce the deviation between the calculated value and the measured value, an empirical correction coefficient is added to eq 7 through the linear fitting. As can be seen from Figure 6, the improved equation can well fit the measured detachment force. Finally, the improved detachment force equation can be expressed as follows:

$$F_d = 1.84 \pi r_{pc} \sigma (\sin \theta_e - \sin \theta_c)$$  \hspace{1cm} (7)

3. CONCLUSIONS

In this paper, dodecane (D), oleic acid (OA), and their mixture (OA–D) were used to treat low-rank coal, and the forces required for bubbles to detach from the low-rank coal surface were measured by a self-developed device. A mechanical model was established to calculate the theoretical detachment force based on the related parameters in the detachment process. The main conclusions are as follows:

The process of bubble detachment from the low-rank coal surface was divided into three stages: relaxation stage, stretching stage, and sliding stage. When introducing the collectors into the coal–air bubble detachment process, the order of detachment force required for bubble detachment from the surface of low-rank coal was OA–D > OA > D. It indicated that there was a synergistic effect between OA and D in improving low-rank coal hydrophobicity to greatly increase the detachment force with OA–D. The n-dodecane can adsorb to the carbonaceous sites on the coal surface, and the oleic acid can adsorb on the oxygen-containing groups on the coal. The improvement of coal surface hydrophobicity increased the equilibrium contact angle, critical contact angle, and contact line length. According to the force balance analysis of the bubble, a theoretical model was established to calculate the detachment force based on the three parameters of equilibrium contact angle, critical contact angle, and contact line length.
The calculated results were in agreement with the measured results.

4. EXPERIMENTAL SECTION

4.1. Materials. The low-rank coal used in this paper came from the Dalitua Coal Plant in Shanxi Province. Bulk clean coal by gravity separation was selected, then the low-rank coal was first cut into flakes with a size of 40 × 20 × 15 mm, then each coal flake went through rough grinding and fine grinding repeatedly, and finally a sandpaper of more than 2000 mesh was used for polishing. Proximate and ultimate analyses of the low-rank coal sample results are shown in Tables 2 and 3.

Table 2. Proximate Analysis (%)a

| M ad | A ad | V daf | FC daf |
|------|------|-------|--------|
| 3.38 | 5.68 | 37.52 | 62.48  |

“M ad stands for air dry base moisture, A ad stands for air dry base ash, and V daf stands for dry ash free base volatile, and FC daf stands for dry ash free base fixed carbon.

Table 3. Ultimate Analysis (%)

| C daf | H daf | O daf | N daf | S daf |
|-------|-------|-------|-------|-------|
| 79.20 | 5.08  | 14.01 | 1.06  | 0.30  |

As can be seen from Table 2, the coal sample had a higher volatilization content of 37.52%, and the content of O was relatively high at 14.01%, which is in the range of O content of low-rank coal,34,35 indicating that the coal sample had great amounts of oxygen-containing functional groups. The ash content of 5.68% meant that the impurity content was low, which was suitable for theoretical research.

The surface morphology of low-rank coal was characterized by SEM measurement. The SEM magnification multiples were 500, 1000, 2000, and 5000, respectively. The test results were shown in Figure 7. The low-rank coal had a relatively homogeneous and smooth surface that could be used for detachment force measurement.

XPS was used to analyze the content of elements and groups on the coal surface. The XPS survey scan result is shown in Figure 8. The elements on the coal surface are mainly C and O, and the absorption peak of C1s was stronger than that of O1s, indicating that the carbon content was significantly higher than the oxygen content. The existing forms of C and O elements can be obtained by the peak fitting of C1s. The fitting results are shown in Figure 9 and Table 4. The functional groups on the coal sample surface were mainly C−C or C−H bonds, whose relative content was 70.61%. The oxygen-containing functional groups were mainly C−O bonds with a relative content of 19.90%. The XPS results indicated that the coal sample had the features of low-rank coal.

X-ray diffraction was conducted using the coal sample, and the result was given in Figure 10 below. The ash was mainly composed of quartz and kaolinite and calcite minerals.

The reagents used in this paper, namely, oleic acid and dodecane, were purchased from Aladdin. The mixed collector was composed of dodecane and oleic acid in the mass proportion of 4:1. When the mass ratio of OA in the mixed collector was changed from 0.2 to 0.3, the interfacial tension between oil and water decreased by about 1.5 mN/m.31,32 Considering that the price of OA was higher than that of common oil collectors, we selected 0.2 as the proportion of OA in the mixed collector.
4.2. Methods. In this paper, a self-developed device was designed to measure the force required for bubble detachment from the low-rank coal. The mechanical test apparatus is shown in Figure 11. The device was composed of a microforce balance, electric lifting platform, acrylic cell, high-speed camera, computer, etc. The Teflon plate was installed at the bottom of the acrylic cell, and the cell was placed on the electric lifting platform. The microforce balance and electric lifting platform were controlled by the computer, and the displacement data of the lifting stage and the microforce balance force data were recorded. Before the test, the low-rank coal was treated with D, OA, and OA−D, respectively, and it was attached to the force sensor of the microforce balance. After that, a small bubble with a diameter of 4 mm produced by a microsyringe was placed on the Teflon plate in the acrylic cell that was filled with deionized water. The lifting platform was moved upward so that the coal sample was immersed into the water, keeping the bubble centerline aligned with the coal centerline. Then, the lifting platform was further moved upward until the bubble and coal were fully contacted and adhered to each other. After 4 s, the lifting platform was moved down, and the bubble was gradually stretched until it detached from the low-rank coal. The lifting platform moved up and down at a speed of 0.01 mm/min. The interaction process between the bubble and low-rank coal was recorded by the experimental system, and the relationship between the detachment force and bubble deformation was analyzed by an image processing software. The force was recorded every 100 ms, and a photo was captured by a high-speed camera every 4 ms. The experimental device was placed in a closed laboratory and kept at room temperature of 20 °C. All test conditions were pH = 8 mainly because the flotation test of low-rank coal was carried out at this pH. The neutral and weak alkaline environment was the common pH range for coal flotation.36,37

The deformation of the bubble outline was characterized by the contact angle and contact line length on the bubble–coal surface that were calculated by the method of image processing as shown in Figure 12. Half of the linear distance between the contact points was defined as the radius of the contact line \((r_{tpc})\) between the bubble and coal surface. The dynamic contact angle was calculated using the \(\theta/2\) method. The method assumed that the adherent bubble was in a spherical bubble. And \(\theta_1 \) was calculated by the distance between the low-rank coal and Teflon \((h)\) and the radius of the contact line \((r_{tpc})\). The calculation is shown in eqs 8, 9, and 10.

\[
\theta_1 = \tan^{-1} \frac{h}{r_{tpc}} \quad (8)
\]

\[
\theta_b = 2\theta_1 \quad (9)
\]

\[
\theta = 180 - \theta_b \quad (10)
\]

where \(r_{tpc}\) is the radius of the three-phase contact line, \(h\) is the distance between the low-rank coal and Teflon plate, and \(\theta\) is the contact angle. And the values of \(\theta_1\) and \(\theta_b\) are shown in Figure 12.

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### Table 4. Contents of Functional Groups on the Surface of the Coal Sample

| functional groups | C−C/C−H (%) | C−O (%) | C≡O (%) | O−C≡O (%) |
|-------------------|-------------|--------|---------|-----------|
| content           | 70.61       | 19.90  | 5.35    | 4.14      |

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Figure 10. X-ray diffraction of the coal sample.

Figure 11. The detachment force test device for the bubble–low-rank coal.

Figure 12. The schematic diagram for calculating the contact angle of bubble–low-rank coal.

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Notes
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REFERENCES
(1) Xing, Y.; Zhang, Y.; Ding, S.; Zheng, X.; Xu, M.; Cao, Y.; Gui, X. Effect of surface roughness on the detachment between bubble and glass beads with different contact angles. Powder Technol. 2020, 361, 812–816.
(2) B. O.; Schreithoffer, N.; Wierink, G.; Heiskanen, K. Particle detachment in flotation; 2009.
(3) Spedden, H. R.; Hannan, W. S. Attachment of mineral particles to air bubbles in flotation. Min. Technol. 1984, 12, 23–54.
(4) Nguyen, A.; Schulze, H. J. Colloidal science of flotation; Marcel Dekker, New York, 2003.
(5) Jameson, G.; Gautam, S. New approaches to particle attachment and detachment in flotation. Soc. mining, Metall. Explor. Inc. SME Meet. Separation Technol. Miner. Coal Earth Resour. 2012, 437–446.
(6) Ralston, J.; Fornsiero, D.; Hayes, R. Bubble-particle attachment and detachment in flotation. Int. J. Miner. Process. 1999, 56, 133–164.
(7) Ahmed, N.; Jameson, G. J. The effect of bubble size on the rate of flotation of fine particles. Int. J. Miner. Process. 1985, 14, 195–215.
(8) Nutt, C. W. Froth Flotation: The adhesion of solid particles to flat interfaces and bubbles. Chem. Eng. Sci. 1960, 12, 133–141.
(9) Wang, G.; Nguyen, A. V.; Mitra, S.; Joshi, J. B.; Jameson, G. J.; Evans, G. M. A review of the mechanisms and models of bubble-particle detachment in froth flotation. Separation and Purification Technology. Elsevier B.V. October 2016, pp. 155–172.
(10) Schulze, H. J. New theoretical and experimental investigations on stability of bubble/particle aggregates in flotation: a theory on the upper particle size of floatability. Int. J. Miner. Process. 1977, 4, 241–259.
(11) Xu, D.; Ametov, I.; Grano, S. R. Detachment of coarse particles from oscillating bubbles—the effect of particle contact angle, shape and medium viscosity. Int. J. Miner. Process. 2011, 101, 50–57.
(12) Knüfer, P.; Fritzsche, J.; Leistner, T.; Rudolph, M.; Peuker, U. A. Investigating the removal of particles from the air/water-interface—modelling detachment forces using an energetic approach. Colloids Surf., A 2017, 513, 215–222.
(13) Kondrat’ev, S. A. Influence of main flotation parameters on detachment of hydrophilic particle from bubble. J. Min. Sci. 2005, 41, 373–379.
(14) Spyridopoulos, M. T.; Simons, S. J. R. Direct measurement of bubble-particle adhesion forces on the effects of particle hydrophobicity and surfactants. Chem. Eng. Res. Des. 2004, 82, 490–498.
(15) Fosu, S.; Skinner, W.; Zanin, M. Detachment of coarse composite sphalerite particles from bubbles in flotation: influence of xanthate collector type and concentration. Miner. Eng. 2015, 71, 73–84.
(16) Jaćzuk, B.; Białoipiotrowicz, T.; Wójcik, W. Influence of n-alkanes and diacetyl alcohol on the detachment force of air bubbles detached from a low-rank coal surface. Chem. Pap. 1990, 44, 303–311.
(17) Wbcjcek, W.; Jarczik, B.; Białoipiotrowicz, T. The stability of coal/n-alkane film-air bubble-water flotation of coal systems and froth. 1991, 67, 223–228, DOI: 10.1039/0032-5910(91)80104.
(18) Li, M.; Xia, Y.; Zhang, Y.; Ding, S.; Rong, G.; Cao, Y.; Xing, Y.; Gui, X. Mechanism of shale oil as an effective collector for oxidized coal flotation: from bubble-particle attachment and detachment point of view. Fuel 2019, 255, 115885.
(19) Hu, H.; Li, M.; Li, L.; Tao, X. Improving bubble-particle attachment during the flotation of low rank coal by surface modification. International Journal of Mining Science and Technology. China University of Mining and Technology March 2020, pp. 217–223.
(20) Xing, Y.; Gui, X.; Cao, Y.; Wang, D.; Zhang, H. Clean low-rank-coal purification technique combining cyclic-static microbubble flotation column with collector emulsification. J. Cleaner Prod. 2017, 657–672.
(21) Wang, D.; Xu, M.; He, J.; Wang, L. Flotation of low rank coal using dodecane after pretreatment by dielectric barrier discharge (DBD) air plasma. Fuel 2019, 251, 543–550.
(22) Xu, M.; Xing, Y.; Cao, Y.; Gui, X. Waste colza oil used as renewable collector for low rank coal flotation. Powder Technol. 2019, 344, 611–616.
(23) Zhen, K.; Zhang, H.; Zheng, C. Wettability modification and flotation intensification of low-rank-coal with dodecyltrimethylammonium chloride addition. J. Therm. Anal. Calorim. 2019, 137, 2007–2016.
(24) Liu, Z.; Liao, Y.; Wang, Y.; An, M.; Lai, Q. Enhancing low-rank coal flotation using a mixture of dodecane and n-valeric acid as a collector. Int. J. Coal Prep. Util. 2019, 1–15.
(25) Jia, R.; Harris, G. H.; Fuerstenau, D. W. Chemical reagents for enhanced coal flotation. Coal Preparation. May 2002, pp. 123–149.
(26) Zhang, R.; Xia, Y.; Guo, F.; Sun, W.; Cheng, H.; Xing, Y.; Gui, X. Effect of microemulsion on low-rank coal flotation by mixing DTAB and diesel oil. Fuel 2020, 260, 116321.
(27) Liu, Z.; Xia, Y.; Lai, Q.; An, M.; Liao, Y.; Wang, Y. Adsorption behavior of mixed dodecane/n-valeric acid collectors on low-rank coal surface: experimental and molecular dynamics simulation study. Colloids Surf., A 2019, 583, 123840.
(28) Zhang, L.; Sun, X.; Li, B.; Xie, Z.; Guo, J.; Liu, S. Experimental and molecular dynamics simulation study on the enhancement of low rank coal flotation by mixed collector. Fuel 2020, 266, 117046.
(29) Özün, S.; Ergen, G. Determination of optimum parameters for flotation of galena: effect of chain length and chain structure of xanthates on flotation recovery. ACS Omega 2019, 4, 1516–1524.
(30) Hadler, K.; Aktas, Z.; Cilliars, J. J. The effects of frother and collector distribution on flotation performance. Miner. Eng. 2005, 18, 171–177.
(31) Liao, Y.; Hao, X.; An, M.; Yang, Z.; Ma, L.; Ren, H. Enhancing low-rank coal flotation using mixed collector of dodecane and oleic acid: effect of droplet dispersion and its interaction with coal particle. Fuel 2020, 280, 118634.
(32) Liao, Y.; Song, X.; An, M.; Yang, Z.; Hao, X.; Ren, H. Effect of dodecane-oleic acid collector mixture on the evolution of wetting film between air bubble and low-rank coal. *Minerals* **2021**, *11*, 58.

(33) Wark, I. The Physical Chemistry of Flotation. I. The significance of contact angle in flotation. *J. Phys. Chem.* **1933**, *37*, 623–644.

(34) Patrakov, Y. F.; Fedorova, N. I. Composition and properties of coals from some deposits in mongolia. *Solid Fuel Chem.* **2011**, *45*, 289–297.

(35) Tan, J.; Cheng, H.; Wei, L.; Gui, X.; Xing, Y. Investigation of CTAB and DBP esters on low-rank coal flotation selectivity. *Energy Sources, Part A* **2020**, *42*, 1225–1234.

(36) Ulusoy, Æ.; Selma, S.; Cebeci, Y. Investigation of the effect of agglomeration time, ph and various salts on the cleaning of zonguldak bituminous coal by oil agglomeration q. *Fuel* **2002**, *81*, 1131–1137.

(37) Kelebek, S.; Demir, U.; Sahbaz, O.; Ucar, A.; Cinar, M.; Karaguzel, C.; Oteyeka, B. The effects of dodecylamine, kerosene and ph on batch flotation of turkey’s tuncbilek coal. *Int. J. Miner. Process.* **2008**, *88*, 65–71.