Supporting Information for "New insights for improving low-rank coal flotation performance via tetrahydrofurfuryl ester collectors"

1. The calculation of evaluation indicators of flotation performance

Combustible material recovery (E_c) and flotation perfection factor (η_{wf}) were used to assess flotation performance[1]. The calculations were based on followed equation:

$$E_c = \frac{\gamma_j(100-A_j)}{100-A_W} \times 100\% \qquad (S1)$$

$$\eta_{wf} = \frac{\gamma_j}{100-A_f} \times \frac{A_f-A_j}{A_f} \qquad (S2)$$

where A_j is the ash content of concentrate (%), A_w is the ash content of tails (%), γ_j is the yield of concentrate (%), A_f is the ash content of feed (%), the E_c is combustible material recovery (%) and η_{wf} is flotation perfection factor (%).

2. Contact angle tests

The contact angle was measured using a powder contact angle analysis system (DSA25B, Krüss, Germany) through the Captive Bubble method, where the air bubbles were generated by a syringe with a needle diameter of 0.258 mm. Firstly, 5.0 g coal sample (74-106 μm) was added to a beaker containing deionized water and pre-wetted for 300 seconds. Then, the collector (kerosene or THF-series) was added and conditioned for 120 seconds, for which the dosage of the collector relative to the mass of coal was 1.0 kg/t. Afterwards, the coal samples were filtered and dried in a vacuum oven at the temperature of 60 °C. Subsequently, 2 g raw coal and treated coal samples were pressed into a coal plate by a tablet machine. The pellet samples were stored in a desiccator under an atmosphere equilibrated with saturated NaCl solution for 48 h before contact angle measurements [2]. In this way, the capillary effect of the pellet was reduced, because the saturated NaCl solution can absorb water from the air and keep the relative humidity constant. Then, the contact angle was determined by capturing the image via the DSA25B analysis system. The images were all captured 10 s after the bubble attached to the pellet surface. The result for each reagent concentration was measured three times at three different positions on the coal plate to obtain the average value.

3. Fourier transform infrared spectroscopy (FTIR) tests

The FTIR study was performed using a ALPHA II (Bruker, DEU, Germany) infrared spectrometer set to a resolution of 4 cm⁻¹ and scanned between 4000 cm⁻¹ and 400 cm⁻¹. The measured samples include raw coal, coal treated with kerosene, and coal treated with THF-series. For the coal treated with different collectors tests, coal powders were treated with collectors under the same as the contact angle measurements. After combining the coal powders with analytical grade KBr in a 1: 100 ratio, the mixture was crushed into a thin slice to perform FTIR measurements. The results were analyzed using Omnic software.

4. X-ray photoelectron spectroscopy (XPS) tests

The surface elements and functional groups of the LRC and various LRC samples treated with different collectors were analyzed using X-ray photoelectron spectroscopy (Thermo Scientific K-Alpha, USA). The XPS measurements were conducted under ultra-high vacuum conditions, with a filament current of 6 mA and a working voltage of 12 kV. The C1s peak was calibrated to a binding energy of 248.8 eV. The sample preparation for this analysis was similar to that used for FT-IR analysis, with a reagent dosage of 1 kg/t. Curve fitting was performed using Avantage software.

5. Adsorption capacity of LRC for collectors tests

Analysis of the adsorption capacity of the reagents on the mineral surfaces was based on the variation in total organic carbon (TOC) in flotation slurry before and after reagents treatment [3]. In this study, the adsorption capacity of LRC for collectors was evaluated based on the mass of total organic carbon (TOC) adsorbed per unit mass of LRC, expressed as q_{TOC}. A higher q_{TOC} value indicates a stronger adsorption capacity of the collector on the LRC surface. The results were obtained by filtering the flotation slurry and measuring the TOC content of the filtrate before and after collector adsorption. TOC analysis was conducted using a vario TOC cube analyzer (Elementar Analysensysteme GmbH, Germany). The collector dosage was set at 1 kg/t. The calculations were based on followed equation:

$$\Delta TOC=(TOC_1-TOC_2) \tag{S3}$$

$$q_{TOC}=\frac{\Delta TOC \times V}{m} \tag{S4}$$

where TOC_1 is the TOC content of collector stock solution before adsorption (mg/L), TOC_2 is the TOC content of filtrate after adsorption (mg/L), V is the volume of flotation slurry (L), m is the mass of LRC used in the flotation process (g), ΔTOC is the change of TOC content of the slurry before and after collector adsorption (mg/L), and q_{TOC} is the mass of TOC adsorbed per gram of LRC (mg/g).

6. Zeta potential tests

The electrical properties of mineral surfaces were analyzed using a ZEN3690 zeta potential instrument (Malvern, UK), and potential variations of the sample at the solid-liquid interface was used to determine the interaction pattern of the reagent with the mineral surface. The measurement procedure was as follows. Coal samples with particle sizes ranging from 74 to 106 μm were selected. The slurry was prepared under the conditions specified in the contact angle experiments. The prepared suspension was then subjected to ultrasonic treatment for 5 minutes to ensure thorough particle dispersion. Finally, the suspension was transferred to the zeta potential measurement cell for testing. To ensure the accuracy of the results, each set of measurements was repeated three times, and the average value was taken as the final result.

7. The tests for bubble adhesion behavior on the LRC surface

The bubble adhesion behavior tests were conducted at room temperature using the Captive Bubble method. It utilized the VEO1310L high-speed camera (Phantom, USA) to study the attachment and adhesion behaviors of a single bubble on the LRC surface before and after treatment with different collectors. The testing apparatus was shown in Figure S1. Firstly, according to the method described in contact angle tests, coal samples were treated with different collectors and pressed into coal plates. The coal plate was then positioned on two fixed brackets inside a rectangular glass chamber. Subsequently, water was added to the glass chamber until the lower surface of the coal plate was submerged. The system was allowed to equilibrate for 8 minutes. Afterward, a bubble with a diameter of approximately 2 mm was released at a distance below the coal surface using a syringe needle. The bubble floated upward and made contact with the coal surface. The attachment and adhesion behaviors were recorded by the high-speed camera at 300 fps.
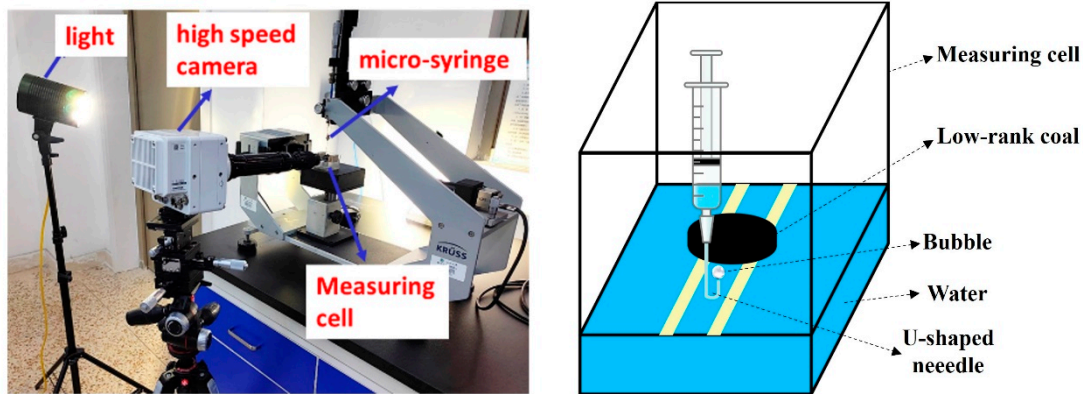
Figure S1. The measurement apparatus and the schematic diagram of measuring cell for bubble adhesion behavior on the LRC surface.

8. The observation for interaction between bubble and collector solution in the flotation system

The flow field characteristics around bubbles and in the wake region in different collector solutions were observed using a particle image velocimetry (PIV) system (TSI, USA). The system consisted of a custom observation device, a laser (rated power: 10 W, wavelength: 532 nm), a CCD camera (resolution: 1928 pixels × 1084 pixels), a synchronizer to synchronize the laser and camera frequencies, and a PC display for data visualization and processing. The laser and camera were positioned perpendicular to each other at two orientations relative to the observation device, with distances of 0.7 m and 0.5 m from the observed bubbles, respectively. To prevent damage from the high-energy laser to both humans and instruments, a black cloth was placed opposite the laser for shielding.

The custom observation device featured an observation zone of 50mm×20mm×100mm (length × width × height). A capillary tube with an outer diameter of 1.50 mm was fixed 15 mm above the bottom. A syringe was used to inject bubbles into the collector solution at intervals of two seconds from one side of the device. During the bubble rising process, the PIV system captured the flow field around the bubbles, recording 200 images per test at a frequency of 15 Hz. The images were imported into Tecplot software for flow field calculation and analysis. Each set of experiments was conducted in five parallel tests to minimize experimental error and ensure the reliability of the results. Figure S2 illustrates the schematic of the observation device.
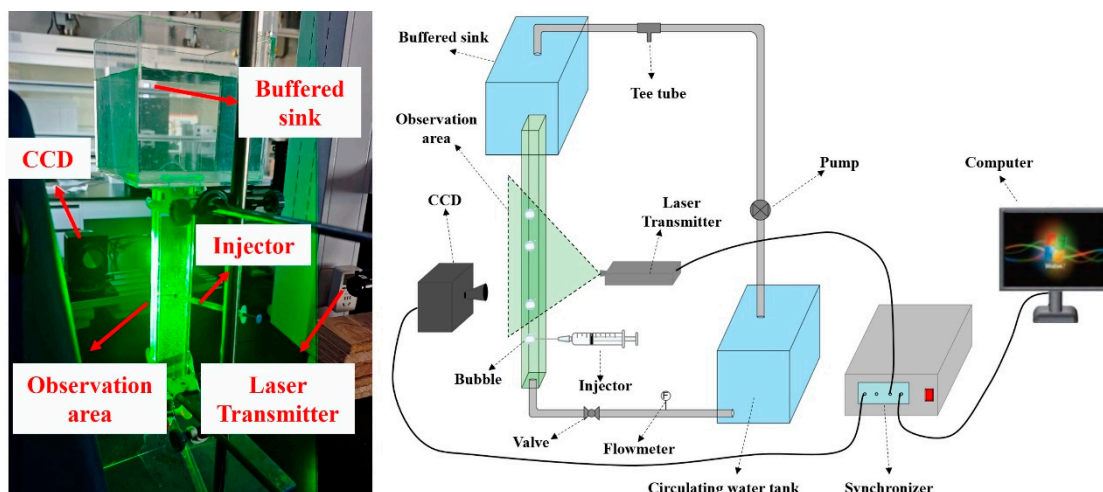

Figure S2. The measurement apparatus and the schematic diagram of measuring cell for interaction between bubble and collector solution.

References

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performance of low-rank coal flotation. Powder Technology 2024, 439, 119727.

2. Lu, Y.; Li, E.; Cheng, H.; Wang, X.; Du, Z.; Cheng, F.; Miller, J.D. Effect of oxygen functional groups on the surface properties and flotation response of fine coal, comparison of rank with oxidation. International Journal of Coal Preparation and Utilization 2021.

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