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Performance study of nonionic surfactant-enhanced Fischer-Tropsch synthesis intermediate products in low-rank coal flotation

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Abstract: Low rank coal has the characteristics of low coalification degree, high volatile matter, and dense pores; therefore, it has problems such as high reagent consumption and high flotation difficulty. This study investigates the effects and mechanisms of surfactant-enhanced Fischer-Tropsch synthesis intermediates (FTI) on the flotation of low-rank coal using a combination of experimental analysis and molecular simulations. When FTI was mixed with 5% surfactant, the collector exhibited improved flotation performance. Three flotation collectors were prepared by blending Span80 and Tween80 with FTI: SFTI-EM (emulsification treatment with Span80 and FTI), SFTI-CO (compound treatment with Span80 and FTI), and TFTI-EM (emulsification treatment with Tween80 and FTI). Flotation test results showed that SFTI-EM and SFTI-CO demonstrated outstanding flotation performance, increasing clean coal yield by 50% compared with diesel collectors. Under identical dosage conditions, SFTI-CO achieved approximately 5% higher clean coal yield than SFTI-EM, while SFTI-EM reduced FTI consumption by about 40%, indicating higher economic value. Molecular dynamics simulations revealed that Span80 molecules adsorbed more firmly on low-rank coal surfaces than Tween80, forming a “bridging” effect between hydrocarbon oil and coal surfaces, thereby enhancing hydrocarbon adsorption on coal. Additionally, the SFTI-EM emulsion exhibited an “oil-water-oil” multiphase droplet structure, facilitating reagent-coal contact. Contact angle measurements further suggested that surfactants contribute to forming more stable mineralized froth, further improving flotation efficiency. This study has not only developed a high-efficiency and economical flotation collector alternative to diesel, but also demonstrated the enhancing effect of non-ionic surfactants combined with FTI on low-rank coal flotation.

Keywords: low-rank coal, flotation, collector, surfactant, molecular simulation

1. Introduction

Against the global backdrop of energy transition and intensified environmental concerns, the efficient development and clean utilization of energy resources have become critical priorities worldwide. In China, low-rank coal already accounts for more than 55% of the total coal output, and this proportion continues to rise. Thus, the clean utilization of this resource is critical to ensuring national energy security (Zheng et al., 2025). However, low-rank coal, characterized by high moisture content, abundant volatile matter, low calorific value, numerous oxygen-containing functional groups, loose structure, and dense pores, presents significant challenges in efficient processing (Chen et al., 2025). Conventional approaches like direct combustion for power generation not only cause severe environmental pollution but also underutilize coal resources (Guo et al., 2025). Flotation technology enhances coal quality by regulating particle hydrophobicity and separating mineral impurities via bubble attachment. Nevertheless, low-rank coal's unique properties lead to excessive collector consumption, unstable froth, low recovery rates, and high operational costs in conventional flotation systems (Wang et al., 2025). Traditional collectors (diesel/kerosene) exhibit limited efficacy while exacerbating petroleum resource

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strain, a critical issue given China's petroleum scarcity (Arab et al., 2025). Developing high-performance, cost-effective, and eco-friendly collectors with clarified mechanisms is essential to overcome these limitations. Furthermore, China has abundant coal resources and a developed coal chemical industry chain. The Fischer-Tropsch synthesis intermediate product (FTI) has stable sources and favorable economic value, which can effectively reduce dependence on petroleum resources, aligning with the strategic demands of national energy security and sustainable development (Huang et al., 2018; Hürpekli et al., 2025).

In recent years, extensive research has focused on developing high-efficiency, environmentally friendly flotation reagents and elucidating their mechanisms. As key reagents directly interacting with coal surfaces during flotation, collectors critically determine flotation performance. Conventional diesel/kerosene collectors exhibit limitations, including excessive dosage and poor efficacy in low-rank coal flotation, driving intensive investigations into novel alternatives. Xu et al. (2023) and Xu et al. (2019) developed environment-friendly plant oil-based collectors (including waste rapeseed oil derivatives) for low-rank coal flotation, demonstrating superior performance to diesel, particularly in reducing oxygen-containing functional groups and enhancing coal hydrophobicity. Wan et al. (2022) pyrolyzed waste thermoplastics into hydrocarbon oils for low-rank coal flotation, achieving lower ash content and higher flotation yield. The presence of C-O and O=C-O bonds in these oils was found to effectively shield oxygen-containing groups on coal surfaces. Yang et al. (2021) validated the enhanced flotation performance of waste engine oil over diesel. Xia et al. (2021) investigated composite collectors combining coal tar with diesel, revealing significantly improved modification effects compared to standalone diesel. Li et al. (2020) extracted light component mixtures from diesel/kerosene to develop CTB collectors containing enriched aromatic compounds and oxygen-containing groups, which substantially improved flotation efficiency and combustible recovery rates.

Research on diverse collector types has expanded technological pathways for low-rank coal flotation, while surfactants significantly optimize reagent performance. Cheng et al. (2024) prepared oil-in-water (O/W) emulsified waste oil for long-flame coal flotation, achieving 3-5% separation efficiency improvement with 60% waste oil reduction compared to diesel. Liu et al. (2023) mechanistically investigated oleic acid (OA) and dodecane (DD) blending ratios, determining the OA:DD=1:3 proportion as optimal for maximizing flotation efficiency. Bao et al. (2022) developed a ternary composite collector (oleic acid/methyl oleate/diesel) that enhanced selective flotation through synergistic adsorption mechanisms, significantly increasing clean coal yield while reducing ash content versus conventional diesel. Du et al. (2023) formulated an SPS microemulsion by microemulsifying Span, Tween, and sodium dodecyl sulfate with diesel, demonstrating improved flotation performance at optimal ratios. These studies collectively demonstrate surfactant-enhanced flotation through three mechanisms: intensified reagent efficacy, optimized adsorption behavior, and surfactant synergism.

Extensive research has been conducted on the flotation mechanisms of low-rank coal, primarily focusing on coal surface properties, coal-water molecular interactions, and coal-collector molecular interactions, which provide important theoretical foundations and technical guidance for flotation process optimization. Studies have revealed that abundant oxygen-containing functional groups on low-rank coal surfaces enhance electrostatic repulsion between coal particles and air bubbles during flotation, consequently suppressing flotation efficiency. Furthermore, the porous structure of low-rank coal surfaces promotes hydration film formation, significantly impeding the adsorption of collector molecules (Liu et al., 2020; Shen et al., 2020). The structural characteristics of collector molecules have also been demonstrated as crucial for low-rank coal flotation performance (Liu et al., 2024). Zhang et al. (2024) proposed the polarity index concept for collector molecules, finding optimal flotation performance when index values range between 6.0-8.0 kcal/mol. The ionic environment in pulp has been verified to significantly influence low-rank coal flotation, with Ren et al. (2021) demonstrating that $Fe(OH)^+$ forms complexes with carboxyl and hydroxyl groups on coal surfaces to enhance flotation efficiency. The critical role of surfactants in low-rank coal flotation has been systematically investigated. For instance, DTAB has been found to enhance coal particle hydrophobicity through "pre-adsorption" effects and promote particle-bubble adhesion, while 160.21 nm microemulsions have been shown to improve flotation performance via electrostatic adsorption (Xia et al., 2019). Synergistic effects between emulsified collectors and CO_2 nanobubbles have been confirmed to increase coal-collector collision probability (Lian et al., 2023). Li et al. (2024) developed biocompatible surfactant-stabilized emulsified kerosene, proposing that surfactants optimize kerosene emulsification and dispersion through "bridging effects", thereby significantly improving flotation efficiency. Mao et al. (2024) further elucidated the critical influence of emulsified oil droplet size on pore wettability and particle-bubble interactions in low-rank coal flotation. These comprehensive investigations into coal surface characteristics, collector molecular interactions, pulp environments, and surfactant optimization have collectively established fundamental mechanisms for low-rank coal flotation, providing a solid foundation for process improvement and resource utilization enhancement.

Although numerous research advancements have been achieved in enhancing low-rank coal flotation performance, current efforts predominantly concentrate on modifying and applying conventional petroleum-based collectors, which heavily rely on fossil fuel resources with high consumption rates and lack clean-energy efficiency. Furthermore, the adsorption behaviors and interaction mechanisms of collectors within the microscopic structures of low-rank coal surfaces remain insufficiently investigated, particularly regarding surfactant-collector synergistic mechanisms. This study, therefore, proposes FTI as an alternative to conventional diesel collectors. Through experimental design analysis and molecular dynamics simulations, the effects of surfactants on FTI's flotation performance and microscopic interaction mechanisms with low-rank coal will be systematically investigated, aiming to develop novel high-efficiency and environmentally friendly collectors for low-rank coal flotation.

2. Materials and methods

2.1. Analysis of low rank coal samples

The test coal sample was collected from long-flame raw coal at Selian No.2 Mine in Ordos, Inner Mongolia Autonomous Region, China. The coal was dried, crushed, and sieved to below 0.5 mm particle size. Selian No.2 Mine coal, classified as low-rank coal, primarily consists of non-caking coal and long-flame coal, characterized by high volatile matter content, weak cohesiveness, high calorific value, and developed pore structure.

2.1.1. Mineral composition of coal samples

Mineralogical composition analysis was conducted using an XRD-6000 X-ray diffractometer on the long-flame coal sample from Selian No.2 Mine. The testing parameters included a Cu target X-ray tube (NF type) with 1×10 mm focal spot, continuous scanning mode across 10°–80° 2θ range (scan rate: 5°/min). The XRD pattern of the coal sample is shown in Fig. 1. Distinct quartz peaks were observed at 2θ position (27°), with multiple secondary quartz peaks detected at other angles, confirming quartz as the dominant mineral component. Kaolinite minerals were also identified, whose strong hydrophilic nature and slime-forming tendency further increase the difficulty of low-rank coal flotation.

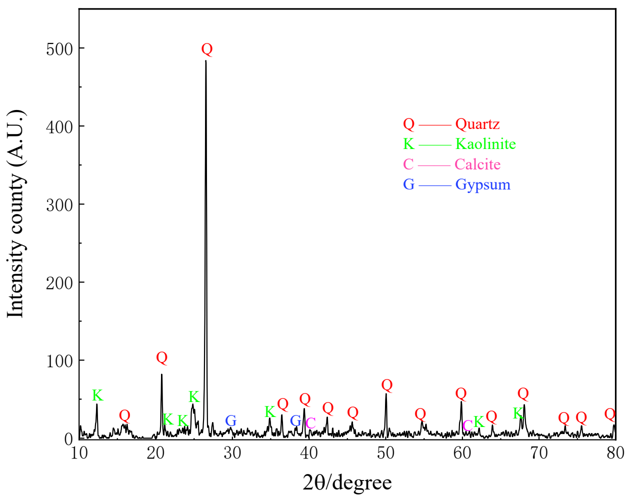

Fig. 1. XRD spectrum of coal sample

2.1.2. Coal sample particle size composition

The coal screening test was performed according to the small-size fractionation procedure specified in Chinese National Standard GB/T 477-2008. Sieves with apertures of 0.5 mm, 0.25 mm, 0.125 mm, 0.075 mm, and 0.045 mm were selected for wet screening using a 200 g coal sample. The particle size distribution results are presented in Table 1. In this context, "yield" refers to the mass percentage of each particle size fraction obtained from sieving the coal sample. The coal sample is primarily composed of particles in the size ranges of 0.5–0.125 mm and below 0.045 mm. The particle size distribution data indicate that the d_{50} and d_{80} values are approximately 0.146 mm and 0.267 mm, respectively. Ultrafine mineral matter (28.51% by mass) with elevated ash content (41.58%) indicates substantial fine high-ash mineral components, which may significantly intensify slime formation in pulp systems and increase flotation difficulty.

Table 1. Small screening data of the coal sample

Grade (mm)	Yield (%)	Ash (%)	Cumulative Oversize		Cumulative Undersize	
			Yield (%)	Ash (%)	Yield (%)	Ash (%)
0.5~0.25	21.46	24.03	21.46	24.03	100.00	30.21
0.25~0.125	34.32	27.94	55.78	26.44	78.54	31.90
0.125~0.075	9.18	21.35	64.96	25.72	44.22	34.97
0.075~0.045	6.53	25.29	71.49	25.68	35.04	38.54
<0.045	28.51	41.58	100.00	30.21	28.51	41.58
total	100.00	30.21				

2.2. Test agents

2.2.1. Test agent

To investigate the enhancement of FTI's performance in low-rank coal flotation by nonionic surfactants, the commonly used nonionic surfactants Span80 and Tween80 were selected. The reagents employed in the experiments comprised Fischer-Tropsch synthesis intermediate (FTI), No. 0 diesel, 2-octanol, Tween80, Span80, Span80-emulsified FTI (SFTI-EM), Span80-compounded FTI (SFTI-CO), and Tween80-emulsified FTI (TFTI-EM). Detailed reagent specifications are provided in Table 2.

Table 2. Experimental reagents

Name	Abbreviation	Role	Source of the Agent
Fischer-Tropsch synthesis intermediate product	FTI	collecting agent	Luan Group
No. 0 diesel	/	collecting agent	Huainan, China
2-octanol	/	foam beater	Aladdin
Tween80	/	emulsifier	Aladdin
Span80	/	emulsifier	Aladdin
Span80 and FTI emulsifying collector	SFTI-EM	collecting agent	self-control
Tween80 and FTI compound collector	SFTI-CO	collecting agent	self-control
Tween80 and FTI emulsifying collector	TFTI-EM	collecting agent	self-control

2.2.2. Analysis of intermediate products of Fischer-Tropsch synthesis

The reagent sample was obtained from a Fischer-Tropsch synthesis process at Shanxi Lu'an Group, where syngas ($CO+H_2$) is catalytically converted into hydrocarbons through this coal-to-liquid technology. Particularly valuable for coal-rich nations, Fischer-Tropsch synthesis enables synthetic fuel production from coal resources. Detailed chemical composition analysis of the Fischer-Tropsch synthesis intermediate (FTI) was performed using a ThermoFisher ISQ7000 gas chromatography-mass spectrometer (GC-MS). As shown in Fig. 2, the FTI sample predominantly contains linear and branched alkanes with carbon chain lengths spanning C10-C21. The major constituents were identified as n-decane (24.7%), n-hexadecane (18.2%), n-heptadecane (15.6%), n-pentadecane (12.1%), n-nonadecane (9.8%), n-tetradecane (6.3%), n-tridecane (5.1%), and n-heneicosane (3.2%). Unlike conventional diesel containing aromatic hydrocarbons (9-15%) and sulfur impurities (<0.035%), FTI's synthetic nature ensures exclusive saturated hydrocarbons, demonstrating significant potential as an environmentally friendly flotation collector.

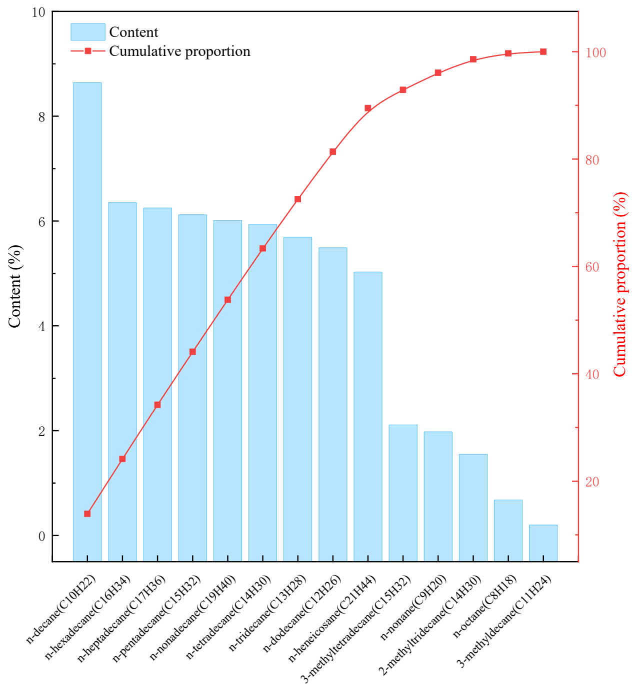

Fig. 2. Composition of Fischer-Tropsch Synthesis Intermediate Products (FTI)

2.3. Preparation of compound and emulsifying collector

Preliminary flotation tests on low-rank coal from Selian No.2 Mine demonstrated the negligible effectiveness of No. 0 diesel collector. At a dosage of 5 kg/Mg, no discernible mineralized froth formation occurred, rendering clean coal yield collection unfeasible. Emulsification and compounding were validated as essential modification strategies for collector performance enhancement, substantially improving flotation efficiency. The preparation procedures for modified collectors are depicted in Fig. 3, with detailed formulation ratios provided in Table 3. For compounded collectors, FTI was stirred using a magnetic stirrer at 1500 rpm according to predetermined ratios, during which Span80 was gradually introduced. Following 2 min of thorough agitation, ultrasonic treatment was administered for 3 min under intermittent operation mode (2s active/ 3s idle) at 42% power output and 20 kHz frequency. The preparation protocol for emulsified collectors mirrored this process, with the critical distinction that water was rapidly injected into the FTI-Span80 mixture after 2 min of magnetic stirring, succeeded by an extended 3-min agitation phase and subsequent ultrasonic processing.

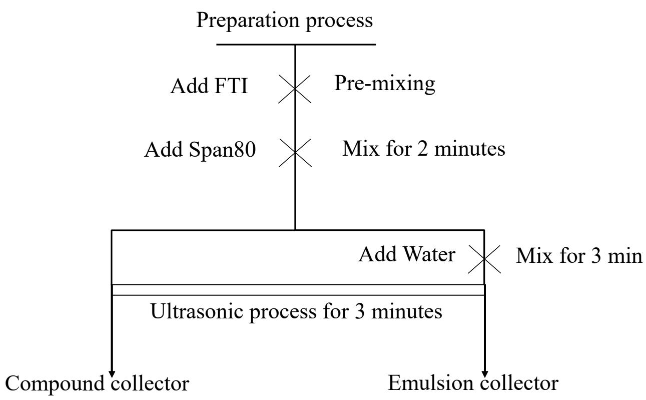

Fig. 3. Flowchart for the preparation of composite collectors

Table 3. Formulation ratio of composite collectors

Name of sample	Type	Constituent	Component ratios
SFTI-EM1	Emulsifying collector	Span80/FTI/water	0.5/6/4
SFTI-EM2	Emulsifying collector	Span80/FTI/water	1.5/6/4
SFTI-EM3	Emulsifying collector	Span80/FTI/water	3/6/4
SFTI-CO1	Compound collector	Span80/FTI	0.5/10
SFTI-CO2	Compound collector	Span80/FTI	1.5/10
SFTI-CO3	Compound collector	Span80/FTI	3/10
TFTI-EM	Emulsifying collector	Tween80/FTI/water	0.5/4/6

2.4. Orthogonal test of flotation of low rank coal

The enhanced flotation performance of modified collectors may be attributed to surfactant addition and processing methodology. To investigate individual factor effects on low-rank coal flotation, a three-factor three-level orthogonal array ($L_9(3^4)$) was designed excluding inter-factor interactions. Span80-FTI compound collectors were prepared according to the formulations in Table 2.3.2 for orthogonal testing. Flotation tests were conducted using an XFG-35II flotation machine (Changsha Instrument Equipment Co., Ltd., China) operated at 3000 rpm main shaft speed. With pulp density maintained at 100 g/dm^3, 150 g coal samples were processed in 1.5 dm^3 cells. After 2-min conditioning period prior to collector addition, 1-min interval was allowed for frother (2-octanol) introduction. Following 20-sec aeration delay, the air supply valve was opened for 3-min froth collection. Final products were filtered and oven-dried at 75°C prior to data recording.

As shown in the experimental header design and the orthogonal array results in Tables 4 and 5, respectively, clean coal yield served as the evaluation criterion. Range analysis revealed factor significance hierarchy: collector dosage > treatment method > surfactant content. Notably, emulsified collectors with 5% surfactant content demonstrated superior performance.

Table 4. Header design

Factor	Level 1	Level 2	Level 3
The content of surfactant on A (%)	5	20	35
B Collector dosage (kg/Mg)	2	5	8
C treatment method	Not processed	Emulsification treatment	Compound treatment
D (blank group)	1	2	3

Table 5. Orthogonal table design and test result analysis

Factor / Test Number	A: Surfactant Content (%)	B: Amount of Collector (kg/Mg)	C: The way of Chemical Treatment	D: Blank Column	Clean Coal Yield
1	5	2	Not processed	1	13.24
2	5	5	Emulsify	2	32.89
3	5	8	Compound	3	49.86
4	20	2	Emulsify	3	20.47
5	20	5	Compound	1	19.95
6	20	8	Not processed	2	35.07
7	35	2	Compound	2	11.78
8	35	5	Not processed	3	23.24
9	35	8	Emulsify	1	48.12
k1	31.997	15.163	23.850	27.103	
k2	25.163	25.360	33.827	26.580	
k3	27.713	44.350	27.197	31.190	
Range	6.833	29.187	9.977	4.610	
Factor primary to secondary			BCAD		
Optimal solution			B3 C2 A1 D3		

2.5. Flotation test of low rank coal

Orthogonal test results demonstrated that emulsified collectors (SFTI-EM/TFTI-EM) and compounded collectors (SFTI-CO) with surfactants achieved enhanced low-rank coal flotation performance. To elucidate the microscopic mechanisms of surfactants in low-rank coal flotation, the adsorption behaviors of Span80-based and Tween80-based collectors on coal surfaces were systematically investigated through molecular-level simulations.

2.6. Molecular dynamics simulation

The orthogonal test results show that emulsifying collectors and mixed collectors with added surfactants perform well in the flotation of low-rank coal. To further understand the microscopic mechanisms of surfactants in the flotation of low-rank coal, adsorption studies were conducted on Span80-type collectors and Tween80-type collectors in the flotation of low-rank coal.

2.6.1. Model construction

Molecular dynamics simulations were performed using Materials Studio 2017 software to investigate atomic/molecular structural properties and interaction behaviors at microscopic scales. The classical Wender lignite model (IRVING et al., 1976) (structural details in Fig. 4) was selected as the low-rank coal molecular framework, containing oxygen-bearing functional groups (-OH, -COOH, -O-, C=O, aromatic rings) that accurately represent long-flame coal surface characteristics. Coal molecular layer construction followed Liu's methodology (Liu et al., 2020): (1) Amorphous Cell module generated initial Wender-based molecular layers with 1.0 g/cm³ density; (2) Graphite sheets were incorporated bilaterally; (3) Forcite module executed iterative geometry optimization until achieving compact coal surface structures with 1.2 g/cm³ density (visualized in Fig. 4).

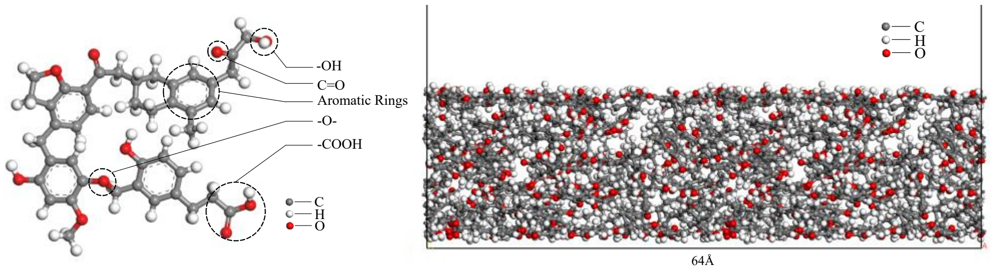

Fig. 4. Coal macromolecular Wender model and coal molecular layer structure model

The adsorption model construction between reagents and coal surfaces was exemplified through an oil-in-water emulsion system, where surfactants establish equilibrium linkage between oil and aqueous phases, achieving interfacial stability. During flotation processes, collector-coal contact occurs under pulp flow field effects as illustrated in Fig. 5. Two comparative systems were constructed: (1) Coal-Water-Surfactant-Oil (CWSO) systems with Span80/Tween80; (2) Coal-Water-Oil (CWO) systems without surfactants (model configurations in Figs. 6-7). Due to the complex composition of Fischer-Tropsch oil (FTI) (as shown in Fig. 2), which consists primarily of linear alkanes with varying chain lengths, n-dodecane was selected as a model compound in this study. As a typical straight-chain saturated alkane, it shares identical functional groups and chemical characteristics with the major constituents of FTI. Therefore, by simplifying the actual multi-component system into a single-component model system, this approach allows for a clearer revelation of the microscopic mechanisms by which surfactants influence the adsorption process, based on well-defined structure–behavior relationships. Simulation cells measuring 64×64×150 Å³ contained 68 n-dodecane molecules ($C_{12}H_{26}$) as FTI substitutes. Using the Amorphous Cell module, surfactant molecules (8 units) were uniformly distributed at the dodecane cluster base, overlaid with a 30 Å thick water layer.

2.6.2. Simulation method

In the MD simulation method, the Forcite module is used, and the condensed phase optimized molecu-

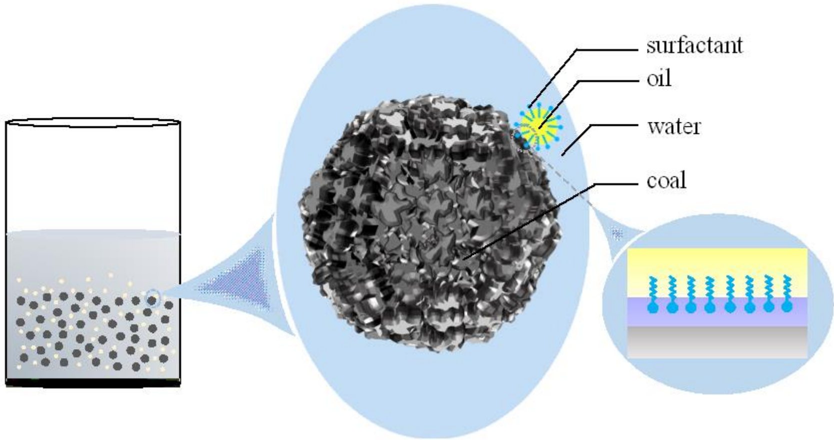

Fig. 5. Schematic diagram of the surface microstructure of coal particles adsorbed by an emulsifying collector

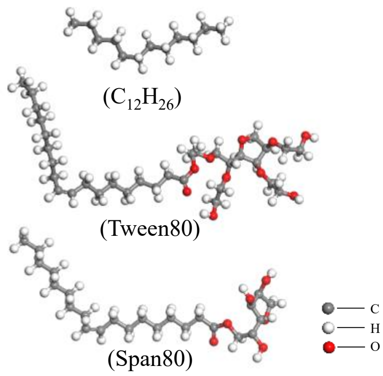

Fig. 6. Molecular model of the agent

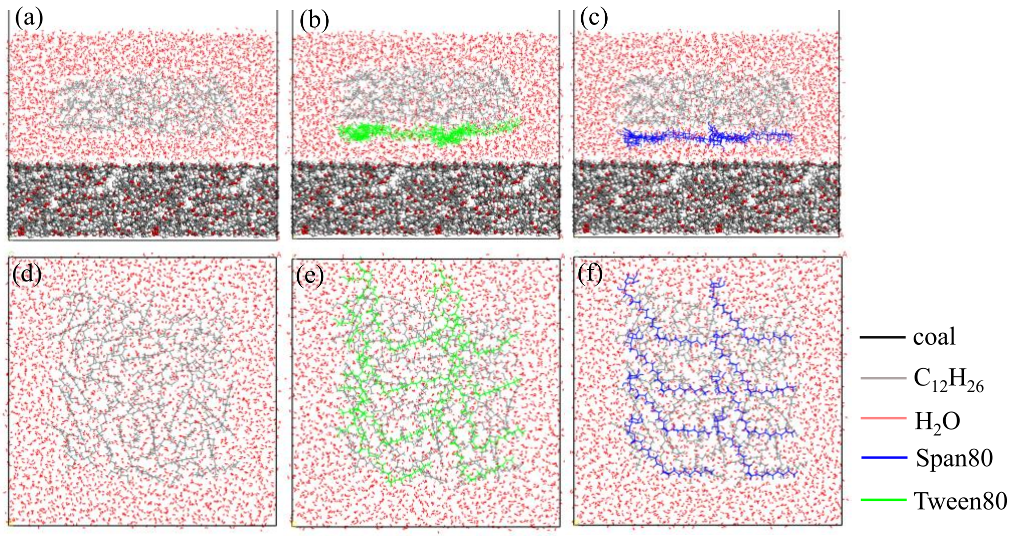

Fig. 7. CWO system model, CW-Tween-O system model and CW-Span-O system model (a. CWO; b. CW-Tween-O; c. CW-Span-O; d. CWO top view; e. CW-Tween-O top view; f. CW-Span-O top view)

lar force field (COMPASS force field) is employed in all simulations. The charge setting is forcefield assigned, with a temperature of 298 K and canonical ensemble set to NVT. A Nose thermostat is used, and the cut-off radius is 12.5 Å, with all coal molecule positions fixed. For the coal-collector system model structure optimization, the maximum iterations are set to 3000, and the charges are selected as Forcefield assigned. The time step for molecular dynamics simulations is 1 fs, and the total simulation time is 500 ps.

2.7. Effect of collectors on surface properties of low rank coal

2.7.1. Microscopic state analysis of emulsions

Optical microscopy was employed to investigate the emulsion system states, with TFTI-EM and SFTI-EM emulsified collectors selected as test specimens. A confocal scanning optical microscope was utilized for characterization. Syringe-collected samples were deposited at the center of glass slides and uniformly spread without cover slip placement to avoid structural deformation from compression. Image processing and analysis were conducted on the acquired images using the MiVnt computer-based microscopic image analysis software.

2.7.2. Particle size analysis of emulsions

To investigate the droplet size distribution within the emulsion system, measurements were conducted using a SALD-7101 laser particle size analyzer (Shimadzu Corporation, Japan). Specifically, 3 cm^3 aliquots of both TFTI and SFTI emulsified collectors were dispensed into the measurement cell. The instrument provides a measurable particle size range of 0.01 to 300 μm.

2.7.3. FTIR test

Fourier-transform infrared (FTIR) spectroscopy was performed using a Thermo Fisher Scientific Nicolet iS50 spectrometer to analyze surface functional groups of low-rank coal samples. Test specimens included: (1) raw low-rank coal, (2) coal treated with SFTI-CO, SFTI-EM, and TFTI-EM collectors, and (3) 0# diesel-treated coal. Coal samples were subjected to mixing under 5 kg/Mg collector dosage and 100 g/dm^3 pulp density conditions, followed by filtration and oven-drying. Dried samples were mixed with KBr at a 1:150 mass ratio, ground into homogeneous powder, pelletized, and analyzed. Spectral data processing and functional group identification were conducted using OMNIC software.

2.7.4. Low rank coal contact angle test

Contact angles were measured for coal samples treated with diesel, emulsified collectors, compounded collectors, and raw coal. Coal samples were prepared at 100 g/dm^3 pulp density by mixing 20 g of coal with 200 cm^3 of water. Magnetic stirring was conducted at 3000 rpm with a collector dosage equivalent to flotation test conditions. After 3-min agitation, products were filtered, oven-dried, and pelletized. A high-speed camera captured droplet images at 0.3-sec intervals, with the initial 0.3-sec droplet profile selected for contact angle determination. Three measurements per sample were averaged. Contact angle images were analyzed using the LB-ADSA plugin in ImageJ software, a Laplace-Young equation-based image processing technique (Aurélien et al., 2010).

3. Results and discussion

3.1. Preparation results of the collector

The collectors prepared according to Section 2.3 are shown in Fig. 8, while Fig. 9 demonstrates the stability of Span80-based collectors after 30-day aging. Emulsified collectors formulated with 5% Span80 exhibited superior stability, maintaining homogeneous dispersion for extended durations suitable for industrial applications, preparation, and storage. In contrast, formulations containing 15% and 35% Span80 developed distinct phase separation layers after one-month storage, indicating inadequate emulsion stability for long-term utilization. Span80-compounded collectors showed no observable stratification under identical aging conditions (Gong et al., 2024).

3.2. Flotation test results of low rank coal

Flotation test results of low-rank coal are presented in Fig. 10. Conventional No. 0 diesel collector demonstrated extremely poor performance, yielding clean coal below 10%. Significant improvements were achieved using SFTI-EM and SFTI-CO collectors. Compared to diesel, SFTI-CO enhanced clean coal yield by 27% at low dosage and 50% at high dosage. In comparison between SFTI-EM and SFTI-CO, compounded collectors exhibited approximately 5% higher clean coal yield than emulsified counterparts. Notably, SFTI-EM (formulated with 40% water and 60% FTI) achieved 40% FTI conservation versus SFTI-CO, indicating superior economic viability. Tween80-based emulsions (TFTI-EM) underperformed Span80 systems, exhibiting inferior ash rejection and elevated clean coal ash content. These results confirm the exceptional flotation efficacy of SFTI-EM and SFTI-CO collectors for low-rank coal, with SFTI-EM demonstrating higher industrial applicability due to cost-effectiveness. Due to the difference in material composition between SFTI-CO (prepared at a Span80/FTI ratio of 0.5:10) and SFTI-EM (prepared at a Span80/FTI/water ratio of 0.5:6:4), and considering that the price of FTI is significantly higher than that of water, the usage cost of SFTI-CO is correspondingly higher (Lian et al., 2023; He et al., 2025).

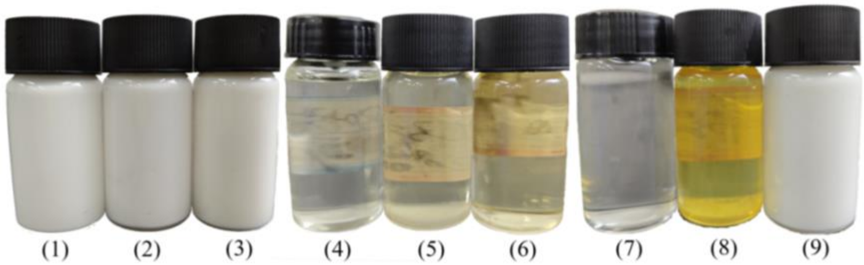

Fig. 8. Test flotation reagents (1. SFTI-EM1; 2. SFTI-EM2; 3. SFTI-EM3; 4. SFTI-CO1; 5. SFTI-CO2; 6. SFTI-CO3; 7. FTI; 8. diesel; 9. TFTI-EM)

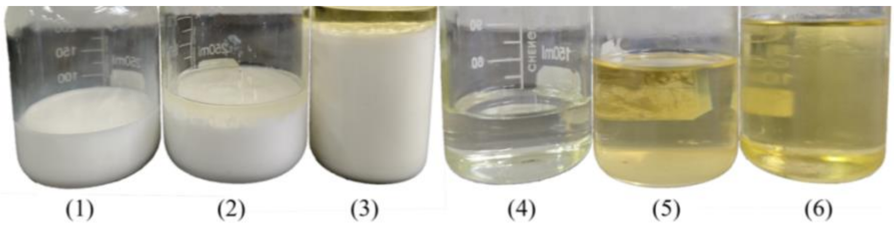

Fig. 9. State of Span80 compound and emulsifying collector after 30 days (1. SFTI-EM1; 2.SFTI-EM2; 3. SFTI-EM3; 4. SFTI-CO1; 5. SFTI-CO2; 6. SFTI-CO3)

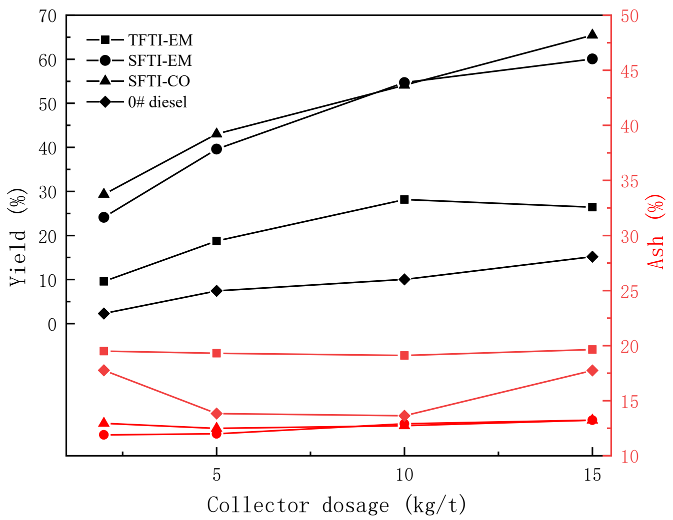

Fig. 10. Flotation test results of different types of collectors on low rank coal

3.3. Molecular dynamics simulation results

Adsorption behaviors in collector-coal molecular models are shown in Fig. 11, displaying the final frame from 500-ps simulations. Analysis reveals that in the CWO system without surfactants, n-dodecane molecules failed to adsorb onto low-rank coal surfaces, being excluded from the aqueous phase without interacting with coal's oxygen-functional groups. The CW-Tween-O system model reveals that among eight surfactant molecules, two Tween80 molecules adsorb onto functional groups on the low-rank coal surface via hydrogen bonding through their hydrophilic moieties (sorbitan and polyoxyethylene chain). Meanwhile, their lipophilic ends (long-chain oleic acid groups) tightly adsorb with dodecane molecular clusters expelled from the aqueous phase, forming a bridge-like connecting structure that indirectly enables the adsorption of dodecane clusters onto the coal surface. In the CW-Span-O system, Span80 aggregates exhibited robust adsorption on coal surfaces while simultaneously binding to dodecane clusters, establishing similar bridging mechanisms. In this process, the hydrophilic moieties (sorbitan rings) of Span80 molecules adsorb tightly onto polar functional groups on the low-rank coal surface through hydrogen bonding, while their hydrophobic tails (long-chain oleic acid groups) simultaneously anchor to dodecane molecular clusters expelled from the aqueous phase (Li et al., 2024).

Relative concentration distribution profiles in Fig. 12 confirm enhanced interfacial accumulation: Span80 molecules displayed higher population density within 5Å of coal surfaces compared to Tween80. Concurrently, n-dodecane in CW-Span-O systems is distributed 30% closer to coal surfaces than in other systems. These molecular simulations conclusively demonstrate that Span80 systems achieve more stable and durable coal surface adsorption than Tween80 counterparts, exhibiting perfect consistency with flotation test results (Xu et al., 2023; Gong et al., 2025).

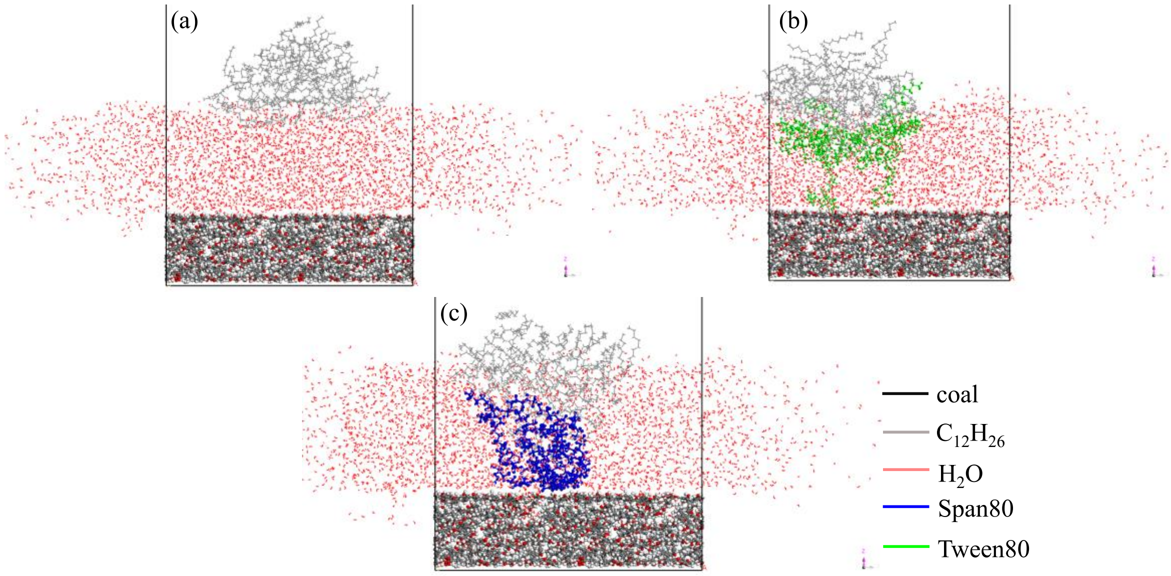

Fig. 11. Adsorption calculation results of the capture agent-coal model (a. CWO model; b. CW-Tween-O model; c. CW-Span-O model)

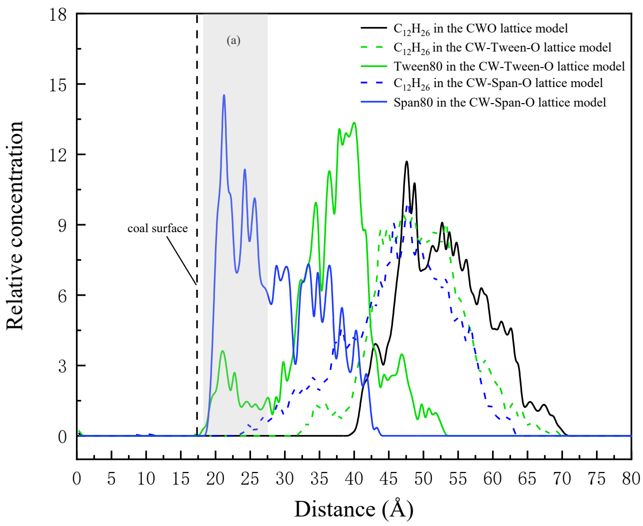

Fig. 12. Relative concentration distribution curves of drug molecules in different models

3.4. Effect of agents on surface modification of low-rank coal

3.4.1. Microscopic states of emulsions

Unlike compounded collectors, emulsified collectors form abundant microdroplets through their "oil-surfactant-water" system configuration. This structural characteristic not only increases interfacial contact area with mineral particles but also enhances collector dispersion and diffusion kinetics within pulp systems, thereby elevating particle-collector collision frequency and adsorption efficiency to improve flotation performance. The liquid phase states differ among various emulsion systems. As shown in Fig. 13, SFTI-EM constitutes a water-in-oil emulsion characterized by numerous droplets ranging from 1 μm to 100 μm in diameter. Notably, multiple microdroplets are observed within larger droplets (labeled as Region 1 in Fig. 13), indicating an internal "O-W-O" multilayer structure. Compared to conventional emulsified collectors, this unique configuration enables the "packaged transport" and "collective release" of numerous oil droplets. It is hypothesized that this mechanism promotes more effective interfacial interactions with coal surfaces during flotation, thereby enhancing the capture and coating efficiency of mineral particles (Lei et al., 2025). TFTI-EM exhibited smaller droplet sizes than SFTI-EM, though both systems contained substantial submicron droplets (Regions 2-3 in Fig. 13). As shown in the results of Fig. 14, the average particle size of SFTI-EM (>10 μm) is coarser than that of TFTI-EM (<1 μm). Therefore, SFTI-EM has a larger emulsion particle size.

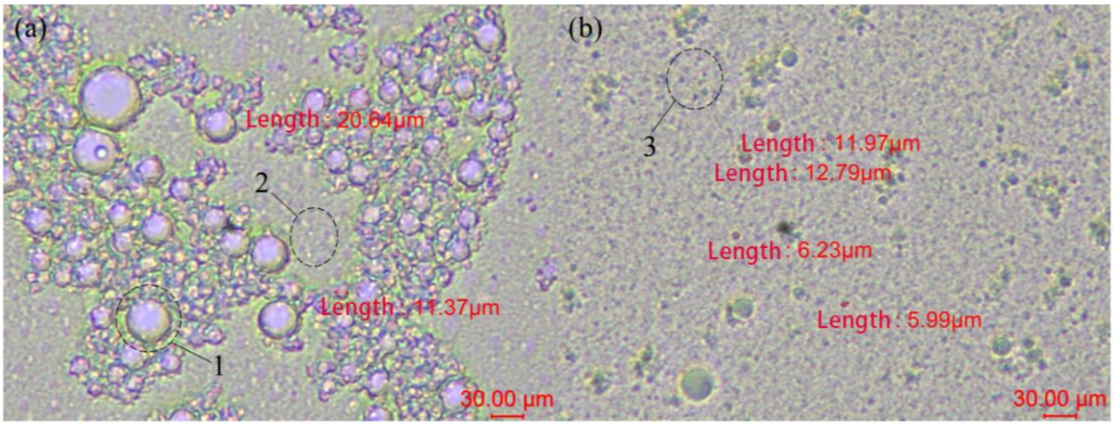

Fig. 13. State of emulsion system under optical microscope (a. SFTI-EM; b. TFTI-EM)

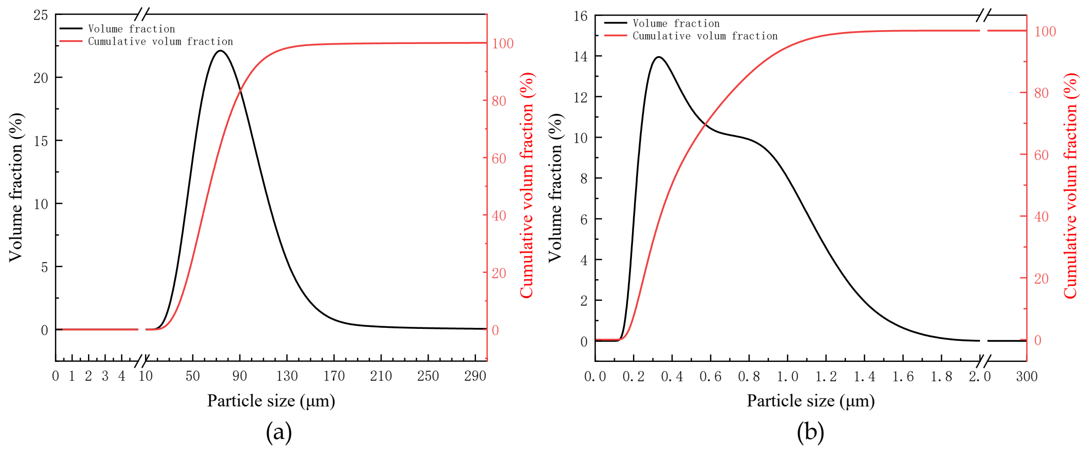

Fig. 14. Droplet size distribution curve in emulsion system (a. SFTI-EM; b. TFTI-EM)

3.4.2. FTIR test

Figure 15 displays the FTIR analysis results of coal samples treated with different collectors. The raw coal spectrum exhibited characteristic absorption bands corresponding to specific functional groups: isolated hydroxyl (-OH) stretching vibrations at 3685.55 cm^{-1} and 3620.05 cm^{-1}, hydrogen-bonded -OH stretching at 3426.7 cm^{-1}; C-H vibrations from methyl ($-CH_3$) and methylene ($-CH_2-$) groups at 2923.38

cm^{-1} and 2855.86 cm^{-1} respectively; aromatic C=C stretching at 1607.37 cm^{-1}; C-O bonds of oxygen-containing functionalities at 1100.97 cm^{-1} and 1034.07 cm^{-1}; The low-wavenumber absorption peaks at 694.63 cm^{-1}, 538.72 cm^{-1}, and 471.2 cm^{-1} are related to the chemical bond vibrations of inorganic minerals in coal and, combined with the XRD results of the coal sample, can be attributed to the characteristic vibrations of minerals such as quartz and kaolinite (Isah et al., 2024). Comparative analysis between untreated and collector-treated coal samples revealed no detectable formation of new functional groups or significant peak shifts, confirming the predominance of physical adsorption mechanisms during collector-coal interactions.

3.4.3. Contact angle test of low rank coal

Figure 16 presents the contact angle measurement results with triplicate-averaged data. The raw coal from Selian No.2 Mine exhibited a contact angle of 25.592°. Collector-treated samples displayed hydrophobicity enhancement in descending order: SFTI-CO > SFTI-EM > TFTI-EM > No. 0 diesel > raw coal. Span80-based collectors demonstrated superior modification of hydrophilic functional groups on coal surfaces compared to Tween80 systems, aligning with flotation performance data. Although No. 0 diesel improved coal hydrophobicity, its practical flotation efficiency remained limited due to unstable froth formation. This discrepancy arises from surfactants' dual functions: enhancing hydrocarbon adsorption while stabilizing mineralized bubbles through interfacial reinforcement (Li et al., 2024; Zakari et al., 2025).

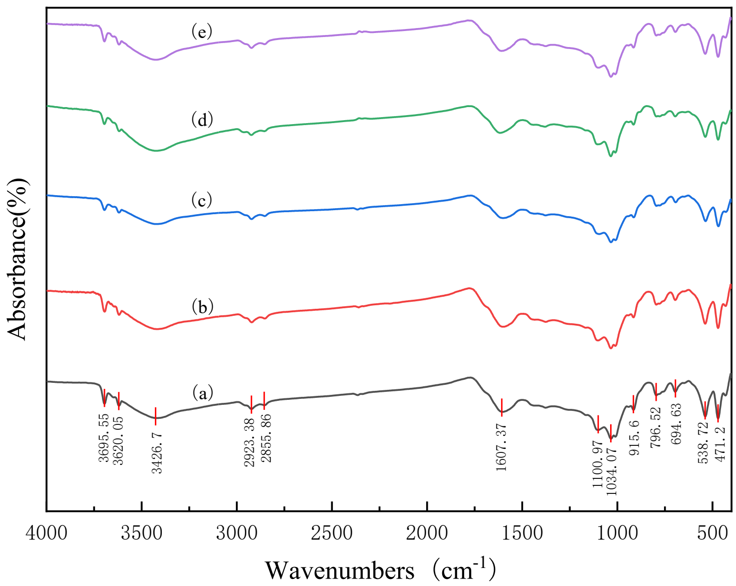

Fig. 15. FTIR detection spectra of low-rank coal after different agents (a. raw coal; b. SFTI-EM; c. SFTI-CO; d. TFTI-EM; e. 0# diesel)

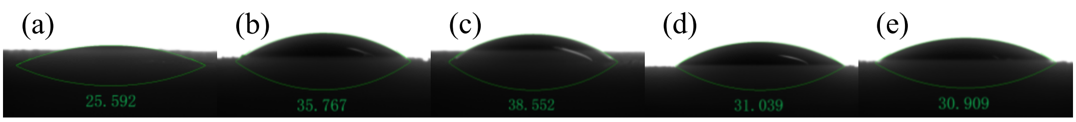

Fig. 16. Results of contact angles of coal samples after different collectors (a. raw coal; b. SFTI-EM; c. SFTI-CO; d. TFTI-EM; e. 0# diesel)

4. Conclusions

The research findings demonstrate that Fischer-Tropsch synthesis intermediates (FTI) exhibit promising application prospects as collectors for low-rank coal flotation. Performance enhancement through emulsification and compounding strategies significantly improves flotation efficiency. The principal conclusions are outlined below.

(1) Mineralogical analysis identified substantial fine high-ash slimes in low-rank coal samples, with 28.51% of particles below 0.045 mm exhibiting 41.58% ash content. FTI primarily consists of linear alkanes (C10-C21), chemically analogous to conventional diesel hydrocarbons but lacking aromatic compounds and sulfur contaminants.
(2) No. 0 diesel showed extremely poor flotation performance for low-rank coal, yielding less than 10% clean coal recovery. Orthogonal tests confirmed the superior efficacy of emulsified collectors containing 5% surfactants. Unit flotation tests revealed Span80-based collectors outperformed both diesel and Tween80 systems, achieving 50% higher recovery than diesel. Notably, Span80-emulsified formulations reduced FTI consumption by 40% while maintaining effectiveness, demonstrating significant economic advantages.
(3) Molecular dynamics simulations revealed stronger adsorption stability of Span80 collectors on low-rank coal surfaces compared to Tween80. Surfactant molecules formed bridge-like linkages between hydrocarbons and coal interfaces, substantially enhancing flotation performance—a phenomenon fully consistent with experimental results.
(4) Comparative emulsion characterization indicated SFTI-EM's larger droplet sizes (1-100 μm) with potential oil-water-oil multiphase structures, contrasting with TFTI-EM's finer dispersions. FTIR analysis confirmed physical adsorption mechanisms without new functional group formation during flotation. Surfactants reinforced hydrocarbon adsorption and stabilized mineralized froth structures, collectively improving flotation yields.

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