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Enhanced separation efficiency of low-rank coal using waste engine oil as a flotation collector

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Abstract: Because of the rich oxygen-containing functional groups and developed pores on the surface of low-rank coal, it is difficult to realize efficient separation during low-rank coal flotation using common oil collectors. Waste engine oil (WEO) is abundant in polar oxygen-containing functional groups and could be an alternative collector. In this study, the effect of WEO on low-rank coal floatation was assessed and engine oil (EO) was also used for comparison. The results show that the separation efficiency of low-rank coal can be significantly improved using WEO; additionally, 96.73% of the clean coal yield can be obtained when the WEO dosage was only 4 kg/t. Compared with EO, the bubble-particle induction time in the presence of WEO shortened from 430 to 220 ms. Moreover, more low-rank coal particles were captured and adhered to the bubble surface using WEO, which indicated a higher probability of bubble-particle attachment. Nonpolar components, polar components and metal ions synergistically promote the flotation separation enhancement of low-rank coal using WEO.

Keywords: low-rank coal, engine oil, waste engine oil, flotation

1. Introduction

China is rich in coal resources, but there are increasingly less high-quality coal deposits for mining and utilization of coal. Thus, increased attention is directed toward low-rank coals and other difficult floating coals instead (Cai et al., 2019; Yang et al., 2019). Low-rank coals, including lignite and long flame, non-caking, and weak-caking coals, comprise approximately 50% of the total coal reserves (Liu and Ohara, 2017; You et al., 2019). In other words, low-rank coals have become increasingly significant energy resources and are additionally used more frequently as industrial materials. However, methods for improving the quality and reducing ash content from coarse coal are mature, while those of fine coal are not well developed. Therefore, numerous fine low-rank coals are accumulated, discarded, or cannot be effectively recycled; this is a waste of coal resources and also results in coal-related environmental pollution. The efficient clean utilization of fine low-rank coals is becoming increasingly essential.

Flotation, an important separation process, is widely used for coal upgrading (Assemi et al., 2008; Brabcová et al., 2015; Brožek and Mlynarczykowska, 2013; Wang et al., 2017; Xia et al., 2019). According to the different surface wettability of coal samples, froth floatation primarily targets fine coal particles less than 0.5 mm (Bedeković, 2016; Xu et al., 2019). Traditional hydrocarbon collectors, such as diesel and kerosene, can obtain hydrophobic coal particles. However, in general, there are multiple oxygen-

containing functional groups and more pores on a low-rank coal surface; consequently, conventional hydrocarbon oil flotation reagents do not easily spread on a low-rank coal surface (Dey et al., 2013; You et al., 2019). When separating this type of fine coal, the high consumption of flotation reagents limits the utilization value (Çınar, 2009; Dey, 2012; Ozdemir et al., 2018).

During recent years, researchers have completed numerous studies to enhance low-rank coal flotation recovery. Microwave (Özbayoğlu et al., 2009), ultrasonic (Ozkan and Kuyumcu, 2006), pore compression (Yang et al., 2019), and other pretreatment methods (Mursito et al., 2010; Ateşok and Çelik, 2000) are used to optimize the surface properties of coal samples. Another way is to add surfactants to improve coal sample hydrophobicity and oil droplet dispersion (Liu and Ohara, 2017; Dey, 2012; Vamvuka and Agridiotis, 2001; Jia et al., 2000). However, it is difficult to fundamentally eliminate the adverse effects of oxygen-containing functional groups on the low-rank coal surface and the cost of the aforementioned two methods is generally expensive. In addition, the development of an efficient flotation collector has attracted extensive attention (Jia et al., 2000; Alonso et al., 1999; Tian et al., 2019; Xia et al., 2017). The method of introducing polar oxygen-containing functional groups in collectors is the most effective and convenient measurement to enhance low-rank coal flotation recovery (Liu et al., 2017). Given recycling and diversified utilization of resources, a variety of vegetable and previous used oils have been studied for enhancing fine coal flotation efficiency (Ramos-Escobedo et al., 2016; Shukla and Venugopal, 2019). Alonso et al. studied the technical and economic feasibility of vegetable oils (used olive oils and original crude soybean oils) as a fine coal flotation reagent (Alonso et al., 2000). Sönmez et al. found that a lubricating oil could be an effective collector to use in froth floatation of Ukrainian coal, which could replace traditional oils such as kerosene and fuel oil as an alternative oil (Sönmez and Cebeci, 2006).

Moreover, the influence of metal ions in the collector on flotation cannot be underestimated. Wang et al. (Wang et al., 2019) noted that metal ions can adsorb onto the mineral surface, which could benefit collector adsorption and change the mineral surface wettability. Xu et al. (Xu et al., 2017) demonstrated that the addition of Pb^{2+} can significantly improve ilmenite flotation recovery using benzohydroxamic acid as a collector. The Pb^{2+} in solution were either adsorbed on the mineral surface, which improved the surface activity of mineral surface, or reacted with benzohydroxamic acid to form complexes of lead and benzohydroxamic acid. Zhao et al. (Zhao et al., 2019) developed an iron chelate reagent for scheelite flotation consisting of ferric chloride and benzohydroxamic acid. Li et al. (Li et al., 2019) found that salicylaldoxime adsorbed onto malachite by forming complexes, in which two salicylaldoxime molecules react with one copper atom by N atom and the O atom bound to benzene ring. However, using a used oil containing nonpolar, polar and metal components as a collector to enhance low-rank coal flotation, particularly the bubble-particle attachment, requires further study.

Engine oil (EO) is mainly composed of base oils and a variety of additives (Srata et al., 2019; Förster et al., 2019). In general, EO is a combination of non-polar hydrocarbons, polar components, calcium, magnesium, zinc, phosphorus, boron, and so on (Maceiras et al., 2017). EO will be mixed with impurities such as other miscellaneous oils and metal powders produced by wear of machine parts during use. In other words, compared with the organic components in EO, that in waste engine oil (WEO) have been changed and some inorganic metal elements may have a higher content. Moreover, there is a great demand for EO every year; WEO accounts for greater than 60% of the used engine oils. Therefore, WEO may be a viable alternative low-rank coal collector.

In this study, the surface properties of low-rank coal were studied, and the chemical components of EO and WEO were analyzed using gas chromatography mass spectroscopy (GC/MS) and inductively coupled plasma optical emission spectrometry (ICP-OES). In addition, the mechanism of bubble-particle attachment in the presence of EO and WEO was explained via induction time and wrap angle tests.

2. Experimental

2.1. Materials

Low-metamorphic lignite coal samples were sourced from Shenhua Group, Inner Mongolia Autonomous Region, China. The coal samples were crushed and screened to achieve the test

requirements of a coal particle size less than 0.5 mm. In addition, EO was purchased from an Automobile 4S Store in Xuzhou and WEO was collected after EO use. The 2-Octanol (analytical grade, purity $\geq 99\%$) was obtained from Sinopharm Chemical Reagent Co., Ltd.

The proximate and ultimate analysis results of coal samples are shown in Table 1. The volatile matter content of coal samples was 39.64% and the oxygen content of the coal sample was 19.02%; this indicated that there could be rich oxygen-containing functional groups on the coal surface.

Table 1. Proximate and ultimate analyses of coal samples

Proximate analysis (ad, %)				Ultimate analysis (daf, %)				
M	A	V	FC#	C	H	O#	N	S
4.88	14.88	39.64	40.60	73.65	5.25	19.02	1.72	0.36

ad: air dry basis; daf: dry ash-free basis; #: by differential subtraction calculation

2.2. X-ray photoelectron spectroscopy tests

An X-ray photoelectron spectroscopy (XPS) system (ESCALAB 250Xi, Thermo Scientific) was adopted to analyze the chemical composition and relative content of oxygen forms on the coal surface (Wang et al., 2013). The coal sample size less than 0.074 mm was required in the XPS tests. XPS wide and narrow scanning models were used according to the difference in the electron binding energy and the position of the photoelectron absorption peak. The binding energy was corrected by setting the C1s hydrocarbon peak to 284.60 eV; the XPS spectra data were fitted using Peak Fit software (Tian et al., 2019).

2.3. Gas chromatography mass spectroscopy tests

The EO and WEO chemical constituents were analyzed using the GC/MS-QP2010 Ultra system (Shimadzu, Kyoto, Japan) including GC and MS detectors. Helium ($> 99.999\%$) was used as a carrier gas and the gas flow rate was 1 mL/min. A capillary column (DB-5MS: 30 mm \times 0.25 mm \times 0.25 μ m, Agilent, J&W Scientific) was heated from 40 to 320 $^{\circ}$ C at a rate of 5 $^{\circ}$ C/min and maintained at 320 $^{\circ}$ C for 10 min. Under the condition of a mass spectrum in electron impact ionization mode, the electron energy was 70 eV and the temperatures of the interface and ion source were 280 $^{\circ}$ C and 220 $^{\circ}$ C, respectively. The relative content of each component was calculated using the peak area normalization method.

2.4. Inductively coupled plasma optical emission spectrometry tests

For the pre-digestion process, 0.2056 g of EO and 0.1831 g of WEO sample was individually weighed and placed into a high-pressure reactor; each sample was heated to 180 $^{\circ}$ C in a concentrated nitric acid environment to digest EO and WEO. Following the digestion, the sample solutions were treated with de-acidification. The trace element contents in the EO and WEO were determined using ICP-OES (Agilent ICPOES730). The RF Power was 1.0 kW. The carrier gas was high purity argon gas and the flow rate of the atomization gas was 0.75 L/min. The axial mode was used.

2.5. Flotation tests

Flotation tests were performed in a 1 L XFD flotation cell. EO and WEO were used as collectors, separately; 2-Octanol was used as a frother. The speed of the flotation machine was set to 1800 r/min. For each flotation test, the minus 0.5 mm fraction was fed into cell at 80 g by mass and agitated for 2 min to ensure the wetting of its surface in advance. Then, the collector was added and stirred for 2 min. Thereafter, the frother was dripped into the pulp and the conditioning progress was conducted for 1 additional minute with mixing. The collector dosage was 2, 4, 6, 8 and 10 kg/t, respectively. The frother dosage was maintained at 500 g/t. The air flow rate remained constant at 0.06 m³/h. Clean coal was collected during the flotation process which occurred for 5 min. The float and sink products were

filtered and dried at 80 °C in an oven; the weight and ash content were used for analysis. The experiments for each group were repeated two times.

2.6. Induction time tests

The induction time system was composed of a light source, camera, displacement table, vibration exciter, computer, as well as other typical components (Fig. 1). Before the test, deionized water and 2 g of coal particles of size between 0.125 and 0.5 mm were mixed in the glass cell and the pulp was stirred for 2 min. It was allowed to stand for 4 min and then the supernatant was poured out. Then, EO or WEO was added at a concentration of 2 kg/t. After the pulp was agitated for 2 min and stood for 4 min, the coal particles were flattened onto the bottom of the glass cell to form a coal bed. An air bubble 4 mm in diameter (d) was formed at the bottom of the capillary with the help of a micro syringe; the initial distance (h) between the bubble and coal bed surface was set to 3 mm. The bubble vertical displacement (z) was 3.5 mm. The bubble approached the coal bed at a uniform speed and returned to the initial position after contact with the coal bed for a given time. When the probability of the bubble-particle attachment was 50%, the time was recorded as the induction time (Verrelli and Albijan, 2015). Each experiment was repeated at least 10 times and the average value was taken as the final induction time.

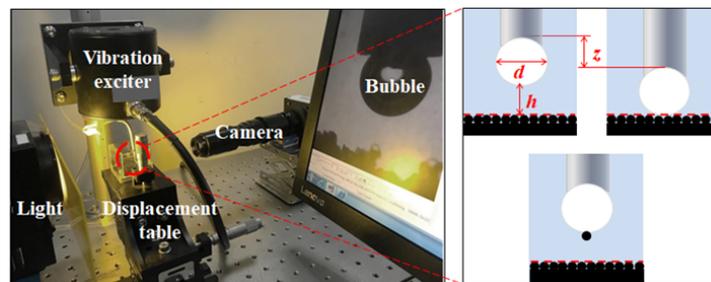


Fig. 1. Schematic diagram of the induction time analysis system

2.7. Wrap angle tests

Fig. 2 shows the wrap angle analysis system. A total of 200 mL of deionized water and 2 g of coal sample (0.125–0.5 mm) were fed to the test cell. The initial speed of the agitator was set to 1000 r/min and the mixture was stirred for 2 min to pre-wet the coal samples fully. Then, the pulp was static for 4 min and the supernatant was discarded. The collector solution with a concentration of 2 kg/t was added and the collector was stirred for another 2 min such that the collector could be adsorbed onto the coal surface. The pulp was also stood for 4 min to remove the supernatant again. The identical amount of deionized water was replenished to the cell. An air bubble, 4.2 mm, in diameter was generated in the cell with the help of a needle tube. Then, the agitator was initiated; the speed was set to 250 r/min.

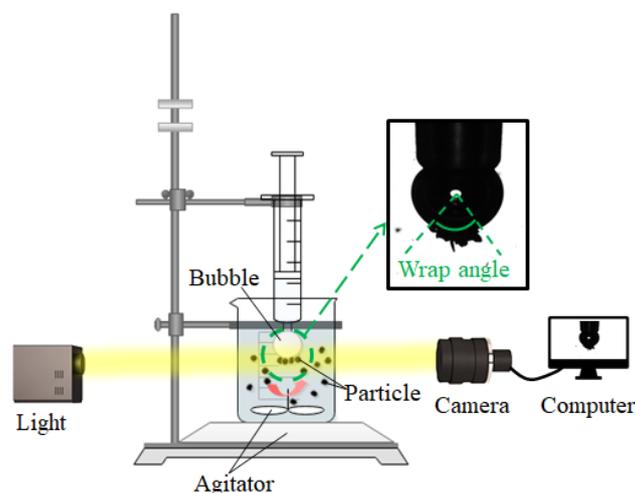


Fig. 2. Schematic diagram of the wrap angle analysis system

Notably, the speed is too fast here to cause bubble instability. The wrap angles of the particles on an air bubble were measured at 10, 20, 40, and 100 s.

3. Results and discussion

3.1. Coal characterization

XPS tests were conducted to obtain additional information regarding the composition of the surface functional groups, etc. The XPS wide sweep spectrum is shown in Fig. 3. The semi-quantitative relative contents of chemical elements on the coal surface are shown in Table 2. It was clear that the O1s and organic component (Si, Al and Ca) contents on the coal surface were relatively high.

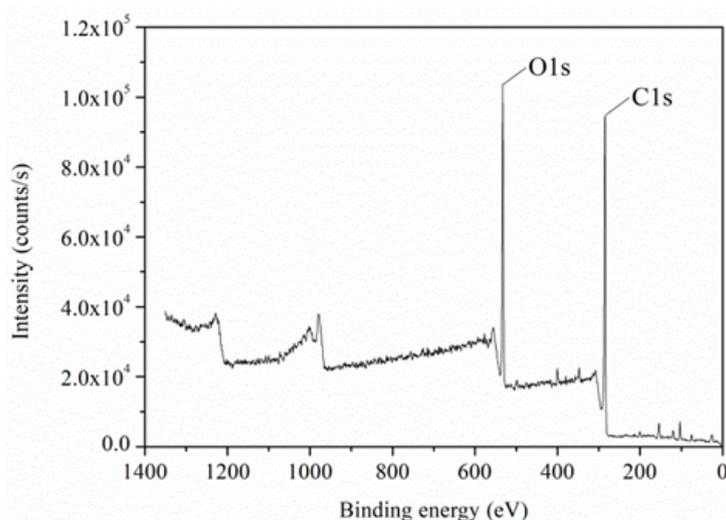


Fig. 3. XPS wide energy spectra of the coal samples

Table 2. Relative contents of chemical elements on the coal surface

Elements	C1s	O1s	N1s	Si2p	Al2p	Ca2p
Relative content, %	64.32	25.17	2.76	3.73	2.99	1.02

The XPS C1s peaks are shown in Fig. 4. The spectra were fitted with four binding energy peaks at 284.60, 285.60, 286.60, and 289.10 eV, representing the C-C/C-H, C-O, C=O, and O=C-O groups, respectively. The relative contents of these groups were calculated according to the peak area; the results are shown in Table 3. The relative content of the C-O was 19.50%. In addition, the C=O and O=C-O groups were observed in coal samples. The oxygen-containing functional groups on the coal surface can increase the hydrophilic points on the coal sample surface; thus, the hydrophilicity is improved.

3.2. Collector characterization

GC/MS tests were performed to determine the organic components in the EO and WEO; the results are shown in Tables 4 and 5, respectively. The organic components in the EO included esters, aromatic hydrocarbons, siloxanes, alkanes and so on. In addition, aromatic hydrocarbons, alcohols, esters, and alkenes are the main organic components in the WEO. There are significant differences between the EO and WEO, even if similarities in the types of the organic components. The compositions of EO were mainly esters, accounting for almost 50%, while the content of aromatic hydrocarbons was relatively low. In contrast, aromatic hydrocarbons were the main components in WEO, and esters were also contained. Moreover, the majority of the retention times of the chemical constituents in the EO were over 30 min while those in the WEO were concentrated in 10 - 20 and 30 - 37 min, indicating that long chain components or macromolecules were dominant in the EO, but long chain components and short chain components coexisted in the WEO.

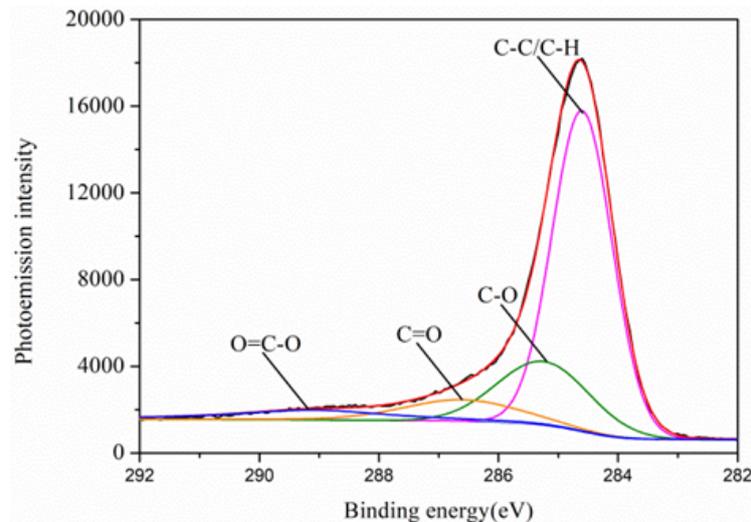


Fig. 4. XPS C1s fitting spectra of the coal samples

Table 3. Relative contents of carbon forms on the coal surface

Carbon forms	C-C/C-H	C-O	C=O	O=C-O
Binding energy, eV	284.60	285.60	286.60	289.10
Relative content, %	63.91	19.50	9.14	7.45

The chemical compositions of the EO and WEO determined their adsorption characteristics on the low-rank coal surface. The aromatic hydrocarbon components in the collectors can form a strong bond with the hydrophobic sites on the low-rank coal surface (Jia et al., 2000). The hydrophobic groups in the collector can be effectively adsorbed in the hydrophobic region of the coal surface and the hydrophobicity of the coal surface can be further improved. In addition, the polar components, such as esters, can mask some of the hydrophilic points on the low-rank coal (Xu et al., 2019). Based on these, the long chain esters in the EO were expected to be well adsorbed on the oxygen-containing sites on the low-rank coal surface. However, the high content (42.09%) and the long carbon chain (12 - 16 carbon atoms) of these esters may lead to the interlacements and entanglements of the non-polar tail chains with each other, which ultimately made it difficult for long chain esters to well disperse on the surface of low rank coal, thus negatively affecting the adsorption efficiency (Fig. 5). On the contrary, the small molecule aromatic hydrocarbons, accounting for more than 50% in WEO, could forcefully occupy the hydrophobic sites, and synergistically adsorbed on the coal surface together with the long chain esters with lower content, so as to the improvement of the hydrophobicity of the coal sample surface as much as possible.

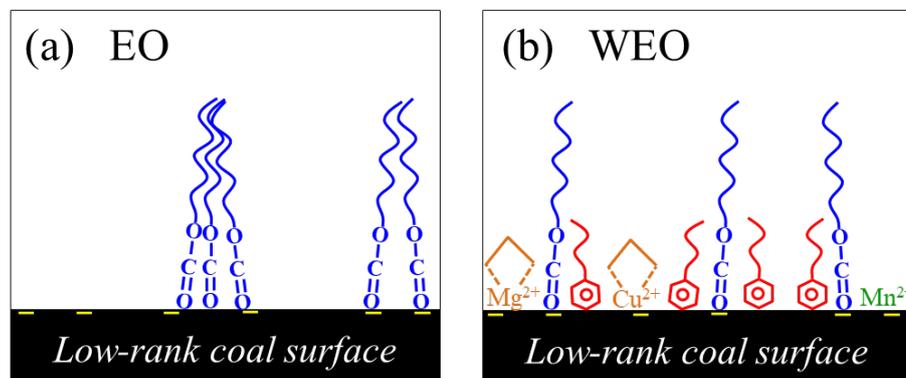


Fig. 5. Adsorption schematic of EO and WEO on low-rank coal surface

Table 4. GC/MS analysis of the EO chemical constituents

Type	Retention time (min)	Chemical substances	Relative content (%)	Total
Esters	32.294	n-Dodecyl methacrylate	23.59	42.09
	35.962	Dibutyl phthalate	1.42	
	36.410	Methacrylic acid, hexadecyl ester	10.01	
	36.983	Sulfurous acid, cyclohexylmethyl Heptadecyl ester	7.06	
Alcohols	12.631	Benzyl alcohol	15.26	16.88
	33.013	1-Tricosanol	1.62	
Siloxanes	29.091	Hexadecamethyl cyclooctasioxane	6.31	15.54
	29.201	Tetradecamethyl hexasiloxane	1.35	
	30.068	Tributyl(ethoxy) silane	1.20	
	32.580	Hexadecamethyl heptasiloxane	5.23	
	35.611	1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-Hexadecamethyl octasiloxane	1.45	
Aromatic hydrocarbons	30.007	9,10-Dibutyl-9,10-dihydroanthracene	5.54	12.95
	35.143	(1-Methyl dodecyl)benzene	2.86	
	37.113	Octadecahydro-benzo[cd]pyrene	4.55	
Olefins	30.136	2,4,4,6,6,8,8-Heptamethyl-2-nonene	6.39	9.67
	30.987	2,4,4,6,6,8,8-Heptamethyl-1-nonene	1.04	
	32.794	3-Eicosene	1.16	
	36.753	1-(1,1-Dimethylethyl)-4-ethenylbenzene	1.08	
Alkanes	32.926	Heptadecane	1.66	2.86
	34.997	Heneicosane	1.20	

The GC/MS analysis results showed the difference in the organic composition between the EO and WEO. Quantitative whole analysis of inorganic elements in the EO and WEO was conducted via ICP-OES tests to distinguish the difference in the metal elements between the EO and WEO (Fig. 6). There was a significant difference between EO and WEO in metal elements. Cu, Mn, and Mg exhibited the most significant differences for the metal elements in the WEO that experienced a percentage increase.

The differences between the EO and WEO in terms of metal elements cannot be ignored. On the one hand, the coal surface is negative, while Cu^{2+} , Mn^{2+} , Mg^{2+} and other metal ions are positively charged. Therefore, metal ions can probably adsorb onto the mineral surface through electrostatic interaction. The adsorbed metal ions and their compounds on the coal surface may benefit collector adsorption and

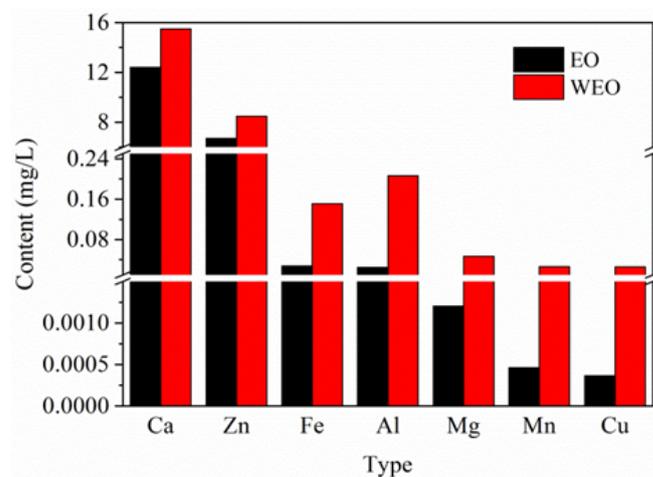


Fig. 6. ICP-OES results for the EO and WEO

Table 5. GC/MS analysis of the WEO chemical constituents

Type	Retention time (min)	Chemical substances	Relative content (%)	Total (%)
Aromatic hydrocarbons	4.395	Toluene	2.53	55.47
	7.279	1,3-Xylene	2.79	
	7.329	1,2-Xylene	1.10	
	7.987	1,4-Xylene	1.81	
	10.256	o-Ethyltoluene	3.91	
	10.359	m-Ethyltoluene	1.73	
	10.536	1,2,3-Trimethyl benzene	1.71	
	10.810	p-Methylethylbenzene	1.62	
	11.336	1,3,5-Trimethylbenzene	8.73	
	12.202	1,2,4-Trimethylbenzene	3.17	
	13.206	1-Methyl-4-propylbenzene	1.53	
	13.359	2-Phenylbutane	1.30	
	13.414	1,3-Dimethyl-5-ethylbenzene	1.59	
	13.986	1,4-Dimethyl-2-ethylbenzene	1.65	
	14.066	o-Isopropyltoluene	1.31	
	14.267	1,2-Dimethyl-4-ethylbenzene	3.68	
	15.263	Prehnitene	1.92	
	15.367	Durene	3.42	
	15.971	4-Methylindan	1.17	
	16.227	5-Methylindan	2.34	
	16.316	1,2,4,5-Tetramethylbenzene	1.59	
	17.347	Naphthaline	3.31	
	20.586	1-Methylnaphthalene	1.57	
Alcohols	12.633	Benzyl alcohol	20.16	20.16
Esters	14.853	Butyric acid, 2-phenyl-, dec-2-yl ester	1.14	14.44
	32.288	n-Dodecyl methacrylate	9.55	
	36.406	Methacrylic acid, tetradecyl ester	3.75	
Alkanes	32.922	Heptadecane	1.30	9.94
	34.995	Heneicosane	2.02	
	36.976	Octacosane	6.62	

change the coal surface wettability (Xu et al., 2017). On the other hand, the existence of metal ions and the formation of complexes with collector may improve the adsorption performance of collector on mineral surface, thus changing the wettability of coal surface (Li et al., 2016; Liu et al., 2015; Tian et al., 2018; Tian et al., 2018; Xiao et al., 2017;).

On the basis of the above analysis, compared with EO, WEO was more conducive to the enhancement of low-rank coal flotation due to the synergistic adsorption of long chain esters and short chain aromatic hydrocarbons on the surface of low rank coal, and the contribution of metal ions (Fig. 5).

3.3. Flotation performance analysis

The flotation results of low-rank coal using EO or WEO are shown in Fig. 7. The concentrate yield of low-rank coal using WEO was observably higher than that using EO. Meanwhile, there was little difference in the concentrate ash content obtained between the EO and WEO. When the WEO dosage used for collecting low-rank coal was 4 kg/t, a clean coal yield of up to 96.73% was obtained. However,

only a 38.80% yield was get using the EO at an identical dosage. Furthermore, when the dosage of WEO was more than 6 kg/t, the concentrate yield remained above 95%; when the EO dosage exceeded 6 kg/t, the clean coal yield dramatically decreased. Therefore, it was evident that WEO can greatly enhance low-rank coal flotation.

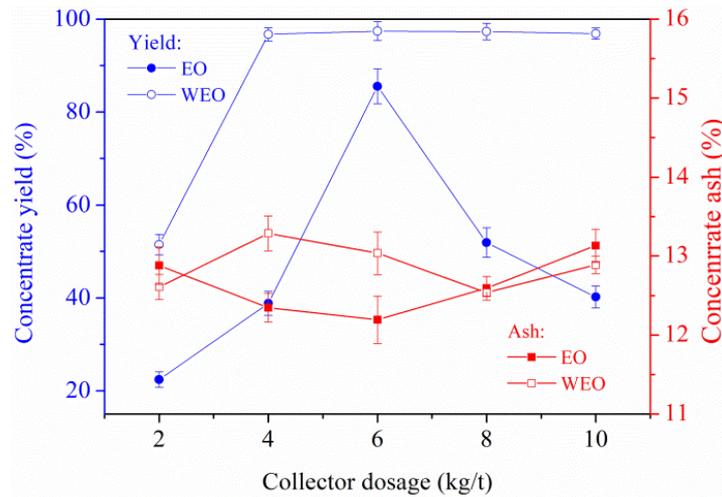


Fig. 7. Flotation results for coal samples using EO and WEO

3.4. Induction time analysis

Without bubble-particle attachment, there is no flotation process (Plbijanic et al., 2010; Phan et al., 2003; Zhang et al., 2019). In other words, bubble-particle attachment is critical to flotation (Xing et al., 2018). Bubble-particle attachment in the presence of EO or WEO was evaluated using induction time. The shorter the induction time, the shorter the time required for bubble-particle attachment; then, bubble-particle attachment was more likely to occur under the same other conditions (Xing et al., 2019). In the presence of EO, the induction time between the bubble and low-rank coal particles was 430 ms, while the induction time was significantly decreased to 220 ms in the presence of WEO (Fig. 8). WEO was more helpful in promoting the attachment between bubbles and low-rank coal particles. Therefore, it was more helpful in improving the recovery rate of low-rank coal flotation at a lower dosage. This result was consistent with the results of the flotation test.

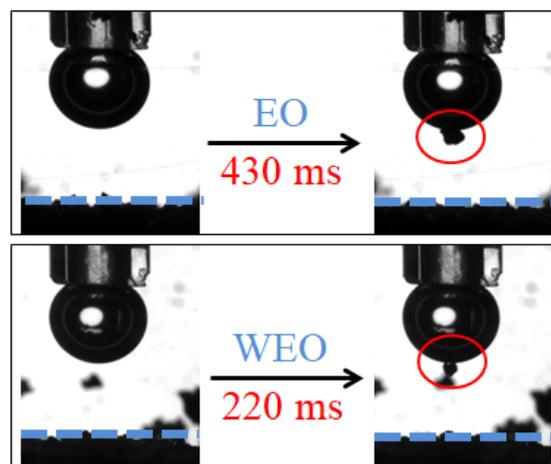


Fig. 8. Induction time results using EO or WEO at the concentration of 2 kg/t

3.5. Wrap angle analysis

The wrap angle refers to the encapsulation of particles on the bubble surface. The larger the wrap angle, the better the attachment effect between particles and bubbles. At the same time, the wrap angle can

directly reflect the difficulty the particles experience in adhering to the surface of the bubbles. With an increase in stirring time, the interaction time between the collector and low-rank coal particle surface gradually increased; additionally, more particles were attached to the fixed bubble surface (Fig. 9). Under the action of EO, when the stirring time was shorter than 40 s, the wrap angle clearly increased; when the stirring time increased to longer than 100 s, the wrap angle remained nearly unchanged. The bubble surface was coated with more low-rank coal particles in the presence of the WEO than in the case of EO. When the mixing time increased to 100 s, the wrap angle was as high as 253.1°; moreover, the bubble was nearly completely coated by low-rank coal particles. The WEO possessed a better collecting ability of low-rank coal particles than EO.

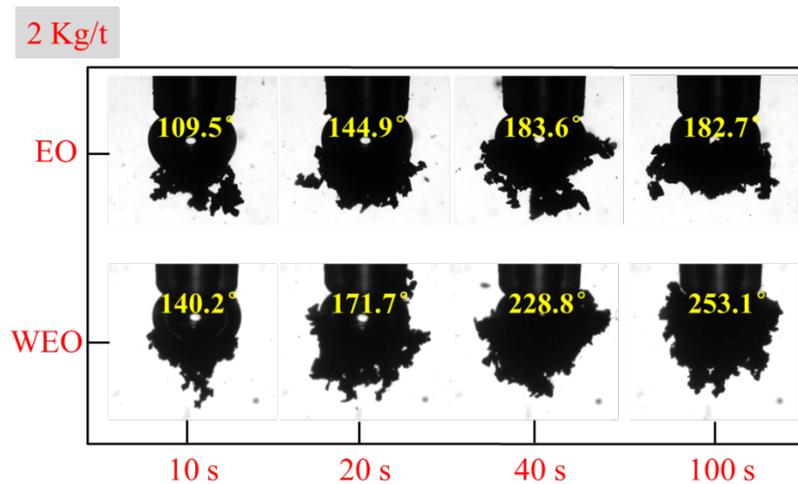


Fig. 9. Wrap angles of low-rank coal particles (pre-treated in EO or WEO environments for different stirring times)

4. Conclusions

WEO can enhance the flotation recovery rate of low-rank coal better than EO. When the WEO dosage was only 4 kg/t, the yield of clean coal was as high as 96.73%. Compared with that of EO, the bubble-low-rank coal particle induction time in the presence of WEO was significantly shortened from 430 to 220 ms. More low-rank coal particles were captured and adhered to the bubble surface. The WEO was more advantageous in promoting the attachment between low-rank coal particles and bubbles; thus, it was more useful in improving the flotation recovery rate of low-rank coal at a lower dosage. The above phenomena and results were attributed to the differences in composition between EO and WEO. The small molecule aromatic hydrocarbons, accounting for more than 50% in WEO, could forcefully occupy the hydrophobic sites, and synergistically absorbed on the coal surface together with the long chain esters with lower content. Meanwhile, the existence of metal ions and the formation of complexes with collector in the WEO was more conducive to the enhancement of low-rank coal flotation. In conclusion, WEO could be an alternative low-rank coal collector.

Acknowledgments

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