

Impact of a Compound Collector on the Recovery of a Low-Rank Coal by Flotation

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Abstract - Flotation remains the cornerstone for recovering low-rank coal leveraging on differences in mineral surface properties. However, the efficiency of standard non-ionic surfactants like kerosene and diesel oil has been suboptimal. This study investigated the impact of combining pine oil (PO) with oleic acid (OA) on low-grade coal flotation response, employing Response Surface Methodology based on a Box-Behnken matrix to design the flotation experiments, with combustible matter recovery (%) as the primary response. Chemical analysis identified the notable presence of silica and alumina, while mineralogical investigations revealed the dominance of kaolinite and anhydrite as major gangue constituents. The coal surface was characterised by roughness, irregular strips and plenty of cracks. Zeta potential studies elucidated collector adsorption states, highlighting the influence of pH on surface charge variations. Fourier-transform infrared spectroscopy analysis indicated the presence of polar functional groups on the coal surface with observed modifications after compound collector addition. Flotation results revealed that the oleic acid-pine oil mixture, particularly at a 1:1 ratio, yields an exceptional recovery of 85.46% at a slurry pH of 8.5. The optimum condition to obtain maximum combustible matter recovery of 86.48% was found to be at an oleic acid dosage of 100 g/t, a pine oil dosage of 100 g/t and a pH of 10. The study highlighted the pivotal role of slurry pH in influencing recovery with higher pH levels correlating with increased recoveries. In conclusion, fatty acids, specifically oleic acid, emerged as potential polar collectors to combine with non-ionic collectors for the recovery of low-grade coal. The findings advocate for further exploration of surface chemistry, mineralogical interactions and alternative collectors. Additionally, scaling up studies and environmental impact assessments are recommended to propel the practical applicability of the compound collector system in industrial settings.

Keywords: Flotation, Low-rank coal, Surfactants, Response surface methodology, Compound collector.

1. Introduction

A significant energy source used worldwide is coal. The South African economy has grown significantly with the aid of the coal mining sector. About 70% of South Africa's primary energy comes from coal, which is likely to continue to be the nation's main energy source despite rising trends towards renewable energy. The current level of energy demand cannot be satisfied by the high and middle-rank coal reserves [1]. A significant area of research and development in the coal business has been the recovery of low-grade coal employing flotation. Their distinguishing characteristics are the high moisture content, poor calorific value and great vulnerability to spontaneous combustion of low-rank coals. [2] stated that, due to these reasons, recovering low-rank coals using conventional methods has been a challenge.

It is well recognized that low-rank coals are challenging to float utilizing typical alkyl non-ionic surfactants, such as dodecane and diesel [3]. This is mostly because low-rank coal contains a lot of oxygenated chemical groups on its surface that are water-loving (including hydroxyl, carboxyl, methoxyl and carbonyl). Hydrogen bonding can unite hydrophilic chemical groups with water. The consequence is an extremely thick hydration film on the exterior of low-grade coal. According to [3], this substantial hydration coating hinders both the connection of coal particles to the bubbles and the surface assimilation of collectors to the coal surface. The use of co-blended collectors in the flotation process is one promising strategy that has been investigated by researchers to upgrade the recovery of low-rank coal.

Utilising a surfactant or collector to complete a coal surface modification has improved flotation performance in recent years. Tetrahydrofuran (THF), a non-ionic surfactant, has been shown by [4] to be an efficient surfactant for lignite flotation. [5] improved the hydrophobicity of low-grade coals by using tetrahydrofuran esters ($C_4H_7O-CH_2-OOC-R$) based on [4]. It

led to the discovery that chemicals with oxygenated chemical groups and benzene rings were more effective on collecting low-rank coals. [6] showed that the surface assimilation of cationic dodecyl ammonium determined the hydrophobicity of blended grains made up of coals and surfactants. [7] added by demonstrating that the surfactants can improve flotation response, but synthesising them is laborious and costly, making them unsuitable for commercial production. Further stress must be placed on the pharmaceutical benzene ring's negative environmental effects.

In numerous industrial applications, compound collectors have additionally been shown to be more efficient, more affordable and less dosage-intensive [8, 9]. [10] used a combination of 4-dodecyl phenol (DDP) and hexadecane (HXD) as a novel collector for the recovery of unburned carbon from fly ash in earlier research. Dodecane and 4-dodecyl phenol (DDP) were successfully combined to increase the flotation performance of lignite [3]. Dodecane and DDP mixture was used as the collector, with the dodecane covering the hydrophilic and DDP covering the water-repellent areas on the lignite exterior respectively [7]. As unconventional flotation reagents, a mixture of diesel oil (hydrocarbon) and oxygenated compounds (aldehyde, ketone and carboxylic acid) was used to increase the flotation efficiency of low-rank coal [2]. The findings of [2] showed that, for the flotation of low-rank coals, chemicals containing oxygenated chemical groups were considerably better collectors than diesel oil due to their higher bonding energy. Only a simple blend can create these mixed collectors. The raw materials are typical chemical reagents with a developed, quick and simple trading market. These organic oil collectors are also typical flotation reagents. Carboxyl, hydroxyl, keto, aldehyde, ether, and other polar organic functional groups are among the most common. According to [7], organic molecules that belong to these classes are typically present in low-rank coal collectors.

The hydrogen bonding between the hydrophilic groups of the collector and the oxygenated chemical groups on the coal surface increases the floatability of low-grade coals [5]. One of the functional groups in organic molecules that contain polar oxygen is the aldehyde group. Between the aldehyde groups, there are no hydrogen bonds or association phenomena. Additionally, aldehydes are very well soluble in organic solvents. The usage and research of collectors containing aldehyde groups for the flotation of low-rank coals, however, have not been done consistently [7]. To improve flotation performance by increasing hydrophobicity, pre-treatments of low-rank or oxidised coals were also investigated. [11] commented that the most crucial pre-treatment techniques are the direct mixing of the chemicals with dry coal prewetting, thermal, microwave, and ultrasound pre-treatments, premixing and preconditioning and grinding.

In the current study, the impact a compound collector made up of oleic acid (polar collector) and pine oil (non-polar collector) on flotation efficiency of a low rank coal is presented.

2. Materials and Methods

2.1 Materials

Low-grade coal with a particle size bigger than 2 mm was acquired from Emalahleni district, South Africa. The proximate analysis of the as-received coal sample revealed the following: Mad = 4.77%, Vad = 26.68%, Aad = 19.03%, FCad = 49.52 % and S = 0.404 %. Where Mad was the moisture content, Vad was the volatile content, Aad was the ash content, FCad was the fixed carbon content and S was the total sulphur content respectively. The flotation reagents used were (pine oil and oleic acid mixture) as a compound collector, MIBC frother, sodium silicate as a depressant, nitric acid and lime as pH modifiers, all sourced from RLS Chemicals Glassware & Equipment, South Africa.

2.2 Experimental methods

2.2.1 Sampling procedure

A 10 kg sample of coal was collected and mixed thoroughly to homogenise it before starting the sampling process. The bulk material was spread out on a clean, flat surface to dry. The sample was then inserted into the Jones riffler, gently agitated to ensure proper randomization of the particles and then flowed into two separate containers. This process provided two primary sub-samples weighing approximately 5kg each. One of the primary sub-samples obtained from the Jones riffler was

then placed into the spinning riffler for further splitting. When the spinning riffler divided the sub-sample into several smaller 10 sub-samples, the resulting sub-samples were inserted into clean and labelled plastic bags. The process was repeated for the other primary sub-sample obtained from the Jones riffler.

2.2.2 Proximate analysis

For proximate analysis, a standard laboratory technique was used to provide valuable information about the composition and characteristics of the as-received coal sample.

2.2.3 Element composition analysis

X-ray fluorescence analysis (XRF) was used to analyse the elemental composition of the coal samples. This method was applied to analyse the mineral matter of the coal. The study of atomic behaviour in contact X-ray radiation enabled the XRF analysis of the components in the coal sample. The chemical makeup of the material was ascertained using an X-ray fluorescent Rigaku ZSX Primus II with SQX software.

2.2.4 Electrokinetic studies

To measure the zeta potential, a potentiometric analyser ZetaPALS was used. The surface charge variation of as-received coal with the collector dosage of 200 g/t and without a collector was measured. The sample used for the test was grounded to a size less than 53 microns. Measurements were taken five times at pH ranges of 3, 5, 7, 9 and 11 using 0.01 M HCl and NaOH solutions.

2.2.5 Functional groups analysis

Fourier-transform infrared spectroscopy (FTIR) was used to study the primary functional groups in the coal sample and compound-collector structures. The specified resolution and several scans of the spectra were captured along the measuring range. After that, baseline variations were removed from all spectra.

2.2.6 Design of flotation Experiments (DoE)

The Response Surface Methodology (RSM), provided by Minitab software, was used to identify the ideal operating conditions for low-rank coal flotation. This approach enables the search for the components' ideal settings to produce the intended result. In order to evaluate the relationship between the three influential factors (X1 - oleic acid dosage, X2 - pine oil dosage and X3- pH) in coal flotation, the Box-Behnken design was utilized.

2.2.7 Flotation procedure

A 2 L Denver flotation cell was used for the flotation experiments. Each run involved mixing 600 g/L of pulp for 2 minutes at a speed of 1500 rpm. Sodium silicate of 500 g/t was added and agitated for 2 minutes. The dosages of oleic acid ranged from 100 to 200 g/t, whereas the pine oil dosages ranged from 100 to 200 g/t for comparison purposes. The compound collector was then agitated for two minutes. The MIBC frother of 150 g/t was added to the cell and agitated for 0.5 minutes. The airflow was then kept constant at 0.25 m³/(m²/min). When necessary, water was injected to keep the pulp level constant while the foam was collected for 5 minutes.

3. Results and Discussions

3.1 Characteristics of the as-received coal sample

3.1.1 Elemental composition of the as-received coal sample

The XRF analysis identified Si (4.60%) and Al (4.38%) as the major components in the mineral matter of the coal sample, as shown in Table 1. These elements were present in the form of silica (SiO₂) and alumina (Al₂O₃), respectively. The significant presence of these oxides suggested that the coal's mineral matter was predominantly composed of silica and alumina. Silica is a common component in coal ash and is derived from the mineral matter present in the coal. Alumina is another significant component of coal ash and originates from the clay minerals and other aluminium-containing minerals

present in the coal. Apart from Si and Al, the XRF analysis also detected the presence of calcium (Ca), iron (Fe), titanium (Ti), and sulphur (S) as other important elements. These elements are likely to be associated with inorganic components present in the coal.

Table 1: Chemical composition of the major elements present in the as-received coal sample

Element	Al	Si	P	S	K	Ca	Ti	Fe
Wt %	4.38	4.60	0.18	0.65	0.14	1.04	0.34	0.89

3.1.2 Electrokinetic studies of coal floatation

The zeta potential in floatation is an important parameter. Since the zeta potential of coal particles varies after the action of different collectors, the zeta potential value can reflect the adsorption state of the collector to some extent. In the test, the average value from five sets of data was taken in a single test and the standard deviation was calculated as the error bar. The results of the zeta potential study, shown in Fig. 1, indicated that the coal surface had a negative charge with increasing pH without the compound collector addition. The negative charge was attributed to the presence of hydrophilic sites on the surface, such as OH and COOH. An increase in hydroxyl and carboxylic functional groups on the coal surface increases the negative zeta potential. The higher the surface charge of the coal, the more hydrophilic the surface of the coal, due to the enhanced localisation of electron density of the chemical compound used as the floatation reagent on the coal surface. As the pH of the solution decreases, the hydronium ions are adsorbed on the coal surface and the coal surface acquires a positive charge. With an increase in pH, the hydronium ions are replaced with hydroxyl ions, and the coal surface contains a negative charge. The average surface charges of pine oil, oleic acid and the treated coal sample were 5.95, -2.35 and -1.91 mV respectively. The zeta potential of pine oil loses stability with increasing pH, while the zeta potential of oleic acid gains stability with increasing pH. The Zeta potential of the treated coal sample showed that the surface charge of coal was reduced with increasing pH. In addition, the zeta potential of the treated sample gradually stabilises, although at a pH of 11, it was unstable.

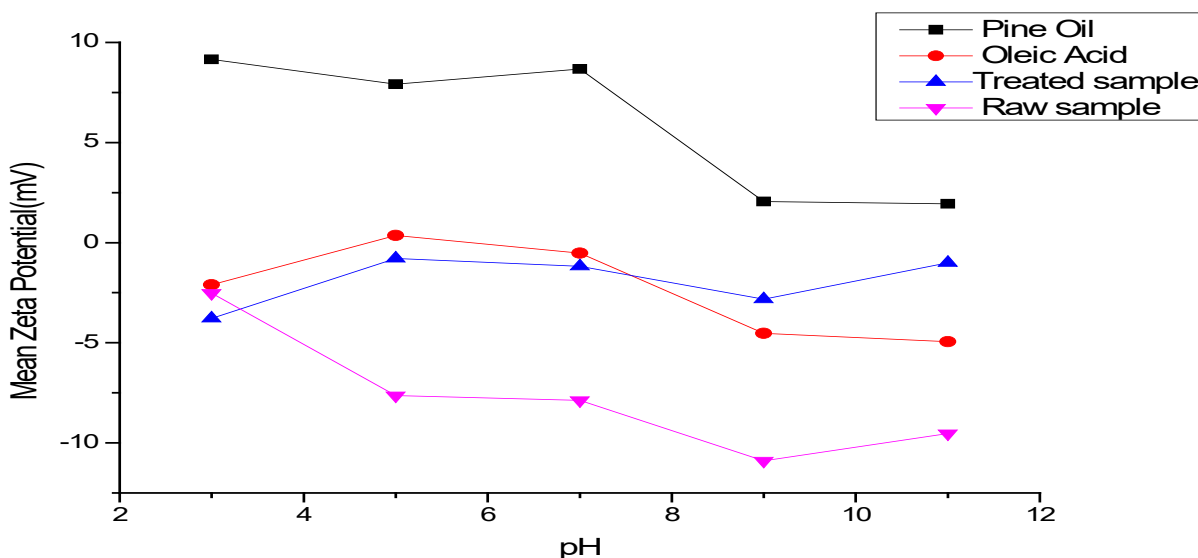


Fig. 1: Zeta potential of the studied collectors individually and in presence of the as-received coal sample

3.1.3 Functional groups and hydrophobicity of the coal sample

The hydrophobicity of the as-received coal sample is closely related to the type and number of functional groups. The FTIR spectrum of the as-received coal sample is shown in Fig. 2. The functional groups correspond to appropriate peaks in the coal samples, according to [2]. The adsorption peak at 3500 cm^{-1} to 3000 cm^{-1} represents the intramolecular hydroxyl (-OH), the absorption peak at 1700 cm^{-1} to 1600 cm^{-1} represents the group of carbonyls (C=O) or carboxyl (COOH), and the characteristic absorption peaks at approximately 1184 cm^{-1} are the stretching vibration of carbonyl. These analyses indicate that the existence of hydrophilic functional groups (C-OH, C=O and COOH) is the material causing poor flotation of low-rank coal.

To confirm the adsorption of compound collectors on low-rank coal surfaces, FTIR tests were also performed on coal samples treated when the PO: OA = 1:1, where the maximum combustible matter recovery (%) was discovered. An FTIR spectrum is illustrated in Fig. 3. It was evident that there were indeed modifications in the functional groups that were present on the treated coal surface, which contributed to the enhanced recoveries. The OH groups were much broader compared to the as-received coal sample. The infrared spectrum of pine oil in Fig. 3 showed several bands of angular deformation C-C and aliphatic C-H between 500 and 1500 cm^{-1} , out of plane deformation of trans alkenes at 911 cm^{-1} and bands with two signals at 1154 cm^{-1} and 1131 cm^{-1} , referring to the C-OH stretch of a secondary alcohol. The methyl band was observed at 1444 cm^{-1} and the geminal methyl, in pairs, at 1379 cm^{-1} and 1371 cm^{-1} . Bands at 1710 cm^{-1} and 1674 cm^{-1} are associated with C=C axial deformation, between 2965 cm^{-1} and 2924 cm^{-1} , referring to the C-H of saturated aliphatic carbon with the high-intensity characteristic of the terpene skeleton and at 3375 cm^{-1} , to the stretch of O-H. A complete characterization of pine oil is not possible as the composition of the material is complex and variable. The FTIR spectrum of pure oleic acid in Fig. 3 shows two bands at 2854 and 2923 cm^{-1} corresponding to the symmetric -CH₂ stretch and the asymmetric -CH₂ stretch respectively. The intense band observed at 1708 cm^{-1} is attributed to asymmetric -C=O stretch and the band at 1285 cm^{-1} corresponds to the C-O stretch. Bands exhibit at 1463 and 935 cm^{-1} represent the O-H stretch in plane and out-of-plane respectively.

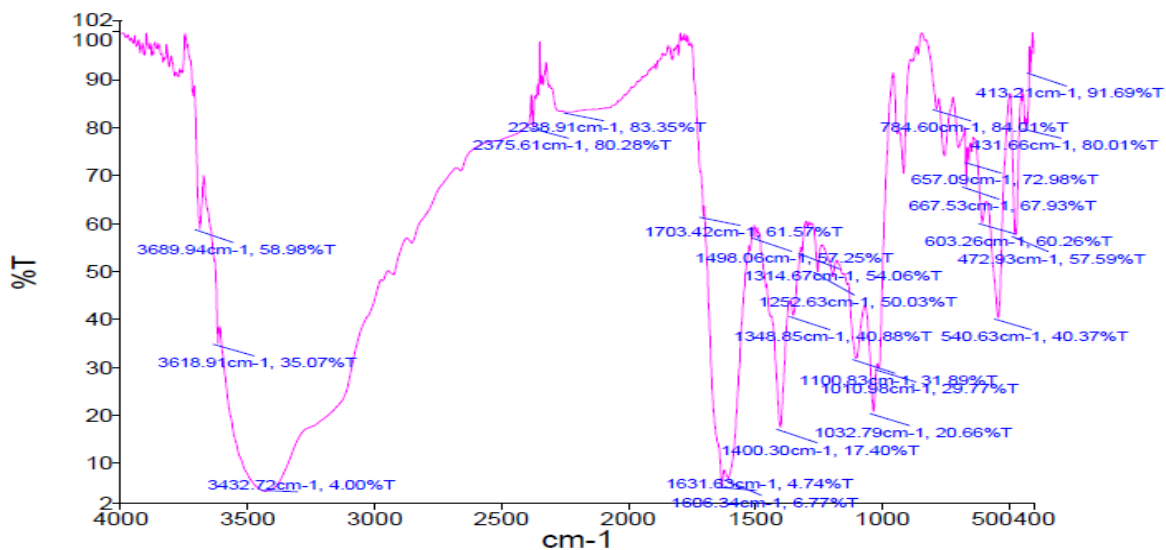


Fig. 2: FTIR spectrum of the as-received coal sample prior treating with collectors

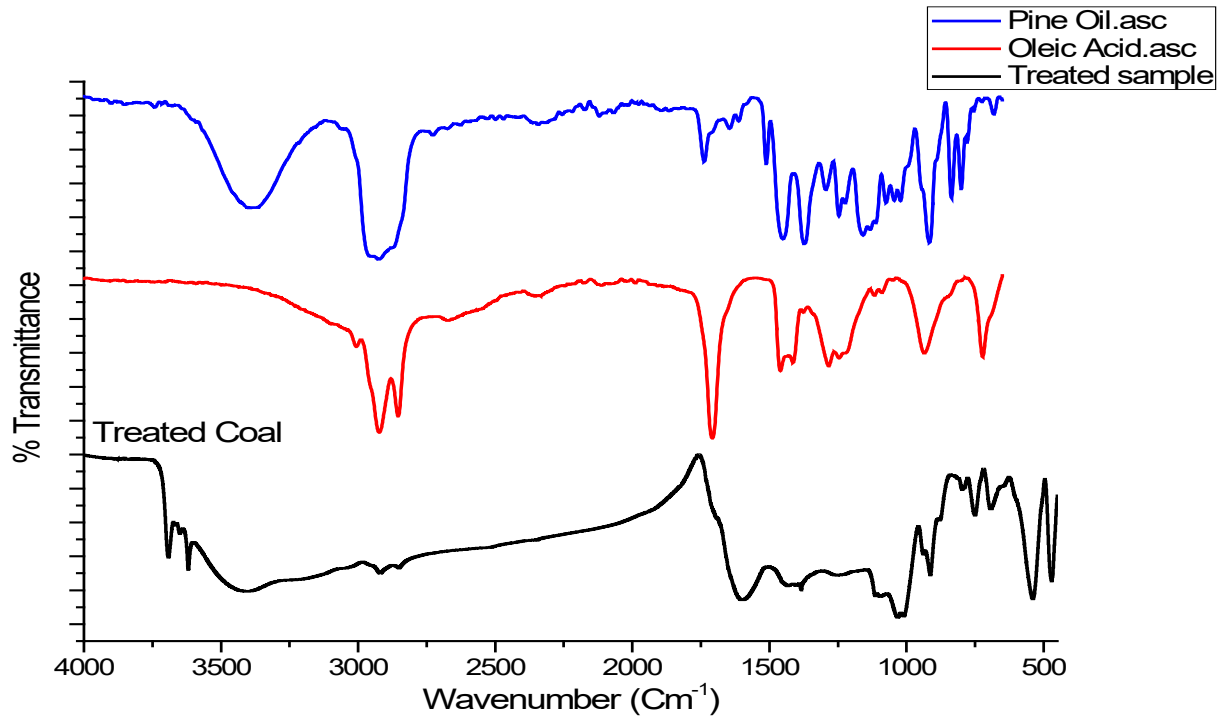


Fig 3: FTIR spectrum of the pine oil, oleic acid and treated sample after conditioning with the compound collector

3.2 Coal flotation results

Due to the considerable number of flotation condition sets, it is difficult to determine the appropriate values of operational parameters that have an impact on flotation performance. With a response surface approach based on Box-Behnken design, the impact of the influential parameters on the flotation behaviour of low-rank coal was thus explored in this study. The combustible matter recovery was calculated using equation (1) to evaluate the flotation effect, which can also be used to evaluate the collecting ability of the collector. The average combustible matter recovery (%) of various combinations of process parameters and levels is shown in Table 2. The highest recovery of 85.46% was obtained in the 3rd experiment, which was conducted under pH = 8.5; oleic acid dosage = 150g/t; pine oil dosage = 150g/t and the lowest recovery of 25.45% was acquired in the 10th experiment, which was conducted under pH = 7; oleic acid dosage = 100g/t; pine oil dosage = 150g/t. It was evident that recovery was directly proportional to pH. It should be noted that at a pH of 8.5, when PO: OA = 1:1, the combustible recovery was the highest. Furthermore, the combustible matter recovery increases with the decrease in PO proportion to OA. The study indicates that the PO: OA = 1:1 compound collector has the best effectiveness to enhance the flotation process. The ability of unsaturated hydrocarbons to increase flotation yield was also confirmed.

$$\text{Combustible matter recovery (\%)} = \left[\frac{M_C (100 - A_C)}{M_F (100 - A_F)} \right] \times 100 \quad (1)$$

where M_C was weight of the concentrate (%), M_F is weight of the feed (%), A_C is the ash content of the concentrate (%) and A_F is the ash content of the feed (%).

Table 2: Box-Behnken Design matrix and measured values of combustible matter recovery

Run	Oleic Acid dosage (g/t)	Pine Oil dosage (g/t)	pH	Combustible matter recovery (%)	% Carbon in concentrate
1	100	200	8.5	61.83	54.46
2	150	200	10	34.22	36.53
3	150	150	8.5	85.46	60.00
4	200	200	8.5	64.90	50.56
5	100	100	8.5	60.90	53.60
6	100	150	10	61.37	77.14
7	200	100	8.5	52.88	71.93
8	200	150	7	50.06	47.06
9	150	100	7	26.53	69.59
10	100	150	7	25.45	36.47
11	150	150	8.5	40.52	75.53
12	150	200	7	71.73	65.54
13	150	150	8.5	50.82	57.16
14	200	150	10	34.55	7.40
15	150	100	10	73.00	32.94
16	100	100	10	66.41	51.84

4. Conclusion

The chemical analysis of the as-received coal sample indicated the prominent presence of silica (SiO_2) and alumina (Al_2O_3). Zeta potential studies on the coal revealed a negative charge correlated with pH variations. The presence of hydrophilic sites, such as OH and COOH groups, played a significant role in shaping the zeta potential. These functional groups played a crucial role in forming a hydration shell on the coal surface, impeding the interaction of traditional hydrocarbon oil collectors with the coal. Some modifications in functional groups after compound collector addition were observed. The flotation results demonstrated that the oleic acid-pine oil mixture, especially at a 1:1 ratio (150g/t each), yielded the highest recovery of 85.46% at a pH of 8.5. The pH of the pulp emerged as a critical factor influencing the flotation process and there is a correlation between pH and recovery. The maximum recovery was achieved at a pH of 8.5. Compound collectors significantly enhances the recovery of low rank coal.

This study contributed valuable insights into the intricate interplay of surface chemistry, collector systems and pH conditions in the flotation of low-grade coal. The exploration of fatty acids as collectors adds depth to the understanding of flotation mechanisms, paving the way for further advancements in coal beneficiation processes.

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