A Comparative Study on Flotation of Coal Using Eco-Friendly Single Reagent and Conventional Dual-Reagent System

N. Vasumathi, M. Sai Kumar, D. S. V. Abhishek, T. V. Vijaya Kumar, and S. J. Gopalkrishna

1 Introduction

Coal, an organic sedimentary rock, is the backbone on which electricity generation and steel making rest. Coal contains mainly carbon, hydrogen, oxygen, nitrogen and sulphur as well as trace amounts of other elements, including the mineral matter that refers to the inorganic constituents of coal [1]. Mineral matter is the principal source of the elements that make up the ash content while the organic matter or the coal macerals contributes to carbon constituents. Most of the high ash coals are subjected to beneficiation for reducing the ash levels so as to make them suitable for various applications. Coking coal or metallurgical coal are coals when baked in absence of air, form a grey, hard, carbonaceous porous residue called 'coke'. These are mainly used for iron and steel manufacturing. Generally coking coals are a part of the bituminous group. While non-coking coals are mainly used for power generation. The mined coal is associated with inorganic impurities during its formation that forms the ash residue in coal which is undesirable for effective utilization of coal for many applications. The high-rank coal with high carbon and less ash content is depleting rapidly. As high-rank coal resources are running out due to the rise in energy demand and steel production, it is therefore imperative to use low-rank, oxidized coal to meet the increasing need for coal [2, 3]. Hence, the need for utilizing low-rank coals with low carbon and high ash is of utmost importance. As these low-rank coal can be effectively utilized after cleaning or washing in order to reduce the ash-forming mineral phases and thereby improving the carbon content of the coal for further suitable utilization.

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A fine coal washery losses ten times as much high-quality coal as a coarse coal washery. Recovering good quality fines will improve the economics of coal washery [4]. Generally, coal washing involves crushing and screening of Run-of-Mine (ROM) coal into smaller fractions, separating the gangue and mineral matter by using physical separation methods such as dense media separation/heavy media separation (HMS) or physico-chemical process, called froth flotation. As flotation process is based on differences in the ability of air bubbles to selectively attach to specific mineral surfaces in a mineral–water slurry and float to the top based on their degree of hydrophobicity [5–7]. Froth flotation is one of the beneficiation methods in fine coal washing by exploiting the surface hydrophobicity difference between coal macerals that are naturally hydrophobic and its associated ash forming minerals impurities that are mostly hydrophilic in nature. This naturally hydrophobic surface property of coal surface provides a high response while processed by flotation as it is a surface-phenomenon-based separation technique. Hence, coal particles have a natural affinity toward air bubbles [8, 9] as they are naturally hydrophobic.

It is generally recognized that recovering coarse coal by flotation is challenging [10, 11]. One factor that should not be overlooked is detachment. To reduce the particle detachment, several techniques have been used and one such way is the addition of flotation reagents which enhances the natural hydrophobicity of the particles that are to be floated. Rahman et al. (2012) discovered that the collector dosage, the aeration rate, and the concentration of fine particles had an impact on how easily the coarse particles detached during the froth phase [12]. In order to enhance this separation process efficacy, certain chemicals called as flotation reagents namely collectors, frothers, etc. are added to transform the coal-water mixture suitable for flotation by enhancing the relative hydrophobicity of coal particles and to maintain froth characteristics [13]. The collectors such as diesel, kerosene, and frothers such as MIBC, and pine oil is the most commonly and widely used reagents in coal flotation to increase the selective hydrophobicity of coal [14, 15]. These non-polar oils are non-environment friendly. As flotation process is very complex and could be balanced only with the appropriate selection of a reagent. Better separation efficiency is obtained when the ability of the flotation reagents gets adsorbed selectively and swiftly onto the coal particle surfaces [16]. Researchers have examined particle size extensively and its significance in flotation in addition to the type and dosage of the reagent and its impact on flotation [17, 18]. Carboxylic, phenolic, and carbonyl groups are the most prevalent types of functional groups on the surface of oxidized coal [19]. Jia et. al. investigated the efficacy of newly developed reagents for flotation of low rank and/or oxidized coals, which are difficult to float using conventional reagents such as fuel oil or kerosene. Experiments were conducted using these Tetra- hydrofurfuryl esters series (THF) as collectors for coal flotation, and the performance of these reagents was compared with that of dodecane and nonylbenzene. Results showed that the nonionic surfactants (THF series) were more effective collectors for both oxidized and unoxidized coals and greatly enhanced the flotation performance when used as a promoter for oxidized coals. Non-ionic tetrahydrofurfuryl ester surfactants are more effective in the flotation of both oxidized and unoxidized coals than dodecane (an oily collector) [20]. The use of dodecane, ethyl esters and dodecane-esters mixed collector on low-rank coal flotation and their interactions with coal particles were studied [21]. Apart from high collecting ability, the specific selectivity of high-efficiency ternary compound collectors such as oleic acid, methyl oleate, and diesel was investigated on low-rank coal [22]. The flotation efficiency of the new oxygenated polar compound collector along with blending frother was compared with conventional diesel (collector) and octanol (frother) on oxidized coals prepared using peroxide oxidation solution [23]. Also, the flotation reagent consumption rate is lower for higher-rank coals than low-rank coals because of their high natural hydrophobicity. It can be observed that most of the coal flotation process involves the usage of a dual reagent system (collector and frother) like hydrocarbon oils and chemically synthesized non-environment friendly collector and frothers. In this study, a single reagent, Collector AB, as an alternative to two reagent practices was developed from a natural percussor without using any harmful synthetic chemicals. This eco-friendly collector AB was used as coal collector-cum-frother and is safe to use in coal washeries as it was synthesized from natural product precursors unlike most commercial coal collectors. The performance of this developed collector AB in effectively separating the ash-forming minerals and collecting the coal particles in terms of its yield was studied. The results obtained were also compared with that of commonly used commercial reagents (collector & frother dual reagent system) to assess their flotation separation efficiency.

2 Material and Methods

2.1 Materials

A coking coal sample collected from one of the mines in Jharkhand was utilized in this flotation study. Commercially available synthetic flotation reagents widely used in coal washeries were used as collectors and frother. An eco-friendly 'Collector AB', synthesized from the natural product was used as coal collector-cum-frother (single reagent), and its flotation separation efficiency was compared with that of commercial dual reagents.

2.2 Methods

Flotation experiments on the coal sample were carried out using a laboratory D12 Denver flotation machine at natural pH (~7.0 pH) and at 12% solids by weight. The flotation experiments were carried out on two different sizes of flotation feed, 100% passing 0.5 and 0.25 mm. The flotation products were dried and subjected to ash analysis.

3 Results and Discussion

3.1 Characterization of Coal Sample

The organic matter or the coal maceral's composition was characterized as different maceral have varied degrees of hydrophobicity [24]. The petrological characterization of the coal sample taken in this study revealed the predominant presence of inertinite along with vitrinite (Fig. 1 and Table 1).

The Mean Reflectance of Vitrinite was found to be 1.1431. The coal maceral composition plays a major role in the surface hydrophobicity of the coal and thereby the selectivity of coal particles influencing the performance of the flotation process.

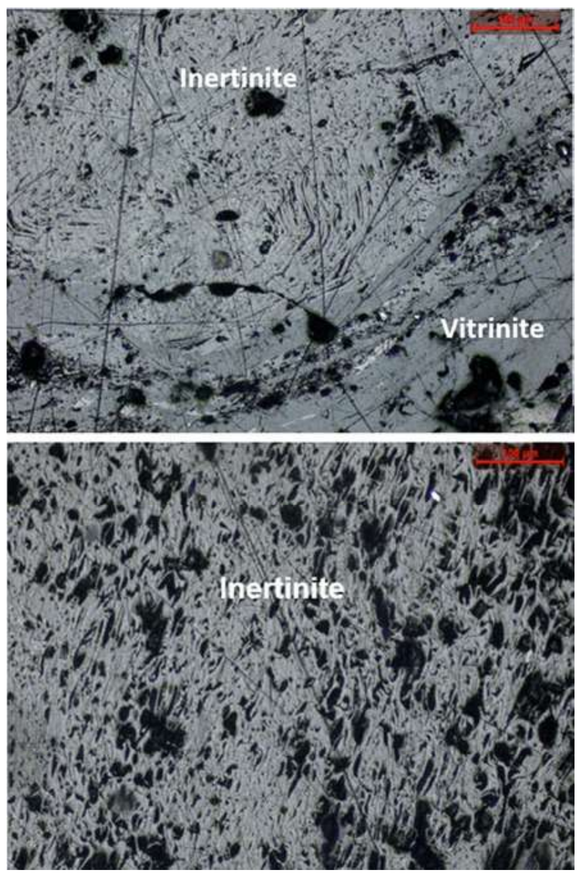


Fig. 1 Petrological image showing the presence of vitrinite and inertinite of the coal sample

Table 1 Maceral composition of coal

Maceral	Volume, %
Vitrinite	24.84
Inertinite	42.08
Heat affected	13.02
Mineral matter	20.06

3.2 Size and Ash Distribution Analysis

The proximate analysis of coal taken for this study is given below. The proximate analysis reveals that the coking coal contains 25.75% ash content and 53.89% fixed carbon with 19.51% volatile matter (Table 2).

The coal sample was size reduced to two size different fractions namely 100% passing 0.5 mm and 100% passing 0.25 mm in order to study the flotation response at these two size fractions. The size distribution and size wise ash analysis were carried out on the coal sample is given in Figs 3 and 4. The sieve analysis indicates that 40.42% of the material is above 300 µm in size, and the rest of the material is distributed in lower-size fractions. Also, the + 300 µm size fraction has higher ash content. From the ash distribution, it can be observed that the coarser fraction contributes higher ash content and below 150 µm is observed to be lower. The + 300 µm size fraction has higher ash content and thus the relatively coarser fractions contribute to higher ash content in comparison to that of below 150 µm size fractions implying that better liberation may be of coal macerals and ash forming minerals on further size reduction (Figs. 2 and 3).

In the sieve analysis on further fine-sized fraction of −0.25 mm coal, it can be observed that ash content gradually decreases with the fineness of the size reduced material. The amount of ash in −75 µm fraction is marginally lower than the coarser size ranges. Relatively lower ash in the finer size ranges could be attributed to better liberation of coal macerals. This size fraction of 100% passing 0.25 mm was also prepared for improved liberation and subjected to flotation studies using a commercial dual-reagent system and synthesized single eco–friendly reagent, 'Collector AB'.

Table 2 Proximate analysis of coal

Parameter	Value, %
Moisture	0.85
Volatile matter	19.51
Ash	25.75
Fixed carbon	53.89

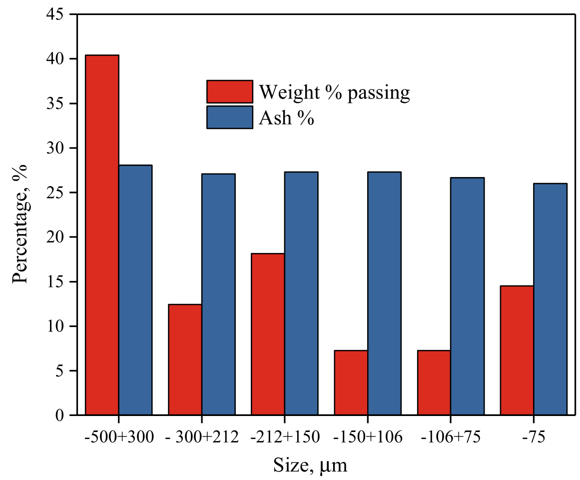


Fig. 2 Size-wise ash analysis of −0.5 mm coal fraction

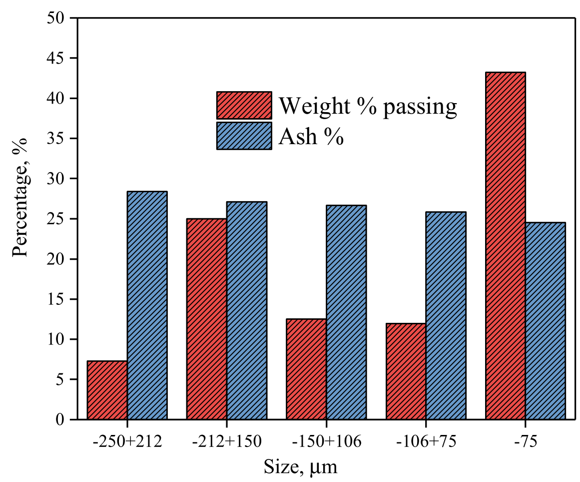


Fig. 3 Size-wise ash analysis of −0.25 mm coal fraction

3.3 FTIR Analysis of Flotation Reagents

The flotation reagents used in this study were characterized by Fourier Transform Infrared Spectroscopy (FTIR, Bruker Alpha II Spectrometer) to decipher the details of the functional group present (Figs. 4, 5 and 6).

The FTIR analysis of the feed coal sample was also studied. The FTIR data reveals that the weak intensity broad peaks in between 3600 to 3700 cm^{-1} indicate the presence of surface hydroxyl groups. The peak at 1600 cm^{-1} indicates the presence of the –C = C-group. The peak at 1023 cm^{-1} shows the presence of sulphate in coking coal. The FTIR of Collector AB suggests that the peaks at 2923 cm^{-1} and 2853 cm^{-1} are the presence of $–CH_3$ and $–CH_2$ groups. The FTIR spectrum and peak values are

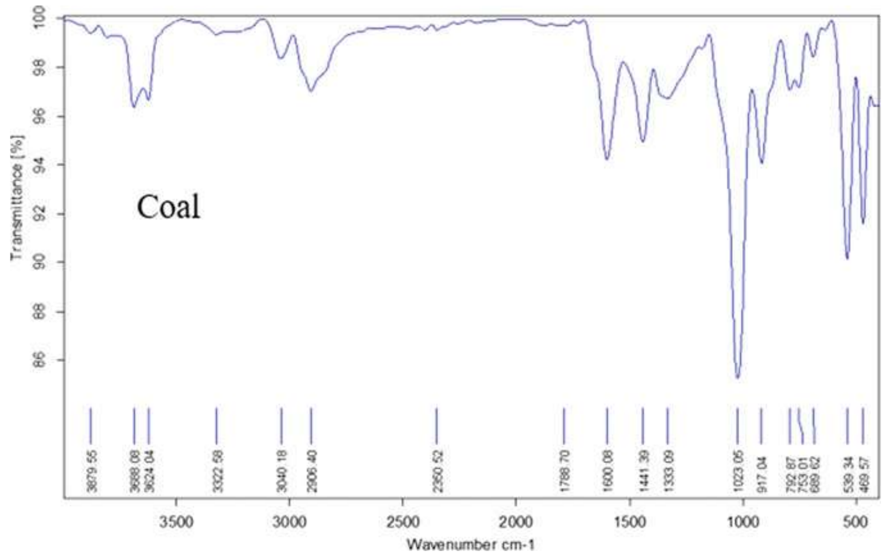


Fig. 4 FTIR analysis of coal

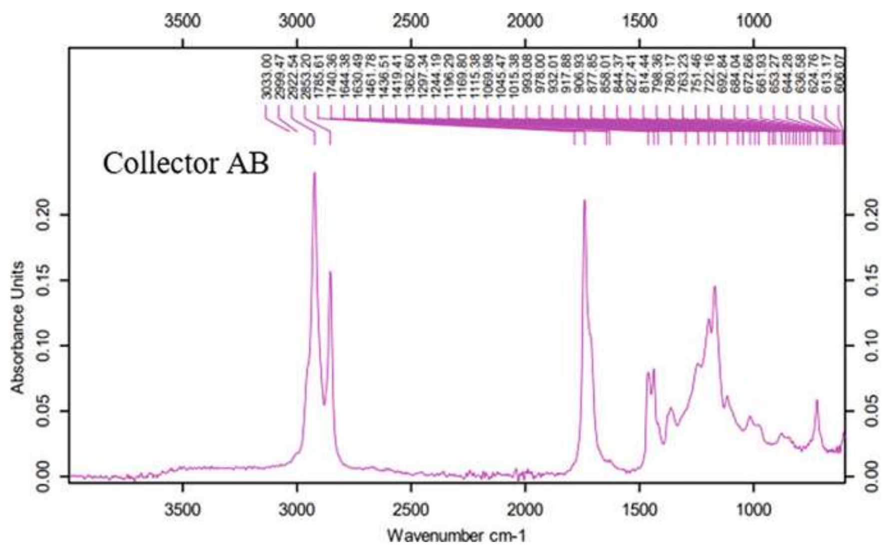


Fig. 5 FTIR analysis of Collector AB

well matched with natural product precursors [25]. The FTIR of commercial frother suggests that the peak in between 3000 to 3550 cm^{-1} of the hydroxyl group. The peaks at 2958 cm^{-1}, 2930 cm^{-1}, and 2873 cm^{-1} clearly indicate the presence of an alkyl chain in the frother.

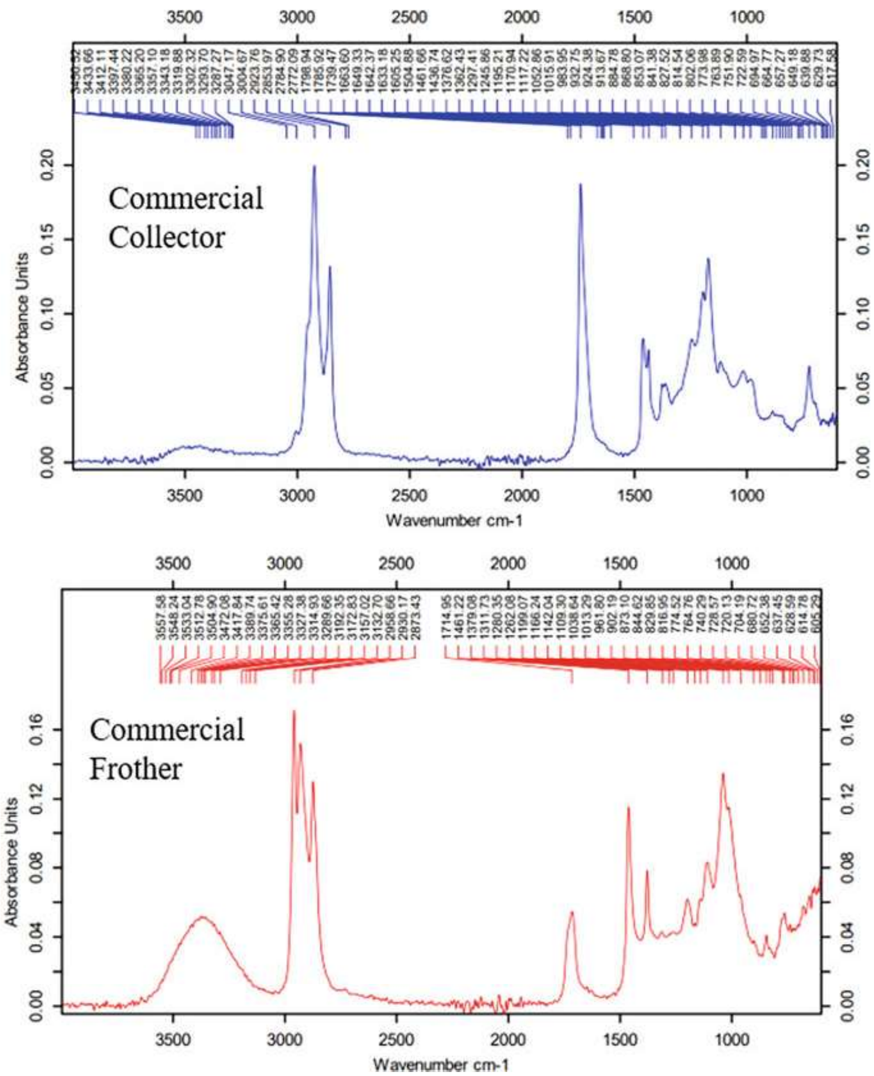
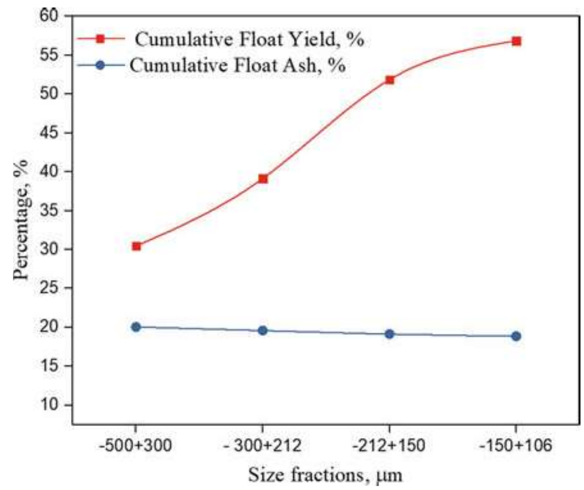


Fig. 6 FTIR analysis of commercial flotation reagents

3.4 HMS of Coarser Size Fraction of 100% −0.5 mm and 100% −0.25 mm

The heavy media separation (HMS) studies of coarser size fractions of two size ranges namely, 100% −0.5 mm and 100% −0.25 mm were carried out. The relatively coarser sieve fractions of 100% −0.5 mm viz., −500 + 300 μm, −300 + 212 μm, −212 + 150 μm, and −150 + 106 μm were subjected to the HMS test to elucidate

Fig. 7 Cumulative yield versus ash of float (−0.5 mm)



information on the liberation of coal macerals. It is observed that in 100% −0.5 mm fraction, the ash in successive floats was found to be decreasing which could be attributed to better liberation of coal macerals at finer sizes. Theoretically, 56.86% by weight (cumulative weight of floats) of the size fraction -500 + 106 μm could be obtained as concentrate/float at 18.83% ash as shown in Fig. 7.

The relatively coarser sieve fractions of 100% −0.25 mm viz., −250 + 212 μm, −212 + 150 μm, and −150 + 106 μm were subjected to the HMS test to study the information on the liberation of coal macerals. In case of 100% −0.25 mm size fraction, the ash in successive floats was found to be decreasing which could be attributed to better liberation of coal macerals at finer sizes than compared to − 0.5 mm size fraction. Theoretically, 32.49% yield (cumulative weight of floats) of the size fraction −250 + 106 μm could be obtained as concentrate/float at 17.43% ash as shown in Fig. 8. This study indicates the possible separation that could be achieved in a washing process. Further these two size fractions were subjected to flotation studies using commercial flotation reagents and the eco-friendly collector AB to study the performance efficacy of the developed reagent.

3.5 Flotation Studies on −0.5 mm and −0.25 mm Size Fractions Using Commercial Collector and Frother and 'Collector AB'

Flotation studies on −0.5 mm coal and −0.25 mm size fractions using commercial collector-frother and the developed single reagent Collector AB were performed. The dosage variation optimization studies were carried out extensively and the main outcome of the tests are highlighted here at comparable ranges of yield and ash

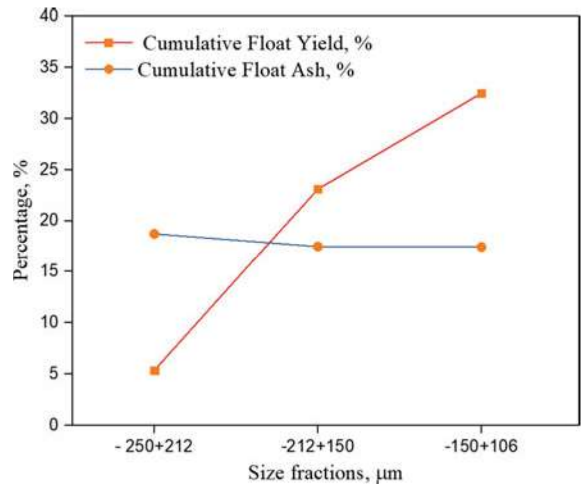


Fig. 8 Cumulative yield versus ash of float (−0.25 mm)

content of the concentrates. Table 3 shows the flotation test results on variation of yield at similar/equivalent ash values in the concentrate (Figs. 9 and 10).

The commercial collector at 0.0412 kg/t and commercial frother at 0.0055 kg/t indicate that a concentrate of 32.45% yield at 16.84% ash could be obtained in −0.5 mm size fraction.

The newly developed single reagent, Collector AB at 0.087 kg/t resulted in a concentrate of 43.83% yield at 16.69% ash which was found to be superior to the commercial reagent dual system at (32.45% yield & 16.84% ash) equivalent ash levels in the concentrate at 0.0412 kg/t collector and 0.0055 kg/t frother dosages. These results indicate that the single reagent, 'Collector AB' has better flotation separation

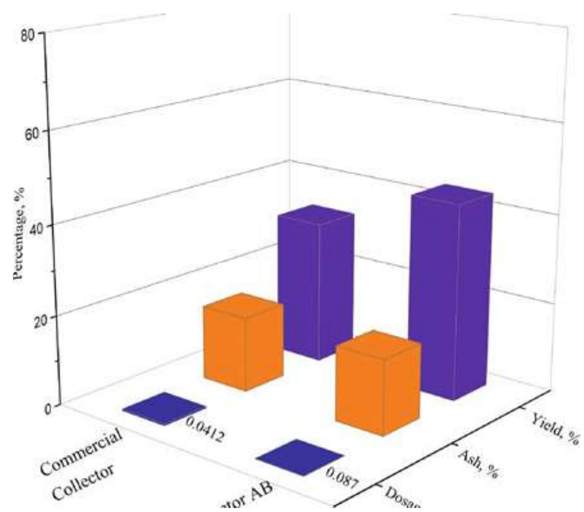


Fig. 9 Flotation results of −0.5 mm coal concentrate

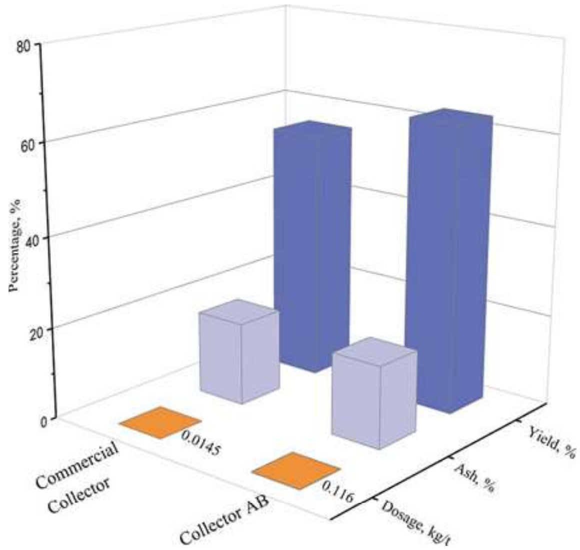


Fig. 10 Flotation results of −0.25 mm coal concentrate

Table 3 Flotation test results of coal

Flotation Reagent	Product	Yield, %	Ash, %	Ash distribution, %
−0.5 mm size coal				
Commercial collector & frother	Concentrate	32.45	16.84	20.61
	Tailings	67.55	31.16	79.39
Collector AB	Concentrate	43.83	16.69	27.28
	Tailings	56.17	34.71	72.72
−0.25 mm size coal				
Commercial collector & frother	Concentrate	55.40	18.23	38.41
	Tailings	44.60	36.33	61.59
Collector AB	Concentrate	63.18	17.92	44.45
	Tailings	36.82	38.45	55.55

efficiency in terms of better yield of concentrate at equivalent ash in the concentrate. This also indicated that the coal macerals are not liberated to the requisite levels for the facilitation of better flotation to improve the yield with lower ash levels. It appears that more coal particles are in an interlocked state as the ash rejection in the tailings/non-float remains low around 30–35%.

A concentrate of 55.40% yield at 18.23% ash could be obtained at a commercial collector dosage of 0.0145 kg/t and frother of 0.0055 kg/t. This is superior to the concentrate obtained on 100% −0.5 mm coal using the same commercial reagents.

Flotation studies were also conducted on 100% −0.25 mm coal. A concentrate of 55.40% yield at 18.23% ash could be obtained using commercial collector (0.0145 kg/t) and frother (0.0055 kg/t). A concentrate of 63.18% yield at 17.92% ash could be obtained using the newly developed 'Collector AB' at 0.116 kg/t dosage. At equivalent ash levels (around 18% ash) in the concentrate, there is an improvement in yield when 100% -0.5 mm coal was reduced to 100% −0.25 mm size.

4 Conclusion

The flotation studies on coal using a commercial dual-reagent system of collector & frother and newly synthesized natural product based 'Collector AB' at two different size fractions indicate that the 'Collector AB' has better flotation performance efficiency with a higher yield of the concentrate. An improvement in yield was observed when 100% —0.5 mm coal was reduced further to 100% —0.25 mm size which could be attributed to better liberation at a relatively finer grind. The Collector AB, a novel single reagent, synthesized from a natural product is eco-friendly in nature and proved to be a good alternative to commercially available flotation reagents and other hydrocarbon oils presently being used for coal flotation. Hence, the developed single reagent for coal flotation paves the way to a sustainable and environmentally friendly solution to the coal washeries in treating coal fines and low-rank coals.

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