Froth flotation beneficiation and physiochemical characterization of coal from Achibo-Sombo-Dabaso area, southwestern Ethiopia

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ABSTRACT

This study was carried out with one of the physiochemical techniques of coal sample beneficiation using froth flotation technique for upgrading the quality of Achibo-Sombo-Dabaso coal, southwestern Ethiopia. The investigations aimed to beneficiate high impure Ethiopian coal and to minimize its impurities present, so that it can replace the imported coal and the environmental pollution generated during combustion is reduced. The proximate and ultimate characterization studies show that the raw coal samples contain 11.81–20.27% moisture, 22.47–36.58% ash, 22.74–34.85% volatile matter, 23.85–38.31% fixed carbon, 1.22–1.44% nitrogen, 0.57–1.9% sulfur with 3243.59–5295.34 kcal/kg calorific value. Froth flotation experiments were carried out on the raw coal samples at varying parameters of collector dosages (0.0095 kg/ton, 0.0283 kg/ton, 0.0472 kg/ton, 0.0661 kg/ton and 0.085 kg/ton of diesel oil), frother dosages (0.0922 kg/ton, 0.1845 kg/ton, 0.2767 kg/ton, 0.3689 kg/ton and 0.4611 kg/ton of n-octanol) and particle size (500–250, 250–125, 125–63 μm). The experimental results for the treated coal samples are 8.12–14.02% moisture, 7.49–13.62% ash, 21.92–30.64% volatile matter, 44.47–55.87% fixed carbon, 0.52–0.92% nitrogen, 0.25–0.41% sulfur content with 5243.40–6531.46 kcal/kg of calorific value. The results of this study indicate that the treated coal samples are relative with high calorific value, fixed carbon and low ash content compared to the raw samples. The coal samples were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and Scanning electron microscopy (SEM) to understand the flotation and size distribution of coal. Therefore, the froth flotation technique at parameters of collector dosages (0.0472 kg/ton of diesel oil), frother dosages (0.3689 kg/ton of n-octanol) and particle size (125–63 μm) is effective to increase the calorific value above 5000 kcal/kg and increment carbon content of Achibo-Sombo-Dabaso coal that suitable as an energy source in cement and steel industries.

1. Introduction

Coal is a combustible fossil fuel from the organic sedimentary rock that contains carbon, oxygen, hydrogen, sulfur, nitrogen, and trace amounts of a variety of other elements (Wakuma and Assaba, 2017; Rao and Anuradha, 2019). It is formed through the coalification processes in which plant debris was transformed from peat to lignite and then to the higher rank anthracite coal (Speight, 2015). According to the American society testing and materials standard (ASTM D-388), coal is classified into four categories as lignite, sub-bituminous, bituminous and anthracite (Suarez-Ruiz et al., 2019). Coal is used as an energy source in the industry, particularly in cement and metallurgical factories due to its higher energy density than other energy sources (Abraham, 2018; Liu et al., 2018a,b). Cement industries use coal as an energy source to burn the raw materials at high temperatures (~1450 °C) in a kiln. Metallurgical (steel or iron) industries are also using coal for smelting of iron at high temperatures (Abraham, 2018; Demoze, 2007).

Commercially coal is mined in more than 50 countries and about 70 countries are using coal. It is estimated that nearly two-thirds of energy supplies in China is from coal resources (Wakuma and Assaba, 2017; Liu et al., 2018a,b; Ilkwuagwu and Ofogbue, 2017). The largest coal-producing countries are the USA, China, Australia, India and South Africa. There is also significant consumption and production of coal in countries like Australia, Indonesia, Russia, South Africa and China for both local use and exports (Demoze, 2007; IEA, 2019). The world Annual consumption of coal is about 5,800 million tons per year, out of this about

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75% is used for the generation of energy having low ash content and high calorific value (above 5000 kcal/kg) and the rest 25% is used for industrial purposes with a calorific value of above 6000 kcal/kg (Abraham, 2018; Mishra et al., 2015).

The available coal resource in Ethiopia is estimated to be around 300 million tons (Demezo, 2007; Abraham, 2018; Habtezgi, 2001). It is widely distributed in the northern (Chilga basin), southwestern (Delbi-Moye, Yayto (Wittete, Achiho, Sombo, Dabaso and Kumbabe), Nejo and Arjo basin) and central Ethiopian plateau (Mush valley and Wuchale basin) (Abraham, 2018; Ahmed, 2008; Haftu et al., 2019; Wagaw, 2007).

Despite its availability, Ethiopian coal is characterized by high impurities (high ash and high sulfur), very low carbon content and calorific values based on ASTM-D-388 standards and degree of metamorphism (Demezo, 2007; Dejene, 2004; Suárez-Ruíz et al., 2019).

The major environmental impact of coal combustion is related to the emissions of particulate gases into the atmosphere. During combustion, the elements in coal are converted to their particular oxides in the form of gaseous or aerosols (liquid droplets) and adsorbed by particulates (fly ash) and continued through the flue gas stream as emissions. The emitted gases include sulfur oxides (SOx), water vapor, carbon dioxide (CO2), and nitrogen oxides (NOx). Other elemental hazardous air pollutants (HAPs) such as mercury and arsenic are also identified as major challenges to coal utilization (Ruiz et al., 2019; Singh, 2016).

Therefore, to solve these problems different researchers have tried to develop different beneficiation technology to minimize the impurity of coal and enhance the energy density (Mishra et al., 2015; Liu et al., 2018a, b; Behera et al., 2018). Coal beneficiation is the process of improving the fixed carbon content to increase the calorific value of the coal by removing the mineral matters. It involves the combustion behavior, reducing slagging, fouling characteristics, and minimizing particulate pollutants and gas emissions (Behera et al., 2018; Moshram et al., 2015).

Different physical, chemical and physiochemical beneficiation techniques are used for upgrading low-rank coals (Behera et al., 2018; Barma, 2019; Qu et al., 2015). The Froth flotation beneficiation technique is the most cost-effective and less expensive physicochemical beneficiation to separate finely dispersed minerals or mineral materials based on the hydrophobicity of coal particles and mineral matters. The method is based on prior surface wetting of fine coal followed by efficient separation by attachment of pure coal on the surface of hydrophobic oil reagents and detachment of impurities matters from the surfaces (Barma, 2019; Ni et al., 2018; Tian et al., 2017; Wen et al., 2017).

The main objective of this research is to upgrade the heating value of coal from the Achiho-Sombo-Dabaso area by minimizing the ash and sulfur content using froth flotation techniques, applying diesel oil as a collector and n-octanol as frother reagents. The selection of this reagent is based on the viscosity, low cost and high molecular weights. In addition, the proximate (moisture content, ash content, volatile matter and fixed carbon), ultimate analysis (carbon, hydrogen, oxygen, nitrogen, sulfur and ash), calorific value (heating value) and surface analysis of the coal before and after froth flotation beneficiation are conducted.

2. Geology of the study area

Geographically, Achiho-Sombo-Dabaso area is bounded between 8°21'30"N–8°24'0"N longitude and 35°55'30"E–36°1'30"E latitude in southwestern Ethiopia covering an area of 9.11 km² with elevation ranging from 1118 to 2331 m above sea level within Geba basin in Yayo coal field (Figure 1). The Achiho-Sombo-Dabaso area is found within the Geba in the southwestern Ethiopian Shield domain (Ahmed, 2010; Tadesse and Mengistu, 1997). The coal-bearing sedimentary sequence is sandwiched between the lower and upper basalts; Inter-Trappean continental sedimentation (Ahmed, 2008; Zerihun et al., 1998).

The sedimentary rocks were formed in the fluviolacustrine environment (Tadesse, 2000). The sedimentary succession at many places overlies uncomfortably the lower basalt and at some places on the basement rocks and mainly consists of a non-systematic sequence of fine-grained clastic sedimentary rocks such as siltstones, claystones, sandstones, mudstones, carbonaceous shales, oil shales and in the middle coal beds. Achiho-Sombo-Dabaso areas are mostly covered with lignite and a few sub-bituminous coal types (Tadesse and Mengistu, 1997; Ahmed, 2008) and the surface mining (strip mining) method is employed in the beginning to mine the coal. During mining, the topsoil and layers of rocks are removed to expose the coal beds as stated in (Figure 2a and b). Currently, the exploitation of coal is operating with three underground openings. Opening one and two are separated by about 11.2 m barrier pillar while opening three is about 9 m towards the south of opening two and 2 m below it and the mined coal was collected as shown in (Figure 2c) (Haftu et al., 2019).

3. Methodology

3.1. The sample preparation

Six coal samples (ARL1, ARL2, ARL3, ARL4, SR and DR) were collected from the Achiho-Sombo-Dabaso area and the collected samples were prepared according to the ASTM standards (ASTM D-2013) of coal preparation methods including crushing, milling and sieving. Crushing is the first stage of reducing the grain size of coal. The bulk sample from the crusher was milled by centrifugal milling and the milled coal sample was separated according to their size by sieve shaker (500–250 μm or 230 mesh; 250–125 μm or 60 mesh, 125–63 μm or 120 mesh) and 125–63 μm or 120 mesh is the optimum particle size, which was collected and stored in airtight plastic bags in order to minimize the oxidation of sample during preparation.

3.2. The preliminary test

The froth flotation experiment is conducted in Addis Ababa institute of Technology (AAIT). Working condition involves particle size, flow rate, a dosage of reagents (Diesel oil and N octanol) and impeller speed in order to test the percentage yield of the coal. The processes of optimization were used to obtain a better yield of the coal recovery and better efficiency, which were performed as a principle of one variable at a time (OVAT). The working ranges of parameters in froth flotation were optimized by fixing the particle size at three ranges of intervals (500–250 μm, 250–125 and 125–63 μm). The diesel oil collectors is varying from 0.0095 kg/ton, 0.0283 kg/ton, 0.0472 kg/ton, 0.0661 kg/ton and 0.085 kg/ton and n-octanol as frother stabilizer (0.0922 kg/ton, 0.1845 kg/ton, 0.2767 kg/ton, 0.3689 kg/ton and 0.4611 kg/ton) so that the yields were collected with corresponding dosage of reagents (Diesel oil and N octanol) and impeller speed in order to produce a better yield of the coal recovery.

The optimized size of 125–63 μm and Wedag flotation machine of 3 L were used to conduct these experiments. 90 g/min of the fine coal sample was mixed with 2.5 L of tap water and stirred for 3 min with an impeller speed of 2800 rpm until the coal particles were completely wetted by closing the air valve. Then 0.0472 kg/ton drops of diesel oil were added as a collector and then agitated again for 2 min and 0.3689 kg/ton of n-octanol was added as a frother and an air valve was opened to supply the air in the flotation cell condition to form the bubble particle. When bubble formation was started 0.5 L of water was added to fill the capacity of the cell. The formed bubble particle started to overflow the cell and the flow particles were collected. The collected and formed foam is continued until the white foam was observed which indicates that the entire solid particles in the cell are attached to the oil collectors. Finally, the collected particle was filtered and dried in a hot oven at 80°C and the flotation concentrate yield is calculated using Eq. (1) (Kumari et al., 2018; Xia et al., 2019; Kaya and Tasdogen, 2019; Shafteeq et al., 2015).

3.3. Flotation test

The optimized size of 125–63 μm and Wedag flotation machine of 3 L were used to conduct these experiments. 90 g/min of the fine coal sample was mixed with 2.5 L of tap water and stirred for 3 min with an impeller speed of 2800 rpm until the coal particles were completely wetted by closing the air valve. Then 0.0472 kg/ton drops of diesel oil were added as a collector and then agitated again for 2 min and 0.3689 kg/ton of n-octanol was added as a frother and an air valve was opened to supply the air in the flotation cell condition to form the bubble particle. When bubble formation was started 0.5 L of water was added to fill the capacity of the cell. The formed bubble particle started to overflow the cell and the flow particles were collected. The collected and formed foam is continued until the white foam was observed which indicates that the entire solid particles in the cell are attached to the oil collectors. Finally, the collected particle was filtered and dried in a hot oven at 80°C and the flotation concentrate yield is calculated using Eq. (1) (Kumari et al., 2018; Xia et al., 2019; Kaya and Tasdogen, 2019; Shafteeq et al., 2015).
\[
\text{Yield} \% = \left( \frac{M_c}{M_f} \right) \times 100
\]

where \( M_c \) is the weight of concentrate and \( M_f \) is the weight of feed of coal sample in grams.

### 3.4. The proximate analysis

This part involves measuring the moisture content (%) (ASTM D-3302), ash content (%) (ASTM D-3174), volatile matter (%) (ASTM D-3175) and fixed carbon (%) (ASTM D-388).

### 3.5. The ultimate analysis

#### 3.5.1. Carbon and hydrogen

These parameters were determined by using EA 1112 flash CHNS/O analyzer in Addis Ababa University, Department of Chemistry. The working conditions of the analyzer were carrier gas flow rate (120 ml/min), reference flow rate (100 ml/min), oxygen flow rate (250 ml/min), furnace temperature (900 °C), oven temperature (75 °C) and oxygen injection time (5 s). For the determination of CHNS, the Flash EA smart Analyzer was operated with the dynamic flash combustion of the powder sample. 3 mg of powder sample was weighed in a tin container that was introduced into the combustion reactor through the Thermo Scientific MAS plus Auto-sampler in the presence of oxygen. After combustion, the resulting gases were conveyed by a helium flow to a layer filled with copper, then swept through a column that provides the separation of the combustion gases. Finally, Thermal Conductivity Detector (TCD) was used for detecting the resulting gases.

#### 3.5.2. Nitrogen determination

For Nitrogen content determination Kjeldahl method is used. 2.00 g of prepared coal sample was weighed and put into a Kjeldahl digestion flask with 20 ml of sulfuric acid with two Kjeldahl tablets as a catalyst.
Then the flask was slightly heated in an inclined position adjusted at 390 °C and allowed to boil for 6 h. During the digestion, the NH₄⁺ ion ((NH₄)₂SO₄) was formed and the mixture was diluted with 100 ml of distilled water for cooling.

To neutralize the solution and convert the NH₄⁺ ion into an ammonia gas excess of 50 ml (50% (w/v)) of sodium hydroxide was added. Then the flask was connected to the Kjeldahl distillation apparatus followed by boiling and condensation of the gas with 70 ml (4% (w/v)) of boric acid. Then 4–7 drops of Tashoro’s (MR and BCG (Bromocresol green indicator)) indicator were added to the receiving flasks for 5 min. Finally, the distillate was titrated against 0.1 M hydrochloric acid. The same procedure was repeated for the blank solution and the percentage of nitrogen (%) was calculated using Eq. (2).

\[
\text{Nitrogen (%) = } \frac{V_2 \ (ml) - V_1 \ (ml) \times 0.1 \ M \times 14.07 \ g/mol}{\text{Weight of sample taken}} \times 100 \quad (2)
\]

where \( V_1 \) and \( V_2 \) are the volumes of HCl consumed blank solution and sample in titration respectively (Ryemshak et al., 2016).

3.5.3. Sulfur determination

To determine the sulfur content using the Eschka method, 1 g of coal sample was weighed in a porcelain crucible and mixed with 3 g of Eschka mixtures (2 g of magnesium oxide and 1 g of anhydrous sodium carbonate). The mixture was covered with another 1 g of Eschka mixture for preventing the loss of sulfur as sulfur dioxide. Then the crucible was put in a cold muffle furnace and heated gradually at 800 °C for 60 min. The compounds of sulfur that evolved during combustion were reacted with the Eschka mixture under oxidized conditions and converted to Sodium Sulfate and Magnesium Sulfate. Then the product was digested by diluting 1 M of HCl solution with intermittent stirring for 45 min. The digested solution was filtered into 400 ml beakers and three drops of methyl orange were added until the color was turned to neutral. Next, the sample was heated to boiling and 10 ml of 10% BaCl₂ was gradually added while stirring in continuous boiling for 30 min. Finally, the solution was filtered after cooling down by thoroughly washing with hot water and the residue BaSO₄ formed was burned at 500 °C and weighed. The formed BaSO₄ was used to calculate the sulfur content applying Eq. (3) (Speight, 2015; Samila et al., 2020; Adekunle et al., 2015).

\[
\text{Sulfur (%) = } \frac{32}{233} \times \frac{\text{Weight of BaSO₄ formed (g)}}{\text{Weight of sample taken (g)}} \times 100 \quad (3)
\]

3.5.4. Oxygen determination

Oxygen content (%) in the given sample was determined by differentiating another ultimate analysis with moisture from 100 and was calculated by using Eq. (4).

\[
\text{Oxygen % = 100} - (C% + H% + N% + S% + A% + M%)
\]

3.6. Caloric value (ASTM D-2015-96)

The analysis of caloric value is made by using the Adiabatic Bomb calorimeter in the central laboratory of the Geological Survey of Ethiopia (GSE). Approximately 1 g of powder coal sample was weighed in nickel crucible and placed in a bomb by supporting over the ring. Then Oxygen supply was purged across the valve into the bomb until the pressure was reached 25–30 atm for completing the combustion. Then the bomb was placed in the nickel bucket of a calorimeter that was filled with 2000 ml of distilled water. After the power was switched on the initial temperature was recorded and when the bucket temperature was equilibrated with the bomb temperature the bomb was fired. Then the maximum temperature was recorded from the reader and the bomb was removed from the bucket and the knop valve was opened gradually to release the residual gas pressure before attempting to remove the cap. All unburned pieces of fuse wire from the bomb electrode were removed, straightened and measured their combined length in cm to know the net amount of wire burned. Finally, the bomb washing was titrated with a standard sodium carbonate solution using a methyl orange indicator.

Then the gross heat combustion was calculated by applying Eq. (5).

\[
\text{GCV} = \frac{tW - e1 - e2 - e3}{m}
\]

where \( t \) = Temperature change in °C, \( W \) = Energy equivalent of calorimeter in Cal/C, \( e1 \) = correction in calories for heat formation of nitric acid (0.0709 N alkali used for titration, \( e2 \) = correction in calories for heat formation of sulfuric acid, \( e3 \) = correction in calories for heat combustion of fuse wire and \( m \) = mass of coal sample taken in grams.

3.7. Scanning electron microscopy (SEM)

For Scanning electron microscope analysis a field emission electron microscope model (Inspect F50) was used to determine the nature of the surface morphology of coal samples at the central laboratory of Addis Ababa Science and Technology University (AASUT). Small amounts of powder sample were put on the conductive carbon tape which is attached to the sample holder. The operating parameters of SEM were adjusted with a voltage of 15.00 kV, a working distance of 11.4 mm and different magnification powers.

3.8. Fourier transforms infrared spectroscopy (FTIR)

The constituent surface functional groups of the original raw and treated coal sample were separately determined by using FTIR (Perkin Elmer spectrum, USA) at central laboratory of AASTU with the wave-number ranges of 4000–400 cm⁻¹, scan rate 32 and resolution 16. Final results were collected and reported by transmittance versus wave-numbers (Liu et al., 2018a,b).

3.9. X-ray diffraction (XRD)

The crystalline structures and mineral matters were identified in both raw and floated samples by using XRD, (SHIMADZU-7000, Japan) equipped with Cu Kα radiation (\( \lambda = 1.5406 \) Å) and 20 ranges from 2 to 70° with continuous scanning at central laboratory of AASTU. The operating parameters were with an applied voltage of 40 kV, a current of 30 mA and with scanning rate of 3 deg/min (Qu et al., 2015).

4. Results and discussion

4.1. Flotation results

As shown in Table 1, the variables that are used during the flotation process are particle size, flow rate, dosages of reagents (diesel oil and n-octanol) and impeller speed. The preliminary of these working parameters in this study was done based on the principles of one variable at a time (OVAT).

After the addition of diesel oil as a collector in the flotation of coal particles and condition for a time of 1-min big bubbles formation was seen in which particles were not attached to the surface of the oily bubbles (Figure 3a). But after the addition of n-octanol as frother and increasing the conditioning time to 5 min, small bubbles were stabilized (Figure 3b). The formed foam particles were skimmed off and filtered by using Whatman filter paper to separate the residue from its solution (Figure 3c). The filtrate of both tailing (residue) and concentrate (foam) was dried and taken for characterization. The result obtained in this study is comparable to the results of other researchers with a maximum mineral removal efficiency of ash content and the pure coal particle recovery yields and accepted particle size for flotation within ranges of 50–250 μm (Chen et al., 2018; Mao et al., 2020, Wang et al., 2018).
4.2. Proximate analysis

The result of proximate analysis of raw and treated coal samples is shown in Figure 4. The moisture content for raw coal is ranging from 11.81% to 20.27% and 8.12%–14.02% for treated coal. As shown in Figure 4, the raw coal at Sombo (sample SR) has the highest moisture content whereas at Dabaso (sample DR) has the smallest moisture content as compared with other samples. The highest value of moisture implies lower carbon contents that lead to lower heating value and higher costs for transportation and storage (Wakuma and Assaba, 2017). The applied flotation technique reduced the moisture contents significantly (Figure 4). Volatile matter for raw coal samples (Achibo, Sombo

| Particle size (μm) | Flowrate (g/min) | Impeller speed (rpm) | Collector | Frother | Yield (%) | Airflow rate | Ash content (%) |
|--------------------|------------------|----------------------|-----------|---------|-----------|--------------|----------------|
| 125–74             | 30               | 2000                 | Diesel oil (10 kg/t) | MIBC (500 g/t) | 80.7 | 18.22 | 8.27 | Chen et al. (2018) |
| 74                 | 90               | 1900                 | Kerosene (3 kg/t) | Sec-ocetyl alcohols (1 kg/t) | 76.41 | 22.64 | 3.3 L/min | 29.87 | Mao et al. (2020) |
| 125–63             | 90               | 2800                 | Diesel oil (0.0472 kg/t) | N-Octanol (0.3689 kg/t) | 77.5 (Achibo) | 20.89 | 7.49 (Achibo) | This study |
|                    |                  |                      |           |         | 73.5 (Sombo) | 24.16 | 10.74 (Sombo) |             |
|                    |                  |                      |           |         | 67.9 (Dabaso) | 29.71 | 12.68 (Dabaso) |             |

Figure 3. Froth flotation procedures and resulting coal particle: (a) Coal sample dispersed in water before the addition of frother and collector (b) After addition of frother and collector and (c) Foam particles filtered using Whatman filter paper.

Figure 4. Graph of proximate analysis of raw and treated coal samples.
and Dabaso) is ranging from 22.74% to 34.85% and for the treated samples is below 30.64%. The Achibo samples have the highest volatile matter with both raw and floated samples (Figure 4). The higher volatile matter in coal indicates the lower rank of the coal and increasing volatile matter also increased the quantities of combustible gases, which directly decreases the amount of fixed carbon and consequently decreases the heating value of the coal. Finally, in this study, it is found that the flotation technique used is effectively increasing the volatile contents of the coal (Figure 4), which in turn increases the staying time in storage rooms.

The ash content of the raw coal is ranging from 22.47% to 36.58% (Figure 4) within the range of the previous study (10.2%–54.6%; average 38%) in the Achibo-Sombo area (Ahmed, 1998). The Achibo second layer (ARL2) has the highest value of ash content of the three sampling sites which is 36.58% and the lower ash content is recorded on Achibo fourth layer (ARL4) which is 22.47%. The increase of ash content led to reducing the burning capacity, affects combustion efficiency, increases handling cost, and causes large slaggings. The ash content and its behavior at high temperatures affect the design and type of ash handling system that is employed in the coal-utilization process. At high-temperature coal ash become sticky and eventually forms molten slag. The increase of the ash content in coal leads to decreased quality or rank because volumes of high impurity reduce the coal efficiency.

After treatment the ash content is reduced on average by about 36% (Figure 4). This confirms that the ash content of the Achibo treated coal sample will be much more reduced after treatment when compared with others that show relatively high fixed carbon and calorific value. The ash yield was related to moisture and volatile matter that was shown in Figure 4, Achibo has high amounts of ash and volatile matters but is lower in moisture content. But Sombo and Dabaso have moderate amounts of ash and volatile matter. Therefore, the ash content of the treated samples is highly reduced so that can be ignited easily and are extremely reactive in combustion. Generally, the relationship of proximate value and the increasing amount of moisture content is leading to increasing the ash and volatile matters. Therefore, the presence of moisture content is decreased relatively with the volatility of the coal increases, and vice versa.

The fixed carbon indicates a rough estimation of the heating value of the coal. The fixed carbon contents for raw coal samples are in the range of 23.15%–38.31% in Figure 4. All raw coal samples were showing less than 40% of the fixed carbon content which implies that lower the carbon content is highly affecting the heating efficiency of the coal. From the studied area Achibo’s fourth layer was the highest amounts of fixed carbon as compared to others, but the first layers of Achibo (ARL1) and Sombo have lower amounts of fixed carbon. The lower amount of fixed carbon is due to ash, volatile matter and moisture content of the coal.

The fixed carbon for the treated coal samples obtained after beneficiation experiments is in the range of 44.47%–55.87% as shown in Figure 4. From the three study areas, the lower layers of Achibo have shown more carbon content and Achibo’s third layers (ARL3) have lower carbon than all other areas. The upgrading of the fixed carbon in lower layers was due to the burial depth increase which increases the ranks of coal, which leads to increasing the carbon number of that coal. The highest fixed carbon observed in Achibo leads to a higher calorific value than the other sites. Therefore, an increasing the fixed carbon content was results in an increase in heating value and decreasing ash contents. Finally, from the observed experimental value of Achibo-Sombo-Dabaso coal, the value of the fixed carbon content for raw samples was in the range of 23.85%–38.31%, but after treatment, the average value of fixed carbon content raised to 55.87%.

4.3. Ultimate analysis

The result of the ultimate analysis is shown in Table 2 and shows clearly the differences between raw and treated coal samples. The carbon content for the raw samples is ranging from 32.90% to 37.54% and for the treated coal samples is ranging from 54.12% to 61.06% as stated in Table 2. During the treatment of coal under high temperature some carbon contents will lost as volatile matter in the case of fixed carbon that is why the ultimate carbon is differing from the proximate fixed carbon. The obtained ultimate carbon content is not confirmed by world a coal standard which specifies greater than 70% (Ryemshak et al., 2016). Therefore, the lowering in the ultimate carbon in coal indicated that the coal is categorized under the low rank.

The hydrogen contents for the raw coal samples are ranging from 4.85% to 5.28% and for treated coal samples hydrogen content was reduced and ranges from 2.98% to 3.26% (Table 2). The higher amount of hydrogen content affects the combustion behavior of the coal and is the characteristic of low-grade coal. But the low value of hydrogen indicates a higher grade category. The obtained result of hydrogen is in agreement with the ASTM standard which specifies hydrogen contents for coal quality in the ranges of 3–5.6% for peat to bituminous coal types and 2–4% for anthracite coal (Ryemshak et al., 2016). Based on the hydrogen result the studied coal samples are classified under lignite and sub-bituminous types of coal and after flotation the Achibo fourth layer is graded into ranges of bituminous types of coal.

The nitrogen content from the experimental value was in the range of 1.28%–1.33% for the raw coal sample and after treatment; the nitrogen content was reduced and is ranging from 0.64% to 0.92% in Table 2. Achibo’s fourth layer sample shows the highest amount of nitrogen contents as compared with the Sombo sample. The presence of nitrogen in coal samples will pollute the environment by releasing nitrogen oxides into the atmosphere in certain combustion conditions. It also decreases the heating values of the coal. Low-rank coal has high amounts of nitrogen content (Ryemshak et al., 2016) but as the grade of the coal increases (matures) the extractable nitrogen content is decreasing. The obtained result of nitrogen content in coal is in agreement with accepted world coal quality standards which contain a maximum limit of 2% (Ruiz et al., 2019; Wang et al., 2018).

The investigated result of sulfur content in raw coal samples is ranging from 0.67% to 1.18% but after treatments, the sulfur content is reduced to a range of 0.25%–0.33% as shown in Table 2. The fourth layer of the Achibo contains the highest amount of sulfur content. The high amount of sulfur in coal was lowering the heating ability of the combusted coal due to the formation of the high ash of sulfur content in the forms of barite (BaSO₄), galena (PbS) and gypsum (CaSO₄.2H₂O). So, the higher sulfur causes an emission of SO₂ gas that is responsible for pollution of the environment that causes acid rain and lung cancer on

Table 2. The ultimate result for both raw and treated coal.

| Area       | Sample raw/Treated for (n = 2) | Carbon (%) | Hydrogen (%) | Sulfur (%) | Nitrogen (%) | Oxygen (%) | Reference |
|------------|--------------------------------|------------|--------------|------------|--------------|------------|-----------|
|            | Raw/Treated                    | Raw/Treated | Raw/Treated  | Raw/Treated | Raw/Treated  | Raw/Treated |           |
| Achibo     | ARL4/AFI                       | 37.54      | 61.06        | 5.28       | 2.98         | 1.18       | 0.25      | 1.28      | 0.92      | 15.77     | 12.58     | Ruiz et al. (2019), Wang et al. (2018), Zhen et al. (2019) |
| Sombo      | SR/SF                          | 32.90      | 54.12        | 4.85       | 3.26         | 0.67       | 0.33      | 1.33      | 0.64      | 12.9      | 16.89     |           |
| Standards  | >70%                           | 2-6%       | <1%          | 0.3-2%     | Less 18%     |           |           |           |           |           |           |           |
human health (Ryemshak et al., 2016; Adekunle et al., 2015). Then beneficiation of coal by flotation technique was used to minimize the amounts of sulfur content in the coal sample which leads to increased calorific values and qualities of the coal. Generally, the sulfur contents in a study are confirming the limit standard for coal quality which contain less than 1% used in the metallurgical and power generation industry (Zhen et al., 2019).

The oxygen content for raw coal samples is ranging from 12.9 to 15.77% and for treated coal samples it ranges from 12.58 to 16.89% as shown in Table 2. The expected value of oxygen content for treated coal would be lower than that of untreated coal samples, due to highly reduced ash content and increment of carbon number. Therefore, values of oxygen content for treated coal samples are higher than that of untreated coal in Sombo.

4.4. Calorific value

The calorific value (heating value) analysis obtained from the result shown in Table 3 is that the raw sample is ranging from 3243.59 to 4506.27 kcal/kg for Achibo’s first to fourth layers. But after the treatment, the calorific value is ranging from 5714.03 to 6531.46 kcal/kg. The Sombo and Dabaso coals also increase in their calorific value to 5462.78 kcal/kg and 5243.40 kcal/kg respectively. This shows that the beneficiation by froth flotation technique is an appropriate approach to increase the calorific value of the coal. Specifically, the calorific value of the top layer of Achibo, Sombo and Dabaso liberated very low amounts of heat due to their high impurities which affect the combustion efficiency of the coal. The top layer also accounted for lower carbon contents and higher amounts of volatile matter than the remaining layers. The results from Table 3 prove that as the burial depth of Achibo increases the organic carbon content increases which are responsible for an increase in the calorific value.

The proximate value is given a rough estimation of the liberating heat value. The fixed carbon in Achibo’s third and fourth layers was higher than in other sites so they liberated more calorific value. Then after treatment, the calorific value of the coal is increased due to the removal of impure materials with the help of chemical reagents. In

| Area       | Sample Raw and Treated respectively | Average Calorific value (n – 2) | Reference                            |
|------------|-------------------------------------|----------------------------------|--------------------------------------|
|            |                                     | kcal/kg                          | MJ/kg (divided by factors of 238.85) |
|            |                                     | Raw                               | Treated                              |
|            |                                     | Raw                               | Treated                              |
| Achibo coal layers | ARL1/AF1                  | 3918.89                         | 5714.03                              | 16.41                             | 23.92 |
|            | ARL2/AF2                  | 3243.59                         | 5642.87                              | 13.58                             | 23.63 |
|            | ARL3/AF3                  | 4448.81                         | 6392.13                              | 18.63                             | 26.76 |
|            | ARL4/AF4                  | 4506.27                         | 6531.46                              | 18.87                             | 27.34 |
| Sombo      | SR/SF                    | 5295.34                         | 5462.78                              | 22.17                             | 22.87 |
| Dabaso     | DR/DF                    | 4975.14                         | 5243.40                              | 26.83                             | 21.95 |
| Standard   | For coal quality          | >5000 kcal/kg                   |                                     |                                    |

In Ilkwuagwu and Ofoegbu (2017), Behera et al. (2018)

| Area       | Sample Raw/treated | Fixed carbon (%) | Calorific value (kcal/kg) | Ranks (categories) of coal |
|------------|--------------------|------------------|----------------------------|---------------------------|
|            |                    | Raw               | Treated                     | Raw                       | Treated                           |
| Achibo     | ARL1/AF1           | 23.85             | 50.82                       | 3918.89                   | 5714.03                           | Lignite A                            | Sub-bituminous B |
|            | ARL2/AF2           | 24.29             | 54.36                       | 3243.59                   | 5642.87                           | Lignite B                            | Sub-bituminous A |
|            | ARL3/AF3           | 33.81             | 44.47                       | 4448.81                   | 6392.13                           | Lignite A                            | High volatile bituminous C |
|            | ARL4/AF4           | 38.31             | 55.87                       | 4506.27                   | 6531.46                           | Sub-bituminous C                    | High volatile bituminous C |
| Sombo      | SR/SF              | 34.21             | 49.91                       | 5295.34                   | 5462.78                           | Sub-bituminous B                    | Sub-bituminous B |
| Dabaso     | DR/DF              | 24.98             | 52.81                       | 4975.14                   | 5243.40                           | Sub-bituminous C                    | Sub-bituminous C |

Table 4. Ranking both treated and untreated coal according to ASTM D-388.

Figure 5. SEM image of Sombo raw (a) and treated coal (b).
Achibo due to increments of the burial depth than all other areas the amount of fixed carbon was highly changed from its value of 38.31%–55.87% in the lower layer. In this way, the more calorific value was recorded by changing from 4506.27 kcal/kg to 6531.46 kcal/kg. The calorific value of the Sombo raw sample is increased from the value of 5295.34 kcal/kg to the treated value of 5462.78 kcal/kg. These increments of heating value were due to the change in fixed carbon from 34.21% to 52.81% and the reduction of ash content from its value of 27.08%–10.74% (Figure 4). The obtained results of calorific value are in agreement with ASTM standards stated that for coal quality greater than 5000 kcal/kg is more used metallurgical and energy source industry (Ilkwuagwu and Ofoegbu, 2017; Behera et al., 2018).

4.5. Coal ranking

ASTM D-388 is used for the classification of coal rank or ages based on the amounts of fixed carbon and calorific values results. As shown in Table 4, the gross calorific value and fixed carbon results of raw samples

| Peak position | Wavenumbers ranges | Functional groups | Compound class |
|---------------|--------------------|-------------------|----------------|
| 675           | 850–550            | C–Cl stretching   | Halo compounds (s) |
| 790           | 840–790            | C–C bending       | Alkene (m) |
| 912           | 920–885            | O–H bend          | Carboxylic acids(m) |
| 1042          | 1060–1020          | Si–O–Si or Si–O–C stretching | Sulfoxide (s) |
| 1456          | 1480–1450          | C–H bending       | Alkane (m) |
| 1605          | 1605–1595          | C=C stretching vibration | The aromatic hydrocarbon of the benzene ring(s) |
| 1618          | 1620–1610          | C=C stretching   | α, β unsaturated ketone (s) |
| 2915, 2922    | 2935–2915          | C–H stretching   | Alkane (m) |
| 3689          | 3695–3600          | Free O–H stretching | Alcohol (m) |

Where s-strong and m-medium.
are used to classify the rank of raw coal that was found in rank between lignite B and sub-bituminous B. According to the results, Sombo and Dabaso have better calorific values than Achibo. Generally, the gross calorific value (Kcal/kg) is increased from its lower value to higher and this enables to rank the coal in the range of sub-bituminous B and high volatile bituminous C according to world coal standards.

4.6. Surface morphology

The surface morphology of coal particles for the raw and treated sample is shown in Figure 5. The SEM result of the surface of raw coal particles indicate the various size of nonuniform and irregular holes with uneven texture (Figure 5a). The holes on the surface will adsorb more
collector reagent rather than spreading on the surface of the coal particles that decrease the performance of the flotation process. By contrast, after treatment with the flotation technique, the surface of the coal demonstrated several physical and chemical changes with homogenous surface morphology (Figure 5b). The SEM image after treatment indicates that the particles are more compacted and increased in the homogeneity of particles. This might be due to the removal of impurities and the increment of carbon content on the sample surface (Cheng et al., 2019).

4.7. Functional groups

FTIR analysis was made to understand the nature of the bonds and to recognize various functional groups which exist on the surface of the coal samples. As shown in Figure 6, the FTIR spectra of the coal surface and the peaks at 2915 cm\(^{-1}\) and 2922 cm\(^{-1}\) correspond to the C–H stretching of alkene. The peaks at 1605 cm\(^{-1}\) and 3689 cm\(^{-1}\) are representing the C=C stretching of aromatic hydrocarbon of benzene rings and O–H stretching of an alcohol group respectively. The peaks at 1042 cm\(^{-1}\) represent the bending vibration of carbon-hydrogen bonds (C–H) on a benzene ring. The peaks at 912, 790, and 681 cm\(^{-1}\) are the substitution of carbon-hydrogen bonds (C–H) and the bending vibration of carbon-hydrogen bonds (H–C–H) as shown in Table 5. The spectral peaks of ash forming minerals in coal analysis were illustrated in the fingerprint region such as at peaks of 532 cm\(^{-1}\) corresponding to aromatic pairs of sulfides–S(–SH (Yu 2017).

To summarize, the results of FTIR confirm that the intensity of the C–H and C=C stretching is increased which may indicate an increase in carbon contents in the treated sample and the surface of low-rank coal has many hydrophilic functional groups (Roya et al., 2020; Zhu et al., 2020; Yang et al., 2020).

4.8. Crystal structures and mineral identification

The crystalline structure and mineral compositions for both raw and treated coal particles are examined by using XRD (Figure 7). The peaks at 2-theta values of 12.55 and 22.14° were recognized as the (310) and (528) planes of SiO\(_2\) respectively (JCPS (Joint Committee on Powder Diffraction Standards) card no. 027-6605 Silicon oxide (Quartz)). But the peaks at 2-theta values of 26°, 33° and 47° were corresponding to (449), (185) and (139) planes of Fe\(_2\)S\(_2\) respectively (JCPS card no. 042-1340 Iron Sulfide (Pyrite)). Whereas the peaks at 2-theta values of 24° and 56° were corresponding to (487) and (232) the planes of TiO\(_2\) respectively (JCPS card no. 021-1272 Titanium oxides (Anatase, syn)). Hence, the XRD results of both samples show that the coal particle contained the minerals of quartz, pyrite and anatase. Both intensities of pyrite and quartz minerals are minimized at treatment, due to the removal of sulfide and silicon in the form of ash that shows a decrement in the intensity of the peaks. XRD results confirm that quartz (SiO\(_2\)), pyrite (Fe\(_2\)S) and anatase (TiO\(_2\)) which are responsible for ash increment in the sampled coal are common and the obtained results are in agreement with (Chen et al., 2018; Jiang et al., 2021).

5. Conclusion

The Achibo-Sombo-Dabaso coal deposit is treated by physiochemical beneficiation using the froth flotation technique to increase the calorific value by using diesel oil and n-octanol to obtain the coal recoveries of 77.5% yield of Achibo, 73.5% yield of Sombo and 67.9% yield for Dabaso. The amount of ash and sulfur content of the area is highly reduced from its maximum value of 36.58% of second layers of raw Achibo to a minimum value of 7.49% of first layers of Achibo treated sample. The grades of raw coal in the study area were categorized under lignite B coal to sub-bituminous B groups with calorific values ranging from 3243.59 to 5295.34 kcal/kg. But after treatment of the samples, the grades of the coal are upgraded to sub-bituminous B-high volatile bituminous C with the calorific values ranging from 5243.40 to 6531.46 kcal/kg. The results of FTIR confirm that the intensity of the C–H and C–C stretching is increased which is a clear indication of an increase in carbon contents in treated samples. The SEM image after treatment indicates that the particles are more compacted and the homogeneity of particles is increased. This might be due to the removal of impurities (mineral matters) and the increment of carbon content in the samples. The results from the XRD confirm that the quartz (SiO\(_2\)), pyrite (Fe\(_2\)S) and anatase (TiO\(_2\)) which are the main source of ash are reduced after treatment. Generally, the overall finding of this study confirms that the calorific value of Achibo-Sombo-Dabaso coal is upgraded to the expected level for the desired application using the froth flotation technique. Finally, the beneficiated coal is upgraded in to ranges of quality coal that contains a higher calorific value of above 5000 kcal/kg and lower sulfur content of less than 1% is suitable for the intended purpose such as in cement and steel industry as energy sources.

Declarations

Author contribution statement

Temam Usman: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

Samuel Abicho: Contributed reagents, materials, analysis tools or data; Wrote the paper.

Daniel Meshesha; Getachew Adam: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

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Data availability statement

Data included in article/supp. material/referenced in article.

Declaration of interest’s statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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