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CLEANING OF BEYŞEHİR (BAYAVŞAR) COAL IN TURKEY WITH HYDROPHOBIC FLOCCULATION USING WASTE MOTOR OIL

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Abstract: In this study, the hydrophobic flocculation behavior of lignite coal obtained from Beyşehir region in Turkey and the effect of some parameters were investigated. These parameters were selected as pH, amount of dispersant, amount of binding liquid, flock growth time, stirring speed, flocculation time and solid ratio. The ash content (ash, %) and combustible recovery (CR, %) of the flocks obtained as a result of the experiments were determined. As a result of the studies, the optimum pH value (3), amount of sodium silicate (1 mL), amount of waste motor oil (3 mL), flock growth time (1 min), stirring speed (1250 rpm), flocculation time (2 min) and solid ratio (5 g) were determined. The hydrophobicity of fine coal grains was increased by using waste motor oil. According to the hydrophobic flocculation results of coal grains, flocks with 17.03% ash content and 99.06% combustion recovery were obtained. While the contact angle of the original coal was 44°, it was observed that the contact angle of the obtained flocks reached 117°. It was determined from experiments that the surfaces of the coal grains have a very high hydrophobicity. As a result, clean coal with a reduced ash content of 53.22% was obtained.

***Keywords*:** Lignite, hydrophobic flocculation, combustion recovery, waste motor oil, contact angle, Beyşehir, Turkey.

Introduction

It is known that there are many countries that provide a significant part of their energy needs from coal. Especially, with the development of

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technology, more than 1/4 of its primary energy needs are supplied from coal.[1] There are many low-quality coal deposits in the world. These deposits have coals with low liberalization grain sizes. For this reason, it is necessary to make them in fine sizes before enrichment.[2] On the contrary, coal particles in the size of dust are wasted in all process stages of coal, although it is produced in large sizes.

Conventional methods are insufficient to separate ultra-fine grains from each other. New methods should be found to recover valuable minerals from wastes and to prevent some environmental problems.[3] Flotation is one of the enrichment methods that can be applied to fine-grained coals. In this method, separation is performed depending on the surface properties of coal and inorganic components.[4] Although flotation is the most common method used, it is not very effective for ultrafine particles.[5] As an alternative to the flotation method; flocculation, oil agglomeration and hydrophobic flocculation methods are used for the enrichment of fine-grained coals.

Hydrophobic flocculation is one of the aggregation methods based on the flocculation of fine particles in aqueous suspension with the effect of hydrophobic interaction and mechanical stirring. It is separated from fine-grained coal impurities depending on the differences of surface properties between organic and mineral matter. Medium-density oils such as non-polar kerosene and diesel are added to the suspension to increase the hydrophobicity of the grains.[6] In addition, dispersants such as sodium silicate, sodium polystyrene sulfonate, tannic acid, sodium hexametaphosphate, sodium phosphate and sodium pyrophosphate are used to prevent non-hydrophobic particles from agglomeration with hydrophobic particles and to increase selectivity.[7] The main purpose of these processes is to cover the hydrophobic grains with oil film in order to increase hydrophobicity and to keep the agglomerated grains together by forming a bridge between the particles.[6,8] Many studies have been conducted on removing impurities from hydrophobic particles by hydrophobic flocculation.[3,5,7,9-15]

In this study, it was aimed to clean the fine-grained coal by using waste motor oil by hydrophobic flocculation. Hydrophobic flocculation behavior was investigated using different parameters during coal enrichment. Ash content, combustion recovery, contact angle, zeta potential and calorific value of the flocks were determined and interpreted in detail.

Materials and Method

Materials

In this study, lignite coal of Beyşehir (Bayavşar) Konya region was used. A sample of 100 kg brought to the laboratory. The coal sample was crushed to under size of 3.5 cm by jaw crusher. Then, the sample was ground at a ball mill Ø180x362 mm with an internal volume of 9 L. After the size reduction process, the entire coal sample was sieved and -212 µm sized sample was obtained. The particle size distribution of the coal sample was determined and the d_{80} value, which is the sieve opening that through 80% of the grains passes, was determined as 75 µm. The sample was dried and analysed. Analysis results were given in Table 1.

Table 1. Proximate analysis of the coal sample.

Sample	Ash, (%)	Volatile Matter, (%)	Fixed Carbon, (%)	Upper Calorific Value, (kcal/kg)
Coal	36.40	42.78	20.82	2529

Calorific value of the coal sample was determined using LECO brand AC-350 adiabatic oxygen bomb calorimeter by ASTM D 5865-11a standard.[16] Ash analysis was carried out in accordance with the standard (ASTM D 3174-04, 2010)[17] using Gemo brand TT107 model ash furnace. Volatile matter determination was carried out using the standard test method (ASTM D3175-18)[18]. The remaining part from moisture, ash and volatile matter in the sample was calculated as the fixed carbon value. In the experiments, Merck brand sodium silicate (1%) and Castrol CRB Turbomax 15/40 brand waste motor oil were used as dispersant and binder, respectively. Solution pH was adjusted with HCl (1%) and NaOH (5%).

Method

Hydrophobic flocculation experiments were carried out in a 400 mL beaker with 4 barriers. These barriers were placed on the inner surface of the beaker both to obtain a homogeneous mixture and to increase the collision efficiency of the grains. After flocculation, non-flocculated particles were removed by a special siphoning system placed in a beaker. The suspension prepared with 300 mL of distilled water and 5 grams of coal sample was mixed for 2 minutes at 1000 rpm. After adjusting the solution pH to the desired value, the dispersant was added and mixed for 2 minutes. Later, waste engine oil was added to the system and mixed for 2 minutes. At the end of this period, the stirring speed was reduced to 180 rpm and flock growth was achieved. Experiments were carried out at different values of pH (3, 5, 7, 9 and 11), amount of dispersant (1, 1.5, 2 and 2.5 mL), amount of binding liquid (1, 2, 3 and 4 mL), flock growth times (1, 3, 5 and 7 min), stirring speed (250, 500, 750, 1000 and 1250 rpm), flocculation time (1, 2, 3 and 4 min) and solid ratio (3, 4, 5 and 6 g). The schematic representation of the steps followed in the experiments was given in Figure 1.

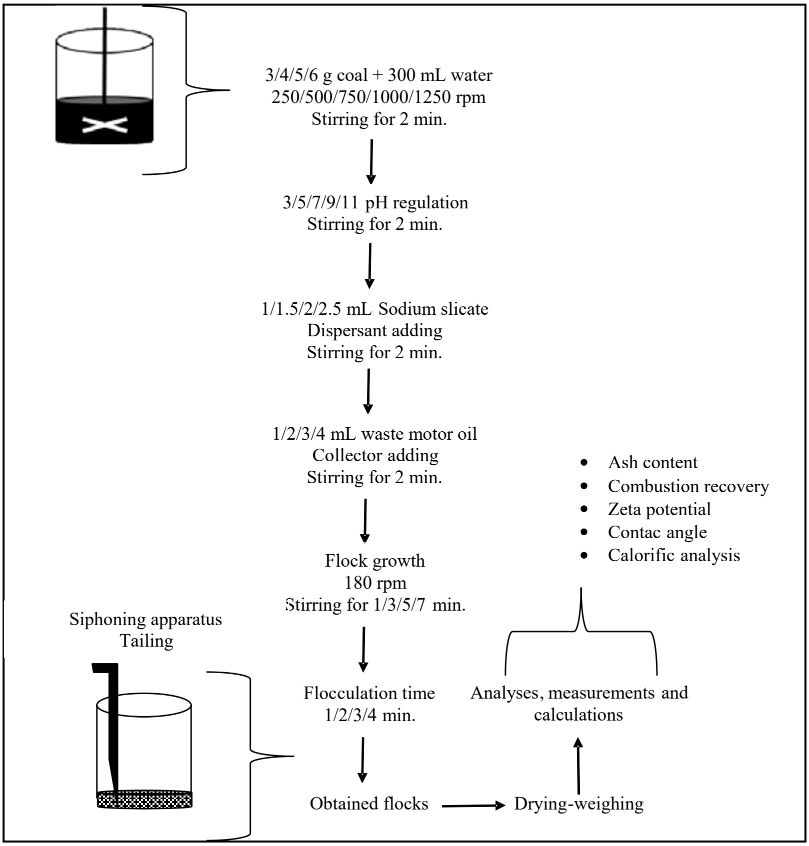

Figure 1. The flow diagram followed in the experiments.

The flocks formed after the experiments were collected on the upper part of the suspension. The other non-flocculated part was removed with a specially designed siphoning system. Flocks were filtered through the filter paper, dried at 105 °C for 4 hours and weighted. The flock recovery (FR%) after flocculation was calculated by Eq. 1. The ash content of the hydrophobic flocks was determined and the combustion recovery (CR%) of the flocks was calculated using Eq. 2.

$$FR,\% = \frac{W_c}{W_f} \cdot 100 \quad (1)$$

$$CR,\% = \frac{FR(100-A_c)}{100-A_f)} \quad (2)$$

where A_c is the ash content of clean coal, A_f is the ash content of feed W_c is weight of clean coal and W_f is weight of feed.

Brookhaven Zeta Plus brand zeta meter (measurement range -150 – +150 mV, standard deviation 2 mV) was used for the zeta potential measurements. The zeta potential of the fine-grained coal sample and mixture of coal-waste motor oil sample were measured at natural pH and different pH values in suspension. Measurement results were given in Figure 2.

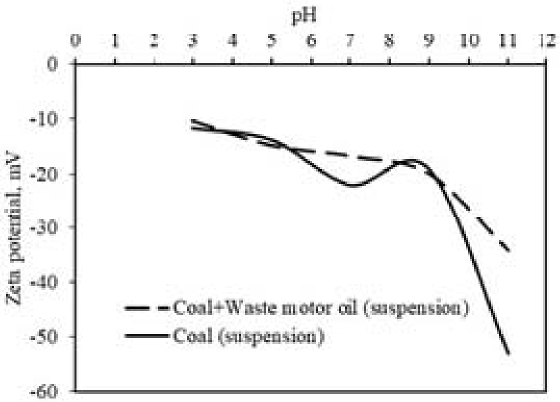

Figure 2. Zeta potential values of suspensions containing coal samples at different pH values.

The coal sample and flocks obtained after hydrophobic flocculation were placed in a specially prepared apparatus. Pellets were formed with the help of a hydraulic press under 20 kN pressure. The static contact angles of these pellets, which were smooth on both surfaces, were measured with the KSV brand Cam 101 model contact angle measuring device (Figure 3). Each measurement was repeated four times and average values were calculated.

Figure 3. The creation of pellets and contact angle measurement.

Results and Discussion

The experiments at different pH values (3, 5, 7, 9 and 11) were carried out to determine the effect of pH on hydrophobic flocculation of the fine-grained coal sample. The results obtained were given in Figure 4. Amount of sodium silicate, amount of waste motor oil, flock growth time, stirring speed, flocculation time and solid ratio were kept constant.

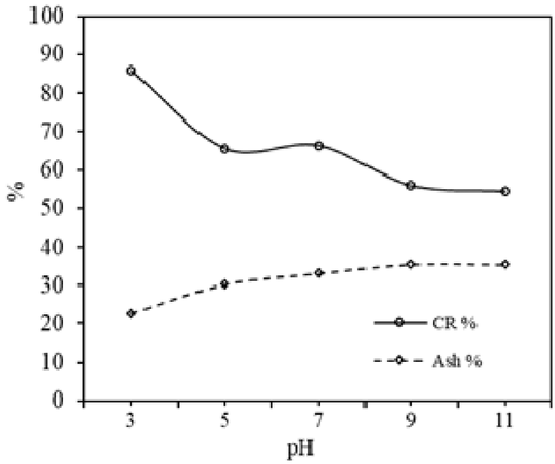

Figure 4. Variations of combustible recovery and ash percentage depending on pH (sodium silicate = 1mL, waste motor oil = 1 mL, stirring speed = 1000 rpm, flock growth time = 1 min, flocculation time = 2 min, solid ratio = 5 g).

As seen in Figure 4, it was seen that the ash content of the hydrophobic flocks increased with increasing pH. However, it was determined that the combustible recovery of the flocks was high at low pH values. The clean coal was obtained at pH = 3 with a combustible recovery of 85.92% and an ash content of 22.78%. The zeta potential measurements of the particle surfaces in the suspension were evaluated depending on the pH values. According to the measurement results, it was determined that the zeta potential at pH 3 was -10.36 mV, the zeta potential at pH 11 was -34.21 mV and at the neutral pH value was -21.99 mV. Electrostatic interactions decrease and hydrophobic interaction between coal particles increases at low pH values. On the contrary, larger zeta potentials are measured in alkaline solutions and are known to increase the electrostatic repulsion between particles.[19,20]

To determine the effect of the amount of sodium silicate added as a dispersant in different values (1, 1.5, 2, 2.5 mL) on the hydrophobic flocculation of the coal sample, experiments were carried out at pH 3 by keeping other parameters constant. The results were given in Figure 5.

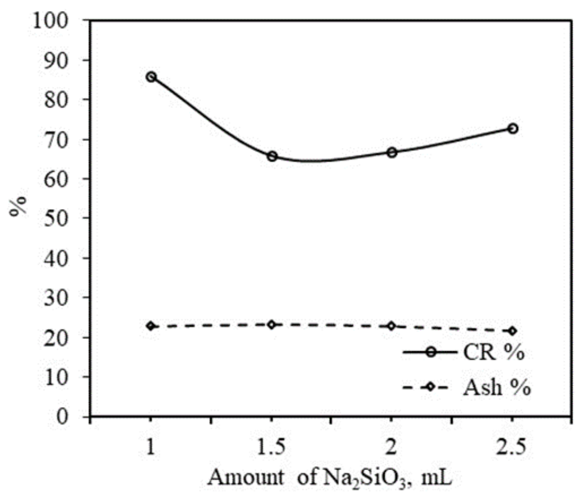

Figure 5. Variations of combustible recovery and ash percentage depending on the amount of sodium silicate (pH = 3, waste motor oil = 1 mL, stirring speed = 1000 rpm, flock growth time = 1 min, flocculation time = 2 min, solid ratio = 5 g).

As can be seen from Figure 5, in the hydrophobic flocculation experiments performed with waste motor oil, there was not much change in ash content with the increase of sodium silicate. The clean coal was obtained with 85.92% combustible recovery and 22.78% ash content using 1 mL sodium silicate. It is stated that dispersants such as sodium silicate, sodium polystyrene sulfonate, tannic acid, sodium hexametaphosphate, sodium phosphate and sodium pyrophosphate are used in hydrophobic flocculation processes to increase the selectivity of non-hydrophobic particles.[7] It is known in the literature that Ermenek coals have similar properties in hydrophobic flocculation with the addition of sodium silicate.[3] In addition, it was determined that sodium silicate had no negative effect on hydrophobic flocculation experiments.[3,15]

The results of hydrophobic flocculation performed with waste motor oil used in different amounts (1, 2, 3.4 mL) were given in Figure 6.

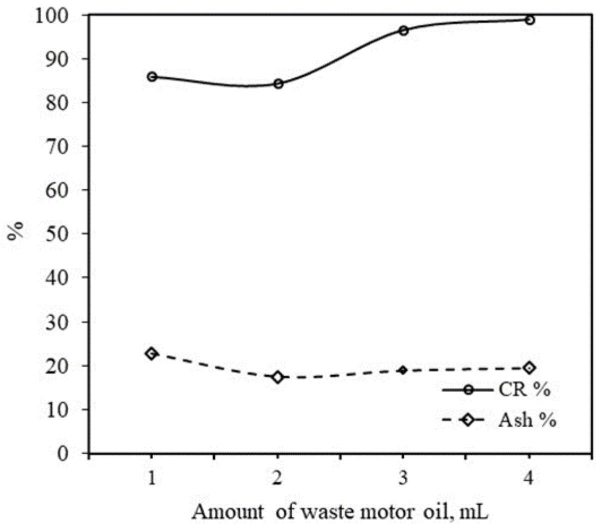

Figure 6. Variations of combustible recovery and ash percentage depending on the amount of waste motor oil (pH = 3, sodium silicate = 1mL, stirring speed= 1000 rpm, flock growth time= 1 min, flocculation time=2 min, solid ratio=5 g).

With the increase in the amount of oil, the ash content decreased while the CR value increased. However, it was found that the ash content increased after a certain amount with the increase in the amount of oil. It is known that the amount of oil creates unstable flocks after a certain value. The unstable nature of the flocks ensures rapid dispersion.[21] Also, it is easier for mineral substances to enter between the flocks.[22] The clean coal was obtained with 96.45% combustible recovery and 18.15% ash content using 3 mL waste motor oil.

In Figure 7, the effect of the flock growth time on the hydrophobic flocculation test results was examined. The stirring speed was reduced to 180 rpm and the flocks were grown at different times (1, 3, 5, 7 min). As can be seen from Figure 7, it is seen that the CR values decrease with the increase of the flock time and the ash values increase even if a little. Therefore, flock growth time was taken as 1 min.

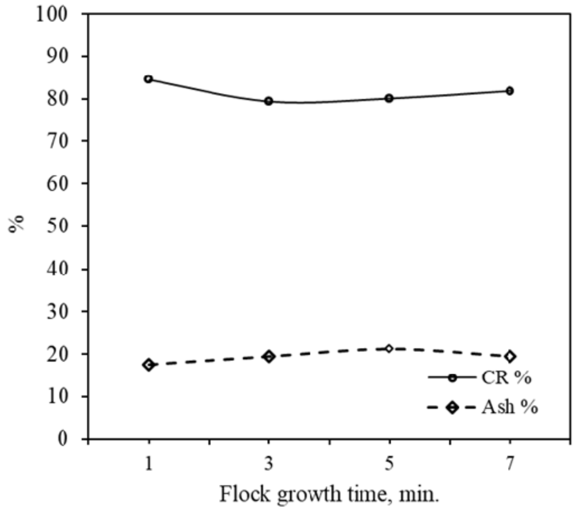

Figure 7. Variations of combustible recovery and ash percentage depending on flock growth time (pH = 3, waste motor oil = 1 mL, sodium silicate = 1 mL, stirring speed = 1000 rpm, flocculation time = 2 min, solid ratio = 5 g).

In order to investigate the effect of stirring speed on hydrophobic coal flocculation, experiments were conducted at different stirring speeds (250, 500, 750, 1000 and 1250 rpm). As can be seen from Figure 8, ash contents decrease with high CR with increasing stirring speed. For this reason, the optimum stirring speed of 1250 rpm was determined. Flocks were obtained with an ash content and combustion recovery, 17.03% and 99.06%, respectively. According to Sahinoglu and Uslu (2008),[21] oils provide better dispersion in suspension with increasing stirring speed and the possibility of particle collision with each other increases. In the literature, it is stated that the flocculation and aggregation effect increases with the increase of the stirring speed and decreases after the critical value.[23,24] On the contrary, it is thought that the decrease in the stirring speed accelerates the entry of ash-forming inorganic materials into the agglomerated coal grains. For these reason, it can be said that ash content (%) has increased.[3,21, 25-27]

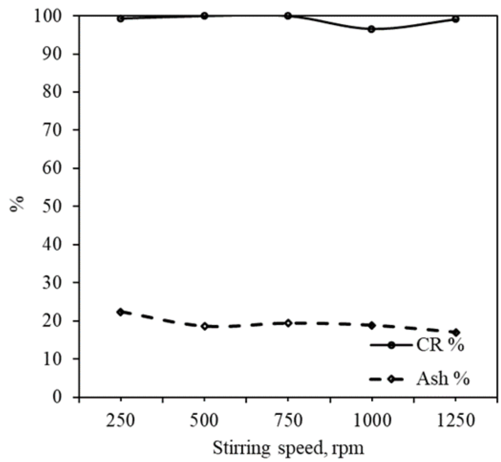

Figure 8. Variations of combustible recovery and ash percentage depending on stirring speed (pH = 3, waste motor oil = 1 mL, sodium silicate = 1mL, flock growth time = 1 min, flocculation time = 2 min, solid ratio = 5 g).

In Figure 9, the effect of different flocculation time (1, 2, 3, 4 min) on hydrophobic flocculation of coal was examined. The flocculation time was determined as 2 min. The clean coal was obtained with 99.06% combustible recovery and 17.03 % ash content. As time increased, there was an increase in very little ash content and a decrease in CR values. A similar situation was mentioned in the literature.[28] With the increase in the flocculation time, the particles were brought together with the oil. However, as the time increased, it was seen that the mineral grains entered the flocks.[29]

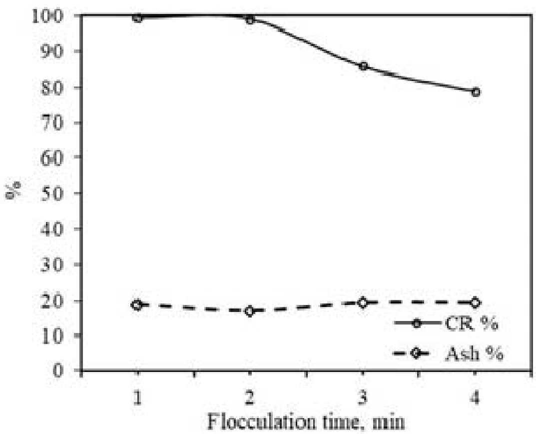

Figure 9. Variations of combustible recovery and ash percentage depending on flocculation time (pH = 3, waste motor oil = 1 mL, sodium silicate = 1 mL, stirring speed = 1250 rpm flock growth time = 1 min, solid ratio=5 g).

As seen in Figure 10, the effect of solid ratio on hydrophobic flocculation was examined. According to the experimental results, optimum results were obtained by using 5 g of coal in the suspension. Although CR values were high in all solid ratios, the lowest ash content (17.03%) was obtained by using 5 g.

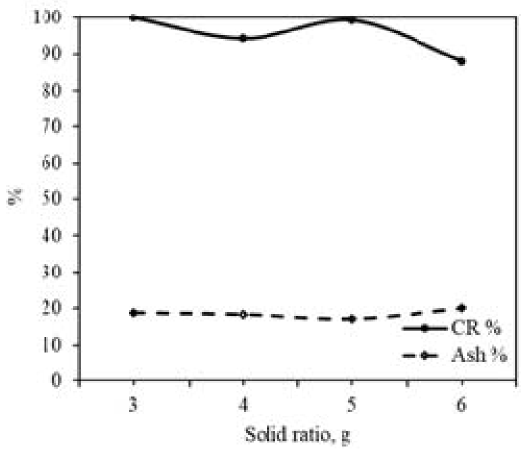

Figure 10. Variations of combustible recovery and ash percentage depending on solid ratio (pH = 3, waste motor oil = 1 mL, sodium silicate = 1 mL, stirring speed = 1250 rpm, flock growth time = 1 min, flocculation time =2 min).

Contact angle measurements, indicative of its hydrophobicity, were carried out by the KSV brand Cam 101 model contact angle measuring device. While the contact angle of the original coal was 44°, the contact angle of the obtained flocks was measured as 117° (Figure 11).

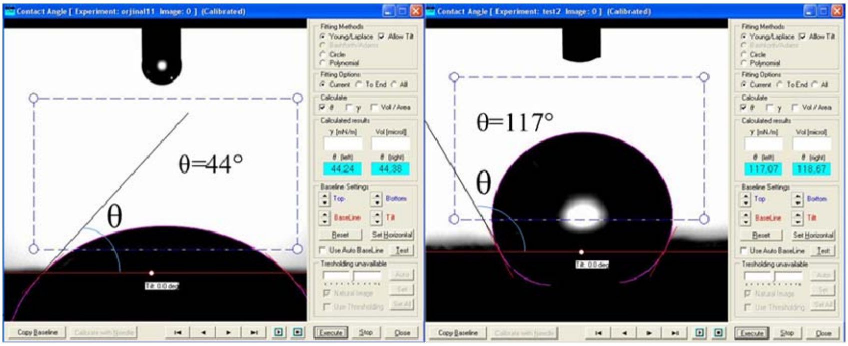

Figure 11. Contact angle measurement results.

This result confirms that the flocked surfaces obtained are highly hydrophobic. Measuring the zeta potential value of -10.93mV also supports these results. In addition, the calorific values of the obtained flocks were measured. The coal sample's calorific value was increased from 2529 kcal/kg to 5447 kcal/kg.

Conclusions

Hydrophobic flocculation experiments were carried out using Beyşehir coal sample. In addition, waste motor oil was used as a binder liquid in the experiments to obtain clean coal. The effects of pH, dispersant (Na_2SiO_3) amount, binder liquid (waste motor oil) amount, flock growth time, stirring speed, flocculation time and solid ratio on hydrophobic flocculation behavior of coal sample were studied in detail. The optimum operating parameters for hydrophobic flocculation were determined as follows: pH= 3, Na_2SiO_3 amount (1 mL), waste motor oil amount (3 mL), flock growth time (1 min), stirring speed (1250 rpm), flocculation time

(2 min) and solid ratio (5 g). According to the optimum results, hydrophobic flocs with 17.03% ash content and 90.06% combustible recovery were obtained. The calorific value of the coal sample, which was 2529 kcal/kg, was increased to 5447 kcal/kg.

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