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Performance Comparison of Waste Cooking Oil on Coal Slime Flotation with Sunflower Oil and Kerosene

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ABSTRACT

This study explores the potential use of waste cooking sunflower oil (WSO) as an eco-friendly collector for coal slime flotation. WSO and coal slime are both waste materials and can be hazardous to human health and the environment, if not disposed of properly. In this study, co-disposal of the two wastes was investigated; a kerosene (petroleum derived oil) and crude sunflower oil (CSO) were used for collector efficiency comparisons. This study also presents a green, low-cost and environmentally friendly alternative. Kinetic flotation tests were carried out to study the flotation selectivity, flammability and combustible recovery. Contact angle measurements were performed with 3 different oils (CSO, WSO and kerosene) by sessile drop method to determine the hydrophobicity and surface properties of coal. Fourier-transform infrared (FTIR) spectroscopy was utilized to analyze for the chemical composition of both WSO and slime coal samples .

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Keywords:
Sunflower oil; Waste cooking oil; Kerosene; Coal slime; Flotation

INTRODUCTION

Waste cooking oil, a liquid waste from kitchens and food sectors, can be hazardous to the environment and human health [1, 2]. The challenges of the treatment of WCOs are primarily involve: the disposal-collection strategy and waste reconversion [3]. In terms of WCO reconversion, they can be employed as primary raw materials in a variety of industrial processes, for instance for the production of biofuel or bio-lubricants, animal feed, and asphalt additives. Other WCO applications are only those that are directly related to their chemical composition.

The mining and washing of coal produces coal slime as a by-product. It is a semi-solid material comprised of water and crushed coal. It is mostly composed of flotation waste from coking coal preparation plants, slurry created after hydraulic coal transportation as well as washing slurry from power plant coal washing facilities [4-6].

Kerosene is a common collector in coal flotation, although it has a high collector consumption (approximately 10 kg/t) and a high cost [7, 8]. Turkey produces 5 million tons of bituminous run of mine coal annually. About 5-7% of these coals are taken under the thickener as "coal slime" or "coal fines wastes" after being washed in dense medium plants. After being dewatered using filter presses, these coals are either disposed of in waste pools or used as fuel for thermal power plants. Concentration of these coal slimes with very fine size (d50 ~ 35 μm) by flotation method is a very costly process. Because it contains high amounts of clay minerals and these clays adsorb large amounts of collectors. Prices per liter of petroleum product in Turkey are higher than in other countries of the world many times over. Therefore, to optimize the coal flotation process in Turkey, an economic collector must be found. In the present case, Turkey does not have any flotation plant for the recovery of coal slime. The biggest reason for this is the collector cost. Kerosene is a petroleum product collector, which is particularly preferred in coal flotation due to its high yield and selectivity. As petroleum products are non-renewable and have extremely flammable properties, there is a need for new research on alternative collectors. In this context, the use of vegetable oils as an alternative collector to petroleum products for coal flotation has been reported by researchers [9-19]. Vegetable oils (VOs) have low concentrations of nitrogen, sulfur,

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and heavy metals, it is also a non-polluting raw material that is renewable and readily available. VOs are being actively researched for alternative applications, such as biodiesel production and utilization as raw materials in the chemical and industrial sectors. These oils contain long-chain fatty acids that possess dual functions as frothers and collectors, thanks to their ester groups that contribute to their frothing abilities [10, 20, 21].Thus, it was assumed that WSO would improve coal particle flotation recovery [9, 12, 22]. Moreover, crude soybean and olive oils, each vegetable oils, were mentioned withinside the literature as collectors for fine coal recovery. For example, Colza oil turned into used as a collector to get high-calorific and low-ash coal. Additionally, Polanga and Mahua oils were utilized as collectors to increase the floatability of high ash Indian non-coking coal [23]. Numerous researchers have indicated the potential use of vegetable oils or waste cooking oils (WSO s) as collectors in coal flotation and agloflotation processes [11, 21]. The use of WSO s as a collector can be cause to as the two main problems that can occur in flotation plants. The first of these is the clogging of the liquid carrier pipes and sluices with oil. This problem can be solved by using various surfactants. The other problem is the oily wastewater that will come out after the process. There are many methods that can be applied to remove oils from oily waste water. For example, gravimetric separators remove free oil from wastewater [24, 25]. According to the US Department of Agriculture (USDA) data for the years of 2021-2022 world vegetable oil production is 214.8 million tones. This oil is used for cooking more than half of it, and on average ~ 100 million tons of WSO is produced every year [26, 27]. In this study, WSO was used as a collector in the coal flotation and the results were compared with the kerosene and sunflower oil as a collector.

MATERIAL AND METHODS

Materials

The coal slime utilized in the flotation studies was sourced from the thickener underflow stream of a coal washing plant in Turkey, where Zonguldak bituminous coal was processed (Fig. 1).

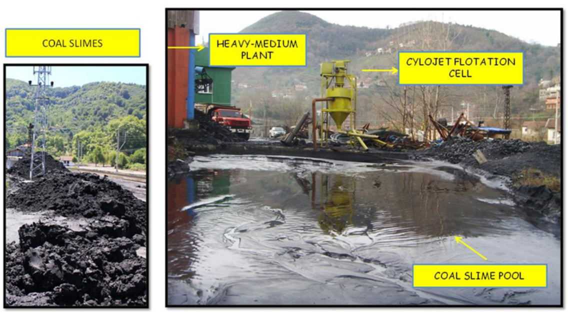

Figure 1. Image of coal slimes and clean coal production from the slime pool by flotation.

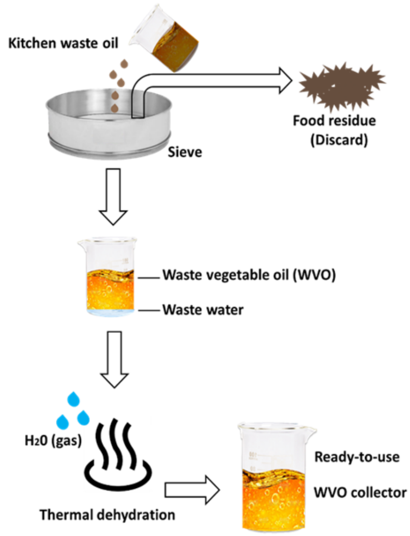

Figure 2. Flowsheet of collector prepared from kitchen waste oil.

The plant operates with a capacity of 150 t/h. Coal with a size of -100 + 1 mm is washed by a heavy-medium cyclone with three products; raw coal with a size of -1 mm is deslimed by a hydrocyclone (Ø400 mm) and the coarser fraction is routed through coal spirals. The hydrocyclone overflow material (coal slime) is sent to a thickener (Ø12 m) and then pumped into the coal sludge pool.

WSO was obtained from the kitchen waste cooking oil. The waste oil was collected in a 500 ml beaker with mixture of oil, waste water and food residue. Due to waste oil contains food residue, firstly the raw materials were sieved for the removal of solid waste and then WSO collector was prepared via filtration and heating processes. For contact angle measurements, we obtained the coal sample as a lump size from the entrance of a washery plant located in Zonguldak, Turkey.

Characterization of Coal Fine Wastes

Proximate analysis was performed to determine the characteristics of the waste coal sample. Proximate analysis was performed on a dry basis and the ash content was 33.75% the total sulfur content was 0.68%. The calculated volatile matter and fixed carbon contents are 29.10% and 37.45%, respectively. According to these results, it can be said that coal has high ash content and low sulfur content. It is in the category of medium volatile coal in terms of volatile matter content.

As a result of the size analysis of the waste coal sample with the Mastersizer 3000 laser diffraction particle size analyzer, the average particle size (d50) of the material was found to be 45 micrometers, and the d80 size was 190 micrometers.

Table 1. Properties of the WSO.

Physical Properties	Value
Viscosity	73 mPa/s
Density	0.91 g/cm³
Oil-water interfacial tension	22.02 mN/m

Collector Types; CSO, WSO and Kerosene

CSO (2000 g/t) was obtained from Kristal company in Izmir, Turkey and used as received in the experiments. WSO (2000 g/t) was used multiple times to cook meat, vegetables, and fish. Properties of the WSO are presented in Table 1.

Kerosene (from Tupras Company in Izmir, Turkey) as a traditional collector was used to compare with the proposed collectors in coal flotation process. Eucalyptus oil is used as a frother.

METHODS

Kinetic Flotation Tests and Release Tests

Flotation tests were carried out in a Denver machine with a 1.5-liter cell capacity. The impeller speed was set to 1100 revolutions per minute. In all experiments, the solid ratio was set at 10%. The sample was mixed well with tap water in the cell for 10 minutes before each flotation test to ensure that the surface was wet. Kinetic flotation tests were performed to determine WSO, CSO and kerosene collection potential (for 30, 60, and 240 seconds of froth scrapping).

The obtained concentrates underwent filtration, followed by washing with acetone and drying in an oven. Prior to initiating the kinetic flotation tests, a "release test" procedure, developed by Dell, was employed to determine the final washability limit of the coal sample [28]. The optimal washability result was achieved by varying stirring speeds in a Denver cell and employing high reagent dosages (10 kg/t WSO , 0.4 kg/t eucalyptus oil). Fig. 3 illustrates a schematic representation of the particle-oil adsorption process during coal flotation, using kerosene, CSO, and WSO.

To assess the flotation performance, various metrics including yield, assay, efficiency index, recovery, and selectivity index were examined. In this study, the comparison of flotation performance was based on the combustible recovery-concentrated ash curve. Additionally, the effectiveness of coal flotation was evaluated using an efficiency index (EI), which was calculated using Eq. 1 [29, 30].

$$EI = CR x \left(\frac{At}{Ac}\right) \quad (1)$$

where CR: combustible recovery, Ac:concentrate ash content, and At: tailing ash content [31].

Contact Angle Measurements

Contact angle is a common technique for determining a material's wettability. As mentioned earlier, wettability is determined by measuring the contact angle formed between the solid and the liquid surface when they come into contact [32].

The contact angle of kerosene, CSO and WSO was measured using the Sessile Drop method on a flat coal surface with an Attention theta contact angle goniometer (Fig. 4).

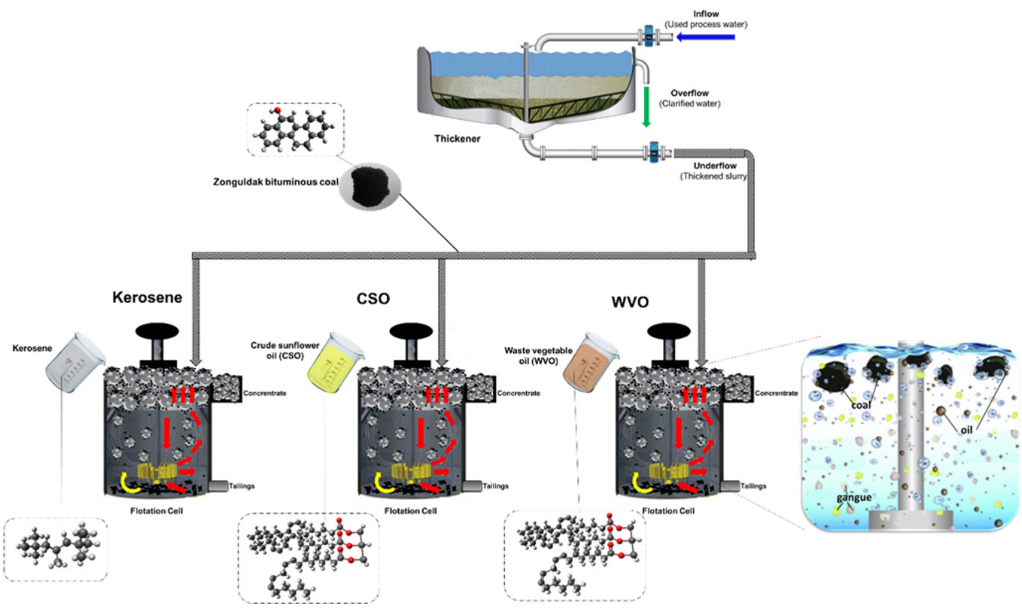

Figure 3. Schematic illustration of coal flotation with Kerosene, CSO and WSO.

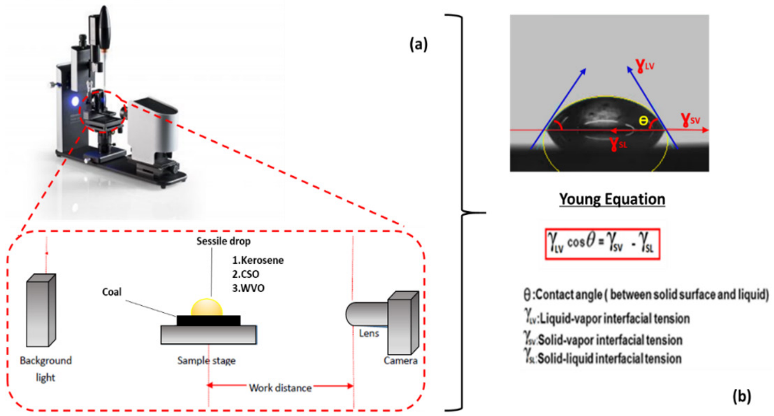

Figure 4. (a) The illustration of the contact angle goniometer (b) schematic representation of wetting statics in Young's equation for solid-liquid-vapor system.

Contact angle measurements were taken after a 15-20 second interval once the water drop size had increased. This approach was utilized to determine the contact angle values. All measurements were conducted at a temperature range of approximately 20-22°C.

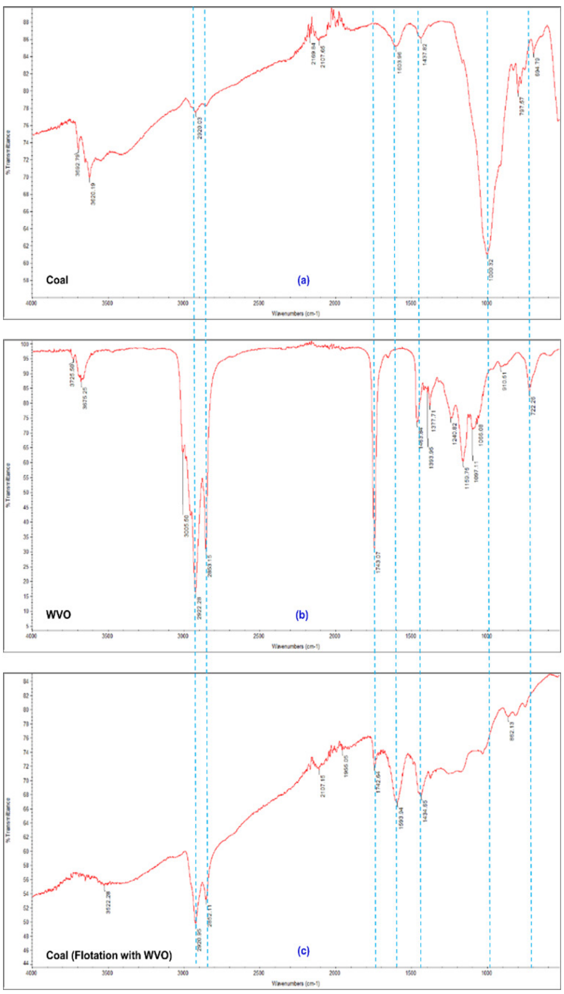

Figure 5. FT-IR spectrums of samples: a) coal, b) WSO, and c) coal floated with WSO.

The contact angle represents the angle created by a liquid droplet on a solid surface, as determined by the Young equation [33]. In Fig. 4 (b), the contact angle of an oil droplet on coal is depicted, influenced by three interfacial tensions: liquid-vapor, solid-vapor, and solid-liquid. This relationship is described by Young's equation, as shown in Eq. 2.

$$\gamma_{LV}\cos\theta = \gamma_{SV} - \gamma_{SL} \qquad (2)$$

where θ is the contact angle, γ_{LV} :liquid-vapor, γ_{SV}:solid-vapor, and γ_{SL}: solid-liquid are the interfacial tensions.

RESULTS AND DISCUSSION

FTIR spectra can be used to evaluate the chemical characteristics of coal, WSO and coal floated with WSO samples , which were recorded with Thermo Scientific Nicolet 6700 FT-IR Spectrometer, over range of 400–4000 cm^{-1}. The FTIR spectrum of coal is presented in Fig. 5.

The band at 1437 cm^{-1} is attributed to vibration of CH_2 group and hydrophobic functional [34, 35]. The peaks at 2853 cm^{-1}, 2922 cm^{-1} are related to C-H stretching. [36]. The peak at 722 cm^{-1} may be the O-H stretching [37]. The peaks at 3522 cm^{-1} and at 1593 cm^{-1} are for OH and COOH group, respectively. The peaks around 1000 cm^{-1} may be attributable to C-O-C. According to literature [30, 35, 38, 39] the bands at 3452 cm^{-1} were assigned to OH vibrations. The peaks observed at 2920 cm^{-1} is due to the aliphatic hydrocarbon groups vibration in coal [40].

Releasing test results for WSO, CSO, and kerosene is important for assessing their suitability for different applications, ensuring compliance with standards, and ensuring optimal performance and efficiency. As seen in Fig. 6, kerosene has a higher collection capacity than WSO. In the experiments using kerosene, 8.97% ash clean coal was recovered with 64.58% combustible recovery value, while in the experiments using WSO, 9.88% ash clean coal was

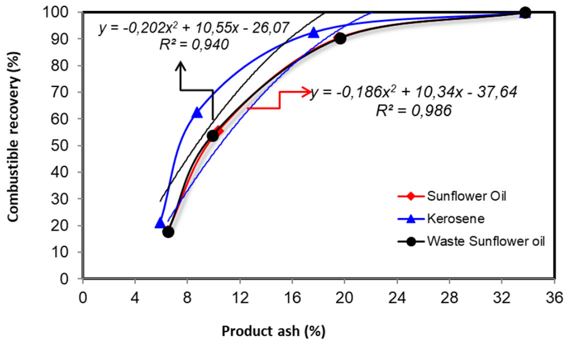

Figure 6. Release test results with WSO, CSO and kerosene.

recovered with 53.73% combustible recovery value. If clean coal product with 10% ash is desired to be sold, the kerosene collector has a combustible recovery rate of approximately 69%, while the WSO has a rate of around 54%. The lower combustible recovery of WSO has been hypothesized to be due to the hydrophilic oxygen bonds present in its structure, which limits its ability to collect. Kerosene is an effective collector due to its absence of oxygen groups and its purely hydrocarbon structure. Recent research suggests that oxygen-containing functional groups, particularly the carboxyl group, play a crucial role in enhancing coal surface wettability [41]. Zhou et al. (2015) have reported that carboxyl and hydroxyl groups are the most effective promoters of surface wettability based on XPS peak-split data. Fig. 7 illustrates the results of kinetic flotation tests conducted using CSO, WSO , and kerosene.

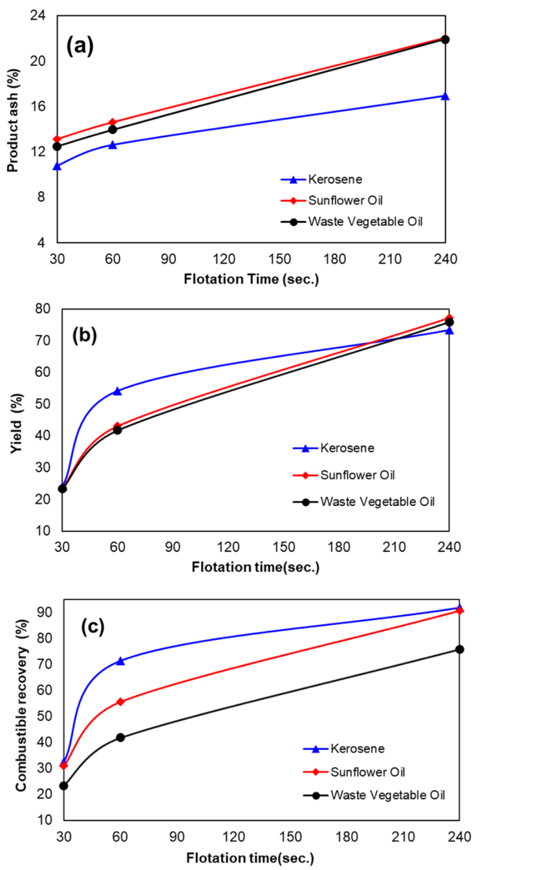

Figure 7. (a) Product ash, (b) yield and combustible recovery values obtained in kinetic tests depending on flotation time with WSO, CSO and kerosene used as collectors.

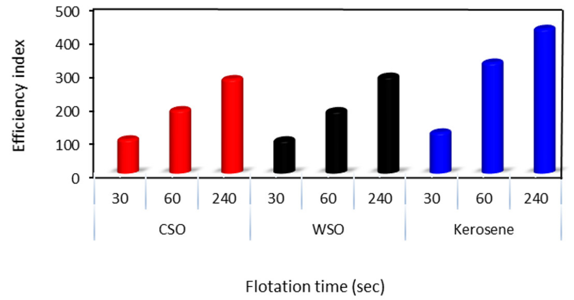

Figure 8. Flotation efficiency index (EI) at various collecting times with WSO, CSO, and kerosene.

Fig. 7 indicates that the combustible recovery of kerosene at the end of 240 seconds flotation time is 94.17%, while the combustible recovery value obtained with WSO is 88.98%. The results indicate that the kerosene collector exhibits higher selectivity compared to CSO and WSO. For instance, after 240 seconds of flotation, the product ash obtained was 17.94% with kerosene, whereas it was 21.73% with the WSO collector.

The efficiency index of CSO, WSO, and kerosene collectors increased as flotation time increased for the three types of collectors, as shown in Fig. 8. At all-time intervals, the efficiency index of kerosene was higher than that of CSO and WSO. For instance, after 240 seconds of flotation time, the efficiency index for kerosene is 471.65, whereas for WSO it is 284.80.

As depicted in Fig. 9, the contact angles measured for kerosene, WSO, and CSO oils on the coal surface were 100o, 91o, and 88o, respectively. The results from Fig. 7 show that kerosene exhibits superior collecting properties on the coal surface compared to CSO and WSO. Hence, these findings support the flotation experiments.

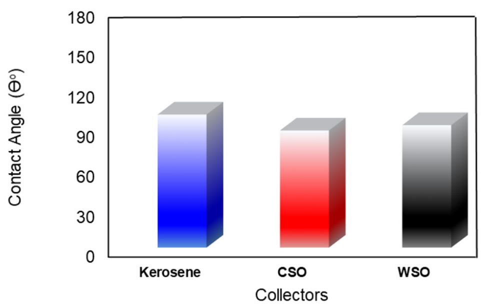

Figure 9. A representation of the contact angles formed by sessile liquid drops (kerosene, CSO and WSO) on the smooth surface of coal.

CONCLUSION

This study shows that using WSO oil in coal slime flotation is applicable, green, efficient, low-cost, and environmentally friendly. The results were evaluated with kerosene and WSO, which have a significant difference between them. Based on the study's findings, WSO effectively lowered the ash content of fine bituminous coal from 33.75% to 6.50%. While WSO can result in clean coal with low ash content, its combustible recovery is lower than that of kerosene. It is most likely due to the WSO 's lower surface coating ability than kerosene. In the release test, WSO achieved a clean coal with 10% ash and a combustible recovery of 54%, while kerosene had a higher recovery of 69%. Kerosene also showed greater selectivity, with a product ash of 17.94% compared to 21.73% for WSO after 240 seconds of flotation. The selectivity index for kerosene was 471.65, while WSO had a lower value of 284.80. Overall, WSO 's performance was approximately 15% lower than kerosene in all aspects, and it had a 40% lower efficiency index compared to kerosene. This is an expected result, but in the near future, oil reserves will be depleted and mankind will turn to renewable resources.

CONFLICT OF INTEREST

Authors approve that to the best of their knowledge, the¬re is not any conflict of interest or common interest with an institution/organization or a person that may affect the review process of the paper.

AUTHOR CONTRIBUTION

All authors contributed to the study conception and de¬sign. Material preparation, data collection and analysis. Dilek Şenol-Arslan: Conceptualization, Methodology, Writing - original draft, Visualization. Hasan Hacıfazlıoğlu: Data curation, Investigation, Supervision, Writing - review and editing.

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