Performance of different oils in oil agglomeration of Zonguldak coal

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In this study, comparison of performance of different oils, in the cleaning of Zonguldak coal, by oil agglomeration was investigated. The feed coal was agglomerated with both classic oils (kerosene, diesel and fuel) used for the coal agglomeration and lubricating oils (spindle, heavy neutral and bright stock) over a wide range of oil concentrations. The performance of the agglomeration process was evaluated by the combustible recovery, ash rejection and efficiency index. It was found that the combustible recovery and ash rejection changed, depending on the type and concentration of oil. The oils were tested for combustible recovery and maximum combustible recovery was obtained on using kerosene. It was found that kerosene, diesel-oil, spindle oil and heavy neutral were suitable for the agglomeration of Zonguldak coal. On considering the efficiency index values, the best results were obtained with heavy neutral. Consequently, it was shown that heavy neutral and spindle oil can be used as alternative oils instead of classic oils for the cleaning of Zonguldak coal by the oil agglomeration.

Modern mining and cleaning processes generate large quantities of fine coal, which create several problems in dewatering, drying, handling, transportation and storage. Significant amounts of these fine coals are lost in the waste streams which results in a significant loss of valuable energy resource and causes considerable environmental problems¹. For making use of the beneficial properties of fine coals, the mineral matter from these is required to be removed. Oil agglomeration has been found to be one of the most effective methods²⁻⁴ for cleaning of a material having very fine sized particles. In comparison to other methods such as flotation and selective flocculation, oil agglomeration is advantageous, due to the simplicity of the process and mineral beneficiation with high recovery. Therefore, oil agglomeration can be regarded as a promising technique for the processing of fine coals. In oil agglomeration process, an immiscible oil (agglomerant) that wets the carbonaceous constituents is added to the coal/water slurry. Due to the difference between the coal particle and mineral matter, the hydrophobic coal particles are preferentially coated by the oil, whereas the hydrophilic mineral matter remains dispersed in the aqueous phase. Upon agitation, the oil coated particles collide with each other and form large agglomerates which can be separated as a clean coal⁵⁻⁶. The agglomerated product is usually separated by using screen. Alternatively, sedimentation and decantation or flotation may be used as means of separation. Basic principles of oil agglomeration and the effects of various operating parameters have been investigated by many researchers³⁻⁶⁻⁹.

The properties of the hydrocarbon oils used for the agglomeration are important as they affect the wetting of the coal and ash-forming mineral matter particles, and hence the selectivity and recovery process⁸. Therefore, the successful use of the oil agglomeration process depends mainly upon selection of oils. The type of oil used is as important as its concentration. In the oil agglomeration process the size and shape of the agglomerates depend upon the amount of oil used.

Oil agglomeration process has not found large-scale commercial acceptance in coal processing or cleaning because of the high cost of oil used in the process. The oil must be effective in terms of high recovery of combustibles and selectivity of the process¹⁰⁻¹². In addition, an ideal oil should be inexpensive and readily available, effective in small quantities, and should beneficiate the coal. There is some difference in opinion on the view, that, heavy oils are more capable of improving the combustible recovery than the light oils, while maintaining separation selectivity²⁻³⁻¹²⁻¹⁶. Therefore, the economic advantage of using cheaper heavy oils can not be reliably confirmed as a general rule. Still no conclusions can be drawn from the published data due...
to lack of control on some important variables and, in particular insufficient knowledge of coal properties. Therefore, the suitable oils for the coal agglomeration must be determined depending on type of the coal. In addition, the effects of new oils such as lubricating oils and vegetable oils instead of only classic oils such as kerosene, fuel-oil, diesel-oil and bitumen are being studied to increase the number of oils those can be used for coal agglomeration.

In this study, Zonguldak coal was agglomerated with both classic oils (kerosene, diesel and fuel) and lubricating oils (spindle oil, heavy neutral and bright stock) over a wide range of oil concentrations. The response of Zonguldak coal to agglomeration with these oils was evaluated by combustible recovery, ash rejection and efficiency index. The influence of oil type and concentration on the results is interpreted here.

**Experimental Procedure**

**Material**

The coal sample was obtained from TTK Zonguldak coal washery. This coal was of bituminous type. The total sulphur content was 0.24%. The result of proximate analysis of the sample is given in Table 1. The coal sample was ground to a nominal top size of -500 μm in a rod mill for oil agglomeration tests. The particle size distribution of the ground sample was determined by wet screening and the results are reported in Table 2.

**Oils**

In the experiments, classic oils (kerosene, diesel-oil and fuel-oil) and lubricating oils (spindle oil, heavy neutral and bright stock) obtained from Tüpraş Aliaga Petroleum refinery were used as agglomerants. All the oils were parafinic hydrocarbon oils. The lubricating oils contain a mixture of hydrocarbons (between C₁₈ and C₃₃) and a small amount (<1%) of wax and aromatic compounds depending on the oil type. The characteristics of the oils used in the study are shown in Table 3.

**Method**

The experiments were performed in a 600 mL beaker with 3 baffles at the borders to create turbulence by using an IKA WERK 20 type mechanical stirrer. The agitation was provided by a centrally located blade which had a slope of 45° turbine impeller (consisting of 2 blades, 58 mm in diameter and 10 mm in width) at fixed distance from the bottom of the beaker. Tap water (pH = 8.50) was used in the experiments. The solid concentration and stirring speed were kept constant at 2.5% by weight and 500 rpm, respectively. The pH of coal suspension was about 8.65 and volume of the suspension subjected to agglomeration was 420 mL. The mixture of coal-water was conditioned for 3 min before the oil addition. Then, coal samples were agglomerated by conditioning with oil for 15 min. After the agglomeration, the contents of the beaker were transferred to 0.5 mm screen. The agglomerates were taken as over screen product. Agglomerates were washed with water to obtain a cleaner product. To remove the oils, the agglomerates were washed with acetone at room temperature and then dried. At the end of drying process, the agglomerated products were weighed. The ash contents (grades) of the agglomerated products were determined. The results

<table>
<thead>
<tr>
<th>Components</th>
<th>As received</th>
<th>Air dried</th>
<th>Dry basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture (%)</td>
<td>4.21</td>
<td>1.25</td>
<td>-</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>14.89</td>
<td>15.36</td>
<td>15.55</td>
</tr>
<tr>
<td>Volatile Matter (%)</td>
<td>25.36</td>
<td>26.14</td>
<td>26.47</td>
</tr>
<tr>
<td>Fixed Carbon (%)</td>
<td>55.54</td>
<td>57.25</td>
<td>57.98</td>
</tr>
<tr>
<td>Calorific value (MJ/kg)</td>
<td>Net 27.09</td>
<td>28.00</td>
<td>28.38</td>
</tr>
<tr>
<td>Gross</td>
<td>28.17</td>
<td>29.04</td>
<td>29.41</td>
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</table>

<table>
<thead>
<tr>
<th>Particle size (μm)</th>
<th>Weight (%)</th>
<th>Cumulative weight (%) passing</th>
</tr>
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<tbody>
<tr>
<td>-500 + 425</td>
<td>0.10</td>
<td>100.00</td>
</tr>
<tr>
<td>-425 + 250</td>
<td>19.80</td>
<td>99.90</td>
</tr>
<tr>
<td>-250 + 160</td>
<td>17.90</td>
<td>80.10</td>
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<tr>
<td>-160 + 125</td>
<td>8.00</td>
<td>62.20</td>
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<tr>
<td>-125 + 90</td>
<td>9.70</td>
<td>54.20</td>
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<tr>
<td>-90 + 63</td>
<td>8.00</td>
<td>44.50</td>
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<tr>
<td>-63</td>
<td>36.50</td>
<td>36.50</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>-</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Oil</th>
<th>Density (kg/m³ at 20°C)</th>
<th>Viscosity (mPa·s at 38°C)</th>
</tr>
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<tbody>
<tr>
<td>Kerosene</td>
<td>780</td>
<td>1.17</td>
</tr>
<tr>
<td>Diesel-oil</td>
<td>840</td>
<td>2.22</td>
</tr>
<tr>
<td>Fuel-oil</td>
<td>940</td>
<td>35.77</td>
</tr>
<tr>
<td>Spindle oil</td>
<td>880</td>
<td>19.19</td>
</tr>
<tr>
<td>Heavy neutral</td>
<td>850</td>
<td>93.27</td>
</tr>
<tr>
<td>Bright stock</td>
<td>830</td>
<td>503.02</td>
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of agglomeration process were evaluated by percentage of combustible recovery and the percentage of ash rejection. The combustible recovery was expressed as the ratio of dry oil and ash-free product to dry ash-free feed coal. The combustible recovery and ash rejection were calculated as follows:

\[
\text{Combustible recovery (CR)} \% = \frac{M_r(100-A_r)}{M_r(100-A_a)} \times 100
\]

\[
\text{Ash rejection (AR)} \% = 100 - \left(\frac{M_a}{M_r} \times A_a / A_r\right) \times 100
\]

where, \(A_a\) = ash content (grade) of the agglomerated product (%); \(A_r\) = ash content of the feed coal (%); \(M_a\) = mass of the agglomerated product (%); \(M_r\) = mass of the feed coal (%).

**Results and Discussion**

**Combustible recovery and ash rejection**

It was reported in the literature that the role of the oil in the oil agglomeration process was to wet the coal surface and to act as a bridging liquid between coal particles. The oil concentration was based on the mass ratio of oil to dry feed coal. Figs 1 and 2 illustrate the effects of oil type and concentration on combustible recovery and ash rejection from the feed coal. As can be seen in Fig. 1, combustible recoveries increased as the oil concentration was increased. However, the combustible recovery depending on oil type did not increase at high concentration of oils except fuel-oil and decreased after a certain concentration value. Therefore, oil concentration had a significant effect on the recovery of combustible material from the feed coal. Thus, as the oil concentration increased from 5 to 30%, the combustible recovery increased from 8.26 to 84.50%, 5.09 to 35.10% and 18.38 to 79.10% for kerosene, fuel-oil and diesel-oil, respectively. For lubricating oils, as the oil concentration increased from 5 to 30%, the combustible recovery increased from 11.90 to 63.50%, 20.90 to 72.65% and 13.56 to 44.73% for spindle oil, heavy neutral and bright stock, respectively.

The minimum combustible recoveries from the feed coal were obtained at the lowest oil concentration (5%) tested. The maximum combustible recoveries were achieved at different oil concentrations depending on oil type. The maximum combustible recoveries were achieved at kerosene, fuel-oil and diesel-oil concentrations of 34, 50 and 34%, respectively. These values were 86.22, 46.15 and 79.10% for kerosene, fuel-oil and diesel-oil, respectively. The maximum combustible recoveries by using lubricating oils (spindle oil, heavy neutral and bright stock) were obtained at spindle oil, heavy neutral and bright stock concentrations of 25, 34 and 30%, respectively. These values were 64.92, 73.51 and 44.73% for spindle oil, heavy neutral and bright stock, respectively. In fact, the maximum combustible recovery from the feed coal was obtained at a kerosene concentration of 34%, this value being 86.22% for oils tested.

At low oil concentrations, the combustible recoveries were low due to the insufficient wetting of coal particles by the oils. As a result, the agglomerates had loose-flock type structure. As the oil
concentration was increased, the agglomerate structure was changed from the loose-floc structure to a more compact structure. Consequently, spherical compact agglomerates were obtained. Therefore, the combustible recoveries increased as the oil concentration was increased. However, at oil concentration of 50%, the spherical shape of agglomerates changed into pasty lumps. The appearance of the agglomerated product changed remarkably and it lost consistency at this concentration. In this situation, the coal particles dispersed in the oil phase to form a coal-in-oil mixture and passed through the screen partly during screening. Therefore, the recovery of combustible material by using oils except fuel-oil decreased at an oil concentration of 50%. These observations are in good agreement with the results given by other investigators.\textsuperscript{7,9} It was reported that the highest combustible recovery and the maximum agglomerate diameter was obtained at the critical oil concentration\textsuperscript{17,21,22}. Based on these results, under the experimental conditions used in this work, concentration of fuel-oil up to 50% may still be considered as maximum. Therefore, the combustible recovery by using fuel-oil increased as the fuel-oil concentration was increased.

The maximum ash rejection percentages from the feed coal were achieved at oil concentration of 5% for oils tested. Unlike combustible recovery, ash rejection from the feed coal tends to decrease with increasing oil concentration up to 30% (Fig. 2). At low oil concentrations, the amount of oil is insufficient to adsorb on to all the coal particles present and, therefore, there is competition for oil wetting among the different types of particles. As a result, only the highest hydrophobic particles, that contain relatively low levels of mineral matter, will be agglomerated. Hence, higher ash rejections are achieved. If the amount of oil is raised the number of oil droplets available for collision with particles to form agglomerates increases, as does the agglomeration of coal particles with much higher proportions of mineral matter. The decrease in ash rejection with increasing oil concentration is variable depending on oil type. These results are similar with the results given in literature.\textsuperscript{17} However, the ash rejection by using oils except fuel-oil increased at oil concentration above 30%. This situation can be attributed to the agglomeration of the more hydrophobic feed particles. On the other hand, the ash rejection by using fuel-oil decreased at concentration of 50%. The reason for this was that the agglomerate became weaker and was easily broken to entrap the water phase including mineral matter. In the present study, the agglomerated product was produced with the ash content of 14.16% by using fuel-oil concentration of 50%.

Efficiency of agglomeration process

The goal of any process used for evaluating feed coals is to achieve maximum ash rejection with virtually quantitative recovery of the combustible material. However, the need to grind the feed coal to extreme fineness so as to totally liberate mineral matter from coal i.e., producing particles constituting pure coal and pure mineral matter, as well as the efficiency of the process used for that particle size make this objective unattainable.\textsuperscript{17} In practice, greater combustible material recovery is obtained at the expense of ash rejection. Therefore, both combustible recovery and ash rejection must be taken into account to evaluate the overall efficiency of the agglomeration process. An efficiency index (EI) was calculated as follows:\textsuperscript{17}:

\[ EI = CR + AR - 100 \]  \hspace{1cm} \text{ ... (3)}

where, CR and AR are the combustible recovery and ash rejection, respectively.

The relationship between efficiency index and oil concentration is shown in Fig. 3. As can be seen in Fig. 3, the efficiency index increased with increasing oil concentration. However, the efficiency index depending on oil type decreased after a certain concentration value. Generally, a decreasing tendency...
of efficiency index was observed at high concentration of oils. The highest EI of 28.92 was achieved with heavy neutral oil concentration of about 33%. The EI values obtained in the agglomeration of the feed coal with oil concentration of 30% were 10.91, 11.31 and 19.13% for kerosene, fuel-oil and diesel-oil, respectively. For lubricating oils, EI values obtained in the agglomeration of the feed coal with oil concentration of 30 were 13.20, 28.62 and 20.95% for spindle oil, heavy neutral and bright stock, respectively. Although high combustible recoveries were obtained by using kerosene, the EI values were very low. This situation was due to the high ash contents of the agglomerated products. The ash contents of the agglomerated products produced with using heavy neutral oil were lower than those of kerosene. For example, the ash contents of the agglomerated products produced using 30% concentration of heavy neutral oil and kerosene were 10.04 and 13.82%, respectively. It was clear that heavy neutral gave the highest index values in the oil concentration investigated. In the oil agglomeration process, the efficiency index values can be used for comparing both, the performance of different oils and the effects of oil concentrations for a known oil. These findings showed that the efficiency index value was used as a quality determining parameter for oil agglomeration process.

The high combustible recoveries obtained on using kerosene and diesel-oil were based on easy dispersion and the increase of the degree of oil coating on the coal particles with these oils is because of low viscosities. If oil is easily dispersed in the slurry during the conditioning phase particle - oil droplet collision probability is enhanced. The ash rejection percentages by using kerosene and diesel-oil were lower than those of other oils. This situation was attributed to the adsorption of kerosene and diesel-oil droplets because of presence of polar groups in their structure on the ash-forming mineral matter. For example, the ash contents of the agglomerated products produced with using oil concentration of 30% of kerosene and diesel-oil were 13.82 and 12.22%, respectively. It was reported in the literature that the oils (kerosene, diesel and fuel) had substances containing polar groups with undetermined structure (amines, resins, asphaltines, etc.) which were relatively more abundant in heavy oils. The low combustible recoveries were obtained with fuel-oil in the oil concentrations investigated. The reason for this was that the fuel-oil had high viscosity in comparison to the kerosene and diesel-oil and was not dispersed sufficiently well in the slurry. Thus, it could not wet the coal particles and cause agglomeration. Besides, the degree of oil coating on the coal particles may decrease by using fuel-oil because of high viscosity. The ash rejections obtained on using fuel-oil were higher than those obtained on using kerosene and diesel-oil. This can be attributed to the recovery of the less amount of ash-forming mineral matter according to the feed coal in the agglomerated product, although the ash contents of the agglomerated products were high due to the less recovery of combustible material. If fuel-oil is not dispersed sufficiently, the adsorption of fuel-oil molecules on the ash-forming mineral matter will be low, although, fuel-oil contains relatively more abundant polar substances.

The low combustible recoveries were also obtained on using bright stock in the oil concentrations tested. This is due to insufficient dispersion of bright stock in the slurry. Bright stock has the highest viscosity of all the oils tested. As a result of the high viscosity, the coal particles can not be wetted sufficiently by bright stock. Besides, the degree of oil coating on the coal particles by using bright stock also decreases. Therefore, the low combustible recoveries are obtained on using bright stock. The ash contents of the agglomerated products were lower than those for other oils. It is due to the high paraffin content of bright stock. As a result, the combustible recoveries obtained with bright stock are higher than those with fuel-oil in the concentrations between 5 and 30%. The ash rejection percentages are also high on using bright stock. This can be attributed to the agglomeration of the highest hydrophobic particles from the feed coal. As a result, the high amount of feed coal can not be agglomerated and, therefore, the high ash rejection percentages are obtained. In fact, it was observed that the agglomerates obtained by using fuel-oil and bright stock were not resistant to mechanical forces during screening.

The combustible recoveries obtained on using spindle oil were higher than those obtained with bright stock. This is due to the easy dispersion of spindle oil and the increase of degree of oil coating on the coal particles because of low viscosity in comparison to that of bright stock. The ash rejection percentages on using spindle oil are lower than those with bright stock. This can be attributed to the high content of aromatic compounds in spindle oil.
Aromatic compounds have greater affinity for ash-forming mineral matters. It was reported that aromatic compounds also decreased the interfacial tension between water and oils. In fact, the agglomerated products with the highest ash contents were obtained with spindle oil among the lubricating oils. It was reported that the agglomerated product with high ash contents were obtained as the aromaticity of oil increased. As a result, the high amount of ash-forming mineral matter was recovered with the agglomerated product and, therefore, ash rejections were decreased on using bright stock.

The highest combustible recoveries were obtained by using heavy neutral oil among the lubricating oils. The viscosity of heavy neutral oil is higher than that of spindle oil. The combustible recoveries obtained using heavy neutral oil are also higher than those with spindle oil. Although, the increase in viscosity has adverse effect on the dispersion of oil, the high combustible recoveries were obtained by using heavy neutral oil. This can be attributed to the presence of aromatic compounds in the structure of heavy neutral. These compounds decrease interfacial tension between water and oils as mentioned previously. Consequently, diffusion ability of oil on water and water-coal interface increases. Therefore, the combustible recoveries are higher than those with spindle oil. In fact, agglomerated products obtained by using heavy neutral have lower ash contents than those of spindle oil. Therefore, it can be said that heavy neutral has the lower aromatic content than that of spindle oil. The ash rejection percentages obtained on using heavy neutral are higher than those for spindle oil. It is due to the low ash contents of the agglomerated products. Since aromatic content of spindle oil was higher than that of heavy neutral, the ash contents of the agglomerated products were higher than those of heavy neutral. For example, the ash contents of the agglomerated products produced, on using oil concentrations of 30%, spindle oil, heavy neutral and bright stock were 12.95, 10.04 and 9.41%, respectively.

A lot of information is available on agglomeration of different coals. However, owing to different characteristics of the feed coals, experimental conditions and type of oils used in agglomeration, comparison between the results of this study and those previously reported by other authors may give different results. Consequently, it was shown that the agglomeration of the Zonguldak coal by using kerosene, diesel-oil, heavy neutral and spindle oil could be achieved under the experimental conditions reported here. It was also evident that both heavy neutral and spindle oil, which are used as lubricating oils could be used as alternative oils instead of kerosene and diesel-oil for the agglomeration of Zonguldak coal. Further improvement in agglomeration performance could be achieved with the determination of optimum conditions of operating parameters (stirring, speed, agglomeration time, solid ratio, etc.).

Conclusion

Thus, it may be inferred that, the maximum combustible recoveries were achieved at different oil concentrations depending on oil type. The combustible recoveries obtained by using fuel-oil and bright stock were lower than those obtained with other oils under the experimental conditions reported here. The maximum combustible recovery was obtained on using kerosene of all the oils tested. Although high combustible recoveries were obtained on using kerosene, the ash rejection percentages were very low due to high ash contents of the agglomerated products. For the oils tested, ash rejection percentages changed, depending on type and concentration of oils.

For lubricating oils, on considering the combustible recovery and ash rejection, the best results were obtained with heavy neutral oil. As the efficiency index values were considered, the best result was obtained with heavy neutral oil depending on oil concentration. Heavy neutral and spindle oils which are used as lubricating oils can be used as alternative oils instead of kerosene and diesel-oil for the agglomeration of Zonguldak coal.

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