Coal Calorific Value after Physical and Chemical Cleaning

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Abstract. In this study a total of 12 coal sample was collected. 7 of these samples are local coal samples and 5 of them is exported coals. These coals samples were fractionated into two size groups, i.e. -10+3.15, -3.15+0.5. Float and sink analysis was performed on this two size groups of samples with Ca(NO₃)₂ medium at the density of 1.50 g/cm³. Latter within the scope of this study, chemical cleaning was employed on this samples. Chemical cleaning on coal samples was carried out with acids (HF and HNO₃) at specific conditions. Samples have different calorific values after physical and chemical cleaning. Although some impurities have been removed with both cleaning methods, physical cleaning resulted in higher ash content coals at the end while with chemical cleaning almost no ash content coals were obtained. However, it was observed the fact that chemical cleaning resulted lower calorific values of samples. This might be because of chemical cleaning results in the decomposition of the coal matrix structure.

1. Introduction
Coal is an organic material and it has some impurities within its structure. These impurities are sometimes hard to remove away. In order to remove these mineral impurities, physical and chemical cleaning methods are employed. Due to higher and higher energy requirements of the world and due to the gradual depletion of high quality coal reserves, coal cleaning gains more importance day by day [1]. Mineral matter in coal have 3 forms; i. true minerals, ii. Dissolved salts in pore water, iii. Elements associated with the hydrocarbonaceous matrix [2]. According to Sharma and Gihar [3], the major minerals in coals are silicates or shales (kaolinite type), quartz and/or sandstone, pyrites and carbonates such as siderites and ankerites.

Various treatments to remove mineral matter can be employed and these treatments result in different mineral matter or ash content at the end [1]. Treatments or methods to remove the mineral matter can be categorized into two main groups, i.e. physical and chemical cleaning. However both methods are affected by the liberation of particles, in other words finer the size higher the rate of mineral matter removal could be. Physical cleaning methods can reduce coal mineral impurities to some degree and it can not lower further and that is why chemical cleaning has to be used to produce clean coal [4, 5]. In terms of chemical cleaning, leaching with nitric acid [6], hydrofluoric acid [7], caustic soda in the Gravimelt process [8], mixtures of hydrofluoric/hydrochloric acids [9], calcium hydroxide/hydrochloric acid [10], sodium hydroxide/hydrochloric acid [11] and different acids [1] have been performed by researchers [1, 6, 7, 8, 9, 10, 11]. Cleaned coal either with physical or chemical methods should be tested in terms of its combustion behaviour [12,13,14,15] since there are some advantages and disadvantages regarding these cleaning methods as such poor reactivity performance is attained [4].
In this study collected coal samples were analysed in terms of their ash removal and calorific value changes respectively before and after physical & chemical cleaning. Ash making mineral matters are removed to some degree with physical cleaning and higher rate of removal was achieved with chemical cleaning method. However, calorific values are higher after physical cleaning and lower after chemical cleaning.

2. Experimental Method
In this study a total of 12 coal samples were collected and physical & chemical cleaning were employed. The collected coal samples and their origins are tabulated in Table 1.

| Coal sample seam identity | Origin of coal sample | Corresponding coding |
|---------------------------|-----------------------|----------------------|
| Çay                       | TTK Karadon           | TB1                  |
| Büyük                    | TTK Kozlu             | TB2                  |
| Azdavay                   | Azdavay-Kastamonu     | TB3                  |
| Çınarlı                   | TTK Amasra            | TB4                  |
| Büyük Damar              | TTK Armutçuk          | TB5                  |
| Sulu                      | TTK Üzülmez           | TB6                  |
| Söğütözü                  | Söğütözü-Kastamonu    | TB7                  |
| Goonyella                 | Queensland-Avusturalya| IT 1                 |
| Weglokoks Typr-R35        | Silesia-Polonya       | IT 3                 |
| South Blackwater          | Blackwater-Avusturalya| IT 4                 |
| Saraji                    | Mackay-Queensland-Avusturalya | IT 6 |
| JWR-Bluecreek, No 7       | Alabama-ABD           | IT 7                 |

In this study, experimental work was carried out on local coal samples (TB1 to TB7) and exported coal samples (IT1 to IT5). Local samples were taken from each coal seam as regards to TS 2942. A total of 50-60 kg of coal was either collected from local coal seams or provided (exported). Schematical representation of experimental procedure (physical cleaning) is provided in Figure 2.

After the process of physical cleaning, chemical cleaning with HF was employed. Chemical cleaning with HF was realized in teflon beaker at various concentrations (1, 2, 3, 4, 5, 6 M). Coal sample (20 g) was objected to 100 ml of acid (HF) solution (at 65 °C) for 3 hours and it was stirred with magnetic stirrer. Latter, the solution was filtrated and filtrate was taken. The filtrate (chemically cleaned coal sample) was dehumidified at 60 °C for 24 h. Corresponding concentration variation with respect to ash removal is provided in Figure 1.

![Figure 1. Concentration (HF) variation with respect to ash removal](image-url)
Figure 2. Schematical representation experimental procedure for physical cleaning.

Referring back to Figure 1, chemical cleaning on all samples was performed with 3.5 M HF solution since highest rate of ash reduction was observed between 3 M and 4 M solution.

3. Results and discussions
The results of ash removal and calorific values after physical & chemical cleaning is provided in Table 2. Corresponding plot (Figure 3) of calorific value change with respect to ash removal is obtained.
Table 2. Results of the ash content and calorific values after physical & chemical cleaning.

| Sample | After Physical Cleaning | After Chemical Cleaning |
|--------|-------------------------|-------------------------|
|        | Ash (%) | Calorific Value (kcal/kg) | Ash (%) | Calorific Value (kcal/kg) |
| TB1    | 8.63    | 7676                      | 0.42    | 6776                      |
| TB2    | 9.68    | 7330                      | 0.55    | 6476                      |
| TB3    | 8.73    | 7683                      | 0.15    | 6157                      |
| TB4    | 7.71    | 6813                      | 0.41    | 5686                      |
| TB5    | 4.32    | 7614                      | 0.32    | 6597                      |
| TB6    | 7.57    | 7484                      | 0.48    | 6723                      |
| TB7    | 8.13    | 7733                      | 0.18    | 6406                      |
| IT 1   | 7.82    | 7908                      | 0.07    | 6672                      |
| IT 3   | 6.64    | 7718                      | 0.22    | 6952                      |
| IT 4   | 5.97    | 7800                      | 0.19    | 6136                      |
| IT 6   | 8.36    | 7934                      | 0.70    | 7169                      |
| IT 7   | 6.61    | 8067                      | 0.67    | 7387                      |

Referring to Table 2, ash content of each coal sample is between 4.32 and 9.68 % after physical cleaning while it is between 0.07 and 0.70 % after chemical cleaning. Corresponding calorific values are between 6813 and 8067 kcal/kg after physical cleaning while they are between 5686 and 7387 kcal/kg after chemical cleaning.

![Graphical representation of ash content removal and corresponding calorific value change.](image-url)
As it can be observed from Figure 3, calorific values decreases after physical cleaning for all coal samples studied. Referring back and forth to the Figure 3 and Table 2, 90-99 % of ash removal was achieved after chemical cleaning. The lowest rate of ash removal (89.9 %) was observed on the sample coded as IT7 and the highest ash removal percentage (99 %) is observed on IT1 sample. However after chemical cleaning calorific values of coal samples decreased within the ratios between 8.4 and 21.3 %. Highest ratio of calorific value decrease was observed on IT4 sample and the lowest one was observed on IT7 sample. In order to tabulate these percentages of calorific value decreases and ash removal rates, Table 3 is provided.

Table 3. Percentages of calorific value decreases and ash removal rates (%) after chemical cleaning.

| Sample | Ash removal rates (%) | Calorific value decrease rates (%) |
|--------|------------------------|------------------------------------|
| TB1    | 95.13                  | 11.72                              |
| TB2    | 94.32                  | 11.65                              |
| TB3    | 98.28                  | 19.86                              |
| TB4    | 94.68                  | 16.54                              |
| TB5    | 92.59                  | 13.36                              |
| TB6    | 93.66                  | 10.17                              |
| TB7    | 97.79                  | 17.16                              |
| IT1    | 99.10                  | 15.63                              |
| IT3    | 96.69                  | 9.92                               |
| IT4    | 96.82                  | 21.33                              |
| IT6    | 91.63                  | 9.64                               |
| IT7    | 89.86                  | 8.43                               |

Table 3 is a good representation of each sample resistance to chemical cleaning. As it is mentioned earlier some coal samples are better convenient for physical cleaning while some are convenient for both cleaning methods. As it can be interfered from Table 3 that, IT4 sample can be regarded as not convenient for chemical cleaning since it loses more than 20 % of its calorific value. However for IT7 sample, chemical cleaning resulted in the removal of almost 90 % of its ash content and its calorific value decreased only 8 %. What can be summarized from these findings, some coal sample (IT7) favours chemical cleaning while some (IT4) have decomposition of coal matrix with chemical cleaning.

As presented earlier, ultra clean coals or fuels have higher demands nowadays and in order to perform this purpose, chemical cleaning is irreplaceable method. However some coals due to their structure and mineral matter forms, chemical cleaning might or might not be convenient method to be employed.

4. Conclusions
In this study, coal ash content removal was employed with physical and chemical methods. Collected coal samples (a total of 12, either local or exported) was physically cleaned in the first place. Right after this physical cleaning their corresponding ash content and calorific values were determined. Secondly, coal samples (physically cleaned) were objected to chemical cleaning at specified conditions. Chemical cleaning resulted in higher rates of ash removal while it resulted in significant decreases in calorific values. Chemical cleaning not necessarily always but most of the time results in decomposed coal matrix and a decrease in calorific value is understandable. However, for some specific coal samples studied have significant amount of calorific value decrease while other samples have respectively 2-3 times lower ratios of this decrease. It was concluded that, some samples are more convenient in terms of chemical cleaning while others have more tendency to have the decomposed coal matrix at the end. In
the order of clean coal production, one should take the findings of this study into account as regards to chemical cleaning. Before chemical cleaning, one should characterize the coal sample tendency or resistance to chemical cleaning, and this study could be beneficial as regards to this characterization. What was concluded in this study is, out of these 12 samples, IT4 sample can be considered as not convenient for chemical cleaning while IT7 sample is rather convenient. A classification method (convenient, inconvenient) should be further proposed within the future scope of this study.

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