Proximate and Ultimate Analysis Before and After Physical & Chemical Demineralization

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Abstract. In this study, a total of 12 coal samples were collected. Physical and chemical cleaning were employed on these collected coal samples. In order to understand the effect of physical & chemical cleaning on these samples, samples characterization were performed in terms of proximate and ultimate analysis. Calorific values of each corresponding clean coal samples were also determined. After chemical cleaning calorific values of each sample decreased, while chemical cleaning resulted in ultra clean coals as regards to ash content (average of 0.5 % ash content). Volatile matter content each corresponding sample after chemical cleaning have higher percentage with respect to the ones after physical cleaning. However for some specific sample, the increase in volatile matter content after chemical cleaning is more than 200 %. Fixed carbon percentages do not show tremendous changes as regards to chemical cleaning, however they decrease for some and increase for some other after chemical cleaning. Calorific values decreases for the all samples after chemical cleaning. Ultimate analysis (C, H, N and O) was also determined after physical and chemical cleaning. Sulphur decreased for all samples after chemical cleaning as expected. Taking these variations into consideration, calorific value decrease were deducted and possible reasons of this decrease was inferred. Corresponding differentiations were compared to calorific value differentiation and the most significant reasoning of the calorific value decrease was evaluated.

1. Introduction
Coal characterization is important in terms its quality determination. Coal has a dominant role in terms of energy production for the time being and near future. Considering this abovementioned dominant role of coal for energy need, produced coals should face some cleaning process before their utilization. This cleaning process does not only improve the coal quality but also it is a considerable factor to reduce transportation costs [1]. According to the same authors [1], removal of ash making minerals and coal beneficiation is a challenging task because of uneven distribution of coal and inorganic components within the coal seams, parting of shale as bands and also the presence of shaly coal. In addition, Kizgut et al. [2] explained the fact that chemical enrichment processes and physical separation methods are being extensively used in ultraclean coal production. Yilmaz [3] has investigated the grindability difference of clean and original coals and he evaluated the proximate analysis and total sulphur differentiation for the grindability prediction of the clean coals. Coal physical and chemical cleaning result in lower ash content (clean coal) and change in proximate analysis data in brief. Some coal samples have a tendency to be cleaned easily some do not. As it is mentioned by [1], or example Indian coals have difficult washability characteristics, because of the following reasons: (1) presence of high
near gravity material content, (2) intricate association of mineral matter with coal, and (3) inconsistency in the homogeneity of coal seams. Depending on this above mentioned nature of coals, coal grindability was predicted for clean coals by the researcher [3]. Majumder et al [4] explained the fact that coal calorific value, which is expressed usually as higher heating value (HHV), is measured experimentally using a bomb calorimeter. According to same authors [4], this method of analysis is cost intensive and it requires a sophisticated equipment and a trained chemist. Referring again to same authors [4], moisture, volatile matter, ash and fixed carbon are determined easily by proximate analysis of coal using a simple furnace and this is way cheaper than a bomb calorimeter and it does not require as much time and experience.

There is a summary of published articles by researchers ([5], [6], [7], [8], [9], [10], [11], [12]) relating to estimate of coal calorific value based on entire proximate and/or ultimate (elemental composition) analysis of data applying linear correlations and artificial neural networks in the study of Majumder et al [4]. Although these models/equations/empirical formulas achieve significant correlations, they have not been widely applicable for power industries as regards to the coal samples’ calorific value prediction. On the other hand, predicting calorific value based on ultimate analysis can also be expensive because it is also time consuming, costly and requires a professional ([11], [12]).

In this study, based on the experimental data of physically clean coals and chemically clean coals, the calorific value differentiation was investigated. Taking into consideration the fact that coal chemical cleaning resulted in lower calorific values, difference between initial calorific values and the ones after chemical cleaning might have been reasoned by the proximate analysis data differentiation, ultimate analysis data differentiation, or the both. Considering 12 samples, calorific values was predicted after chemical cleaning by employing proximate analysis and ultimate analysis data.

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.

Table 1. Collected coal samples origins, locations and their corresponding codings.

| 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, IT3, IT4, IT6, IT7). 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). After 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.

Proximate and ultimate analysis was carried out as regards to the standards (Collection of gross sample ASTM D-2234, Preparation of laboratory sample ASTM D-2103, Proximate analysis of coal and coke ASTM D-3172, ash in the analysis sample of coal and coke ASTM D-3174, volatile matter in the analysis sample of coal and coke ASTM D-3175, and total sulphur in the sample of coal and coke ASTM D-3177).

3. Results and discussions
Collected samples are analysed in terms of proximate analysis after physical cleaning (Table 2) and chemical cleaning (Table 2). Results of each analysis are tabulated in Table 2 and Table 3.

| Sample | Proximate analysis | Ultimate analysis |
|--------|--------------------|------------------|
|        | Ash (%)            | Volatile Matter (%) | Fixed Carbon (%) | Calorific value (kcal/kg) | C (%) | H (%) | N (%) | O (%) | S (%) |
| TB1    | 8.63               | 31.02             | 60.35            | 7676              | 80.93 | 4.48  | 1.18  | 4.45  | 0.33  |
| TB2    | 9.68               | 27.33             | 62.99            | 7330              | 78.65 | 4.38  | 1.71  | 5.00  | 0.58  |
| TB3    | 8.73               | 29.20             | 62.07            | 7683              | 78.48 | 4.65  | 0.69  | 5.86  | 1.59  |
| TB4    | 7.71               | 38.13             | 54.16            | 6813              | 69.92 | 4.96  | 0.26  | 16.60 | 0.65  |
| TB5    | 4.32               | 33.13             | 62.55            | 7614              | 79.09 | 4.78  | 1.54  | 9.77  | 0.50  |
| TB6    | 7.57               | 29.03             | 63.40            | 7484              | 80.81 | 4.35  | 1.03  | 5.80  | 0.44  |
| TB7    | 8.13               | 10.11             | 81.76            | 7733              | 82.70 | 3.40  | 1.22  | 3.58  | 0.97  |
| IT 1   | 7.82               | 25.22             | 66.96            | 7908              | 82.25 | 4.81  | 0.75  | 3.83  | 0.54  |
| IT 3   | 6.64               | 27.00             | 66.36            | 7718              | 81.82 | 4.42  | 0.43  | 5.95  | 0.74  |
| IT 4   | 5.97               | 29.52             | 64.51            | 7800              | 78.95 | 4.78  | 1.30  | 8.49  | 0.54  |
| IT 6   | 8.36               | 19.80             | 71.84            | 7934              | 81.65 | 4.38  | 0.92  | 4.05  | 0.64  |
| IT 7   | 6.61               | 20.59             | 72.80            | 8067              | 84.16 | 4.42  | 1.48  | 2.61  | 0.72  |

As regards to Table 2, ash content is the lowest for TB5 sample (4.32 %) and it is highest (9.68 %) for the TB2 sample after physical cleaning. Volatile matter changes between 19.80 % and 38.13 %. Fixed carbon percentages are between 54.16 % and 81.76 %. Calorific values after physical cleaning are considerably high and they change in a range of 6813 and 8067. In terms of ultimate analysis, C (%) is highest for IT7 sample (84.16 %) and it is lowest for TB4 sample (69.92 %). Total sulphur percentages are low after physical cleaning as expected and they are about 0.5 %, average.
Ash content and total sulphur percentages decreased after chemical cleaning for all samples. Ash content after chemical cleaning changes between 0.07 and 0.67 % and this can be regarded as ultraclean coal can be produced at the end of this treatment. Volatile matter contents show a trend to increase after chemical cleaning and fixed carbon percentages change in negligible ratios. However calorific values decreased up to %20 percent considering the before and after chemical cleaning.

This study aims to observe the differences in proximate and ultimate analysis data with respect to calorific value differentiation before and after chemical cleaning. That is why each analysis differentiation was calculated and tabulated in Table 4. In terms of this differentiation calculation, the value (ash, volatile matter, fixed carbon, C, H, N, O, S) after physical cleaning is subtracted from the value after chemical cleaning and the difference is divided by the value after physical cleaning and then it is multiplied by 100. This is carried out in order to have an idea by what percentage the proximate analysis and ultimate analysis changes before and after chemical cleaning. In addition to these above mentioned tabulated data, calorific value differentiation (%) was also calculated and tabulated in Table 4. At the end, these tabulated data of each analysis differentiation was compared to calorific value differentiation. This is performed due to better understand which proximate/ultimate analysis data corresponds to calorific value differentiation more. Differentiation of proximate/ultimate analysis data and calorific values were plotted against and regression coefficients of each plots were determined (See Figure 1-8).

| Sample | Proximate analysis | Ultimate analysis |
|--------|-------------------|------------------|
|        | Ash (%) | Volatile Matter (%) | Fixed Carbon (%) | Calorific Value (kcal/kg) | C (%) | H (%) | N (%) | O (%) | S (%) |
| TB1    | 0.42    | 34.61            | 64.97            | 6776                        | 71.90 | 3.72  | 3.90  | 19.77 | 0.29  |
| TB2    | 0.55    | 37.96            | 61.49            | 6476                        | 70.50 | 3.43  | 4.03  | 21.00 | 0.49  |
| TB3    | 0.15    | 42.24            | 57.61            | 6157                        | 67.99 | 3.95  | 3.71  | 23.25 | 0.95  |
| TB4    | 0.41    | 54.01            | 45.58            | 5686                        | 62.43 | 3.99  | 4.20  | 28.42 | 0.55  |
| TB5    | 0.32    | 38.93            | 60.75            | 6597                        | 69.91 | 4.06  | 3.72  | 21.75 | 0.24  |
| TB6    | 0.48    | 34.45            | 65.07            | 6723                        | 72.57 | 3.76  | 4.12  | 18.71 | 0.36  |
| TB7    | 0.18    | 35.00            | 64.82            | 6406                        | 70.70 | 2.78  | 4.40  | 21.24 | 0.70  |
| IT 1   | 0.07    | 34.60            | 65.33            | 6672                        | 71.53 | 3.58  | 3.62  | 20.74 | 0.46  |
| IT 2   | 0.22    | 32.07            | 67.71            | 6952                        | 74.33 | 3.73  | 3.89  | 17.31 | 0.52  |
| IT 4   | 0.19    | 41.93            | 57.88            | 6136                        | 66.47 | 3.39  | 3.45  | 23.05 | 0.36  |
| IT 6   | 0.70    | 28.76            | 70.54            | 7169                        | 75.56 | 3.54  | 3.60  | 16.01 | 0.59  |
| IT 7   | 0.67    | 26.43            | 72.90            | 7387                        | 78.92 | 3.84  | 3.72  | 12.23 | 0.62  |
Table 4. Differentiation (%) of proximate and ultimate analysis data before and after chemical cleaning

| Sample | Proximate analysis Differentiation (%) | Ultimate analysis Differentiation (%) |
|--------|----------------------------------------|---------------------------------------|
|        | Ash Diff. (%) | Volatile Matter Diff. (%) | Fixed Carbon Diff. (%) | Calorific Value Diff. (%) | C Diff. (%) | H Diff. (%) | N Diff. (%) | O Diff. (%) | S Diff. (%) |
| TB1    | 95.13        | -11.57                     | -7.66                     | 11.72                     | 11.16       | 16.96       | -230.51     | -344.27     | 12.12       |
| TB2    | 94.32        | -38.89                     | 2.38                      | 11.65                     | 10.36       | 21.69       | -135.67     | -320.00     | 15.52       |
| TB3    | 98.28        | -44.66                     | 7.19                      | 19.86                     | 13.37       | 15.05       | -437.68     | -296.76     | 40.25       |
| TB4    | 94.68        | -41.65                     | 15.84                     | 16.54                     | 10.71       | 19.56       | -1515.38    | -71.20      | 15.38       |
| TB5    | 92.59        | -17.51                     | 2.88                      | 13.36                     | 11.61       | 15.06       | -141.56     | -122.62     | 52.00       |
| TB6    | 93.66        | -18.67                     | -2.63                     | 10.17                     | 10.20       | 13.56       | -300.00     | -222.59     | 18.18       |
| TB7    | 97.79        | -246.19                    | 20.72                     | 17.16                     | 14.51       | 18.24       | -260.66     | -493.30     | 27.84       |
| IT 1   | 99.10        | -37.19                     | 2.43                      | 15.63                     | 13.03       | 25.57       | -382.67     | -441.51     | 14.81       |
| IT 3   | 96.69        | -18.78                     | -2.03                     | 9.92                      | 9.15        | 15.61       | -804.65     | -190.92     | 29.73       |
| IT 4   | 96.82        | -42.04                     | 10.28                     | 21.33                     | 15.81       | 29.08       | -165.38     | -171.50     | 33.33       |
| IT 6   | 91.63        | -45.25                     | 1.81                      | 9.64                      | 7.46        | 19.18       | -291.30     | -295.31     | 7.81        |
| IT 7   | 89.86        | -28.36                     | -0.14                     | 8.43                      | 6.23        | 13.12       | -151.35     | -368.58     | 13.89       |

Differentiation for each proximate and ultimate analysis data and total sulphur was calculated and tabulated as seen in Table 4. Referring back and forth to the Table 4, some values are negative since their corresponding results (physical cleaning) are lower than the ones after chemical cleaning. However as it is seen from Table 3 that, differentiation of ash (proximate analysis), carbon and hydrogen (ultimate analysis) and total sulphur is positive. Differentiation of volatile matter (proximate analysis), nitrogen and oxygen (ultimate analysis) is negative. However, differentiation of fixed carbon is kind of complicated which is positive for some samples and negative for others. Based on these above provided tabulated results, plots were obtained for each data (proximate or ultimate) with respect of calorific value differentiation (%).

Considering each plots obtained (Figure 1-8), regression coefficients (R^2) changes between 0.004 and 0.8. Highest regression coefficient was obtained for “C” carbon differentiation (%) and the lowest one was obtained for “O” oxygen differentiation (%), respectively. Taking into consideration this finding, “C” carbon (ultimate analysis) differentiation is the most responsible for the calorific value differentiation after chemical cleaning. So, what can be claimed in this context briefly is the fact that increase in “C” carbon (ultimate analysis) differentiation (%) results in an increase in calorific value differentiation (%). So, as regards to prediction which is already reported by many researchers, carbon content should be the one most focused in order to have significant and successful correlations.
Figure 1. Ash Diff (%) vs Calorific Value Diff (%).

Figure 2. Volatile Matter Diff (%) vs Calorific Value Diff (%).

Figure 3. Fixed Carbon Diff (%) vs Calorific Value Diff (%).

Figure 4. “C” Diff (%) vs Calorific Value Diff (%).

Figure 5. “H” Diff (%) vs Calorific Value Diff (%).

Figure 6. “N” Diff (%) vs Calorific Value Diff (%).

Figure 7. “O” Diff (%) vs Calorific Value Diff (%).

Figure 8. “S” Diff (%) vs Calorific Value Diff (%).
4. Conclusions
In this study, 12 coal samples were collected and their physical & chemical cleaning were performed. Right after these cleaning processes, proximate and ultimate analysis were performed for each samples. Along with these analysis, calorific value determination and total sulphur measurements were carried out. Considering these analysis results, after chemical cleaning calorific value of each sample decreased in some ratios, while some proximate and ultimate analysis data change in different manners. Differentiation of each proximate, ultimate analysis parameter along with calorific value and total sulphur was tabulated in percentages and in order to carry out this calculation the results after chemical cleaning is subtracted from the results after physical cleaning and the subtraction is divided by the result after physical cleaning. And at the end it is multiplied by 100 to have percentage values. Tabulating these abovementioned percentage differentiations helped to observe possible relations of calorific value differentiation, since some parameter resulted in a positive manner like the one as calorific value would not be enough for correct addressing of calorific value. All in all, this study would help future researcher in this field as regards to calorific value prediction, since the contribution of carbon should definitely be taken into consideration, only proximate analysis would not be enough for correct addressing of calorific value.

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