Reactivity of Physically and Chemically Clean Coals

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Abstract. In this study, a total of 12 coal samples were collected. In order to have reactivity determination samples were thermo-gravimetrically analysed. Thermo-gravimetric analysis was carried out not only on physically clean coal samples but also on chemically clean coal samples. Reactivity program within thermogravimetric analysis consists of volatiles burning in N$_2$ atmosphere which is fast reaction and residual carbon burning in dry air atmosphere which takes places right after. Reactivity parameter for each coal sample is considered as an important parameter since it characterize the burning profile of residual carbon matter after devolatilization. In order to have reactivity determination, samples were objected to temperature increase up to 700 $^\circ$C in N$_2$ atmosphere and then the temperature was set to 500 $^\circ$C in dry air atmosphere. Reactivity of each corresponding sample after physical and physical-chemical cleaning was determined. The determined reactivity ($R_{500}$) values changed between 0.06 and 0.221 for physically clean coal samples and they are between 0.11 and 0.24 for the chemically clean coal samples. Reactivity ($R_{500}$) values increased after chemical cleaning. Due to coal structure difference, the increase in reactivity ($R_{500}$) after chemical cleaning is different for each sample. For example for TB6 sample, reactivity ($R_{500}$) increased more than 60 % while for TB5 sample it only increased by 6 % after chemical cleaning. Chemical cleaning followed by physical cleaning results in increase in reactivity and this increase depends on the nature of the coal type.

1. Introduction

Coal depending on its organic matrix and depending on thermal decomposition kinetics have different reactivity. Reactivity of a coal is determined with thermos-gravimetric methods and coal reactivity is mostly depending on its own structure. The reactivity changes as coal type changes and different reactivity is determined after coal preparation, i.e. coal cleaning. Coal cleaning is either employed by physical methods mostly or chemical treatments are also applicable for further ultra clean coal production purposes. Coal reactivity is a way to address to understand the behaviour of that specific coal sample in all major conversion processes such as combustion, gasification, carbonization and liquefaction and coal pyrolysis is one of the most important aspects of this behaviour [1]. Coal contains inorganic and organic matter together and coal cleaning is employed to remove some parts of these inorganics from the body. Many researchers have tried to address the relationships between inorganic body of coal and the reactivity of organic body in coal during coal pyrolysis ([2], [3], [4], [5], [6], [7], [8], [9], [10]). Selective demineralization of coals with acids has usually been used to investigate the effect of each element in coal in terms of reactivity ((([2], [3], [4], [5], [6]). However still, in literature there is a lack of study about the relationship between inorganic matter and the kinetics/reactivity of coals and coal pyrolysis. Liu et al. [1] have worked with Chinese low-rank coals, Shenfu subbituminous
coals and Huolingele lignite. In their work, authors [1] have the coals demineralized and they added several inorganics. Coal samples (original, demineralized, and demineralized coal with inorganics added) were analysed in terms of thermo-gravimetric during coal pyrolysis, and this thermo-gravimetric analysis was used to investigate the effects of mineral matter on the reactivity of coal pyrolysis. What they [1] have concluded is as following: “i. Inherent mineral in coal has no evident effect on the reactivity and kinetics of coal pyrolysis, ii. When some inorganic materials such as CaO, K₂CO₃ and Al₂O₃ were added into the demineralized coal it showed a positive effect on reactivity, iii. Addition of inorganic materials will make the activation energy of coal pyrolysis decrease”.

In this study, 12 coal samples were cleaned with physical and chemical methods. After each cleaning process, reactivity of each sample were determined. The reactivity values for each sample before and after chemical cleaning was compared and effect of chemical cleaning was understood. Depending on coal sample characteristics, reactivity increase after chemical cleaning was compared for each sample and some deductions were done.

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, 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.

Thermogravimetric analyses were carried out as described by Kizgut et al. [11]. The thermogravimetric analyses were carried out by using a PL TGA 1500 thermogravimetric analyser. Employed reactivity program is represented in Figure 1.
Following, the calculation method (Eqn 1) for reactivity is provided.

\[ R = \left( -1 / W_0 \right) \times \left( \frac{dW}{dt} \right) \]  

(1)

Here,

\( W_0 \) : Initial weight of the residual carbon (char) (% dry ash free basis)

\( dW/dt \) : The maximum level of weight loss (min\(^{-1}\))

3. Results and discussions

Collected samples were cleaned physically in the beginning and latterly chemical cleaning was employed. The samples after physical cleaning were analysed in terms thermo-gravimetric methods and their reactivities were determined. In order to determine the reactivity of a sample TG and DTG curves should be obtained. The obtained TG and DTG curves for the samples after physical and chemical cleaning is provided in Figure 2-25.
Figure 2. TG/DTG profiles of TB1 sample after physical cleaning.

Figure 3. TG/DTG profiles of TB2 sample after physical cleaning.

Figure 4. TG/DTG profiles of TB3 sample after physical cleaning.

Figure 5. TG/DTG profiles of TB4 sample after physical cleaning.

Figure 6. TG/DTG profiles of TB5 sample after physical cleaning.

Figure 7. TG/DTG profiles of TB6 sample after physical cleaning.

Figure 8. TG/DTG profiles of TB7 sample after physical cleaning.

Figure 9. TG/DTG profiles of IT1 sample after physical cleaning.

Figure 10. TG/DTG profiles of IT3 sample after physical cleaning.

Figure 11. TG/DTG profiles of IT4 sample after physical cleaning.

Figure 12. TG/DTG profiles of IT6 sample after physical cleaning.

Figure 13. TG/DTG profiles of IT7 sample after physical cleaning.
Based on the TG/DTG profiles, reactivity of each sample was determined. Reactivity determination was performed for the clean samples after chemical treatment as well. The results obtained are tabulated in Table 2 and Table 3.
Table 2. Reactivity of each sample after physical cleaning.

| Sample | W_0  | dW/dT | R_{500} |
|--------|------|-------|---------|
| TB1    | 81.78| 15.29 | 0.19    |
| TB2    | 81.83| 8.28  | 0.10    |
| TB3    | 80.85| 8.59  | 0.11    |
| TB4    | 68.38| 15.11 | 0.22    |
| TB5    | 77.01| 14.29 | 0.19    |
| TB6    | 81.56| 6.93  | 0.09    |
| TB7    | 87.97| 5.49  | 0.06    |
| IT 1   | 83.16| 7.41  | 0.09    |
| IT 3   | 81.48| 8.33  | 0.10    |
| IT 4   | 78.33| 8.15  | 0.10    |
| IT 6   | 85.75| 5.16  | 0.06    |
| IT 7   | 85.85| 12.66 | 0.15    |

Table 3. Reactivity of each sample after chemical cleaning.

| Sample | W_0  | dW/dT | R_{500} |
|--------|------|-------|---------|
| TB1    | 61.52| 13.82 | 0.22    |
| TB2    | 58.88| 14.01 | 0.24    |
| TB3    | 54.05| 12.37 | 0.23    |
| TB4    | 49.59| 12.26 | 0.25    |
| TB5    | 58.95| 11.73 | 0.20    |
| TB6    | 62.38| 13.4  | 0.21    |
| TB7    | 61.97| 7.01  | 0.11    |
| IT 1   | 62.32| 12.62 | 0.20    |
| IT 3   | 64.58| 13.71 | 0.21    |
| IT 4   | 57.1 | 11.76 | 0.21    |
| IT 6   | 71.59| 13.73 | 0.19    |
| IT 7   | 73.37| 15.42 | 0.21    |

As previously explained, reactivity of a coal sample is obtained TG/DTG profiles and each sample after physical and chemical cleaning was analysed in terms of thermo-gravimetric methods for the characterization of these profiles. Referring to figures (Figure 2-25) each reactivity parameters for the corresponding sample was determined and these results are tabulated in Table 2 and Table 3. As regards to the reactivity results presented in Table 2 and Table 3, reactivity is increased after chemical cleaning. However for some samples it increased in specific percentages, for example for the sample TB2, it was 0.1 initially after physical cleaning and it increased to 0.24 after chemical cleaning. Same dramatic
increase was also observed for the sample IT6 (initially 0.06 and finally 0.19). And for some samples it did not increase as much dramatically, for example for sample TB5, it was 0.19 initially and it increased to 0.20 finally. These corresponding variations are represented in Figure 2.

![Figure 2. Reactivity after physical and chemical cleaning.](image)

Referring to Figure 2, it is easily observed the fact that reactivity increases after chemical cleaning. However for the samples except TB4 and TB5, the increase in reactivity can be claimed as significant. In order to have higher reactivity, chemical cleaning can be employed. For the samples TB4 and TB5, chemical treatment should be followed by some mineral adding as suggested by Liu et al. [1].

4. Conclusions

In this study, 12 coal samples were collected and their physical & chemical cleaning were performed. Thermo-gravimetric analysis was employed to obtain TG/DTG profiles of each sample after physical & chemical cleaning. Reactivity values for each samples were obtained from these abovementioned TG/DTG profiles. Reactivity values calculated are tabulated and examined. Increase in reactivity after chemical cleaning was observed. Chemical cleaning resulted in an increase for all the samples studied. The reactivity increase is restricted for TB4 and TB5 samples. These abovementioned samples should be chemically cleaned and right after this cleaning some minerals as suggested by Liu et al. [1] could be added in order to have higher reactivity. Reactivity of a coal sample has been addressed for coal further utilization like gasification and combustion. In order to understand the coal behaviour in these abovementioned processes, reactivity of coal sample or coal blends should be characterized. In the order of reactivity determination TG/DTG profiles should be previously obtained. However this study summarizes the fact that for higher reactivity purposes, coal can be chemically treated and significant increase is observed for 10 samples out of 12 samples studied. This study would be helpful in terms of better understanding the parameters resulting an increase in reactivity and it would contribute to future researchers/engineers in this field of coal combustion/pyrolysis/ gasification.

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