Activation Energies of Physically and Chemically Clean Coals

Mehmet Bilen

1 Department of Mining Engineering, Zonguldak Bülent Ecevit University, 67100, Zonguldak, Turkey
mehmetubilen@yandex.com

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 characterize the kinetics of each coal sample, activation energies of each corresponding coal sample were determined. Arrhenius equation was employed for the determination of above mentioned activation energies. Activation energies for both physically and chemically clean coal samples were determined. Activation energy of coal sample after chemical cleaning is observed to be higher the one that is obtained after physical cleaning. Referring to these differences, increase in activation energy after chemical cleaning was considered to be side effect of chemical cleaning, since higher activation energy means higher heat requirement for sample to be activated. Corresponding differences of activation energies were compared with the calorific values change respectively after physical cleaning and after chemical cleaning.

1. Introduction
Coal depending on its organic matrix and depending on thermal decomposition kinetics have different activation energy requirements. Activation energy for each coal can be different due to its thermal kinetics differentiation. The activation energy of the same coal sample before and after either physical or chemical treatment have differences, and this difference is expected and understandable.

Coal oxidation is an irreversible exothermic process and the reaction rate increases with temperature [1, 2, 3, 4, 5]. Thermogravimetric analysis is commonly employed method to address and investigate the thermal behaviour with kinetics [1, 6, 7, 8]. Coal activation energies not only determines the speed of coal oxidation reaction but also it reflects the tendency of spontaneous combustion [9, 10, 11]. In the study of Gao et al. [1], authors investigated the coal apparent activation energies at different oxygen concentrations and different heating rates. Referring to abovementioned authors’ findings [1], increase in oxygen concentrations resulted an increase of activation energy, while increase in heating rate resulted in a decrease of activation energies. Kizgut et al., [10], examined the effect of chemical demineralization on thermal behaviour of bituminous coals. And they [10] also expressed the fact that TG/DTG is being used to obtain burning profile and parameters like characteristic temperatures and reactivity derived from these profiles. These abovementioned parameters do not totally reflect burning conditions, they can be employed for the assessment of relative burning profiles of various coals and coal blends [10, 11, 12, 13, 14, 15]. Coal calorific value is already a sign for the corresponding effect of physical and chemical cleaning. However there is no any study concerning the change in calorific value and activation energy at the same time for both after physical and chemical treatment.
In this study, corresponding calorific value and activation energy change for 12 coal samples right after physical and chemical cleaning were investigated. Activation energies and calorific values show a decrease after chemical treatment. In order to understand the relationship between calorific value and activation energy, they were compared and possible relations between each were proposed. With this new proposed approach, one can have idea about sample activation energy (assuming first order reaction rates) considering the calorific value of that specific sample.

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                  |
| Çınarılı                 | TTK Amasra             | TB4                  |
| Büyük Damar             | TTK Armutçuk           | TB5                  |
| Sulu                     | TTK Üzülmez            | TB6                  |
| Söğütözü                 | Söğütözü-Kastamonu     | TB7                  |
| Goonyella                | Queensland-Avustralya  | IT 1                 |
| Weglokoks Typr-R35       | Silesia-Polony         | IT 3                 |
| South Blackwater         | Blackwater-Avustralya  | IT 4                 |
| Saraji                   | Mackay-Queensland-Avustralya | 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. [12]. The thermogravimetric analyses were carried out by using a PL TGA 1500 thermogravimetric analyzer. The tests were carried out with a 10±0.1mgcoalsample in a platinum crucible. The sample was heated to850°C at 10°C min⁻¹ in air with a flow rate of 15 cm³ min⁻¹ to determine the characteristic temperatures. The loss of mass, time and temperature were recorded simultaneously. This data then transferred to a computer to establish TG and DTG curves. The characteristic temperatures were designated as follows:

• Tic=temperature of initial chemisorption
• Tmc=temperature of maximum rate of chemisorption
• Ti=initial temperature where mass loss reaches to a rate of 1% per minute
• Tp=peak temperature at maximum mass loss rate
• T1/2 = temperature at which 50% burn off (mass, ash free basis) occurs, and
• Tb = burnout temperature where DTG profile reaches 1% combustion rate at tail end of the profile.

Considering thermogravimetric characterisations, Arrhenius equation was employed to obtain activation energies of each coal sample. Arrhenius equation is given as following:

\[ k = A \cdot e^{-\frac{E_a}{RT}} \]  

\( k \) = constant (first order) \( (\text{time}^{-1}) \)
\( E_a \) = Activation energy \( (\text{kJ.mol}^{-1}) \)
\( R \) = Universal gas constant \( (8,314 \text{ J/(gmol)(K)}) \)
\( T \) = Temperature \( (273+0^\circ\text{C}) \)

Taking the natural logarithm of Arrhenius equation;

\[ \ln k = \text{constant} - \frac{E_a}{RT} \]  

when \( \ln k \) is plotted against \( 1/T \), the slope of the linear curve equals to \(-E_a/R\), and from these abovementioned expressions, activation energies could be determined.

3. Results and discussions

Collected samples were analysed in terms of thermal analysis and their corresponding calorific values were determined. Thermal characterization was carried out on each sample after physical and chemical cleaning respectively. Thermal parameter results are tabulated in Table 2 and Table 3, respectively for physically and chemically clean coal samples.

Table 2. Thermal parameter results for physically clean coal samples.

| Thermal Parameters | Samples |
|--------------------|---------|
| \( T_{ic} (^\circ\text{C}) \) | TB1 142 TB2 129 TB3 141 TB4 163 TB5 142 TB6 179 TB7 149 IT 1 132 IT 3 140 IT 4 138 IT 6 161 IT 7 129 |
| \( T_{mc} (^\circ\text{C}) \) | 284 280 283 241 261 273 298 277 277 259 292 294 |
| \( T_i (^\circ\text{C}) \) | 360 352 349 343 358 343 344 339 340 327 353 353 |
| \( T_p (^\circ\text{C}) \) | 508 496 502 463 511 479 537 450 465 439 466 480 |
| \( T_{1/2} (^\circ\text{C}) \) | 502 493 494 464 504 475 533 456 466 444 475 473 |
| \( T_b (^\circ\text{C}) \) | 584 580 578 552 589 549 605 553 550 547 564 556 |

Table 3. Thermal parameter results for chemically clean coal samples.

| Thermal Parameters | Samples |
|--------------------|---------|
| \( T_{ic} (^\circ\text{C}) \) | - - - - - - - - - - - - |
| \( T_{mc} (^\circ\text{C}) \) | - - - - - - - - - - - - |
| \( T_i (^\circ\text{C}) \) | 328 310 324 227 324 330 384 330 331 309 345 341 |
| \( T_p (^\circ\text{C}) \) | 461 456 468 469 468 453 489 460 450 453 476 468 |
| \( T_{1/2} (^\circ\text{C}) \) | 458 454 464 449 464 453 487 463 456 450 476 468 |
| \( T_b (^\circ\text{C}) \) | 546 552 553 531 553 543 573 561 555 553 560 555 |

Based on the thermal parameter results tabulated in Table 1 and Table 2, activation energies of each sample (after physical and chemical cleaning) were calculated as following the procedure given in Experimental Method Section. Calculated activation energy (Ea) values for each sample are tabulated...
in Table 4. Determined calorific values for each corresponding sample (after physical and chemical cleaning) are tabulated in Table 5.

**Table 4.** Calculated activation energy values for each sample (after physical and chemical cleaning).

| Sample | After Physical Cleaning | After Chemical Cleaning |
|--------|-------------------------|-------------------------|
|        | Activation Energy       | Activation Energy       |
|        | (kJ mol⁻¹)              | (kJ mol⁻¹)              |
| TB1    | 95.77                   | 101.74                  |
| TB2    | 108.18                  | 124.31                  |
| TB3    | 89.01                   | 112.04                  |
| TB4    | 88.71                   | 94.59                   |
| TB5    | 82.93                   | 101.18                  |
| TB6    | 99.31                   | 117.76                  |
| TB7    | 163.29                  | 149.36                  |
| IT 1   | 114.14                  | 107.03                  |
| IT 3   | 96.26                   | 103.58                  |
| IT 4   | 93.19                   | 118.86                  |
| IT 6   | 120.89                  | 116.29                  |
| IT 7   | 123.00                  | 120.51                  |

**Table 5.** Determined calorific values of each sample (after physical and chemical cleaning).

| Sample | After Physical Cleaning | After Chemical Cleaning |
|--------|-------------------------|-------------------------|
|        | Calorific Value         | Calorific Value         |
|        | (kcal/kg)               | (kcal/kg)               |
| TB1    | 7676                    | 6776                    |
| TB2    | 7330                    | 6476                    |
| TB3    | 7683                    | 6157                    |
| TB4    | 6813                    | 5686                    |
| TB5    | 7614                    | 6597                    |
| TB6    | 7484                    | 6723                    |
| TB7    | 7733                    | 6406                    |
| IT 1   | 7908                    | 6672                    |
| IT 3   | 7718                    | 6952                    |
| IT 4   | 7800                    | 6136                    |
| IT 6   | 7934                    | 7169                    |
| IT 7   | 8067                    | 7387                    |

Referring to Table 3 and Table 4, calorific value differentiation after physical cleaning was thought be in relation with activation energies differentiation. As it can be noticed, activation energies decrease after chemical cleaning as calorific values do. In order to determine activation energy of a specific sample, thermo-gravimetric analysis should be performed. However, calorific value differentiation could be employed to predict the final activation energy after the cleaning steps. For this purpose, calorific value differences after cleaning were determined. (Table 6).
Table 6. Calorific value differences after physical & chemical cleaning.

| Sample | After Physical Cleaning | After Chemical Cleaning | Difference (%) |
|--------|-------------------------|-------------------------|----------------|
|        | Calorific Value (kcal/kg) | Calorific Value (kcal/kg) | [(CV_{apc}-CV_{acc})/CV_{apc}]*100 |
| TB1    | 7676                    | 6776                    | 11.72           |
| TB2    | 7330                    | 6476                    | 11.65           |
| TB3    | 7683                    | 6157                    | 19.86           |
| TB4    | 6813                    | 5686                    | 16.54           |
| TB5    | 7614                    | 6597                    | 13.36           |
| TB6    | 7484                    | 6723                    | 10.17           |
| TB7    | 7733                    | 6406                    | 17.16           |
| IT 1   | 7908                    | 6672                    | 15.63           |
| IT 3   | 7718                    | 6952                    | 9.92            |
| IT 4   | 7800                    | 6136                    | 21.33           |
| IT 6   | 7934                    | 7169                    | 9.64            |
| IT 7   | 8067                    | 7387                    | 8.43            |

CV_{apc}: Calorific value after physical cleaning; CV_{acc}: Calorific value after chemical cleaning.

Here note that the highest decrease was observed for the sample IT4 (21.33 %) and the lowest one was observed for the IT 7 (8.43 %). Taking these variations into consideration, activation energies after chemical cleaning was predicted. In order to carry out this prediction, activation energy values (after physical cleaning) was considered to increase as the ratio of calorific value decrease (after chemical cleaning). More clearly, activation energy values (after physical cleaning and chemical cleaning) and predicted activation energies (after chemical cleaning) are all provided in Table 7.

Table 7. Predicted activation energies with respect to originally determined ones.

| Sample | After Physical Cleaning | After Chemical Cleaning (Determined) | Predicted Values After Chemical Cleaning |
|--------|-------------------------|---------------------------------------|------------------------------------------|
|        | Activation Energy (kJ mol^{-1}) | Activation Energy (kJ mol^{-1}) | A_{E_{apc}}*(1+Diff (%))/100 |
| TB1    | 95.77                   | 101.74                               | 107.00                                   |
| TB2    | 108.18                  | 124.31                               | 120.78                                   |
| TB3    | 89.01                   | 112.04                               | 106.69                                   |
| TB4    | 88.71                   | 94.59                                | 103.38                                   |
| TB5    | 82.93                   | 101.18                               | 94.01                                    |
| TB6    | 99.31                   | 117.76                               | 109.41                                   |
| TB7    | 163.29                  | 149.36                               | 191.31                                   |
| IT 1   | 114.14                  | 107.03                               | 131.98                                   |
| IT 3   | 96.26                   | 103.58                               | 105.81                                   |
| IT 4   | 93.19                   | 118.86                               | 113.07                                   |
| IT 6   | 120.89                  | 116.29                               | 132.55                                   |
| IT 7   | 123.00                  | 120.51                               | 133.37                                   |

A_{E_{apc}}: Activation energy after physical cleaning, Diff: Difference calculated in Table 5.
Referring to Table 6, predicted activation energy values (after chemical cleaning) are between 94.01 and 191.31 while the determined ones change between 94.59 and 149.36. However for some specific samples, activation energies either determined or the predicted one are almost similar, i.e. refer to the sample IT3 (determined one is 103.58, predicted one 105.81). In order to better represent the achievement as regards to above mentioned prediction method, plot between determined activation energies and the predicted ones is provided (Figure 1).

Figure 1. Determined and predicted activation energy values for the chemically clean samples.

As it can be observed from Figure 1, significant correlation coefficient was obtained between determined and predicted activation energy values. Basically having the calorific values after physical and chemical cleaning and employing the difference between them would enable one to have idea about activation energy of coal samples after chemical cleaning. This would ease to have initial estimates of what the activation energy of clean sample would if their activation energy and calorific values differences are previously determined.

As previously explained, activation energy and calorific value are somehow in relation with each other. Referring back and forth to the tables (Table 3-6), activation energy increases while calorific value decreases. After either physical or chemical treatment or the both, calorific value changes for that specific sample, and decrease mostly after chemical cleaning. In addition, activation energy increase after chemical cleaning. After chemical treatment, decrease in calorific value and increase in activation energy make sense since chemical treatment disrupt the structure. Thermo-gravimetrical analysis is commonly employed method to characterize the coal thermal behaviour with kinetics, but sometimes it should not be necessary to evaluate. More clearly, after some physical or chemical treatments, the activation energy should/could change in a manner like the calorific value does or the opposite. After chemical treatment samples calorific values decreased within a range of 8 to 20 %. And after chemical treatment the activation energy values increased in some ratios. With this study, after physical or chemical treatment one can easily have an idea about the activation energy corresponding changes.

4. Conclusions
In this study, 12 coal samples were collected and their physical & chemical cleaning were performed. Activation energy of each sample after physical and chemical cleaning was determined with thermo-gravimetric methods. Not only the activation energy values of each sample but also the corresponding calorific values were obtained. As regards to the obtained results, after chemical cleaning, calorific values shows a decrease trend while activation energy values increase. This makes sense since chemical treatment harms the structure of coal and calorific values decrease and the activation takes longer. Corresponding differentiation of calorific values might/might not have the information about the activation energy increase. Taking this above-mentioned into consideration, a new prediction method
was proposed to predict the activation energy values of chemically cleaned coal samples. This prediction method takes the calorific value differentiation into account and the predicted activation energy values shows significant correlation with those determined. With this method proposed, one can easily have idea about activation energy values of coal samples after chemical cleaning, if she or he has the information of the activation energies of pre-cleaning process and calorific values differentiation.

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