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# Effect of demineralization on the reactivity of lignites

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## Abstract

In this study, effect of demineralization on the combustion reactivity of 25 lignite samples, originating from different areas of Turkey, was investigated. Non-isothermal thermogravimetry, where the sample was heated in air where temperature increased at a linear rate of 40 K/min to 1273 K, has been used to investigate the combustion reactivities of the original and demineralized lignite samples. The activation energies calculated by two different methods and the burning profiles of the original and demineralized samples were compared and discussed. It was observed that the combustion reactivity of the samples was considerably influenced by the demineralization process applied. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Lignite; Mineral matter; Reactivity

## 1. Introduction

Coal contains variable amounts of mineral matter which includes clay minerals, sulfides, carbonates, sulfates, chlorides, silicates, oxides, hydroxides and phosphates. Mineral matter is generally considered to be the sum of all inorganic minerals and elements that are present in coal. Thus, all elements in coal, except organically combined C, H, N, O and S, are classified by this definition as mineral matter [1,2].

Mineral matter in coal has been classified in different ways, but for practical purposes it is useful to classify it as inherent or adventitious mineral matter [1,3]. Inherent mineral matter represents the material that is too closely associated with the coal substance to be readily separated from it by physical methods, and the adventitious represents the material that is less intimately associated with the coal substance and thus more readily removable on coal cleaning [1,3].

The amount and composition of the mineral matter can influence the combustion characteristics of coal, which is important in the design of coal-fired boilers [4–7]. Two models have been proposed to explain catalysis of carbon reactions: the first is the oxygen-transfer model, the second is the electron-transfer mechanism [8]. The first model emphasizes the catalyst–gas interaction; the second emphasizes the catalyst–carbon interaction [8].

The objective of the research described in this study is to investigate the effects of demineralization on the combustion reactivity of 25 lignite samples originating from different areas of Turkey.

## 2. Experimental

In the experiments, 25 lignite samples originating from different areas of Turkey were used. Samples

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were ground and sieved into a powder with a particle size of 250 μm. The proximate analysis and the calorific value measurements of the lignite samples were performed according to ASTM standards. Determination of the total mineral matter content of the lignite samples was carried out according to the ISO-602 standard. The demineralization of the lignite samples was achieved by the treatment with hydrochloric and hydrofluoric acids under the conditions described in the ISO-602 standard.

Thermogravimetric analysis of the original and demineralized lignite samples was carried out using a Shimadzu TG 41 thermal analyzer. Forty-milligram samples were spread uniformly on the bottom of the crucible made of alumina. The temperature was raised at a heating rate of 40 K/min to 1273 K and held for 30 min at this temperature. During the studies, the flow rate of the air was fixed at 40 cm$^3$/min.

## 3. Results and discussion

The analyses results of the lignite samples are shown in Table 1.

The best way to estimate the combustion reactivity of a coal sample is to determine activation energy value from its burning profile. Experimental non-isothermal TG data has been used to calculate the activation energy values of the original and demineralized lignite samples by the methods of Coats–Redfern [9]. and Zsako [10,11]. The activation energy values calculated by the methods of Coats–Redfern and Zsako for the combustion reactions of original lignite samples ranged between 64–139 and 84–147 kJ/mol, respectively (Table 2). Activation energy values calculated by the same methods for the combustion reactions of the demineralized lignites varied between 77–144 and 88–175 kJ/mol, respectively (Table 3).

Table 1
The results of analysis of the original lignite samples

| Sample code | Moisture (wt.%) | Volatile matter (wt.%) | Fixed carbon (wt.%) | Ash (wt.%) | Mineral matter (wt.%) | Net calorific value (MJ/kg) |
|---|---|---|---|---|---|---|
| L-01 | 10.5 | 32.2 | 25.1 | 32.2 | 41.9 | 10.5 |
| L-02 | 4.4 | 22.2 | 32.8 | 40.6 | 44.4 | 14.5 |
| L-03 | 15.7 | 36.1 | 16.4 | 31.8 | 46.2 | 11.4 |
| L-04 | 9.6 | 39.2 | 40.2 | 11.0 | 11.9 | 21.7 |
| L-05 | 10.5 | 36.8 | 40.6 | 12.1 | 16.5 | 20.8 |
| L-06 | 19.9 | 30.3 | 35.8 | 14.0 | 16.4 | 17.0 |
| L-07 | 27.6 | 39.8 | 22.8 | 9.8 | 12.3 | 16.9 |
| L-08 | 24.2 | 38.4 | 31.2 | 6.2 | 7.7 | 17.2 |
| L-09 | 2.0 | 32.0 | 51.6 | 14.4 | 17.0 | 27.1 |
| L-10 | 14.0 | 36.1 | 23.3 | 26.6 | 34.8 | 14.2 |
| L-11 | 7.2 | 46.4 | 39.1 | 7.3 | 12.5 | 26.0 |
| L-12 | 25.3 | 28.7 | 16.7 | 29.3 | 38.3 | 11.6 |
| L-13 | 16.2 | 40.9 | 10.3 | 32.6 | 44.1 | 12.1 |
| L-14 | 15.9 | 41.0 | 36.4 | 6.7 | 13.7 | 20.0 |
| L-15 | 35.4 | 32.2 | 23.4 | 9.0 | 15.3 | 13.4 |
| L-16 | 12.5 | 32.3 | 32.3 | 22.9 | 27.7 | 19.2 |
| L-17 | 17.9 | 37.3 | 26.1 | 18.7 | 28.9 | 16.1 |
| L-18 | 27.0 | 34.4 | 18.0 | 20.6 | 26.8 | 14.6 |
| L-19 | 14.1 | 33.4 | 39.8 | 12.7 | 15.1 | 19.7 |
| L-20 | 13.9 | 24.6 | 22.3 | 39.2 | 48.0 | 12.1 |
| L-21 | 40.4 | 32.1 | 12.3 | 15.2 | 35.6 | 12.8 |
| L-22 | 6.4 | 28.6 | 37.4 | 27.6 | 33.9 | 19.0 |
| L-23 | 5.9 | 31.8 | 53.4 | 8.9 | 8.8 | 27.7 |
| L-24 | 27.5 | 34.4 | 24.0 | 14.1 | 27.6 | 12.3 |
| L-25 | 48.0 | 28.2 | 11.8 | 12.0 | 30.2 | 10.3 |

Table 2
Activation energy values of the original lignite samples

| Sample code | Coats–Redfern (kJ/mol) | Zsako (kJ/mol) |
|---|---|---|
| L-01 | 87.7 | 92.1 |
| L-02 | 124.1 | 129.7 |
| L-03 | 86.4 | 92.1 |
| L-04 | 95.0 | 100.4 |
| L-05 | 108.1 | 100.4 |
| L-06 | 85.0 | 87.9 |
| L-07 | 97.3 | 104.6 |
| L-08 | 95.4 | 100.6 |
| L-09 | 138.5 | 146.7 |
| L-10 | 89.4 | 96.3 |
| L-11 | 103.7 | 113.0 |
| L-12 | 104.2 | 113.0 |
| L-13 | 87.5 | 92.1 |
| L-14 | 64.2 | 83.7 |
| L-15 | 83.2 | 87.8 |
| L-16 | 81.5 | 83.7 |
| L-17 | 84.3 | 87.9 |
| L-18 | 87.1 | 96.3 |
| L-19 | 88.9 | 96.3 |
| L-20 | 122.8 | 129.7 |
| L-21 | 72.4 | 83.7 |
| L-22 | 96.9 | 100.4 |
| L-23 | 100.1 | 104.6 |
| L-24 | 78.1 | 83.7 |
| L-25 | 84.4 | 87.9 |

Table 3
Activation energy values of the demineralized lignite samples

| Sample code | Coats–Redfern (kJ/mol) | Zsako (kJ/mol) |
|---|---|---|
| L-01 | 113.5 | 146.5 |
| L-02 | 126.8 | 131.2 |
| L-03 | 92.7 | 104.6 |
| L-04 | 102.5 | 113.0 |
| L-05 | 110.9 | 104.6 |
| L-06 | 109.1 | 133.9 |
| L-07 | 108.3 | 121.4 |
| L-08 | 104.9 | 120.3 |
| L-09 | 143.7 | 156.5 |
| L-10 | 92.8 | 98.1 |
| L-11 | 112.3 | 125.6 |
| L-12 | 108.5 | 117.2 |
| L-13 | 96.2 | 100.4 |
| L-14 | 95.0 | 108.8 |
| L-15 | 86.3 | 96.3 |
| L-16 | 86.0 | 96.2 |
| L-17 | 90.0 | 104.6 |
| L-18 | 90.5 | 108.8 |
| L-19 | 89.8 | 98.3 |
| L-20 | 126.3 | 146.5 |
| L-21 | 77.4 | 87.9 |
| L-22 | 111.2 | 121.4 |
| L-23 | 133.7 | 142.3 |
| L-24 | 80.9 | 87.9 |
| L-25 | 90.4 | 117.2 |

The comparison of the activation energy values calculated for the combustion reactions of original and demineralized lignites clearly show that the removal of mineral matter causes a decrease in combustion reactivity. The combustion activation energies of the demineralized lignite samples are found to be higher than those of the original samples. The maximum differences were determined as 48% between values calculated by the Coats–Redfern method and 57% between values calculated by the Zsako method.

It is known that the demineralization process performed by treatment with hydrochloric and hydrofluoric acids is not successful in removing iron-containing mineral species. This means that the demineralized lignite samples contain iron which has catalytic effect on combustion of coal [8]. Therefore, lignite samples with high iron content did not show a considerable reactivity decrease after demineralization as expected.

The burning profiles of the original and demineralized lignite samples are also compared. The characteristic temperatures of the burning profiles are listed in Table 4. The ignition temperature corresponds to the point where the burning profile curve underwent a sudden rise. The ignition temperatures of the original lignite samples derived from their burning profiles lie in the range of 420–498 K, whereas the ignition temperatures of the demineralized samples range between 442 and 656 K. Demineralization causes an increase in ignition temperature between 4 and 158 K.

The point of the burning profile at which the rate of weight loss due to combustion is a maximum is called the ‘peak temperature’. Burning profile peak temperature is taken as a measure of the reactivity of a coal: the lower the maximum peak temperature, the more reactive a coal may be considered [12,13]. The peak temperatures of the original and demineralized lignite samples range between 533–804 and 485–879 K, respectively. Demineralization causes an increase in the peak temperature of 17 lignite samples between 4 and 95 K; however, the peak temperature of eight samples decreases after demineralization.

Table 4
Characteristic temperatures of the burning profiles obtained for original and demineralized lignite samples

| Sample code | Original lignite sample | | Demineralized lignite sample | |
|---|---|---|---|---|
| | Ignition temperature (K) | Peak temperature (K) | Ignition temperature (K) | Peak temperature (K) |
| L-01 | 435 | 631 | 516 | 668 |
| L-02 | 478 | 793 | 506 | 879 |
| L-03 | 463 | 623 | 486 | 670 |
| L-04 | 473 | 649 | 511 | 660 |
| L-05 | 438 | 766 | 521 | 715 |
| L-06 | 438 | 691 | 489 | 600 |
| L-07 | 458 | 665 | 462 | 688 |
| L-08 | 448 | 702 | 502 | 577 |
| L-09 | 498 | 763 | 656 | 722 |
| L-10 | 438 | 657 | 514 | 668 |
| L-11 | 488 | 676 | 497 | 680 |
| L-12 | 429 | 722 | 447 | 637 |
| L-13 | 443 | 623 | 484 | 485 |
| L-14 | 421 | 642 | 487 | 711 |
| L-15 | 446 | 620 | 477 | 624 |
| L-16 | 443 | 714 | 465 | 724 |
| L-17 | 443 | 621 | 482 | 670 |
| L-18 | 420 | 609 | 484 | 598 |
| L-19 | 430 | 665 | 471 | 737 |
| L-20 | 483 | 804 | 525 | 820 |
| L-21 | 418 | 533 | 451 | 568 |
| L-22 | 463 | 678 | 497 | 720 |
| L-23 | 463 | 797 | 501 | 757 |
| L-24 | 444 | 594 | 457 | 684 |
| L-25 | 423 | 580 | 442 | 594 |

Jenkins et al. [14] suggested that the additional porosity produced by mineral removal enhances the reactivity of coals which have particularly small pore structure. If this increase in reactivity of a coal becomes dominant and exceeds the reduction in catalytic activity, the overall reactivity of coal increases as a result of demineralization. The removal of the inherent mineral matter during demineralization process can improve the porosity of coal. But the pore structure of coal could not be affected by the removal of the adventitious coal mineral matter which has been liberated during crushing.

The experimental results obtained in this work show that the application of demineralization generally shifts the burning profiles of the lignite samples to higher temperatures.

The conversion values calculated for the combustion reactions of the original and demineralized lignite

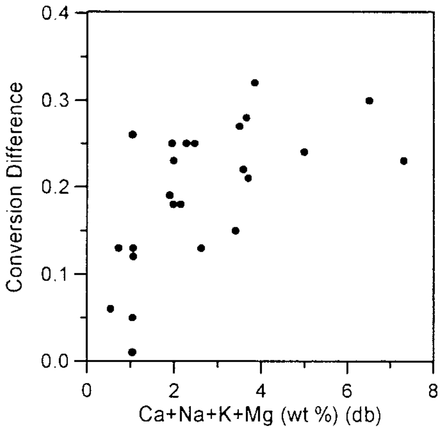

Fig. 1. Relationship of the conversion differences between original and demineralized lignite samples at 1273 K with the sum of the Ca, Na, K and Mg contents (dry basis) of the original lignite samples.

Table 5
Conversions of the original and demineralized lignite samples at 873 and 1273 K

| Sample code | Original lignite sample | | Demineralized lignite sample | |
|---|---|---|---|---|
| | 873 K | 1273 K | 873 K | 1273 K |
| L-01 | 0.51 | 0.90 | 0.37 | 0.58 |
| L-02 | 0.34 | 0.72 | 0.28 | 0.53 |
| L-03 | 0.52 | 0.97 | 0.44 | 0.69 |
| L-04 | 0.41 | 0.76 | 0.40 | 0.71 |
| L-05 | 0.35 | 0.64 | 0.34 | 0.63 |
| L-06 | 0.45 | 0.80 | 0.38 | 0.67 |
| L-07 | 0.48 | 0.86 | 0.43 | 0.68 |
| L-08 | 0.49 | 0.83 | 0.44 | 0.71 |
| L-09 | 0.16 | 0.67 | 0.15 | 0.41 |
| L-10 | 0.67 | 0.99 | 0.45 | 0.72 |
| L-11 | 0.67 | 0.67 | 0.35 | 0.61 |
| L-12 | 0.46 | 0.99 | 0.43 | 0.69 |
| L-13 | 0.55 | 0.99 | 0.50 | 0.76 |
| L-14 | 0.56 | 0.90 | 0.43 | 0.65 |
| L-15 | 0.51 | 0.90 | 0.45 | 0.67 |
| L-16 | 0.48 | 0.80 | 0.42 | 0.67 |
| L-17 | 0.50 | 0.86 | 0.46 | 0.71 |
| L-18 | 0.53 | 0.93 | 0.48 | 0.71 |
| L-19 | 0.45 | 0.77 | 0.41 | 0.69 |
| L-20 | 0.41 | 0.82 | 0.32 | 0.57 |
| L-21 | 0.57 | 0.96 | 0.51 | 0.75 |
| L-22 | 0.37 | 0.95 | 0.30 | 0.54 |
| L-23 | 0.31 | 0.60 | 0.22 | 0.47 |
| L-24 | 0.55 | 0.90 | 0.43 | 0.65 |
| L-25 | 0.56 | 0.99 | 0.49 | 0.74 |

samples at 873 and 1273 K are listed in Table 5. It is apparent that the conversions of the original lignite samples are greater for both the temperatures examined. The differences at 1273 K are greater than those at 873 K (except 4 samples). Therefore, it can be concluded that the catalytic effects of the mineral species on the combustion reactivity of coal increase with increasing temperature in the temperature range investigated.

An inspection of Table 5 indicates that the combustion of the original lignite samples was nearly completed at 1273 K. However, an important part of the demineralized lignite samples combusted during holding the temperature at 1273 K.

The relationship of the conversion differences between original and demineralized samples at 1273 K with the sum of the Ca, Na, K and Mg contents of the original lignite samples is shown in Fig. 1. As the concentration of these elements in the original lignite samples increases, the effect of the demineralization processes on the conversion increases.

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