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Comparison of the Combustion Characteristics of Three Different Fossil Fuels from Turkey

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ABSTRACT: In this study, thermal features and reaction kinetics of the raw Çorum-Alpagut Lignite, Zonguldak-Üzülmez Bituminous Coal and Şırnak-Avgamasya Asphaltite were investigated through a qualitative and quantitative comparison via Thermogravimetric Analysis (TG/DTG) and an Arrhenius Type Kinetic Model, in order to determine the liability to ignite and effectiveness of the combustion of the concerned fuels as well as the critical points during their reaction periods. At the end of experiments, Alpagut Lignite, Üzülmez Bituminous Coal and Avgamasya Asphaltite resulted in different combustion features in terms of residue left, peak temperatures and activation energies from which the combustion behaviour of these fuels can be interpreted in details. In this study, thermal features and reaction kinetics of the raw Çorum-Alpagut Lignite. Zonguldak-Üzülmez Bituminous Coal and Şırnak-Avgamasya Asphaltite were investigated through a qualitative and quantitative comparison via Thermogravimetric Analysis (TG/DTG) and an Arrhenius Type Kinetic Model, in order to determine the liability to ignite and effectiveness of the combustion of the concerned fuels as well as the critical points during their reaction periods. At the end of experiments, Alpagut Lignite, Üzülmez Bituminous Coal and Avgamasya Asphaltite resulted in different combustion features in terms of residue left, peak temperatures and activation energies from which the combustion behaviour of these fuels can be interpreted in details.

1 INTRODUCTION

Rather than oil, lignite, bituminous coal and asphaltite are the most important fossil fuel types in Turkey with considerable reserves all around the country. These energy sources are utilized extensively for electricity production and heating purposes. For the determination of the appropriate fuel among the alternatives for specific purposes and the design of the combustor facilities, it is essential to have considerable information related to the thermal behaviour of such fuels. Ignition and proceeding combustion reactions of fossil fuels are accompanied by weight loss, thermal decomposition of the mineral matrix, diffusion and heat transfer to the surroundings. These subsequent phases are excessively influenced by various parameters such as the reactivity of the fuel, its liability to react with Oj, as well as physical features arising in accordance to the origin *of* the fuel. Thermal analysis methods proved to be a sucessful tool in the investigation of the combustion behaviour of the fossil fuels (Kanikowski and Stenberg, 1988), especially in the previous two decades. The reliability of the process in reflecting the consecutive thermal processes (i.e. loss of moisture, devolatilization, oxidation of fixed carbon, pyrolysis reactions, etc.) and the flexibility in the application of various temperature regimes attracted great interest to thermal analysis methods like DSC (differential scanning calorimetry), DTA (differential thermal analysis) TGA/DTG (thermo-gravimetric analysis/differential thermogravimetry) DSC and TGA techniques were effectively utilized for the characterization of Ohio Bituminous Coals by Rosenvold et al. (1981). Twentyone coal samples from Ohio were analyzed for the determination of the distinct volatilization and oxidation regions as well as endothermic and exothermic peak points. Chemical reactions corresponding to the related individual temperature values which have dictated the on-going combustion process were dealt and compared in details with respect to the coal type. Khulbe et al. (1984) performed pyrolysis studies with the asphaltene fraction derived from Cold-Lake (Canada) bitumen by using TGA and the kinetics of the conversion process was determined via an Arrhenius type kinetic model. Combustion behaviour of 10 different coals of lignite, sub-bituminous and bituminous type was compared qualitatively through DSC and TGA by Janikowski and Stenberg (1988). For all the coals studied, two definite regions of chemical reactivity were

Table 1. Proximate Analysis and Sulphur Content of the Samples (original basis)

	Alpagut Lignite	Avgamasya Asphallite	Üzülmez Bituminous Coal
Moisture *(%)*	7.56	0.66	0.36
Volatile Matter (7r)	II 09	33.25	25.75
Fixed Carbon (%)	35.20	21.23	58.71
Ash(%)	46.15	44 86	15.18
Sulphur (tf)	1.80	5.53	0.35
Calorific Value (Kcal/Kg)	4300	4515	6754

determined, but at varying temperature ranges. All these and parallel studies claimed that thermogravimetric methods were very well adopted to researches concerning fossil fuels This study deals with the comparison of three most important energy sources in Turkey of different type, lignite, bituminous coal and asphaltite. In this respect, the combustion behaviour of these solid fossil fuels were investigated by means of non-isothermal TG/DTG analyses. Both quantitative and qualitative determined, but at varying temperature ranges. All these and parallel studies claimed that thermogravimetric methods were very well adopted to researches concerning fossil fuels This study deals with the comparison of three most important energy sources in Turkey of different type, lignite, bituminous coal and asphaltite. In this respect, the combustion behaviour of these solid fossil fuels were investigated by means of non-isothermal TG/DTG analyses. Both quantitative and qualitative evaluations were made and the results related to the thermal features of the competing fuels were complemented by a successive reaction kinetics approach.

2 EXPERIMENTAL

For the study, Alpagut Lignite (Çorum), Üzülmez Bituminous Coal (Zonguldak) and Avgamasya Asphaltite (Sımak) were used whose proximate analyses are given in Table 1. At this point, it should be noted that, Avgamasya asphaltite consists of considerably high sulphur amount when compared with the lignite and bituminous coal, which is one of its distinct characteristics.

The calorific values of the samples were measured with a Parr Oxygen Bomb Calorimeter For commencing the thermogravimetric analyses, firstly, the bulks were crushed to -100 mesh and then represantative samples were taken to be combusted in a Polymer Laboratories PL TGA-1500 analyzer (Fig. 1). Non-isothermal TG method enables the observation of the weight loss of a sample as a function temperature and time through a pre-determined temperature regime and/or period. In addition, it is possible to obtain and collect series of numerical data of weight, temperature and time changes at any desired interval. For each experiment, samples of approximately 25 mg were placed in a platinum crucible and installed to the furnace of the TG unit. The initial temperature was set to ambient and it was continuosly increased upto 900 "C with a constant heating rate of 10 "C/min through a full controlled temperature programme. A uniform airflow of 15 mL/min was supplied to the combustion cell during the whole experiment. Prior to the experiments, the TGA instrument was calibrated for reliable results. At the end of each session, data required for the determination of the thermal characteristics and application of the kinetic analyses were obtained by means of thermogravimetric and differential weight loss curves of the realized combustion reactions.

3 RESULTS AND DISCUSSION

3. J Thermal Features

Although the combustion profiles of most of the fossil fuels possess a number of common phases such as loss of moisture and volatiles, oxidation of fixed carbon and evolution of heat, the differences related to those dictate the nature and efficiency of the combustion reaction. The temperature ranges of such individual intervals, their effect on the overall combustion period, importance on the whole reaction series and similar phenomena all rely on the composition, origin, mineral matrix, etc. of the concerned fuel type. Owing to these distinct features, various fuels result in considerably different combustion behavior efficiency and consequences.

At the end of experiments, the thermograms of lignite, bituminous coal and asphaltite showed characteristic combustion profiles. These differences were apparently noticed through the complementary DTG curves. The TG/DTG profiles of Alpagut lignite, Avgamasya asphaltite and Üzülmez bituminous coal are shown in Figures 2, 3 and 4, respectively.

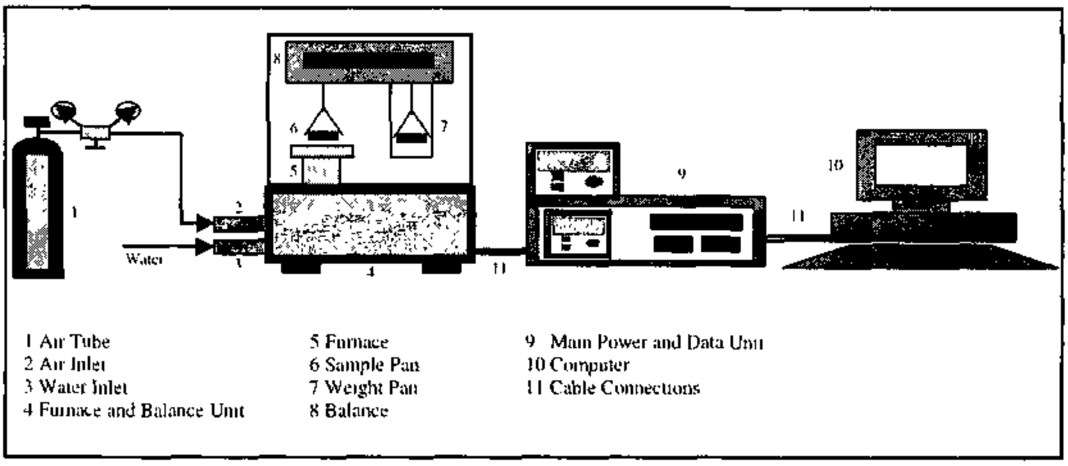
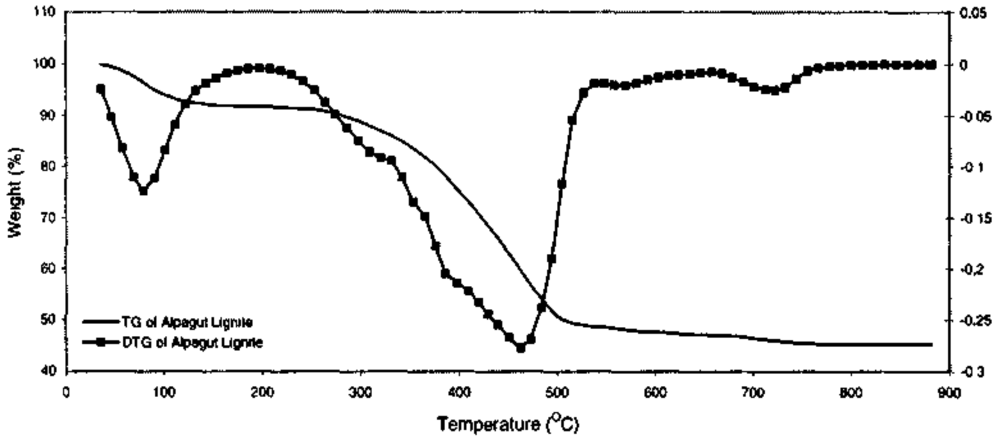


Figure I. Schematic form of the TG/DTG analyzer.

It was seen that Alpagut Lignite lost its moisture and the volatiles in two distinct regions around 35-180 "C and 210-360 "C, respectively (Fig. 2). After these periods, the onset of fixed carbon oxidation was seen aprroximately at 365 "C. It was observed that combustion occurred at two successive regions, between 365-541 "C and 551-787 "C, respectively. However, the weight loss realized during the second region was so slight compared to the primary one, indicating that the reactions dictating the combustion behaviour mainly occurred during the first one (Fig. 2). Like Alpagut lignite, the release of the moisture and the volatiles fraction occurred as particular processes between 60-165 "C and 274-380 "C, respectively for Avgamasya asphaltite. Oxidation reactions were realized at two distinct phases, between 385-558 "C and 630-836 "C (Fig. 3). Ft is obviously seen from Figures 2 & 3 that the second oxidation region of asphaltite is broader than lignite's in terms of weight loss. Gorman and Walker (1973) reported that inorganic minerals occunng in fossil fuels such as various clays or carbonates tend to decompose beginning from 600-650 "C upto 800-850 °C. Thus, this distinct second oxidation region may be well attributed to the decomposition of calcitc and dolomite which were reported to exist in considerable amounts in the mineral matrix of Avgamasya asphaltite (Hicyilmaz & Altun, 2002). For the combustion of Üzülmez bituminous coal, it can be claimed that no significant moisture release was observed (Fig. 4). It is seen from the proximate analysis (Table 1) that moisture content of Üzülmez coal is very low. Thus, it is normal not to observe any distinct region corresponding to the loss of moisture in the TG and/or DTG profiles. However, beginning from approximately 180 "C, the weight of the sample happened to increase gradually upto 290 °C. This peculiar segment in the TG/DTG profile of Üzülmez bituminous coal corresponds to the ehemisorption of oxygen to the pores (Crelling et al., 1992) due to which the sample gains weight (Fig. 4). The loss of volatiles was realized between 290-386 "C. The onset of combustion was observed beyond 395 °C and oxidation of the combustible species occurred in one apparent region that lasted around 770 "C.

In thermogravi metric studies, one of the distinctive aspects is the maximum peak temperature which accounts for the point where the rate of weight loss is at its highest level. Relative reactivity of the coal samples may be determined by using these peak temperatures, which can be directly interpreted from the DTG curves, in this respect, Alpagut lignite can be claimed to be more reactive than Üzülmez bituminous coal with a lower maximum peak temperature at 463.80 "C (Table 2). The reactivity order of the coal samples involved in this study may be well attributed with the rank concept. The reactivity order given here is in confirmation with the literature (Ceylan et al., 1999), where young coals (lignite in this study) which are of low rank proved to be more reactive than the old ones of higher rank (bituminous coal in this study). However asphaltite can be narrated with neither the reactivity nor the rank relation owing to its petroleum origin (Orhun, 1969). The residue left after the non-isothermal thermogravimelry runs is also one of the indicators providing clues about the thermal behaviour and combustion quality of the fossil fuels. Although, Üzülmez bituminous coal was found to be the least reactive sample, it proved to result in the most efficient combustion from the view of residue with the lowest residue value of 15.68 %. Furthermore, it was seen that Alpagut lignite involved a high amount of incombustible material which was approximately 45 % (Table 2)



Figuie 2 TG/DTG Profiles ot Alpagut Lignite

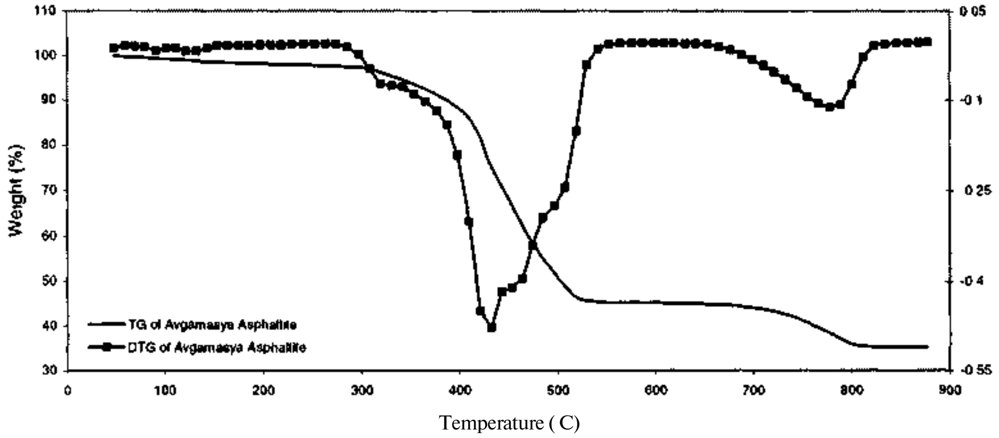


Figure 3 TG/DTG Piofiles ot Avgamasya Asphaltite

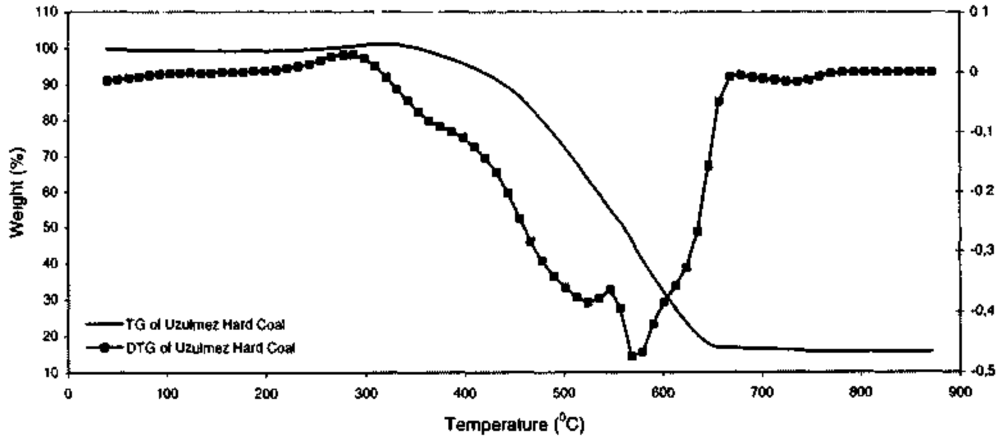


Figure 4 TG/DTG Pıotıles of Üzülmem Bituminous Coal

Table 2. Thermal Features of the Samples

	Alpagut Lignite	Avgamasya Asphaltite	Üzülmez Bituminous Coal
Maximum Peak Temperature ("O	463.80	427.55	572.70
Burnout Temperature ("O	786.64	836.01	768.32
Residue (%)	45.26	35.06	15.68

3.2 Kinetic Analysis

As well as thermal features, evaluating the overall combustion process in view of reaction kinetics provides considerable data related to the reactivity degree of the fossil fuels. Kinetic analysis enables the interpretation of the very complex subsequent series of reactions comprising the overall combustion profile in a very rapid, reliable and more understandable way. In this study, the thermal findings of the concerned fossil fuels were complemented with the determination of their activation energies, since activation energy is the measure of the easiness of a sample to begin combusting and complete the reaction. Arrhenius type kinetic model is one of the most appropriate concepts in expressing the reaction kinetics of the samples, which can be successfully adopted and relied to TG/DTG data. Hence, kinetic characteristics of the samples were analysed and investigated by this method

According to the model;

$$\frac{dw}{dt} = kW^n \qquad (1)$$

$$k = Ar\exp(\frac{-E}{RT}) \qquad (2)$$

Combining 1 and 2 gives;

$$\frac{dw}{dt} = Ar\exp(\frac{-E}{RT})W^n \qquad (3)$$

In this equation, dw/dt shows the rate of weight change of the reacting material, Ar is the Arrhenius Constant, E is the activation energy, T is the temperature, R is the gas constant, and n is the reaction order.

For analysing the TG/DTG data, the model assumes that the rate of weight loss of the total sample depends only on the rate constant, the weight of the sample remaining and the temperature with assumed unity reaction order. Thus, the equation takes the following form;

$$\frac{1}{W}\left(\frac{dw}{dt}\right) = Ar\exp\left(\frac{-E}{RT}\right) \qquad (4)$$

Taking the logarithm of both sides provides;

$$\log\left[\frac{1}{W}\left(\frac{dw}{dt}\right)\right] = \log Ar - \frac{E}{2.303RT} \qquad (5)$$

TG/DTG data provides directly the variation of weight with respect to temperature (i.e. dw/dt) and weight of the reacting material at each temperature level. Thus, plotting log[l/W(dw/dt)] against 1/T, results in the experimental interpretation of the model. The normalization of this curve results in a straight line whose slope explicitly equals to -E/2.303R(Koketal., 1997).

As has been stated, the overall combustion reaction of fossil fuels is comprised of a number of individual events taking place subsequently. The individual activation energies for each reaction region may rely on and can be notionally attributed to different mechanisms. However, they do not give any indication of the contribution of each region to the overall reactivity of the sample as singular ones. Hence, the Arrhenius type kinetic model is complemented with the concept of weighted mean activation energy, E_{wm} (Cumming 1984), to involve the participation of each individual region so as to determine the overall reactivity of the sample at all;

$$E_{wm} = F_1E_1 + F_2E_2 + F_3E_3 + ...+ F_nE_n \qquad (6)$$

where Fi, F:.........F„ are the mass fractions of the combustible content of the sample oxidized during each region of Arrhenius linearity, and Ei, Ei......., E„ are the individual apparent activation energies corresponding to each region.

In Table 3, the activation energies of the samples are given. As seen from this table, the activation energy of Üzülmez bituminous coal is twofold of Alpagut lignite and higher than Avgamasya asphaltite. Alpagut lignite resulted in the lowest activation energy value with 17.52 KJ/mol. These results suggested that, Alpagut lignite was the most liable fuel to ignite and combust. The ignition and the on-going combustion reactions became harder and harder as shifted to Avgamasya asphaltite and Üzülmez bituminous coal. Consequently, the combustion of the lignite sample occurred in the most favorable way when compared to asphaltite and bituminous coal. When the observations about thermal and kinetic features of the fuels are evaluated together, it can be proposed that having a high calorific value and/or a low amount of inorganic constituents are not the determining features for an easy ignition and favorably proceeding combustion when the comparison is among fuels of different types. Despite having the most adverse residue and calorific value, Alpagut lignite was found to be the most reactive fuel, proving this approach.

Table 3. Activation Energies of the Samples

Sample Type	Activation Energy (KJ/mol)
Alpagut Lignite	17.52
Avgamasya Asphaltite	29.56
Üzülmez Bituminous Coal	36.18

4 CONCLUSIONS

In view of the findings of the study, the following conclusions can be derived;

1. It was seen that Alpagut lignite, Avgamasya asphaltite and Uzulmez bituminous coal resulted in significantly different combustion profiles in terms of thermal features and kinetic behaviour.
2. The oxidation of the combustible matter of Alpagut lignite and Avgamasya asphaltite occurred in two succeeding regions. It is noteworthy to mention that the weight loss during the second oxidation region of asphaltite was significantly higher than that of lignite. The combustion profile of Üzülmez bituminous coal resulted in a very characteristic weight gain region corresponding to the oxygen chemisorption.
3. From the view of thermal features, Üzülmez bituminous coal appeared to be the highest quality fuel among the supplements in the study, providing the lowest residue and highest calorific value. However, in terms of reaction kinetics combustion of Üzülmez bituminous coal gave rise to the highest activation energy, indicating that initiating and proceeding the combustion reactions were considerably harder when compared to lignite and asphaltite.
4. Although, Alpagut lignite was observed to be the most unfavorable fuel with the highest residue and lowest calorific value, it was found to be the most reactive fuel with the earliest combustion onset and the lowest activation energy. Thus, ignition and oxidation of the combustible matter occurred more easily and efficiently when compared to asphaltite and bituminous coal.
5. The thermal and kinetics features of Avgamasya asphaltite were observed somewhere in between lignite and bituminous coal. Hence, it may be accepted as a considerable supplement to lignite and bituminous coal where exists. However, the high sulphur content may be an obstacle, which should be evaluated further.

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