

Effect of pyrolysis temperature on burning reactivity of lignite char

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Abstract

Elbistan lignite is low-quality Turkish lignite with high ratio of volatile matter/fixed carbon contents that causes very high thermal reactivity. Partly elimination of volatiles from lignite was performed by pyrolysis at different temperatures to study effects of volatile matter removal on thermal reactivity. Hence, it was subjected to pyrolysis in both a horizontal tube furnace and a thermal analyzer at temperatures between 300-700 °C. Then, the semi-chars were burned in a thermal analyzer up to 900°C to compare the effects of pyrolysis temperature on char burning reactivity. Seven different criteria were considered to compare the thermal reactivity of the pyrolytic semi-chars during non-isothermal burning process. It was concluded that the extent of volatile matter removal (especially in oxygen content) provides enrichment in carbon content, and accordingly reduction in reactivity. The severity of pyrolysis step determines the thermal history of char which affects the reactivity in sequential processes. Increasing final temperature in pyrolysis step reduced the burning reactivity of the forming char. Ignition temperature shifted to higher temperatures owing to reducing reactivity, and complete burning of the char occurred at elevated temperatures and took longer times. This successively affected many reactivity-related parameters such as burn-out levels, maximum burning rate and its temperature, conversion levels, heat flow rates, etc.

Keywords: Lignite; Pyrolysis temperature; Burning; Reactivity
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1. Introduction

Coal combustion is still the leading alternative for power generation worldwide, and any possible measure to improve the combustion efficiency of coal and to lower emissions from combustion is of great importance. However, coal combustion is a complex process and has several stages such as pyrolysis, homogenous combustion of volatiles, and heterogeneous combustion of solid char. That is, pulverized coal particles undergo to rapid drying and pyrolysis in combustors, producing the char, and then this char burns rather slowly. The rate of burning of char controls the overall combustion rate since it is the slowest stage. Therefore, it is quite impossible to achieve any improvement strategy without getting detailed experience on char burning characteristics of individual coal samples. In addition, inorganics found in coal play critical roles such as catalytic effects and undesirable deposit formations [1].

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The heterogeneous combustion of char is the most complicated stage of combustion and it is consisted of various steps. These steps are diffusion of oxygen to the char surface from the bulk gas, adsorption of oxygen on the char surface, rearrangement of adsorbed surface species (surface reactions), internal diffusion of oxygen from the char surface to porous matrix, reaction of carbon with oxygen, and exterior diffusion of product gases to the bulk gas from the char surface [1-3]. Therefore, char oxidation is largely diffusion controlled [1].

The importance of char burning from technological point of view is that it directly affects unburned carbon content in ash which is very critical in boiler design. Accordingly, intrinsic char reactivity has been taken into account as an important factor influencing the char burn-out under pulverized fuel (PF) burning conditions [4]. Therefore, char burning is vital for both pulverized coal-fired boilers and fluidized-bed (FB) boilers. Besides, the combustion characteristics of chars from solid fuels including coal and biomass are also closely related to char morphology and the thermal history of char [5-7]. Of which, thermal history is mostly characterized by heating rate and final temperature applied during the charring process, and it plays significant role on the reactivity of the produced pyrolytic char [3].

Coal chars are comprised of non-uniform structures containing micro-, meso-, and macropores [8]. It is also reported that the chars obtained under rapid heating conditions have rather porous structures [6]. The mean particle size as well as the size distribution of the particles affect both aerodynamics and heat transfer characteristics which are crucial for proper modeling of char combustion. Almost all steps of char burning that take place in both inner surface and outer surface are highly dependent on diffusional effects which are influenced by pore structure of the char. Therefore, chars from different coals having dissimilar pore structures show different gas diffusion rates, and consequently their apparent combustion rates may also show important differences [7]. For an instance, it is reported that very low porosity may be in question in chars obtained from coals with high inertinite and high mineral matter contents [8]. The porosity of char is not only affected by intrinsic coal properties but also pyrolysis conditions are highly effective. That is, configuration of the combustion system and the operational variables such as heating rate, final temperature, residence time as well as usage of catalysts closely influence the combustion characteristics.

Reactivity of a given char/semi-char sample cannot be precisely predicted by the available experience from other chars, since differentiations in many properties such as morphology and history of char, amounts of active sites on surface, and catalytic or inhibiting effects of inorganics change the thermal behavior seriously [9, 10]. The studies in literature focused directly on the burning of pyrolytic chars mostly cover low ash content relatively high-rank coals [11]. On the other hand, char oxidation for high ash fuels is influenced by the presence of inorganic compounds since these compounds absorb some heat to drive reactions [1]. Besides, devolatilization of lower rank coals, for instance lignites, usually produces chars with large surface areas and reactivities in comparison to high rank coals [10].

Turkish lignites which have low calorific value and high mineral matter content are so important national energy sources that 8 % of world lignite consumption is carried out in Turkey by lignite-fired power stations. For instance, Elbistan lignite which is the highest-deposit Turkish lignite is burned in Afsin-Elbistan power station that has two units (A and B units) in operation. The unit A established in 1984 has a capacity of 1355 MW, while the unit B established in 2004 has a capacity of 1440 MW. Also, several new units are planned to be constructed in near future. Unfortunately, the unburned carbon content in ash from such pulverized-fuel burning power stations is relatively higher than efficient combustion systems which employ up-to-date technology. Moreover, there is not sufficient information about char burning characteristics of such high mineral matter Turkish lignites. In this context, this paper focuses on the char burning characteristics of Elbistan lignite.

Another distinctive point of this paper is that there are several different criteria in literature to evaluate thermal reactivity of char samples. However, since each criterion was applied to individual experimental data obtained under specific conditions, it is too difficult to compare their outcomes with each other. From this point of view, this paper offers a compilation of seven different criteria to check the char reactivity, and these criteria were applied to three sets of experiments.

2. Materials and methods

2.1. Lignite and char characterizations

Lignite was provided from the coal mine in Elbistan region located in mid-south of Turkey. Lump coal was kept in laboratory for two weeks to dry under ambient conditions. Then, representative samples were taken, and the particle size was reduced to $\sim 250\ \mu\text{m}$ by dry milling. Proximate analysis and the higher calorific value measurement of the sample were performed according to ASTM standards, while an elemental analyzer (Eurovector EuroEA3000) was used for ultimate analysis.

Pyrolysis experiments were conducted in both a horizontal tube furnace and a thermal analyzer in which dynamic nitrogen flow assured non-oxidative inert medium.

The tube furnace equipped with a PID temperature controller provided sensitive control of temperature inside the furnace in which nitrogen flow rate was 100 mL/min. Nitrogen flow was initiated to sweep away any likely oxygen in the furnace before placing the lignite into the furnace in silica crucible. Then, the sample (10 g) was heated from ambient to given final temperatures such as 300, 400, 500, 600, and 700°C by heating rates of either 10 or 40°C/min, and a hold time of one hour was allowed at these final temperatures. Heating at a rate of 10°C/min in experiments of charring or char burning is very common for such investigations [12]. Hereafter, the heating rate of 10°C/min will be denoted as “slow heating”, while the heating rate of 40°C/min will be assumed as “moderately heating”. After completion of the hold time, the char was allowed to cool down to room temperature, and then it was rapidly removed from the furnace and stored in a desiccator.

Alternatively, TA Instruments SDTQ600 model thermal analyzer was used to pyrolyse the lignite under nitrogen flow of 100 mL/min from ambient to the same final temperatures, which mentioned for tube furnace, by a heating rate of 10°C/min. Hold times were allowed at the final temperatures until getting unchanged weights. These tests were performed using an initial sample weight around 10 mg. After the test, the thermally treated sample was kept in the thermal analyzer to cool down to room temperature under nitrogen flow. Then, the gaseous atmosphere turned from nitrogen to dry air (100 mL/min) for in-situ burning test of the solid product (char) that remained after pyrolysis. For this purpose, temperature was increased up to 900°C by a heating rate of 10°C/min. Thus, burning profiles were obtained from the thermal analyzer through the simultaneously obtained curves of Thermogravimetry (TG), Derivative Thermogravimetry (DTG), Differential Thermal Analysis (DTA), and Differential Scanning Calorimetry (DSC).

On the other hand, the pyrolytic chars produced in the tube furnace and stored in desiccator were also burned in the same thermal analyzer. The char obtained in tube furnace with a heating rate of 10°C/min was burned with a heating rate of 40°C/min in thermal analyzer, while the heating rate of burning was 10°C/min for the char produced at 40°C/min to compare the combined effects of heating rate and reactor configuration. Hereafter the experiments will be classified as Set I, Set II, and Set III experiments basing on the heating rates during charring and burning, and the configuration used. That is, “Set I” denotes charring in tube furnace at 10°C/min and burning in thermal analyzer at 40°C/min, while “Set II” employs charring in tube furnace at 40°C/min and burning in thermal analyzer at 10°C/min. Besides, “Set III” experiments were performed using only thermal analyzer for both charring and burning at 10°C/min.

The produced chars were named as C300, C400, C500, C600, and C700 chars depending on the final temperature applied in the stage of pyrolysis no matter how the reactor type.

All of the characterization tests, pyrolysis- and combustion- experiments were repeated several times to check the accuracy and the precision of the results, and the mean values of the close results

were used.

Scanning Electron Microscopy (SEM) images of both parent lignite and the chars were obtained using a Hitachi TM 1000 Tabletop Microscope linked with an energy dispersive (EDS) attachment.

Particle size distribution tests of the samples were performed using Malvern Instruments Hydro Mastersizer 2000 that employs water as dispersant to classify the particles in the range of 0.020-2000 μm . Mineralogical tests of lignite and chars were conducted using Panalytical - X'Pert Pro PW 3040/60 model device with software of X'Pert HighScore Plus which provides high accuracy in interpretation of the phases.

2. 2. Methods used for comparison of char reactivity

The following criteria have been considered to compare the apparent reactivities of the pyrolytic chars during combustion:

1. Temperatures at which conversion is as much as 5 % of the initial weight.
2. Burn-out levels at the final temperature of burning (900°C) calculated as follows:

$$\text{Burn-out (\%)} = \frac{(W_0 - W_f)}{(W_0)} \cdot 100 \quad (1)$$

where; W_0 : Initial Weight (mg), W_f : Final Weight (mg)

3. Conversion at any temperature as a percentage of the total conversion calculated from the following equation:

$$\text{Conversion (\%)} = \frac{(W_0 - W)}{(W_0 - W_f)} \cdot 100 \quad (2)$$

where; W : Weight at Time t (mg)

4. "Burning Profiles"-related parameters. Maximum burning rate [R_{max}] and its temperature [T_{max}] from DTG, maximum heat flow rate [$(H. F.)_{\text{max}}$] and its temperature [$T_{(H. F.)_{\text{max}}}$] from DSC, and maximum temperature difference [ΔT_{max}] and its temperature [$T_{(\Delta T_{\text{max}})}$] from DTA were considered.
5. Calculation of reactivity using following equation:

$$r = \frac{(W_0 - W)}{W_0} \cdot \left(\frac{1}{t}\right) \quad (3)$$

Where; r : Reactivity (min^{-1}), t : Time (min)

6. t_{50} value which has been rather applied to isothermal burning tests was also incorporated to this study. This method bases on determination of time at which the sample weight reduces to 50 % of the initial one.
7. Comparison of Activation Energy. The data taken from DSC tests was used to calculate the activation energies. For this purpose, the following equation of Borchardt-Daniels' kinetic model which is a non-isothermal model based on a single-heating rate measurement assuming n^{th} order kinetics was used [13,14]:

$$\ln\left(\frac{dH}{dt} \frac{1}{\Delta H_0}\right) = \ln A - \frac{E}{RT} + n \ln\left(1 - \frac{\Delta H_T}{\Delta H_0}\right) \quad (4)$$

where, dH/dt : Heat Flow, ΔH_0 : Total Heat of Reaction, ΔH_T : Partial Heat of Reaction at Temperature T , A : Pre-Exponential Factor, E : Activation Energy, R : Gas Constant

3. Results and discussion

3. 1. Lignite and char characterization

Analysis results of lignite are given in Table 1, and it obvious that this lignite is a low rank

coal with high ash and sulfur contents, and low calorific value. Table 2 presents the comparison of some properties of untreated lignite and its pyrolytic chars. It is clear from this table that carbon contents and accordingly the higher calorific values of the pyrolytic chars almost increase in parallel with the increase in the pyrolysis temperature. In contrast to this, hydrogen contents decrease as temperature increases and it is known that the decrease in hydrogen content is a reliable predictor to evaluate the severity of the pyrolytic process [3]. On the other hand, sulfur content was not affected from the pyrolytic process unless temperature reaches 700°C, and this indicates that an effective desulfurization of this lignite can be carried out by thermal treatment at around 700°C. Besides, influence of the pyrolysis process on nitrogen content is rather complicated that it causes to enrichments as temperature rises up to 600°C, and then it drops to some extent at 700°C. It is reported in literature in this context that a considerable part of nitrogen could be remained in char although temperature during pyrolysis reaches even 900°C [15, 16].

Table 1. Analysis Results of Elbistan lignite

Proximate Analysis (%, dry)	Volatiles	46.1
	Fixed Carbon*	17.1
	Ash	36.8
Ultimate Analysis (%, dry-ash-free)	C	50.60
	H	3.63
	N	1.79
	S	6.20
	O*	37.78
Higher Calorific Value (MJ/kg, dry)		15.4

*calculated by difference.

Table 2. Effects of Pyrolysis Temperature on Properties

	Untreated	C300	C400	C500	C600	C700
Higher Cal. Val. (MJ/kg) (dry basis)	15.4	18.9	19.4	19.6	19.8	21.1
C (%)	50.60	56.10	60.25	60.10	62.15	65.30
H (%)	3.63	2.99	2.13	1.90	1.60	1.76
N (%) (dry-ash-free)	1.79	2.08	2.20	2.22	2.20	1.07
S (%)	6.20	5.61	5.70	6.01	6.00	0.70
O (%)	37.78	33.22	29.72	29.77	28.05	31.15
Surface Area (m ² /g)	0.304	0.290	0.251	0.239	0.217	0.232
Surface Weighted						
Mean Diameter (µm)	19.754	20.688	23.916	25.144	27.713	25.876
Volume Weighted						
Mean Diameter (µm)	63.412	51.160	62.343	60.354	54.935	60.692
d(0.1) (µm)	12.146	11.710	12.738	12.606	13.650	12.530
d(0.5) (µm)	41.726	34.523	44.108	42.591	38.640	44.228
d(0.9) (µm)	149.151	116.904	140.625	135.853	122.046	134.554

Oxygen content which is a reliable predictor of thermal reactivity showed significant decreases at temperatures of 300 and 400°C in comparison to their own previous measurements. However, the changes in oxygen content at temperatures of 500 and 600°C are not as obvious as at the previous temperatures, while the pyrolysis at 700°C lead to some increase in oxygen content. Nevertheless, combination of the losses in hydrogen and oxygen contents should lead to formation of more condensed char structure [17].

The results for surface area, mean diameter, and diameters for some fractions such as d(0.1), d(0.5), and d(0.9) of the samples were also given in Table 2. Surface areas for both untreated lignite and its chars have rather low values that change in very narrow range of

0.217-0.304 m²/g. This is in contrast to the findings of other authors who mention that increasing pyrolysis temperature results in enlargement in surface area up to 600°C, and beyond that surface area reduces [18]. The low surface areas that are irrespective of pyrolysis conditions in this study may be attributed to the abundance of mineral matter in lignite [8]. Besides, surface weighted mean diameter results showed that all of the chars have larger mean diameters than the untreated lignite to some extent. In contrast to this, untreated lignite has the highest volume weighted mean diameter. On the other hand, there is not an apparent trend in d(0.1) size fraction that all the values are around 12.5 μm, while other size fractions of d(0.5) and d(0.9) showed relatively more differentiations. For instance, the highest d(0.9) belonged to untreated coal, indicating that thermal treatment made some reduction in size of the particles. However, surface area measurements did not reflect the abundance of finer particles. This may be resulted from shrinking and collapsing of the particle structure due to thermal treatment.

Mineralogical analysis results from XRD technique indicated that the compounds of silicon, calcium, iron, and magnesium exist in the original lignite as well as the pyrolytic chars. Of which, SiO₂ was detected as the most characteristic mineral. Also, CaSO₄, the presence of which was detected in chars after 400°C, is the other frequent mineral. In addition, the sulfur bearing minerals such as Fe₇S₈, MgS, and CaSO₄ are responsible for the high sulfur contents in this lignite and its pyrolytic chars.

SEM micrographs of lignite and chars can be seen in Fig. 1. It can be concluded that although these images are substantially similar to each other, faint differentiations on surface can be noticed as pyrolysis temperature increases. That is, the surface of lignite changed in such a way that some cracks and splits became more apparent in comparison to the untreated lignite. Some studies in literature in which pyrolytic chars has been obtained from biomass addresses that release of volatile matter leads to development of pores of different sizes. Also, progressive increases in micropore developments were reported with increasing pyrolysis temperature, while a maximum development of larger pores took place at 600°C [16].

3. 2. Char reactivity

3. 2. 1. Method 1

This method is rather used to predict the ignition point when temperature around a particle is difficult to measure [19]. For this, the moisture-free weights of the samples were taken into account in determination of the temperatures at conversion of 5 % of the initial weights. The values of Set I experiments were determined as 153, 275, 370, 408, 431, and 433°C for parent lignite, C300, C400, C500, C600, and C700 char samples, respectively. Similarly, the values of 179, 289, 350, 373, 392, and 413°C for Set II experiments, and 179, 286, 301, 319, 349, and 395°C for Set III experiments were measured, respectively. These results showed that the higher the pyrolysis temperature, the higher the temperature for reaching 5 % conversion of the initial weight. This is related to the extent of the previously elimination of the volatiles from lignite during pyrolysis process. Thus, the heating of lignite to high temperatures led to less reactive pyrolytic chars containing little amounts of volatile matter. For instance, the char that produced at 700°C had so low thermal reactivity that 5 % of its initial weight could be lost at temperature region of 395-433°C under investigated burning conditions.

3. 2. 2. Method 2

Burn-out level of a fuel is a good indicator to evaluate its burning efficiency in combustor. From this point of view, low values of burn-out predict the fact that some of the organic

materials leave the combustor as unburned, leading reduction in combustion efficiency [20]. In char burning, however, burn-out levels at any temperature are lower than those for original

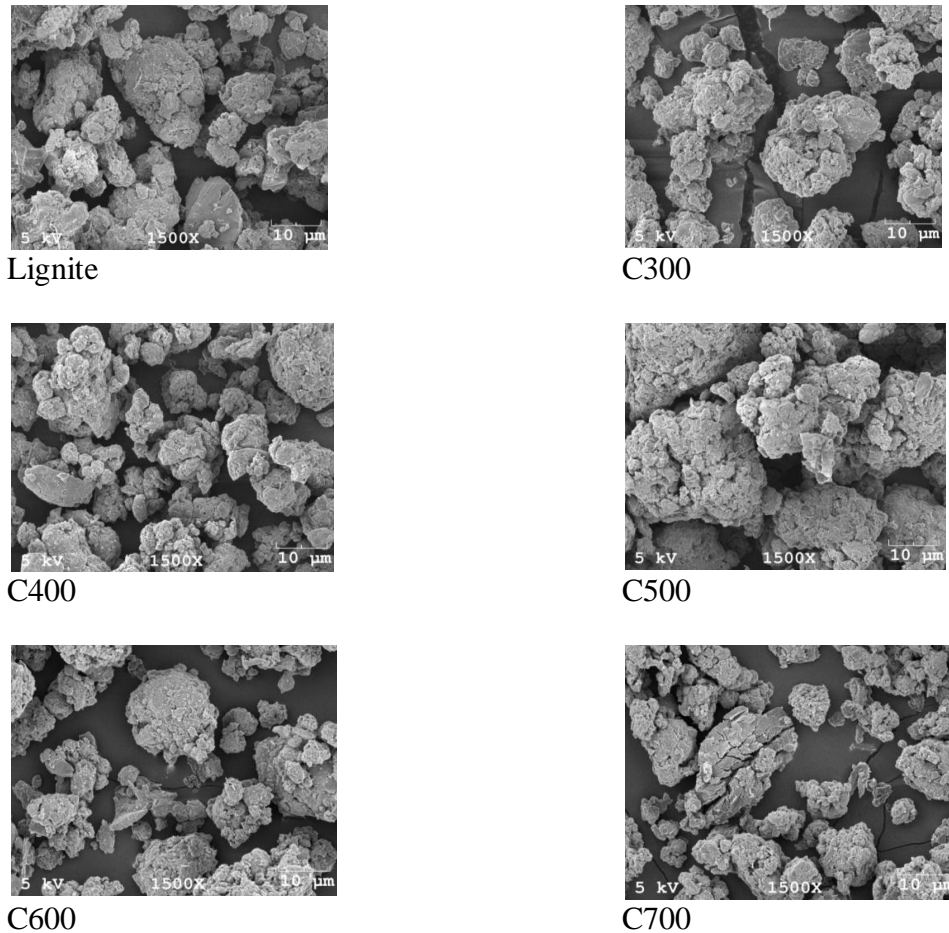


Fig. 1. SEM micrographs of lignite and chars.

fuel sample due to the fact that easily decomposable part of the fuel has already been eliminated during charring. The char structure also changes as burning proceeds, and finally it becomes annealed, deteriorating the heat transfer inside the particle [9]. This reduces the reactivity of the remaining char, and enhances the formation of unburned carbon. On the other hand, enrichment of inorganics in char may also inhibit the burning reactivity. So, the burn-out levels of thermally treated chars cannot be compared with original fuels, and they should be evaluated regarding the temperature regions to which the sample was exposed.

So close burn-out levels were measured from the three sets of experiments for the chars subjected to the same charring temperatures that the deviations from the arithmetic mean values were within (+/-) 3 % for the parent lignite and the chars of C300, C400, C500, and C600. That is, the mean burn-out levels for the three sets of experiments were 80.9, 72.0, 69.1, 67.3, and 65.5 % for lignite, C300, C400, C500, and C600 chars, respectively. On the other hand the burn-outs of 62.7, 67.2, and 58.8 % were determined for C700 char from Set I, Set II, and Set III experiments, respectively.

It can be concluded from these results that the increasing pyrolysis temperature causes reductions in the burn-out levels, and the lowest burn-out was detected for the char obtained at 700°C. In other words, the chars obtained at lower temperatures showed relatively more reactivity during burning.

3. 2 .3. Method 3

Conversions calculated by Eq. 2 as percentages of the total conversion are tabulated in Table 3 for each temperature increment of 100°C. The data on Table 3 indicate that the major part of the mass losses during combustion takes place at temperatures between 300 and 500°C. Additional mass losses taking place between 600 and 900°C are only account for 5 % of the total conversions. This is an indication of the presence of a region in which most of the organic material burns and thermal reactivity reaches high values. It is reported in literature that the decrease in reactivity of lignite chars happens in the conversion range of 88-93 % [20]. On the other hand, the mass losses arisen from at temperatures higher than 600°C may be neglected since decomposition of some minerals such as carbonates begins thereafter [20]. Alternatively, Krzesinska et al. [21] reported that the temperature dependency of weight loss and carbon content tends to saturate above 600°C, while the true density and elastic parameters still increase up to 900°C. This means that further heating (above 600°C) does not remove any compounds from material, but there exists probably reorganization of carbonised structure forming more compact matrix.

Table 3. Percentages of total conversion at given temperatures

Pyrolysis		Burning		Sample						
Equip.	Heating Rate (°C/min)	Equip.	Heating Rate (°C/min)	Temperature (°C)	Lignite	C300	C400	C500	C600	C700
Percentage of Total Conversion (%)										
Tube Furnace	10	Thermal Analyzer	40	100	10.2	8.5	7.4	7.0	8.7	7.4
				200	20.0	14.6	11.9	10.1	12.1	9.7
				300	29.7	17.3	12.5	10.6	12.6	9.3
				400	60.8	38.1	20.8	13.8	14.1	10.7
				500	93.5	94.3	73.7	57.9	44.0	43.4
				600	96.5	98.1	96.7	96.1	96.3	97.8
				700	98.3	99.1	97.9	96.7	96.8	99.0
				800	98.5	99.6	98.2	97.4	97.4	99.0
				900	100.0	100.0	100.0	100.0	100.0	100.0
Tube Furnace	40	Thermal Analyzer	10	100	12.9	9.2	8.9	7.0	9.2	11.7
				200	20.3	13.0	11.8	9.2	11.8	14.2
				300	35.4	17.6	12.4	9.5	12.4	15.3
				400	82.4	72.6	44.4	21.9	18.2	17.7
				500	93.5	93.2	93.5	92.5	94.6	94.2
				600	97.7	96.6	96.2	95.2	96.3	100.0
				700	98.5	97.2	97.1	96.1	96.7	99.1
				800	98.9	98.3	98.0	97.7	97.8	98.9
				900	100.0	100.0	100.0	100.0	100.0	100.0
Thermal Analyzer	10	Thermal Analyzer	10	100	12.9	2.6	1.8	1.0	0.1	0.2
				200	20.3	3.0	1.2	0.0	0.0	0.0
				300	35.4	13.5	8.6	3.3	0.0	0.0
				400	82.4	76.0	74.0	69.7	53.2	10.6
				500	93.5	93.0	88.6	87.4	87.3	89.8
				600	97.7	98.3	95.4	94.5	94.0	95.3
				700	98.5	99.2	96.8	96.4	95.8	96.2
				800	98.9	99.2	97.5	97.1	96.7	96.5
				900	100.0	100.0	100.0	100.0	100.0	100.0

The decrease in reactivity at high conversion levels may be resulted from possible collapse in char structure during pyrolysis, blocking the diffusion of oxygen to solid remnant. Also, consumption of organic material that leaves less decomposable potential for higher temperatures is another reason for the small contribution of high temperatures to the total conversion level. Besides, the increases in burn-out that observed in conversion at 900°C may be attributed to the disintegration of some mineral matter, leaving additional mass losses [20]. In addition, increasing elemental carbon content (Table 2) is regarded to be responsible for the decrease in thermal reactivity [22].

More detailed inspection of the data also reveals that C500, C600, and C700 chars have their highest thermal reactivities in the region of 400-500°C. Besides, mass losses at 300°C cannot be ignored for the original lignite as well as low temperature chars of C300 and C400. Thus, C500, C600, and C700 chars can be distinguished from C300 and C400 chars.

3. 2. 4. Method 4

Method 4 bases on determination of some reactivity-related parameters from burning profiles. Determination of $[R_{\max}]$, $[T_{\max}]$, $[(H. F.)_{\max}]$, and $[\Delta T_{\max}]$ from burning profiles was illustrated schematically in Fig. 2, and results are given in Table 4 for not only these parameters but also temperatures such as $[T_{(H. F.)_{\max}}]$ and $[T_{(\Delta T_{\max})}]$. Many investigators consider $[T_{\max}]$ temperature as a reliable reactivity indicator that its low values indicate high thermal reactivity [20]. Similarly, $[R_{\max}]$ representing the maximum rate of burning is another important indicator for char burning reactivity [22].

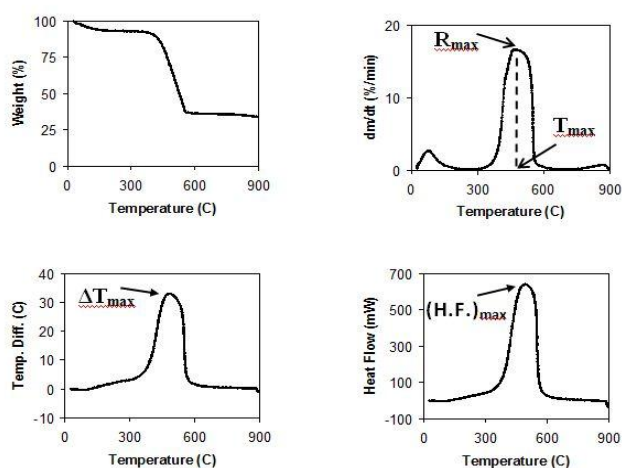


Fig. 2. Patterns for TGA, DTG, DTA, and DSC burning profiles.

It is clear from Table 4 that chars obtained in the same equipment with the same heating rate show similar trends with respect to $[T_{\max}]$ values that this parameter increases as a result of rise in the final temperature of charring stage. This is an indication of diminishing reactivity due to heating process applied during pyrolysis, and consequently the $[R_{\max}]$ rates regularly shifted to higher temperatures. This shift is more apparent in case of moderate heating rate since the time is shorter to reach a given temperature due to relatively higher heating rate, and accordingly the heat transfer to the particle is relatively limited.

As to the extent of $[R_{\max}]$ values, it is likely to say that $[R_{\max}]$ values are much more sensitive to the heating rates of burning than the heating rates applied during pyrolysis process. For instance, the chars obtained with a heating rate of $10^{\circ}\text{C}/\text{min}$ in either equipment showed different trends of $[R_{\max}]$ values under different heating rates of burning. That is, the chars produced under moderately heating condition gave such $[R_{\max}]$ values that they changed in a narrow range of 14.8-16.6 %/min. In contrast, the chars produced under slow heating condition showed $[R_{\max}]$ values that change rather in a wider interval of 5.7-18.5 %/min.

Of slowly heated chars from tube furnace, C500 char showed the highest $[R_{\max}]$ value during combustion with moderately heating rate. Whereas, slowly heated chars from thermal analyzer had two maxima of $[R_{\max}]$ which were determined for C600 and C700 chars.

The values of $T_{(H. F.)_{\max}}$ were determined to increase as the charring temperature rises, accordingly the highest value belonged to C700 char, indicating the maximum heat flows shifted to high temperatures as the severity of pyrolysis enhances. This is another indication of the decreasing reactivity as a result of increasing heat effects. Similarly, the amounts of the heat flow from the chars have an increasing tendency with charring temperature.

Temperature difference which is determined from DTA thermogram is the difference in

Table 4. Results from Burning Profiles

Pyrolysis		Burning		Sample						
Equip.	Heating Rate (°C/min)	Equip.	Heating Rate (°C/min)	Parameter	Lignite	C300	C400	C500	C600	C700
Tube Furnace	10	Thermal Analyzer	40	R_{max}	13.7	15.5	16.1	16.6	15.5	14.8
				T_{max}	394	424	451	475	500	502
				$(H.F.)_{max}$	54.2	59.1	54.6	65.0	59.9	67.6
				$T_{(H.F.)_{max}}$	452	464	475	493	512	513
				ΔT_{max}	2.9	3.2	2.9	3.4	3.0	3.4
Tube Furnace	40	Thermal Analyzer	10	$T_{\Delta T_{max}}$	448	446	458	480	501	504
				R_{max}	4.6	7.1	10.8	13.0	12.8	14.2
				T_{max}	380	377	387	420	442	465
				$(H.F.)_{max}$	18.1	29.0	42.6	55.8	55.3	54.2
				$T_{(H.F.)_{max}}$	386	384	399	423	446	467
Thermal Analyzer	10	Thermal Analyzer	10	ΔT_{max}	1.1	1.7	2.5	3.1	3.0	2.9
				$T_{\Delta T_{max}}$	385	383	398	423	444	467
				R_{max}	4.6	5.7	6.4	6.6	18.5	18.5
				T_{max}	380	362	354	347	375	421
				$(H.F.)_{max}$	18.1	23.5	28.6	29.2	54.5	75.0
Thermal Analyzer	10	Thermal Analyzer	10	$T_{(H.F.)_{max}}$	386	374	358	350	381	435
				ΔT_{max}	1.1	1.5	1.8	1.9	3.3	4.1
				$T_{\Delta T_{max}}$	385	368	358	350	381	435

R_{max}	: maximum burning rate (%/min).
T_{max}	: temperature of maximum burning rate (°C).
$(H.F.)_{max}$: maximum heat flow (W/g).
$T_{(H.F.)_{max}}$: temperature of maximum heat flow (°C).
ΔT_{max}	: maximum temperature difference on DTA curve (°C/mg).
$T_{\Delta T_{max}}$: temperature of maximum temperature difference on DTA curve (°C).

temperature between sample and furnace, and positive values indicate exothermicity in which sample temperature is higher. In fact, reaction of carbon with oxygen is highly exothermic, and the temperature on char surface may be several hundred degrees higher than the surrounding temperature in big scale combustors [23]. There is a strong similarity between DTA and DSC results. Also, (ΔT_{max}) values for untreated lignite and low temperature chars (C300 and C400) could not reach those for C500, C600, and C700 chars.

DSC and DTA curves confirm the presence of the region mentioned in method #3 in which most of the organic material burns and thermal reactivity reaches high values.

3. 2. 5. Method 5

Patterns for the change in reactivity values that calculated according to Eq. 3 are shown in Fig. 3 for burning with moderate- and slow- heating rates, respectively. Rise in heating rate led to serious increases in the values of reactivity too, so the reactivity values for different heating rates should not be compared, and it is safer to use them to trace the variation trend of an individual sample's reactivity depending on temperature. Nevertheless, the general trend in

both figures is that there exists an increase in reactivity until reaching a maximum and beyond that it slows down as temperature increases. Alonso et al.[10] also reported that the maximum reactivity is seen in a definite conversion region. They also found that the conversions of 10-20 % belong to the maximum reactivity.

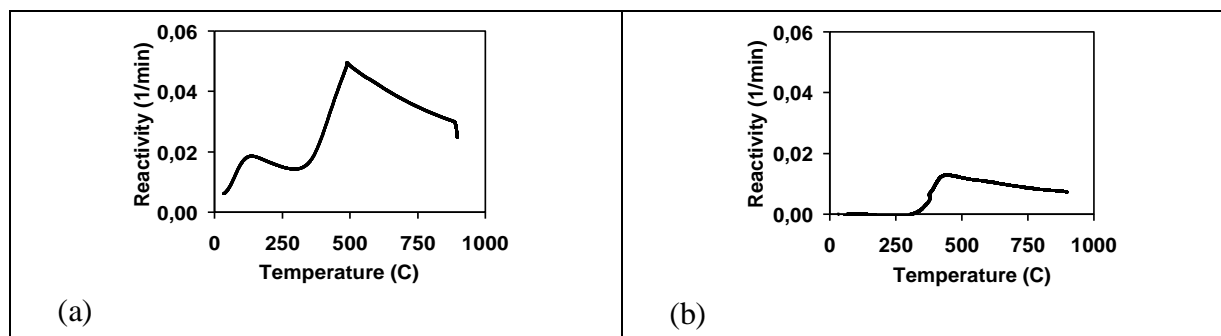


Fig. 3. Change of reactivity [(a): for moderate heating rate, (b) for slow heating rate].

The maximum reactivity values and the temperatures of which are given in Table 5. The burning tests of the chars revealed that the increase in charring temperature results in decrease in the char reactivity. In addition, none of the chars are as reactive as the original lignite under investigated conditions. Besides, the reactivities for both slow heating sets are in good agreement with each other.

Table 5. Maximum Reactivities (1/min) and Their Temperatures (°C)

Pyrolysis		Burning		Sample						
Equip.	Heating Rate (°C/min)	Equip.	Heating Rate (°C/min)	Parameter	Lignite	C300	C400	C500	C600	C700
Tube Furnace	10	Thermal Analyzer	40	Max. Reactivity	0.0592	0.0494	0.0475	0.0423	0.0393	0.0421
				T	474	491	533	551	589	596
Tube Furnace	40	Thermal Analyzer	10	Max. Reactivity	0.0180	0.0157	0.0143	0.0142	0.0137	0.0135
				T	412	425	442	452	469	504
Thermal Analyzer	10	Thermal Analyzer	10	Max. Reactivity	0.0180	0.0161	0.0147	0.0133	0.0128	0.0115
				T	412	426	425	433	446	467

3. 2. 6. Method 6

Although this method has been commonly used at isothermal thermogravimetric analysis tests [4, 10], we tried to apply this method to non-isothermal burning tests. Times determined for conversion of 50 wt % of the initial weight (t_{50}) for Set I experiments were 10.5, 11.9, 12.3, 13.6, 14.4, and 13.1 min for lignite, C300, C400, C500, C600, and C700 chars, respectively. Whereas, the values for Set II experiments were 33.4, 36.2, 38.3, 39.3, 41.0, and 44.2 min, and for Set III were 33.4, 35.5, 36.1, 38.6, 39.8, and 43.5, respectively.

The times for getting the conversion level of 50 % are about threefold longer in case of slow heating experiments, and these values also indicate that the final temperature applied during pyrolysis lengthen the time to reach the mentioned conversion level. In addition, the chars obtained in tube furnace at moderate heating rate had a bit longer time in comparison to the chars obtained in thermal analyzer under the same heating rate of burning. Nonetheless, the results from both sets of experiments are consistent with each other.

3. 2. 7. Method 7

Activation energies and pre-exponential factors calculated from Equation 4 were evaluated. In order not to deal with evaporation of moisture and decompositions of minerals, the temperature range for kinetic calculations was limited from 200 to 600°C. However, as an exception, this range was broadened to 200-650°C for the set of burning runs with moderately heating rate, since the main exothermic regions in DSC curves were not completely ended at 600°C due to higher heating rate. It was determined that activation energies and pre-exponential factors change in the ranges of 64.7 - 117.0 kJ/mol and 4.49 – 7.76 min⁻¹ for Set I experiments, 55.0 – 163.7 kJ/mol and 3.35 – 11.50 min⁻¹ for Set II experiments, and 45.3 – 100.6 kJ/mol and 2.23 – 6.46 min⁻¹ for Set III experiments, respectively.

The activation energies for burning of chars produced in tube furnace revealed that burning of untreated lignite needs much more energy than C300 char. This indicates the high reactivity of the low temperature char. However, the other chars produced at higher temperatures required higher activation energies than untreated lignite, and the highest values were measured for C600 char that is even higher than C700 char. From this point of view, C600 char can be accepted as the less reactive char. On the other hand, increasing pyrolysis temperature from 600 to 700°C caused marked decreases in activation energy. Similarly, Li et al. [24] found out that the activation energy for semi-cokes rises slightly with increasing final pyrolysis temperature except that at 750°C. They explained this event with secondary char formation through tar deposition. Besides, the possible catalytic effects of the minerals in char should be considered since they are capable of lowering the activation energy. Pre-exponential factors also gave similar behavior in parallel with the change in activation energy.

Activation energies for the chars produced in thermal analyzer revealed a highly different situation that except for C700 char, activation energies for other chars were considerably lower than that for the untreated lignite. Basing on this, it is likely to say that increasing pyrolysis temperature to 700°C caused a rapid decrease in the burning reactivity.

Hu et al. [23] investigated burning of chars in a temperature range of 1000-1300°C, and they found that activation energy is about 20 kcal/kg which is within the activation energy range of the present study. Similarly, the level of the activation energies found here, especially for high temperature chars, are also consistent with results by Kastanaki and Vamvuka [20], who reported that activation energy for coal char is around 115 kJ/mol, and it was lower than those for biomass chars.

4. Conclusion

Elbistan lignite is an extremely reactive low-rank coal with high oxygen and mineral matter contents. The ratio of the contents of volatile matter/fixed carbon is very high, and this is the source of such a high reactivity. In order to investigate effects of volatiles removal on thermal reactivity, partly elimination of volatiles from lignite was studied through pyrolysis at regularly increasing temperatures. For this purpose, pyrolytic chars were produced under different temperature and heating rate conditions and then combusted in thermal analyzer. It was found that the extent of volatile matter removal (in particular in oxygen content) from lignite provides the increase in carbon content, and accordingly the reduction in reactivity. Therefore, none of these chars were as reactive as the untreated lignite which is very rich in oxygen content. Also, enrichment of inorganics which are mainly comprised of silicon and calcium compounds may have influence on thermal behavior.

Burning data from thermal analyzer were evaluated regarding a couple of criteria representing several specified parameters which are relevant in reactivity. The common point for outcomes of these criteria is that the severity of pyrolysis step determines the thermal

history of char which affects the reactivity in sequential stages. Namely, increasing final temperature in the pyrolysis step reduces the burning reactivity of the forming char significantly. However, variations in surface area and particle size of the chars owing to thermal treatment were not as much as the burning reactivity and it is thought that high mineral matter content of this lignite plays no ignorable role on this situation.

As a result of reducing reactivity, ignition temperature shifts to higher temperatures, and therefore complete burning of the char needs much more heat and longer residence times. This successively affects many reactivity-related parameters such as burn-out levels, maximum burning rate and its temperature, conversion levels, heat flow rates etc. Also, a characteristic region is available for each char in which most of the organic material rapidly burns and thermal reactivity reaches its peak value. It was seen that this region also shifts to higher temperatures in parallel with the increase in the final temperature of charring process.

The major part of the mass losses during combustion was observed to take place at temperatures between 300 and 500°C. Additional mass losses taking place between 600 and 900°C are only account for 5 % of the total conversion.

It was found that C500, C600, and C700 chars have their maximum burning reactivities between 400°C and 500°C. Besides, mass losses at 300°C cannot be ignored for the original lignite as well low temperature chars of C300 and C400. From this point of view, C500, C600, and C700 chars can be distinguished from C300 and C400 chars.

References

- [1] Miller B G, Tillman D A. *Combustion Engineering Issues for Solid Fuel Systems*. Elsevier, New York, 2008.
- [2] Dennis JS, Lambert RJ, Milne AJ, Scott SA, Hayhurst AN. The kinetics of combustion of chars derived from sewage sludge. *Fuel* 2005;84:117-126.
- [3] Zhu Q, Jones JM, Williams A, Thomas KM. The predictions of coal/char combustion rate using an artificial neural network approach. *Fuel* 1999;78:1755-1762.
- [4] Gurgel Veras CA, Saastamoinen J, Carvalho Jr JA, Aho M. Overlapping of devolatilization and char combustion stages in the burning of coal particles. *Combust Flame* 1999;116:567-579.
- [5] Gani A, Naruse I. Effect of cellulose and lignin content on pyrolysis and combustion characteristics for several types of biomass. *Renew Energ* 2007;32:649-661.
- [6] Cloke M, Wu T, Barranco R, Lester E. Char characterization and its application in a coal burnout model. *Fuel* 2003;82:1989-2000.
- [7] He R, Suda T, Fujimori T, Sato J. Effects of particle sizes on transport phenomena in single char combustion. *Int J Heat Mass Tran* 2003;46:3619-3627.
- [8] Everson RC, Neomagus HWJP, Kasaini H, Njapha D. Reaction kinetics of pulverized coal-chars derived from inertinite-rich coal discards: Characterisation and combustion. *Fuel* 2006;85:1067-1075.
- [9] Backreedy RI, Jones JM, Pourkashanian M, Williams A, Burn-out of pulverised coal and biomass chars. *Fuel* 2003;82:2097-2105.
- [10] Alonso MJG, Borrego AG, Alvarez D, Parra JB, Menrnde R. Influence of pyrolysis temperature on char optical texture and reactivity. *J Anal Appl Pyrol* 2001;58:887-909.
- [11] Jayanti S, Maheswaran K, Saravanan V. Assessment of the effect of high ash content in pulverized coal combustion. *Appl Math Model* 2007;31:934-953.
- [12] Hossain MK, Strezov V, Chan KY, Ziolkowski A, Nelson PF, Influence of pyrolysis temperature on production and nutrient properties of wastewater sludge biochar. *J Environ Manage* 2011;92:223-228.
- [13] Dominguez J C, Oliet M, Alonso MV, Gilarranz MA, Rodriguez F. Thermal stability and pyrolysis kinetics of organosolv lignins obtained from Eucalyptus globules. *Ind Crop Prod* 2008;27:150-156.

- [14] Vinayagamoorthi S, Vijayakumar CT, Alam S, Nanjundan S. Structural aspects of high temperature thermosets –Bismaleimide/propargyl terminated resin system-polymerization and degradation studies. *Eur Polym* 2009;45:1217-1231.
- [15] Zhao Z, Li W, Qiu J, Li B. Effect of Na, Ca and Fe on the evolution of nitrogen species during pyrolysis and combustion of model chars. *Fuel* 2003;82:1839-1844.
- [16] Bonelli PR, Della Rocca PA, Cerrella EG, Cukierman AL, Effect of pyrolysis temperature on composition, surface properties and thermal degradation rates of Brazil nut shells. *Biores Technol* 2001;76:15-22.
- [17] Bruun EW, Nielsen HH, Ibrahim N, Egsgaard H, Ambus P, Jensen PA, et al. Influence of fast pyrolysis temperature on biochar labile fraction and short-term carbon loss in a loamy soil. *Biomass Bioenerg* 2011;35:1182-1189.
- [18] Onay O. Influence of pyrolysis temperature and heating rate on the production of bio-oil and char from safflower seed by pyrolysis, using a well-swept fixed-bed reactor. *Fuel Process Technol* 2007;88:523-531.
- [19] Shen B, Qinlei. Study on MSW catalytic combustion by TGA. *Energ Convers Manage* 2006;47:429-1437.
- [20] Kastanaki E, Vamvuka D. A comparative reactivity and kinetic study on the combustion of coal–biomass char blends. *Fuel* 2006;85:1186-1193.
- [21] Krzesinska M, Zachariasz J. The effect of pyrolysis temperature on the physical properties of monolithic carbons derived from solid iron bamboo. *J Anal Appl Pyrol* 2007;80:209-215.
- [22] Janse AMC, Biesheuvel PM, Prins W, van Swaaij WPM. A novel interconnected fluidised bed for the combined flash pyrolysis of biomass and combustion of char. *Chem Eng J* 1999;75:121-130.
- [23] Hu YQ, Nikzat H, Nawata M, Kobayashi N, Hasatani M. The characteristics of coal-char oxidation under high partial pressure of oxygen. *Fuel* 2001;80:2111-2116.
- [24] Li AM, Li XD, Li SQ, Ren Y, Chi Y, Yan JH, et al. Pyrolysis of solid waste in a rotary kiln: influence of final pyrolysis temperature on the pyrolysis products. *J Anal Appl Pyrol* 1999;50:149-162.