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Investigation of catalytic pyrolysis of Erzurum-Umutbaca coal by using the thermal analysis method

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In the study, the catalytic pyrolysis behavior of low-rank Umutbaca coal with the addition of CaO was examined using thermal analysis methods. For this purpose, the effect of adding CaO to coal on both the pyrolysis temperatures of the coal and the composition of the gas and solid product (char) was investigated. Also, the kinetic analysis was carried out to characterize the catalytic pyrolysis process by adding CaO to coal. Using the data obtained in TGA at heating rates of 2.5, 5, and 10 °C/min, the activation energies required for the pyrolysis process of coal both with and without CaO were calculated by KAS and FWO methods. Thermodynamic parameters including ΔH, ΔG, and ΔS were calculated with activation energies obtained from the FWO method. The thermodynamic suitability of adding CaO to a low rank coal such as Umutbaca for the pyrolysis process was investigated.

Keywords: Low-rank coal, pyrolysis, CaO addition, TG-DTG, thermodynamics parameters.

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INTRODUCTION

Coal is a product of organic life on our planet and its history dates back 360 million years[1].Thanks to developing technologies, interest in alternative energy sources is increasing. However, considering the advantages of coal over other energy sources such as its current amount, production cost, usage area, and portability, it is obvious that it will be an indispensable energy source in the future. There are large coal reserves in almost every region of the world[2].

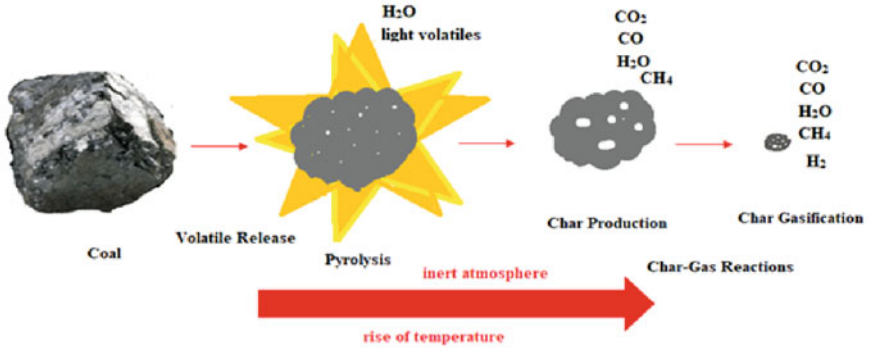
Coal is the primary energy source in the world and in our country, more than 90% of the electrical energy produced is provided by coal-fired power plants. Due to the high prices and low reserves of oil and natural gas, coal-based electrical energy production is considered economically more attractive for coal-rich countries[3]. However, coal-fired thermal power plants have huge negative effects on the environment and human health. Direct use of coal pollutes the atmosphere due to it emits too CO_2 gas. In addition, when coal does not burn completely and efficiently, carbonaceous particles are either carried into the air with gases or become inert as ash. It is a huge economic loss.

It is extremely important to use clean coal technologies to meet energy needs while protecting our environment[4]. Pyrolysis is one of the most preferred processes in the beneficial use of coals (Scheme 1). Additionally, pyrolysis is the thermochemical degradation of carbon-based materials such as biomass, plastic, rubber, coal, etc., in the inert atmosphere, at high temperatures of 200 °C and above. Coal pyrolysis forms the basis of many important processes such as coking, hydrogenation, combustion, and gasification. which are carried out in closed systems, usually in inert, reducing, or oxidative atmospheres, at different pressures and residence times[5].

In the pyrolysis process (at low temperatures), fully efficient carbon conversion cannot be achieved. In gas production process, a certain amount of carbon may remain in the ash obtained as a result of pyrolysis. It is possible to achieve high carbon conversion, that is, to increase the efficiency, by adding a suitable catalyst without increasing the pyrolysis process to high temperatures. The use of catalysts not only increases carbon conversion, but also reduces the formation of tar and harmful gaseous products such as HCN, NH_3, and causes a significant decrease in tar yield.

Coal and biomass samples can generally be pyrolyzed using alkaline catalysts (KCl, CaO, KOH, NH_4CO_3, and Fe_2O_3), and activated char and metal catalysts (K, Ca, Ni, Fe). In addition, instead of a single catalyst, pyrolysis of coal can be carried out by preparing catalysts in binary or triple mixtures[6].

Catalytic pyrolysis of coal with alkali metal salts is a well-known process, although its catalytic mechanism is not yet fully understood. In the literature, it is pro-



Scheme 1. The pyrolysis process of coal

posed that the catalytic activity enhances the amount of active sites, alters the identity of surface intermediates, accelerates the formation rate of products, and reduces the activation energy[6–8].

The pyrolysis is a useful method for elucidating coal structure and evaluating coal reactivity. In particular, it provides kinetic data as well as many valuable data about the degradation of coal by non-isothermal pyrolysis process at the constant heating rate in a thermal analyser (TG-DTG/DSC)[9–11]. The results from TG-DTG analysis for the catalytic pyrolysis may be helpful to the design of systems such as coal gasification, and combustion. Moreover, the thermodynamic feasibility of coal pyrolysis requires to be demonstrated to optimize pyrolysis conditions and promote efficient thermal conversions.

The purpose of the study is to investigate the catalytic action of CaO on the pyrolysis behaviour of Umutbaca coal. It examined the effect of heating rate on the pyrolysis process of both raw coal and coal with CaO and studied pyrolysis kinetic characteristics of these samples. In addition, gaseous products formed during pyrolysis was monitored by TG-FTIR analysis, and the char obtained from pyrolysis was analysed by FT-IR. Kinetic analysis of the pyrolysis process was also be carried out by using KAS (Kissinger-Akahira-Sunose), FWO (Flynn-Wall-Ozawa) methods[2–15]. Also, it was calculated by utilizing FWO method the thermodynamic parameters (ΔH, ΔS, and ΔG). To our knowledge, there is no study on the thermodynamic evaluation of coal catalytic pyrolysis along with its kinetics. In the study, examining the effect of CaO addition to coal on the pyrolysis process by utilizing TGA may provide information for further development in the pyrolysis of low-rank coals such as Umutbaca coal.

EXPERIMENTAL SECTION

Materials

Coal was supplied from Erzurum Oltu (Umutbaca). In our study, the coal with grain size of 125–250 μm were used. It was kept in the vacuum desiccator. Elemental and ultimate analysis was carried out on a LECO CHNS 932 device (Table 1).

Preparation of Coal Samples with CaO

CaO salts with the proportion 1%, 2.5%, and 5% (wt) were added directly to the coal, and thoroughly mixed. The dry samples were kept in a desiccator. It used NETZSCH STA 409 PC Luxx analyser for catalytic pyrolysis of coal. The raw coal and the samples with CaO were placed in the pan. TG-DTG analysis was carried out in nitrogen environment (90 ml/min) and at different heating rates of 2.5, 5, and 10 °C/min from 25 °C to 800 °C. The important temperatures for the pyrolysis behavior of the samples were obtained from the TG-DTG profiles.

In addition, FTIR analysis of the samples (raw coal, raw coal after pyrolysis, and the coal with CaO after pyrolysis) was carried out to observe the structural changes in coal. For FT-IR analysis of solid samples, Bruker VERTEX 70v brand instrument was used, spectra were recorded between 4000 and 400 cm^{-1}. For the emitted gases during pyrolysis, it was used the Perkin Elmer STA 8000 Thermogravimetric Analysis & Spectrum 1 FT-IR Spectrometer device. Experiments were performed in the temperature range of 25–1000 °C under N_2 atmosphere at a heating rate of 10 °C min^{-1}. FTIR spectra of the gases have been recorded between 4000 and 500 cm^{-1}.

Kinetics analysis

The pyrolysis of coal can be expressed as:

$A_{(coal)} \rightarrow B_{(coke\ or\ char)} + C_{(volatile\ matters,\ e.g.\ tar,\ gas)}$

The rate equation is written as follows (Eq. (1)):

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (1)$$

α is the conversion rate, f(α) is a function depending on the reaction mechanism, and k is the specific rate constant given by the Arrhenius equation.

$$k = A\exp\left(-\frac{Ea}{RT}\right) \quad (2)$$

A is the pre-exponential factor (min^{-1}), Ea is the activation energy (kJ/mol), R is the universal gas constant (J/mol/K), and T is the absolute temperature (K).

If k is written in the Eq. (1), Eq. (3) is obtained.

$$\frac{d\alpha}{dt} = Aexp(\frac{-Ea}{RT}f(\alpha) \quad (3)$$

Eq. (4) is getting from Eq. (3)

$$\frac{d\alpha}{dt} = \frac{d\alpha}{dT}.\frac{dT}{dt} = A\exp\left(-\frac{Ea}{RT}\right)f(\alpha) \quad (4)$$

If β=dT/dt (heating rate) is substituted into the Eq. (4), Eq. (5) is obtained.

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\exp\left(\frac{E_a}{RT}\right)f(\alpha) \quad (5)$$

It can be defined g(α) (new temperature function) by integrating Eq. (5).

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_0^T exp\frac{-E_a}{RT}dT \quad (6)$$

Eq. (6) has no analytical solution. It is solved by using different approaches.

KAS method (Eq. (7)) is obtained by differentiating Eq. (5) and rearranging the terms.

$$\ln\frac{\beta}{T^2} = \ln\left[\frac{AEa}{Rg(\alpha)}\right] - \frac{Ea}{RT} \quad (7)$$

In KAS method, Ea is calculated from the slope of $\ln(\beta/T^2)$ versus 1/T graph.

FWO method uses Eq. (8).

$$ln\beta = ln\left[\frac{AEa}{Rg(\alpha)}\right] - 2.315 - \frac{0.457Ea}{RT} \quad (8)$$

In FWO method, Ea is calculated from the slope of ln(β) versus 1/T graph.

Table 1. Elemental and Ultimate Analysis of Umutbaca Coal

Proximate Analysis (wt %)				Ultimate Analysis (wt %)				
A	M	V	FC	C	H	N	S	O*
17.33	4.84	37.39	40.44	62.46	5.04	1.37	0.55	8.41

*: By difference

Thermodynamics parameters

Thermodynamics parameters (ΔH, ΔG, ΔS) for the pyrolysis process of raw coal and CaO-coal were calculated by using Eyring equations[16, 17].

$$A = \beta . Ea . \exp\left(\frac{Ea}{R\,T_{peak}}\right) R . T_{peak}^{2} \quad (9)$$

$$\Delta H = Ea - R . T \quad (10)$$

$$\Delta G = Ea + R . T_{peak} \ln\left(\frac{K_B T_{peak}}{hA}\right) \quad (11)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T_{peak}} \quad (12)$$

K_B is Boltzmann constant (1.381×10^{-23} J/K), h is Plank constant (6.626×10^{-34} J/s), and Tpeak is the peak temperature of DTG curve.

RESULTS AND DISCUSSION

Pyrolysis of Umutbaca coal

The pyrolysis curves (TG, DTG) of the raw Umutbaca coal were displayed in Figure 1. There are two degradation steps in the pyrolysis of Umutbaca coal.

Stage 1: (25–220 °C): A mass loss of 6.4% is observed in the stage. For 10 °C/min, the peak with a peak of 108°C indicates that the water adsorbed in the pores is removed.

Stage 2: (220–700 °C) It is the main pyrolysis zone and there is a 33% mass loss. The complex chemical reactions and carbonization occur. It is understood that Umutbaca coal has strong bond structures and pyrolytic decomposition occurs at high temperatures[18]. According to the DTG graph in Figure 1, it is seen very dominant temperature peak.

The peak temperature (Tpeak-max) is 450 °C. for a heating rate of 10 °C/min. Pyrolysis of coal continues at these temperatures[19]. The amount of char from the pyrolysis process is 61.08% (at a heating rate of 10 °C/min).

According to the DTG curves obtained from the pyrolysis of raw coal, Tpeak-max for 2.5 °C/min: 427 °C, Tpeak-max for 5 °C/min: 431 °C, Tpeak-max for 10 °C/min: 450 °C.

Catalytic pyrolysis of Umutbaca Coal

TG-DTG graphs of the samples by adding 1%, 2.5%, 5% CaO were performed at the heating rate of 10 °C/min. TG-DTG graphs of the samples with CaO are displayed in Figure 2. According to the DTG curves, the pyrolysis process took place in two steps, like that of raw coal.

Stage 1: (25–210 °C) There is a mass loss of 6.95%. Tpeak-max temperature is 102.6 °C. The water adsorbed in the region moves away.

Stage 2: (220–700 °C) is the main pyrolysis zone where 29.76% mass loss occurs. The amount of a residue (char) obtained from pyrolysis is approximately 66%. Tpeak-max of coals with 1% and 2.5% CaO are 450 °C.

The coal with 5% CaO is 440 °C. When compared to raw coal Tpeak-max of the samples with CaO for the same heating rate, it is understood that CaO added to coal reduces the Tpeak-max temperature, and accelerates the pyrolysis process. As the concentration of CaO increases, the catalytic effect of CaO becomes more evident. Samples with 1% and 2.5% CaO have behaved like raw coal. Additionally, the effects of heating rate for coal with 5% CaO were also investigated in Figure 3 (2.5, 5, 10 °C/min).

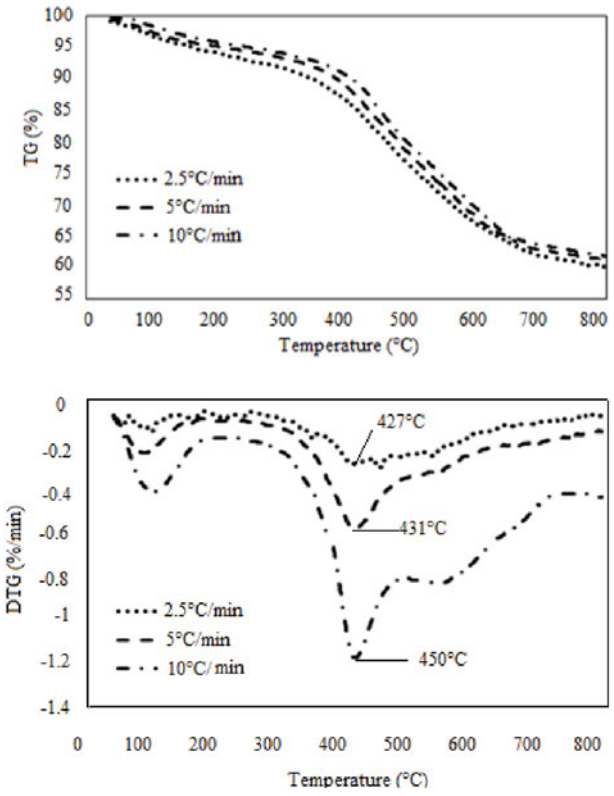


Figure 1. TG-DTG curves of Umutbaca coal in N_2 atmosphere, respectively

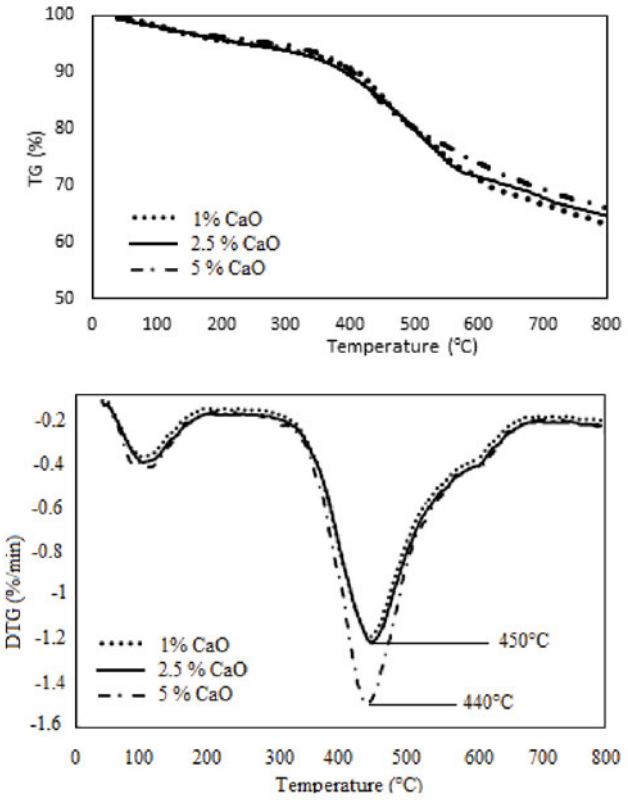


Figure 2. TG/DTG curves of Umutbaca coal with different concentrations of CaO in N_2 atmosphere

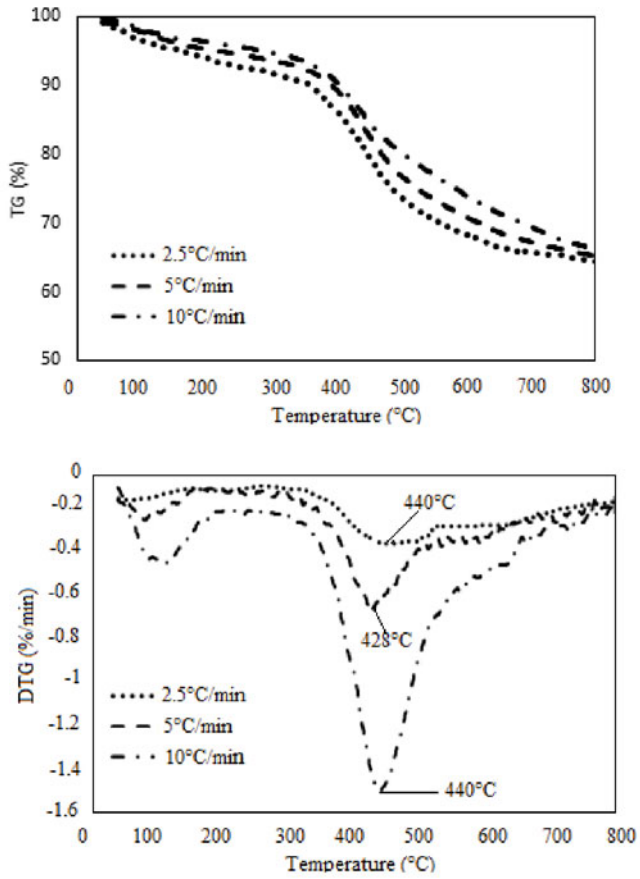


Figure 3. TG-DTG curves the pyrolysis of Umutbaca coal with 5% CaO in N_2 atmosphere

TG and DTG curves of the coal with 5% CaO consist of two stages, similar to the pyrolysis process of raw coal.

Stage 1: (25–210 °C) There is a mass loss of 6.95%. For a heating rate of 10 °C/min, the Tpeak-max temperature is 102.6 °C. In the region, the water adsorbed moves away.

Stage 2: (220–700 °C) It is the main pyrolysis zone where 29.76% mass loss occurs.

According to the DTG curves for the coal with 5% CaO, Tpeak-max is for 2.5 °C/min: 440 °C, Tpeak-max for 5 °C/min: 428 °C, Tpeak-max for 10 °C/min: 440 °C.

When compared to the Tpeak-max temperatures obtained for the same heating rate in the coal, it is understood that CaO reduces the Tpeak-max temperatures except for a heating rate of 2.5 °C/min. As the heating rate increases, the differences between the Tpeak-max temperature values of raw coal and the coal with CaO also increase. CaO added to coal reduced the Tpeak-max temperatures, that is, it accelerated the pyrolysis process.

The increase in heating rate shifted both TG and DTG curves to the right. Thus, the Tpeak-max temperature in coal shifted towards higher temperatures. It is known that in TG, DTG graphs, the degradation curves tend to the right as the heating rate increases. Because as the heating rate increases, the difference between the sample and the furnace temperature will increase, meaning a thermal delay will be observed.

TG-FTIR and FT-IR Analyses

FTIR spectra of the gases released from the TGA during pyrolysis process are obtained at 270 °C, 430 °C, and 660 °C. FTIR spectra of the coals without additives and with 1%–5% CaO are shown in Figure 4. The methane, water vapour, aromatic structures, CO_2, and CO gases were detected at 430 °C in Figure 4.

Complex and numerous reactions occur during pyrolysis. These reactions consist of variations of aliphatic and aromatic groups, bond breaking, evaporation, condensation, and cross-linking. The pyrolysis process begins with the breaking of weak bonds such as straight bonds between ring systems and continues with the formation of free radical groups (-CH_2, -O-). Free radicals are highly reactive and combine easily in the gas phase, especially to form CH_4 and H_2O. The formation and increase in the amount of CH_4 and the increase in the amount of H_2O are in harmony with each other, as can be seen from the TG-FTIR results, especially in Figure 5. Water formed after 300 °C acts as a methane precursor for coals. CO is produced by the decomposition of heterocyclic oxygen groups at high temperatures. Moreover, the amount of CO_2 obtained from the pyrolysis of coals with 1% and 5% CaO is quite low compared to the pyrolysis of raw

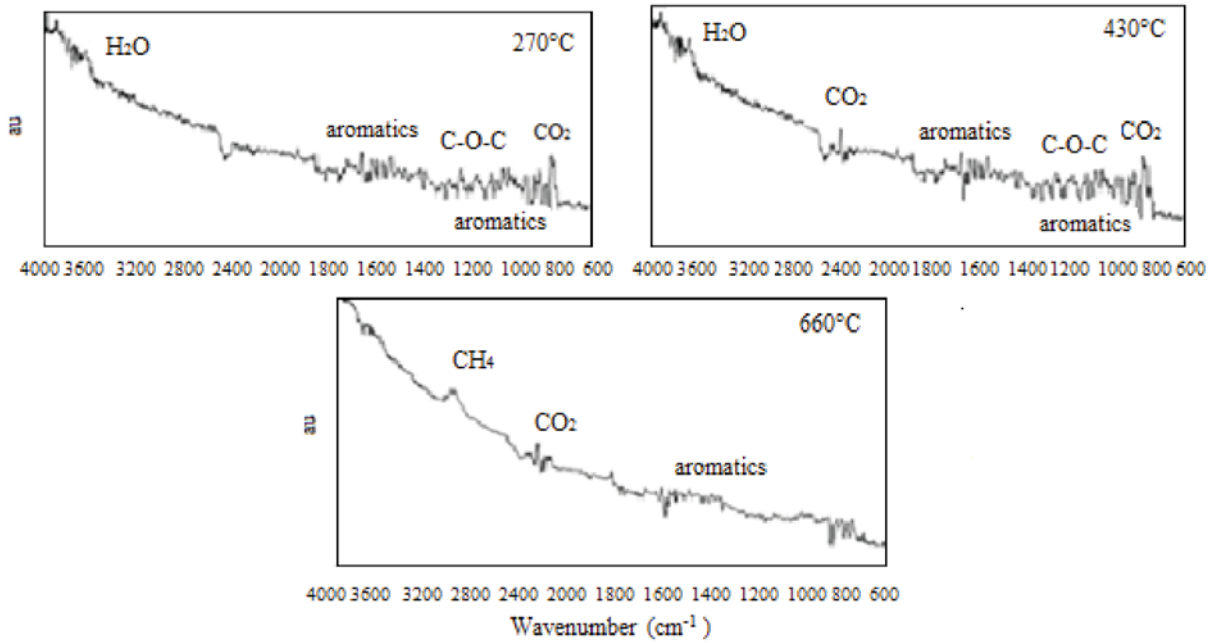


Figure 4. TG-FTIR analysis of gases evolved at certain temperatures during pyrolysis of Umutbaca coal in (10 °C/min)

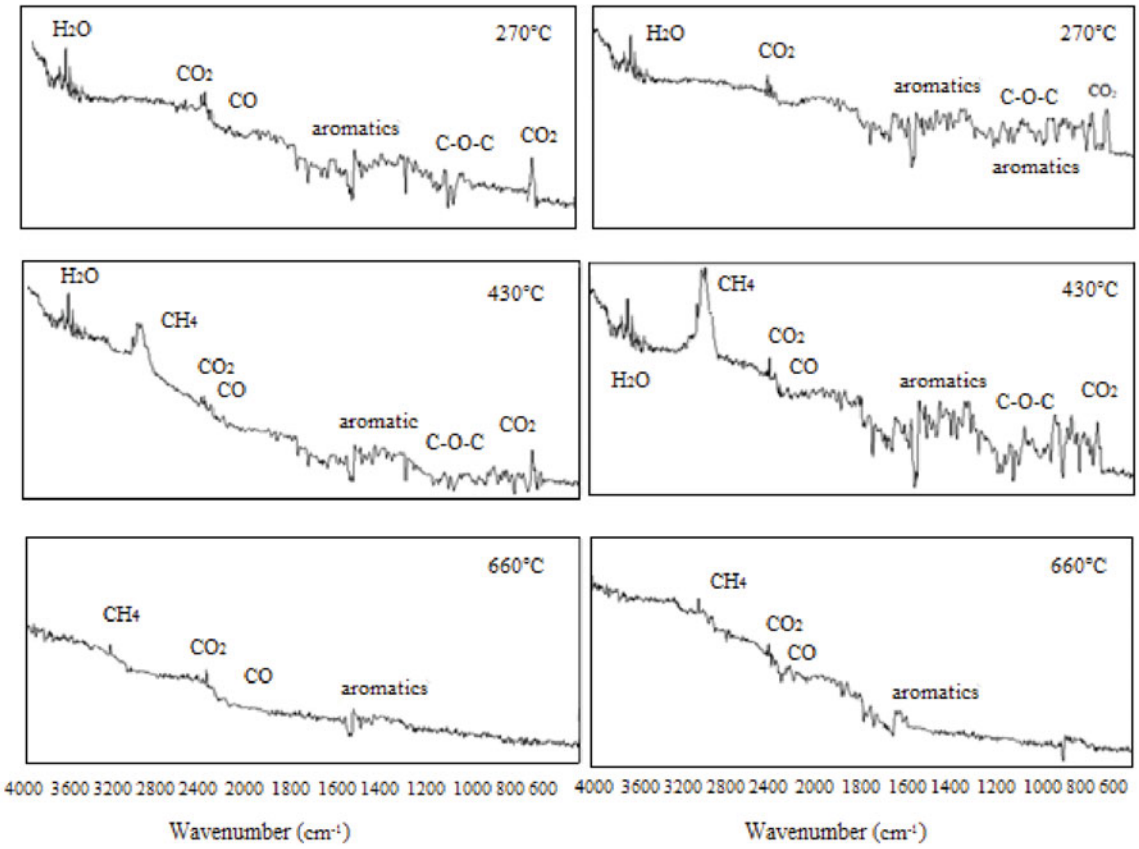


Figure 5. TG-FTIR analysis results of gases formed at certain temperatures during the pyrolysis of 1% CaO+ %5 CaO with Umutbaca coal in N_2 environment (10 °C/min)

coal in Figure 5. The situation was also observed in the literature[20].

In the literature, it is stated that CaO promotes the release of volatile substances during pyrolysis, and increases methane (CH_4) gas formation, accelerates the pyrolysis of aromatic compounds in structure, and has considerable catalytic impact on the gasification of low-rank coal[21, 22].

In Figure 6, FTIR results of chars (raw coal and the coal with CaO (5%)) obtained after pyrolysis at 600 °C are included.

FT-IR analysis was performed to better understand the changes occurring in the structure of Umutbaca coal during pyrolysis (Fig. 6). The O-H group is located in the range of 3700–3200 cm^{-1}. It is the vibration of $–CH_3$ (aliphatic) groups in the range of 3000–2800 cm^{-1}. In aromatic structures, C=C and C=O bonds are located at 2000–1500 cm^{-1}, aromatic carbonyl/carboxyl C=O groups are located at 1830–1600 cm^{-1}, and aromatic C=C rings are located at 1600–1500 cm^{-1}. Aliphatic CH is particularly striking at 1450 cm^{-1}. Aliphatic structures in the range of 1300–1000 cm^{-1} are larger and denser in coal. Vibrations of Si-O groups in the range of 1100–960 cm^{-1} are noticeable. In the literature, it is mentioned that various functional groups such as long aliphatic chains, aryl methyl, methylene and aromatic heterocyclic must be degraded in order to produce methane gas[23]. The structures are dominant in Umutbaca coal.

In the FT-IR analysis of chars obtained at 600 °C, the vibration of $–CH_3$ (aliphatic) groups in the range of 3000–2800 cm^{-1} is not visible in 5% CaO doped coal, and there are also significant decreases in groups carbonyl/carboxyl groups, aromatic, aliphatic structure in

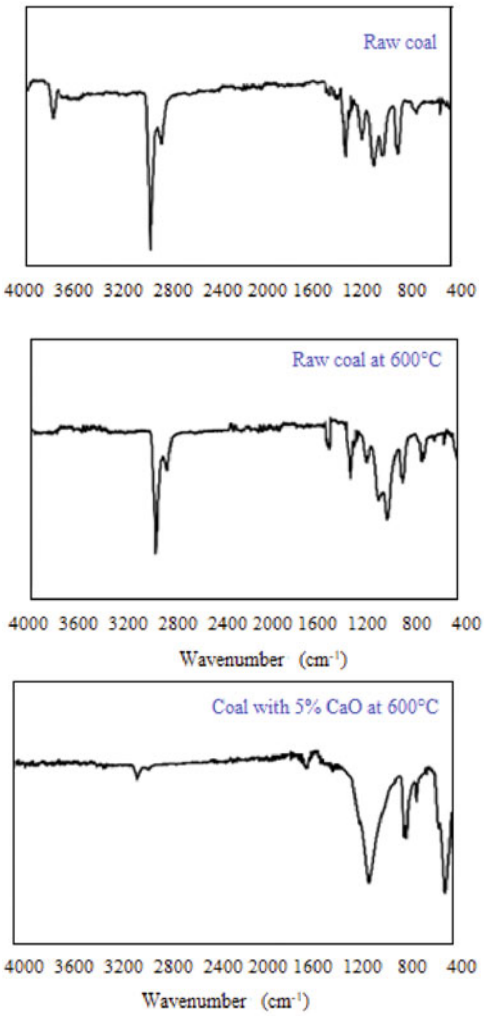


Figure 6. FTIR analysis the raw coal, the raw coal at 600 °C, the coal with 5% CaO at 600 °C

the range of 2000–1000 cm^{-1}. According to the results, it is understood that the methyl groups in the structure are removed between 430 °C and 660 °C and methane gas is formed.

In the TG-FTIR analysis of 1% and 5% CaO-added coals, there is a predominant methane formation at 430 °C, which is not found in raw coal. In the literature, an increase in CH_4 gas concentration is mentioned in the pyrolysis of the coals with Ca-based salt[21, 24]. According to TG-FTIR and FTIR analysis results of chars after pyrolysis, it is understood that the addition of CaO increases the formation of methane gas.

In the literature, it is stated that the formation of gaseous products is enhanced by calcium oxide, which can effectively catalyse secondary reactions of primary products[25]. It is assumed that the polarity of the active sites of CaO can affect the stability of primary products (especially containing aromatic compounds). It increases the decomposition of heavy alkanes and polycyclic aromatic compounds to form light alkanes and gaseous species, thus reducing tar yield. The higher CH_4 production may really be provided to the demethylation of methyl groups in the primary products.

Kinetics Analysis of the pyrolysis of Umutbaca-Raw Coal

The kinetics analysis of the pyrolysis process was conducted by using TG-DTG data. It can be seen that the pyrolysis process occurs in two steps at the TG-DTG degradation curves in Figure 1. Kinetic analysis was carried out in the Excel program using the conversion values obtained from TG analysis.

Figure 7 displays the $\ln(\beta/T^2)$-1/T and $\ln\beta$-1/T graphs of the KAS and FWO methods, respectively. Activation energies belonging to the main pyrolysis stage were calculated from the slope of these graphs. There are the required activation energies of the main pyrolysis stage of Umutbaca coal according to the conversion rate, A, and R^2 values in Table 2. Arrhenius constant (A) is determined by using Equation 7. Examined Table 2, it is seen constantly increasing activation energy values in the range of 0.1–0.4. The conversion range of 0.1–0.4 corresponds to approximately 350–490 °C.

In the temperature range, aliphatic groups (carboxyl and carbonyl) in the structure of coal decompose, causing the formation of CO_2 and CO. Firstly, there is almost a stabilization and then there is an increase in the 0.4–0.9 conversion range. In the temperature range, pyrolytic decomposition continues and very little CH_4 formation occurs. Activation energy values of raw coal according to the KAS and FWO methods are as high as the values obtained in the N_2 atmosphere of Soma and Orhaneli lignite in the literature[26].

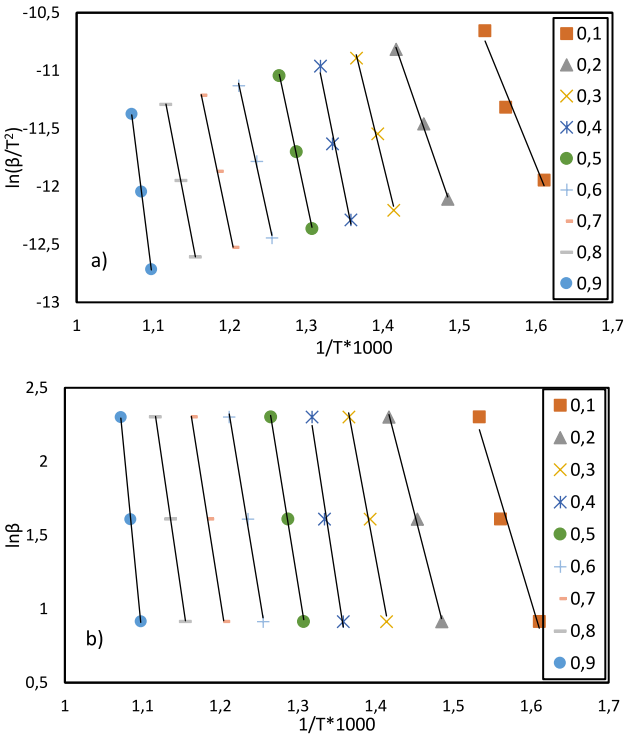


Figure 7. Temperatures according to conversion fractions (α) of the main pyrolysis state and different heating rates a) KAS, b) FWO

Kinetic Analysis of the pyrolysis of Umutbaca coal with CaO

Kinetic analysis was carried out to understand whether there is a catalytic effect on pyrolytic decomposition in the coal with CaO (5%). Activation energies were calculated by using KAS, FWO methods from the TG data in Figure 8.

Activation energies obtained by the KAS-FWO method for raw Umutbaca and the coal with 5% CaO are given in Table 3. It can be seen a significant decrease in the Ea values for each transformation after a conversion rate of 0.4. Table 3 reveals clearly the catalytic effect of 5% CaO addition on the pyrolysis process of Umutbaca coal according to the conversion rate and temperature change. When we compare with the values obtained from the pyrolysis of raw coal, it is seen that there is a slight decrease in the Ea values of the coal with CaO.

Thermodynamics parameters for the pyrolysis process

The thermodynamic parameters (ΔH, ΔG, ΔS, and Ea) obtained from FWO method (for 10°C/min) are shown in Figure 9. The enthalpy change (ΔH) shows the energy required for the formation of the activated complex. It is calculated from the energy difference

Table 2. The activation energies, A, and R^2 values for the pyrolysis of raw coal

	KAS method		FWO method		
α	Ea (kJ/mol)	R^2	Ea (kJ/mol)	R^2	A
0.1	134.6286	0.9668	138.0187	0.9712	3.00E+09
0.2	158.5563	0.9979	161.6172	0.9982	1.78E+11
0.3	223.1311	0.9930	223.498	0.9937	7.32E+15
0.4	271.0198	0.9841	269.4305	0.9854	1.84E+19
0.5	257.1354	0.9993	256.7224	0.9993	2.12E+18
0.6	250.9331	0.9968	251.3483	0.9971	8.48E+17
0.7	262.8887	0.9999	263.2503	0.9999	6.43E+18
0.8	284.8875	0.9999	284.7229	0.9999	2.48E+20
0.9	440.5589	0.9996	427.8944	0.9996	8.29E+30

Table 3. The activation energies, A, and R^2 values for the pyrolysis of coal with CaO (5%)

	KAS method		FWO method		
α	Ea (kJ/mol)	R^2	Ea (kJ/mol)	R^2	A
0.1	112.1226	0.9923	116.4276	0.9934	9.29E+7
0.3	244.0242	0.9848	242.9553	0.9861	3.59E+17
0.4	211.0259	0.949	211.9438	0.954	1.68E+15
0.5	149.6769	0.9995	154.0382	0.9995	6.99E+10
0.6	97.75601	0.9954	105.1974	0.9965	1.26E+7
0.7	76.29592	1	85.39237	1	3.63E+5
0.8	70.72969	0.9811	80.8086	0.9862	1.59E+5
0.9	88.04526	0.9997	98.43239	0.9998	3.77E+6

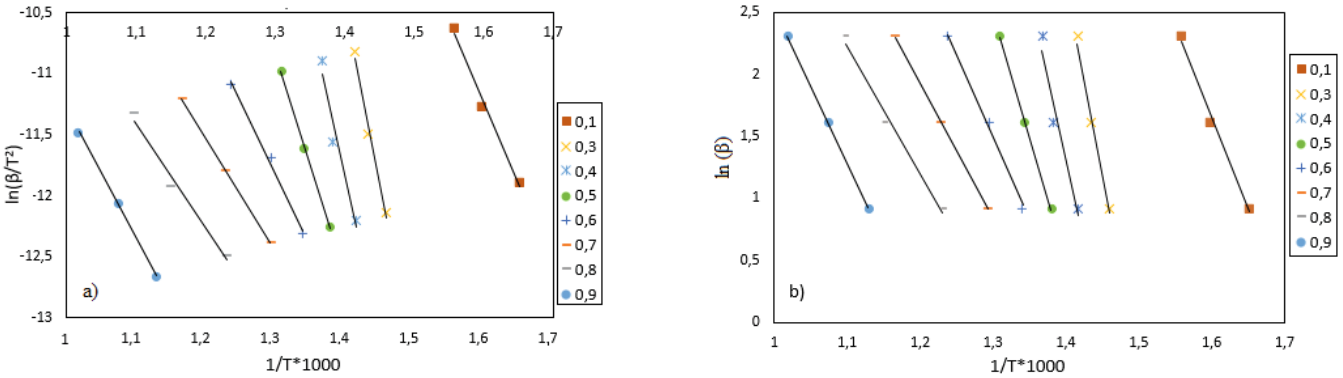


Figure 8. Temperatures according to conversion fractions (α) and different heating rates of the main pyrolysis state of 5% CaO coal a) KAS method b) FWO method

between the activated complex and the reactant. It is seen that ΔH (endothermic process) has the positive values for the pyrolysis process, the values of ΔH are compatible with Ea in Figure 9. ΔH and Ea values are very close to each other (the difference is ~5-8 kJ/mol for the pyrolysis of raw coal, ~4-6 kJ/mol for the coal with CaO. It means that the potential energy barrier is low, and the formation of activated complex is easy, however as the reaction progresses, the pyrolysis gets more difficult. ΔH value for raw coal increases significantly with the increase of α. However, the enthalpy value of the coal with CaO enthalpy value of the coal with CaO

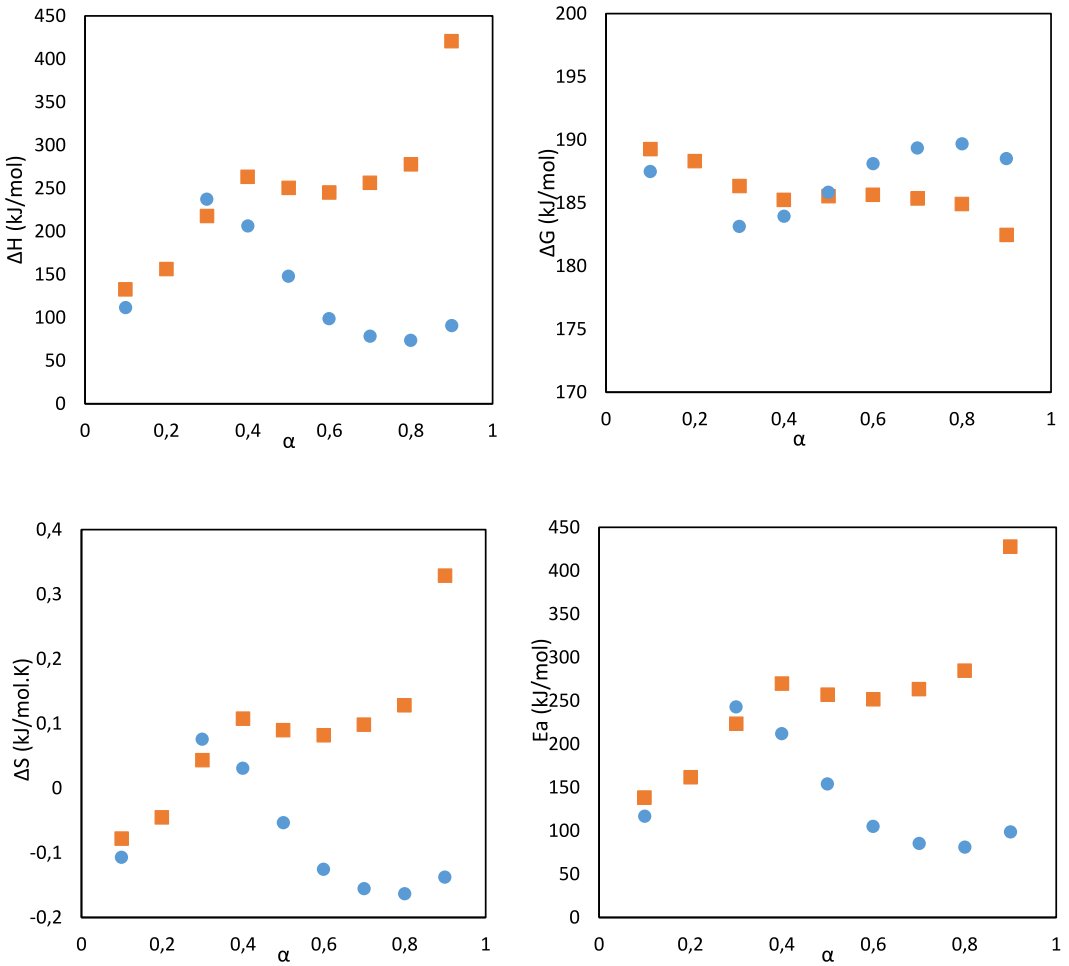


Figure 9. ΔH, ΔG, ΔS, and Ea versus at 10 °C/min heating rate for FWO method ■: raw coal, ●: the coal with CaO

decreases with the rising of α. The addition of CaO to coal reduces remarkably both the activation energy and the enthalpy of coal pyrolysis.

It should be noticed that ΔH tries to produce the energy required to break chemical bonds and decrease the degree of disorder (ΔS) during process. In the other words, the absorbed heat overcomes the energy barrier to break chemical bonds on the other hand, transforms disordered structures into ordered structures[27]. There are the significant decreases in activation energy and enthalpy values, especially after 0.3 conversion.

ΔG displays the thermodynamic favourability of process, so large and (+) ΔG values suggest that process is a non-spontaneous reaction and gets more difficult as the conversion rate increases. In fact, with increases in conversion, pyrolysis needs more energy to proceed. ΔS is the index of the degree of disorder of a system. ΔS for the pyrolysis of raw coal increases from negative to positive values. The negative values of entropies of the formation of the activated complex stated that the activated complex can be defined by a much higher 'degree of arrangement'. The negative ΔS values in the pyrolysis process of the coal with CaO meant that the activated complexes were more organized structure, compared to the initial substance[28, 29].

It can be stated that the CaO addition to Umutbaca coal ensured that the structures that were not broken during pyrolysis were easily degraded. The situation can also be understood from the TG-FTIR results. While the formations of methane and aromatic chain structures are low in raw coal, the formation is quite high in the coal with CaO, especially in coal with 5% CaO.

The activation energy and the enthalpy change of the coal with CaO is much lower than the raw coal. It is understood that at high conversion values of the coal with CaO, ΔG values increase slightly compared to raw coal. For the pyrolysis of coals with negative ΔS, when ΔG values are higher than ΔH, it can be said that a significant part of the heat energy supplied to the system is excess or free[30]. The findings may reveal the pyrolysis potential of Umutbaca coal with its CaO contribution.

On the other hand, low or minus values of ΔS for the coal with CaO display that the thermal equilibrium has been reached in reaction system after many physical/chemical changes. Thus, it appears from a thermodynamic perspective that the coal with CaO is potentially beneficial in optimizing pyrolysis conditions relative to raw coal and promoting efficient coal thermal transformations for clean coal use.

CONCLUSIONS

TG-DTG and TG-FTIR analysis indicate that CaO can promote the pyrolysis of Umutbaca coal, by decreasing the pyrolysis temperature, especially the adding 5%CaO. It is understood that the adding of 5% CaO to Umutbaca coal can cause the useful catalyst for the pyrolysis of coal. It exhibits that the gas product yield from the pyrolysis of Umutbaca coal by adding CaO catalyst can increase. The yields of CH_4, CO, the aromatic groups increase with the catalyst addition. The adding of 5% CaO was observed from the kinetics analysis (KAS and FWO method) that the activation energy of the pyrolysis process was significantly reduced. Thermodynamic parameters (ΔH, ΔG and ΔS) were calculated based on the Ea values in FWO method (for only 10 °C/min), The positive ΔH value for raw coal increase with α consistently with the variation of Ea, revealing that pyrolysis is endothermic and thermodynamic favourability reduced with α rises. However, the adding of 5% of CaO reduce ΔH. The negative ΔS, obtained by adding CaO to coal, means that the reactivity is high and the system can react faster to produce the activated complex, which results in short reaction times. These results may indicate that the addition of CaO to Umutbaca coal can be potentially useful for the coal pyrolysis.

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