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Determination of thermal decomposition kinetics of low grade coal employing thermogravimetric analysis

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Abstract−The decomposition kinetics of low grade coals was studied and compared with the kinetics of higher grade coals using thermogravimetric analysis. The effect of atmospheres (air, O_2 and N_2) on coal decomposition kinetics was also investigated. Experiments were carried out under non-isothermal conditions from room temperature to 950 °C at a heating rate of 10 °C/min. Three kinetic models--multiple linear regression equation, unreacted shrinking core and continuous reaction--were used to determine the kinetic parameters of coal decomposition. From the kinetic parameters determined through the multiple linear regression equation, coal type and the atmosphere had an effect on coal decomposition kinetics. Also, there was some variation in the kinetic parameters of coal decomposition determined by the chosen kinetic models. However, the model employing multiple linear regressions yielded consistent results with respect to theoretical background. Under air, the order of the secondary decomposition of coal samples was found to be 0.88, 1.33, 1.69 and 1.52 for samples A, B, C and D, respectively. The order of the secondary decomposition of coal samples when operated under O_2 was 1.09, 1.45, 2.36 and 1.81 for samples A, B, C and D, respectively. Under N_2, the order of the secondary decomposition of coal samples was 0.72, 0.79, 1.15 and 1.02 for samples A, B, C and D, respectively.

Keywords: Low Grade Coal, Decomposition, Thermogravimetric Analysis, Kinetics, Kinetic Parameters

INTRODUCTION

Coal, the most widely excavated mineral in the world [1], serves and will continue to serve as the primary energy resource at least for the next century [2]. Till the recent past, coal was used as a direct fuel, but now coal is being transformed into convenient secondary fuels [1,3]. Hence, a study on the thermal properties of coal is of essential importance for its effective application. Particularly, an understanding of coal decomposition is very essential for the design of the burner, exhaust hood and as a whole in the design of boilers [4,5]. However, the decomposition of coal is a complicated and tricky process, which involves due understanding. The decomposition reactions can happen either simultaneously or subsequently, which depends on the operating conditions such as temperature, heating rate, pressure, coal particle size, reactor configuration, oxidizing atmospheres, *etc.* [6-8].

Inherently, coal is composed of moisture, volatile matter, fixed carbon and ash. When coal undergoes thermal decomposition, first the liberation of water molecules occurs, followed by reactions of volatiles and fixed carbon [9,10]. The coal decomposition process comprises homogeneous decomposition of volatiles and heterogeneous decomposition of fixed carbon. Several authors have studied the behavior of coal combustion and successfully classified the coal combustion process. Some have categorized the combustion process into homogeneous (involving combustion of volatiles) and heterogeneous (concerning the combustion of volatiles-fixed carbon) [11,12].

A few others have divided the combustion phenomena into primary and secondary combustion [13]. The primary combustion pertains to combine devolatilization and simultaneous fixed carbon combustion. Secondary combustion takes care of only fixed carbon combustion.

Irrespective of the equipment used, the rate of a coal decomposition reaction depends on chemical kinetics and also on the mass transport taking place inside and outside of the coal particle [5]. The rate of coal decomposition is hindered by various resistances, such as movement of reactive gas species through the gas film, diffusion of gas through the outer layer of ash, diffusion of gas through the pores of the particle and resistance due to chemical kinetics [14].

The thermal behavior of coal can be determined by thermogravimetric analysis (TGA). TGA is a simple, inexpensive and less time consuming technique which can be used to predict the thermal response of coal when it undergoes decomposition [15-17]. TGA can be used to determine the decomposition temperature range of coal components, initial degradation temperature of coal, peak temperature of coal decomposition, and to determine the kinetics of coal decomposition. Determination of kinetics provides information on the pre-exponential factor, activation energy and order of reaction. From thermal analysis, the kinetic parameters can be determined using two different approaches [18,19]. One approach deals with applying thermal analytical data on global reaction rate equations integrated over the whole range of decomposition temperature. In the other approach, a global reaction rate expression is made into linear equations, and linear regression equations are used to

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derive kinetic parameters. In this work, we adopted the latter approach.

Research findings on the thermal behavior of coal using TGA have been reported. Otero et al. [20] attempted to study kinetics of the combustion of coal, sludge and their blends using TGA. It was reported that TGA can be used as an easy, rapid tool not only to predict the weight loss, but also to determine the kinetics of materials. Hence, in this study TGA was employed to study the kinetics of coal decomposition. Biswas et al. [21] carried out a TGA study to investigate the combustion behavior of a mix of high ash and low ash coal. They reported that high ash coal exhibited better TGA reactivity than low ash coal, and stated that the high reactivity of high ash coal could be due to the synergy effect of minerals and their intrinsic nature. Hence, in this study TGA was used for high grade and low grade coals to study their decomposition behavior. Gil et al. [17] conducted TGA study to understand the thermal characteristics and kinetics of coal, biomass and their blends. They reported that combustion of biomass occurs in three steps, while combustion of coal takes place in only one step, particularly between 315-615 °C. Nonetheless, in the current study we divided the decomposition process of coal into three stages and attempted to determine the kinetics. Yuzbasi and Selcuk [22] performed TGA-FTIR (Fourier Transform Infra-red Radiation) study on biomass/lignite blends. Experiments were conducted in four different O_2/CO_2 gas concentrations. It was reported that high O_2 levels can help combustion to shift to lower temperatures and can increase the decomposition rate. Hence, in this study TGA was performed under three atmospheres such as air, O_2 and N_2 to analyze the influence of atmospheres on the kinetic parameters of coal decomposition. Filho [5] conducted TGA study to understand the combustion of Brazilian bituminous coal. TGA was used to determine the kinetics of combustion. The combustion process was classified into primary and secondary combustion. The above study assumed nth order reaction model. Nevertheless, in the present study, order was not assumed rather the kinetics of decomposition was determined using multiple linear regression equation employing modified Arrhenius equation. Nunes and Marcilio [23] conducted Oxy-fuel combustion of coal char employing a thermo balance at various temperatures and different O_2/CO_2 gas concentration. Three kinetic models such as unreacted core, continuous reaction and Langmuir-Hinshelwood models were used to determine kinetic parameters of Oxy-fuel combustion of char. While using unreacted core model, it was found that the chemical reaction controlled the combustion process. It was also observed that the continuous reaction model was unfit for the experimental data as consumption of particles was inconsistent during the combustion process. It was also found that the Langmuir-Hinshelwood model did not yield an accurate value for the reaction and desorption steps. Hence, it can be perceived that the unreacted core model is effective in determining kinetic parameters of Oxy-fuel combustion of char. Sheeba et al. [24] identified three zones while studying the reaction kinetics of coir pith pyrolysis using TGA. Due to the difference in exhibition of thermal degradation, the same kinetic parameters were not used to define the degradation process. The kinetic parameters were determined individually for all three zones. Mansaray and Ghaly [25], while investigating the kinetics of rice husk in TGA, noticed two distinct zones of degradation. The behavior of degradation and kinetics of degradation for the two zones was analyzed separately, as the two zones displayed different degradation trends. Hence, in the current study the degradation trends were divided into zones and an attempt has been made to study the kinetics of coal components as like the aforementioned works.

We determined the kinetic of coal combustion and pyrolysis here using three kinetic techniques, such as multiple linear regression equation, making use of the modified Arrhenius equation, unreacted shrinking core model, and continuous reaction model. Although the concept of determination of kinetics through multiple linear regression has been already established in biomass decomposition, it has not been attempted in coal decomposition [26]. Hence, we endeavored to determine the kinetics of decomposition of coal using multiple linear regression equation. The advantage of the method is that the order of the decomposition process can be determined, whereas in existing methods the order is assumed; then pre-exponential factor and activation energy are calculated accordingly. The characteristics of indigenous low rank coals and imported Russian high rank coals (as Russian high rank coals are imported in South Korea) were studied. Also, earlier studies have not investigated the effect of different atmospheres on the kinetics of decomposition of coal. Nonetheless, in this study the effect of atmospheres such as air, O_2 and N_2 on the kinetics of decomposition of coal was studied and compared. The kinetic parameters determined through the unreacted shrinking core model and the continuous reaction model are also presented in this work.

MATERIALS AND METHODS

1. Coal Samples

Two low grade and two high grade coal samples were chosen for this study. The two low grade coal samples, A and B, were mined from Jangseong mining station, Taebaek-Si, Gangwon-do, South Korea. Here, these coals are generally used as fuel in power plants and in briquette making. The high grade coal samples C and D were from Russian mines. Coal lumps as such were of a size less than 2.5 mm.

2. Physical, Chemical and Thermal Analysis

For TGA, usually samples of size less than 250 μ are employed. This is to avoid heat and mass transfer limitations [27]. For particles of small diameters, mass transfer is assumed to occur with no resistance [28]. Hence, in this study, samples were sieved following ASTM D4749-87 standard and only samples of size less than 212 μ were used for further TGA studies. The mean particle diameter of the coal samples was determined in accordance with the method suggested by Cheremisinoff and Cheremisinoff [29]. The method suggested by Tolvanen et al. [30] was followed to determine the true density of coals. This method gives a density value close to the actual true density of coal. The true density was measured by dropping a small lump of 10 g of coal in a measuring jar filled with water. The difference in volume of water was noted and true density was calculated. As a sample of size less than 212 μ was used for TGA study, bulk density of those sized samples (<212 μ) were measured. The bulk density of samples was measured by using the ASTM E873-06 standard. The proximate analysis of coal samples was determined by using the Leco TGA 701 Analyzer. The analysis was carried out thrice to check for consistency of results. The average of the values was considered. ASTM D 3176 standard, which deals with the standard practice for the ultimate analysis of coal and coke was followed using Thermo scientific FlashEA1112 automatic elemental analyzer. The correlation developed by Channiwala and Parikh [31] was used to determine the HHV (higher heating value) of the coal samples from elemental analysis. The correlation can be given by

$$\text{HHV}=349.1\text{C}+1178.3\text{H}+100.5\text{S}-103.4\text{O}-15.1\text{N}-21.1\text{ASH kJ/kg} \quad (1)$$

where C, H, S, O and N denote their elemental percentage, while the composition of ash was taken from the proximate analysis.

The correlation can be valid only when the elements in the samples fall in the following range: $0<\text{C}<92\%$; $0.43<\text{H}<25\%$, $0<\text{O}<50$; $0<\text{N}<5.6\%$, $0<\text{ASH}<71\%$; $4745<\text{HHV}<55{,}345$ kJ/kg. From the calculated HHV, lower heating value (LHV) can be computed. The correlation suggested by Basu [32] was used to determine LHV from HHV. The correlation is as follows:

$$\text{LHV}=\text{HHV}-h_{st}\,(0.09\text{H}+0.01\text{H}_2\text{O})\text{ kJ/kg} \quad (2)$$

where h_{st} denotes enthalpy of steam (2,260 kJ/kg), H represents % of hydrogen and H_2O denotes % of moisture.

Scanning electron microscope (SEM) coupled with energy dispersive X-ray spectrometer (EDS) has been widely used to detect and identify the nature and composition of mineral matter present in coals [33]. For the analysis, SEM model SNE-3000M SEC integrated with EDS model XFlash 410-H-Bruker was employed. In this study, TGA was performed using Leco TGA 701 instrument. The instrument is known for an accuracy of 2% of set point or ±2 °C, whichever is greater and this deviation could reflect in the TG and DTG curves. Operating conditions of the TGA and their necessity are presented in Table 1 [5,22,27,34,35]. TGA runs were repeated thrice to eliminate the test error [36]. The deviations of the results were less than 5%.

KINETICS ANALYSIS

1. Multiple Linear Regression Equation

Global kinetics of the devolatilization reaction can be given as [37]

$$-\frac{dM}{dt}=kM^n \quad (3)$$

where M denotes fractional weight remaining (established by Goldfarb et al. [38]), while k denotes reaction rate constant and n represents order of the reaction.

It is well known that the study of kinetics is related to weight loss. For the convenience of the kinetic study, the weight terms are expressed in fractional form. The concentration of the reactants is zero at the completion of the reaction, and hence the weight terms are corrected for residual weight which remains after decomposition. Mansaray and Ghaly and Kumar et al. adopted the same procedure for the study of kinetics [26,39].

The fractional weight reamaining M can be expressed as

$$M=\frac{w-w_f}{w_0-w_f} \quad (4)$$

where w denotes instantaneous weight of sample undergoing decomposition, w_f represents weight of residue at the end of the reaction (kg) and w_o denotes initial weight of sample (kg).

Applying the Arrhenius equation,

$$k=Ae^{-E/RT} \quad (5)$$

where A represents pre-exponential factor (1/min), E denotes activation energy (kJ/mol), R denotes universal gas constant (kJ/mol K) and T denotes absolute temperature (K).

Eq. (3) can be expanded as follows:

$$\ln\left[\frac{-1}{w_o-w_f}\frac{dw}{dt}\right]=\ln A-\left(\frac{E}{RT}\right)+n\ln\left(\frac{w-w_f}{w_0-w_f}\right) \quad (6)$$

where dw/dt represents the change in weight of sample with respect to time.

The above equation takes the form

$$y=B_1+B_2x+B_3z \quad (7)$$

The parameters y, x, z, B_1, B_2 and B_3 in Eq. (5) can be defined as

$$y=\ln\left[\frac{-1}{w_0-w_f}\frac{dw}{dt}\right] \quad (8)$$

$$x=\frac{1}{RT} \quad (9)$$

$$z=\ln\left(\frac{w-w_f}{w_0-w_f}\right) \quad (10)$$

$B_1=\ln A$

$B_2=-E$

$B_3=n$

B_1, B_2 and B_3 are constants which can be determined using multi-

Table 1. Operating conditions of TGA

Condition	Range	Reason
Non-isothermal	-	To have an instantaneous and well defined physical conditions
Temperature range	25.00-950.00 °C	To facilitate propagation and completion of degradation.
Heating rate	10 °C/min	High heating rates provide large temperature gradient thereby affecting the kinetics. Hence, small heating rate was employed.
Carrier gas flow rate	7 lpm	To provide sufficient degradation atmosphere
Sample weight	Close to 20 mg	To eliminate the heat and mass transfer limitations.
Sample size	<212 µm	

linear regression method [26].

2. Unreacted Core Model

In this model, it is assumed that the reaction starts from the periphery of the particles. Then, the reaction proceeds into the core of the particle leaving behind converted particles termed as 'ash'. It is also assumed that at any point of time, there prevails an unreacted core of the particle which undergoes shrinking. The model was first established by Yagi and Kunii [40-42]. This model assumes five continuous steps occurring in sequence during the reaction. They are

i. Diffusion of gas reactant through the stagnant film of gas surrounding the particle to the surface of the solid core

ii. Penetration of gas reactant through the ash layer to the surface of the solid core

iii. Reaction of gas reactant with solid at the surface of solid core

iv. Penetration of the gaseous products through the ash layer to the stagnant layer of gas

v. Diffusion of gaseous products through the stagnant film back to the main body of the fluid

All these steps can be modeled using mathematical equations based on the decomposition occurring over a certain period of time. In this study, the first three steps were considered as they were expected to offer high resistance.

The reaction model for the diffusion of gas reactant through the stagnant film of gas can be given by the equation as established by Barranco et al. and Levenspiel [14,43]

$$\frac{t}{\tau}=X \tag{11}$$

$$\tau=\frac{\rho r}{3k_g P_{O_2}} \tag{12}$$

where X is the conversion of samples, t is the time taken for the conversion X (s), τ is the time taken for the full conversion (s), ρ is the density of the coal particle (kg/m^3), r is the radius of the coal particle (m), k_g is the mass transfer coefficient between coal particle and gas reactant while PO_2 is the partial pressure of oxygen (kPa). The reaction model for the penetration of gas reactant through the ash layer can be given by

$$\frac{t}{\tau}=1-3(1-X)^{2/3}+2(1-X) \tag{13}$$

$$\tau=\frac{\rho r^2}{6D_e P_{O_2}} \tag{14}$$

where D_e is the coefficient of effective diffusivity (m^2/s).

The reaction model for the reaction of gas reactant with solid can be given by

$$\frac{t}{\tau}=1-(1-X)^{1/3} \tag{15}$$

$$\tau=\frac{\rho r}{k'PO_2} \tag{16}$$

where k′ is the superficial first-order reaction rate constant (kg/m^{2}skPa) [23].

To implement the model, TGA was also conducted at 925 and 950 °C under air and O_2 atmosphere for samples A, B, C and D. To determine the rate determining step among the resistances (resistance of the stagnant gas film, resistance of the ash layer and the resistance of the chemical reaction), graphs were plotted between X vs. time, $1-3(1-X)^{2/3}+2(1vx)$ vs. time and $1-(1-X)^{1/3}$ vs. time for the chosen temperatures under air and O_2 atmosphere. The unreacted shrinking core model cannot be applied for N_2 atmosphere as O_2 is not involved.

It was found that the curve plotted between X vs. time was more linear, which was evident from the R^2 values. This indicated that the decomposition process was determined by diffusion of gas reactant through the stagnant film of gas surrounding the particle to the surface of the solid core. For the above case, the reaction model can be given by Eqs. (11) and (12).

The rate of reaction ($-r_A$) was assumed to obey the below equation.

$$(-r_A)=k'P^n_{O_2} \tag{17}$$

where k′ is the superficial first-order reaction rate constant (kg/m^{2}skPa), n is the order of the reaction (was assumed to be one) (no unit) and P_{O_2} is the partial pressure of oxygen (kPa) [23].

The rate of reaction ($-r_A$) can be calculated by the equation

$$(-r_A)=\frac{r\rho}{\tau} \tag{18}$$

where ($-r_A$) is the rate of reaction (kg/m^{2}s), r is the radius of coal sample (m) (values in Table 2), ρ is the density of the coal sample (kg/m^3) and τ is the taken for the full conversion of coal sample (s) which was obtained from the TGA runs.

3. Continuous Reaction Model

In this model, it is assumed that the reaction occurs across the entire core when the reagent gas comes into contact with the solid core. Further, it is assumed that the penetration of the gas reactant is much faster than the chemical reaction.

The model can be represented by the below equation since the reaction is of irreversible first order type [14].

$$-\ln(1-X)=kt \tag{19}$$

RESULTS AND DISCUSSION

1. Physical and Chemical Analysis

Results from the physical, chemical and thermal analysis of the coal samples are presented in Table 2. The mean particle diameter of the sample A was the highest and sample B was the lowest. Coal samples A and B had higher density than samples C and D. In general, feedstock with higher densities is beneficial as it considerably reduces the size of conveying and handling equipment [44]. The transportation cost and the energy required for conveying and handling of feedstock also diminish. Hence, the handling of coal samples A and B would be more convenient than samples C and D. From the bulk density measurement, it was noted that coal sample A and B exhibited higher bulk density than sample C and D. The proximate analysis indicated that all coal samples had very low moisture (<4.08%). This indicates that only minimum heat energy would be consumed to expel the water molecules from the

Table 2. Physical, chemical and thermal analysis results of samples

Analysis	Samples			
	Coal A	Coal B	Coal C	Coal D
Particle size				
Mean particle diameter (μm)	138	137	126	119
Density				
True density (kg/m^3)	2,560	2,792	1,261	1,408
Bulk density (kg/m^3)	1,366	1,369	889	1,020
Proximate analysis				
Moisture (%)	3.79	3.54	2.74	4.08
Volatile matter (%)	7.34	7.83	10.07	12.14
Fixed carbon (%)	52.74	57.72	77.59	67.58
Ash (%)	36.15	30.92	9.61	16.21
Ultimate analysis (Dry and ash free basis)				
C (%)	55.31	60.54	79.61	71.65
H (%)	1.02	0.98	2.99	2.57
N (%)	0.43	0.39	1.62	1.50
S (%)	0.24	0.26	0.35	0.38
O* (%)	43.00	37.83	15.43	23.90
Heating value				
HHV (kJ/kg)	8,899	11,408	25,860	20,053
LHV (kJ/kg)	8,688	11,197	25,265	19,543
Grade identified				
	Lignite	Lignite	Bituminous	Sub-bituminous
Ash analysis				
Al (%)	41.25	44.55	35.71	26.09
Si (%)	43.13	44.55	46.43	52.17
K (%)	4.38	4.95	N.D*	21.74
Fe (%)	10.00	5.94	N.D*	N.D*
Ni (%)	1.25	N.D*	N.D*	N.D*
Ca (%)	N.D*	N.D*	17.86	N.D*
Total (%)	100.00	100.00	100.00	100.00

*By difference

*N.D: Not detected

samples. Also, all samples had less volatile content (<12.14%). Hence, it is expected that there would be some delay in the ignition of samples. It was noted that the fixed carbon content of samples C and D were higher relative to samples A and B. Hence, it is likely that sample C and D would display more heating value than sample A and B [45]. Also, samples A and B showed higher ash content. High ash content is always disadvantageous as it consumes more heat energy during decomposition. Further, high ash coals are prone to clinkering, sintering and agglomeration issues, which are undesirable [46]. Hence, in samples A and B, the ash handling issues are more probable. From the elemental analysis, coal samples C and D had high carbon content. Hence, it is likely that these samples would deliver more heating value than samples A and B. Presence of high concentration of oxygen was found in samples A and B. This indicates that the samples A and B would release more condensable gases than samples C and D [32]. In all the samples, the presence of nitrogen and sulfur was found. Hence, it is highly probable that these samples would release NO_X and SO_X emissions [47] during combustion. It was noticed that the coal sample C had the highest heating value (LHV 25,625 kJ/kg). Lowest heating value (LHV 8,688 kJ/kg) was found for coal sample A. The heating values of samples were compared to general category of coals to identify which grade or rank they fell under. It was found that coal sample A and B were of lignite type. Coal C was noted to be the bituminous type, while coal D was sub-bituminous grade [48-50]. The ash analysis indicated that samples showed the existence of minerals such as alumina, silica, potassium, iron, nickel and calcium. The presence of Ni was found only in sample A. Nickel in coal has also been validated in the report of WHO and also in the work of Jia and Anthony [51,52]. Hence, while handling sample A, appropri-

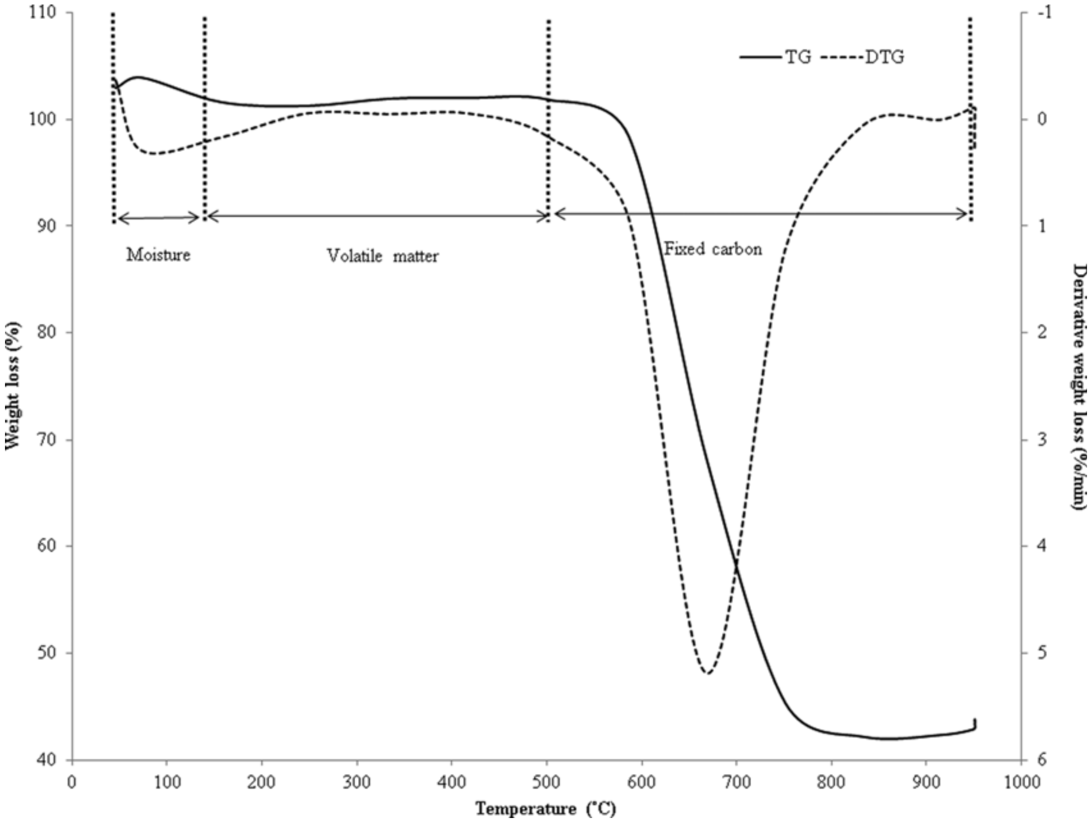

Fig. 1. TG-DTG curve of coal sample A in air.

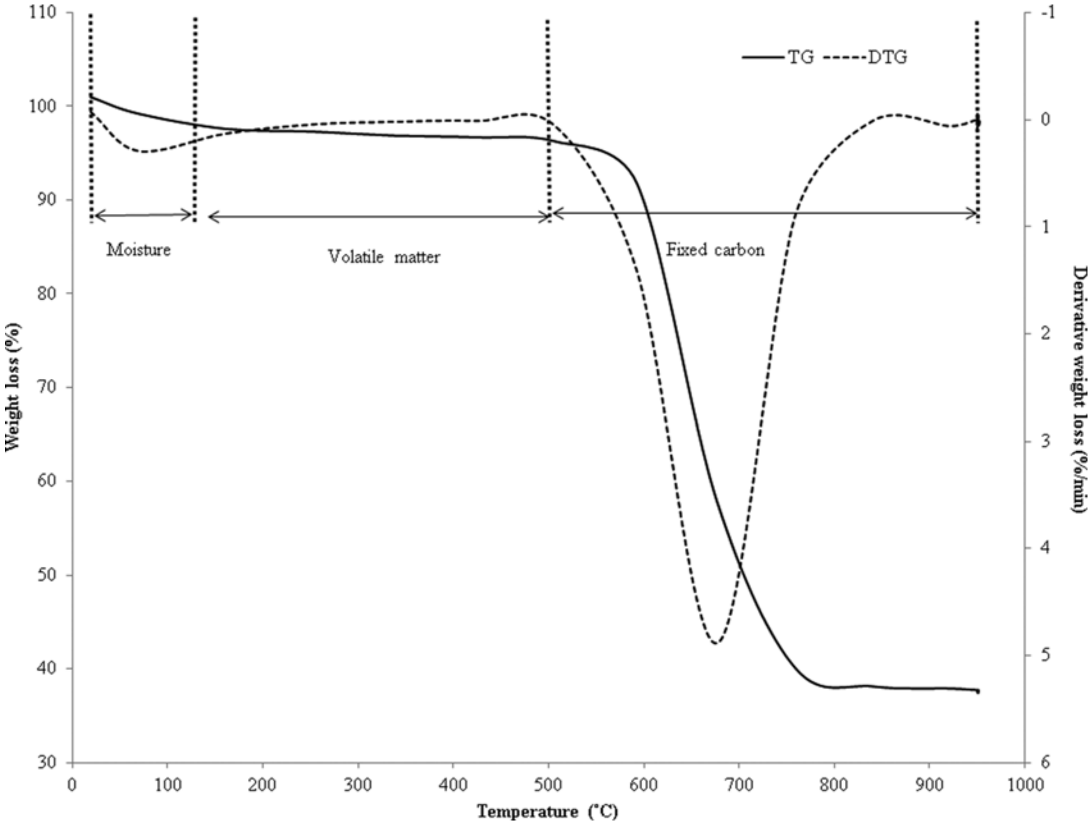

Fig. 2. TG-DTG curve of coal sample A in O_2.

ate emission control equipment should be in place. Interestingly, sample C exhibited relatively high Ca content. The oxides of Ca have the tendency to adsorb CO_2. As adsorption of CO_2 is an exothermic process, the phenomenon can increase the rate of decomposition reaction. Also, the presence of high CaO reduces the consumption of limestone used for the capturing of SO_2 [53]. Hence, it is expected that the rate of decomposition of sample C would be relatively faster as presence of Ca minerals would play a role as catalyst for the decomposition reaction [54]. Also, sample C may consume less amount of limestone intended for SO_2 capture. A high concentration of K was found in sample D. Such high K presence has the tendency to reduce melting temperatures of ash causing ash agglomeration [55]. Hence, it is likely that sample D is prone to undergoing ash agglomeration.

2. Thermal Analysis-thermogravimetric Analysis

The TG (thermogravimetry) and DTG (derivative thermogravimetry) curves of coal sample A obtained for air, O_2 and N_2 atmospheres are presented in Figs. 1-3, respectively. As all the curves look similar, only TG-DTG curves of coal sample A obtained for air, O_2 and N_2 atmospheres are provided. However, the inference of TG-DTG curves for all coal samples has been detailed below. The continuous line in the figures represents the TG curve, while the dotted line typifies DTG curve. During coal decomposition, moisture evolution happens first, followed by degradation of volatile matter and fixed carbon. This indicates that coal components would exhibit different degradation temperature.

From Fig. 1, degradation of the sample A started close to 25.00 °C, while the decomposition ended near to 950.00 °C. From the TG and DTG curves, the components of coal can be classified into three zones. The region of each zone was identified from the inflection point of the TG curve [36]. The region of moisture was noticed between 25.00 to 137.68 °C, while the zone of volatile matter was determined between 137.68 to 535.91 °C. The region of fixed carbon decomposition was between 535.91 to 950.64 °C. In DTG curve, the flatter curve resembles homogeneous reaction of decomposition, while the steep curve demonstrates heterogeneous reaction [56]. Hence, the region of heterogeneous reaction ranges from 535.91 to 950.64 °C. Barring this zone, all the zones are representatives of homogeneous reactions. There is also a possibility that degradation of a component can occur in other component regions. However, it would not be that much more significant.

The identified degradation temperature range of coal components of samples under different atmospheres is presented in Table 3. It can be noted that the low degradation temperature range of fixed carbon in samples C and D could be due to the high quality (mainly lower ash and higher volatile and fixed carbon content) of the coals C and D. The difference in the degradation temperature range of components and their weight loss composition could be due to a discrepancy in the proportion of components [57]. The difference existing in the bondage of components could also have contributed to the varying degradation temperature range and weight loss of components.

Table 4 presents the composition of fixed carbon decomposition (% of decomposition of fixed carbon) and residual weight of coal

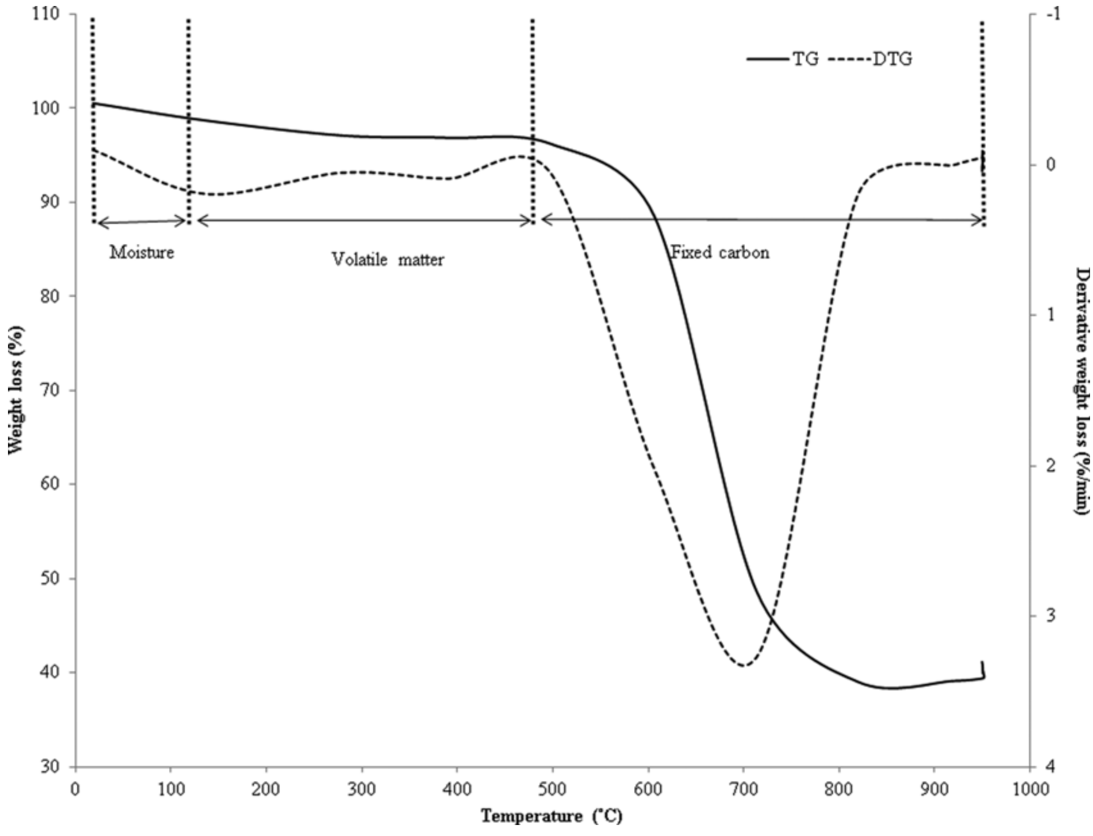

Fig. 3. TG-DTG curve of coal sample A in N_2.

Table 3. Degradation temperature range of coal components

Coal samples	Atmosphere	Temperature range of moisture (°C)	Temperature range of volatile matter (°C)	Temperature range of fixed carbon (°C)
A	Air	25.00-137.68	137.68-535.91	535.91-950.64
B		25.00-121.78	121.78-539.60	539.60-950.65
C		25.00-107.45	107.45-408.65	408.65-950.66
D		25.00-137.77	137.77-365.30	365.30-950.17
A	O_2	25.00-123.66	123.66-512.64	512.64-949.63
B		25.00-129.57	129.57-473.54	473.54-949.60
C		25.00-110.40	110.40-380.27	380.27-950.00
D		25.00-115.28	115.28-395.45	395.45-949.74
A	N_2	25.00-124.82	124.82-520.65	520.65-949.56
B		25.00-98.60	98.60-525.44	524.44-949.66
C		25.00-106.00	106.00-379.24	379.24-949.813
D		25.00-111.71	111.71-383.98	383.98-949.74

Table 4. Composition of secondary decomposition and residual weight of combustion and pyrolysis

Coal samples	Atmosphere	Decomposition of fixed carbon (%)	Residual weight (%)
A	Air	57.63	43.67
B		63.69	38.24
C		89.24	15.77
D		75.14	23.25
A	O_2	58.86	37.26
B		68.72	31.18
C		88.17	12.54
D		78.15	21.98
A	N_2	55.50	41.06
B		64.21	33.84
C		89.96	10.19
D		83.27	14.90

samples. For all the three atmospheres, the percentages of fixed carbon decompositions for samples C and D were higher as these samples inherently possess more fixed carbon. It can be noticed that the residual weight of all coal samples was higher than their ash content. This could be due to partially decomposed carbon particles.

The weight loss owing to moisture and volatile matter degradation was very little. For samples A and B, the residual weight was observed to be relatively higher as they intrinsically contain more ash content. The decomposition of fixed carbon and residual weight was not greatly influenced by reaction atmospheres.

3. Determination of Kinetic Parameters

3-1. Multiple Linear Regression Equation

The parameters of kinetics were determined following the method adopted by Mansaray and Ghaly (a), Mansaray and Ghaly (b), Nassar and Wang et al. [39,58-60]. Different components exhibit different kinetic properties. As coal is mainly composed of four different components, during thermal degradation of coal the same conditions (initial weight, final weight, change in weight, degradation temperature range, time and temperature) should not be used to determine the kinetic parameters of coal. Hence, the kinetic parameters for each component need to be determined. Based on the inflection point of the TG curve, regions were identified as zones of moisture, volatile matter and fixed carbon. The operating conditions for each component were considered according to the degradation temperature range of components. As discussed in the theoretical background, the kinetic parameters were determined employing modified Arrhenius equation.

Basic kinetic parameters were comprised of pre-exponential factor, activation energy and order of the reaction. As the composition of weight loss happening in the region of moisture and volatile matter was meager, the kinetic parameters for the decomposition of moisture and volatile matter (primary decomposition) could not be determined. A similar methodology of kinetics determination, *i.e.*, employing a modified form of Arrhenius equation and applying multiple linear regression equation was followed by Kumar et al. [26]. Like the present study, the TGA plot of the chosen biomass was divided into three stages. It was reported that the first stage was due to moisture evolution, the second stage was because of the degradation of hemicellulose-cellulose, and the third stage was due to the decomposition of lignin. In that study, only the kinetics of the second stage (degradation of hemicellulose-cellulose) was reported, as the degradation (weight loss) was very active in this stage. The kinetics of the first stage (dehydration) and third stage (decomposition of lignin) was not reported, as the weight loss was insignificant in these stages. The determined kinetic parameters for fixed carbon decomposition (secondary decomposition) for all the samples conducted at different atmospheres are presented in Table 5.

3-2. Influence of Coal Grade on Kinetic Parameters of Secondary Decomposition

For all atmospheres, samples C and D exhibited high pre-exponential factor than samples A and B. The highest pre-exponential factor was found for sample C followed by D, B and A. This indicates that high grade coal displays high pre-exponential factor. Not only coal type, pre-exponential factors are also influenced by order of reaction and reaction stages [5]. It can also be noticed from Table 5 that the quality of coal influences the activation energy. The

Table 5. Kinetic parameters of secondary decomposition of combustion and pyrolysis determined using multiple linear regression equation

Coal samples	Atmosphere	Pre-exponential factor (1/s)	Activation energy (kJ/mol)	Order of reaction
A	Air	2.87E+09	242.68	0.88
B		3.43E+09	220.17	1.33
C		4.69E+14	106.82	1.69
D		9.16E+11	154.24	1.52
A	O_2	4.57E+10	182.37	1.09
B		1.65E+16	122.85	1.45
C		3.35E+19	91.03	2.36
D		8.89E+16	104.92	1.81
A	N_2	7.44E+06	270.65	0.72
B		5.37E+07	246.97	0.79
C		2.54E+10	143.68	1.15
D		8.78E+09	178.47	1.02

activation energy for coal sample A was the highest (242.68 kJ/mol for air, 182.37 kJ/mol for O_2 and 270.65 kJ/mol for N_2). However, the coal sample is regarded as low quality coal. Next to sample A, the activation energy was more for sample B followed by samples D and C. The lowest activation energy was found for the sample C (106.82 kJ/mol for air, 91.03 kJ/mol for O_2 and 143.68 kJ/mol for N_2).

The current findings imply that the low rank coal consumes more external energy for secondary decomposition than high grade coals. Kaitano [61] also observed higher activation energy for coals with rich ash content. It was reasoned that the high activation energy was due to the presence of the high inertinite content of coal. Also, it was found that the order of the reaction increases with respect to the increase in coal quality. In other words, the high rank coal displayed high order. The order of reaction was maximum for coal C followed by D, B and A. It was consistent for all atmospheres. The current findings were also consistent with the fact that coal with high activation energy would display low reactivity [62].

Gunes and Gunes [63] conducted a similar study like the present study. About 12 Turkish coals of various grades were studied for their thermal decomposition kinetics. Among the 12 coals, Amasra coal was the highest grade coal with Ash 9.7%, and fixed carbon 49.8%. The lowest rank coal amongst the coal samples was Esme. It was 32.0% ash and 27.3% fixed carbon. Single-first order reaction model was applied to non-isothermal TGA and kinetic parameters were determined. Both Amasra and Esme displayed three zoned thermal decomposition behavior. When the kinetic parameters were compared, the Esme coal (low rank coal) exhibited higher activation energy than Amasra coal in all the three zones. This indicates that low rank coal requires more activation energy than high rank coal. The finding was very consistent with the inference of the current study.

3-3. Influence of Atmosphere on Kinetic Parameters of Secondary Decomposition

The coal samples exhibited high pre-exponential factor when conducted under O_2 than air and N_2 atmosphere. Compared to N_2 atmosphere, air was favored for high pre-exponential factor. For N_2 atmosphere, all the samples displayed high activation energy. After N_2, air exhibited more activation energy than O_2. This indicates that the external energy requirement to initiate the decomposition reactions is less for O_2 than for air. It can also be inferred that O_2 favors for decomposition than air. The more activation energy for N_2 atmosphere indicates that more external energy is needed to initiate pyrolysis than combustion process.

When the order of the reaction was compared for various atmospheres, the degradation process occurring in the presence of O_2 displayed a higher rate. The order of reaction was lowest for the degradation process under N_2 atmosphere. This indicates that O_2 atmosphere is more favorable for decomposition reactions than air. Also, it can also be inferred that the combustion is much faster than pyrolysis process. Ghaly and Mansaray [64] studied thermal degradation of rice husks for three heating rates in air, oxygen and nitrogen atmospheres using TGA. It was found that degradation rate was higher in oxygen atmosphere than in air and nitrogen. The findings were very similar to the inferences of the current study. In the current study too, the rate of degradation was found to be higher for O_2 than for air and N_2. In another study, Peterson et al. [65] investigated thermal degradation of polystyrene, polyethylene and polypropylene in nitrogen and air atmospheres using thermogravimetry and differential scanning calorimeter. Samples were heated at nominal heating rates of 0.5-0.2 K/min up to 600 °C. Model-free iso-conversional method was applied to determine activation energy. In air atmosphere, polymers demonstrated lower activation energy than in nitrogen atmosphere. The observed activation energy for polystyrene, polyethylene and polypropylene in air was 125, 80 and 90 kJ/mol, respectively. Conversely, in nitrogen atmosphere the activation energy was 200, 240 and 250 kJ/mol for polystyrene, polyethylene and polypropylene, respectively. The findings were quite consistent with the current inference.

4. Unreacted Core Model

Eqs. (17) and (18) were linearized for 925, 950 and 975 °C under air and O_2 atmosphere and the values of k were determined for all samples. The pre-exponential factor, A (kmol/sm^{-2}) and the activation energy of the reaction, E (kJ/kmol) were determined using the Arrhenius equation.

The values of A and E were determined from plots of ln (k) versus (1/T). The linearized Arrhenius equation for sample A, B, C and D under air atmosphere is presented in Figs. 4-7, respectively.

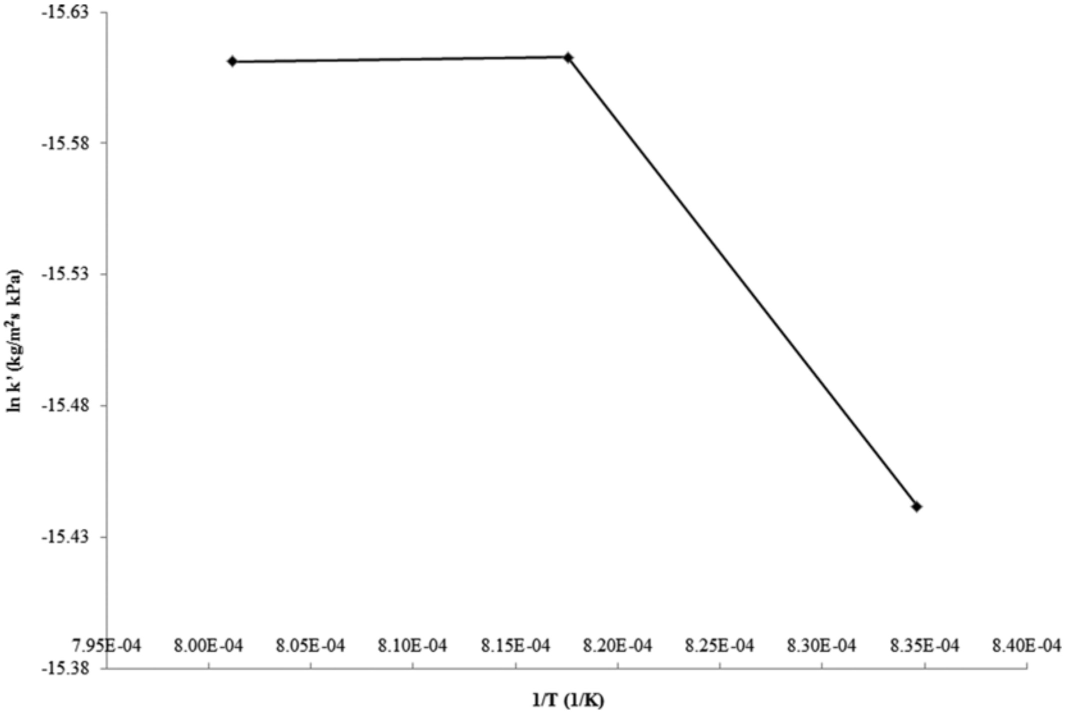

Fig. 4. Linearised Arrhenius equation for coal sample A operated under air.

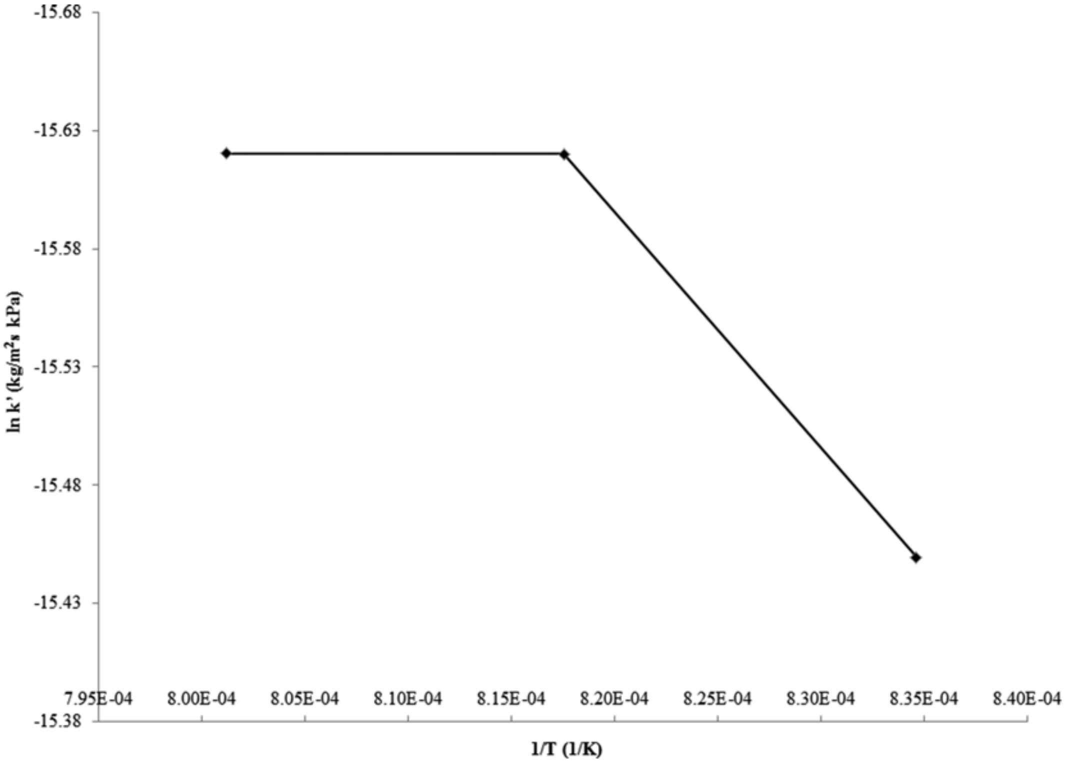

Fig. 5. Linearised Arrhenius equation for coal sample B operated under air.

The linearized Arrhenius equation for samples A, B, C and D under O_2 atmosphere is presented in Figs. 8-11. The obtained kinetic parameters are presented in Table 6.

The pre-exponential factor and activation energy were calculated assuming the order of the reaction to be one [23]. The kinetic parameters for samples operated under N_2 could not be determined, as partial pressure of O_2 was not involved in the decomposition process. Eqs. (19) and (20) were linearized for 925, 950 and 975 °C, then

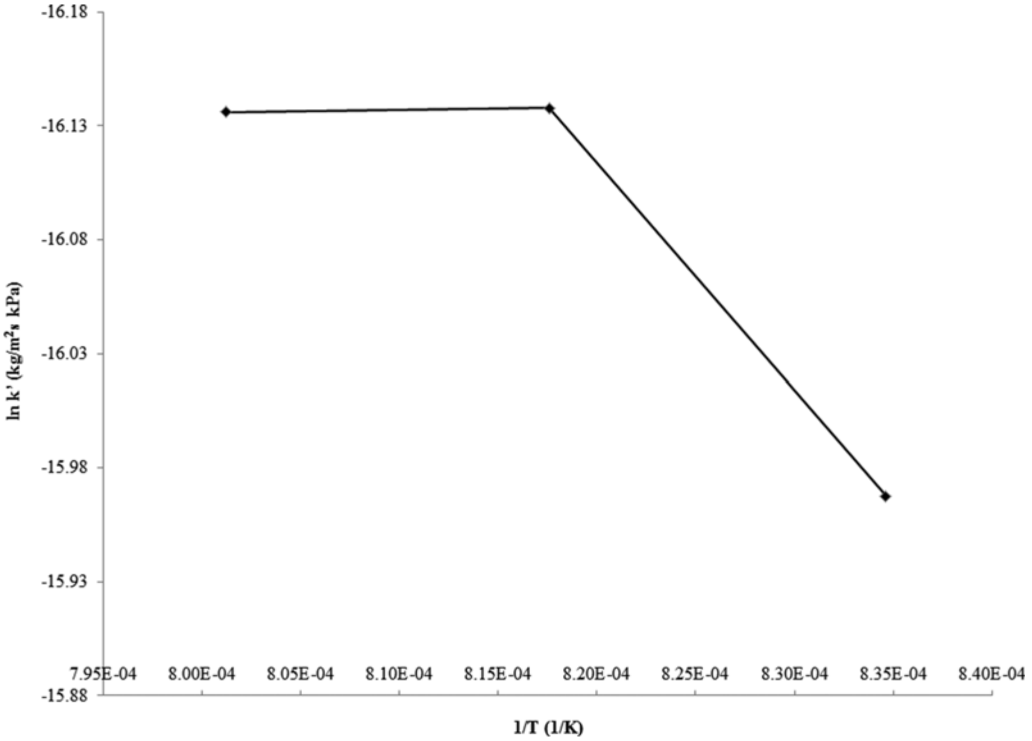

Fig. 6. Linearised Arrhenius equation for coal sample C operated under air.

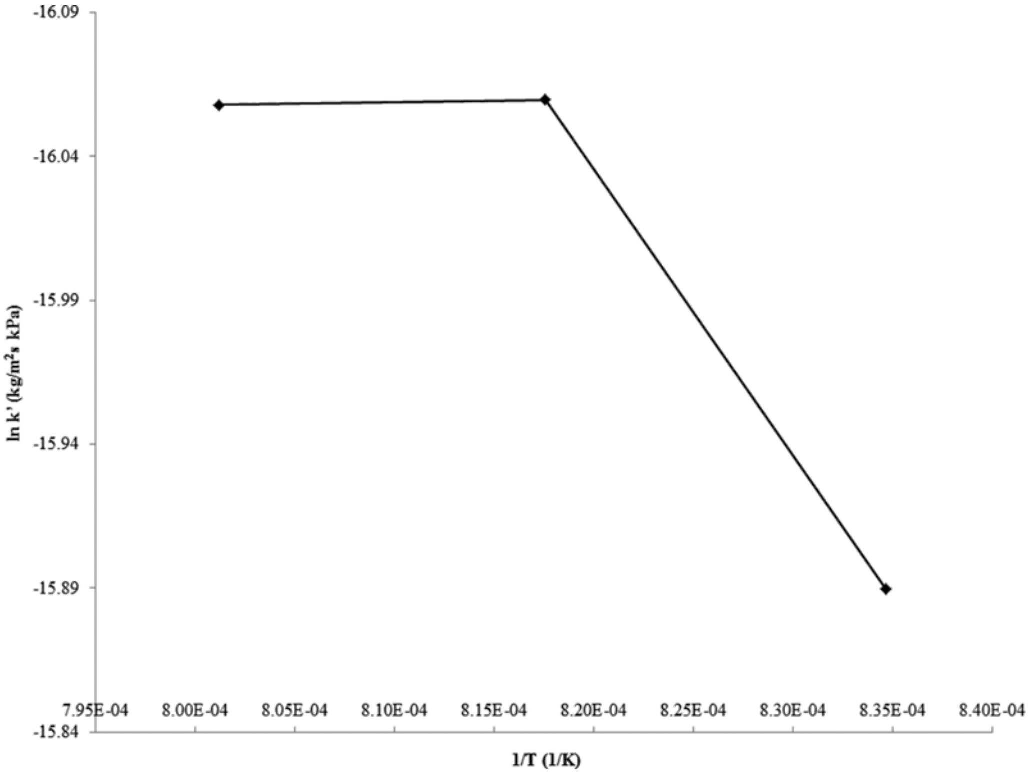

Fig. 7. Linearised Arrhenius equation for coal sample D operated under air.

the kinetic parameters were determined. Hence, the obtained kinetic parameters correspond to the temperature range of 925-975 °C. The value of pre-exponential factor of low-rank coals was higher than that of high-rank coals. Furthermore, barring sample B, the pre-exponential factor was found to be more for air than O_2 atmosphere. This was not consistent with the results found through

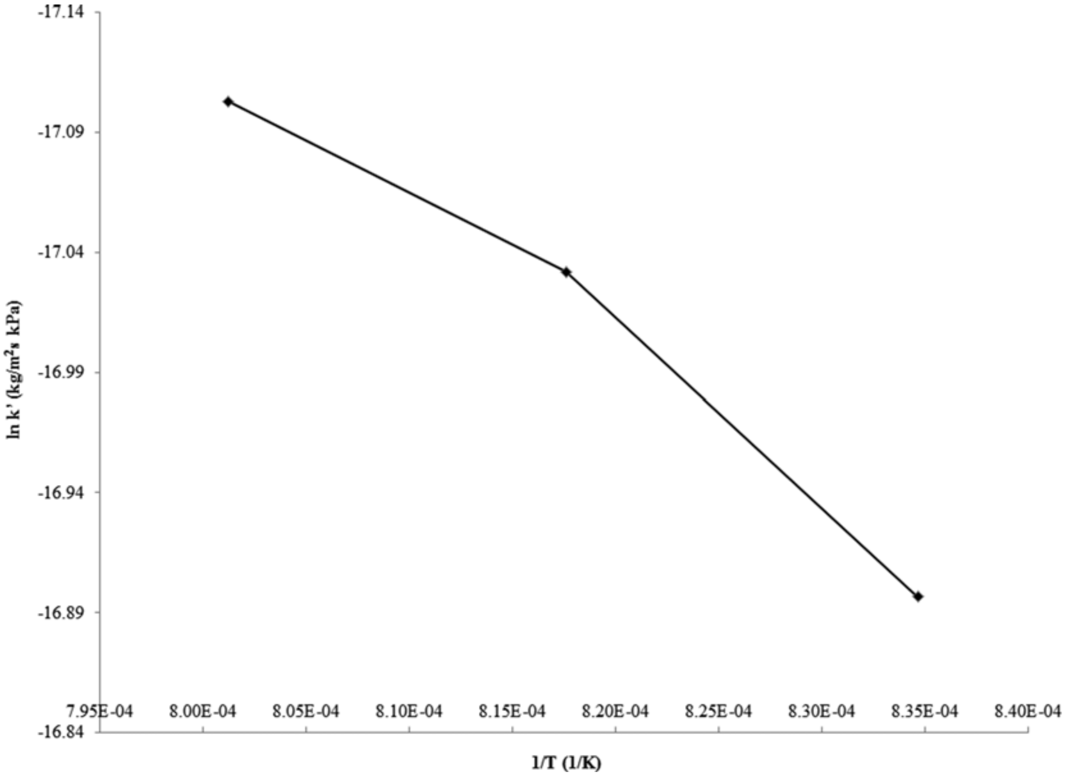

Fig. 8. Linearised Arrhenius equation for coal sample A operated under O_2.

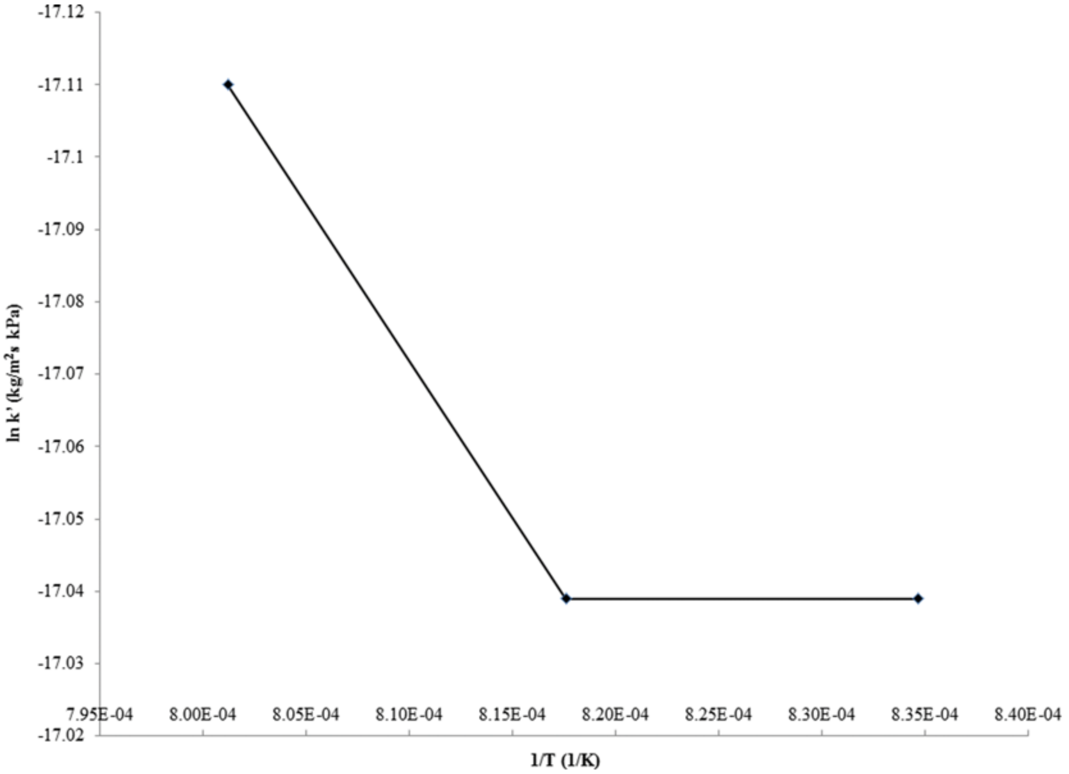

Fig. 9. Linearised Arrhenius equation for coal sample B operated under O_2.

multiple linear regression model. It can be observed from Table 6 that there was almost no change in activation energy for all samples under air atmosphere. The activation energy for all samples was close to 42.0 kJ/mol. However, the activation energy for sam-

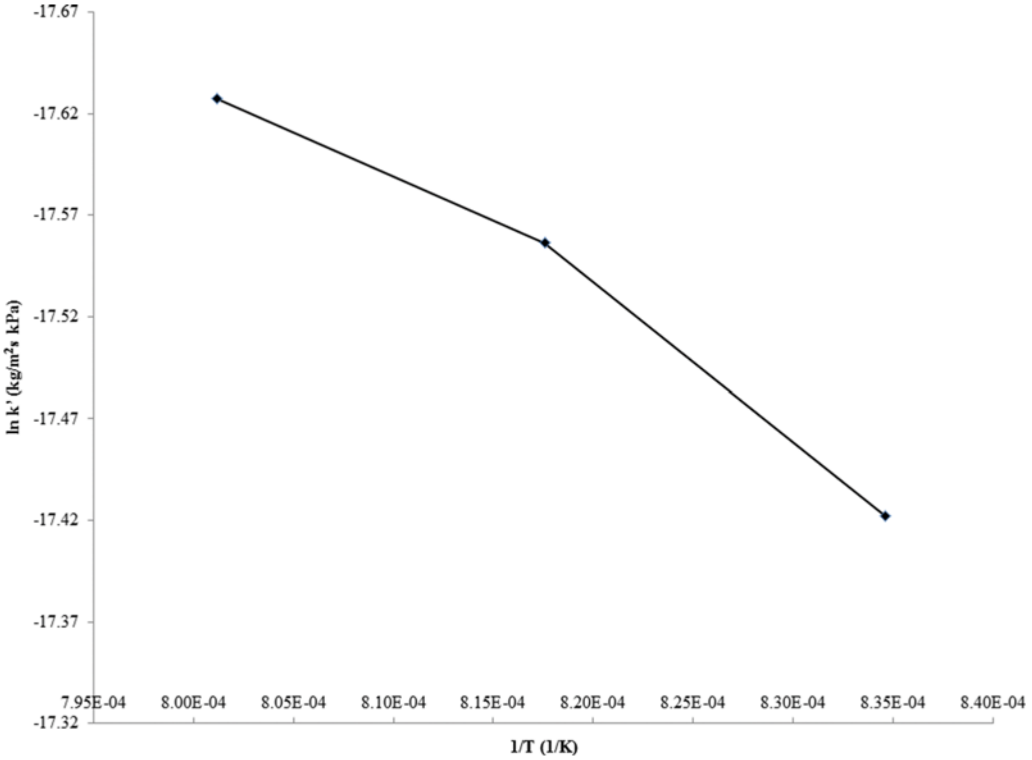

Fig. 10. Linearised Arrhenius equation for coal sample C operated under O_2.

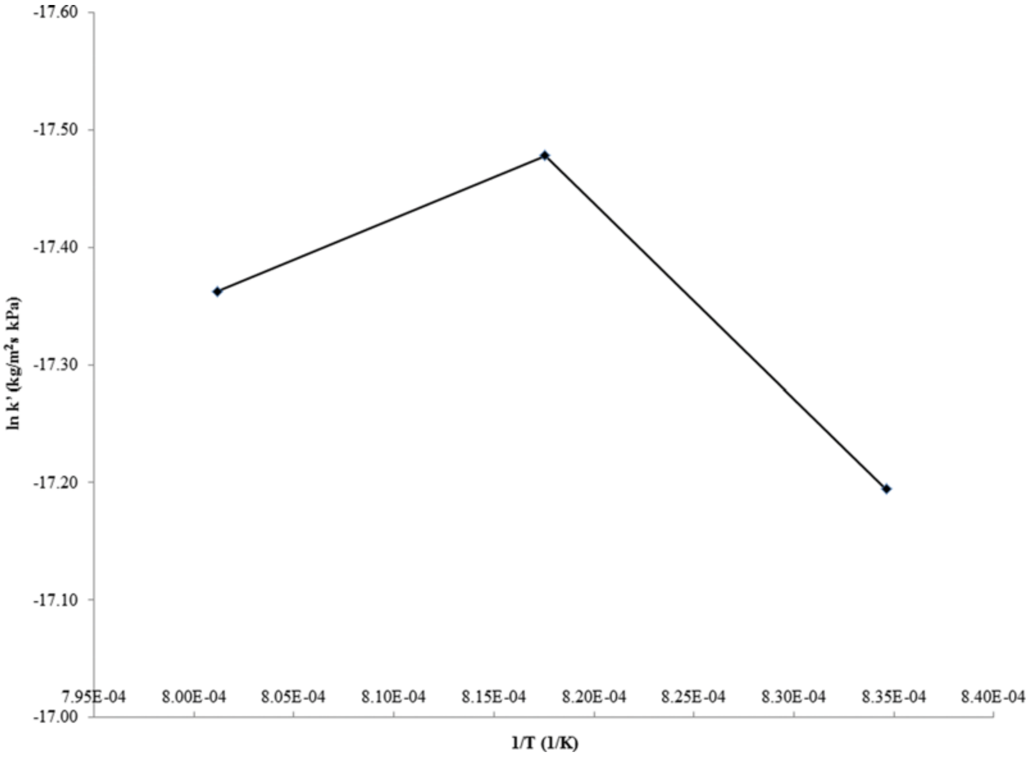

Fig. 11. Linearised Arrhenius equation for coal sample D operated under O_2.

ples A, B, C and D operated under O_2 was different. It was 51.40. 17.55, 51.15 and 42.49 kJ/mol for samples A, B, C and D, respectively. Also, apart from sample B, all samples exhibited higher activation energy when operated in O_2 atmosphere. This was not consistent with the results obtained by multiple linear regression equation model.

Table 6. Kinetic parameters of coal decomposition determined using unreacted shrinking core model

Coal samples	Atmosphere	Pre-exponential factor (1/s)	Activation energy (kJ/mol)
A	Air	2.71E-09	42.41
B		2.59E-09	42.76
C		1.64E-09	42.18
D		1.78E-09	42.11
A	O_2	2.61E-10	51.40
B		6.92E-09	17.55
C		1.58E-10	51.15
D		4.48E-10	42.49

Table 7. Kinetic parameters of coal decomposition determined using continuous reaction model

Coal samples	Atmosphere	Pre-exponential factor (1/s)	Activation energy (kJ/mol)
A	Air	1.98 E+02	114.46
B		1.47 E+09	236.75
C		6.84 E+08	201.922
D		1.51 E+01	81.49
A	O_2	1.42 E-03	17.04
B		2.07 E-03	18.51
C		1.04 E-03	17.82
D		2.52 E-03	18.05
A	N_2	2.5 E-04	8.89
B		3.21 E-04	12.87
C		2.12 E-02	34.49
D		4.40 E-04	13.99

5. Continuous Reaction Model

By taking the value of X from Eq. (19) and t from the experimental runs, the value of k′ at 950 °C under air, O_2 and N_2 was determined for all samples. Then, the Arrhenius equation was employed. The plot of ln (k′) versus (1/T) and the values of A and E were calculated as in the unreacted shrinking core model. The kinetic parameters determined using continuous reaction model are in Table 7.

Here also, the order of the reaction was assumed to be unity, the pre-exponential factor and activation energy were determined accordingly [23]. From the table, the activation energy of samples under air was higher than O_2 and N_2 atmosphere. There was not much difference in activation energy of samples for O_2 and N_2 atmosphere. Also, the pre-exponential factor for samples operated under air was much higher than O_2 and N_2. This was not consistent with the findings of multiple linear regression equation model.

6. Comparison of the Techniques

Although the kinetic parameters of coal decomposition can be determined through techniques such as multiple linear regression equation, unreacted core model and continuous reaction model, only multiple linear regression equations have provided consistent results in the current study. This could be due to the adoption of three-step nature of coal decomposition reactions. Based on that, different kinetic parameters were employed to define the degradation process, which has yielded acceptable results. The interpretations of the technique are also logically based on theoretical background. Furthermore, models like unreacted core model cannot be used for the determination of thermal decomposition of coal under N_2 atmosphere, as O_2 is not involved. In unreacted core and continuous reaction models, the order of the reaction was assumed, whereas in multiple linear regression equations the order of the reaction is not assumed, rather can be determined. This indicates that a multiple linear regression equation is the best technique among the chosen techniques for determination of kinetic parameters of coal decomposition. The obtained kinetics is valid for the considered coal samples and the undertaken operating conditions. Hence, it should be noted that kinetics may vary as they are influenced by temperature, heating rate, sample size, amount of sample, carrier gas, type of analyzer, operator skill, methodology followed to determine the kinetics [56].

CONCLUSION

We used three kinetic model techniques, such as multiple linear regression equation (using Modified Arrhenius equation), unreacted core model and continuous reaction model, to determine the kinetic parameters (pre-exponential factor, activation energy and order of the reaction) of coal decomposition. Among the three models, the model employing multiple linear regression yielded consistent results with respect to theoretical background and hence its findings are only concluded here. It was found that coal type and atmosphere influence the kinetic parameters of coal decomposition. The low rank coals consumed more external energy (activation energy) for secondary decomposition than high grade coals. The order of reaction of secondary decomposition of coal was higher for high grade coals. This indicates that the high grade coals were more reactive than low grade coals. Also, the coal samples (both high and low grade) exhibited high pre-exponential factor when conducted under O_2 than air and N_2 atmosphere. Further, the degradation process that occurred in the presence of O_2 displayed a higher order than in air and N_2 atmospheres. The order of reaction was the lowest for the degradation process happening under N_2 atmosphere.

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