

Fluidized bed combustion of coal: effect of heating rate and particle size on activation energy

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Abstract- Coal is a heterogeneous substance and as it is not a good conductor of heat, so, in all pyrolysis and combustion processes the reaction occurs in non-isothermal conditions. In this work the effect of heating rate and particle size of a single coal particle during pyrolysis by thermogravimetric (TG/DTG) analysis is reported. All the experiments were conducted at non-isothermal conditions in the temperature range of $298-1123^{\circ}K$ in argon gas atmosphere. TG/DTG curves have shown variation in, peak temperatures and residual values for particle sizes and heating rates. The experimental data were evaluated by different existing kinetic model. A third order model fitted to the data very well. Kinetic parameters were evaluated by existing non isothermal methods. Activation energy and pre-exponential factor A has been found to vary with heating rate. As the heating rate increases the activation energy and pre-exponential factor A increases. Correlations have been given. It has been found that extrapolated activation energy resembles data in literature.

Index terms: activation energy, Coal, fluidized bed, heating rate, Kinetic analysis, Particle size, pre-exponential factor

1. INTRODUCTION

Pyrolysis is the first step in all thermo chemical coal conversion processes. Many investigators have considered pyrolysis as the first step for all thermo chemical conversion [1],[2],[3], for evaluation of kinetic data and for establishing reliable models. But, available kinetic data are not sufficient for application and extrapolation to different feed stocks and process conditions and, on the other hand, the models are complicated. Thermo gravimetric analysis (TGA) provides a rapid quantitative method to examine the overall pyrolysis, especially under non isothermal conditions, and enables one to estimate the effective kinetic parameters for the overall decomposition reactions. Coal pyrolysis is a very complicated physical and chemical process which is sensitive to many factors such as coal rank, heating rate, heat and mass transfer effects [2], [4],[5].

Coal pyrolysis is not easily described by mathematical models because of the complex array of thermal decomposition reactions and because of the complicating effects of heat and mass transport phenomena. First order single-reaction models provide adequate description of the pyrolysis process if they are applied to isothermal conditions [6]. A more descriptive pyrolysis model is obtained if no specific order is assumed for the Arrhenius single-reaction equation. The order has been found to vary from two to eight [7]. Solomon et al [4] discussed the choice of pyrolysis models that allow extrapolation between heating rates (in their case, 0.5-333K/s). They considered that a model with distributed activation energy would give the best fit. However, a simple model (without activation energy distribution) can give reasonable prediction if the reaction rates are defined over a sufficiently large range of heating rates, provided that the coal particles being pyrolyzed are isothermal and the temperature measurements are correct. Burnham and Braun [8] analyzed a variety of global kinetic models on coal pyrolysis and claimed that the best simple model is an nth-order reaction, referring to the reaction profile, consisting of several discrete first-order reactions with different activation energies but the same frequency. Burnham and Braun [8] suggest that a deviation from first-order kinetics is often either due to the existence of a distribution of activation energies, or, to the propagation of a decomposition front through the solid. The propagation of decomposition front was investigated by Chern and Hayhurst [9] and found that the devolatilization of coal can be explained by the shrinking-core model assuming no change in the size of the particles. Chern and Hayhurst [9] also indicated that the reaction front proceeds at a constant velocity. Wiktorsson et al [5] studied the

range of extrapolation of discrete kinetic parameters for species evolved in coal pyrolysis and concluded that a second order ethane parameters shows good reliability of extrapolation to a very high heating rate, however tar kinetic parameters of second order could be extrapolated with reasonable accuracy in the heating range 3-16200

$K \text{ min}^{-1}$.

The average particle sizes used in a fluidized bed are comparatively large in comparison to pulverized coal combustion boiler. It has been reported that in a fluidized bed different particle sizes experiences different rate of heating [10]. There is no work reported in literature on the study of effect of heating rate on particle sizes relevant to fluidized bed combustion. There are two distinct parameters which go on changing for the particle sizes in a fluidized bed. Heating rate varies inversely to the particle size. The volatile yields are reported to be less for large particles in comparison to small particles in fluidized bed [11],[12]. To study whether heating rate or particle diameter is responsible or both, one has to study one parameter at a time keeping the other parameter constant i.e. either diameter has to be varied keeping heating rate constant or heating rate has to be varied keeping the diameter constant. It is difficult to heat different particle sizes at one heating rate. In a DTA-TGA equipment although linear rate of heating is applied, large particles will not be heated at the same rate. Similarly if we vary the particle size in a wide size range it will be difficult to maintain constant rate of heating. It is only possible to make a comparative study for a narrow particle size range keeping the linear heating rate constant and to study the effect of heating rate, the particle size has to be kept constant. In this report pyrolysis of coal has been studied in DTA-TGA equipment by varying one parameter at a time and keeping the other parameter constant. Effect on particle diameter has been studied for a very narrow range of particle diameters keeping heating rate constant, so that inaccuracies arising out of particle sizes of wide range being heated at different heating rate are at the minimum. To study the effect of heating rate, coal particle of constant particle size was heated at three different heating rates. Kinetic parameters were evaluated in inert atmosphere by employing non-isothermal methods.

2. EXPERIMENTAL

2.1 Analysis of the coal samples

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The proximate and ultimate analyses of the coal samples were carried out by the methods outlined in IS: 1350 (Part I, Proximate Analysis) [13] and IS: 1350 (Part IV/Section 1, Determination of Carbon and Hydrogen) [14], IS: 1350 (Part IV/Section 2, Determination of Nitrogen) [15], IS: 1350 (Part III, Determination of Sulphur) [16]. The calorific values were determined using the methods prescribed in IS: 1350 (Part II, Determination of calorific value of coal) [17]. The results of these analyses are presented in Table 1. Mass equivalent diameter of the coal particles were calculated using equation given by Borah et al. [18], assuming the particle to be spherical.

2.2 Apparatus and procedure

The TG/DTG of the coal sample were carried out in an inert atmosphere of argon gas (purity 99.99% and moisture free) and a flow rate of 100 ml minute⁻¹ in a thermo gravimetric analyzer (Model: TGA/SDTA 851⁰/LF/1100; Make: Mettler-Toledo, Switzerland). The accuracy in the measurement of temperature inside the furnace is ±0.3⁰K. The accuracy of measurement of mass in the balance of the analyzer is ±0.001mg. The experiments were carried out using alumina crucible having volume of 900 µL. The analyzer is operated through a Hewlett-Packard PC loaded with STAR^e software.

3. RESULT AND DISCUSSION

3.1 Effect of particle size on pyrolysis of coal

Four coal particles of a typical north East Indian coal (properties as given in table 1) of diameter 3.7, 3.9, 4.2 and 4.4 mm respectively were taken for study of effect of particle sizes. The experiments were performed at a heating rate of 20⁰K min⁻¹ and heated up to 1123⁰K. The pyrolysis reaction is significant in the temperature range of 623–1123⁰K. The fractional conversion (X) in pyrolysis is expressed on a normalized basis i.e. $X = \frac{(W_0 - W)}{(W_0 - W_f)}$, where, W , W_0 and W_f are present, initial and final masses of the coal samples, respectively. The variation of X with temperature (T) is illustrated in Fig.1. From the yield curve it is evident that up to a temperature 773–823⁰K the higher the particle size the lower is the value of X for the same temperature. After 823⁰K the yield of higher particle sizes are higher than the smaller size particle. This may be the effect of heat transfer to the particles. Higher the particle size lower is the heat transfer rate which is also could be seen from the results of Ross et al [10]. In the temperature range of 700–1100K the yield of volatile matter increases as the particle size increases.

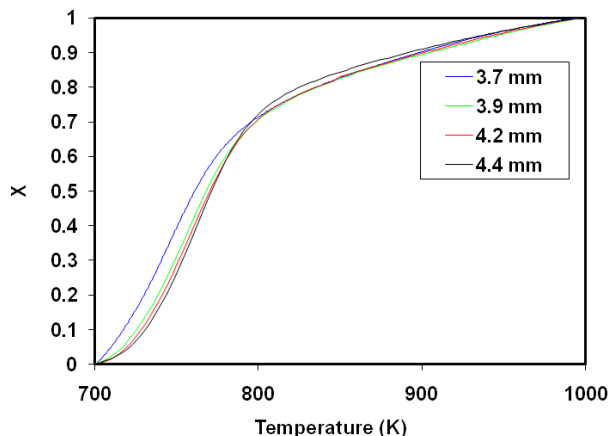


Fig.1 Conversion vs. Temperature for different particle size

3.2 TG and DTG curves of pyrolysis of coal of different size

The TG and DTG curves of pyrolysis of a typical north East Indian coal (properties given in table 1) were obtained for particle diameters of 3.7, 3.9, 4.2 and 4.4 mm in inert atmosphere of Argon gas. All the thermo gravimetric curves are asymmetric, Fig.2, and moves to higher temperature with increase in particle sizes. The peak conversion rate and the maximum peak temperature and the corresponding conversion can be identified from Fig.2. Higher particle size results in higher yield, higher peak value of reaction rate and a higher temperature for its occurrence. Values of peak temperature T_p, X_{max} and $\left(\frac{dX}{dt}\right)_{max}$ for particle sizes are given in table 2. It can be observed that as the particle size increases the peak temperature is shifted to higher temperature. This may be due to the differences in heat transfer rates to the particles. Higher the size of the coal particle lower is the heat transfer rate which is also could be seen from the results of Ross et al [10].

TG and DTG curves of pyrolysis of coal at different heating rate

The TG and DTG curves of pyrolysis of a typical north East Indian coal (properties given in table 1) with approximately same particle sizes

Table 1 Proximate and ultimate analyses of the coal samples

Analysis	Parameter	(%)
Proximate analysis (air-dried)	Volatile matter	38.1
	Fixed carbon	45.6
	Ash	14.4
	Moisture	1.9
	Gross specific energy (MJ/kg)	28.1
Ultimate analysis (daf)	Carbon	81.6
	Hydrogen	5.3
	Nitrogen	1.3
	Sulfur	4.9
	Oxygen (by difference)	6.9

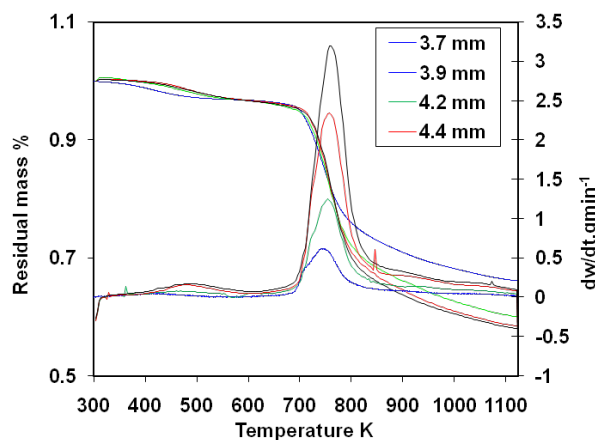


Fig.2 Mass loss rate vs. temperature for different particle size were

Table 2 Values of T_p , X_{max} , $\left(\frac{dW}{dt}\right)_{max}$ and $\left(\frac{dX}{dt}\right)_{max}$ of coal particle of different particle diameter

Diameter of Coal particle, mm	$T_p, ^\circ K$	X_{max}	$\left(\frac{dW}{dt}\right)_{max}$ $g \text{ min}^{-1}$	$\left(\frac{dX}{dt}\right)_{max}$ min^{-1}
3.7	742	0.28098	0.00062	0.20334
3.9	754	0.33756	0.00125	0.21510
4.2	758	0.35945	0.00234	0.21492
4.4	758	0.36288	0.00320	0.22914

obtained at heating rates of 20, 40 and 50 $K \text{ min}^{-1}$ in inert atmosphere of Argon gas. The variations of X with temperature are shown in Fig.3. From the curves it can be seen that for the same conversion X the temperature of occurrence is higher at higher heating rate. This may be for the heat and mass transfer effect for which although outside temperature has reached a higher level of temperature in less time, the inside of the particle temperature has not experienced the same temperature. At lower heating rate more time is allowed for the particle to reach the same temperature and hence the conversion is higher. Moreover, the devolatilization of coal starts only after attaining a temperature of around 700 $^\circ K$. Devolatilization reaction is energy intensive. At lower heating rate more time is being allowed and there is more energy input, so, the devolatilization is more at lower

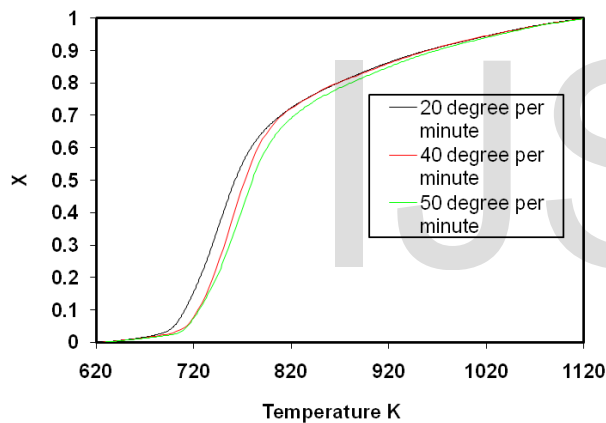


Fig.3 Conversion vs. temperature at different heating rates

temperature. At higher rate of heating similar energy will be available at higher temperature. However after reaching a temperature of approximately 773-823K the conversion has no significant difference. The pyrolysis reaction is significant in the temperature range of 623-1123K. All the thermo gravimetric curves are asymmetric (Fig.4), and moves to higher temperature with increase in heating rates. The peak conversion rate and the maximum peak temperature and the corresponding conversion can be identified from Fig.4. A higher heating rate results in higher peak value of reaction rate and a higher temperature for its occurrence. Values of T_p , X_{max} and $\left(\frac{dX}{dt}\right)_{max}$ at various heating rate are given in Table 3.

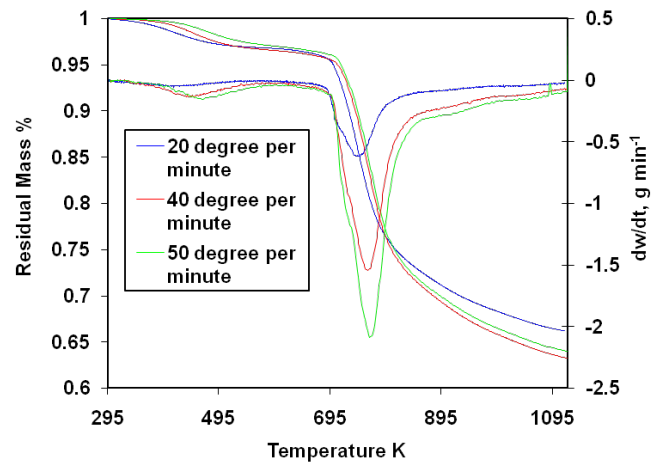


Fig.4 Mass loss rate vs. temperature at different heating rate

Table 3 Values of T_p , X_{max} , $\left(\frac{dW}{dt}\right)_{max}$ and $\left(\frac{dX}{dt}\right)_{max}$ of coal particle at different heating rate

Heating rate, $K \text{ min}^{-1}$	$T_p, ^\circ K$	X_{max}	$\left(\frac{dW}{dt}\right)_{max}$ $g \text{ min}^{-1}$	$\left(\frac{dX}{dt}\right)_{max}$ min^{-1}
20	746	0.338682	0.61801	0.05444
40	763	0.367586	1.54666	0.11985
50	766	0.360415	2.08709	0.15208

3.3 Kinetic studies

The rate of the pyrolysis process can be described by Equation (1).

$$\frac{dX}{dt} = k(T)f(X) \quad (1)$$

Where X is the extent of conversion, $k(T)$ a temperature dependent reaction rate constant and $f(X)$ is a dependent kinetic model function. There is an Arrhenius type dependence between $k(T)$ and temperature according to equation (2).

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

Where A is the pre-exponential factor, E the apparent activation energy, T , the absolute temperature and R is the universal gas constant. For non-isothermal conditions, when the temperature varies with time with a constant heating rate $\beta = \frac{dT}{dt}$, Equation (2) can be modified as follows:

$$\beta \frac{dX}{dT} = A \exp\left(\frac{-E}{RT}\right) f(X) \quad (3)$$

Separating the variables and on integration we get,

$$\int_0^X \frac{dX}{f(X)} = \frac{A}{\beta} \int_{T_0}^T \exp\left(\frac{-E}{RT}\right) dT \approx \frac{AE}{\beta R} \int_0^x \frac{\exp(-x)}{x^2} dx = \quad (4)$$

Where T_0 is the initial temperature, $g(X)$ the integral form of the reaction model and $p(x)$ is the temperature integral ($x = \frac{E}{RT}$),

which does not have analytical solution. At $T = T_0$, $X = 0$, so the lower limit of the integral on the right-hand of equation (4) can be approximated to be equal to 0.

Model-fitting approach

Coats and Redfern method [19],[20]

For non-isothermal experiments, model fitting involves fitting different models to X -temperature curves and simultaneously determining E and A [21]. There are numerous non isothermal model fitting methods; one of the most popular is the Coats and Redfern method. This method utilizes the asymptotic series expansion in approximating $p(x)$ producing the following equation,

$$\ln \frac{g(X)}{T^*} = \ln \left[\frac{AR}{\beta E} \left\{ 1 - \left(\frac{2RT^*}{E} \right) \right\} \right] - \frac{E}{RT^*} \quad (5)$$

where T^* is the mean of the experimental temperatures. Plotting the left-hand side (which includes the model $g(X)$ of equation (5) versus $\frac{1}{T}$ gives E and A from the slope and intercept respectively. The model that gives the best linear fit is selected as the model of choice. The most commonly used reaction models for solid-state processes are listed in Table 4 [22]. Kennedy and Clark method [23]

The method proposed by Kennedy and Clark is based on the expression:

$$T = \beta t + T_0 \quad (6)$$

Where T_0 is the initial temperature (the temperature at the start of the reaction).The basic equation is

$$\frac{\beta g(X)}{T - T_0} = A \exp\left(\frac{-E}{RT}\right) \quad (7)$$

and taking the logarithm of both sides of this equation gives:

$$\ln \left[\frac{\beta g(X)}{T - T_0} \right] = \ln(A) - \frac{E}{RT} \quad (8)$$

Plotting the left-hand side of this equation against $\frac{1}{T}$ should give a straight line of slope $\frac{-E}{R}$ and intercept $\ln(A)$, assuming a reaction model $g(X)$ listed in Table 4. T_0 is the temperature at which the pyrolysis process starts. The experimentally determined value of T_0 at the considered heating rates is 623K. The non-isothermal kinetic data of coal pyrolysis were fitted to each of the 19 reaction models listed in Table 4. The values of activation energy E , pre-exponential factors $\ln(A)$ and the Pearson correlation coefficients \bar{R}^2 for the two kinetic models which fitted the pyrolysis data well at constant heating rates of 20, 40 and 50Kmin⁻¹ are given in Table 5.

As shown in Table 5 the third order reaction model gives the highest Pearson correlation coefficients with Coats and Redfern method for all the particle diameters. It can be observed from the Table 5 and Fig. 5 that the Activation energies have been found to increase with particle size, when the heating rate has been kept constant. The

Activation energies have been found to increase with particle size following the equation given below

$$E = 30d_p^2 - 210d_p + 557 \quad \bar{R}^2 = 0.99 \quad (9)$$

Where, d_p is the particle diameter of coal particles. For the cases where particle diameter has been kept constant and the heating rates were varied the apparent activation energy increases as the heating rate increases as shown in Fig. 6 and Table 6. Activation energies

Table 4

Algebraic expressions of $f(X)$ and $g(X)$ for the reaction models considered for the present work			
NO.	Reaction Model	$f(X)$	$g(X)$
1	Power law	$4X^{3/4}$	$X^{1/4}$
2	Power law	$3X^{2/3}$	$X^{1/3}$
3	Power law	$2X^{1/2}$	$X^{1/2}$
4	Power law	$2/3X^{-1/2}$	$X^{3/2}$
5	Zero-order(Polany-Winger equation)	1	X
6	Phase-boundary controlled reactions(contracting area,bidimensional shape)	$2(1-X)^{1/2}$	$[1-(1-X)^{1/2}]$
7	Phase-boundary controlled reactions(contracting volume,Tridimensional shape)	$3(1-X)^{2/3}$	$[1-(1-X)^{1/3}]$
8	First-order(Mampel)	$(1-X)$	$-\ln(1-X)$
9	Three-halves order	$(1-X)^{3/2}$	$2[(1-X)^{-1/2} - 1]$
10	Second-order	$(1-X)^2$	$(1-X)^{-1} - 1$
11	Third-order	$(1-X)^3$	$(1/2)[(1-X)^{-2} - 1]$
12	Avrami-Erofeev(n=1.5)	$(3/2)(1-X)[- \ln(1-X)]^{1/3}$	$[- \ln(1-X)]^{2/3}$
13	Avrami-Erofeev(n=2)	$2(1-X)[- \ln(1-X)]^{1/2}$	$[- \ln(1-X)]^{1/2}$
14	Avrami-Erofeev(n=3)	$3(1-X)[- \ln(1-X)]^{2/3}$	$[- \ln(1-X)]^{1/3}$
15	Avrami-Erofeev(n=4)	$4(1-X)[- \ln(1-X)]^{3/4}$	$[- \ln(1-X)]^{1/4}$
16	One-dimensional diffusion	$1/2X$	X^2
17	Two-dimensional diffusion(bidimensional particle shape) Valensi equation	$1/[- \ln(1-X)]$	$(1-X)\ln(1-X) + X$
18	Three-dimensional diffusion(tridimensional particle shape) Jander equation	$3(1-X)^{1/3}/2[(1-X)^{-1/3} - 1]$	$[1-(1-X)^{1/3}]^2$
19	Three-dimensional diffusion(tridimensional particle shape) Ginstling Brounshtein	$3/2[(1-X)^{-1/3} - 1]$	$(1-2X/3) - (1-X)^{2/3}$

Table 5

Arrhenius parameters determined by Coats-Redfern and Kennedy-Clark methods (model fitting) for two kinetic models which best describe the coal pyrolysis for different particle size

	$g(\alpha)$	3.7mm			3.9mm			4.2mm			4.4mm		
		lnA	E (kJmol ⁻¹)	\bar{R}^2	lnA	E (kJmol ⁻¹)	\bar{R}^2	lnA	E (kJmol ⁻¹)	\bar{R}^2	lnA	E (kJmol ⁻¹)	\bar{R}^2
CR Method	$(1-\alpha)^{-1} - 1$	4.83	118	0.8996	5.84	126	0.8995	6.81	132	0.8979	7.7483	139	0.9097
	$(1/2)[(1-\alpha)^{-2} - 1]$	16.8	191	0.9046	17.2	196	0.9296	18.5	204	0.9332	20.0	215	0.9439
KC Method	$(1-\alpha)^{-1} - 1$	9.61	69	0.8522	11.1	81	0.8942	12.1	88	0.9007	13.034	94	0.9173
	$(1/2)[(1-\alpha)^{-2} - 1]$	21.6	143	0.8321	22.5	151	0.8968	23.8	159	0.9079	25.349	170	0.9235

have been found to increase with heating rate following the equation given below

$$E = 141.3\beta^{0.1} \quad \bar{R}^2 = 0.99 \quad (10)$$

The pre-exponential factor A also behave similarly (Fig.7). The pre-exponential factor A have been found to increase with heating rate following the equation given below

$$A = 24,266\beta^{2.25} \quad \bar{R}^2 = 0.99 \quad (11)$$

M.V.Kok et al have also reported similar trend of increase in activation energy with particle size from 400 mesh sizes to 48 mesh sizes which have been stated as due to the ease of penetration of gas through the particles [24].

If we extrapolate the activation energy vs. heating rate curve to the heating rate of fluidized bed than we find that the activation energy to be equal to 302 KJ/mole for a particle size of 3.74 mm. The

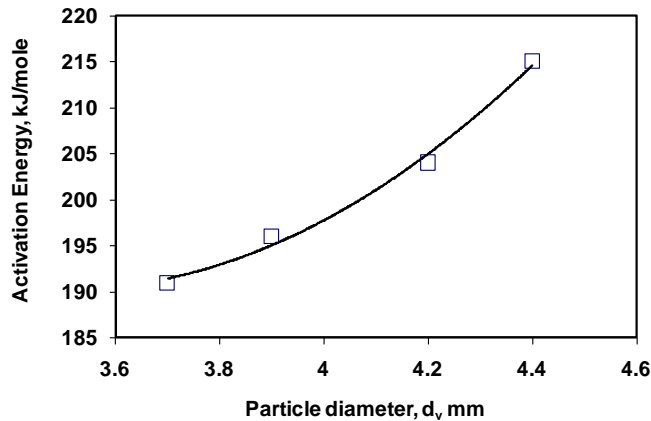


Fig.5 Activation energy vs. particle diameter

heating rate of 3.74mm particle diameter coal particle was taken from a plot of heating rate vs. particle diameter (by extrapolation) given in Borah et.al [25]. The value was 1980 K min^{-1} . Activation energy used in kinetics of devolatilization parameters in devolatilization models in fluidized bed ranges from $142\text{-}326 \text{ KJmole}^{-1}$ [26]. So, the extrapolated value seems to be quite reasonable. Also L.-P.Wiktorsson et al [5] studied the range of extrapolation of discrete kinetic parameters for species evolved in coal pyrolysis and concluded that a second order ethane parameters shows good reliability of extrapolation to a very high heating rate, however tar kinetic parameters of second order could be extrapolated with reasonable accuracy in the heating range $3\text{-}16200 \text{ K min}^{-1}$. Since tar constitutes a major component of the volatile matter hence extrapolation of activation energy and pre-exponential factor seems to be reasonable. Pre-exponential factor A

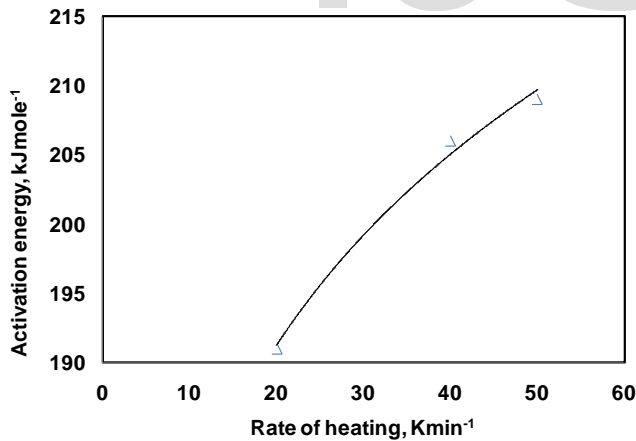


Fig.6 Activation Energy vs. heating rate

Table 6
Arrhenius parameters determined by Coats-Redfern and Kennedy-Clark methods (model fitting) for two kinetic models which best describe the coal pyrolysis at the three heating rates

	$g(\alpha)$	20 K/minute			40 K/minute			50 K/minute		
		lnA	$E \text{ (kJmol}^{-1}\text{)}$	R^2	lnA	$E \text{ (kJmol}^{-1}\text{)}$	R^2	lnA	$E \text{ (kJmol}^{-1}\text{)}$	R^2
CR Method	$(1-\alpha)^{-1}-1$	4.83	118	0.8996	6.81	133	0.9005	7.14	136	0.9068
	$(1/2)[(1-\alpha)^{-2}-1]$	16.8	191	0.9046	18.5	206	0.9205	18.8	209	0.9291
KC Method	$(1-\alpha)^{-1}-1$	9.93	72	0.8427	12.7	89	.891	13.2	90	0.9063
	$(1/2)[(1-\alpha)^{-2}-1]$	21.8	144	0.8369	24.4	161	0.8807	24.9	162	0.8938

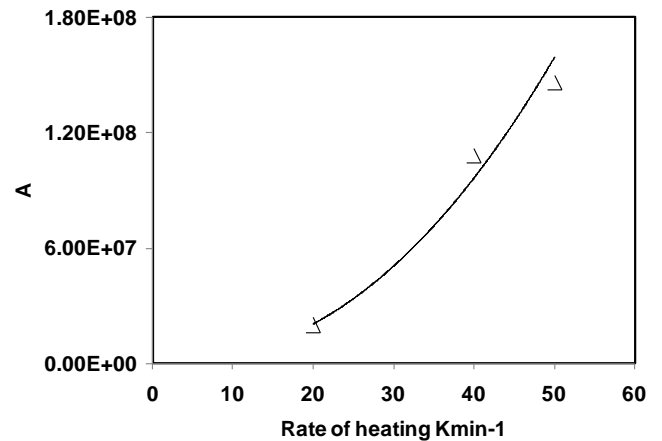


Fig.7 Pre-exponential factor A vs. heating rate

has been reported to be equal to 1.06×10^{10} at a heating rate calculated from the table given in literature [27]. When extrapolated to a heating rate of 1980 K min^{-1} for a 3.74 mm coal particle in fluidized bed, the pre-exponential factor A, has been found to be equal to 6.15×10^{11} . It has been stated that the temperature dependence of pre-exponential factor A is negligible in normal cases compared to the temperature dependence of the $\exp\left(\frac{-E}{RT}\right)$ factor, except in the case of "barrier less", diffusion limited reactions, in which case the pre-exponential factor A is dominant and is directly observable. In the present case since the pyrolysis of coal is dependent on heat transfer inside the particle i.e. thermal diffusion inside the particle, so, this may be the cause of the variation of the pre-exponential factor A with heating rate and particle size.

4. CONCLUSIONS

Effect of heating rates on single large coal particle was studied at three different heating rates. Activation energies have been found to increase with heating rates. Effect of particle size is also significant. Activation energies have been found to increase with particle size. Correlations have been given. Kinetic parameters were evaluated using a model which best fitted the experimental data. Nineteen different models have been fitted to the experimental data and it has been found that coal conversion obeys a third order model. Pre-exponential factor A has also been found to increase with heating rates. Correlation has been given. The temperature dependence of pre-exponential factor A is negligible in normal cases, but in present case it seems that it is not negligible. The reason may be that for pyrolysis of large coal particles thermal diffusion is dominant. It is possible to extrapolate the activation energy evaluated at lower heating rate to higher heating rate. However further work is necessary for other particle sizes of coal.

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