[Boraha., 3(1): January, 2016] ISSN 2349-4506
Impact Factor: 2.265
Global Journal of Engineering Science and Research Management

ZnO NANOPARTICLE DEPENDENT NON-ISOTHERMAL PYROLYSIS OF ASSAM COAL (INDIA). PART II: THERMODYNAMIC STUDY

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KEYWORDS: Coal pyrolysis, ZnO nanoparticles, activation energy, thermodynamic parameters).

ABSTRACT

Non-isothermal pyrolysis of coal of varying sizes, in presence of ZnO nanoparticles, have been carried out in this study. Activation energy values for raw coal and blended coal samples were determined and these values were used for the evaluation of thermodynamic parameters. In most of the ZnO blended coal samples, the activation energy values are higher than the unblended coal samples revealing role of nanoparticles on more thermal stability of the coal molecule. Moreover, during the pyrolysis process, association reactions were quite likely to take place. Thermodynamic studies reveal endothermic behaviour, low randomness and non-spontaneous nature of the pyrolysis process. This work has some technological interest.

INTRODUCTION

Coal is the abundant fossil fuel on the earth comprising about 75% of the world's total resources of fossil fuels [1]. It consists of a large polymeric matrix of aromatic structures which is known as macromolecule; however, the aromatic content varies with the rank of coal. High aliphatic side chains and oxygen containing functional groups are generally found in low rank coals. When coal is heated non-isothermally in inert or non-inert atmosphere, some structural modification, kinetic and thermodynamic changes occur besides emission of volatile species. Coal plants are responsible for the bad effects of volatiles in ecosystems and organisms; however, some studies have been undertaken as a remedial measure [2].

Pyrolysis of coal is the initial step in most coal conversion processes. Some changes of the coal macormolecule occur during pyrolysis and these include pore structure, volatiles, physical and chemical environments. Pyrolysis of blended coal, i.e., the presence of zinc chloride [3-7], aluminium chloride [6], stannous chloride [5], etc., in coal have been known. The effect of the presence of metals and metal oxides during thermal treatment of coal have been extensively studied. Moreover, the use of sodium and calcium based compounds for the pyrolysis and gasification of coal have been known in literature. Since pyrolysis yields a solid product known as char, the nature of this product determines some characteristics of the parent coal. Wang et al [8] have reported that transition metal oxides have excellent catalytic activity due to the free movement of electrons in the valence band and conduction band. Recently, Baruah et al [9] studied the effect of magnetic nanoparticles on the structural changes of coal during the non-isothermal pyrolysis. To understand the chemical and physical changes during non-isothermal pyrolysis, the magnitude of activation energy is very essential. The aims of the present study are to determine the activation energy and thermodynamic parameters in the non-isothermal pyrolytic process at low temperature and their effects.

MATERIALS AND METHODS

Coal sample and its preparation

Coal sample was collected from the Tirap colliery of the Makum Coal Field, Upper Assam. The coal was ground and two different sizes (72BS and 100BS). The coal sample was treated with dilute HCl followed by dilute HNO_3 as reported in ASTM. The material was filtered out, washed with distilled water, dried and finally collected. The proximate and ultimate analysis of the coal sample are given in Table 1.

Table 1. Proximate and ultimate analyses of coal sample

Proximate	Wt.%	Ultimate	Wt.%*
Moisture	4.9	Carbon	79.3
Ash	28.5	Hydrogen	5.5
Volatile matter	33.8	Nitrogen	1.3
Fixed carbon	32.8	Sulphur	3.7

	Oxygen (by diff.)	10.2

- Moisture free basis

Preparation of ZnO nanoparticles

The preparation and characterization of zinc oxide nanoparticles have been reported elsewhere [10]. The alkali solution was added to the zinc nitrate solution with constant stirring till the pH of the solution attained 11.0. Soluble starch (0.1%) was used as stabilizing agent. The solid material was centrifuged out followed by washing with ethanol and then dried in air. The material was then heated in an oven at 70°C for two hours and finally white material is obtained.

Preparation of ZnO blended coal samples

Blended coal samples were prepared by mixing different amounts of ZnO nanoparticles with coal sample. Two sets of blended samples for two different sizes (BS and 100BS) of coal were prepared. The composition of the blemded samples are given in Table 2.

Table 2. Composition of different blended coal samples

Sl. No.	Coal particle size	Sample	Amount of	
			Coal (mg)	ZnO (mg)
1	72BS	UC1	100	0
2		BC11	100	5
3		BC12	100	7.5
4		BC13	100	10
5	100BS	UC2	100	0
6		BC21	100	5
7		BC22	100	7.5
8		BC23	100	10

Thermal analysis

Non-isothermal thermogravimetric analysis offers certain advantages over the isothermal method. First, this method eliminates the errors introduced by the thermal induction period, and the second, it permits a rapid scan of the whole temperature range of interest.

In this study, thermogravimetric analysis were carried out in a DTA-TGA equipment model SDT 2960 of M/s TA Instruments, USA under nitrogen atmosphere up to 305°C. The heating rate was maintained at 5°C per minute. The thermodynamic data were derived from the TG analysis.

Determination of Activation energy

The kinetics of pyrolysis reaction of coal in presence and absence of ZnO nanoparticles have been studied [11]. For thermodynamic study, the activation energy is an important component. Three equations have been used to determine the activation energy of the coal decomposition reaction in inert atmosphere. The average values of the activation energy obtained from these three model equations are used for subsequent calculations.

The final form of the Arrhenius equation is

$$\log \mathrm{K} = -\frac{\mathrm{E}}{2.303RT} + \log A$$

Activation energy is evaluated graphically from the slope (-E/2.303R) of the straight line obtained by plotting log K against (1/T).

The final form of the Coats and Redfern equation [12] is

$$\log \frac{[\mathrm{a}^{1-n} - (\mathrm{a}-\mathrm{x})^{1-n}]}{(1-\mathrm{n})\mathrm{T}^2} = -\frac{E}{2.303RT} + \log \frac{\mathrm{AR}}{\mathrm{E}}\left[1 - \frac{2\mathrm{RT}}{\mathrm{E}}\right]$$

A plot of $\log \frac{[\mathrm{a}^{1-n} - (\mathrm{a}-\mathrm{x})^{1-n}]}{(1-\mathrm{n})\mathrm{T}^2}$ vs. $\frac{1}{T}$ for $n \neq 1$ and $\log [-\log (a-x/a) / T^2]$ against for n = 1 should result in a straight line with a slope of $\left(-\frac{E}{2.303R}\right)$wherefrom activation energy can be calculated.

The final form of Borah and Baruah equation [13] is

$$\log\frac{T1}{T2} + \log\frac{\log\left[\frac{w-X2}{w}\right]}{\log\left[\frac{w-X1}{w}\right]} = \frac{E}{2.303R}\left[\frac{T2-T1}{T1T2}\right]$$

Where x_1 and x_2 are weight loss at T_1 and T_2 respectively and w is the final weight loss, the temperature of which is greater than T_2 (may be 0.5 ^{O}C more).

This equation is free from rate constant, and therefore, the principal advantage of this equation is that the knowledge of the rate constant and the graphical work are not necessary for the determination of activation energy.

Determination of thermodynamic parameters

Although three equations were used to calculate the activation energy of the pyrolysis process, but the average values are taken for calculating the thermodynamic parameters. A correlation of the activation energy (E_a) and the internal energy of activation (ΔU*) of the pyrolysis process can be given as:

$$Ea = RT + \Delta U *$$

$$\text{Again, } \Delta H *= \Delta U * + \Delta(PV) *$$

Where ΔH* is the enthalpy of activation.
The term $\Delta(PV) *$ can be neglected as its value is negligible for a condensed system.
Thus

$$\Delta H *= \Delta U *$$
$$\text{Hence, } Ea = RT + \Delta H *$$
$$or, \Delta H *= Ea - RT$$
$$\Delta H *= \Delta U *$$

It is apparent that, Δ U* and, $\Delta H *$ have almost identical values of corresponding ΔU and ΔH for the complete reaction. Similarly, entropy of activation (, Δ S*) and Gibbs free energy of activation (, Δ G*) should be almost identical with Δ S andΔ G, respectively. Therefore, the thermodynamic parameters,Δ U, Δ H, Δ S and Δ G are used in this study.

For the determination of ΔH, the equation is:

$$\Delta H = \Delta E_a - RT$$

ΔS is calculated by using the following equation:

$$K = \frac{kT}{h} e^{\Delta S/R} e^{\Delta H/RT}$$

K is the rate constant, □ is the Boltzman constant and h is the Plank constant.
Δ G has a good relation with Δ H and ΔS as:
,

$$\Delta G = \Delta H - T\Delta S$$

RESULTS AND DISCUSSION

Activation energy

The activation energy for each sample was estimated from the thermogravimetric analysis in the temperature range 373 – 573^{o}K, therefore, the value obtained is the sum of effective activation energies for various chemical and physical changes occurring simultaneously during pyrolysis. In this study, activation energy was calculated by using three model equations: Arrhenius equation, Coats and Redfern equation and, Borah and Baruah equation. In the first two dynamic kinetic equations, evaluation of the activation energy relay on graphically which is cumbersome. The advantage of the Borah and Baruah equation [13] is that activation energy can be determined without graphical work and also without the knowledge of rate constant. The values of activation energy calculated using three equations are almost similar despite the difference in the method of calculation.. The average values, for different samples, of activation energy obtained from these equations are also presented in the Table 3. The frequency factor was calculated by using the Arrhenius equation and the values are also given in Table 3.

Table 3. Activation energy and frequency factor of the non-isothermal pyrolysis of coal samples.

Sample	Activation energy (KJ mol^{-1})				Frequency factor (s-^{1})
	Arrhenius equation	Coats and Redfern equation	Borah and Baruah equation	Average	Using Arrhenious equqtion
UC1	10.37	8.61	8.09	9.02	9.91×10^{-4}
BC11	13.36	13.55	13.71	13.54	8.13×10^{-4}
BC12	10.53	10.79	10.74	10.69	9.55×10^{-4}
BC13	12.34	12.66	12.34	12.45	8.91×10^{-4}
UC2	10.97	10.21	10.06	10.41	9.12×10^{-4}
BC21	13.20	13.26	13.87	13.44	7.76×10^{-4}
BC22	11.10	10.22	10.78	10.70	8.91×10^{-4}
BC23	10.17	10.40	9.90	10.16	9.55×10^{-4}

Table 3 reveals that activation energies for BC11, BC12 and BC13 coal samples are higher than that of the UC1 sample. In the larger size coal, BC21 and BC22 samples have higher and BC23 sample has lower activation energies than the UC2 sample. However, in both the size of coals, the blended samples, BC11 and BC21 samples, have exceedingly high activation energies than the unblended samples (UC1 and UC2) (Table 3). It appears that there is almost no significant influence of ZnO nanoparticles during non-isothermal pyrolysis in case of BC22 and BC23 samples.

The activation energy is an important parameter since it indicates the thermal stability of a material and its magnitude reflects the extent of transformation. Here, increase of activation energy in the blended coal samples (Table 3) suggests that ZnO nanoparticles hinder the evaluation of volatile species from coal by increasing the activation energy in most of the samples. Thus the thermal stability of the molecules during pyrolysis increased and as a result, reduction of evolution of volatile matters is quite possible. This observation is supported by the nature of evolution of volatiles in the non-isothermal process; however, it is more noticeable in lower size coal samples [11].

The frequency factor or pre-exponential factor gives some information on various changes during pyrolysis process. The physical significance of the frequency factor is the number of successful collisions in forming the activated complex. The pre-exponential factors for all the samples have been calculated from the intercepts of the Arrhenius plots, and are presented in Table 3. The values are quite low in magnitude but the order is same (Table 3). Low value of frequency factor reveals that the pyrolysis process is non-spontaneous in nature. It has been observed in Table 3 that the degree of non-spontaneity of the pyrolysis process is different for different samples as is evident from different values of the frequency factors. However, the frequency factor is not the only means to qualify a process of spontaneous or non-spontaneous, but it is better governed by the thermodynamic functions. It is known in literature that association reactions have low frequency factor [14]. Thus during the pyrolysis process, association reactions were quite likely to take place. It is apparent that before cleavage of bonds in the coal mass, an associated complex could have been formed involving molecules and ion-radicals in the unblended samples while for blended samples, involvement of ZnO and coal molecule in the formation of activated complex is quite likely. Higher activation energy and probable formation of activated complex specially in the blended samples strongly suggest that ZnO nanoparticles in its influence shows inertness of the activated complex and consequently, hindering the emission of volatiles from coal during pyrolysis.

Thermodynamic study

Thermodynamic parameters, enthalpy change (ΔH), entropy change (ΔS) and Gibbs free energy change (ΔG) were evaluated for the non-isothermal pyrolysis of coal samples and are presented in Table 4. The average values of activation energy (Table 3) have been used for the evaluation of ΔH.

Table 4. Thermodynamic parameters, ΔH, ΔS and ΔG for the non-isothermal pyrolysis of 72 BS size coal samples.

Sample	Temperature (^{o}K)	ΔH (KJ mol^{-1})	ΔS (JK^{-1}mol^{-1})	ΔG (KJ mol^{-1}) x 10^{2}
UC1	373	5.91	- 277.89	1.10
	423	5.50	-284.38	1.26
	473	5.09	- 293.19	1.44
	523	4.67	- 297.98	1.61
	573	4.26	-302.35	1.78
BC11	373	10.44	- 266.35	1.10
	423	10.23	- 275.13	1.26
	473	9.61	- 282.68	1.43
	523	9.19	- 288.72	1.60
	573	8.78	- 294.38	1.77
BC12	373	7.59	- 273.01	1.09
	423	7.17	- 281.81	1.26
	473	6.76	- 288.49	1.43
	523	6.34	- 294.17	1.60
	573	5.93	- 299.36	1.77
BC13	373	9.35	- 268.71	1.10
	423	8.93	- 277.97	1.27
	473	8.52	- 284.89	1.43
	523	8.10	- 290.67	1.60
	573	7.69	- 296.28	1.78

Table 5. Thermodynamic parameters, ΔH, ΔS and ΔG for the non-isothermal pyrolysis of 100 BS size coal samples.

Sample	Temperature (^{o}K)	ΔH (KJ mol^{-1})	ΔS (JK^{-1}mol^{-1})	ΔG (KJ mol^{-1}) x 10^{2}
UC2	373	7.31	- 273.59	1.09
	423	6.89	- 282.64	1.27
	473	6.48	- 289.30	1.43
	523	6.06	- 294.88	1.60
	573	5.65	- 299.84	1.77
BC21	373	10.34	- 265.64	1.09
	423	9.92	- 274.47	1.26
	473	9.51	- 283.39	1.44
	523	9.09	- 289.39	1.60
	573	8.68	- 294.83	1.78
BC22	373	7.60	- 272.94	1.09
	423	7.18	- 282.02	1.27
	473	6.77	- 288.82	1.43
	523	6.35	- 294.48	1.60
	573	5.94	- 299.57	1.78
BC23	373	7.06	- 274.01	1.10
	423	6.64	- 283.27	1.27
	473	6.23	- 289.82	1.43
	523	5.81	- 295.51	1.60
	573	5.40	- 300.51	1.78

The system, under study, is a condensed system, the values of ΔU and ΔH are identical, and therefore, only ΔH values are presented in Tables 4 and 5. As thermal energy was supplied in the non-isothermal process, the nature of the process should be endothermic. The positive values of ΔH for all the samples strongly support the endothermic nature of the pyrolysis process. The samples BC11, BC12 and BC13 have higher ΔH values than that of the UC1 sample, suggesting that the presence of ZnO nanoparticles in the coal increases the endothermic behaviour of the pyrolysis process. There is a strong likelihood that ZnO could form strong bonding with coal components resulting in stable activated complex. During non-isothermal process, large amounts of free radicals could be formed in the blended samples relative to the unblended sample (UC1) and these free radicals could immediately polymerise in presence of ZnO to form bigger molecules with high thermal stability. This assumption indicates lower emission of volatile species from the blended samples. This is exactly so as we have found decrease of evolution of volatiles in the blended samples [11] this is the reason why greater values of ΔH are observed for BC11, BC12 and BC13 samples (Table 4).

On the other hand, the samples of coal particles of lower size have shown nature of ΔH values which are not alike with the bigger size samples. However, the trend of ΔH values for UC1 and BC11 and UC2 and BC21 are almost identical. In case of BC22 and BC23 samples, the values of ΔH are not at all significant suggesting that ZnO nanoparticles have negligible effect on the pyrolysis process.

The bond dissociation energies of some common bonds of coal molecule viz. C-C (180-210 KJ mol^{-1}), C-H (376.2 KJmol^{-1}), C-O (344.4 KJmol^{-1}), C-S (476.5 KJmol^{-1}), C-N (305.1 KJ mol^{-1}) and O-H bonds (KJmol^{-1}) [15] may be considered here. The dissociation energy values are found to be higher than that of the activation energy (Table 3). The low values of activation energy strongly suggest that significant rupture of these bonds during non-isothermal pyrolysis process is not possible. The cleavage of any bond is possible which has very low bond dissociation energy. The C-C bond has lowest bond dissociation energy among all the studied bonds here. The generation of free radicals by the cleavage of C-C bonds in presence of ZnO during pyrolysis could be possible and recombination of these free radicals yielding polymeric molecules is also quite likely. This mechanism is quite probable because low values of frequency factor correlate the association reaction, mentioned above; however, this mechanism may not account for a large number of free radical formation as coal is a mixture of heterogeneous molecules and, therefore, breakdown of all molecules is not occurred at a definite time.

The change of entropy (ΔS) values are all negative suggesting very low ramdomness of the species. On blending the coal particles with ZnO nanoparticles, the ΔS values decreases further. This may be due to the fact that the role of the nanoparticles is to decrease the ramdomness resulting in stability of the coal molecule. The change of free energy (ΔG) signifies whether a process is spontaneous or not. In this study, the ΔG values are all positive (Tables 4, 5), revealing non-spontaneous nature of the pyrolysis processes which is supported by the low frequency factor (Table 3). Thus on considering the thermodynamic parameters it can be definitely said that the presence of ZnO in the blended coal increasers the thermal stability of the coal molecule.

Low magnitude of activataion energy (Table 3) reveals predominance of physical change rather than chemical change during pyrolysis. One thermophysical property of coal is phase transition from solid coal to a softening state. Recently, the softening behavior of coal has been studied [16]. Other important thermophysical property of coal is also under consideration.

CONCLUSIONS

The role of a green catalyst, ZnO nanomaterials, in the non-isothermal pyrolysis at low temperature strongly indicates low activation energy. Low absorption of energy. And decrease of randomness of species during thermal treatment suggest different behavior of the blended samples than the parent coal. This study has shown the dependence of ZnO nanoparticles on the pyrolysis of coal resulting in non-spontaneous nature of the pyrolytic process. As a very few literature is available on the thermodynamics of blended coal during pyrolysis, this work may contribute something for the technological advancement of coal utilization.

ACKNOWLEDGEMENT

The authors are thankful to the Principal, Dr L Baruah, NNS College, for facilities and the Director, CSIR-NEIST, Jorhat for instrumental facilities.

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