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ZnO NANOPARTICLE DEPENDENT NON-ISOTHERMAL PYROLYSIS OF ASSAM COAL (INDIA) PART I: KINETIC STUDY

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ABSTRACT

To promote the use of abundant low rank Assam coal resources, it is necessary to understand the extent of emission of volatile species from the coals on thermal treatment. As no pyrolysis work seems to be done with most of the coals so far using a green catalyst, ZnO nanoparticles, this study is an attempt to visualize the magnitude of volatile species released from the thermal treatment of Assam coal in nitrogen atmosphere which is a great environmental concern. The evolution of volatile species for the 72 BS sized unblended coal, have been found to be higher than those samples containing varying amounts of ZnO. For 100BS sized coal particles, similar amounts of volatiles from the unblended coal as well as blended coal of (coal : ZnO for100:5 and 100:7.5) have been observed but for 100:10 ratio ZnO blended samples decrease of volaties has been found. Kinetic study reveals that the rate of reaction was initially very fast and then gradually declined. Moreover, the rate constants for the blended samples have been observed to be lower than that of the unblended samples.

The presence of ZnO nanoparticles increases the thermal stability of the coal particles. The present work is a new approach of using ZnO nanoparticles for low emission of volatiles from thermal treatment of coal and understanding the kinetics of pyrolysis process and therefore, has to some extent environmental and technological interests.

INTRODUCTION

The scientific community of the world is looking for development of some beneficial technologies of coal processing so that preservation of biodiversity at all levels can be achieved. The main criteria of the beneficial technology include low cost, low emission of volatiles and low ash deposit after utilization of coal, among others. Both volatile species and ash deposits have serious impact on the deterioration of environment which require prime importance during processing of coal. Restoration of ecology is need of the hour not only for human lives but also for the plant and animal kingdoms [1]. Thus the exploitation of fossil fuel resources not only providing energy for the development of national economy but also causing damage to the ecological environment.

Development of Indian society and economy largely depend on the clean energy consumption, maintaining positive economy and social benefits. A major economic significance of India is the huge deposits of coal. In 2014, a total of 301.56 Billion tonnes of coal reserve are estimated by Geological Survey of India [2]. Deposits of lignite in Neyveli of Tamil Nadu, low-rank high sulphur coals in the North-East India and comparatively high-rank coals in some states like Jharkhand, Odisha, Chattishgarh, Madhya Pradesh, Andhra Pradesh, West Bengal, etc., are largely found in India. These coals have tremendous utilization for various small and large scale industrial establishments including power generation, as well as R&D purposes. High ash content and also high sulphur content in some of these coals are the major concerns, therefore, these coals require some treatment for their efficient utilization.

Coal is primarily used as a fuel. The main volatile species released during thermal treatment of coal are carbon dioxide (CO_2) in large scale, sulphur dioxide (SO_2), nitrogen oxides (NO_x), some organic substances, etc.[3]. Depletion of carbon in coal is due to dehydration reactions which are favoured by the presence of low-molecular weight organic compounds [4]. Evolution of small organic molecules, decomposition of functional groups like carboxyl groups, as well as formation of free radicals are quite likely [4] and, therefore, attempts have been made to reduce emission of volatile species during isothermal and non-isothermal processes using suitable catalysts.

Nanomaterials are believed to be the promising catalysts for various thermal and coal conversion processes. Since nanomaterials have many desirable features including high surface area, therefore, application of these materials in the thermal processes of coal could give encouraging results. The development and use of new catalyst that can restrict the emission of volatile species from coal [5] is important in order to obtain products of high energy content more efficiently. Since pyrolysis of coal has been drawing much attention worldwide for various coal conversion processes in recent times, in the present study, non-isothermal pyrolysis of coal in the low temperature region will be attempted in presence of ZnO nanoparticles as a green catalyst. Here, our main aim is to study the effect of ZnO nanomaterials for the reduction of volatile species emission during thermal treatment of coal in inert atmosphere and to determine kinetic parameters during pyrolysis of coal.

MATERIALS AND METHODS

Coal sample

For the present investigation, coal sample was obtained from the Tirap colliery of the Makum Coal Field, Upper Assam. This coal is a sub-bituminous coal contains high sulphur content. The coal was ground and two different sizes (72BS and 100BS) were prepared for this study.

Preparation of coal sample

The coal sample was treated with dilute HCl followed by dilute HNO3 to remove sulphate and minerals specially pyrite as reported in ASTM. The solid material was filtered out, washed with distilled water, dried and finally collected in an air tight polypropylene bottle.

Preparation of ZnO nanoparticles

The preparation and characterization of zinc oxide nanoparticles have been reported elsewhere [6]. In short, these were prepared from 0.45M $Zn(NO_3)_2.6H_2O$ and 0.9M NaOH and soluble starch (0.1%) was used as stabilizing agent. The alkali solution was added dropwise to the zinc nitrate solution with constant stirring till the pH of the solution attained 11.0. The solid material was centrifuged out followed by washing with ethanol and then dried in air. Further the material was heated in an oven at 70°C for two hours. The dried white material is ZnO nanoparticles. Characterization of these particles are reported elsewhere [6].

Preparation of ZnO blended coal samples

The blended samples were prepared by mixing different amounts of ZnO nanoparticles with coal sample. Two sets of blended samples for 72BS and 100BS size coal were prepared which are prepared as follows (Table 1). All the samples were kept in air tight polypropylene bottles.

Table 1. 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 kinetics and thermodynamic data were derived from the TG analysis.

X-ray diffraction (XRD)

The XRD measurements of ZnO nanoparticles particles was carried out using a Bruker AXS and the X-ray diffraction was determined with CuKα radiation with wavelength, λ = 1.54178A° at the Bragg angle (2 theta) ranging from 10 – 100° at a scan rate of $5^{o}\ min^{-1}$.

THEORY

Determination of rate constant

During thermal treatment coal, a large volume of nitrogen gas was used in this study. The rate of reaction depends primarily on one component only, i.e., coal or blended coal. Thus the decomposition of coal follows pseudo-first order kinetics. The first order equation is

$$K = \frac{2.303}{t} + \log\frac{a}{a-x}$$

Where K is the rate constant, a is the initial concentration of coal and x is the amount of loss at time t.

RESULTS AND DISCUSSION

The coal sample used in this study is a sub-bituminous Assam coal. The proximate and ultimate analyses of coal, under investigation, are presented in Table 2.

Table 2. 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

1. Moisture free basis

XRD of ZnO nanoparticles

The XRD spectra of synthesized ZnO nanoparticlesis is presented in Figure 1. By using the Debye-Scherrer equation [7]; the crystallite size of the nanoparticles was calculated the crystallite sizes of the particles are in the range 39.5-53.1 nm. The surface area of the nanomaterials was calculated [8] and found to be 27.1 g/m^2. Characterization of these nanoparticles have been done by SEM, EDX, FESEM and IR and are reported elsewhere [6].

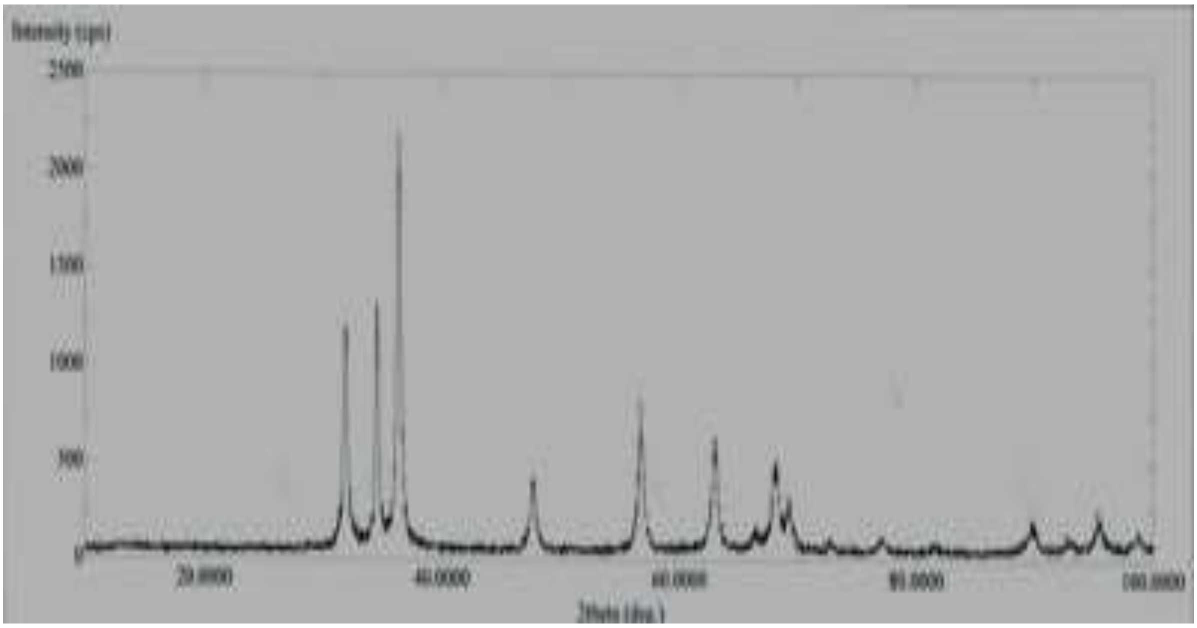

Figure 1. XRD spectra of ZnO nanoparticles

The magnitude of 2θ, d- values and intensities of Ni nanomaterials obtained from the XRD pattern (Figure 1) are presented in Table 3. It is observed from Table 3 that highest

Table 3. Magnitude of 2θ, d- values and intensities of Ni nanomaterials obtained from XRD pattern.

Sl. No.	2θ	d-value	Intensity	I/Io
1	31.980	2.7962	1171	54
2	34.560	2.5932	1321	61
3	36.380	2.4675	2175	100
4	47.680	1.9058	408	19
5	56.740	1.6211	813	38
6	63.020	1.4738	638	30
7	68.080	1.3761	504	24
8	69.200	1.3565	333	16
9	89.860	1.0907	229	11
10	95.320	1.0421	254	12

Intensity for ZnO nanoparticles is observed at 36.38^{O} followed by 34.56^{O} and 31.98^{O}. These values reveal fine crystallinity of the nanoparticles.

Thermogravemetric (TG) analysis

The percentage of volatile matter (VM) released from the unblended and bended coal samples for both 72BS and 100 BS sizes of coal particles are presented in Figure 2. The data have been evaluated from the TG curves. It is seen from the Figure 2 that for 72 BS sized coal blended samples with increasing ZnO content, there is gradual decrease of emission of volatile species. Further the release of volatile species in the blended samples is less than that obtained from the unblended sample. In case of 100 BS sized samples, the amount of emitted volatile species in UC2 as well as BC21 and BC22 (Figure 2 a-c) are almost same but in case of BC23, the evolved volatile species decreases.(Figure 2 d). Decrease of volatile matter in blended samples than the unblended sample in either sized coal particles strongly reveals increase of thermal stability of the coal molecule in the presence of ZnO nanoparticles. It is evident that ZnO nanomaterials have possessed positive effect on the reduction of volatile species during non-isothermal pyrolysis of Assam coal.

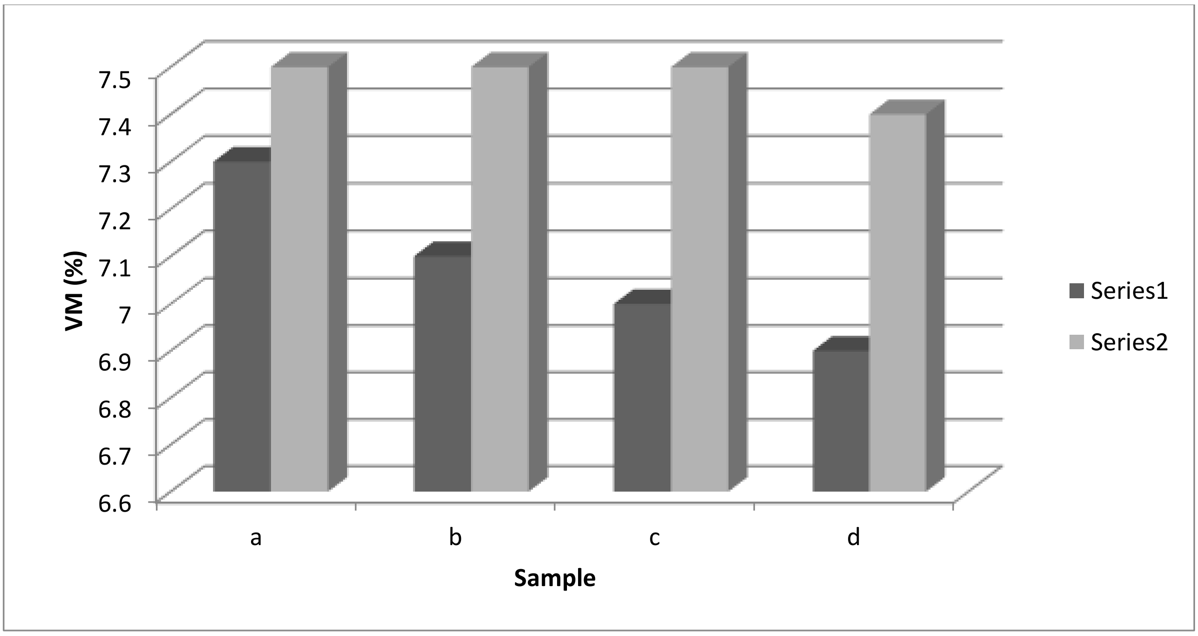

Figure 2. Volatile matter (VM) released from 72BS (series 1) and 100 BS (series 2) samples: a, unblended (UC1 and UC2), and blended b, (BC11 and BC21), c, (BC12 and BC22) and d, BC13 and BC23)

Kinetic study

The kinetic parameters viz. rate constant and frequency factor are evaluated from the TG data. The rate constant values for unblended and blended samples of two different sizes of coal particles are presented in Tables 4 and 5.

Table 4. Rate constant during non-isothermal pyrolysis of 72 BS size unblended and blended samples in the temperature range 373-573K

Sample	Temperature (°K)	Time	Rate constant, k (sec^{-1})
UC1	373	15 min 30 sec	3.51×10^{-3}
	423	25 min 30 sec	2.60×10^{-3}
	473	35 min 30 sec	1.32×10^{-3}
	523	45 min 30 sec	1.02×10^{-3}
	573	55 min 30 sec	0.74×10^{-3}
BC11	373	15 min 30 sec	3.31×10^{-3}
	423	25 min 30 sec	2.18×10^{-3}
	473	35 min 30 sec	1.48×10^{-3}
	523	45 min 30 sec	1.10×10^{-3}
	573	55 min 30 sec	0.80×10^{-3}
BC12	373	15 min 30 sec	3.72×10^{-3}
	423	25 min 30 sec	2.20×10^{-3}
	473	35 min 30 sec	1.52×10^{-3}
	523	45 min 30 sec	1.10×10^{-3}
	573	55 min 30 sec	0.80×10^{-3}
BC13	373	15 min 30 sec	3.54×10^{-3}
	423	25 min 30 sec	2.12×10^{-3}
	473	35 min 30 sec	1.50×10^{-3}
	523	45 min 30 sec	1.12×10^{-3}
	573	55 min 30 sec	0.80×10^{-3}

Table 5. Rate constant during non-isothermal pyrolysis of 100 BS size unblended and blended samples in the temperature range 373-573K

Sample	Temperature (°K)	Time	Rate constant (sec^{-1})

UC2	373	15 min 30 sec	3.80 x 10^{-3}
	423	25 min 30 sec	2.16 x 10^{-3}
	473	35 min 30 sec	1.48 x 10^{-3}
	523	45 min 30 sec	1.08 x 10^{-3}
	573	55 min 30 sec	0.80 x 10^{-3}
BC21	373	15 min 30 sec	3.72 x 10^{-3}
	423	25 min 30 sec	2.44 x 10^{-3}
	473	35 min 30 sec	1.45 x 10^{-3}
	523	45 min 30 sec	1.04 x 10^{-3}
	573	55 min 30 sec	0.78 x 10^{-3}
BC22	373	15 min 30 sec	3.74 x 10^{-3}
	423	25 min 30 sec	2.14 x 10^{-3}
	473	35 min 30 sec	1.46 x 10^{-3}
	523	45 min 30 sec	1.06 x 10^{-3}
	573	55 min 30 sec	0.78 x 10^{-3}
BC23	373	15 min 30 sec	3.92 x 10^{-3}
	423	25 min 30 sec	2.15 x 10^{-3}
	473	35 min 30 sec	1.48 x 10^{-3}
	523	45 min 30 sec	1.06 x 10^{-3}
	573	55 min 30 sec	0.77 x 10^{-3}

The rate constants have been found to decrease with the progress of time in both 72 BS and 100 BS coal samples (Tables 4 and 5). This trend reveals that the rate of reaction was initially very fast and then gradually declined; thus suggesting that the non-isothermal pyrolysis of coal proceeds with a sluggish course as time progresses. When pyrolysis proceeded from 15 min 30 sec (373^{o}K) to 25 min 30 sec (423^{o}K), the difference of rate constants for ZnO blended samples of 72 BS size (BC11, BC12 and BC13), have been found to be higher than that of the unblended sample (UC1) in the same time period. This strongly supports the effect of ZnO nanoparticles on the pyrolysis process in the temperature range 373 – 423^{o}K. On the other hand, when pyrolysis proceeded from 25 min 30 sec (423^{o}K) to 35 min 30 sec (473^{o}K), the difference of rate constants for the blended samples have been observed to be lower than that of the unblended sample (UC1) (Table 4). Similar trends have not been found in the 100 BS coal samples (Table 5).

CONCLUSIONS

This study has explained the role of a green catalyst, ZnO nanomaterials, in the non-isothermal pyrolysis at low temperature.for the emission of volatile. Species. Under the effect of ZnO nanoparticles, the orientation of the macromolecular structure becomes locally stronger.and therefore, stability of the molecules were enhanced. Decrease of the rate constants with the rise of temperature revealing great impact of the nanoparticles on the coal molecule. It is observed that the rate constants are of the same order. Same order of rate constant reveals that the pyrolysis process follows pseudo-first order kinetics. Low value of rate constant supports that the decomposition reaction leading to the slow evolution of volatiles and the reaction is kinetically very slow. The effect of ZnO nanoparticle is significant because it shows inertness of the activated complex with a consequent decrease of weight loss. Thus the presence of ZnO nanoparticles. Is not only the reason for reducing the emission of volatile species which is technologically significant but also plays a very important role for the restoration of ecological system?

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