



Experimental Study on Pyrolysis of coal by Thermogravimetric Analysis (TGA) under Different Temperature Conditions

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ARTICLE INFO

Received : 13 February 2018
Revised : 12 April 2018
Accepted : 22 April 2018

Keywords:

Pyrolysis, coal, thermo gravimetric, heating rate, Nitrogen environment.

ABSTRACT

In this study the pyrolysis characteristics of four different particle size (25-36, 36-52, 52-72, 100-150 μm) coal samples were performed by using thermogravimetric analysis (TGA). The experiments were conducted in nitrogen atmosphere for four different heating rates (50, 100, 160, 200 K/min) for the temperature range from 30 °C to 950 °C with purge flow rate of 40 ml/min. The peak temperature, mass loss, maximum mass loss rate for all different particle size coal samples were evaluated. All thermogravimetric (TG) and differential thermogravimetric (DTG) curves shows that the overall pyrolysis can be divided into different stages according to temperature profiles and each stage has its unique characteristics. The characteristic parameters of different particle size coals increased significantly with increasing the heating rate. Coal pyrolysis in this experiment can be divided in to three stage: moisture release, devolatilization and char gasification in higher temperature zone. Corresponding calculated mean value of activation energy for coal is found 241.132 KJ/mol. The results might have important implication for understanding the mechanism of pyrolysis of coal.

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1. Introduction

The thermal decomposition of coal particles is an important part and also an essential step in the gasification of coal. Pyrolysis is one of the most important thermal conversion processes and it is also the first step in the process of combustion and gasification. Large amounts of clean solid, liquid and gas products can be obtained from pyrolysis process, such as high heating value semi-char and hydrogen enriched gaseous products. For determine the pyrolysis behaviour of solid fuels like coal, thermogravimetric analysis (TGA) is one of the most prevalent method. It is also used to study the physical and chemical properties of samples as a function of temperature [kelebpile et al. 2011]. Many co-processing studies have been performed with thermo-gravimetric analysis in both co-pyrolysis and co-gasification [zhang et al. 2015]. Two types of process occurs when coal is heated. First is depolymerisation in this stage gas, water vapour and tar are formed and second is repolymerization in which char formed [Seo et al. 2011]. Thermal analysis method is widely used for research of combustibility and oxidation behaviours of coal. When thermal curves of different coals varied a lot, the practical combustibility of them is different, when the curves are close to each other, the practical combustibilities are normally the same. The current work focus on pyrolysis of coal with different particle size on different heating rate. The pyrolysis of coal is chemically complex as it involves simultaneous chemical reaction process and also used to determine the physical and chemical properties of different particle size coal samples as a function of temperature. Coal conversion heavily relies on coal reactivity. The

reactivity of Coal basically affected by several factors like thermo-chemical processing condition, coal rank as well as particle size. By coupling pyrolysis and gasification process in any fluidized bed reactors to produce the syngas is one of the most efficient coal utilization technology. The main objective of the present work is to experimental study of physico-chemical and thermal characteristics of coal in nitrogen environment at four different heating rates (50, 100, 160, 200 K/min). So proposed study could increases the use of coal, minimise wastages, pertaining the storage of coal.

2. Materials & Methods

2.1 Sample Preparation-

Indian coal samples were collected from Eastern Coalfield Limited Raniganj (West-Bengal) for this study. Collected coal samples were kept for sun drying for three days. Sun dried sample was grinded using mortar and pestle. The fine powder was allowed to pass through a 105 μm sieve to confirm the uniform particle size distribution. These different particle size coal samples were crushed and sieved to obtain four different particle size (25-36, 36-52, 52-72, 100-150 μm) suitable for TGA pan and kept in air tight bag. The experimental setup for TGA is shown in Fig. 1.

2.2 Proximate and ultimate analysis-

Proximate and ultimate analysis of coal sample were carried out in CSIR-Central Institute of Mining & Fuel Research (CIMFR), Dhanbad (Jharkhand) according to American Society for Testing and Materials

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Fig 1. Experimental Set up

(ASTM) D-5373 standard. Table 1 and Table 2 show the proximate and ultimate analyses for coal sample.

Table 1 Proximate Analysis (%)

Sample	Volatile Matter	Ash	Moisture	Fixed Carbon
Coal	20.4	11.23	3.7	48.6

Table 2 Ultimate Analysis (%).

Sample	C	H	N	S	O
Coal	76.4	4.5	1.0	0.2	10.4

2.3 Experimental apparatus and procedure-

All TGA experiments were carried out by using NETZSCH (TG 209 F3 Tarsus) thermal analyzer in nitrogen environment with a purge flow rate of 40 ml/min. At the beginning of each experiment, Ten gram of the coal sample was placed on an Al_2O_3 crucible in the temperature range from 30 to 950 °C in TGA. During the experiment, different heating rates 50, 100, 160 and 200 K/min were used.

2.4 Kinetic Methods

Kinetic studies of coal pyrolysis has an important role to design and operation of gasification plants. The kinetic analysis tests for different particle size coal samples were carried out on NETZSCH thermal gravimetric analyser (TG 209 F3 Tarsus). Generally, the rate of reaction for a heterogeneous Arrhenius equation can be calculated as follows:

$$\frac{d\alpha}{dt} = A e^{-\frac{E}{RT}} f(\alpha) \quad (1)$$

In above equation (1), α shows the conversion degree, T shows the reaction temperature, t shows the time, A shows the value for pre-exponential function, R shows the value of ideal gas constant (8.314 J/mol K), E shows the value of activation energy and f(α) means the function for reaction model. Basically α (T) indicate the combustion rate of fuel up to temperature T. Data obtained from TG analysis is utilized to evaluate the value for α (T) as shown in following equation.

$$\alpha = \frac{m_o - m_T}{m_o - m_f} \quad (2)$$

Where m_o means mass of the coal sample at initial, m_T is the mass of sample at temperature T and m_f is the final mass of the coal sample.

The function f(α) can be expressed as shown in equation (3).

$$f(\alpha) = (1-\alpha)^n \quad (3)$$

Where n represent the order of reaction.

For a constant heating rate ($\beta = \frac{dT}{dt}$) in order to find out reaction rate as a function of temperature we can convert equation (1) into non isothermal experiment as shown in equation (4).

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-\frac{E}{RT}} f(\alpha) \quad (4)$$

There are so many methods to calculate the kinetic parameters like A, E and n of Arrhenius equation based on the TG analysis. Particularly, the activation energy for coal is evaluated by Friedman method.

The expression for this Friedman analysis is as below-

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

According to equation (5) the slope of $\ln \left(\beta \frac{d\alpha}{dT} \right)$ against $-\frac{1}{T}$ (K) can describe the value of activation energy related to low rank coal samples.

3. Results & Discussion

3.1 Physico-chemical characteristics of the materials

To estimate the physical and chemical properties of coal samples, proximate and ultimate analysis were carried out. Proximate analysis results showed that moisture, volatile matter, fixed carbon and ash contents were 3.7, 20.4, 48.6 and 11.23%, respectively as shown in Table 1. Ultimate analysis showed the amount of carbon contents (76.4%) as shown in Table 2.

3.2 Influence of heating rate on the thermal decomposition of coal sample

The mass loss (TG) curves and the differential mass loss (DTG) curves for coal samples at four different heating rate (50, 100, 160, 200 K/min) from 30 to 950 °C in nitrogen gas atmosphere are shown from Figures 2-5. For these all four heating rate, the weight loss of coal particle was due to water releases and secondly due to devolatilization. Different curves for weight loss versus temperature are shown in Figures 2-5. The thermal degradation took place towards the right as the heating rate continuously increased. From DTG curves (Figure 2-5), the influence of different heating rates could be found; the maximum rate of degradation was at active pyrolysis stage and increased with increasing the heating rate because at maximum heating rate, thermal energy was gained by coal samples. Possible devolatilization for least amount of adsorbed gases and very light hydrocarbons might have occurred below 250 °C.

3.3 Effect of particle size

In general, the coal pyrolysis is affected by the coal particle size. To explore the effect of coal type, different experiments were performed on four different heating rate (50, 100, 160, 200 K/min.) for different particle size (25-36, 36-52, 52-72, 100-150 μ m) as shown in Figures 2-5. During the experiments, with increasing particle size, pyrolysis of coal was also affected in terms of weight loss with respect to temperature and time. To further illustrate the effect of coal particle size on coal pyrolysis reaction, some characteristics parameters were also considered such as initial temperature (T_i), final temperature (T_f) and peak temperature (T_p). The initial temperature of different coal particle size decreased from 535 °C to 612 °C.

3.4 Kinetic parameters

The kinetic parameters for pyrolysis of coal samples were obtained by iso-conversional model free method known as Friedman method under nitrogen atmosphere by using the TGA curves at four different heating rates. This model free analysis was applied as first order reaction kinetics.

Thus, a plot of $\ln \left(\beta \frac{d\alpha}{dT} \right)$ against $-\frac{1}{T}$ (K), should

result in a straight line. In this study, the average value of activation energy of the different particle size coal samples were in the range 241.132 KJ/mol. During the pyrolysis, when heating rate increased, value for activation energy of coal samples also continuously decreased, because energy was supplied by supporting fuel with high heating rate. The analysis by Friedman method was free from mathematical assumption resulting in minimum system error.

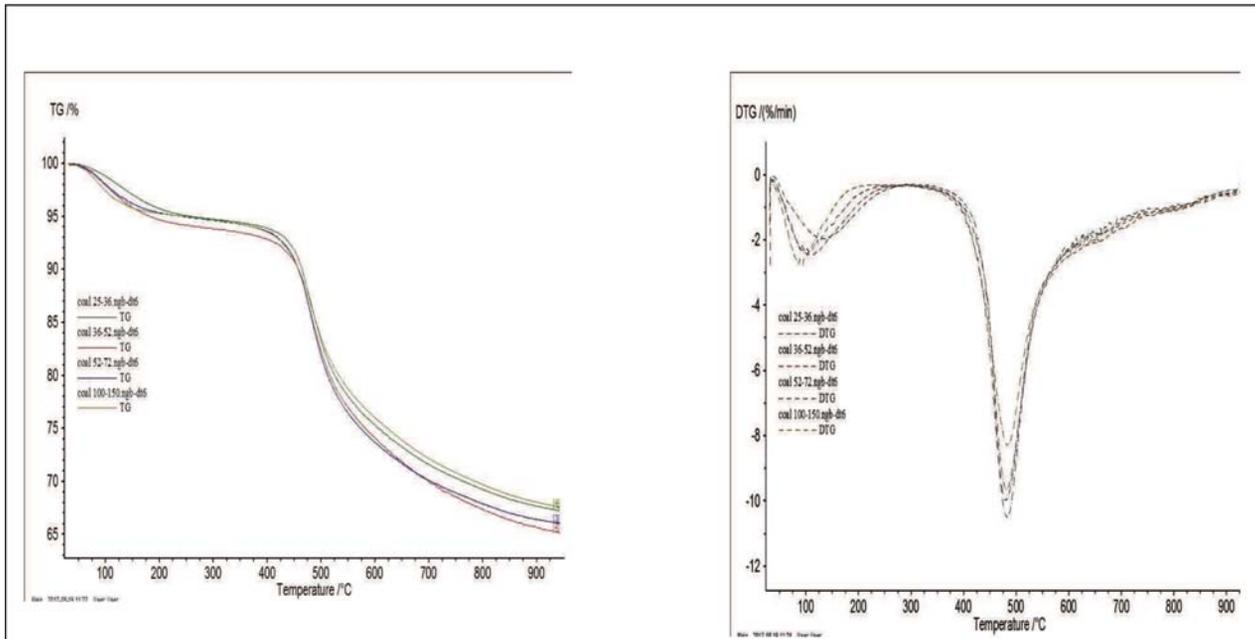


Figure 2. TG & DTG curves for heating rate of 50 k/min

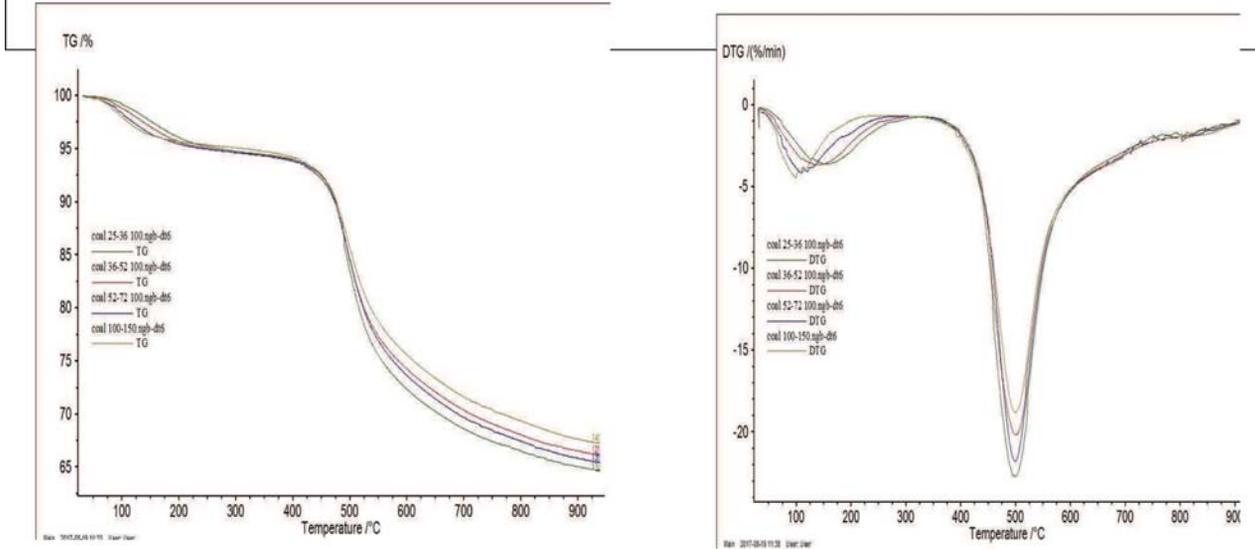


Figure 3. TG & DTG curves for heating rate of 100 k/min

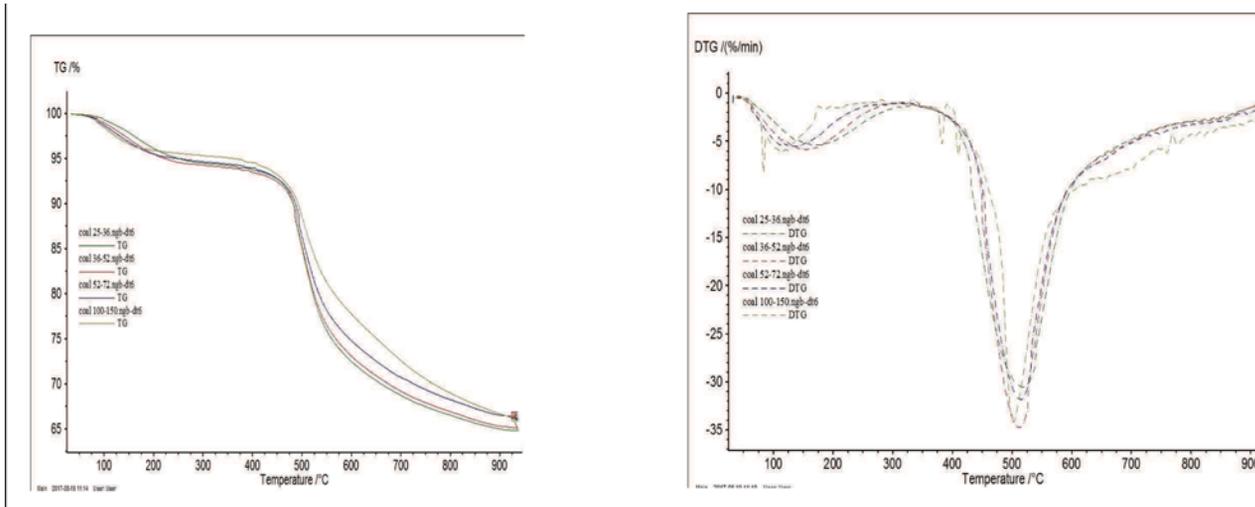


Figure 4. TG & DTG curves for heating rate of 160 k/min

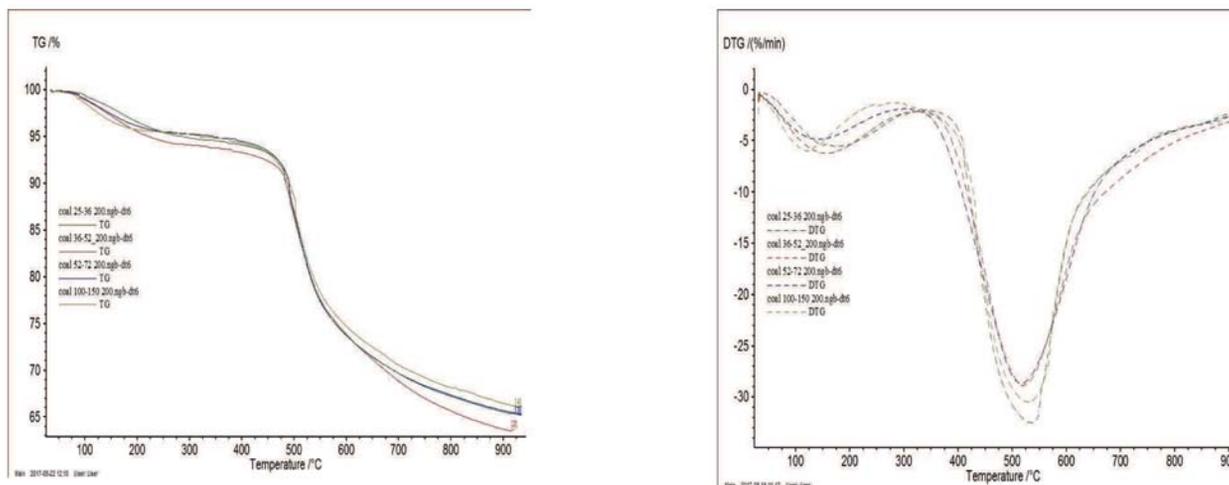


Figure 5. TG & DTG curves for heating rate of 200 k/min

4. Conclusion

The results showed that the pyrolysis characteristic of coal varied from its coalification and chemical composition. The ignition temperature of coal samples was affected by some volatile matter. For all heating rate the maximum weight loss was between the temperature range 100-400 °C. The order of reactivity of different particle size samples still increased with increasing particle size, which was considered reasonable to reburn with large particle size in a circulating fluidized bed gasifier. The activation energy were estimated as 241.1 KJ/mol. (mean value). In other words, the pyrolysis behaviour of coal could be determined in terms of the weight percentages of coal samples. From the results it could be inferred that Indian coal was a valuable resource.

Acknowledgements

The authors thankfully acknowledge Director NIT-Durgapur and the Director CSIR - Central Mechanical Engineering Research Institute (CSIR-CMERI), Durgapur, India for their continuous support and encouragement in carrying out this research work.

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