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High ash coal pyrolysis at different heating rates to analyze its char structure, kinetics and evolved species

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ABSTRACT

Mass losses of high ash coal and the mole fractions of evolved species were measured during pyrolysis using a thermo-gravimetric analyzer (TGA) and a mass spectrometric analyzer, respectively. Coal samples of three sizes from Bilaspur, India were pyrolyzed using the TGA in an argon atmosphere under dynamic conditions at atmospheric pressure under the heating rates of 40, 100, 500, and 1000 °C/min until the furnace temperature reached 1000 °C and maintain the temperature to complete the pyrolysis process. The structural properties of the produced char such as pore surface area (BET) obtained by N_2 adsorption method and SEM analysis were performed in order to explain the differences in structure based on char generation method. The BET surface area is increased by more than twofold when the heating rate is raised from 40 °C/min to 1000 °C/min. The kinetic parameters of activation energies (E) and Arrhenius constant (A) of thermal pyrolysis for different sized coal particles at various conversion levels were correlated from the thermogravimetric data under four heating rates. The dependencies of kinetic parameters on particle size and conversion levels during coal pyrolysis were estimated. The results revealed that higher pyrolysis rate of coal would greatly increase the yield of light gases such as CO, H_2 when compared to slower pyrolysis process.

1. Introduction

Low grade coals with high ash contents have gradually become essential energy resources due to their availability as abundant minable reserves and the substantial consumption of high-quality coals. However, the ash present in these coals largely inhibits its effective use and extensive utilization techniques such as carbonization and gasification. The research to improve inferior coal quality has been widely carried out, which mainly includes the drying, washing and pyrolysis techniques. The suitable thermal decomposition of coal presents a potentially low-cost alternative for yielding gaseous fuels from volatile matter and upgrading char as value-added carbon products. Coal devolatilization is considered as the first step and also of primary importance in coal thermal conversion techniques, such as coal coking, gasification, combustion and so on [1–5]. Laboratory-scale testing provides useful and necessary information on solid fuel behavior during pyrolysis. This information can be used later on when designing larger power plants and burning facilities. Borah et al. [6] have reported that heating rate, ultimate temperature and coal rank are the most important parameters influence the yield and composition of the products evolved during devolatilization as coal devolatilization is complex in nature. The maximum temperature and the heating rate are varied in different coal utilization processes. Coal devolatilization is continued for several hours (with a heating rate of 10^{-1} to 10^{1} K/s) in a coking plant, order of few seconds or less (with a heating rate of 10^{2}–10^{4} K/s) in the processes of gasification or combustion [7], and within several milliseconds (with a heating rate of 10^{4}–10^{6} K/s) in a plasma process [8,9]. Hence, the basic information of coal pyrolysis under different heating rate and ultimate temperature is required to establish efficient coal utilization processes. Seo et al. [10] have reported that the knowledge of the thermal decomposition of fuels is essential to assess the performance of gasification processes.

Several researchers [10–15] and recently authors [16–20] have reported that thermal analysis techniques such as thermogravimetric analysis and mass spectrometry (TGA-MS) have been widely used to estimate the rapid quantitative methods for the examination of processes under isothermal or non-isothermal conditions and allow for the estimation of effective kinetic parameters for various decomposition reactions and evolved gas analyzes, respectively. Due to its complexity of structure and the heterogeneity of components, the determination of the coal pyrolysis process is very difficult, which consists of a lot of physical changes and

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Table 1
Proximate and ultimate analysis of the coal.

Proximate analysis				Ultimate analysis (dry basis)					Heating value	
Moisture (%)	Ash (%)	V.M (%)	Fixed carbon (%)	C (%)	H (%)	N (%)	O (%)	S (%)	LCV kcal/kg	HCV kcal/kg
2.95	45.85	25.62	25.58	39.43	2.52	0.97	10.78	0.45	3486	3642

chemical reactions. Generally, two processes occur competitively when coal is heated. First one is the depolymerisation process through which gas, water vapor, and tar are formed. Another one is the condensation or repolymerization process, which leads to char/coke formation [10]. Kobayashi et al. [21] investigated the devolatilization of a bituminous coal at high temperatures under fast heating conditions and found that the yield of volatiles increased significantly with the ultimate temperature. Pyrolysis process of coal is greatly influenced by various factors, which includes intrinsic factors of coal and external factors. Generally speaking, the intrinsic factor covers structure, composition, particle size [22] and rank of coal [15], while the external factors include temperature [23], pressure [24], heating rate [25] and reaction atmosphere [26]. Tyler et al. [27] have reported that the coal conversion and the yield of volatiles increased significantly up to 1000 K, and then it became invariant with the temperature under fast heating rate conditions. Some researchers [28,29] have stated that the yields of gaseous products had different trends with the variation of ultimate temperature. Solomon et al. [30] have explained the effect of temperature using the primary and secondary decomposition reactions. Ladner et al. [31] have reported that the increase in heating rate resulted in an increase in oil and tar yields as well as coal conversion. However, Sunberg et al. [32] have described that heating rate on the yields of the pyrolysis products are insignificant. The contradictory results of these experiments might be arised often due to the secondary reactions from volatiles interactions which cannot be prevented in experimental systems. The nature of coal makes it very difficult to perform unambiguous experiments to determine the conversion rates, mechanisms and volatiles in coal pyrolysis. Therefore, although a number of new experimental and theoretical approaches have been used to investigate the effects of these parameters on coal devolatilization [33], the fundamental knowledge of coal pyrolysis at sequentially from low to high heating rate effects in single system is further investigated in this paper.

There have been a number of approaches to modelling the complex coal pyrolysis process. Several types of kinetic models have already been presented in the literature and employed to describe the fast pyrolysis process of solid fuel particles [34]. Recently, several empirical kinetic models are used in different pyrolysis studies, such as single model [10,11,35,36], parallel model [10,11,37,38], or parallel-series model [39,40]. Porada [37] have studied the coal pyrolysis under non-isothermal conditions, and determined kinetic parameters of a number of constituent reactions using gas analysis (GA). Otero et al. [41] have reported the Arrhenius activation energies of various blends of coal and sludge using a non-isothermal iso-conversional method for TGA (thermo-gravimetric analysis) results. Kim et al. [42] have investigated the volatilization characteristics of five Australian coals experimentally using TGA reactor using a simple empirical model.

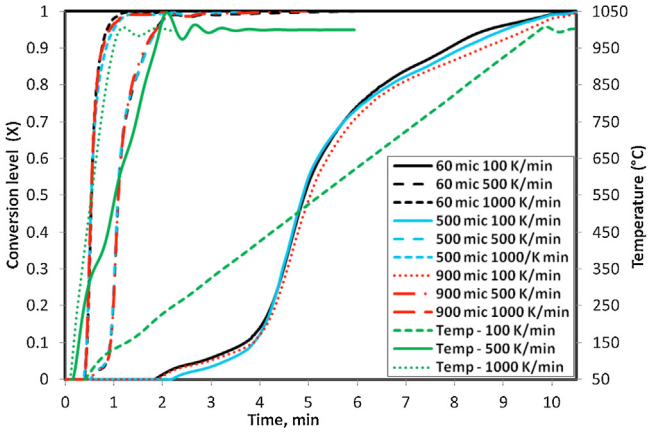

Fig. 1. Curves of conversion of coal pyrolysis at different heating rates.

The present study is investigated with the Indian coal of two sizes which are pyrolyzed under the heating rates from 40 °C/min to 1000 °C/min and the associated gas evolution using mass spectrometry. The scientific significance is clear that gas evolution and coal-char structure is mainly depends on devolatilisation/pyrolysis rate. The char structure is characterized using SEM (Scanning Electron Microscope) micro graphs and Brunauer–Emmett–Teller (BET) analysis. Experimental data were interpreted using a single model to obtain kinetic parameters.

2. Materials and methods

High ash Indian coal with the average particle sizes of 60 μm, 500 μm and 900 μm are used for this study. The coal sample was partially dried at low temperature (<35 °C) and then ground and sieved using standard sieves to obtain the average particles size ranges about 60 μm, 500 μm and 900 μm. A NETZSCH STA 429 thermal analyser with platinum furnace is used to prepare the char particles. The char particles are produced using the heating rates of 40 °C/min, 100 °C/min, 500 °C/min and 1000 °C/min in argon ambience. The experimental setup used for the gasification tests was described in a previous study [16–20]. After pyrolysis, chars were cooled to ambient temperature in argon ambience. The system recorded the weight loss using a highly sensitive analytical balance with a resolution of 10^{-3} mg. Thermocouples measuring the sample temperatures were connected to the bottom portion

Table 2
Proximate and ultimate analysis of the Indian coal-char produced at 40 °C/min.

Proximate analysis				Ultimate analysis (dry basis)				Heating value
Particle size	Moisture (%)	Ash (dry basis) (%)	V.M (dry basis) (%)	C (%)	H (%)	N (%)	S (%)	HCV kcal/kg
60 μm	2.44	64.4	2.33	36.6	0.39	0.75	0.59	2871
900 μm	2.25	72.2	2.62	28.3	0.34	0.44	0.5	2340

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