Fuel 90 (2011) 3299–3305

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Application of chemometrics to study the kinetics of coal pyrolysis: A novel approach

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ARTICLE INFO

Article history:
Received 26 October 2010
Received in revised form 17 March 2011
Accepted 19 May 2011
Available online 1 June 2011

Keywords:
Chemometric
Principal component analysis
Hierarchical clustering analysis
Coals

ABSTRACT

In present investigation, chemometric tools, principal component analysis (PCA) and Hierarchical clustering analysis (HCA) are used to get the linkage between the coal properties and kinetics of pyrolysis. Thermo gravimetric analysis (TGA) of 10 perhydrous Indian coals was done. Devolatilization of these coals showed five independent reactions. Kinetic parameters were calculated for individual reaction. Activation energy and weight loss of each reaction has been analyzed as a function of coal properties (moisture, volatile matter, ash, fixed carbon, carbon, hydrogen, nitrogen and sulfur). By applying chemometric, was extracted information about the linkage between activation energies of each reaction and coal properties. The mathematical treatment of data has provided conclusions on properties of coal and kinetic parameters.

1. Introduction

Pyrolysis is an important intermediate stage in coal gasification, combustion, and liquefaction, and also considered as a simple and effective method for a clean conversion of coal [1]. The application of thermal analysis to study the behavior of fossil fuels during pyrolysis has gained much industrial importance [2].

Thermal analysis characterizes the physical and chemical properties of substances, depending on the temperature at defined heating rate (dynamics measurement) or on the time at a constant temperature (static measurement) [3]. In recent years, the application of thermal analysis techniques to study the combustion and pyrolysis behavior of fuels has gained a wide acceptance among research workers [4–6]. Kinetics of devolatilization is useful for accurate estimation of the reactivity of fossil fuels during their utilization and conversion processes (gasification, liquefaction). Devolatilization of solid fuel occurs by processes like dehydration, primary and secondary devolatilization and thermal degradation. Accurate knowledge of the devolatilization processes is necessary to develop predictive models for coal conversion processes.

Application of chemometrics to TGA data at different steps of the devolatilization is of interest and useful. Chemometrics is a chemical discipline that uses mathematics, statistics and formal logic: (1) To design or to select optimal experimental procedures, (2) To provide maximum relevant chemical information by analyzing chemical data, and (3) To obtain knowledge about the chemical systems [7].

In present investigation, perhydrous Indian coals, which are suitable for conversion processes like liquefaction and coke making used for thermo gravimetric analysis. The kinetic parameters extracted from TGA are combined with differing chemometric tools such as correlation, principal component analysis (PCA) and cluster analyses. A general overview of the application of chemometrics, particularly in PCA techniques and soft modeling to TGA data is presented in the paper giving special attention to the more recent contribution on fuel conversion processes. The database can be interpreted in many ways, we have highlighted the usefulness of PCA in order to 1. Develop a relationship between the coal properties and kinetic parameters obtained from TGA. 2. Suitability of coal for particular conversion process i.e. by combining the physico-chemical properties of coal with that of the kinetic parameters obtained from TGA.

2. Materials and methods

The freshly mined low rank coal samples from different coalfields of northeastern India were used in this study. The air-dried samples were ground to 0.211 mm before use. The proximate, ultimate and sulfur analyses were done by using a TGA 701 (Leco), True spec elemental analyzer (Leco) and S 144 DR sulfur determinator (Leco). Physico-chemical characteristics of these coals are summarized in Table 1.

2.1. TGA and DTG

Differential thermal analysis was used to determine the pyrolysis behavior of perhydrous coals. Experiments were carried out in a

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doi:10.1016/j.fuel.2011.05.017

Table 1
Physico-chemical characteristics of sub-bituminous coals, and weight loss (%) for five reactions during pyrolysis.

	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
M	2.9	3.1	1.5	2.7	2.9	3.4	2.8	2.1	3.2	2.8
Ash	20	11.5	11.5	12	7.1	11.9	17.6	14.4	3.9	16.3
VM	35.6	41.4	40.5	35.5	42.7	37.2	36	38.1	40.4	36.1
FC	41.5	44	46.5	49.8	47.3	47.5	45.6	45.4	52.5	44.8
C	74.6	64.1	64.3	70.1	68.6	70.8	71.4	81.8	75.9	82.3
H	7.5	5.72	6.07	6.1	5.5	4.7	2.7	5.8	5.3	5.9
N	1.2	1.4	1.1	1.3	1.1	1.1	1.1	1.4	1.1	1.4
S	2.9	2.9	4.46	3.98	3	4	4.5	2.2	2	2.4
H/C	1.21	1.07	1.13	1.04	0.96	0.80	0.45	0.85	0.84	0.86
W_1	0.22	0.39	0.15	0.21	0.25	0.32	0.27	0.25	0.26	0.31
W_2	2.82	7.33	3.4	2.67	2.88	6.4	2.67	2.1	2.65	1.92
W_3	19.36	18.97	20.27	19.2	19.67	18.2	19.01	18.1	18.3	17.2
W_4	8.63	10.85	9.87	11.2	10.3	11.4	8.6	8.2	9.99	10.2
W_5	16.24	18.98	18.91	20.6	20.1	19.2	19.8	18.7	17.2	18.2

VM: volatile matter, FC: fixed carbon; W1-W5: Weight loss during the reactions 1–5, respectively.

Leco TGA 701 thermal analysis system with 0.5 g each of coal samples in a stream of nitrogen with a flow rate of 40 ml/min and linear heating rate of 10 °C/min. Several preliminary thermo gravimetric runs were performed in order to investigate the sample mass influence on the devolatilization behavior. Variation in mass has negligible effect on the devolatilization of coal.

2.2. Calculation of kinetic parameters

The kinetic parameters, activation energies and pre exponential factors of coal pyrolysis were determined by the integral method by applying Arrhenius equation. Arrhenius equation can be expressed as

$$dx/dt = Aexp(-E/RT)(1-x) \quad (1)$$

where A is pre-exponential factor, E activation energy, T temperature, t time, X weight loss fraction or decomposition during pyrolysis and which can be calculated by

$$x = \frac{W_0 - W_t}{W_0 - W_f} \quad (2)$$

where W_0 is the original mass of the test sample, W_t is the mass at time t or T and W_f is the final mass at the end of pyrolysis.

The constant heating rate during pyrolysis is $H = dT/dt$ for H being the heating rate. Rearranging the Eq. (1) and on integration gives

$$In[-ln(1-x)/T2] = In[AR/HE(1-2RT/E)] - E/RT \quad (3)$$

The expression ln{AR[1-(2RT/E)]/HE in Eq. (3) is essentially constant for most of the values of E and temperature range of the pyrolysis. By plotting the left side of Eq. (3) against $1/T$, a straight line is obtained indicating the process to be of first order reaction. From the slope, $-E/R$, the activation energy E can be determined.

2.3. Data treatment and chemometric analysis

Statistical treatment of data including correlation analysis, and principal component analysis (PCA) and Hierarchical clustering analysis (HCA) were performed using SPSS 15 statistical software.

Principal component analysis (PCA) techniques have been widely applied in the treatment of datasets of such a high complexity [8]. PCA provides a new set of orthogonal variables, the principal components (PCs), generated so that each PC accounts for the maximum possible amount of variance contained in the original dataset. The PCs are obtained as linear combination of the original descriptors and are aligned along the directions of covariance of the data [9].

PCA technique extracts the Eigen values and Eigen vectors from the covariance matrix of original variables. It allows finding out association between variables, thus, reducing the dimensionality of the data set. The Eigen values of PCs are the measure of their associated variance, the participation of the original variables in the PCs is given by the loading, and the individual transformed observations are called scores [9,10]. PCA was performed on normalized (z-scale transformation) variables after sorting out the highly correlated variables from the data sets. The Bartlett's sphericity test was applied to the correlation matrix of variables for assessing the adequacy of PCA [11]. PCs with Eigen value greater than 1 were considered. Here, PCA was performed with a view to establish linkage between the coal properties and kinetic parameters extracted from TGA. To validate the model result, correlation were also drawn to calculate theoretical activation energy.

Cluster analysis is an exploratory multivariate method that can be used to describe the relationships among variables. Several mathematical criteria can be used to examine the similarity (or difference/distance) between variables and cases. For Hierarchical clustering analysis (HCA), the Ward's method was used to get cleaner picture of clusters. This method is distinct from all other methods because it uses an analysis of variance approach to evaluate the distances between clusters. This method attempts to minimize the sum of square (SS) of any two clusters that can be formed each step. This method is regarded as a very efficient one. The joining or tree clustering method uses the dissimilarities (similarities) or distances between objects when using the clusters. Similarities (distance) are a set of rules that serves as criteria for grouping or separating items elucidean distance is chosen for the analysis.

3. Results

3.1. Thermal behavior and kinetics of coal pyrolysis

The curves of thermal analysis (TGA and DTG) of one of the coal samples are shown in Fig. 1. It is evident from the shape of the curves that pyrolysis proceeds through five different temperature regions. Hence devolatilization may occur via five reactions i.e. dehydration (reaction 1), primary devolatilization /thermal desorption of gases (reaction 2), thermal degradation (reaction 3), depolymerization/secondary devolatilization (reaction 4), and dehydrogenation/condensation (reaction 5) [12,13]. The activation energies are determined for each process reaction by applying first order Arrhenius equation on each independent reaction (calculation is given in the materials and methods). Activation energy (E_a) with standard deviation and r^2 for each linear regression is shown for