The influence of chemical structure on the kinetics of coal pyrolysis

M.D. Casal, M.F. Vega, E. Diaz-Faes, C. Barriocanal*

Instituto Nacional del Carbón (INCAR-CSIC), Apdo 73, 33080 Oviedo, Spain

ARTICLE INFO

ABSTRACT

The pyrolysis characteristics of a series of bituminous coals, along with an anthracite and a lignite, were studied by means of thermogravimetric analysis (TGA). The kinetic parameters were determined by the integral method assuming that coal pyrolysis is a first-order reaction. The chemical coal structure was determined by means of diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS), whereas the thermoplastic properties of the coals were studied by applying Gieseler plastometry.

The kinetic parameters obtained are discussed in relation to the chemical structure, thermoplastic properties, rank and volatile matter evolution of the coal. In addition, the origin of the "kinetic compensation effect" between the activation energy and the pre-exponential factor for these bituminous coals was investigated.

1. Introduction

Coal continues to be one of the main sources of energy worldwide and is indispensable in the steel-making industry. Of the coals of different rank, bituminous coals are the most widely employed in the coke-making industry because of their thermoplastic properties (e.g. their ability to soften and resolidify when heated in the absence of oxygen) (Loison et al., 1989). Coal pyrolysis is an important thermal conversion process, which involving a series of complex reactions and is the first step in coal conversion processes, such as combustion and gasification (Casal et al., 2005; van Heek and Hodek, 1994). When coal is heated in an inert atmosphere it undergoes physical and chemical transformations. This process is affected by internal factors, including structure, composition and coal rank, and external factors such as temperature, catalysts or heating rate (Alonso et al., 2001; Liu et al., 2004; Zhang et al., 2016, 2013).

Thermogravimetric analysis (TGA) is one of the most important techniques used to study the thermal events and kinetics of coal pyrolysis (Arenillas et al., 2001; Geng et al., 2016; Zhang et al., 2013). Among the advantages it offers are its easy implementation and good repeatability of results. To determine the kinetic parameters of coal processes it is important to be able to understand and predict the physical and chemical changes during the thermal process.

Many researchers have attempted to develop methods to quantify the kinetic behaviour of coal combustion (Naidu et al., 2016; Sarwar et al., 2012; Slyusarskiy et al., 2017). In coal pyrolysis, several researchers have focused on the kinetic study of non-coking coals (Gao et al., 2016; Niu et al., 2016; Toloue Farrokh et al., 2017) or low-rank coals (Song et al., 2017; Xu et al., 2015). However, few researchers have focused on the kinetics of bituminous coals. In a recent study, Alonso et al. managed to develop an Arrhenius-based deconvolution model to establish systematic trends in the kinetic parameters with coal rank and maceral composition (Alonso et al., 2001). Zhang et al. centered their research on the relationship between the thermal properties and kinetic parameters of vitrinite-rich and inertinite-rich concentrates and coal rank (Zhang et al., 2016). Conversely, Epshtein et al. correlated the kinetic parameters of coal pyrolysis and combustion with coal rank and degree of aromaticity (Epshtein et al., 2017).

The present research work focuses on the pyrolysis of a series of bituminous coals, that go through a plastic stage when heated in an inert atmosphere. The main goal of this study was to establish a relationship between the kinetic parameters obtained from the thermogravimetric analysis with coal rank, the indices derived from infrared spectroscopy, thermoplastic properties and volatile matter evolution during the pyrolysis process. Furthermore, two non-bituminous coals (i.e. a lignite and an anthracite) have been included in order to broaden the scope of the study.

2. Materials and methods

2.1. Coals

The present work has been carried out using one anthracite, eleven bituminous coals and a lignite (Table 1).

Proximate analyses were performed following the ISO562 and ISO1171 standard procedures for volatile matter and ash content,

---

Table 1
Proximate and ultimate analysis of all the coals studied.

Coal	Ash (%)	VM (%)	C (%)	H (%)	N (%)	S (%)	O (%)
A	13.3	3.2	83.6	1.1	0.9	0.9	1.8
LV1	6.6	16.7	84.0	4.3	1.4	1.0	2.4
LV2	10.2	17.4	79.8	4.2	2.8	0.5	4.0
LV3	5.6	17.7	85.6	4.4	1.6	0.6	3.6
LV4	6.6	18.3	83.9	4.4	1.5	0.7	2.6
MV1	9.8	20.7	79.9	4.4	2.1	0.5	3.9
MV2	9.0	24.0	80.2	4.7	2.2	0.6	4.9
MV3	8.5	24.9	79.9	4.7	1.3	0.8	4.9
MV4	4.6	26.0	85.4	4.7	1.1	0.4	3.9
HV1	7.7	31.6	79.8	4.9	1.6	0.7	6.6
HV2	8.6	33.0	77.9	5.1	2.2	0.6	6.7
HV3	7.4	33.4	79.1	5.0	1.5	1.1	6.1
L	22.8	34.6	55.3	3.6	0.9	7.4	14.2

All data is on a dry basis (db) expressed as % weight.

respectively. The elemental analysis was determined in a LECO CHN-2000 instrument for C, H and N (ASTM D-5773), a LECO S-144DR device (ASTM D-5016) for sulphur and a LECO VTF-900 instrument for the direct determination of the oxygen content.

A petrographic examination of the samples was carried out on a MPV II Leitz microscope under reflected white light using immersion objectives ($32\times$) in accordance with the ISO 7404-5 standard for vitrinite reflectance and the ISO 7404-3 procedure to determine the maceral group content.

2.2. Diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS)

Coal samples with a particle size of < 0.063 mm were left to dry at 35 °C overnight before analysis. The spectra of the coals were measured using a collector diffuse reflectance accessory fitted to a Nicolet Magna-IR560 spectrometer. A mercury cadmium telluride detector (MCT-A) that operates at sub-ambient temperature was used for the analysis. Data were collected in the range of 650–4000 cm^{-1}, by applying 128 scans at a resolution of 4 cm^{-1} to each sample. Semiquantitative analyses were carried out using the integrated area (A) of selected absorption bands.

2.3. Thermoplastic properties

The thermoplastic properties of the bituminous coals were assessed by means of the Gieseler fluidity test. The Gieseler test was carried out in a R.B. Automazione Gieseler plastometer PL 2000 following the ASTM D2639-08 standard procedure, explained in detail in a previous paper (Díaz-Faes et al., 2007).

2.4. Thermogravimetric analysis (TG/DTG)

The TG/DTG analysis of the coals was carried out using a TA Instruments STD 2960 thermoanalyser. The samples (10 mg) with a particle size of < 0.212 mm were heated up to 1000 °C at a rate of 3 °C/min under a nitrogen flow of 100 mL/min. From the data obtained by thermogravimetric analysis the derivative weight loss curve (DTG curve) was calculated. The maximum volatile matter evolution (DTGmax) and the temperature at which the maximum occurred (Tmax) was derived from the TG/DTG curves (Barriocanal et al., 2003; Díaz-Faes et al., 2007). No heat and mass transfer limitations were observed under the experimental conditions used.

2.5. Kinetic study

Thermal gravimetry data were used to calculate kinetic parameters for coal devolatilization. First order reaction was assumed and the integral method was used to study the kinetics of the process (Liu et al.,

2004; Yangali et al., 2014). The kinetics of the reaction can be described as follows:

$$dx/dt = A \exp(-E/RT)(1 - x) \tag{1}$$

where A is a pre-exponential factor (min^{-1}), E is the activation energy (J/mol), R is the universal gas constant ($R = 8.314\,\mathrm{Jmol^{-1}K^{-1}}$), T is the thermodynamic temperature (K) and x is the pyrolysis conversion, which is calculated as follows:

$$x = (m_0 - m_t)/(m_0 - m_f) \tag{2}$$

where m_0 is the initial mass of the sample, m_t is the sample mass at time t during thermal de and m_f is the final mass at the end of the pyrolysis.

For a constant heating rate, β, during pyrolysis the expression $\beta = dT/dt$ was introduced in Eq. (1) and after integration it transforms into:

$$\ln(-\ln(1 - x)/T^2) = \ln(AR/\beta E(1 - 2RT/E)) - E/RT \tag{3}$$

Given that for most values of E and for the temperature range of the pyrolysis, the expression $\ln(AR/\beta E(1 - 2RT/E))$ in Eq. (3) can be considered essentially constant, if the left side of Eq. (3) ($\ln(-\ln(1 - x)/T^2)$) is plotted versus 1/T, a straight line is obtained. The activation energy, E, can be calculated from the slope of the line, E/R. In addition, the pre-exponential factor, A, can be calculated from the intercept.

The method used, although simple, has been reported to be useful for comparing different samples. (Arenillas et al., 2001).

3. Results and discussion

The present work was carried out using thirteen coals of different rank: an anthracite (A), eleven bituminous coals divided into low-volatile coals (LV1-4), medium-volatile coals (MV1-4), high-volatile coals (HV1-3), and a lignite coal (L). The results of the proximate and ultimate analyses are collected in Table 1, where the coals are listed by decreasing rank according to their volatile matter content. As expected, the main variations observed with increasing rank were a gradual decrease in hydrogen and oxygen content and an increase in carbon content.

The vitrinite reflectance and the maceral composition of the coals are presented in Table 2. The coals were selected from different geographical origins: SP (Spanish coals) USA (North American coals), AU (Australian coals), CZ (Czech coal) and PL (Polish coal. As can be seen the mean reflectance, varies between 4.9 and 0.34%. The vitrinite content is high (70.4–91.3 vol% mmf), whereas the percentage of the liptinite-group is relatively low, the highest value corresponding to HV3 (9.9 vol% mmf). In coal A and LV coals at a reflectance of 4.9 to 1.55 the liptinite macerals disappear (Table 2) because in coals with

Table 2
Origin and petrographic analysis of the coals.

Coal	Country	R_o[a] (%)	Vitrinite (vol% mmf[b])	Liptinite (vol% mmf[b])	Inertinite (vol% mmf[b])
A	SP	4.9	91.3	0.0	8.7
LV1	USA	1.62	86.3	0.0	13.7
LV2	AU	1.52	75.7	0.0	24.3
LV3	USA	1.58	76.7	0.0	23.3
LV4	USA	1.55	85.9	0.0	14.1
MV1	AU	1.35	75.4	0.9	23.7
MV2	AU	1.24	81.2	1.4	17.4
MV3	USA	1.18	83.0	2.6	14.4
MV4	CZ	1.44	81.1	0.4	18.5
HV1	PL	0.95	70.4	8.3	21.3
HV2	AU	0.87	84.4	2.7	12.9
HV3	USA	0.79	74.9	9.9	15.2
L	SP	0.34	71.6	1.1	27.3

[a] Mean vitrinite reflectance.
[b] Mineral matter-free.