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

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.

Keywords *bituminous coal, pyrolysis, kinetic, TGA*

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, 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×) 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 less than 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 (DTG_{max}) and the temperature at which the maximum occurred (T_{max}) 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:

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

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

$$x = (m_0 - m_t)/(m_0 - m_f) \quad (2)$$

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:

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

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 $R_o > 1.5$ %, the optical properties of liptinite converge with those of vitrinite and display the same reflectance, which makes it difficult to distinguish between them (Borrego et al., 2000). Inertinite ranges from 5.8 vol.% mmf in anthracite to 18.4 vol.% mmf in lignite. The inertinite group in the bituminous coals, ranges from 9.2 vol.% mmf for coal HV2 to 18.3 vol.% mmf for coals LV2 and LV3.

There is a direct relationship between the volatile matter content of coal and its maceral composition which can be expressed by means of the following equation (Borrego et al., 2000):

$$VM_{calcd} = \phi_V(R_o) \cdot X_V + \phi_L(R_o) \cdot X_L + \phi_I(R_o) \cdot X_I \quad (4)$$

where ϕ_m is the fractional volatile matter content of the macerals present in the coal, which can be calculated by means of expressions defined by Borrego et al. (Borrego et

al., 2000), and X_m is the percentage of each maceral expressed in vol.% mmf (Table 2).
Eq. (4) has been used for the coals in the present research work, as shown in Figure 1.

Figure 2 displays the infrared spectra corresponding to coals A, LV1, MV3, HV3 and L. A comparison of the DRIFT spectra of the studied coals reveals the following changes with increasing rank: a decrease in the absorbance band of the OH-containing functional groups (band centered at ca. 3300 cm^{-1}), an increase in the aromatic C-H stretching absorption bands (at ca. 3000-3100 cm^{-1}) and a diminution of the aliphatic C-H stretching absorption bands (at ca. 2800-3000 cm^{-1}). In the case of coal L, the strong O-H band overlaps the aromatic C-H stretching absorption bands. The C=O absorption band (ca. 1800-1650 cm^{-1}) is more prominent for coal L than in the case of the bituminous coals. The low-rank coals have more groups with oxygen functionalities, such as ketones, aldehydes and carboxylic acids, that are the responsible for the strong absorption observed at 1710 cm^{-1} (Iglesias et al., 1995). As reported by Chen et al., nearly all the vibration signals disappear for anthracite, except the aromatic C=C stretching absorption bands (at ca. 1600 cm^{-1}) (Chen et al., 2012). Finally, the bands assigned to the aromatic C-H out-of-plane bending modes (ca. 700-900 cm^{-1}) are only noticeable in the spectra of the bituminous coals.

A series of indices from the literature have been used to quantify some of the chemical structures present in the coals studied (Table 3) (Chen et al., 2012; Menéndez et al., 1996). Data corresponding to A and L have not been included in the table due to the poor level of accuracy achieved in determining the peak area. It can be seen that the AR1 and the AR2 indices, increase with increasing coal rank (Table 4). The variation is less noticeable, however, in the case of the AR2 index due to the possible interference from the mineral matter and long aliphatic chains in the 700-900 cm^{-1} region (Chen et al., 2012; Iglesias et al., 1995). The degree of condensation of the aromatic rings, as measured

by means of the DOC1 and the DOC2 indices, also increase with increasing coal rank because the fraction of aromatic hydrogen in the coal increases and the C=C bonds decrease, while the amount of aliphatic compounds decreases.

The ratio between the methylene and methyl groups in the aliphatic structures (CH_2/CH_3) was also calculated. This index represents the length or degree of branching of the aliphatic chains. Table 4 shows that the lower the rank is, the greater the length of the structures present in the coal and the higher the degree of branching.

Bituminous coals, with volatile matter content between 15-40 % soften at a temperature of ca. 375-400 °C when pyrolyzed. Table 5 summarizes the main parameters derived from the thermoplastic analysis of the coals except for A and L that do not pass through a plastic stage. The thermoplastic properties of the coals are related to coal rank and their maceral composition. In general, as the coal rank increases, the curves shift to higher temperatures, maximum fluidity decreases, and the plastic range (T_r - T_s) narrows. This behaviour is related to the extent of cross-linking and the size of the planar macromolecules which make up the coals. Generally high fluidity is favoured by the presence of aliphatic and hydroaromatic compounds with bridging bonds that can be easily thermally cleaved (Loison et al., 1989; Barriocanal et al., 2003).

Figure 3 shows the DTG curves for A, L and six of the bituminous coals (LV2, LV3, MV2, MV4, HV1, HV2). The main parameters derived from the thermogravimetric analysis of all the coals studied are presented in Table 6. The evolution of volatiles is dependent on coal rank, due to the difference in the molecular structures of the coals (Barriocanal et al., 2003). This is reflected in the displacement to higher values of the temperatures at which weight loss begins and ends with increasing rank. Moreover, the maximum rate of volatile matter evolution (DTG_{max}) decreases and takes place at a higher temperature in the case of the low-volatile coals (Table 6). As can be seen in Figure

3 this effect is more noticeable in the case of coal A, whose DTG_{max} increases to 618 °C though it is much lower (0.05 %min⁻¹) than in the rest of the coals included in the present study (0.35-0.89 %min⁻¹). This fact can be attributed to the highly condensed aromatic structure of anthracite that impedes devolatilization. The DTG profiles of the bituminous coals are similar, with a sharp peak at ca. 450 °C due to the evolution of high molecular weight species (tar) and light hydrocarbons coinciding with the plastic stage. However, the DTG curve corresponding to coal L presents a two-stage pattern. The first stage occurs between 250 and 500 °C and corresponds to the degradation of the carbonaceous matrix and the release of relatively high molecular weight species (Figure 3)., since lignites have a higher aliphatic C–H content, consisting of labile groups that are easily evolved when heated (Cheng et al., 2017). Moreover, this stage occurs over a wider range of temperatures than in the rest of the coals studied. The second stage (ca. 500 °C), is attributed to the release of secondary gases resulting from the condensation of aromatic rings and the decomposition of mineral matter (Han et al., 2016).

3.1. Kinetic parameters

Table 7 collects the kinetic parameters and correlation coefficients obtained by applying Eq (3). Figure 4 shows as an example the pyrolysis mechanism of coal LV1 and the lignite.

The kinetic parameters were calculated in the temperature range from 146-180 °C to 900 °C, which represents the main region of devolatilization. The square of the correlation coefficient is always higher than 0.90, indicating that the corresponding independent first-order reaction model fits well to the experimental data.

The pyrolysis of coal is a complex process which involves the rupture of different types of chemical bonds with different energies. The whole process can be divided into four regions. At $T < 140$ °C, any water is removed and the activation energy is very low.

Consequently, this stage was not considered when calculating the kinetic parameters. In the following stage, Stage I, at temperatures between 146 °C-180 °C and 323 °C-551 °C, gas starts to be released in the form of CO₂, H₂ and other lower molecular weight hydrocarbons. A comparison of all the samples shows that the activation energy is low and almost constant, ranging from 35 to 51 kJ/mol for coals L and MV3, respectively.

Stage II which ranges from 324 °C-552 °C to 502 °C-660 °C is the key step in the pyrolysis process as all the coals suffer the highest mass loss with the breakdown of complex organic molecules. The chemical reactions involved include: the rupture of C-C bonds and aromatic side-chains, aromatic condensation and dehydrogenation, the ring opening reaction of cycloalkane and the decomposition of long chain alkanes. The main volatile products released are condensable and non-condensable gas and light hydrocarbons. In addition, during this stage, the bituminous coals pass through the plastic stage. The activation energy increases with respect to the previous stages and the values obtained range from 245 kJ/mol for coal A to 86 kJ/mol for coal L.

In Stage III, from 503 °C-661 °C to 900 °C, the activation energy is again very low (around 50 kJ/mol). During this step, coal evolves CO, non-condensable hydrocarbons and H₂ due to ring condensation. Most of the stable bonds have broken and therefore, less activation energy is required for decomposition.

To calculate the total activation energy of each sample (E_T), the following equation, involving the activation energy of each independent step, was used (Cumming, 1984) :

$$E_T = \sum_{i=1}^{i=3} F_i E_i$$

where E_i is the individual activation energy value obtained in each corresponding stage of Arrhenius linearity and F_i is the weight fraction of the coal pyrolyzed during each stage, expressed as:

$$F_i = (m_a - m_b) / (m_0 - m_f)$$

where m_a and m_b are the mass of the sample at the beginning and at the end of each stage, respectively.

The total activation energy, for all the coals studied is between 138 and 73 kJ/mol (Table 7). These values agree with those found for similar coals by other authors (Sarwar et al., 2012; Zhang et al., 2013). It can be observed that there is a direct relationship between E_T and the coal rank ($R^2=0.941$). This behavior agrees with the tendency of E_2 and $\ln A$ calculated from Stage II (Figure 5), which is the most important stage of the pyrolysis.

In light of the relationship between the VM and the maceral composition (Figure 1), E_a must be related to petrographic composition. The presence of vitrinite corresponds to high values of E_a (Table 2 and Table 7). This agrees with changes in the elemental composition of the vitrinite from lignite to anthracite, as reflected by the increase in aromaticity and the loss of aliphatic and oxygen containing structures (Chen et al., 2012). On the other hand, a high liptinite content is associated with bituminous coals of low rank and a low E_a (Table 2 and Table 7) which agrees with the low aromaticity and high long-chain aliphatic compounds that make liptinite the most thermally unstable maceral.

Figure 6 shows the relationship between the kinetic parameters (activation energy and pre-exponential factor) usually referred to as the “isokinetic effect” that has been widely reported to take place in coal pyrolysis (Alonso et al., 2001; Liu et al., 2017). When dealing with reactions in gas phase, the kinetic theory of gases attributes the pre-exponential factor to the frequency of collisions between reactant molecules. The process

of coal pyrolysis comprises a set of complex thermal reactions, starting with the molecular breakdown of large molecules which are in a vibrational state inside the coal matrix. Therefore, if one draws a parallel with the kinetic theory of gases, it can be assumed that the pre-exponential factor in the pyrolysis process is related to the vibration frequency at which the rupture of the molecules takes place. An increase in coal rank implies that the condensation and cross-linking of aromatic clusters also increases, resulting in a higher molecular ordering. Consequently, the higher the rank of a coal is, the greater its structural ordering and, as a consequence, a higher vibrational frequency is needed for pyrolysis to take place. This association, which is based on the assumption indicated above, explains the direct relation between the pre-exponential factor and the rank observed in [Figure 5](#). On the other hand, molecular structures that need high vibrational frequencies to break down will also require high activation energies to induce a vibrational state and this is presumably the cause of the compensation effect observed in [Figure 6](#). This hypothesis is similar to that of the enthalpy-entropy compensation that associates the decrease in enthalpy (exothermic changes) with tauter bonding and consequently with less entropy (freedom of movement) (Benson, 1976).

In the present study, all the kinetic data points for coals with a $T_{\max}$ range of 415 °C to 483 °C ([Table 6](#)) follow closely the linear relationship between $\ln A$ and E_2 observed in [Figure 6](#) except for anthracite, which also has a significantly higher $T_{\max}$ value (618 °C). It must be remembered that the pyrolysis process is not just one process that can be represented by a single value of activation energy, but rather a combination of competing reactions that display different values of homogeneously distributed activation energy. According to Marbán and Cuesta (Marbán and Cuesta, 2001), activation energies at the low-end of the distribution would appear preferentially at DTG peaks with comparatively low values of $T_{\max}$, and conversely activation energies at the high-end of

the distribution would appear at the DTG peaks corresponding to the higher $T_{\max}$ values, as in the case of anthracite, which deviates from the trend observed in Figure 6.

Differences in the chemical structure due to coal rank will affect the pyrolysis reactivity of coals. In fact, several factors affect the reactivity of a coal during the pyrolysis process. One factor which has positive effect on pyrolysis reactivity is the presence of long aliphatic chains and bridge bonds which is related to a high CH_2/CH_3 index. On the other hand, a factor that has a negative impact on pyrolysis reactivity is the presence of a large proportion of highly condensed aromatic compounds, i.e. a relatively high content in aromatic to aliphatic hydrogen (-high AR1 and AR2 indices-) and low aromatic C=C bonds (-high DOC1 and DOC2 indices-). With the combination of both the positive and negative factors just mentioned, the Infrared Reactivity Index (IRI) can be defined, as follows:

$$\text{IRI} = (\text{CH}_2/\text{CH}_3) / (\text{AR1} + \text{DOC1} + \text{DOC2})$$

As Figure 7 shows, there is a good correlation between the IRI and the activation energy values. That is, the larger the IRI values are, the lower the E_a and the higher the pyrolysis reactivity are. It can be seen that in the case of the high rank bituminous coals, the presence of aromatic compounds of high macromolecular size, which contributes negatively to pyrolysis reactivity, gives rise to high E_a values and to low IRI values. On the other hand, the low rank bituminous coals are characterized by high IRI values, due to the presence of aliphatic compounds whose bonds are easier to break, and therefore they require a lower energy of activation.

Another important factor to be taken into account is coal plasticity. Bonds between different molecules must first be broken to pass from a solid to a liquid state and after further heating to pass back from a liquid to solid state again. Logically, a certain amount of the calculated activation energy will be required to bring about these physical changes.

For this reason, a relationship has been established between the Gieseler maximum fluidity and the E_a , for the bituminous coals used in the present research work (Figure 8). As the plastic range (T_r - T_s) is always inside Stage II, the relationship established is valid only over the limited range of temperatures corresponding to Stage II. Figure 8 shows that a decrease in $\ln MF$ is accompanied by high E_2 values. It seems reasonable to assume that as the plasticity decreases, the viscosity increases and so the pyrolysis process needs a higher activation energy. The plastic behavior of bituminous coals is dependent on coal structure. The co-presence of small aliphatic compounds with high amounts of transferable hydrogen that stabilize cleaved fragments contributes to a high fluidity. Low volatile bituminous coals, or high rank coals with a high E_a , have large macromolecular compounds and an insufficient aliphatic character that inhibit plasticity. Conversely, in the case of low rank bituminous coals, the presence of small aromatic compounds and branched aliphatic compounds, which cleave easily, to produce a high concentration of transferable hydrogen, increases fluidity in agreement with the low E_a values obtained for low rank coals.

By focusing on the parameters derived from the thermal analysis, a relationship between the thermal events during pyrolysis and E_a can be established. In the case of bituminous coals, as the activation energy increases, the decomposition temperature range (T_f - T_i) also increases, devolatilization proceeds at a higher temperature (a higher T_{max}) and thermal decomposition occurs at a slower rate (a lower DTG_{max}) (Table 7). As mentioned before, by increasing the coal rank, the compounds become more thermally stable. Consequently, the pyrolysis requires a higher E_a and takes place at a higher temperature. In the case of lignite, devolatilization proceeds at a slower rate and over a broader range of temperatures, due to the large amount of aliphatic and small cross-linked oxygen compounds.

Given that the reactions which affect the E_a values most occur during Stage II, corresponding to the interval from 324 °C-552 °C to 502 °C-660 °C, it is worthwhile to calculate the amount of volatile matter released by each coal in this temperature range. The results obtained, normalized up to 100 %, are shown in Table 7. It can be seen that the amount of volatile matter released in Stage II decreases with the increase in E_2 (Figure 9). Once again, the point corresponding to anthracite diverges from the regression line, due to its structure and pyrolysis behavior, which differs from that of the bituminous coals.

This result correlates with the fact that for coals with a low E_a and highly reactive species, the release of volatile matter is more drastic and intense, whereas, the devolatilization process in coals that require a high E_a , is much milder and more enduring and the volatile matter released contains a large amount of high molecular weight compounds.

4. Conclusions

It has been demonstrated that the kinetic parameters -the activation energy of Stage II (E_2) and the pre-exponential factor- of the samples studied exhibit a “kinetic compensation effect” which is not statistically related.

These kinetic parameters correlate not only with rank but also with: (i) the Infrared Reactivity Index, which integrates various structural indices associated with coal chemical structure; (ii) the Gieseler maximum fluidity in the case of coals that pass through a plastic stage and (iii) the amount of volatile matter released in Stage II, when coals experience the greatest loss of mass.

The highest activation energy during pyrolysis corresponded to anthracite (138 kJ/mol), whereas lignite had the lowest (73 kJ/mol). In the case of the bituminous coals

364 Ea varied between 117 and 97 kJ/mol. The values obtained are dependent on the chemical
365 structure of each coal which in turn determines pyrolysis reactivity.

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References

- Alonso, M.J.G., Alvarez, D., Borrego, A.G., Menéndez, R., Marbán, G., 2001. Systematic effects of coal rank and type on the kinetics of coal pyrolysis. *Energy Fuels* 15, 413–428. <https://doi.org/10.1021/ef000170x>.
- Alonso, M.J.G., Alvarez, D., Borrego, A.G., Menéndez, R., Marbán, G., 2001b. Systematic effects of coal rank and type on the kinetics of coal pyrolysis. *Energy Fuels* 15, 413–428. <https://doi.org/10.1021/ef000170x>.
- Arenillas, A., Rubiera, F., Pevida, C., Pis, J.J., 2001. A comparison of different methods for predicting coal devolatilisation kinetics. *J. Anal. Appl. Pyrolysis* 58–59, 685–701. [https://doi.org/10.1016/S0165-2370\(00\)00183-2](https://doi.org/10.1016/S0165-2370(00)00183-2).
- Barriocanal, C., Díez, M.A., Alvarez, R., Casal, M.D., Canga, C.S., 2003. On the relationship between coal plasticity and thermogravimetric analysis. *J. Anal. Appl. Pyrolysis* 67, 23–40. [https://doi.org/10.1016/S0165-2370\(02\)00012-8](https://doi.org/10.1016/S0165-2370(02)00012-8).
- Benson, S.W., 1976. Thermochemical kinetics: methods for the estimation of thermochemical data and rate parameters. Wiley.
- Borrego, A.G., Marbán, G., Alonso, M.J.G., Álvarez, D., Menéndez, R., 2000. Maceral effects in the determination of proximate volatiles in coals. *Energy Fuels* 14, 117–126. <https://doi.org/10.1021/ef990050t>.
- Casal, M.D., Canga, C.S., Díez, M.A., Alvarez, R., Barriocanal, C., 2005. Low-temperature pyrolysis of coals with different coking pressure characteristics. *J. Anal. Appl. Pyrolysis* 74, 96–103. <https://doi.org/10.1016/j.jaap.2004.10.012>.
- Chen, Y., Mastalerz, M., Schimmelmann, A., 2012. Characterization of chemical functional groups in macerals across different coal ranks via micro-FTIR spectroscopy. *International Journal of Coal Geology* 104, 22–33. <https://doi.org/10.1016/j.coal.2012.09.001>.

400 Cheng, J., Zhang, Y., Wang, T., Norris, P., Chen, W.-Y., Pan, W.-P., 2017.
 401 Thermogravimetric-Fourier Transform Infrared Spectroscopy-Gas
 402 Chromatography/Mass Spectrometry Study of Volatile Organic Compounds from Coal
 403 Pyrolysis. *Energy Fuels* 31, 7042–7051.
 404 <https://doi.org/10.1021/acs.energyfuels.7b01073>.
 405 Cumming, J.W., 1984. Reactivity assessment of coals via a weighted mean activation
 406 energy. *Fuel* 63, 1436–1440. [https://doi.org/10.1016/0016-2361\(84\)90353-3](https://doi.org/10.1016/0016-2361(84)90353-3).
 407 Díaz-Faes, E., Barriocanal, C., Díez, M.A., Alvarez, R., 2007. Characterization of
 408 different origin coking coals and their blends by Gieseler plasticity and TGA. *J. Anal.*
 409 *Appl. Pyrolysis* 80, 203–208. <https://doi.org/10.1016/j.jaap.2007.02.008>.
 410 Diessel, C.F.K., 1983. Carbonization reactions of inertinite macerals in Australian coals.
 411 *Fuel* 62, 883–892. [https://doi.org/10.1016/0016-2361\(83\)90154-0](https://doi.org/10.1016/0016-2361(83)90154-0).
 412 Díez, M.A., Alvarez, R., Barriocanal, C., 2002. Coal for metallurgical coke production:
 413 Predictions of coke quality and future requirements for cokemaking. *Int. J. Coal Geol.* 50,
 414 389–412. [https://doi.org/10.1016/S0166-5162\(02\)00123-4](https://doi.org/10.1016/S0166-5162(02)00123-4).
 415 Epshtein, S.A., Kossovich, E.L., Kaminskii, V.A., Durov, N.M., Dobryakova, N.N.,
 416 2017. Solid fossil fuels thermal decomposition features in air and argon. *Fuel* 199, 145–
 417 156. <https://doi.org/10.1016/j.fuel.2017.02.084>.
 418 Gao, Z., Zheng, M., Zhang, D., Zhang, W., 2016. Low temperature pyrolysis properties
 419 and kinetics of non-coking coal in Chinese western coals. *J. Energy Inst.* 89, 544–559.
 420 <https://doi.org/10.1016/j.joei.2015.07.002>.
 421 Geng, C., Li, S., Yue, C., Ma, Y., 2016. Pyrolysis characteristics of bituminous coal. *J.*
 422 *Energy Inst.* 89, 725–730. <https://doi.org/10.1016/j.joei.2015.04.004>.

423 Han, F., Meng, A., Li, Q., Zhang, Y., 2016. Thermal decomposition and evolved gas
 424 analysis (TG-MS) of lignite coals from Southwest China. *J. Energy Inst.* 89, 94–100.
 425 <https://doi.org/10.1016/j.joei.2015.01.007>.

426 Iglesias, M.J., Jiménez, A., Laggoun-Défarge, F., Suárez-Ruiz, I., 1995. FTIR Study of
 427 Pure Vitrains and Associated Coals. *Energy Fuels* 9, 458–466.
 428 <https://doi.org/10.1021/ef00051a010>.

429 Liu, J., Ma, J., Luo, L., Zhang, H., Jiang, X., 2017. Pyrolysis of superfine pulverized coal.
 430 Part 5. Thermogravimetric analysis. *Energy Convers. Manag.* 154, 491–502.
 431 <https://doi.org/10.1016/j.enconman.2017.11.041>.

432 Liu, Q., Hu, H., Zhou, Q., Zhu, S., Chen, G., 2004. Effect of inorganic matter on reactivity
 433 and kinetics of coal pyrolysis. *Clean Coal Technol.* 83, 713–718.
 434 <https://doi.org/10.1016/j.fuel.2003.08.017>.

435 Loison, R., Foch, P., Boyer, A., 1989. *Coke: Quality and Production*. Elsevier, London.

436 Marbán, G., Cuesta, A., 2001. On the cause of deviation of arrhenius-parameters from the
 437 isokinetic trend in carbon gasification reactions. *Energy Fuels* 15, 764–766.
 438 <https://doi.org/10.1021/ef000145r>.

439 Menéndez, J.A., Pis, J.J., Alvarez, R., Barriocanal, C., Fuente, E., Díez, M.A., 1996.
 440 Characterization of petroleum coke as an additive in metallurgical cokemaking.
 441 Modification of thermoplastic properties of coal. *Energy Fuels* 10, 1262–1268.
 442 <https://doi.org/10.1021/ef960091e>.

443 Mui, E.L.K., Cheung, W.H., Lee, V.K.C., McKay, G., 2010. Compensation effect during
 444 the pyrolysis of tyres and bamboo. *Waste Manag.* 30, 821–830.
 445 <https://doi.org/10.1016/j.wasman.2010.01.014>.

446 Naidu, V.S., Aghalayam, P., Jayanti, S., 2016. Evaluation of CO₂ gasification kinetics
 447 for low-rank Indian coals and biomass fuels. *J. Therm. Anal. Calorim.* 123, 467–478.
 448 <https://doi.org/10.1007/s10973-015-4930-4>.
 449 Niu, Z., Liu, G., Yin, H., Zhou, C., Wu, D., Yousaf, B., Wang, C., 2016. In-situ FTIR
 450 study of reaction mechanism and chemical kinetics of a Xundian lignite during non-
 451 isothermal low temperature pyrolysis. *Energy Convers. Manag.* 124, 180–188.
 452 <https://doi.org/10.1016/j.enconman.2016.07.019>.
 453 Sarwar, A., Nasiruddin Khan, M., Azhar, K.F., 2012. Kinetic studies of pyrolysis and
 454 combustion of Thar coal by thermogravimetry and chemometric data analysis. *J. Therm.*
 455 *Anal. Calorim.* 109, 97–103. <https://doi.org/10.1007/s10973-011-1725-0>.
 456 Slyusarskiy, K.V., Larionov, K.B., Osipov, V.I., Yankovsky, S.A., Gubin, V.E., Gromov,
 457 A.A., 2017. Non-isothermal kinetic study of bituminous coal and lignite conversion in air
 458 and in argon/air mixtures. *Fuel* 191, 383–392. <https://doi.org/10.1016/j.fuel.2016.11.087>.
 459 Song, H., Liu, G., Zhang, J., Wu, J., 2017. Pyrolysis characteristics and kinetics of low
 460 rank coals by TG-FTIR method. *Fuel Process. Technol.* 156, 454–460.
 461 <https://doi.org/10.1016/j.fuproc.2016.10.008>.
 462 Toloue Farrokh, N., Askari, M., Fabritius, T., 2017. Investigation of Tabas anthracite coal
 463 devolatilization: Kinetics, char structure and major evolved species. *Thermochim. Acta*
 464 654, 74–80. <https://doi.org/10.1016/j.tca.2017.05.015>.
 465 van Heek, K.H., Hodek, W., 1994. Structure and pyrolysis behaviour of different coals
 466 and relevant model substances. *Coal Struct.* 92 73, 886–896.
 467 [https://doi.org/10.1016/0016-2361\(94\)90283-6](https://doi.org/10.1016/0016-2361(94)90283-6).
 468 Xu, Y., Zhang, Y., Zhang, G., Guo, Y., Zhang, J., Li, G., 2015. Pyrolysis characteristics
 469 and kinetics of two Chinese low-rank coals. *J. Therm. Anal. Calorim.* 122, 975–984.
 470 <https://doi.org/10.1007/s10973-015-4801-z>.

471 Yangali, P., Celaya, A.M., Goldfarb, J.L., 2014. Co-pyrolysis reaction rates and
472 activation energies of West Virginia coal and cherry pit blends. *J. Anal. Appl. Pyrolysis*
473 108, 203–211. <https://doi.org/10.1016/j.jaap.2014.04.015>.
474 Zhang, L., Hower, J.C., Liu, W., 2016. Devolatilization and kinetics of maceral
475 concentrates of bituminous coals. *Fuel Process. Technol.* 154, 147–155.
476 <https://doi.org/10.1016/j.fuproc.2016.08.026>.
477 Zhang, S., Zhu, F., Bai, C., Wen, L., Zou, C., 2013. Thermal behavior and kinetics of the
478 pyrolysis of the coal used in the COREX process. *J. Anal. Appl. Pyrolysis* 104, 660–666.
479 <https://doi.org/10.1016/j.jaap.2013.04.014>.
480

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.

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.

Table 3. Definition of the semi-quantitative indices derived from the DRIFT spectra (Chen et al., 2012a; Menéndez et al., 1996).

Semi-quantitative index	Index calculation	Band region (cm ⁻¹)
Aromaticity 1 (AR1)	CHar stretching/CHal stretching	A(3000-3100)/A(2800-3100) ^a
Aromaticity 2 (AR2)	CHar out of plane/CHal stretching	A(700-900)/A(2800-3100) ^a
Degree of condensation 1 (DOC1)	CHar stretching/C=C stretching	A(3000-3100)/A1600 ^a
Degree of condensation 1 (DOC2)	CHar out of plane/C=C stretching	A(700-900)/A1600 ^a
Methylene to methyl ratio	CH ₂ /CH ₃	A1445/A1375 ^a

^a Area

Table 4. DRIFTS indices for the bituminous coals.

Coal	AR1	AR2	DOC1	DOC2	CH ₂ /CH ₃
LV1	0.37	0.57	0.65	0.96	13.18
LV2	0.34	0.64	0.50	0.93	13.49
LV3	0.38	0.64	0.65	1.07	14.90
LV4	0.35	0.69	0.50	1.00	14.74
MV1	0.28	0.60	0.41	0.88	14.17
MV2	0.25	0.47	0.39	0.75	17.10
MV3	0.26	0.47	0.42	0.76	18.95
MV4	0.27	0.58	0.43	0.93	18.07
HV1	0.19	0.44	0.28	0.66	19.31
HV2	0.15	0.37	0.14	0.36	24.76
HV3	0.17	0.45	0.25	0.66	25.83

Table 5. Gieseler parameters of the coals.

Coal	Ts (°C) ^a	Tf (°C) ^b	Tr (°C) ^c	Tr – Ts (°C) ^d	MF (ddpm) ^e
LV1	459	474	498	39	1.8
LV2	450	477	495	45	8
LV3	445	475	502	57	44
LV4	440	470	491	51	8
MV1	434	464	494	60	89
MV2	417	458	494	77	672
MV3	402	455	494	92	1642
MV4	414	452	486	72	631
HV1	401	441	473	72	816
HV2	393	438	472	79	3184
HV3	394	436	473	79	5061

^a Softening temperature, defined as the temperature at which the stirrer starts to rotate.

^b Maximum fluidity temperature.

^c Resolidification temperature, defined as the temperature at which the stirrer stops rotating.

^d Plastic range.

^e Maximum fluidity expressed in dial divisions per minute (ddpm).

Table 6. Parameters derived from the thermogravimetric analysis of the coals performed at 3 °C/min.

Coal	Ti(°C) ^a	Tf(°C) ^b	Tf-Ti(°C)	DTGmax (%min ⁻¹) ^c	Tmax (°C) ^d	CY(%) ^e
A	348	1000	652	0.05	618	93.5
LV1	359	903	544	0.35	483	80.9
LV2	357	890	533	0.35	484	80.9
LV3	360	888	528	0.40	486	80.3
LV4	368	951	583	0.40	477	78.3
MV1	349	849	500	0.47	477	77.6
MV2	345	807	462	0.56	466	74.9
MV3	358	849	491	0.57	467	74.4
MV4	345	800	455	0.63	461	73.2
HV1	346	878	532	0.83	445	66.5
HV2	343	773	430	0.89	446	66.7
HV3	324	757	433	0.85	446	67.3
L	302	915	613	0.52	415	62.2

^a Temperature at 5 % conversion.

^b Temperature at 95 % conversion.

^c Maximum rate of volatile matter evolution.

^d Temperature of maximum volatile matter release.

^e Coke yield at 1000 °C.

Table 7. Kinetic parameters obtained for the pyrolysis of the coals.

Coal	T (°C)	E _i (kJ/mol)	Ln A	R ²	E _T (kJ/mol)	VM (% , daf)
A	180-551	43	3.1	0.9483	138	41.6
	552-660	245	30.8	0.9904		53.6
	661-900	53	2.2	0.9737		19.4
LV1	166-402	39	4.2	0.9745	117	8.5
	403-536	177	25.7	0.9819		55.2
	537-900	56	2.9	0.968		42.5
LV2	158-402	41	4.6	0.9713	116	9.6
	403-536	172	24.8	0.9831		58.4
	537-900	57	3.2	0.9655		42.7
LV3	166-402	41	4.5	0.9765	119	8.4
	403-536	174	25.1	0.9932		56.9
	537-900	58	3.4	0.9644		39.9
LV4	157-398	46	5.6	0.9793	114	8.7
	399-535	165	23.8	0.9886		59.1
	536-900	54	2.6	0.9555		38.9
MV1	153-382	43	5.3	0.9729	112	8.4
	383-521	161	23.6	0.989		62.3
	522-900	52	2.6	0.9572		39.5
MV2	151-360	44	5.8	0.9779	106	6.7
	361-514	142	20.7	0.9888		67.4
	515-900	51	2.5	0.9422		35.2
MV3	154-355	51	7.1	0.9842	104	5.4
	356-515	137	19.8	0.9897		68.9
	516-900	49	2.2	0.9474		34.6
MV4	151-360	44	5.7	0.9787	110	6.4
	361-514	146	21.3	0.9927		66.2
	515-900	55	3.0	0.9491		32.9
HV1	148-332	42	5.9	0.9690	102	4.3
	333-502	134	19.9	0.9920		70.3
	503-900	43	1.4	0.9359		0.3
HV2	150-326	46	6.6	0.9707	101	3.8
	327-514	123	17.8	0.9887		77.8
	515-900	48	2.2	0.9528		27.4
HV3	146-326	44	6.3	0.9701	97	5.5
	327-514	117	16.9	0.9896		77.3
	515-900	49	2.3	0.9505		24.7
L	158-323	35	4.3	0.9587	73	7.8
	324-534	86	11.3	0.9496		82.9
	535-900	57	3.0	0.9354		37.3

Figure 1. Relationship between the calculated volatile matter ($VM_{\text{calcd}} = \phi_V(R_o) \cdot X_V + \phi_L(R_o) \cdot X_L + \phi_I(R_o) \cdot X_I$) and the experimental (proximate) volatile matter.

Figure 2. DRIFT spectra of L, HV3, MV3, LV1 and A coals.

Figure 3. DTG curves corresponding to A, LV2, LV3, MV2, MV4, HV1, HV2, and L coals.

Figure 4. Plot of $\text{Ln}(-\text{Ln}(1-X)/T^2)$ against $1/T$ for coals LV1 and L.

Figure 5. Relationship between the volatile matter content (VM) and the activation energy (E_2) calculated from Stage II and $\ln A$.

Figure 6. Linear dependency between LnA and E_2 calculated from Stage II, for all the coals studied.

Figure 7. Relationship between the activation energy calculated from Stage II (E_2) and the Infrared Reactivity index, IRI, $(CH_2/CH_3)/(AR1+DOC1+DOC2)$.

Figure 8. Relationship between the activation energy calculated from Stage II (E_2) and the Ln of the Gieseler maximum fluidity (MF).

Figure 9. Relationship between the activation energy calculated from Stage II (E_2) and the amount of volatile matter released in Stage II and normalized up to 100%.