

Thermokinetic analysis of the decomposition of Ukrainian coals from the Donetz Basin

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Abstract. Thermogravimetry was applied to the investigation of Donetz bituminous coals formed under low-reduced (LRC) and reduced (RC) conditions. Thermokinetic analysis has demonstrated that thermal decomposition of the RC coal samples proceeds more intensely than for the LRC samples.

Key words: coal genetic type, low-reduced coal (LRC), reduced coal (RC), thermogravimetry

Introduction

It is well known that the properties of coal depend on its genetic type, rank level, and petrographic composition. One of the most important genetic features of coal is its susceptibility to vitrinite reduction. This property has rarely been investigated and consequently has not been adequately described. However, this does not affect the International Coal Classification. The reductivity of vitrinite depends on the facies to which the coal belongs. Coal facies can be described as alluvial or marine, where deposits are laid down in swamp lakes, ponds, rivers, or seas.

Coals deposited in brackish marine areas are characterized by distinct properties: high proportions of hydrogen, nitrogen, and sulphur, and the presence of fine crystalline pyrite concretions (Teichmüller 1974, Matsenko 1984, Volkova and Bogdanova 1989; Marinov et al. 2000a; Marinov et al. 2000b). The structure and reactivity of these coals have not yet been thoroughly studied because their high sulphur content is a serious problem for their utilisation. This is also a problem for Donetz Basin coals, which are associated with polyfacies deposits.

In earlier studies, pyrolysis in water vapour at atmospheric pressure (Minkova et al. 1991) was applied to the investigation of Donetz coals of different genetic types by reductivity. It has been shown that ether -O- and thioether -S- bonds dominate in the reduced coals (RC) and in semi-cokes prepared from such samples, i.e. they have interconnected structures that correspond to the agglutinate material. In contrast, the aforementioned bonds are destroyed during the heating of low reduced coals (LRC), while semi-cokes with high values of specific surface area (adsorbents) are formed (Marinov et al. 2000a).

The purpose of the present paper is a detailed study of the kinetics of RC and LRC coals during pyrolysis, through the use of thermogravimetry. We further wish to elucidate the utility of thermokinetic analysis for the determination of coal genetic type.

Materials and methods

Samples of reduced and low reduced coals were collected from neighbouring coal seams of the Donetz Basin (the distances between which were less than 100 m). Coal reductivity was estimated by inspecting the seam roof character. The content of finely crystalline pyrite in the coal samples was also determined. The petrographic, proximate and ultimate analysis of the samples, including the total (S_t), organic (S_o), pyritic (S_p), and sulphate (S_s) sulphur were determined according to standard procedures. A selective catalytic decomposition was applied to determine the proportion of non-thiophenic sulphur (S_{n-t}) (Marinov et al. 2000b).

Thermogravimetric analyses were performed in an OD-103 Derivatograph. The initial weight of the sample was close to 300 mg, and the heating rate was 10 K · min⁻¹ under an argon atmosphere (flow rate 2.6 cm³ · s⁻¹). Platinum crucibles with covers were used. The samples were heated from ambient temperature to 1073 K. Temperatures and mass losses were recorded as TG and DTG curves on light-sensitive paper.

Two types of thermokinetic models were used for this analysis:

1. a kinetic and diffusion model (Mianowski and Radko 1995, Radko and Mianowski 1998) used for determining the Arrhenius equation parameters in the conventional kinetic and diffusion area,
2. a three-parameter model (Mianowski 2000, 2001).

This comparative analysis makes use of the following assumptions:

The value of the average reaction rate is calculated as:

$$\bar{k} = \frac{A}{T_f - T_i} \int_{T_i}^{T_f} \exp\left(-\frac{E}{RT}\right) dT \quad (1)$$

After integrating (Błażejowski 1984), this can be formed into:

$$\bar{k} = \frac{AR}{E(T_f - T_i)} \left[T_f^2 \exp\left(-\frac{E}{RT_f}\right) - T_i^2 \exp\left(-\frac{E}{RT_i}\right) \right]$$

The value of the average reaction rate is calculated for the temperature of maximum reaction rate (T_m), according to the standard Arrhenius equation:

$$k_m = A \exp\left(-\frac{E}{RT_m}\right) \quad (3)$$

The variation of the a_2 coefficient and the $\frac{a_1}{a_2} = T^*$ ratio is given by a three-parameter equation:

$$\ln \alpha = a_0 - \frac{a_1}{T} - a_2 \ln T \quad 0 < \alpha \leq 1, a_2 > 0 \quad (4)$$

depending upon the assumed c value ($c \in [0.5, 1.0]$), which limits the range of the conversion degree analysed $0 \leq \alpha < c$.

From equation (4) the relative ratio of the thermal decomposition results in the following form (Mianowski 2001):

$$r = \frac{d\alpha}{\alpha dT} T^2 = \frac{-DTG}{m_i - TG} T^2 = a_1 - a_2 T \quad (5)$$

This equation was also used for the comparison of the LRC and RC pyrolysis processes.

The characteristics of the two types of coals tested are shown in Tables 1 and 2. As can be seen from Table 1, the samples of reduced coals indicate higher total sulphur contents, H/C ratios, and yields of volatile matter than the low reduced coals corresponding to the same degree of coalification.

The petrographic composition of the coals is uniform, and a predominant proportion of vitrinite can be observed (Table 2). Lower values of vitrinite reflectance (R_m^o) and higher contents of lithotypes with finely crystalline pyrite are recorded in the RC samples. The organic sulphur S_o is the main form of sulphur for the coals concerned in the present study. However, in all pairs higher S_p^d and S_o^d (including S_{n-t}) contents were determined for reduced coals.

Results and discussion

The thermogravimetric curves of the LRC and RC samples are shown in Fig. 1, while the calculated data for the pyrolysis are gathered in Table 3. It can be seen from Table 3 that kinetic and diffusion models can adequately describe the conventional kinetic range for the LRC coal. However, this model is slightly less appropriate for the RC samples. Comparing the decomposition rates of coals knowing only their activation energy (E) is problematic, particularly without the pre-exponential factor (A). This is why the additional criterion for the reaction rate was assumed in accordance with equation (2) and the Arrhenius equation (3). According to Mianowski and Radko (1993), this value amounts to $k_m \approx 0.2 \text{ min}^{-1}$ for typical bituminous coals from the Upper Silesian Coal Basin. A clear deviation from this value was observed for the RC sam-

Table 1. Characteristics of the studied coals

No.	Coal mine (seam)	Type	W^a	A^d	V^{daf}	C^{daf}	H^{daf}	$\left(\frac{H}{C}\right)^{af}$	$(O + S + N)^{diff}$	S_t^d	S_s^d	S_p^d	S_o^d	S_o^{daf}	S_{n-t}	$\frac{S_{thioph}}{S_{n-t}}$
1	Kurakhovskaya (I ₄)	LRC	9.4	5.3	37.2	79.3	5.07	0.77	15.63	1.04	0.12	0.07	0.85	0.90	0.36	1.36
2	Kurakhovskaya (I ₂)	RC	5.5	8.6	43.0	76.1	5.22	0.82	18.68	5.60	0.02	2.44	3.14	3.43	0.65	3.83

S_{n-t} – non-thiophene, S_o – organic, S_p – pyrite, S_t – total, S_{thioph} – thiophene, S_s – sulfate sulphur

Table 2. Vitrinite reflectance and petrographic composition of the studied coals

No.	Coal mine (seam)	Type	R_m^o %	Petrographic components vol. %			Mineral components vol. %	Lithotype with finely crystalline pyrite vol. %
				Vt	L	I		
1	Kurakhovskaya (I ₄)	LRC	0.66	89	7	4	3	0
2	Kurakhovskaya (I ₂)	RC	0.52	80	9	11	7	63

R_m^o – vitrinite reflectance, Vt – vitrinite, L – liptinite, I – inertinite

Table 3. Thermokinetic parameters for the studied coals^{a)}

No.	Coal mine (seam)	Type	T_i K	T_f K	A min^{-1}	E $\text{kJ} \cdot \text{mole}^{-1}$	r^2 %	$T_m^{b)}$ K	\bar{k} acc. to (2) min^{-1}	k_m acc. to (3) min^{-1}
1	Kurakhovskaya (I ₄)	LRC	658.0	832.2	$8.90 \cdot 10^8$	144.6	99.1	782.6	0.169	0.197
2	Kurakhovskaya (I ₂)	RC	641.9	795.5	$1.97 \cdot 10^{15}$	225.1	97.6	747.2	0.499	0.364

^{a)} concern kinetic range only

^{b)} temperature of maximum reaction/process rate

ples, which indicates that at the temperature of the maximum reaction rate (T_m) the decomposition rate is twice that of typical bituminous coals. This can be explained by the increased sulphur content, especially S_o^d in non-thiophenic form, which is the most unstable of all organic sulphur structures (Marinov et al. 2000). Therefore, the thermal treatment is more effective for coals with higher S_{n-t} contents (Table 1). For reduced coal the harmonised kinetic and diffusion processes run together with the high pyrolysis rate (Fig. 2b). This explains the favourable conditions for the formation of the systematic semi-coke structure (Butuzova 2002).

For investigating the influence of decreasing the thermal conversion degree in the range of

$$0 \leq \alpha < c \text{ where } 0.5 \leq c < 1 \quad (6)$$

for the variation of the parameters in equation (4), we calculated the maximum values of the a_2 coefficient (Fig. 3). Clearly, the thermal decomposition ratio estimated for the RC samples according to the a_2 coefficient value is much higher than that for LRC coal.

In Fig. 4 (Mianowski 2000) we illustrate the dependence of the relative thermal decomposition ratio on temperature according to a three-parameter model (4) for typical bituminous coal. It is observed that the data points group along the straight line of the coefficients (5), which complies with the kinetic range. Next, the coefficient $a_2 = 0$ decays and the points form a line parallel to the temperature axis, while the a_1 in the conventional diffusion range is proportional to the dissociation enthalpy (Mianowski 2001).

A comparison of the temperature dependence of the relative thermal decomposition ratio [according to equation (5)] for the coal samples under analysis (Fig. 5) to the similar dependence for typical coals (Fig. 4) reveals a clear deviation from a straight line (5). This effect is especially distinct for the RC samples. At temperatures above $T^* = 795$ K we observe a calm, which reflects the rapid atrophy of the kinetic range (Fig. 5b).

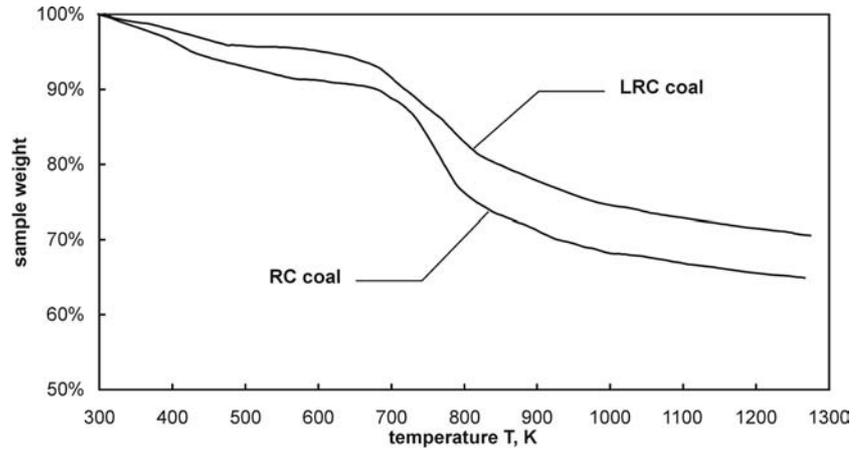


Figure 1. Thermogravimetric curves of the studied coals.

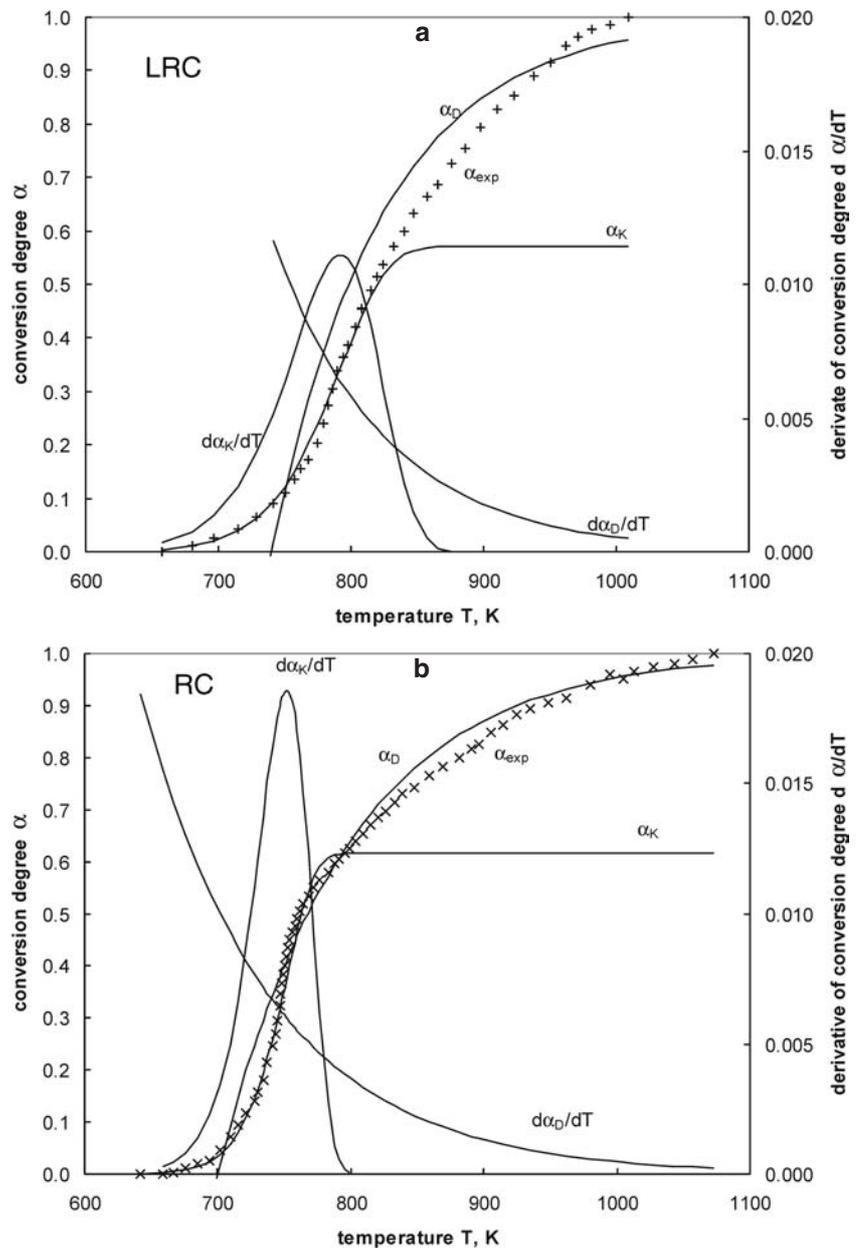


Figure 2. Graph of the kinetic and the diffusion model of thermal decomposition for: a – LRC coal, b – RC coal.

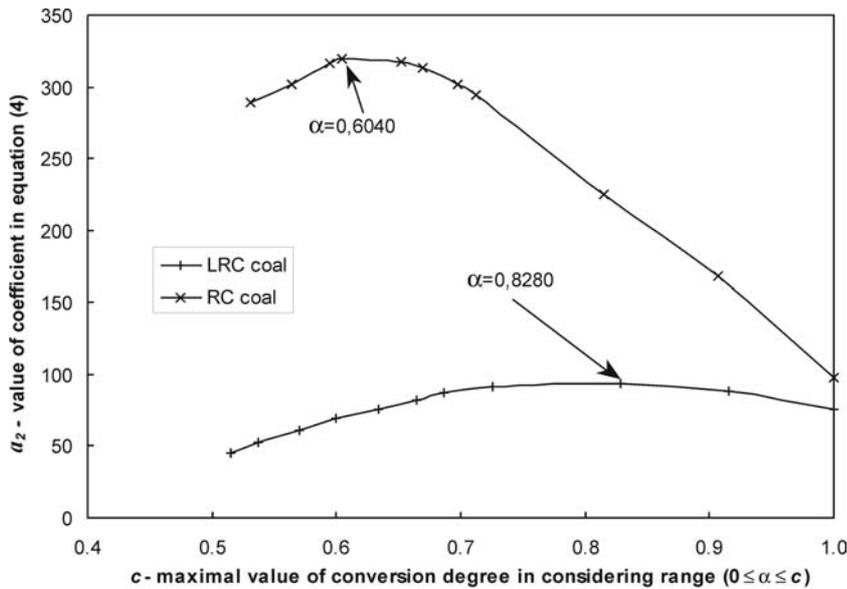


Figure 3. The dependence of the value of a_2 coefficient on the final value of the conversion degree for the studied coals.

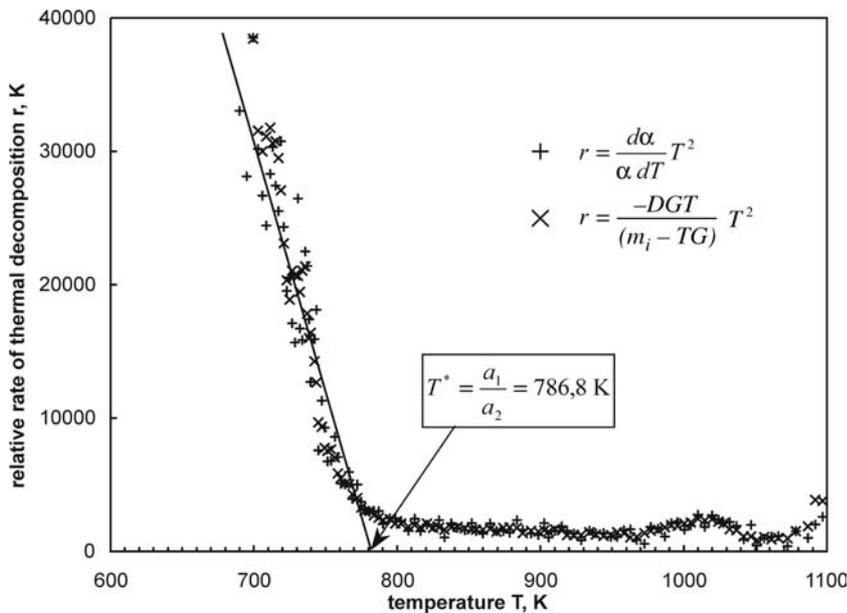


Figure 4. The dependence of the relative thermal decomposition ratio on temperature for typical bituminous coals (Mianowski 2000).

List of symbols

- a_0, a_1, a_2 – coefficients of the three-parameter equation, according to equation (4)
- A – pre-exponential factor, min^{-1}
- c – maximum value of conversion degree in the range $0 \leq \alpha \leq c$
- DTG – first derivative of the TG, $\text{mg} \cdot \text{K}^{-1}$
- E – activation energy, $\text{J} \cdot \text{mole}^{-1}$
- k – decomposition rate constant, min^{-1}
- \bar{k} – integral average rate constant, min^{-1}
- m – mass, mg
- r – relative rate of thermal decomposition, K
- r^2 – determination coefficient, %
- R – universal gas constant, $\text{J} \cdot \text{mole}^{-1} \text{K}^{-1}$ ($R = 8,314 \text{ J} \cdot \text{mole}^{-1} \text{K}^{-1}$)
- T – temperature, K
- T^* – temperature from condition $r = 0$ in equation (5), K
- TG – mass loss form thermogravimetry analysis, mg
- α – conversion degree, $0 \leq \alpha \leq 1$
- subscripts:
 - d – diffusion area
 - f – final state
 - i – initial state
 - k – kinetic area
 - m – maximum reaction rate

Conclusions

The kinetics of the thermal decomposition of isomorphous LRC and RC coal types of distinct elemental compositions (especially regarding sulphur content) are different. Using the thermokinetic approach (with two different models and several estimators) it was demonstrated that the thermal decomposition of the RC samples proceeds more intensely than for the LRC samples. The harmonised kinetic and diffusion processes run together with the high pyrolysis rate for RC coal, favouring the formation of carbonized coals of systematic structure, despite the high process rate. These probably result from the

catalytic effects of pyrite decomposition on the coal pyrolysis process.

It has been shown that equations (4) and (5) can be used for determining a coal’s genetic type. Furthermore, the coefficient a_2 can be used for the efficient scaling of the coal’s thermal decomposition ratio for volatile-rich samples, including those with high sulphur and oxygen contents.

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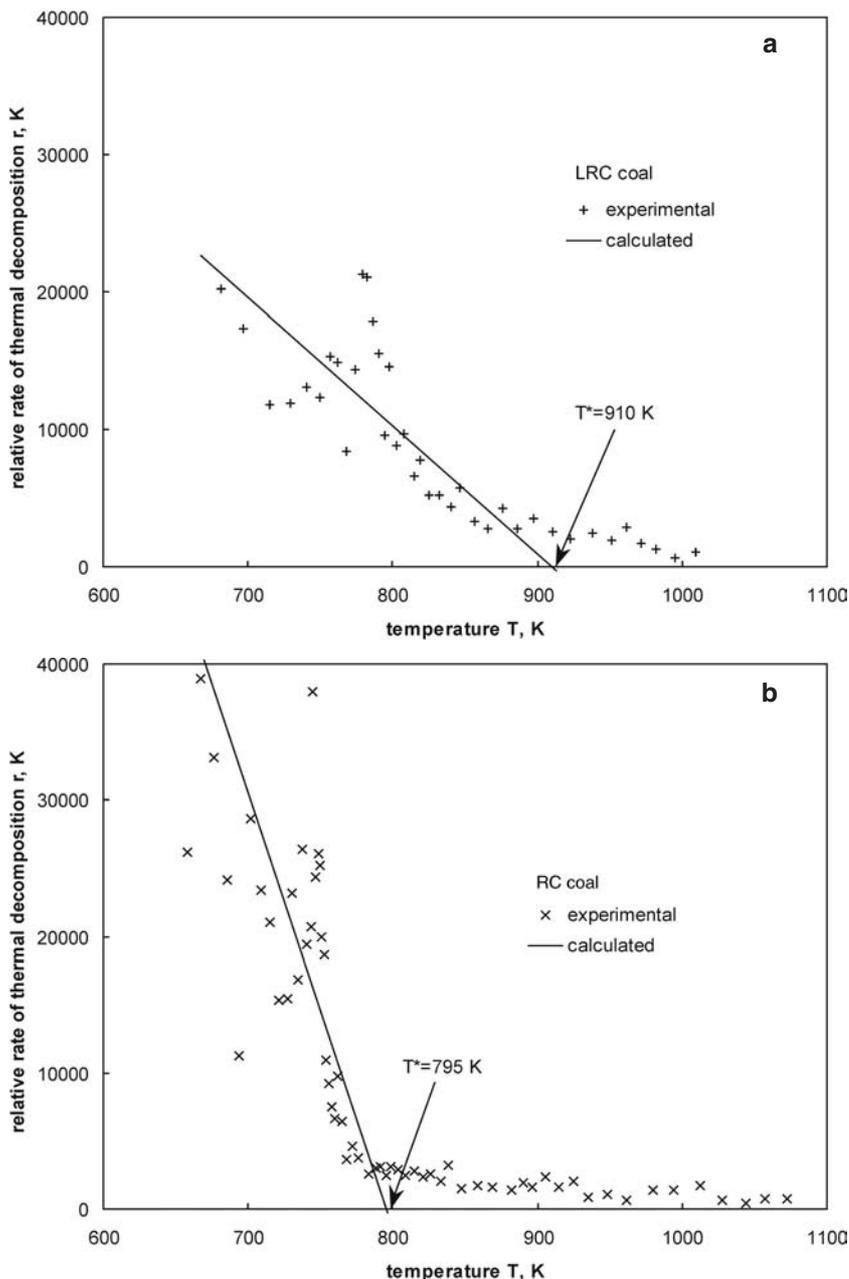


Figure 5. The dependence of the relative thermal decomposition ratio on temperature for: a – LRC coal, b – RC coal.