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THERMOKINETIC ANALYSIS OF COAL PYROLYSIS PROCESS

A. Mianowski and T. Radko

Department of Chemical Technology of Coal and Petroleum of the Silesian Technical University, 44–101 Gliwice, ul. Bolesława Krzywoustego 8, Poland

Abstract

The main problems of the kinetic description of the coal pyrolysis process have been discussed. A few possible methods for estimating the kinetic parameters of the process, on the basis of thermogravimetrical analysis in non-isothermal conditions have been presented.

Keywords: coal pyrolysis, kinetics, TG

Kinetic studies of the coal pyrolysis

Kinetic description of the coal thermal decomposition is possible only if appropriate model for characteristic conversion of the coal into coke is being assumed. This interconversion is determined by the coal quality, thermal conditions in which the process takes place, the method of gaining gaseous and liquid products and many other factors. Figure 1 [1] shows the general scheme of the coal thermal decomposition. Usually in the literature four models are being used to describe the process:

1. single irreversible decomposition reaction

$$\text{coal} \longrightarrow \text{char} + \text{gaseous products}$$

2. consecutive decomposition reactions

$$\begin{tikzcd}
\text{coal} \arrow[r] & \text{metaplast} \arrow[r] & \text{char} \arrow[d] & + & \text{primary volatile matter} \\
 & & \text{coke} & + & \text{secondary volatile matter}
\end{tikzcd}$$

3. two parallel irreversible decomposition reactions

$$\begin{tikzcd}
 & \text{solid residue} + \text{volatile matter} \\
\text{coal} \arrow[ur] \arrow[dr] & \\
 & \text{solid residue} + \text{volatile matter}
\end{tikzcd}$$

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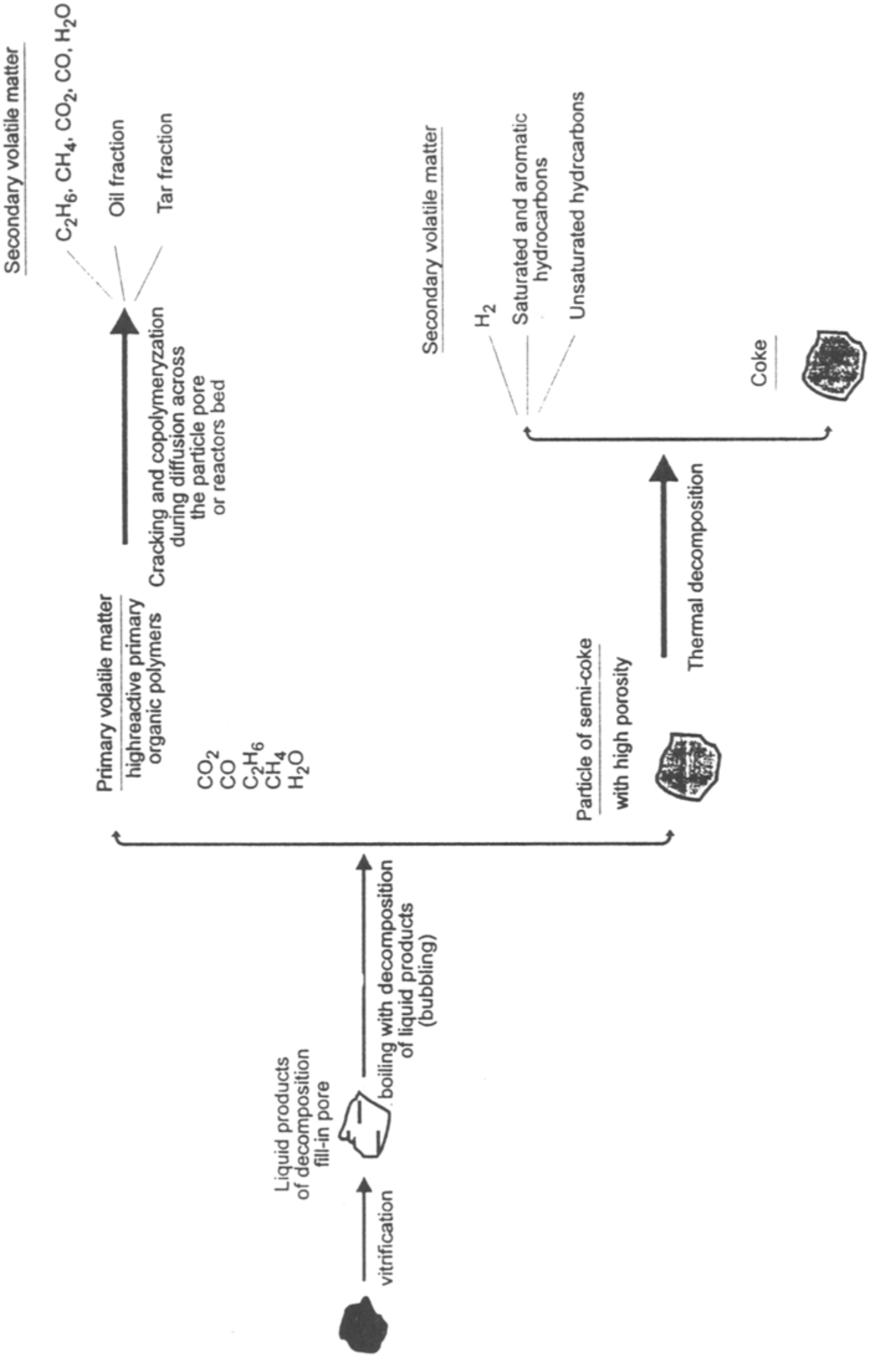
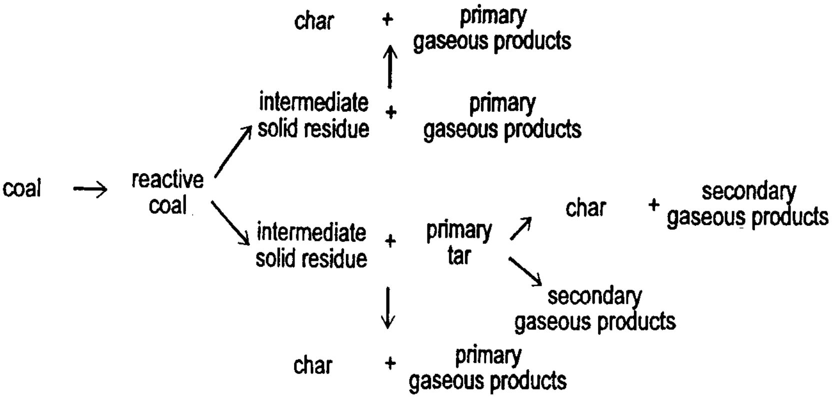


Fig. 1 General scheme of the coal pyrolysis process

4. manifold consecutive and parallel reactions



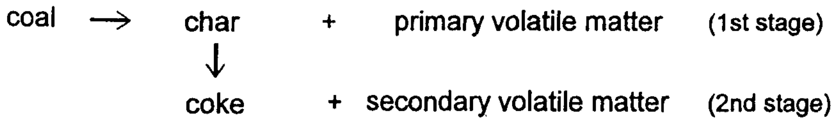
It is worth noticing however, that the more precise is the description of the process the more complex character has its mathematical model.

Two main types of the approaches can be found in the literature. The first one consists in analysing the kinetics of coal pyrolysis on the basis of the individual reaction yielding gaseous or liquid products [2–6]. The kinetic parameters obtained by this procedure are unambiguous, but their technological implementation are limited by the narrow ranges within they are obeyed. Very precise analytical equipment, that is desired in this particular case, poses further problems.

The second approach based on the analysis of the pyrolysis as a 'gross process'. The rate of gaseous products formation, determined by thermobalance is used to measure the reaction rate. Van Krevelen model for isothermal conditions, assuming three stages pyrolysis process [7] should be seen as a typical one coming from this point of view. The model has been developed also by Skliar and co-workers [8, 9]. The kinetics of the first order, in relation to the products formed, was assumed in the above mentioned approaches. Some other results indicated however that coal pyrolysis process can be of the order higher than two (e.g. 3–6.6 [10, 11]).

Basic approach

The general aim of our studies is to perform a kinetic interpretation of the coal thermogravimetrical curves assuming the general pyrolysis model as follows:



We realised that theoretical meaning of the kinetic parameters obtained for such simplified model is limited. Thus for example no possibility of the identification of elementary reaction is offered by the method. We believe however that correlation of the parameters obtained with some technological features determined by standard methods should develop thermogravimetry into a powerful analytical method of carbochemistry.

Assumptions

Our analyses are based on the assumption that in non-isothermal (dynamic) conditions standard Eq. (1) is obeyed:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}=\frac{A}{q}f(\alpha)\,e^{-E/RT} \tag{1}$$

where: $\alpha \in <0,\ 1>$ and q = i d e m > 0

We present here the implementation of two possible solutions of (1), which depending on the weight integrals $g(\alpha)$ forms (2) or (3) respectively [12]:

$$g(\alpha)=\frac{ART^2}{qE}\,e^{-E/RT} \tag{2}$$

or

$$g(\alpha)=\left(\frac{T}{T_m}\right)^2 e^{[E/RT_m(1-T_m/T)]}\,, \qquad A=\frac{qE}{RT_m^2}\,e^{E/RT_m} \tag{3}$$

where:

$$g(\alpha)=\int_0^{\alpha}\frac{\mathrm{d}\alpha}{f(\alpha)} \tag{4}$$

for the evaluation of the kinetic parameters of the pyrolysis process basing on the hard coal thermogravimetric analyses.

Among many works dealing with the analysis of the kinetics of the various processes there are only few using the Eq. (1) to describe hard coal pyrolysis. Besides just mentioned [10, 12] some other examples are given in [13]. The main reason for little interest in the pyrolysis kinetics is the complex nature of the process. The lack of the general scheme of the chemical reactions proceeding and their unknown stoichiometry in particular, force a lot of oversimplifications in the kinetic models developed. Such oversimplifications result in the fact that kinetic parameters calculated do not always preserve their physical meaning. So calculating of them for the purposes of the basic science do not have any sense. From the technological point of view the kinetic parameters estimated can be anticipated as ones reflecting some features of the coals studied.

On the other hand simplifications must be introduced not only into the reactions schemes but also into the definitions of some kinetic parameters. As there is no possibility to determine molar weight of the coal substance we define the conversion degree for any given pyrolysis stage as (Fig. 2):

$$\alpha = \frac{m_i - m(T)}{m_i - m_f}, \quad \alpha \in <(0,1>) \tag{5}$$

Pyrolysis can be divided into stages according to peaks on DTA curve which are characteristic for coals, TG inflexion points or some other criteria.

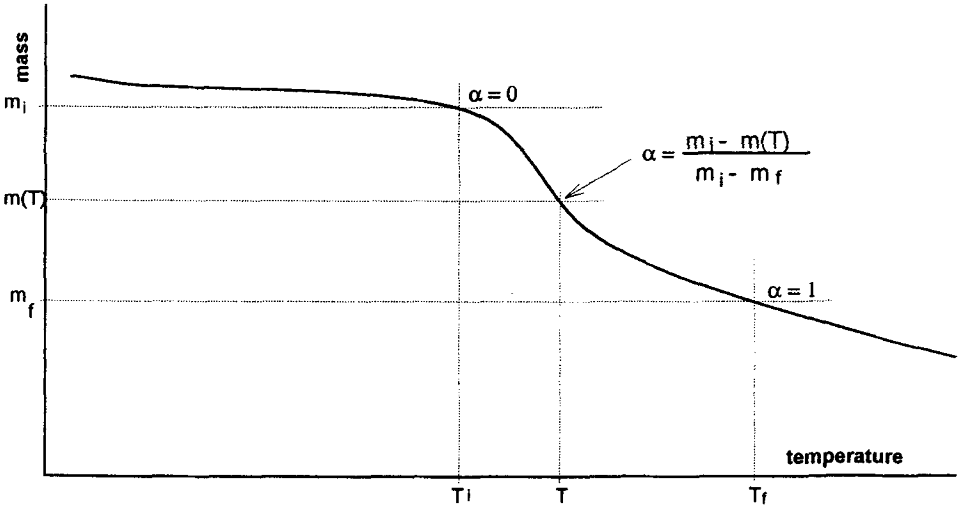


Fig. 2 Graphical interpretation of the conversion degree assumed for kinetic analysis of the pyrolysis process

Results and discussion

Estimation of kinetic parameters according to known procedures

The kinetic parameters we estimated using Eqs (2) or (3), while basing on the experimental data measured in our laboratory. The orthocoking coal of 35.1 type (or 534 type according to International Classification) is taken as the example from many analysed polish coals of the different metamorphism degrees and coal blends. The samples were analysed by means of thermogravimetry in inert atmosphere using MOM OD 103 Derivatograph.

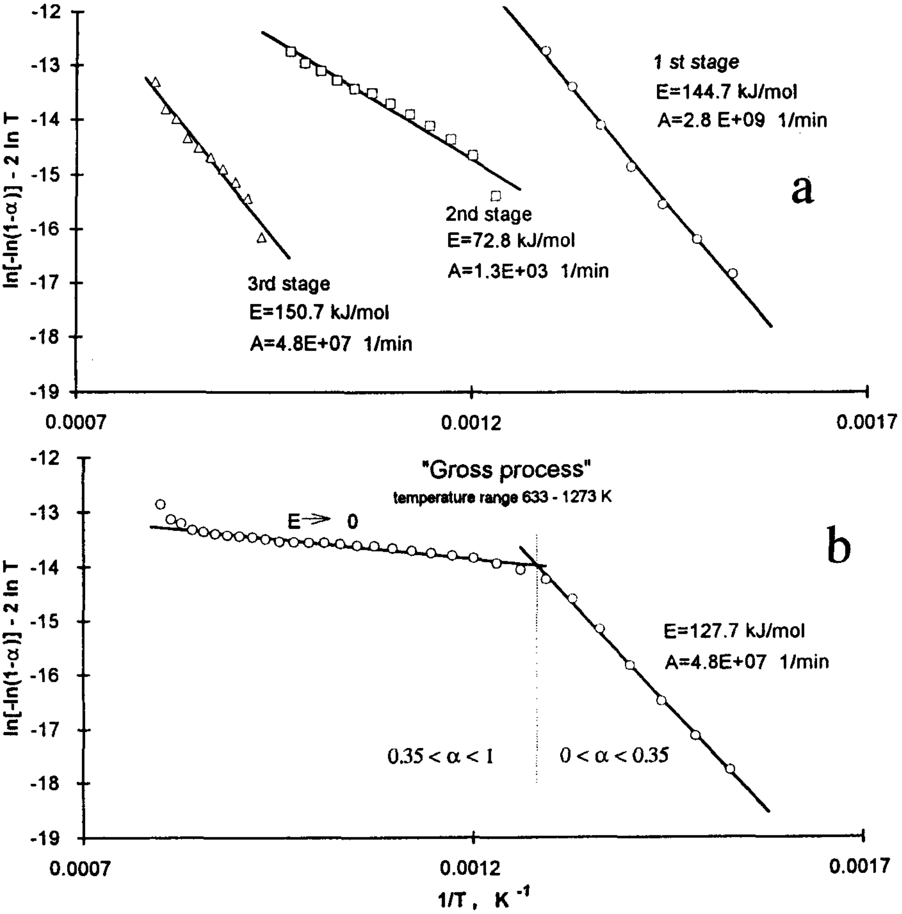


Fig. 3 Kinetic description of the coal pyrolysis, provided that F1 mechanism and solution (2) is assumed: a) if dividing the process into three stages, b) if analysing 'gross process'

In Figs 3a and 6 the analysis of pyrolysis process is shown, provided that F1 mechanism and solution (2) is assumed. Two possible procedures are presented in Figs 3a and 3b respectively. The one in Fig. 3a consists in dividing of the whole temperature range analysed (360–1000°C) into three appropriate stages [14]. For each individual stage the conversion degree takes values from $\alpha \in <0, 1>$. At the border of the intervals the $\alpha = 1$ value of the given stage corresponds to $\alpha = 0$ of the next one. The procedure results in three *E* and *A* pairs, each for every stage. Following problems in finding temperature ranges to define individual stages, due to the lack of the characteristic peaks on DTA curves for some coals type, the kinetic parameters evaluated can include some randomness and their usability to comparative analysis is limited.

The second version (Fig. 3b) consists in analysis of the pyrolysis in the whole temperature range 360–1000°C as the one 'gross process' in which $\alpha \in <0, 1>$, as previously assumed by Elder [10]. If one assumes once more the adequacy of the kinetic description e.i. F1 mechanism and solution (2), it can be observed that initially the activation energy takes value of 128 kJ/mol in the relatively narrow temperature range for $\alpha < \sim 0.3$, while next its value jumps close to zero. The fact should be explained by the change in the mechanism of the coal substance decomposition involved in pyrolysis e.g. transfer from the kinetic area into the diffusion one.

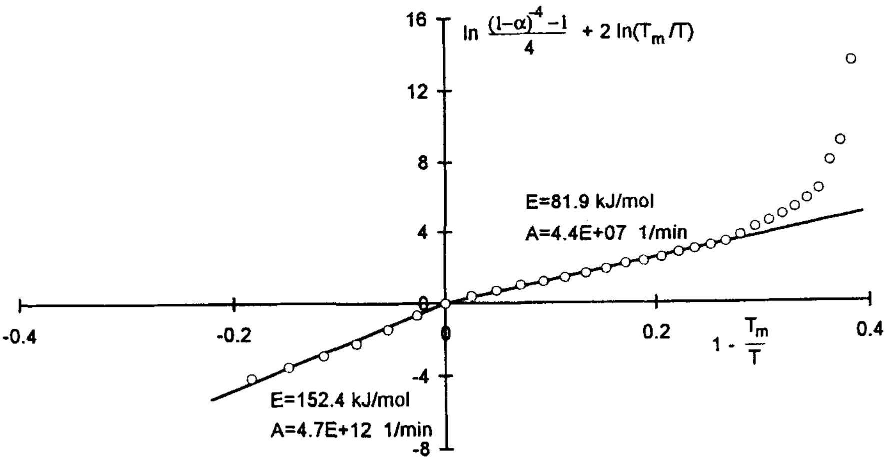


Fig. 4 Kinetic description of the coal pyrolysis, provided that F5 mechanism and solution (3) is assumed

Figure 4 shows another possibility to describe the kinetics of the pyrolysis process when using F5 mechanism (Fn for $n \cong 5$) and the solution (3). The n value was calculated basing on [12]:

$$\alpha_m = 1 - n^{1/1-n} \qquad \text{for} \quad T = T_m \text{ and } n \neq 1 \tag{6}$$

for the experimental conversion degree value determined at the temperature of the maximal conversion rate (α_m). This procedure indicates at least two stage nature of the pyrolysis and results in the different kinetic parameters E and A.

Estimation of the kinetic parameters for two step pyrolysis model

The analysis indicates that thermal decomposition of the dry hard coal ($W^a = 0\%$) proceeds in two stages. Therefore in further evaluations we assumed the two stages kinetic description of the process. We show the actual division of the pyrolysis into two stages in Fig. 5 which in fact is the more detail image of the Fig. 2. Non-linear weight losses *vs.* temperature dependence ($-\mathrm{d}m/\mathrm{d}T$ = v a r) describes the first stage. In the second stage, e.i. secondary degassing the same relationship acquire the linear form ($-\mathrm{d}m/\mathrm{d}T$ = i d e m). Previous analyses suggest that the first stage is of the more complex nature and covers quick physicochemical conversions of the coal which involves forming the phases of high plasticity. The above mentioned processes proceeds in the kinetic area, but the step include also consolidation of the coal structure which

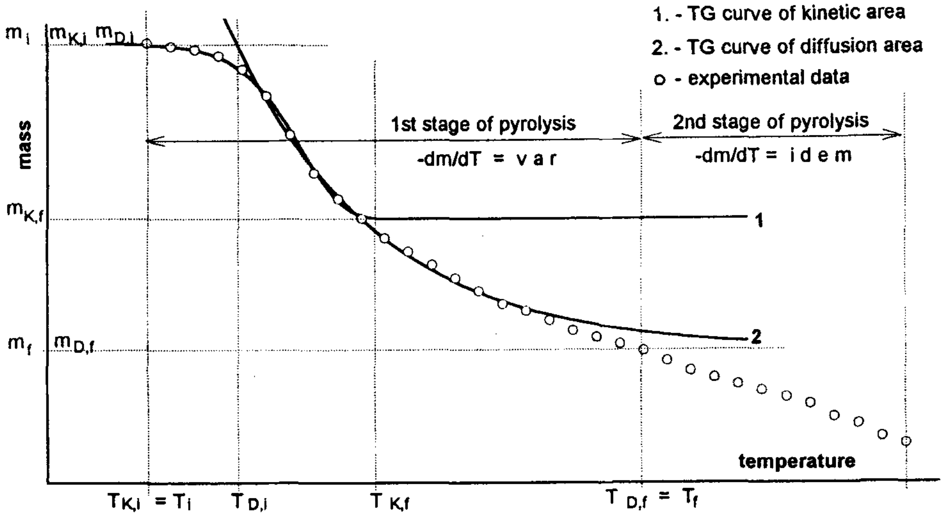


Fig. 5 Two stage division of the pyrolysis process. Interpretation of the kinetic and diffusion areas

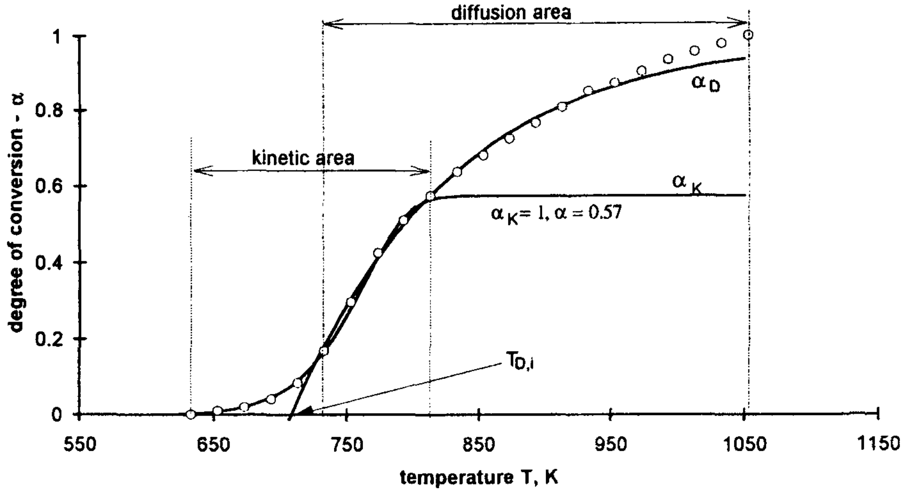


Fig. 6 The α_K and α_D functions for the coking coal of the 534 type

proceeds in the slower diffusion area. Kinetic and diffusion areas can interfere in some temperature ranges indicating the actual nature of the samples analysed. Two stages model should result in introducing indices I and II into our description. As we however limit our analysis to the first stage only we omit the indices and all symbols refer to the first pyrolysis stage.

We propose two equation types (notation according to Figs 5 and 6) to describe the kinetics of the first stage:

– the first order kinetics – F1 mechanism with additional conditions as specified previously [13] assumed for the conversions in the kinetic area results in the following equation form:

$$-\ln(1-\alpha_K) = \frac{A_K R T^2}{qE} e^{-E/RT} \qquad \alpha_K \in <0,1> \tag{7}$$

where:

$$\alpha_K = \frac{m_{K,i} - m(T)}{m_{K,i} - m_{K,f}}$$

$$m_{K,f} \le m(T) \le m_{K,i} \tag{8}$$

$$0 \le \alpha_K \le 1$$

– for the kinetics of the first order if assumed that according to Fig. 3b $E \cong 0$ in Eq. (1) one obtains for the diffusion area final form of:

$$-\ln(1-\alpha_D) = \frac{A_D}{q} \Delta T \qquad \Delta T = T - T_{D,i} \tag{9}$$

where:

$$\alpha_D = \frac{m_{D,i} - m(T)}{m_{D,i} - m_{D,f}}$$

$$m_{D,f} \le m(T) \le m_{D,i}$$

$$0 \le \alpha_D \le 1 \tag{10}$$

The model (7) should be analysed before the (9) one (Figs 3b and 5).

Kinetics of the first order as described by Eq. (7) is obeyed only in a part of the first pyrolysis stage as comes from the procedure of the kinetic area range determination indicated in [13]. So the dependence of the conversion degree in the kinetic area – α_K *vs*. conversion degree of the coal substance in the whole first stage – α is described by (Fig. 5):

$$\alpha = C \cdot \alpha_K\ , \quad \alpha_K \in <0,1> \tag{11}$$

$$\text{where: } C = \frac{m_{K,i} - m_{K,f}}{m_{K,i} - m_{D,f}} = \frac{m_{K,i} - m_{K,f}}{m_{D,i} - m_{D,f}} = i\ d\ e\ m$$

or:

$$\alpha = \alpha_D\ , \quad \alpha_D \in < 0.1> \tag{12}$$

According to the definition (5) for the maximal value of the conversion degree in the kinetic area $\alpha_K = 1$, the conversion degree for the whole first stage equals to C from (11) e.g. the value of $\alpha = 0.57$ corresponds to $\alpha_K = 1$ for the analysed coal of the 543 type, Fig. 6. The changes of the conversion degree for the diffusion area α_D corresponds to the changes of the conversion degree in the whole first stage.

Figure 6 shows the curves α_K and α_D for the coal type 543 analysed. The good agreement of the experimental data with the functions (7) and (9) can be observed. Moreover it is the diffusion area (9) which is followed by the most of the measurements. The activation energy evaluated for kinetic area according to (7) (E = 138.9 kJ/mol) closes both to the value obtained from the temperature criterion procedure [15]:

$$\ln\alpha = -\frac{E}{RT} + constant, \qquad 0 < \alpha < 0,2 \tag{13}$$

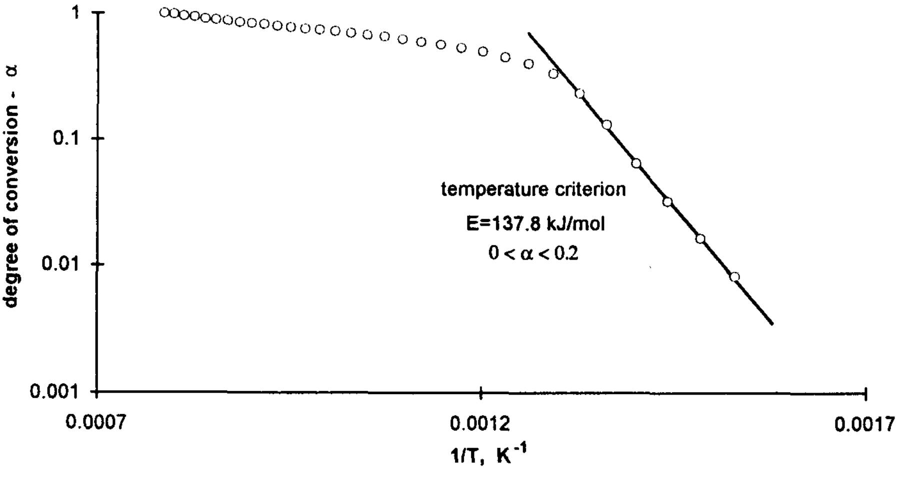


Fig. 7 Activation energy of the pyrolysis process evaluated on the base of the temperature

(E = 137.8 kJ/mol – Fig. 7), and to the initial activation energy estimated for the 'gross process' (E = 127.7 kJ/mol – Fig. 3b). These results seems to prove the existence of the kinetic pyrolysis area. It is short and quick but on the other hand very important from the coking theory point of view.

The analysis of the α_K and α_D functions for different coals types (Figs 8a–c) indicates that Eqs (7) and (9) describes the measurements in different ranges. The kinetic, diffusion and combined areas can be told. Moreover such important technological features as sintering or plasticity are obviously reflected in forms of kinetic and diffusion areas. This is the distinctively formed kinetic and combined area (coherent α_K and α_D) which indicates well sintering coals and the proper plasticity. So the individual area dimensions and further their inter-

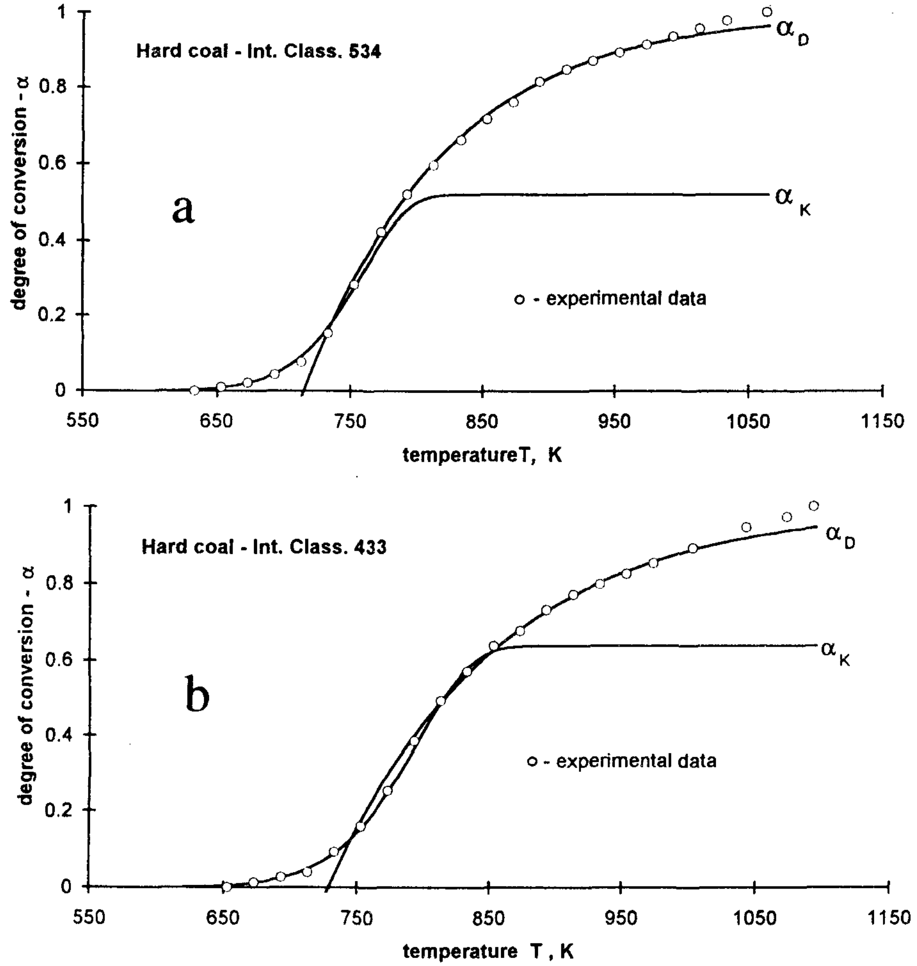


Fig. 8 Examples of the α_K and α_D functions for the different coking types: a) Int. Class. 534; b) Int. Class. 433

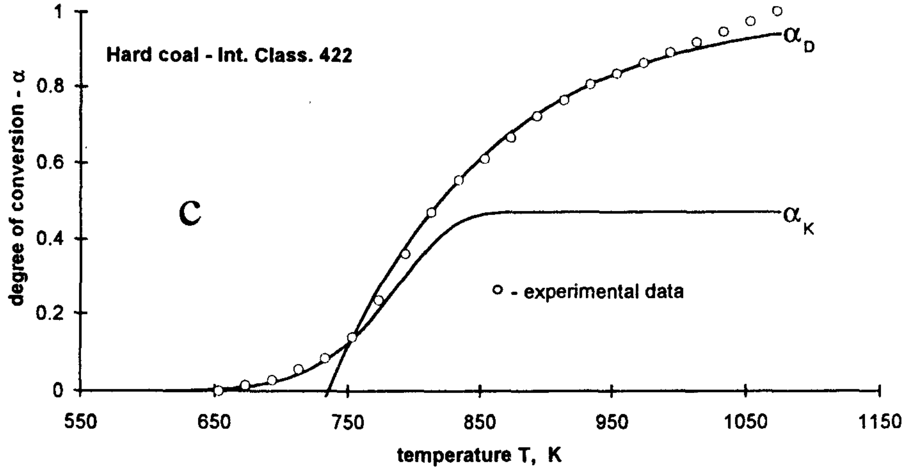


Fig. 8 Examples of the α_K and α_D functions for the different coking coal types: c) Int. Class. 422

dependencies reflects their technological features of the coals analysed. It can be concluded that Eqs (7) and (9) adequately describes the first pyrolysis stage.

Conclusions

The analysis of the possibility of kinetic description of hard coal pyrolysis indicates that using Eqs (7) and (9) gives an opportunity for unambiguous evaluation of the kinetic parameters of the process. Moreover the parameters and functions α_K and α_D obtained for the first pyrolysis stage can be used to estimate the technological quality of the coals and/or the resulted cokes. The important advantage of the equations proposed is their simple mathematical form. It makes possible the quick and effective evaluation of the kinetic parameters for a great deal of technological samples.

Symbols:

A – pre-exponential factor of the Arrhenius equation, min^{-1}
e – Euler's number, $e = 2.718\ldots$,
E – activation energy, kJ/mol,
$f(\alpha)$ – function symbol of the argument α,
$g(\alpha)$ – weight integrals,
m – mass of the sample, mg,
n – order of reaction,
q – rate of heating, $\mathrm{deg \cdot min}^{-1}$,

R – universal gas constant, $R = 0.008314$ kJ·(mol·K)$^{-1}$
T – absolute temperature, K,
T_m – temperature of maximal conversion rate, K,
$T_{D,i}$ – temperature at $\alpha_D = 0$, K,
..(T) – at temperature T,
α – degree of conversion, $\alpha \in <0,1>$.

Subscript:

i – initial stage,
f – final stage,
m – at the maximal conversion rate,
K – refers to kinetic area,
D – refers to diffusion area.

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Zusammenfassung — Es werden die Hauptprobleme der kinetischen Beschreibungsweise von Kohlenpyrolyseprozessen besprochen und einige mögliche Methoden zur Abschätzung der kinetischen Parameter des Prozesses auf der Basis thermogravimetrischer Analyse unter nichtisothermen Bedingungen dargelegt.