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THE DETERMINATION OF COAL COMBUSTION KINETICS WITH THERMOGRAVIMETRY

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This investigation concerns the determination of the kinetics of coal combustion. It is not well possible to use an exact analytical formula for the rate equation. For that reason a stepwise method is proposed, giving the activation energy as function of the reaction parameter α, without assumption of any specific rate equation.

In the description of the kinetics of coal combustion it is often assumed that the reaction is a simple n-th order process. The reaction parameter α changes as

$$d\alpha/dt = k(1-\alpha)^n, \text{ with } k = k_0 \exp(-E_A/RT) \tag{1}$$

In most cases it is assumed that $n = 1$ [1, 2]. However, such an assumption is not valid in the real combustion of bituminous coals with high volatile content. Here at least three parallel processes occur:

a) Volatilization of compounds, and the combustion of volatiles in the gas phase (fraction α_1)
b) Combustion of volatiles directly on the coal particles (α_2)
c) Combustion of the char (α_3).

The general kinetic description of the process can then only be given in terms of averaged or effective quantities according to $d\alpha/dt = \bar{k}\ \bar{f}(\alpha)$; $\bar{f}(\alpha)$ is some function of α, and the effective functions $\bar{k}$ and $\bar{f}$ may be composed of different terms, like

$$\bar{k}\,\bar{f}(\alpha) = k_1 f_1(\alpha) + k_2 f_2(\alpha) + \ldots \tag{2}$$

Clearly the use of a simple, particular function of α like in Eq. 1 is then only warranted in a limited range of experimental conditions. For those conditions it is possible to evaluate quantities, such as k_0, n and the activation energy E_A from one, nonisothermal TG experiment [1, 2]. According to Newkirk one writes:

$$\ln F = \ln\{(d\alpha/dt)/(1-\alpha)^n\} = \ln k_0 - E_A/RT \tag{3}$$

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and obtains k_0 and E_A from a plot of ln F as a function of $1/T$. In this approach an a priori value for the exponent n has been assumed. One may alternatively use combinations of two experimental points, i and j, and following Freeman and Carroll [3] obtain n with

$$Y = \frac{\ln(\mathrm{d}\alpha/\mathrm{d}t)_i - \ln(\mathrm{d}\alpha/\mathrm{d}t)_j}{\ln(1-\alpha_i) - \ln(1-\alpha_j)} \tag{4}$$

$$X = \frac{1/T_i - 1/T_j}{\ln(1-\alpha_i) - \ln(1-\alpha_j)} \tag{5}$$

$$Y = -(E_A/R)\,X + n \tag{6}$$

This method is normally applied for linear heating rate curves, and gives a mean value for E_A and n. When E_A and n vary with α, this method is not well suitable.

Another alternative is not to attempt finding an explicit expression for $f(\alpha)$, and only assume that $f(\alpha)$ is the same function under different experimental conditions in which α is the same. Then it is necessary to determine $\mathrm{d}\alpha/\mathrm{d}t$ for equal α at different temperatures, with different samples, and at different heating rates or combustion temperatures. Experimentally this creates reproducibility problems between different samples and different thermogravimetric test runs. We have [4] developed a "stepping" method for this situation, in which data are extracted from a series of isothermal and non-isothermal experiments with one sample.

First one obtains $(\mathrm{d}\alpha/\mathrm{d}t)_R$ from isothermal steps with varying α at one reference temperature T_R. Then, the combination with data obtained at other temperatures T gives

$$Z = \{(\mathrm{d}\alpha/\mathrm{d}t)_T/(\mathrm{d}\alpha/\mathrm{d}t)_R\} = \exp\{-E_A/R)\,(1/T-1/T_R)\} \tag{7}$$

A plot of ln Z vs $1/T$ will show a straight line for a particular, well defined region of α-values. The determination of E_A is such a region is then straightforward. We have used these alternative approaches in an attempt to unravel the kinetics of coal combustion.

Experimental results

For our experiments we used coal samples delivered by the Dutch Centre for Coal Specimens SBN, with particle sizes $0 < d_p < 3000\ \mu m$.

Grinding the samples might have given more reproducible results but we decided against it, to allow application of the results to technical coal combustion experiments, with also a broad particle size distruibution [5].

The composition of the different coal samples which were used in the TG experiments are given in Table 1.

Table 1 Composition of coal samples (dry weight)

Sample* No	code	Composition (wt %) volatiles	fixed Carbon	ash
I	513DE38	37.8	54.1	8.1
II	504FR45	41.2	48.4	10.4
III	anthracite	9.9	86.2	3.9
IV	511US43	41.5	46.9	11.6
V	502GB14	14.9	73.5	11.6
VI	515US38	36.6	55.3	8.1

* I, II, IV, V, VI Dutch Centre for Coal Specimens SBN
III Anthracite from Niederberg AG, FRG

It may be expected that the relative contribution to the overall process of each of the three processes, mentioned in the introduction, depends on factors like volatile content, sample geometry, layer thickness, particle size distribution, gas flow rate and temperature. A high layer thickness, high reaction rate and low exchange rate with the gas phase will promote the simultaneous occurrence of all reactions together.

For this reason the reaction was performed on samples with a small layer thickness in an open cylindrical crucible. This crucible was made of alumina with the following dimensions: height 5 mm. diameter 7 mm.

Amounts of 50–90 mg were heated in flowing air (5 lh^{-1}, STP) in a thermobalance of the type described in [6]. After drying the samples for 15 min at 130° the temperature was raised to the desired reaction temperature. This reaction temperature was deliberately kept low to ensure that the reaction rate is indeed limited by chemical kinetics, and not by e.g. gas diffusion.

The stepping method then consists of determining the reaction rate $d\alpha/dt$ from TG data at many different reaction temperatures. As the reaction proceeds, and the sample is consumed, α changes from 0 to 1. Approximately one fifth of all the, relatively short, isothermal $d\alpha/dt$ measurements were obtained at one "reference temperature" T_R. From there one could plot $d\alpha/dt$ at T_R for $0 < \alpha < 1$. From this one could obtain the isothermal reference curve as described above, and calculate the kinetic parameters from the complete set of data as indicated.

In most cases the reaction rate at reference temperature became so slow in the course of the reaction, that a higher reference temperature had to be chosen for the remainder of the combustion reaction.

The figures 1 and 2 demonstrate the characteristic irreproducibility of isothermal experiments under identical process conditions, but with different coal samples. In Fig. 1 anthracite is used with relatively small particle sizes ($0 < d_p < 150$ μm) and with a low content of volatiles. Here the reproducibility is reasonable, expecially at higher α-values, where the combustion of volatiles has become of minor importance. In contrast, the experiments of Fig. 2, with coal of a high content of volatiles, remain irreproducible over the whole α-range. The experiments of Fig. 2 were made with powdered samples. With coarser samples ($0 < d_p < 3000$ μm) the irreproducibility was even worse.

These results indicate that an approach to unravel the kinetics of coal combustion on the basis of such formalisms as Eq. (1) is only of limited

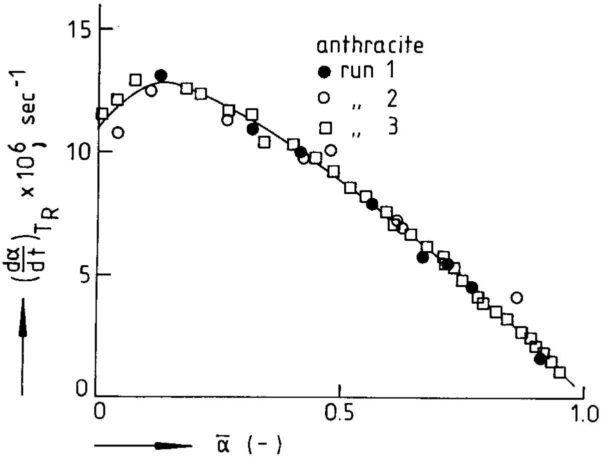

Fig. 1 Combustion of anthracite (sample III) at 345°C. The particle size is 0–150 μm. Run 1 and 2: stepwise method, run 3: completely isothermal experiment

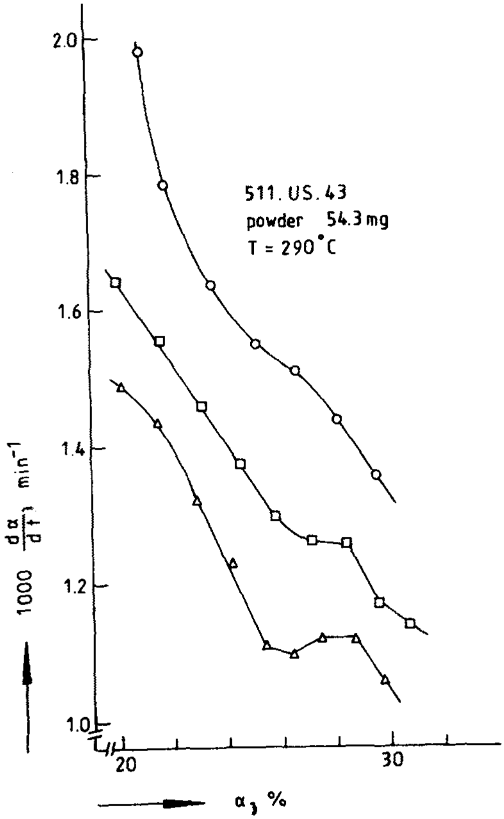

Fig. 2 Combustion of three different samples of powdered coal (sample IV) at 290°C

value. Moreover, in Fig. 1 the maximum in $d\alpha/dt$ is a clear indication that the combustion process could never be described by an expression like Eq. 1 with a fixed order of n. On the basis of these observations analysis of coal combustion in terms of equations 3–6 will always be fraught with complications, due to irreproducibility between samples and changes in kinetics as a function of α. The "stepping" method seems the more promising approach.

The results of this method are shown in Figs 3–5. Figure 3 gives $d\alpha/dt$ as a function of α for the reference temperature T_R. Figure 4 reveals that these data may be grouped in regions with different reaction orden n. Figure 5 then represents the results of the stepping method for the region $0.5 > \alpha > 0.7$, obtained with Eq. (7). Indeed one obtains here a straight line, and consequently one activation energy describing the combustion of this coal sample (IV) at this stage.

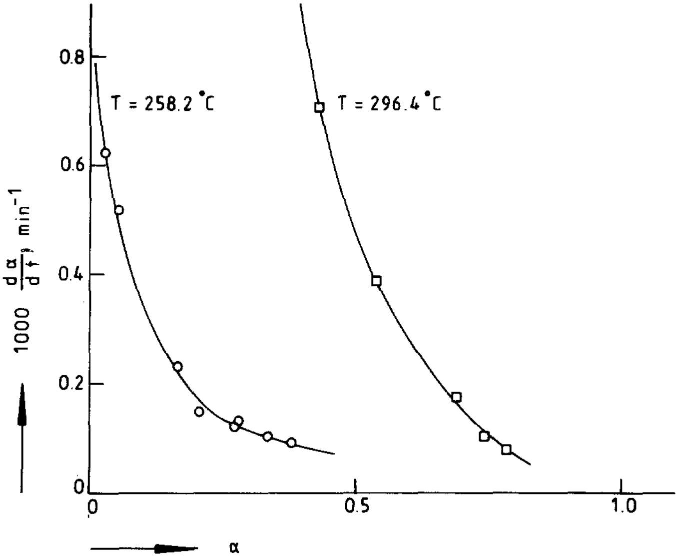

Fig. 3 Reference curves for the combustion of sample IV, according to the stepwise method. The particle size is 0–3000 μm

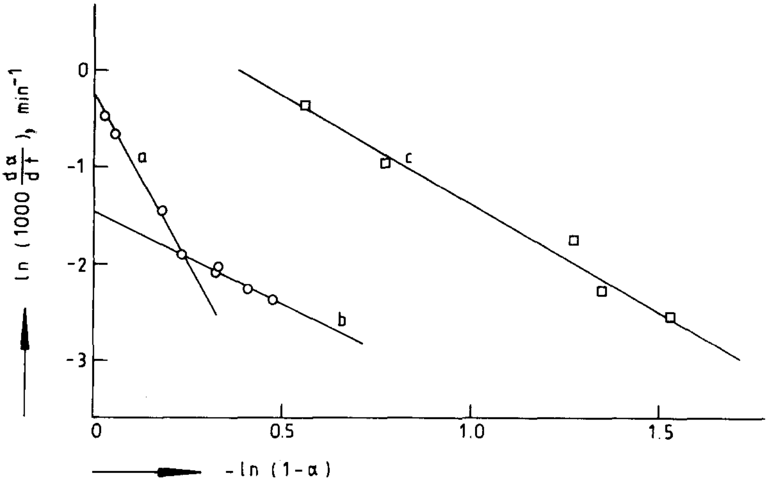

Fig. 4 Determination of the reaction order n from the reference curves of sample IV at T_R = 258.2°C (a and b) and 296.4°C (c). a: n = 6.85; b: n = 2.01; c: n = 2.26

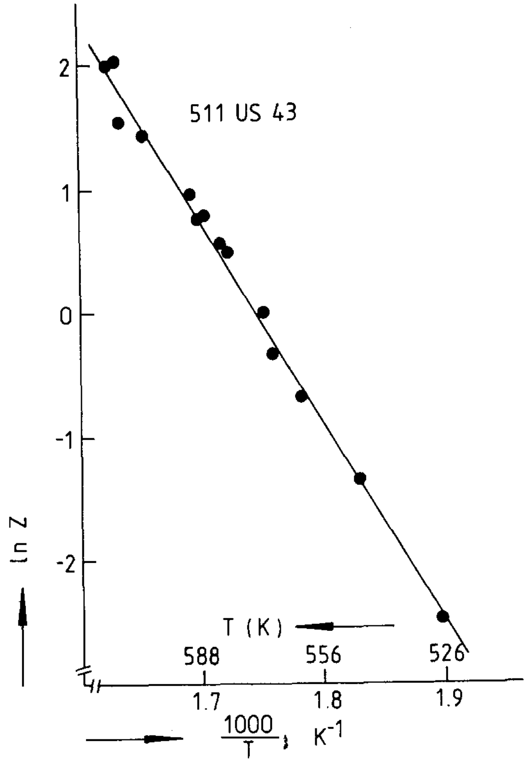

Fig. 5 Determination of the activation energy for sample IV, according to the stepwise method (equation 7) for $\alpha = 0.5$–0.7

Discussion of the results

The results of sample IV are given in Table 2, where kinetic parameters are calculated for specific α-regions, according to three methods (first order, n-th order and stepwise method). The inaccuracy of the calculated values of E_A is about 6 kJ/mol, assuming that the measured temperature is accurate within 0.5 K and the rate $d\alpha/dt$ within 10%. Comparison of the activation energies, calculated with these methods, shows that the first order method gives too low results. The other two methods lead to about the same E_A in each α-region. Still, we must keep in mind that the value of n, calculated from the experiments at T_R, is only an arithmetic constant with no other physical meaning than that it identifies the α-regions. The value of $n = 6.85$, for $\alpha = 0$–0.2, indicates that the isothermal combustion rate decreases much

Table 2 Stepwise measurements of sample IV.
Evaluation according to the methods 1: $d\alpha/dt = k(1-\alpha)$, 2: $d\alpha/dt = k(1-\alpha)^n$ and 3: "stepwise" method; $d\alpha/dt = kf(\alpha)$.
The inaccuracy of E_A is about 6 kJ/mol.

α-region	T,	method 1		method 2	method 3
–	°C	E_A, kJ/mol	n	E_A, kJ/mol	E_A, kJ/mol
0.0–0.2	235–266	107	6.85	128	122
0.2–0.4	254–307	102	2.01	132	132
0.4–0.6	254–307	135	2.26	138	139
0.6–0.7	296–340	145	2.26	141	142
0.7–0.8	296–340	115	2.26	124	122
0.0–0.8	(mean value)	119	–	133	131

faster at the beginning of the process than in a first order process. Such a fast decrease of rates at the beginning of the combustion reaction is observed in all samples with high volatiles content. The evaporation and combustion of volatiles is the most important process at this stage. If it is assumed that this first part of the process can be described by first order kinetics, in which the terms with α_1 (Eq. (2)) dominate, then

$$d\alpha_1/dt = k_1(1-\alpha_1) \text{ with } \alpha_1 = z.\alpha \tag{8}$$

It can be calculated that this is valid for $z = 4$, which implies that 25% of the total weight loss should correspond to the combustion of volatiles during this stage. In Table 1 we see that the volatile fraction is 41.5%, so the remainder of the volatiles burns during later stages of the reaction. The values of $n = 2.01$ and 2.26 for the rest of the combustion reaction also indicate faster rate decrease than in a first order process. This decrease of the rate is, at least partially, an effect of particle sizes: the smallest particles will burn first. Their disappearance decreases the coal surface area and consequently the overall reaction rate.

The activation energy appears to be low in the first part of the reaction and to increase during the rest of the reaction. Therefore we may assume that here the combustion of volatiles has a relatively low activation energy in comparison with the char combustion. In ref. [7] the outgassing of powdered coal in N_2 has been studied. In a temperature region of 523–938 K activation energies of 115–206 kJ/mol are found at reaction orders $n = 0.14$–1.83 for linear heating rate curves. The initial activation energy of 122 kJ/mol fits well with these linear heating rate experiments. The present value of $n = 6.85$ seems to be too high, but this is caused as discussed before, by a different definition of α.

In Table 2 also the mean values of the activation energy E_A are calculated, according to the method given by Cumming [1]:

$$E_m = (F_1 E_1 + F_2 E_2 + ..) / (F_1 + F_2 + ..) \tag{9}$$

In this formula F_1 is the α-region, for which the activation energy E_1, is valid. The first order activation energy is 119 kJ/mol. Cumming [1] reported, for powdered bituminous coal samples with about 40% volatile content, values between 72 and 113 kJ/mol. The somewhat higher value of 119 kJ/mol will be caused by the difference in particle sizes between both experiments: in big particles the reaction needs a higher activation energy for growing inwards than is smaller particles, where the surface reaction dominates.

As can be seen in Table 2, the mean value of E_A according to the first order method is about 12 kJ/mol lower than the values of E_A for the other methods. Since two methods (the first order and the n-th order with constant n) have no reliable physical background, and lead to incorrect results, compared to the stepwise method, only this last method is applied for calculation of E_A as a function of α for the other samples in Table 3. From this Table it can be seen:

– the course of E_A with α differs for every experiment, depending on the kind of sample and the sample size. For most samples the initial E_A is low and increases with α to a maximum value (I, IV and V), while the other samples (III and VI) initially start with the highest activation energy. It is possible that in the first few percent of the combustion reaction a lower activation energy exists, but this would not be detected by the stepwise method, since a little fraction of the coal has already reacted before the first step is reached. Cumming [1] reported for an anthracite (< 210 μm) an activation energy of 52.8 kJ/mol in the first 2% and 149.3 kJ/mol in the rest of the reaction (calculated assuming a first order process). So it is well possible that we in some cases have missed this first part with the stepwise method. This explanation is not valid for sample VI, with a high volatile content. Here we must assume that the volatiles are bound very strongly, resulting into a high initial activation energy.

Table 3 Activation energy E_A, kJ/mol as function of α, calculated with the "stepwise" method. The inaccuracy of E_A is about 6 kJ/mol.

Sample*	E_A at values of α: 0.1	0.3	0.5	0.7	0.9	mean value of E_A
I	102	109	114	117	99	108
I	99	104	125	116	100	109
II	108	106	111	118	–	111
II	92	119	104	132	–	112
IIIa	179	148	139	135	108	142
IIIb	147	112	128	130	–	129
IV	122	132	139	132	–	131
V	124	126	149	147	127	135
VI	145	–	119	126	–	130

* sample size: sieve fraction 0–3000 μm, except sample IIIa (0–150 μm) and IIIb (212–250 μm)

At the end of the combustion reaction, where only the bigger particles remain, the activation energy decreases. The figures given in ref [1, 2] also indicate this behaviour, although the authors do not further go into this fact. A possible explanation could be the ash content. At the end of the reaction diffusion processes through the ash layer will cause a lowering of the experimental E_A.

The mean values of E_A (108–135 kJ/mol) seem a little high compared to values for high volatile containing samples, mentioned in ref. [1, 2], being 72–113 kJ/mol, but we have to keep in mind that the litterature values are calculated with assumption of a first order process and for particle sizes of 0–210 μm.

– Experiments with different samples of the same coal with high volatile content show a bad reproducibility of the E_A-α curve, but the mean values of the activation energy agree very well (samples I and II). Particularly the two experiments with sample II show this behaviour. The activation energy shows several maxima with varying α and is initially high for the first experiment and low for the second one.

Probably this irreproducibility is caused by differences in particle sizes. It is possible that, in view of the broad particle size distribution and the small sample weights, the relative amount of big particles differs for both experiments. Perhaps the reproducibility would be better by taking bigger samples or more narrow sieve fractions.

Different particle sizes give different activation energies. This is demonstrated for anthracite (sample III). Sieve fractions of 0–150 μm; respectively 212–250 μm give mean activation energies of 142, respectively 129 kJ/mol.

This can be compared to first order values in ref [1, 2] being 108–153 kJ/mole for a sieve fraction of 0–210 μm.

So for anthracite the activation energy is higher for smaller crystals, just opposite to what we expect for high volatile samples. This could be explained when assuming that the first start of the reaction (nuclei formation) is extra difficult compared to the growth of nuclei [8]. For most of the high volatile coals the start of the reaction is activated by the combustion of volatiles, leaving disordered coal "crystals". Now we can understand that anthracite with big particles has a lower activation energy: the nuclei formation is relatively less important, compared to the growth mechanism.

Sample VI, a high volatile coal, has a different behaviour compared to the other high volatile coals, but behaves more like anthracite. Also in this case, the start of the combustion reaction needs a high activation energy. Further experiments with different sieve fractions and sample sizes, would be necessary for finding an explanation.

There is no good relation between coal composition and activation energy.

Conclusions

The kinetic equation for coal combustion cannot well be described by a first order or a n-th order process, according to $d\alpha/dt = k(1-\alpha)^n$.

On behalf of the irreproducibility of different samples, kinetics are to be determined with use of one sample.

The stepwise method, giving for the same sample isothermal and non isothermal information, is a good method for calculation of kinetic parameters, since no assumptions are necessary about the kinetic mechanism or dependance on reaction parameter α. This stepwise method eliminates specific effect of surface area and sample size distribution since each measurement on a sample is related to the same reference curve.

The shape of E_A-α curves may differ strongly for identical experiments, but the average value of the activation energy, determined with the stepwise method, is nearly constant.

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Zusammenfassung – Diese Arbeit beschäftigt sich mit der Kinetik der Kohleverbrennung. Für die Reaktionsgeschwindigkeit ist es jedoch nicht möglich, eine exakte analytische Gleichung anzuwenden. Aus diesem Grunde wird ein schrittweises Vorgehen vorgeschlagen, das die Aktivierungsenergie ohne Voraussetzung jeglicher spezifischer Geschwindigkeitsgleichungen als Funktion des Reaktionsparameters α liefert.

Резюме – Исследование касается определения кинетики горения угля. Не представилось возможным применить какое-либо точное аналитическое выражение уравнения скорости реакции. В связи с этим предложен ступенчатый метод, дающий энергию активации как функцию реакционного параметра α , без предположения какого-либо характерного уравнения скорости реакции.