

CHARACTERISATION OF PYROLYSIS KINETICS BY ROCK-EVAL BASIC DATA

I. JOHANNES^{*(a)}, K. KRUSEMENT^(a), R. VESKI^(b),
J. A. BOJESEN-KOEFOED^(c)

^(a) Department of Oil Shale Technology,
Tallinn University of Technology
5 Ehitajate Rd., 19086 Tallinn, Estonia

^(b) Peat Info Ltd, 233-48 Sõpruse Rd, 13420 Tallinn, Estonia

^(c) Geological Survey of Denmark and Greenland (GEUS)
10 Øster Voldgade, DK-1350K Copenhagen, Denmark

A possibility for evaluation of pyrolysis kinetics of two Estonian shales and six biomass samples by Rock-Eval basic data is described. A pseudo-first-order kinetic model is proposed basing on S1, S2 and T_{max} determined only at one heating rate for calculating 1) the apparent activation energy (E) and frequency factor (A) for evolution of total hydrocarbons, 2) the current yields of hydrocarbons in time and temperature, 3) the kinetic constants (A_i and E_i) for release of hydrocarbons from thermolabile ingredients. A linear relationship is revealed between kinetic constants of the samples studied: $\ln A_i = -4.455 + 0.228E_i$, $r = 0.9947$, $n = 8$.

Introduction

Abbreviations

- S1 – free and/or thermolabile hydrocarbons, mg/g sample, evolved at 300 °C
S2 – cracked hydrocarbons, mg/g sample, evolved between 300–650 °C
TC – total carbon, % from sample
TOC – total organic carbon, % from sample
 T_{max} – temperature for maximum of surface S2, °C
OI – oxygen index
HI – hydrogen index
BI – bitumen index

* Corresponding author: e-mail address ille.johannes@ttu.ee

RC	–	residual carbon
E	–	activation energy, kJ/mol
A	–	frequency factor
FID	–	flame ionisation detector
HC	–	hydrocarbons
R	–	gas constant, 8.314 J/mol
β	–	heating rate, °/min

Rock-Eval pyrolysis [1] has been a widely used method in organic geochemistry for examining the oil and gas potential and maturity of different ancient and recent sediment samples [2-8]. The method was extended to biomass samples in the paper [9]. Besides, a software OPTKIN was developed [10] for description of pyrolysis kinetics using the Rock-Eval measurements. The kinetic study is based on the temperature pattern, the integration ranks and the parameters defined for the basic method, while different heating rates for pyrolysis (1, 2, 5, 10, 15, 20, 25 °/min) are programmed. As results, distribution of activation energies (E_i) for multi-component parallel reactions and the computed values of frequency factor (A_i) can be obtained.

In this work, an approach is proposed for estimation of the apparent kinetic constants A and E for pseudo first-order formation of total hydrocarbons, and A_1 and E_1 for evolution of hydrocarbons from thermolabile ingredients. Algorithms are deduced for prediction of co-effects of time and temperature on the yield of total hydrocarbons using the data S_1 , S_2 and T_{\max} obtained only at one constant heating rate.

Experimental

Materials and methods

The source materials studied were Estonian Ordovician kukersite oil shale and Dictyonema argillite, and six biomass samples – peat, reed, willow, pine bark, pine sawdust and spruce branches, characterised in our previous paper [9].

The analyses were performed at the Geological Survey of Denmark and Greenland using a *LECO CS-200* instrument, and Rock-Eval analyser *RE6* at standard conditions [1] under the heating rate 25 °/min.

In the paper [9] it was shown that the basic data of Rock-Eval were excellent for kukersite and Dictyonema argillite, but gave by 21.3–56.6% underestimated values of the total organic carbon (TOC) when biomass samples were analysed. The discrepancy was explained by the presence of a notable part of acid-soluble organic matter in the “non-geological” samples being extracted before estimation of TOC. The true values of TOC, OI, HI, BI and RC for the biomass samples were calculated using TC instead of TOC stated. The basic data obtained by Rock-Eval instrument and the corrected values are given in Table 1.

Table 1. Rock-Eval data

	Kuker-site	Dictyonema	Peat	Reed	Willow	Pine sawdust	Pine bark	Spruce branches
TOC %	36.40	10.8	38.2	26.2	29.70	36.65	35.6	28.4
TC %	40.96	10.70	45.28	37.66	40.6	43.63	44.7	43.0
T _{max}	423	411	332	308	319	338	319	312
S1 mg/g	1.30	1.11	25.8	66.3	58.1	41.5	52.7	67.4
S2 mg/g	365.7	46.2	99.5	98.4	131.5	183.2	118.0	133.8
TOC*%	–	–	45.28	37.56	40.60	43.63	44.70	43.02
HI*	–	–	220	262	324	429	264	311
OI*	–	–	180	183	168	94	139	154
BI*	–	–	57	176	143	95	118	157
RC*%	–	–	34.88	23.89	24.87	24.98	30.53	26.32

*) – corrected values

Results and discussion

Non-isothermal kinetics

The kinetics of non-isothermal pyrolysis with a constant heating rate has been studied earlier for interpretation of pyrolysis thermogravimetric curves. For this aim, an integrated approximate relationship has been used [11, 12]

$$\ln[-\beta \ln(1-x)/RT^2] - \ln(1-2RT/E) \approx \ln(A/E) - E/RT \quad (1)$$

where x is transformation ratio of the component, and the values of kinetic constants A and E are found by the least squares optimisation.

In this work, for preliminary description of kinetics of the total hydrocarbon evolution by means of the basic data ($S1$, $S2$, T_{max} and β) of Rock-Eval analysis Equation (1) is expressed as

$$A = \beta E \exp\{\ln[-\ln(1-x)/T^2] + E/(RT)\} [R(1-2RT/E)]^{-1} \quad (2)$$

The two unknown constants A and E can be found by means of the two-equation system obtained when the variables for the two conditions:

$$1) x_1 = S1/(S1 + S2); \quad T_1 = 273 + 300 \text{ K}$$

$$2) x_2 = (S1 + 0.5S2)/(S1 + S2); \quad T_2 = 273 + T_{max} \text{ K.}$$

are introduced into Equation (2). The value of E is varied until the values of A_1 and A_2 for the two conditions coincide. The apparent kinetic constants estimated for the samples studied according to the procedure above are given in the first rows of Table 2.

Table 2. Apparent kinetic constants for evolution of total hydrocarbons by Rock-Eval pyrolysis

	Kukersite	Dictyo- nema	Peat	Reed	Willow	Pine sawdust	Pine bark	Spruce branches
E (Eq. 2)	132.3	90.35	115.7	285.3	148.4	105.2	147.6	221.2
$\ln A$ (Eq. 2)	22.4	15.1	23.0	60.2	30.5	20.5	30.4	46.3
a (Eq. 10)	9.33	2.38	10.02	46.55	17.38	7.66	17.2	32.78
b (Eq. 9)	-15858	-10785	-13862	-34334	-17812	-12590	-17704	-26575
E (Eq. 11)	131.8	89.7	115.2	285.5	148.1	104.7	147.2	220.9
$\ln A$ (Eq. 12)	22.3	15.0	22.9	60.2	30.5	20.4	30.3	46.2

We propose for estimation of A and E a direct arithmetic solution. Namely, Equation (1) can be written in the form

$$\ln[-\ln(1-x)T^{-2}] = \ln[AR(1 - 2RTE^{-1})(\beta E)^{-1}] - E(RT)^{-1}, \quad (3)$$

where the first member in the right-hand side can be approximated to a constant value. So, Equation (3) should express a linear regression

$$Y = a - bX \quad (4)$$

where

$$Y = \ln[-\ln(1-x)/T^2] \quad (5)$$

$$X = 1/T \quad (6)$$

$$a = \ln[AR(1 - 2RT/E)/(\beta E)] \quad (7)$$

$$b = E/R \quad (8)$$

The regression coefficients in Equation (4) can be found by means of X_1 , Y_1 and, Y_2 , X_2 obtained introducing into Equations (5) and (6) two known pairs (T_{300} , x_{300} and T_{max} , x_{Tmax}) of Rock-Eval data as follows:

$$b = (Y_1 - Y_2)(X_2 - X_1)^{-1} \quad (9)$$

and

$$a = Y_1 + X_1(Y_1 - Y_2)(X_2 - X_1)^{-1} \quad (10)$$

Thereafter, the values of apparent activation energy and frequency factor can be found by replacements in Equations (8) and (7) as follows:

$$E = bR^{-1} \quad (11)$$

$$A = \beta b(1 - 2Tb^{-1})^{-1} \quad (12)$$

Table 2 proves suitability of the approximation (4) by the practical coincidence of E and A found by means of a and b , with the values found feeding E values into the two-equations system expressed as Equation (2).

The coefficients a and b allow calculation of any current transformation ratio during a non-isothermal pyrolysis as follows:

$$x = 1 - \exp[-T^2 \exp(a + b/T)] \quad (13)$$

Since Equations (3) and (4) explain a proportional change in a with $\ln(1/\beta)$, the model proposed allows to predict the kinetics at any heating rate. The current yield of the total hydrocarbons from the initial samples is expressed as $0.1x(S1 + S2)\%$, and the reaction time as $(T - T_0)/\beta$.

Figure 1 shows the effect of temperature on the transformation ratios of the oil potential (S1+S2) at heating rates 5 and 25 min^{-1} predicted using Equation (13) and constants in Table 2. It is evident that an increase in the heating rate swifts the transformation curves to the region of higher temperature. As it could be expected, a non-isothermal pyrolysis process takes less time at the higher heating rate (Fig. 2).

The pyrolysis kinetic constants found arrange the samples as follows: Dictyonema argillite > pine sawdust < peat < kukersite < pine bark < willow < spruce branches < reed.

It is noteworthy that the values of E and A obtained for the different samples prove the phenomenon reported earlier [13, 14] – an increase in frequency factors and activation energy in hydrocarbon generation according to a linear regression

$$\ln A = b_0 + b_1 E \quad (14)$$

Figure 3 shows that the kinetic constants found for bulk of the samples studied in this work (Table 2) result in a good correlation ($r = 0.995$), the value for b_0 is $-4.46 (\pm 1.61)$ and for b_1 is $0.228 (\pm 0.010)$.

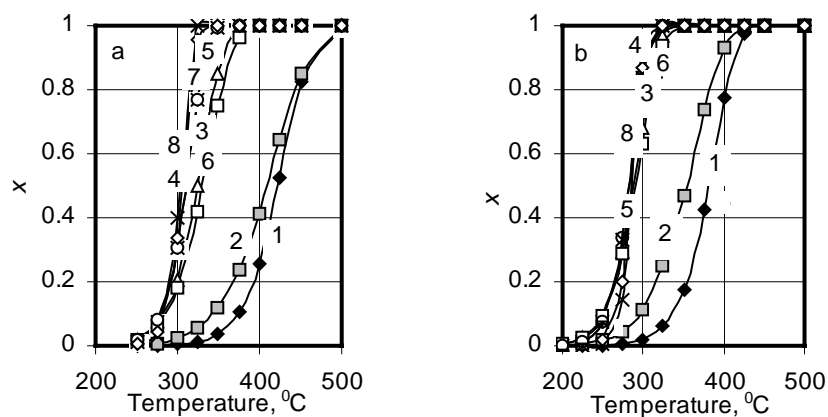


Fig. 1. Effect of temperature on the total yield of hydrocarbons from 1 – kukersite, 2 – Dictyonema argillite, 3 – peat, 4 – reed, 5 – willow, 6 – pine sawdust, 7 – pine bark, 8 – spruce branches. Heating rate: a – 25, b – 5 $^{\circ}\text{C}\text{min}^{-1}$

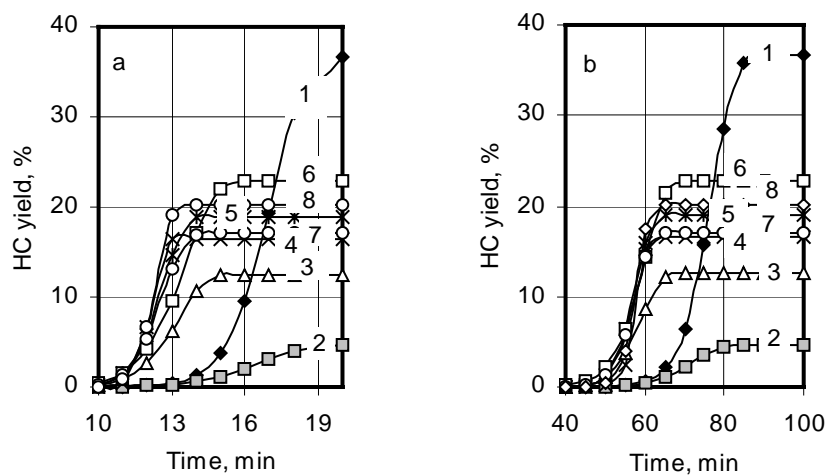


Fig. 2. Effect of time on total yield of hydrocarbons.
See the heating rates and initial samples in Fig. 1

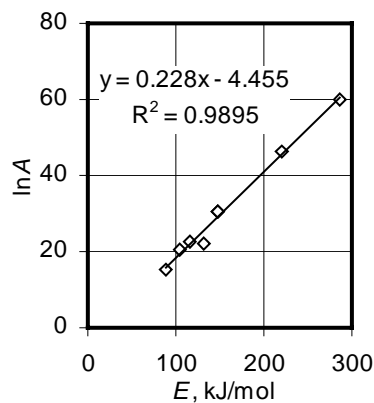


Fig. 3. Plot of $\ln A$ versus E .

Isothermal kinetics for evolution of hydrocarbons from thermolabile compounds

The apparent rate coefficient at a temperature T for the total single first order reaction is expressed as

$$k_T = -[\ln(1 - x_1)]/t \quad (15)$$

where x_1 is the evolution degree of the total volatiles from thermolabile compounds. Admitting that the first maximum is attained at half-time value

where $x_1 = 0.5$, the rate coefficients at 300 °C can be found introducing into Equation (15) the pyrolysis time at the first FID maximum for S1 (Table 3).

Table 3. Rate coefficients for evolution of hydrocarbons at 300 °C

	Kukersite	Dictyo-nema	Peat	Reed	Willow	Pine sawdust	Pine bark	Spruce branches
$t_{\max 1}$, min	0.27	0.39	1.08	0.888	1.08	0.873	0.641	0.473
k_{573}	2.56	1.77	0.64	0.78	0.64	0.79	1.08	1.46
E_1	93.2	89.3	76.7	79.4	76.7	79.6	83.5	87.1
$\ln A_1$	16.8	15.9	13.0	13.6	13.0	13.7	14.6	15.4

The percentage of hydrocarbons expelled from an initial sample at time t (α) can be calculated as follows:

$$\alpha = 0.1S1[1 - \exp(-k_T t)] \quad (16)$$

Fig. 4 illustrates the time-dependencies of the yields of the fragments from thermolabile OM of the samples calculated using Equation (16) and the values of S1 estimated by Rock-Eval procedure at 300 °C.

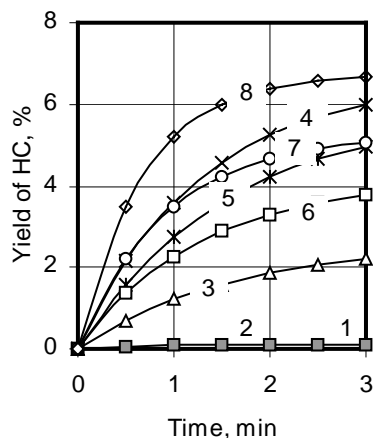


Fig. 4. Effect of time on the yield of hydrocarbons from thermolabile compounds at 300 °C. See the initial samples in Fig. 1

The Rock-Eval data and the regression (14) allow estimating the apparent values of kinetic constants for evolution of the total thermolabile and/or adsorbed organic components (A_1 and E_1) despite the process has been carried out only at one temperature. For this aim, the member $\ln A$ in the Arrhenius equation

$$\ln k = \ln A - E/RT \quad (17)$$

is replaced by its expression (14). After replacements the following equations are obtained for the kinetic constants

$$E_1 = (\ln k_{573} - b_0)/[b_1 - 1/(573R)] \quad (18)$$

and

$$\ln A_1 = k_{573} + E_1/(573R) \quad (19)$$

The values of E_1 and $\ln A_1$ found and given in the last rows of Table 3 allow prediction of the time dependence of x_1 at any temperature by means of Equations (17) and (15). For estimation of the percentage of hydrocarbons expelled from the thermolabile ingredients in time according to Equation (16), the S1 value for this temperature should be determined.

Conclusions

1. The basic Rock-Eval analysis can give a defined information on the pyrolysis kinetics.
2. Mathematical models are proposed basing on the data of Rock-Eval analysis (S1, S2 and T_{\max}) obtained only at one heating rate for estimation of the apparent activation energy (E) and frequency factor (A) of the total evolution of hydrocarbons, and for prediction of current yields of hydrocarbons in time and temperature.
3. A linear relationship ($r = 0.995$) is revealed between the kinetic constants for the bulk of eight samples studied: $\ln A = -4.46 + 0.228E$.
4. A mathematical model is proposed for estimation of apparent kinetic constants, A_1 , and E_1 , for evolution of hydrocarbons from thermolabile ingredients by means of S1 and the equation presented in p. 3.

The data obtained by Rock-Eval analysis characterise the oil potential and pyrolysis kinetics at traditional pyrolysis. The pyrolysis kinetics and yield of hydrocarbons can be improved using special catalysts, and specific technologies.

Acknowledgements

Authors are grateful for financial support from the Estonian Science Foundation (Grants 5357 and 5360).

REFERENCES

1. Rock-Eval 6. User's Guide // <http://www.vinci-technologies.com>.
2. Lafargue, F., Marquis, E., Pillot, D. Rock-Eval 6 applications in hydrocarbon exploration, production, and soil contamination studies // Rev. Inst. Fr. Pet. 1998. Vol. 53, No 4. P. 421–437.

3. Sykes, R., Snowdon, L. R. Guidelines for assessing the petroleum potential of coaly source rocks using Rock-Eval pyrolysis // *Org. Geochem.* 2002. Vol. 33, No. 12. P. 1441–1455.
4. Dahl, B., Bojesen-Koefoed, J., Holm, A., Justwan, H., Rasmussen, E., Thomsen, E. // A new approach to interpreting Rock-Eval S2 and TOC data for kerogen quality assessment // *Org. Geochem.* 2004. Vol. 35, No. 11–12. P. 1461–1477.
5. Copard, Y., Disnar, J. R., Becq-Giraudon, J. F. // Erroneous maturity assessment given by T_{\max} and HI Rock-Eval parameters on highly mature weathered coals // *Int. J. Coal Geol.*, 2002. Vol. 49, No. 1. P. 57–65.
6. Ariztegui, D., Chondrogianni, C., Lafargue, E., McKenzie, J. A. Compositional variations in sedimentary organic matter in Lake Albano Holocene record: ecosystem reaction to environmental changes // In: P. Guilizzoni and F. Oldfield (eds), *Paleoenvironmental Analysis of Italian Crater Lake and Adriatic Sediments*. Mem. Ist. Ital. Idrobiol., 1996. Vol. 55. P. 111–117.
7. Wilkes, H., Ramrath, A., Negendank, J. F. W. Organic geochemical evidence for environmental changes since 34,000 yrs BP from Lago di Mezzano, central Italy // *J. Paleolimn.* 1999. Vol. 22, No. 4. P. 349–365.
8. Disnar, J. R., Guillet, B., Keravis, D., Di-Giovanni, C., Sebag, D. Soil organic matter (SOM) characterization by Rock-Eval pyrolysis: scope and limitations // *Org. Geochem.* 2003. Vol. 34, No. 3. P. 327–343.
9. Johannes, I., Bojesen-Koefoed, J. A., Kruusement, K., Palu, V., Veski, R. Evaluation of oil potential of Estonian oil shales and biomass using Rock-Eval pyrolysis // *Oil Shale*. Vol. 23, No. 2. P. 110–118.
10. Optkin 3.0 Software. <http://www.vinci-technologies.com>.
11. Torrente, M. C., Galan, M. A. Kinetics of the thermal decomposition of oil shale from Puertollano // *Fuel*. 2001. Vol. 80, No. 3. P. 327–334.
12. Li, S., Yue, C. Study of different kinetic models for oil shale pyrolysis // *Fuel Process. Technol.* 2004. Vol. 85, No. 1. P. 51–61.
13. Burnham, A. K., Braun, R. L. Global kinetic analysis of complex materials // *Energy Fuel*. 1999. Vol. 13, No. 1. P. 1–22.
14. Ansong G., Zewen, L. Kinetic studies of asphaltene pyrolysis and their geochemical application // *Appl. Geochem.* 2002. Vol. 17, No. 12. P. 1529–1541.

Presented by J. Soone

Received May 17, 2005