EVALUATION OF OIL POTENTIAL OF ESTONIAN SHALES AND BIOMASS SAMPLES USING ROCK-EVAL ANALYZER

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A possibility for evaluation of oil potential of two Estonian shales and six biomass samples by Rock-Eval data is described. The amount of hydrocarbons volatilized from thermo-labile ingredients of the samples at 300 ^{0}C (S1) is found to increase from 1.1 to 66.3 mg/g in the row: Dictyonema < kukersite < peat < pine sawdust < pine bark < willow < reed ≈ spruce branches. The total oil potential by pyrolysis at 300–650 ^{0}C (S1+S2) increases from 47.4 to 367 mg/g in the row: Dictyonema < peat < reed < pine bark < willow energy crop < spruce needles < pine sawdust < kukersite. An increase in oxygen index decreases the temperature at the pyrolysis maximum rate and S2 but increases S1 of the samples according to relationships approximated to linear regressions.

Introduction

Rock-Eval pyrolysis has been a widely used method in organic geochemistry as a rapid standard tool for examining the oil and gas potential and maturity of different rock samples [1–4], including sediments cored within the framework of the Ocean Drilling Program [5]. Also some soils, Holocene and Pleistocene lake sediment samples and contaminated soils have been examined [6, 7] with the aim to elucidate ecosystem's reaction to environmental changes. Thereby, we cannot find any Rock-Eval investigations related to biomass, in spite particular woody material is a common minor part of young sediments.

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The Rock-Eval instrument was developed at Institut Francais du Pétrole (IFP) in 1977 [8] and later modified by Lafargue [9] and Behar [10]. The detailed user's guide can be found in [11]. The method consists in estimating petroleum potential of rock samples by pyrolysis according to a programmed temperature pattern. The temperature programs are defined in order to distinguish, by a flame ionization detector (FID), thermo-vaporized free hydrocarbons and/or fragments from thermolabile compounds at 300 °C (peak S1), and potential hydrocarbons that can be released during thermo-destruction of organic matter (OM) within the range 300–650 °C (peak S2). In addition, CO and CO_2 released during pyrolysis are monitored by means of an IR cell, providing information on the oxidation state of OM. The method is completed by oxidation of the rock sample according to a programmed temperature pattern. This complementary stage allows determination of total organic carbon and mineral carbon content of samples.

The main parameters estimated by the basic Rock-Eval method, their abbreviations, and the parameters found from Rock-Eval data by simple calculations have been given in the User's Guide [11] and are presented in Tables 1 and 2.

The recent works of our laboratory attended to destruction of Estonian oil shale kerogen, oil generation from reed, and oil shale pyrolysis kinetics are described in the papers [12–15].

Table 1. **Rock-Eval parameters and their abbreviations**

	Detector / Oven	Unit	Name
S1	FID / Pyrolysis at 300 ^{0}C	mg HC/g sample	Free hydrocarbons
S2	FID / Pyrolysis at 300–650 ^{0}C	mg HC/g sample	Oil potential
T_{max}	Pyrolysis, thermocouple	°C	Temperature for maximum of curve S2
S3	IR / Pyrolysis, 850 ^{0}C	mg CO_2/g sample	CO_2 from organic source
S3 CO	IR / Pyrolysis, 850 ^{0}C	mg CO/g sample	CO from organic source
S4 CO_2	IR / Oxidation	mg CO_2/g sample	CO_2 from organic source

Table 2. **Calculated Rock-Eval parameters and their abbreviations**

	Unit	Formula	Name
PI		S1/(S1 + S2)	Production index
PC	wt.%	0.1[0.83(S1 + S2) + 0.273S3 + 0.429(S3CO + 0.5S3'CO)]	Pyrolysable organic carbon
TOC	wt.%	PC +RC	Total organic carbon
BI		100S1/TOC	Bitumen index
HI		100S2/TOC	Hydrogen index
OI		100S3/TOC	Oxygen index
RC CO	wt.%	0.0428S4 CO	Residual carbon organic (CO)
RC CO_2	wt.%	0.0273S4 CO_2	Residual carbon organic (CO_2)
RC	wt.%	RC CO + RC CO_2 = TOC – PC	Residual carbon organic.

In this work, application of Rock-Eval pyrolysis for characterization of fuel potential of different biomass samples and two Estonian shales is studied.

Experimental

Materials and methods

The source materials studied were two samples of Estonian Ordovician shales (kukersite rich in carbonates, and alumosilicate "black shale"– Dictyonema argillite), and six biomass samples (peat, common reed, willow, pine sawdust, pine bark and spruce branches).

The samples were powdered by a disintegration-type mill and dried at room temperature. The percentages of OM in the biomass samples were found by the amount of ash at 850 °C [16] and hygroscopic water [17], and for the oil shales by ash of the acid-treated samples counting the contributions of hygroscopic water and pyrite. Carbon content of OM for kukersite was found excluding the contribution from carbonates (12.8% CO_2). Characteristics of the initial samples are presented in Table 3.

Table 3. **Characteristics of the initial samples, %**

	Moisture	Ash (A^d)	Carbonate (CO_2)^d	Organic matter (OM)
Kukersite	0.6	37.2	12.8	50.5
Dictyonema	1.4	81.2	0	16.0
Peat	12.9	6.8	0	93.2
Reed	7.5	3.0	0	97.0
Willow	7.2	1.6	0	98.4
Pine sawdust	9.1	0.4	0	99.6
Pine bark	8.8	2.1	0	97.9
Spruce branches	7.9	3.5	0	96.5

The elemental and Rock-Eval analyses were performed at the Geological Survey of Denmark and Greenland using an elemental analyser *CHN-2000*, and a Rock-Eval instrument *RE6* at standard conditions [11] under the heating rate 25^0/min. The values of TS (total sulphur), TC and TOC (for the residue remained after treatment with acidic solution) were obtained on the instrument *LECO CS*-200.

Results and discussion

The data obtained by elemental analysis (Table 4) and Rock-Eval analysis (Table 5) show large variability between the samples studied. At that, noteworthy high values of S1 (25–66 mg/g) and PI (0.18–0.40) are characteristic of biomass samples.

Table 4. **Elemental composition, %**

	Initial samples (air dry)			Organic matter			
	C	H	N	C	H	N	$O^{1)}$
Kukersite	41.46	4.77	0.15	79.32	9.50	0.30	10.88
Dictyonema shale	11.52	1.45	0.42	73.02	9.19	2.66	15.12
Peat	46.33	5.87	2.15	57.07	7.23	2.65	33.05
Reed	39.25	5.83	0.56	43.74	6.50	0.62	49.13
Willow	42.14	6.10	0.61	46.15	6.68	0.67	46.50
Pine sawdust	45.47	6.45	0.13	50.22	7.12	0.14	42.51
Pine bark	45.47	6.24	0.43	52.01	6.99	0.48	40.52
Spruce branches	44.37	6.33	0.93	49.92	7.12	1.05	41.91

$^{1)}O = 100 - (C + H + N)$

Table 5. **Rock-Eval data**

	Kuker-site	Dictyonema	Peat	Reed	Willow	Pine sawdust	Pine bark	Spruce branches
TOC, %	36.40	10.81	38.19	26.19	29.70	36.65	35.59	28.36
TC, %	40.96	10.70	45.28	37.56	40.60	43.63	44.70	43.02
TS, %	2.01	2.90	0.79	0.35	0.22	0.16	0.12	0.13
T_{max}	423	411	332	308	319	338	319	312
S1, mg/g	1.30	1.11	25.78	66.29	58.07	41.53	52.71	67.40
S2, mg/g	365.73	46.24	99.48	98.43	131.47	183.17	118.02	133.77
S3, mg/g	4.85	4.30	81.48	68.98	68.09	40.95	62.09	66.51
HI	1005	428	260	376	443	500	332	472
OI	13	40	213	263	229	112	174	234
PI	0.003	0.023	0.206	0.402	0.306	0.184	0.309	0.335
PC	30.46	3.93	10.40	13.67	15.73	18.65	14.17	16.70
RC, %	5.94	6.88	27.79	12.52	13.97	18.00	21.42	11.66

Figure 1 demonstrates that
- the data of TC obtained by *LECO CS*-200 are fairly close to those obtained by elemental analysis;
- the content of TOC is 5–16 absolute % less than the content of TC, except Dictyonema shale in which TOC ≈ TC (see discussion below);
- TOC increases from 10.81 to 38.19 mg/g in the row: Dictyonema < reed < spruce branches < willow < pine bark < kukersite < pine sawdust < peat;
- OI giving information about oxidation state increases from 13 to 263 in the row: kukersite < Dictyonema < pine sawdust < pine bark < peat < willow < spruce branches < reed.
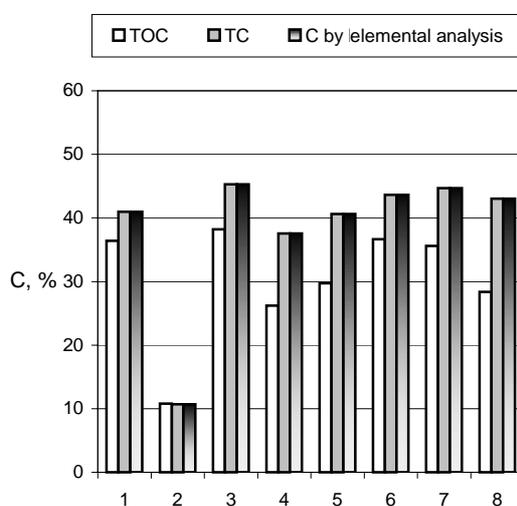
Fig. 1. Values of TOC and TC, and carbon content obtained by elemental analysis of the samples: 1 – kukersite, 2 – Dictyonema, 3 – peat, 4 – reed, 5 – willow, 6 – pine sawdust, 7 – pine bark, 8 – spruce branches

It is clear that for kukersite TOC should be less than TC due to carbonates, and for Dictyonema argillite the values of TC and TOC should coincide. For biomass samples in which the percentage of OM reaches 93.2–99.6 and no mineral carbon was found (Table 3), the values of TOC and TC should coincide. The differences revealed can be explained by a substantial hydrolysis and solution of biomass ingredients (sugars, starch, pectin, hemicelluloses) at the acid treatment before determination of TOC by LECO CS-200 instrument. Figure 2 depicts a good linear correlation between the percentage of dissolved carbon (difference between TC and TOC) and S1 values for the not matured biomass samples. So, in further discussions the corrected value TOC*, equal to TC, is applied instead of TOC for the biomass samples. The corrected values of the Rock-Eval characteristics calculated using the TOC* value are given in Table 6.

Several researchers have tried to evaluate S2 or HI as predictors of oil-generative potential of coals by their correlation with atomic H/C. The results were generally disappointing [1]. Figure 3 demonstrates imperfection of the relationship for the bulk of biomass studied in this work, too.

The values of RC have a tendency to decrease with an increase in PC. For the corrected values, excluding Dictyonema argillite, the relationship can be approximated to a linear regression with correlation coefficient r = 0.954 (Fig. 4).
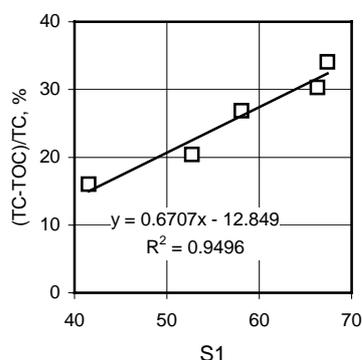
Fig. 2. Relationship between S1 and underestimation percentage of TOC for biomass samples

Table 6. **Corrected Rock-Eval data for biomass samples**

	Peat	Reed	Willow	Pine sawdust	Pine bark	Fir branches
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
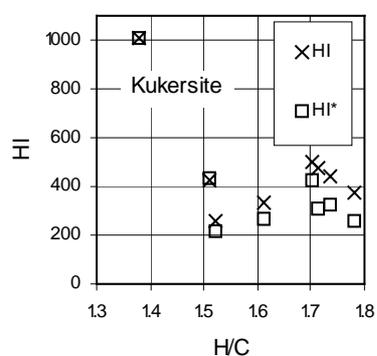
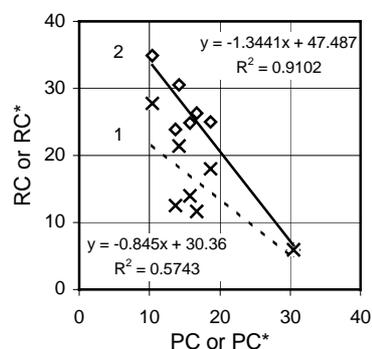*Fig. 3.* Effect of H/C (g/g) on the values of HI and on the corrected values HI*

Fig. 4. Relationship between RC and PC (curve 1), and between their corrected values (curve 2)

The value of T_{max} for rocks and sediments is known to be determined by their thermal evolution formerly undergone. For the biomass (with zero thermal history) and oil shales studied the row according to the increase of T_{max} is as follows: spruce branches < reed < pine bark = willow < peat < sawdust < Dictyonema < kukersite. Such a succession can be explained by two reasons:

- the more matured is an OM, the higher is its T_{max};
- the facile breakage of weak bonds of carbon atoms with oxygen decreases T_{max}.

The latter is illustrated by a negative linear dependence of T_{max} on the oxygen index (Fig. 5) which has a good correlation for the total samples. At that, the effect of the corrected values, OI*, is more intensive than that of OI.

Great variations in the oil yield (S1 and S2) from the different biomass samples are related with their oxygen content, alike T_{max} is related with OI. This effect is proved by satisfactory linear negative relationships of the plots of S2 and S2/OM versus OI or OI* when Dictyonema or kukersite is excluded (Fig. 6a and 6b, curves 2 and 2*). Noteworthy is an oppositely, positive, effect of OI on the S1 and S1/OM values for all the samples studied (Fig. 6a and 6b, curves 1 and 1*).
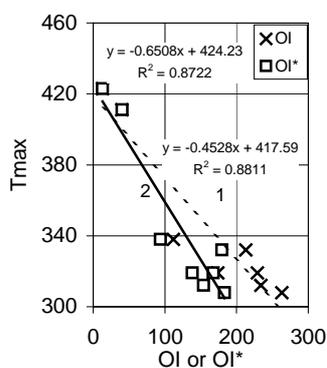

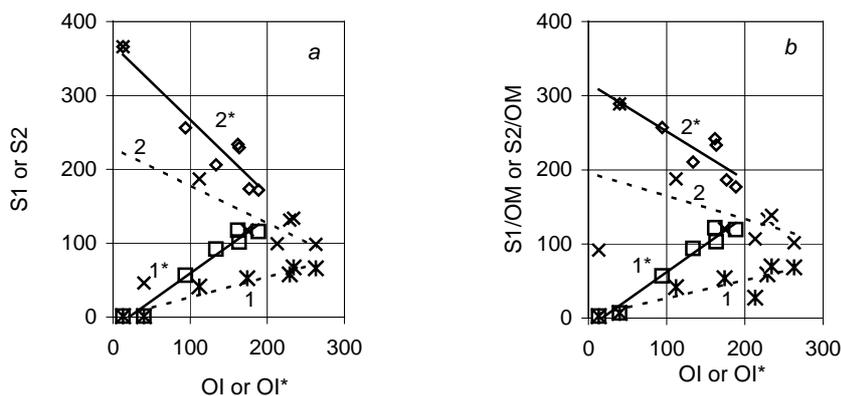*Fig. 5.* Effect of OI (curve 1) or OI* (curve 2) on T_{max}

Fig. 6. Effect of OI and OI* on the values of S1 and S2 for the initial samples (*a*) and for their organic matters (*b*) at temperature 300 °C (curves 1, 1*) and at 300– 650 °C (curves 2, 2*)

Conclusions

1. The Rock-Eval analysis can give an essential information on the oil potential of Estonian oil shales and six biomass samples studied. At that, the basic data of Rock-Eval are excellent for kukersite and Dictyonema argillite, but the procedure applied gives in 16–34 relative % under-estimated values of the total organic carbon (TOC) for the biomass samples. The discrepancy is resulted by a notable part of acid-soluble organic matter in the "non-geological" samples being extracted before estimation of TOC. So, for the biomass samples the true values of TOC, OI, HI, BI and RC should be calculated using TC instead of TOC stated.

2. The corrected values for RC increase with a decrease in PC according to a linear relationship from 5.94% to 34.8% in the row: kukersite < reed < willow < pine sawdust < spruce branches < pine bark < peat.

3. The amount of hydrocarbons volatilized from thermolabile ingredients of the samples at 300 °C (S1) increases from 1.1 to 67 mg/g in the row: Dictyonema shale < kukersite < peat < pine sawdust < pine bark < willow < reed ≈ spruce branches.

4. The total oil potential at pyrolysis under 300–650 °C (S1+S2) increases from 47.4 to 367 mg/g in the row: Dictyonema < peat < reed < pine bark < willow < spruce branches < pine sawdust < kukersite.

5. The corrected oxygen index of the samples increases from 13 to 188 in the row: kukersite < Dictyonema < pine sawdust < pine bark < spruce branches < willow < peat < reed. An increase in OI decreases the temperature at the maximum rate of pyrolysis (T_{max}) and S2 but increases S1 of the samples according to relationships approximated to linear regressions.

Acknowledgements

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