

Genetic potential of the Histria petroliferous basin

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Abstract: - The paper identifies geochemically the petroliferous system Histria on the Romanian shelf of the Black Sea from the extension the orogene from north Dobrogea. This petroliferous system consists from the following two subsystems: the first is of generation-expulsion type and is formed by the oligocene source rock and the second one is of migration-accumulation type and is formed by the accumulations of gases and oil which belong to the cretacic and eocene natural reservoirs. We have noticed through Rock-Eval analyses that the organic matter from the source rocks is of continental nature and generates gases and at the same time is of algae nature (lacustrine and/or marine) and generates oil and gases.

Key-Words:- Rock-Eval analysis, petroliferous basin, subsidence, hydrocarbons.

1 Introduction and geological background

The Dobrogea county of Romania consists of the following tectonic units: North Dobrogea Orogen, Central Dobrogea Massif and South Dobrogea Platform. These units extend eastwards beneath the Black Sea into the Romanian shelf, and are separated by major faults Sf. Gheorghe, Peceneaga-Camena, Capidava-Ovidiu and Intramosică (Călărăși-Fierbinți, Fig.1). The shelf portion of the North Dobrogea Orogen consists of three thrust sheets, with the thrusting direction towards north-west: the Tulcea thrust, the Niculitel thrust and the Macin thrust. These structural elements form the basement for the sedimentary succession that accumulated during the evolution of the Black Sea in the offshore extension of the North Dobrogea Orogen. Within this tectonic setting, the northern portion of the Romanian offshore includes a continental shelf and a deeper-water basin; the latter defines the Histria Basin („Histria Depression”), which has actively received sediments starting with the Aptian. The continental slope that outlines the Histria Basin is partly controlled by basement faults (e.g., the Peceneaga-Camena fault to the south). This slope formed in relation to the extensional regime that accompanied the opening of the intra-cratonic rift basin of the Black Sea during the late Aptian-Albian.

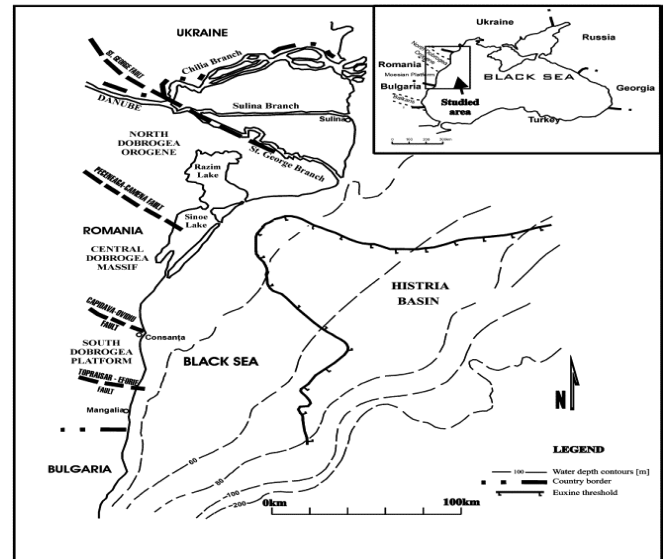


Fig. 1 Location of the Romanian offshore

All hydrocarbon-bearing reservoirs which are presently known within the Histria Basin (Sinoe, Delta, West Lebăda, East Lebăda and Pescăruș fields) were deposited during the Albian-Eocene interval.

The Histria Basin entered a compressional regime starting with the beginning of the Oligocene.

The transition from extension, which dominated the evolution of the basin until the end of the Eocene, to

WELL	DEPTH	TOC ^o	S ₁ ^o	S ₂ ^o	f _{ci} ^o = 1 - 0.085 · (S ₁ ^o + S ₂ ^o) / TOC ^o
-	m	%	mgHC/g rock		-
31	812.5	1.16	0.18	0.44	0.955
Sinoe	922.5	1.85	0.15	1.23	0.937
813	952.5	1.38	0.20	1.07	0.922
Lebăda V.	1082.5	1.60	0.18	1.80	0.890
31	1087.5	1.03	0.15	0.77	0.924
Sinoe	1202.5	1.07	0.08	0.53	0.951
Mean	-	-	-	-	0.929

Table 1. The computation of the initial fraction of residual organic carbon from the oligocene source rock

compression starting with the Oligocene, generated significant tectonic inversion, and was accompanied by high rates of subsidence in the basin. This tectonic inversion resulted in the uplift of the basement along the edge of the Histria Basin during the Oligocene, as well as in the progradation of the depocenter. High sediment supply following the Oligocene basin-margin uplift resulted eventually in the complete fill of the Albian-Eocene 'depression' [4].

Oligocene sediments in the Histria Basin are generally of pelitic character. The Oligocene Sea was initially opened to the east and north-east of the Histria depression. In the center and the north-west part of the depression, the environmental conditions were typical of a restrictive, closed basin of anoxic type. Subsidence within the basin led to rapid burial of the sediments and the preservation of organic matter, conducive to the formation of source rocks.

Following burial, the source rocks entered a geothermic field adequate to the maturation and expulsion of hydrocarbons. Starting with the late Lower Miocene, the Oligocene source rocks have generated and expelled hydrocarbons. These hydrocarbons accumulated in traps with reservoirs of Eocene, Upper Cretaceous and Albian age, following the process of primary and secondary migration. The Oligocene shales played both the role of source rocks in the Histria Basin, and seal for the underlying Albian to Eocene reservoirs. This relationship between the Albian – Eocene reservoirs and the Oligocene source rocks and seals defines the petroleum system of the Histria Basin. This petroleum system has been studied by means of chemical analyses of the oil produced from the Sinoe, Delta, West Lebăda, East Lebăda and Pescăruș fields, as well as of the natural bitumen collected from the Oligocene source rocks.

2 The generation and expulsion of hydrocarbons: the method

We consider a source rock analyzed through combustion. By using this method, one can measure the amount of total organic carbon content TOC as the ratio between the mass of organic carbon C obtained during burning and the mass m_{rs} of the source rock:

$$TOC = \frac{C}{m_{rs}}, [\%] \text{ or } [g \text{ OC}/100 \text{ g rock}]. \quad (1)$$

From relation (1) we obtain the quantity C of organic carbon:

$$C = 10 \cdot TOC \cdot m_{rs}. [\text{mg OC}]. \quad (2)$$

A source rock stores a certain quantity of organic matter which may vary through time as the organic matter matures and hydrocarbons are released. If we analyzed the rock through combustion at an initial reference moment in time, when the initial quantity of total organic carbon is TOC^o , then the corresponding initial quantity of organic carbon is:

$$C^o = 10 \cdot TOC^o \cdot m_{rs}. [\text{mg OC}]. \quad (3)$$

As the source rock is buried gradually during the evolution of the sedimentary basin, it may reach an adequate geothermal field that may lead to the maturation of the organic matter and to the expulsion of hydrocarbons. It is assumed that the rock has already released a certain quantity of hydrocarbons within the sedimentary basin at the moment of extraction from the producing fields.

The quantity of organic carbon corresponding to the expelled hydrocarbons ΔOC is given by the difference between the initial quantity of organic carbon C^o and the residual (present-day) quantity of organic carbon C as determined through combustion on the analyzed source rock:

$$\Delta OC = (C^o - C), [g \text{ OC}] \quad (4)$$

From (2), (3) and (4) we have:

$$\Delta OC = 10 \cdot (TOC^o - TOC) \cdot m_{rs}, [\text{mg OC}] \quad (5)$$

or:

$$\Delta OC = 10 \cdot TOC^o \cdot (1 - TOC / TOC^o) \cdot m_{rs}, [\text{mg OC}]. \quad (6)$$

We define the following factor of hydrocarbons expulsion:

$$f_{ex} = 1 - TOC / TOC^o \quad (7)$$

From (6) and (7) we have:

$$\Delta OC = 10 \cdot f_{ex} \cdot TOC^o \cdot m_{rs}, [\text{mg OC}], \quad (8)$$

or:

$$\Delta OC / m_{rs} = 10 \cdot f_{ex} \cdot TOC^o, [\text{mg OC}/g \text{ rock}], \quad (9)$$

Relation (9) enables us to calculate the quantity of hydrocarbons expelled from the source rock. The conversion of the quantity of organic carbon $\Delta OC / m_{rs}$ into expelled hydrocarbons $\Delta HC / m_{rs}$ is possible using a „w” coefficient.

WELL	DEPTH	TOC	S ₁	S ₂	f _{ci}	TOC ^o	f _{ex}	f _{ex} ^{ph}	1/2 · f _{ex} ^{ph}
-	m	%	mg HC/g rock		-	%	-	-	-
10 Tomis	1487.5	0.95	0.11	1.19	0.884	1.00	0.0500	0.0111	0.0055
	1832.5	1.49	0.09	1.17	0.928	1.49	0	0	0
817 Lebăda V.	2067.5	1.31	0.09	1.31	0.909	1.34	0.0224	0.0050	0.0025
816 Lebăda V.	2215.0	3.93	0.71	22.12	0.506	7.21	0.4549	0.1871	0.0936
75 Cobălcescu	3497.0	2.27	0.50	3.93	0.834	2.53	0.1028	0.0228	0.0114
	3995.5	1.87	0.27	4.29	0.793	2.19	0.1461	0.0341	0.0170

Table 2. The initial content of total organic carbon and the expulsion factors from the oligocene source rock

According to Pepper and Corvit [3] this coefficient depends upon the number of carbon atoms in the molecule, and varies between 0.75 and 0.87 mg OC/mg HC (0.75 for methanol and 0.87 for n-alcans with infinite length).

Cooles et al. [1] and Lewan et al. [2] considered an average value of $w = 0.85$ mg OC/mg HC. According to this approach, the quantity of hydrocarbons expelled from a source rock is:

$$\Delta HC/m_{rs} = 10 \cdot f_{ex} \cdot TOC^o / 0.85 \text{ [mg HC/ g rock]}. \quad (10)$$

In order to estimate the quantity of hydrocarbons expelled by a source rock using relation (10) it is necessary to know its initial total organic carbon content TOC^o . The amount of initial total organic carbon of the source rock may be estimated by using an algorithm as described below.

We consider a source rock analyzed through combustion and pyrolysis (Rock-Eval analysis). The analysis through combustion allows the measurement of the total organic carbon content TOC ; pyrolysis allows one to determine the S_1 , S_2 and S_3 peaks, which have the following meaning:

◆ The S_1 peak represents the free (mobile) hydrocarbons generated by the organic matter in the source rock;

◆ The S_2 peak represents the fixed hydrocarbons generated by the organic matter in the source rock as a result of pyrolysis;

◆ The S_3 peak relates to residual organic matter which does not contribute to the generation of hydrocarbons. According to the principle of mass balance, the following relation is true:

$$TOC = S_1 + S_2 + S_3. \quad (11)$$

The TOC is expressed in terms of % or gOC/100grock; the S_1 and S_2 peaks are expressed in terms of mgHC/grock; and the S_3 peak is expressed in terms of mg CO₂/g rock. In order to homogenize relation (11) we consider the following homogenization factor:

$w = 0.85$ mg OC/mg HC. Consequently:

$$10 \cdot TOC = 0.85 \cdot (S_1 + S_2) + S_3, \text{ [mg OC/g rock]}. \quad (12)$$

We denote as f_{ci} the fraction of residual organic carbon from the total organic carbon content:

$$f_{ci} \cdot TOC = 0.1 \cdot S_3, \text{ [mg OC/g rock]} \quad (13)$$

From relations (12) and (13) we have:

$$f_{ci} \cdot TOC = TOC - 0.085 \cdot (S_1 + S_2) \quad (14)$$

and

$$f_{ci} = 1 - 0.085 \cdot (S_1 + S_2) / TOC. \quad (15)$$

The following relation between the ratio of total organic carbon content and the ratio of the corresponding fractions of the residual organic carbon can be established:

$$TOC^o / TOC = f_{ci}^o / f_{ci}, \quad (17)$$

or:

$$TOC^o = f_{ci}^o / f_{ci} \cdot TOC, \text{ [%]}. \quad (18)$$

The following workflow can be used to determine the initial total organic carbon content TOC^o in the source rock:

◆ We perform analyses of combustion and pyrolysis on rocks from the same sedimentary basin, which are similar from a petrographic standpoint with the studied source rock, but with immature organic matter. We thus determine TOC^o and the S_1^o and S_2^o peaks. We then use these values in relation (16) in order to determine the fraction f_{ci}^o of residual organic carbon from the initial content of total organic carbon for every immature rock. We then calculate their mean value:

$$f_{ci}^{med} = 1/n \cdot \Sigma f_{ci}^o \quad (19)$$

where (n) is the number of the analyzed samples;

◆ We use the TOC , S_1 and S_2 values known from the analysis of the actual source rock in relation (15) in order to calculate the f_{ci} fraction of residual organic carbon from the total organic carbon content;

◆ We then use the relation (18) written under the following form:

$$TOC^o = f_{ci}^{med} / f_{ci} \cdot TOC, \text{ [%]} \quad (20)$$

to determine the initial content of residual organic carbon of the analyzed rock.

3 The generation and expulsion of hydrocarbons

The Oligocene sedimentary formations from the Histria Basin consist generally of compact shales, immature organic matter and thus are representative for the initial conditions of formation of the source rock. Table 1 presents the initial content of organic carbon TOC^o and the values of the S_1^o and S_2^o peaks for each sample.

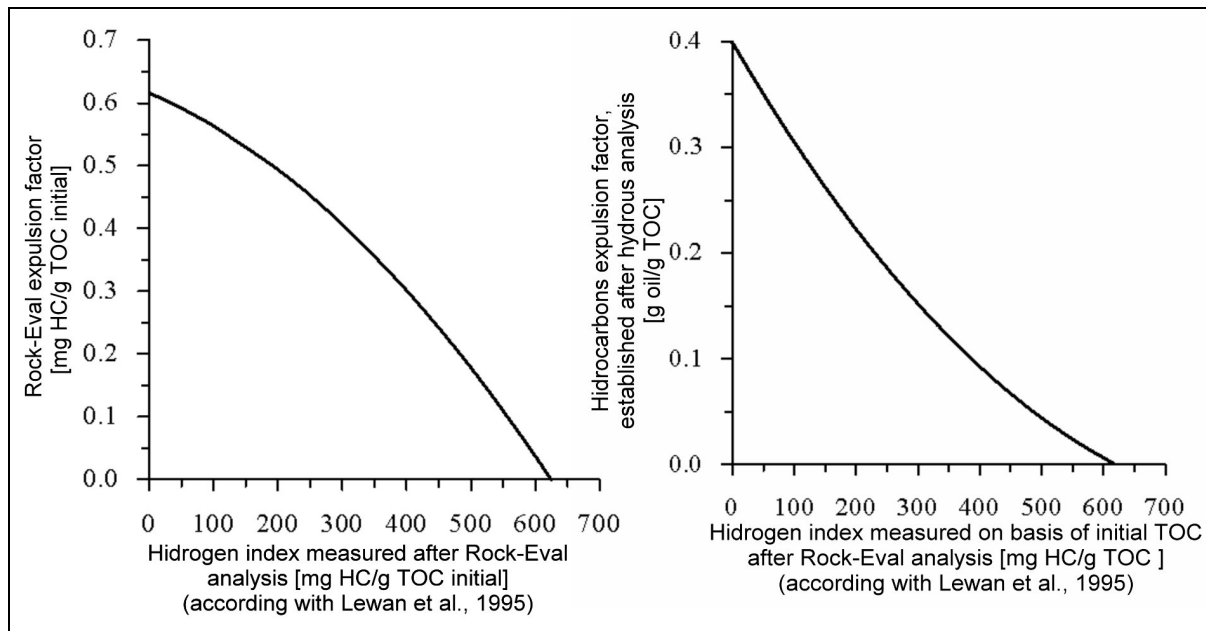


Fig. 2 Expulsion factor obtained through dry and hydro pyrolysis (Rock-Eval)

We then use the relation (16) to calculate the fractions f_{ci}^o of residual organic carbon from the initial contents of total organic carbon. The calculated mean value for the fractions f_{ci}^o is $f_{ci}^{med} = 0.929$.

Table 2 includes samples that contain mature organic matter and are likely to have expelled hydrocarbons in the past. Samples in the table are listed according to depth, and the corresponding values of TOC and of the S_1 and S_2 peaks are indicated as well. We use the relations (15), (20) and (7) to compute the fraction f_{ci} of residual organic carbon from the total organic carbon, the initial content in total organic carbon TOC^o , and the expulsion factor f_{ex} .

Lewan et al., [2] estimated the quantities of expelled hydrocarbons from the New Albany shale in the Illinois Basin. They noticed that the expulsion factor of the hydrocarbons determined according to the Rock-Eval pyrolysis method is overestimated. They proposed that a more realistic expulsion factor may be determined by using a hydro pyrolysis technique.

According to Lewan's et al. [2] experiments, a quantity of 300÷500 g of rock (with cuttings ranging in size from 0.5 cm to 2 cm) is introduced in a reactor which contains water at a constant temperature of 250÷365 °C. During hydro pyrolysis, water heating takes place in a closed circuit installation during a 3 to 6-day time interval. The pressure within the reactor may vary between 10 and 20 MPa, depending on temperature, the content of organic matter of the source rock and the duration of heating. The pressure is the result of the water vapours and of the presence of gases at the upper part of the reactor. If the rock sample is a potential source rock subjected to adequate conditions and duration for the experiment, the rock expels a quantity

of oil that accumulates at the surface of water in the reactor. The molecular and isotopic composition of the expelled oil is similar to that of natural oil. This suggests that the analysis through hydro combustion does simulate closely the natural process of hydrocarbon expulsion from source rocks. The analysis of the New Albany shales has demonstrated that the expulsion factor through hydro pyrolysis is smaller than the one obtained from Rock-Eval pyrolysis (Fig.3). We have used this conclusion to calibrate the results obtained in the case of the Oligocene source rocks in the Histria Basin. Figure 3 illustrates the correlation between the expulsion factor determined through the Rock-Eval method and the expulsion factor determined through hydro pyrolysis. The mathematical expression of this correlation is given by:

$$f_{ex}^{ph} = -304.802 \cdot 10^{-6} + 0.252828 \cdot f_{ex} - 0.781901 \cdot f_{ex}^2 + 6.27273 \cdot f_{ex}^3 - 13.65 \cdot f_{ex}^4 + 11.7165 \cdot f_{ex}^5$$

Table 3 presents the values of the expulsion factors f_{ex}^{ph} by taking into account the hydro pyrolysis. Even though hydro pyrolysis simulates the natural expulsion of hydrocarbons from the source rock, the expulsion factors obtained through hydro pyrolysis seem to overestimate the natural ones. Considering the variables which may lead to an overestimation of the expulsion factors determined through hydro pyrolysis (e.g., the increased solubility of the water from the network of natural bitumen; the decrease in pressure during the experiment; and the thermal expansion of the hydrocarbons) it was proposed that the expulsion factor under natural conditions is half of the expulsion factor measured with the method of hydro pyrolysis.

WELL	DEPTH	TOC ^o	$\frac{1}{2} \cdot f_{ex}^{ph}$	$\Delta HC/m_{rs}$	TYPE OF ORGANIC MATTER
-	m	%	-	mg HC/g rock	-
10 Tomis	1487.5	1.00	0.0055	0.065	Continental, produce gases
817 Lebăda V	2067.5	1.34	0.0025	0.039	
816 Lebăda V	2215.0	7.21	0.0936	7.939	Marine, produce parafinic and condensed oil
75 Cobălcescu	3497.0	2.53	0.0114	0.339	Continental, produce gases
	3995.5	2.19	0.0170	0.438	

Table 3. The unit quantities of expulsion hydrocarbons from the oligocene source rock

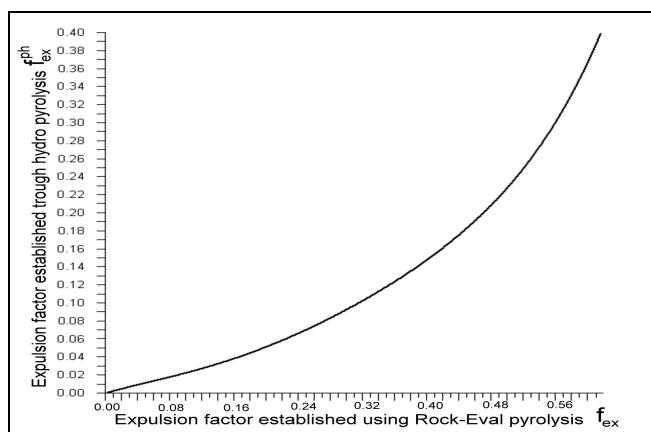


Fig. 3 Expulsion factor hydro depending with expulsion factor from Rock-Eval pyrolysis

Based on this conclusion, as well as considering relation (10), we have calculated in Table 3 the quantities of the hydrocarbons expelled in the case of the Histria Basin. It can be observed that the source rocks from the wells 10 Tomis, 817 West Lebăda and 75 Cobălcescu have expelled small amounts of gases, while the sample from the 816 Lebăda Vest well has expelled a much higher quantity of oil and gases.

4 Conclusions

The petroleum system of the Histria Basin develops along the offshore extension of the North Dobrogea orogen, within the deep-water setting of the Black Sea (Fig. 1). This system has a hydrocarbon generation-expulsion component, represented by Oligocene source rocks, and a migration-accumulation component that involves reservoirs of Albian to Eocene age.

This study focuses on the geochemical analysis of the Oligocene source rocks. Rock-Eval analyses indicate a complex origin for the organic matter in the source rocks, from a continental nature, generating gases, to a lacustrine and/or marine algal nature, generating oil and gases.

The expulsion potential of these rocks has been estimated to 0.039÷0.438 Kg gases/t rock and to 7.939 Kg oil/t rock.

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