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Maria-Fernanda Romero-Sarmiento, Daniel Pillot, Géremie Letort, Violaine Lamoureux-Var, Valérie Beaumont, et al.. New Rock-Eval Method for Characterization of Unconventional Shale Resource Systems. Oil & Gas Science and Technology - Revue d'IFP Energies nouvelles, 2016, 71 (3), pp.37. 10.2516/ogst/2015007 . hal-01395102

HAL Id: hal-01395102
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Oil & Gas Science and Technology – Rev. IFP Energies nouvelles (2016) **71**, 37
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DOI: 10.2516/ogst/2015007

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New Rock-Eval Method for Characterization of Unconventional Shale Resource Systems

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Abstract — *Unconventional resources such as tight, fractured and hybrid shale gas and oil plays as well as oil or kerogen shale systems, are considered exploitable self-contained source and reservoir rocks. A better understanding of the thermal cracking of sedimentary organic matter, hydrocarbons generation, expulsion, storage and retention mechanisms constitutes a key point, estimating the oil and gas in-place, free or adsorbed, for their exploration and exploitation. Herein, we introduce a new "ready to use" method of analysis and interpretation for the Rock-Eval 6 device for better assessment of free or sorbed hydrocarbons in unconventional shale plays. This method was developed at IFP Energies nouvelles (France) and was tested on 15 actual or potential unconventional shale samples from Silurian Shale (Algeria), Mississippian Barnett Shale (USA), Early Jurassic Shale (France), Late Jurassic Bazhenov Shale (Russia) and Eocene Green River Shale at different thermal maturity stages. Results indicate a better quantification of free and/or sorbed hydrocarbons (Sh0 and Sh1 peaks) as well as a more accurate determination of the Rock-Eval* T_{max} maturity parameter.

Résumé — **Nouvelle méthode de pyrolyse Rock-Eval pour la caractérisation des hydrocarbures de roches mères non conventionnels** — Les ressources non conventionnelles, en particulier les hydrocarbures de roches mères et les schistes bitumineux sont actuellement considérées comme des roches réservoirs pétroliers exploitables. Une meilleure compréhension sur le craquage thermique de la matière organique sédimentaire, sur les mécanismes de production/génération, d'expulsion, de stockage et de rétention des hydrocarbures constitue un point essentiel à la fois pour l'estimation mais également pour l'exploration et l'estimation du pétrole et du gaz en place (libre ou adsorbé) présents dans ces systèmes. Ici, nous présentons une nouvelle méthode d'analyse et d'interprétation pour le Rock-Eval 6 permettant une meilleure estimation/évaluation des hydrocarbures libres ou adsorbés au sein d'une roche mère non conventionnelle. Cette méthode, développée à l'IFP Energies nouvelles (France), a été élaborée et testée sur 15 échantillons de schistes actuels ou potentiels provenant : du Silurien *Shale* (Algérie), du Mississippien *Barnett Shale* (USA), du Jurassique Inférieur du Bassin de Paris (France), du Jurassique Supérieur *Bazhenov Shale* (Russie) et de l'Eocène *Green River Shale* (USA) et ce, à des stades différents de maturité thermique. Les résultats

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indiquent une meilleure quantification d'hydrocarbures libres et/ou adsorbés (pics Sh0 et Sh1) ainsi qu'une détermination plus précise du paramètre de maturité thermique le T_{max} du Rock-Eval.

INTRODUCTION

Over the last 30 years, the Rock-Eval pyrolysis has been widely used to identify organic matter occurrence, type and thermal maturity level. This technique has been also used to quantify the Total Organic Carbon (TOC) content as well as the mineral carbon content of both reservoir and source rocks (Espitalié *et al.*, 1986; Lafargue *et al.*, 1998; Behar *et al.*, 2001). The Rock-Eval 6 device is equipped with two ovens for pyrolysis and combustion processes, respectively. The hydrocarbons generated during a Rock-Eval analysis are monitored by a Flame Ionization Detector (FID) whereas the non-hydrocarbons compounds like CO_2 and CO released during pyrolysis and oxidation stages are monitored by an infra-red detector (Behar *et al.*, 2001). This pioneering device, thanks to the built-in "Basic/Bulk-Rock" and "Pure Organic Matter" methods, provides relevant parameters to respectively characterize any source rocks and isolated kerogens, in a petroleum system perspective. Applied to exploration purposes, the S2 peak, which is assigned to the hydrocarbon residual potential, is the main focus of these methods. It is widely accepted that the quantity of hydrocarbons released beyond 300°C is associated to the thermal cracking of the organic matter (kerogen) and is then refereed as the pyrolysis stage from Rock-Eval analyses. During this pyrolysis stage, hydrocarbons detected between 300 and 650°C or 300 and 800°C, according to user choice, correspond to the S2 peak surface from typical "Basic/Bulk-Rock" and "Pure Organic Matter" analyses.

In addition, the classical Rock-Eval thermal maturity parameter T_{max} is calculated from the temperature at which the S2 peak reaches its maximum. More details about the corresponding pyrolysis and oxidation conditions for these classical Rock-Eval methods are described in Lafargue *et al.* (1998) and Behar *et al.* (2001). When the S1 peak is the main concern, *e.g.* for reservoir units studies, an alternative built-in method, the "Reservoir" method, is available. This method is usually performed on cutting or core samples and is based on a pyrolysis temperature program allowing an improved recovery of "free" hydrocarbons, as a result of a lower initial temperature, and a better deconvolution of the released components. Moreover, the "Reservoir" method was shown to provide an estimation of API gravity of hydrocarbon fluids from cuttings (Trabelsi *et al.*, 1994). The "Reservoir" method pyrolysis temperature program is also designed to estimate the occurrence and nature of heavy oils and tars-mats intervals during drilling operations (Carpentier *et al.*, 1995, 1998). For the "Reservoir" method, the initial starting pyrolysis temperature is reduced to 180°C, in order to monitor the low-molecular weight hydrocarbons, which are not considered with the Basic/Bulk-Rock method as it starts at 300°C. The lower initial starting temperature is combined with a longer temperature plateau of 10 minutes for a more complete capture of the low-molecular weight hydrocarbons, resulting in a more realistic quantification of the hydrocarbons associated to the S1 peak, comparing to the Basic/Bulk-Rock method. The "Reservoir" method therefore provides two peaks designated as S1r and S2a, which in turn can be calculated to produce a "S1 peak" more equivalent to the conventional S1 peak from the Basic/Bulk-Rock method for reservoir oil and tar samples (Trabelsi *et al.*, 1994). S1r represents the very lightest fractions detected during the temperature plateau at 180°C whereas the S2a peak detects hydrocarbon compounds between 180 and 325°C (Trabelsi *et al.*, 1994). More details about the corresponding pyrolysis and oxidation conditions for the "Reservoir" method are described in Trabelsi *et al.* (1994).

Meanwhile, the increasing interest in unconventional gas and oil shale plays requires the development of a new method providing relevant parameters devoted to exploration and production of these new plays. The proposed method is designed to consider the specificity of the dual attributes of unconventional gas and oil shale plays: being a source rock and a reservoir. Herein, we introduce a specific IFPEN Shale Play method® (Patent 14/55.009, Pillot *et al.*, 2014) for any Rock-Eval 6 device, including a new pyrolysis program and associated parameters for evaluation of unconventional shale resources such as tight, fractured and hybrid shale gas and oil plays as well as oil or kerogen shale systems. This new method was elaborated and tested from 15 worldwide unconventional shale samples, *i.e.* Silurian Shale (Algeria), Mississippian Barnett Shale (USA), Early Jurassic Shale (France), Late Jurassic Bazhenov Shale (Russia) and Eocene Green River Shale (USA). This specific Rock-Eval method attempts to optimally quantify hydrocarbons still present within unconventional dual source/reservoir rocks.

1 MATERIAL AND METHODS

1.1 Description: The IFPEN Shale Play Method®

The *IFPEN* Shale Play method® is characterized by a specific temperature program, which allows a more exhaustive

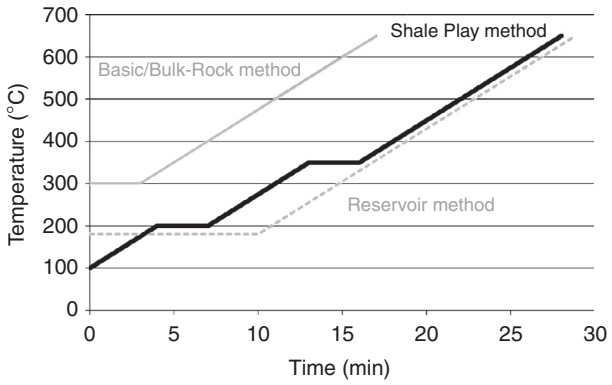


Figure 1

Rock-Eval temperature program for hydrocarbons characterization for the new IFPEN Shale Play method compared to the classical "Basic/Bulk-Rock" and "Reservoir" methods.

recovery and separation of the thermovaporizable hydrocarbons (which tentatively can be assigned to both free and sorbed hydrocarbons in shale plays). Figure 1 displays the thermovaporization and pyrolysis conditions defined for this new *IFPEN* Shale Play method® in comparison to the existing Reservoir and Basic/Bulk-Rock methods:

- Reservoir,
- Basic/Bulk-Rock.

The specific analytical conditions for the *IFPEN* Shale Play method® are described as follow:

- the pyrolysis step starts at T_1 = 100°C. This temperature is chosen as the most appropriate to initiate thermovaporization and capture eventually the quantity of the lightest hydrocarbons, still present in the sample;
- from initial T_1, the temperature is programmed to increase at a rate of 25°C/min, up to T_2 = 200°C. T_2 is maintained as a plateau for 3 minutes. During this step, the more easily thermovaporizable hydrocarbons are released and monitored;
- from T_2 plateau, the temperature is then increased at a rate of 25°C/min, up to T_3 = 350°C. This temperature is maintained for a plateau of 3 minutes. During this step heavier molecular weight compounds are thermovaporized. T_3 is assumed to correspond to the limit for onset of kerogen thermal cracking;
- from T_3, the temperature is raised again according to a linear temperature program defined by a rate of 25°C/min, up to a final temperature T_4 = 650°C, designed to release the pyrolyzable part of the remaining organic matter.

TABLE 1

Rock-Eval methods *versus* type of samples

Methods	Type of samples
Basic/Bulk-Rock	Source rocks
Reservoir	Reservoir oils and tars
Shale Play	Tight, fractured and hybrid shale gas and oil plays Oil or kerogen shale systems
Pure Organic Matter	Kerogen and coals

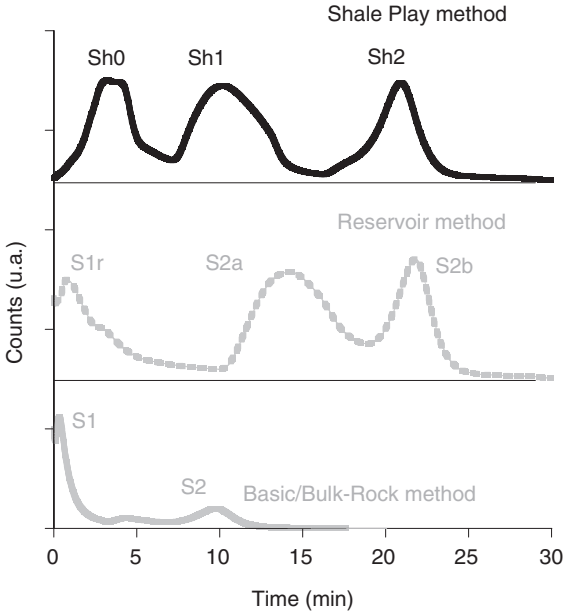


Figure 2

Rock-Eval pyrograms comparing the 3 Rock-Eval methods: Basic/Bulk-Rock, Reservoir and Shale Play.

Depending of the scientific purpose and the type of samples to be analyzed, it is mandatory for the user to select the appropriate Rock-Eval method to ensure an useful meaning of the Rock-Eval results. Table 1 summarizes different types of geological samples that can be run using the currently available Rock-Eval methods.

1.2 New Acquired Parameters from the IFPEN Shale Play Method®

The *IFPEN* Shale Play method® provides 3 key parameters: Sh0, Sh1 and Sh2. These parameters are derived from

TABLE 2
Acquired parameters for the Basic/Bulk-Rock and the new IFPEN Shale Play methods (completed from Behar *et al.*, 2001)

Methods	Basic/ Bulk-Rock	Shale Play	Name	Units
Acquired parameters	S1	Sh0	Free or sorbed hydrocarbons	mg HC/g rock
		Sh1		
	S2	Sh2	Remaining hydrocarbon potential	mg HC/g rock
	T_{max}	T_{max}	T_{max}	°C

the surface areas of the 3 recorded peaks (Fig. 2). They correspond to the quantities of HC compounds monitored by a FID. These acquired parameters are expressed in milligrams of HC compounds per gram of initial rock, as provided by all Rock-Eval methods. Figure 2 also displays the Rock-Eval pyrograms comparing the 3 now available Rock-Eval methods: Basic/Bulk-Rock, Reservoir and Shale Play.

The Sh0 peak is assigned to the lightest thermovaporized hydrocarbons released between T_1 (100°C) and T_2 (200°C). The Sh1 peak is assigned to heavier thermovaporized hydrocarbons released between T_2 (200°C) and T_3 (350°C). Finally, the Sh2 peak is assigned to HC issued from both the pyrolysis of sedimentary organic matter, but also to the ultimate thermovaporization of the high-molecular weight hydrocarbons detected between T_3 (350°C) and T_4 (650°C). The acquired parameters for the new Rock-Eval method are shown in Table 2.

1.3 New Calculated Parameters from the IFPEN Shale Play Method®

The total quantity of thermovaporized hydrocarbons detected in Sh0 and Sh1 peaks, is assumed to provide an estimation of total available free and sorbed hydrocarbons occurring in unconventional shale samples, from which is defined the HC Content Index (HCcont):

$$\text{HCcont} = \text{Sh0} + \text{Sh1} \ [\text{Unit: mg of HC/g of initial rock}]$$

The relative quantity of lighter molecular weight HC provides information about the quality of reservoired fluids. The HC Quality Index (HQI) is calculated from Sh0 and Sh1 as follow:

$$\text{HQI} = \frac{\text{Sh0}}{(\text{Sh0} + \text{Sh1})} \times 100 \ [\text{Unit: wt\%}]$$

TABLE 3
Calculated parameters for the new IFPEN Shale Play method

Calculated parameters	Shale Play method	Name	Units
T_{max}	T_{max}	T_{max}	°C
HI	$\frac{\text{Sh2} \times 100}{\text{TOC}}$	Hydrogen index	mg HC/g TOC
HCcont	Sh0 + Sh1	HC content index	mg HC/g rock
HQI	$\frac{\text{Sh0}}{\text{Sh0} + \text{Sh1}} \times 100$	HC quality index	wt%
PIShale	$\frac{\text{Sh0} + \text{Sh1}}{\text{Sh0} + \text{Sh1} + \text{Sh2}} \times 100$	Production index of Shale Plays	wt%

A Production Index of Shale Plays (PIShale) provides a guiding information likely to define sections of interest within a shale play unit:

$$\text{PIShale} = \frac{(\text{Sh0} + \text{Sh1})}{(\text{Sh0} + \text{Sh1} + \text{Sh2})} \times 100 \ [\text{Unit: wt\%}]$$

The calculated parameters for the new IFPEN Shale Play method® are given in Table 3.

1.4 Samples

The investigated samples are derived from 5 source rocks of different origins and ages (Tab. 4), potentially being unconventional shale resource systems at different thermal maturity stages: Silurian Shale (Algeria), Mississippian Barnett Shale (Fort Worth Basin, Texas, USA), Early Jurassic Shale (Paris Basin, France), Late Jurassic Bazhenov Shale (Russia) and Eocene Green River Shale (Uinta Basin, USA). The Silurian Shale samples come from sections in southern Algeria, North Africa Platform (Ghadamis Basin). The Silurian silty-shale succession of the Ghadamis Basin consists of the organic-rich black shales and marls considered as a candidate for shale play production. The geological setting of this basin is described in detail by Underdown and Redfern (2008). The Barnett Shale samples are from two boreholes (Mesquite 1, Blakely 1) and an outcrop (San Saba County) (Romero-Sarmiento *et al.*, 2014) in the Fort Worth Basin (Texas, USA). The geological setting of the Mississippian Barnett Shale play has been the object of several publications and will not be reviewed here (Montgomery *et al.*, 2005; Ewing, 2006; Pollastro *et al.*, 2007; Romero-Sarmiento *et al.*, 2013, 2014). The Torcian Shale

TABLE 4

Geographic and geological information for studied samples showing Rock-Eval data on the initial samples from Basic/Bulk-Rock method

Country	Age	Basin	Formation	T_{max} (°C)	TOC (wt%)	HI (mg/g)	OI (mg/g)
Algeria	Silurian	Ghadamis	Argileux	437	6.3	105	8
Algeria	Silurian	Ghadamis	Argileux	422	16.2	313	7
Algeria	Silurian	Ghadamis	Argileux	448	1.4	11	8
USA	Mississippian	Fort Worth	Barnett Shale	416	11.6	418	14
USA	Mississippian	Fort Worth	Barnett Shale	436	4.4	140	4
USA	Mississippian	Fort Worth	Barnett Shale	457	9.3	163	0
USA	Mississippian	Fort Worth	Barnett Shale	451	3.5	172	1
USA	Mississippian	Fort Worth	Barnett Shale	450	4.1	155	0
USA	Mississippian	Fort Worth	Barnett Shale	543	2.8	15	1
France	Early Jurassic	Paris	Torcian Shale	442	3.1	238	12
France	Early Jurassic	Paris	Torcian Shale	441	4.5	161	10
Russia	Late Jurassic	West Siberian	Bazhenov	428	15.3	587	2
Russia	Late Jurassic	West Siberian	Bazhenov	438	11.2	463	3
Russia	Late Jurassic	West Siberian	Bazhenov	435	5.3	67	2
USA	Eocene	Uinta	Green River Shale	438	13.4	799	19

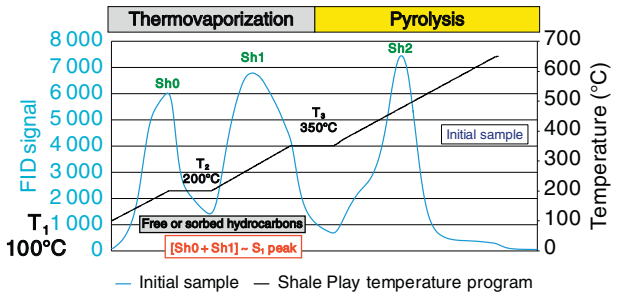


Figure 3

New Rock-Eval pyrogram generated by *IFPEN* Shale Play method for selected sample from Late Jurassic Bazhenov Shale (Russia).

samples come from Early Jurassic intervals of the Paris basin (France). The current petroleum potential of this basin is mainly associated to the Liassic interval where the prospective "Banc de Roc" limestone (prone for hydraulic fracking) is stratigraphically located between the Lower Domerian Shale and the Toarcian Shale (Espitalié *et al.*, 1987; Perrodon and Zabek, 1990; Brigaud *et al.*, 2009). The Bazhenov Shale samples were collected from three boreholes located in the West Siberian Basin (Russia). The Late Jurassic Bazhenov Shale is the main source rock of the largest petroleum basin in the world. More details about the depositional setting of the Bazhenov Shale are found in Peters *et al.* (1993) and Littke *et al.* (1999). Finally, a sample from the Green River Shale (Uinta basin, USA) was also investigated. This immature sample forms part of the Parachute Creek Member of the Green River Formation (Ruble *et al.*, 2001; Behar *et al.*, 2010).

2 RESULTS AND DISCUSSION

Figure 3 illustrates the Rock-Eval pyrogram generated by the *IFPEN* Shale Play method®. For instance, the Late Jurassic Bazhenov Shale sample clearly shows the definition of Sh0, Sh1 and Sh2 peaks. We suggest that the thermovaporized hydrocarbons (Sh0 and Sh1; Fig. 3) that can be detected between T_1 (100°C) and T_3 (350°C), are assigned to the part of free or sorbed hydrocarbons still present within shale sample.

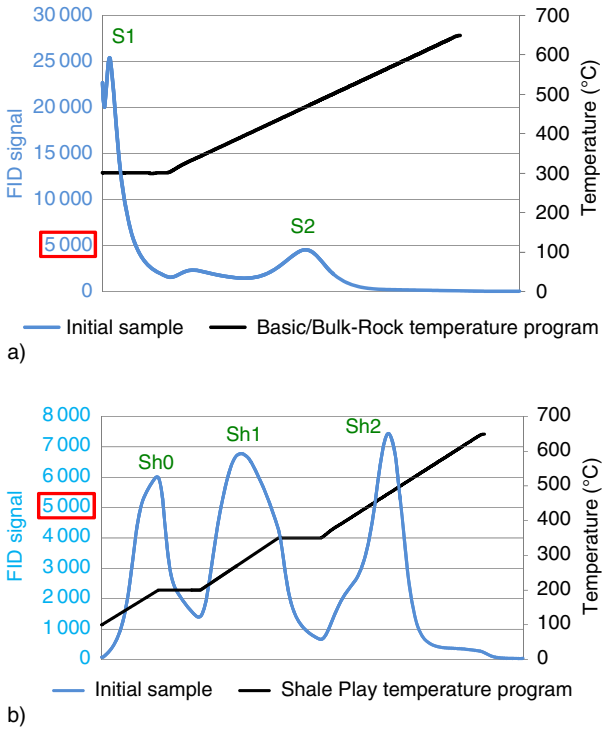


Figure 4

Rock-Eval pyrograms showing a) S1 and S2 peaks from Basic/Bulk-Rock method; b) Sh0, Sh1 and Sh2 peaks from IFPEN Shale Play method: Late Jurassic Bazhenov Shale sample.

Here, the investigated samples were run using both Basic/Bulk-Rock and Shale Play methods in order to compare the generated Rock-Eval pyrograms corresponding to each method (Fig. 4a and 4b, respectively). Figure 4a shows that a part of the free or sorbed low-molecular weight hydrocarbons is lost because the thermovaporization stage of the Basic/Bulk-Rock method starts at a too high temperature (300°C). In contrast, with the new *IFPEN* "Shale Play" method® (Fig. 4b), we can observe that the selected low temperature (T_1 = 100°C) is more appropriate to optimize the recovery of most of the thermovaporizable hydrocarbons.

The "S1 peak" equivalent (S1 = Sh0 + Sh1) acquired from *IFPEN* Shale Play method can be compared, even if not directly, to the concept of S1 peak obtained by the standard Basic/Bulk-Rock method (Fig. 5). Most investigated samples show that "S1 peaks" equivalents from Shale Play method are substantially higher than S1 peaks obtained by the classical Basic/Bulk-Rock method (Fig. 5). Consequently results indicate an improved assessment of extractable hydrocarbon compounds in unconventional shale systems.

In order to investigate the type of hydrocarbons detected by each new acquired Rock-Eval parameter, samples from Bazhenov and Silurian Shale were also selected due to their significant Sh0 and Sh1 values. Following the extraction procedure described in Behar *et al.* (1989), six samples were firstly extracted with *n*-pentane (*n*-C_5) in order to recover, on one hand, the *n*-C_5 extracts and, on the other hand, the *n*-C_5 extracted solid residues. These solid residues were then extracted with DiChloroMethane (DCM) to finally recover DCM extracts and the so-called more extensively "extracted samples" corresponding, by the end, to the solid residue of two successive extractions (*n*-C_5 and DCM). The *n*-C_5 and DCM extracts as well as the extracted sample were then analyzed by the new *IFPEN* Rock-Eval Shale Play method®. It should be noted that aliquots of *n*-C_5 and DCM extracts were weighed (*i.e.* 8 to 12 mg) in Rock-Eval crucibles, previously filled by silica following procedures also described in Trabelsi *et al.* (1994). Table 5 provides *n*-C_5 and DCM extract weights from investigated samples.

Today, it is widely accepted that the *n*-C_5 extract contains saturates, aromatics and resins that are soluble in *n*-pentane whereas the following DCM extract contains more polar compounds, which include the total asphaltenes and remaining resins that are not soluble in *n*-pentane (Behar *et al.*, 1989, 2008). The proportions of the new Rock-Eval parameters for both the *n*-C_5 and DCM extracts are illustrated in Figures 6a and 6b, respectively.

In this study, we assume that the *n*-C_5 extract mostly contains the thermovaporized hydrocarbons of low-molecular weight released between 100 and 200°C (Sh0 peak; Fig. 6a). The *n*-C_5 extract also contains a non-negligible part of the thermovaporized hydrocarbons of high-molecular weight (Sh1 peak; Fig. 6a). Sh0 and Sh1 peaks probably correspond to low and high-molecular weight thermovaporized hydrocarbons, respectively (*i.e.* tentatively saturates and aromatics soluble in *n*-pentane). The low Sh2 peak from the *n*-C_5 extract probably corresponds to resins that are soluble in *n*-pentane (Fig. 6a). In contrast, the DCM extract mainly contains the high-molecular weight hydrocarbons detected between 200 and 650°C. Here, the Sh2 peak from the DCM extract probably corresponds mainly to resins and asphaltenes (Fig. 6b). Finally, the extracted sample only contains the "insoluble" organic matter as shown in Figure 7, which is cracked by pyrolysis. The Sh2 peak from the extracted sample after *n*-C_5 and DCM extractions therefore corresponds to the kerogen fraction (Fig. 7).

Furthermore, in order to compare the new Rock-Eval T_{max} (TpSh2 - ΔT_{max}) calculated by the proposed new pyrolysis method with the widely accepted T_{max} from Basic/Bulk-Rock method, we plotted the average T_{max} values from "extracted samples" obtained by the classical Basic/Bulk-Rock method *versus* the average T_{max} values from

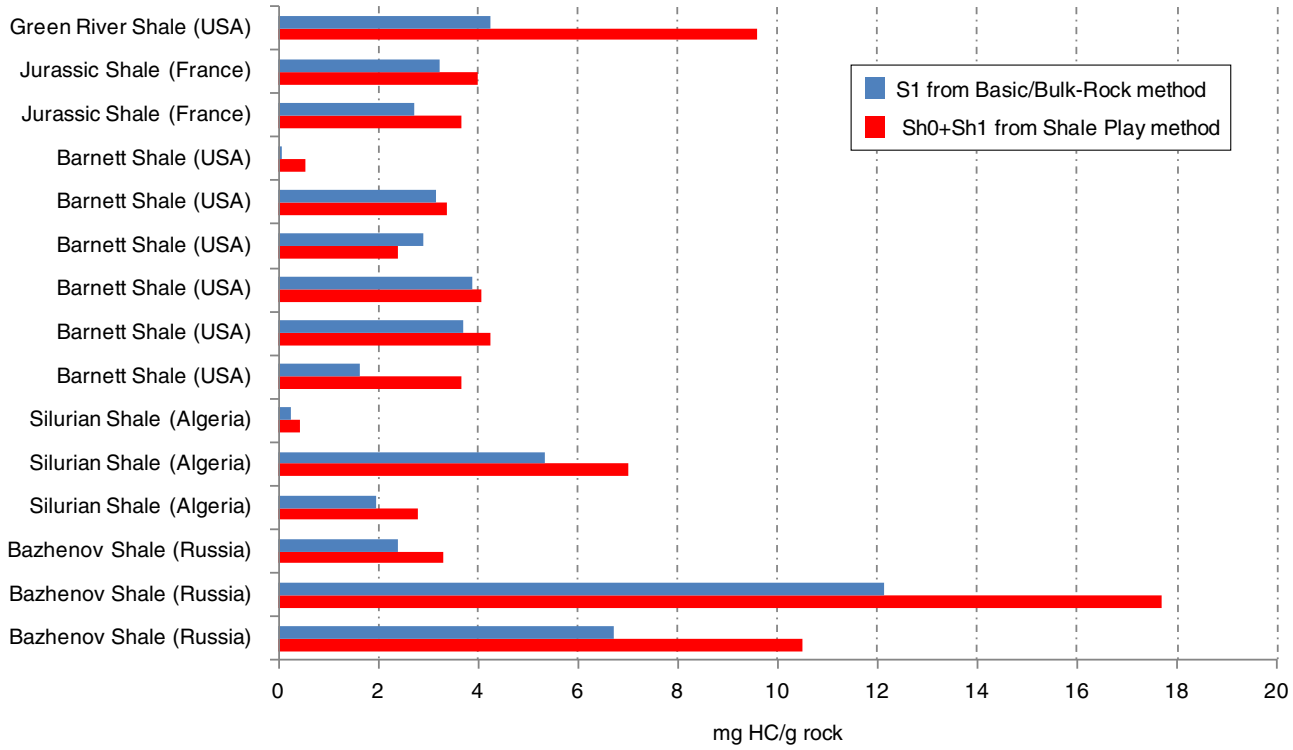


Figure 5

Comparison of S1 peak from Basic/Bulk-Rock method and Sh0 + Sh1 peaks from IFPEN Shale Play method for investigated samples.

TABLE 5

n-C_5 and DCM extract weights from investigated samples

Country	Age	Formation	Initial mass (g)	n-C_5 extract (mg/g)	DCM extract (mg/g)
Algeria	Silurian	Argileux	7.75	1.24	1.13
Algeria	Silurian	Argileux	10.38	0.56	0.51
Algeria	Silurian	Argileux	8.01	1.35	5.21
Russia	Late Jurassic	Bazhenov	11.23	7.02	7.33
Russia	Late Jurassic	Bazhenov	9.97	22.15	12.43
Russia	Late Jurassic	Bazhenov	7.71	5.53	1.39

"initial samples" obtained by the new Shale Play method (Fig. 8). It should be noted that the Rock-Eval T_{max} from Basic/Bulk-Rock method measured on unconventional shale samples could be affected by the possible occurrence of hydrocarbons still present in the rock after thermovaporization step. Consequently, in order to avoid any T_{max} bias, solvent extractions of initial samples are performed. Results indicate that T_{max} parameter of "extracted samples" obtained from Basic/Bulk-Rock method is consistent with the T_{max} parameter of "initial samples" obtained by the Shale Play method. Figure 8 shows that the T_{max} parameter, depending on thermal cracking of organic matter, is not affected by the temperature program dedicated to the thermovaporization of free and sorbed hydrocarbons into Sh0 and Sh1 peaks. Moreover, the optimization of thermovaporization enables a Rock-Eval T_{max} parameter determination more representative of original organic matter in source rock (previous to oil formation). A noticeable implication for operational purposes is that extraction by organic solvents is probably not necessary to obtain a representative and accurate T_{max} parameter directly on "impregnated" samples.

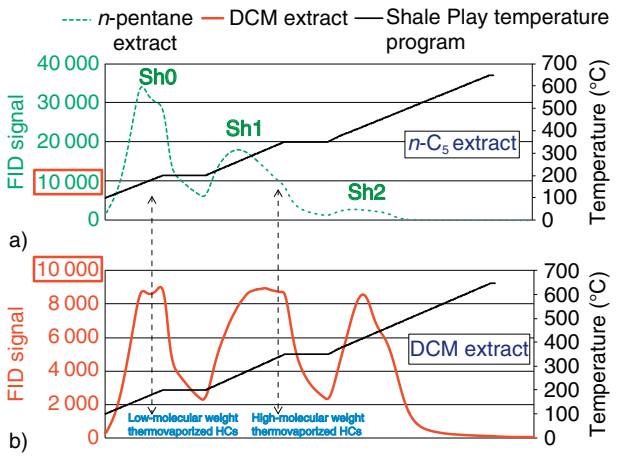


Figure 6

Rock-Eval pyrograms from the new IFPEN Shale Play method: a) n-C_5 and b) DCM extracts: Late Jurassic Bazhenov Shale.

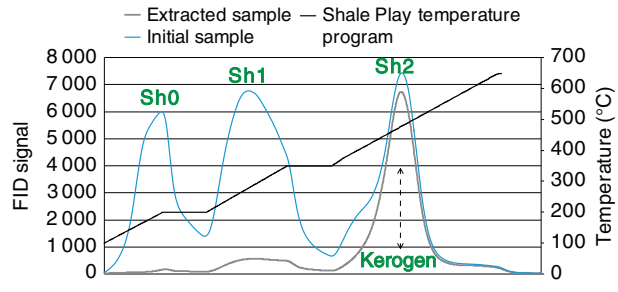


Figure 7

Rock-Eval pyrograms from the new IFPEN Shale Play method comparing initial *versus* extracted sample after successive n-C_5 and DCM extractions: Late Jurassic Bazhenov Shale.

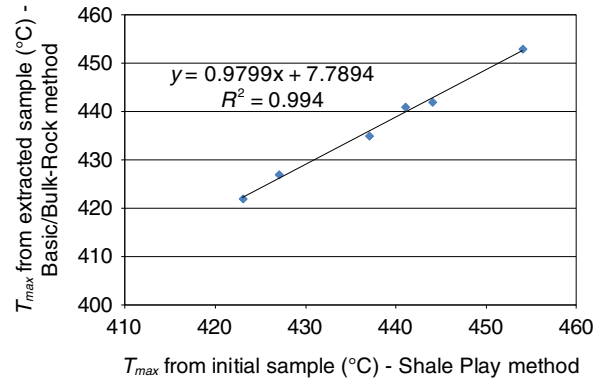


Figure 8

The average Rock-Eval T_{max} values from "extracted samples" obtained by the classical Basic/Bulk-Rock method *versus* the average T_{max} values from "initial samples" obtained using the new Shale Play method.

CONCLUSIONS

The proposed method can be easily programed within any Rock-Eval 6 instrument. It provides an efficient, fast and ready to use tool informing on the quantities of "free and sorbed" hydrocarbons in shale plays. Moreover, key parameters are proposed to define sections of interest and this pyrolysis program is likely to provide a meaningful T_{max} value by avoiding "contamination" by heavy free hydrocarbons which might bias this crucial parameter in shale plays.

Even if some future works are still necessary to evaluate with precision both the amount and the type of hydrocarbons detected by each new acquired Rock-Eval parameters (Sh0, Sh1 and Sh2), the present contribution shows that the new *IFPEN* Shale Play method may provide original and pertinent indicators of the hydrocarbon retention within unconventional source rocks such as tight, fractured and hybrid shale plays and improves the assessment of thermal maturity (T_{max}) directly from non-extracted rocks.

ACKNOWLEDGMENTS

The authors acknowledge *IFP Energies nouvelles* for providing approval to publish the cited patent 14/55.009, Pillot *et al.*, 2014. We thank GASH consortium for providing *Barnett Shale* samples. The editor-in-chief of OGST and two anonymous reviewers are acknowledged for useful and constructive comments on the manuscript.

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Manuscript submitted in January 2015
Manuscript accepted in March 2015
Published online in August 2015

Cite this article as: M.-F. Romero-Sarmiento, D. Pillot, G. Letort, V. Lamoureux-Var, V. Beaumont, A.-Y. Huc and B. Garcia (2016). New Rock-Eval Method for Characterization of Unconventional Shale Resource Systems, *Oil Gas Sci. Technol* **71**, 37.