Geochemical screening of source rocks and reservoirs: The importance of using the proper analytical program

H. Carvajal-Ortiz*, T. Gentzis*

Core Laboratories, 6316 Windfern Road, Houston, TX 77040, USA

A B S T R A C T

Geochemical screening is routinely integrated into larger exploration (and sometimes development) programs that also include assessments of the geological setting, petrophysics, mechanical properties of the rock, etc. The Rock-Eval analytical equipment and its classical Basic/Bulk-Rock method have been developed mainly to characterize potential source-rock intervals in petroleum systems. However, with the increasing interest in unconventional plays, it has been recently demonstrated that the use of modified pyrolysis-temperature regimes improves the quantification of hydrocarbons still present in oil-impregnated samples. In spite of their availability, the use of such modified pyrolysis-temperature regimes still remains scarce among users of pyrolysis data (e.g., exploration geologists and geochemists, reservoir engineers, petrophysicists, and other geoscientists).

Several cases were selected to portray how different analytical programs are necessary to obtain less biased and more accurate answers to critical questions during prospect and play evaluations and appraisals. Samples originating from conventional and unconventional plays in the Greater Permian Basin of West Texas (Wolfcamp & Spraberry formations), the DJ Basin in Colorado (Niobrara Formation), the Williston Basin (Lower Bakken Shale), and source-rock reservoirs in the Middle East were analysed each using three known different pyrolysis methods, namely the Institut Français du Pétrole's "Basic/Bulk-Rock", "Reservoir", and "Shale Play". The Shale Play and Reservoir pyrolysis methods yield oil-in-place estimates 20–42% higher than those yielded by the Basic/Bulk-Rock method on the same sample (e.g., for the Niobrara Formation – 87 bbl oil/ac-ft Bulk method, 118 bbl oil/ac-ft Reservoir method, 119 bbl/ac-ft Shale method; for the Lower Bakken – 194 bbl oil/ac-ft Bulk method, 246 bbl oil/ac-ft Shale method). In addition, a mature, source-rock interval believed to contain gas-prone organic matter (Type III) based solely on TOC and pyrolysis data, was re-interpreted as composed mainly of amorphous oil-prone kerogen, following a multi-component study (which included transmitted and reflected-light organic petrography). These results present unequivocal evidence that underestimating the importance of selecting the proper analytical program can change interpretations dramatically.

1. Introduction

Source-rock characterizations by classical organic geochemistry workflow have been widely performed by several previous studies, starting in the late 1970s (e.g., Espitalié et al., 1977; Peters, 1986; Langford and Blanc-Valleron, 1990; Peters and Cassa, 1994; Lafargue et al., 1998; Behar et al., 2001, and many others). Geochemical screening of source rocks via open-system programmed pyrolysis (commonly referred to as Rock-Eval, which is a registered trademark of Institut Français du Pétrole-IFP), TOC determinations, and organic petrography are nowadays part of the standard protocol in exploration campaigns (Hart and Steen, 2015; Dembicki, 2009, 2016; Carvajal-Ortiz and Gentzis, 2015; Romero-Sarmiento et al., 2015, 2016, in press; Sanei et al., 2015), especially when dealing with unconventional

systems such as shale-gas and shale-oil systems (e.g., Curiale and Curtis, 2016; Jarvie, 2012a, 2012b). The information provided by these analyses is routinely integrated into larger exploration (and sometimes development) programs that also include assessments of the geological setting, petrophysics, mechanical properties of the rock, etc. (e.g., Chen and Jiang, 2016; Jarvie, 2014; Modica and Lapierre, 2012). In addition, the fact that organic matter within source rocks is not homogeneous adds even more complexity to the geochemical screening of both conventional and unconventional petroleum systems. Assuming that the Rock-Eval data will indicate the type of kerogen present in a particular source rock, what Dembicki (2009) referred to as "The Rock-Eval Fallacy" is a common mistake, and a consequence of widespread lack of understanding of the true nature of organic matter heterogeneity in source rocks (i.e., mixtures of various kerogen types and preservation

states rather than the ubiquitous occurrence of kerogen end-members). The Rock-Eval fallacy results from misinterpretation of basic source-rock parameters and, hence, miscalculation during resource evaluation and assessment. For instance, a common mistake found in technical presentations and peer-reviewed publications is the qualification of organic matter as gas-prone (usually Type III), based solely on Rock-Eval pyrolysis results. Such misidentification of kerogen types is often due to misinterpretation of results from oil-prone organic matter (usually marine Type II) that has already experienced significant transformation of reactive kerogen into hydrocarbons because of thermal maturation (Dembicki, 2009, 2016; Tyson, 2016).

An additional source of complexity when geochemically screening hydrocarbon plays is the selection of the proper analytical protocol. Just as petrographers approach and examine reservoirs containing siliciclastics and carbonates differently, so it should be when geochemically screening different hydrocarbon plays. Organic matter in source-rock reservoirs (like those found in unconventional systems) have some similarities (i.e., similar kerogen type and thermal maturity), but when parameters such as thermal maturity and petrophysical properties vary, the analytical procedures available should be flexible enough to accommodate this inherent variability.

Although originally developed for classical source-rock evaluation (mainly on immature source-rocks), open-system programmed pyrolysis or Rock-Eval pyrolysis (Espitalié et al., 1985) is an analytical tool that can customize temperature programs to best suit the geochemical and geological characteristics of particular hydrocarbon plays (e.g., Lafargue et al., 1998). Customizing the pyrolysis program is a trivial task in newer versions of pyrolysis instruments (e.g., Rock-Eval™ 6, HAWK™, and soon in Rock-Eval™ 7). With the advent of unconventional resources, the need for a flexible analytical protocol for the screening of source-rock reservoirs is critical (Curiale and Curtis, 2016). In spite of the existence of such analytical flexibility (e.g., Trabelsi et al., 1994; Romero-Sarmiento et al., 2015; Sanei et al., 2015), the use of modified temperature programs remains scarce among users of pyrolysis data (e.g., exploration geoscientists, reservoir engineers, petrophysicists, etc.).

The main purpose of this study is to highlight the importance of selecting the appropriate open-system pyrolysis method to obtain accurate results and interpretations. To achieve this objective, we will present a series of cases which demonstrate how different analytical programs are necessary to obtain less biased and more accurate answers to critical questions during prospect and play appraisals. The cases selected come from different basins worldwide, covering a wide range of thermal maturities and organic richness. Additionally, we will show how a multi-analyses approach, including organic petrography and Rock-Eval pyrolysis modified methods, is always the best protocol when screening both conventional and unconventional plays.

2. Materials and methods

2.1. Methods

2.1.1. Open-system programmed pyrolysis (Rock-Eval pyrolysis)

The instruments utilized were Rock-Eval 6 Turbo units (RE6). Temperature programs for the detection of free hydrocarbons (S1), thermally-cracked hydrocarbons (S2), and CO and CO_2 from thermal decomposition (S3) and oxidation (S4) of organic matter are described below terminology is presented in Fig. 1. The different programs are described in detail by Behar et al. (2001), Romero-Sarmiento et al. (2015), and Trabelsi et al. (1994) (Table 1):

- Basic/Bulk-Rock (by IFP Rock-Eval methods®): 300 °C isothermal for 3 min (thermal extraction of the free hydrocarbons, S1), then programmed pyrolysis up to 650 °C at 25 °C/min (presumed to be thermal cracking of reactive kerogen, S2). More details are available in Behar et al. (2001). It should be emphasized that the Basic/Bulk-

Rock method is used mainly to characterize any *source rock* in "conventional" petroleum systems.

- Reservoir Pyrolysis (by IFP Rock-Eval methods®): The "Reservoir" method has been developed at the IFP to characterize any reservoir oil and tar samples in reservoir studies. The IFP Reservoir temperature program has an initial temperature of 180 ± 50 °C. The two methods used in our study are the modified temperature programs that are described in the registered "Reservoir" method listed by IFP Rock-Eval methods®. The Reservoir pyrolysis method used in this study had an initial oven temperature of 150 °C (30 °C lower than the default isothermal of 180 °C), isothermal for 10 min (thermal extraction of the lightest hydrocarbon fraction, S1r). Temperature was then increased to 650 °C at 25 °C/min and 10 °C/min (for thermal extraction of the medium/heavy hydrocarbon fraction up to 325 °C, S2a; thermal cracking of the NSO or kerogen fraction from 325 °C to 650 °C, S2b). See Trabelsi et al. (1994) and Sanei et al. (2015) for more details.

- Shale Play® Pyrolysis (by IFP Rock-Eval methods®): The Shale Play® method has been developed to characterize any tight, fractured and hybrid shale play as well as shale oil systems (oil-impregnated samples). Initial oven temperature is 100 °C ± 50 °C, as described by Romero-Sarmiento et al. (2015). In our study, we used the modified temperature programs that are described in the registered IFP's Shale Play® method (Romero-Sarmiento et al., 2014, 2015), with initial temperatures of 100 °C and a lower initial temperature of 80 °C (20 °C lower than the default Shale Play® method); the temperature was immediately increased to 200 °C at 25 °C/min. Lowering the initial temperature (from 100 °C to 80 °C) was necessary in some samples with high quantities of light hydrocarbons remaining. The oven was held isothermal for 3 min at 200 °C to complete the thermal extraction of the lightest hydrocarbon fraction (Sh0). From 200 °C the oven temperature increased to 350 °C at 25 °C/min, staying isothermal at this temperature for 3 min (for thermal extraction of the medium/heavy hydrocarbon fraction, Sh1). The last temperature step consisted of a temperature ramp from 350 °C to 650 °C at 25 °C/min (thermal cracking of the NSO or kerogen fraction from 350 °C to 650 °C, Sh2). See Romero-Sarmiento et al. (2014, 2015, 2016) for more details.

Analytical QA/QC protocol followed the guidelines outlined by Carvajal-Ortiz and Gentzis (2015). For Rock-Eval 6 analysis, the samples were crushed to ∼ 100 μm size. For samples that had been in contact with oil-based (OBM), contaminants were extracted using organic solvents. We used an azeotropic mixture of chloroform-methanol (89:11 *v/v*) and extraction time ranged from 24 to 72 h. For all samples analysed with each temperature ramp, samples were analysed in triplicate to quality-check the homogeneity of the aliquots taken and to assess analytical precision. Analytical error for total pyrolysis yields (i.e., S1 + S2) was better than ± 0.5 mg/g.

2.1.2. Reflected-light microscopy: vitrinite reflectance (R_o) and fluorescence of organic matter

Detailed sample preparation and analysis procedures are described in the ASTM D7708 standard test method (2014) and by Hackley et al. (2015). Briefly, whole-rock (WR) samples are crushed to 20 mesh (850 μm or 0.85 mm size) particles. Ground particles are placed in specially-designed plastic moulds (1.5 in. or 3.3 cm in diameter) where they are mixed with epoxy resin and hardener (ratio of 2:1), leaving it to harden overnight. Sample grinding and polishing was performed using Buehler EcoMet/AutoMet 250 automated polishing equipment. We attempted to achieve a sample surface that was scratch- and relief-free for reliable VRo measurements because poorly polished surfaces can lower the R_o values by 0.1–0.2%.

Reflectance in oil (R_o) and fluorescence analyses were performed using a Carl Zeiss Axio Imager A2m microscope, equipped with a white (halogen) light source (from a 12 V/100 W halogen lamp with