



Thermo-vaporization for decontaminating hydrocarbon source rocks

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ABSTRACT

Although use of oil based mud (OBM) benefits drilling engineers, it creates complications for analyses and interpretations of geochemical samples. Pyrolysis of such samples frequently displays masking effects on the true pyrolysis Tmax (e.g., true maturity). When this phenomenon goes undetected, erroneously reported Tmax-based thermal maturity may wrongly influence exploration efforts. The consequences can be even more dramatic when such data is used for calibration of basin models that aim to reconstruct burial and temperature histories and determine hydrocarbon generation from source rock(s).

Solvent extraction is generally an effective and commonly employed method for removal of solvent-soluble organic contaminants from samples, but it is expensive and time consuming. Here, we report a new and a faster method called “thermo-vaporization” (TV) that is capable of replacing solvent-extraction processes, thereby eliminating the need for lengthy solvent extraction. This can lead to further contamination. Careful thermo-vaporization conducted below kerogen cracking temperatures guarantees that the solid organic matter (kerogen) is not affected, excluding low level effects determined for immature sulfur-rich kerogen containing samples. The thermo-vaporization method saves time and reduces the potential effect of sample contamination. It provides a rapid workflow to assess thermal maturity with greater confidence.

The study described in this article confirms that solvent extractable organic contaminants can be removed from samples by the novel thermo-vaporization method. The method is based on programmed pyrolysis and can be performed with a variety of available pyrolysis apparatus. After optimization, it was found that TV at 350 °C for 60 min or 375 °C for 30 min are both sufficient for removal of contaminants similar to the traditional solvent extraction method. A workflow for a thermo-vaporization based sample cleaning prior to pyrolysis is provided.

1. Introduction

Source rock evaluation is the most critical step for initial assessment of hydrocarbon potential of sedimentary basins. Screening analyses of source rocks aim for fast determination of the quantity, quality, and thermal maturity of sedimentary organic matter. These assessments are routinely made using open system pyrolysis (Espitalié et al., 1977; Delvaux et al., 1990; Behar et al., 2001). Pyrolysis is an inexpensive and fast screening method for selecting samples for more detailed geochemical and petrographic analyses. Very often sampling at one-foot intervals is made. Pyrolysis enables operators to generate immense amounts of data by pyrolyzing many samples, as received with little need for sample preparation. These features make pyrolysis an indispensable and largely dependable technique for fast geochemical screening and data acquisition in the petroleum industry. This relatively practical approach is unfortunately susceptible to potential erroneous assessment of source rock richness and thermal maturity, due to both low quality of samples and misinterpretations by impatient

users. While continuous effort has been made to produce guidelines for conducting pyrolysis and interpreting results (e.g., Katz, 1983; Peters, 1986; Espitalié, 1986; Jarvie, 1991; Peters and Cassa, 1994; Snowdon, 1995; Ohm et al., 2007; Dembicki, 2009; Carvajal-Ortiz and Gentzis, 2015; İnan et al., 2017), heavy reliance upon pyrolysis for source-rock assessment can, in some instances, produce misleading conclusions. Consequently, this simple approach bears significant potential for erroneous assessment of source rock quality and thermal maturity due to contamination with oil based mud (OBM); contamination by drilling diesel is not an issue since it evaporates at initial isothermal hold temperature of pyrolysis (300 °C), i.e., before pyrolysates are generated and released. Petersen et al. (2017) recently showed how OBM contamination leads to erroneous geochemical analyses as well as kinetics.

Organic (e.g., oil) additives in drilling muds are known to have a significant adverse effect on the thermal maturity parameter (Tmax), which is determined from pyrolysis of source rock samples. Pyrolysis analyses of samples acquired from wells drilled by OBM frequently display masking effects on the true pyrolysis Tmax (e.g., true maturity)

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as well as the total hydrocarbon yields. This can lead to inaccurate interpretations of the source rock potential and thermal maturity, which in turn may wrongly influence exploration efforts. Based on the composition of the organic additives, the T_{max} might shift to a lower or a higher values. For instance, wrongly reporting an oil window maturity for a gas-maturity source rock in a given area will obviously discourage shale gas exploration activities. Reporting a higher maturity for an immature source rock will mislead and raise expectations of hydrocarbon potential of the source rock. It is, therefore, crucial to detect and remove contaminants that could affect T_{max} estimates prior to pyrolysis analysis. As Carvajal-Ortiz and Gentz (2015) noted, geochemical screening techniques (i.e., pyrolysis) provide results that are relatively easy to interpret, but users should be aware of the multiple analytical pitfalls and significant attention must always be given to data quality issues.

It is worth noting that solvent extraction is an established method that geochemists widely utilize to extract source rock bitumen for characterization (Tissot and Welte, 1984). Solvent extraction is also a traditional method for decontaminating samples prior to analysis. Solvent extraction for cleaning samples is time consuming, expensive and in most cases environmentally unfriendly and may lead to health-related issues resulting from exposure to organic solvents.

Researchers have developed methods to identify various thermally vaporized hydrocarbon types, but no effort has been spent to use pyrolysis chambers as a thermo-vaporization medium for the purpose of decontaminating samples. Geochemists use thermo-vaporization for purging hydrocarbons out of a pyrolysis furnace. For example, thermo-vaporization has been widely used to remove pyrolysate out of pyrolysis chambers for further analysis and characterization by GC and GC-MS (e.g., Horsfield et al., 2015, and references therein), but these methods are beyond the scope of the present work. Another recent example of thermo-vaporization use is given by Romero-Sarmiento et al. (2016). They introduced a new Rock-Eval method for characterization of different classes of hydrocarbons within source rocks by utilizing a multi-ramping approach to enable successive liberation of free and adsorbed hydrocarbons. This approach is valuable for detecting light and heavy hydrocarbons but isn't optimal, and certainly was not suggested as a method for removing contaminants from the samples.

Recently, İnan et al. (2017) introduced a new thermal maturity indicator, called oxidation T_{max}. This indicator is based on recording the temperature of the S4 (oxidation) peak position. This peak is less influenced by OBM contamination and so produces more reliable maturity measurements for contaminated source rocks. The method can be performed by using either a LECO instrument and/or standard Rock Eval. It is expected that oxidation T_{max} will find its place in applications for maturity assessment of contaminated samples. We presume that pyrolysis T_{max} will continue to be used widely and so decontaminating the samples prior to pyrolysis analysis is a worthy and justifiable exercise.

The main aims of this study are to 1) demonstrate the adverse effects of OBM on pyrolysis analyses of source rocks for thermal maturity determination, and 2) to develop a new practical and rapid method to replace existing solvent extraction methods for removal of OBM from source rocks; with as little influence as possible on the source rock's indigenous kerogen.

2. Samples and methods

2.1. Samples

Source rock samples used in this study are core fragments from a shale member of the Silurian Qusaiba Formation and a carbonate mud rock sample of the Middle-Upper Jurassic Tuwaiq Mountain Formation obtained from exploration wells drilled with water-based mud in the Saudi Arabian Basin; the samples were uncontaminated. Shale samples

Table 1
Pyrolysis analysis results for “as-received” QS, QA, QG, and TC samples, OBM-contaminated QS, QA, and QG samples and solvent-extracted QA samples.

Sample	TOC	S1	S2	S3	T _{max} (°C)
A. Pyrolysis results of “as-received” samples					
QS ^a	8.40	2.85	42.01	0.49	419
QA ^a	3.16	1.06	2.14	0.12	462
QG ^a	2.26	1.24	2.11	0.24	481
TC ^a	8.22	2.11	70.76	0.84	414
OBM	22.0	156.5	28.63	1.33	432–436
ASE-FP-new	–	6.30	262.26	13.85	338
ASE-FP-used	–	45.91	96.5	16.82	328
B. Pyrolysis results of samples contaminated with OBM					
QA + 40 mg OBM	8.55 ^b	47.30	8.71	0.42	437
QA + 20 mg OBM	6.30 ^b	18.11	4.14	0.18	448
QA + 10 mg OBM	4.87 ^b	16.65	3.41	0.14	452
QA + 5 mg OBM	4.06 ^b	10.87	3.2	0.13	454
QG + 20 mg OBM	5.55 ^b	71.72 ^c	16.96	0.88	432
QS + 20 mg OBM	10.71 ^b	102.3 ^c	36.2	1.63	429
C. Pyrolysis results of samples after solvent extraction					
QA + 40 mg OBM	–	0.31	2.02	0.24	454
QA + 20 mg OBM	–	0.27	2.12	0.16	460
QA + 10 mg OBM	–	0.25	1.91	0.17	459
QA + 5 mg OBM	–	0.20	1.65	0.18	458

Explanations: OBM: Oil Based Mud, ASE: Automated Solvent Extraction, ASE-FP: Filter paper used in the ASE system. TOC = total organic carbon (wt%); S1: Free hydrocarbons (mg HC/g sample); S2: Pyrolyzable hydrocarbons (mg HC/g sample); S3: Pyrolyzable CO₂ (mg CO₂/g sample); T_{max}: pyrolysis temperature (°C) at which kerogen breakdown is maximum.

^a Vitrinite Reflectance Equivalent (% VRE) maturity for QS, QA, and QG samples (as given İnan et al., 2016) are 0.61, 1.43, and 1.62, respectively. VRE for TC sample is 0.41% based on the relation %VRE = (0.0134 * T_{max}) – 4.9706 given by İnan et al. (2016).

^b Calculated from the mixture ratio of shale sample and OBM.

^c High values due to DCM addition for better mixing. Qusaiba shale samples used in each mixture was 100 mg.

are known to contain dominantly amorphous kerogen with less contribution from algae, lamalginite, graptolite and chitinozoan (İnan et al., 2016). Three samples for OBM removal study were selected from different thermal maturity levels to investigate effects of OBM on pyrolysis S2 T_{max} position. This selection criteria is essential for the applicability of the method of this study as OBM has a direct effect on the thermal evolution of the S2 peak. Samples QS, QA and QG represent low maturity (T_{max} = 419 °C), high maturity (T_{max} = 462 °C) and over-maturity (T_{max} = 481 °C), respectively (Table 1). Vitrinite reflectance equivalent (%VRE) maturity converted from graptolite reflectance for these samples (as reported by İnan et al., 2016) have also been included in Table 1. The carbonate sample (TC) selected for this study is immature (T_{max} = 414 °C) and it contains abundant sulfur-rich kerogen of dominantly algal origin (Hakami and İnan, 2016). Justification for selecting this sample is simply that its quite labile (sulfur-rich) kerogen is expected to be the most affected upon thermal treatment (thermo-vaporization) and will be discussed later. The pyrolysis data and calculated VRE for this sample (TC) are also given in Table 1.

An OBM sample was obtained and pyrolyzed to obtain a pyrogram and a T_{max} value. For further characterization of the OBM sample, Thermogravimetric Analyses (TGA) and Fourier Transform Infrared (FTIR) analyses were also performed.

In the final step of sample preparations, OBM was diluted with DCM to decrease its viscosity and various amounts (ranging from 5 to 40 mg) of OBM were added to the crushed splits of each uncontaminated Qusaiba sample (approximately 100 mg) to obtain OBM contaminated samples. The OBM-contaminated samples, prepared by mixing crushed shale sample with OBM, in this study are definitely different than that of OBM-well contaminated core samples. It seems that intact shale core samples retrieved from OBM-well may be less prone to OBM contamination. However, mud pressure in the well may lead easier penetration of OBM into the shale.

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