CORRELATION OF TMAX AND MEASURED VITRINITE REFLECTANCE
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In 2001 a poster presentation at AAPG indicated a correlation between Tmax and vitrinite reflectance for the Barnett Shale (Jarvie et al., 2001). Unfortunately, the data were not presented nor preserved for this calculated correlation. As was stated in the poster (Figure 1), the correlation equation was:

Equivalent %Ro from Tmax = (0.018 x Tmax) - 7.16 where Tmax is reported in °C

![Tmax-based calculation of %Ro for the Barnett Shale](image)

Figure 1. Slide from Jarvie et al. (2001) poster, AAPG National Convention. The data for this correlation were not reported nor archived, but is based on fresh Barnett Shale core samples. The equation was not anticipated to be widely utilized, but was utilized to show Tmax in terms of equivalent Ro with which independent geologists were more familiar.

The validity of this correlation has been questioned particularly when calculated data does not match measured vitrinite reflectance or measured organic particles, the latter as in Lewan and Pawlewicz (2017). Thermal maturity should always be confirmed using all available maturity data ranging from Tmax (esp. on extracted rocks), measured vitrinite reflectance, measured and corrected bitumen reflectance using both the Jacob (1987) and Landis and Castano (1995) equations, gas composition with carbon and deuterium isotopes, aromatic GCMSMS maturity equivalency, pyrolysis gas chromatography, and any other maturity techniques including hydrogen indices assuming a database relationship of HI to maturity.

The most important aspect of thermal maturity assessments is the determination of product type such as black or volatile oil, condensate-wet gas, or dry gas. Thus, the maturity to product type must be confirmed by early production history of a given area of interest.

One of the key issues related to unconventional organic-rich and associated hybrid resource plays is the fact that little, if any, indigenous land plant debris would be expected to be found in deep marine settings where excellent source rocks were deposited. This was certainly illustrated in Dembicki (1984) that showed very poor interlaboratory correlation for measured vitrinite reflectance on marine shale source rocks.

Vitrinite particles for reflectivity measurements are most likely to be found in Type III and Type II/III shales. It is necessary to provide appropriate samples to the petrologist for vitrinite reflectance
measurements such as Type II/III or III kerogens. Coaly and terrigenous organic matter contain abundant vitrinite particles and such samples can be selected by study of the geology and visual examination of samples. Additionally, suitable samples may be selected using basic geochemical analyses such as TOC and pyrolysis data, which allow computation of hydrogen indices. Keep in mind that HI is affected by maturation (kerogen type designations only apply to immature to very early mature samples).

Samples with greater than 0.50% TOC original and HI original values less than 350 mg/g TOC are suitable for organic petrology. The lower the TOC, the more rock material that must be supplied to the laboratory especially for isolated kerogen analysis. Remember that if the measured TOC is 1.00 wt.%, the volume percent is only ca. 2.00 vol. %, meaning 98% of the rock is non-organic and a lesser amount is present as vitrinite particles. Approximately 30 grams of sample is preferred although organic petrology may be completed on less material depending on the presence of vitrinite.

Measurement of non-vitrinitic organic particles presents a different issue, i.e., correlation to a true vitrinite reflectivity value. Measurements performed on organic matter, whether bitumen, pyrobitumen or other organic particulate matter, also show considerable variation from measured vitrinite reflectance (e.g., Jacob, 1987; Landis and Castaño, 1995) (see comparison in Jarvie, 2017). The above issues say more about the samples utilized for such measurements than the actual measurements. A useful approach is to profile an entire well rather than just the zone(s) of interest. This was recommended in the early days of organic geochemistry (Tissot and Welte, 1984) and stands true to this day. As typical paleogeothermal gradients only result in about 0.10%Ro per 1000 feet, it would be optimum to measure good samples up hole at 500-1000 ft intervals as well as high grading the most likely samples to find vitrinite particles.

As such one criterion that is often overlooked is the quality of samples. Fresh cuttings provide reliable results unless such samples were taken from a well drilled with oil-based mud (OBM). Such samples should be thoroughly solvent extracted prior to pyrolysis or kerogen isolation although this is not commonly done (oil and acid do not interact readily, like mixing oil and water).

The sample type must also be considered particularly the age and length of archival of cuttings especially. Samples older than the Siluro/Devonian will not have significant indigenous land plant debris. Archived cuttings may present a less obvious issue.

In early work on the Barnett Shale archived cuttings samples were the primary source of data in the 1980s and 1990s. There were some core data available through the Bureau of Economic Geology (BEG) and data from the T.P. Sims #1, Anadarko Oliver #1 were added at later dates. The only other core samples and data were proprietary to Mitchell Energy. However, what we learned was that archived cuttings from pre-1990 were yielding lower TOC, S2, and maturity data (Jarvie, 2016). A correction to Barnett Shale maturity from cuttings was estimated to be about 0.15%Ro (Jarvie et al., 2005), although they ranged from about 0.05 to 0.30%Ro. Thus, the position of the condensate-wet gas window was estimated to occur at about 1.15%Ro (Jarvie et al., 2005). This is substantiated by the cracking of the C19+ biomarkers in samples at about this thermal maturity suggesting significant oil cracking.

When analyzing archived cuttings, one must be concerned about possible oxidation of organic matter, both kerogen and any bitumen that is present (Jarvie, 2016). When archived cuttings were compared to fresh cuttings and core, it was generally noted that the TOC and S2 were significantly lower (often by more than a factor of two).

To test this phenomenon, an ideal set of samples was provided by Gunn Oil Co as they offset an older well where archived cuttings were available from the Midland sample library. Gunn Oil also provided fresh cuttings and SWC for comparison. There was a three-fold increase in inorganic carbon in
the archived cuttings compared to fresh cuttings, whereas TOC decreased by a factor of two and S2 by a factor of three (Figure 2). As the effluent from pyrolysis is split 50:50, an increase in non-hydrocarbon gases such as CO₂ from oxidation) will lower S2 due to dilution. A similar phenomenon is sometimes observed in weathered outcrop samples where the FID (flame ionization detector) may be extinguished by high non-hydrocarbon gas content especially carbon dioxide from oxidized outcrops (Figure 3). The mass balance shows that the reduction in TOC and S2 was related to the dilution within 15% accuracy.

This oxidation effect appears to be the cause of the difference between recent samples of the Barnett Shale and cuttings from a Humble Geochemical Services Barnett Shale assessment in the middle 1990s. The Humble cuttings data do not show a comparable relationship to recent samples, primarily core, in terms of HI (hydrogen index) versus thermal maturity (Fig. 4). However, when publicly available core samples utilized by Humble from the middle 1990s are reported, the relationship is comparable to fresh samples reported in Lewan and Pawlewicz (2017) (see Fig. 4).

It should also be noted that there are different ways to prepare and measure the reflectivity of vitrinite particles. The two basic methods are whole rock and isolated kerogen analysis. Whole rock methodologies utilize chips of the sediment samples that are polished and any indigenous particles of vitrinite are measured by reflectivity. This technique provides a good setting to determine whether vitrinite particles are indigenous by their orientation in the mineral matrix. However, this technique provides a low number of readings, almost always fewer than 20 readings and often only a couple.
readings. Measurement of reflectivity of vitrinite on isolated kerogen provides a good yield of vitrinite on suitable samples due to the dissolution of the rock matrix. Unfortunately, this also makes it more difficult to ascertain which particles are indigenous. In this latter case the petrologist may measure a large number of particles but have a degree of uncertainty as to which are indigenous.

Figure 3. Example pyrograms. a) Pyrogram of a typical fresh cuttings or core analysis showing pyrolysis peak from 350-600°C; (b) pyrogram of a highly oxidized sample where the FID is extinguished resulting in an incomplete recording of the pyrolysate. The latter results from a high amount of non-hydrocarbon gases that result in an imbalance in the hydrogen and air flows to maintain the flame.

Figure 4. Comparison of HI and maturity (reflectivity of organic matter, not vitrinite). This shows the good relationship of archived core analysis by Humble to the recent work of the USGS and Klentzman on the Barnett Shale. However, it also shows the poor correlation of analytical results from archived cuttings (1970s-80s vintage). This supports the hypothesis that the archived cuttings are oxidized as shown in Figure 2.
Likewise, Tmax has numerous limitations and is especially affected by oil-based mud, organic contaminants in water-based mud, low pyrolysis response resulting in no peak, poorly resolved peaks, FID outages, and salt ionization (Espitalie et al., 1985). Source rocks that are not solvent extracted generally have lower Tmax values than source rocks that have been solvent extracted. This is due to volatilization of extractable organic matter that skews the kerogen peak to lower values. It has been shown that Monterey Shale samples can have 16°C variation in Tmax (Kruse, 1983), Bakken Shale up to 8°C (Figure) (Jarvie et al., 2011), and Vaca Muerta Shale (5°C) (Jarvie, unpublished data) between whole rock and solvent extracted rock. The solvent extracted rock is the more accurate assessment of kerogen maturity. This is also important when samples are selected for kinetic analysis (Jarvie, 1991).

Tmax is dependent upon the S2 measurement in various pyrolysis instruments. The shape of the S2 peak is a key part of Tmax. If the peak is flat as in organic lean or overly mature samples, Tmax will virtually be a random number. If the S2 is skewed due to the presence of extractable organic matter (EOM) or organic contamination from oil-based mud or organic additives in water-based muds, Tmax will also vary and is generally lowered in such cases. The best Tmax values are obtained on samples having greater than 0.50 mg/g rock for S2 and after solvent extraction in a strong, polar solvent such as chloroform-methanol.

Of course, Tmax accuracy is also dependent upon true temperature and calibration of any pyrolysis instrument. The problem is that in most pyrolysis instruments the true temperatures vary instrument to instrument. While not all pyrolysis instruments have comparable absolute temperatures, they will yield the same result for Tmax on a standard, but not necessarily on unknowns. Thus, they may be reproducible on the calibration standard, but inaccurate in terms of Tmax.

Figure 5. Comparison of unextracted and extracted samples of Upper Bakken Shale. Tmax values of solvent-extracted rock average 5°C higher Tmax. The average Tmax value for whole rocks is 432°C versus 437°C Tmax for solvent-extracted rock or a calculated equivalent %Roe(Tmax) of 0.62% versus 0.71% (using the 2001 equation). This is the difference between immature and early mature Bakken Shale. Modified from Jarvie et al. (2011).
Wildcat Technologies’ HAWK pyrolysis instrument was designed so that all instruments have the same absolute temperature, thus eliminating the issue when non-standard (unknowns) are analyzed. In addition, the HAWK allows for heat measurements to be initiated as low as 50°C (Fig. 6a), thereby enabling accurate measurement of volatile hydrocarbons extending to carbon number 4 to 5 organic compounds. HAWK pyrolysis measurements provide the whole range of Tmax data needed to correlate with Ro measurements. In addition to initiating of temperature programming as low as 50°C, it also has a maximum oven temperature of 850°C. The five-program ramp in Figure 6b allows more accurate determination of Tmax on whole rock samples.

Tmax will also vary with kerogen type and is not very applicable to kerogens with a single activation energy such as most lacustrine shales. Tmax changes as a function of the bond disassociation kinetics that vary in a Type II and Type III kerogen with a broad distribution of activation energies and probability factors (Arrhenius constants). Kerogens that do not have such a distribution, i.e., those with 90% of the decomposition described by a single activation energy and probability factor, decompose at a higher temperature, but also at a higher rate. For example, Tmax on samples of immature Lower Green River Shale core samples average 442°C for Tmax (n=127) with HI values as high as 980 mg/g indicative of limited conversion (<10% TR). However, interbedded coal lenses average 420°C Tmax (n=7) showing the dramatic difference in Tmax between two dramatically different sets of kerogen decomposition kinetics. A type II clay-rich shale would likely have a Tmax of about 430°C and a type II marine carbonate about 425°C. A very low maturity Monterey Shale (Type II-ONS) (Jarvie and Lundell, 2001) would have a Tmax of about 395°C. Thus, Tmax must be evaluated carefully for reliability and for kerogen type constraints.

Figure 6 a-b. Classical (a) and HAWK-PAM (b) thermal extraction and pyrolysis analysis. Classical pyrolysis (a) shows a large free oil peak (S1) but the pyrolysate has a shoulder that is also volatile (extractable) organic matter; it is necessary to extract the rock to obtain the total oil and the S2 Tmax value is skewed to a lower value. The HAWK-PAM methodology (b) separates the total oil peak into four different compositional ranges and removes the shoulder from the kerogen peak yielding a more reliable Tmax value. See Maende, 2016, for full details on HAWK-PAM.

Thus, given the analytical and sample limitations in both Tmax and measured vitrinite reflectance or other organic particles, it is not surprising that such a correlation will sometimes be poor. It again suggests the need to risk thermal maturity by all available data and then relate that to early production. Cumulative production will not provide an assessment of product type (phase) as GOR will increase with ongoing production.

To document a relationship between Tmax and vitrinite reflectance, a search of literature provided substantial amounts of data, or in the absence of data, provided a correlation equation. This
A compilation of Tmax and measured vitrinite reflectance data or correlations from published sources are presented in Appendix I. The correlation graphic and fitting result is shown in Figure 7.

When all the correlations are utilized over the Tmax window from 430 to 485°C (i.e., 10 data points per correlation), the following equation is obtained:

$$2018 \text{ Equivalent } \%Ro = (0.0165 \times \text{Tmax}) - 6.5143 \text{ where Tmax is reported in } ^\circ\text{C}$$

Comparison of the 2001 and new equation is shown in Table 1. This comparison shows little difference in the calculated %Ro from Tmax. In addition both equations fall near the centerpoint of the Teichmuller and Durand (1983) Tmax vs %Ro plot until very high thermal maturities where Tmax is not likely reliable in most cases.

All correlation data are provided in an Excel file that may be downloaded.

![Figure 7](image-url)
Table 1. Comparison of the 2001 and 2018 equations for converting Tmax to an equivalent %Ro. The two equations yield essentially the same %Roe.

Risking Thermal Maturity

Although measured vitrinite reflectance and Tmax have been discussed in some detail in the above, there are certainly other factors in their assessment and applicability to a given play. Furthermore, additional maturity assessments will aid in derivation of an interpreted thermal maturity (%iRo) (Jarvie, 2017). This requires a geochemical expert to derive using all available data as it could be expected that not all data will agree and provide a simple interpretation of thermal maturity. Finally, it is important to be able to predict the product type (phase-related product) for best application in exploration and production. It is insufficient to provide only an indication of oil or gas window thermal maturity for unconventional resource plays. A more useful guide for thermal maturity interpretation for unconventional plays is shown in Figure 8.

Position of Various Oil and Gas Windows

A key point of assessing thermal maturity is to be able to predict petroleum type and quality. The following guidelines from geochemical and engineering perspectives provide an indication of the petroleum type and quality (Jarvie, 2016).
Comparison of interpreted thermal maturity values to product type is achieved using guidelines from SPE Monograph 20 (Whitson and Brulé) (Figure 9). Black oil in terms of phase usually (not always as such determination requires PVT analysis) falls below about 1,500 to 1,000 scf/stb. Volatile oils, the ideal target for tight oil plays, falls between about 1000 to 3500 scf/stb. This overlap in GOR values shows that these values are guidelines, not absolutes. Above 3500 scf/stb, a condensate wet gas phase will exist. This can be broken down into condensate-wet gas, rich wet gas (high BTU), or lean wet gas before reaching the dry gas window, i.e., > 100,000 scf/stb. These guidelines are shown in Table 2.

Synopsis

Thermal maturity is an essential ingredient in assessing petroleum systems and the likely charge. This is especially true in unconventional resource systems where maturity and product are directly related. Various techniques may yield different interpretive results. These results must be interpreted to provide an accurate thermal maturity analysis. It may be necessary and is generally desirable to have other data (gas composition, carbon isotopes, quantitative aromatic hydrocarbons, etc.) to further resolve these differences. Ultimately, the final interpretation must be related to product type.

Table 2. Approximate description of various petroleum phases. Note the overlap of volatile and black oil phases that requires PVT analysis, which is true for all phase predictions. The windows are very close once the gas condensate window is reached due to the exponential increase in gas at those maturity levels. Ref: Whitson and Brulé, 2000.
References


Jacob, H., 1989, Classification, structure, genesis, and practical importance of natural solid oil bitumen (“migrabitumen”), Int. Coal Geol., 11, 65-79.


### Appendix I

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