Investigation and Identification of Pyrolysis Attributes that Can Assist in Predicting Producible Hydrocarbon in the Unconventional Eagle Ford Formation*

Albert Maende¹, Brian Horsfield², Sascha Kuske², Brian Jarvie³, Dan Jarvie¹, and W. David Weldon¹

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Abstract

Prediction of producible hydrocarbons in unconventional formations, is vital because it governs returns on investments. Kuske et al., 2019 used a PhaseSnapShot workflow to model target well hydrocarbon phases based on PVT data and nearest slightly less mature well. Gorynski et al., 2019, showed low-maturity shales can be dominated by heavy (C32+) oils and that the ratios of SARA components in the C15+ fraction of produced fluid and core extract can be used to estimate the mobile oil. Pepper et al., 2019 discriminated fluid saturation from sorbed oil.

Prediction of producible hydrocarbons in unconventional formations is complicated by the co-occurrence of sorbed oil with fluid saturation. Our objective was to investigate and identify pyrolysis attributes that can assist in predicting producible hydrocarbon in unconventional formations. Seven core samples spanning the Eagle Ford Formation’s early mature, oil window and condensate/wet gas zones were analyzed on the HAWK pyrolysis instrument using both classical bulk-flow pyrolysis and HAWK-PAM the latter of which provides insights into boiling ranges. Hydrocarbons were extracted using DCM, while the extracted rock was analyzed using both pyrolysis methods. The extract was quantified and fingerprinted using both gas chromatography and PAM. The suppression effect of ‘S2 shoulders’ on maturity was evident on four cores.

While the S1 mg HC/g rock values for the seven core samples were 5.3, 2.23, 2.82, 2.19, 8.33, 6.68, and 3.94 for Tmax (°C) maturity values of 436, 442, 458, 465, 443, 434, and 435 respectively, their S1+ (S2whole rock - S2extract rock) values were 20.07, 5.13, 5.18, 3.41, 15.32, 25.6, and 12.54 mg HC/g rock respectively. These two measurements, however, do not enable the discrimination of producible hydrocarbons because of the presence of sorbed oil which is highest in early mature cores.
Conversion of mg HC/g rock measurements to their respective organic carbon using the assumption that 85% of hydrocarbons content is organic carbon, together with conversion of the quantified extracted organic matter (EOM) from ppm to weight % enabled the identification of a new set of pyrolysis attributes: For the Tmax (°C) maturity values of 436, 442, 458, 465, 443, 434, and 435 respectively, S1 organic Carbon/EOM was 0.18, 0.27, 0.34, 0.3, 0.42, 0.18, and 0.23: The (C4 - C19)/EOM ratio was 0.05, 0.1, 0.14, 0.14, 0.17, 0.05, and 0.09 while that of (C4 - C36)/EOM was 0.31, 0.36, 0.5, 0.39, 0.55, 0.24, and 0.34 respectively. The ratio of (C4 - C19)/(C4 - C36) yielded values of 0.17, 0.27, 0.28, 0.37, 0.31, 0.22, and 0.25. These four pyrolysis attributes enable ranking of predicted producible hydrocarbons, with the highest to lowest values in each of the attributes, corresponding to highest to lowest producible hydrocarbon contents. Determination of these pyrolysis attributes for a producing interval can provide calibration for predicting similar production.

**References Cited**


Investigation and Identification of Pyrolysis Attributes that can Assist in Predicting Producible Hydrocarbon in the Unconventional Eagle Ford Formation

Presented at: AAPG 2020 Annual Convention & Exhibition, Houston, Texas, USA, September 29th – October 1st by Albert Maende¹, Brian Horsfield², Sascha Kuske², Brian Jarvie³, Dan Jarvie¹, and W. David Weldon¹

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Talk Outline

- Objective and previous work
- Two current pyrolysis methods invoked in this study and their limitations
- New method for investigation for pyrolysis attributes
- Analyses of Eagle Ford Formation’s core and extracted core samples; Classical pyrolysis, HAWK-PAM, quantification of extractable organic matter and gas chromatography
- Results and Interpretation
- Graphical plots of selected pyrolysis parameters against maturity (Tmax)
- Pyrolysis parameters demarcation of immature, oil window and condensate/wet gas zones
- Comparison of pyrolysis and maturity measurements of cores and extracted cores
- Gas chromatography fingerprinting of the core extracts and evaporative loss determination
- Pyrolysis attributes of the Shale Prospectivity Tool
- Cut-off values of the Shale Prospectivity Tool for determination of producible oil zones
- Shale Prospectivity Tool mapping of the drilled structure
- Conclusions

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Objective and Previous Work

Introduction

Seven core samples spanning the Eagle Ford Formation’s early mature, oil window and condensate/wet gas zones (Figure 1 and Figure 2) were analyzed as whole rock, extracts and extracted rock, with the objective of investigating and identifying pyrolysis attributes that can assist in predicting producible hydrocarbons in unconventional formations.

This is a vital need because it governs returns on investments.

Kuske et al., 2019 used a PhaseSnapShot workflow to model target well hydrocarbon phases based on PVT data and nearest slightly less mature well.

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Previous Work and Current Pyrolysis Methods

Gorynski et. al., 2019, showed low-maturity shales can be dominated by heavy (C_{32+}) oils and that the ratios of SARA components in the C_{15+} fraction of produced fluid and core extract can be used to estimate the mobile oil.

Pepper et.al., 2019 discriminated fluid saturation (producible hydrocarbons) from sorbed oil.

Prediction of producible hydrocarbons in unconventional formations is complicated by the co-occurrence of sorbed oil with fluid saturation.

The current pyrolysis methods that are invoked in this study are Classical Pyrolysis and HAWK-PAM

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Classical Pyrolysis and HAWK-PAM

**Classical Pyrolysis**, are analyses to determine thermally released oil (S1 in mg HC/g rock) at 300 °C, hydrocarbons yield from pyrolysis of kerogen (S2 in mg HC/g rock) through heating in an inert environment using a ramp rate of 25 °C from 300 to 650 °C, pyrolysis measurements of both CO and CO$_2$ (S3CO in mg CO/g rock and S3CO$_2$ in mg CO$_2$/g rock) and maturity (Tmax in °C) determined as the temperature at the maximum generation of hydrocarbons on the S2 peak.

**HAWK-PAM**, are analyses whereby, a ramp rate of 25°C was utilized to generate five petroleum peaks – four on oil fractions and one on kerogen. It is a pyrolysis method through which, determination of the occurrence of carbon number groupings corresponding to $C_4 - C_5$ (Oil-1) at ~50 – 100 °C, $C_6 - C_{10}$ (Oil-2) at 100 °C, $C_{11} - C_{19}$ (Oil-3) at 100 – 180 °C, $C_{20} - C_{36}$ (Oil-4) at 180 – 350 °C and $C_{37+}$ (K-1; Kerogen plus any $C_{37+}$) at 350 – 650 °C, is done. In addition, maturity (K-1 Tmax in °C) is determined as the temperature at the maximum generation of hydrocarbons on the K-1 peak (Maende et. al., 2017).

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Statement of the Limitations of both Classical Pyrolysis and HAWK-PAM

Classical Pyrolysis and HAWK-PAM measurements, however, do not enable the discrimination of producible hydrocarbons because of the presence of sorbed oil which is highest in early mature cores.

New Method of Investigation for Pyrolysis Attributes

Conversion of mg HC/g rock measurements to their respective organic carbon using the assumption that 85% of hydrocarbons content in petroleum is organic carbon, together with conversion of the quantified extracted organic matter (EOM) from ppm to weight % enabled the identification of a new set of pyrolysis attributes, collectively referred to as the “Shale Prospectivity Tool”. Seven core samples from the Eagle Ford Formation were analyzed.

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Location and Stratigraphy of Eagle Ford Shale Play

Figure 1. Eagle Ford Shale Play, Western Gulf Basin, South Texas (EIA, 2014)

Figure 2. Stratigraphy of Western Gulf Basin, South Texas (Ononogbu, 2012)
Analyses

Analyses of core and extracted core samples from the Eagle Ford Formation

The seven core and extracted core samples from the Eagle Ford Formation were analyzed on the HAWK pyrolysis instrument using both classical bulk-flow pyrolysis and HAWK-PAM, the latter of which provides insights into boiling ranges.

Hydrocarbons were extracted using dichloromethane (DCM), while the extracted rock was analyzed using both pyrolysis methods. The extract was quantified and fingerprinted using gas chromatography and will later be quantified and fingerprinted using PAM.

HAWK® Pyrolysis

The seven core and extracted core samples were analyzed on the HAWK Pyrolysis, TOC & Carbonate Carbon instrument using two pyrolysis methods, namely; Classical Pyrolysis and HAWK-PAM.

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Extractable Organic Matter (EOM)

Quantitative extraction of extracts for Gas Chromatography analyses was done using the Dionex ASE 350 model.

For Dionex extraction, the rock sample is ground to 60 mesh size, after which a weight of sample ranging from 5 to 20 grams is placed into the Dionex’ steel extraction cell and then using dichloromethane as the solvent, extraction of the oil is done within the 40 °C to 100 °C operating temperature range of the Dionex.

The extract is then dried under a fume hood and weighed for quantification.
Gas Chromatography (GC)

Gas Chromatography (GC) Whole Oil Gas Chromatography on the extracted oil was performed using an Agilent GC. Petroleum extracted from rock samples can be fingerprinted by gas chromatography (GC).

A fingerprint of petroleum provides an indication of the distribution and yield of resolvable compounds, i.e., basically a histogram of the individual compounds that can be separated by this analytical technique.

An oil or extract with an internal standard(s) is injected into a GC inlet which vaporizes the petroleum in the presence of an inert carrier gas onto a capillary column that may range from 10 to 150 meters in length.
Gas Chromatography (GC)

The internal surface of the column is coated with a chemical phase utilized for the required analytical need.

This chemical phase interacts with the hydrocarbon molecules moving through the length of the column resulting in separation of the alkanes as well as many iso-alkanes, cyclo-alkanes, and some aromatic hydrocarbons.

The end of the column passes the effluent into a flame ionization detector (FID).

Integration of the fingerprint provides the weight or mole percent of each compound relative to the internal standard(s) and is used to characterize the alkane fraction of the petroleum (Jarvie, 2015).
Results and Interpretation

Classical Pyrolysis, HAWK-PAM, Extractable Organic Matter (EOM) & Gas Chromatography (GC)

Table 1. Classical Pyrolysis, HAWK-PAM and Extractable Organic Matter

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Method</th>
<th>Sample Type</th>
<th>S1 (mg HC/g rock)</th>
<th>S2 (mg HC/g rock)</th>
<th>S3 (mg CO2/g rock)</th>
<th>Tmax (°C)</th>
<th>Production index (S1/S1 + S2)</th>
<th>Extractable Organic Matter (EOM) (ppm)</th>
<th>S1sum - S1rock + S2sum - S2rock (Jarvie, 2012)</th>
<th>Sample ID</th>
<th>Method</th>
<th>Sample Type</th>
<th>S1 (mg HC/g rock)</th>
<th>S2 (mg HC/g rock)</th>
<th>S3 (mg CO2/g rock)</th>
<th>Tmax (°C)</th>
<th>Production index (S1/S1 + S2)</th>
<th>Extractable Organic Matter (EOM) (ppm)</th>
<th>S1sum - S1rock + S2sum - S2rock (Jarvie, 2012)</th>
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<tbody>
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<td>Classical Pyrolysis</td>
<td>Core</td>
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<td>0</td>
<td>0.03</td>
<td>0.27</td>
<td>44.99</td>
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</table>

The suppression effect of ‘S2 shoulders’ on maturity was evident on four cores (those of Tmax 436, 458, 465 and 443). The “S2 shoulder” which is an overlap of the heavier oil component from S1 into S2 is quantifiable through the almost equality of the “S2 – K1” value with the “Sum(Oil-1, Oil-2, Oil-3 and Oil-4 – S1” value of the cores of Tmax 442 and 443 which are of mid oil window maturity (Table 1).

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Graphical Plots of Selected Pyrolysis Measurements against Maturity (Tmax)

Core Samples; Tmax vs S1

S1 (mg HC/g rock)

Core Samples; Tmax vs EOM

EOM (ppm) (Ext wt / Rock wt) x 1,000,000 x 10^4

Core Samples; Tmax vs S2/S3

S2/S3 x 10

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Graphical Plots of Selected Pyrolysis Measurements against Maturity (Tmax)

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Graphical Plots of Selected Pyrolysis Measurements against Maturity (Tmax)

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Graphical plots of selected pyrolysis measurements against Tmax (Figure 3) demonstrate that the immature, oil window and condensate to wet gas zones plot along elliptical arcs that have specified exponential equations with correlation values that range from an $R^2$ of 0.59 to 0.93. The highest $R^2$ values are in the 0.90 to 0.93 range and are those of Tmax vs S2, Tmax vs S2/S3, and K-1 Tmax vs K-1.

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Ranges of Pyrolysis Parameters that Demarcate the Immature, Oil Window and Condensate to Wet Gas Zones

Table 2. Summary of the Various Ranges of Pyrolysis Parameters that Demarcate the Immature, Oil Window and Condensate to Wet Gas Zones

<table>
<thead>
<tr>
<th>Maturity</th>
<th>S1 (mg HC/µg rock) from Tmax vs S1</th>
<th>EOM (ppm) from Tmax vs EOM</th>
<th>S2/S3 from Tmax vs S2/S3</th>
<th>Sum(S1 + S2) (mg HC/µg rock) from Tmax vs Sum(S1 + S2)</th>
<th>K-1 Tmax (°C) from K-1 Tmax vs Sum(Oil-1, Oil-2 &amp; Oil-3)</th>
<th>K-1 Tmax (°C) from K-1 Tmax vs Sum(Oil-2, Oil-3 &amp; Oil-4)</th>
<th>K-1 (mg HC/µg rock) from K-1 Tmax vs K-1</th>
<th>K-1 (mg HC/µg rock) from K-1 Tmax vs EOM</th>
<th>K-1 (mg HC/µg rock) from K-1 Tmax vs Sum(Oil-1, Oil-2, Oil-3 &amp; Oil-4)</th>
<th>S2 (mg HC/µg rock) from Tmax vs S2</th>
<th>K-1 (mg HC/µg rock) from K-1 Tmax vs S2/S3</th>
<th>K-1 (mg HC/µg rock) from K-1 Tmax vs S3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Immature (&lt; 435 °C Tmax)</td>
<td>3.5 - 10</td>
<td>1.3 - 4</td>
<td>5 to 15</td>
<td>25 - 80</td>
<td>12 - 34</td>
<td>55 - 12</td>
<td>21 - 60</td>
<td>1.4 - 3.5</td>
<td>27 - 80</td>
<td>27 - 50</td>
<td>48 - 60</td>
<td></td>
</tr>
<tr>
<td>Oil Window (435 °C - 455 °C Tmax)</td>
<td>2 to 10</td>
<td>0.5 - 1.8</td>
<td>2.5 to 5</td>
<td>10 to 25</td>
<td>0.7 - 3.5</td>
<td>1.5 - 12</td>
<td>9 to 21</td>
<td>0.5 - 1.8</td>
<td>11 to 27</td>
<td>7 to 46</td>
<td>5 to 48</td>
<td></td>
</tr>
<tr>
<td>Condensate to Wet Gas (455 °C - 475 °C Tmax)</td>
<td>0 - 0.5</td>
<td>0 - 0.8</td>
<td>0 to 2.5</td>
<td>0 to 10</td>
<td>0.7 - 1.2</td>
<td>0 - 4.3</td>
<td>0 to 9</td>
<td>0.5 - 0.8</td>
<td>0 - 11</td>
<td>0 - 8</td>
<td>0 - 5</td>
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Comparison of Pyrolysis and Maturity Measurements of Core and Extracted Core Samples that were analyzed using Gas Chromatography (GC) and for which Evaporative Loss was Determined

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Sample Type</th>
<th>S1 (mg HC/g rock)</th>
<th>S2 (mg HC/g rock)</th>
<th>S3 (mg CO2/g rock)</th>
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</tr>
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<tr>
<td>G014171</td>
<td>Core / Extracted Core</td>
<td>5.3 / 0.16</td>
<td>25.55 / 10.78</td>
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</tr>
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<td>G014174</td>
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<td>442 / 443</td>
</tr>
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<td>G014177</td>
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<td>458 / 465</td>
</tr>
<tr>
<td>G014180</td>
<td>Core / Extracted Core</td>
<td>2.19 / 0.25</td>
<td>2.91 / 1.69</td>
<td>0.29 / 0.26</td>
<td>465 / 476</td>
</tr>
<tr>
<td>G014183</td>
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<td>11.99 / 5.00</td>
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<td>443 / 458</td>
</tr>
<tr>
<td>G014185</td>
<td>Core / Extracted Core</td>
<td>6.68 / 0.13</td>
<td>58.08 / 39.16</td>
<td>0.45 / 0.31</td>
<td>434 / 440</td>
</tr>
<tr>
<td>G014188</td>
<td>Core / Extracted Core</td>
<td>3.94 / 0.13</td>
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Gas Chromatography (GC) Fingerprints of the Extracts of the Seven Core Samples that were Analyzed

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<th>Sample ID</th>
<th>Sample Type</th>
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Gas Chromatography (GC) Fingerprints of the Extracts of the Seven Core Samples that were Analyzed and Restored Yields

Samples G014177, G014180 and G014183 whose Tmax values are 458, 465 and 443 respectively, have evaporative losses of 82.6% for nC$_{19}$, 83.7% for nC$_{19}$, and 84.2% for nC$_{20}$, respectively (Table 4).
Gas Chromatography (GC) Fingerprints of the Extracts of the Seven Core Samples that were Analyzed and Restored Yields

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</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Core Tmax (°C)</th>
<th>Evaporative Loss</th>
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</thead>
<tbody>
<tr>
<td>G014177</td>
<td>458</td>
<td>82.6% nC\textsubscript{19}</td>
</tr>
<tr>
<td>G014180</td>
<td>465</td>
<td>83.7% nC\textsubscript{19}</td>
</tr>
<tr>
<td>G014183</td>
<td>443</td>
<td>84.2% nC\textsubscript{20}</td>
</tr>
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Gas Chromatography (GC) Fingerprints of the Extracts of the Seven Core Samples that were Analyzed and Restored Yields

Samples G014177, G014180 and G014183 whose Tmax values are 458, 465 and 443 respectively, have evaporative losses of 82.6% for nC\textsubscript{19}, 83.7% for nC\textsubscript{19} and 84.2% for nC\textsubscript{20}, respectively (Table 4).

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Sample ID</th>
<th>Tmax (°C)</th>
<th>Core_Tmax (°C)</th>
<th>Evaporative Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>G014177</td>
<td>458</td>
<td>82.6%_nC\textsubscript{19}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G014180</td>
<td>465</td>
<td>83.7%_nC\textsubscript{19}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G014183</td>
<td>443</td>
<td>84.2%_nC\textsubscript{20}</td>
<td></td>
<td></td>
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</tbody>
</table>
Gas Chromatography (GC) Fingerprints of the Extracts of the Seven Core Samples that were Analyzed

Figure 4 shows the gas chromatography (GC) fingerprints of the extracts of the seven core samples. Samples G014177, G014180 and G014183 whose Tmax values are 458, 465 and 443 respectively, have evaporative losses of 82.6% for nC_{19}, 83.7% for nC_{19} and 84.2% for nC_{20} respectively.
Pyrolysis Attributes of the Shale Prospectivity Tool

As a result of this study, the Shale Prospectivity Tool has been developed.

The objective of the Shale Prospectivity Tool is to utilize Six Pyrolysis Attributes to Predict the Occurrence of Producible Hydrocarbons and in addition, also map Structures.

The six pyrolysis attributes are determined through conversion of two Classical Pyrolysis rock measurements and four HAWK-PAM rock measurement’s mg HC/g rock (milligram hydrocarbons per gram rock), values to their respective organic carbon using the assumption that 85% of hydrocarbons content in petroleum is organic carbon.

These values are then normalized to either their respective TOC (Total Organic Carbon) or Extractable Organic Matter (EOM) measurements.

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Definitions of Pyrolysis Attributes of the Shale Prospectivity Tool

The Six Pyrolysis Attributes of the Shale Prospectivity Tool are defined as shown below:

**Pyrolysis Attribute 1:** Classical Pyrolysis’ S1 organic carbon content in hydrocarbons normalized to either EOM or TOC. i.e., S1*C in HCs/EOM or TOC

Pyrolysis Attributes 2, 3, 4 and 5 are all derived from HAWK-PAM measurements:

**Pyrolysis Attribute 2:** Oil4 (C_{20} - C_{36})*C in HCs/EOM or TOC

**Pyrolysis Attribute 3:** Sum of Oil1, Oil2, & Oil3 (C_{4} - C_{19})*C in HCs/EOM or TOC

**Pyrolysis Attribute 4:** Sum of Oil1, Oil2, Oil3 & Oil4 (C_{4} - C_{36})*C in HCs/EOM or TOC

**Pyrolysis Attribute 5** is the Mobility Index: Sum(Oil1, Oil2 & Oil3)/Sum(Oil1, Oil2, Oil3 & Oil4) (C_{4} - C_{19}/C_{4} - C_{36})

**Pyrolysis Attribute 6:** Classical Pyrolysis’ S2 kerogen pyrolyzed hydrocarbons normalized to either EOM or TOC. i.e., S2*C in HCs/EOM or TOC
Cut-off Values of Pyrolysis Attributes of the Shale Prospectivity Tool for Determination of Producible Oil Zones

Each of these five pyrolysis attributes has been assigned a cut-off value that it needs to either equal or exceed in order for it to be a candidate to be utilized in identifying a producible oil zone. An analyzed sample that has at least three of these pyrolysis attributes either equating or exceeding the cut-off value is considered to be indicative of a producible oil zone. Table 5 and Figure 5 show that all the seven core samples fulfill the Shale Prospectivity Tool’s conditions for being identified as being in a producible oil zone. However it is only the G014180 core of Tmax 465 °C (K-1 Tmax 464 °C) that equates or exceeds the Mobility Index cut-off value.

Table 5. Pyrolysis Attributes of the Shale Prospectivity Tool

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Sample ID</th>
<th>$S_1$°C in HCs/EOM; Pyrolysis Attribute 1_0.1 as cut off</th>
<th>Oi14 ($C_{20}$)°C in HCs/EOM; Pyrolysis Attribute 2_0.05 as cut off</th>
<th>Sum of Oi11, Oi12, Oi13 ($C_{20}$)°C in HCs/EOM; Pyrolysis Attribute 2_0.05 as cut off</th>
<th>Sum of Oi11, Oi12, Oi13 ($C_{20}$)°C in HCs/EOM; Pyrolysis Attribute 2_0.05 as cut off</th>
<th>Mobility Index; Sum(Oi11, Oi12 &amp; Oi13) \sum_{Oi11, Oi12 &amp; Oi13}($C_{20}$)°C in HCs/EOM; Pyrolysis Attribute 5_0.35 as cut off</th>
<th>Mobility Index; Sum(Oi11, Oi12 &amp; Oi13) \sum_{Oi11, Oi12 &amp; Oi13}($C_{20}$)°C in HCs/EOM; Pyrolysis Attribute 5_0.35 as cut off</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core</td>
<td>G014171</td>
<td>0.18</td>
<td>0.25</td>
<td>0.05</td>
<td>0.31</td>
<td>0.17</td>
<td>0.21</td>
</tr>
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<td>Core</td>
<td>G014174</td>
<td>0.27</td>
<td>0.27</td>
<td>0.10</td>
<td>0.36</td>
<td>0.27</td>
<td>0.27</td>
</tr>
<tr>
<td>Core</td>
<td>G014177</td>
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<td>0.36</td>
<td>0.14</td>
<td>0.50</td>
<td>0.28</td>
<td>0.28</td>
</tr>
<tr>
<td>Core</td>
<td>G014180</td>
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<td>0.25</td>
<td>0.14</td>
<td>0.39</td>
<td>0.37</td>
<td>0.37</td>
</tr>
<tr>
<td>Core</td>
<td>G014183</td>
<td>0.42</td>
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<td>0.55</td>
<td>0.31</td>
<td>0.31</td>
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<tr>
<td>Core</td>
<td>G014185</td>
<td>0.18</td>
<td>0.19</td>
<td>0.05</td>
<td>0.24</td>
<td>0.22</td>
<td>0.22</td>
</tr>
<tr>
<td>Core</td>
<td>G014188</td>
<td>0.23</td>
<td>0.26</td>
<td>0.09</td>
<td>0.34</td>
<td>0.25</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Figure 5. Graphical Plot of Five Pyrolysis Attributes of the Shale Prospectivity Tool
Shale Prospectivity Tool Mapping of the Drilled Structure

A graphical plot of the Shale Prospectivity Tools’ Pyrolysis Attribute 1 ($S_1^\ast C$ in HCs/EOM against Pyrolysis Attribute 6 ($S_2^\ast C$ in HCs/EOM maps the drilled structure and show the separation between these values to be widest in the immature zone, of intermediate width in the oil window and so close to each other as to be virtually touching in the condensate to wet gas zone (Figure 6). The down-dip direction can also be discerned. Kuske et al., 2019 showed that Hydrogen Index values of two of the Eagle Ford suites of samples that they analyzed, systematically varied with structural dip direction.

Figure 6. Two Pyrolysis Attributes of the Shale Prospectivity Tool used to Delineate Maturity Zones and Map Structure

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Conclusions

Seven core samples spanning the Eagle Ford Formation’s early mature, oil window and condensate/wet gas zones were analyzed both as whole rock and extracted rock, whereby, six pyrolysis attributes that can assist in predicting producible hydrocarbon in unconventional formations and also map structures were identified and collectively labelled as “the Shale Prospectivity Tool”.

The six pyrolysis attributes are determined through conversion of two Classical Pyrolysis rock measurements and four HAWK-PAM rock measurement’s mg HC/g rock values to their respective organic carbon using the assumption that 85% of hydrocarbons content in petroleum is organic carbon. These values are then normalized to either their respective TOC or EOM measurements.
Conclusions

The suppression effect of ‘S2 shoulders’ on maturity was evident on four cores (those of Tmax 436, 458, 465 and 443). The “S2 shoulder” which is an overlap of the heavier oil component from S1 into S2 is quantifiable through the almost equality of the “S2 – K1” value with the “Sum(Oil-1, Oil-2, Oil-3 and Oil-4 – S1” value of the cores of Tmax 442 and 443 which are of mid oil window maturity.

Graphical plots of selected pyrolysis measurements against Tmax (Figure 3) demonstrate that the immature, oil window and condensate to wet gas zones plot along elliptical arcs that have specified exponential equations with correlation values that range from an $R^2$ of 0.59 to 0.93.
Conclusions

The highest $R^2$ values are in the 0.90 to 0.93 range and are those of $T_{max}$ vs $S_2$, $T_{max}$ vs $S_2/S_3$, and $K_1$ $T_{max}$ vs $K_1$. Samples G014177, G014180 and G014183 whose $T_{max}$ values are 458, 465 and 443 respectively, have evaporative losses of 82.6% for $nC_{19}$, 83.7% for $nC_{19}$ and 84.2% for $nC_{20}$ respectively.

**Classical Pyrolysis** and **HAWK-PAM** measurements, however, do not enable the discrimination of producible hydrocarbons because of the presence of sorbed oil which is highest in early mature cores. Conversion of mg HC/g rock measurements to their respective organic carbon using the assumption that 85% of hydrocarbons content in petroleum is organic carbon, together with conversion of the quantified extracted organic matter (EOM) from ppm to weight % enabled the identification of a new set of pyrolysis attributes, which collectively are referred to as the Shale Prospectivity Tool.

An analyzed sample that has at least three of the Shale Prospectivity Tools’ pyrolysis attributes either equating or exceeding the cut-off value is considered to be indicative of a producible oil zone.

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Conclusions

All the Eagle Ford Formation’s seven analyzed core samples, fulfill the Shale Prospectivity Tool’s conditions for being identified as being in a producible oil zone. However it is only the G014180 core of Tmax 465 °C (K-1 Tmax 464 °C) that equates or exceeds the Mobility Index pyrolysis attribute cut-off value.

A graphical plot of the Shale Prospectivity Tools’ Pyrolysis Attribute 1 (S1*C in HCs/EOM) against Pyrolysis Attribute 6 (S2*C in HCs/EOM) maps the drilled structure and show, the separation between these values to be widest in the immature zone, of intermediate width in the oil window and so close to each other as to be virtually touching in the condensate to wet gas zone.

The Shale Prospectivity Tools’ Pyrolysis Attributes enable ranking of predicted producible hydrocarbons, with the highest to lowest values in each of the attributes, corresponding to highest to lowest producible hydrocarbon contents. Determination of these pyrolysis attributes for a producing interval can provide calibration for predicting similar production.
Acknowledgements and References

Acknowledgements
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References
References


Pepper, A., S. Perry, and L. Heister, 2019, Saturation Isn’t What It Used to Be: Towards More Realistic Petroleum Fluid Saturations and Produced Fluid Compositions in Organic-Rich Unconventional Reservoirs, Unconventional Resources Technology Conference (URTeC) DOI 10.15530/urtec-2019-196. This paper was prepared for presentation at the Unconventional Resources Technology Conference held in Denver, Colorado, USA, 22-24 July 2019.