218 Higgins Street
Humble, TX 77338
(281) 540-3208

Application Note (052016-1)

Wildcat Compositional Analysis for Conventional and Unconventional Reservoir Assessments

HAWK Petroleum Assessment Method™ (HAWK-PAM)

Albert Maende, Wildcat Technologies, albertmaende@wildcattechnologies.com

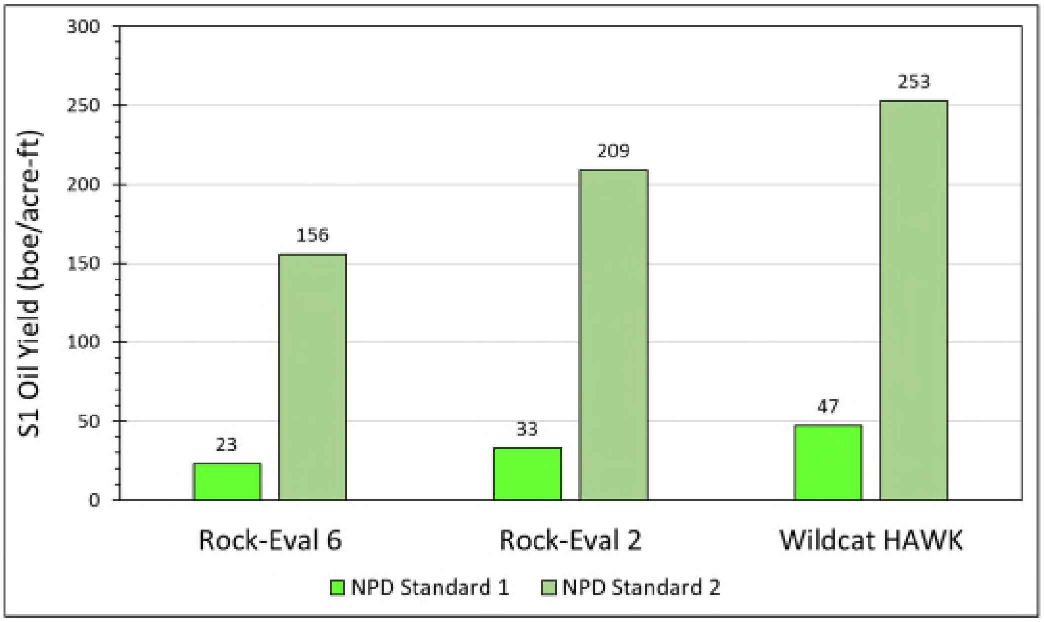
Pyrolysis in Petroleum Exploration

Pyrolysis has been used to characterize petroleum source rocks for over 40 years now (Barker, 1974; Espitalie et al., 1977). Up to the present date, pyrolysis instrumentation has been utilized to evaluate source rock formations (e.g., Jones, 1984; Peters, 1986; Peters and Caasa, 1994). Jarvie (2012) sought to directly address identification of sweet spots in unconventional reservoir intervals in his promulgation of the pyrolysis interpretation parameter referred to as "Oil Saturation Index" or Normalized Oil Content (Jarvie et al., 2001; Jarvie and Baker, 1985).

Wildcat Technologies has advanced the capabilities and utility of bulk thermal extraction/pyrolysis instrumentation with its advanced HAWK instrument that provides highly accurate and reliable measure of TOC, oil and kerogen yields as well as thermal maturity. Wildcat Technologies has advanced this technology further by announcing the launch of its recently developed multiramp/multizone pyrolysis method that is now operational on the HAWK Pyrolysis instrument. This HAWK Petroleum Assessment Method whose registration is currently underway, is geared at reservoir assessment in both unconventional and conventional systems.

It is useful to note that oil yields can vary according to the instrumentation used. The figure below utilizes standard rock analysis reported by the Norwegian Petroleum Directorate (NPD) showing higher values in Rock-Eval 2 and more recently, by HAWK compared to Rock-Eval 6 (Jarvie, 2014).

HAWK (Hydrocarbon Analyzer with Kinetics) system provides oil and kerogen yields on petroleum source rocks, oil yields on reservoir rocks, and thermal maturity assessment with an equivalent vitrinite reflectance value (%Roe) derived from Tmax. For kinetic experiments, HAWK measures true temperatures using highly conductive helium (not nitrogen) carrier gas.



Comparison of oil (S1) yields reported by the Norwegian Petroleum Directorate on their standard rock samples.

HAWK Petroleum Assessment Method™ (HAWK-PAM)

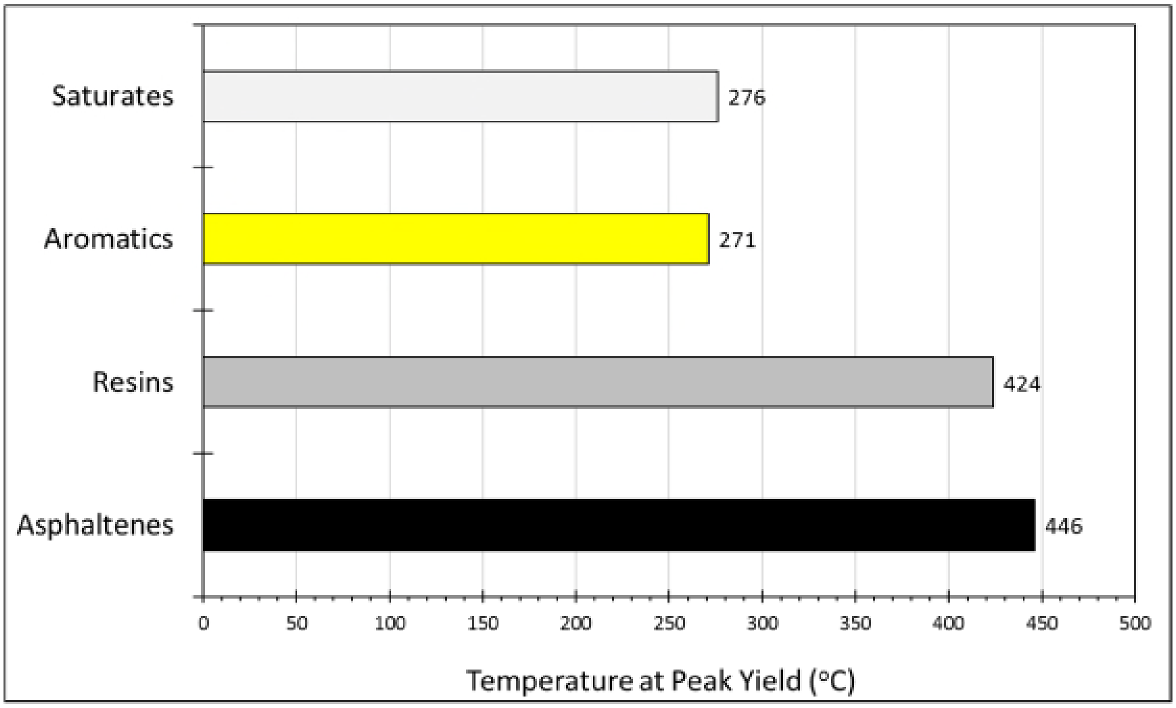
A multiple ramp and isotherm capability is now available on the HAWK Instrument. HAWK Petroleum Assessment Method utilizes five zones using multiple ramp and isotherm routines assigned during a single sample analysis. A ramp rate of 25°C is utilized to generate five petroleum peaks – four on oil fractions and one on kerogen. Each isotherm has its own specific Tmax indicative of the maximum evolution temperatures. The peak names and associated temperature of occurrence are as shown in the table below:

Peak (zone) Name	Oil-1	Oil-2	Oil-3	Oil-4	K-1
Temperature Range (°C) within which Tmax is designated	~50 °C to ~100 °C, hold for 5 minutes	100 °C, hold for 5 minutes	Ramp 100 °C to 180 °C at 25 °C per minute. Hold for 5 minutes	Ramp 180°C to 350 °C at 25 °C per minute. Hold for 5 minutes	Ramp 350°C to 650 °C at 25 °C per minute. Hold for 5 minutes
Petroleum Fraction	C4-C5	C6-C10	C11-C19	C20-C36	Kerogen (plus any C37+)
SARA disposition	Saturates and Aromatics			Polars	n/a

Approximation of carbon number ranges and SARA fraction disposition utilized in one of the multiple ramp and isotherm programs used in the HAWK PAM.

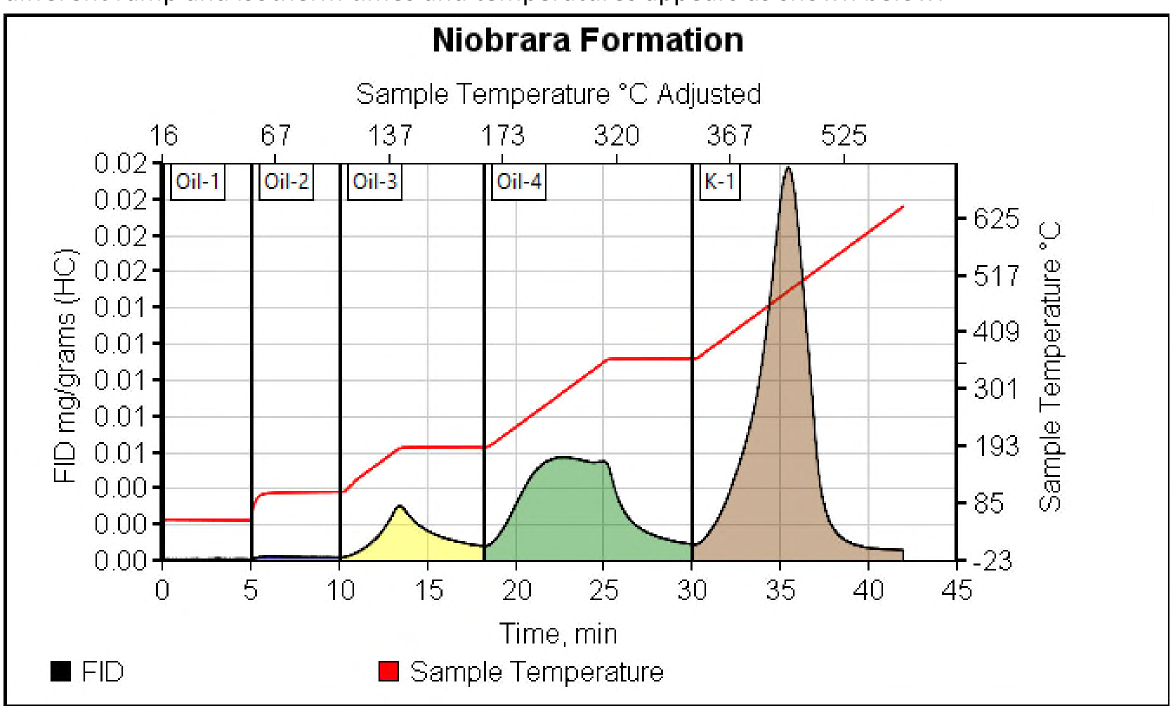
The generalized categories for these five HAWK Petroleum Assessment Method peaks as well as polar constituents (resins vs asphaltenes) are depicted above.

Additional methodologies partially segregate the polars into resin and asphaltenes fractions based on their Tmax differences. This was shown by Jarvie et al. (2015) where the saturates and aromatics largely volatilize whereas the resins and asphaltenes decompose during pyrolysis at different temperature (Tmax) values.



Volatilization and Tmax temperatures for saturates and aromatics and resins and asphaltenes, respectively.

A typical pyrogram generated using the HAWK Petroleum Assessment Method using five different ramp and isotherm times and temperatures appears as shown below:



Five ramp temperatures and isotherms using a HAWK PAM program. Programming can be assigned for any given ramp and isotherm values in the methodology.

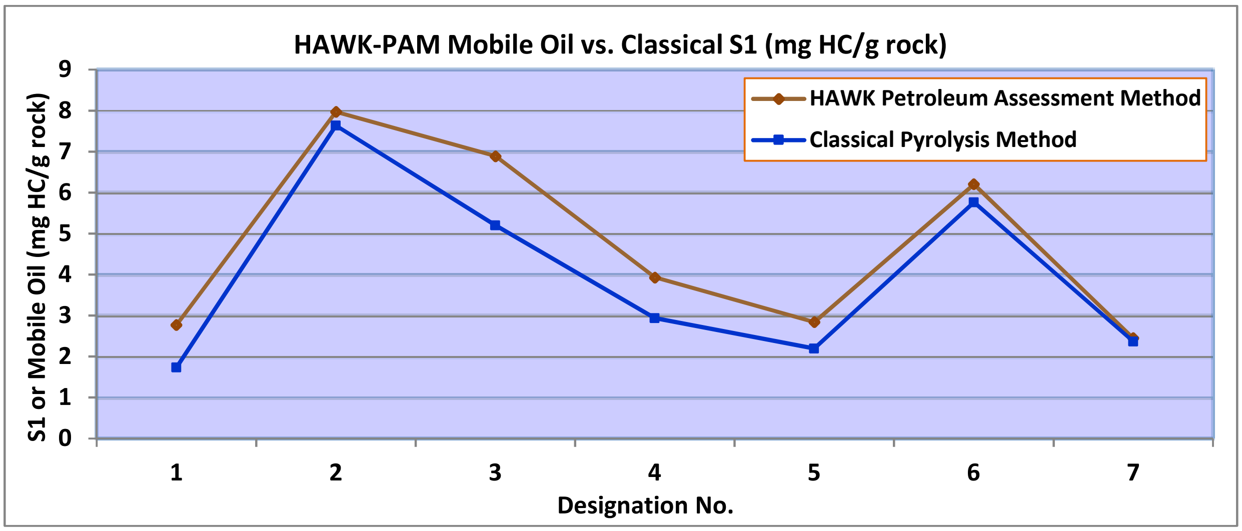
Reservoir Assessment using the HAWK Petroleum Assessment Method™ (HAWK-PAM)

Results on analyses of samples from seven source rocks using this new method are shown below and so are the results of analysis of this same group of samples when the classical pyrolysis method (initiate pyrolysis at 300 °C and ramp at 25 °C up to 650 °C) is utilized.

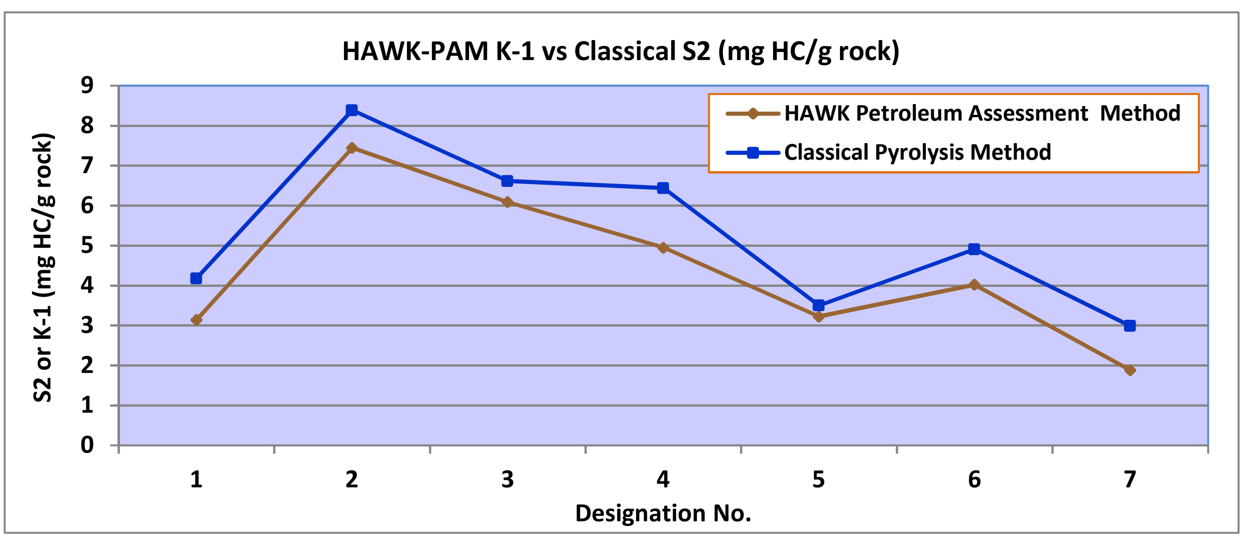
Comparison of results of HAWK Petroleum Assessment Method™ with those of the Classical Pyrolysis Method

The tables and charts below show a comparison of various unconventional resource plays using HAWK.

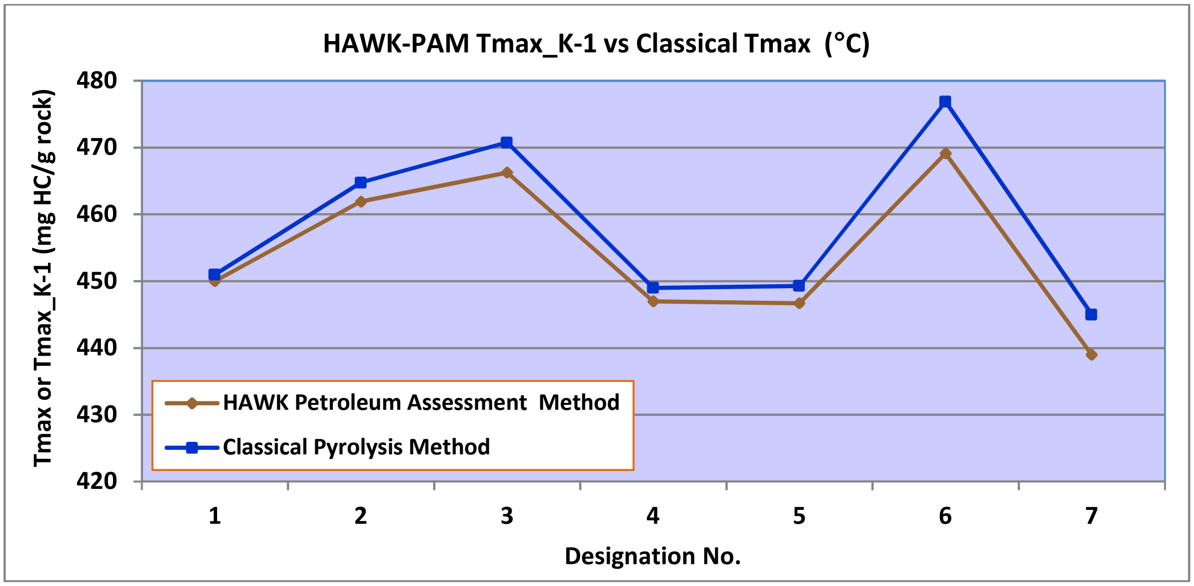
Formation	Barnett	Marcellus	Burkett	Niobrara	Upper Avalon	Eagle Ford	Bazhen
Mobile Oil	2.77	7.97	6.89	3.93	2.84	6.2	2.45
S1	1.74	7.64	5.2	2.94	2.2	5.76	2.37



Formation	Barnett	Marcellus	Burkett	Niobrara	Upper Avalon	Eagle Ford	Bazhen
K-1	3.14	7.45	6.09	4.95	3.23	4.02	1.88
S2	4.18	8.39	6.62	6.44	3.5	4.91	2.99



Formation	Barnett	Marcellus	Burkett	Niobrara	Upper Avalon	Eagle Ford	Bazhen
K-1 Tmax	450	462	466	447	447	469	439
Tmax	451	465	471	449	449	477	445



Comparison of Classical Pyrolysis Method and HAWK Petroleum Assessment Method™ Parameters

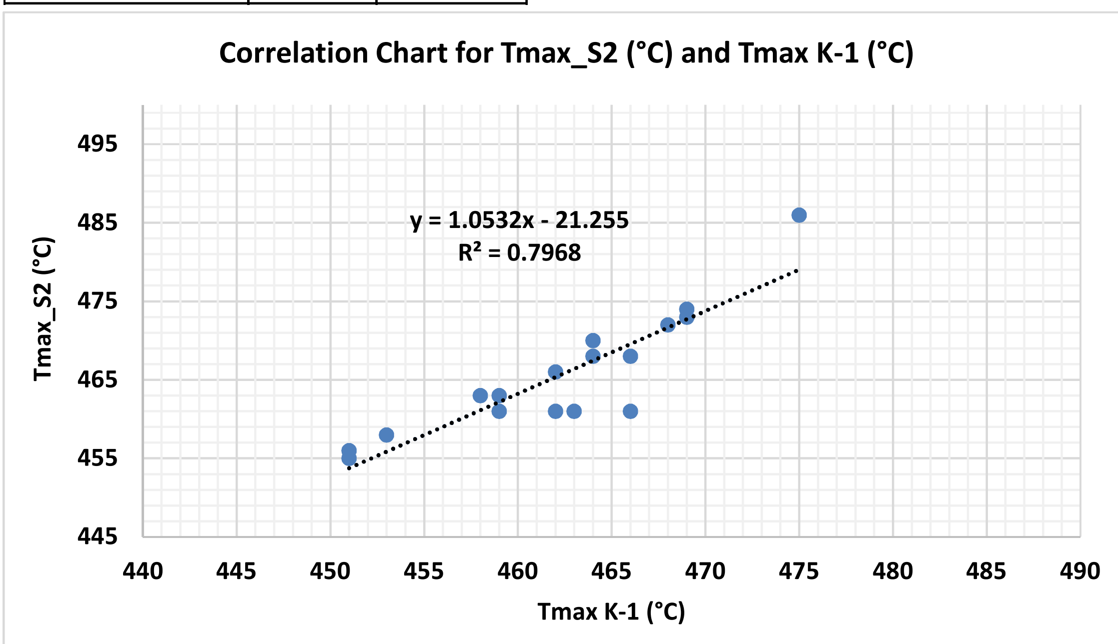
This comparison shows that for all the analyzed samples, the mobile oil computed using the HAWK Petroleum Assessment Method exceeds the S1 value obtained from the Classical Pyrolysis Method.

Whenever the Tmax K-1 turns out to be a number of degrees different from the classical pyrolysis Tmax, the implication is that the rock sample is impregnated with petroleum or is contaminated by oil-based mud additives. It is only through the Petroleum Assessment method that separation of the heavy oil/asphaltene from kerogen is almost completely achieved thereby enabling a more accurate kerogen Tmax.

Correlation of Classical Pyrolysis Method Maturity Parameter (Tmax_S2 (°C)) with HAWK Petroleum Assessment Method™ Tmax K-1 (°C) Parameter

The Classical Pyrolysis Method maturity parameter, Tmax_S2 (°C) correlates closely with the HAWK Petroleum Assessment Method's Tmax K-1 (°C) parameter as is depicted in the table and graph below:

Sampled Formation	Tmax_S2 (°C)	Tmax K-1 (°C)
Marcellus Shale	461	466
Marcellus Shale	466	462
Marcellus Shale	461	463
Marcellus Shale	468	466
Marcellus Shale	461	462
Marcellus Shale	463	458
Marcellus Shale	461	459
Marcellus Shale	463	459
Marcellus Shale	456	451
Marcellus Shale	455	451
Marcellus Shale	458	453
Marcellus Shale	486	475
Marcellus Shale	474	469
Burkett Formation	473	469
Burkett Formation	472	468
Burkett Formation	468	464
Burkett Formation	470	464

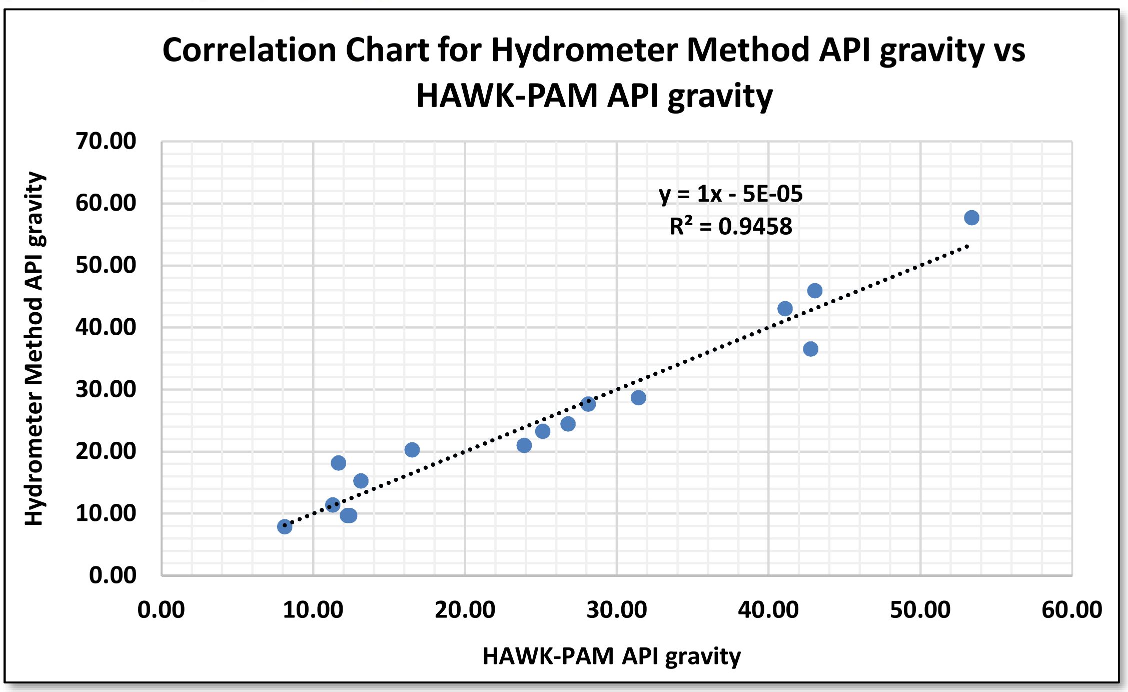


Correlation of Classical Pyrolysis Method Tmax_S2 (°C) and HAWK Petroleum Assessment Method™ Tmax K-1 (°C) Parameters.

Prediction of API gravity

A derivation from the HAWK Petroleum Assessment method parameters is of use in predicting API gravity as can be seen from the table and graph below which were obtained from running the HAWK Petroleum Assessment method on oils.

Hydrometer Method API gravity	HAWK-PAM API gravity
57.70	53.39
9.72	12.26
20.30	16.51
28.70	31.42
43.05	41.09
45.96	43.05
36.57	42.77
23.30	25.12
24.50	26.79
21.00	23.89
27.70	28.12
11.41	11.28
9.72	12.41
7.91	8.12
15.31	13.14
18.16	11.67

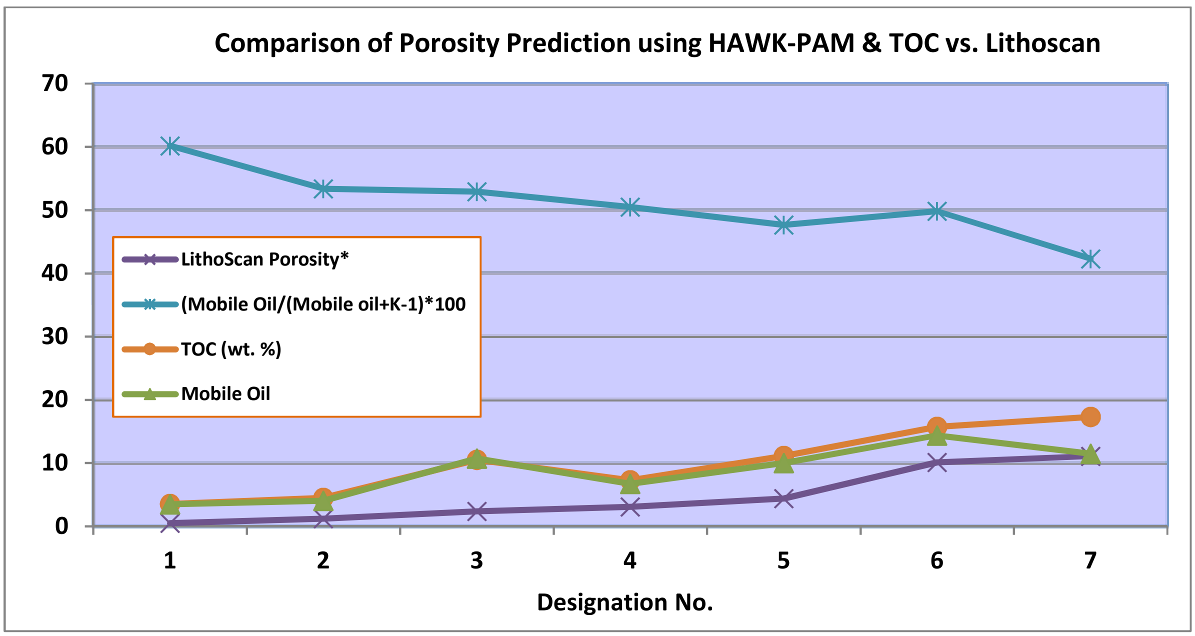


API prediction using HAWK. This can be used on source/reservoir rocks calibrated to oils.

Prediction of Porosity

A comparison of the HAWK Petroleum Assessment Method's mobile oil(oil-1+oil-2+oil-3+oil-4) to (mobile oil + K-1) ratio with measured porosity values as can be seen in the table and graph below show that this ratio is of use for predicting porosity. Evidently the mobile oil(oil-1+oil-2+oil-3+oil-4) to (mobile oil + K-1) ratio has an inverse relationship with porosity in that the lower this ratio is, the higher the porosity. Comparisons of mobile oil (Oil-1 + Oil-2 + Oil-3 + Oil-4) in mg HC/g rock and TOC (wt. %) values are also shown in the graph and table below.

Comparison of Porosity Prediction Marcellus Shale							
Designation No.	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Mobile Oil	3.49	4.04	10.73	6.73	10.04	14.38	11.46
LithoScan Porosity*	0.5	1.20	2.40	3.10	4.40	10.10	11.1
(Mobile Oil/(Mobile oil+K-1)*100	60	53	53	51	48	50	42
TOC (wt. %)	3.55	4.51	10.5	7.27	11.11	15.72	17.32



Note: LithoScan Porosity* is from LithoSCAN®FEI Wellsite®SEM-EDX

Porosity prediction using HAWK.

References

Barker, C., 1974, Pyrolysis techniques for Source-Rock Evaluation, AAPG Bull., v. 58, no. 11, p. 2349-2361.

Espitalie, J., M. Madec, B. Tissot, J.J. Mennig, and P. Leplat, 1977, Source rock characterization method for petroleum exploration, OTC paper #2935, 6p.

Jarvie, Daniel M., Alejandro Morelos, and Zhiwen Han, 2001, Detection of Pay Zones and Pay Quality, Gulf of Mexico: Application of Geochemical Techniques, Gulf Coast Assoc. of Geol. Soc. Transactions, Volume LI, 2001, pp. 151-160.

Jarvie, D. M., 2012, Shale resource systems for oil and gas: Part 2 – Shale-oil resource systems, in J. A. Breyer, ed., Shale reservoirs – Giant resources for the 21st century: AAPG Memoir 97, p. 89 – 119.

Jarvie, D.M., B.M. Jarvie, W.D. Weldon, and A. Maende, 2015, Geochemical assessment of in situ petroleum in unconventional resource systems, URTeC paper 2173379, 20p.

Jarvie, D.M., 2014, Components and processes affecting producibility and commerciality of shale resource systems, Geologica Acta, v. 12, no. 4, ALAGO Special Publication, p. 307-325.

Jones, R., 1984, Comparison of carbonate and shale source rocks, in Petroleum Geochemistry and Source Rock Potential of Carbonate Rocks, AAPG Studies in Geology 18, J. Palacas, ed., pp. 163-180.p. 163-177.

Peters, K. E., 1986, Guidelines for Evaluating Petroleum Source Rock Using Programmed Pyrolysis, AAPG Bull. v. 70, No. 3, p. 318-329.

Peters, K.E. and M.R. Cassa, 1994, Applied source rock geochemistry, in Magoon, L.B. and W.G. Dow, eds., The petroleum system – from source to trap, AAPG Memoir 60, p. 93-120.