Adventures in Programmed Pyrolysis*

Richard Drozd[1], Jarrod Dall[1], and Stephen Palmer[1]

Search and Discovery Article #80659 (2018)**
Posted November 19, 2018

*Adapted from oral presentation given at AAPG 2018 Annual Convention & Exhibition, Salt Lake City, Utah, United States, May 20-23, 2018
 DOI:10.1306/80659Drozd2018

[1]Weatherford Laboratories, Weatherford International, Houston, TX, United States (dick.drozd@weatherfordlabs.com)

Abstract

Programmed pyrolysis has been used to evaluate source rocks for 50 years. The “standard” method was developed and has been used to assess the potential for generation of conventional petroleum accumulations. It has now been applied to unconventional reservoirs. Recently, alternative pyrolysis programs have been suggested to improve identification of moveable and immovable hydrocarbons in unconventional systems. We have investigated two of these alternate methods, one using multiple steps in heating rate (IFP Shale Play Method) and the other a single ramp (Extended Slow Heating, Sanie et al 2015) and compared the results to the standard method. This discussion will focus on a comparison of the standard and multi ramp methods. Twenty core and outcrop samples containing primarily Type II kerogen were analyzed pre and post solvent extraction using both SRA and RE6 instruments. Aliquots of each sample were retained for eventual mineral and elemental analyses.

The programs for the standard method consist of two peaks: S1 volatile hydrocarbons distilled from the sample at 300°C, and the S2 peak theoretically the hydrocarbons derived from the conversion of kerogen between 300°C and 650°C. The multi-ramp method produces three peaks, Sh0 the most volatile compounds distillable at 200°C, Sh1 compounds that distill between 200° and 350°C, and Sh2 theoretically attributed to kerogen breakdown. Total pyrolysis yields for both methods were equivalent. The average difference between Tmax values of the kerogen peak, pre and post extraction is 1.9°C for both methods.

Solvent extraction removes the S1 peak, but also reduces the size of the S2 peak in most samples. The S2 peak pre extraction contained some soluble compounds, which may or may not be moveable within a reservoir. The multi-ramp method is designed to better separate potentially moveable hydrocarbons from those generated by kerogen conversion. Multi-ramp analysis of

extracted samples removed the Sh0 and most of the Sh1 hydrocarbons. However, some samples showed evidence of kerogen conversion at temperatures below ~350°C. This observation indicates that not all the Sh1 signal can be attributed to hydrocarbons that were previously generated by the kerogen and have the potential to be moveable. Some of these are being generated in the laboratory. The reasons some sample show low temperature generation and some do not are twofold: kerogen thermal maturity and organic matter type, as will be presented in detail.

ADVENTURES IN PROGRAMMED PYROLYSIS

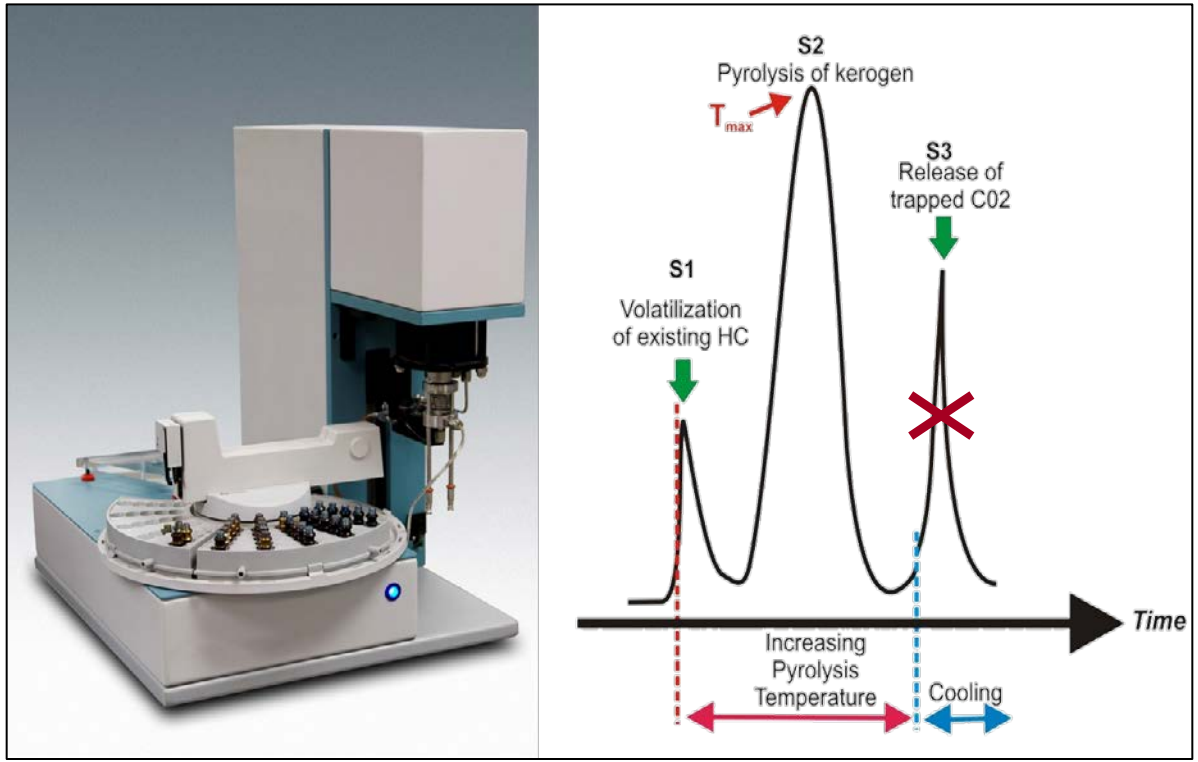
Richard Drozd
Jarrod Dall
Stephen Palmer
Weatherford Laboratories

January 15, 2018

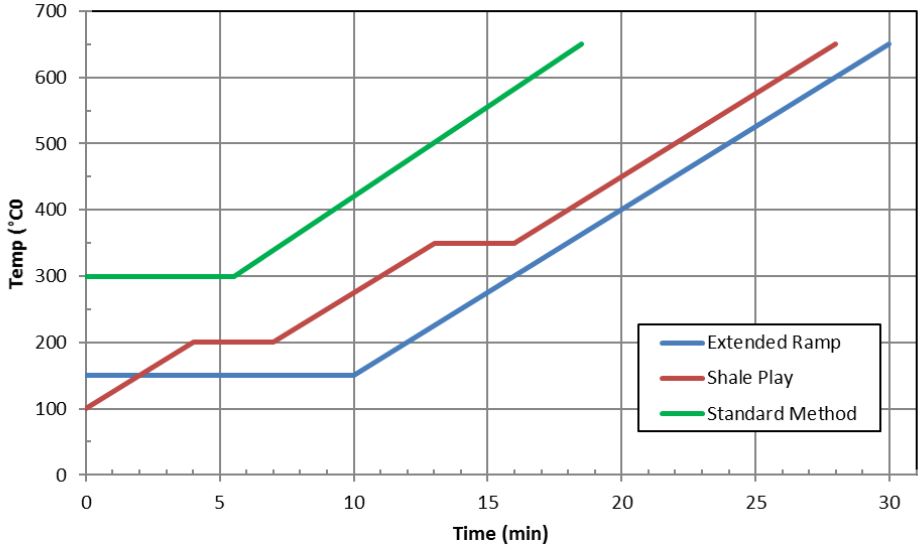
Weatherford®

WHAT IS PROGRAMMED PYROLYSIS?

- A standard technique for evaluation of source rock potential
- Long history in conventional exploration
- Now routinely applied for assessment of unconventional units



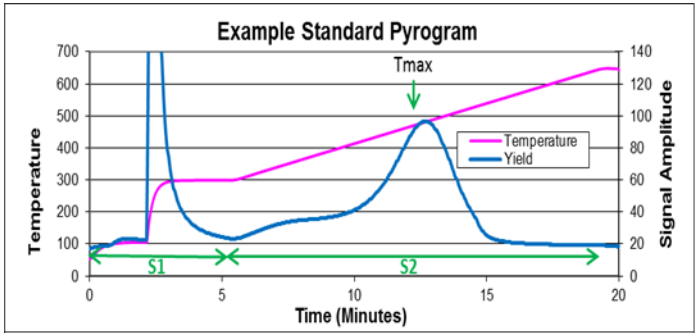
PYROLYSIS EXPERIMENTS

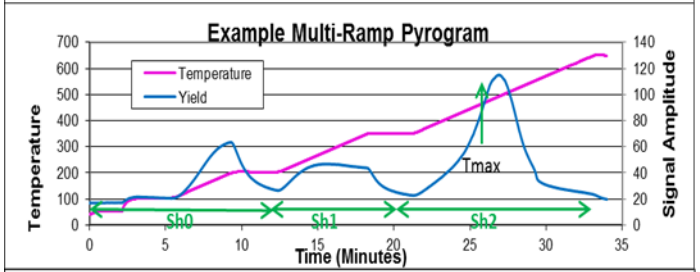


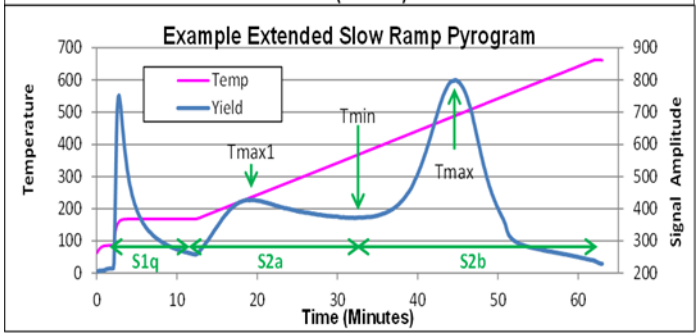
SHALE PLAY METHOD
100°C Initial,
ramp 25°/min to 200°C,
hold 3 min,
ramp 25°/min to 350°C,
hold 3 min,
ramp 25°/min to 650°C

STANDARD METHOD
300°C Initial, hold 5.5 min,
Ramp 25°/min to 650°C

EXTENDED RAMP METHOD
150°C Initial, hold 10 min,
Ramp 25°/min to 650°C



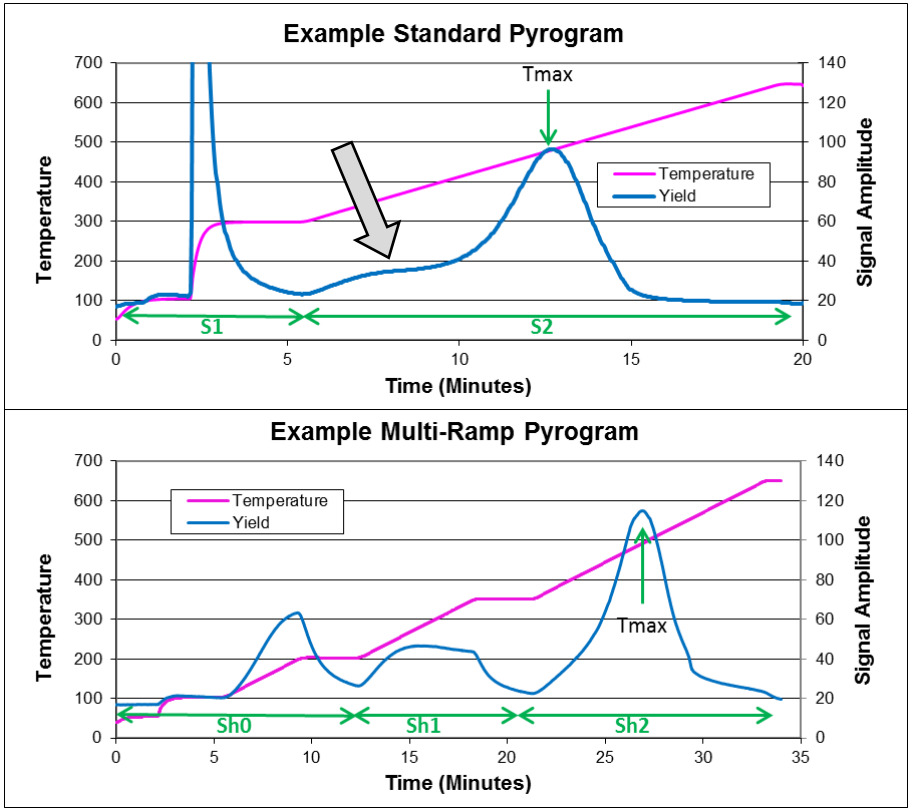




COMPARISON OF MULTI- AND STANDARD- RAMPS

Low temperature shoulder

- May be volatile (moveable) hydrocarbons that are not released at 300°C in the lab
- May be compounds generated from the kerogen at lower temperatures
- May be contamination due to OBM, drilling additives, migrated hydrocarbons
- Analysis of extracted aliquots to remove “shoulder”



NOMENCLATURE AND SAMPLES

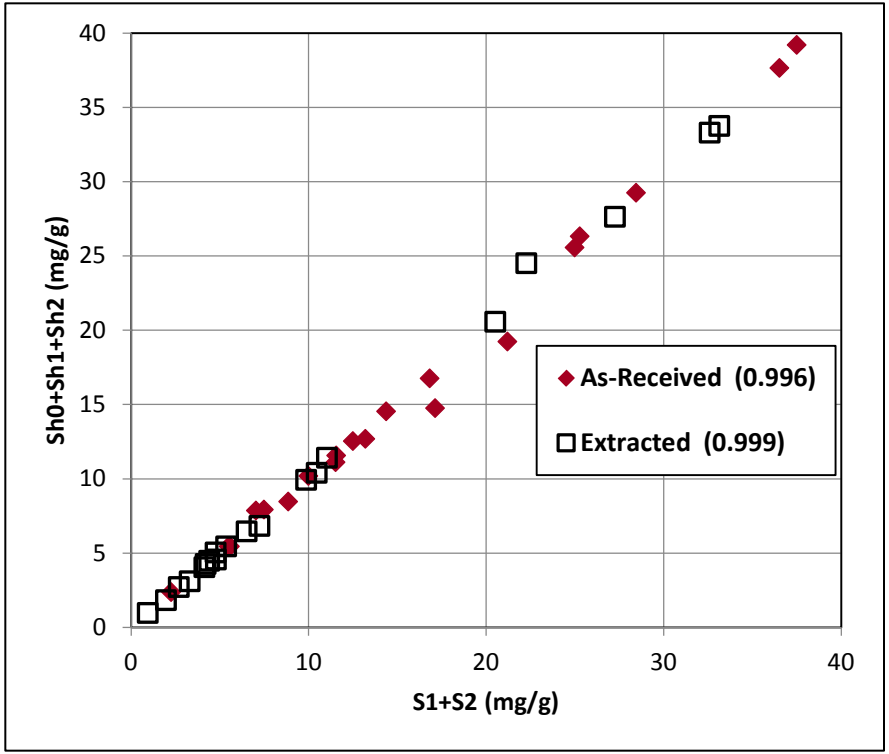
Standard		Shale Multi-Ramp	
S1	Most volatile hydrocarbons	Sh0	Most volatile hydrocarbons
		Sh1	Volatile hydrocarbons, may be producible
S2	Kerogen conversion, may include producible fraction	Sh2	Kerogen conversion
Tmax	Max release S2	Tmax	Max release Sh2

"As-Received" Aliquot (AR)
Solvent Extracted Aliquot (Extr)

1 Miocene
1 Eocene
5 Cretaceous
5 Permian
2 Mississippian
5 Devonian
1 Ordovician

Formation	Well	Depth	County	State	
Black Marker	Mashburn 3H-33X	13041	Stephens	OK	Mississippian
Bone Spring	Collier 1201	8123-25	Pecos	TX	Permian
Bone Spring Lower	Chilton 5601	9416-18	Pecos	TX	Permian
Bone Spring Upper	Chilton 5601	8786-88	Pecos	TX	Permian
Boquillas	Outcrop		Val Verde	TX	Cretaceous
Brushy Canyon	Chilton 5601	6635-36	Pecos	TX	Permian
Caney	Mashburn 3H-33X	14195.2-6.0	Stephens	OK	Mississippian
Eagle Ford	Patteson 3M	7405-08	Gonzales	TX	Cretaceous
Green River Shale	Outcrop Mahogany		Uintah	UT	Eocene
Marcellus	511391 BIG57H1	7098-101	Wetzel	WV	Devonian
Monterey	Outcrop SB-15 to 21	Pismo	Shell Beach	CA	Miocene
Mowry	Hayden Trust 44-9 MH	9648-65	Campbell	WY	Cretaceous
New Albany	Phillips#1	3604-08	Effingham	IL	Devonian
New Albany	Brooks#1	1829-76	Christian	IL	Devonian
Niobrara	Hayden Trust 44-9 MH	8232-46	Campbell	WY	Cretaceous
Point Pleasant	Mitchell #1	6471-92	Guernsey	OH	Ordovician
Storm King Mountain	Outcrop		Garfield	CO	Cretaceous
Wolfcamp	Collier 1201	10653-55	Pecos	TX	Permian
Woodford Core	Mashburn 3H-33X	14777	Stephens	OK	Devonian
Woodford Outcrop	Outcrop		Carter	Ok	Devonian

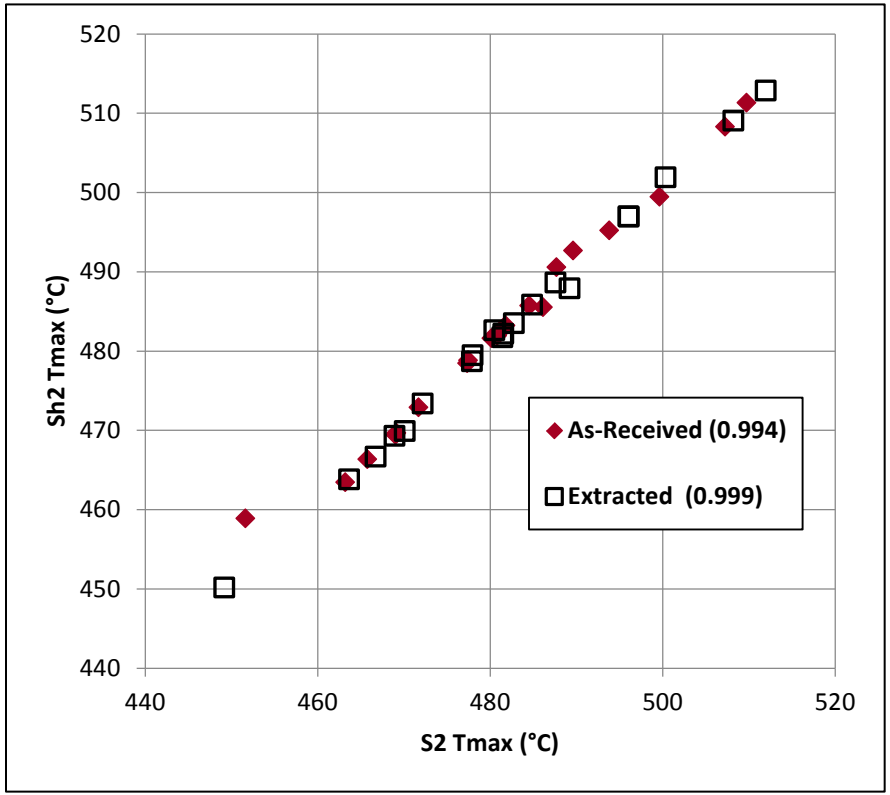
COMPARISON OF PYROLYSIS YIELDS



- Because temperature programs are different, can only compare total pyrolysis yields
- Correlation of yields between methods:
  - As-received 0.996
  - Extracted 0.999

COMPARISON OF PYROLYSIS T_{MAX}

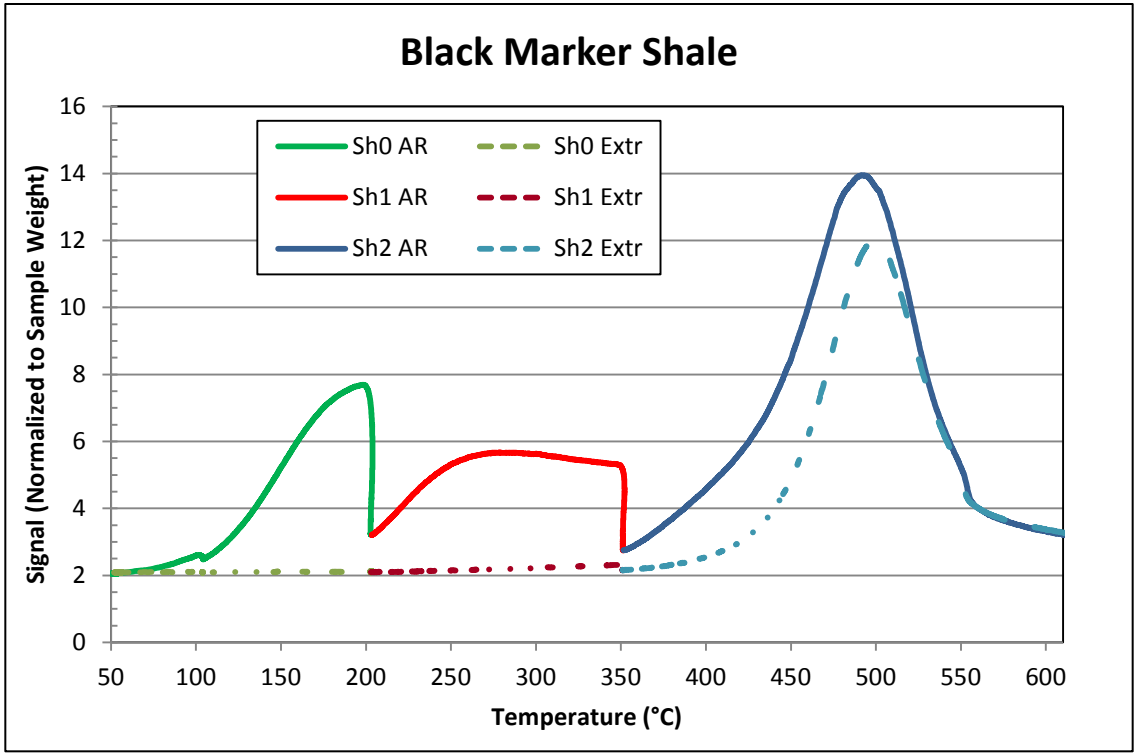
- S2 Tmax and Sh2 Tmax should both reflect kerogen conversion to hydrocarbons
- Correlation of Tmax values between methods:
  - As-received 0.994
  - Extracted 0.999



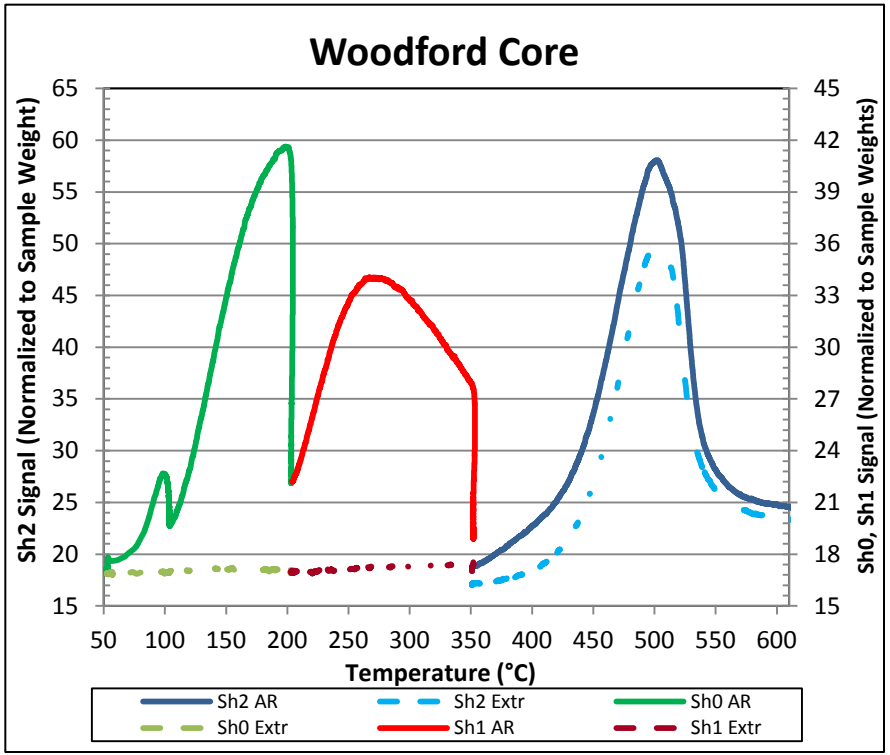
COMPARISON OF AS-RECEIVED & EXTRACTED SAMPLES

- Anticipated pattern
  - Sh0 & Sh1 removed
  - Slight drop in Sh2
  - Shift to higher Tmax on extracted sample

Note that horizontal axis is now *temperature* instead of time. Removes any minor impact of heating rate variations



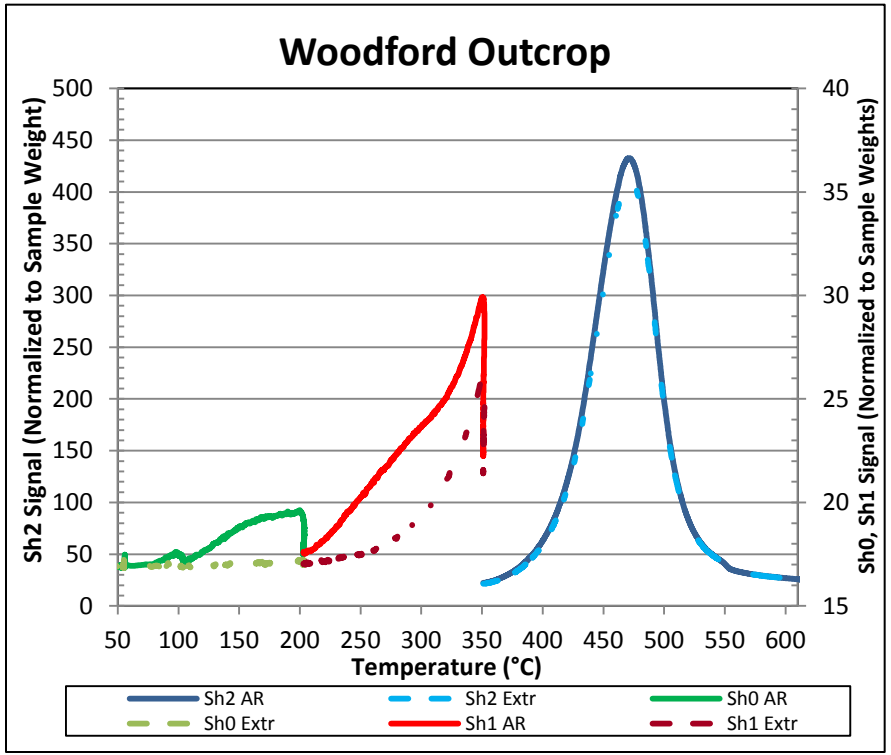
ALL IS NOT WELL, HOWEVER



- Pyrogram from Woodford core sample
- Pre-extraction Sh1 yield drops with increasing temperature – larger at 270°C dropping to 350°C
- Characteristic of volatilization
- After extraction Sh1 << Sh1 as received

ALL IS NOT WELL, HOWEVER

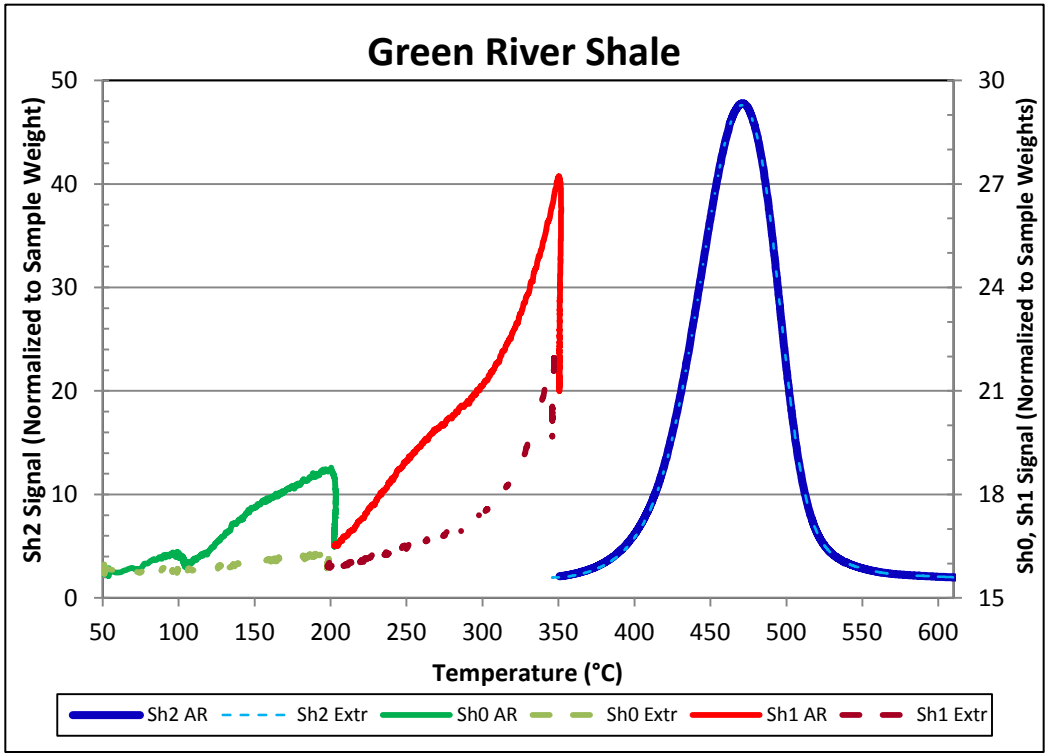
- Pyrogram from Woodford outcrop sample
- Pre-extraction Sh1 yield increases with increasing temperature – smaller at 270°C increasing to 350°C
- Extracted Sh1 < Sh1 as-received
- Character of kerogen cracking



MORE OBVIOUS CASE

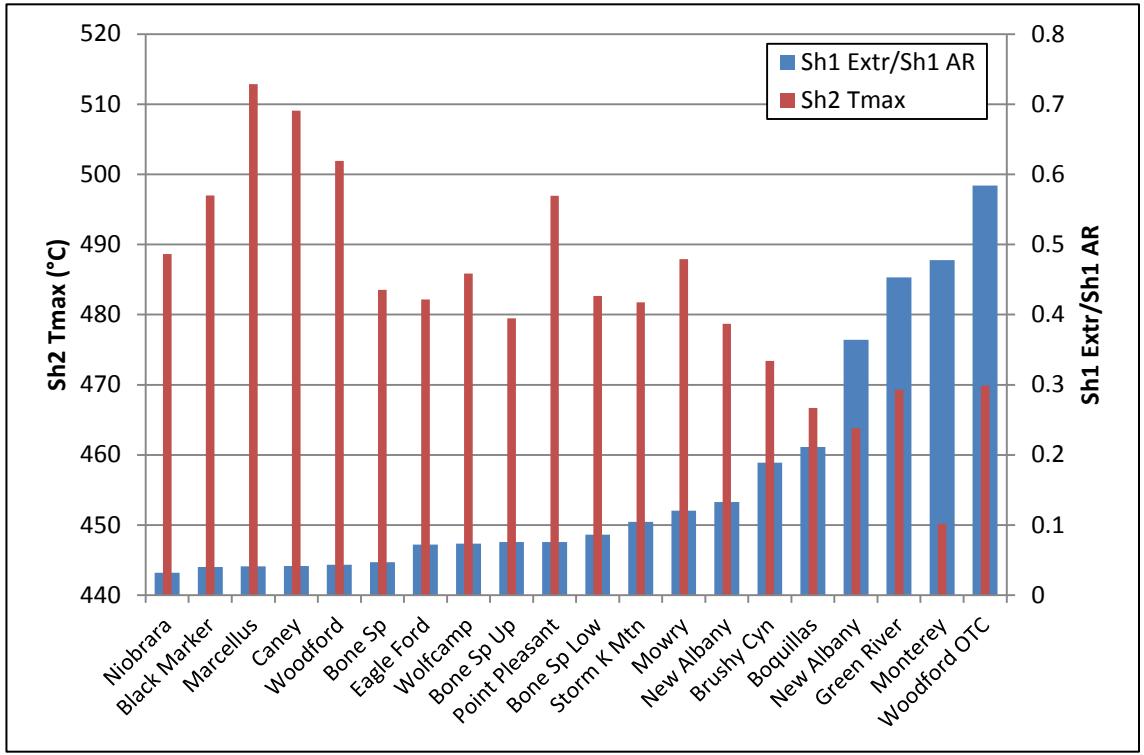
- Sh1 peak shows a definite increase with temperature unlike Woodford core but like Woodford outcrop
- Is this common or unusual?
- Calculate a ratio

  Sh1 Extr/ Sh1 AR



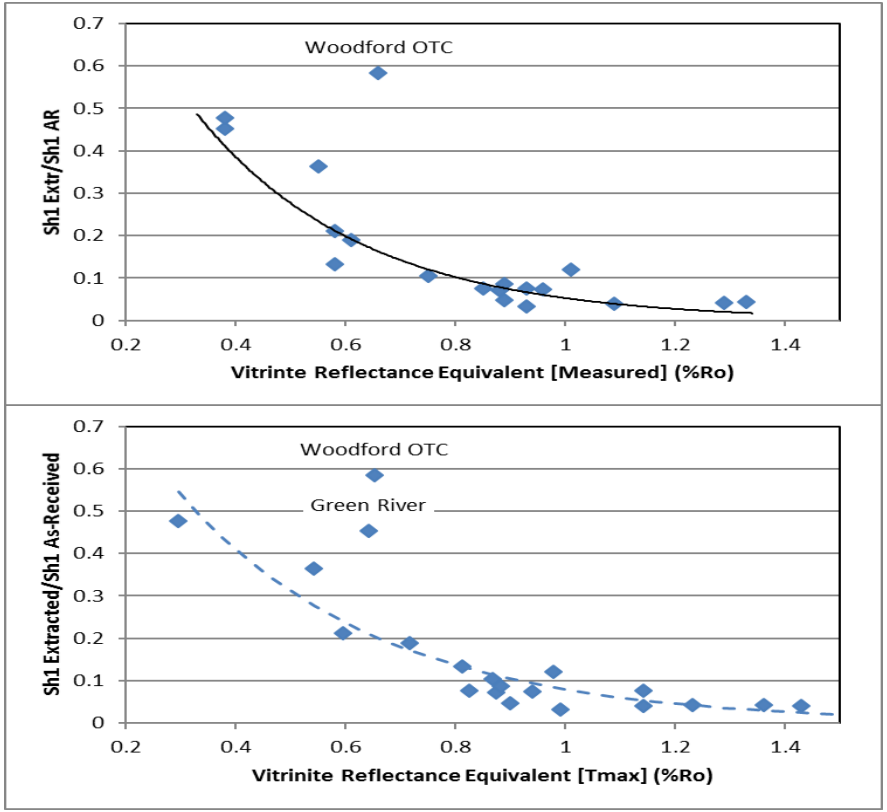
CONDITIONS FOR HIGH RETENTION OF Sh1 AFTER EXTRACTION

- The highest Sh1 Extr/Sh1 AR are confined to Tmax values < 470°C
- Samples with Tmax ≳ 480°C have ratios <0.1
- Extraction removes 90% or more of the Sh1 peak → volatile compound

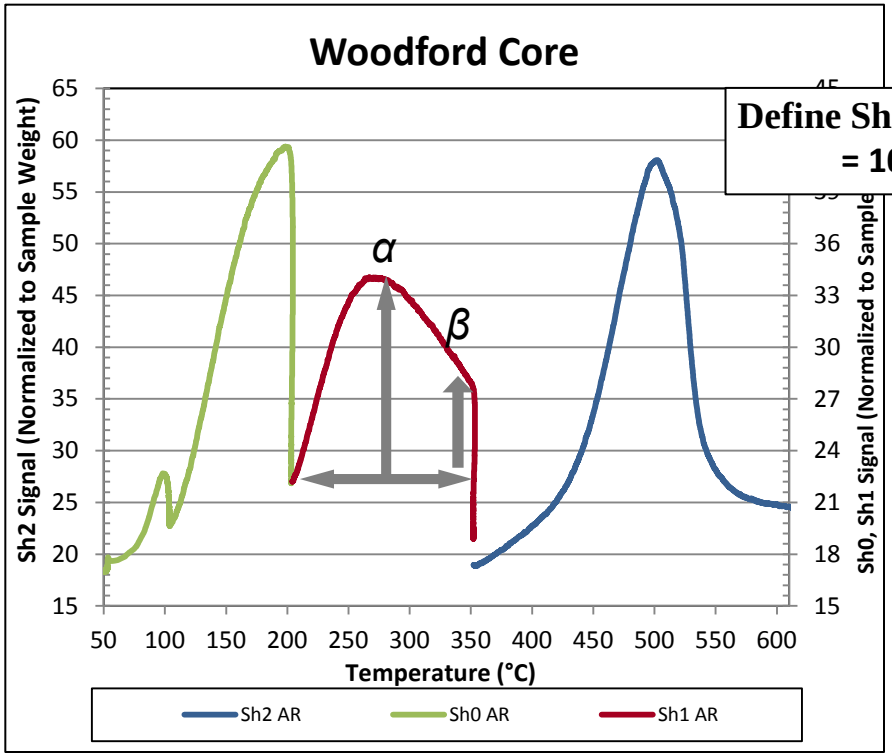


MATURITY & HIGH RETENTION OF Sh1 AFTER EXTRACTION

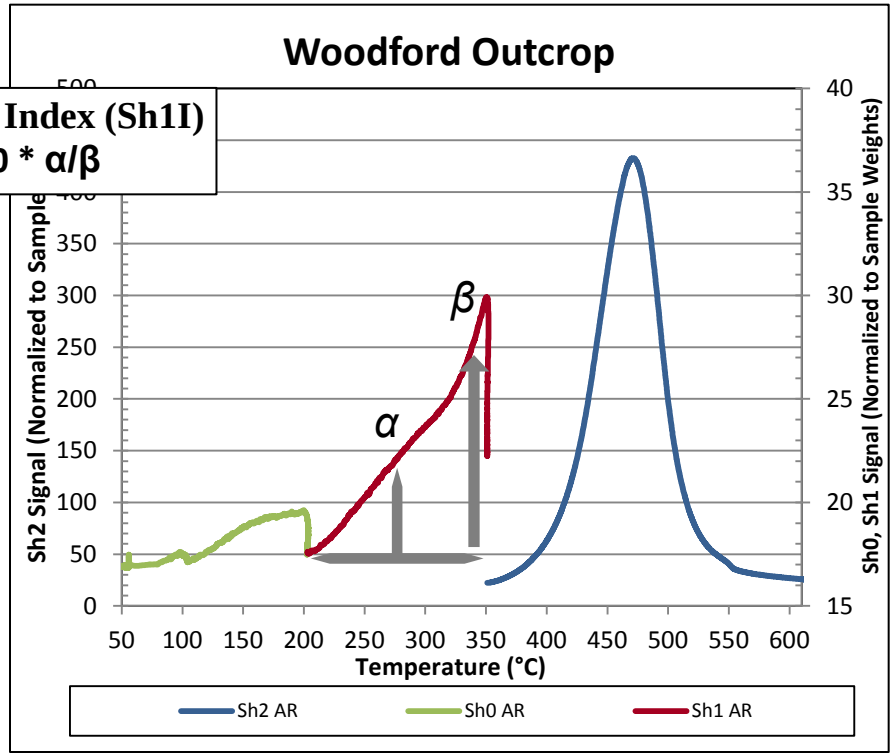
- Two thermal maturity indicators Sh2 Tmax and measured vitrinite reflectance or equivalent (solid bitumen, pyrobitumen, chitinozoa, graptolites)
- Lowest thermal maturity samples have highest retained Sh1 after extraction
- For such samples Sh1 will not correlate to movable hydrocarbons



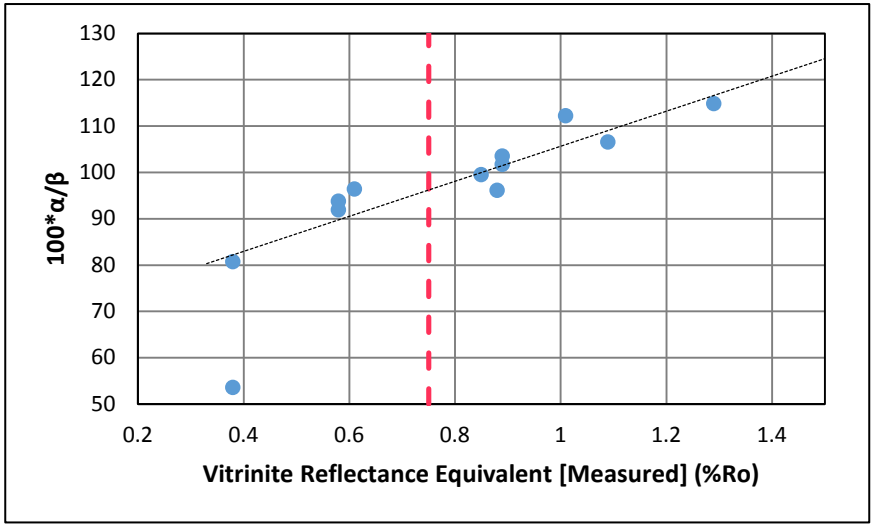
ALTERNATE PARAMETERIZATION



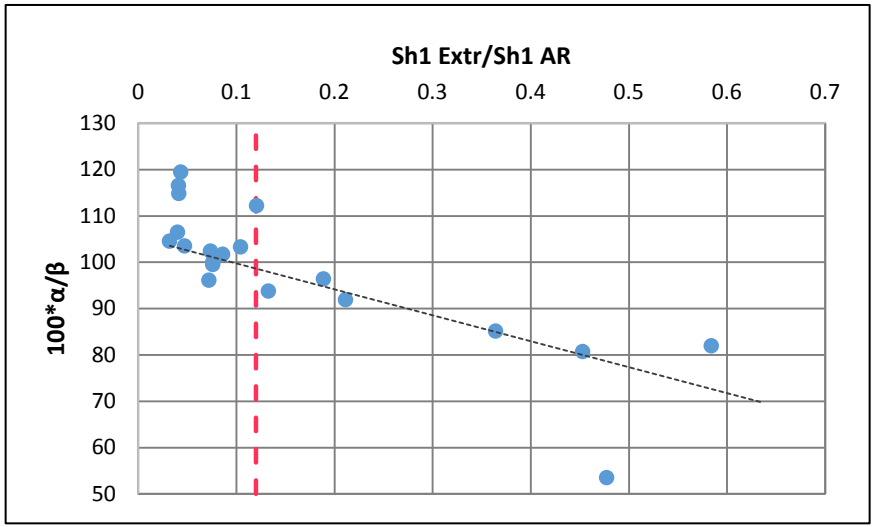
Define Sh1 Index (Sh1I)
= 100 * α/β



LIMITS FOR THE SH1I PARAMETER



Sh1I as a function of vitrinite reflectance equivalent. Samples with Ro ≲ 0.75% need extraction prior to pyrolysis. This diagram suggests that limit corresponds to Sh1I ≲ 100.



Sh1I versus Sh1 Extr/Sh1 AR ratio. Samples with Sh1 Extr ≳ 12% of Sh1 Ar need extraction. On this diagram that corresponds to Sh1I ≲ 95. Therefore, extraction of samples with Sh1I ≲ 100 is recommended.

CONCLUSIONS

- Twenty whole core and outcrop samples were analyzed by the standard and step pyrolysis methods, both as-received and solvent extracted
- Hydrocarbon yields are equivalent for both methods
- Tmax values are equivalent for both methods
- In some samples, the Sh1 peak is completely removed by solvent extraction – supporting assignment as volatile compounds
- In other cases, a residual Sh1 remains after extraction
- The residual fraction is inversely related to thermal maturity – high maturity implies low residual whereas low maturity has high residual.
- A parameter is defined based upon the shape of the Sh1 peak [Sh1 Index] which can be used to identify those samples where solvent extraction is appropriate
- “Blind” application of multi ramp pyrolysis methods without consideration of thermal maturity can lead to over-estimation of the movable hydrocarbon content.

ACKNOWLEDGEMENTS

- Weatherford Laboratories and Weatherford International for support and permission to present this talk.
- Thank my colleagues within Weatherford Laboratories and Oil Tracers for provision of the outcrop samples and constructive comments.
- Industry partners that donated core material to this research project:

BALLARD PETROLEUM HOLDINGS LLC

NEWFIELD

EQT Where energy meets innovation.

sabine oil & gas

FOREST OIL 1916

Plus anonymous donors

THANK YOU!