

Investigating laboratory-generated pyrobitumen precursors for unconventional reservoir characterization: a geochemical & petrographic approach.

A. J. Mort*, Geological Survey of Canada, 3303 33rd St NW, Calgary, AB. T2L 2A7

andy.mort@nrcan.gc.ca

and

H. Sanei, Geological Survey of Canada, 3303 33rd St NW, Calgary, AB. T2L 2A7

Summary

The use of bulk parameters such as the Rock-Eval S2 curve to characterize organic matter in gas shales can lead to the erroneous identification of kerogen (autochthonous; derived from sedimentary organic matter) instead of pyrobitumen (allochthonous, derived from earlier oil charge). Analysis of the pyrobitumen using geochemical and petrological techniques shows that there is wide variation in many of the properties of pyrobitumen as a function of both the precursor oil composition and thermal maturity. It is furthermore believed that many of the properties of pyrobitumens deviate from those of kerogens at similar levels of maturity. This ongoing study aims to characterize some of these properties to provide tools to better identify pyrobitumen and its influence on shale gas reservoir properties.

Introduction

The recent rapid gains in understanding of tight gas plays suggest that organic porosity hosts a volumetrically significant proportion of reservoir hydrocarbons in gas shales, hence the relationship between adsorbed gas and kerogen as a function of organic matter type and particular maturity has attracted a good deal of attention. Pyrobitumen, like kerogen, is an insoluble organic solid found ubiquitously in variable quantities in sediments known to contain organic matter. A key genetic difference between these two organic solids is that while kerogen is sedimentary in origin, pyrobitumen occurs as a by-product of the thermal degradation of petroleum generated from kerogen. In petroleum systems where the generated hydrocarbons have largely remained within the source rock, e.g. the Barnett Shale, the organic matter will be a mixture of kerogen and pyrobitumen. However in other tight gas plays (e.g. Montney, Marcellus; (Laughrey *et al.*, 2010)), petrographic analysis indicates that pyrobitumen is the dominant, sometimes only form of organic solid, therefore the primary reservoir for (adsorbed) gas.

Despite the genetic difference in origin of kerogen and pyrobitumen, there is tendency to classify all shale organic matter as kerogen. This is particularly apparent in the interpretation of Rock-Eval pyrolysis results for the organic geochemical characterization of shale plays. Rock-Eval was originally and historically used for the assessment of hydrocarbon generation potential in source rocks. However, the interpretation of Rock-Eval analysis of tight oil/gas samples should be performed with an awareness

that these sediments contain a mixture of kerogen and its (often highly mature) generation products (oil + gas + pyrobitumen (Ruble *et al.*, 2010)).

The assumption that the Rock-Eval S2 peak only represents kerogen (i.e. remaining hydrocarbon generation potential) is at odds with the increasing acceptance that all tight gas plays have individually unique characteristics. It is likely that the porosity models developed for kerogens at variable levels of thermal maturity may not be appropriate for those of pyrobitumen since the structural evolution of each is dependent on precursors which are genetically distinct.

Method

The aim of this research is to improve current geochemical and petrologic understanding of the compositional and nanostructural differences in pyrobitumens with respect to their role in shale gas and shale oil systems. Although kerogen and pyrobitumen can display similar bulk responses for the basic Rock-Eval parameters (S1, S2, S3, T_{max} , TOC), the Rock-Eval 6 apparatus is nonetheless capable of providing greater detail concerning samples. Although there is virtually no published data on Rock-Eval response of oils, (considered here as the precursors for pyrobitumens) a knowledge of the Rock-Eval response to reservoir oil samples of varying composition will provide a valuable baseline for the interpretation of oil-derived and oil-related samples.

In order to study the porosity and chemical response of pyrobitumen to increasing thermal maturity and precursor oil composition, we have synthesized pyrobitumen in the laboratory using offline isothermal pyrolysis of oils at a range of temperatures.

An initial series of five oils was selected from different petroliferous basins in Canada, reflecting a wide range of source rock ages and oil types. It has been demonstrated that pyrobitumen yield from precursor oils is strongly dependent on oil composition, with NSO-enriched heavy oils producing large amounts of pyrobitumen when subjected to thermal stress by comparison with mid to high gravity oils and condensates (Mort, 2004). The samples selected for this pilot study were thus relatively viscous, heavy crudes in order that sufficient product (pyrobitumen) would be generated for subsequent analysis by both geochemical and petrographic methods.

Table 1 List of oil samples selected for the initial part of this study including summary location/age data

Sample	Depth (m)	Location	Source age
King's Cove A-26	1540-1560	Atlantic Offshore	Jurassic
Quintana Wiegand	2910-2918	Alberta	Devonian
Waterton 12-9-3-30	1859	Alberta	Devonian
Cape Allison C-47	1504-1509	Arctic Offshore	Cretaceous
Sarnia 1-1-RIII	784	Ontario	Silurian

The oils were mixed with pure silica sand acting as a substrate to produce a thick semi-solid material representing the pyrobitumen precursor. These precursor oil-sand samples were analyzed by bulk (Rock-Eval) and molecular geochemical methods to establish a geochemical baseline to which the

pyrolyzates and residues can be compared. The initial results produced by Rock-Eval are intriguing, and are worthy of standalone discussion, given the lack of comparable published data.

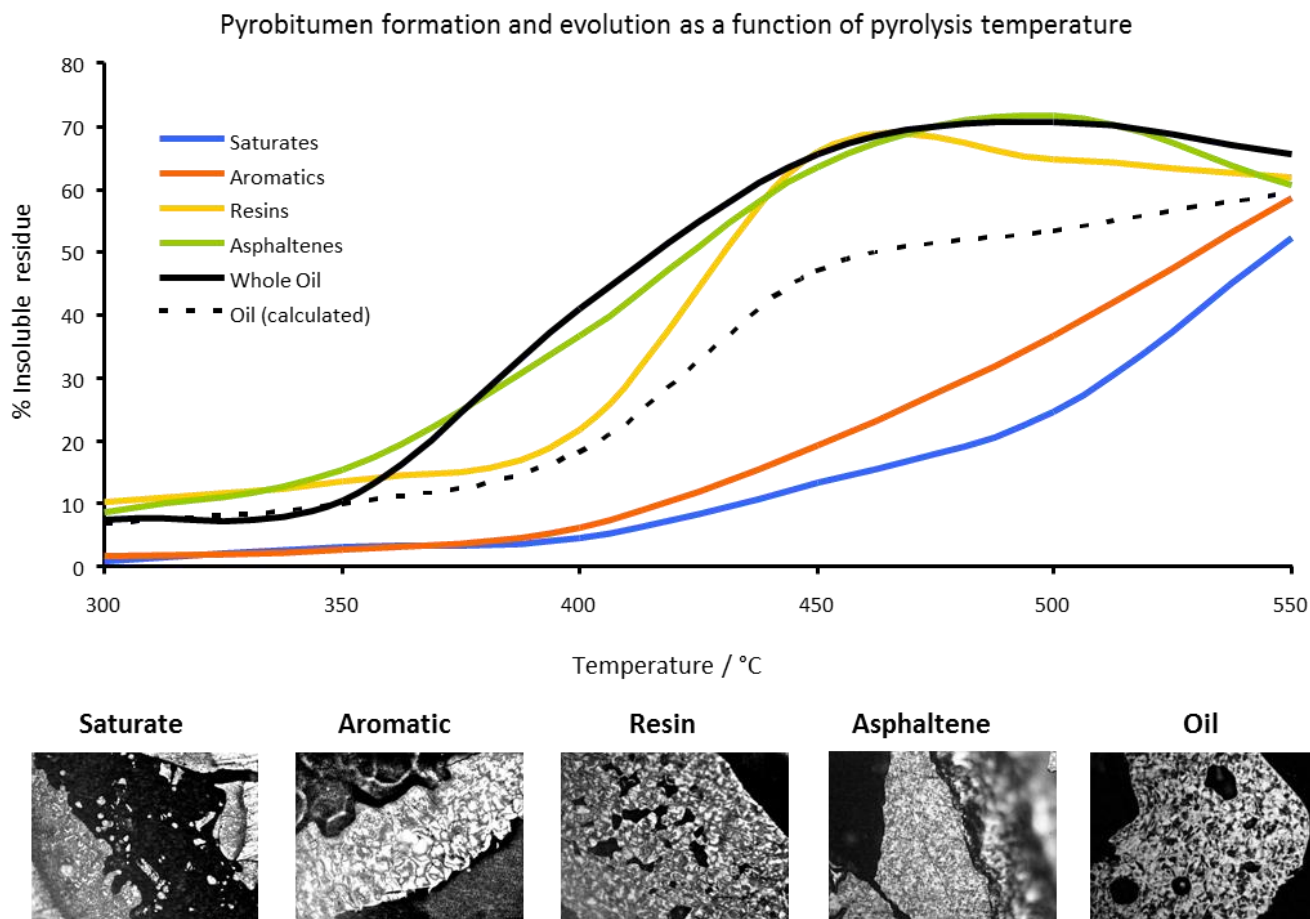
Aliquots of the oil-sand mixtures were pyrolyzed under inert conditions at a range of temperatures from 300-550°C in a specially designed muffle furnace at the University of Manitoba. The pyrolysis products were recovered and are subject to an ongoing multidisciplinary analytical program at the Organic Geochemistry and Petrology laboratory of the GSC in Calgary.

1. DCM extractable organic matter was isolated and analyzed using high resolution molecular geochemical GCMS and GCGC-TOF-MS to both (1) monitor the fate of the parent compounds in the original oil and (2) observe the potential neoformation of metastable intermediates which may play a role in the thermal conversion of the oil and evolution of the solid residue.
2. Insoluble residue (pyrobitumen) was isolated from the extractable fraction and analyzed using high resolution petrographic techniques to monitor the evolution of the nature and distribution of porosity as well as the overall pore volume.

Initial Results

Previously unpublished results (Mort, 2004) indicate that pyrobitumen can be formed from all sub-fractions of an oil. Figure 1 shows the results of earlier isothermal (24h) anhydrous pyrolysis experiments on the SARA sub-fractions of an asphaltic oil. It is apparent that the volume of insoluble residue is strongly dependent on the composition of the precursor oil, with the heavy ends playing a disproportionate role in the formation of insoluble residue at high temperatures

Figure 1 Plot of pyrobitumen formation potential of SARA fractions of an asphaltic oil, including the parent oil (black line). The dotted line represents the theoretical pyrobitumen formation potential of the whole oil, assuming a weighted mean contribution from all sub-fractions. Optical microscopy of the residues obtained at 500°C (see below) suggest significant variation in their petrophysical properties. Micrograph field of view is approximately 25µm



Earlier petrographic analysis (see micrograph images in Figure 1) has shown that the reflectance behaviour and coking propensity of the insoluble residues from different petroleum varies considerably. It is likely that the variation in petrophysical properties of these organic solids is also considerable. The ongoing investigation will attempt to further characterize the residues resulting from pyrolysis of the oils in Table 1, considering properties pertinent to gas shale characterization, such as gas generation potential, brittleness, porosity distribution and pore volume.

Conclusions

Laboratory pyrolysis has been used to synthesize pyrobitumen from a suite of precursor oils. Initial results suggest that the volume of insoluble bitumen formed is strongly dependent on precursor oil composition. Optical properties of the residues from oil fractions are also highly variable. Ongoing research using both geochemical and petrologic techniques is designed to elucidate the properties of pyrobitumen from a tight oil/gas play perspective.

Acknowledgements

The authors would like to thank Jesse Carrie at the University of Manitoba for performing the pyrolysis experiments on the oils. Marina Milovic and Rachel Robinson at the Geological Survey of Canada in Calgary have provided excellent technical assistance in the molecular analysis of the oils and pyrolyzates. Danielle Kondla and Rochelle Bank (both University of Calgary) are thanked for their rigorous work on sample preparation and Rock-Eval deconvolution / interpretation during internships at the Geological Survey of Calgary

References

- Laughrey, C.D., Lemmens, H., Ruble, T.E., Butcher, A.R., Walker, G., Kostelnik, J., Barnes, J., Knowles, W., 2010. Black Shale Diagenesis: Insights from Integrated High-Definition Analyses of Post-Mature Marcellus Formation Rocks, Northeastern Pennsylvania. In: AAPG Hedberg Conference, Austin, TX, p. 6.
- Mort, A.J., Huc, A.Y., Trichet, J., 2004. Mécanismes de formation et évolution des pyrobitumes dans les réservoirs pétroliers : cas naturels et approches expérimentales. Institut des Sciences de la Terre.
- Ruble, T.E., Lemmens, C.D.L.H., Walker, G., Knowles, W.R., 2010. Assessing the importance of pyrobitumen in unconventional reservoirs. In: TSOP Annual Meeting. TSOP, Denver, CO, p. 1.