

URTeC Control ID Number: 2670700

Determining Quantity and Quality of Retained Oil in Mature Marly Chalk and Marlstone of the Cretaceous Niobrara Formation by Low-Temperature Hydrous Pyrolysis

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This paper was prepared for presentation at the Unconventional Resources Technology Conference held in Austin, Texas, USA, 24-26 July 2017.

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SUMMARY

Low-temperature hydrous pyrolysis (LTHP) at 300°C (572°F) for 24 h released retained oils from 12- to 20-mesh-size samples of mature Niobrara marly chalk and marlstone cores. The released oil accumulated on the water surface of the reactor, and is compositionally similar to oil produced from the same well. The quantities of oil released from the marly chalk and marlstone by LTHP are respectively 3.4 and 1.6 times greater than those determined by tight rock analyses (TRA) on aliquots of the same samples. Gas chromatograms indicated this difference is a result of TRA oils losing more volatiles and volatilizing less heavy hydrocarbons during collection than LTHP oils. Characterization of the rocks before and after LTHP by programmable open-system pyrolysis (HAWK) indicate that under LTHP conditions no significant oil is generated and only preexisting retained oil is released. Although LTHP appears to provide better predictions of quantity and quality of retained oil in a mature source rock, it is not expected to replace the more time and sample-size efficacy of TRA. However, LTHP can be applied to composited samples from key intervals or lithologies originally recognized by TRA. Additional studies on duration, temperature, and sample size used in LTHP may further optimize its utility.

INTRODUCTION

The quantity and quality of oil retained in mature source rocks are important attributes in determining the potential of tight-oil accumulations. Retort methods using crushed rock such as “Tight Rock Analysis” (TRA) have been used to determine oil quantities (Handwerger et al. 2011 and 2012). Released-TRA oil quantities are determined by volatilization of the retained oil in open-system pyrolysis at 316°C (600°F). Although this retort approach provides a rapid method for evaluating retained oil in numerous core samples in a timely manner, volatilization is not operative in the subsurface extraction of oil from tight-oil accumulations. As a result, TRA may not provide an accurate account of the quantity or quality of retained oil. Low-temperature hydrous pyrolysis (LTHP) provides an alternative to acquiring quantities and quality of retained oil in mature source rocks. LTHP, like TRA uses mature source rocks that are crushed between 12 and 20 mesh size. However, LTHP heats the rock in the presence of liquid water in a closed system at 300°C (572°F) for 24 hours. This condition is below the thermal-stress level typically required to generate oil from the thermal decomposition of bitumen and kerogen, but sufficient to release retained oil in a mature source rock. Under this condition, thermal expansion of pore fluids and reduced capillary forces releases retained oil, which accumulates on the water surface in the reactor during heating. The chalk and marlstone sequence of the Cretaceous Niobrara Formation in the Denver Basin provides an excellent test of this approach with both lithologies being a source and reservoir of retained oil to different degrees.

METHODS

Samples of marly chalk and marlstone were taken from 7-inch intervals of a core in the “B” horizon of the Smoky Hill Member of the Niobrara in the producing Horsetail #19N-1924M well between depths of 5500 and 5784 feet in Weld County, Colorado. The cores were initially wrapped in Saran wrap after collection and stored in a refrigerator upon being received at the U.S. Geological Survey. Cold samples were crushed and sieved from 12- to 20-mesh size, and within 1.5 hours after crushing, 507 grams of sample were loaded into one-liter Hastelloy-C276 reactor

(SS-316 gaskets) with ~490 grams of distilled water. The head space was evacuated for several minutes and then charged with ~1000 psia of helium to check for leaks with a gas leak detector. The head-space helium pressure was then reduced to 25 psia and the reactor weighed to a tenth of a gram. The reactor was heated up to 300°C (572°F) in less than one hour and held at that temperature ($\pm 0.5^\circ\text{C}$) for 24 h. Final gauge pressure at temperature was ~1,300 psig. After heating, the reactor was allowed to cool to room temperature within the following 18 hours. The reactor was weighed to a tenth of a gram to verify no leaks had occurred during the heating. The reactor was connected to an evacuated known-volume manifold for collecting duplicate gas samples and collection pressure and temperature were recorded. Collected gases were analyzed with a Wason ECE gas analyzer as described by Lewan and Kotarba (2014). Gas analyses showed no argon, oxygen, alkenes, hexanes, or benzene at or greater than 1 mg. Accuracy of the analyses are checked by comparing moles of initial He loaded into the reactor head space with the moles of He analyzed in the collected gas. The difference is less than 4% on a mole basis for these experiments. Specifics on the LTHP experimental conditions are given in **Table 1**.

| HP Lab Number | HP-3836 | HP-3837 |
|-----------------------------------|-----------------|---------------|
| Sample | "B" Marly Chalk | "B" Marlstone |
| 12/20 Crushed Rock (g) | 507.2 | 507.1 |
| Distilled Water (g) | 494.0 | 484.3 |
| Helium (psia) | 25.4 | 25.3 |
| Helium (mmol) | 24.2 | 20.9 |
| Warm-up Time (h) | 0.79 | 0.76 |
| Time at 300°C (h) | 24.17 | 24.12 |
| Mean Temperature (°C) | 300.1 | 300.3 |
| Std. Dev. Temperature (\pm °C) | 0.5 | 0.4 |
| Final Pressure at Temp. (psig) | 1310 | 1280 |
| Recovered Rock (g) | 500.2 | 498.2 |
| Recovered Water (g) | 484.5 | 473.1 |
| Pressure at Room Temp. (psig/°C) | 32.9 | 55.3 |
| Recovered Analyzed Helium (mmol) | 24.4 | 21.6 |

After the remaining head-space gas in the reactor was slowly vented, the reactor was opened and the height of the head space above the floating oil was measured for calculating head-space volume. A Pasteur pipette was used to quantitatively collect the released oil floating on the water surface and is referred to as released free oil. A benzene rinse was then used to recover released oil film that adheres to the reactor walls and collection pipette. The benzene solvent was evaporated in a fume hood and the quantity of the released rinsed oil was mathematically added to the quantity of released free oil for a total quantity of released oil. The released oil collected by the pipette was characterized by gas chromatography using a flame-ionization detector. Produced crude oil from the same well was also characterized by gas chromatography for comparison with the LTHP-released oils.

Aliquots of the same 12 to 20 mesh-size sample were submitted to TerraTek-Schlumberger Reservoir Laboratory for tight-rock analyses (TRA). This retort method is described in detail by Handwerker et al. (2011 and 2012). Briefly, as-received (AR) bulk density, porosity, and grain density were first determined before fluid saturations were determined at a series of temperatures in a retort vessel using 27 g of 12- to 20-mesh-size sample. The collection of interstitial water was defined by the volatilized water at 132°C (270°F) and held at this temperature until released water ceased. The retort vessel was then heated to and held at 316°C (600°F) until all of the released capillary water, clay-bound water, and retained oil ceased. At this temperature and atmospheric pressure, these fluids are volatilized, condensed, and collected in a glass collection tube. The water and oil separate as immiscible phases in the collection tube and were quantified on a volume basis. This TRA-released oil (T2 cumulative) was compared with the LTHP-released oil and the produced crude oil from the same well. The final TRA temperature was 704°C (1300°F), which volatilizes structured water from clay minerals and generates hydrocarbon products from the cracking of kerogen and bitumen, which was not the subject of this study. The small amounts of collected TRA oil were characterized by gas chromatography in the same way as described for the LTHP-released oils.

LECO total carbon (TC) and total organic carbon (TOC), and HAWK-pyrolysis parameters (i.e., S_1 , S_2 , S_3 , and T_{max}) were determined on the original rocks and recovered LTHP rocks. The marly chalk and marlstone had total carbon contents of 13.65 and 8.48 wt%, respectively, and total organic carbon contents of 2.38 and 3.06 wt%, respectively. These contents equate to calculated carbonate ($\text{CO}_3^{=}$) contents of 56.4 and 27.1 wt % for the marly chalk and marlstone, respectively. The HAWK conditions are similar to other open-system programmable-pyrolysis

instruments (e.g., Source Rock Analyzer and Rock Eval) with initial heating to 300°C and held for 3 minutes, followed by heating at 25°C/min to 650°C and held for 22 minutes.

RESULTS

Released Oil

Table 2 gives the LTHP-released oil and gas yields for the two lithologies in units of grams collected and mg/g of original rock. Comparing these LTHP yields with the retained oil from TRA requires conversion of mass to volume. LTHP-released oil from the marly chalk was sufficient to determine a reliable density of 0.859 g/cm³ (API gravity of 33.2) that was used to calculate volumes of released oil from both lithologies. Marly chalk and marlstone volumes used in the LTHP were calculated using the TRA as received (AR) bulk rock densities of 2.384 and 2.494 g/cm³, respectively (**Table 3**). Both lithologies release oil, but the marly chalk releases 1.3 and 2.9 times more oil than the marlstone based on TRA and LTHP, respectively. These differences in quantities of TRA and LTHP are significant (**Tables 2 and 3**). Based on volume % of the marly chalk and marlstone, LTHP-released oils are 2.11 and 0.73, respectively, and TRA-released oils are 0.62 and 0.46, respectively.

Table 2: Low-temperature hydrous pyrolysis (LTHP) yields.

| HP Lab Number | HP-3836 | HP-3837 |
|---------------------------------|-----------------|---------------|
| Sample | "B" Marly Chalk | "B" Marlstone |
| Released Oil | | |
| Released Free Oil (g) | 2.146 | 0.726 |
| Released Rinse Oil (g) | 1.712 | 0.551 |
| Total Released Oil (g) | 3.858 | 1.277 |
| Total Released Oil (mg/g rock) | 7.61 | 2.52 |
| Total Released Oil (vol% rock)* | 2.11 | 0.73 |
| Released Gas | | |
| Methane (g) | 0.002 | 0.000 |
| Ethane (g) | 0.000 | 0.000 |
| Propane (g) | 0.000 | 0.003 |
| Butanes (g) | 0.001 | 0.013 |
| Pentanes (g) | 0.000 | 0.011 |
| Hydrogen (g) | 0.003 | 0.002 |
| Carbon Dioxide (g) | 0.312 | 1.163 |
| Hydrogen Sulfide (g) | 0.006 | 0.012 |
| Nitrogen (g) | 0.009 | 0.005 |
| Total Released Gas (g) | 0.333 | 1.209 |
| Total Released Gas (mg/g rock) | 0.66 | 2.38 |

* based on oil density of 0.859 g/cm³ (API gravity = 33.2) and bulk rock density of 2.384 g/cm³ for marly chalk and 2.494 g/cm³ for marlstone.

Table 3. Tight Rock Analyses (TRA) results.

| Sample | "B" Chalk | "B" Marl |
|--|-----------|----------|
| TRA Raw Data | | |
| Bulk Density (g/cm ³) | 2.384 | 2.494 |
| Retort AR Sample Weight (g) | 27.004 | 27.018 |
| Bulk Volume of Sample (cm ³) | 11.328 | 10.831 |
| Gas Saturated Pore Volume (cm ³) | 0.87 | 0.28 |
| Pore Water Volume (T1, cm ³) | 0.00 | 0.02 |
| Pore Oil Volume (T2 cumulative, cm ³)* | 0.07 | 0.05 |
| Total Fluid Volume (cc) | 0.94 | 0.35 |
| Volume % of Rock | | |
| Gas | 7.65 | 2.60 |
| Water | 0.00 | 0.18 |
| Oil | 0.62 | 0.46 |
| Total Fluids | 8.27 | 3.25 |

* based on a density of 0.815 (API Gravity = 42)

Gas chromatographs of the LTHP-released oils and the produced crude oil are shown in **Figure 1**. With the exception of differences in the amount of light alkanes (n -C₁₄) in the LTHP-released oils, the distribution on n -alkanes and isoprenoids are similar. Released oil from the marly chalk has the most light hydrocarbon loss with the alkane distribution decreasing at n -C₁₅ (**Figure 1A**). Released oil from the marlstone maintains an increasing light hydrocarbon distribution to n -C₁₁ (**Figure 1B**). The produced crude oil has no significant volatile loss of light hydrocarbons with an increasing alkane distribution to n -C₇ (**Figure 1C**). The differences in light hydrocarbons in the LTHP-released oils are assumed to be a result of evaporative losses prior to core refrigeration, during crushing to 12- to 20-mesh size, or while collecting the oil from the reactor. The greater loss of light n -alkanes in the released oil from the marly chalk may be a result of greater atmospheric exposure during an earlier prolonged examination of the unwrapped core. All of the gas chromatographs show heavier n -alkanes (n -C₁₅₊) extending beyond n -C₃₅. The various calculated oil properties displayed with the gas chromatographs in **Figure 1** are similar between the LTHP oils and the produced crude oil.

Gas chromatographs of the TRA-released oils and the produced crude oil are shown in **Figure 2**. Unlike the produced and LTHP oils, the TRA oils show a more limited distribution of n -alkanes that ranges from n -C₉ to n -C₂₈ with steep declines at carbon numbers greater and less than n -C₁₅. This distribution is characteristic of the kerosene and diesel distillation fractions (C₁₂-C₂₅) of crude oil. This distribution is expected for an oil product derived from the condensation of volatile hydrocarbons released during the T2 stage of TRA. Light volatile hydrocarbons (C₁₅-) are not condensed and lost with the exhaust gases from the retort. Conversely, heavy hydrocarbons (C₁₅₊) are less likely to be volatilized at 316°C (600°F) with increasing carbon number. As a result, the TRA-released oil only represents a distillation product of the retained oil. The various properties posted with the gas chromatographs in **Figure 2** have similar alkane ratios, but the TRA-released oils are translucent and not opaque like the produced crude oil and LTHP-released oil (**Figure 1**). As expected, their API gravities are also higher than the produced crude oil and LTHP-released oil.

Released gas

Composition of the LTHP-gas released is given in **Table 2**. Carbon dioxide is the dominant gas, which we suggest is the result of dissolution of some of the carbonate minerals or thermal decomposition of weakly bound carboxyl groups in the organic matter during LTHP. Similarly, the small amounts of hydrogen sulfide may be a product of thermal decomposition of weakly bound organic sulfide linkages in the organic matter. The hydrocarbon contents are low with only 0.003 g and 0.027 g released from the marly chalk and marlstone, respectively. Interestingly, the higher hydrocarbon content released from the marlstone consists predominantly of butanes and pentanes with no detectable methane or ethane. This scarcity of hydrocarbon gases suggests that the LTHP condition of 300°C (572°F) for 24 h is not sufficient to generate thermogenic gas, and these gases may be residual gases that were not displaced by air upon bringing the core to the surface or during exposure to the atmosphere in preparing the crushed sample. The atmospheric air is best represented by the nitrogen content with accompanying oxygen and argon being below detection limits. The source of the low hydrogen contents remains uncertain.

Recovered rock

LECO carbon and HAWK pyrolysis parameters of the original samples and the samples recovered after LTHP are given in **Table 4**. The percent change in TC, TOC, S₂, and HI are minimal (< 15%), which suggests the petroleum generative potential of the organic matter is not significantly affected by LTHP. Conversely, the HAWK pyrolysis parameters involving pre-existing petroleum in the rock (i.e., S₁, PI, and S₁/TOCx100) is significantly reduced by LTHP by 49 to 68 %.

DISCUSSION

The oil released by LTHP is considered to be oil retained in the Niobrara “B” marly chalk and marlstone. The LTHP oil is thought to be released by reducing capillary forces and increasing thermal expansion of the retained non-compressible oil and water at 300°C (572°F). As a result, oil displacement by water and pore structures are enhanced as observed in hot-water injection experiments on tight reservoirs (Yongmao et al., 2016). It remains to be determined whether the amount of oil released by LTHP is fully representative of production from tight-shale accumulations. However, its ability to release an oil that is similar to produced crude oil is encouraging. The importance of liquid water being present in LTHP is that retained hydrocarbon-rich oil (i.e., saturates and aromatics) is immiscible with polar-rich bitumen (i.e., resins and asphaltenes) within the source rock (Lewan, 1997). This immiscibility is a result of dissolved water in the bitumen. As a result, phase separation differentiates between

released hydrocarbon-rich oil and retained polar-rich bitumen. This differentiation between oil and bitumen cannot be made solely by organic solvent extractions (e.g., Dean Stark methods).

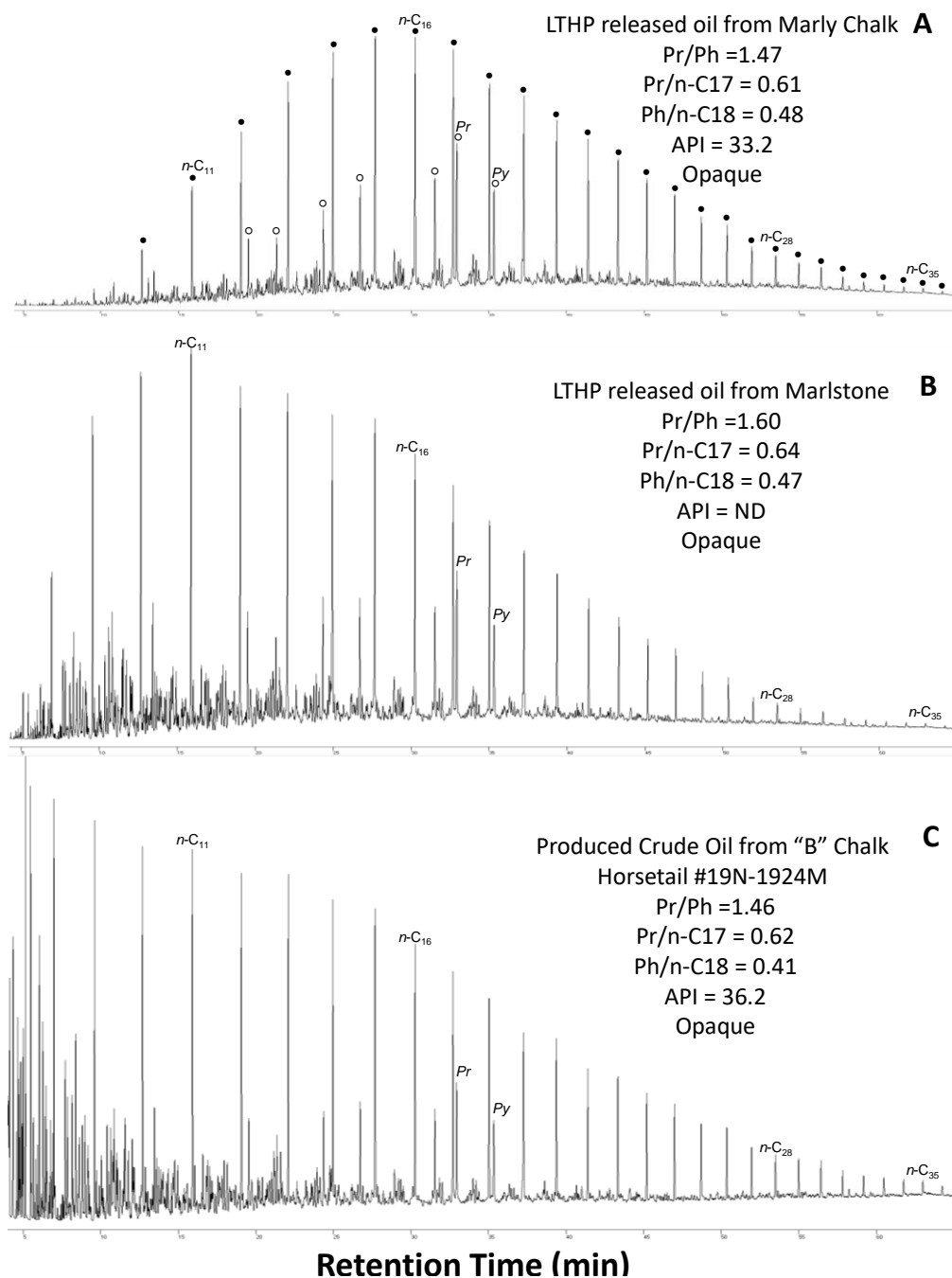


Figure 1. Gas chromatograms of **A)** LTHP-oil released from the "B" Marly Chalk, **B)** LTHP oil released oil from the "B" marlstone, and **C)** produced crude oil from the Horsetail #19N-1924M. Solid dots denote *n*-alkane peaks with specific *n*-alkanes labeled with carbon numbers 11, 16, 28, and 35. Open dots denote isoprenoid peaks with specific isoprenoids labeled as *Pr* for pristane and *Ph* for phytane. All gas chromatograms are normalized to *n*-C₁₇ peak.

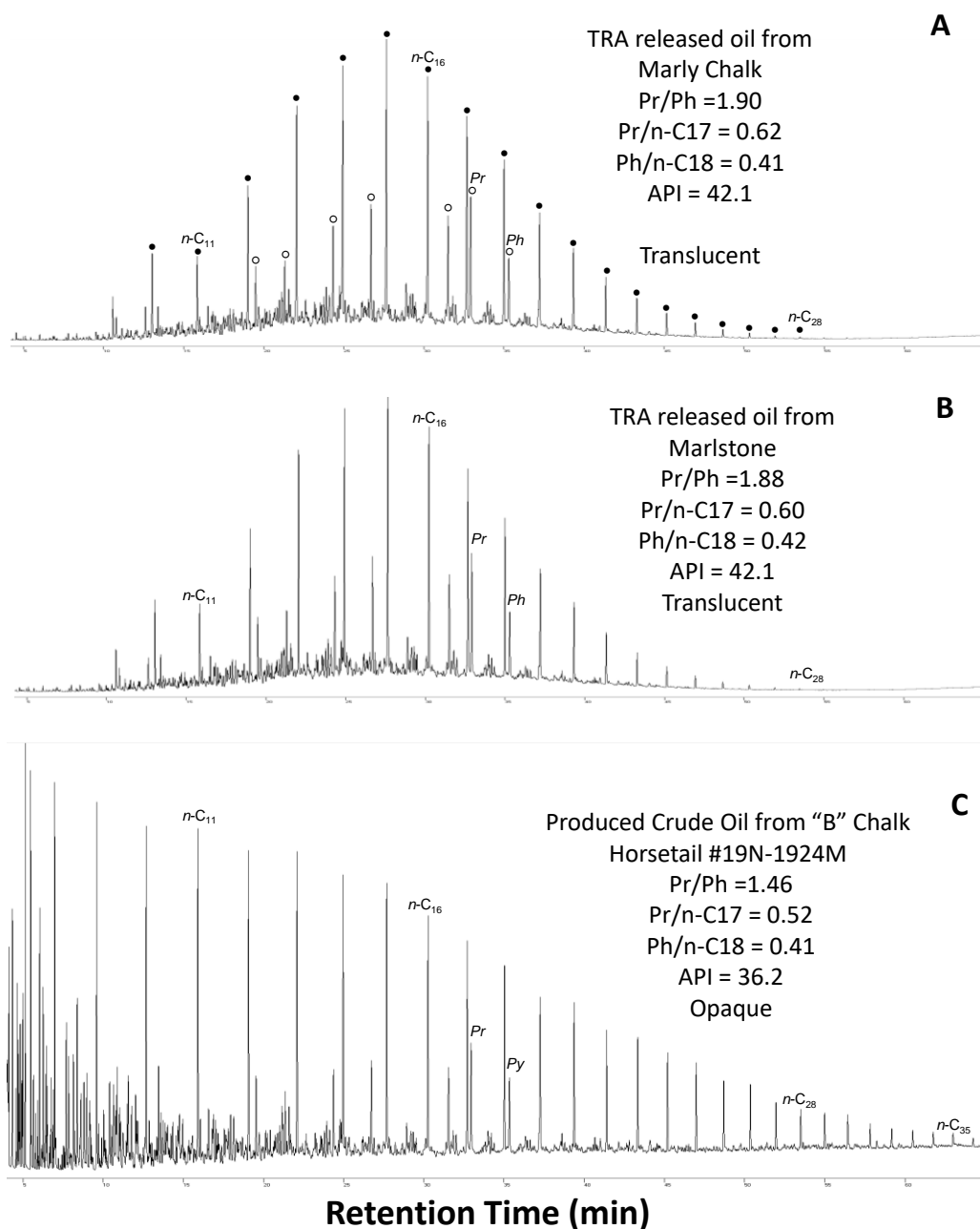


Figure 2. Gas chromatograms of **A)** TRA oil from the "B" Marly Chalk, **B)** TRA oil released from the "B" marlstone, and **C)** produced crude oil produced from the Horsetail #19N-1924M. Solid dots denote *n*-alkane peaks with specific *n*-alkanes labeled with carbon numbers 11, 16, and 28. Open dots denote isoprenoid peaks with specific isoprenoids labeled as *Pr* for pristane and *Ph* for phytane. All gas chromatograms are normalized to *n*-C₁₇ peak.

The marly chalk may have oil that has migrated from the adjacent marlstone. This is reflected in the significantly higher $S_1/TOC \times 100$ parameter of the original marly chalk relative to that of the marlstone (**Table 4**). The question that arises is how much of the produced crude oil is from the marly chalk and how much is from the marlstone. The TRA results (**Table 3**) indicate that the marly chalk may contribute 35 volume % more retained and producible oil than the marlstone. The LTHP results (**Table 2**) indicate that the marly chalk may contribute 189 volume % more

retained and producible oil than the marlstone. These are significant differences with the LTHP results indicating the marly chalk is the main source of the produced oil.

Table 4. LECO and HAWK analyses of original sample and LTHP recovered sample.

| | Marly Chalk | | | Marlstone | | |
|--|--|-----------|-----------|-----------|-----------|-----------|
| | Original | Recovered | % Change* | Original | Recovered | % Change* |
| LECO Total C (wt%) | 13.65 | 12.95 | 5.1 | 8.45 | 8.12 | 3.9 |
| LECO TOC (wt%) | 2.38 | 2.08 | 12.6 | 3.06 | 3.01 | 1.6 |
| S ₁ (mg/g rock) | 8.1 | 2.6 | 67.9 | 2.3 | 0.9 | 60.7 |
| S ₂ (mg/g rock) | 10.0 | 8.7 | 13.1 | 9.7 | 9.0 | 7.1 |
| S ₃ (mg/g rock) | 0.2 | 0.3 | -12.5 | 0.2 | 0.3 | -23.8 |
| T _{max} (°C) | 442 | 443 | -0.2 | 447 | 447 | 0.0 |
| HI (mg S ₂ /g TOCx100) | 421.4 | 419.2 | 0.5 | 315.7 | 298.0 | 5.6 |
| OI (mg S ₃ /g TOCx100) | 10.1 | 13.0 | -28.7 | 6.9 | 8.6 | -25.9 |
| PI (S ₁ /[S ₁ +S ₂]) | 0.5 | 0.2 | 48.9 | 0.2 | 0.1 | 52.6 |
| S ₁ *100/TOC | 339.5 | 124.5 | 63.3 | 76.5 | 30.6 | 60.0 |
| | *(Original - Recovered)/Original x 100 | | | | | |

There remain some aspects of LTHP that need to be investigated. These include determining the optimum mesh size and time-temperature conditions used. Grain sizes from 1 mm to 20 mm and confined versus unconfined cores have been shown not to have a significant effect on the amount of oil generated and expelled during high temperature hydrous pyrolysis (Lewan, 1993 and Lewan and Birdwell, 2013; respectively). However, release of retained oil in a source rock by LTHP may be grain-size dependent and additional studies are needed. Although LTHP conditions of 300°C (572°F) for 24 h avoid significant thermal decomposition of the organic matter to generate oil and gas, durations shorter than 24 h or temperatures lower than 300°C (572°F) may work equally well. This may be especially important when working with source rocks containing high-sulfur Type-IIS kerogen, which can initiate thermal decomposition of organic matter to oil at lower thermal maturities (Lewan, 1985).

TRA remains an informative and practical means of evaluating petrophysical properties of source rocks in tight-shale plays and will not be replaced by LTHP, which requires significantly more sample, longer operational time, and does not provide gas or water saturations. However, LTHP does appear to provide a better estimate of amount and type of oil retained in a source rock. In conjunction with TRA, LTHP could serve as a calibration for oil saturations by using composited samples over key intervals or lithologies within tight-shale accumulations.

CONCLUSIONS

LTHP at 300°C (572°F) for 24 h of Niobrara “B” marly chalk and marlstone from the Horsetail #19N-1924M core release an opaque, black oil comparable to crude oil produced from the well. With the exception of some minor volatile losses, the released LTHP oils also have similar chromatographic characteristics and API gravities to crude oil produced from the well. The quantities of released oil by LTHP are 3.4 to 1.6 times greater than the oil released by TRA, which involves volatilization and condensation of retained oil in the rock. The translucent, yellow oil released by TRA has chromatogram characteristics more like petroleum distillation products with *n*-alkane distributions unlike the produced crude oil. Conversely, LTHP oils are released by opening of tight pore throats as a result of thermal expansion of the retained oil and water in the rock and the immiscibility of the oil in the dissolved-water bearing polar-rich bitumen of a rock. LTHP results show that the chalky marlstone is the major source of produced oil by almost a factor of 3 relative to the marlstone. This proportionality is significantly greater than the TRA results, which has the chalky marlstone as a major source of produced oil by only a factor of 1.3 relative to the marlstone. Compositions of released gases and HAWK-pyrolysis parameters of recovered rocks indicate that at 300°C (572°F) for 24 h no significant thermal decomposition of organic matter to oil or gas is occurring. However, refinement of LTHP is needed with respect to mesh sizes, temperatures, and durations employed. LTHP is not envisioned to replace TRA, but rather supplement it with more realistic amounts and types of oil retained in specific intervals or lithologies of tight-shale accumulations.

ACKNOWLEDGEMENTS

The authors appreciate Whiting Petroleum Corporation for making the core material available for this pilot study and funding for TRA of the samples. We acknowledge the coordination of sample analyses at the USGS by

Augusta Warden and the gas chromatograph by Zach Lowry and LECO and HAWK analyses by Mark Drier. The paper has benefited from discussions about TRA with John Keller, Chris Batzer, and Chad Fuller at TerraTek Schlumberger Reservoir Laboratories. Technical reviews by Justin Birdwell at the USGS and by Lyn Canter and Steve Cumella were especially helpful. Editorial reviews by David Ferderer and Janet Slate at the USGS were most helpful in the final version of the manuscript. Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

REFERENCES

- Handwerger, D.A., Suarez-Rivera, R., Vaugh, K.I., Keller, J.F., 2011. Improved petrophysical core measurements on tight shale reservoirs using retort and crushed samples, SPE Paper 147456 presented at the SPE Annual Technical Conference and Exhibition, 30 October-2 November, Denver, Colorado, 21 p.
- Handwerger, D.A., Willberg, D., Pagels, M., Rowland, B., Keller, J.F., 2012. Reconciling retort versus Dean Stark measurements of tight shales, SPE Paper 159976 presented at the SPE Annual Technical Conference and Exhibition, 8-10 October, San Antonio, Texas, 14 p.
- Lewan, M.D., 1985, Evaluation of petroleum generation by hydrous pyrolysis experimentation: Philosophical Transactions of the Royal Society, London, Series A315, p. 123-134.
- Lewan, M.D., 1993, Laboratory simulation of petroleum formation-hydrous pyrolysis, *in* Engle, M. H. and Macko, S. A., eds., Organic Geochemistry-Principles and Applications, Plenum Press, New York, p. 419-442.
- Lewan, M. D., 1997, Experiments on the role of water in petroleum formation, *Geochimica et Cosmochimica Acta* v. 61, p. 3692-3723.
- Lewan, M.D. and Birdwell, J.E., 2013, Application of uniaxial confining-core clamp with hydrous pyrolysis in petrophysical and geochemical studies of source rocks at various thermal maturities: Unconventional Resource Technology Conference Proceedings, Denver, CO, August 12-14, Paper No. 1571475, 8 p.
- Lewan M.D. and Kotarba, M.J., 2014. Thermal-maturity limit for primary gas generation from humic coals as determined by hydrous pyrolysis: American Association of Petroleum Geologists Bulletin, v. 98, p. 2581-2610.
- Yongmao, H., Mingjing, L., Chengshun, D., Jianpeng, J., Yuliang, S., Guanglong, S., 2016, Experimental investigations on enhanced oil enhancement mechanism of hot water injection in tight reservoirs, *Open Physics* v. 14, p. 703-713.