
Components and processes affecting producibility and commerciality of shale resource systems

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| A B S T R A C T |

Unconventional shale resource systems have provided North America with abundant energy supplies and reserves for present and future decades. This energy resource was largely overlooked until the new millennium. Prior 2000 only a few small oil and gas companies were pursuing such plays led by independent, Mitchell Energy and Development Corporation of The Woodlands, TX. Mitchell's successful commercial development of the Mississippian Barnett Shale of the Ft. Worth Basin, Texas spawned an energy renaissance in North America. In the last decade the development of unconventional shale resource systems has been phenomenal in the United States with abundant new supplies of natural gas and oil. These resource systems are all associated with petroleum source rocks, either within the source rock itself or in juxtaposed, non-source rock intervals. Three key characteristics of these rocks, apart from being associated with organic-rich intervals, are their low porosity (less than 15%), ultra-low permeability ($<0.1\text{mD}$), and brittle or non-ductile nature. These characteristics play a role in the storage, retention, and the requirement of high-energy stimulation to obtain petroleum flow. Organic richness and hydrogen content certainly play a role in petroleum generation, but they also play a role in retention and expulsion fractionation of generated petroleum. Often a substantial portion of the porosity evolves from the decomposition of organic carbon that creates organoporosity in addition to any matrix porosity. Open fracture-related porosity is seldom important. Hybrid systems, *i.e.*, organic-lean intervals overlying, interbedded, or underlying the petroleum source rock, are the best producing shale resource systems, particularly for oil due to their limited adsorptive affinities and the retention of polar constituents of petroleum in the source rock. Paradoxically, the best shale gas systems are those where the bulk of the retained oil in the source rock has been converted to gas by cracking. Such conversion cracks the retained polar constituents of petroleum as well as saturated and aromatic hydrocarbons to condensate-wet gas or dry gas at high thermal maturity. Such high level conversion also creates the maximum organoporosity, while enhancing pore pressure. Bitumen (petroleum)-free total organic carbon (TOC) is comprised of two components, a generative and a non-generative portion. The generative organic carbon (GOC) represents the portion of organic carbon that can be converted to petroleum, whereas the non-generative portion does not yield any commercial amounts of petroleum due to its low hydrogen content. Organoporosity is created by the decomposition of the generative organic carbon as recorded in volume percent. In the oil window, this organoporosity is filled with petroleum (bitumen, oil and gas) and is difficult to identify, whereas in the gas window any retained petroleum has been converted to gas and pyrobitumen making such organoporosity visible under high magnification microscopy. Production decline analysis shows the variable production potential of many North American shale gas and oil systems and their high decline rates. The most productive North American shale gas systems are shown to be the Marcellus and Haynesville shales, whereas the best shale oil systems are the hybrid Bakken and Eagle Ford systems.

KEYWORDS | Unconventional. Shale-Gas. Shale-Oil. Organoporosity. Production.

INTRODUCTION

The objectives of this paper are to provide basic knowledge on shale resource systems as well as advancing specific points for their assessment. Shale resource systems that include hybrid systems have had a dramatic impact on the energy portfolio of the United States. Such energy resource plays are characterized by low porosity and ultra-low permeabilities that were largely bypassed as pay zones due to the inability to obtain commercial flow of gas or oil in the absence of open fractures. Adoption and advancement of approaches to stimulate enhanced flow has made it possible to commercialize these plays. However, the characteristics of shale resource plays are highly variable and require investigation and testing of the most efficacious techniques to reach commercial petroleum flow rates. This paper focuses on select geochemical processes in evaluation of these plays.

Shale resource systems include, not only source rocks, but also hybrid systems where a non-source rock is juxtaposed to a good to excellent source rock and receives charge from it (Jarvie, 2012a). These plays are often appropriately referred to as ‘tight oil’ as they require stimulation to forcibly fracture the rock matrix. These plays have enabled the U.S. to take on a semblance of energy independence after the hollow rhetoric of the last forty years since the oil embargos of the 1970s.

In 2013 crude oil imports into the USA declined 9% and have declined 17% since 2010 (U.S. Census Bureau, 2014). This decrease represents over an 800 million barrel decline from 3.59 billion barrels in 2012 to 2.81 billion barrels in 2013 (U.S. Census Bureau, 2014) due almost exclusively to tight oil production. Production of shale oil in the U.S. increased from 0.2 million barrels per day (mmbod) in 2000 to over 2.27mmbod in 2012 (EIA, 2014). In 2008 shale oil accounted for about 12% of U.S. crude oil production, but had grown to approximately 35% in 2012 (EIA, 2014). Total U.S. crude oil production increased to approximately 7.7 mmbod in 2013, which represents an 18% increase over 2012 (EIA, 2014). Economically, this increased production represents a \$63 billion decline in the overall trade deficit for the USA (U.S. Census Bureau, 2014). Between 2008 and 2012 the energy sector created 1.7 million jobs all in oil and gas drilling (IHS CERA, 2014) helping restrain the economic fallout from the 2008 financial disaster.

Similarly, a dramatic increase in gas production due to shale gas resource plays is also evident. In 1998 shale gas systems only supplied about 2% of gas reserves in the USA with production primarily from five plays including the Lewis, Barnett, New Albany, Ohio, and Antrim shales, whereas in 2013, this total reached 23% (EIA, 2014). The bulk of shale gas production is derived from Marcellus, Haynesville, Barnett,

and Fayetteville shales. Despite decreased or shut-in production due to low gas prices in the USA, shale gas production in 2013 increased to 10.371 trillion cubic feet (tcf) (EIA, 2014).

Production from shales is not a new phenomenon. Production from Devonian shales in the northeastern USA began in the 1820s (Peeples, 1980). These were low flow-rate wells where ‘pipelines’ were created from hollowed-out logs (Curtis, 2002). However, sufficient gas was produced to allow gas lighting in the city of Fredonia, N.Y.. In the 1860s shale gas was discovered and led to production in western Kentucky that later spread to West Virginia and Ohio (Curtis, 2002). The Big Sandy field in eastern Kentucky was the largest known gas accumulation in the world in the 1920s (Curtis, 2002). More recently, production of biogenic gas from the Antrim and New Albany shales and thermogenic gas from Lewis Shale and in select locales, New Albany Shale, has been ongoing, albeit in modest volumes of gas.

Neither is hydraulic fracturing a new process. Developed in 1947 for use in conventional wells, over two million wells have been stimulated (Montgomery and Smith, 2010). However, these have not been the high-energy stimulation as used in shale resource plays today. Today’s high-energy hydraulic stimulations use millions of gallons of water and pump millions of pounds of proppant to create a fracture network among pores (*i.e.*, stimulated rock volume or SRV), allowing flow of petroleum to the well bore. Surfactants are added to the water (thereby creating ‘slick’ water) and proppants are typically sand of varying mesh sizes that both prop open the fractures and also divert the flow of high-pressure water to create a more dendritic fracture network.

Mitchell Energy and Development Corporation’s marginally commercial play in the Barnett Shale began in 1981, and took about 17 years to truly reach commercial levels of production. The Barnett Shale was frequently thought to be one-of-a-kind, a unique play type. However, it eventually led to the development of a multitude of highly productive major shale gas and oil plays in North America, including the Fayetteville, Marcellus, Haynesville, Muskwa, and Montney shales. The largest of these shale gas systems, the Marcellus Shale, has estimated ultimate recovery (EUR) of 471tcf of natural gas (EIA, 2011). The total EUR for North America is 750tcf of natural shale gas (EIA, 2011). It must be noted that estimates of EUR are based on somewhat limited production data; thus, EUR can and will be highly variable. For the most part, projected EURs have increased through time due to advancements in completion strategies.

Shale oil drilling in the Monterey Shale in California began in the early 1900s and yielded large volumes of oil

from fractured shale in structural traps. In the late 1980s and early 1990s horizontal drilling in the Upper Bakken Shale in the Williston Basin yielded high flow rate oil wells with short production lives due to oil storage in open fractures. Similarly, the Bazhenov Shale of West Siberian Basin has also yielded significant oil production volumes from open fractures (Lopatin *et al.*, 2003). These are certainly shale oil resource plays, but did not require high energy stimulation due to open fracture storage.

Unconventional shale oil resource plays began initially in the Middle Member of the Bakken Formation. at Elm Coulee field in eastern Montana in about 2001 and subsequently in 2006 at Parshall field in North Dakota. These areas were complemented in 2008–2009 by another major shale oil resource play in south-central Texas, the Eagle Ford Shale. More recently a huge shale oil resource play has evolved in the Permian Basin of west Texas that includes Wolfcampian and Leonardian mudstones and hybrid sands as well as the Ordovician Utica Shale in eastern Ohio.

One characteristic of shale resource plays is their massive and readily identifiable areal extent. Identifying continuous shale plays from a geological and geophysical viewpoint is more obvious than identifying conventional structural traps that are petroleum charged. Source rocks are certainly the most likely place to find petroleum, however, they are also the most difficult reservoir to develop due to their low porosity (<15%) and ultra-low permeability (<0.1md) (Williams, 2012), often with permeabilities less than 1μD. In addition they may be ductile depending on the percentage of clay content and may contain swelling clays that inhibit stimulation and production.

Even though shale resource plays have high volumes of oil-in-place, their low porosities and permeabilities seemingly locked the petroleum in these systems. While kicks or even flow were noted in such systems, there appeared to be minimal possibility of achieving commercial flow rates of petroleum. Vertical wells could only create limited SRV when stimulated, but did eventually achieve commercial rates in the Barnett Shale with slick water fracs that were more effective and less expensive. Horizontal drilling technology alone, which was used successfully in open-fractures in the Bakken Shale and Austin Chalk reservoirs in the late 1980s and early 1990s, did not lead to the success found in North America's shale resource systems. The key was the ability to drill horizontal wells and perform high energy stimulation, generally written as 'fracing' by industry (or 'fracking' in public media sources), to create much larger SRVs. High-energy stimulation of shale resource systems has been completed on over 60,000 shale resource systems in the USA to date. Even with horizontal drilling combined with fracing, these wells

are not high flow rate systems due to poor connectivity of pores and narrow pore throats as well as sorptive effects particularly in organic-rich rocks. Typical recovery factors range from approximately 4 to 20% of in-place reserves. However, increase in EURs has shown continual improvement due to advances in understanding of these systems especially concerning completion techniques and down-spacing of wells. High-level commercial success requires drilling of hundreds to thousands of wells to develop these resources due to their modest flow rates and lack of connectivity between or among wells. Such high-volume drilling requires resources (*e.g.* water, sand, salt water disposal (SWD) wells and infra-structure (*e.g.* roads, pipelines, gas processing), which is complicated and more disruptive in heavily populated areas.

There has been an environmental rebuff to this development that cites ground-water contamination, low level maximum moment magnitude scale (Mw or M) 2 or lesser earthquakes, and high water usage. Based on over 60,000 stimulated wells, it is proven that ground water contamination has not occurred as a result of hydraulic stimulation. The reported cases of water well contamination in the Fort Worth and Appalachian basins are as a matter of public record, pre-existing conditions. Water wells drilled in areas of the Fort Worth Basin have often reported gas and these gases have been proven to result from natural migration, *e.g.*, Range Resources vs. U.S. Environmental Protection Agency (EPA), which was dismissed without prejudice (U.S. District Court, 2012). In a case of apparent water contamination in the Marcellus, well cementing was the culprit, not the stimulation. Unfortunately this latter issue is similar to the conventionally-drilled Deep Water Gulf of Mexico Macando well that had cementing issues (OSC, 2011) among several factors resulting in tragic loss of life and environmental contamination. This is another issue for industry and regulators to address: to insure that current regulations meet the requirements for added safety to drilling operations for both personnel and the environment.

M2 or lower level earthquakes have occurred primarily from SWD wells. SWD wells are necessary and are an essential part of drilling operations in both conventional and unconventional wells. SWD wells drilled near existing natural fractures are thought to be the cause of seismicity related to unconventional shale development (Frolich and Potter, 2013).

Of the issues surrounding shale resource development, another key factor is fresh water usage. However, it is not necessary to use fresh water exclusively because many fluids such as gels, nitrogen foam, propane and even salt water can be used for such efforts (N. Steinsberger, 2010, personal communication). They are,

however, more costly to employ and have proven to be less effective than slick water.

Apart from the USA having secure energy resources and the related economic benefits, the lowest level of carbon dioxide (CO₂) emissions was reported in the first quarter of 2012 covering the last 20 years (EIA, 2012). Electricity generation accounts for the highest percentage of CO₂ emissions in the USA and the switch to natural gas from coal has aided this reduction.

Globally, shale resource systems have not achieved the success of North America to date. This is due, not only to the characteristics of these shale resource systems, but also because development requires expertise, services, and infrastructure as well as societal and political acceptance. As shown by the Barnett Shale, developing shale resource plays is not a fast process (Steward, 2007). The first wells are typically the least successful and require optimization, usually in completion strategies. It is often stated by industry experts that ten or more wells are required to test a play adequately, and this presumes that the operator already has experience with unconventional shale resource systems.

Nonetheless, some of the international attempts have been in systems where such a basic factor as organic richness has been at minimal levels. In other cases the mudstone matrix was less amenable to stimulation, *i.e.*, less brittle and having rock mechanical properties that are not amenable to stimulation techniques to date.

However, some success has been reported in China as well as Argentina. Other regions or countries where success may be expected in the future include the Middle East (Saudi Arabia, United Arab Emirates), Africa (Algeria), Australia, Mexico, and various countries in South America most likely Colombia, but also other countries having source rocks with high carbonate content.

DISCUSSION

An unconventional shale resource system is comprised of a source rock and possibly juxtaposed organic-lean lithofacies, either of which can produce petroleum without further heating (Jarvie, 2012a). Perhaps it would be appropriate to add to this definition the requirement for high energy stimulation, but this is not necessary for open fracture plays as has been shown historically. When petroleum is stored in a juxtaposed organic-lean lithofacies, these systems are referred to as hybrids. These are systems with overlying, underlying or inter-bedded organic-lean lithofacies. Such intervals usually have low permeabilities and porosities comparable to the juxtaposed organic-rich

shales and therefore, require high-energy stimulation. However, these organic-lean lithofacies are typically brittle and do not have the retentive (sorptive) capacity of the abundant kerogen and bitumen found in organic-rich shales. Certainly petroleum is produced from some organic-rich shales, but the best production wells have been from juxtaposed, organic-lean lithofacies.

The term 'shale' can be equivocal among geologists as it can be thought of being defined either by particle size or by mineralogy. The term 'shale' will be used throughout this paper to describe what are typically mudstones of highly variable mineralogy.

Shale gas systems can contain either biogenic or thermogenic gas (Jarvie *et al.*, 2007). There can be mixing of the two, but this has seldom been the case. Biogenic shale gas systems are typically shallow with dry gas stored in open fractures such as the Devonian Antrim Shale of the Michigan Basin, USA (Curtis, 2002). Biogenic and low to moderate maturity thermogenic gases typify low volume gas wells in terms of flow rates or volume recovery of gas. Typical Antrim Shale wells recover about 0.3bcf/well (billion cubic feet (of gas) per well) and low maturity, thermogenic shale gas wells, as found in certain areas of the Devonian New Albany Shale of the Illinois Basin, USA, have low flow rates of gas (ca. 135mcf/d) (thousand cubic feet (of gas) per day).

High thermal maturity shale gas systems (>1.0% vitrinite reflectance in oil (%Ro) are typified by the more prodigious gas producers, such as Barnett, Fayetteville, Haynesville, and Marcellus shales. In these plays gas flow rates and recovery volumes are

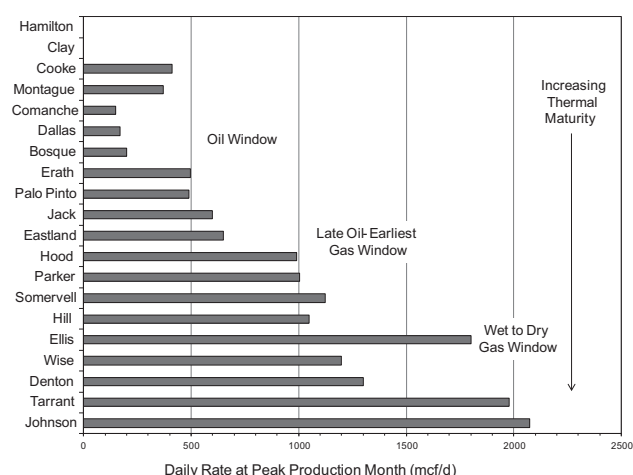


FIGURE 1. Comparison of gas yields from the Barnett Shale, Fort Worth Basin, Texas, at varying thermal maturity. These data show the month of peak gas production by county. As maturity increases from oil window to dry gas window, the gas yields increase.

closely correlated to thermal maturity as shown by Barnett Shale production data by county (Fig. 1). This figure shows the daily rate for peak production month by county from the Barnett Shale in the Fort Worth Basin, Texas. The best producing areas are Wise, Denton, Tarrant, and Johnson counties, where thermal maturities range from 1.2 to 1.6%Ro. This is due, in part, to increased gas content due to cracking of residual kerogen, but primarily due to cracking of retained petroleum, which also removes the heavier and more polar components of petroleum that can restrict petroleum flow. Decomposition of such organic matter is also accompanied by the development of organoporosity within organic matter including kerogen, bitumen and pyrobitumen.

High thermal maturity thermogenic shale gas systems typically have recoveries of over 1 bcf most often being in the 2 to 8bcf per well range. A hybrid shale gas system is typified by the Montney Shale, where organic-lean to rich shale is inter-bedded with silty sands. Hybrids generally do not show good correlation between porosity and TOC (Fig. 2). When there is correlation between porosity and TOC, storage is inferred to be largely due to organoporosity.

Shale oil systems are thermogenic and are distinctly different from oil shale systems that require anthropogenic heating to convert immature organic matter to petroleum. Shale oil systems differ from oil shale systems because they can be made to produce naturally generated petroleum. Thus, a major

unconventional oil resource system, oil shale, is not included in the above definition of shale oil.

The term ‘petroleum’ includes gas and oil as well as hydrocarbons and non-hydrocarbons. Hydrocarbons include only compounds containing carbon and hydrogen, such as saturated and aromatic compounds. However, petroleum also includes non-hydrocarbons, *i.e.*, compounds containing additional elements beyond carbon and hydrogen. These are commonly referred to as polar compounds or resins and asphaltenes, and often described as ‘NSO’ (nitrogen, sulfur, oxygen) bearing compounds. In addition minor amounts of metals are also found in crude oil, most commonly, nickel and vanadium. Bitumen is an overlapping term as it is often referred to in the context of the earliest products generated from kerogen. Bitumen is comprised of all the above constituents, although enriched in non-hydrocarbons.

A difference in petroleum composition between source rocks and reservoirs they sourced was first noted by Brenneman and Smith (1958). They reported that source rocks had higher concentrations of NSO-compounds and lower concentration of paraffins than nearby associated reservoir rocks. However, in another source-reservoir pair, there were more aromatics and lesser amounts of paraffins and NSO-compounds in the reservoir oil, suggesting a fractionation process. Gimplevich (1960 as cited in Hunt, 1979), Baker (1962) and Vandenbroucke (1972) reported differences in saturate-to-aromatic (S/A) ratios, where related oils had higher S/A ratios than related source rock extracts. Another comparison showed increased polar compounds in shale extracts compared to extracts of sands sourced by the same shale (Vyshemirsky *et al.*, 1974). This fractionation between source rock and reservoir was suggested to be primarily due to sorption of polar compounds by the organic matter (Young and McIver, 1977). Sandvik *et al.* (1992) quantified the retention of polar compounds in source rocks versus expelled oil using gold tube pyrolysis. Retention by the source rock causes expulsion fractionation, verifying the previous field data with experimental proof. Expulsion fractionation can even affect biomarker compounds, where measurements by Gimplevitch (1960, as cited by Hunt 1979) showed source rocks to have two to three times higher concentrations of pentacyclic triterpanes. In terms of unconventional shale versus hybrid systems, this shows that expulsion and short distance migration over centimeters fractionates oil into a higher quality oil than found retained in the source rock.

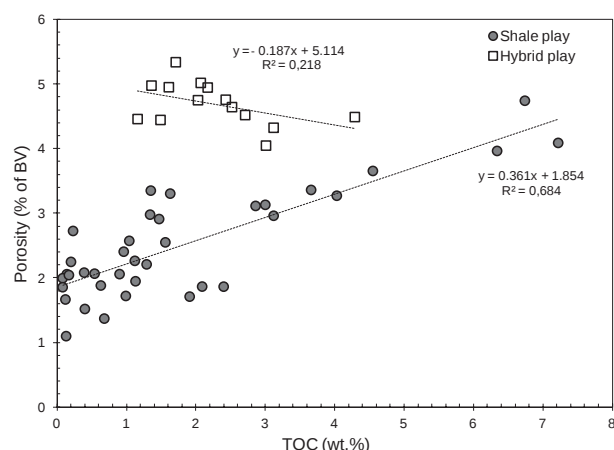


FIGURE 2. Comparison of a shale and hybrid system based on total organic carbon TOC and porosity. A source rock juxtaposed with organic-lean rock is a hybrid system. In such a system TOC and porosity do not show correlation, which is indicative of porosity unrelated to organoporosity development. On the other hand, a shale source rock play may have organoporosity development from organic matter decomposition. A positive correlation between TOC and porosity implies that this is organoporosity rather than matrix porosity.

In order to evaluate a source rock or hybrid as a potential resource system, it is necessary to evaluate a variety of geochemical components and processes as part of a larger program assessing the geological setting and rock properties such as petrophysics and rock mechanics.

TOTAL ORGANIC CARBON (TOC)

TOC is determined by combustion in a Leco Corp. (St. Joseph, MI) carbon analyzer, e.g. Leco model C230. Samples are weighed prior to dissolution of carbonates by hydrochloric acid. After rinsing and drying, the decarbonated sample is reweighed and the carbonate carbon content is determined gravimetrically. Subsequently, the decarbonated sample is combusted at high temperature (ca. 1200°C) in the Leco instrument. Comparison of the unknown analysis to a standard value allows computation of the organic carbon content in weight percent.

TOC is comprised of two key components: a portion that can generate petroleum upon thermal maturation, and a portion that will not generate significant amounts of petroleum. These have been referred to as labile and inert carbon (Cooles *et al.*, 1986), but referred to by Jarvie (2012a) as Generative Organic Carbon (GOC) and Non-Generative Organic Carbon (NGOC). GOC converts to petroleum and pyrobitumen. With increasing temperature, petroleum also cracks to lighter oil, gas, and

additional pyrobitumen until at very high temperatures or maturity, all GOC and petroleum has been converted to gas and pyrobitumen (Fig. 3).

NGOC will yield only small amounts of dry gas (Jones, 1984), but may act as a sorbent and possibly a catalytic site and is thus, not inert. NGOC is volumetrically important for kerogen density calculations, but will have higher density than the GOC portion of TOC due to its more highly condensed structure and related lower concentration of hydrogen.

The petroleum generation potential of a source rock is directly proportional to the amount of original GOC (GOC_o) and its thermal history. The percentage of GOC_o in original TOC (TOC_o) is determined by dividing original hydrogen index (HI_o) by 1176 (Jarvie, 2012a). A HI_o of 1176 is derived from an assumption of approximately 85% carbon in petroleum, i.e., $1/0.085$. Many authors have used 83% carbon in petroleum, which yields a maximum HI_o of 1200mg/g TOC (e.g. Espitalie *et al.*, 1984). TOC_o is multiplied by the percentage GOC_o , which yields GOC_o in weight percent. This value is subsequently divided by 0.085 to obtain original petroleum generation potential (S_2) (S_{2o}) in mg petroleum/g rock.

To demonstrate the importance of HI_o values, assume a one foot thick shale has a TOC_o of 1.00wt.%, but in one case a Type II kerogen with HI_o of 350mg/g TOC and a second case where the HI_o is 700mg/g TOC. In this example, the lower HI_o value will have a S_{2o} of approximately 3.50mg hydrocarbons/g rock, whereas the higher HI_o yields approximately 7.00mg hydrocarbons/g rock. Obviously the petroleum generation potential as determined by S_{2o} is directly proportional to HI_o and TOC_o .

As such, S_{2o} may be used to compute the petroleum generation potential taking into account thermal maturity or kerogen conversion. Assuming a 35°API (American Petroleum Institute) oil (0.85g/cc) and a matrix density of 2.5g/cc, a conversion factor of 22.82 is used to convert S_{2o} from mg petroleum/g rock to barrels of oil equivalent/acre-foot (boe/acre-ft). Barrels of oil equivalent (boe) does not distinguish between the amounts of gas versus oil. At 50% transformation ratio (TR), the yield of petroleum is approximately 80 barrels of oil equivalent per cubic foot (boe/ft³) for the 350 HI_o sample and 160boe/ft³ for the 700 HI_o sample. Multiplication of this value by the source rock thickness and 640 (acres/mile² or acres/section) provides the estimated petroleum generation potential in boe/section. Of course expulsion losses must be accounted for to assess retained oil-in-place values or potential petroleum charge into a hybrid.

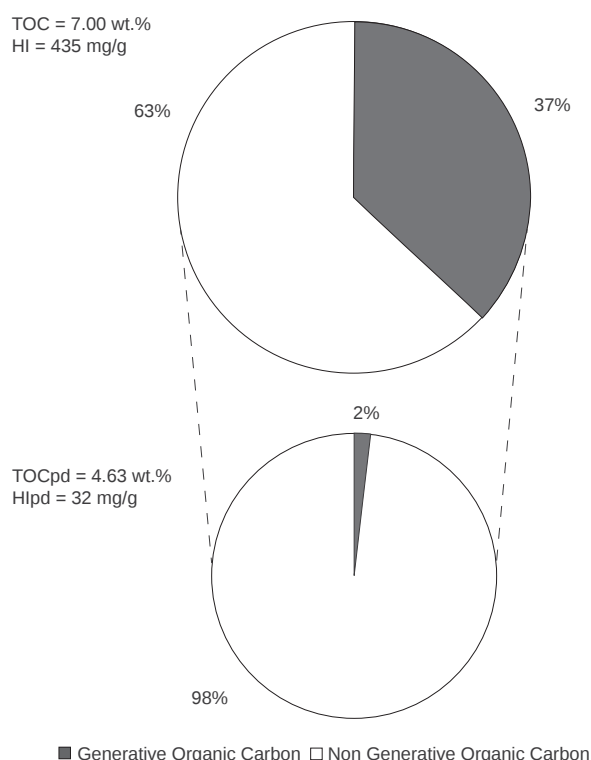


FIGURE 3. Diagrammatic illustration of total organic carbon (TOC) with generative organic carbon (GOC) and non-generative organic carbon (NGOC) fractions. Thermal maturation reduces TOC as a result of conversion of GOC (petroleum potential or S_2) to petroleum. TOC decreases by the carbon lost in petroleum generation. There is a slight increase in NGOC with maturation due to pyrobitumen formation.

There is also organic carbon in kerogen-derived carbon dioxide and carbon monoxide (recorded as S3), but they are a minor component of TOC in terms of mass ($0.027 \times S3$ value) and is unrelated to petroleum generation potential. However, this carbon dioxide may play a role in formation of carbonic acid that could result in dissolution of associated or juxtaposed carbonates.

With an increase in thermal maturity, TOC decreases due to the conversion of GOC or S2 to petroleum. The maturation-reduced TOC is referred to as present-day TOC (TOC_{pd}). Most basins have source rocks that have undergone maturation, often to varying levels. Shale gas systems are at a high level of conversion having vitrinite reflectance values of greater than 1.0% Ro and TR greater than 80% (TR as defined by the change in HI_o). Therefore, in order to assess the original petroleum generation potential, TOC_o needs to be determined, which is primarily restoring GOC_o , although there is also a need to reduce the NGOC present-day ($NGOC_{pd}$) by the amount of added pyrobitumen from conversion of GOC and oil cracking (Jarvie, 2012a).

One way to determine TOC_o , $S2_o$ and HI_o is to identify and analyze samples that are immature that match the organofacies of those in more mature areas. This typically results in a range of TOC_o and HI_o values. For example, immature Barnett Shale samples have TOC_o and HI_o values of about 7.00wt.% and 435mg/g, respectively (Jarvie *et al.*, 2007). Standard deviations from such average values within a single organofacies are about 1.00 and 55, respectively. Therefore, even when immature samples are available, it will still likely be necessary to evaluate a range of values and perhaps establish probability factors akin to P90, P50, and P10 values used in petroleum reserve calculations. For example, these factors can be used to state that 90% of the samples will have a TOC_o greater than 6wt.%, only 10% will have an TOC_o greater than 8wt.%, and there is 50% likelihood that the TOC_o will be 7wt.%. This provides an assessment of risk for various geochemical characteristics and a sensitivity analysis of the total petroleum generation potential.

In the absence of immature source rocks, other means of establishing TOC_o and HI_o can be utilized. These include the methods presented by various authors such as Daly and Edman (1985), Peters *et al.* (2005), Jarvie *et al.* (2007), and Jarvie (2012a), the latter using a nomograph from estimates of HI_o .

Daly and Edman (1985) suggested guidelines for the extent of conversion of various kerogen types. They showed values of 80%, 50%, and 20% for the total amount of TOC that could be converted for kerogen types I, II, and III, respectively. These percentages were then used in

TABLE 1. Classical kerogen types based on original hydrogen index (HI_o) definitions of Jones (1984) with the range of percentages calculated for generative original organic carbon (GOC_o). This assumes 85% carbon in petroleum, which yields a maximum HI_o of 1176mg/g total organic carbon (TOC). This clearly shows dependency of the degree of convertibility of organic carbon on hydrogen content

Kerogen Type	HI_o Range	GOC_o Range
Type I	> 700	> 60%
Type II	350 - 700	30% - 60%
Type II / III	200 - 349	17% - 29%
Type III	50 - 199	4% - 28%
Type IV	< 50	< 4%

conjunction with estimates of TR to compute how much petroleum could be generated.

Taking their approach one step further, the portion of TOC_o that can be converted, *i.e.*, GOC_o , can be calculated or any original hydrogen index (HI_o) using assumptions cited above (Jarvie, 2012a) (Table 1).

However, the most basic issue with these calculations is how to establish a value for HI_o when the appropriate immature series cannot be located. As cited previously, even with an immature series, HI_o values can be quite variable. In fact, many immature source rocks are located along the basin margin where the organofacies may not be representative of those in the central part of the basin. As such more than one organofacies and HI_o value may have to be assumed for different portions or regions for a source rock.

The extent of kerogen conversion, *i.e.*, TR, can be used to estimate HI_o by reverse modeling. Thermal maturity needs to be appropriately constrained using thermal maturity indicators, such as vitrinite reflectance (%Ro), temperature at the maximum evolution of the pyrolysis peak (T_{max}) equivalent (%Roe(T_{max})), equivalent %Roe values from carbon isotopes (Schoell, 1984), or other estimates of thermal maturity such as biomarker ratios or aromatic hydrocarbons. Certainly a simple 1D basin model can be used for this purpose either based on measured kinetics or default values by organofacies. The thermal and burial history model would necessarily be optimized using thermal maturity data and the resulting TR computed.

Based on data available from the Barnett Shale, which is a low sulfur Type II kerogen, a T_{max} of 441°C is indicative of ca. 50% TR (Fig. 4). If, at this TR, present-day petroleum potential ($S2_{pd}$) values average about 14.92mg/g rock at a TOC_{pd} of 5.61wt.%, then $S2_o$ is readily calculated ($S2_{pd}/0.50$). The organic carbon that has been converted to petroleum is the difference

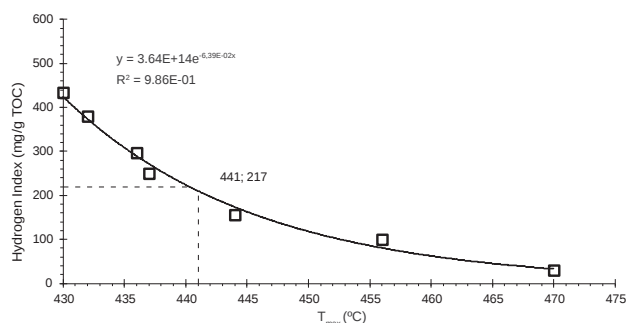


FIGURE 4. Relationship of temperature at the maximum evolution of the pyrolysis peak (T_{max}), an indication of thermal maturity, to hydrogen index (HI) for a maturation series of the Barnett Shale, Fort Worth Basin, Texas. A maturation series such as this may be used to estimate original hydrogen index (HI_o) if the same organofacies is assumed. A T_{max} of 441°C indicates a present-day hydrogen index (HI_{pd}) of 217 or 50% conversion of organic matter based on the change in HI_o .

between $S2_o$ and $S2_{pd}$ times 0.085 (1.23wt.%). TOC_o is then TOC_{pd} plus the weight percent organic carbon calculated from the difference between $S2_o$ and $S2_{pd}$ or in this example, 6.88wt.%. HI_o is then calculated from the $S2_o$ and TOC_o values of 29.84mg/g rock and 6.88wt.%, respectively, resulting in a HI_o of 434mg/g TOC (Table 2).

These Barnett Shale data suggest that the GOC_o is approximately 37% of the TOC_o or 2.54wt.% of the TOC. This is the amount of TOC that can be converted to petroleum and pyrobitumen as well as potential for organoporosity development in the Barnett Shale. Support for 37% conversion of TOC_o is provided by immature Barnett Shale samples from the Lampasas, Texas area, that show nearly identical percentages for GOC_o . Given the range of HI_o values for Type II kerogens, it is apparent that GOC_o can be quite variable too, *e.g.*, while the Barnett Shale has about 37% of its TOC_o as GOC, various organofacies of the Eagle Ford and Bakken shales have about 58–60% of their TOC_o as GOC based on HI_o values of about 700mg/g TOC.

In the absence of any reasonable data, a sensitivity analysis can be utilized for Type II kerogens with a P50 HI_o value of 475mg/g TOC with P10 and P90 values of

645 and 340mg/g TOC, respectively (Jarvie, 2012a). In this case it is assumed that 90% of Type II kerogens have a HI_o of 340mg/g TOC or higher; similarly, these data suggest only 10% of Type II kerogens have a HI_o greater than 645mg/g TOC. Overall, there is a 50% probability that a Type II kerogen will have a HI_o of 475mg/g TOC.

ORGANOPOROSITY DEVELOPMENT

A portion of porosity in source rocks has been shown to be related to organic carbon content (Jarvie, 2005; Reed and Loucks, 2007; Loucks *et al.*, 2009). This concept of porosity potential was speculated to be available for Type III kerogens by Tissot and Welte (1978). The change in mass of TOC due to petroleum generation is directly proportional to the volume of organoporosity that is possible. In the oil window, this porosity is filled with oil and bitumen, whereas in the dry gas window the organoporosity is filled with gas and is readily visible using argon-ion milling and SEM imaging. This type of organic storage capacity can be estimated by conversion of GOC_o in mass to volume percent. This requires knowledge of the rock density as well as TOC density. Typically, shale source rocks have a rock matrix density between 2.4 and 2.7g/cc. An average density value for TOC is ca. 1.15g/cc. However, it is likely that the GOC portion of TOC is ca. 1.00g/cc, whereas the NGOC is likely ca. 1.40g/cc. This is based on density assessments by Okiongbo *et al.* (2005) and Vandenbroucke and Largeau (2007). Table 3 illustrates the total organoporosity potential of a source rock with 2.5wt.% GOC_o at full conversion. Obviously at lower levels of conversion, the volume percentage of organoporosity will be fractionally lower.

In shale oil systems organo-pores are not readily visible and their existence is reasonably questioned. However, although not visible, first principles suggest that there must be organic porosity as a result of conversion. With 2.50wt.% GOC_o , at 0.80%Ro or near 50% TR for low sulfur, Type II kerogens, approximately 2.5 vol.% organoporosity would be possible, but is usually not apparent (Fig. 5). It is proposed that this organoporosity is not visible under ion milling/SEM analysis as the

TABLE 2. Calculation of original $S2$ ($S2_o$), original total organic carbon (TOC_o), and original hydrogen index (HI_o) from the present-day (pd) values and the estimated level of kerogen conversion at a given maturity level as shown in Figure 4. OC is organic carbon; subscript 'o' represent original values. TR is kerogen transformation ratio in percent

$S2_{pd}$ (mg/g rock)	TOC_{pd} (wt.%)	T_{max} (°C)	TR (est)	$S2_o$ (mg/g rock)	OC in $S2_o - S2_{pd}$ (wt.%)	TOC_o (wt.%)	HI_o (mg/g TOC)
14.92	5.61	441	50%	29.84	1.27	6.88	434

TABLE 3. Calculation of the potential for organoporosity at 70% and at full (100%) conversion for a source rock with $S2_{pd}$, TOC_{pd} , and T_{max} to determine GOC_o , TOC_o , and HI_o . The density assumption for GOC is based on low density, oil prone organic matter (amorphous, alginite), whereas NGOC is based on high density organic matter. Ranges for organic matter density as a function of thermal maturity are found in Okiongbo *et al.* (2005)

	mass (g)	density (g/cc)	volume (cc)	volume (%)	TR
Rock-1	93.12	2.70	34.49	87.8%	na
GOC _{pd-1} to Porosity	1.63	1.00	1.63	4.1%	70%
NGOC _{pd-1}	4.49	1.40	3.21	8.1%	70%
TOC volume	6.12	1.40	4.37	12.2%	70%
Rock-2	86.10	2.70	34.49	86.1%	na
GOC _{pd-2} to Porosity	2.32	1.00	2.32	6.3%	100%
NGOC _{pd-1}	4.56	1.40	3.26	8.3%	100%
TOC-2 volume	4.56	1.40	3.26	8.3%	100%

petroleum is sorbed in the kerogen matrix (this includes hydrocarbons sorbed in bitumen as well as hydrocarbons and bitumen sorbed in kerogen). Thus, any available organopores will be filled with petroleum and the kerogen will swell in such solvating agents. Such oil window organoporosity is now starting to be identified in various shales (*e.g.* Rowe, 2014).

From polymer chemistry it is known that polymer swelling occurs when select solvents are added. This has also been reported for kerogen when petroleum solvents are used (Ertas *et al.*, 2006). These authors also report that aromatics are fractionated from saturated hydrocarbons under such conditions. Possible substantiation of this phenomenon include the fractionation of petroleum that occurs during expulsion, and also by the Bakken

Formation, where shale rock extracts and produced shale and Middle Member oils can be compared. Bakken Shale source rock extracts show elevated light aromatic content (toluene) when normalized by heptane compared to produced early to middle mature oils using high resolution light hydrocarbon extraction/fingerprinting technique (Jarvie *et al.*, 2011) (Fig. 6). This effect is not due to evaporative fractionation or the presence of carbonate source rocks as the Bakken Shale is a tight reservoir rock and is siliclastic.

Organic matter has been shown to have forty-four times more adsorptive affinity than quartz, for example (Schettler and Parmely, 1991). However, swelling would suggest a more complex situation in source rocks where both adsorption and absorption are occurring. Adsorption is a low energy, physical attraction of gas or liquid molecules to a solid material; absorption is also a physical effect related to solubility. It is best to describe the interaction in organic matter as ‘sorption’, thereby including both phenomena.

In general, higher matrix porosity yields better gas or oil retrieval because sorption is reduced in the absence of original organic matter. In an organic-rich shale, sorption results in retention of petroleum, especially polar components such as resins and asphaltenes. This is a key point in evaluation of production potential from shale versus hybrid plays. Organic-rich shales may have much higher oil-in-place values but may be far more difficult to produce due to sorption of petroleum constituents to TOC. Using the results from Sandvik *et al.*, (1992) and Pepper (1992), a sorption index (SI) can be used to relate oil retention to organic matter content. This value is between 80 to 100mg of oil per gram of TOC.

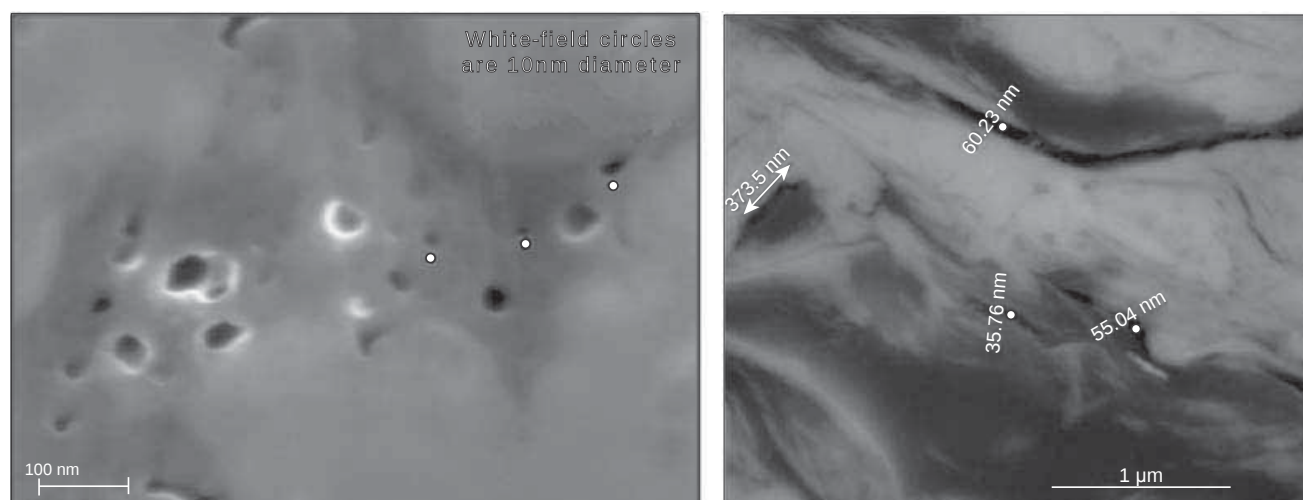


FIGURE 5. SEM micrographs of a shale resource system in the gas window (Barnett Shale, Fort Worth Basin) (Reed and Loucks, 2007) and oil window (Bakken Shale, Williston Basin) courtesy of Core Labs. Pores associated with organic matter are obvious in the Barnett Shale, but not in the Bakken Shale. It is hypothesized that organopores in the Bakken Shale are filled with oil and bitumen entrained in a swollen kerogen matrix.

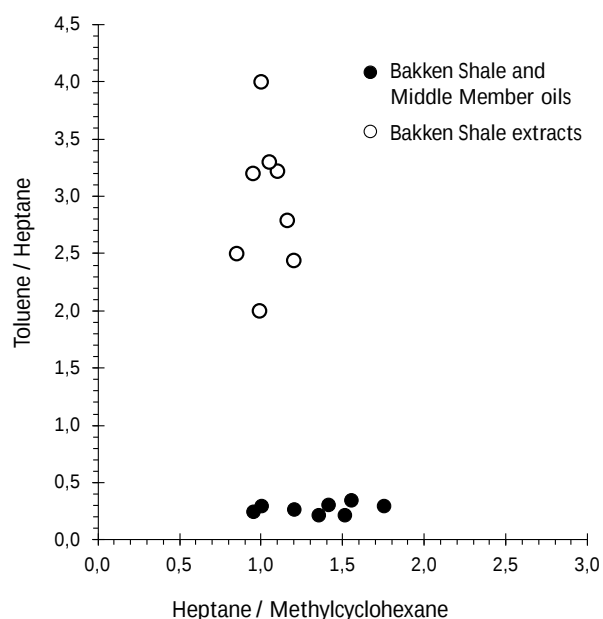


FIGURE 6. Thompson's paraffinicity and aromaticity ratios from produced oils from the Middle Member of the Bakken Shale (an organic-lean dolomite) compared to Bakken Shale extracts. The produced oils all have low aromaticity as shown by the toluene/heptane ratios being less than 0.50, whereas Bakken Shale extracts have aromaticity values from 0.90 to 1.45. This suggests fractionation of oil in terms of normalized toluene content from source rock to reservoir rock.

GEOLOGICAL FACTORS

Understanding the geology and burial history of unconventional shale resource plays is an essential component for evaluating their potential for oil or gas. Many of the shale resource plays in the U.S. have undergone substantial uplift. As is well known, thermal maturity represents the maximum paleo-temperature, thereby often permitting quantification of the amount of uplift. This is important, as the storage capacity of a shale is affected by temperature and pressure. Under present-day temperature and pressure conditions and at 5% porosity, the Barnett Shale has about 450mcf/acre-ft storage capacity for gas (Jarvie *et al.*, 2007). However, at maximum paleo-temperature and pressure, the storage capacity increases to 710mcf/acre-ft, almost a 60% increase.

This assumes that no gas is lost during uplift, which is sometimes a point of contention. However, in the case of the Barnett Shale, where the primary storage is in organoporosity, there would be essentially only minor loss of gas even with fracturing due to the isolated storage. Because maximum generation from the Barnett Shale is thought to have occurred at 250Ma, diffusion loss appears to be insignificant. However, if the storage is primarily in matrix or fracture porosity, this could result in greater

loss. One issue that could occur if liquids are present is condensation. Most Barnett Shale gas wells have minor amounts of liquids associated with production up to about 1.7% Ro. Gas wells are classified as dry gas when the gas-to-oil (GOR) ratio is over 100,000scf/stb (standard cubic feet per stock tank barrel) or yields of 10 or less barrels per million cubic feet (Whitson and Brulé, 2000).

PETROLEUM CONTENT

Shale oil resource systems depend either on high oil saturation in the shale itself or juxtaposed organic-lean lithofacies, *i.e.*, a hybrid system. Identifying potential reservoir zones in conventional or unconventional shale oil systems with producible oil can be as simple as identifying rocks with elevated normalized oil yields or S1/TOC ratios (Jarvie and Baker, 1984; Jarvie *et al.*, 2001; 2012b) referred to as the oil crossover effect (Jarvie, 2012b). Typically, values exceeding the sorption capacity of a rock, *i.e.*, whenever S1/TOC exceeds unity or approximately 100mg oil/g TOC, is indicative of producible oil. This was utilized in determination of perforation points in the Monterey Shale (D. Jarvie, 1984, unpublished data) and in an Anadarko Basin, Oklahoma conventional play (Jarvie and Baker, 1984). Interestingly, this is the approximate value for the expulsion threshold as described by Sandvik *et al.* (1992) and Pepper (1992) meaning the source rock is highly saturated with oil.

The Laurel #1 well, Colombia, drilled and cored in the 1990s, illustrates the use of the oil crossover effect to identify potentially producible oil (Fig. 7). In the intervals from 1676–1722 and 1776–1840m. producible oil is indicated, although this does not imply commerciality. Strong sorption effects are expected because TOC values are high and the maturity is modest, indicative of only minor cracking of resins and asphaltenes that results in a strong polarity component to the retained petroleum.

S1/TOC values less than 100mg/g may still indicate producible oil due to evaporative losses in S1 as a result of depressurization, sampling handling and processing, and petroleum carryover into the pyrolysis (S2) peak. Evaporative losses can be very high depending on a number of factors: i) rock permeability, ii) TOC, iii) rock lithofacies, iv) volatility of oil, v) sample type (core, cuttings), vi) sampling handling, vii) storage conditions, viii) sample preparation, and ix) even the analytical instrument used for analysis. In an organic-lean sandstone, for example, loss of petroleum will be high especially if a condensate. In an organic-rich, tight shale, evaporative losses will be much less. Espitalie *et al.* (1984) reported that maximum loss of C1–C8 hydrocarbons from air-dried cuttings occurred after

about 12–15 minutes. Thus, after a short drying time, the yield of these compounds began to decrease rapidly.

Some petroleum will also be found in pyrolysis yields. In organic-rich source rocks often 10% of petroleum will be imbibed in kerogen. Organic-rich Bakken Shale will often have very high yields of petroleum when comparison of whole and extracted rock pyrolysis (S2) yields is completed (Jarvie *et al.*, 2011). In heavy oil plays, such as the Monterey Shale, oil carryover into pyrolysis yields can be very high sometimes accounting for over 50% of the extractable organic matter. This carryover often affects $T_{\max}$ measurements by skewing the pyrolysis peak toward lower temperatures. Bakken Shale extracted rocks have about 5°C higher $T_{\max}$ values (Jarvie *et al.*, 2012b), whereas Monterey Shales have been reported to have $T_{\max}$ values up to 16°C higher than unextracted rocks (Kruege,

1983). Thus, extracted rocks provide a more accurate assessment of S2 yields (and hence, HI) as well as more representative $T_{\max}$ values. The difference between the whole and extracted rock S2 yields can be added to S1 to obtain the yield of oil less evaporative losses.

Evaporative losses from shale oil resource systems can be estimated by analyzing rock extracts by gas chromatography and comparing them to produced oils from the same horizon. A gas chromatographic (GC) fingerprint of the Upper Bakken Shale, the produced oil, and the reservoir rock, the Bakken Formation Middle Member, at Parshall field, Mountrail County, North Dakota, shows the presence of C_{15} - hydrocarbons in the shale and produced oil, but their absence in the produced reservoir rock (Fig. 8). The rock samples are core chips and were analyzed after one year of storage at the North

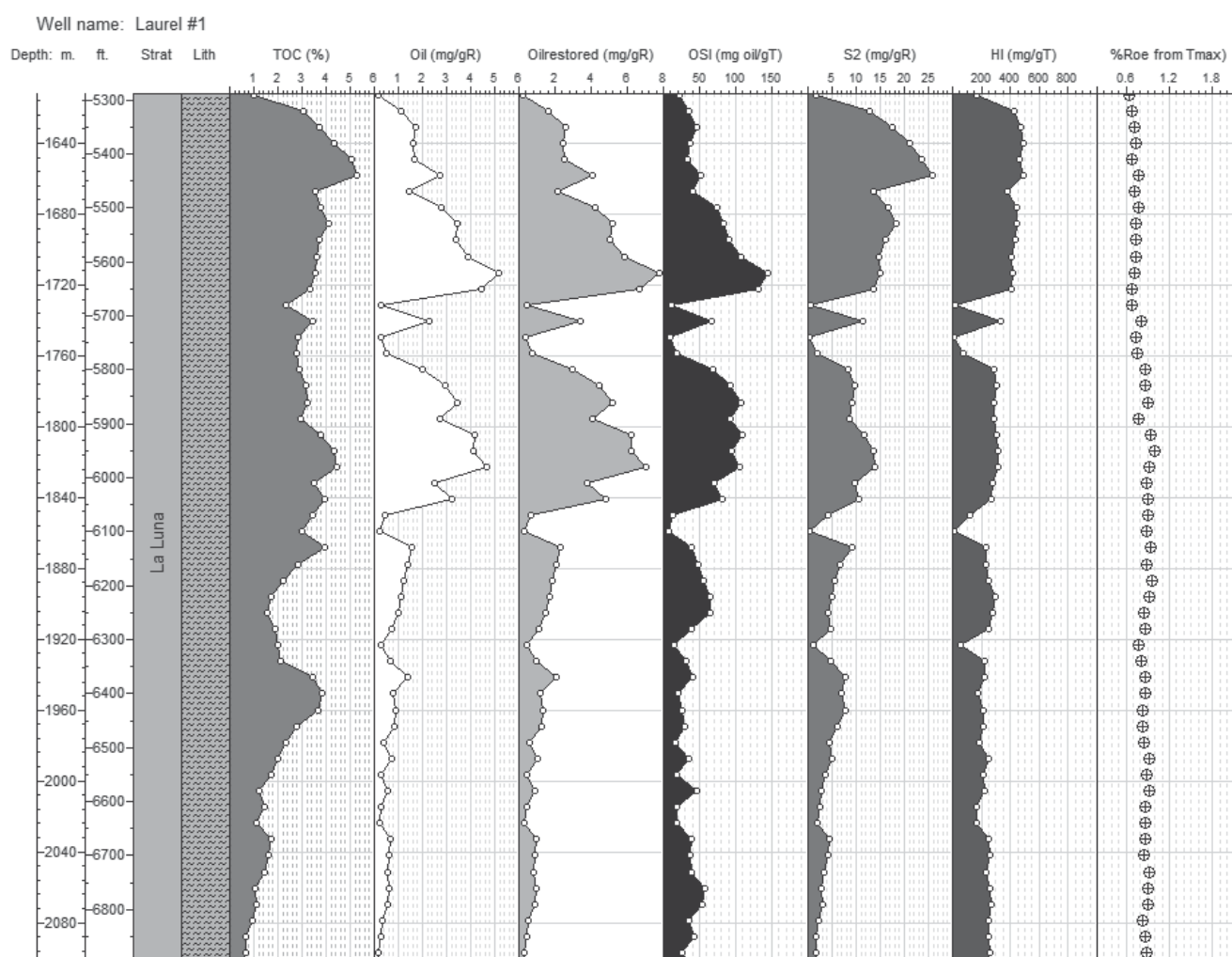


FIGURE 7. Geochemical log of a La Luna (Colombia) well showing the oil crossover effect, where the oil saturation index ($S1 \times 100/TOC$) exceeds 100mg oil/g TOC. In this well zones of elevated oil content are between 1676–1722 and 1776–1840m. OSI is the oil saturation index or normalized oil content ($S1 \times 100 / TOC$); S2 is the petroleum potential, HI is hydrogen index, %Roe is the equivalent vitrinite reflectance value derived from $T_{\max}$, and $T_{\max}$ is the temperature at the maximum evolution of the pyrolysis peak and is related to thermal maturity.

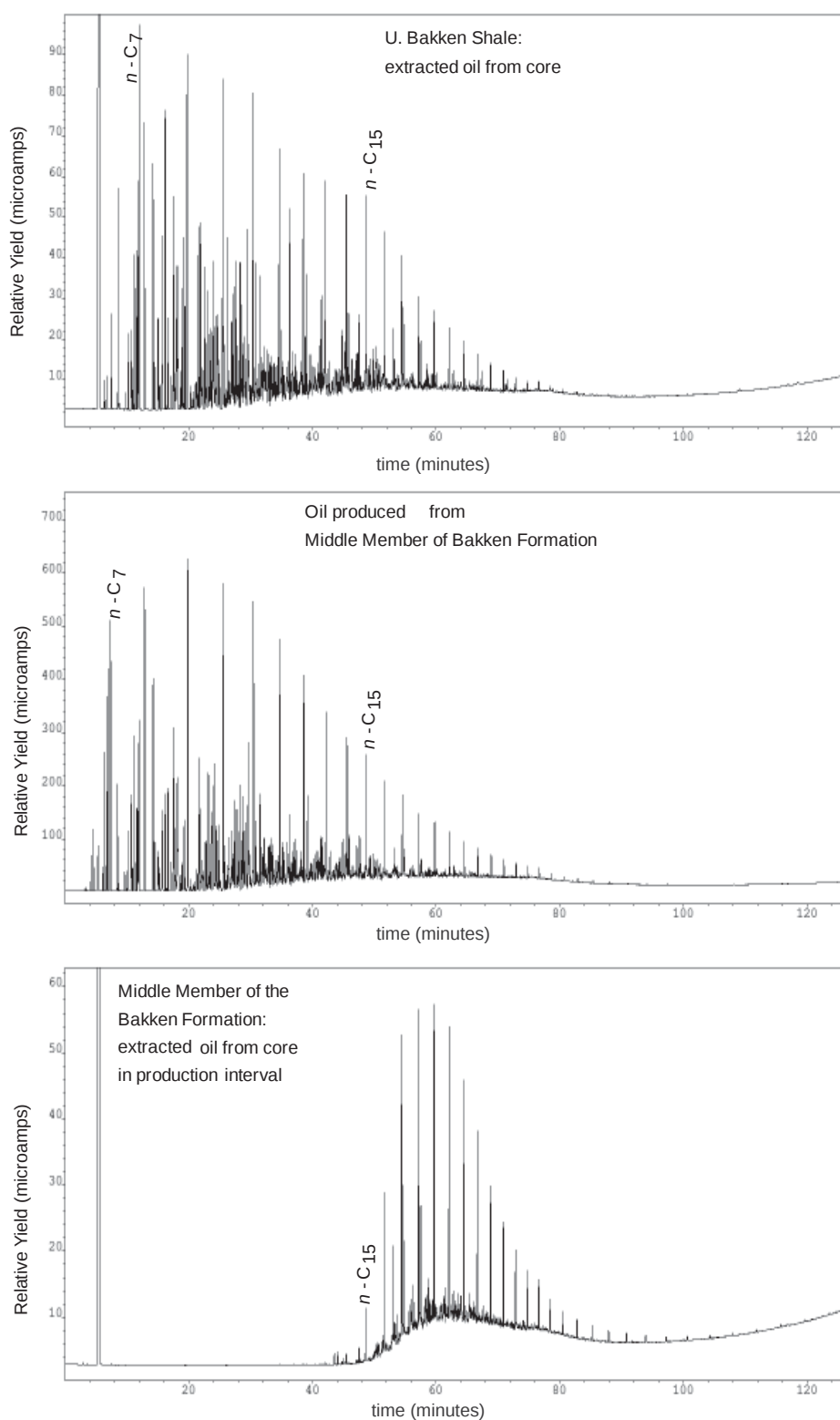


FIGURE 8. High-resolution gas chromatographic (GC) fingerprints of extracts from the Upper Bakken Shale and the Bakken Middle Member as well as a produced oil. The produced oil is from the Middle Member. The Upper Bakken Shale is very organic-rich (ca. 15 wt.% TOC) and is highly oil saturated, whereas the Middle Member (dolomitic limestone) is organic-lean (<0.50 wt.% TOC) and is also highly oil saturated. However, there is strong sorption of oil in the shale due to its organic content, whereas the Middle Member readily releases its volatile oil as shown by the absence of C₁₅-hydrocarbons in the Middle Member extract fingerprint.

Dakota Geological Survey so the same conditions were experienced by the rock samples. Topping (evaporation) of the produced oil allows reconstruction of the S1 value as it takes about 80% evaporation of the produced oil to match the fingerprint of the Middle Member; thus, the measured S1 value is about 80% low. This also clearly demonstrates why the organic-lean Middle Member is a much better reservoir rock – it readily gives up its oil. The Upper Bakken Shale strongly retains even the light end hydrocarbons under the identical storage and analytical conditions due to retention by organic matter, which is absent in the Middle Member.

Oil contained in S1 and any oil loss by evaporation is more mobile than any oil imbibed in organic matter in the source rock. Thus, the total S1 value provides an indication of the total oil-in-place assuming the evaporative loss can adequately be restored. However, the measured S1 yield plus restored evaporative losses are more indicative of mobile oil, whereas oil in kerogen is less mobile, *i.e.*, less producible. This goes to the heart of the matter: oil is more readily producible from organic-lean hybrid systems that have fractionated, higher quality (less polar) oil composition.

The underestimation of free oil is also evident in old cuttings samples when compared to fresh cuttings and rotary sidewall cores (RSWC) (Fig. 9). A well was drilled in 2011 that offset a previously drilled well

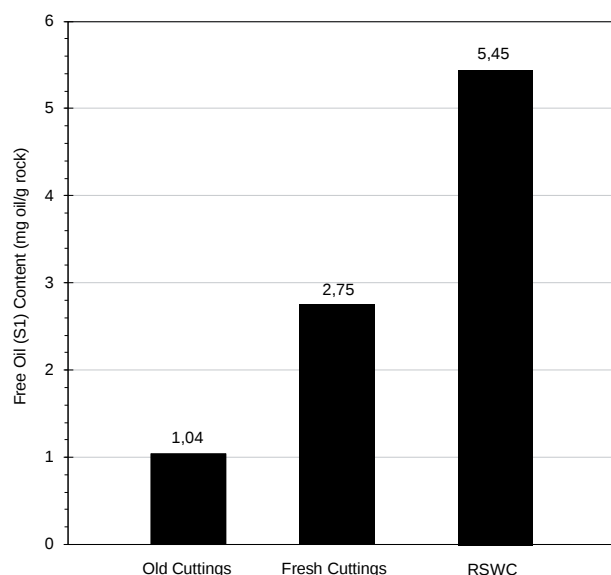


FIGURE 9. Comparison of measured oil contents (S1) from archived (old) cuttings versus fresh cuttings and fresh rotary sidewall core (RSWC). The archived well was drilled in the 1980s and so oil has evaporated from the cuttings. The fresh cuttings are about double the old cuttings, but the RSWC samples are about five times higher. Using the GC fingerprinting approach aids the restoration of S1 oil contents.

from the 1980s, where cuttings were available from a sample repository. The old cuttings ($n=24$) have a median S1 value of 1.04mg oil/g rock, whereas fresh cuttings ($n=19$) from the new well yield 2.75mg oil/g rock. RSWC ($n=11$) average five times higher at 5.45mg/g. These data show an increase in oil yield from approximately 24boe/acre-ft to 124boe/acre-ft. For a 100ft thick section this represents the difference between 1.5mmboe/section and 8.0mmboe/section. This substantiates the fact that old cuttings represent the minimum S1 oil values at best.

The typical acquisition of Rock-Eval S1 (mg oil/g rock) is programmed at 300°C for 3 minutes to vaporize oil out of the rock sample. This is the standard and most widely used program estimated to be completed on 99% of shale resource plays in the USA. In fact this is the standard analysis program for nearly all programmed pyrolysis. Reservoir assessment programs, such as Saudi Aramco's POPI procedure (*e.g.* Jones *et al.*, 2007), have a programmed isotherm starting at 180 to 215°C, but this is for estimating physico-chemical properties such as API gravity of retained oil. For detecting high oil saturations in shale resource plays, it is desired that S1 oil yields be optimized without cracking any bitumen or kerogen. Thus, 300°C is the standard.

Using identical programmed S1 isotherm data at 300°C demonstrates that S1 values from the Rock-Eval® 6 instrument (Vinci Technologies, Suresnes, France) are 25–35% lower than in the Rock-Eval® 2 instrument (NIGOGA, 2000) and even lower than the S1 values from the HAWKSM pyrolysis instrument (Wildcat

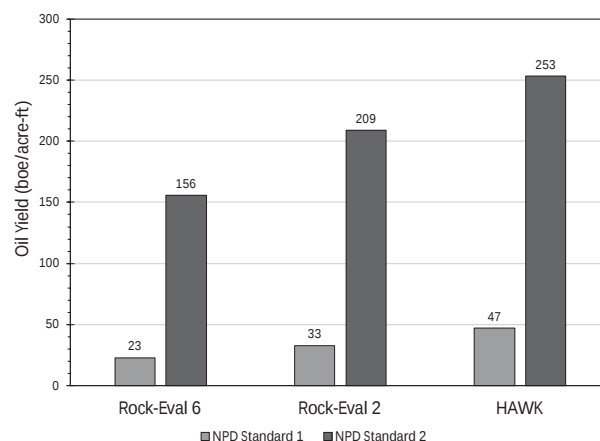


FIGURE 10. Relationship of free oil contents (S1) as measured by Rock-Eval 6, Rock-Eval 2, and HAWK instruments. All instruments were programmed to the same temperatures and times for S1 analysis. The Rock-Eval 6 instrument records lower free oil contents than either the Rock-Eval 2 or HAWK instruments leading to 25–35% lower estimates of oil contents. NPD is the Norwegian Petroleum Directorate.

Technologies, Humble, TX) (Fig. 10). If the values were recorded in a 200ft-thick shale, the yield would be lower by 6.7mmboe/section versus 12.4 million boe in the Wildcat HAWK. The reasons for these different yields are related to oven closing and sealing mechanics, carrier gas type and flow, and true temperatures in the oven.

GOR ESTIMATION

In drilling unconventional reservoirs it is important to determine the product type prior to drilling, *i.e.*, gas versus oil. Determination of oil and gas windows via thermal maturity determinations is the first step in such assessments, but this is further refined by description of the petroleum phase ranging from black to volatile oil, gas condensate and dry gas. These terms are often loosely applied, but a good approach is to utilize gas-to-oil ratios as a descriptive term in such assessments. For example, the SPE uses greater than 100,000scf/stb (standard cubic feet per stock tank barrel) to define the dry gas phase (Whitson and Brulé, 2000; Jarvie, 2014). The volatile oil window, which is perhaps the most important window for effective shale oil production, is about 1000 to 3500scf/stb. Less than 1000scf/stb is a typical black oil with higher resins and asphaltenes than a volatile oil. API gravities in volatile oils are usually 40–50°API, whereas black oils are less than 40°API.

In addition input to reservoir assessments by petroleum engineers requires estimation of initial GOR (gas-to-oil ratios). This is done by narrowing the value based on known reservoir pressures and temperatures and then estimating the GOR that best fits these results.

Using light hydrocarbon data, Mango and Jarvie (2001) correlated concentrations of select C_6 and C_7 isoalkanes to reported GOR values in the Williston Basin, USA. Various oils were used in this correlation, including carbonate-sourced Mississippian oils, shale-sourced Upper Devonian Bakken oils, and Ordovician Red River-sourced oils. This same approach was extended to petroleum source rocks using a proprietary solvent extraction technique that preserve the light hydrocarbons, when present. This allows prediction of the reservoir state, in some cases prior to drilling from existing core or cuttings samples, or after drilling to assist reservoir engineering efforts. The calculated GOR from light hydrocarbons is referred to as the “intrinsic” GOR as it reflects in situ reservoir, not surface conditions.

GOR is difficult to ascertain as there are many operational parameters that affect GOR at production

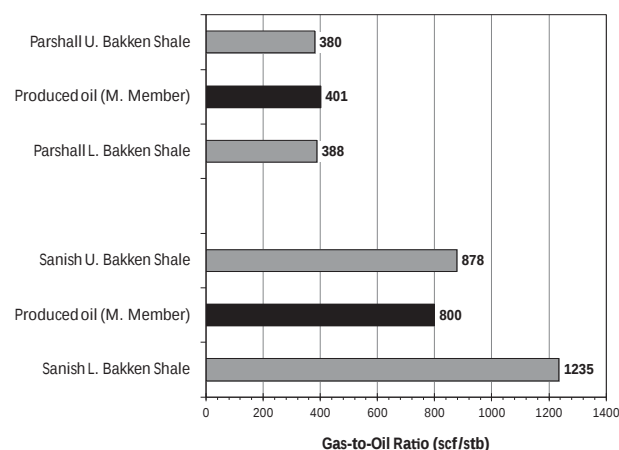


FIGURE 11. Intrinsic gas-to-oil ratio (GOR) values calculated from C_6 and C_7 hydrocarbons on Upper and Lower Bakken Shales compared to production GOR. The average values of the Bakken Shales from Parshall compare favorably to the production GOR. At Sanish Field, the intrinsic GOR of the Upper Bakken Shale compares favorably to production GOR, whereas the Lower Bakken Shale is higher.

facilities. These include how a well is choked (restrained), condensate-banking, and where the gas and oil measurements are taken. On the other hand, intrinsic GOR calculations provide another basis for assessment of the state of petroleum in the reservoir rock itself.

When intrinsic GOR values are compared to reported production values in the Middle Member of the Bakken Formation at Parshall Field, Williston Basin, the Upper Bakken Shale averaged 377scf/stb, whereas production GOR averages about 400scf/stb (Jarvie *et al.*, 2011). At Sanish Field, just a few miles northwest of Parshall Field, the Upper Bakken Shale averages 821scf/stb for intrinsic GOR, whereas production is about 800scf/stb (Jarvie *et al.*, 2011) (Fig. 11). However, the intrinsic GOR on the Lower Bakken Shale averages 1207scf/stb suggesting it is not the primary source of the Middle Bakken oil at Sanish Field.

Comparison of intrinsic GOR values in the Eagle Ford Shale are shown to vary by maturity regime. For example, low maturity Eagle Ford oils in Frio County, Texas have low API gravity (20–29°API). Typical production GOR values are 100–300scf/stb, whereas computed intrinsic values are comparable. As thermal maturity increases, GOR increases rapidly. When very high maturity condensates are encountered such as in the Haynesville Shale in East Texas and Western Louisiana, production GOR values are very high typically ranging from 30,000 to greater than 100,000scf/stb. Intrinsic GOR values are typically lower than production reported values, but are still indicative of the reservoir phase.

Prediction of the product type or phase of petroleum is a critical factor in successful production.

TABLE 4. Approximate values for desired product or phase. The best production from shale oil resource plays is usually when volatile is present in the reservoir, whether in the shale itself or a hybrid. However, the best shale gas production is from shales where the gas is very dry, *i.e.*, polar oil components removed from the system by cracking

Product	TR (%)	°API	GOR (scf/stb)	Yield (bbls/mmcf)
Black oil	< 65	< 40	< 1,500	na
Volatile oil	65 - 79	40 - 49	1,500 - 3,499	667 - 286
Gas condensate	80 - 89	50 - 54	3,500 - 9,999	285 - 101
NGLs	90 - 95	55 - 60	10,000 - 99,000	100 - 10
Dry gas	> 95	> 60	> 100,000	< 10

These predictions have typically been based on thermal maturity parameters such as measured vitrinite reflectance or other chemical maturity parameters. These are good techniques when the data can be acquired accurately, which is not always a trivial process on marine shales or carbonates that have minimal vitrinite particles, have oil carry-over into pyrolysis affecting T_{max} , and other caveats. Application of intrinsic GOR values provide another means of estimating product and phase (Table 4). Various data can be used to further optimize the maturity – phase relationship, but intrinsic GOR provides a direct indication of phase.

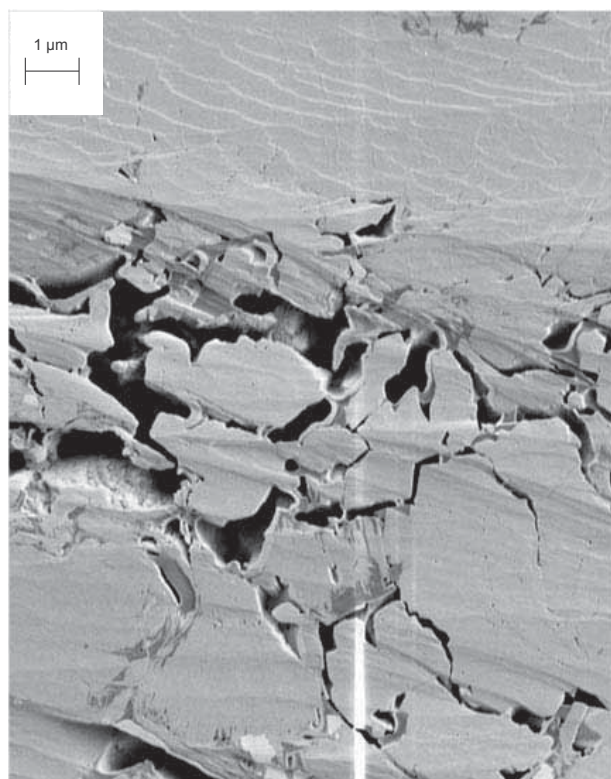


FIGURE 12. Micrograph of acid etched carbonate source rock. This picture shows evidence of acidic action on a carbonate source rock.

ORGANIC ACIDS

In the late 1980s and early 1990s publications on the potential impact of organic acids on creation of secondary porosity in conventional reservoir systems was investigated (*e.g.* Bjorlykke, 1984; Surdam *et al.*, 1984; Stoessler and Pittman, 1990; Barth *et al.* 1990; 1992). This potential was largely discounted and discussion discontinued. However, in unconventional systems there is physical evidence of acid etching, acid-derived migration conduits, and secondary porosity. This is evident in hybrid systems with carbonates closely associated with organic-rich mudstones (Fig. 12). There is considerable carbon dioxide and water released during kerogen diagenesis and continued carbon dioxide and organic acids release during petroleum generation. While carbonic acid is a very weak acid, dissolution of carbonates occurs when in contact with even slightly acidic waters. Etching and secondary porosity has been imaged in Middle Member Bakken Formation carbonates, Eagle Ford shale carbonates, and Brown Dense (Smackover) hybrid shale resource systems.

PRODUCTION DECLINE ANALYSIS

Shale Gas

The yield of gas from shale gas systems varies dramatically as illustrated by generalized production decline curves of various North American shale gas systems (Fig. 13). The Haynesville Shale yields the most gas based on this generalized comparison, yet it has approximately the same gas content as the Barnett Shale. The difference is related to increased storage and higher pressures in the Haynesville Shale. Porosity in the Haynesville Shale averages about 7%, whereas in the Barnett Shale porosity is typically about 4.5% (and is highly correlated

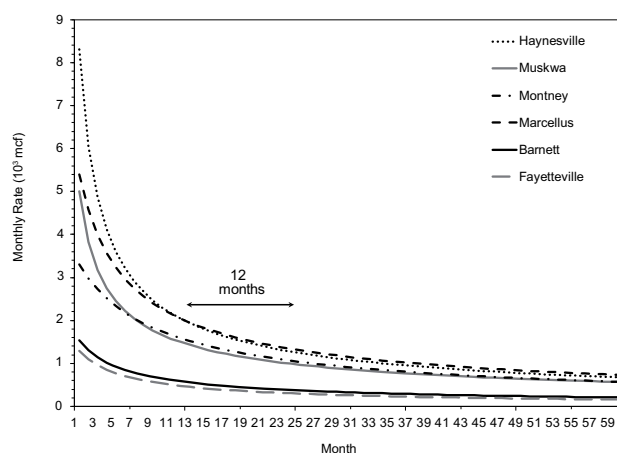


FIGURE 13. Production decline curves from the top six shale gas plays in North America by month in thousand cubic feet (mcf).

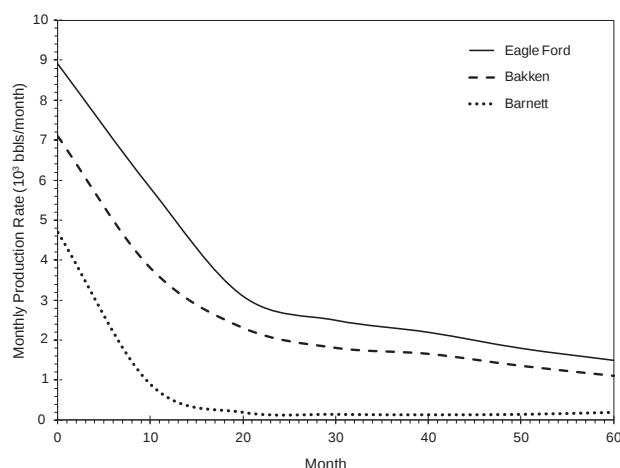


FIGURE 14. Production decline curves from three shale oil plays in the United States by month in barrels of oil.

to TOC). The free gas content is about 80% in the Haynesville Shale, whereas the Barnett Shale has only about 55% on average. Free gas flows from connected storage much more readily than adsorbed gas. Adsorbed gas flow occurs primarily after pressure draw down and is of lower economic return than free gas. Also the pressure gradient is very different between the two shales. While the Barnett Shale is over-pressured at about 0.52psi/ft, the Haynesville Shale is highly over-pressured at about 0.80psi/ft. These factors combine to give the variable gas flow rates between these two systems with much higher initial rates and EURs from the Haynesville Shale.

Shale Oil

Analysis of production data of shale oil systems provides insights into the difference between an organic-rich source rock system and a hybrid system. The Eagle Ford Shale and Middle Member Bakken Formation production decline curves show higher oil production than the Barnett Shale oil system (Fig. 14) (Lewis *et al.*, 2012). Both the Barnett and Eagle Ford shales are mudstones, each with about 5wt.% TOC. The Eagle Ford Shale is estimated to have a much higher HI_o at 600+ mg/g TOC (D. Jarvie, 2011, unpublished data) compared to the Barnett Shale at about 435mg/g HI_o (Jarvie *et al.*, 2007). With the lower production flow and EUR in the Barnett Shale compared to the Eagle Ford Shale, the key factors appear to be the Eagle Ford's less sorptive nature, higher storage capacity and permeability. The Barnett Shale is quartz-rich and brittle, thereby susceptible to excellent stimulation, however, the porosity is primarily organoporosity and the quartz content is biogenic, meaning the pores are closely associated with organic carbon and its sorptive capacity. One test for the presence of biogenic silica is any correlation between quartz content and TOC; if there is good correlation, the quartz content is likely biogenic rather than detrital.

The Eagle Ford Shale has double to almost triple the porosity with about three times more matrix porosity than organoporosity. The porosity is associated with carbonates that have very low adsorption affinities compared to kerogen. In addition the permeability is about ten times greater than the Barnett Shale. Finally, the higher HI_o in the Eagle Ford means that about 50–60% of the organic matter is convertible to petroleum, whereas only about 37% of the Barnett Shale is convertible to petroleum.

Similarly, Bakken Formation production is from the organic-lean and dolomitic Middle Member at Parshall Field, meaning lower retentive capacity than the organic-rich Bakken Shale, and because oil was expelled from the organic-rich shales, it has been fractionated into a higher quality oil (lower amounts of polar compounds) than in the shale itself.

LATIN AMERICA POTENTIAL FOR SHALE RESOURCE PLAYS

In Mexico and South America, numerous source rock systems have potential for shale gas or oil. In Mexico, the Eagle Ford Shale equivalent is the Boquillas Shale. It is exposed at road cuts in south Texas, where immature TOC values average about 4wt.% (n=10) with HI values of over 600mg/g TOC (D. Jarvie, 2011, unpublished data). There are also well known Tithonian source rocks that are organic-rich and age equivalent to the Bossier Shale.

Argentina leads the list with the most potential for shale resource systems, which include Cretaceous Vaca Muerta and Los Molles source rocks in the Neuquen Basin, Lower Cretaceous–Upper Jurassic Aguada Banders, Lower Cretaceous D-129, and Upper Jurassic Asfalto source rocks in the San Jorge Basin. The Austral Basin contains the Cretaceous Springhill source rock and the lacustrine Cacheuta Formation is found in the Cuyana Basin. Finally the Upper Cretaceous Yacoraite source rock is present in the Northwest Basin. It should be noted that lacustrine resource systems have proven to be difficult systems to produce.

In Venezuela the Cretaceous La Luna Shale is present and is also found in Columbia, which also has the Villeta Shale, both of which are carbonate and TOC-rich source rocks. In Ecuador and Peru, a carbonate source rock, the Napo Formation, holds promise as a shale oil resource play. Brazilian Devonian shales in the Solimoes Basin average 6wt.% TOC and are prospective for gas. In Uruguay Cretaceous lacustrine shales average 1–2wt.% TOC in the Santa Lucia Basin, whereas Paraguay has the Paleocene Upper Palo Santo source rock with 1–1.5wt.% TOC, most

likely in the gas window. Onshore Suriname may have shale oil potential as it has oil fields likely sourced by Cretaceous source rocks of Upper Albian to Cenomanian age.

Middle Devonian Tequeje, Limoncito, and Los Monos Formation source rocks are found in the Bolivian foothills and foreland basins (Moretti *et al.*, 1996). Other source rocks of significance include the Upper Devonian Tomachi Formation and the Upper Carboniferous–Lower Permian Copacabana Formation in the northern Sub-Andean Zone (Moretti *et al.*, 1996).

CONCLUSIONS

Unconventional shale resource systems hold substantial quantities of oil and gas, but because they are low porosity and often ultra-low permeability systems, they require high-energy stimulation. These systems consist of organic-rich source rocks or combination source rocks with juxtaposed organic-lean lithofacies that contain expelled oil from these source rocks. The source rock shale is the most obvious petroleum resource, but can be the most difficult to produce due to its sorptive affinity, more polar content in the oil window, and potentially lower brittleness than sands, silts, and carbonates. On the other hand, hybrid shale resource systems often provide optimum recoveries of unconventional petroleum as they have expulsion-fractionated oil of higher quality and are not organic-rich, thus lacking the sorptive (retentive) capacities of their organic-rich sources.

TOC is comprised of two principal components: a generative and a non-generative fraction referred to as generative organic carbon (GOC) and non-generative organic carbon (NGOC). GOC provides all the petroleum that is generated from a source rock and also provides an indication of the potential for organoporosity development. It may contain either oil or gas prone organic matter or a mixture of both.

Free oil content (S1) measured on any rock represents a minimum value due to losses inherent in sample retrieval, processing, storage, and handling. Oil content is minimized by evaporation of volatile compounds and carryover of petroleum into the pyrolysis peak. Yields of S1 are also variable depending on the instrumentation used for analysis. Some constituents of petroleum carry-over into pyrolysis but this can readily be determined by analyzing a whole and solvent extracted rock. However, S1 oil yields with restored evaporative losses represent the highly mobile oil fraction, whereas oil carried over into the pyrolysis yield is less mobile.

GOR is measured after production flow and usually higher GORs (>1000scf/stb) are necessary to move oil out of source rocks. Intrinsic GOR is calculated from light hydrocarbons and is useful for pre- or post-drill assessments of reservoir phase. It is an indication of the GOR in the reservoir rock itself rather than surface flow. The fact that source rocks retain hydrocarbons from ca. C5 and upward in carbon number illustrates how well organic-rich source rocks retain hydrocarbons as opposed to other organic-lean lithofacies.

Carbonic and other organic acids may play an important role in systems with high amounts of carbonate in the source rock or in juxtaposed lithofacies. Carbonic acid forms as water and carbon dioxide are generated from kerogen in the early oil window through the gas generation window. Although not a strong acid, the action of even slightly acidic water on carbonates is well documented and may be part of the enhanced storage created in such systems.

Production decline analysis shows inherent differences among various shale gas and oil systems. Organic-rich shale plays often have poorer performance than hybrids especially in the oil window. The decline rates for most systems are very high, averaging ca. 60% in the first year. The drainage volumes of these wells are limited, meaning many in-fill wells are needed to reasonably drain acreage held by operators. The modest production yields and limited drainage of given wells means that hundreds to thousands of wells are necessary to tap the total energy resource of these plays.

In Latin America many potential shale resource systems are present and show potential for either gas or oil. While success is not yet obvious given the short exploration history for such plays, it is likely that advances in technology will open these resources for parts of Latin America.

Organic geochemistry is only one part of the assessment required for unconventional shale oil or gas production. Rock mineralogy and mechanics are particularly important as they relate to the ability to stimulate a sufficient volume of rock filled with petroleum. Of course, the ultimate production result is related to the ability to complete and flow the petroleum-charged horizon successfully.

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