

# *Unconventional shale-gas systems: The Mississippian Barnett Shale of north-central Texas as one model for thermogenic shale-gas assessment*

**Daniel M. Jarvie, Ronald J. Hill, Tim E. Ruble, and Richard M. Pollastro**

## **ABSTRACT**

Shale-gas resource plays can be distinguished by gas type and system characteristics. The Newark East gas field, located in the Fort Worth Basin, Texas, is defined by thermogenic gas production from low-porosity and low-permeability Barnett Shale. The Barnett Shale gas system, a self-contained source-reservoir system, has generated large amounts of gas in the key productive areas because of various characteristics and processes, including (1) excellent original organic richness and generation potential; (2) primary and secondary cracking of kerogen and retained oil, respectively; (3) retention of oil for cracking to gas by adsorption; (4) porosity resulting from organic matter decomposition; and (5) brittle mineralogical composition.

The calculated total gas in place (GIP) based on estimated ultimate recovery that is based on production profiles and operator estimates is about 204 bcf/section ( $5.78 \times 10^9 \text{ m}^3/1.73 \times 10^4 \text{ m}^3$ ). We estimate that the Barnett Shale has a total generation potential of about 609 bbl of oil equivalent/ac-ft or the equivalent of 3657 mcf/ac-ft ( $84.0 \text{ m}^3/\text{m}^3$ ). Assuming a thickness of 350 ft (107 m) and only sufficient hydrogen for partial cracking of retained oil to gas, a total generation potential of 820 bcf/section is estimated. Of this potential, approximately 60% was expelled, and the balance was retained for secondary cracking of oil to gas, if sufficient thermal maturity was reached. Gas storage capacity of the Barnett Shale at typical reservoir pressure, volume, and temperature conditions and 6% porosity shows a maximum storage capacity of 540 mcf/ac-ft or 159 scf/ton.

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A point of concern for reviewers was the use of personal communications, unpublished data and presentations, and abstracts. Their concerns are well founded because such materials are not readily available to all readers of *AAPG Bulletin* and certainly have not been subjected to rigorous peer review. We share those concerns but did use those materials because of the dearth of publications on the Barnett Shale. These references may be subjective and may rely on personal opinions, antidotal observations, or strictly empirical data. Care should be exercised in extending information from these references until they are verifiable by rigorous study and peer-reviewed publication. In addition, we thank the Oil Information Library of Fort Worth and its curator, Roy English, and the Bureau of Economic Geology, especially Steve Ruppel and colleagues in Austin, as well as James Donnally and Randy McDonald, for their assistance in providing information and access to samples.

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### INTRODUCTION

Unconventional shale gas has evolved into an important resource play for the United States, accounting for more than 14% of produced gas in the United States by the end of 2004 (Energy Information Administration [EIA], 2004). These are typically source rocks that also function as reservoir rocks and are a class of continuous petroleum accumulations (Schmoker, 1995). An unconventional, continuous petroleum system consists of an accumulation of hydrocarbons that are found in low-matrix-permeability rocks that depend on fracture permeability (either natural or as a result of stimulation) for production and contain large amounts of hydrocarbons, but with low gas recovery factors (Schmoker, 1995).

Shale-gas systems are of two distinct types: biogenic and thermogenic (Claypool, 1998), although there can also be mixtures of the two gas types. Biogenic shale-gas plays, such as the Antrim Shale of the Michigan Basin (Martini et al., 2003), contain dry gas adsorbed to organic matter. After dewatering, these wells will have modest initial gas flow rates in the 50–400 mcf/day (1416–11,327 m<sup>3</sup>/day) range, but with production histories upward of 30 yr.

Several types of continuous, thermogenic shale-gas systems exist, including (1) high-thermal-maturity shales (e.g., Barnett Shale of the Fort Worth Basin); (2) low-thermal-maturity shales (e.g., some New Albany Shale in areas of the Illinois Basin); (3) mixed lithology intraformational systems containing shale, sands, and silts (e.g., Bossier Shale of east Texas); (4) interformational systems where gas is generated in a mature shale and stored in a less mature shale (e.g., Tertiary Waltman Shale Member of the Wind River Basin, Wyoming); and (5) combination plays that have both conventional and unconventional production (e.g., some vertical Anadarko Basin wells producing from Wapanucka and Hunton reservoirs, as well as the Woodford Shale). There may also be mixed systems containing both thermogenic and biogenic gas (e.g., possibly some New Albany Shale gas systems) (Jarvie et al., in press).

The Barnett Shale of the Fort Worth Basin, Texas, has evolved into the preeminent shale-gas resource play because of the long-term development efforts of Mitchell Energy Corporation (now part of Devon Energy) and subsequent operators in the basin (Givens and Zhao, 2004; Steward et al., 2006; Steward, in press). The estimated ultimate recovery (EUR) from this low-porosity and low-permeability black shale is 2.5–3.5 bcf (7.08–9.91 × 10<sup>7</sup> m<sup>3</sup>) of gas from horizontal wells drilled in the core producing areas (counties with the highest production to date) (Mortis, 2004). The Barnett Shale is found at depths of generally 6500–8500 ft (1981–2591 m), with average thickness of about 350 ft (106.7 m) in the core areas, although values range from 50 or less to more than 1000 ft (15.2 or less to more than 304.8 m) across the basin (Pollastro, 2003; Pollastro et al., 2003; Montgomery et al., 2005). Although these shale-gas wells have modest gas flow rates compared to conventional plays, they also have modest drilling costs, so the rate of return (ROR) is commonly 100% within 1 yr in the core area and 65% in noncore areas

(areas where production is not well established; EOG Resources Inc., 2006).

Gas storage in the Barnett Shale is primarily as free gas with lesser amounts of adsorbed gas. Gas is derived from both thermogenic cracking of kerogen and from cracking of any retained oil in the shale (Jarvie et al., 2003; Montgomery et al. 2005). Areas where the Barnett Shale is in the oil window (0.60–0.99%  $R_o$ ) (see appendix for explanation of terms) generally have gas flow rates or EURs that are lower than wells in the core area (Bowker, 2003a) because only oil-associated gas is generated in this maturity window.

Mineralogy appears to be a key factor characterizing the best wells (Bowker, 2003a). The best Barnett Shale production comes from zones with 45% quartz and only 27% clay (Bowker, 2003a). The brittleness of the shale is key to stimulation whereby a fracture network is created, providing linkage between the wellbore and the microporosity (average 6%). Pore throats are typically less than 100 nm in the Barnett Shale (Bowker, 2003a). Although fractures in the Barnett Shale are necessary for good production, macrofractures near major fault zones are less productive because fractures are being filled with carbonate cement and are less responsive to stimulation (Bowker, 2003a). Faults are also conduits for stimulation energy instead of fracturing the indurated shale. Such stimulation generally will not reach much of the microporosity, and the result is poor shale-gas wells.

The Barnett Shale gas system is sealed by limestone above the Barnett Shale and in some areas below the shale. These limestones generally have higher fracture thresholds than the shale itself, thereby providing barriers to stimulation to optimize fracturing of the gas-bearing shale (Martineau, 2001). However, Barnett Shale has been shown to be highly productive in areas where the lower stimulation barrier is not present using horizontal wells and rigorous stimulation without breaking into the underlying brine-bearing limestones of the Ellenburger Formation (Marble, 2004, 2006).

Although it is known that the Barnett Shale is organic rich, has high gas contents, and responds to stimulation efforts, it is not evident why it is such a prodigious shale-gas system. The goal of this article is to understand the geochemical criteria that make the Barnett Shale of the Fort Worth Basin a prodigious gas resource given its unconventional low porosity and permeability reservoir characteristics. To evaluate this hydrocarbon resource system, it is important to understand various geochemical processes and shale characteristics controlling generation, storage, and access to this gas resource.

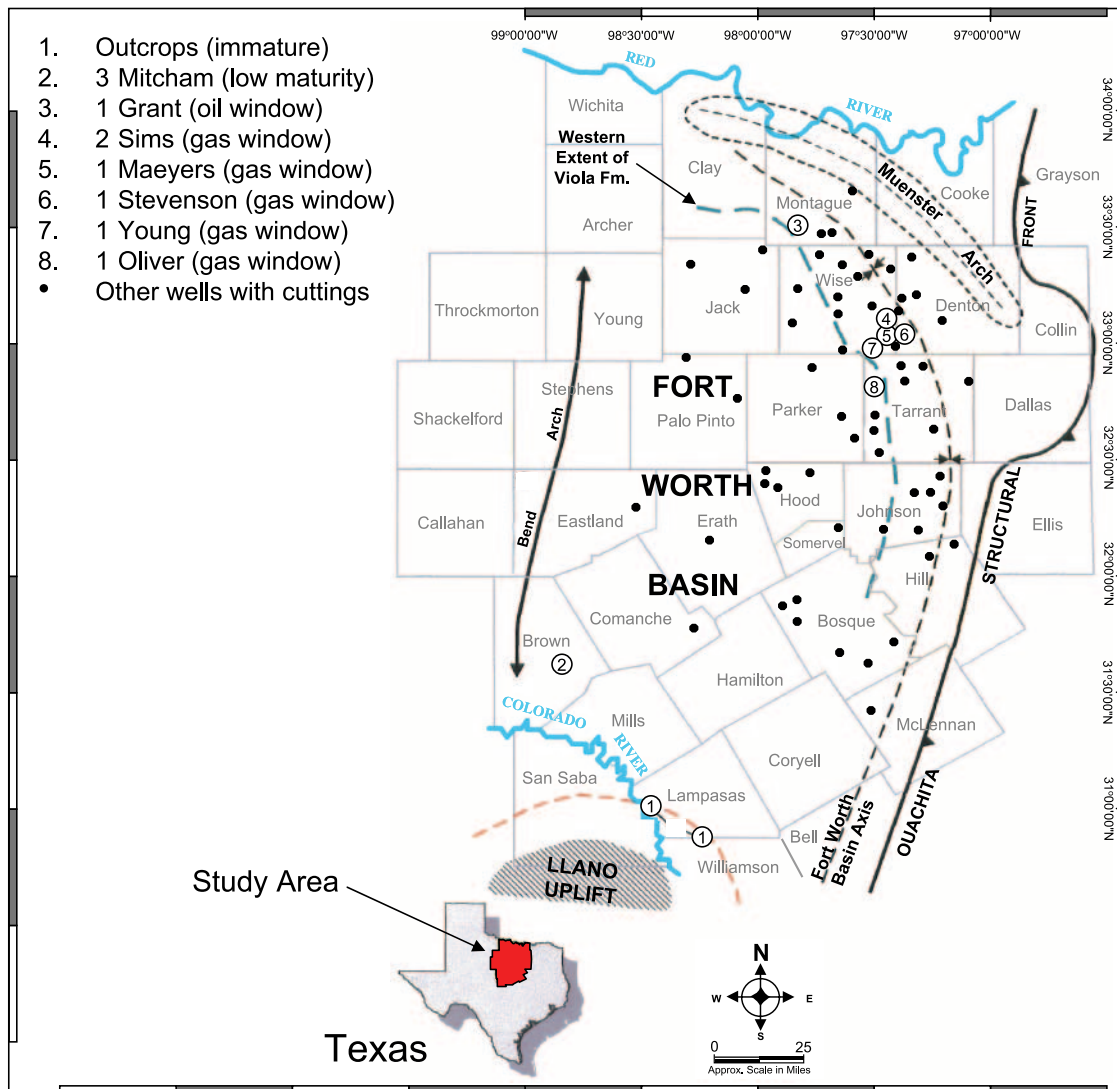
## GEOLOGIC SETTING

The Barnett Shale occurs in a 38-county area of the Fort Worth Basin in north-central Texas, with the main producing areas north and south of Fort Worth, Texas (Figure 1). Montgomery et al. (2005) and Pollastro et al. (2007) provide a summary of the geologic evolution of the Fort Worth Basin. The Barnett Shale occurs in other nearby basins, such as the Hardeman, Kerr, Marfa, and Permian basins. Age-equivalent shales, as well as underlying Devonian black shales, are present along the eastern flank of the Ouachita thrust front in the Delaware, Arkoma, and Black Warrior basins and along the Appalachian Mountains, extending into the northeastern parts of the United States.

The Barnett Shale can be divided into five lithofacies: (1) black shale, (2) lime grainstone, (3) calcareous black shale, (4) dolomitic black shale, and (5) phosphatic black shale (Henk et al., 2000; Henk, 2005; Hickey and Henk, 2006; Loucks and Ruppel, 2007). All lithofacies yield high gamma-ray responses ( $>100^\circ$  API), with the phosphatic shales having the highest response. Micropores in thin sections show no evidence of connectivity, consistent with the low permeability of the shale. Thin sections also reveal the presence of pyrite, scattered calcite shell fragments, occasional silicified *Tasmanites* (algal fragments), and conodonts. Poorly sorted lime grainstones are indicative of sediment gravity flows.

Figure 2 is a generalized Fort Worth Basin stratigraphic column (Flippin, 1982). The Barnett Shale unconformably overlies limestones of the Ordovician Viola Limestone in eastern parts of the basin. The Viola Formation in this area provides the basal seal and stimulation barrier to prevent Ellenburger Group waters from entering the wellbore during completion, although it is now evident that wells can be completed with high flow rates where the Viola Limestone is missing (Marble, 2004, 2006). The Devonian section is absent in the Fort Worth Basin as is the entire Permian section.

The Barnett Shale is conformably overlain by Pennsylvanian Marble Falls Limestone. In the eastern part of the basin, the upper quarter of the Barnett Shale is separated from the lower Barnett Shale by the Forestburg limestone. Original completions in the Barnett Shale by Mitchell Energy were only made in the lower Barnett Shale, and they later put the upper Barnett Shale under stimulation, adding about 25% to the EUR of their wells (Bowker, 2003a). Minor amounts of Cretaceous rock occur in certain parts of the basin, and Tertiary rocks are absent.



**Figure 1.** Generalized structure and well and outcrop location map. Well core samples are shown with numbers; other wells where cuttings only were available are shown with solid black circles (modified and with permission from the Fort Worth Oil Information Library).

**BACKGROUND: BARNETT SHALE GAS AND OIL SYSTEMS**

A petroleum system comprises various components, including source rock, migration pathway, reservoir rock, seal, and overburden (Magoon and Dow, 1994). Processes inherent to such a system include generation, expulsion, accumulation, overburden deposition, and preservation of hydrocarbons (Magoon and Dow, 1994). In addition, petroleum adsorption and its impact on expulsion and secondary cracking of any retained oil (Stainforth and Reinders, 1990; Thomas and Clouse, 1990; Pepper, 1992; Sandvik et al., 1992) are also important processes that are critical to un-

derstanding the gas in place (GIP) in the Barnett Shale.

The Barnett Shale has been buried to sufficient depth and/or exposed to hot fluid flow to reach oil- or gas-generation stages in most parts of the Fort Worth Basin. In areas where the Barnett Shale reaches gas-window thermal maturity ( $> 1.0\% R_o$ ) (vitrinite reflectance in oil) and especially above  $1.4\% R_o$ , there are large continuous commercial gas resources. The Newark East gas field, now the largest gas field in Texas, has estimated mean gas resources of 26.2 tcf ( $7.4 \times 10^{11} \text{ m}^3$ ) (Pollastro et al., 2003) and has grown from the 87th largest in the early 1990s to the second largest gas field in the United States (EIA, 2006).

GENERALIZED SUBSURFACE STRATIGRAPHIC SECTION					
SYSTEM	STAGE	GROUP	FORMATION		
CRETACEOUS	LOWER	COMANCHE	FREDRICKSBURG	GOODLAND PALUXY	
			TRINITY	GLEN ROSE	
			THRIFTY	BRECKENRIDGE KING	
PENNSYLVANIAN	UPPER	CISCO	GRAHAM	GUNSIGHTS SWASTIKA BUNGER	
			CANYON	CADDO CREEK	HOME CREEK LIMESTONE COLONY CREEK SHALE
				BRAD	RANGER LIMESTONE PLACID SHALE
		GRAFORD		WINCHELL CEDAR TOWN ADAMS BRANCH UPPER BROWNWOOD SHALE	
		WHITT	PALO PINTO KEECHI CREEK ALESVILLE		
		MIDDLE	STRAWN	LONE CAMP	CAPPS LIME MORRIS SANDSTONE GARNER
	MILLSAP LAKE			GRINDSTONE CREEK LAZY BEND	
	KICKAPOO CREEK			CADDO I	RAVILLE PARKS CADDO POOL
	ATOKA		CADDO II AND III PREGNANT SHALE BIG SALINE	SMITHWICK ATOKA CLASTICS	
	LOWER	MORROW	MORROW	SMITHWICK	
	MISSISSIPPIAN	CHESTER		COMYN	
		MERAMEC	<b>BARNETT SHALE</b>		
OSAGE			CHAPPEL		
ORDOVICIAN		VIOLA	VIOLA		
		SIMPSON	SIMPSON		
	CANADIAN	ELLENBURGER	HONEYCUT		
			GORMAN		
		TANYARD			
CAMBRIAN	OZARKIAN		WILBERNS		
	UPPER		RILEY HICKORY		
PRECAMBRIAN					

**Figure 2.** Generalized stratigraphic column in the Fort Worth Basin (modified from Flippin, 1982). Used with permission from the Dallas Geological Society.

The Barnett Shale is the primary source for petroleum in the Fort Worth Basin, sourcing conventional reservoir systems with both oil and gas (Jarvie et al., 2003; Montgomery et al., 2005; Hill et al., 2007). The Newark

East gas field initially comprised gas produced from the Pennsylvanian Bend Conglomerate (locally known as the Boonsville conglomerate), which is sourced from the Barnett Shale. These reservoirs are charged by gas generated

during the oil window at inferred maturities of 0.70–1.00%  $R_o$  based on carbon isotopic values (Jarvie et al., 2003; Hill et al., 2007). In addition, the Barnett Shale has sourced petroleum in conventional oil reservoirs, including Ellenburger, Chappel, Strawn, and various other stratigraphically distinct reservoir units based on high-resolution gas chromatography, carbon isotopes, and biomarkers (Jarvie, 2000; Jarvie et al., 2001, 2005, 2006; R. J. Hill, D. M. Jarvie, R. M. Pollastro, K. A. Bowker, and B. L. Claxton, 2004, unpublished work; Hill et al., 2007). High-resolution light hydrocarbon data suggest some terrigenous oil input to a few production oils, which is possibly caused by organofacies variations within the Barnett Shale or mixing with Pennsylvanian Smithwick Shale hydrocarbons (Jarvie et al., 2003). The Smithwick Shale has excellent TOC values (1–3 wt.%), but with low initial hydrogen indices (<200 mg HC/g rock), making it a type III gas-prone kerogen (Jarvie and Henk, 2006). No other horizons in the Fort Worth Basin have been identified that have petroleum source potential.

## SAMPLES AND EXPERIMENTAL RESULTS

A geochemical database consisting of 315 cores, 488 cuttings, and 6 outcrop samples of the Barnett Shale in the Fort Worth Basin was used to determine its geochemical characteristics including gas-generation potential. Core samples from six different high-thermal-maturity Fort Worth Basin wells obtained from the Texas Bureau of Economic Geology were analyzed at 1-ft (0.3-m) intervals with average values reported in Table 1. Oryx provided core samples from the Oryx 1 Grant well located in Montague County, which is in the middle oil window (0.80%  $R_o$ ). Cuttings samples are from 35 wells in 17 different counties, with average values for all samples and for lower-thermal-maturity samples ( $T_{max} < 440^\circ\text{C}$ ) reported in Table 1 (see the appendix for definition of Rock-Eval parameters). In addition, six outcrop samples from two locations in the far south-western Fort Worth Basin provided thermally immature Barnett Shale samples, as does one set of cuttings from the Explo Oil 3 Mitcham well in Brown County.

## KEROGEN TYPE

The average original hydrogen index ( $HI_o$ ) value of immature Lampasas County outcrop samples (1, Figure 1) is 475 mg HC/g TOC, indicative of type II marine oil-prone kerogen (Jones, 1984). Cuttings samples from the

Explo Oil 3 Mitcham well in Brown County (2, Figure 1) are low thermal maturity ( $\sim 0.60\%$   $R_o$ ) and have lower  $HI_o$  than the Lampasas outcrops averaging 392 mg HC/g TOC. Thus, measured  $HI_o$  values for low-thermal-maturity samples range from 392 to 475 mg HC/g TOC. When these low-maturity cuttings and the immature outcrop samples are combined on a plot of Rock-Eval  $S_2$  vs. TOC, the slope of the best-fit line gives  $HI_o$  of 533 mg HC/g TOC (Langford and Blanc-Valleron, 1990; Cornford et al., 1998) (Figure 3). Thus,  $HI_o$  covers a range of values from 392 to 533 mg HC/g TOC based on both measured and graphical interpretation of measured data.

Visual assessments of kerogen indicate the presence of 95–100% amorphous (structureless) organic matter with occasional algal *Tasmanites*, confirming the chemical kerogen type. Minor amounts of terrestrial organics may also be found. Although this kerogen type is associated with anoxia, this can first develop at topographic lows in the basin from density stratification, meaning that there can be minor oxidized organic matter occurring with well-preserved organic matter (Jones, 1984).

The hydrocarbons generated from a siliceous marine type II kerogen are predominantly low-sulfur oil and cogenerated gas in the maturity range of 0.60–0.99%  $R_o$ . Organic matter from the Barnett Shale generates about 30% gas in the oil window from primary cracking based on laboratory experiments (Jarvie et al., 2003). At increasing thermal maturity, present-day HI ( $HI_{pd}$ ) is less than  $HI_o$ , and  $HI_{pd}$  will not be indicative of the original kerogen type, but will provide an indication of the primary products that can be generated (e.g., oil, mixed, wet gas, dry gas).

## ORGANIC RICHNESS

Determination of the original total organic carbon ( $TOC_o$ ) of a source rock provides a quantitative means to estimate the total volume of hydrocarbons that it can generate depending on kerogen type. Heavily explored areas generally have source rocks that are thermally mature, so it is not straightforward to determine original values. Consideration of the components of TOC assists in understanding how to restore highly mature TOC to  $TOC_o$ .

Total organic carbon in a source rock comprises three basic components: (1) organic carbon in retained hydrocarbons as received in the laboratory ( $C_{HC}$ ); (2) organic carbon that can be converted to hydrocarbons,  $C_C$ , called convertible carbon (Jarvie, 1991a) or

**Table 1.** Average TOC, Rock-Eval, and Vitrinite Reflectance Values and Computations from Core, Cuttings, and Outcrop Samples of the Barnett Shale, Fort Worth Basin\*

Thermal Maturity	Map Number	Operator and Well**	County	TOC (wt.%)	S <sub>1</sub> (mg HC/g Rock)	S <sub>2</sub> (mg HC/g Rock)	HI*** (mg HC/g TOC)	T <sub>max</sub> (°C)	Calculated R <sub>o</sub> (%) (from T <sub>max</sub> ) <sup>†</sup>	Measured R <sub>o</sub> (%)	Oil in Rock from S <sub>1</sub> (bbl oil/ac-ft) <sup>††</sup>	Generation Potential from S <sub>2</sub> (bbl oil/ac-ft) <sup>††</sup>	Number of Samples
Immature	1	Outcrops (average)	Lampasas	11.47	2.93	54.43	475	425	0.48	0.48	64	1192	6
Immature	2	Explo 3 Mitcham	Brown	4.67	2.60	18.17	392	434	0.66	0.62	57	398	3
		Cuttings (all)	Various	2.72	0.74	1.97	72	462	1.16	1.21	16	43	488
		Cuttings (low maturity – T <sub>max</sub> < 440°C)	Various	2.91	1.26	6.59	227	439	0.75	0.67	28	144	51
		Cuttings (high maturity) (HI < 100)	Various	2.62	0.53	0.86	33	nr	nr		12	19	402
Oil window	3	Oryx 1 Grant (core)	Montague	4.70	3.60	14.09	300	446	0.86	0.86	79	308	25
Gas window	4	MEC 2 Sims (core)	Wise	4.21	0.33	1.07	25	491	1.67	1.67	7	23	99
Gas window	5	MEC 1 Maeyers (core)	Wise	4.45	0.61	0.97	22	477	1.43	na	13	21	9
Gas window	6	MEC 1 Young (core)	Wise	4.73	1.95	2.78	59	468	1.27	na	43	61	111
Gas window	7	MEC 1 Stevenson (core)	Wise	4.68	0.76	0.96	20	470	1.30	na	17	21	12
Gas window	8	APC 1 Oliver (core)	Tarrant	4.30	0.26	0.59	14	544	2.64	na	6	13	59
		Average of high-maturity cores		4.48	0.78	1.27	28	490	1.66	1.67	17	28	

\*Samples are divided into immature, oil-window, and gas-window thermal-maturity categories.

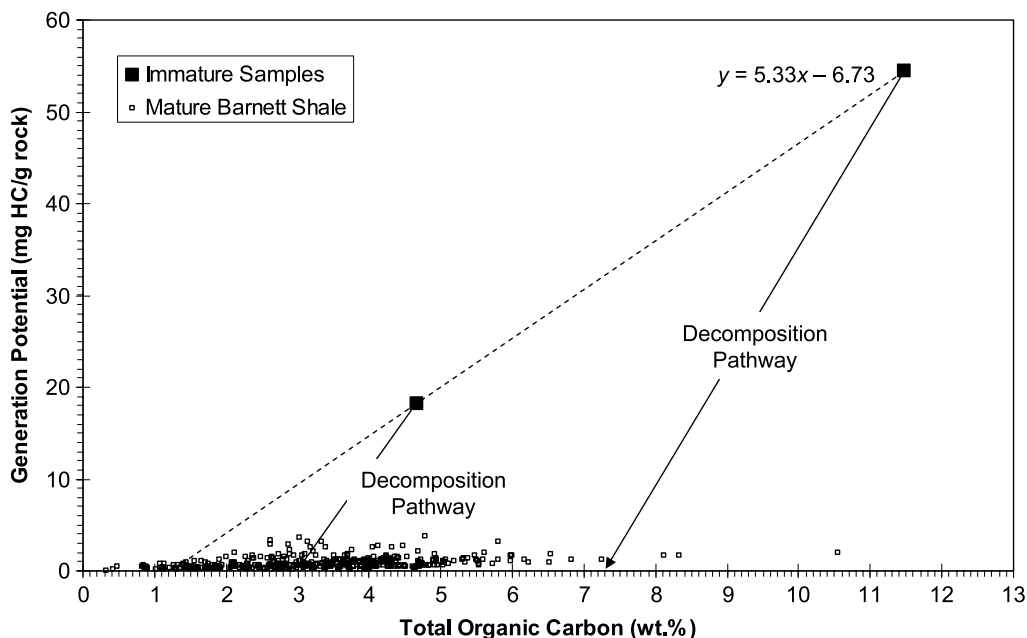
\*\*MEC = Mitchell Energy Corporation; APC = Anadarko Petroleum Corporation.

\*\*\*HI = Hydrogen Index.

<sup>†</sup>Calculated R<sub>o</sub> from T<sub>max</sub> = 0.0180 × T<sub>max</sub> – 7.16 (Jarvie et al., 2001).

<sup>††</sup>Conversion factor for S<sub>1</sub> or S<sub>2</sub> to bbl oil/ac-ft = 21.89.

**Figure 3.** Plot of generation potential ( $S_2$ ) vs. organic richness (TOC). Solid large squares are immature to early mature samples that provide measured indications of  $HI_o$  and  $C_R$  from the slope and  $x$ -intercept. Open, small squares are high-maturity (average 1.8%  $R_o$ ) core data. Solid lines from solid squares to  $x$ -axis are projected decomposition lines from immature to high thermal maturity.



reactive or labile carbon (Cooles et al., 1986); and (3) a carbonaceous organic residue that will not yield hydrocarbons because of insufficient hydrogen commonly referred to as inert carbon (Cooles et al., 1986; Jarvie, 1991a), dead carbon, or residual organic carbon ( $C_R$ ). As organic matter matures,  $C_C$  is converted to hydrocarbons and a carbonaceous residue eventually resulting in a reduced TOC when expulsion occurs.

Immature (0.48%  $R_o$ ) outcrop samples of the Barnett Shale ( $n = 6$ ) have high TOC values averaging 11.47%. Their average generation potential (Rock-Eval  $S_2$  yield) is 54.43 mg HC/g rock or 1192 bbl of oil equivalent/ac-ft ( $0.15 \text{ m}^3/\text{m}^3$ ). However, low-maturity cuttings from Explo Oil Inc. 3 Mitcham well in Brown County at the far southwestern flank of the basin average 4.67 wt.% TOC with  $S_2$  values of 18.17 mg HC/g rock (398 bbl of oil equivalent/ac-ft or  $0.05 \text{ m}^3/\text{m}^3$ ).

The present-day average TOC from 290 high-thermal-maturity Barnett Shale core samples from six wells in the principal producing area of Wise and Tarrant counties (average %  $R_o$  of 1.67) is 4.48 wt.% (see Table 1). Because TOC values commonly show log-normal distributions (Cornford et al., 1998), average values may not always be representative of TOC. However, these values are consistent with well-to-well averages that are in the range of 4–5% TOC. Removal of the residual  $C_{CHC}$  in Rock-Eval  $S_1$  and  $S_2$  yields a  $C_{Rpd}$  of 4.43 wt.%.

From Figure 3, the  $x$ -axis intercept is the amount of dead carbon that does not yield any hydrocarbons (Cornford et al., 1998) and is 1.26 wt.%. However, or-

ganic matter decomposition results in  $C_R$  at high thermal maturity increasing by about 10–20% versus the original  $C_R$  value (Burnham, 1989). The increase in  $C_R$  may be from aromatization and condensation reactions (Muscio and Horsfield, 1996) or from the carbon-rich residue of secondary cracking of petroleum to gas. The open-system maturation data (i.e., free of secondary cracking) of Jarvie and Lundell (1991) on low-maturity cuttings showed a  $C_{Rpd}$  intercept of 3.20%.

We developed another approach for determining  $TOC_o$  that consists of first determining  $HI_o$  based on visual kerogen type percentages and using average  $HI_o$  for four kerogen types (averages derived from range of HI in Jones, 1984) (equation 1, appendix).

The transformation ratio ( $TR_{HI}$ ) is the change in  $HI_o$  to present-day values ( $HI_{pd}$ ) that includes a correction for early free oil content from the original production index ( $PI_o$ ) and present-day oil content ( $PI_{pd}$ ) (Peters et al., 2006) (equation 2, appendix). Once  $TR_{HI}$  is determined,  $TOC_o$  can be calculated (equation 3, appendix). From equations 1 to 3, the calculated  $TOC_o$  value for Barnett Shale is 6.41% based on 95% type II and 5% type III with fractional conversion at 0.95. This yields an average original HI value of 434 mg HC/g TOC. This yields a  $C_{R_o}$  of 4.09 wt.%.  $C_C$  of 2.32 wt.% is the amount of organic carbon that is converted to hydrocarbons, which computes to 27.84 mg HC/g rock for  $S_{2o}$  or 609 bbl of oil equivalent/ac-ft ( $0.082 \text{ m}^3/\text{m}^3$ ). The change in these values with increasing thermal maturity based on the calibration data from Jarvie and Lundell (1991) and Montgomery et al. (2005) is shown in Table 2.



**Table 2.** Experimental Data from Jarvie and Lundell (1991) Showing Change in TOC<sub>o</sub>, C<sub>C</sub>, and C<sub>R</sub>, and Porosity Increase with Increasing Thermal Maturity

Approximate R <sub>o</sub> (%)	TOC <sub>pd</sub> (wt.%)	Change in from TOC <sub>o</sub> (%)	C <sub>C</sub> * (wt.%)	C <sub>C</sub> Conversion (%)	TR <sub>HI</sub> (f) (%)	C <sub>R</sub> ** (wt.%)	Increase in C <sub>R</sub> (%)	Potential Porosity from C <sub>C</sub> Decomposition (vol. %)
0.55	6.41	0.0	2.32	0	0	4.09	0.0	0
0.85	5.50	14.2	1.16	50	41	4.34	6.1	2.4
1.40	4.85	24.3	0.23	90	86	4.62	13.0	4.3

\*C<sub>C</sub> = organic carbon that can be converted to hydrocarbons and carbonaceous residue.

\*\*C<sub>R</sub> = residual organic carbon.

The TOC<sub>o</sub> (6.41%) is less than estimates that would be made from both Daly and Edman (1985) and Jarvie and Lundell (1991), who used corrections of 50 and 36%, respectively, to compute original TOC values from C<sub>R</sub> on high-maturity samples for type II kerogens. This is likely caused by excluding the increase in C<sub>R</sub> because of oil cracking or other reactions in these earlier studies.

## THERMAL MATURITY

### Vitrinite Reflectance

High gas content in the Barnett Shale is caused by the volumes of hydrocarbons generated (a result of organic richness, generation potential, and shale thickness), thermal maturity, and retention of a part of liquid hydrocarbons for subsequent cracking to gas. Where lower maturity Barnett Shale is found, gas flow rates are lower, and this is hypothesized to be caused by both lower volumes of generated gas and the presence of residual hydrocarbon fluids that occlude pore throats. The high gas flow rates, achieved in many high-maturity Barnett Shale wells, result from the large increase in gas generation because of both kerogen and oil cracking. Thus, thermal maturity is a key geochemical parameter to assess the likelihood of high-flow-rate shale gas.

Thermal maturity provides an indication of the maximum paleotemperature reached by a source rock. Two basic approaches exist to this determination: visual and chemical. Vitrinite reflectance is the most common approach for the determination of thermal maturity, which is completed by microscopic examination of kerogen or whole rock mounts and recording the reflectivity of the particle via a photomultiplier. For a review of the history and methods of thermal-maturity assessment, the reader is referred to Burgess (1975). Numerous pitfalls exist to determining the indigenous

population of vitrinite, and we commonly use additional chemical assessments to supplement visual measurements. These include Rock-Eval  $T_{max}$ , organic matter transformation ratio, residual hydrocarbon fingerprints (extract fingerprints), gas composition, and carbon isotopes, when available.

To be a fully useful parameter in assessment of oil and gas generation, thermal maturity must be directly related to the extent of organic matter conversion and, ultimately, the preservation of generated hydrocarbons. Maturity windows are dependent on the rates of decomposition (kinetics) of organic matter. Waples and Marzi (1998) demonstrated that because the kinetics of vitrinite and hydrocarbon generation overlap, they are related, but cannot provide a universal correlation.

Variation in rates of kerogen decomposition by kerogen type was illustrated by Espitalie et al. (1984), and precise measurements for various source rocks were reported by Jarvie and Lundell (2001). For example, using kinetic data from various kerogen types, they found that at 0.80% R<sub>o</sub> at a constant heating rate of 3.3°C/m.y., a low-sulfur type II kerogen such as the Barnett Shale would be approximately 27% converted, whereas a typical type III coal would only be about 9% converted, and a high-sulfur, high-oxygen Monterey Formation sample would be about 56% converted. Thus, oil and gas windows vary depending on source rock type and inherent decomposition rates as well as thermal histories.

### Organic Matter Conversion (Transformation)

Although maturity parameters such as vitrinite reflectance are empirically related to the oil and gas windows, it is feasible to evaluate conversion directly by measuring changes in organic matter yields, i.e., the extent of kerogen conversion by calculation of the kerogen transformation ratio.

The conversion of organic matter can be assessed by the change in TR<sub>HI</sub> values from low maturity to high

maturity. Commonly referred to as transformation ratio (TR), this term has conflicting meanings in the literature (e.g., Espitalie et al., 1984; Tissot and Welte, 1984; Pelet, 1985). Therefore, we add the subscript HI to transformation ratio ( $TR_{HI}$ ) and convert to percent to define how it applies to kerogen conversion calculations. This is the same as the fractional conversion,  $f$ , of Claypool (Peters et al., 2006). Assuming an average  $HI_o$  value of 434 mg HC/g TOC for the Barnett Shale (from equation 1 of the appendix),  $TR_{HI}$  can be calculated for any  $HI_{pd}$  value. For example,  $HI_{pd}$  of 28 mg HC/g TOC (e.g., high-maturity Barnett Shale cores, Table 1) suggests about 93% conversion of Barnett Shale organic matter to hydrocarbons and carbonaceous residue. For the lower-thermal-maturity Oryx 1 Grant core samples with a  $HI_{pd}$  of 300 mg HC/g TOC, the  $TR_{HI}$  is only 31%, explaining why high amounts of recoverable gas are not found and oil is found in conventional reservoirs in Montague County.

We emphasize that  $HI_o$  and hence,  $TR_{HI}$  is kerogen specific and does not apply to other kerogen types.  $TR_{HI}$  can be assessed from extensive analysis of samples of varying thermal maturity or derived by determining  $HI_o$  from maceral compositions as shown in equation 1.

$HI_{pd}$  and  $TR_{HI}$  are effective to predict oil versus gas windows in the Barnett Shale. The sensitivity of  $TR_{HI}$  to  $HI_o$  is critical around approximately 80% conversion of organic matter (onset of primary condensate–wet gas window). As can be seen in the immature Barnett Shale data in Table 1,  $HI_o$  values can readily vary by  $\pm 50$  mg HC/g TOC. However, even with this range of  $HI_o$ , the error in  $TR_{HI}$  is only  $\pm 2.5\%$  (at very high maturity, it is  $\pm 1.4\%$ , whereas at middle maturity, it is about  $\pm 10\%$ ). For the high-maturity Barnett Shale thermogenic gas system, an approximation of  $TR_{HI}$  to equivalent vitrinite reflectance values is derived from data points from the earliest oil window to the end of the gas window (Jarvie et al., 2005). The  $TR_{HI}$  needed for the earliest gas window is approximately 80%, but the dry-gas window requires values upward of 90%.

To illustrate the effectiveness of this approach to assess oil and gas windows for the Barnett Shale in the Fort Worth Basin, contour maps of both  $HI_{pd}$  and  $TR_{HI}$  are shown in Figure 4a and b. These maps complement a vitrinite reflectance maturity map with a pyrolysis-based chemical assessment of thermal maturity. Interestingly, these maps suggest potential gas production farther to the west in the Fort Worth Basin than do vitrinite reflectance data (e.g., Montgomery et al., 2005).

For evaluation of plays and prospects, it is useful to overlay the predicted oil and gas windows from vi-

sual and chemical interpretations of geochemical data; where the interpretations agree, risk is lower, and where they disagree, risk is higher. Further interpretation or analysis may be required to resolve differences.

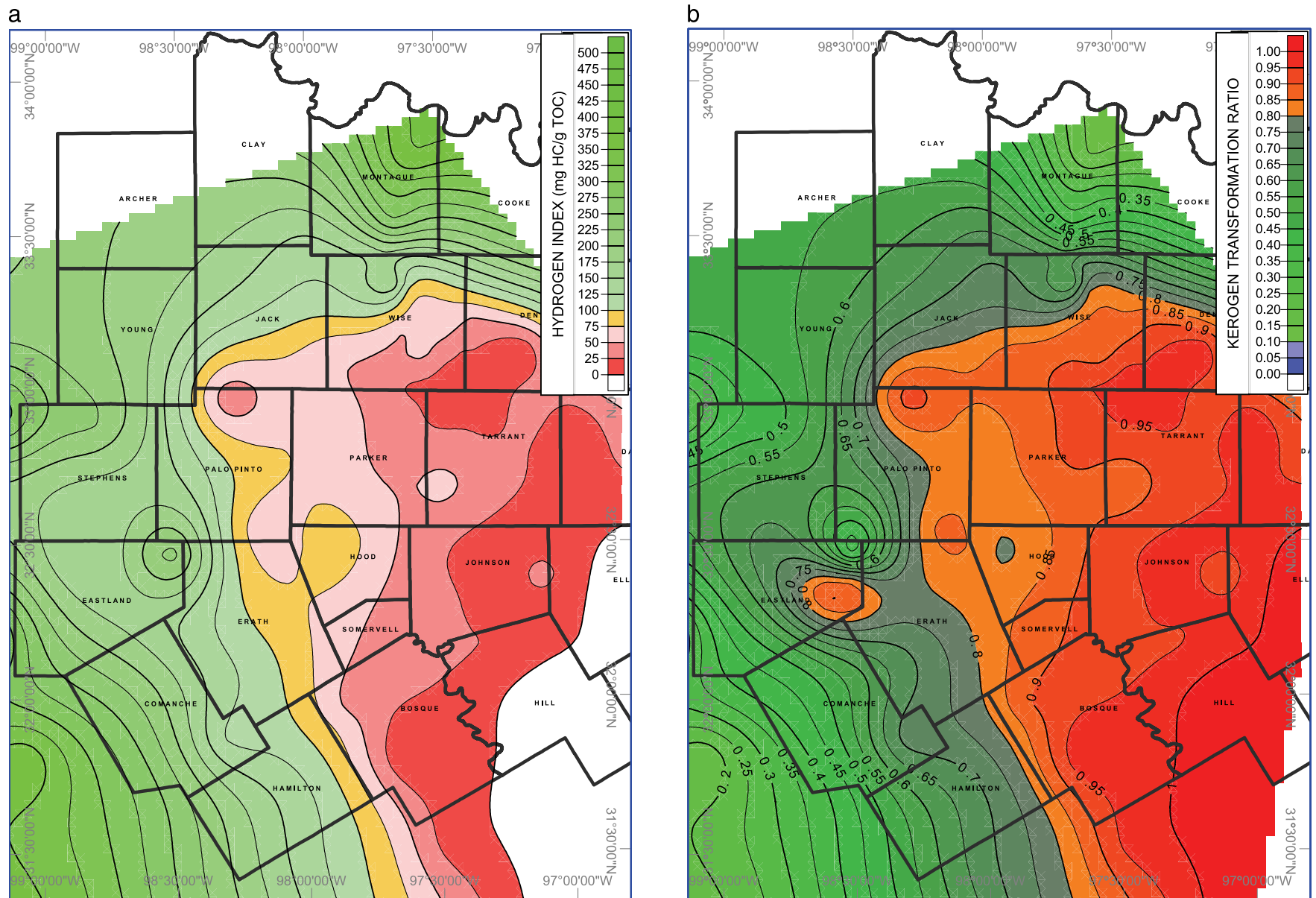
## COMPOSITION OF RESIDUAL HYDROCARBON FLUIDS

Because conversion of organic matter depends on kerogen type and thermal history, it is also imperative to evaluate the residual hydrocarbons in shale. The presence of liquid hydrocarbons in Barnett Shale is coincident with lower gas flow rates, faster gas production decline curves, and less-recoverable gas. Shales containing paraffins above  $C_{20}$  or with large unresolved complex mixtures (UCM) on gas chromatographic fingerprints have much lower gas flow rates than shales with only  $C_{20}$  residual hydrocarbon content and no UCM. Samples with high  $C_{20+}$  paraffins in extractable organic matter will have lower gas-to-oil (GOR) values consistent with the black-oil maturity window, whereas samples with low  $C_{20+}$  hydrocarbons ( $< 5\%$ ) will have higher GOR values ( $> 3500$  scf/bbl of oil;  $623 \text{ m}^3/\text{m}^3$ ).

A gas chromatographic fingerprint of residual hydrocarbons extracted from the Barnett Shale reveals the presence of problematic petroleum products, such as extended paraffins or UCM that are hypothesized to occlude pore throats restricting gas flow (Figure 5a). If the percentage of  $C_{20}$  to total area of the gas chromatographic fingerprint is greater than 95% (i.e., only condensate-like liquid hydrocarbons are present, e.g., Figure 5b), then high gas flow rates and high GOR values are predicted, all other factors being equal.

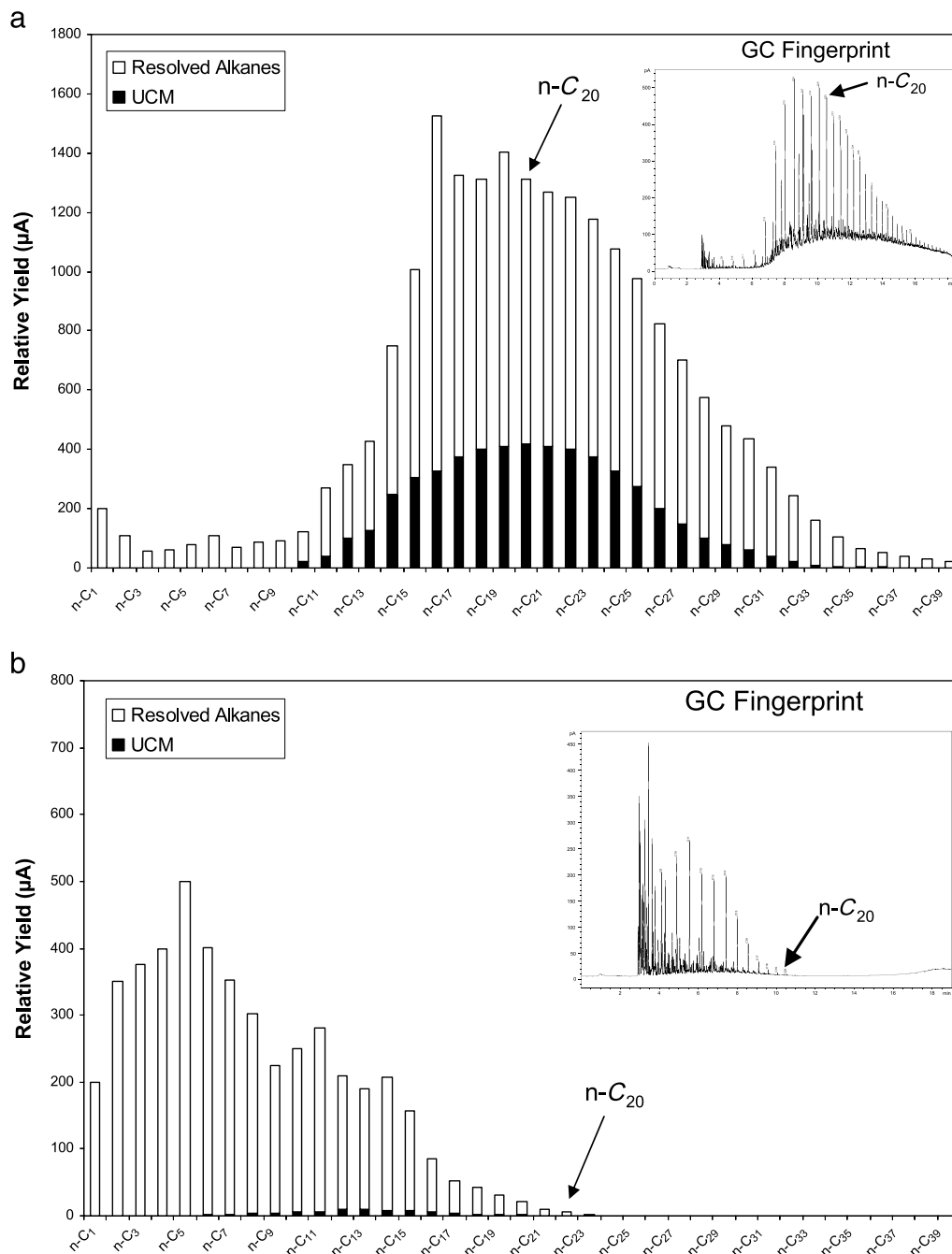
## INTERPRETED THERMAL MATURITY

Thermal maturity derived from visual and chemical methods can be compared using a conversion routine and polar plot of various maturation parameters. This requires careful calibration of various thermal maturity parameters. For the Barnett Shale, a range of optimum maturity values to achieve economic gas flow rates are shown in Table 3. A maturity risk plot modified from Jarvie et al. (2005) is a simple means to compare various maturity parameters and their application to initial economic assessment of low-permeability shale-gas systems such as the Barnett Shale or other low-maturity gas systems such as the New Albany or Antrim shales (Figure 6).



**Figure 4.** Maps of Barnett Shale kerogen conversion based on (a) HI and (b) HI-based transformation ratio ( $TR_{HI}$ ). These show excellent correlation to the vitrinite reflectance based maturity map of Montgomery et al. (2005), but suggest an expansion to the gas-productive window farther to the west.

**Figure 5.** Gas chromatographic (GC) histograms and fingerprints (inset) from Barnett Shale solvent extracts in the (a) oil window and (b) gas window. A GC fingerprint is basically a histogram of the yield (y-axis) and distribution (x-axis) of various resolvable compounds from GC analysis. The presence of extended paraffins and a large unresolved complex mixture (UCM) causes gas flow reduction or occlusion in the Barnett Shale.



### COMPUTATION OF POROSITY CAUSED BY ORGANIC CARBON CONVERSION

The thermal conversion of kerogen to petroleum results in the formation of a carbon-rich residue ( $C_R$ ) and increased porosity in the rock matrix, which impacts gas storage capacity. Although TOC is reported in weight percent, its volume percent is about two times higher. For an average TOC of 6.41 wt.% (mass),

the volume percent TOC is about 12.7 vol.% using 1.18 g/cm<sup>3</sup> density for organic matter. When thermal maturation is in the dry-gas window (e.g., > 1.4%  $R_o$ ), approximately 4.3 vol.% porosity is created by organic matter decomposition (see Table 2).

During thermal maturation,  $C_R$  also becomes more dense, reaching 1.35 g/cm<sup>3</sup> for amorphous organic matter (Okiongbo et al., 2005). However, that still does not exclude microporosity in  $C_R$ . At high maturity,

**Table 3.** Minimum and Best Values for Determining Whether a Low-Porosity, Low-Permeability Shale Has High Thermal Maturity Using Both Visual and Chemical Maturity Parameters

	$R_o$ (%)	$T_{max}$ (°C)	TR (%)	$HI_{pd}$ (mg HC/g TOC)	Dry Gas (%)	$C_{20+}$ (%)
Minimum	1.00	455	80	76–100	80	5
Better	1.20	465	90	50–75	90	3
Best	1.40	475	95	<50	95	1

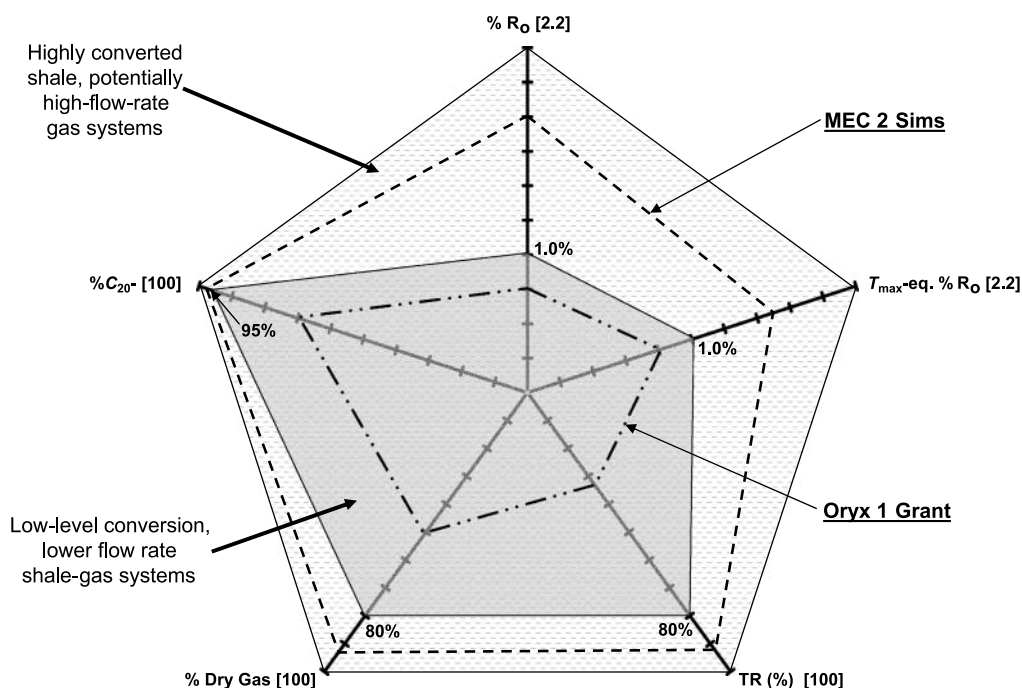
stacked layers of polyaromatic rings are separated by about 0.34–0.80 nm (Oberlin et al., 1980). Behar and Vandenbroucke (1987) report pore sizes of 5–50 nm, depending on kerogen type. These values are typical of the pore dimensions reported for Barnett Shale (Bowker, 2003a).

### ADSORPTION OF OIL AND GAS

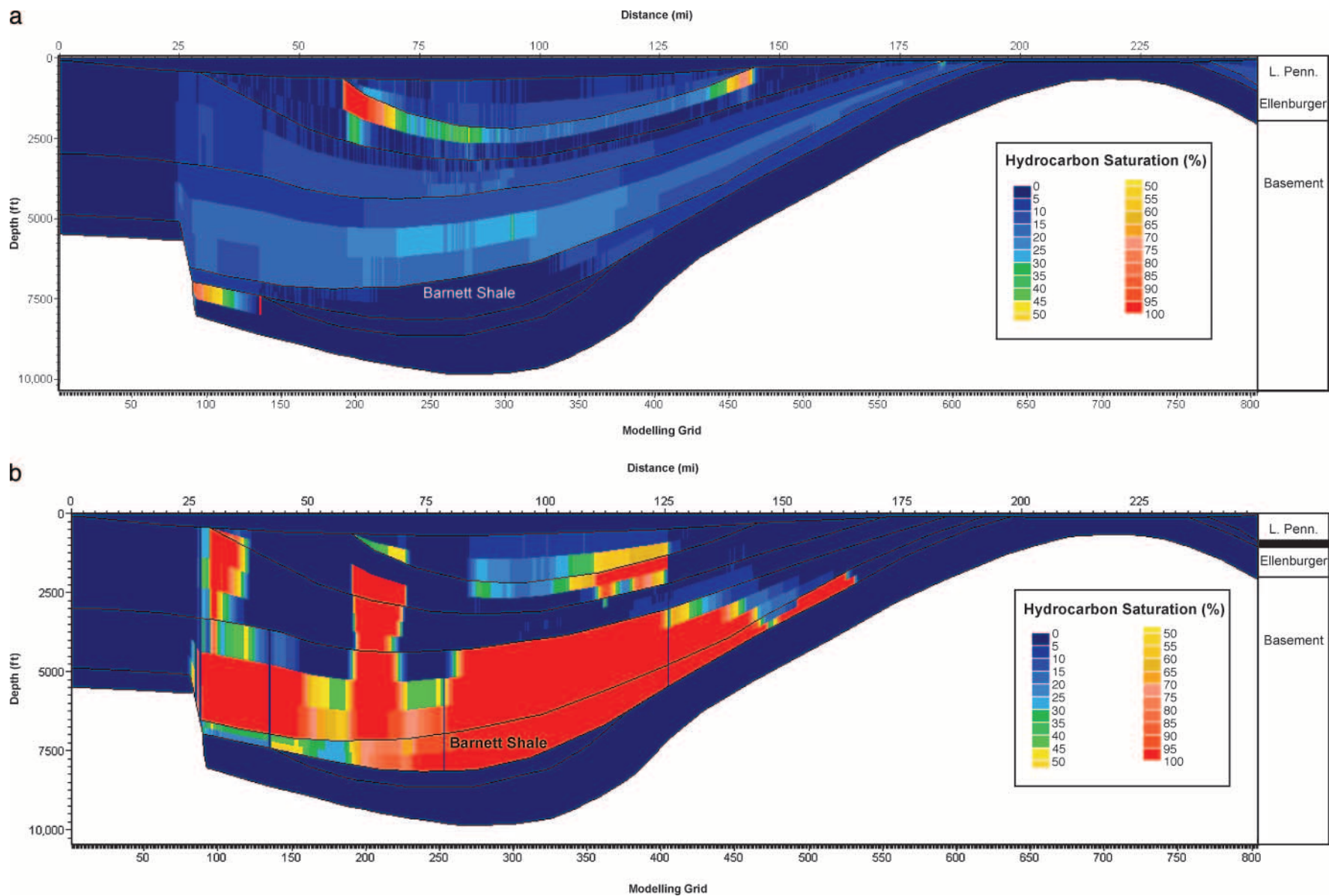
Gas is stored in shale source rocks in two principal ways: (1) as gas adsorbed (chemical) and absorbed (physical) (or sorbed to include both physicochemical possibilities) to or within the organic matrix and (2) as free gas in pore spaces or in fractures created either by organic matter decomposition or other diagenetic or tectonic processes. Organic richness, kerogen type, and

thermal maturity impact the sorptive capacity of organic matter.

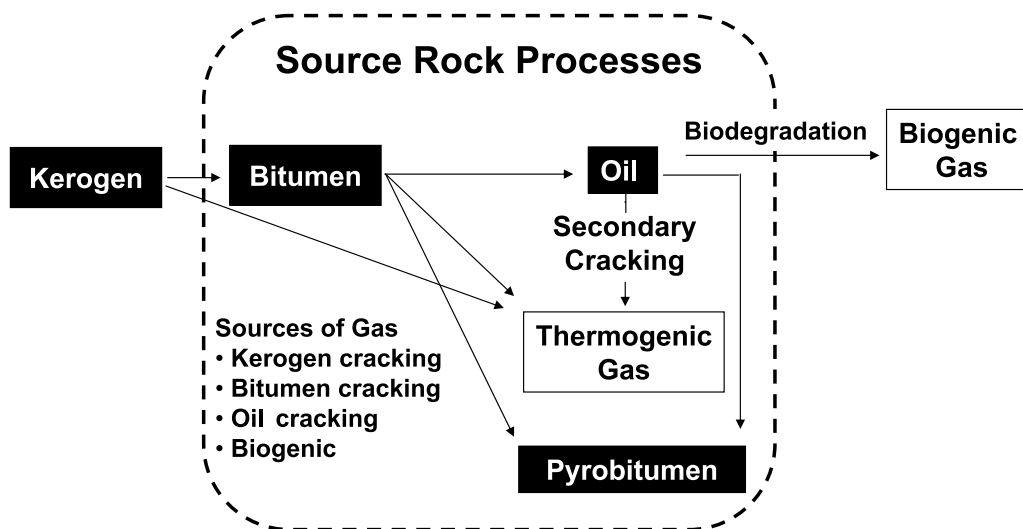
Sorption capacity also affects expulsion efficiency. Although expulsion efficiency is generally cited as related to saturation levels in source rock, it is also a function of sorption capacity, which may be the principal control (Pepper, 1992). Adsorptive sites must be filled before expulsion can proceed (Pepper, 1992), which is independent of saturation thresholds. The function of adsorption and saturation thresholds is illustrated by the numerical simulation of hydrocarbon generation and expulsion from the Barnett Shale in the Fort Worth Basin using the PetroMod<sup>®</sup> one-dimensional basin modeling software (IES). In the first simulation, a standard (default) pore saturation-based simulation of 20% is used (Figure 7a). This is equivalent to about 54 mg HC/g TOC. However, values for adsorption in



**Figure 6.** Polar shale-gas risk plot with various visual and chemical assessments of organic matter conversion or thermal maturity. Low-porosity and low-permeability shales at high levels of organic matter conversion have potential for high gas flow rates (>1 mmcf/day) will plot in the light-gray hatched area, whereas flow rates will be lower for similar shales at low levels of conversion (dark hatched area). Values for the productive MEC 2 Sims and the nonproductive Oryx 1 Grant well are shown with dashed and dash-dotted lines, respectively. Values for high-maturity shale gas are listed in Table 3.



**Figure 7.** Numerical simulation of hydrocarbon generation from the Barnett Shale in the Fort Worth Basin with and without adsorption. (a) When a saturation threshold default value is used, the numerical simulation shows only residual oil remaining in the Barnett Shale as the balance has been expelled. (b) When adsorption is included (200 mg HC/g TOC), hydrocarbons are retained and cracked to gas as shown by the calculated high gas contents.



**Figure 8.** Processes in a source rock leading to oil, gas, and carbon-rich residue (pyrobitumen). High-maturity shale-gas systems derive high gas contents from the indigenous generation of gas from kerogen, bitumen, and oil cracking.

the oil window are estimated to range from 130 to 200 mg HC/g TOC (Pepper, 1992). In the second simulation, an adsorption saturation of 200 mg HC/g TOC (Figure 7b) is used and illustrates the dramatic impact that adsorption plays in the final product composition in the shale-gas reservoir system. Large differences exist in the amount and types of hydrocarbons that were expelled and, consequently, the amount of oil that was retained for cracking to gas. This dramatically impacts the calculated product composition (gas vs. oil) that is present today in the Barnett Shale.

Adsorption may also impact the formation of gas by the decomposition of paraffins (alkanes), which have very high bond decomposition energies. Recent work on the cracking of alkane carbon-carbon bonds shows that adsorption of straight-chain alkanes to a solid matrix results in the structural flex in carbon-carbon bonds and breakage at lower-than-expected energies (Sheiko et al., 2006). Adsorption may also provide the intimate contact between generated hydrocarbons and transition metals, for example, which is required for the catalysis of paraffins to methane and a carbonaceous residue (Mango and Jarvie, 2006).

## GAS GENERATION

As a type II oil-prone source rock, what makes the Barnett Shale in the Fort Worth Basin such an exceptional gas system? The first consideration is how large volumes of gas can be formed, and the second is how gas can be stored. Three distinct processes result in the formation of thermogenic gas within shale (Figure 8): (1) the decomposition of kerogen to gas and bitumen;

(2) the decomposition of bitumen to oil and gas (steps 1 and 2 are primary cracking); and (3) the decomposition of oil to gas and a carbon-rich coke or pyrobitumen residue (secondary cracking). The latter process depends on the retention or adsorption of oil in the system, which is a key to the large resource potential of the Barnett Shale gas system.

Primary kerogen cracking occurs between temperatures of 80 and 180°C (176 and 356°F), for 10 and 90% conversion, respectively, based on kinetic data and average heating rates (Jarvie and Lundell, 2001). Most source rocks reach 50% conversion between 130 and 145°C (266 and 293°F). Secondary oil to gas cracking has been suggested to begin at about 150°C (302°F) depending on heating rate (e.g., Claypool and Mancini, 1990; Waples, 2000). However, based on whole extract (Jarvie, 1991b) and asphaltene cracking kinetics (di Primio et al., 2000), some volatile bitumen components consisting primarily of asphaltenes and resins crack at the same time or soon after their formation from kerogen. Kinetic experiments and liquid chromatographic analysis indicate that approximately 10% of Barnett Shale-sourced oil cracks over the same temperature window as most kerogens. These fractions average 10–20% of Barnett Shale solvent extracts. The balance of Barnett Shale extracts are composed of about 80% paraffins and aromatics that require higher temperatures to decompose (>175°C; >347°F) excluding any adsorption-induced reduction in cracking rates (Sheiko et al., 2006).

For the most part, the Barnett Shale is a closed system; i.e., products are not released immediately after generation. Pressure buildup caused by the generation of hydrocarbon and nonhydrocarbon gases such as carbon dioxide exists. Carbon dioxide is likely derived from the

early stages of Barnett Shale organic matter decomposition, although carbonate thermal decomposition and decarboxylation reactions may also increase concentrations of this gas. With increasing thermal maturity, secondary cracking of retained oil results in the formation of hydrocarbon gas, an increase in GOR, a concomitant increase in pressure, and microfracturing. Estimates suggest that 1% oil cracking in a closed system creates sufficient pressure to exceed the fracture threshold of the rock fabric (Gaarenstroom et al., 1993). Thus, microfractures and migration pathways in the Barnett Shale originate, at least in part, from early hydrocarbon and nonhydrocarbon (primarily carbon dioxide and nitrogen) gas generation and secondary cracking of hydrocarbons in the oil and gas windows. This and mass balance considerations suggest episodic expulsion from the Barnett Shale. This process likely occurred many times in the core area, and the range of maturities (0.70–1.0%  $R_o$ ) of gas samples in the Boonsville field supports this hypothesis (Jarvie et al., 2003, 2004; R. J. Hill, D. M. Jarvie, R. M. Pollastro, K. A. Bowker, and B. L. Claxton, 2004, unpublished work; Hill et al., 2007).

The creation of microporosity from organic matter decomposition appears to reasonably explain the measured porosity values and the residual organic carbon content. Solvent extraction, which will remove most extractable organic matter, does not remove all adsorbed and trapped hydrocarbons from highly mature Barnett Shale, and further analysis of occluded gas demonstrates the presence of high-maturity gas in the MEC 2 Sims well core samples (Jarvie et al., 2004). These microreservoirs are gas-filled compartments at about 1.70%  $R_o$ , and their lack of connectivity provides an explanation for the efficacy of restimulation, releasing more gas.

Below 1.0%  $R_o$ , these microreservoirs are filled with retained petroleum consisting of both oil and gas that restricts gas flow rates and increases production decline rates. This may be a function of discontinuous pore throats or pore throats constricted by adsorbed hydrocarbons, requiring elevated energy to break through exits blocked by adsorbed hydrocarbons or an activated exit (Lindgreen, 1987), i.e., sufficient energy or pressure to overcome adsorption by high-molecular-weight petroleum constituents that have higher adsorption activities than gas resulting in occluded pore throats with pressure drawdown. At some locations, paleotemperature and pressure regimes in the Barnett Shale have provided sufficient energy to overcome these activation barriers resulting in expulsion. Data from a variety of sources demonstrate that compositional fractions with-

in crude oil are not equally amenable to expulsion because of sorption (e.g., McAuliffe, 1980; Stainforth and Reinders, 1990; Sandvik et al., 1992).

Overall, lower gas flow rates and faster production decline rates in the oil window (0.50–0.99%  $R_o$ ) are likely caused by (1) low quantities of gas generated only from primary kerogen cracking (low GOR); (2) restricted release of hydrocarbons caused by the adsorption and occlusion of pore throats by adsorbed bitumen, asphaltenes, and other components of black oil; and (3) lower initial pressures with faster pressure drawdown, or a combination of these and other factors. However, above 1.0–1.4%  $R_o$  (paleotemperature of more than 150°C [302°F]), much of the higher-molecular-weight crude oil components have been cracked to gas, shale pores are filled with gas, and adsorption affinity is reduced because of the reduction in size of hydrocarbons. Under these conditions, the Barnett Shale has more gas caused by secondary cracking, and stimulation allows a part of the exposed free and adsorbed gas (high GOR) to escape into the wellbore. Pepper (1992) estimated that adsorption is reduced by a factor of 10 at high maturities from 200 mg HC/g TOC in the oil window to about 20 mg HC/g TOC in the gas window. Instead, this may be a function of the reduced energy by which lower-molecular-weight paraffins are adsorbed, but in either case, gas flow is enhanced. Secondary cracking can occur in other nonshale reservoir rocks such as the Bossier Shale gas system of east Texas, where the presence of pyrobitumen in tight sands and silts indicates such a process (Emme and Stancil, 2002; Chauouche, 2005).

### Volumes of Hydrocarbons Generated

The remaining hydrocarbon-generation potential of source rocks is typically measured by Rock-Eval pyrolysis ( $S_2$ ) yields. Based on available data, an average, immature Barnett Shale original pyrolysis or original generation potential ( $S_{2o}$ ) contains 27.84 mg HC/g rock (Table 4). This pyrolysis amount can be converted to barrels of oil equivalent per acre-foot and, using an average thickness of 350 ft (106.7 m), results in a yield of 136.5 MMBO equivalent per section (where a section is 640 ac [2.59 km<sup>2</sup>]) ( $8.90 \times 10^{13}$  m<sup>3</sup>/m<sup>3</sup>) or, in gas equivalent, 820 bcf/section ( $8.93 \times 10^3$  m<sup>3</sup>/m<sup>3</sup>).

The cracking of oil to gas is limited by the amount of available hydrogen in the system needed to form wet and dry gas. The atomic H/C ratio for oil is about 1.8 H/C depending on composition, whereas methane



**Table 4.** Gas Storage Capacity of the Barnett Shale under Various PVT Conditions for Present-Day and Paleotemperatures and Pressures\*

Description	GIP Low Estimate	GIP Median Estimate	GIP High Estimate
Estimated ultimate recoverable (EUR) (55-ac [22-ha] well spacing)** (bcf)	1.30	1.75	2.50
Estimated recovery (estimated between 8 and 12%) <sup>†</sup>	10%	10%	10%
Estimated gas in place (GIP) based on well EUR and estimated recoveries (bcf/section)	151	204	291
TOC <sub>o</sub> (wt.% estimated average) <sup>††</sup>		6.41	
TOC <sub>c</sub> (wt.% measured average) <sup>††</sup>		2.32	
Original generation potential (Rock-Eval S <sub>20r</sub> , mg HC/g rock) <sup>‡</sup>		27.84	
Estimate of amount of oil generated from kerogen (70% of total hydrocarbons) (bbl oil/ac-ft) <sup>‡‡</sup>		427	
Estimate of amount of gas generated from kerogen (30% of total hydrocarbons) (mcf/ac-ft) <sup>¶</sup>		1097	
Source rock thickness (ft)		350	
Primary oil generated from kerogen with above thickness converted to gas equivalent (bcf/section)		573	
Primary gas generated from kerogen from shale with above thickness (bcf/section)		247	
Total hydrocarbons (gas and oil) generated from primary cracking of kerogen (gas equivalent bcf/section)		820	
Expulsion factor		0.60	
Oil expelled (bbl oil/ac-ft)		256	
Gas expelled (mcf/ac-ft)		658	
Retained hydrocarbons			
Primary oil retained in shale (bbl oil/ac-ft)		171	
Primary gas retained in shale (mcf/ac-ft)		439	
Correction factor for insufficient hydrogen in oil		0.47	
Gas yield from secondary cracking of oil (mcf/ac-ft)		482	
Total retained gas (primary gas plus secondary gas from oil cracking) (mcf/ac-ft)		921	
Total retained hydrocarbons under these assumptions (bcf/section)		206	

\*PVT = pressure, volume, temperature.

\*\*EUR from Adams (2001), Bowker (2003a), Montgomery et al. (2005).

<sup>†</sup>Estimated recovery percentage from Bowker (2003a), Montgomery et al. (2005).

<sup>††</sup>See Table 2.

<sup>‡</sup>Conversion of wt.% CC to mg HC/g rock, divide by 0.08333.

<sup>‡‡</sup>Conversion of Rock-Eval S<sub>2</sub> in mg HC/g rock to bbl oil/ac-ft, multiply by 21.89.

<sup>¶</sup>Conversion of Rock-Eval S<sub>2</sub> in mg HC/g rock to mcf/ac-ft, multiply by 131.34 (btu basis).

formation requires 4.0 hydrogens per carbon. Thus, there is about 55% hydrogen shortage in oil when it is cracked to methane. Gases in the Barnett Shale are typically less than 100% methane, and a reasonable average is about 90% methane across the entire productive area. Even at 90% methane, the H/C requirement for condensate wet-gas formation is about 3.8, so hydrogen deficiency is still approximately 53%. Taking hydrogen deficiencies into account, gas-generation potential for the Barnett Shale is about 550 bcf/section ( $5.99 \times 10^3 \text{ m}^3/\text{m}^3$ ) although 148 bcf/section of gas has likely been expelled. However, reductions caused by the expulsion of petroleum will further reduce the gas-generation potential of the Barnett Shale system.

## Expulsion Efficiency

The Barnett Shale has expelled hydrocarbons into conventional oil and gas reservoirs based on the correlation of black oils and condensates to Barnett Shale-produced oils, condensates, and extracts (Jarvie et al., 2001, 2003; R. J. Hill, D. M. Jarvie, R. M. Pollastro, K. A. Bowker, and B. L. Claxton, 2004, unpublished work; Hill et al., 2007). In fact, the Boonsville field contains 2–3 tcf ( $5.66\text{--}8.50 \times 10^{10} \text{ m}^3$ ) of wet gas and condensate, and the combined produced oil in the Fort Worth Basin is more than 2 billion bbl (318 million  $\text{m}^3$ ; Pollastro et al., 2004). Accounting for the amount of expelled hydrocarbons is not a simple task because reconciliation

of reserves plus losses during migration or to the surface is not readily estimated. An empirical approach uses EUR and recovery factors cited by operators in the Newark East field to evaluate the expulsion efficiency.

The EUR for Barnett Shale wells ranges from about 1.0 to 3.0 bcf/well ( $2.8$  to  $8.5 \times 10^7 \text{ m}^3$ ), depending on whether a well is vertical or horizontal (Pollastro et al., 2004), but a reasonable average is about 1.75 bcf/well. If recovery estimates of 8–12% (Bowker, 2003a) or an average of 10% is used, the EUR per section is 17.50 bcf ( $4.96 \times 10^8 \text{ m}^3$ ). Most wells have been drilled on 55-ac (22-ha) spacing, so the GIP per section is about 204 bcf ( $5.78 \times 10^9 \text{ m}^3$ ). This is higher by about 54 bcf/section than reported estimates of GIP in the Barnett Shale (150 bcf/section [ $640 \text{ m}^3/\text{m}^3$ ]; Adams, 2003; Bowker, 2003b), although these authors used a thickness of 300 ft (91.44 m) for the Barnett Shale.

The total hydrocarbon-generation potential of Barnett Shale at high thermal maturity ( $>1.4\% R_o$ ) based on original generation potentials from Rock-Eval pyrolysis, corrected for hydrogen mass balance for mixed wet and dry gas, and an average thickness of 350 ft (106.7 m) is about 550 bcf/section ( $5987 \text{ m}^3/\text{m}^3$ ). Compared to GIP based on EUR, approximately 324 bcf/section ( $3530 \text{ m}^3/\text{m}^3$ ) has been expelled from the Barnett Shale either in the form of gas or oil equivalent. This indicates about 60% expulsion from the Barnett Shale based on the above computed GIP.

Another variable in this calculation is the assumption of original generation potentials. Table 4 shows our best estimate calculation as well as low and high average values based on low-maturity Barnett Shale from Brown County and Barnett Shale outcrop samples collected in Lampasas County, respectively. The average value of these two locations approximate our best values arrived at independently based on  $HI_o$  and  $TOC_o$  equations.  $TOC_R$  values greater than 8% ( $\sim 12\% TOC_o$ ) in Barnett Shale are not common, indicating that the rich outcrop samples are an end member of organic-rich Barnett Shale. In addition, the Explo 3 Mitcham samples are cuttings and are early mature (about  $0.62\% R_o$ ), with a slight understatement of  $TOC_o$  and  $S_{2o}$ . We think, therefore, that expulsion efficiencies are about 60%, although the range is likely 50–70%. This is lower than conventional wisdom for source rock expulsion efficiency, but explains the high gas contents of gas-window mature Barnett Shale.

Considering  $TOC_o$  and its components,  $C_C$  and  $C_R$ , a reasonable explanation of the expelled carbon as hydrocarbons, retained carbon as gas and some liquids, and the slight increase in  $C_R$  are reasonably accounted for

as shown in Figure 9. At 60% expulsion, only 0.91 wt.% carbon is cracked to gas and a carbonaceous residue. The cited hydrogen deficiency results in an increase in  $C_R$  by 0.31 wt.%, which, when added to the original  $C_R$ , yields 4.40 wt.%  $C_R$  at high maturity. This is comparable to the measured average value of 4.48 wt.% for  $C_R$  from the database of high-maturity Barnett Shale (see Table 1). The remaining 0.32 wt.% of hydrocarbons is cracked to gas at high thermal maturity and yields about 911 mcf/ac-ft ( $18.5 \text{ m}^3/\text{m}^3$ ) of gas under these assumptions.

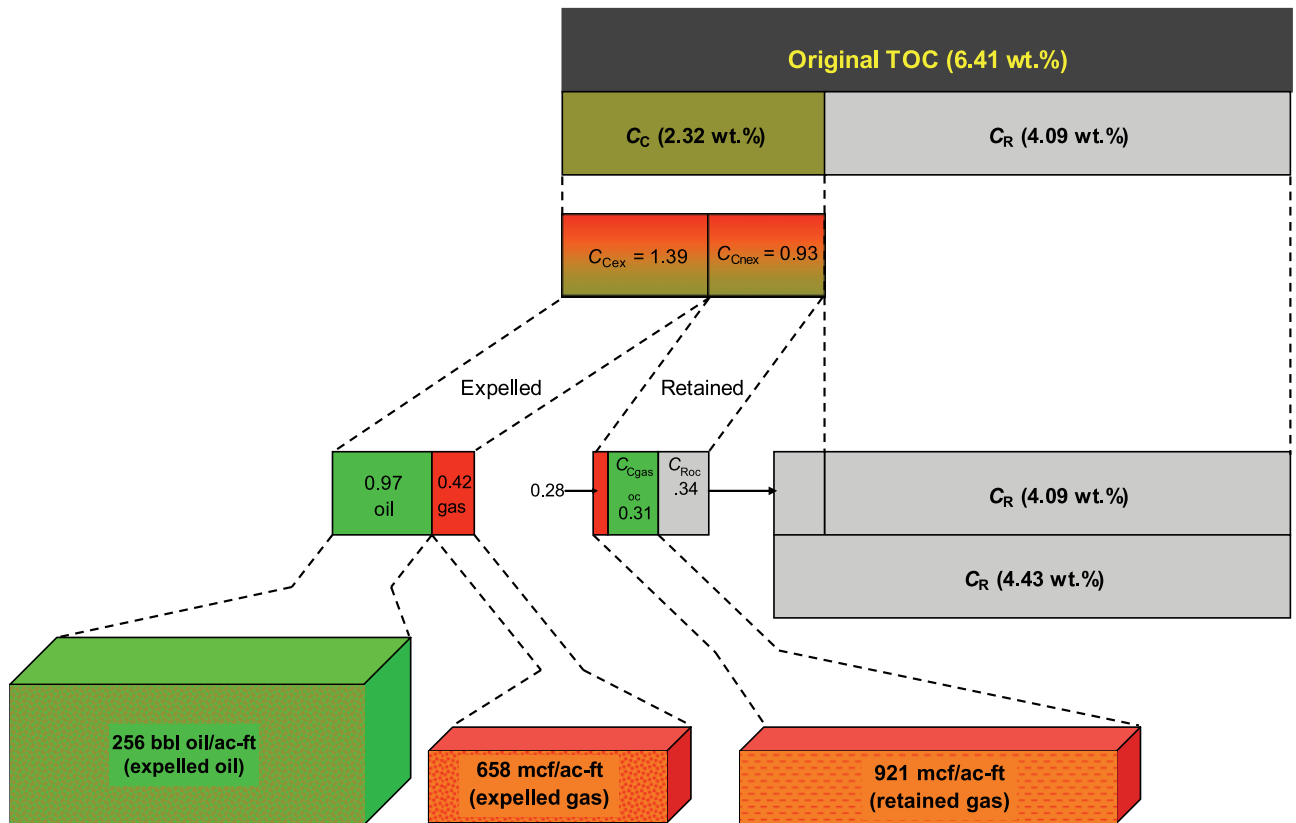
## GAS STORAGE CAPACITY

Scientists have shown that the Barnett Shale has the capacity to generate enormous amounts of gas, but can these volumes be stored in a low-permeability shale? Modeling gas storage using pressure, volume, and temperature (PVT) properties assuming nonideal gas, typical porosity values (5–8%), 3800 psi (26.2 MPa), and  $70^\circ\text{C}$  ( $34^\circ\text{F}$ ) indicates that the storage capacity of the Barnett Shale is also enormous, ranging from 450 to 720 mcf/ac-ft ( $103 \text{ m}^3/\text{m}^3$ ) (Table 5). For a 6% porosity shale under these temperature and pressure conditions, there is approximately 159 scf/ton (4.96 cubic meters/metric ton), consistent with the estimates of Mavor (2001).

At maximum burial depth ( $>250 \text{ Ma}$ ), high-maturity Barnett Shale ( $>1.40\% R_o$ ) was at much higher temperatures and pressures. An additional 5000 ft (1524 m) of burial or hydrothermal water movement would likely have elevated temperatures and pressures to about  $180^\circ\text{C}$  ( $356^\circ\text{F}$ ) and 8000 psi (55.2 MPa). Oil would be cracked to gas; organic matter decomposition would be near completion, providing additional pore storage capacity; and adsorption would be at a maximum in the burial and thermal history of the Barnett Shale. With uplift, temperature and pressure would be reduced, resulting in less adsorbed gas and easier release of gas.

## MINERALOGY

Although mineralogical analysis is generally not included in organic geochemical assessments, it is an important factor in gas production from the Barnett Shale and other tight shale systems that require stimulation. Paraphrasing Bowker (2002), the Barnett Shale produces so much gas because it is brittle and responds to stimulation (and



**Figure 9.** Depiction of TOC components and values that result from thermal maturation of organic matter in Barnett Shale. A part of the  $\text{TOC}_o$ ,  $C_c$  at 2.32 wt.% is converted to hydrocarbons, whereas there is also a hydrogen-poor component,  $C_r$  at 4.09 wt.%. With thermal maturation, hydrocarbons are generated and an estimated 60% of carbon in generated hydrocarbons ( $C_{cex}$ ) is expelled from the Barnett Shale. The expelled products are approximately 70% petroleum and 30% gas. A portion of carbon is not expelled ( $C_{cnex}$ ) as hydrocarbons, but is further cracked to ( $C_{cgas}$ ). Carbon in gas totals 0.28 wt.% unexpelled gas from primary cracking of kerogen and 0.31 wt.% carbon in unexpelled oil that was cracked to gas. Additional dead carbon is formed from secondary cracking of oil ( $C_{croc}$ ), yielding a high thermal maturity  $C_r$  of 4.43 wt.% comparable to the database average for high-maturity cores (4.48 wt.%; see Table 1). Only 0.59 wt.% carbon is retained in the Barnett Shale as gas, but this totals 921 mcf/ac-ft.

because it has high gas contents). Although the organic matter is capable of generating, retaining, and storing huge amounts of hydrocarbons, gas flow is limited if the individual microreservoir compartments cannot be connected via well stimulation. This brittleness is related to mineralogy, and the Barnett Shale contains high percentages of quartz derived from biogenic silica (data from Gas Research Institute, 1991) (Figure 10). Although a shale by name and particle size, clay contents range from more than 40 to less than 5%. Clay, quartz, and carbonate contents are highly variable in the Barnett Shale and result in variable fracture gradients (Martineau, 2001), so it would be expected that some zones are more fractured during stimulation than others. Without these mineralogical characteristics, stimulation and fracturing of the Barnett Shale gas system would not be as successful given current technologies.

## PROJECTED INITIAL GAS PRODUCTION RATES

With the integration of source rock volumetrics (total generation potential and thickness) and natural and induced fracture presence, gas flow rates can be estimated. A schematic for this is shown in Figure 11 based on Barnett Shale vertical wells. The goal of this schematic is to provide risk assessment. Obviously, a variety of non-geochemical factors affect flow rates, including geological and engineering issues such as the presence of faults and structures, stimulation barriers, stimulation technique and size, and the ability of the rock to fracture.

This flow-risk assessment has been applied to Barnett Shale wells in the Fort Worth Basin in addition to wells in the Delaware and Arkoma basins to predict flow rates from Barnett and Woodford shales. For example, in the core area of the Fort Worth Basin, the Mitchell Energy

**Table 5.** Estimated Values for EUR and GIP\*

Porosity (%)	mcf/ac-ft at 70°C and 3800 psi	mcf/ac-ft at 180°C and 8000 psi
5	450	710
6	540	850
7	630	990
8	720	1130

\*Used to compute expulsion and retained oil percentage from calculated original HI, TOC, and S<sub>2</sub> with corrections for oil cracking.

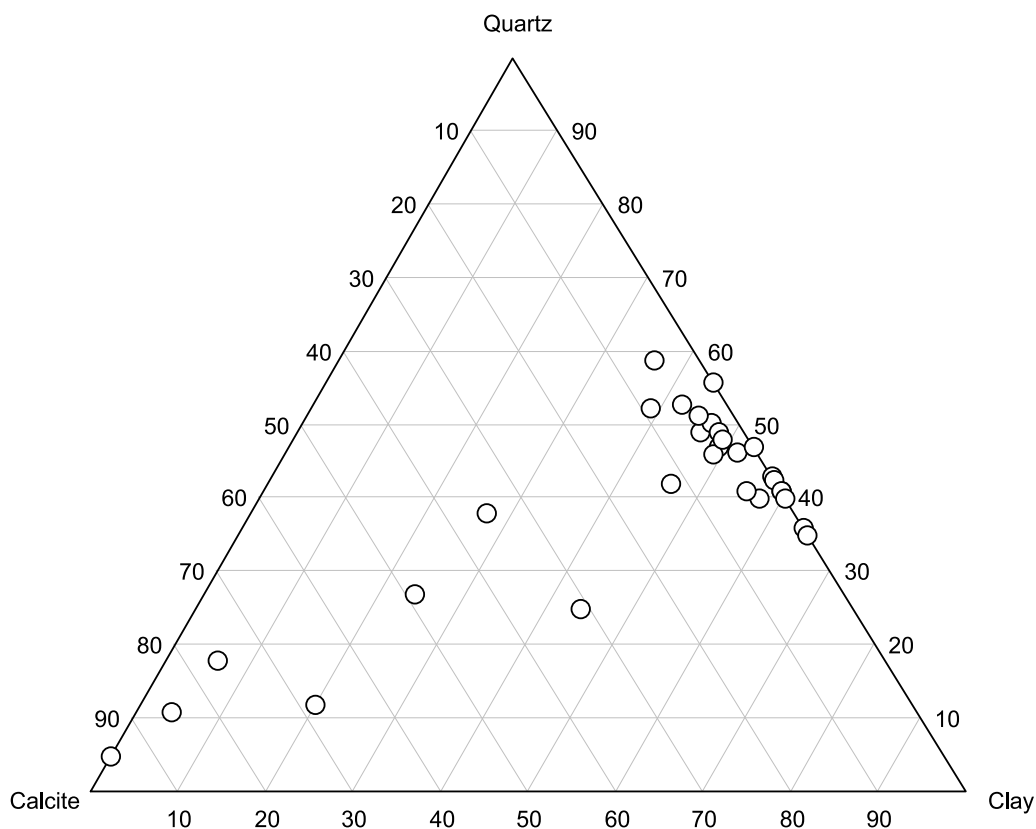
Corporation 2 T.P. Sims vertical well in Wise County has a maturity value of 1.65% R<sub>o</sub>, and the well has flowed more than 1 mmcf/day (28.3 million m<sup>3</sup>/day). In noncore areas, Barnett Shale wells in the thermal-maturity window of 0.80–0.90% R<sub>o</sub> range have initial production rates of 100–500 mcf/day (2.83–14.2 million m<sup>3</sup>/day). More recently, Infinity Oil and Gas has completed horizontal wells in Erath County that have mapped maturities of approximately 1.0% R<sub>o</sub> that have flowed more than 1 mmcf/day (28.3 million m<sup>3</sup>/day; Infinity Energy Resources, 2006).

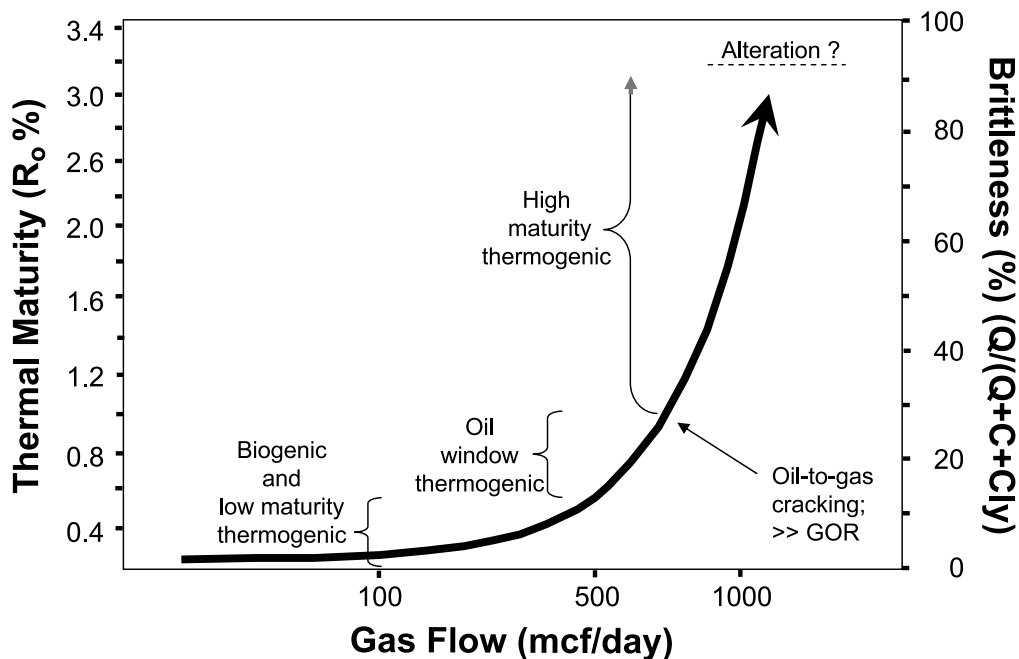
However, oil-window thermal-maturity Barnett Shale wells (0.60–0.99% R<sub>o</sub>) average less than 500 mmcf/day (14.2 × 10<sup>6</sup> million m<sup>3</sup>/day) over the first month of production and are not commercial depending on economic conditions (drilling costs, gas prices, etc.). Gas flow from shales in the oil window have lower EUR and ROR because less gas has been generated, and the wells also have even faster decline rates.

Structurally, it is also necessary to know the location of sink holes, karsts, macrofractures, faults, or other conduits in the sedimentary package. These features conduct stimulation energy away from the shale using current stimulation techniques, resulting in poor stimulation. One of the reasons for acquiring seismic data in the Fort Worth Basin is to identify areas not to drill based on the presence of sink holes or other structurally complex areas (Bowker, 2003a; Marble, 2006), although these may be found to be productive in the future as new completion technologies are developed.

Restimulation of productive wells commonly results in rates exceeding the original production flow rates (Bowker, 2003a). Mitchell Energy Corporation’s 2 Sims well in Wise County shows the impact of restimulation at about 122 months as the initial restimulation flow

**Figure 10.** Mineralogical distribution of quartz (Qz), calcite (Ca), and clay (Cly) in the Barnett Shale from the Mitchell Energy Corp. 1 Young, W. C. well showing a high amount of quartz, an indication of brittleness in some sedimentary facies of the Barnett Shale. Other factors being equal, high-maturity, brittle shales are most likely to yield high gas flow rates.





**Figure 11.** Diagrammatic illustration of increasing gas flow rates with increasing source rock organic richness (TOC), thermal maturity, GOR, and fractures found in shale-gas systems. Play economics can be evaluated using projected gas flow rates and EUR versus drilling and development costs.

rate exceed 2 mmcf/day ( $5.66 \times 10^4 \text{ m}^3/\text{day}$ ) (Figure 12). Changes in stress field orientation following production as well as improved stimulation techniques are the principal reasons for the increase in flow rates (Montgomery, 2004).

## CONCLUSIONS

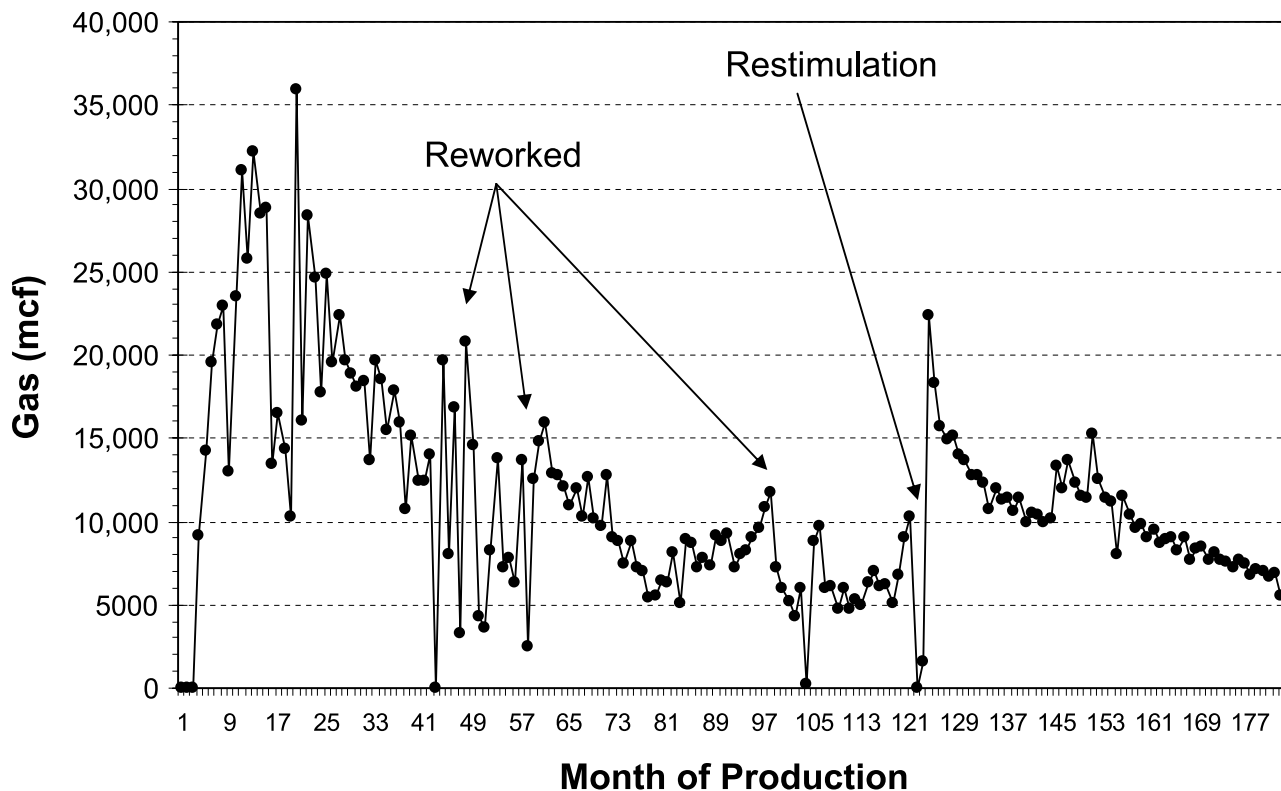
A variety of unconventional shale-gas resource plays and gas types associated with these plays exist. Gases may be biogenic or thermogenic, and although most gas is indigenous, in some cases, shale systems contain migrated gas. Shale-gas resource plays may be extremely tight (low permeability) to highly fractured, with variable bulk mineralogical composition controlling the brittle versus ductile nature of the shale. To evaluate the likelihood of economic shale-gas production, it is essential to determine whether the gas is thermogenic or biogenic and to evaluate the geologic characteristics of the shale-gas system to properly apply geochemical measurements and interpretation.

The Barnett Shale is an organic-rich, type II, oil-prone marine shale that originally averaged about 6.41% TOC, with a hydrogen index of about 434 mg HC/g TOC. Computation of original generation potentials yields about 27.84 mg HC/g rock or 609 bbl of oil equivalent/ac-ft ( $0.083 \text{ m}^3/\text{m}^3$ ). The low permeability of the Barnett

Shale and its adsorptive capacity result in the retention of abundant petroleum, which can be cracked to gas given sufficient thermal maturation. Combined with primary kerogen-to-gas cracking, this yields the high gas contents, accounting for the high GIP and EUR from Barnett Shale gas wells. However, expulsion from the Barnett Shale has occurred as evidenced by gas production from the overlying Boonsville conglomerate as well as oil fields in the less mature northern and western parts of the Fort Worth Basin. Expulsion is estimated to be about 50–70% of the total generation potential of the Barnett Shale, but this estimate is highly dependent on the determination of the original generation potential and GIP.

Because there is insufficient hydrogen (53%) in oil to convert it entirely to gas, the retained gas content is reduced from 324 bcf/section ( $3530 \text{ m}^3/\text{m}^3$ ) to about 204 bcf/section ( $2223 \text{ m}^3/\text{m}^3$ ). Free gas is stored in microporosity created by organic matter decomposition, generation-induced microfractures, and any intergranular pores preserved during deposition. With a  $C_{Co}$  of 2.32 wt.%, a net porosity increase of 4.3 to 4.6% results from the conversion of kerogen to hydrocarbons. This provides a considerable part of the known porosity of the Barnett Shale and results in a multiplicity of compartmentalized microreservoirs. Subsequently, to achieve gas flow in Barnett Shale wells, rigorous stimulation is required to rupture these microreservoir compartments.

Gas storage in the Barnett Shale at reservoir PVT conditions demonstrates that at 6% porosity, 70°C



**Figure 12.** Production decline curve for the MEC 2 T.P. Sims vertical well that has produced 2.025 bcf of gas. The well was restimulated during the 122 months resulting in an increase in gas flow.

(158°F), and 3800 psi (26.2 MPa), a maximum storage of 540 mcf/ac-ft or 159 scf/ton (4.96 cubic meters/metric ton) is possible.

To locate high flow rate thermogenic Barnett Shale gas in the Fort Worth Basin, it is essential to determine the extent of organic matter conversion using visual and chemical means of maturity assessment combined with numerical-simulation models. Vitrinite reflectance is commonly used to assess thermal maturity, but should be complemented by chemical measurements. It is helpful to complete vitrinite reflectance profiles over the entire wellbore because in marine shales, vitrinite particles are sparse. Chemical assessments of organic matter maturity and conversion such as Rock-Eval  $T_{max}$ , HI-derived transformation ratios ( $TR_{HI}$ ), gas composition, and carbon isotopes are complementary chemical techniques. It is also essential to evaluate residual hydrocarbon products to ensure that no high-molecular-weight black-oil components remain in the system. These components are hypothesized to restrict or occlude flow by adsorption as noted by lower gas flow in less mature (more oily) areas. They disappear at different levels of thermal maturity depending on kerogen type. Thus, a

multiparameter visual and chemical assessment of the extent of organic matter conversion should be undertaken to assess shale-gas producibility.

The Barnett Shale has proven to be a commercial thermogenic shale-gas system, but other systems, some with similar geochemical, petrophysical, and mineralogical characteristics have excellent potential for commercial gas production. Other gas systems with quite different types of gas as well as varying geochemical, petrophysical, and mineralogical characteristics also have good potential for commercial gas and long-term production, but may have lower flow rates compared to Barnett Shale wells in the Fort Worth Basin given current completion technologies. The economics of production of gas from each of these systems are dependent on geological, geochemical, petrophysical, and engineering, as well as drilling costs and gas prices. Thus, one shale-gas model cannot be expected to explain all other shale-gas system plays, and each must be studied in its own right with application of appropriate technologies and, sometimes, the enduring patience that was required for commercial development of Barnett Shale in the Fort Worth Basin.

## APPENDIX: TERMS AND COMPUTATION OF $HI_o$ , $TR_{HI}$ , AND $TOC_o$

### Terms

- $R_o$  = vitrinite reflectance (in percent)  
 $TOC$  = total organic carbon (in wt.%)  
 $C_C$  = convertible organic carbon or carbon in free oil or kerogen in a rock (wt.%)  
 $C_R$  = residual organic carbon or carbon remaining after pyrolysis (wt.%)  
 $S_1$  = free volatile hydrocarbons thermally flushed from a rock sample at 300°C (nominal) (in mg HC/g rock)  
 $S_2$  = products that crack during standard Rock-Eval pyrolysis temperatures (300–600°C [nominal]) (in mg HC/g rock)  
 $S_3$  = organic carbon dioxide released from rock samples between 300 and 390°C (nominal) (mg  $CO_2$ /g rock)  
 $T_{max}$  = the temperature at peak evolution of  $S_2$  hydrocarbons (in °C)  
 $HI$  (hydrogen index) = remaining potential ( $S_2$ ) divided by  $TOC \times 100$  (in mg HC/g  $TOC$ )  
 $PI$  (production index) = free oil content as measured by  $S_1$  only divided by the sum of  $S_1$  plus the remaining generation potential ( $S_2$ ) or  $S_1/(S_1 + S_2)$  (values from 0.00 to 1.00)  
 $TR_{HI}$  = transformation or conversion ratio calculated from  $HI_o$  and  $HI_{pd}$  (see equation below)

Subscripts used with terms:

- $o$  = original  
 $pd$  = present day

### Computation of $HI_o$ , $TR_{HI}$ , and $TOC_o$

$HI_o$  value can be computed from visual kerogen assessments and assigned kerogen-type  $HI_o$  average values using the following equation:

$$HI_o = \left( \frac{\% \text{ type I}}{100} \times 750 \right) + \left( \frac{\% \text{ type II}}{100} \times 450 \right) + \left( \frac{\% \text{ type III}}{100} \times 125 \right) + \left( \frac{\% \text{ type IV}}{100} \times 50 \right) \quad (1)$$

This equation requires input of maceral percentages from visual kerogen assessment of a source rock. For example, using Barnett Shale that is 95% type II and 5% type III, the calculated  $HI_o$  value is 434 mg HC/g  $TOC$ . At 100% type II,  $HI_o$  would be 450 mg HC/g  $TOC$ . These values are comparable to those measured on immature to low-thermal-maturity Barnett Shale that ranged from 380 to 475 mg HC/g  $TOC$ .

Using the equations of Claypool (Peters et al., 2006), the fractional conversion, i.e., the extent of organic matter conversion, can be determined. The fractional conversion,  $TR_{HI}$ , is derived from the change in  $HI_o$  to present-day values ( $HI_{pd}$ ) (Espitalie et al., 1984; Pelet, 1985; Peters et al., 2006), where  $PI$  is the production index ( $S_1/(S_1 + S_2)$ ) as  $PI_o = 0.02$  to  $PI_{pd}$  (Peters et al., 2006):

$$TR_{HI} = 1 - \frac{HI_{pd} [1200 - HI_o (1 - PI_o)]}{HI_o [1200 - HI_{pd} (1 - PI_{pd})]} \quad (2)$$

This incorporates the formula of Pelet (1985) for computing kerogen transformation where 1200 is the maximum amount of hydrocarbons that could be formed assuming 83.33% carbon in hydrocarbons. The  $PI$  is a ratio of hydrocarbons already formed to the total hydrocarbons (determined from the ratio of  $S_1$  to  $S_1 + S_2$  from

Rock-Eval data; Espitalie et al., 1977), but the solution is not overly sensitive to these values.

Once values for  $HI_o$  and  $TR_{HI}$  are determined by calculation or by measurements from low-maturity samples,  $TOC_o$  can be calculated:

$$TOC_o = \frac{HI_{pd} \left( \frac{TOC_{pd}}{1+k} \right) (83.33)}{\left[ HI_o (1 - TR_{HI}) \left( 83.33 - \left( \frac{TOC_{pd}}{1+k} \right) \right) \right] - \left[ HI_{pd} \left( \frac{TOC_{pd}}{1+k} \right) \right]} \quad (3)$$

where 83.33 is the average carbon content in hydrocarbons and  $k$  is a correction factor based on residual organic carbon being enriched in carbon over original values at high maturity (Burnham, 1989). For type II kerogen, the increase in residual carbon  $C_R$  at high maturity is assigned a value of 15% (whereas for type I, it is 50%, and for type III, it is 0%) (Burnham, 1989). The correction factor,  $k$ , is then  $TR_{HI} \times C_R$ .

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