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Geochemical Limitations of Shale Gas Resource Assessment

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Abstract: *Assessment of any shale gas potential is normally made using original S_2 value calculated from the present day S_2 values of the rock-eval analysis. The present day S_2 itself has got technical limitation and to get the original S_2 it is necessary to evaluate the original TOC which is also bound by many limitations. The technical limitation of S_2 suggests available hydrocarbons above C_{24} composition cannot come as S1 thus increasing amount of S2 although the cracked S2 amount may not be very high. Calculation of the original TOC value is also made by different methods. Based on the previous works it is accepted that type-1 kerogen loose TOC up to 80% , type-II up to 50% and type-III up to 20% to generate petroleum. Original TOC is calculated as equal to Present day TOC / (1-%converted). Calculation of the converted percentage should be very definite to conclude the percentage of original TOC. Jarvy has shown a calculation method using iso-decomposition and iso-original HI profiles. This method is limited to the fact that original HI can only be known once the original TOC is known. In this work attempt has been made to develop a mathematical equation using vitrinite reflectance (Vro) to calculate the original TOC. This method is also limited to the correct measure of Vro data and the equation is valid only based on the assumption that the cracking of kerogen to generate petroleum is same.*

I. Introduction

Shale gas although costlier to produce than conventional gas, is a major technical achievement during the present declining conventional resources. United States, the path finder of this technology, has been upgraded to a status of petroleum exporter because of huge resource of shale gas. The improvement of commercial shale gas production started with technology improvement of hydraulic fracturing after 1947 yet till 2004 the shale gas production remained marginal and it became commercial in 2005 due to huge production from horizontal wells. It is necessary to evaluate the resource potential before development of shale gas because development of shale gas field is costlier.

The resource evaluation for shale gas is also not like conventional volumetric calculation because its porosity evaluation and saturation calculations are not directly possible by conventional laboratory techniques. Shale gas is not migrated gas like conventional hydrocarbons that filled the pore space of the shale reservoir. It is the left over gas that failed primary migration from the source rock. Gas resource is partly remained adsorbed with kerogen and clay minerals and partly remained as free gas in the pore. Typical analysis techniques for shale-gas reservoir rocks include: TOC, X-ray diffraction, adsorbed/canister gas, vitrinite reflectance, detailed core and thin-section descriptions, porosity, permeability, fluid saturation, and optical and electron microscopy (Passey et al, 2010). Sometimes cuttings are also used in impermeable bottles (Jarvey, 2005) to evaluate the resource. All the techniques have their own limitations like canisters evaluations are mainly due to high cost for which sometimes cuttings in impermeable bottles are used to for direct assessment of the amount of gas in shale. However both the techniques are also limited to the loss of gas during cores/cuttings extraction which is tried to resolve statistically. Although these are the direct and dependable means of resource assessment but geochemical means are also dependable and much cheaper for resource evaluation.

To evaluate gas resource Jarvey et al (2005) used geochemical methods to calculate original S2 and transformation ratio. These geochemical calculations need assessment of original TOC for which Jarvey et al (2005) assumed present day TOC is 64% of the original TOC in Barnett Shale. The generation of gas cannot be uniform throughout the shale because of variations of maturity. Therefore, the uniform value of 64% is also not acceptable for original TOC calculation. In this work attempt has been made to develop a mathematical equation to find the left over present day TOC fraction using vitrinite reflectance data. This can help to calculate original TOC based on present day TOC and its thermal maturation.

II. Methodology

Geochemical assessment of the generation potential of the source rock needs evaluation of original TOC. To calculate the original TOC first attempt has been made to develop a relation between TOC and vitrinite reflectance. It is already known that higher vitrinite reflectance indicate more maturity of the source rock and TOC of the rock decrease with higher maturity. Thus TOC of source rock is inversely proportional with vitrinite reflectance values. Also it is known that the early generation of hydrocarbons starts with Vro value of 0.6. Therefore we can write,

$$(Vro - 0.6) \propto 1/TOC^* \quad (1)$$

Also it is known that the increase of vitrinite reflectance is exponential, therefore the proportionality equation (1) can be re-written as -

$$(Vro - 0.6) = \log_e(K / TOC^*) \quad (2)$$

Where, TOC* = Left over % TOC and K= constant

When, Vro = 0.6, TOC is the Original value. Therefore,

$\log_e K = \log_e TOC_{original}$ = 100% TOC

K= ln 100 = 4.6

$$\text{Therefore, } (Vro - 0.6) = 4.6 - \log_e \text{TOC} * \quad (3)$$

$$\text{Or, } \log_e TOC * = 4.6 - (Vro - 0.6) \quad (4)$$

$$\text{Log}_e\text{TOC}^* = 5.2 - \text{vro} \quad (5)$$

$$\text{Therefore, leftover TOC\% is } TOC * = e^{(5.2 - Vro)} \quad (6)$$

Using equation (6) we can find the converted percentage of TOC for the particular Vro and the original TOC can be calculated using equation:

$$\boldsymbol{Original\,TOC = 100\left(\frac{Present\ day\ TOC}{TOC*}\right)} \quad \textbf{(7)}$$

Re-calculation of the resource assessment is made using published data (Jarvie et al, 2005).

Table-1: List of Data used

Well	TOC(%)	HI	T_{max}(^{0}C)	Vro% Calculated	Vro% Measured	TR
1. Mitcham#1	4.67	396	434	0.65	nd	0
2. Heirs#1	3.40	68	454	1.01	0.9	83
3. T.P.Sims#2	4.45	25	487	1.61	1.66	94
4. W.C.Young#1	4.93	56	468	1.26	nd	86
5. Oliver#1	4.30	13	544	2.63	nd	97
6. Truitt-A#1	4.13	261	445	0.85	nd	34
7. Grant#1	4.70	299	446	0.86	nd	35
8. Gage#1	2.66	39	485	1.57	1.37	90

III. Results

Geochemical data of Barnett Shale samples published by Jarvey et al. (2005) has been used here to recalculate original TOC, original HI and Transformation Ratio (TR) for comparison(Table-2). Although recalculation is made based on the above data but Vro 2.63 of sample 5 is not dependable because above 2.0 Vro mainly pyrobitumens remain as organic matter (Mort & Sanei, 2013). The same sample when analyzed with 2.0 Vro show nearly same transformation ratio 98.6 in place of 98.8 but definitely the generation potential cannot be reliable if it is not kerogen. Re-calculations of each individual sample are shown below.

1. Present TOC = 4.67% and present Vro = 0.65% , Calculated TOC* = 94.6% and calculated original TOC = 4.93%, Present S2 = 18.5, Original S2 = 21.68, Original HI = 439.4 and Tr = 9.88%

2. Present TOC = 3.40% and present Vro = 1.01%, Calculated TOC* = 66.0% and calculated original TOC = 5.15%, present S2= 2.31, original S2 = 23.39
   Original HI= 454 and Tr = 85%

3. Present TOC= 4.45% and present Vro = 1.66%, Calculated TOC*= 34.5% and calculated original TOC = 12.9%, present S2= 1.11, original S2= 103.0 and
   Original HI= 798 and Tr=96.9%

4. Present TOC = 4.93% and present Vro = 1.26%, Calculated TOC* = 51.4% and calculated original TOC = 9.59%, present S2 = 2.76 and original S2 = 58.9, Original HI = 614 and Tr = 91%

5. Present TOC = 4.3% and present Vro = 2.63%, Calculated TOC* = 13.1% and calculated original TOC = 32.8%, present S2 = 0.56 and original S2 = 345.3, Original HI = 1049 and Tr = 98.8%

6. Present TOC = 4.13% and present Vro = 0.85%, Calculated TOC* = 77.5% and calculated original TOC = 5.33%, present S2 = 10.78 and original S2 = 25.24, Original HI = 473.6 and Tr = 44.9%

7. Present TOC = 4.7% and present Vro = 0.86%, Calculated TOC* = 76.7% and calculated original TOC = 6.1%, present S2 = 14.05 and original S2 = 31.25, Original HI = 510 and Tr = 41%

8. Present TOC = 2.66% and present Vro = 1.57%, Calculated TOC* = 37.7% and calculated original TOC = 7.05%, present S2 = 1.04 and original S2 = 53.97, Original HI = 765 and Tr = 95%

Table-2: Comparison of the original TOC, Original HI and Transformation ratios

Well	TOC_O1	TOC_o2	HI_o1	HI_o2	TR-1	TR-2
1	7.30	4.93	687.2	439.4	0	9.9
2	5.31	5.15	477.3	454.3	83	85.0
3	6.95	12.91	449.7	798.2	94	96.9
4	7.70	9.59	469.6	614.1	86	90.9
5	6.72	32.91	442.1	1049.1	97	98.8
6	4.80	5.33	395.5	473.6	34	44.9
7	5.71	6.13	460.0	510.0	35	41.4
8	4.16	7.05	458.6	765.2	90	94.9

Where, TOC_01, HI_01,TR-1 are accepted data by Jarvey et al (2005) and TOC_02, HI_02 and TR-2 are recalculated values.

IV. Discussion

Results above show re-calculations of the data vary to a limited extent. Because the original TOC calculation is based on the Vro values it is necessary that the Vro values should be dependable. Particularly for sample-5, original TOC 32.91% deposited during sedimentation is not acceptable. To get more dependable results it is also necessary to know the type of organic matter.

Assessment of the shale gas potential can be measured as the left over gas after primary migration from the total generation of the shale. Total amount generated from the shale is calculated as follows

$$Amount\ generated\ = Shale\ mass\ x\ TOC\ (change) x\ (HIo - HIp) \quad (8)$$

Where, HIo = Original HI and HIp = present HI

Assuming shale density as 2.5g/cc, shale of 1sq.ft area with 1ft thickness amounts to mass of 70,792.12 g. Further, 1g of shale hold 0.4cc volume of which pore volume is 0.024cc (6% porosity). For Barnett Shale reservoir pressure gradient is known to be 0.5psi/ft suggesting reservoir pressure at a depth of 2300m (7545.93ft) = 3772.96psi. 6 mg organic matter per gram of rock when converted to gas creates sufficient pressure (3858.5psi) that may develop fracture for primary migration. This calculation is made following ideal gas equation. In 1ft^3 rock the generated oil may create a pressure gradient of 0.3psi/ft suggesting generated oil when exceeds 2times the pore volume may create sufficient pressure for primary migration. Individual calculations for each sample for asset evaluation are shown below.

Sample 1: original TOC is 4.94% and present day TOC is 4.67% suggests 0.27% TOC only used for hydrocarbon generation. The amount of the carbon mass for hydrocarbon generation equals to 191.1g/sq.ft. The present HI for this is 396 and original HI is 440 suggesting amount of generated hydrocarbon is equal to 0.0084kg/sq.ft or 0.12mg/g of rock.

The total amount of generated hydrocarbon if oil (density 0.8g/cc) is 0.006 times the volume of the pore suggesting no primary migration. The maturity of the shale is seen to be 0.65 Vro suggesting it has not entered gas window. The generated oil volume is therefore stored as shale oil and assessment is 2.6BO/AF.

Sample 2: Original TOC is 5.15% and present day TOC is 3.40% suggests 1.75% TOC has been used for hydrocarbon generation. The amount of the carbon mass used for hydrocarbon generation is equal to 1238.86g/sq.ft. The present HI for this is 68 and original HI is 454 suggesting the amount of generated hydrocarbon is equal to 0.48kg/sq.ft or 6.75mg/g of rock.

The total amount of generated hydrocarbon if oil (density 0.8g/cc) is equal to 0.35 times the volume of the pore. The maturity of the shale is seen to be 1.01 Vro suggesting it remained manly in oil window.. Therefore all the generated oil remained as shale oil and the shale oil assessment is 147.76 BO/AF.

Sample 3: Original TOC is 12.89% and present TOC is 4.45%, amounts the carbon mass for hydrocarbon generation equal to 5974.85g. The present HI for this is 25 and original HI is 798 suggesting the amount of generated hydrocarbon is equal to 4.62kg/sq.ft or 65.2mg/g of rock.

The total amount of generated hydrocarbon if oil (density 0.8g/cc) is 3.4 times volume of the pore and if gas (gas density as 710 mg/litre), the volume of generated gas is 0.092litre/g of rock which is 3826 times the pore volume. The maturity of the shale is seen to be 1.66 Vro suggesting 60% remained in oil window and 40% remained in gas window. Therefore 39.1mg/g is generated oil and 26.1mg/g is generated as gas. The generated oil volume is 2 times more than the pore volume for which probably primary migration was possible. It is possible that the some amount of oil might have undergone the secondary cracking that helped primary migration as gas. Last pulse of 6mg/g shall be preserved as shale gas that amounts to 298scf/tonne and 131MCF/AF.

Sample 4: Original TOC is 9.59% and present TOC is 4.93% amounts the carbon mass equal to 3299.0g. The present HI for this is 56 and original HI is 614 suggesting original generation potential is equal to 1.8kg/sq.ft or 26mg/g of rock.

The total amount of generated hydrocarbon if oil (density 0.8g/cc) is 1.35 times volume of the pore and if gas (gas density as 710 mg/litre), the volume of generated gas is 0.0366 litre/g of rock which is 1526 time the pore volume. The maturity of the shale is seen to be 1.26 Vro suggesting 90% remained in oil window and 10% remained in gas window. Therefore 23.4mg/g is generated oil and 2.6mg/g is generated as gas. The generated oil is thus nearly 1.2 times more than the pore volume and generated gas 152.6 time more than the pore volume. It is possible that the generated oil trapped in the pore might have undergone secondary cracking and helped to succeed primary migration. Therefore last 6 mg/g of generated hydrocarbon is contributed as shale gas. This corresponds to 298 scf/tonne and 131 MCF/AF of shale.

Sample 5: Original TOC is 32.8% and present day TOC 4.3% suggest the amount of TOC used is 28.5% for hydrocarbon generation. The amount of carbon mass used for hydrocarbon generation is equal to 20175.75g. For this sample present HI is 13 and original HI is 1048 suggesting amount of generated hydrocarbons equal to 20881905.6 mg/sq.ft. or 295mg/g of rock.

The total amount of generated hydrocarbon if oil (density 0.8g/cc) is 15 times volume of the pore and if gas (gas density as 710 mg/litre), the volume of generated gas is 0.415litre/g of rock which is 17312 time the pore volume. The maturity of the shale is seen to be 2.63 Vro suggesting 33% remained in oil window and 67% remained in gas window. Therefore 97.3mg/g is generated oil and 197.7mg/g is generated as gas. The generated gas is thus nearly 11561 times more than the pore volume. The generated oil volume is 5 times the pore volume suggesting some pulses of primary migration of oil. Oil left behind will be cracked to generate gas. Amount of shale gas stored correspond to generated 6 mg/g of rock which is equivalent to 298 scf/tonne of rock.

Sample 6: Original TOC is 5.33% and present day TOC 4.13% suggest the amount of TOC used is 1.2% for hydrocarbon generation. The amount of carbon mass used for hydrocarbon generation is equal to 849.5g. For this sample present HI is 261 and original HI is 473 suggesting amount of generated hydrocarbons equal to 180095 mg/sq.ft. or 2.54mg/g of rock.

The total amount of generated hydrocarbon if oil (density 0.8g/cc) is nearly 0.13 times volume of the pore and if gas (gas density as 710 mg/litre), the volume of generated gas is 0.036litre/g of rock which is 149 times the pore volume. The maturity of the shale is seen to be 0.85 Vro suggesting the sampe remained in oil window only. Therefore, entire 2.54mg/g is generated oil and remained as shale oil equivalent to 55.6 BO/AF..

Sample 7: Original TOC is 6.1% and present day TOC 4.7% suggest the amount of TOC used is 1.4% for hydrocarbon generation. The amount of carbon mass used for hydrocarbon generation is equal to 991.1g. For this sample present HI is 299 and original HI is 507 suggesting amount of generated hydrocarbons equal to 206,148.8 mg/sq.ft. or 2.9mg/g of rock.

The total amount of generated hydrocarbon if oil (density 0.8g/cc) is nearly 0.15 times the pore volume and if gas (gas density as 710 mg/litre), the volume of generated gas is 0.0041litre/g of rock which is 170 time the pore volume. The maturity of the shale is seen to be 0.86 Vro suggesting it remained entirely in oil window. Therefore whole 2.9mg/g is generated oil and the generated gas is small amount simultaneously produced with oil. Since it is less than the pore volume it is expected the entire generated oil is stored as shale oil equivalent to 63.5 BO/AF.

Sample 8: Original TOC is 7.05% and present day TOC 2.66% suggest the amount of TOC used is 4.39% for hydrocarbon generation. The amount of carbon mass used for hydrocarbon generation is equal to 3107.8g. For this sample present HI is 39 and original HI is 764 suggesting amount of generated hydrocarbons equal to 2253155 mg/sq.ft. or 31.8mg/g of rock.

The total amount of generated hydrocarbon if oil (density 0.8g/cc) is 1.65 times volume of the pore and if gas (gas density as 710 mg/litre), the volume of generated gas is 0.045litre/g of rock which is 1866 time the pore volume. The maturity of the shale is seen to be 1.57 Vro suggesting 50% remained in oil window and 50% remained in gas window. Therefore 15.9mg/g is generated oil and 15.9mg/g is generated as gas. Generated oil in the oil window is 0.71 times the pore volume suggesting no primary migration. The generated gas in gas window together with secondary cracked oil is therefore 1866 times more than the pore volume. Amount of shale gas stored correspond to generated 6 mg/g of rock which is equivalent to 298 scf/tonne of rock

V. Conclusions

Calculations above show reasonable assessments of generated hydrocarbons in the study area. Limitation of the evaluation of generated hydrocarbons mainly depends on the calculation of original TOC. Assessment of the unconventional resource is limited to the generation potential and effective primary migration. Re-calculation of the available published data suggests sample 2, 6 and 7 remained in oil window are sweet spots for shale oil. Sample 2 is near the end of oil window and may have some more associated gas also compared to sample 6 and 7. Sample 3, 4, 5 and 8 are sweet spots of shale gas and expected potential is nearly 298 scf/tonne of the rock. This research is mainly focused on technology but the values in wells may not relevant because all calculations are made based on same pressure of 3772.96psi which is not correct. However well-wise pressure data, lithology, porosity, density may upgrade the work for dependable values.

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