Chapter 4: Organic Geochemistry

Introduction

The organic geochemistry of shales in terms of its organic richness, hydrocarbon source potential, thermal maturity, depositional environment etc. are essential stipulations for shale gas resources assessment. Rock Eval Pyrolysis technique has been widely used to evaluate the hydrocarbon generation potential, organic matter type, maturity etc of shale rock (Espitalié (1986), Peters (1986), and Jarvie and Lundell (1991), Farhaduzzaman *et al* (2012), etc. This chapter presents the organic matter richness, petroleum generation potential, type of organic matter and maturity evaluation of Barren Measures shales. A total of 32 core samples from different depth interval of the Barren Measures Formation were selected from four boreholes (B#1, B#2, B#3 and B#4). All the samples were analyzed using LECO EC-12 carbon analyzer and Rock Eval Pyrolysis-6 to understand the geochemical properties of Barren Measures shale. The shale is found to be rich in TOC (3.75 to 20.9 wt. %) with kerogen type III (gas prone). The study analysed the effect of burial history on the preservation and maturation of organic matters. The organic richness, kerogen type, thermal maturity of Barren Measures are signifying fair to excellent gas generation potential.

Total Organic Content (TOC)

The Total Organic Content (TOC) was determined by using LECO EC-12 carbon analyser (Lafargue *et al*, 1998). Approximately 0.2 grams of the samples were weighed, treated with concentrated hydrochloric acid to remove carbonates, and vacuum filtered on glass fiber paper. The LECO EC12 system is a microprocessor based instrument for determining carbon content in coal, coke, petroleum products, shale, ores and many other nonmetallic materials. The EC 12 is used to combust the samples in an oxygen atmosphere at about 1000º C where the carbon oxidizes to carbon dioxide. Moisture and dust were removed and CO_2 gas was measured by solid state infrared detector (Knies *et al,* 2002; Farhaduzzaman *et al*, 2012)

The dark grey to black colour of the studied shale samples of Barren Measures indicates high content of organic matter (Potter, 1980; Pettijohn, 1984; Varma *et al*, 2014). The laboratory measured TOC value ranges from 3.75 wt. % to 20.9 wt. %. Generally, the variation in TOC content is caused due to climatic variations of sediment deposition, decomposition, weathering effect and/ or thermal maturation with burial (Hunt, 1995; Stein, 2007; Wang and Carr, 2013). Oxygen depleted or anoxic, low energy environment is the best media for preserving organic matter (Demaison and Moore, 1980). The considerably low measured TOC for the samples belonging to borehole B#4 indicates the vertical TOC variation with depth of burial. Post depositional diagenesis processes, increasing pressure and temperature with burial depth etc. causes thermal alteration of organic matter which may lead to TOC variation, i.e. TOC loss with depth is due to maturation, hydrocarbon generation and expulsion. Previous studies strongly suggested that such differences are due to conversion of organic matter to hydrocarbons in the subsurface (Montgomery *et al*, 2005; Jarvie *et al,* 2007). In this study, the original TOC (TOC_O) of the samples was calculated from measured TOC values, using numerical methods (Jarvie and Lundell, 1991; Jarvie, 2004). The original TOC differs from the present day TOC (TOC_P) content ($TOC_P/0.64 = TOC_O$) and it is higher than present day TOC. The calculated original TOC ranges from 5.85 to 32.65 wt. % for the studied shale samples.

Rock Eval Pyrolysis Analysis

Rock-Eval pyrolysis technique has been used to determine the petroleum potential and the thermal maturity of the kerogen occurring in a rock (Barker, 1974; Espitalie, 1986; Jarvie and Lundell, 2001; Banerjee *et al*, 2006; Jarvie *et al*, 2007; Maky and Ramadan, 2008). Details of the analytical methods have been described by Espitalie (op. cit.), Tissot and Welte (1984) and Peters (1986). Here, the hydrocarbon generation potential of Barren Measures shale samples (n=32) was assessed using the Rock Eval 6 pyrolyser (Turbo version-Vinci Technologies). The complete process was carried out in the two ovens i.e. pyrolysis and oxidation (combustion) of Rock Eval pyrolyser. Pyrolysis continues with an isothermal temperature program of 300 °C to 650 °C in an inert atmosphere of nitrogen with a rise of 25°C per minute. The pyrolyzed hydrocarbons were controlled by a flame ionization detector (FID). Pyrolysis analysis provides four vital parameters: (1) thermo vaporized free hydrocarbons (S1 peaks); (2) pyrolysis hydrocarbon from cracking of organic matter (S2 peaks), the amount of hydrocarbon not yet released from the rock by natural processes. It represents the residual petroleum potential; (3) the amount of carbon dioxide (CO_2) released through heating organic matter (S3 peaks); and (4) the highest temperature for generating a maximum amount of hydrocarbon during pyrolysis (Tmax). The Tmax value is a maturity parameter and corresponds to the temperature at which maximum amount of hydrocarbons are released from the thermal degradation of kerogen, i.e. S2 peak. It is used as an indicator of the thermal maturity of rock (Espitalie, op. cit.). The calculated parameters of Rock Eval i.e. the hydrocarbon potential or hydrogen index (HI) is defined by 100 × S2/TOC. The oxygen index (OI) is defined as 100 × S3/TOC, where S3 is the CO_2 released during the pyrolysis. Both the measured and calculated parameters from Rock Eval pyrolysis, helps in determination of kerogen type, hydrocarbon generation efficiency and maturation. The hydrocarbon generation and maturation processes are highly controlled by time, temperature, pressure, depth of burial etc. (Peters, 1986; Hunt, 1995; Jarvie *e al*, 2007). Therefore, the experimental temperatures were set comparatively higher than normal subsurface conditions, so that appreciable reaction for the generation of hydrocarbons can occur in a reasonably short time and amount of generated hydrocarbons relative to the total potential of the source rock can be estimated (Peters, 1986; Espitalie, 1986; Banerjee *et al*, 2006; Mani *et al*, 2014). The Rock Eval Pyrolysis generated parameters are S1, S2, S3 and Tmax whereas calculated parameters are hydrogen index (HI), oxygen index (OI), production index (PI), genetic potential (PI), maturity etc. The important parameters obtained from the pyrolysis of shales using Rock Eval 6 are furnished in Table 4.1, 4.2, 4.3 and 4.4.

Table 4.1: *Rock Eval Pyrolysis results of Borehole B #1*

Depth Intervals (m)	**S1** (mg HC/g rock)	**S2** (mg HC/g rock)	**S3** (mg CO_2/g rock)	**TOC** Wt.**%**	**Tmax** (ºC)	**PI**	**HI** (mg HC/g TOC)	**OI** (mg CO_2/g TOC)	**VRo%**
150-155	1.20	10.59	0.20	12.98	445	0.101	81.587	1.540	0.85
155-160	1.91	14.99	0.56	20.90	445	0.113	71.722	2.679	0.85
170-175	0.98	8.90	0.56	12.00	446	0.099	74.166	4.666	0.868
175-180	0.94	6.98	0.34	11.56	446	0.118	60.380	2.941	0.868
180-185	0.92	6.30	0.41	6.78	447	0.127	92.920	6.047	0.886
185-190	1.94	5.98	0.45	8.37	447	0.244	71.445	5.376	0.886
190-195	0.71	3.56	0.33	6.09	448	0.166	58.456	5.418	0.904
195-200	0.33	2.57	0.85	3.75	448	0.113	68.533	22.666	0.904

__Table 4.2:__ Rock Eval Pyrolysis results of Borehole B #2

Depth Intervals (m)	**S1** (mg HC/g rock)	**S2** (mgHC/ g rock)	**S3** (mgCO$_2$/g rock)	**TOC** wt.%	**Tmax** (ºC)	**PI**	**HI** (mgHC/g TOC)	**OI** (mg CO$_2$/g TOC)	**VRo%**
91-95	0.80	4.12	0.42	4.74	433	0.162	86.919	8.860	0.634
96-100	0.74	6.03	0.50	6.67	435	0.109	90.404	7.496	0.67
100-105	0.95	9.89	0.40	7.89	437	0.087	125.348	5.069	0.706
105-120	0.88	5.45	0.30	6.78	439	0.139	80.383	4.424	0.742
110-115	0.98	8.41	0.52	10.69	441	0.104	78.671	4.864	0.778
115-120	0.73	6.31	1.45	9.94	443	0.103	63.480	14.587	0.814
120-125	1.94	17.05	0.29	17.88	443	0.102	95.357	1.621	0.814
125-130	1.66	14.2	0.30	19.98	444	0.104	71.071	1.501	0.832
130-135	1.94	12.23	0.60	17.88	444	0.136	68.400	3.355	0.832
135-140	1.19	10.34	0.80	12.00	445	0.103	86.166	6.666	0.85
150-155	1.03	12.59	0.80	13.69	445	0.075	91.964	5.843	0.85
155-160	1.84	18.49	0.57	20.88	445	0.090	88.553	2.729	0.85
185-190	1.44	6.68	0.42	9.73	446	0.177	68.653	4.316	0.868
190-195	0.81	4.83	0.33	4.97	447	0.143	97.183	6.639	0.886

__Table 4.3:__ Rock Eval Pyrolysis results of Borehole B#3

Depth Interval (m)	**S1** (mg HC/g rock)	**S2** (mg HC/g rock)	**S3** (mg CO$_2$/g rock)	**TOC** wt%	**Tmax** (ºC)	**PI**	**HI** (mg HC/g TOC)	**OI** (mg CO$_2$/g TOC)	**VRo%**
110-115	1.80	12.23	0.42	12.85	441	0.128	95.175	3.268	0.778
115-120	1.39	9.85	1.02	11.26	442	0.123	87.477	9.058	0.796
120-125	1.19	12.06	0.83	13.08	443	0.089	92.201	6.345	0.814
150-154	0.67	7.60	0.79	8.56	443	0.081	88.785	9.228	0.814
157-160	0.52	8.02	0.43	9.65	444	0.060	83.108	4.455	0.832
160-162	1.88	8.75	1.85	11.48	446	0.176	76.219	16.114	0.868

__Table 4.4:__ Rock Eval Pyrolysis results of Borehole B#4

Depth Interval (m)	**S1** (mg HC/g rock)	**S2** (mg HC/g rock)	**S3** (mg CO_2/g rock)	**TOC** wt %	**Tmax** (ºC)	**PI**	**HI** (mg HC/g TOC)	**OI** (mg CO_2/g TOC)	**VRo%**
301-305	0.40	3.12	0.61	5.13	456	0.113	60.818	11.890	1.048
305-310	0.94	4.08	0.68	5.20	456	0.187	78.461	13.076	1.048
310-315	0.41	3.06	0.74	4.81	457	0.118	63.617	15.384	1.066
320-321	0.55	4.64	0.58	5.77	458	0.105	80.415	10.051	1.084

a. Genetic Potential (GP): A genetic potential is the summation of the amount of free hydrocarbon (S1) and the quantity of remaining hydrocarbon which has not yet been converted to hydrocarbons (S2). This can be mathematically expressed as (S1+S2) measured in mg/g of rock (Tissot and Welte, 1984). Genetic potential values and comparable source rock evaluations are shown in Table 4.5. The excellent genetic potential is observed in the most of studied samples. The average GP of the studied samples are 9.54 mg HC/g Rock varying from 2.9 to 20.33 mg HC/g Rock. The maximum genetic potential of 20.33 mg HC/g Rock was observed at the depth interval of 155-160m of borehole B#2. The cross plot between GP and TOC illustrate that the samples are having good to excellent hydrocarbon generation potential (Figure 4.1).

__Table 4.5:__ Generation Potential of studied samples

Borehole	**GP (mg HC/g TOC)**			**Evaluation**
	min	**max**	**avg**	
B#1	2.9	16.9	8.6	Moderate to good
B#2	4.92	20.33	10.96	
B#3	8.27	14.03	10.99	Good
B#4	3.47	5.19	4.30	Moderate

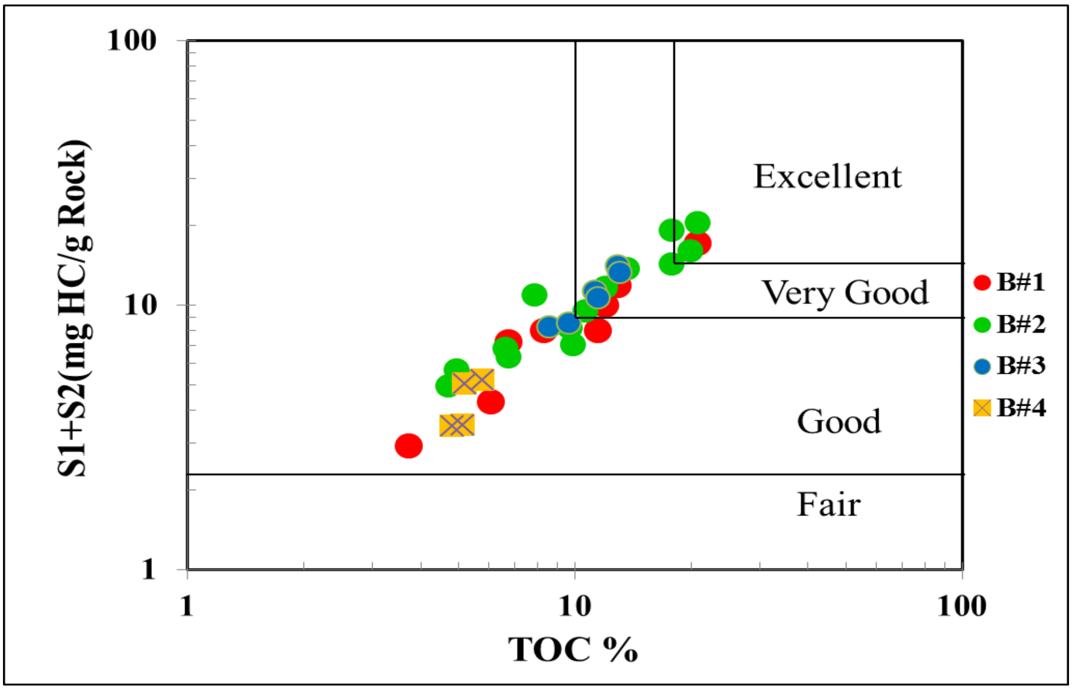

Figure 4.1 *Cross plots of Generation potential (GP) versus TOC (after Ghori, 2002).*

b. Productivity Index (PI)

The productivity index (PI) or production index or transformation ratio, is a proportionality between the hydrocarbons that already generated (S1) from kerogen and a quantity of whole hydrocarbons that can be obtained from kerogen. The production index or productivity index (PI) is derived from the relationship S1/ (S1+S2). The PI of studied samples shows a range of 0.06 to 0.24mg HC/ g TOC and indicates in situ petroleum generation (Peters & Moldowan 1993) of matured sediments (Peters 1986). The highest PI is observed at the depth interval of 185-190m (B#1). The weathering processes or oxidation removes hydrogen and adds oxygen to the kerogen which can slightly alter the original PI value. Generally, the commercial gas shale producing horizons show PI values ranges from 0.6 to 1.5, where shales with greater than 0.1 PI can generate excellent quantity of hydrocarbon.

c. S2 versus TOC

The plot of S2 vs TOC was plotted (Figure 4.2) and it reflects very good to excellent genetic potential.

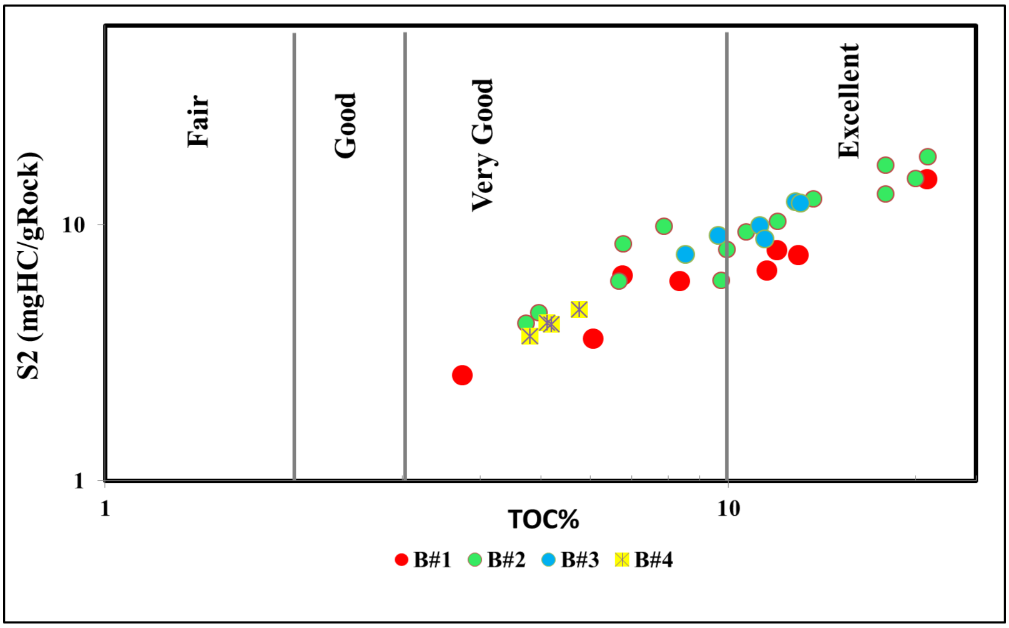

Figure 4.2*: Cross plot between S2 versus TOC (Ghori, 2002).*

Kerogen Type Determination from Pyrolysis

a. Hydrogen Index and Oxygen Index (OI)

These indices are mathematically expressed as [(100 x S2)/TOC] and [(100 x S3)/TOC] for the hydrogen index and the oxygen index, respectively (Hunt 1995; Tissot and Welte, 1984; Peters and Cassa, 1994). At early thermal maturity stages: (1) type I kerogen usually contains HI values >600 mg HC/g TOC and OI values <50 mg CO_2/g TOC; (2) type II kerogen normally has HI values 300–600 mg HC/g TOC and OI values <50 mg CO_2/g TOC; (3) a mixture of type II and type III has a low hydrogen index 200–300 mg HC/g TOC; (4) type III kerogen generally contains HI values 50–200 mg HC/g TOC and OI values of 5–100 mg CO_2/g TOC; and (5) type IV kerogen commonly has HI values of <50 mg HC/g TOC (Tissot and Welte, 1984; Peters and Cassa, 1994).

It is observed that the samples of Barren Measures shale have the HI ranging from 58.45 to 125.34 mg HC/g TOC with an average HI of 80.56 mg HC/ g Rock (Table 4.6). Low HI (<125.34 mg HC/g TOC) indicates a greater potential to generate gaseous hydrocarbon (Boyer *et al*, 2006). The original S2 and original HI were determined using the mathematical equations (Espitalie, 1986; Peter, 1986; Peter and Cassa, 1994; Jarvie, 2004; Jarvie *et al,* 2007). The original generation potential (original S2 mg hydrocarbons / g rock) of studied sample is calculated numerically i.e. original S2=TOC change / 0.083 + present S2. The original S2 values ranges from 5.11 to 32.6 mgHC/g rock. Thus original HI value is calculated using the equation Original HI = Original S2 / Original TOC x 100 (Jarvie 2004; Jarvie *et al*, 2007). The studied samples show original HI value of 80.78 to 138 mg HC/g TOC. OI value ranges from 1.50 to 22.66 mg CO_2/g TOC with an average of 7.13 mg CO_2/g TOC. The cross plot between HI and OI of samples (Figure 4.3) denotes the presence of type III, gas prone kerogen (Hunt, 1995). OI trends to decrease while PI increases with burial depth (Espitalie 1986). In the present study, slight increase in trend of PI was noticed.

Table 4.6: *HI and OI values of studied Boreholes*

Borehole	HI (mg HC/g Rock)		OI (mg HC/g Rock)		Evaluation
	min	max	Min	max	
B#1	58.45	92.92	1.54	22.66	TYPE III
B#2	63.48	125.34	1.5	14.58	
B#3	76.21	95.17	3.2	16.11	
B#4	60.81	80.41	10.05	15.38	

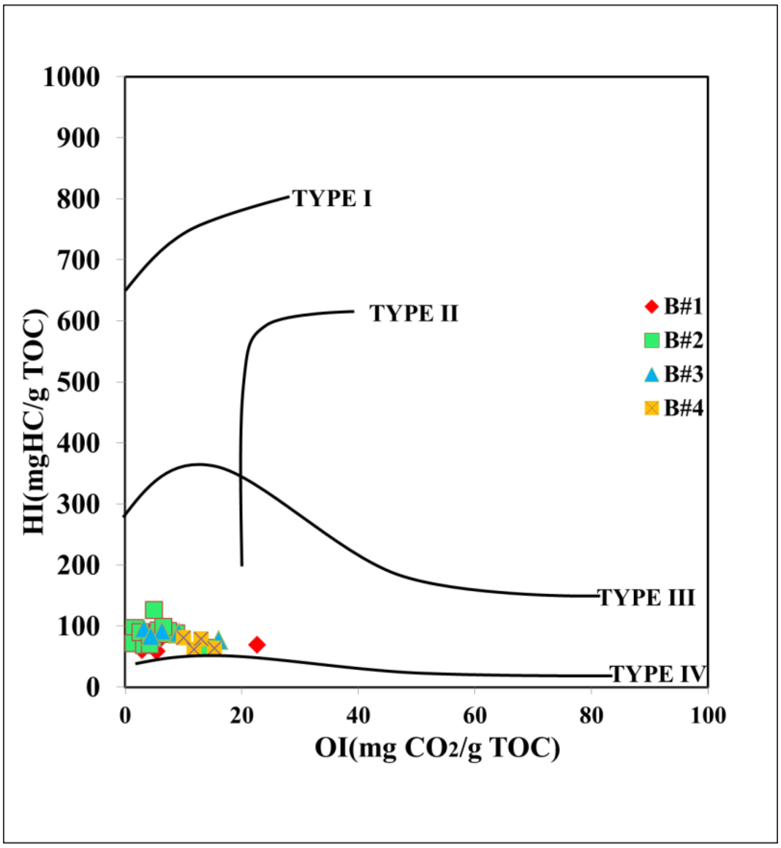

Figure 4.3 *Modified Van Krevelen diagram indicating the kerogen type for Barren Measures Shale.*

b. HI versus Tmax

HI versus Tmax cross plot was analysed for kerogen type determination (Hunt, 1995) and presence of type III kerogen was identified (Figure 4.4). The samples from Barren Measures are III kerogen and capable to produce mainly gas.

c. TOC versus S2

The plot of TOC versus Rock-Eval pyrolysis S2 was interpreted to determine the type of organic matter (Figure 4.5). The figure shows that samples are of type III kerogen The Rock Eval study reveals the presence of kerogen type (III) gas prone. Type III consists of humic, coaly material derived from continental higher plants. It has a low H/C ratio and high oxygen content and therefore is usually gas prone (Van Krevelen, 1961; Tissot and Walte, 1984). It produces natural gas and occasionally associated condensate if the thermal maturation is adequate. Type III kerogen has low H/C (<1.0) and high O/C (up to ~0.3). Such low hydrogen organic matter is polyaromatic. The cross plots of studied samples from boreholes represents the type III kerogen.

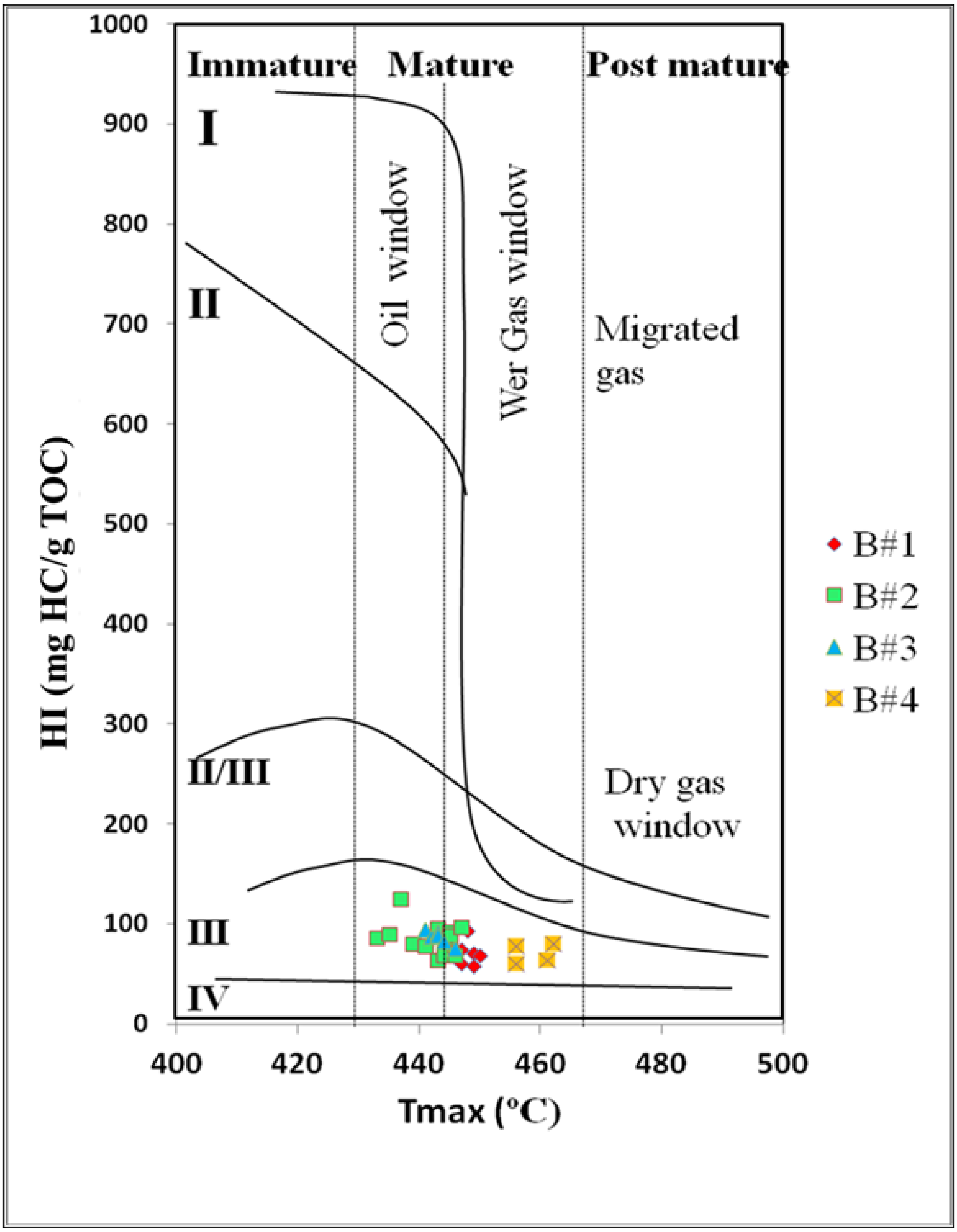

Figure 4.4 *HI versus Tmax cross plot. The plot shows the kerogen type and maturity range of the samples (after Espitalie, 1986).*

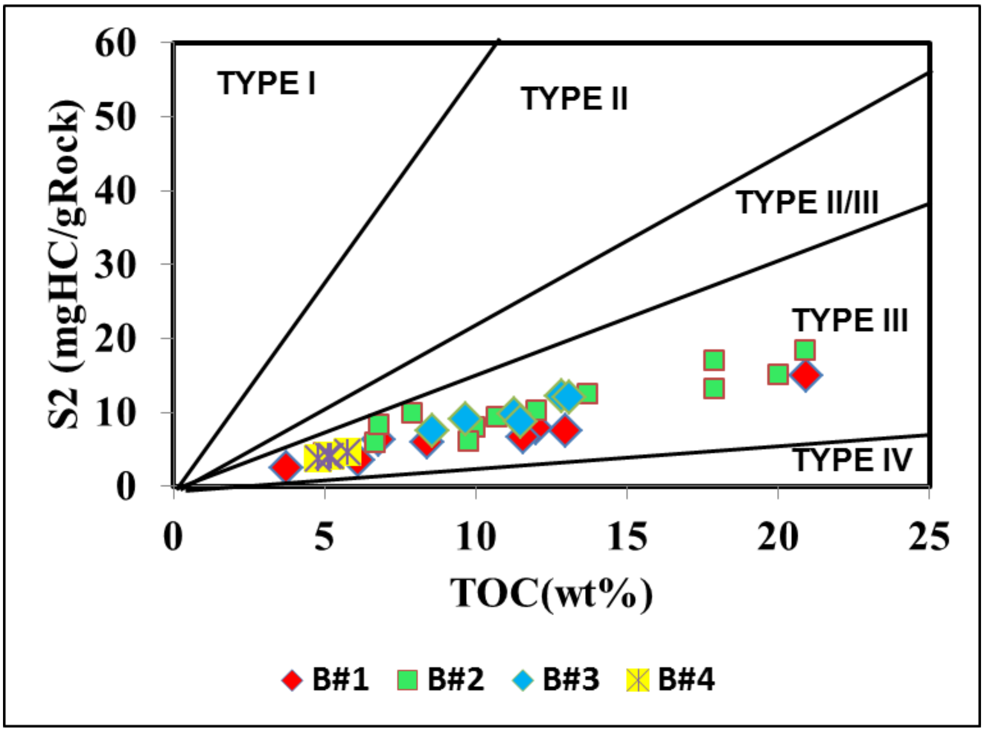

Figure 4.5: *Cross plot of remaining hydrocarbon potential (S2) and TOC (wt. %) for Barren Measures shales. All the samples are falling in the type III zone (Hunt, 1995).*

Thermal Maturity Determination

The Maturation of the organic matter can be estimated by Tmax range, Tmax versus HI and Numerical maturity calculation method. According to Espitalie(1986), for Type III organic matter, a Tmax of 434ºC is the boundary between immature and mature kerogen (oil production zone) whereas a Tmax of 465ºC as the boundary between mature and over-mature kerogen (gas-production zone) The highest Tmax value during pyrolysis analysis of organic material was recorded for samples from B#4 at a depth of 350-355 m. Analysis of all the crucial Rock-Eval parameters (HI, OI and Tmax) refers early to late maturity level of the shales.

a. Tmax versus PI

Combining and finding relations between the essential Rock-Eval parameter, Tmax, and calculated Rock-Eval parameter, PI, is a valuable method for indicating the thermal maturity of organic matter (Figure 4.6).

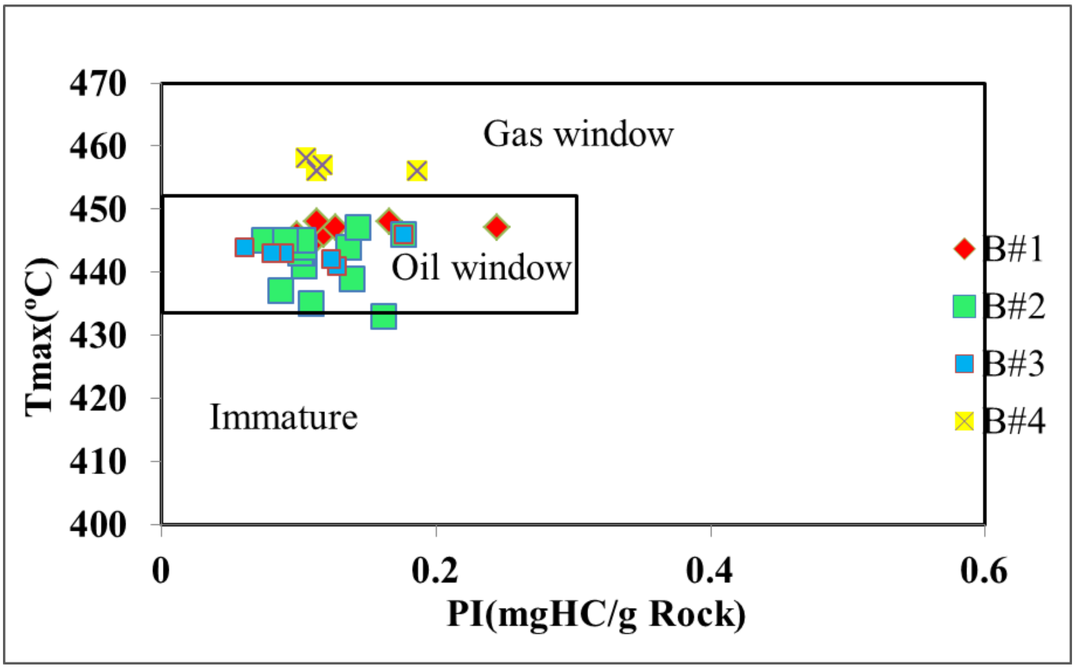

Figure 4.6 *Tmax versus Production Index (Ghori, 2002).*

b. Vitrinite Reflectance (Ro)

The Vitrinite reflectance is an optical method for measuring the source rock maturity (Tissot and Welte, 1984). Vitrinite includes material derived from vascular plants (Hunt, 1995). With increasing maturity of organic matter, the reflectance (Ro) of light also increases. Since Tmax obtained from Rock-Eval pyrolysis indicates the level of thermal maturity, it is possible to convert Tmax to Ro (Dembicki 2009). The conversion can be mathematically expressed as Ro (calculated) = (0.018) (Tmax) – 7.16 (Jarvie and Lundell, 2001; Jarvie *et al*, 2007). The samples are showing the maturity range of 0.6-1.0% (Figure 4.7).

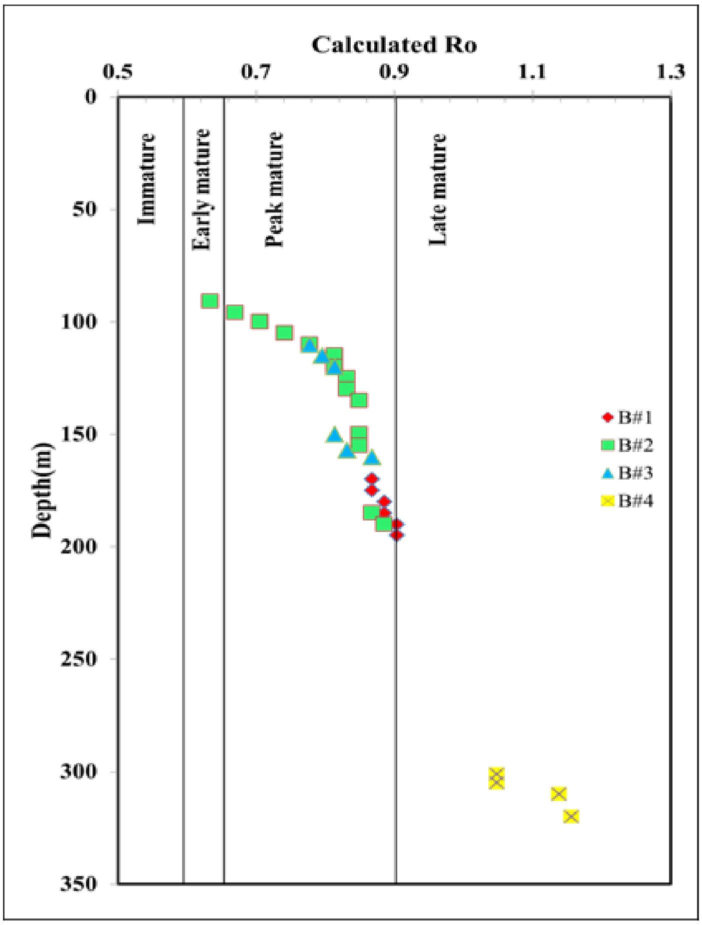

Figure 4.7 *Depth versus calculated maturity values of Barren Measures. The samples of borehole B#4 are showing maximum maturity values (modified after Peters and Cassa, 1994).*

Figure 4.8 illustrates in general terms the temperature dependence of hydrocarbon generation in the subsurface from the kerogen-type III. The present temperature and depth level of shale is not necessarily an indicator of its maturity: Maximum burial and maximum subsurface temperature exposure may have occurred at some time in the geologic past. The maximum oil and gas generation, and termination of generation are all kerogen-type specific. A shale can generate oil or/and gas based on kerogen type, burial history, temperature, etc. Although, a source rock can generate maximum gas within gas window, however, limited gas generation starts from oil window level. In case of kerogen type III, a source rock can generate gas during the early stage of maturity too.

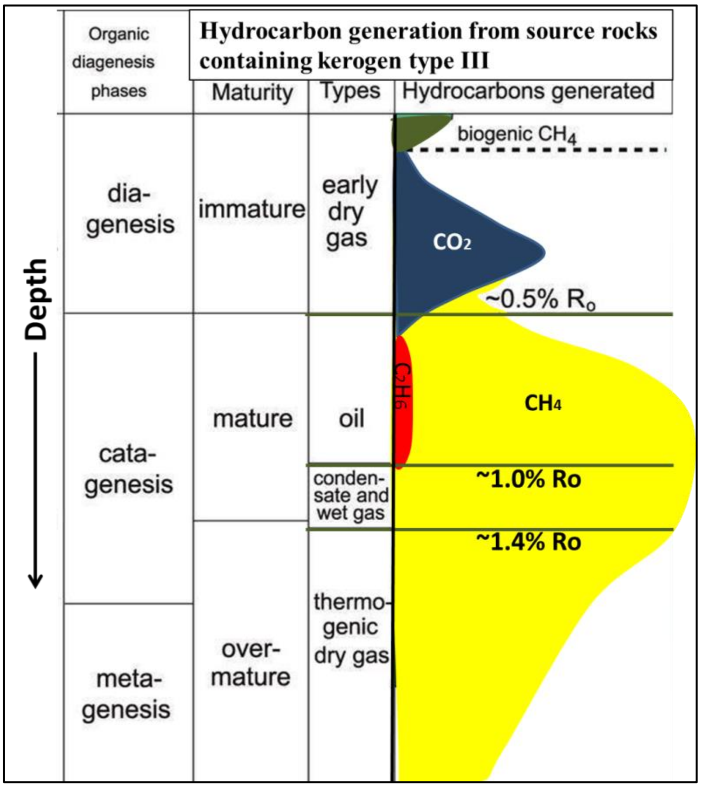

Figure 4.8 *Depth versus hydrocarbon (Kerogen type III) generation stages (modified after Hunt, 1995)*

Migrated Hydrocarbons

The comparison of production indices with the thermal maturity stage of samples was used to identify migrated hydrocarbons (Hunt, 1995). The high S1 values are either: (1) normal, which indicate prospective source rocks; or (2) abnormal, resulting from a combination with migrated oil, or coming from drilling additives (Peters and Cassa, 1994). When S1 is high and the TOC is low, nonindigenous hydrocarbons can be detected (Hunt, 1995). Figure 4.9 separates migrated from non-migrated hydrocarbons for the samples in different boreholes. The dividing line on the plot is where S1/TOC = 1.5. Values belonging to nonindigenous hydrocarbons appear above this line while indigenous hydrocarbon values emerge below it (Hunt, 1995). The cross plot of S1 versus TOC% was used to distinguish migrated hydrocarbons and contaminants from indigenous hydrocarbons (Hunt, op cit). Figure 4.9

represents the plot of S1 versus TOC for the analysed samples in this study. The findings suggest indigenous organic matter in Barren Measures.

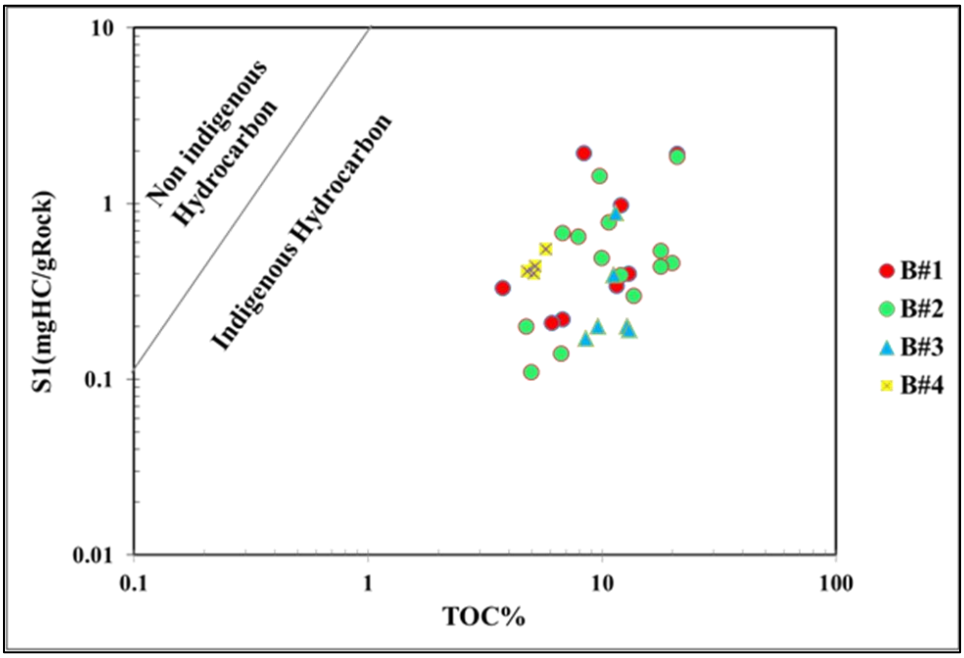

Figure 4.9 *S1 versus TOC (wt %) cross plot shows all the samples are in the zone of indigenous hydrocarbon (after Hunt 1995).*

Depth of Expulsion or Primary Migration

Primary migration, or expulsion from fine-grained organic rich shales to the migration pathways, is the first migration phase for organic material following conversion to petroleum (Hunt, 1995). The depth at which a source rock starts to expel hydrocarbon can be determined by plotting depth against S1/TOC (Figure 4.10). According to Hunt (1995), the expulsion starts when the ratio of S1 to TOC ranges between 0.1 and 0.2. Thus, the present analyses confirm the insitu gas generation competency of Barren Measures Shale, even though it requires integrated geological, petro-physical, geo-mechanical investigations in finding sweet spots for shale gas exploration in the field. Therefore, an attempt has been made to assess the reservoir quality of the Barren Measures in the next chapter.

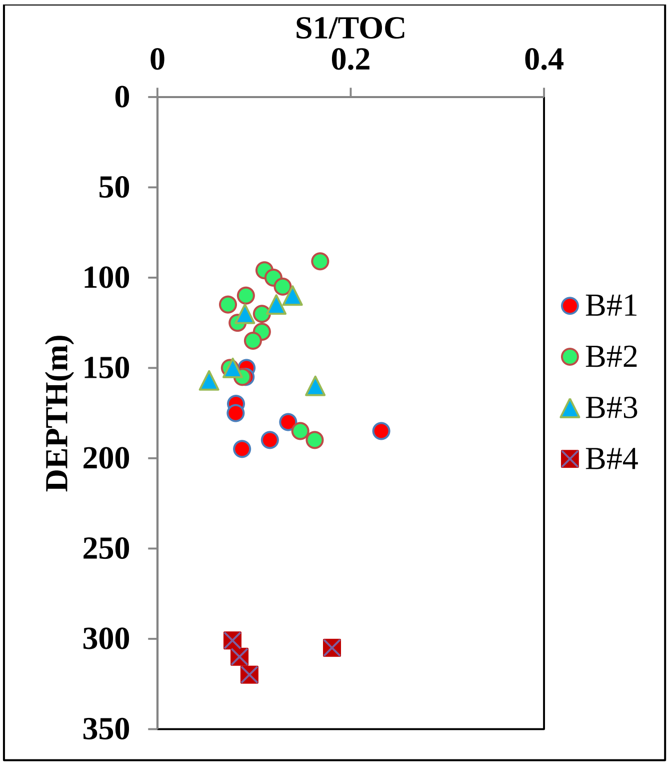

Figure 4.10 *Depth versus S1/TOC graph (after Ghori, 2002).*

Organic geochemistry analyses suggest the Barren Measures shales are having TOC content ranges from 3.75 to 20 wt% and thermally mature, consist of mainly Kerogen type III, deposited in anoxic condition and matured comparatively at shallower depth. The shale of Barren Measures has very good source rock generative potential and has obtained thermal maturity levels equivalent to the oil window (Boruah and Ganapathi, 2015). The thermal maturity of the shales is controlled by the burial history of the sediments. The Barren Measures may have excellent prospects for shale gas exploration if the exploration strategies are focused considering the reservoir properties.

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