

Convergence of shale gas reserve estimates from a high pressure water pyrolysis procedure and gas adsorption measurements

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Introduction

Shale gas is thermogenic gas (composed mainly of methane), that is largely generated at high thermal maturities. Produced gas data from the Barnett Shale have shown methane contents of 80% from condensate-wet gas mature, and >90% for dry gas mature source rocks (Jarvie et al. 2005). Jarvie (2012), suggested that the best shale resource systems have a source rock maturity (VR) of > 1.4% Ro. However, Andrews (2013) estimated the UK Bowland shale resources assuming a lower thermal maturity range of 1.1-1.9% Ro for shale gas generation based on studies of conventional UK borehole cores using Rock Eval pyrolysis. Regarding using laboratory pyrolysis procedures for shale gas estimate, the estimate will depend upon the maturity range over which dry gas generation is assumed to occur and the pyrolysis procedure used. This assumes that the gas generated can be retained in the shale and to test whether this is the case, the results need to be compared with those from high pressure gas (methane) adsorption.

This study correlates, for the first time, results from closed system pyrolysis and high pressure methane adsorption isotherms. Pyrolysis experiments were conducted sequentially under non-hydrous and water pressure (180-800 bar) conditions, on an immature source rock (0.58% Ro, HI of 410 mg HC/g TOC, Tmax of 436 °C, and TOC of 6.69%) (from Rempstone-1 well) from the UK Upper Bowland Shale. The source rock (2-5 mm particles) was successively heated 5 times with increasing temperature (350 °C 24 h, 380 °C 24 h, 420 °C 24 h, 420 °C 48 h, and 420 °C 120 h). After each run, the reactor contents (pyrolysed rock, expelled oil and gas) were recovered, before re-charging the pyrolysis vessel with the same source rock.

Results

Fig. 1 shows that for the sequential 800 bar experiments, maximum C₁-C₅ gas yields was generated from source rock with initial VR of 1.26% Ro (21 mg/g TOC), the methane content was only 50%. Dry shale gas containing *ca*. 80% and 90% methane was generated from initial VR's of 2.03% Ro (7.4 mg/g TOC of C₁-C₅ gas) and 2.25% Ro (4.7 mg/g TOC of C₁-C₅ gas) respectively. All the lower water pressure runs followed the same trend as the 800 bar run. Experiments conducted in the absence of water (non-hydrous) for comparison, produced much higher gas yields because the oil remained in contact with the source rock and cracked to a greater extent. This resulted in the gas generated at the highest maturity containing < 70% methane, showing that only sequential water pyrolysis can properly simulate dry shale gas. Gas in place (GIP) estimates calculated using the 800 bar expelled dry gas yield indicate that the UK Upper Bowland Shale may contain 22-33 tcf of shale gas, significantly less than 164-447 tcf suggested by Andrews (2013) using a much wider maturity range.

The high pressure methane adsorption isotherms were Type I for the initial and pyrolysed shales (Fig. 2) with pore water present. The monolayer capacity (using duel-site Langmuir equation) for the 800 bar mature shale (2.03% Ro) was 4.2 mg/g at 25 °C and this reduced by about 57% at 100 °C. This range of values (1.8-4.2 mg/g) is between 38 and 57% of the GIP estimated from 800 bar pyrolysis gas yield (4.7-7.4 mg/g). This implies that there is just



sufficient capacity to adsorb dry gas containing >90% methane. If this is correct then the GIP volume estimate will reduce even further to between 8-19 tcf.

Conclusions

Although the GIP estimates from the high pressure methane adsorption measurements are lower than the amounts of dry gas generated, the range of values overlap quite strongly. This study have shown that the amount of shale gas contained in the UK Bowland shale will be significantly less, due to the reduced hydrocarbon generative potential (HI < 20 mg HC/g TOC) that will be remaining in the rocks (Figure 1) at high maturity when dry gas generation commences. The methane adsorption isotherms provide certainly strong evidence that there is insufficient capacity within Bowland Shale source rocks to store large quantities of gas if generated at relatively low maturities as suggested by Andrews (2013).



Figure 1. Total hydrocarbon (C_1 - C_5), C_2 - C_5 and methane yields (mg/g TOC of initial rock TOC) for 800 bar sequential pyrolysis.



Figure 2. Methane adsorption isotherm at 25 and 100 °C for 800 bar 420 °C 48h sample.

References

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