Impact of high water pressure on oil generation and maturation in Kimmeridge Clay and Monterey source rocks: Implications for petroleum retention and gas generation in shale gas systems

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Abstract

This study presents results for pyrolysis experiments conducted on immature Type II and IIs source rocks (Kimmeridge Clay, Dorset UK, and Monterey shale, California, USA respectively) to investigate the impact of high water pressure on source rock maturation and petroleum (oil and gas) generation. Using a 25 ml Hastalloy vessel, the source rocks were pyrolysed at low (180 and 245 bar) and high (500, 700 and 900 bar) water pressure hydrous conditions at 350 °C and 380 °C for between 6 and 24 h. For the Kimmeridge Clay (KCF) at 350 °C, Rock Eval HI of the pyrolysed rock residues were 30 – 44 mg/g higher between 6 h and 12 h at 900 bar than at 180 bar. Also at 350 °C for 24 h the gas, expelled oil, and vitrinite reflectance (VR) were all reduced by 46%, 61%, and 0.25% Ro respectively at 900 bar compared with 180 bar. At 380 °C the retardation effect of pressure on the KCF was less significant for gas generation. However, oil yield and VR were reduced by 47% and 0.3% Ro respectively, and Rock Eval HI was also higher by 28 mg/g at 900 bar compared with 245 bar at 12 h. The huge decrease in gas and oil yields and the VR observed with an increase in water pressure at 350 °C for 24 h and 380 °C for 12 h (maximum oil generation) were also observed for all other times and temperatures investigated for the KCF and the Monterey shale. This shows that high water pressure significantly retards petroleum generation and source rock maturation. The retardation of oil generation and expulsion resulted in significant amounts of bitumen and oil being retained in the rocks pyrolysed at high pressures, suggesting that pressure is a possible mechanism for retaining petroleum (bitumen and oil) in source rocks. This retention of petroleum within the rock provides a mechanism for oil-prone source rocks to become potential shale gas reservoirs. The implications from this study are that in geological basins, pressure, temperature and time will all exert significant control on the extent of petroleum generation and source rock maturation for Type II source rocks, and that the petroleum retained in the rocks at high pressures may explain in part why oil-prone source rocks contain the most prolific shale gas resources.

Keywords: Kimmeridge Clay, Monterey shale, hydrocarbon generation, maturation, vitrinite reflectance, hydrous pyrolysis, high water pressure, pressure retardation, shale gas.

1. Introduction

Increasing interest in shale gas exploration has raised some questions regarding petroleum generation in organic rich shales that are both source and reservoir rocks. In conventional petroleum exploration the source rock generates and expels the petroleum which then migrates into the trap with a seal preventing further migration from the reservoir (Magoon and Dow, 1994). Geochemical parameters used to identify source rocks in conventional petroleum systems include source richness, kerogen type and maturity. A variety of analytical and optical techniques are available for the identification of kerogen type, with one of the most widely used laboratory methods being pyrolysis to evaluate the amount and composition of hydrocarbons generated, as well as investigating the mechanisms by which the hydrocarbons are generated. Additionally, pyrolysis has also been used to derive the kinetic parameters for the different kerogen types, so that the volume, composition and timing of petroleum generation can be predicted by petroleum system modelling, which has become an essential tool in the evaluation of the prospectivity of petroleum basins.

In conventional petroleum systems, petroleum (oil and gas) generation and source rock maturation occur in hydrostatically or overpressured basins. The geochemical models currently used to predict petroleum generation and source rock maturation assume that both petroleum generation and source rock thermal maturation are determined by the thermal history of the source rock alone (e.g. Pepper and Corvi, 1995), with pressure being considered to have no effect. The absence of pressure from geochemical models arises from the studies which have produced conflicting results, with some finding that pressure had no or very little effect (Michels et al. 1994; Monthioux et al. 1986, 1985), while others have observed that pressure retarded both maturation and petroleum generation (Carr et al. 2009; Landais et al. 1994; Michels et al. 1995; Uguna et al. 2012a, 2012b, 2015). The different findings about the importance of pressure were considered to be due to the different pyrolysis methods used (Uguna et al. 2012a). Most of the pyrolysis methods (e.g. Rock-Eval, MSSV and hydrous pyrolysis) heat the source rocks and kerogens under vapour pressure, which has implications for the mechanical (pV) work required during petroleum generation. The pV work arises from the volume expansion as kerogen is converted into modified kerogen, liquid and gaseous hydrocarbons, and the movement of the generated hydrocarbons into the porosity of the source rock. Vapour-based pyrolysis methods require only very small amounts of energy to account for the pV work due to the high compressibility of vapour. However the pore water present in source rocks in geological basins is highly incompressible, and therefore requires a much larger amount of pV work to displace the water to provide the space for the generated petroleum. Consequently, the thermal energy used for bond breakage in low pressure vapour-based pyrolysis (e.g. MSSV) systems, has to be divided between both bond breakage and pV work at high water pressures. This reduction in the amount of bond breakage accounts for the retardation when maturation and petroleum generation occurs under water pressure as in geological basins. Indeed, when the pyrolysis methods are modified to include water pressure, these studies show retardation of bitumen, oil and gas generation and vitrinite reflectance under water pressure (Carr et al. 2009; Landais et al. 1994; Michels et al. 1995; Uguna et al. 2012a, 2012b, 2015).

Another method widely used for source rock pyrolysis studies is the sealed gold-bag technique where a crushed sample is placed inside a gold-bag, and heated in an autoclave pressure vessel (Michels et al. 1994; Monthioux et al. 1986, 1985). In high pressure studies using gold bags/capsules, either in the presence or absence of water where the gold bag/capsule is pressurised with water or inert gas applied to the external surface, have shown little or no pressure effect on petroleum generation or source rock maturation (Freund et al. 1993; Huang, 1996; Michels et al. 1994; Monthioux et al. 1986, 1985). It has been suggested that gold-bag pyrolysis accurately replicates subsurface conditions in the laboratory (Monthioux, 1988). However, the results obtained from gold-bag pyrolysis investigations showed that the gas yields increased with increasing pressure (Tao et al. 2010), which is the opposite trend to that predicted by thermodynamics.

In complex self-contained “unconventional” shale gas exploration, the same geochemical methods as used for conventional exploration have also been widely applied, although the nature of the inorganic components that form the bulk of the source rock must be included, as they form the main reservoir, which controls gas storage after generation and the potential for production (Scotchman, 2015). Although the amount of research has vastly increased during the past decade, there are a number of unknowns concerning the petroleum generation and retention processes that account for the success of these systems. The formation of thermogenic gas arises from several processes; the decomposition of primary kerogen to bitumen and gas, the decomposition of generated bitumen to oil and gas, the secondary cracking of the oil to gas and pyrobitumen, and the direct generation of gas from kerogen during the gas window (Jarvie et al. 2007). The generated gas is stored as free gas in either intergranular porosity and fractures in shales, nanoporosity in kerogens that developed during maturation, adsorbed onto the kerogen and clay particle surfaces, or absorbed in either kerogen or bitumen (Bernard et al. 2012a; Curtis, 2002; Jarvie et al. 2007; Jenkins and Boyer, 2008; Loucks et al. 2010; Montgomery et al. 2005; Ross and Bustin, 2009; Scotchman, 2015).

Unconventional shale gas resource systems are generally slightly to highly over-pressured (Jarvie, 2012), and the few published studies so far have used either open system pyrolysis (Rock Eval and pyrolysis gas chromatography), or low pressure MSSV closed system pyrolysis, to investigate gas generation and retention in shale gas resource systems (Hartwig et al. 2010; Mahlstedt and Horsfield, 2012; Slowakiewicz et al. 2015). The retention of gas in shales depends partly on the adsorption of the generated gas by the kerogen and inorganic minerals (Williams, 2013). Adsorption is the adhesion of gas and liquid molecules to the adsorbent (kerogen and shale), and is an exothermic process favoured in high pressure conditions. This study investigates the impact of high water pressure on oil and gas generation, and source rock maturation during experiments on immature oil prone Type II and IIs source rocks (Kimmeridge Clay and Monterey respectively), using a pressure range of 180-900 bar and temperatures of 350 and 380 °C. This is to investigate previous findings that gas generation in shale gas resource systems results from cracking of petroleum (bitumen and oil) retained in low porosity shale source rocks at high maturities (Bernard et al. 2012a, 2012b; Hill et al. 2007; Jarvie et al. 2007).

In geological basins, the hydrostatic pressure increases at ~100 bar/km, and the pressures used in this study therefore correspond to petroleum generation with the depth interval of 1.8 to 9 km. Assuming a temperature range for petroleum generation of 60 to 200 °C (Peters and Cassa, 1994), and an average geothermal gradient of 30 °C/km, then the depth interval of petroleum generation occurs between 2 and 7 km, then petroleum generation in hydrostatically pressured basins occurs between 200 and 700 bar. In the case of basins with lower geothermal gradients or those with overpressures, the pressure at which petroleum generation occurs could extend to 900 bar and higher. With overpressures of up to 60 MPa (600 bar) in Jurassic reservoirs in the Central Graben, North Sea, and when combined with the hydrostatic pressure in the Jurassic reservoirs at depths of 4 km and deeper, and with the source rock also of Jurassic age, then the total pore pressure can be as high as 1000 bar. The pressures used in this study are therefore comparable with those occurring during petroleum generation. However, the experimental temperatures are much higher, due to the necessity for the reaction to occur in 24 h as opposed to the millions of years in geological basins.

No analyses were undertaken on the generated oils, as this study was aimed at investigating generation in unconventional source systems. The authors recognise that the generation of oil from the bitumen generated by the source rock/kerogen plays a role in determining the composition of the bitumen that subsequently generates gas in the gas window, but the main focus of this work was on studying the effect that pressure plays on controlling the amount of bitumen and oil that survives the oil window to be available to generate gas in the gas window. We also acknowledge that under the supercritical water conditions (380 °C) used in some of these experiments, water will have the properties of an organic solvent, which is completely different from the liquid water conditions present in the 350 °C experiments and those in nature. This will surely lead to more oil being expelled at 380 °C compared to 350 °C. However, it was necessary to use a temperature as high as 380 °C to be able to achieve high (gas window) maturity and conversion in reasonable time. As we have previously shown that 900 bar water pressure experiments retarded vitrinite reflectance of oil prone Svalbard coal by 0.15% Ro and 0.16% Ro at 350 °C and 380 °C respectively for 24 h compared to low pressures (Uguna et al. 2015).

2. Experimental

The Monterey shale sample studied is from the lower Altamira shale member, outcrop located East of Lunada Bay, Palos Verdes, California. The Kimmeridge Clay Formation (KCF) source rock was from Kimmeridge Bay outcrop, Dorset, UK. Both source rocks were immature, with the Kimmeridge Clay containing 30.4% total organic carbon (TOC), with a hydrogen index (HI) of 639 mg/g, T_{max} of 419 °C, and a vitrinite reflectance (VR) of 0.39% Ro. The Monterey shale contains 13.8% TOC, with HI of 544 mg/g, T_{max} of 386 °C, and VR of 0.36% Ro. The pyrolysis equipment used was a 25 ml Hastalloy cylindrical pressure vessel rated to 1400 bar at 420 °C, connected to a pressure gauge and rupture disc rated to 950 bar. The experiments being conducted on non-extracted rocks (sample size 2-4 mm) at 350 and 380 °C for 6-24 h under low pressure hydrous (180 and 245 bar) and high water pressure (500, 700 and 900 bar) conditions using 3.29 g of Kimmeridge Clay and 1.44 g of Monterey shale. The experimental procedure used was described in detail by Uguna et al. (2012a, 2015).

After pyrolysis, the generated gases were collected at ambient temperature with a gas tight syringe and transferred to a gas bag (after the total volume had been recorded), and immediately analysed for the C_1-C_4 hydrocarbon composition by gas chromatography as described previously by Uguna et al (2012a). The expelled oil floating on top of the water after the experiments was collected with a spatula and recovered by washing with cold dichloromethane (for runs where expelled oil was generated), after which the water in the vessel was decanted. The floating oil on top of the water, together with oil stuck to the side the reactor wall (recovered by washing with cold dichloromethane), as well as the oil on the outside of the pyrolysed rock (recovered by quickly washing with cold dichloromethane for 30 seconds prior to drying of the rock), were all combined and referred to as expelled oil. The reacted rock was then vacuum dried at 45 ºC for 3-4 h, crushed and soxhlet extracted using 150 ml dichloromethane/methanol mixture (93:7 volume: volume) for 48 hours to recover the bitumen, and any non-expelled oil retained in the rock, both being referred to as bitumen. It should be noted that the use of crushed rock in the 2-4 mm size range in the experiments probably favours increased amounts of oil and gas expulsion from the pyrolysed source rock compared with larger masses in geological basins, and the term expelled oil does not indicate the amount of oil that can be expected to have been expelled from the much larger source rock layers present in geological basins.

Vitrinite reflectance measurement, Rock Eval and TOC analysis were made on both the initial non extracted rocks and pyrolysed solvent extracted rocks residues. Vitrinite reflectance measurement was performed using the same method and instrument described in our previous study (Uguna et al. 2012a). Rock Eval pyrolysis used a Vinci Technologies Rock Eval 6 standard instrument, with about 60 mg of crushed powdered rock being heated using an initial oven programme of 300 °C for 3 min and then from 300 °C to 650 °C at the rate of 25 °C min^{-1} in an N_2 atmosphere. The oxidation stage was achieved by heating at 300 °C for 1 min and then from 300 °C to 850 °C at 20 °C min^{-1} and held at 850 °C for 5 min. Hydrocarbons released during the two-stage pyrolysis were measured using a flame ionisation detector (FID) and CO and CO_2 measured using an infra-red (IR) cell. Rock Eval parameters reported in this study were S1 (free hydrocarbons in mg HC/g of rock TOC), S2 (generated hydrocarbons in mg HC/g of rock TOC), HI (hydrogen index calculated from S2 X 100/TOC), TOC and $T_{max.}$ (temperature of maximum S2 peak).

3. Results

3.1. Kimmeridge Clay

3.1.1. Pyrolysis at 350 °C

The individual and total (C_1-C_4) gas yields (mg/g of initial rock TOC) obtained for the KCF source rock at 350 °C are presented in Table 1, with the total gas yields presented in Figure 1. The total (C_1-C_4) gas yields obtained between 6 and 24 h reached a maximum at 180 bar for each period of heating, but then progressively decreased with an increase in water pressure. The total gas yield increases as the duration of the experiment increased from 6 to 12 and then to 24 h for all pressures investigated. Ethene (C_2H_4) and propene (C_2H_6) yields were also higher at 6, 12 and 24 h under 180 bar conditions compared to the amounts present at higher pressures.

Table 1. Individual and total (C_1–C_4) hydrocarbon gas yields (mg/g TOC of initial rock TOC) for Kimmeridge Clay and Monterey Shale pyrolysis at 350 °C for 6-24 h.

KCF samples	Time (h)	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_{10}	Total C_1-C_4	Gas wetness
180 bar	6	2.6	0.13	2.3	0.32	1.7	0.8	8	0.33
500 bar	6	1.5	0.02	1.3	0.07	1.0	0.5	4	0.38
700 bar	6	1.0	0.01	0.8	0.03	0.6	0.3	3	0.33
900 bar	6	0.9	0.01	0.7	0.02	0.5	0.3	2	0.45
180 bar	12	4.9	0.13	4.7	0.44	3.7	1.5	15	0.33
500 bar	12	4.0	0.01	3.6	0.08	2.7	1.5	12	0.33
700 bar	12	3.0	0.01	2.7	0.06	2.1	1.1	9	0.33
900 bar	12	2.4	0.01	2.3	0.05	1.9	1.0	8	0.30
180 bar	24	7.6	0.09	7.4	0.50	5.5	2.6	24	0.32
500 bar	24	5.7	0.01	5.5	0.10	4.5	2.5	18	0.32
700 bar	24	4.8	0.01	4.5	0.04	3.3	1.5	14	0.34
900 bar	24	4.8	0.00	3.9	0.04	2.9	1.4	13	0.37
Monterey samples									
180 bar	6	8.2	0.39	4.6	0.79	2.8	1.2	18	0.46
500 bar	6	5.1	0.07	2.7	0.16	1.7	0.7	10	0.51
700 bar	6	4.1	0.04	2.2	0.11	1.4	0.6	9	0.46
900 bar	6	4.5	0.03	2.4	0.10	1.5	0.7	9	0.50
180 bar	24	11.4	0.23	7.4	0.77	4.7	2.0	27	0.42
500 bar	24	7.5	0.03	4.6	0.16	3.2	1.5	17	0.44
700 bar	24	6.1	0.02	3.9	0.09	2.6	1.2	14	0.44
900 bar	24	5.4	0.01	3.5	0.08	2.3	1.1	12	0.45

Gas wetness – $C_1/(C_1$-$C_4)$

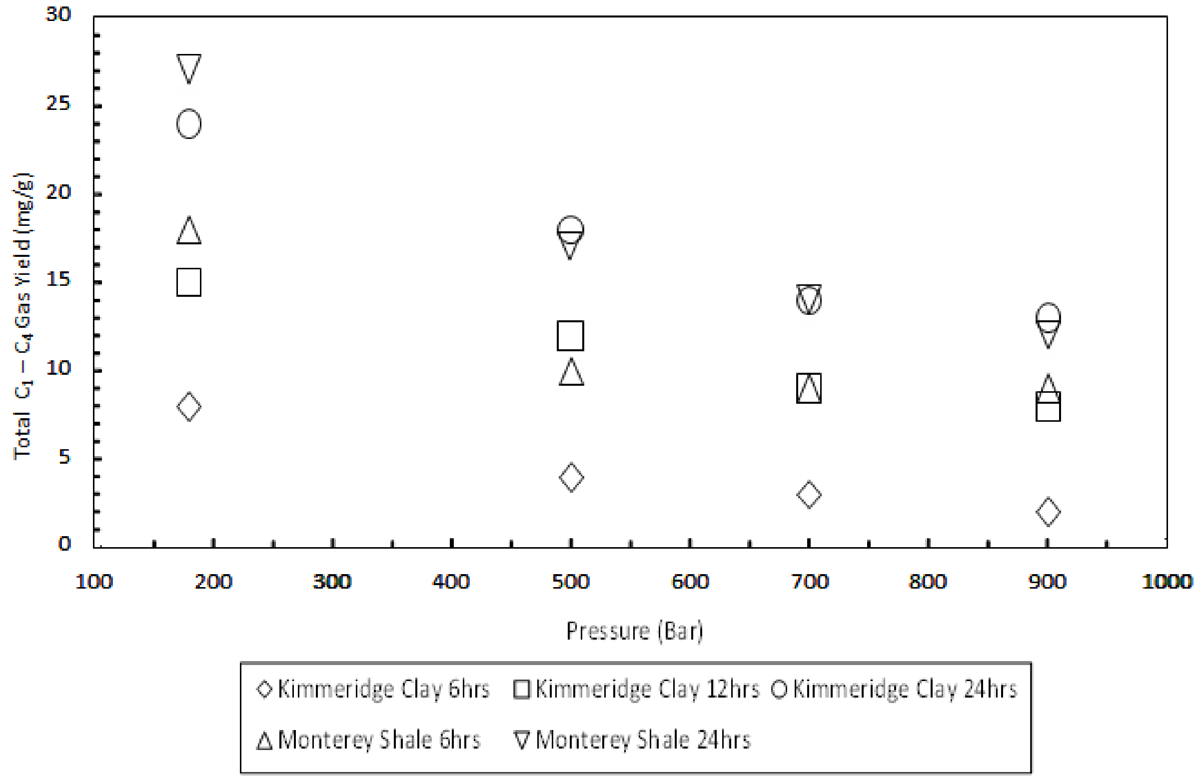

Figure 1. Total hydrocarbon (C_1-C_4) gas yields (mg/g TOC of initial rock TOC) for Kimmeridge Clay and Monterey Shale pyrolysis at 350 °C for 6-24 h.

The expelled oil and bitumen yields (mg/g of initial rock TOC) generated for the KCF source rock at 350 °C are presented in Figure 2 and Table 2. At 6 h only bitumen was generated, as oil generation had not yet commenced. The bitumen yield reduced slightly at 900 bar compared to 180 bar. Pyrolysis for 12 h resulted in the onset of oil generation, and extending the duration to 24 h resulted in increased oil yields at all pressures compared with the 12 h values. The oil yields at 12 and 24 h reached a maximum at 180 bar, and decreased as the pressure increased to 900 bar (Table 2 and Figure 2). The trend in bitumen yields was opposite to that obtained from the oil yield, with the bitumen progressively increasing going from a minimum at 180 bar to a maximum at 900 bar (Table 2).

Table 2. Bitumen and oil yields, and residual rock individual and mean VR for Kimmeridge Clay and Monterey Shale pyrolysis at 350C for 6-24 h.

KCF samples	Time (h)	Expelled oil (mg/g TOC)	Bitumen (mg/g TOC)	Residual rock individual VR readings (% Ro)	Residual rock mean VR (% Ro)[a]
180 bar	6	0	994	0.62, 0.72, 0.69, 0.65, 0.67	0.67 (4)
500 bar	6	0	968	0.74, 0.63, 0.69, 0.58, 0.61, 0.50, 0.65, 0.64, 0.73, 0.60, 0.57, 0.67, 0.57, 0.66	0.63 (14)
700 bar	6	0	961	0.68, 0.60	0.64 (2)
900 bar	6	0	932	0.55, 0.64, 0.64	0.62 (3)
180 bar	12	201	740	0.78, 0.69, 0.63, 0.68, 0.76, 0.74, 0.71, 0.77, 0.82	0.73 (9)
500 bar	12	161	764	0.61, 0.77, 0.69, 0.74, 0.63, 0.79, 0.66, 0.74	0.70 (8)
700 bar	12	138	807	0.74, 0.71, 0.69	0.71 (3)
900 bar	12	127	829	0.69, 0.60, 0.55, 0.67, 0.73, 0.68, 0.61	0.65 (7)
180 bar	24	339	398	0.87, 0.80, 0.89	0.85 (3)
500 bar	24	257	517	0.72, 0.76	0.74 (2)
700 bar	24	157	614	0.67, 0.63	0.65 (2)
900 bar	24	133	809	0.64, 0.56	0.60 (2)
Monterey samples					
180 bar	6	314	244	0.70, 0.67, 0.54, 0.64	0.64 (4)
500 bar	6	245	262	0.57, 0.49	0.53 (2)
700 bar	6	244	274	0.52, 0.58, 0.53	0.54 (3)
900 bar	6	228	269	0.44, 0.51, 0.46, 0.44	0.46 (4)
180 bar	24	365	127	1.22, 1.12	1.17 (2)
500 bar	24	291	141	1.07, 1.20	1.14 (2)
700 bar	24	253	180	0.95, 1.05, 1.01, 1.00	1.00 (4)
900 bar	24	246	179	0.89, 0.94	0.92 (2)

[a] numbers in bracket are the numbers of vitrinite particles measured.

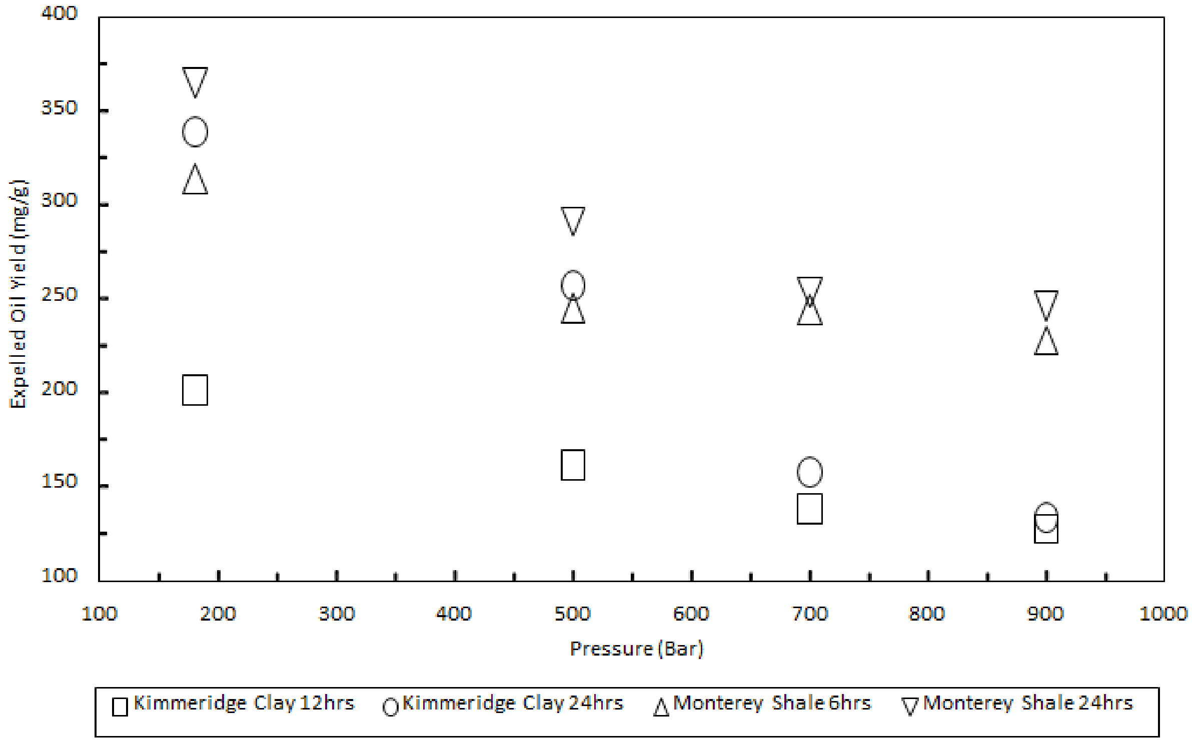

Figure 2. Oil yields (mg/g TOC of initial rock TOC) for Kimmeridge Clay and Monterey Shale pyrolysis at 350 °C for 6-24 h.

The Rock-Eval pyrolysis data (S1, S2, HI, and T_{max}) obtained from the pyrolysed residual extracted KCF source rock at 350 °C are listed in Table 3. The S2 data show values at 900 bar that are higher than those at 180 bar at both 6 and 12 h. In contrast at 24 h S2 show lower values at 900 bar compared with 180 bar. The S2 values obtained at 180 and 500 bar after 24 h are higher than those obtained from either the 6 or 12 h experiments at both pressures, and also when compared to 700 and 900 bar. The HI data do not show a consistent trend with increasing pressure and time. The HI values were higher in the 6 h than in the 12 h experiments under all pressure conditions, and the 12 h values are higher than the 24 h data apart from the 12 h 500 bar run, which has a higher HI at 24 h than at 12 h. The S2 and HI relationships with pressure and time appear to be complex, with the variations being due to the presence of modified bitumen that did not convert completely to petroleum in the residues that generated more oil. During Rock Eval pyrolysis, any modified bitumen (insoluble in the DCM/methanol solvent mixture used for extracting bitumen from the source rocks) present in the residual rock will be released as volatiles alongside the unconverted hydrocarbon as S2 peak, thus increasing the S2 yield. The fact that modified bitumen that did not convert completely to petroleum in the 180 and 500 bar rock residues contributes to S2 yield, suggests that such partially modified bitumen can contribute to secondary gas generation at high maturity in geological basins. T_{max} increased with increasing time going from 6 to 24 h under all experimental conditions due to increase in thermal maturity, but no significant effect of pressure was observed apart from 24 h where T_{max} was slightly higher at 180 bar compared to the high pressures (500-900 bar).

The residual individual and mean vitrinite reflectance (VR) values obtained for the KCF source rock after pyrolysis at 350 °C are listed in Table 2 with the mean values presented in Figure 3. After 6 and 12 h pyrolysis, the mean VR was higher at 180 bar, stayed about the same at 500 and 700 bar, but were only reduced slightly by 0.05% Ro (at 6 h) and 0.08% Ro (at 12 h) at 900 compare to 180 bar. At 24 h the mean VR was also higher at 180 bar (0.85% Ro), but reduced by 0.11% Ro to 0.74% Ro at 500 bar water pressure. The mean VR reduced further to 0.65% Ro and 0.60% Ro at 700 and 900 bar respectively, such that the 700 and 900 bar values were 0.20% Ro and 0.25% Ro respectively lower than the 180 bar VR value. The gas wetness varied between 0.30 and 0.45 (Table 1), which is consistent with the oil window maturities (0.60-0.85% Ro) indicated by the VR data.

Table 3. Kimmeridge Clay and Monterey shale TOC and Rock Eval data for initial and residual rock pyrolysed at 350 °C for 6-24 h.

KCF samples	Time (h)	S1 (mg/g)	S2 (mg/g)	HI (mg/g)	T*max* (°C)	Residual rock TOC (%)
Initial KCF		4.6	194	639	419	30.4
180 bar	6	0.04	10.8	229	437	4.7
500 bar	6	0.03	12.3	248	437	5.0
700 bar	6	0.03	12.3	254	438	4.9
900 bar	6	0.04	13.9	273	438	5.1
180 bar	12	0.05	10.6	181	441	5.9
500 bar	12	0.02	8.0	164	440	4.9
700 bar	12	0.04	9.0	172	442	5.3
900 bar	12	0.01	11.2	211	440	5.3
180 bar	24	0.11	18.7	167	446	11.2
500 bar	24	0.11	16.6	177	443	9.4
700 bar	24	0.04	8.4	152	440	5.6
900 bar	24	0.05	8.1	153	441	5.3
Monterey samples						
Initial Monterey		4.2	75	544	386	13.8
180 bar	6	0.10	7.1	116	433	6.1
500 bar	6	0.07	8.4	142	432	5.9
700 bar	6	0.13	8.8	151	431	5.8
900 bar	6	0.18	9.4	157	432	6.0
180 bar	24	0.13	3.5	63	439	5.6
500 bar	24	0.16	4.5	80	438	5.6
700 bar	24	0.10	5.9	104	436	5.7
900 bar	24	0.09	5.7	98	437	5.9

3.1.2. Pyrolysis at 380 °C

In pyrolysis experiments at 380 °C for 6-24 h, the total (C_1-C_4) gas yields in mg/g of initial rock TOC (Table 4 and Figure 4) generated for the KCF source rock were higher at 500 bar compared to 245 bar. Increasing the pressure to 700 and 900 bar produced a slight decrease in the gas yield compared with 500 bar. Ethene (C_2H_4) and propene (C_3H_6) yields were higher at 245 bar, and also reduced going to high pressures (500 to 900 bar) as observed at 350 °C.

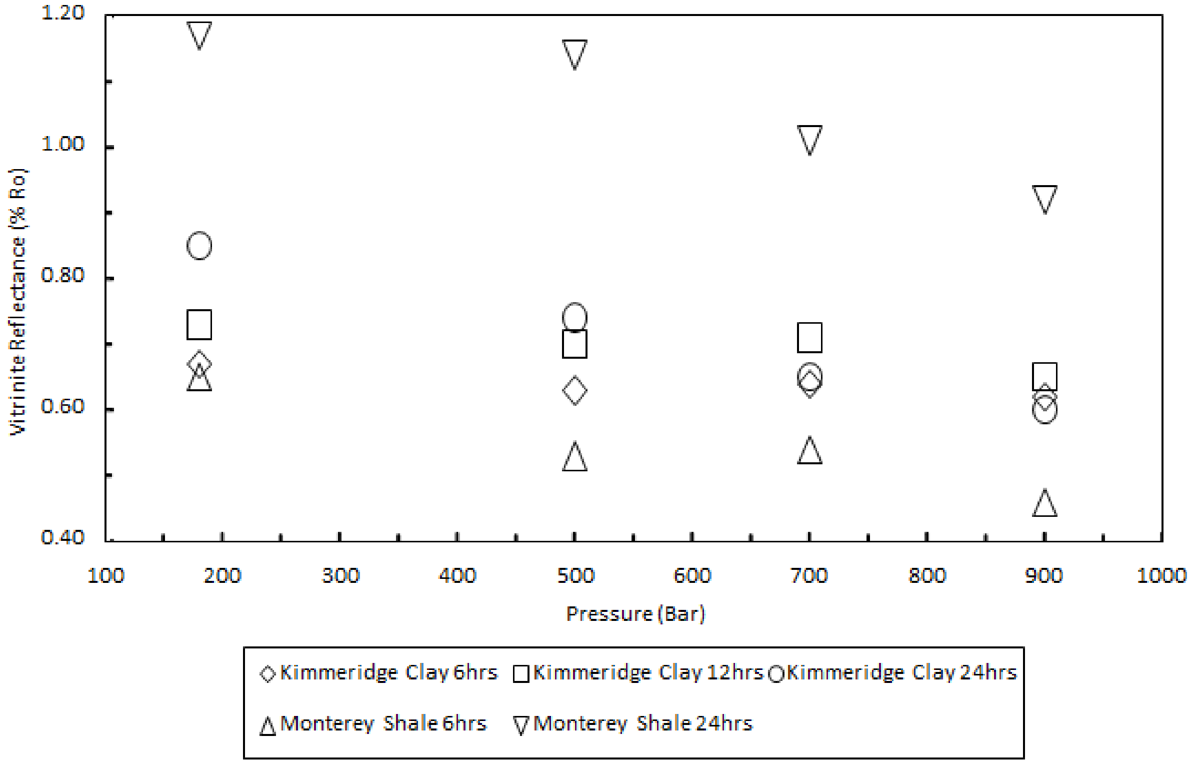

Figure 3. Mean VR (% Ro) for Kimmeridge Clay and Monterey Shale pyrolysis at 350 °C for 6-24 h.

Table 4. Individual and total (C_1–C_4) hydrocarbon gas yields (mg/g TOC of initial rock TOC) for Kimmeridge Clay and Monterey Shale pyrolysis at 380 °C for 6-24 h.

KCF Samples	Time (h)	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_{10}	Total C_1-C_4	Gas Wetness
245 bar	6	7.4	0.15	6.9	0.84	4.8	2.0	22	0.34
500 bar	6	12.5	0.04	11.0	0.41	7.5	2.9	34	0.37
700 bar	6	11.2	0.04	10.1	0.27	7.1	2.7	31	0.36
900 bar	6	10.7	0.02	9.6	0.19	6.8	2.8	30	0.36
245 bar	12	9.1	0.11	8.2	0.78	5.3	1.9	25	0.36
500 bar	12	16.5	0.02	15.2	0.44	11.8	5.3	49	0.34
700 bar	12	16.2	0.03	14.9	0.32	11.5	5.3	48	0.34
900 bar	12	15.9	0.03	14.4	0.20	10.1	3.9	45	0.35
245 bar	24	15.3	0.08	13.9	0.90	10.2	3.9	44	0.35
500 bar	24	19.1	0.03	15.4	0.32	13.3	7.2	55	0.35
700 bar	24	17.1	0.04	14.8	0.39	12.6	7.0	52	0.33
900 bar	24	16.9	0.00	14.4	0.34	12.2	7.2	51	0.33
Monterey samples									
245 bar	6	7.6	0.48	5.4	1.30	2.5	1.2	19	0.40
500 bar	6	12.2	0.07	7.9	0.36	5.3	2.1	28	0.44
700 bar	6	8.7	0.05	5.7	0.21	3.8	1.5	20	0.44
900 bar	6	8.9	0.03	5.7	0.16	3.7	1.4	20	0.45
245 bar	24	15.4	0.59	9.9	2.15	6.3	2.6	37	0.42
500 bar	24	21.1	0.05	13.9	0.29	10.6	5.2	51	0.41
700 bar	24	22.2	0.05	14.1	0.21	10.4	4.6	52	0.43
900 bar	24	20.9	0.05	13.4	0.24	10.0	4.8	49	0.43

Gas wetness – $C_1/(C_1\text{-}C_4)$

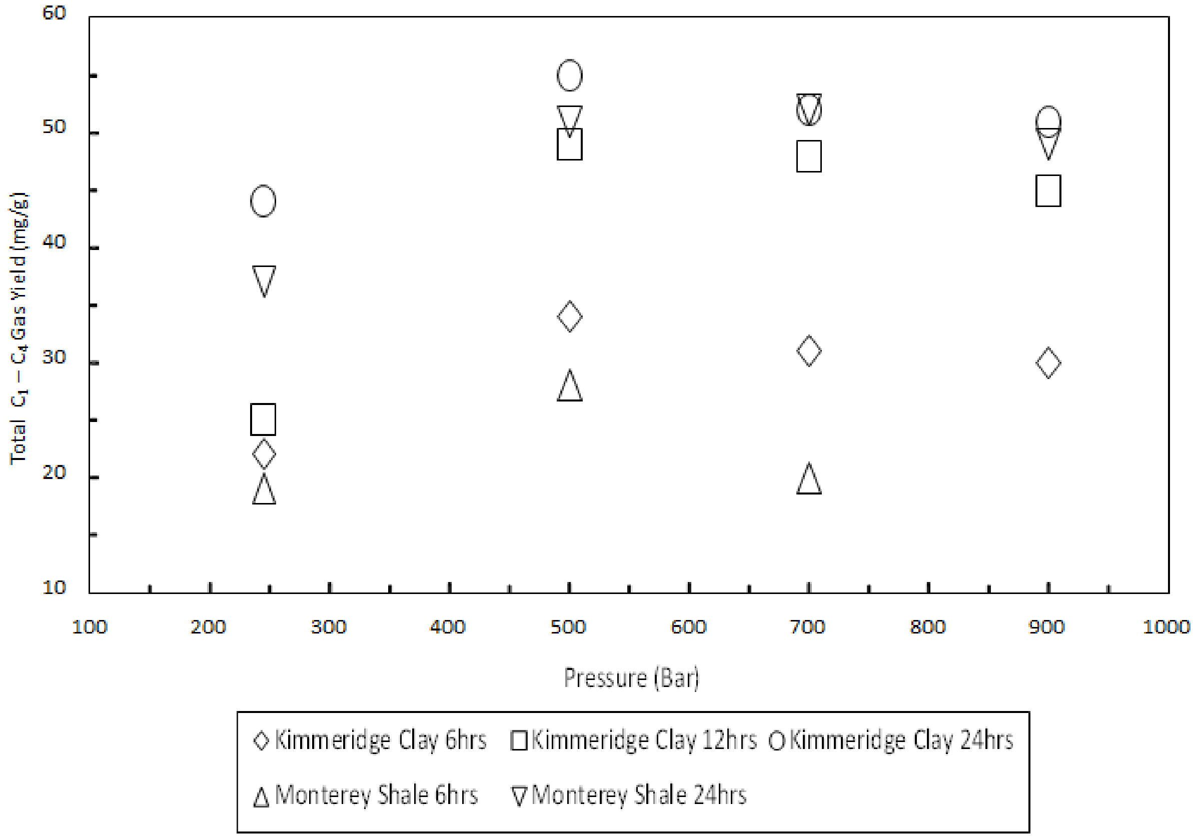

Figure 4. Total hydrocarbon (C_1-C_4) gas yields (mg/g TOC of initial rock TOC) for Kimmeridge Clay and Monterey Shale pyrolysis at 380 °C for 6-24 h.

The oil yields in mg/g of initial rock TOC (Table 5 and Figure 5) from pyrolysis at 380 °C reached a maximum at 500 bar for 6 h, before reducing by 29% and 47% at 700 and 900 bar respectively. The oil yield increased as the residence time was raised from 6 to 12 h under all pressure conditions as expected, with maximum oil generation occurring at 245 bar for 12 h. The oil yield decreased consistently in both the 12 h and 24 h experiments as the pressure was increased from 245 to 900 bar, although the 24 h 700 and 900 bar oil yields are higher compared to 12 h at the same pressures. The bitumen yield in mg/g of initial rock TOC (Table 5) at 6 h decreased from 245 bar to a minimum at 500 bar, before increasing significantly going to 700 and 900 bar. In contrast to the 6 h yields, the bitumen yield at 12 h increased continuously as the pressure increased from 245 to 900 bar, while at 24 h the bitumen yield was higher at 245 bar, similar at 500 and 700 bar and increased slightly going to 900 bar.

Table 5. Bitumen and oil yields, and residual rock individual and mean VR for Kimmeridge Clay and Monterey Shale pyrolysis at 380 °C for 6-24 h.

KCF samples	Time (h)	Expelled oil (mg/g TOC)	Bitumen (mg/g TOC)	Residual rock individual VR readings (% Ro)	Residual rock mean VR (% Ro)
245 bar	6	321	304	0.87, 0.83, 0.73, 0.82, 0.81, 0.76	0.80 (6)[a]
500 bar	6	382	243	0.74, 0.68, 0.79, 0.82, 0.78	0.76 (5)
700 bar	6	272	432	0.67, 0.66, 0.72, 0.75, 0.63	0.69 (5)
900 bar	6	201	508	0.71, 0.64, 0.69, 0.57, 0.60, 0.61, 0.53	0.62 (7)
245 bar	12	499	120	0.90, 0.98	0.94 (2)
500 bar	12	434	141	0.83, 0.87, 0.93, 0.84	0.87 (4)
700 bar	12	314	162		NDP[b]
900 bar	12	262	233	0.74, 0.63, 0.55	0.64 (3)
245 bar	24	411	120	1.36, 1.20, 1.27, 1.31, 1.25	1.28 (5)
500 bar	24	426	78	1.25, 1.06, 1.17, 1.12, 1.14, 1.11	1.14 (6)
700 bar	24	397	78	1.05, 0.98, 1.04, 1.08	1.04 (3)
900 bar	24	338	85	0.98, 0.94, 1.04	0.99 (4)
Monterey samples					
245 bar	6	229	157	0.86	0.86 (1)
500 bar	6	334	136	0.88, 0.93, 0.89	0.90 (3)
700 bar	6	312	138	0.84, 0.77	0.81 (2)
900 bar	6	268	158	0.80, 0.74	0.77 (2)
245 bar	24	225	91	1.46, 1.37, 1.42, 1.36	1.40 (4)
500 bar	24	301	98	1.48, 1.54, 1.59	1.54 (3)
700 bar	24	241	109	1.37, 1.36	1.37 (2)
900 bar	24	242	109	1.23, 1.14, 1.18, 1.19	1.19 (4)

[b] numbers in bracket are the numbers of vitrinite particles measured.

[b] no determination of vitrinite particles possible.

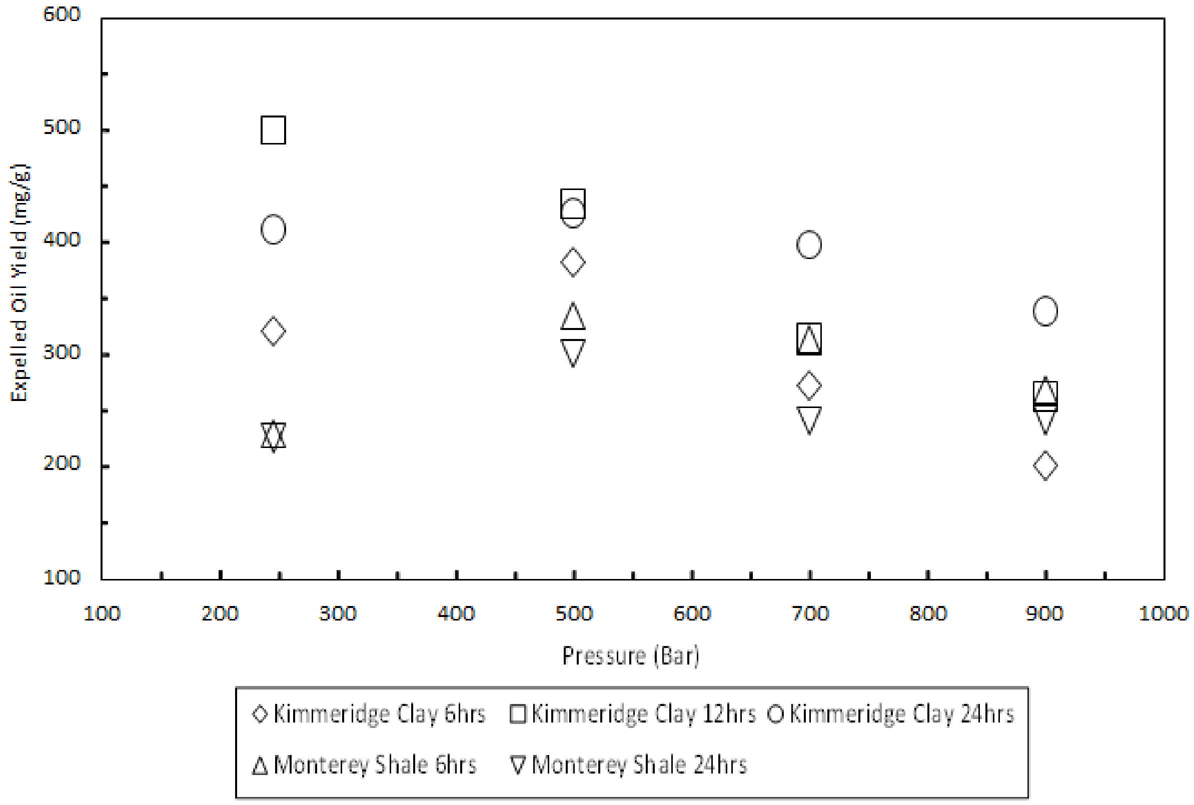

Figure 5. Oil yields (mg/g TOC of initial rock TOC) for Kimmeridge Clay and Monterey Shale pyrolysis at 380 °C for 6-24 h.

The Rock-Eval pyrolysis data (S1, S2, HI, and T_{max}) for the KCF at 380 °C (Table 6) show no consistent trend for either S2 and HI at 6 h, whereas at 12 and 24 h both S2 and HI increase with increasing pressure. Apart from the 900 bar residue at 12 h, the S2's at other pressures are lower compared to the same pressures at 6 h, while the 24 h data are consistently lower than the 12 h samples. The HI also reduce as the time was increased from 6 to 12 h, and then from 12 to 24 h at all pressures. T_{max} was similar under all experimental conditions at 6 h and 12 h, but was higher at 24 h under 245 bar conditions compared to those between 500 and 900 bar.

Table 6. KCF and Monterey shale TOC and Rock Eval data for initial and residual rock pyrolysed at 380 °C for 6-24 h.

KCF samples	Time (h)	S1 (mg/g)	S2 (mg/g)	HI (mg/g)	T*max* (°C)	Residual rock TOC (%)
Initial KCF		4.6	194	639	419	30.4
245 bar	6	0.63	13.5	110	448	12.3
500 bar	6	0.11	12.7	114	448	11.1
700 bar	6	0.11	13.2	119	444	11.1
900 bar	6	0.12	11.1	105	446	10.6
245 bar	12	0.07	7.5	63	453	12.0
500 bar	12	0.09	9.1	72	449	12.6
700 bar	12	0.08	10.2	80	448	12.8
900 bar	12	0.10	11.2	88	448	12.8
245 bar	24	0.06	5.8	44	496	13.2
500 bar	24	0.08	5.8	50	464	11.7
700 bar	24	0.09	6.8	53	460	12.7
900 bar	24	0.08	7.2	59	458	12.2

Monterey samples						
Initial Monterey		4.2	75	544	386	13.8
245 bar	6	0.10	3.0	44	449	6.9
500 bar	6	0.08	2.4	44	441	5.4
700 bar	6	0.07	2.2	43	441	5.1
900 bar	6	0.09	2.4	43	443	5.6
180 bar	24	0.05	1.7	23	521	7.3
500 bar	24	0.06	1.1	22	527	4.9
700 bar	24	0.11	1.2	24	537	5.1
900 bar	24	0.06	1.4	26	514	5.3

The KCF individual and mean VR obtained at 380 °C for 6-24 h are presented in Table 5 and the mean VR also presented Figure 6. The mean VR at 6 h was higher at 245 bar (0.80% Ro), and was not significantly affected by pressure at 500 bar. However, at 700 and 900 bar the mean VR were reduced to 0.69% Ro and 0.62% Ro respectively. Increasing the residence time to 12 h resulted in higher mean VR compared to 6 h, except for the 900 bar residue which had about the same VR as that obtained after 6 h. The mean VR value at 12 h (Table 5 and Figure 6) was higher at 245 bar, and was not significantly affected by pressure going to 500 bar as observed at 6 h. At 700 bar no VR measurement was possible due to the absence of any recognisable vitrinite. At 900 bar the mean VR was reduced by 0.3% Ro compared with the 245 bar VR. At 24 h the mean VR (Table 5 and Figure 6) increased under all pressure conditions as expected. The mean VR was higher at 245 bar, reduced by 0.14% Ro and 0.24% Ro with increase in pressure to 500 bar and 700 bar respectively. At 900 bar the VR reduced further by 0.29% Ro compared to the 245 bar value. The higher VR observed at 24 h under 245 bar, and the reduction going to high pressures (500-900 bar) is consistent with T_{max} which was higher at 245 bar and reduced between 500 and 900 bar. The gas wetness varied between 0.33 and 0.37 (Table 4), and are consistent with VR data in the range 0.62 to 1.28% Ro (oil window).

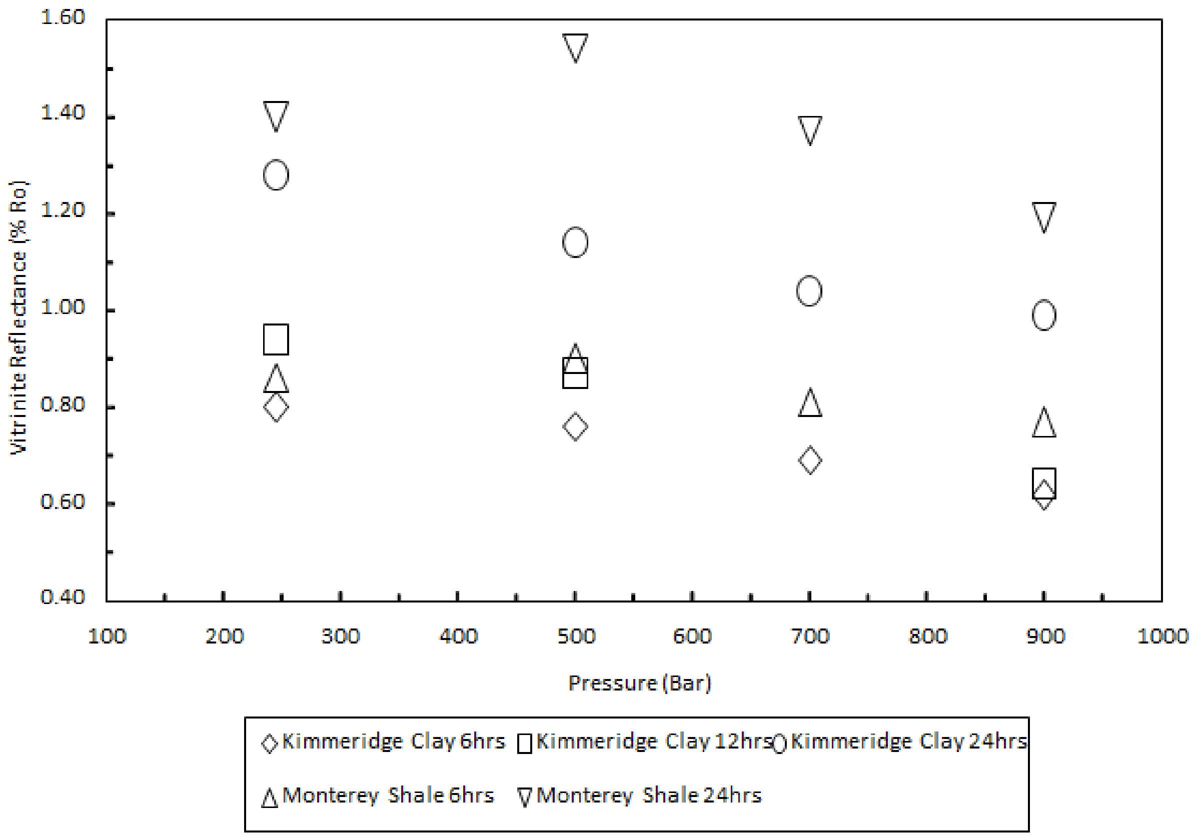

Figure 6. Mean VR (% Ro) for Kimmeridge Clay and Monterey Shale pyrolysis at 380 °C for 6-24 h.

3.2. Monterey Shale

3.2.1. Pyrolysis at 350 °C

The individual and total (C_1-C_4) gas yields (mg/g of initial rock TOC) obtained for the Monterey shale source rock at 350 °C are presented in Table 1 and Figure 1. The total (C_1-C_4) gas and alkenes yields obtained from the Monterey samples follows the same trends as already described for the KCF, viz. a reduction with increasing pressure in both the 6 and 24 h pyrolysis. At 6 h the Monterey shale source rock had started generating oil. This is in contrast to the KCF source rock, and can be attributed to the Monterey shale being more reactive than the KCF, primarily due to the presence of Type IIs kerogen in the Monterey shale rather than Type II in the KCF. The expelled oil yields (Figure 2 and Table 2) decreased while the bitumen yields (Table 2) increased at both 6 and 24 h as the pressure increased from 180 to 900 bar, again a similar trend to that observed for the KCF at 350 °C.

The Monterey shale Rock Eval data (S1, S2, HI, and $T_{\max}$) obtained from the 350 °C pyrolysed extracted rock residues are presented in Table 3. The trend in S2 and HI is the same as observed for the KCF source rock at 6 and 12 h. The 6 h S2 increased consistently as pressure increased from 180 to 900 bar. The HI at 180 bar was also lower, and also increased with increase in pressure to 900 bar. An increase in the residence time to 24 h resulted in reductions in both S2 and HI under all pressures, with the reduction being primarily due to more petroleum generation with time. Both the S2 and HI values obtained from the samples pyrolysed at 700 and 900 bar for 24 h are higher than the values obtained at 245 and 500 bar. $T_{\max}$ was similar under all experimental conditions at both 6 h and 24 h. The residual individual and mean VR values obtained for the Monterey shale source rock after pyrolysis at

350 °C are listed in Table 2 and the mean VR also presented in Figure 3. The VR also reduced by 0.18% Ro and 0.25% Ro at 6 h and 24 h respectively going from 180 bar to 900 bar as observed for the KCF source rock. The wet gas ratios range between 0.42 and 0.51 (Table 1), which are consistent with the mainly late immature to oil window vitrinite reflectance data (0.46 to 1.17% Ro).

3.2.2. Pyrolysis at 380 °C

The Monterey shale individual and total (C_1-C_4) gas yields (mg/g of initial rock TOC) are presented in Table 4 and Figure 4. The total gas yields show a slightly different trend to that observed at 350 °C, in that maximum gas yields occurred at 500 bar for both 6 and 24 h runs, and not low pressure as in the 350 °C experiments. At 6 h the gas yield was higher at 500 bar and reduced at 700 and 900 bar to a similar value as that obtained at 245 bar. At 24 h the total gas yield also increased going from 245 bar to a maximum at 500 bar, but stayed the same at 700 and 900 bar. Ethene and propene yields were higher at 6 and 24 h under low pressure conditions, and reduced at high pressures as observed at 350 °C. The expelled oil yield (mg/g of initial rock TOC) obtained at 380 °C for 6 and 24 h (Table 5 and Figure 5) also follows the same trend as the KCF source rock, increasing from 245 bar to a maximum at 500 bar, before decreasing at 700 and 900 bar. At 24 h the oil yield decreased slightly under all pressure conditions compared to the yields at 6 h, and is due to the oil starting to crack to gas. The bitumen yield (Table 5) for 6 h decreased going from 245 bar to a minimum at 500 and 700 bar, before increasing at 900 bar to the same value obtained at 245 bar. At 24 h the bitumen yields were similar at 245 and 500 bar, and increased slightly to the same value at both 700 and 900 bar.

The Rock Eval pyrolysis data (S1, S2, HI, and T_{max}) obtained from extracted rock residues from Monterey shale pyrolysis at 380 °C for 6 and 24 h are presented in Table 6. The S2 and HI values at 24 h were approximately half the size of the values at 6 h under all experimental conditions, this is due to significant petroleum generation from the source rocks with increase in residence time. Overall S2 and HI were not affected by pressure at 380 °C. T_{max} was slightly higher at 6 h under 245 bar compared to between 500 and 900 bar. At 24 h T_{max} initially increased from 245 bar to maximum at 700 bar, before reducing to 900 bar. The individual and mean VR at 380 °C for 6 and 24 h are presented in Table 5, with the mean VR plotted against pressure in Figure 6. Overall the mean VR values are higher than those at 350 °C, indicating either oil window to early gas window (range 0.81 to 1.54% Ro). The VR values are consistent with gas wetness values of 0.40 to 0.45 which are slightly lower than those in the 350 °C samples. The VR values are the same range as those obtained from pyrolysis of oil-prone Svalbard coal samples at 380 °C for 24 h at pressures between 235 and 900 bar (Uguna et al. 2015). The mean VR increased going from 245 to 500 bar, with the increase most evident at 24 h. An increase in the pressure from 500 bar to 700 and 900 bar resulted in a reduction of the VR at both 6 and 24 h, which was also observed for the KCF source rock. At 6 h increase in pressure from 500 bar to 700 and 900 bar reduced the mean VR by 0.09% Ro and 0.13% Ro respectively, and at 24 h the mean VR also reduced by 0.17% Ro and 0.35% Ro at 700 and 900 bar respectively compared with the 500 bar VR value.

3.3. Experimental carbon mass balance

Tables 7 and 8 present the carbon mass balances for KCF and Monterey shale respectively at 350 and 380 °C for 6-24 h. The residual TOC of the source rocks, hydrocarbon gas, oil and bitumen yields have been used to derive these balances. The carbon content of one bitumen and one oil sample generated from the KCF analysed were 80% and 80.5% respectively, and therefore a value of 80% was assumed to derive the carbon balances for all the oils and bitumens for both source rocks. The balances exclude C_4 alkenes, iso butane and C_5 gases, lower molecular weight hydrocarbons e.g. gasolines, CO and CO_2 which were not measured. The gasoline hydrocarbons could not be recovered due to evaporative losses during product recovery and solvent extraction of the pyrolysed rock to recover the bitumen and un-expelled oil.

The carbon balances were between 84 and 88% at 350 °C for the KCF source rock at the bitumen generation stage (6 h) and the onset of bitumen cracking to oil (12 h), and they would have been closer to 100% if C_4 alkenes, iso butane, C_5 gases, CO and CO_2 data had been available to be included. Extending the residence time to 24 h at 350 °C (bitumen cracking to oil stage), the KCF carbon recovery was between 81 and 85% (except for the experiment at 700 bar). At 380 °C the KCF recoveries were between 74 and 79% in both the 6h and 12 h experiments except for the 700 and 900 bar runs which gave 68% recovery, these being lower than the recoveries obtained at 350 °C. This is again probably due to increased lighter hydrocarbon products being generated at 380 °C, and as noted above, these lighter hydrocarbons were not recovered. At 380 °C for 24 h the KCF recoveries were between 69 and 81%. The carbon recovery for the Monterey shale is generally lower than the KCF source rock under all experimental conditions. This is because the Monterey shale is more reactive, thus probably generated more lighter hydrocarbons than the KCF at the same temperature, pressure and time conditions.

Table 7. Carbon balances (products and residual rock in mg of carbon) for Kimmeridge Clay pyrolysis.

Sample	Temperature (°C)	Time (h)	Total (C_1-C_4)	Bitumen	Oil	Residual rock	Total recovered	(%) Recovery
180 bar	350	6	6	795	0	83	884	88
500 bar	350	6	3	774	0	93	870	87
700 bar	350	6	2	769	0	86	857	86
900 bar	350	6	2	746	0	94	842	84
180 bar	350	12	12	592	161	105	870	87
500 bar	350	12	9	611	129	89	838	84
700 bar	350	12	7	646	110	91	854	85
900 bar	350	12	6	663	102	93	864	86
180 bar	350	24	19	318	271	219	827	83
500 bar	350	24	15	414	206	174	809	81
700 bar	350	24	11	491	126	107	735	74
900 bar	350	24	10	647	106	88	851	85
245 bar	380	6	17	243	257	258	775	78
500 bar	380	6	27	194	306	211	738	74
700 bar	380	6	25	346	218	205	794	79
900 bar	380	6	24	406	161	202	794	79
245 bar	380	12	20	96	399	267	782	78
500 bar	380	12	39	113	347	251	750	75
700 bar	380	12	38	130	251	258	677	68
900 bar	380	12	35	186	210	253	684	68
245 bar	380	24	35	96	329	345	805	81
500 bar	380	24	44	62	341	304	751	75
700 bar	380	24	41	62	318	310	731	73
900 bar	380	24	40	68	270	312	690	69

Table 8. Carbon balances (products and residual rock in mg of carbon) for Monterey Shale pyrolysis.

Sample	Temperature (°C)	Time (h)	Total (C_1-C_4)	Bitumen	Oil	Residual rock	Total recovered	(%) Recovery
180 bar	350	6	14	195	251	334	794	80
500 bar	350	6	8	210	196	325	739	74
700 bar	350	6	7	219	195	313	734	73
900 bar	350	6	7	215	182	323	727	73
180 bar	350	24	21	102	292	313	728	73
500 bar	350	24	13	113	233	301	660	66
700 bar	350	24	11	144	202	317	674	67
900 bar	350	24	10	143	197	315	665	67
245 bar	380	6	15	126	183	375	699	70
500 bar	380	6	22	109	267	291	689	69
700 bar	380	6	16	110	250	278	654	65
900 bar	380	6	16	126	214	302	658	66
245 bar	380	24	29	73	180	399	681	68
500 bar	380	24	40	78	241	252	611	61
700 bar	380	24	40	87	193	271	591	59
900 bar	380	24	39	87	194	284	604	60

4. Discussion

4.1. Effect of pressure on petroleum generation at 350 °C

The reduction in expelled oil yield at 350 °C observed under high water pressure (500, 700 and 900 bar), compared with the values obtained under lower pressure (180 bar) conditions for both source rocks (Table 2), is the result of pressure retarding the generation of oil. This occurs due to retardation of the rate of bitumen conversion to oil. This resulted in more extractable bitumen being retained in both source rocks at high water pressures (500-900 bar), such that for 24 h at 350 °C (maximum oil generation at all pressures) for the KCF source rock (Table 2), the 900 bar bitumen yield (809 mg/g TOC) was more than double the 180 bar yield (398 mg/g TOC). In the Monterey shale for 24 h the 900 bar bitumen yield (179 mg/g TOC) was 30% more than the 180 bar yield (127 mg/g TOC). The increase in bitumen yield observed with an increase in pressure for the KCF source rock at 350 °C for 24 h is consistent with the decreases in residual rock TOC (from 11.2% at 180 bar to 5.3% at 900 bar) (Table 3), and the recovered residual rock carbon content (from 219 mg/g carbon at 180 bar to 88 mg/g carbon at 900 bar) (Table 7) from 6 to 24 h. These reductions in the carbon content of the rocks confirm that high water pressure prevented pyrobitumen formation by inhibiting the conversion of bitumen to oil and gas for the KCF source rock at 350 °C for 24 h. This is consistent with previous observations on the Type IIs phosphatic Retort Shale at high pressure (Price and Wenger, 1992). Although pressure retarded bitumen conversion to oil in the Monterey shale, the trend in reduced rock carbon content observed at 900 bar for the KCF was not apparent for Monterey shale, and can be attributed to the difference in kerogen or source rock types.

In addition to the reduction in the oil yield, the gas yield also decreased significantly (with the alkenes most affected) with an increase in pressure. The huge reduction in alkene gases is either due to pressure suppressing alkenes generation or the hydrogenation of alkenes to alkanes or a combination of both (Uguna et al. 2015). The trend in gas yield is entirely consistent with our previous studies conducted at 350 °C (Carr et al. 2009; Uguna et al. 2012a, 2012b). The retardation of both oil and gas generation at 350 °C for both source rocks at pressures of 500, 700 and 900 bar is consistent with the increase in Rock Eval S2 and HI, observed at high pressures for the KCF source rock between 6 and 12 h and Monterey shale for 6 and 24 h. The increase in S2 and HI going to high water pressure indicates that petroleum generation from source rock/kerogen was retarded by high water pressures. This means that hydrocarbon generation potential was retained in the rocks pyrolysed at high pressures, and is consistent with previous studies (Price and Wenger, 1992; Uguna et al. 2012a). The slight reduction in bitumen yield observed going to 900 bar at 6 h for the KCF shows that the retardation effect of pressure on bitumen generation is not as significant as that observed for gas and oil generation under high pressures. The intermediate bitumen phase is thought to have a lower density (closer to kerogen) and will occupy a smaller volume (within the rock) compared to oil and gas; consequently the mechanical (pV) work required to displace the water from the source rock pores to accommodate bitumen is smaller than that required to accommodate the same mass of oil or gas within the source rock porosity (Uguna et al. 2012b). This accounts for the relative minor effect of pressure on bitumen generation. Overall the results obtained at 350 °C show that the retardation effect of pressure was more significant for both oil and gas and lesser for bitumen generation.

4.2. Effect of pressure on petroleum generation at 380 °C

At 380 °C, oil generation and expulsion was retarded by an increase in pressure for both source rocks, which resulted in more extractable bitumen remaining in the high pressure rocks between 6 and 24 h. However, the retardation effect of pressure was more significant for the KCF, when the drop in oil yield going to 900 bar was compared for both source rocks. At 6 h (at 500 bar) and 12 h (at 245 bar) the KCF oil yield was 47% higher, and at 24 h (at 500 bar), it was 20% higher compared to the same times at 900 bar (Table 5). While for the Monterey shale the oil yield was 20% higher at both 6 and 24 h at 500 compared to 900 bar (Table 5). The lesser retardation effect of pressure on oil generation observed for the Monterey shale is thought to arise from the more reactive nature of the Monterey shale kerogens compared to the KCF, and it is also the higher reactivity of the kerogen that explains why Rock Eval S2 and HI were not affected with increase in pressure to 900 bar in the Monterey source rock at 380 °C. While for the KCF, the retardation of oil generation and expulsion at 700 and 900 bar is consistent with the increase in Rock Eval S2 and HI at 380 °C between 12 and 24 h (Table

6). This means that pressure is retarding petroleum generation from the source rock/kerogen by preserving hydrocarbon generative potential to high pressures as observed at 350 °C.

Compared with the 350 °C experiments, the retardation effect of pressure on gas generation was less significant at 380 °C for both source rocks. The gas yield was not affected between 500 and 900 bar, except for the Monterey shale at 6 h that showed a 29% drop in gas yield at 700 and 900 bar. This is considered to be a combination of two factors for both source rocks. Firstly, temperature becomes dominant over pressure at 380 °C, such that 900 bar pressure was still not enough to significantly retard gas generation from the kerogen/source rocks as observed at 350 °C. This is due to the additional 30 °C promoting the catalytic effect of the clay minerals present, as well as providing sufficient thermal energy to undertake the (pV work) required against the pressurised water to provide the space to accommodate the additional volume of gas generated (Carr et al. 2013). Secondly, the retardation of oil generation and expulsion allowed some of the bitumen and oil retained in the rock to crack to gas and gasoline hydrocarbons at high pressures. The fact that the KCF bitumen yield at 900 bar reduced by 148 mg/g with only a corresponding increase in oil yield of 76 mg/g, and no significant increase in gas yield going from 12 to 24 h (Table 4) provide evidence that the main product from the cracking of petroleum (bitumen and oil) retained in the rocks at high pressures might be gasolines that were retarded from cracking further to gas. Although 12 h runs were not conducted for the Monterey shale, the similar gas yields (Table 4) between 500 and 900 bar to the KCF at 24 h indicates that the same reaction pathway giving higher gas yield occurred for both source rocks at high pressures. As our experimental design could not allow the recovery of light petroleum fractions, we believe the gasolines were lost during products recovery and solvent extraction of the rocks to recover retained petroleum. Hence the lower product recovery obtained at 700 and 900 bar compared to 245 and 500 bar for both source rocks (Tables 7 and 8).

To confirm that some direct cracking of petroleum (bitumen and oil) retained in the rocks at high pressure occurred at 380 °C, the carbon content of the 700 and 900 bar rock residues were compared to those of 245 and 500 bar. The carbon content of the KCF residual rock (Table 7) increased by 87 mg/g (258-345 mg/g) and 93 mg/g (211-304 mg/g) at 245 bar and 500 bar respectively going from 6 to 24 h, while the increases were 105 mg/g (205-310 mg/g) and 110 mg/g (202-312 mg/g) at 700 bar and 900 bar respectively from 6 to 24 h. The recovered residual rock carbon content for the Monterey shale (Table 8) at 6 and 24 h was also higher at 700 and 900 bar compared to 500 bar. The lower residual rock carbon contents under conditions (245 to 500 bar) that produced the highest oil yields for both source rocks, suggest that the rate of bitumen conversion to oil, and oil expulsion from the source rocks were faster, hence less pyrobitumen was formed from direct cracking petroleum within the rocks. However, at 700 and 900 bar the higher carbon contents of the residual rocks produced from experiments that generate less oil for both source rocks suggests that additional pyrobitumen (compared to 245 and 500 bar) was being formed by cracking of petroleum within the rocks as oil generation and expulsion from the source rocks were delayed. The increase in residual rock carbon content at 380 °C at 700 and 900 bar shown here is entirely consistent with the increase in residual coal TOC observed in our previous study on Svalbard coal pyrolysed at 420 °C for 24 h (Uguna et al. 2015). The increase in residual coal TOC for the Svalbard coal was also thought to be due to the direct cracking of bitumen or oil in the coals at high pressures. Overall the 380 °C results for both source rocks show that pressure had a higher retardation effect on oil generation and expulsion, and a lesser effect on gas generation. The higher retardation effect of pressure on oil generation is due to a combination of pressure slowing down the rate of bitumen conversion to oil, and the physical effect of pressurised water restricting expulsion of the generated oil from the rock. While the lesser effect of pressure on gas generation arises from the higher temperature used. As such gas generation occurred from some cracking of the expelled oil, directly from the kerogen/source rocks and via cracking of petroleum retained in the rocks with clay minerals catalysing the reaction. Due to the lower viscosity of gas they could easily escape from the rock hence gas generation was not retarded compared to oil that was being restricted from escaping from the rock due to its higher viscosity.

4.3. Pressure retardation of oil generation and expulsion as a mechanism for petroleum retention in gas shales, and gas generation in unconventional petroleum system

The fact that petroleum (bitumen and oil) in the rock at high temperature (380 °C) is contributing to gas generation at high pressures in this study, suggests that in geological basins bitumen or oil trapped in source rocks to high maturity will potentially generate more gas than expelled oil due to interaction with the kerogen and mineral matter adjacent to the source rock pores. The generation of gas at 380 °C and high pressures via cracking of bitumen and oil trapped in rock observed is this study have also been reported as the source of gas in shale gas systems (Bernard et al. 2012a, 2012b; Hill et al. 2007: Jarvie et al. 2007). However, Lewan (1993) showed that under the low pressure hydrous pyrolysis, bitumen can escape from the kerogen into the surrounding source rock. It has been suggested that the retention of bitumen in unconventional shale gas systems occurs due to the inability of bitumen to migrate out of low permeability shale source rocks. In the case of oil, bitumen that could not migrate from low porosity shale rocks fills the pores, and consequently prevents oil migration (Bernard et al. 2012a, 2012b). In addition to the low permeability of shale contributing to the retention of bitumen that is then cracked to gas, this study indicates that pressure retardation of oil generation and expulsion is also a possible mechanism for the retention of petroleum (bitumen and oil) in Type II and IIs shale rocks. The trapped bitumen or oil if preserved into the gas window, then becomes a potential source of shale gas at high maturity.

Having shown that bitumen, oil and gas generation are retarded in source rocks by high pressures, the question then arises as to how so much gas can occur in gas shales generated from bitumen or oil cracking. The shale gas reservoirs in the USA, such as the Barnett, Woodford and Marcellus shales, occur in onshore uplifted basins and are generally overpressured (Jarvie et al. 2007). Overpressure in geological basins can arise due to a number of mechanisms, e.g. disequilibrium compaction (Osborne and Swarbrick, 1997). One of the most commonly considered mechanisms (petroleum generation and oil to gas cracking) was discounted by Osborne and Swarbrick (1997) due to the self-limiting effect of pressure in sealed, i.e. overpressured systems because any increase in pressure could inhibit further generation or cracking. Petroleum generation and oil to gas cracking reactions are retard by high pressures, as confirmed by the results presented in this and previous studies (e.g. Carr et al. 2009; Landais et al. 1994; Michels et al. 1995; Uguna et al. 2012a, 2012b, 2015), and thus preclude these processes as being major contributors of overpressure generation in subsiding geological basins as suggested by Osborne and Swarbrick (1997). The subsidence of the basin prior to inversion will have generated and expelled conventionally reservoir petroleum from the source rocks, e.g. Barnett Shale, Fort Worth Basin, USA (Hill et al. 2007). This issue could be resolved by the inversion process itself producing increased heat flow due to the tectonic processes responsible for the inversion, e.g. compression in the crust beneath the inverting basin, also producing higher heat flows (Carr and Uguna, 2015). This compression generates friction between the moving masses, which accounts for the increased heat flow during inversion. The reduction in pressure coupled with the slight reduction in temperature during uplift could result in a renewed phase of gas generation, the gases generated could be sourced from any remaining potential in the matured kerogen, and from petroleum (bitumen and oil) retained in the pores under the high pressures developed during subsidence.

4.4. Effect of pressure on source rock thermal maturity

The reduction in VR observed for both source rocks at high water pressures between 6 and 24 h at 350 and 380 °C is due to high water pressure retarding source rock maturation by reducing the rate of aromatisation reactions (Carr, 1999). This result is entirely consistent with our previous studies (Uguna et al. 2012a, 2012b, 2013). At 380 °C in contrast to 350 °C, the increase in VR from 245 to 500 bar observed for the Monterey shale (an opposite trend to the KCF source rock) is the result of the retardation effect of pressure being shifted beyond 500 bar, and is due to the higher reactivity of the Monterey shale. The higher VR observed for the Monterey shale under 500 bar pressure conditions at 380 °C is consistent with the higher gas and oil yield. The KCF and Monterey shale are Type II and IIs source rocks respectively, and contain very small amounts of autochthonous vitrinite, and so the numbers of individual vitrinite particles that were available for measurement were small. The few numbers of vitrinite particles measured for each of the rocks residues mean that the VR differences between the various samples might be regarded as statistically insignificant. However, the consistency in the reduction in gas and oil yields (for both source rocks at 350 and 380 °C) the preservation of S2 and HI for the KCF (at 350 and 380 °C) and Monterey shale (at 350 °C) together with the observed reduction in Rock Eval T_{max} at 380 °C (for both source rocks) with pressure increase indicates that the observed decrease in VR with increase in pressure is correct. Also the fact that the decrease in VR observed with increasing pressures in this study is consistent with results obtained for coals pyrolysed at 350 °C (Uguna et al. 2012a) and 380-420 °C (Uguna et al. 2015). In these coal pyrolysis studies 100 VR measurements were obtained from each coal sample, and the VR values decreased with increasing pressure as in this study, indicating that while the results in this study are not as statistically reliable as those obtained in the coal studies, the trends are consistent indicating that the decrease in VR with increasing pressure is correct.

5. Conclusions

The results obtained at 350 °C for both the KCF and Monterey shale Type II and IIs source rocks show that gas, expelled oil yields and vitrinite reflectance were all higher under 180 bar pressure than under high water (500 to 900 bar) pressures. The bitumen contents however, increase as the pressure was increased from 180 to 900 bar, which occurs due to high pressures retarding the conversion of bitumen into oil and gas, and the retarded petroleum generation is also seen in the vitrinite reflectance values being lower at higher pressures. The retardation of petroleum generation resulted in more hydrocarbon potential remaining in the high pressure rocks. This increased Rock Eval HI's in the rocks pyrolysed between 500 and 900 bar for both KCF and Monterey source rocks. The retardation of bitumen cracking to oil prevented pyrobitumen formation at high pressures (700 and 900 bar) for the KCF as shown by the lower TOC contents of the pyrolysed residues obtained from the 700 and 900 bar high pressure experiments at 24 h.

At 380 °C, the data are far more complex than those at 350 °C, due in part to the different reactivities of the kerogens in the two source rocks, the additional 30 °C enabling more endothermic reactions, e.g. oil generation, to occur, but there are also the physical effects of the pressurised water restricting expulsion of oil from the pyrolysed samples. The effect of increasing the pressure at any temperature increases the activation energy (E_a) for endothermic reactions, due mainly to the pressure increasing the size of the pV term within the E_a. Pyrolysis of both KCF and Monterey source rocks at 380 °C for 24 h, resulted in gas generation being higher at high pressures (500 to 900 bar) than at 245 bar. The oil yields increase as the experiment duration increases from 6 to 12 and then to 24 h at the same pressures. However, unlike the oil yield results at 350 °C, the oil yields show a maximum at 500 bar, while the bitumen yields show minima at 500 bar in both the KCF and Monterey samples pyrolysed for 6 h, while in the results from 12 h KCF and 24 h Monterey samples show increasing bitumen yields occur with increasing pressure. The bitumen yields for the KCF pyrolysed for 24 h show much lower values at 500, 700 and 900 bar than at 245 bar, suggesting that the bitumen in the KCF pyrolysed for periods as long 24 h was converted into other products, e.g. gas and gasolines. As the gasolines were not recovered in the experimental method, the higher loss of gasolines in the samples pyrolysed at 380 °C probably accounts for the low total carbon recoveries in the mass balance calculations (Tables 7 and 8) than those produced in the 350 °C experiments. Comparisons between the mass balance residual rock carbon contents in the KCF samples pyrolysed between 6 and 24 h at 380 °C show that the difference is 87 mg/g at 245 bar and 110 mg/g at 900 bar, which probably reflect the increased pyrobitumen formation in the KCF samples pyrolysed at 900 bar. The mass balance of the residual rock carbon contents are similar in the Monterey to those occurring in the KCF, and are also probably indicators of pyrobitumen formation. The low total carbon recoveries at 700 and 900 bar for the KCF (between 12 and 24 h) and the Monterey shale (for 6 and 24 h) at 380 °C is consistent with the formation of gasolines along with the formation of pyrobitumen, while for the Monterey pyrolysed at 350 °C for 24 h is consistent with formation of lighter petroleum products.

The implications from this study are that in geological basins, pressure, temperature and time will all exert significant control on the extent of the early and main stages of source rock maturation and petroleum (oil and gas) generation. In geological basins temperatures are much lower, and the pressures (regardless of whether overpressure is present) can be as high as the 900 bar used in this study, indicating that the retardation effect of pressure could be more significant than shown here. In particular, the increase in un-expelled oil and bitumen being retained in the source rock as bitumen, and the preservation of hydrocarbon potential, as observed in the highest pressure experiments is likely to have important implications for the further generation potential of the source rocks in the gas window. More so the cracking of petroleum (bitumen and oil) retained in the source rocks to gas under high pressures at 380 °C provides further evidence on how gas may likely be generated in shale gas systems. Indeed this may explain the observation that Type II source rocks matured to gas window conditions form the most prolific shale gas reservoirs, such as the Woodford, Marcellus and Barnett shales in the USA (Jarvie et al. 2007).

While the effect of pressure retards petroleum generation during the subsidence phase of the basin, the presence of gas shales in inverted basins is potentially the result of a combination of factors associated with the basin inversion. The oil-prone source rocks generated oils and gases during the subsidence of the basin, but were not exhausted as regards hydrocarbon generation potential. Although temperatures are reduced in the inverted basin, the reduction in temperature was not as much as the reduction in pressure, due to the elevated heat flows that must accompany inversion. It is the effect of the reduced pressure that probably enabled the gas generation to occur from potential still remaining in the kerogens after the subsidence, and also from petroleum (bitumen and oil) that may have been retained in the source rock porosity by the high pressures during the basin subsidence.

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