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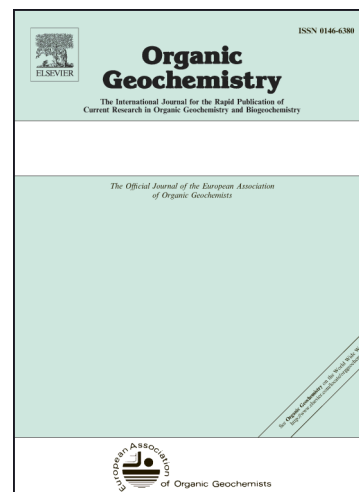Clement N. Uguna, Andrew D. Carr, Colin E. Snape, Will Meredith

High pressure water pyrolysis of coal to evaluate the role of pressure on hydrocarbon generation and source rock maturation at high maturities under geological conditions

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Abstract

This study investigates the effect of water pressure on hydrocarbon generation and source rock maturation at high maturities for a perhydrous Tertiary Arctic coal, Svalbard. Using a 25 ml Hastalloy vessel, the coal was pyrolysed under low water pressure (230-300 bar) and high water pressure (500, 700 and 900 bar) conditions between 380 °C and 420 °C for 24 h. At 380 °C and 420 °C, gas yields were not affected by pressure up to 700 bar, but were reduced slightly at 900 bar. At 380 °C, the expelled oil yield was highest at 230 bar, but reduced significantly at 900 bar. At 420 °C cracking of expelled oil to gas was retarded at 700 and 900 bar. As well as direct cracking of the coal, the main source of gas generation at high pressure at both 380 °C and 420 °C is from bitumen trapped in the coal, indicating that this is a key mechanism in high pressure geological basins. Vitrinite reflectance (VR) was reduced by 0.16 %Ro at 380 °C and by 0.27 %Ro at 420 °C at 900 bar compared to the low pressure runs, indicating that source rock maturation will be more retarded at higher maturities in high pressure geological basins.

1. Introduction

In geological basins hydrocarbon generation is an endothermic process which involves the conversion of immature kerogen into gaseous and liquid hydrocarbons, and a residual mature solid kerogen. This conversion results in the product (gas, liquid and residual kerogen) final volume being greater than the reactant (immature kerogen) initial volume. Hydrocarbon generation reactions occur under saturated, high water pressure conditions and according to chemical theory, reactions like hydrocarbon generation whose products occupy a greater volume than its reactant should be influenced by pressure. Previous pyrolysis studies on the role of pressure during hydrocarbon generation and source rock maturation have been reviewed in detail by Uguna et al. (2012a), with the findings appearing to be in conflict, due to variety of pyrolysis methods used. Most high pressure pyrolysis studies performed under confined conditions using gold bags or gold capsules, in which the sample being pyrolysed is either not in contact or in contact with only a limited amount of water, produced little or no significant pressure effects (e.g. Monthioux et al., 1985, 1986; Freund et al., 1993; Michels et al., 1994; Huang, 1996; Knauss et al., 1997; Shuai et al., 2006; Tao et al., 2010). In contrast, under high pressure conditions in fixed volume vessels, in which the pyrolysed sample is in direct contact with water, pressure has been found to significantly retard both hydrocarbon generation and source rock maturation (Price and Wenger, 1992; Landais et al., 1994; Michels et al., 1995; Carr et al., 2009; Uguna et al., 2012a, b, 2013).

A recent study by Uguna et al. (2012a) conducted on two coals (an orthohydrous Longannet UK coal and a perhydrous Svalbard coal) at 350 °C for 24 h in the pressure

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range of 175-900 bar, showed that high water pressure retarded hydrocarbon (gas and bitumen) generation and source rock maturation as measured by vitrinite reflectance (VR). We also recently showed for Kimmeridge Clay pyrolysis at 350 °C that gas and bitumen generation, and VR were all retarded at 500 bar, while at 420 °C VR was retarded but gas and the bitumen plus oil yields were not affected by pressure at 450 bar when compared to results obtained at lower pressures (Uguna et al., 2012b). We interpreted these results as the effect of pressure being insufficient when temperatures as high as 420 °C are used.

To investigate if the retardation effect of water pressure observed at 350 °C on a coal will be the same at 420 °C, experiments were conducted at 380 °C and 420 °C and pressures up to 900 bar, that is, higher than the 450 bar previously used by Uguna et al. (2012b) for a Kimmeridge clay source rock. The sample studied is the same Svalbard perhydrous coal used by Uguna et al. (2012a). The results obtained at 380 °C and 420 °C will be compared with the results obtained from the same coal at 350 °C (Uguna et al., 2012a) to assess the effects of pressure and temperature on gas generation, oil generation and cracking, and source rock maturation.

2. Experimental

The sample studied is a perhydrous high volatile bituminous coal from the Arctic archipelago of Svalbard of Paleocene age (particle size 2-4 mm), with a total organic carbon content (TOC) of 78.5%, Hydrogen Index (HI) of 347 mg/g and VR of 0.68 %Ro (Table 1). The pyrolysis equipment (Fig. 1) comprised 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 were conducted using 2.0 g of coal

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at 380 °C and 420 °C (temperature accuracy ±1 °C) for 24 h under low and high water

pressure conditions. The low pressure experiments at 380 °C (230 bar) and 420 °C

(300 bar) were performed by adding 12 ml and 10 ml water respectively to the vessel,

while the high water pressure experiments at both temperatures were conducted at 500,

700 and 900 bar. The experimental procedure used has been described in detail

previously (Uguna et al., 2012a) and summarised below.

The reactor vessel was heated by means of a fluidised sand bath, controlled by

an external temperature controller. Temperature was also monitored independently by

means of a K-Type thermocouple attached to the outside of the vessel and recorded by

computer every 10 seconds. The un-extracted coal sample to be pyrolysed was first

weighed and transferred to the vessel, after which the volume of water needed for the

experiment was added. For all experiments the reaction vessel was flushed with

nitrogen gas to replace air in the reactor head space, after which 2 bar pressure of

nitrogen was pumped into the pressure vessel to produce an inert atmosphere during the

pyrolysis runs. The sand bath (connected to a compressed air source) was pre-heated to

the required experimental temperature and left to equilibrate, after which the pressure

vessel was then lowered in to the sand bath by lifting up the sand bath using the jack

(Fig. 1), and the experiment left to run with a constant air flow through the sand bath.

The pressure observed for the low pressure experiments, 230 bar and 300 bar at 380 °C

and 420 °C, respectively, was generated by the vapour of the water 12 ml (230 bar at

380 °C) and 10 ml (300 bar at 420 °C) added to the vessel at the start of the experiment.

High liquid water pressure (500, 700 and 900 bar) experiments were performed

similarly to the low (230 bar and 300 bar) pressure hydrous runs, with the vessel

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initially filled with 20 ml water. After lowering the pressure vessel into the sand bath, the vessel was connected to the high water pressure line and allowed to attain its maximum vapour pressure (in about 30 minutes), before the addition of more water to increase the pressure. This procedure is employed to prevent too much water being added to the vessel which might lead to the generation of over pressure in excess of the pressure limit of the system. To apply high liquid water pressure to the system (with the aid of a compressed air driven liquid pump), the emergency pressure release valve B was first closed, and valve A opened until a pressure slightly higher than the vapour pressure of the experiment is displayed on the external pressure gauge. This was undertaken to avoid the loss of any of contents of the vessel when the reactor valve C is opened. High liquid water pressure was then applied to the system by first opening valve C and immediately gradually opening valve A to add more distilled water into the reaction vessel. When the required pressure was attained, valve C was closed to isolate the reactor from the high water pressure line, and valve A was also closed to prevent more water going to the pressure line. Valve B was opened to vent the excess pressure on the line. The experiment was then allowed to run (leaving valve C tightly closed to avoid losing generated products) for the required time, after which the sand bath was switched off and left to cool to ambient temperature before product recovery.

To recover the generated gas, the high water pressure line was disconnected and a connector attached to valve C. The gas was collected with the aid of a gas tight syringe via the connector by opening valve C and transferred to a gas bag (after the total volume had been recorded), and immediately analysed on a Clarus 580 gas chromatograph (GC) fitted with a FID and TCD detectors operating at 200 °C. 100 μl of gas samples were injected (split ratio 10:1) at 250 °C with separation performed on an

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alumina plot fused silica 30 m x 0.32 mm x 10 µm column, with helium as the carrier gas. The oven temperature was programmed from 60 °C (13 min hold) to 180 °C (10 min hold) at 10 °C/min. Individual gas yields were determined quantitatively in relation to methane (injected separately) as an external gas standard. The total yield of the hydrocarbon gases generated was calculated using the total volume of generated gas collected in relation to the aliquot volume of gas introduced to the GC, using relative response factors of individual C_2-C_5 gases to methane predetermined from a standard mixture of C_1-C_5 gases. The oil floating on top of the water after the experiments (collected with a spatula and recovered by washing the spatula in dichloromethane) together with oil stuck to the side of the reactor wall (recovered by washing with cold dichloromethane) were combined and referred to as expelled oil. The reacted coals were vacuum dried at 45 °C for 3-4 hours, crushed and Soxhlet extracted using 150 ml dichloromethane:methanol mixture (93:7 v:v) for 48 hours to recover the bitumen and any non-expelled oil retained in the coal, with both being referred to as bitumen.

Under the supercritical water conditions (380 °C and 420 °C) used in these experiments water will have the properties of an organic solvent, as such it is difficult to differentiate oil expulsion during the experiments and solvent extraction of the pyrolysed coal after the experiment to obtain the bitumen and non-expelled oil retained in the coals. In order to differentiate the amounts of oil expelled during the experiments from the bitumen and non-expelled oil retained in the coals, the floating oil on top of the water after the experiments together with those on the side of the reactor wall was called expelled oil, and the bitumen and non-expelled oil solvent extracted from the coals called bitumen.

3. Results

3.1. Pyrolysis at 380 °C

The gas yields (mg/g of starting coal) generated at 380 °C are presented in Table 2 and Fig. 2. The total (C_1-C_5) hydrocarbon gas generated at 380 °C was slightly higher at 230 bar (34 mg/g) compared to pyrolysis at 500 and 700 bar (31 mg/g), but was reduced by 20% to 27 mg/g at 900 bar when compared to the amount generated at 230 bar. The methane, ethane and propane gas yields (Table 2) showed reductions between 230 and 900 bar, while butane and pentane contents (Table 2) were the same at 230 bar and 500 bar, both showing small increases at 700 bar, before showing a reduction at 900 bar. The unsaturated alkenes contents (Table 2) were found to be highest at 230 bar, but decreased significantly as pressure increased to 500, 700 and 900 bar. The expelled oil yields (mg/g of starting coal) generated are presented in Fig. 3, and also listed in Table 3 together with the bitumen and bitumen plus oil yields. The oil yield at 380 °C reached a maximum at 230 bar (174 mg/g), and was reduced by 22% as the pressure was increased to 500 bar and 700 bar (136 mg/g). At 900 bar the oil yield was reduced further to 114 mg/g, which is 34% less than at 230 bar, indicating less generation and expulsion at high pressure in the coal chips used here. The bitumen yield (Fig. 3) was similar at 230 bar and 500 bar, but increased going to 700 bar and 900 bar. The residual coal VR values (mean of 100 measurements) obtained are listed in Table 3 and also presented in Fig. 4. The VR values were similar at 230 bar (1.35 %Ro) and 500 bar (1.31 %Ro). A slight reduction in VR was observed with increase in pressure to 700 bar (1.29 %Ro) compared to 230 bar, while at 900 bar the VR reduced further to 1.19 %Ro, which is 0.16 %Ro lower than the 230 bar VR value.

3.2. Pyrolysis at 420 °C

The gas yields obtained at 420 °C are listed in Table 2, and also presented in Fig. 5. The total (C_1-C_5) gas yield increased slightly going from 300 bar (105 mg/g) to a maximum at 500 bar (115 mg/g) and 700 bar (111 mg/g), before decreasing slightly at 900 bar (99 mg/g). The individual hydrocarbon gas yields (Table 2) show the same trend as the total gas yields except for the unsaturated alkenes which decreased significantly with an increase in pressure as observed at 380 °C. The expelled oil yield in mg/g TOC of initial coal (Table 3 and Fig. 6) was lowest at 300 bar, and increased by 66% as the pressure increased to 500 bar pressure. The oil yield increased further with an increase in pressure by 27% and 21% for the 700 bar and 900 bar runs respectively in comparison to the 500 bar run. The bitumen yield (Table 3 and Fig. 6) was lower and similar at 300 bar (81 mg/g) and 500 bar (89 mg/g), but reduced at 700 bar (51 mg/g) and 900 bar (54 mg/g). The residual coal VR values (mean of 100 measurement) (Table 3 and Fig. 4) was 1.76 %Ro at 300 bar, and decreased by 0.15 %Ro at 500 bar (1.60 %Ro) and 700 bar (1.61 %Ro). An increase in the pressure to 900 bar caused the VR to further decrease to 1.49 %Ro, with the 900 bar value being 0.27 %Ro lower than the 300 bar value, and 0.11 %Ro and 0.12 %Ro lower than the 500 bar and 700 bar values, respectively.

3.3. Experimental carbon mass balance

The experimental carbon mass balance obtained previously at 350 °C for 24 h (Uguna et al., 2012a) are presented in Table 4, while those obtained for pyrolysis at 380 °C and 420 °C are presented in Table 5. The extracted residual coals (carbon content determined using the residual TOC of the pyrolysed coals), hydrocarbon gases, oil and

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bitumen yields were used to determine these balances. The Svalbard coal bitumen at 350 °C contained 85% carbon (Uguna et al., 2012a), and this value has been used to calculate the carbon contents of the bitumen and oil generated at 380 °C and 420 °C. The balances exclude lower molecular weight hydrocarbons e.g. gasoline ($C_6 – C_{12}$) hydrocarbons, together with CO and CO_2 which were not measured. The gasoline hydrocarbons could not be recovered due to evaporative losses during products recovery and solvent extraction of the pyrolysed coals to recover the bitumen and non-expelled oil, while CO and CO_2 generation was not investigated in the study.

At 350 °C (bitumen generation stage) the carbon recoveries was 93-96% of the initial starting coal. At 380 °C and 420 °C the carbon recoveries were 84-90% and 84-88% respectively. The drop in recovery at 380 °C and 420 °C compared to 350 °C is due to an increased generation of lighter hydrocarbons that could not be recovered as the bitumen is cracked to oil at higher temperature. The carbon recoveries would have been greater if CO and CO_2 could have been included. The high carbon recoveries obtained considering the fact that light hydrocarbons, CO and CO_2 were not included indicate that product recovery in our experiments is good. The similar carbon recovery obtained under low and high pressure conditions at 350, 380 and 420 °C shows that the changes in product yields observed with pressure increase is due to pressure effect and not loss of product either during the experiments or product recovery after the experiments.

4. Discussion

The bitumen, gas and VR results obtained previously for the same Svalbard coal at 350 °C for 24 h and already published (Uguna et al., 2012a) will be discussed

together with those obtained at 380 and 420 °C. The gas and bitumen yields (mg/g of

starting coal) obtained at 350 °C for 24 h are presented in Table 6 and Fig. 7. At 350 °C

only bitumen was generated, as oil generation and expulsion had not yet commenced.

However given the starting maturity of the coal (0.68 %Ro), extending the duration of

heating in excess of 24 h, might well have resulted in the onset of oil generation from

this coal. The bitumen yield was higher at 175 bar, and reduced by only about 10% at

900 bar in relation to 175 bar. The small reduction in bitumen yield observed with

increase in pressure to 900 bar indicates that pressure has a slight retardation effect on

bitumen generation. At 380 °C the coal had started to generate and expel oil. The

higher oil yield obtained at 230 bar shows that more oil was generated and expelled

under low pressure conditions, and the reduction in oil yield observed going from 230

bar to 500, 700 and 900 bar is due to pressure retarding the generation and expulsion of

oil. This is due to both the rate at which bitumen is converting to oil and the rate at

which oil is expelled from the coal being slower under high water pressure conditions,

which resulted in more bitumen remaining in the coal pyrolysed at 900 bar (124 mg/g

TOC) compared to 230 bar (102 mg/g TOC). An increase in the temperature to 420 °C

resulted in a decrease in the oil and bitumen yields at all pressures compared to 380 °C,

and is due to increased cracking. The increase in oil yield observed going from 300 bar

to high pressures (500-900 bar) is due to maximum oil generation having been shifted to

high pressures at 420 °C.

At 350 °C the total (C_1-C_4) gas yield (Fig. 7 and Table 6) was higher at 175 bar

and decreased by 22% and 55% going from 175 bar to 500 and 900 bar, respectively.

The huge reduction in gas yields observed with increase in pressure indicates that

pressure significantly retarded gas generation, and the 10% reduction in bitumen yield

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in comparison to the 55% reduction in gas yield observed at 900 bar, shows that the retardation effect of pressure is more significant for gas than bitumen generation. The huge retardation effect of pressure on gas generation relative to bitumen generation observed at 350 °C going from 175 to 900 bar arises from the volume expansion required to accommodate the gaseous product (Uguna et al., 2012a). With gas having a lower density and higher volume than bitumen, the energy (pV work) required to displace the surrounding water at 900 bar to create the volume needed to accommodate the generated gas is far greater than that required to create the volume needed to accommodate the bitumen within the coal, hence pressure retardation effect is less for bitumen than gas generation (Uguna et al., 2012a).

At 380 °C the total (C_1-C_5) gas yield was reduced at 900 bar by 20% in comparison to 230 bar, while at 420 °C the gas yield only reduced slightly by 14% at 900 bar compared to the maximum yield generated at 500 bar. At both 380 °C and 420 °C the unsaturated alkene gases were reduced under high water pressure to a much greater extent than the saturated alkane gases. This is due to the retardation of alkene gas generation by pressure or hydrogenation of alkenes to alkanes, or the addition of free radicals to alkenes to form branched short chain alkanes being favoured under high water pressure. The reduction in the yields of alkene gases with pressure increase observed in this study might explain why alkenes are not formed under pressure conditions in geological basins. Overall, the results indicate that at 380 °C and 420 °C, gas yields are not markedly affected by pressure as observed at 350 °C, and this is considered to be a combination of two factors. Firstly, the increase in temperature results in the physical retardation induced by 900 bar pressure, becoming less significant, due to the increased chemical reactions between the supercritical water and

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kerogen, such that gas generation was not significantly retarded as observed at 350 °C. The additional 30 °C provides the thermal energy to enable the system to have sufficient energy available to undertake both the bond breakage (to generate the hydrocarbons) and pV work to create the space in the pressurised water to accommodate the additional volume required by the generated hydrocarbons. Secondly, due to high water pressure delaying the conversion of bitumen to oil and the expulsion of oil from the coal, some cracking of bitumen and/or oil retained in the coal to gas and gasoline hydrocarbons occurred at high pressures. The cracking of bitumen and/or oil to gas and gasoline hydrocarbons, explains why the increase in extracted bitumen yield with an increase in pressure going from 230 bar to 900 bar at 380 °C is relatively small when the reduction in oil yield is considered. This means that the retained bitumen is decreasing due to cracking to gas and gasoline range hydrocarbons, as oil generation is retarded by pressure. At 380 °C the 500, 700 and 900 bar gas yields did not show any significant increase due to cracking of bitumen, suggesting that gasoline hydrocarbons, which were prevented from cracking further to gas under high pressures were the main products from the cracking of bitumen and/or oil retained in the coal at high pressures. The formation of more gasoline hydrocarbons from cracking of retained bitumen and/or oil in the coal at high pressures is evident from carbon mass balance obtained at 380 °C (Table 5) which showed a steady decrease in total recovered carbon from 90% (at 230 bar) to 84% (at 900 bar). The decrease in total recovered carbon being due mainly to the loss of unrecovered gasoline hydrocarbons and CO_2. The cracking of the retained bitumen and/or oil at high pressure is also supported by the small gradual increase in TOC at 380 °C going from 230 bar (77.6%) to 500 bar (78.9%), 700 bar (78.8%), and 900 bar (80.5%), which is due to pyrobitumen formation. The lower residual TOC

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obtained at 230 bar indicate that less pyrobitumen was formed, suggesting that oil was generated and expelled at a faster rate, which in turn reduced the rate at which bitumen and/or oil in the coal was cracked directly to gas. This explains why the expelled oil yield at 380 °C (Table 3 and Fig. 3) was higher at 230 bar in comparison to the 500, 700 and 900 bar results.

At 420 °C the oil yield increased with increasing pressure going from 300 bar (29 mg/g) to 500 (85 mg/g), 700 (117 mg/g) and 900 bar (108 mg/g), while the bitumen yield decreased going from 300 bar (81 mg/g) and 500 bar (89 mg/g) to 700 bar (51 mg/g) and 900 bar (54 mg/g). The trend in oil and bitumen yield is opposite to that observed at 380 °C, and might be due to enhanced generation and expulsion of oil with increase in pressure resulting in less extractable bitumen remaining in the coal at 700 bar and 900 bar. Alternatively it might be due to direct cracking of bitumen and/or oil retained in the coal, while pressure is also preserving the expelled oil from further cracking to gas at 700 bar and 900 bar. We believe that the alternative direct cracking is the more likely reason why the oil yields were higher and the bitumen yields lower at 700 bar and 900 bar. This can be explained using the residual coal TOC (Table 3), which was higher at 300 bar (79.5%), reduced by 5.6% to a minimum at 500 bar (73.9%) before increasing again by 4.8% and 5.1% to 700 bar (78.7%) and 900 bar (79.0%), respectively. Under 300 bar conditions 10 ml water was used and the experiment was under superheated steam conditions which might not have favoured oil generation and expulsion, resulting in the bitumen and/or oil retained in the coal being cracked mainly to gas, with the formation of pyrobitumen or coke as shown by the highest residual TOC obtained. At 500 bar pressure the lower residual TOC is due to less pyrobitumen or coke being formed, which is as a result of oil generation and

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expulsion being favoured due to the moderate pressure, supercritical water conditions as a result of the additional water in the vessel. The lower residual TOC observed at 420 °C under 500 bar conditions is entirely consistent with the lowest residual TOC observed for the 230 bar experiment, under which pressure the maximum amount of oil was generated at 380 °C. This suggests that maximum oil generation and expulsion occurred under 500 bar conditions at 420 °C, indicating that the lower expelled oil yield obtained at 500 bar in relation to 700 bar and 900 bar values is due to cracking of oil to gas and gasolines.

The increase in the residual TOC with increasing pressure to 700 bar and 900 bar at 420 °C is ascribed to pyrobitumen or coke formation resulting from the direct cracking of trapped bitumen and/or oil to gas, entirely consistent with lower bitumen yields at 700 bar and 900 bar. The fact that pressure retarded oil generation and expulsion at 420 °C under 700 bar and 900 bar pressure conditions suggests that the higher expelled oil yield obtained in comparison to the 500 bar value, is due to pressure retarding oil cracking to gas, consistent with the slight reduction in gas yield observed at 900 bar. Although some cracking of retained bitumen and/or oil occurred at 420 °C under 500 bar conditions, the fact that oil cracking to gas is evident suggests that oil cracking was a significant contributor to gas generation at 500 bar. On the other hand the fact that oil cracking to gas is retarded at 700 bar and 900 bar at 420 °C is further evidence that gas generation at 700 bar and 900 bar was mainly from the cracking of bitumen, although direct generation of gas from kerogen due to high temperature is a possible alternative, without requiring the bitumen intermediate to be formed. The contribution of bitumen and/or oil retained in the coals to gas generation and the retardation of the expelled oil from cracking to gas at 700 bar and 900 bar observed in

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this study, suggest that in geological basins bitumen or oil trapped in source rocks to high maturities can be converted to gas at a later period. This potentially might occur as a result of a combination of increased heat flow required during uplift (all gas shales currently in production occur in inverted basins), with the reduction in pressure.

The residual coal VR values (mean of 100 measurements) obtained previously at 350 °C for 24 h and already published (Uguna et al., 2012a) are presented in Table 6 and Fig. 4. The VR follow the same trend as those obtained in this study at 380 °C and 420 °C, reducing by 0.15 %Ro from maximum at 175 bar (1.07 %Ro) hydrous conditions to a minimum at 900 bar (0.92 %Ro). The reduction in VR observed at 350, 380 and 420 °C with an increase in pressure is due to high water pressure retarding source rock maturation, which is as a result of the rate of aromatisation reactions being reduced under high water pressure conditions (Uguna et al., 2012a). Comparison of the VR results (Fig. 4, Tables 3 and 6) obtained at all three temperatures shows that VR was reduced by the same value at 350 °C (0.15 %Ro) and 380 °C (0.16 %Ro) going from low pressure hydrous to 900 bar water pressure. However, at 420 °C the VR reduced by 0.27 %Ro at 900 bar compared to the 300 bar VR. This indicates that the retardation effect of pressure on source rock maturation becomes more significant with increase in source rock maturity, and is due to the coal becoming less reactive at higher maturities due to loss of volatiles.

The increase in gas yield at 420 °C going from 300bar to 500 bar before reducing going to 900 bar, and the retardation of VR between 500 bar and 900 bar at 350 °C to 420 °C observed in this study has been observed previously for oil cracking conducted at 350 °C and 400 °C (Hill et al., 1996) and coal pyrolysed at 300 °C and 340

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°C (Hill et al., 1994) using the anhydrous, confined gold bag pyrolysis method. Both studies showed that hydrocarbon gas yield and VR increased to a maximum at 690 bar before decreasing at 2000 bar. The high pressure (2000 bar) reached by Hill et al. (1996, 1994) using gold bags before pressure retardation occurred compares with this study, in which pressure retardation was observed between 500 bar and 900 bar. This difference has been attributed to the different pyrolysis methods used (Landais et al., 1994; Michels et al., 1995). As mentioned earlier in the introduction, pressure retardation effects have been shown to be generally more significant for high water pressure unconfined pyrolysis than high pressure confined gold bag pyrolysis. The high retardation effect of pressure observed under high water pressure pyrolysis conditions has been attributed to the pressurising medium (water) been in contact with the sample been pyrolysed (Landais et al., 1994; Michels et al., 1995). On the other hand under confined gold bag pyrolysis the sample is not in contact with the pressurising medium, and the pressure applied to the outside of the gold bag may be reduced by the pressure generated from products generation, hence the pressure retardation effect is less (Uguna et al., 2012a, b).

In the transition state theory, reaction rates are controlled by the activation volume ($\Delta^{\ddagger}V^{o}$) which is the volume difference between the activated complex and reactant. If the reaction is bimolecular (where the volume of the transition state is smaller than the sum of the volumes of the reactants) $\Delta^{\ddagger}V^{o}$ is negative and the reaction rate constantly increases with increasing pressure, thus reaction is enhanced. Conversely, if a reaction is unimolecular (where the volume of the transition state is larger than the volume of the initial species) high pressure will reduce the reaction rates, thus retarding the reaction (Al Darouich et al., 2006). Hill et al. (1996) using gold bags

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to study oil cracking calculated ($\Delta^\ddagger V^o$) values of +47 cm^3/mol in the 90-483 bar range at 400 °C, while between 345 and 690 bar at 350 and 380 °C, and 483 and 690 bar at 400 °C, ($\Delta^\ddagger V^o$) is 14 cm^3/mol. Al Darouich et al. (2006) also using gold bags to study oil cracking, calculated ($\Delta^\ddagger V^o$) values in the range 40-140 cm^3/mol. Given the relatively large size of the molecules in kerogen and petroleum, it would be realistic to expect quite large changes upon activation, depending upon the exact nature of the activated complex (Uguna et al., 2012a). The situation is complicated by the fact that $\Delta^\ddagger V^o$ (like all volume parameters) must be pressure dependent, but no theory is currently available to predict the variation in activation volume with pressure. Consequently in the case of such complex reactions such as the conversion of kerogen into bitumen, oil, gas, pyrobitumen and modified kerogens, an alternative approach is required, if the relationship between $\Delta^\ddagger V^o$ cannot be derived.

5. Conclusions and implications

5.1. Conclusions

At 350 °C under 900 bar pressure conditions gas and bitumen generation, and source rock maturation were all retarded by pressure, with the retardation effect of pressure being more significant for gas generation and source rock maturation than bitumen generation.

At 380 °C and 420 °C gas generation was retarded by pressure to a lesser extent than at 350 °C, due to a combination of the higher temperature (which reduced the effect of pressure) and the cracking of bitumen retained in the coal to gas.

However at 380 °C, high water pressure significantly retarded oil generation and expulsion by delaying bitumen conversion to oil. At 420 °C, oil cracking to gas was retarded at 700 bar and 900 bar.

At 350 and 380 °C VR was retarded by 0.15 %Ro going from low pressure to 900 bar, and at 420 °C VR was retarded by 0.27 %Ro going from low pressure to 900 bar.

5.2. Implications

Gas and oil generation, oil cracking to gas and source rock maturation will be retarded to a greater extent than bitumen generation in high pressure geological basins for perhydrous coals, in common with Type II source rocks.

The retardation effect of pressure observed in this study implies that in addition to temperature and time, pressure will have a significant control on the extent of hydrocarbon (oil and gas) generation and source rock maturation in geological basins.

The retardation effect of pressure could be more significant in geological basins than shown in this study, because in geological basins, temperatures are much lower and the pressures can be much higher than the temperatures and pressure used in this study.

The un-expelled oil and preserved bitumen retained in the coal as bitumen which contributed to gas generation in the high pressure experiments and the observed pressure retardation of oil cracking to gas suggests that in geological basins oil and bitumen preserved in source rocks to the gas window will potentially generate more gas due to kerogen and mineral matter interaction than expelled oil.

The higher retardation of VR (source rock maturation) observed at 420 °C in comparison to 350 °C and 380 °C under high pressure suggest that in geological basins the retardation effect of pressure on source rock maturation will be more significant at higher maturities.

Acknowledgments

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Figure captions

Fig. 1. Schematic diagram of pyrolysis equipment.

Fig. 2. Total hydrocarbon (C_1-C_5) gas yields (mg/g TOC) for pyrolysis at 380 °C.

Fig. 3. Expelled oil and bitumen yields (mg/g TOC) for pyrolysis at 380 °C.

Fig. 4. Vitrinite reflectance for pyrolysis at 350, 380 and 420 °C.

Fig. 5. Total hydrocarbon (C_1-C_5) gas yields (mg/g TOC) for pyrolysis at 420 °C.

Fig. 6. Expelled Oil and bitumen yields (mg/g TOC) for pyrolysis at 420 °C.

Fig. 7. Bitumen and total hydrocarbon (C_1–C_4) gas yields (mg/g TOC) for pyrolysis at

350 °C from Uguna et al., (2012a).

Table 1. Initial Svalbard coal data.

TOC (%)	S_1 (mg/g)	S_2 (mg/g)	HI (mg/g)	T_{max} (°C)	Mean VR (%Ro)	Vitrinite (%)	Liptinite (%)	Inertinite (%)
78.5	12.0	273	347	440	0.68	92.6	4.0	3.4

Table 2. C_1–C_5 hydrocarbon gas yields (mg/g TOC of initial coal TOC) for pyrolysis at 380 °C and 420 °C for 24 h.

Sample	Temp (°C)	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4 alkenes	C_4 alkanes	C_5 alkenes	C_5 alkanes	Total C_1-C_5
230 bar	380	14.0	0.06	8.9	0.38	6.1	0.42	2.8	0.30	1.3	34
500 bar	380	13.2	0.02	7.9	0.10	5.8	0.13	2.8	0.10	1.3	31
700 bar	380	12.6	0.01	7.7	0.09	5.7	0.13	2.9	0.11	1.5	31
900 bar	380	11.2	0.01	6.9	0.07	5.1	0.09	2.6	0.07	1.2	27
300 bar	420	42.9	0.11	24.2	0.69	19.6	0.92	10.8	0.72	5.3	105
500 bar	420	45.1	0.05	25.2	0.50	21.5	0.87	13.4	0.84	7.1	115
700 bar	420	45.0	0.04	25.0	0.35	20.8	0.57	12.5	0.52	6.0	111
900 bar	420	40.9	0.03	22.1	0.30	18.2	0.52	10.8	0.48	5.4	99

Table 3. Expelled oil, bitumen and bitumen plus oil yields (mg/g TOC of initial coal TOC), residual coal TOC and VR values for pyrolysis at 380 °C and 420 °C.

Sample	Temp (°C)	Expelled oil	Bitumen	Bitumen plus oil	Residual coal TOC (%)	Mean VR (%Ro)	SD[a]
230 bar	380	174	102	276	77.6	1.35	0.12
500 bar	380	136	105	241	78.9	1.31	0.14
700 bar	380	136	117	253	78.8	1.29	0.16
900 bar	380	114	124	238	80.5	1.19	0.12
300 bar	420	29	81	110	79.5	1.76	0.23
500 bar	420	85	89	174	73.9	1.60	0.23
700 bar	420	117	51	168	78.7	1.61	0.33
900 bar	420	108	54	162	79.0	1.49	0.33

[a] Standard deviation of the 100 VR measurements of each sample.

Table 4. Carbon balances (products and residues in mg of carbon/g of initial TOC) for pyrolysis at 350 °C for 24 h from Uguna et al., (2012a).

Sample	C_1-C_4	Bitumen	Residual Rock	Total Recovered	(%) Recovery
175 bar	4.80	295	631	928	93
500 bar	3.73	292	660	956	96
900 bar	2.19	264	664	930	93

Table 5. Carbon balances (products and residues in mg of carbon/g of initial TOC) for pyrolysis at 380 °C and 420 °C.

Sample	Temp (°C)	C_1-C_5	Oil	Bitumen	Residual Rock	Total Recovered	(%) Recovery
230 bar	380	27	148	87	641	902	90
500 bar	380	25	115	89	640	869	87
700 bar	380	24	115	99	616	855	86
900 bar	380	21	97	105	621	844	84
300 bar	420	83	25	69	707	883	88
500 bar	420	91	72	76	602	841	84
700 bar	420	87	99	43	642	872	87
900 bar	420	78	92	46	633	848	85

Table 6. Bitumen, C_1–C_4 hydrocarbon gas yields (mg/g TOC of initial coal TOC) and VR values for pyrolysis at 350 °C for 24 h from Uguna et al., (2012a).

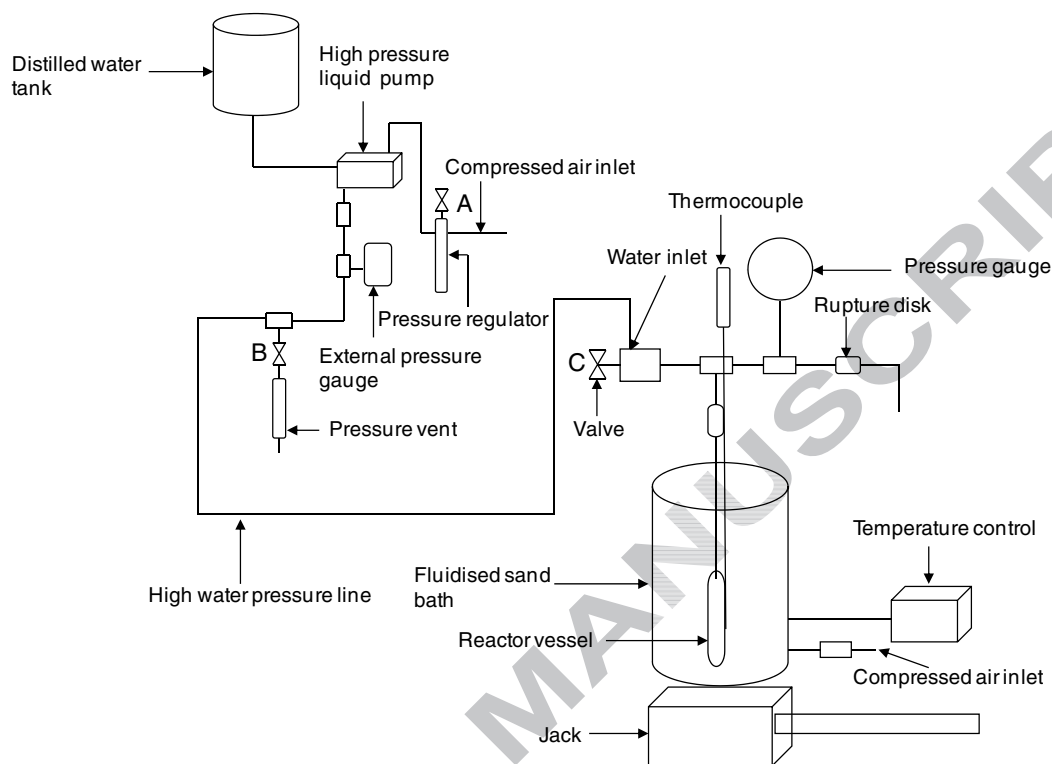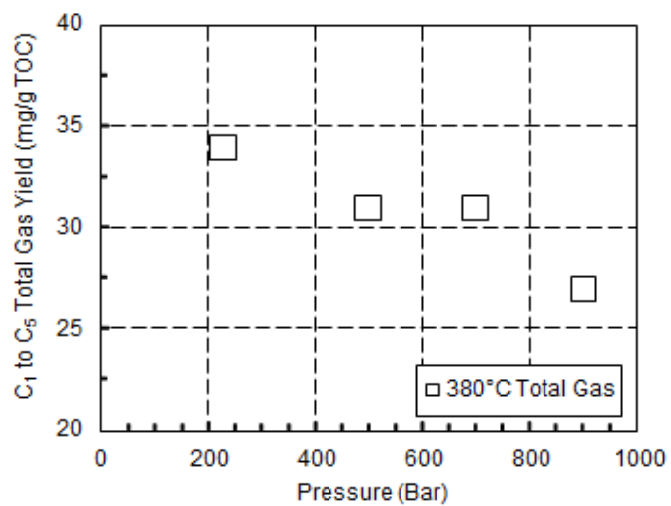| Sample	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_{10}	C_1-C_4	Bitumen	Mean VR (%Ro)
Initial coal	-	-	-	-	-	-	-	128	0.68
175 bar	2.65	0.01	1.75	0.09	1.21	0.41	6.12	348	1.07
500 bar	2.04	0.00	1.30	0.02	1.02	0.37	4.75	344	0.94
900 bar	1.19	0.00	0.76	0.01	0.60	0.23	2.79	311	0.92

Fig. 1

Fig. 2 (380 °C gas yield)

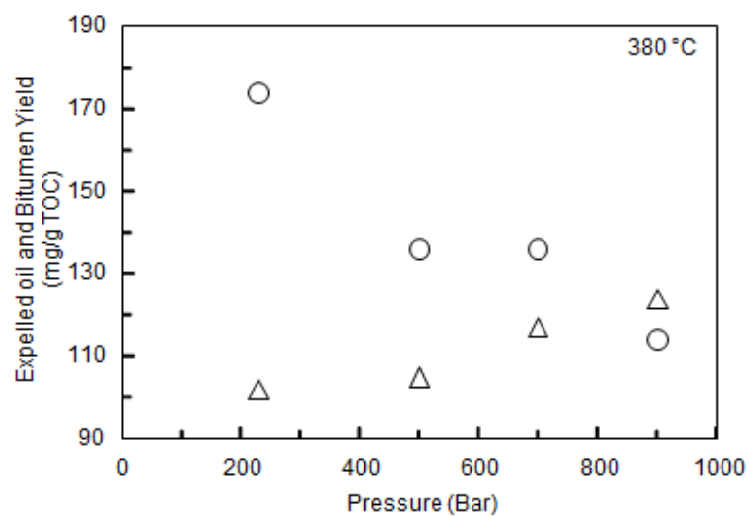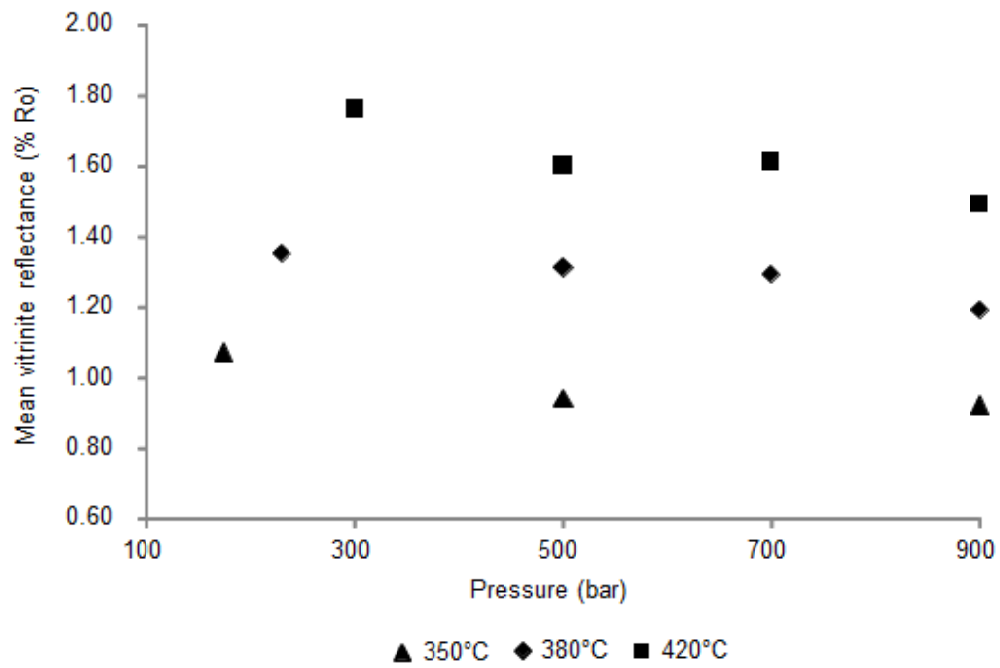Fig. 3 (380 °C expelled oil and bitumen yields)

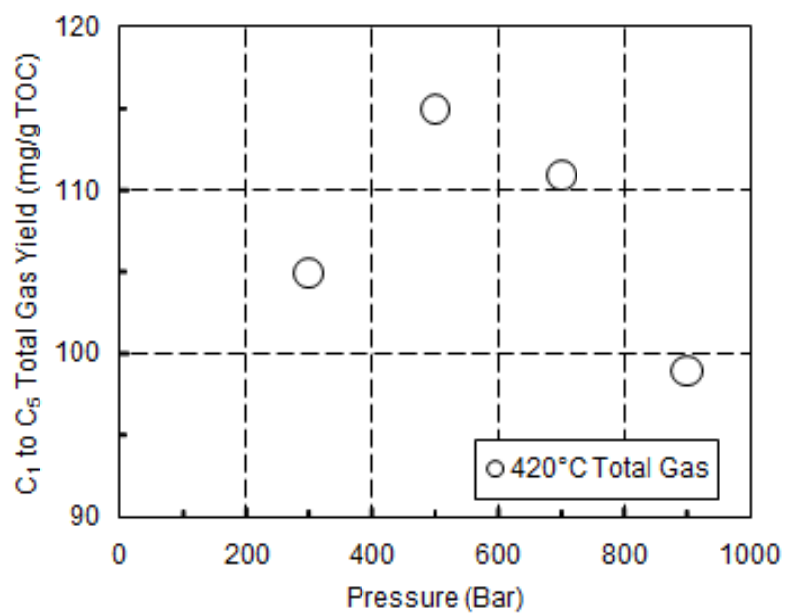Fig. 4 (350, 380 and 420 °C VR)

Fig. 5 (420 °C gas yield)
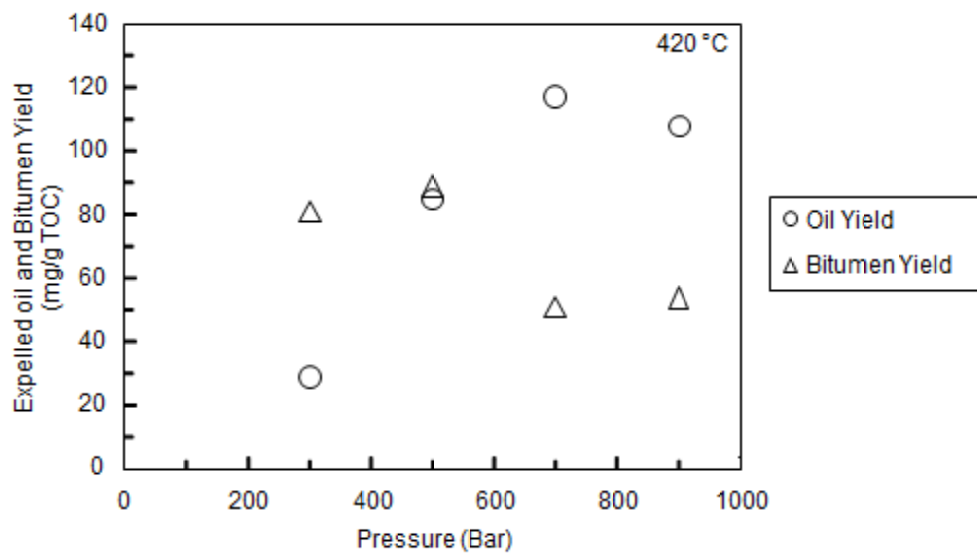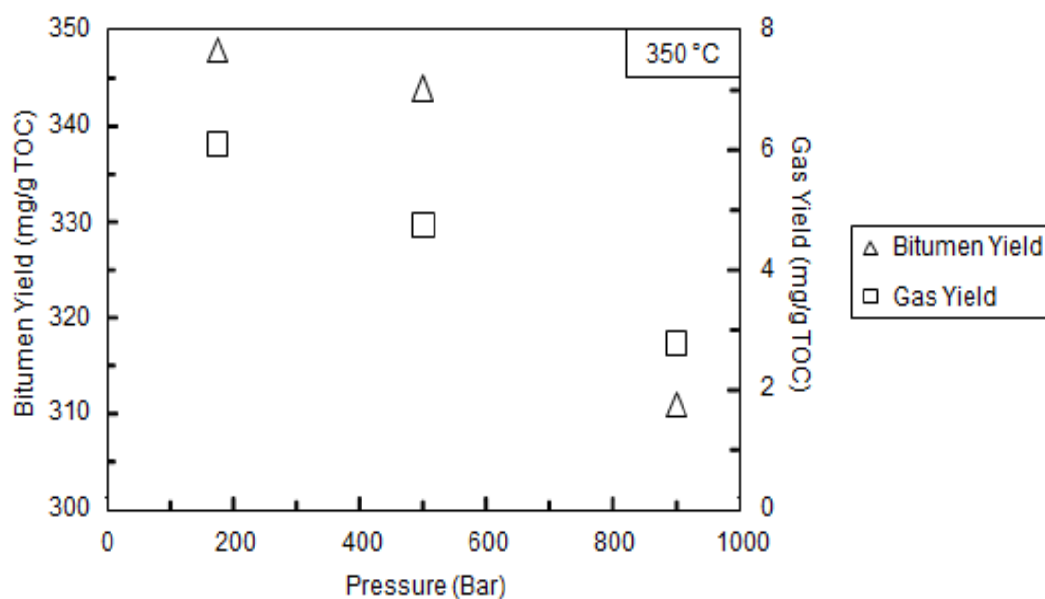
Fig. 6 (420 °C expelled oil and bitumen yields)

Fig. 7 (350 °C gas and bitumen yields)

Highlights

- We report the first study using water pressure of 900 bar and temperature of 420°C.
- The gas yield from coal was retarded at 900 bar compared to lower pressures.
- Oil yield and VR for coal were reduced at 500 & 900 bar compared to low pressures.
- Oil cracking to gas was retarded at high pressures compared to low pressures.