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.

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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; Uguna et al., 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 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 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 s. 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 into 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 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 min), 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 (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 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 alumina plot fused silica 30 m × 0.32 mm × 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 h, crushed and Soxhlet extracted using 150 ml dichloromethane:methanol mixture (93:7 v:v) for 48 h 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

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