

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

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15

16 **Abstract**

17

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

32

33 **Keywords:** Coal, hydrocarbon generation, maturation, vitrinite reflectance, hydrous
34 pyrolysis, high water pressure.

35

36 **1. Introduction**

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

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

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

67 To investigate if the retardation effect of water pressure observed at 350 °C on a
68 coal will be the same at 420 °C, experiments were conducted at 380 and 420 °C and
69 pressures up to 900 bar, which is higher than the 450 bar previously used by Uguna et
70 al. (2012b) for a Kimmeridge clay source rock. The sample studied is the same
71 Svalbard perhydrous coal used by Uguna et al. (2012a). The results obtained at 380 and
72 420 °C will be compared with the results obtained from the same coal at 350 °C (Uguna
73 et al., 2012a) to assess the effects of pressure and temperature on gas generation, oil
74 generation and cracking, and source rock maturation.

75 **2. Experimental**

76 The sample studied is a perhydrous high volatile bituminous coal from the
77 Arctic archipelago of Svalbard of Paleocene age (particle size 2-4 mm), with a total
78 organic carbon content (TOC) of 78.5%, Hydrogen index (HI) of 347 mg/g and VR of
79 0.68% Ro (Table 1). The pyrolysis equipment (Fig. 1) comprised a 25 ml Hastalloy
80 cylindrical pressure vessel rated to 1400 bar at 420 °C connected to a pressure gauge
81 and rupture disc rated to 950 bar. The experiments were conducted using 2.0 g of coal

82 at 380 and 420 °C (temperature accuracy ± 1 °C) for 24 h under low and high water
83 pressure conditions. The low pressure experiments at 380 °C (230 bar) and 420 °C
84 (300 bar) were performed by adding 12 ml and 10 ml water respectively to the vessel,
85 while the high water pressure experiments at both temperatures were conducted at 500,
86 700 and 900 bar. The experimental procedure used has been described in detail
87 previously (Uguna et al., 2012a) and summarised below.

88 The reactor vessel was heated by means of a fluidised sand bath, controlled by
89 an external temperature controller. Temperature was also monitored independently by
90 means of a K-Type thermocouple attached to the outside of the vessel and recorded by
91 computer every 10 seconds. The un-extracted coal sample to be pyrolysed was first
92 weighed and transferred to the vessel, after which the volume of water needed for the
93 experiment was added. For all experiments the reaction vessel was flushed with
94 nitrogen gas to replace air in the reactor head space, after which 2 bar pressure of
95 nitrogen was pumped into the pressure vessel to produce an inert atmosphere during the
96 pyrolysis runs. The sand bath (connected to a compressed air source) was pre-heated to
97 the required experimental temperature and left to equilibrate, after which the pressure
98 vessel was then lowered in to the sand bath by lifting up the sand bath using the jack
99 (Fig. 1), and the experiment left to run with a constant air flow through the sand bath.
100 The pressure observed for the low pressure experiments, 230 bar and 300 bar at 380 °C
101 and 420 °C respectively was generated by the vapour of the water 12 ml (230 bar at 380
102 °C) and 10 ml (300 bar at 420 °C) added to the vessel at the start of the experiment.

103 High liquid water pressure (500, 700 and 900 bar) experiments were performed
104 similarly to the low (230 and 300 bar) pressure hydrous runs, with the vessel initially

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

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

129 an alumina plot fused silica 30 m x 0.32 mm x 10 μm column, with helium as the carrier
130 gas. The oven temperature was programmed from 60 $^{\circ}\text{C}$ (13 min hold) to 180 $^{\circ}\text{C}$ (10
131 min hold) at 10 $^{\circ}\text{C min}^{-1}$. Individual gas yields were determined quantitatively in
132 relation to methane (injected separately) as an external gas standard. The total yield of
133 the hydrocarbon gases generated was calculated using the total volume of generated gas
134 collected in relation to the aliquot volume of gas introduced to the GC, using relative
135 response factors of individual $\text{C}_2\text{-C}_5$ gases to methane predetermined from a standard
136 mixture of $\text{C}_1\text{-C}_5$ gases. The oil floating on top of the water after the experiments
137 (collected with a spatula and recovered by washing the spatula in dichloromethane)
138 together with oil stuck to the side of the reactor wall (recovered by washing with cold
139 dichloromethane) were combined and referred to as expelled oil. The reacted coals
140 were vacuum dried at 45 $^{\circ}\text{C}$ for 3-4 hours, crushed and soxhlet extracted using 150 ml
141 dichloromethane/methanol mixture (93:7 volume: volume) for 48 hours to recover the
142 bitumen and any non-expelled oil retained in the coal, with both being referred to as
143 bitumen.

144 Under the supercritical water conditions (380 and 420 $^{\circ}\text{C}$) used in these
145 experiments water will have the properties of an organic solvent, as such it is difficult to
146 differentiate oil expulsion during the experiments and solvent extraction of the
147 pyrolysed coal after the experiment to obtain the bitumen and non-expelled oil retained
148 in the coals. In order to differentiate the amounts of oil expelled during the experiments
149 from the bitumen and non-expelled oil retained in the coals, the floating oil on top of the
150 water after the experiments together with those on the side of the reactor wall was called
151 expelled oil, and the bitumen and non-expelled oil solvent extracted from the coals
152 called bitumen.

153 3. Results

154 3.1. Pyrolysis at 380 °C

155 The gas yields (mg/g of starting coal) generated at 380 °C are presented in Table
156 2 and Fig. 2. The total (C₁-C₅) hydrocarbon gas generated at 380 °C was slightly higher
157 at 230 bar (34 mg/g) compared to pyrolysis at 500 and 700 bar (31 mg/g), but was
158 reduced by 20% to 27 mg/g at 900 bar when compared to the amount generated at 230
159 bar. The methane, ethane and propane gas yields (Table 2) showed reductions between
160 230 and 900 bar, while butane and pentane contents (Table 2) were the same at 230 bar
161 and 500 bar, both showing small increases at 700 bar, before showing a reduction at 900
162 bar. The unsaturated alkenes contents (Table 2) were found to be highest at 230 bar, but
163 decreased significantly as pressure increased to 500, 700 and 900 bar. The expelled oil
164 yields (mg/g of starting coal) generated are presented in Fig. 3, and also listed in Table
165 3 together with the bitumen and bitumen plus oil yields. The oil yield at 380 °C reached
166 a maximum at 230 bar (174 mg/g), and was reduced by 22% as the pressure was
167 increased to 500 and 700 bar (136 mg/g). At 900 bar the oil yield was reduced further
168 to 114 mg/g, which is 34% less than at 230 bar, indicating less generation and expulsion
169 at high pressure in the coal chips used here. The bitumen yield (Fig. 3) was similar at
170 230 and 500 bar, but increased going to 700 and 900 bar. The residual coal VR values
171 (mean of 100 measurements) obtained are listed in Table 3 and also presented in Fig. 4.
172 The VR values were similar at 230 bar (1.35% Ro) and 500 bar (1.31% Ro). A slight
173 reduction in VR was observed with increase in pressure to 700 bar (1.29% Ro)
174 compared to 230 bar, while at 900 bar the VR reduced further to 1.19% Ro, which is
175 0.16% Ro lower than the 230 bar VR value.

176 3.2. Pyrolysis at 420 °C

177 The gas yields obtained at 420 °C are listed in Table 2, and also presented in
178 Fig. 5. The total (C₁-C₅) gas yield increased slightly going from 300 bar (105 mg/g) to
179 a maximum at 500 bar (115 mg/g) and 700 bar (111 mg/g), before decreasing slightly at
180 900 bar (99 mg/g). The individual hydrocarbon gas yields (Table 2) show the same
181 trend as the total gas yields except for the unsaturated alkenes which decreased
182 significantly with an increase in pressure as observed at 380 °C. The expelled oil yield
183 in mg/g TOC of initial coal (Table 3 and Fig. 6) was lowest at 300 bar, and increased by
184 66% as the pressure increased to 500 bar pressure. The oil yield increased further with
185 an increase in pressure by 27% and 21% for the 700 bar and 900 bar runs respectively in
186 comparison to the 500 bar run. The bitumen yield (Table 3 and Fig. 6) was lower and
187 similar at 300 bar (81 mg/g) and 500 bar (89 mg/g), but reduced at 700 bar (51 mg/g)
188 and 900 bar (54 mg/g). The residual coal VR values (mean of 100 measurement) (Table
189 3 and Fig. 4) was 1.76% Ro at 300 bar, and decreased by 0.15% Ro at 500 bar (1.60%
190 Ro) and 700 bar (1.61% Ro). An increase in the pressure to 900 bar caused the VR to
191 further decrease to 1.49% Ro, with the 900 bar value being 0.27% Ro lower than the
192 300 bar value, and 0.11 and 0.12% Ro lower than the 500 and 700 bar values
193 respectively.

194 3.3. Experimental carbon mass balance

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

199 bitumen yields were used to determine these balances. The Svalbard coal bitumen at
200 350 °C contained 85% carbon (Uguna et al., 2012a), and this value has been used to
201 calculate the carbon contents of the bitumen and oil generated at 380 and 420 °C. The
202 balances exclude lower molecular weight hydrocarbons e.g. gasoline ($C_6 - C_{12}$)
203 hydrocarbons, together with CO and CO₂ which were not measured. The gasoline
204 hydrocarbons could not be recovered due to evaporative losses during products recovery
205 and solvent extraction of the pyrolysed coals to recover the bitumen and non-expelled
206 oil, while CO and CO₂ generation was not investigated in the study.

207 At 350 °C (bitumen generation stage) the carbon recoveries was 93-96% of the
208 initial starting coal. At 380 and 420 °C the carbon recoveries were 84-90% and 84-88%
209 respectively. The drop in recovery at 380 and 420 °C compared to 350 °C is due to an
210 increased generation of lighter hydrocarbons that could not be recovered as the bitumen
211 is cracked to oil at higher temperature. The carbon recoveries would have been greater
212 if CO and CO₂ could have been included. The high carbon recoveries obtained
213 considering the fact that light hydrocarbons, CO and CO₂ were not included indicate
214 that product recovery in our experiments is good. The similar carbon recovery obtained
215 under low and high pressure conditions at 350, 380 and 420 °C shows that the changes
216 in product yields observed with pressure increase is due to pressure effect and not loss
217 of product either during the experiments or product recovery after the experiments.

218 **4. Discussion**

219 The bitumen, gas and VR results obtained previously for the same Svalbard coal
220 at 350 °C for 24 h and already published (Uguna et al., 2012a) will be discussed
221 together with those obtained at 380 and 420 °C. The gas and bitumen yields (mg/g of

222 starting coal) obtained at 350 °C for 24 h are presented in Table 6 and Fig. 7. At 350 °C
223 only bitumen was generated, as oil generation and expulsion had not yet commenced.
224 However given the starting maturity of the coal (0.68% Ro), extending the duration of
225 heating in excess of 24 h, might well have resulted in the onset of oil generation from
226 this coal. The bitumen yield was higher at 175 bar, and reduced by only about 10% at
227 900 bar in relation to 175 bar. The small reduction in bitumen yield observed with
228 increase in pressure to 900 bar indicates that pressure has a slight retardation effect on
229 bitumen generation. At 380 °C the coal had started to generate and expel oil. The
230 higher oil yield obtained at 230 bar shows that more oil was generated and expelled
231 under low pressure conditions, and the reduction in oil yield observed going from 230
232 bar to 500, 700 and 900 bar is due to pressure retarding the generation and expulsion of
233 oil. This is due to both the rate at which bitumen is converting to oil, and the rate at
234 which oil is expelled from the coal being slower under high water pressure conditions,
235 which resulted in more bitumen remaining in the coal pyrolysed at 900 bar (124 mg/g
236 TOC) compared to 230 bar (102 mg/g TOC). An increase in the temperature to 420 °C
237 resulted in a decrease in the oil and bitumen yields at all pressures compared to 380 °C,
238 and is due to increased cracking. The increase in oil yield observed going from 300 bar
239 to high pressures (500-900 bar) is due to maximum oil generation having been shifted to
240 high pressures at 420 °C.

241 At 350 °C the total (C₁-C₄) gas yield (Fig. 7 and Table 6) was higher at 175 bar
242 and decreased by 22% and 55% going from 175 bar to 500 and 900 bar respectively.
243 The huge reduction in gas yields observed with increase in pressure indicates that
244 pressure significantly retarded gas generation, and the 10% reduction in bitumen yield
245 in comparison to the 55% reduction in gas yield observed at 900 bar, shows that the

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

255 At 380 °C the total (C₁-C₅) gas yield was reduced at 900 bar by 20% in
256 comparison to 230 bar, while at 420 °C the gas yield only reduced slightly by 14% at
257 900 bar compared to the maximum yield generated at 500 bar. At both 380 and 420 °C
258 the unsaturated alkene gases were reduced under high water pressure to a much greater
259 extent than the saturated alkane gases. This is due to the retardation of alkene gas
260 generation by pressure or hydrogenation of alkenes to alkanes, or the addition of free
261 radicals to alkenes to form branched short chain alkanes being favoured under high
262 water pressure. The reduction in the yields of alkene gases with pressure increase
263 observed in this study might explain why alkenes are not formed under pressure
264 conditions in geological basins. Overall, the results indicate that at 380 and 420 °C, gas
265 yields are not markedly affected by pressure as observed at 350 °C, and this is
266 considered to be a combination of two factors. Firstly, the increase in temperature
267 results in the physical retardation induced by 900 bar pressure, becoming less
268 significant, due to the increased chemical reactions between the supercritical water and
269 kerogen, such that gas generation was not significantly retarded as observed at 350 °C.

270 The additional 30 °C provides the thermal energy to enable the system to have sufficient
271 energy available to undertake both the bond breakage (to generate the hydrocarbons)
272 and pV work to create the space in the pressurised water to accommodate the additional
273 volume required by the generated hydrocarbons. Secondly, due to high water pressure
274 delaying the conversion of bitumen to oil and the expulsion of oil from the coal, some
275 cracking of bitumen and/or oil retained in the coal to gas and gasoline hydrocarbons
276 occurred at high pressures. The cracking of bitumen and/or oil to gas and gasoline
277 hydrocarbons, explains why the increase in extracted bitumen yield with an increase in
278 pressure going from 230 bar to 900 bar at 380 °C is relatively small when the reduction
279 in oil yield is considered. This means that the retained bitumen is decreasing due to
280 cracking to gas and gasoline range hydrocarbons, as oil generation is retarded by
281 pressure. At 380 °C the 500, 700 and 900 bar gas yields did not show any significant
282 increase due to cracking of bitumen, suggesting that gasoline hydrocarbons, which were
283 prevented from cracking further to gas under high pressures were the main products
284 from the cracking of bitumen and/or oil retained in the coal at high pressures. The
285 formation of more gasoline hydrocarbons from cracking of retained bitumen and/or oil
286 in the coal at high pressures is evident from carbon mass balance obtained at 380 °C
287 (Table 5) which showed a steady decrease in total recovered carbon from 90% (at 230
288 bar) to 84% (at 900 bar). The decrease in total recovered carbon being due mainly to
289 the loss of unrecovered gasoline hydrocarbons and CO₂. The cracking of the retained
290 bitumen and/or oil at high pressure is also supported by the small gradual increase in
291 TOC at 380 °C going from 230 bar (77.6%) to 500 bar (78.9%), 700 bar (78.8%), and
292 900 bar (80.5%), which is due to pyrobitumen formation. The lower residual TOC
293 obtained at 230 bar indicate that less pyrobitumen was formed, suggesting that oil was

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

298 At 420 °C the oil yield increased with increasing pressure going from 300 bar
299 (29 mg/g) to 500 (85 mg/g), 700 (117 mg/g) and 900 bar (108 mg/g), while the bitumen
300 yield decreased going from 300 bar (81 mg/g) and 500 bar (89 mg/g) to 700 bar (51
301 mg/g) and 900 bar (54 mg/g). The trend in oil and bitumen yield is opposite to that
302 observed at 380 °C, and might be due to enhanced generation and expulsion of oil with
303 increase in pressure resulting in less extractable bitumen remaining in the coal at 700
304 and 900 bar. Alternatively it might be due to direct cracking of bitumen and/or oil
305 retained in the coal, while pressure is also preserving the expelled oil from further
306 cracking to gas at 700 and 900 bar. We believe that the alternative direct cracking is the
307 more likely reason why the oil yields were higher, and the bitumen yields lower at 700
308 and 900 bar. This can be explained using the residual coal TOC (Table 3) which was
309 higher at 300 bar (79.5%), reduced by 5.6% to a minimum at 500 bar (73.9%) before
310 increasing again by 4.8 and 5.1 to 700 bar (78.7%) and 900 bar (79.0%) respectively.
311 Under 300 bar conditions 10 ml water was used, and the experiment was under
312 superheated steam conditions which might not have favoured oil generation and
313 expulsion, resulting in the bitumen and/or oil retained in the coal being cracked mainly
314 to gas, with the formation of pyrobitumen or coke as shown by the highest residual
315 TOC obtained. At 500 bar pressure the lower residual TOC is due to less pyrobitumen
316 or coke being formed, which is as a result of oil generation and expulsion being
317 favoured due to the moderate pressure, supercritical water conditions as a result of the

318 additional water in the vessel. The lower residual TOC observed at 420 °C under 500
319 bar conditions is entirely consistent with the lowest residual TOC observed for the 230
320 bar experiment, under which pressure the maximum amount of oil was generated at 380
321 °C. This suggests that maximum oil generation and expulsion occurred under 500 bar
322 conditions at 420 °C, indicating that the lower expelled oil yield obtained at 500 bar in
323 relation to 700 and 900 bar values is due to cracking of oil to gas and gasolines.

324 The increase in the residual TOC with increasing pressure to 700 and 900 bar at
325 420 °C is ascribed to pyrobitumen or coke formation resulting from the direct cracking
326 of trapped bitumen and/or oil to gas, entirely consistent with lower bitumen yields at
327 700 and 900 bar. The fact that pressure retarded oil generation and expulsion at 420 °C
328 under 700 and 900 bar pressure conditions suggests that the higher expelled oil yield
329 obtained in comparison to the 500 bar value, is due to pressure retarding oil cracking to
330 gas, consistent with the slight reduction in gas yield observed at 900 bar. Although
331 some cracking of retained bitumen and/or oil occurred at 420 °C under 500 bar
332 conditions, the fact that oil cracking to gas is evident suggests that oil cracking was a
333 significant contributor to gas generation at 500 bar. On the other hand the fact that oil
334 cracking to gas is retarded at 700 and 900 bar at 420 °C is further evidence that gas
335 generation at 700 and 900 bar was mainly from the cracking of bitumen, although direct
336 generation of gas from kerogen due to high temperature is a possible alternative,
337 without requiring the bitumen intermediate to be formed. The contribution of bitumen
338 and/or oil retained in the coals to gas generation, and the retardation of the expelled oil
339 from cracking to gas at 700 and 900 bar observed in this study, suggest that in
340 geological basins bitumen or oil trapped in source rocks to high maturities can be
341 converted to gas at a later period. This potentially might occur as a result of a

342 combination of increased heat flow required during uplift (all gas shales currently in
343 production occur in inverted basins), with the reduction in pressure.

344 The residual coal VR values (mean of 100 measurements) obtained previously at
345 350 °C for 24 h and already published (Uguna et al., 2012a) are presented in Table 6
346 and Fig. 4. The VR follow the same trend as those obtained in this study at 380 and 420
347 °C, reducing by 0.15% Ro from maximum at 175 bar (1.07% Ro) hydrous conditions to
348 a minimum at 900 bar (0.92% Ro). The reduction in VR observed at 350, 380 and 420
349 °C with an increase in pressure is due to high water pressure retarding source rock
350 maturation, which is as a result of the rate of aromatisation reactions being reduced
351 under high water pressure conditions (Uguna et al., 2012a). Comparison of the VR
352 results (Fig. 4, Tables 3 and 6) obtained at all three temperatures shows that VR was
353 reduced by the same value at 350 °C (0.15% Ro) and 380 °C (0.16% Ro) going from
354 low pressure hydrous to 900 bar water pressure. However, at 420 °C the VR reduced by
355 0.27% Ro at 900 bar compared to the 300 bar VR. This indicates that the retardation
356 effect of pressure on source rock maturation becomes more significant with increase in
357 source rock maturity, and is due to the coal becoming less reactive at higher maturities
358 due to loss of volatiles.

359 The increase in gas yield at 420 °C going from 300 to 500 bar before reducing
360 going to 900 bar, and the retardation of VR between 500 and 900 bar at 350 to 420 °C
361 observed in this study has been observed previously for oil cracking conducted at 350
362 and 400 °C (Hill et al., 1996) and coal pyrolysed at 300 and 340 °C (Hill et al., 1994)
363 using the anhydrous, confined gold bag pyrolysis method. Both studies showed that
364 hydrocarbon gas yield and VR increased to a maximum at 690 bar before decreasing at

365 2000 bar. The high pressure (2000 bar) reached by Hill et al. (1996, 1994) using gold
366 bags before pressure retardation occurred compares with this study, in which pressure
367 retardation was observed between 500 and 900 bar. This difference has been attributed
368 to the different pyrolysis methods used (Landais et al., 1994; Michels et al., 1995). As
369 mentioned earlier in the introduction, pressure retardation effects have been shown to be
370 generally more significant for high water pressure unconfined pyrolysis than high
371 pressure confined gold bag pyrolysis. The high retardation effect of pressure observed
372 under high water pressure pyrolysis conditions has been attributed to the pressurising
373 medium (water) been in contact with the sample been pyrolysed (Landais et al., 1994;
374 Michels et al., 1995). On the other hand under confined gold bag pyrolysis the sample
375 is not in contact with the pressurising medium, and the pressure applied to the outside of
376 the gold bag may be reduced by the pressure generated from products generation, hence
377 the pressure retardation effect is lesser (Uguna et al., 2012a & b).

378 In the transition state theory, reaction rates are controlled by the activation
379 volume ($\Delta^\ddagger V^0$) which is the volume difference between the activated complex and
380 reactant. If the reaction is bimolecular (where the volume of the transition state is
381 smaller than the sum of the volumes of the reactants) $\Delta^\ddagger V^0$ is negative and the reaction
382 rate constantly increases with increasing pressure, thus reaction is enhanced.
383 Conversely, if a reaction is unimolecular (where the volume of the transition state is
384 larger than the volume of the initial species) high pressure will reduce the reaction rates,
385 thus retarding the reaction (Al Darouich et al., 2006). Hill et al. (1996) using gold bags
386 to study oil cracking calculated ($\Delta^\ddagger V^0$) values of +47 cm³/mol in the 90-483 bar range
387 at 400 °C, while between 345 and 690 bar at 350 and 380 °C, and 483 and 690 bar at
388 400 °C, ($\Delta^\ddagger V^0$) is 14 cm³/mol. Al Darouich et al. (2006) also using gold bags to study

389 oil cracking, calculated ($\Delta^\ddagger V^\circ$) values in the range 40-140 cm³/mol. Given the
390 relatively large size of the molecules in kerogen and petroleum, it would be realistic to
391 expect quite large changes upon activation, depending upon the exact nature of the
392 activated complex (Uguna et al., 2012a). The situation is complicated by the fact that
393 $\Delta^\ddagger V^\circ$ (like all volume parameters) must be pressure dependent, but no theory is
394 currently available to predict the variation in activation volume with pressure.
395 Consequently in the case of such complex reactions such as the conversion of kerogen
396 into bitumen, oil, gas, pyrobitumen, and modified kerogens, an alternative approach is
397 required, if the relationship between $\Delta^\ddagger V^\circ$ cannot be derived.

398

399 **5. Conclusions and implications**

400

401 **5.1. Conclusions**

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

406 2. At 380 and 420 °C gas generation was retarded by pressure to a lesser extent than at
407 350 °C, due to a combination of the higher temperature (which reduced the effect of
408 pressure), and the cracking of bitumen retained in the coal to gas.

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

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

414 **5.2. Implications**

415 The implications from this study are that:

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

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

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

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

430 5. The higher retardation of VR (source rock maturation) observed at 420 °C in
431 comparison to 350 and 380 °C under high pressure suggest that in geological basins the

432 retardation effect of pressure on source rock maturation will be more significant at
433 higher maturities.

434

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437 review and suggestions which improved this paper. We also thank David Clift here at
438 the University of Nottingham for doing the vitrinite reflectance measurement.

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504 partially matured source rock and bitumen in isolation compared to their whole
505 source rock. Journal of Analytical and Applied Pyrolysis 103, 268-277.

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508 **Figure captions**

509 Fig. 1. Schematic diagram of pyrolysis equipment.

510 Fig. 2. Total hydrocarbon (C₁-C₅) gas yields (mg/g TOC) for pyrolysis at 380 °C.

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

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

513 Fig. 5. Total hydrocarbon (C₁-C₅) gas yields (mg/g TOC) for pyrolysis at 420 °C.

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

515 Fig. 7. Bitumen and total hydrocarbon (C₁-C₄) gas yields (mg/g TOC) for pyrolysis at
516 350 °C from Uguna et al., (2012a).

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520 Table 1. Initial Svalbard coal data.

521

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

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523

524 Table 2. C₁–C₅ hydrocarbon gas yields (mg/g TOC of initial coal TOC) for pyrolysis at
525 380 and 420 °C for 24 h.

526

Sample	Temp (°C)	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H 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

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

531

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

532 ^a Standard deviation of the 100 VR measurements of each sample.

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534

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

537

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

538

539

540 Table 5. Carbon balances (products and residues in mg of carbon/g of initial TOC) for
 541 pyrolysis at 380 and 420 °C.
 542

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

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545 Table 6. Bitumen, C₁-C₄ hydrocarbon gas yields (mg/g TOC of initial coal TOC) and
 546 VR values for pyrolysis at 350 °C for 24 h from Uguna et al., (2012a).
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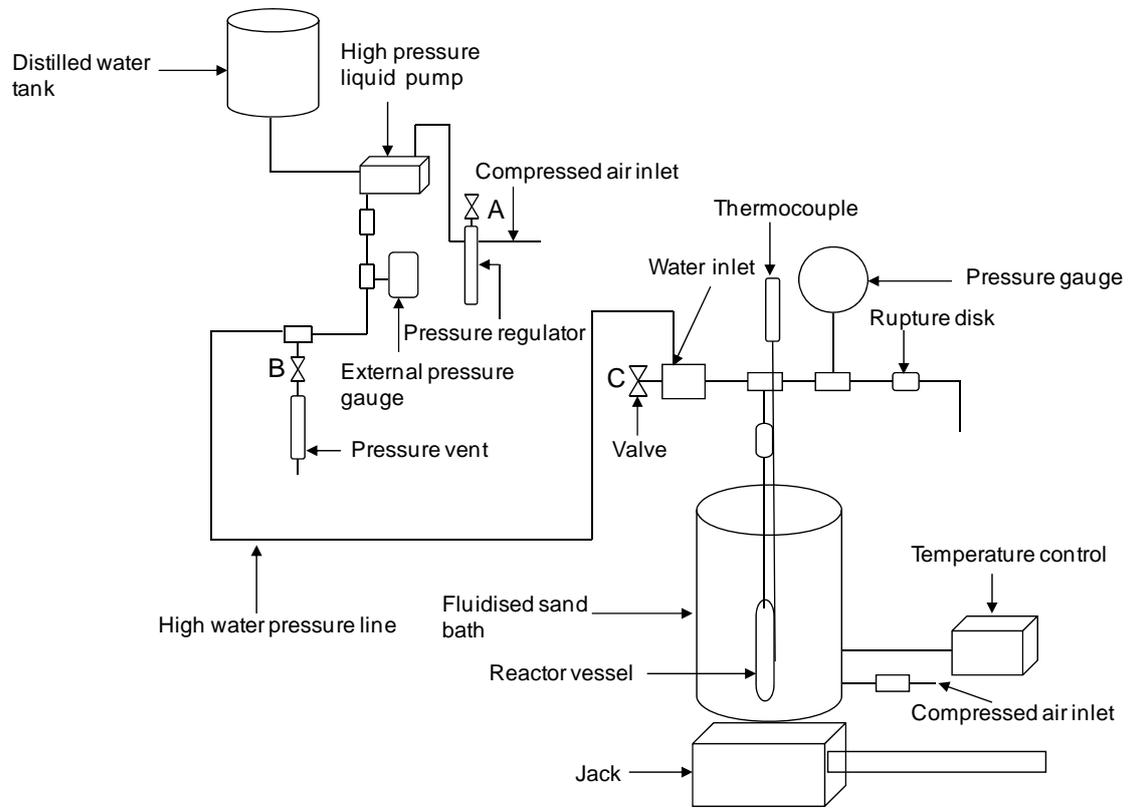
Sample	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₁ -C ₄	Bitumen	Mean VR (% Ro)
Initial coal	-	-	-	-	-	-	-	128	0.68
175 bar	2.65	0.01	1.75	0.09	1.21	0.41	6.12	348	1.07
500 bar	2.04	0.00	1.30	0.02	1.02	0.37	4.75	344	0.94
900 bar	1.19	0.00	0.76	0.01	0.60	0.23	2.79	311	0.92

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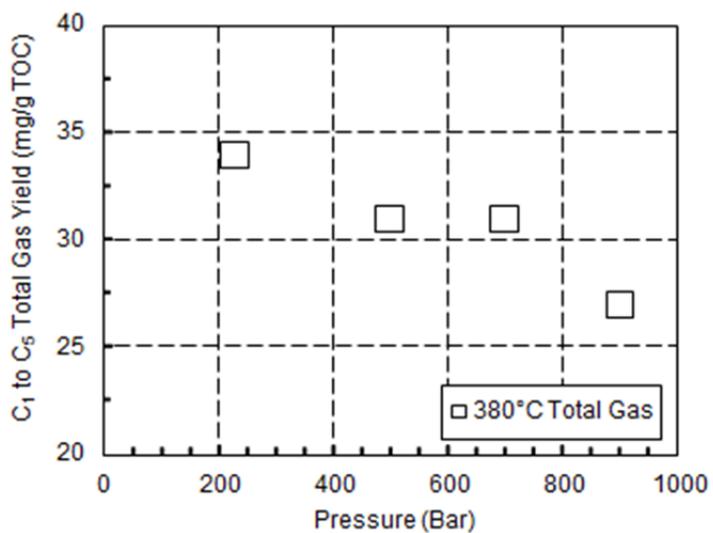
551 Fig. 1
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554 Fig. 2 (380 °C gas yield)

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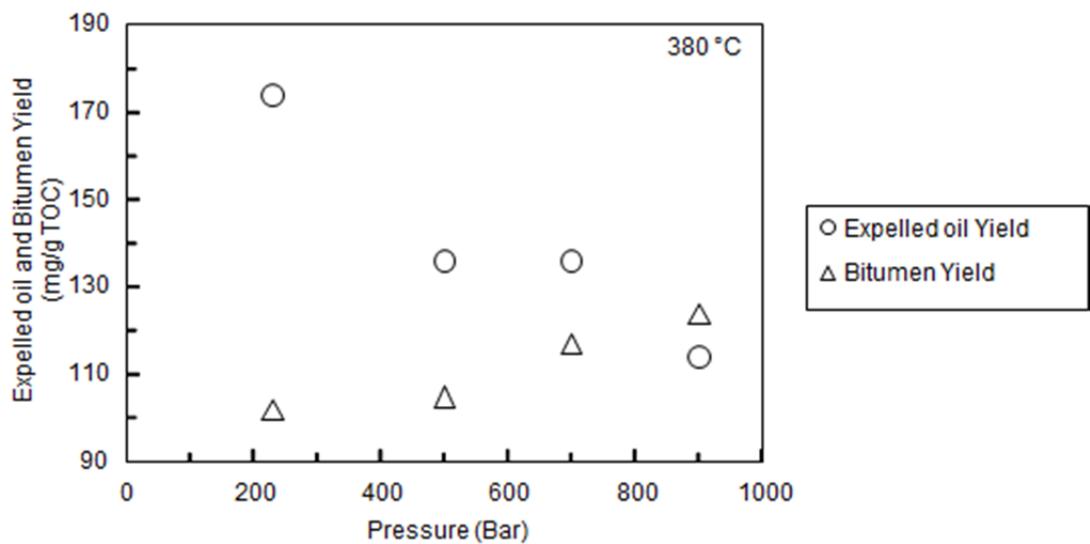
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571 Fig. 3 (380 °C expelled oil and bitumen yields)

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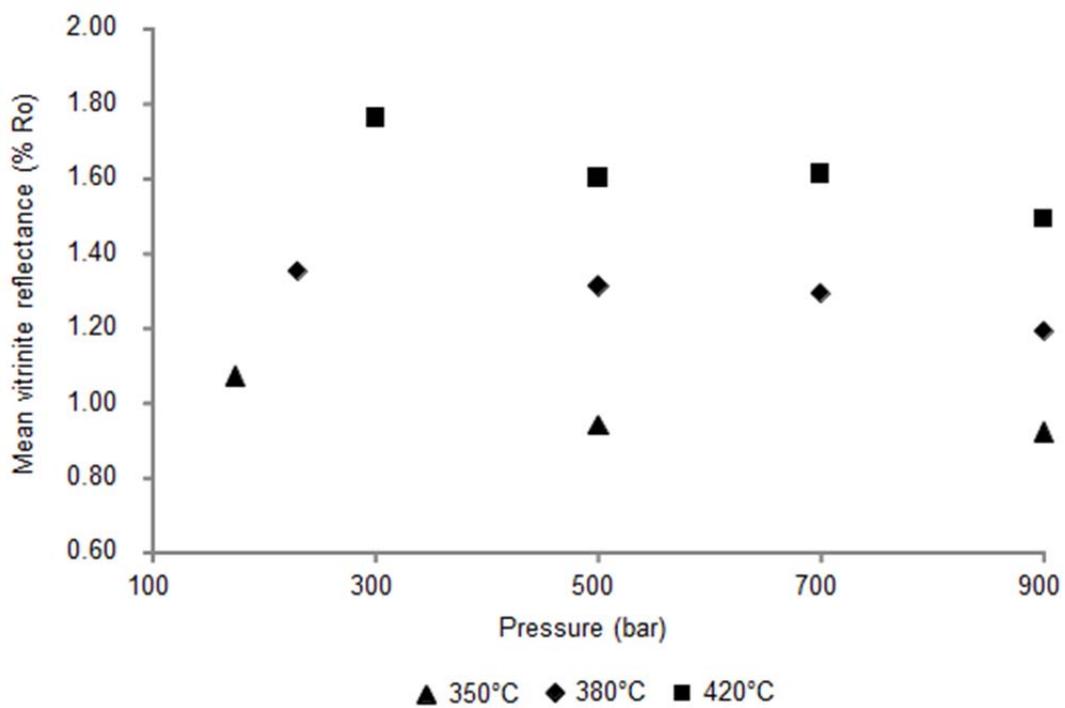
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588 Fig. 4 (350, 380 and 420 °C VR)

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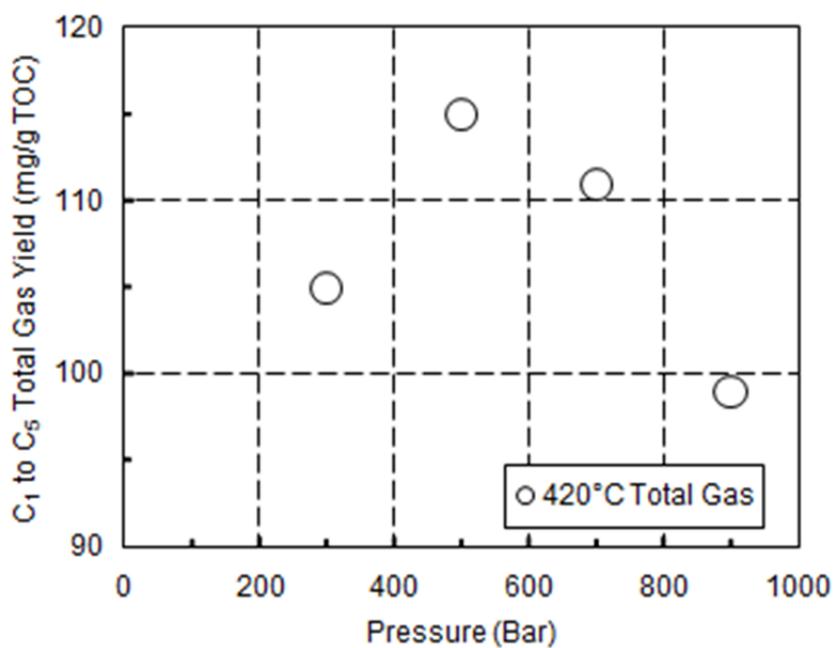
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603 Fig. 5 (420 °C gas yield)

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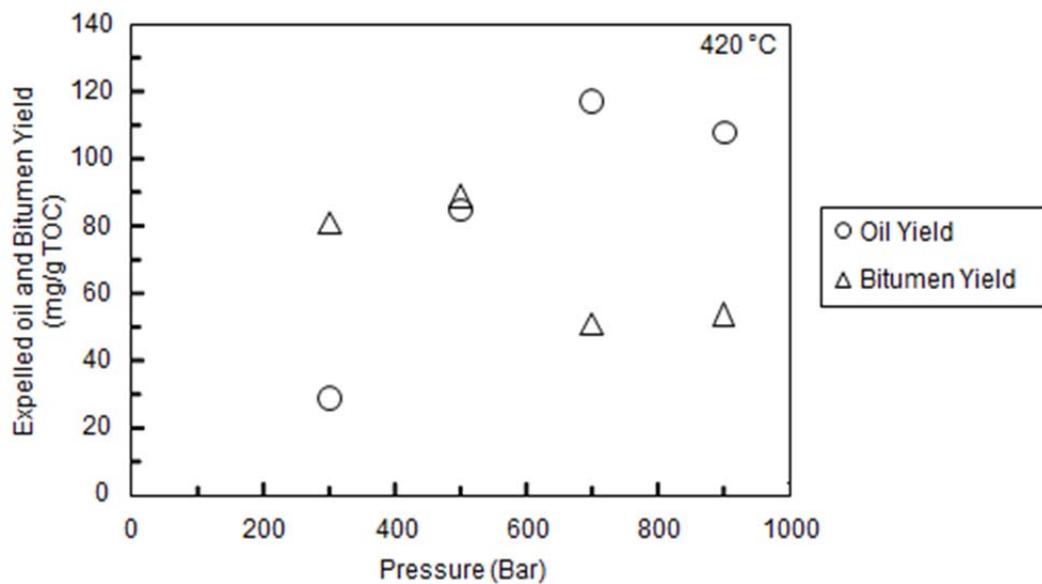
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619 Fig. 6 (420 °C expelled oil and bitumen yields)

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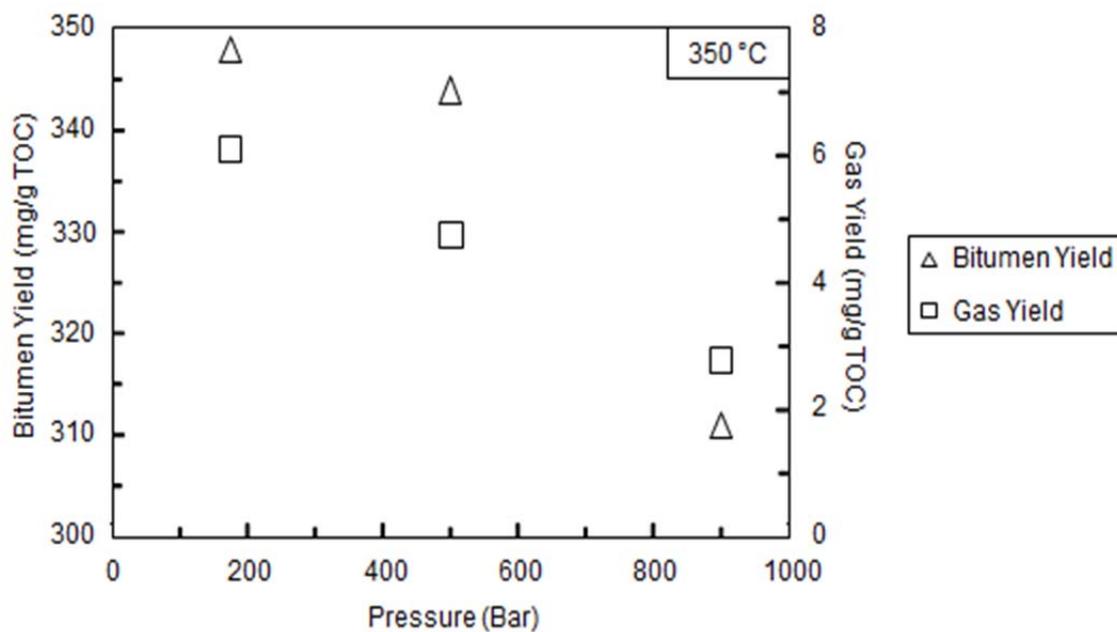
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635 Fig. 7 (350 °C gas and bitumen yields)

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