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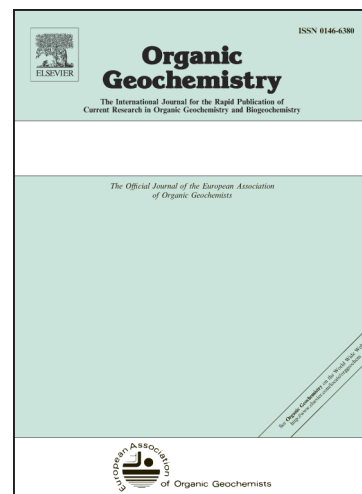Clement N. Uguna, Andrew D. Carr, Colin E. Snape, Will Meredith

Retardation of oil cracking to gas and pressure induced combination reactions to account for viscous oil in deep petroleum basins: Evidence from oil and *n*-hexadecane pyrolysis at water pressures up to 900 bar

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Abstract

This study reports a laboratory pyrolysis experimental study on oil and *n*-hexadecane to rationalise the thermal stability of oil in deep petroleum reservoirs. Using a 25 ml Hastalloy pressure vessel, a 35° API North Sea oil (Oseberg) and *n*-hexadecane (*n*-C_{16}), were pyrolysed separately under non-hydrous (20 bar), low pressure hydrous (175 bar) and high liquid water pressure (500 and 900 bar) at 350 °C for 24 h. This study shows that the initial cracking of oil and *n*-hexadecane to hydrocarbon gases was retarded in the presence of water (175 bar hydrous conditions) compared to low pressures in the absence of water (non-hydrous conditions). At 900 bar water pressure, the retardation of oil and *n*-hexadecane cracking was more significant compared to 175 bar hydrous and 500 bar water pressure conditions. Combination reactions have been observed for the first time in pressurised water experiments during the initial stages of cracking, resulting in the increased abundance of heavier *n*-alkane hydrocarbons ($>C_{20}$), the amount of unresolved complex material (UCM), as well as the asphaltene content of the oil. These reactions, favoured by increasing water pressure provide a new mechanism for rationalising the thermal stability of oils, and for producing heavy oils at temperatures above which biodegradation can occur. Indeed, we demonstrate that bitumen from the high pressure Gulf of Mexico basin has been formed from lighter oil components and it possesses similar characteristics to the laboratory oils generated.

Keywords: Oil cracking, *n*-hexadecane cracking, oil viscosity, high water pressure, pressure retardation, combination reactions.

1. Introduction

The thermal cracking of petroleum and its conversion into gas and pyrobitumen in geological basins appears to occur between 150 and 200 °C, and has been the subject of extensive investigations using field data (e.g. Price et al., 1979; Price et al., 1981; Price, 1982; Mango, 1991; Hayes, 1991), laboratory pyrolysis investigation of oils (e.g. Ungerer and Pelet, 1987; Ungerer et al., 1988; Behar et al., 1992; Behar et al., 1997a; 1997b; Schenk et al., 1997; Dieckmann et al., 1998; Lewan and Ruble, 2002; Hill et al., 2003; Lehne and Dieckmann, 2007a; 2007b; Behar et al., 2008), or theoretical calculations (e.g. Dominé et al., 1998). Undegraded crude oils generally show an increase in both API gravity and gas to oil ratio (GOR) with increasing depth of burial (Tissot and Welte, 1984), which can result from the conversion of oil into lighter hydrogen-rich products (gas and condensate) and heavy carbon rich solid residues (coke or pyrobitumen). Pyrobitumen forms either by aromatic condensation reactions (Ungerer et al., 1988; Behar et al., 1992), or directly from nitrogen sulphur and oxygen (NSO) compounds (Hill et al., 2003). Oil cracking to gas was described as occurring via hydrogen transfer reactions (Bailey et al., 1974; Connan et al., 1975), although it also appears that the mechanism involves free radical reactions (Rice and-Herzfeld 1934), with initiation, hydrogen transfer, decomposition of carbon-carbon bonds by ß-scission, radical isomerization, addition and termination processes in the oil (e.g. Bounaceur et al. 2002a; Burkle-Vitzthum et al., 2004).

In addition to actual oils, numerous studies have also been conducted using individual aliphatic hydrocarbons between *n*-hexane and *n*-hexadecane to investigate the thermal cracking of oil (e.g. Fabuss et al., 1964; Ford, 1986; Dominé, 1989; 1991;

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Khorasheh and Gray, 1993a; 1993b; Song et al., 1994; Jackson et al., 1995; Behar and Vandenbroucke, 1996). The thermal cracking of aliphatic hydrocarbons involves their conversion into lower molecular weight alkanes and alkenes, and with minor yields of aromatic compounds (Rice, 1931; 1933; Voge and Good, 1949; Ford, 1986; Zhou et al., 1987; Bounaceur et al., 2002a) together with branched alkanes of higher molecular weight than the starting alkane. Experimental observations show that the concentration of alkenes decrease with increasing conversion, while the alkanes increase in concentration, especially those with a higher number of carbon atoms than the reactant (Khorasheh and Gray, 1993a; Ford, 1986; Dominé, 1989; Dominé et al., 1990).

The cracking of aromatic compounds has been investigated (Savage and Klein, 1987; Freund and Olsmtead, 1989; Poutsma, 1990; Smith and Savage, 1991; 1994; Burnham et al., 1998; Yu and Eser, 1998; Behar et al., 1999; 2002; Bounaceur et al., 2000; Burklé-Vitzthum et al., 2003; 2004; 2005; Dartiguelongue et al., 2006; Leininger et al., 2006). The thermal stability of alkylaromatics depends on the number of aromatic rings and length of the side chain (Smith and Savage, 1991; Behar et al., 2002). The main degradation products appear to be a combination of heavy aromatics (e.g. phananthrenes), lighter aromatics (e.g. naphthalene, toluene), alkanes and gases (Behar et al., 2002). The effect of co-reactions between aromatics and hydrocarbon mixtures in laboratory pyrolysis was studied by Burkle-Vitzthum et al. (2004; 2005) and by Lannuzel et al. (2010). Benzene does not have any kinetic effect on the thermal cracking of alkanes (Burkle-Vitzthum et al., 2004), although addition reactions with methyl radicals leads to the formation of toluene, and depending on the temperature and pressure conditions, toluene is potentially a strong inhibitor of n-alkanes cracking (Burkle-Vitzthum et al., 2004; 2005; Lannuzel et al., 2010). The inhibition of n-alkane

cracking by monoaromatics, e.g. alkylbenzenes, tertralin, hydronaphthalenics, has also been widely observed (e.g. Behar et al., 2002; Bounaceur et al., 2002b; Burkle-Vitzthum et al., 2005; Burnham et al., 1997; McKinney et al., 1998). The composition of oils in subsurface reservoirs in geological basins ranges between heavy oils with relatively low alkane-aromatic ratios, to light, condensates with high alkane-aromatic ratios, means that there are many potential interactions between the different components depending on the temperature and pressure histories of the reservoir.

While much of the work on the stability of hydrocarbons has concentrated on the stability with temperature, the other physical factor that needs to be considered is pressure. Given that the oil to gas process results in a volume increase (Barker, 1990), then such changes should be controlled by the system temperature and pressure. The influence of pressure has not received as much attention as that devoted to temperature. It is important to recognise that the experimental design used to simulate the effects of pressure need to be assessed. In most of the experiments undertaken up to this point, the experiments investigating the effects of pressure have used gold-bags (confined pyrolysis), in which the sample (oil or model compound) is sealed within a gold-bag (having removed vapour from inside the gold-bag prior to sealing), and the gold-bag is then inserted within a vessel in which pressure is applied to the external surface of the gold-bag. The important point is that the oil or model compounds being pyrolysed are not in contact with the water. Most of the work on the effect of pressure has been undertaken on model compounds, e.g. saturates and aromatics, although Hill et al. (1996) pyrolysed the C_9+ fraction of a saturate-rich, West Canadian Devonian oil in sealed gold tubes at temperatures between 350 and 400 °C for 72 h and at pressures between 90 and 2000 bar, and found that the effect of pressure on the rate of oil

cracking and product generation was small. In a number of studies, a retardation effect was observed during the pyrolysis of saturated hydrocarbons at pressures higher than 400 bar (Fabuss et al., 1964; Dominé, 1991; Behar and Vandenbroucke, 1996). At lower pressures, Fabuss et al. (1964) concluded that pressure accelerates cracking between 1 and 400 bar while a decrease was observed at higher pressure (800 bar). This trend of an initial increase followed by a decrease at higher pressure has been confirmed for oil cracking (Behar and Vandenbroucke, 1996; Hill et al., 1996). On the contrary, Jackson et al. (1995) observed a continuous retarding effect for *n*-hexadecane pyrolysis between 120 and 600 bar. Al Darouich et al. (2006) (using the light aromatic fraction of a crude oil pyrolysed at 375 °C under pressures of 400, 800 and 1200 bar) showed that a pressure increase from 100 to 400 bar reduced the cracking of light aromatic fractions, unstable charge-classes, and secondary cracking of the C_{15}–C_{20} and C_{20+} compounds, which reduced the production of gas and insoluble residue. However further increase in pressure produced only minor changes compared with those produced by increasing the pressure from 100 to 400 bar.

Unlike the confined pyrolysis non-hydrous studies reported above, water is present in most rocks in geological basins, even if only as the irreducible water saturating hydrocarbon reservoirs. Although source rocks have been pyrolysed in the presence of water (hydrous pyrolysis), relatively few studies have been undertaken using water and oil in the pyrolysis experiment. It must be recognised that in addition to the presence of liquid water and not steam, other factors such as the physical state of the water as the solubility of hydrocarbons in water depends strongly on water phase state, and the chemical effect of the water need to be considered. Some work on the effect of water on the stability of hydrocarbons has been undertaken, Abbott et al.

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(1995) showed that 5α(H)-cholestane was more degraded under anhydrous compared to hydrous conditions. Hydrous pyrolysis experiments on a Japanese oil derived from a type II source rock by Tsuzuki et al. (1999) showed that the cracking reaction rates were retarded compared with non-hydrous experiments. Brooks et al. (1971) as well as Hesp and Rigby (1973) also showed that the pyrolysis of oil in the presence of water and under inert gas pressure retarded oil to gas cracking reactions compared with non-hydrous and absence of pressure, while oil cracking to gas was retarded between 700 and 900 bar water pressure for coal pyrolysed at 420 °C for 24 h (Uguna et al., 2015). In an attempt to evaluate the role of water, Hoering (1984) undertook a series of hydrous pyrolysis experiments with pulverized rock, model compounds, and D_2O. This study demonstrated deuterium exchanged with hydrogen in hydrocarbons that were cleaved from decomposing kerogen, but the specific role of water in the pyrolysis reactions and its ability to promote oil expulsion from an organic-rich rock was not determined. The objective of the Hoering (1984) study was to address this uncertainty through a series of experiments designed to evaluate various roles water may play in petroleum formation. Although this study uses petroleum rather than kerogen, similar processes involving the cleavage of carbon-carbon bonds in free radical reactions in petroleum as opposed to kerogen can be expected to occur.

The studies by Brooks et al. (1971) and Hesp and Rigby (1973) used a maximum pressure of 210 atm. (213 bar equivalent to hydrostatic pressure at 2.4 km) at 375 °C under hydrous conditions. Although oil cracking was retarded in the presence of water, the effect that the increase in pressure has on oil cracking was not fully investigated, as temperature was only the parameter varied in their experiment. In our previous studies, we have investigated gas and oil generation, and oil cracking from

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petroleum source rocks and coal under high water pressure conditions. The aim of this study is to take further the earlier findings by Brooks et al. (1971) as well as Hesp and Rigby (1973) that oil cracking to gas was retarded in the presence of water by comparing the effect of increased water pressure on the cracking of expelled oil in deep water petroleum saturated reservoirs. It presents results for laboratory pyrolysis experiments conducted on a 35° API North Sea oil and n-hexadecane (n-C$_{16}$) at 350 °C under non-hydrous low pressure conditions (20 bar), normal hydrous pressure (175 bar), and high water pressure (500 and 900 bar) conditions for 24 h. The aim of this study is also to investigate the gross changes in oil quality expected to occur as they are buried to greater depths and higher temperatures and pressures after emplacement in a reservoir. Having investigated the effect of water pressure on oil generation and expulsion from the Kimmeridge Clay (Uguna et al., 2016) which is the equivalent of Draupne source rock that generated the Oseberg oil in the Norwegian North Sea (Dahl and Speers, 1985), the oil was chosen to investigate the potential cracking of oil to gas. Given the preliminary nature of this work, no attempt has been made to understand the mechanisms involved. However, at high pressures, bimolecular reactions (radical addition and hydrogen abstraction) are favoured over the unimolecular radical decomposition (Khorasheh and Gray, 1993a) which also have higher activation energies than bimolecular reactions and are favoured at higher temperatures. The physical effect played by the virtual incompressible nature of high-pressure water has never been investigated for oil cracking, but it would be expected to play an important role due to the effect that it has on the reaction kinetics. As the pressure increases, for endothermic volumetric expansion reactions, such as cracking, the amount of energy required to achieve the activated complex increases, due to the increased positive pV work

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component of the activation energy. In contrast for exothermic, e.g. combination, reactions the pV work is subtracted from the activation energy, and thus high pressure favours such reactions. This is also likely to arise from the pre-exponential A factor increasing due to the higher collision rates between reacting species.

When considering the results from laboratory experiments under 175 bar hydrous, 500 and 900 bar water pressures as reported in this study, it is always important to compare the laboratory conditions to those present in geological basins. In this study the temperature of 350 °C is far higher than the temperatures at which oil is found in geological reservoirs, while pressures of 175 bar, 500 bar and 900 bar are the hydrostatic pressures at 1.7 km, 5 km and 9 km respectively, assuming no overpressure in all cases. The pyrolysed oil was also compared to a Gulf of Mexico (GOM) bitumen sample from a depth of 20,353 ft. and reservoir pressure of 822 bar. The GOM bitumen used here was not a solvent soluble bitumen fraction of a source rock, but a tar like solid bitumen (containing gasoline range hydrocarbons) soluble in dichloromethane. This bitumen was chosen because of the depth and reservoir pressure it was obtained from to compare it to the oil residue after pyrolysis, and to further investigate if the bitumen was formed from oil cracking. The GOM bitumen and its asphaltene were analysed by gas chromatography (GC), gas chromatography-mass spectrometry (GC-MS) and hydropyrolysis (HyPy). Hydropyrolysis is an open-system continuous flow pyrolysis technique, which in the presence of a molybdenum catalyst and high hydrogen gas pressures (15 MPa) possesses the unique ability to produce high yields of hydrocarbon biomarkers from source rock kerogens and petroleum asphaltenes, whilst minimising structural alteration by isomerisation and cracking. The hopane and sterane biomarkers covalently bound within the macromolecular structure of the asphaltenes and released

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by HyPy, are found to undergo the same epimerisation reaction pathways as their free

counterparts in the maltene fraction. They are however for most oils generally less

mature then the free biomarkers in terms of isomerisation at both ring and side-chain

chiral centres (Murray et al., 1998; Russell et al., 2004).

2. Experimental

2.1. Pyrolysis experiments

Pyrolysis experiments were conducted using 1.2 g of *n*-hexadecane and 2.0 g of

oil at 350 °C (temperature accuracy ±1 °C) for 24 h under non-hydrous (no water

added), low pressure hydrous (175 bar) and high liquid water pressure (500 and 900

bar) pyrolysis conditions. The *n*-hexadecane and oil pyrolysis experiments were

performed separately using the same pyrolysis equipment and experimental procedure

that has been published previously (Uguna et al., 2012a; 2015) and also described here.

The pyrolysis equipment (Figure 1) comprised a Hastalloy (25 ml cylindrical) pressure

vessel (rated to 1400 bar at 420 °C, designed by Strata Technology, Sunbury-on-

Thames, UK) connected to an Autoclave Engineers pressure gauge and rupture disc

rated to 950 bar. Heat was applied 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 low pressure hydrous experiments were conducted

with the addition of 15 ml distilled water to the vessel, generating a pressure of 175 bar.

The oil or *n*-hexadecane to be pyrolysed was directly weighed into the empty vessel,

after which 12 g of pre-extracted glass beads (80 mesh particle size) was added to the

vessel before the volume of water needed for the experiment was added. It is

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noteworthy here that the reaction product distributions during the hydrous pyrolysis of a sterane model compound were very similar in a comparison of the reactions carried out in stainless steel-316 and borosilicate glass reactors (Abbott et al., 1995). Glass beads were to adsorb the oil or *n*-hexadecane to ensure the samples were submerged in water during the 175, 500 and 900 bar experiments. 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 (350 °C) and left to equilibrate, after which the pressure vessel was then lowered into the sand bath and the experiment left to run with a constant air flow through the sand bath. The pressure observed for the low pressure (175 bar) experiment was generated by the vapour of the water (15 ml) added to the vessel at the start of the experiment.

High liquid water pressure (500 and 900 bar) experiments were performed similarly to the low (175 bar) pressure hydrous runs, with the vessel initially filled with 20 ml water. After lowering the pressure vessel onto the sand bath, the vessel was connected to the high liquid water pressure line and allowed to attain its maximum vapour pressure of 175 bar (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

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undertaken to avoid losing any content 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 is switched off and left to cool to ambient temperature before product recovery.

The total internal volume of the empty pressure vessel and its associated pipe work and pressure gauge was estimated to be about 31 ml by pressurising with nitrogen gas from a nitrogen cylinder set to 2 bar, and measuring the volume of gas released. It is important to note that overpressure was not generated during the low pressure (175 bar) or 500 bar and 900 bar experiments due to the small amount of gas generated, and the recorded final pressure after 24 h being the same as pressure at the start of the experiment.

In order to test if any gas in the system was lost in the process of pressurising the vessel, a control experiment was conducted at 350 °C for 50 minutes at a pressure of 500 bar using the same oil sample being studied. The short time used for the control experiment was to ensure the oil did not thermally crack. The volume of gas collected after the control experiment was found to be equal to the volume of nitrogen pumped into the system at 2 bar before the experiment started. This indicated that gas has not been lost either during pressurisation, pressure build up in the vessel or during gas

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sampling from the reactor after the experiments. A flow chart showing the pyrolysis

conditions, products recovery and analysis are shown in Figure 2, and the four separate

experiments carried out on both the oil and *n*-hexadecane as listed below:

    i.   20 bar (low pressure non-hydrous pyrolysis)

    ii.   175 bar (15 ml water, normal low pressure hydrous pyrolysis)

    iii.   500 bar (high liquid water pressure pyrolysis)

    iv.   900 bar (high liquid water pressure pyrolysis)

No attempt has been made to separate the effects of water and inert pressure at low

pressures since the emphasis here is understanding the impact high water pressures on

the initial stages of cracking.

2.2. Gas analysis

To recover the generated gas, the high water pressure line was disconnected and

a connector attached to valve C. The generated gas was collected at ambient

temperature (via the connector by opening valve C) with the aid of a gas tight syringe

and transferred to a gas bag (after the total volume had been recorded) and immediately

analysed. The gas generated from the *n*-hexadecane experiments were analysed on a

Carlo Erba HRGC 5300 GC fitted with a FID detector operating at 200 °C. 10 µl of gas

samples were injected at 100 °C with separation performed on a Varian Poraplot-Q

fused silica 25 m x 0.32 mm x 10 µm column, with helium as the carrier gas. The oven

temperature was programmed from 70 °C (2 min hold) to 90 °C (3 min hold) at 40 °C

min^{-1}, then to 140 °C (3 min hold) at 40 °C min^{-1}, and finally to 180 °C (49 min hold) at

40 °C min^{-1}. The gas from the oil cracking experiments were analysed on a Clarus 580 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 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^{-1}. 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 C_5 gases were not reported for *n*-hexadecane because only C_1-C_3 and butane gases were correctly identified because of the age of the instrument and the old software used for the GC.

2.3. GC and GC-MS analysis of GOM bitumen, oils and *n*-hexadecane

After gas analysis, aliquots of oil and *n*-hexadecane were collected for GC and GC-MS analysis respectively, and the asphaltene content of the oil left was determined based on the weight of oil remaining as previously described elsewhere (Russell et al., 2004). The GC analysis of the initial, cracked whole oil and GOM bitumen fractions were carried out using an Agilent 6890 GC fitted with FID at 350 °C. Injections were performed in split mode (split ratio 100:1), with separation achieved on a DB-1 fused silica capillary column (100 m). Helium was employed as the carrier gas, with a temperature programme of -20 °C cryogenic (hold for 0 min) to 320 °C (hold for 30 min) at 10 °C min^{-1}. GC-MS analysis of the cracked *n*-hexadecane products were

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performed on a Varian CP-3800 GC interfaced to a Varian 1200 MS (ionising energy

70 eV, source temperature 280 °C). Injections were performed in split mode (split ratio

30:1) and eluted components monitored in full scan mode (m/z 50-450), turning off the

instrument at the elution time of n-hexadecane to avoid damaging the filament.

Separation was achieved on a VF-1MS fused silica capillary column (50 m x 0.25 mm

internal diameter, 0.25 m thickness), with helium as the carrier gas, and an oven

programme of 50 °C (hold for 2 min) to 300 °C (hold for 20.5 min) at 4 °C min⁻¹.

2.4. Hydropyrolysis of GOM bitumen asphaltene and GC-MS analysis

The asphaltene fraction isolated from the GOM bitumen was subjected to

hydropyrolysis as described in detail elsewhere (Murray et al., 1998; Russell et al.,

2004). Briefly, the sample (50 mg) was pyrolysed on a bed of sulphided molybdenum

catalyst (250 mg), with resistive heating from 50 °C to 250 °C at 300 °C min⁻¹, and then

250 °C to 520 °C (hold for 2 min) at 8 °C min⁻¹, under a hydrogen pressure of 15 MPa.

A hydrogen sweep gas flow of 5 l min⁻¹, (measured at ambient temperature and

pressure), ensured that the products were quickly removed from the reactor vessel, with

the products trapped on dry ice cooled silica. The aliphatic, aromatic and polar fractions

of the hydropyrolysates were separated by silica gel / alumina adsorption

chromatography with successive elutions of n-hexane, n-hexane/DCM (3:2 v/v) and

DCM/methanol (1:1 v/v), with the aliphatic fraction then analysed using the same GC-

MS as used for n-hexadecane above using an oven programme of 50 °C (hold for 2 min)

to 300 °C (hold for 33 min) at 5 °C min⁻¹. Analysis were performed in full scan mode

(m/z 50-450) and selected ions monitoring m/z 191 (hopanes) and m/z 217 (steranes)

separately.

3. Results and discussion

3.1 Gas yields

Table 1 presents the individual and total (C_1-C_5) gas yields (mg/g of carbon of pyrolysed oil and *n*-hexadecane). The gas yields are low as expected for the initial stages of cracking for both the oil and *n*-hexadecane. However, they are highest under non-hydrous low pressure (20 bar) conditions and reduce in going to normal hydrous pressure (175 bar), with the C_1-C_5 yield 44% lower compared to the non-hydrous (20 bar) yield for the oil. This confirms that a combination of increasing pressure and water retards oil cracking to gas, consistent with previous studies (Brooks et al., 1971; Hesp and Rigby 1973). The gas yields continue to fall with increasing water pressure, with the alkene formation strongly suppressed. At 500 bar, the C_1-C_5 hydrocarbon gas yields decrease slightly compared to 175 bar, while at 900 bar the gas yield is 36% and 23% lower in relation to the 175 bar and 500 bar yields, respectively. The trends in gas yields for both the initial stages of cracking for oil and *n*-hexadecane pyrolysis are consistent to those observed for our previous studies for the pyrolysis of coals between 500 and 900 bar water pressure at 350 °C (Uguna et al., 2012a) and for Kimmeridge Clay Type II source rock pyrolysed between 310 and 350 °C at 500 bar water pressure (Carr et al., 2009; Uguna et al., 2012b; 2013). However, when the gas yields obtained here at 500 and 900 bar are compared to our previous studies on coals and Kimmeridge Clay type II source rock (Carr et al., 2009: Uguna et al., 2012a; 2012b; 2016) the sequence of the retardation effect of pressure is *n*-hexadecane (most retarded) > oil > perhydrous coals > Type II source rocks (least retarded). The C_1-C_5 gas yield for oil pyrolysis at 900 bar in this study is 6.5 times lower compared to Kimmeridge clay also

pyrolysed at 900 bar under the same temperature and time (Uguna et al., 2016). This suggests that the retardation effect of pressure is greater for the initial stages of oil cracking than for source rock maturation.

The reduction in gas yield in the presence of water (175 bar hydrous conditions) compared to the absence of water (non-hydrous conditions) observed here is the opposite observed previously for source rocks and kerogens. It has been widely reported that gas and liquid hydrocarbon yields from kerogens, petroleum source rocks and coals are significantly higher under hydrous compared to non-hydrous conditions (Comet et al., 1986; Andresen et al., 1993; Kuangzong et al., 1994; Michels and Landais 1994; Lewan 1997; Behar et al., 2003). The higher products yield under hydrous conditions reported in the above studies is due to water playing the role of a reactive medium by transferring hydrogen and oxygen to kerogen termed the chemical effect of water. Our previous study (Carr et al., 2009) investigated the chemical effect of water on hydrocarbon gas generation by comparing non-hydrous pyrolysis to hydrous pyrolysis using different volumes of water for Kimmeridge Clay pyrolysed at 350 °C for 24 h. This study showed that hydrocarbon (C_1-C_4) gas yields was higher (24 mg/g TOC) with 10 ml water (155 bar) in the vessel compared to non-hydrous (15 bar) yield (16 mg/g TOC), and when the water volume was doubled to 20 ml (180 bar) the gas yield reduced to 11 mg/g TOC. Also in our previous study comparing gas and bitumen yields under hydrous (20 ml water, 175 bar pressure) and non-hydrous conditions showed that hydrocarbon (C_1-C_4) gas yields was lower and bitumen yield higher under hydrous compared to non-hydrous conditions for coals pyrolysed at 350 °C for 24 h (Uguna et al., 2012a).

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These studies show that water has a chemical effect in promoting kerogen conversion to liquid and gaseous hydrocarbon under hydrous conditions. However, the reduction in gas yield in the presence of water under normal hydrous conditions (175 bar) observed in this study confirms that water is an inhibitor in both oil and *n*-hexadecane cracking reactions as opposed to a reactive medium in kerogen conversion reactions (Comet et al., 1986; Andresen et al., 1993; Kuangzong et al., 1994; Michels and Landais 1994; Lewan 1997; Behar et al., 2003; Carr et al., 2009). The retardation of oil and *n*-hexadecane cracking with increasing pressure reflects the increase in the Ea (activation energy) of the reactions with increasing pressure.

3.2 Cracked oils and *n*-hexadecane

The whole oil GC traces are presented in Figures 3a and 3b. Under non-hydrous and 175 bar conditions, no discernible changes were observed in the *n*-alkane distribution in the whole oil GC since the overall extent of cracking is low at a temperature of 350 °C for a period of 24 h, consistent with the low extent of cracking. The 500 and 900 bar GC traces visually show higher abundance of heavier *n*-alkanes (>C_{20}) compared to the initial, non-hydrous (20 bar) and 175 bar oils. The 500 and 900 bar oils GC traces also shows unresolved complex mixture (UCM). This was very evident in the 900 bar oil when compared to the 175 bar oil (Figure 3b). The GC-MS total ion chromatograms for *n*-hexadecane cracking are presented in Figures 4a and 4b. The non-hydrous (20 bar) trace show a complex mixture of straight and branched chain alkanes in the C_{18}-C_{31} region. Under 175 bar hydrous conditions, the C_{18}-C_{31} alkanes mixture were completely absent, but increase in water pressure to 500 and 900 bar resulted to their formation with their abundance visually more at 900 bar.

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The higher abundance of higher molecular weight n-alkanes ($>C_{20}$) observed for the 500 and 900 bar oils (Figures 3a and 3b) indicate that water pressure conditions gave rise to higher boiling, higher gravity viscous oils, the trend being most pronounced for the 900 bar oil (Figures 3a and 3b). The unresolved complex mixture (UCM) was also very evident in the 900 bar oil when compared to 175 bar oil (Figure 3b), and arises from combination reactions involving the higher boiling materials ($>C_6$). These combination reactions are exothermic unlike cracking reactions which are endothermic, and exothermic reactions are more favoured under high pressures than cracking reactions, as shown by the retardation of coal to gas conversion reactions at 350 °C under pressures of 500 and 900 bar (Uguna et al., 2012a). To show that the 500 and 900 bar oils are heavier (contain higher abundance of n-alkanes $>C_{20}$) than the initial, non-hydrous and 175 bar oil, some peak area ratios from the whole oil GC trace and the asphaltene contents of the oils were used below. The use of peak area ratios of n-alkanes to determine their abundance in the oils was preferred to the use of an internal standard to quantify their concentrations. This was to avoid introducing organic solvent to the oils which will have resulted in the light ends (gasoline range hydrocarbons) being lost due to co-elution with the solvent front. The peak area ratios used are; toluene/nC_7, toluene/nC_{28}, methylcyclohexane/nC_7, short to long chain n-alkanes [($nC_6+nC_7+nC_8$)/($nC_{27}+nC_{28}+nC_{29}$) and ($nC_6+nC_7+nC_8$)/($nC_{30}+nC_{31}+nC_{32}$)], initial oil/pyrolysed oil short chain ($nC_6+nC_7+nC_8+nC_9$) n-alkanes, and initial oil/pyrolysed oil long chain ($nC_{27}+nC_{28}+nC_{29}+nC_{30}$) and ($nC_{31}+nC_{32}+nC_{33}+nC_{34}$) n-alkanes.

Considering the peak area ratios of toluene to C_{28} n-alkane and short to long chain n-alkanes for the initial and pyrolysed oils (Figure 5), these ratios initially increase from the initial oil to a maximum at 175 bar before decreasing with an increase

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in pressure to values lower than the initial oil. The increase shown going from the

initial to non-hydrous and 175 bar shows that the non-hydrous and 175 bar oil contains

lower abundance of C_{27}-C_{32} n-alkanes than the initial oil which resulted from their

cracking to form more C_6-C_8 n-alkanes. However, the lower values shown at 500 and

900 bar compared to the initial oil indicates that the 500 and 900 bar oils contain higher

abundance of C_{27}-C_{32} n-alkanes than the initial oil, which should not be the case if

cracking is occurring. This again occurs due to the preferential combination of smaller

hydrocarbon molecules into more complex higher boiling point hydrocarbons. The

toluene to n-heptane and methylcyclohexane to n-heptane peak area ratios (Figure 5)

show that the relative amounts of these compounds are the same for both the initial and

pyrolysed oils, suggesting that their relative stabilities are similar under the

experimental conditions used.

When the ratio of the initial to pyrolysed oil short chain n-alkanes (Figure 6) is

considered, the values change from 0.89 and 0.93 under non-hydrous (20 bar) and 175

bar conditions respectively to 1.24 at 500 bar and 1.48 at 900 bar. The ratio of <1

obtained under non-hydrous and 175 bar shows that the oils contains more C_6-C_9 n-

alkanes than the initial oil due to some cracking of high molecular weight hydrocarbons.

However, the change in the ratio from being <1 under 175 bar hydrous conditions in

which very small cracking occurred to >1 at 500 and 900 bar suggests that the cracking

to smaller hydrocarbons is being increasingly restricted, and the 500 and 900 bar oils

contain lesser amounts of C_6-C_9 n-alkanes than the initial oil. This is again due to

combination reactions involving lower molecular hydrocarbons into larger and more

complex hydrocarbons.

Figure 6 also presents the initial to pyrolysed oils long chain n-alkanes, the initial to pyrolysed oil (nC_{31}-C_{34}) ratio initially increased going from 1.24 at 20 bar (non-hydrous) to 1.59 at 175 bar before reducing significantly with increase in water pressure to 0.79 and 0.67 at 500 and 900 bar respectively. The initial to pyrolysed oils (nC_{27}-nC_{30}) ratios were 1.08 (non-hydrous) and 1.12 (175 bar), but were 0.73 and 0.66 in the 500 and 900 bar oils. The higher ratios (>1) obtained for the initial to non-hydrous and 175 bar oil again indicate that the abundance of C_{27}-C_{34} n-alkanes are lower in the non-hydrous and 175 bar pyrolysed oils than in the initial oil, which shows that the higher molecular weight (C_{27}-C_{34}) alkanes were being cracked to lighter hydrocarbons (<C_{10}) and gas. The reduction in both ratios (<1) going to 500 and 900 bar indicate that the abundance of C_{27}-C_{34} n-alkanes in the 500 and 900 bar oils is higher than in the initial oil which should not be the case if cracking is occurring. The change in the values between 20 bar (non-hydrous) and 175 bar for both the (nC_{27}-nC_{30}) and (nC_{31}-nC_{34}) ratios between the initial oil and the pyrolysed oils shows that the largest increase occur in the longer chain n-alkanes, suggesting that these were cracked more easily under low pressure conditions than the nC_{27}-nC_{30} alkanes. Interestingly, the values for both the (nC_{27}-nC_{30}) and (nC_{31}-nC_{34}) ratios between the initial oil and the pyrolysed oils are very similar at 500 and 900 bar at 350 °C.

The increase in abundance of C_{27}-C_{34} n-alkanes together with the reduction in C_6-C_9 n-alkane abundance in the oils with increase in water pressure provide more evidence that the higher amounts of long chain hydrocarbons in the 500 and 900 bar oils results from combination reactions involving lower molecular weight hydrocarbons. The fact that the amount of C_6-C_9 n-alkanes is lowest and the C_{27}-C_{34} n-alkanes is highest in the 900 bar oil, indicate that combination reactions are more favoured over

cracking reactions at 900 bar and 350 °C, meaning cracking reactions were being

replaced by combination reactions at high pressures. The asphaltene content of the

cracked oils also increased significantly from 0.4% (initial oil) to 1.1% and 1.3% for the

non-hydrous and 175 bar oils respectively due to cracking. The 900 bar oil asphaltene

increased further to 1.9% despite the extent of cracking decreasing with increase in

pressure. Like the combination reactions observed involving lower molecular weight

hydrocarbons, asphaltene formation is a volume reduction process and should be

favoured also at high pressures.

For *n*-hexadecane, the product distribution from the non-hydrous (20 bar)

pyrolysis (Figures 4a and 4b) was entirely consistent with previous studies using similar

conditions (Ford, 1986; Wu et al., 1996), with the lower molecular weight ($<C_{14}$)

hydrocarbons being mainly straight chain alkenes and alkanes, and the higher molecular

weight ($>C_{18}$) hydrocarbons containing branched and straight chain alkanes in the C_{18}-

C_{31} region. Ford (1986) and Wu et al. (1996) concluded that the C_{18}-C_{31} straight and

branched chain alkanes were formed by alkylation reactions between lower molecular

weight ($<C_{14}$) alkenes and C_{16} radicals. Under normal pressure (175 bar) hydrous

conditions (Figures 4a and 4b), the concentration of $<C_{14}$ alkenes decreased and the

formation of C_{18}-C_{31} alkanes was completely suppressed. The reduction in $<C_{14}$ alkenes

concentration at 175 bar is due to hydrogenation of alkenes to alkanes, as well as

suppression of alkene generation reactions under normal hydrous conditions. The

absence of C_{18}-C_{31} alkanes in the 175 bar product is due to insufficient $<C_{14}$ alkenes (as

they were hydrogenated to alkanes) that can react with C_{16} radicals to form C_{18}-C_{31}

alkanes. The 500 and 900 bar water pressure products lacked $<C_{14}$ alkenes but contain

C_{18}-C_{31} straight and branched chain alkanes (Figures 4a and 4b), with the concentration

increasing further to 900 bar. In a study on the effects of pressure on the cracking of *n*-tetradecane (*n*-C$_{14}$) at temperatures between 250 and 450 °C and at pressures between 0.001 and 1000 bar in gold-bag pyrolysis experiments, Michels et al. (2015) observed maxima in the bell-shaped *n*-alkane conversion curve. The pressure at which the maxima occurred increased with increasing temperature. The proportion of monomolecular vs bimolecular reactions controls the extent of conversion (bell shape curves) under the conditions used, i.e. confined, non-hydrous pyrolysis. For each temperature the curve profile changed. Many contradictions into the effects of pressure on hydrocarbon pyrolysis published ("retardation vs acceleration" of reaction) arise from the lack of understanding of this complex behaviour. While this issue is undoubtedly correct, the effect that water has on the reactions as highlighted by the studies of Brooks et al. (1971), Hesp and Rigby (1973), and Hoering (1984) was ignored by Michels and co-workers (e,g. Michels et al., 2015; Panifolva et al., 2015), who claimed that non hydrous experimental conditions can replicate the cracking of oil in deeply buried reservoirs. Comparing the results at 900 bar with those obtained at either 175 bar (hydrous) or 500 bar water pressure for both Oseberg oil and *n*-hexadecane here shows that at high water pressure the gas yield is reduced, the presence of alkenes is virtually eliminated, and the high molecular weight products are increased. The high-pressure results are inconsistent with the more efficient cracking observed by Michels et al. (1995) for the results obtained from hydrous as opposed to confined (gold-bag) pyrolysis. As already discussed, this effect is due to the conservation of energy law, and the absence of sufficient thermal energy (even at 350 °C) to provide the energy for both bond rupture to create the radicals required for the generation of low molecular weight compounds, i.e. gases, and pV work required for the product

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formation. Lannuzel et al. (2010) observed the absence of alkenes in high pressure (700 bar) gold-bag pyrolysis at 350 °C, and the absence of alkenes in the high-water pressure results in this study appears to be consistent with this.

The fact that the formation of the C_{18}-C_{31} normal and branched alkanes were hindered at 175 bar indicates that their formation at 500 and 900 bar water pressure is due to combination reactions induced by water pressure, and we believe the reaction involves $<C_{14}$ alkenes and C_{16} radicals since $<C_{14}$ alkenes were absent under the high water pressure conditions. The absence of $<C_{14}$ alkenes under 500 and 900 bar is due to a combination of their suppression, and combination reactions. Combination reaction occurred under 500 and 900 bar pressures conditions because the vessel is predominantly full of water and there was no vapour present where the alkenes can be hydrogenated to alkanes as was the case at 175 bar. The hydrogenation of alkenes to alkanes and suppression of alkene formation observed in this study under high water pressure conditions explains why alkenes are not present in natural oils, and provide evidence that high water pressure pyrolysis closely simulates natural conditions present in geological basins.

3.3 Evidence for bitumen formation by combination reactions

The GOM bitumen is not biodegraded containing light *n*-alkanes, contains 52% asphaltene, and the GC chromatogram (Figure 7a) resembles those of the 500 and 900 bar pyrolysed oils (Figures 3a and 3b), in showing an unresolved complex mixture (UCM), below the chromatogram baseline in the region of the extended ($>nC_{20}$) *n*-alkanes. The asphaltene content of the bitumen is significantly higher than the 900 bar oil, and the unresolved complex mixture more pronounced. Solli and Leplat (1986),

Jones et al. (1988), and Sofer (1988) all reported that alkanes were generated by asphaltene hydrous pyrolysis by cracking, which is in contrast to the asphaltene formation by high pressure pyrolysis observed in this study. We believe that combination reactions which increased the asphaltene content and higher molecular weight n-alkanes of the 500 and 900 bar oils and the formation of C_{18}-C_{31} straight and branched alkanes for n-hexadecane pyrolysis at 500 and 900 bar is also responsible for the high asphaltene content of the GOM bitumen. To investigate this, the maturities of the free biomarkers were compared to the asphaltene bound biomarkers released by catalytic hydropyrolysis (Murray et al., 1998; Russell et al., 2004). The C_{29} $\alpha\alpha\alpha$ S / ($\alpha\alpha\alpha$ S + $\alpha\alpha\alpha$ R) and C_{29} $\alpha\beta\beta$ / (($\alpha\alpha\alpha$ S + $\alpha\alpha\alpha$ R) + $\alpha\beta\beta$) free sterane (Figure 7b) ratios were 0.52 and 0.49 respectively. This was similar to the ratios of 0.53 (C_{29} $\alpha\alpha\alpha$ S / $\alpha\alpha\alpha$ S + $\alpha\alpha\alpha$ R) and 0.52 [C_{29} $\alpha\beta\beta$ / ($\alpha\alpha\alpha$ S + $\alpha\alpha\alpha$ R) + $\alpha\beta\beta$] obtained for the asphaltene bound steranes (Figure 7c). The C_{31} and C_{32} $\alpha\alpha\alpha$ S / ($\alpha\alpha\alpha$ S+ $\alpha\alpha\alpha$ R) free hopane ratios were 0.60 and 0.58 respectively, also similar to the asphaltene bound hopane ratios 0.60 (C_{31} $\alpha\alpha\alpha$ S / ($\alpha\alpha\alpha$ S+ $\alpha\alpha\alpha$ R)) and 0.59 (C_{32} $\alpha\alpha\alpha$ S / ($\alpha\alpha\alpha$ S+ $\alpha\alpha\alpha$ R)). Asphaltene bound biomarkers have been found to be generally less mature than free biomarkers (Murray et al., 1998; Russell et al., 2004). The fact that the free and asphaltene bound biomarkers for the GOM bitumen are of similar maturity further suggest that the bitumen may have been formed from oil by combination reaction induced by pressure and the free phase biomarkers may have been incorporated into the asphaltene during this process.

3.4 General discussion

The magnitude of the retardation effects of pressure on the initial stages of oil cracking is much greater than found in previous studies using confined gold bags pyrolysis method (Hill et al., 1996; Al Darouich et al., 2006) that generally show less retardation effect compared to the unconfined water pyrolysis method used here. The decomposition of oil to gas occurs via beta scission of hydrocarbons to generate free radicals. Two types of radicals play a part in the pyrolysis mechanism of saturated hydrocarbons (Bounaceur et al., 2002a): radicals that decompose by monomolecular reactions and radicals that react by bimolecular reactions. Clearly, the former involve volume expansion and intuitively will be considerably more retarded by pressure. The results also need to be considered with respect to transition state theory where pressure is likely to increase the pV work term in the activation energy, Ea. In the case of oil cracking in reservoirs in geological basins, the pore spaces not filled with oil are initially filled with water prior to oil cracking, and as noted above the incompressible nature of the water can be viewed as increasing the pV work term required as the forces opposing the formation of the activated complex increase.

The ability of high water pressure to promote combination reactions resulting in more viscous oil have been observed for the first time under laboratory water pressure conditions. This explains why oils can be stable, becoming heavier and potentially even forming bitumens like the GOM bitumen shown here, under the high water pressure regimes found in geological basins. Indeed, for Caillou Island (Louisiana) oils, Price (1990) reported an increase in API from 30° at 9000 ft. to 50° at 19000 ft., before reducing rapidly to 35° API at 20000 ft., a trend that might be expected if increasing water pressure was producing heavy oil. Combination reactions are exothermic, which means that they would be favoured in cooler high pressure basins, e.g. the Gulf of

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Mexico, and lower API gravity oils with higher asphaltene content than used in this study will more likely favour this process. Moreover, much of the bitumen previously described as the pyrobitumenic residue after oil cracking has possibly been incorrectly identified. Indeed characterisation of the supposed 'pyrobitumens' in the high temperature (190 °C) high pressure North Sea Upper Jurassic Fulmar Formation (Scotchman et al., 2006) have shown that the 'pyrobitumens' are degraded residues of normal oil window mature North Sea oils, e.g., deasphaltation (Wilhelms and Larter, 1995), and have not formed by oil cracking as proposed by Vandenbroucke et al. (1999). In this case may be the high temperatures are preventing the exothermic combination reactions, whereas the high pressures are preventing the endothermic cracking reactions. Much more work is required into this area of research to fully understand heavy oil formation in geological basins.

To attempt extrapolation from 350 °C to the temperatures in geological basins, the chemical effects of water in promoting conversion will possibly be lowered due to lower water solubility of hydrocarbons. However, the physical effect of pressurised water will probably be emphasised even more because the viscosity of oil will increase significantly. Also in conjunction with pressure, it is recognised that other variables, such as pH, Eh, mineralogy and porosity could all have a significant role to play. Further, Michels et al. (1995) concluded that as well as the chemical composition of the diagenetic fluids (aqueous solutions and gases), their physical relationship with bitumen and oils, and the interactions between water and the organic compounds within the organic phases, as well as temperature and pressure parameters need to be considered when extrapolating the chemical mechanisms observed in laboratory to the natural environment. However, whilst all these factors must be considered, the reduced

cracking observed in conjunction with the combination reactions favoured by high water pressure provides a new means for rationalising the observed thermal stability of oils and heavy oil formation in high pressure basins.

4. Conclusions and implications

1. The cracking of oil and *n*-hexadecane to hydrocarbon gases was retarded in the presence of water under 175 bar low pressure hydrous conditions compared to non-hydrous (absence of water). The retardation effect of pressure was more significant at 500 and 900 bar water pressure compared to 175 bar with the alkene gases most retarded.

2. The cracking of oil and *n*-hexadecane to lower molecular weight (C_6-C_9) hydrocarbons was retarded under 500 and 900 bar water pressure compared to 175 bar, with the effect being most significant at 900 bar.

3. At 500 and 900 bar water pressure combination reactions occurred, replacing cracking reactions. These increased the abundance of heavier *n*-alkanes ($>C_{20}$) present in both oil and *n*-hexadecane, the amount of unresolved complex material (UCM) and asphaltene content of the oil.

4. Combination reactions observed at high water pressure for the first time in this study provide a new mechanism for rationalising the thermal stability of oils, and producing heavy oils at temperatures above those at which biodegradation can occur.

5. This study have demonstrated from the maturity of the bound biomarkers released by hydropyrolysis that bitumen from the high pressure Gulf of Mexico basin have been formed from lighter oil components via combination reactions.

The implications from this study are that in deep petroleum basins and reservoirs with high pressures, the retardation effect of pressure on oil cracking will be far more significant than is currently thought. Oil will be far more thermally stable, and combination reactions resulting in more viscous oil will be far more likely to occur than observed in this study. This is due to temperature been lower and pressures (regardless of whether overpressure is present) higher in geological basins than temperature of 350 °C and maximum pressure of 900 bar used in this study.

Acknowledgments

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straight-chain alkanes. Industrial and Engineering Chemistry Research 26, 846–

852.

Figure captions

Fig. 1. Schematic diagram of pyrolysis equipment.

Fig. 2. Flow chart showing pyrolysis conditions, products recovery and analysis.

Fig. 3. (a) GC profiles of the initial and pyrolysed oils, (b) GC profiles of 175 and 900 bar oils [normalised to abundance of methylcyclohexane (MCH)] comparing extent of UCM under both conditions.

Fig. 4. (a) GC-MS total ion chromatograms profiles for the cracked *n*-hexadecane under non-hydrous (20 bar) , 175 bar, 500 bar and 900 bar conditions, (b) Expanded GC-MS total ion chromatograms for C_{18}-C_{31} hydrocarbons from *n*-hexadecane cracking under non-hydrous (20 bar), 175 bar, 500 bar and 900 bar.

Fig. 5. Toluene to C_7 *n*-alkane, methylcyclohexane to C_7 *n*-alkane, and short to long chain *n*-alkane peak area ratios for initial and pyrolysed oils.

Fig. 6. Short and long chain *n*-alkane ratios of initial to pyrolysed oil with increase in pressure.

Fig. 7. (a) GC profile for Gulf of Mexico bitumen whole oil, (b) Gulf of Mexico bitumen free sterane biomarker GC-MS trace, (c) Gulf of Mexico bitumen asphaltene bound sterane biomarker GC-MS trace.

Table 1. Hydrocarbon gas yields (mg/g carbon) for the oil and *n*-hexadecane.

Oseberg oil Samples	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
Non-hydrous (20 bar)	0.86	0.07	0.62	0.26	0.68	0.18	0.78	0.08	1.77	5.30
175 bar	0.35	0.02	0.15	0.03	0.25	0.01	0.74	0.00	1.41	2.95
500 bar	0.07	0.00	0.03	0.00	0.23	0.01	0.85	0.00	1.27	2.45
900 bar	0.07	0.00	0.02	0.00	0.14	0.01	0.63	0.00	1.02	1.89
n-hexadecane samples	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_{10}				Total C_1-C_4
Non-hydrous (20 bar)	0.55	0.04	0.36	0.31	0.37	0.22				1.85
175 bar	0.08	0.02	0.20	0.09	0.18	0.07				0.65
500 bar	0.01	0.00	0.01	<0.01	0.01	0.01				0.04
900 bar	0.01	0.00	0.01	<0.01	0.01	0.01				0.04

Fig. 1

Fig. 2

Pyrolysis at 350 °C for 24 h

↓

Reactor allowed to cool to ambient temperature followed by analysis of generated gases by GC

↓

Pyrolysed oil and *n*-hexadecane recovered, and a small amount analysed by GC and GC-MS

↓

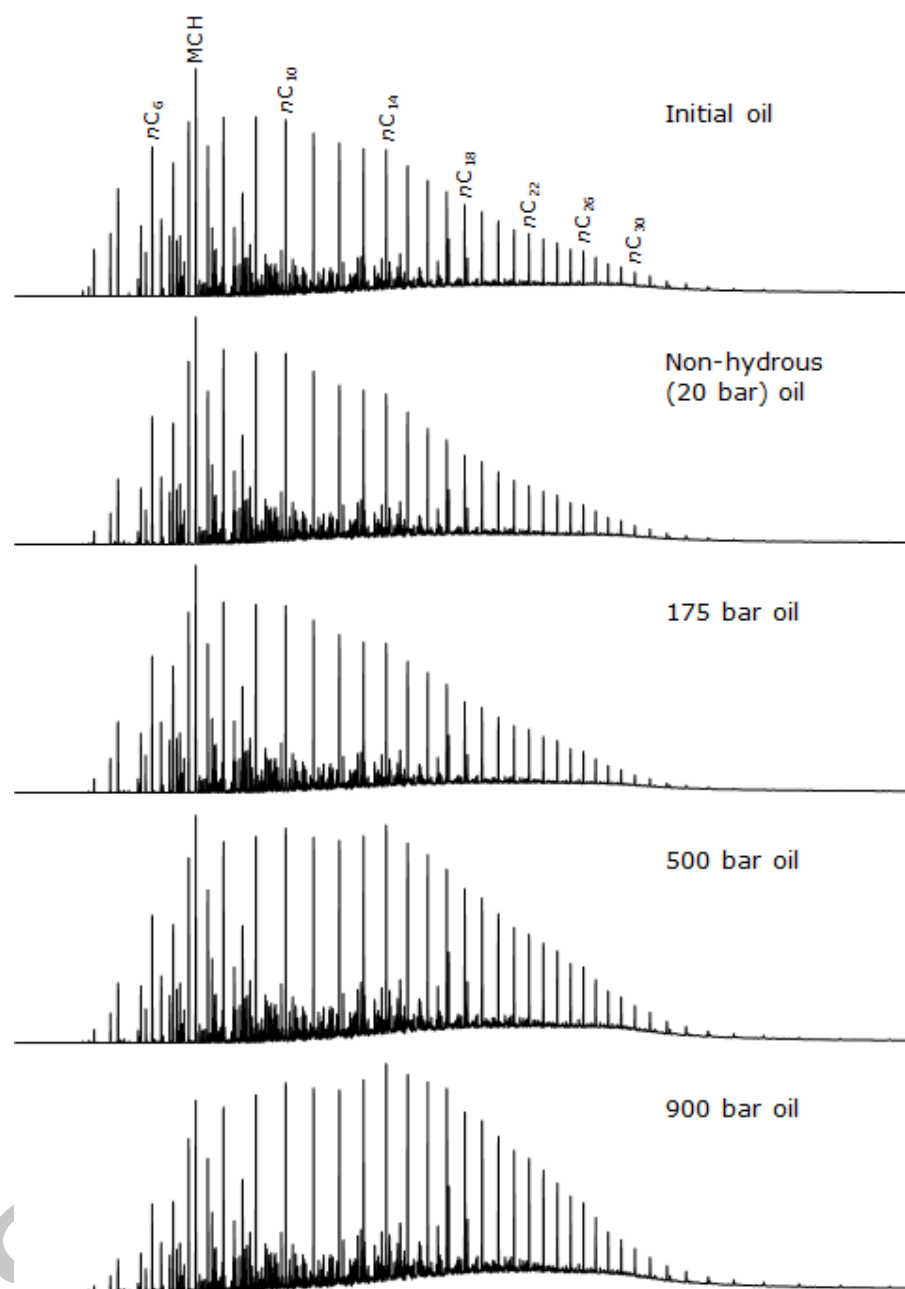Asphaltene contents of the remaining pyrolysed oils determined by *n*-heptane precipitation

Fig. 3a

Fig. 3b

MCH

nC$_{14}$

175 bar oil

900 bar oil

Fig. 4a

Fig. 4b

Fig. 5

$\diamond$ Toluene/nC_{28} $\triangle$ $(nC_6+nC_7+nC_8)/(nC_{27}+nC_{28}+nC_{29})$ $\ast$ Methylcyclohexane/nC_7

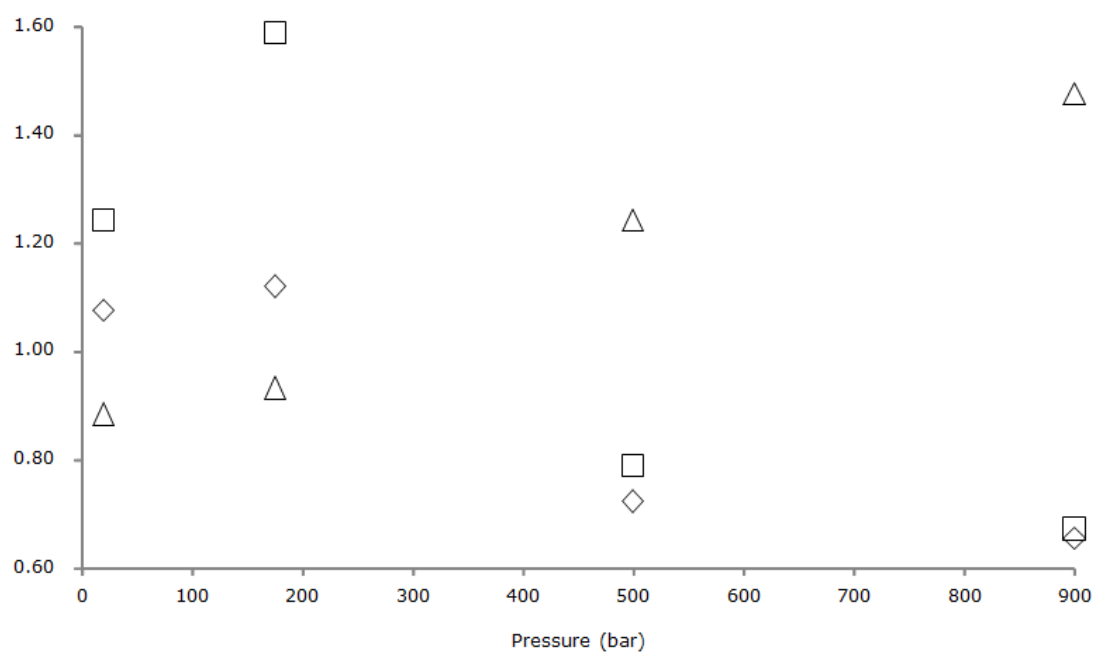$\square$ Toluene/nC_7 $\times$ $(nC_6+nC_7+nC_8)/(nC_{30}+nC_{31}+nC_{32})$

Fig. 6

◇ (Initial oil $nC_{27}+nC_{28}+nC_{29}+nC_{30}$)/(Pyrolysed oil $nC_{27}+nC_{28}+nC_{29}+nC_{30}$)

□ (Initial oil $nC_{31}+nC_{32}+nC_{33}+nC_{34}$)/(Pyrolysed oil $nC_{31}+nC_{32}+nC_{33}+nC_{34}$)

△ (Initial oil $nC_6+nC_7+nC_8+nC_9$)/(Pyrolysed oil $nC_6+nC_7+nC_8+nC_9$)

Fig. 7a

Fig. 7b
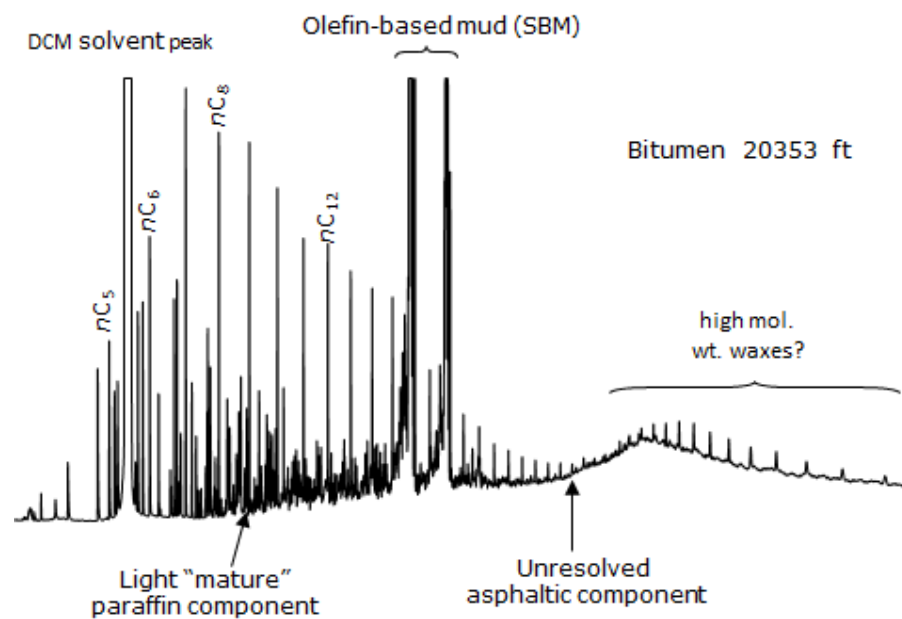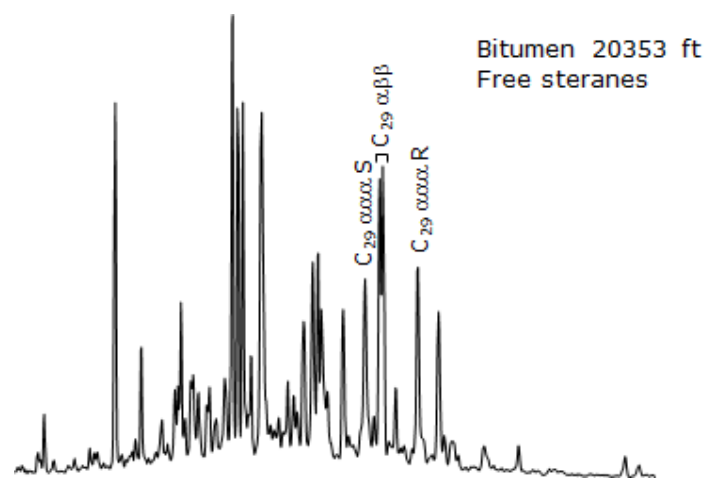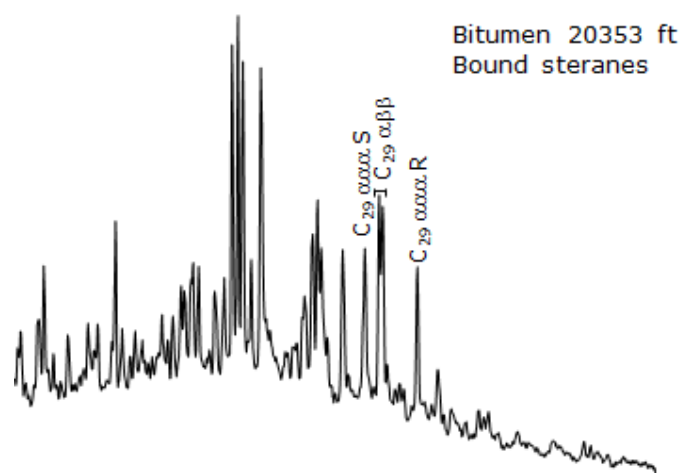

Bitumen 20353 ft
Free steranes

$C_{29} \alpha\alpha\alpha S$ $C_{29} \alpha\beta\beta$

$C_{29} \alpha\alpha\alpha R$

Fig. 7c

Bitumen 20353 ft
Bound steranes

C_{29} ααα S

C_{29} αββ

C_{29} ααα R

- 900 bar water pressure increased the viscosity of oil via combination reaction.
- Oil and n-C_{16} cracking to gas is retarded at 900 bar compared to lower pressures.
- Oil may be more thermally stable in deep petroleum basins than currently thought.