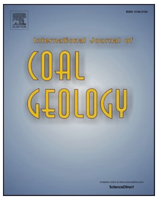
International Journal of Coal Geology 300 (2025) 104708

Contents lists available at ScienceDirect

International Journal of Coal Geology

journal homepage: www.elsevier.com/locate/coal



The effect of high pressure on hydrocarbon generation from Type-I kerogen source rocks: Implications for petroleum system evolution

Ahmed Khairy[a,b,*], Clement N. Uguna[a], Christopher H. Vane[c], Waleed Sh. El Diasty[d], Kenneth E. Peters[e], Colin E. Snape[a], Sherif Farouk[f], Will Meredith[a]

[a] *Low Carbon Energy and Resources Technologies Group, Faculty of Engineering, Energy Technologies Building, Triumph Road, University of Nottingham, Nottingham NG7 2TU, UK*

[b] *Geology Department, Faculty of Science, South Valley University, Qena 83523, Egypt*

[c] *British Geological Survey, Organic Geochemistry Facility, Keyworth, Nottingham NG12 5GG, UK*

[d] *Geology Department, Faculty of Science, Mansoura University, Mansoura 35516, Egypt*

[e] *Schlumberger NExT Training, Kentfield, CA 94904, USA*

[f] *Exploration Department, Egyptian Petroleum Research Institute, Nasr City 11727, Egypt*

ARTICLE INFO

Keywords:
Duwi Formation
Hydrous pyrolysis
High water pressure
Hydrocarbon generation
Sulphur content
Pressure retardation

ABSTRACT

This study examines the effect of high water pressure (up to 900 bar) on hydrocarbon generation from Type-I kerogen-rich source rocks and compares the results with previously observed effects on Type-II and Type-III kerogens. An immature Type-I oil shale sample from the Duwi Formation, Egypt, was pyrolysed under anhydrous, low-pressure hydrous, and high water-pressure conditions at 320 °C (end of bitumen generation) and 350 °C (oil window) for 6 and 24 h, respectively.

Pyrolysis at 320 °C showed that bitumen generation was promoted in the presence of water under low-pressure hydrous compared to anhydrous conditions but retarded at high water pressures. At 350 °C, oil generation was also retarded by increasing pressure, with maximum oil yield at 500 bar before dropping by 72% at 900 bar. Lower bitumen yields at 500 bar and higher yields at 900 bar confirm more retention of oil and bitumen in the rock at higher pressure. High water pressure systematically decreased hydrocarbon gas yields, with a more prominent effect at 320 °C because of temperature's dominant impact over pressure at 350 °C. Similarly, non-hydrocarbon gas yields decreased as water pressure increased, with maximum yields under anhydrous and low-pressure hydrous conditions. The retardation effect on bitumen generation was less significant than that on oil and gas generation.

This study highlights pressure's impact on petroleum generation, particularly in overpressured basins. Elevated pressures on Type-I kerogen source rocks retard oil expulsion, and the retained oil and bitumen within the rock can be directly cracked to gas, suggesting that under such conditions, oil yields may be lower, while unconventional gas resources are likely to be more abundant.

1. Introduction

Deeply buried source rocks in geological basins are affected by both high temperature and pressure. However, it was generally believed that pressure has minimal impact on source rock maturation and petroleum generation. Tissot and Welte (1984) stated that the exact role of pressure in petroleum generation is unclear and is likely subordinate to the influence of temperature. Stainforth (2009) reported that pressure has only a second-order effect on petroleum formation. However, recent exploration resulted in petroleum production from high-pressure, high-temperature (HPHT) strata in many basins worldwide. HPHT wells have extreme downhole conditions, including temperatures above 149 °C and pressures over 1,034 bar (Agwu et al., 2021). For instance, Chevron's Anchor project in the Gulf of Mexico successfully achieved oil production from ultra-high-pressure wells (up to ~1,300 bar), demonstrating the importance of understanding petroleum systems under such extreme conditions (Chevron, 2024; Falcon et al., 2024; Reuters, 2024; Sauer et al., 2024). This highlights the significance of this study in

---

* Corresponding author at: Low Carbon Energy and Resources Technologies Group, Faculty of Engineering, Energy Technologies Building, Triumph Road, University of Nottingham, Nottingham NG7 2TU, UK.

E-mail address: ahmed.khairy@nottingham.ac.uk (A. Khairy).

https://doi.org/10.1016/j.coal.2025.104708
Received 23 November 2024; Received in revised form 27 January 2025; Accepted 28 January 2025

investigating the effects of pressure on hydrocarbon generation, particularly in overpressured basins and HPHT conditions. Other examples of worldwide HPHT fields include the Victoria Field in the UK North Sea, which exhibits downhole pressures of 1,034 bar, while the Elgin-Franklin Field in the UK Central Graben records a downhole pressure of 1,100 bar. In the Gulf of Mexico, the downhole pressure of the Joseph HPHT gas well exceeds 1,724 bar (Agwu et al., 2021 and references therein).

Laboratory pyrolysis experiments are powerful tools to examine hydrocarbon generation and the maturation of source rocks within geological basins (e.g., Carr et al., 2009; Uguna et al., 2015, 2016a, 2016b). However, conflicting results were obtained by several experimental attempts to examine the influence of pressure on hydrocarbon generation and maturation based on various experimental procedures and different kerogen types. Several studies reported that high pressure has either no or a minor effect on petroleum generation and maturation (e.g., Monthioux et al., 1985, 1986; Freund et al., 1993; Michels et al., 1994; Huang, 1996; Knauss et al., 1997). In contrast, some authors reported an enhancing effect of high pressure on hydrocarbon generation (Shuai et al., 2006; Tao et al., 2010), while others concluded that high pressure retards the generation of hydrocarbons as well as the maturation of source rocks (e.g., Dominé, 1991; Price and Wenger, 1992; Hill et al., 1994; Landais et al., 1994; Michels et al., 1995; Dalla Torre et al., 1997; Wang et al., 2006). Uguna et al. (2012a) provided a detailed review of these studies, highlighting the conflicting nature of their findings. Data interpretation from geological basins also provided contradictory conclusions about the impact of pressure on petroleum generation and maturation. While some studies reported that pressure has no effect (Khorasani and Michelsen, 1994; He et al., 2002), other studies suggested that pressure retards hydrocarbon generation and maturation (Hao et al., 1995; McTavish, 1998; Zou and Peng, 2001; Huijun et al., 2004). Hao et al. (2007) reported that the retardation effect of overpressure varies across three Chinese basins, possibly due to differences in the volumes of volatiles produced by kerogen in each basin.

The confusion about the impact of pressure on petroleum generation mainly arises from variations in pyrolysis methods in addition to lack of consideration for the significance of the pressurising phase within the pyrolysis vessel (i.e., whether vapour or a fluid phase partially or completely fills the vessel, along with the pyrolysed sample) (Carr et al., 2009; Uguna et al., 2016b).

In geological basins, source rocks are typically water-saturated, and organic matter maturation occurs in the presence of water. Therefore, the role of water in laboratory pyrolysis experiments should not be underestimated (e.g., Lewan, 1997). Water contributes hydrogen, which promotes radical disproportionation reactions during petroleum generation. These reactions favour the aromatisation of organic matter and increase the expulsion of saturated hydrocarbons. In contrast, anhydrous conditions result in less aromatic and more cross-linked residues due to the absence of hydrogen (Hackley et al., 2022, 2025). Additionally, it is crucial to consider the physical properties of water. While vapour within the pyrolysis vessel can be compressed to accommodate the volume expansion produced during hydrocarbon generation, water is largely incompressible. As a result, retardation of reactions generally occurs under water-pressure pyrolysis conditions compared to those with compressible vapour.

High-pressure pyrolysis experiments based on vapour pressure and gold bags, in which the pyrolysed sample has no or limited contact with water, generally reported no or minimal evidence for pressure retardation of petroleum generation and maturation (Uguna et al., 2012a and references therein). High-pressure pyrolysis experiments utilising gold bags or capsules apply external pressure to the walls of the gold bag or capsule, with the pressurising medium not directly in contact with the pyrolysed sample. During pyrolysis, the generated liquid and gaseous products result in a volume increase, leading to the expansion of the gold bag or capsule because of the high flexibility of gold. Therefore, the internal pressure within the gold bag or capsule remains relatively constant and counteracts the externally employed pressure, with the walls of the gold bag acting as a pressure barrier. On the other hand, vapour-based pyrolysis methods, such as micro scale sealed vessel (MSSV, e.g., Erdmann and Horsfield, 2006) and hydrous pyrolysis (e.g., Lewan et al., 1979; Lewan, 1993), are affected by the compressibility of the vapour phase, which allows volume expansion compared to incompressible water.

Recent high water-pressure pyrolysis experiments conducted in closed autoclave vessels, where the pressurised water is directly in contact with the pyrolysed rock sample, revealed that pressure significantly retards source rock maturation and petroleum generation (e.g., Carr et al., 2009; Uguna et al., 2012a, 2016b). Applying this pyrolysis technique indicated that both temperature and pressure substantially control petroleum generation and maturation. While temperature increases thermal maturity and total hydrocarbon yields, pressure has the opposite or retardation effect. These experimental conditions are analogous to natural conditions in geological basins, with virtually no barrier acting against pressure. Because the pyrolysis vessel is filled with water, oil expulsion from the source rock is retarded (Uguna et al., 2016b), and gas yields are reduced due to the limited or absent vapour space available to accommodate the generated gaseous compounds (Uguna et al., 2012a).

Although high water-pressure pyrolysis experiments were performed on Type-II kerogen from Kimmeridge Clay (Carr et al., 2009; Uguna et al., 2012b), Type-III kerogen from Longannet and Svalbard coals (Uguna et al., 2012a, 2015), and Type-IIS kerogen from Monterey shale (Uguna et al., 2016b), no previous studies were conducted on source rocks enriched in Type-I kerogen. Thus, this study is the first to examine the impact of high water pressure (up to 900 bar) on hydrocarbon generation from rocks enriched in Type-I kerogen using an immature oil shale sample from the Duwi Formation, Eastern Desert, Egypt. Additional data were also provided on generated non-hydrocarbon gases and the sulphur content of the pyrolysed rock and generated oil. The outcomes of this study were compared with previously published data on Type-II and Type-III kerogens to determine whether similar trends occur. This study contributes to understanding Type-I kerogen source rocks and how pressure in geological basins impacts petroleum generation from these rocks.

2. Rock sample

An immature Type-I kerogen rock sample from the Duwi Formation was used in this study. The kerogen-type characterisation is based on bulk rock geochemistry (HI vs. OI) and is unrelated to the depositional environment (see Section 4.1). The sample was collected from El Nakheil underground phosphate mine in the Quseir area, Eastern Desert, along the Red Sea coast, Egypt. Due to mining activities, an unweathered rock sample was collected from a freshly exposed surface within the mine. The organic-rich black shale from the Duwi Formation at El Nakheil mine is classified as oil shale by several authors (e.g., El-Kammar, 2017; Barakat et al., 2019; Abou El-Anwar et al., 2024), with considerable economic potential due to its metalliferous and organic content (Makled et al., 2014; El-Kammar, 2017; Abou El-Anwar et al., 2024). These shales are generally immature with T_{max} and vitrinite reflectance (Ro) less than 430 °C and 0.40%, respectively (e.g., El-Kammar, 2017).

The proposed age of the investigated sample is Late Campanian-Early Maastrichtian (e.g., El Beialy, 1995; Makled et al., 2014). Based on visual kerogen analysis, previous studies reported that this interval is enriched with homogeneous, structureless marine amorphous organic matter (Makled et al., 2014). Previous organic petrographic investigations confirmed Type-I kerogen, consistent with organic geochemical parameters, and revealed high enrichment of liptinite (100%), consisting of alginite (63%), bituminite (22%), and liptodetrinite (15%) (Abou El-Anwar et al., 2024). Alginite is composed mainly of prasinophytes (telalginite), while bituminite was attributed to faecal pellets (Abou El-Anwar et al., 2024). However, Pickel et al. (2017) reported that zooplankton faecal pellets are unlikely to be the direct precursors of bituminite, as they contain only 1–4% organic carbon (Porter and Robbins, 1981). Therefore, bituminite in this interval is likely derived from the degradation of various organic precursors formed under predominantly anoxic and suboxic conditions. In addition to the absence of freshwater *Botryococcus*-related telalginite, the marine origin of the preserved organic matter was confirmed by the presence of sediment inclusions, primarily planktonic foraminifera, fish remains, and bivalve shells (Baioumy and Tada, 2005; Baioumy and Lehmann, 2017; Tahoun and Mohamed, 2020; Abou El-Anwar et al., 2024).

Based on geochemical and palynological evidence, these oil shale layers were deposited in highstand system tracts during periods of high palaeo-productivity and active upwelling (Makled et al., 2014; Tahoun and Mohamed, 2020). Redox-sensitive trace elements indicated that these layers were deposited in stratified and stagnant waters of the Tethys Sea, with oxygen-poor bottom conditions (Baioumy and Lehmann, 2017). The anoxic settings during the deposition of these shales resulted from high-productivity upwelling that lasted for approximately 20 million years along the southern Tethys (Baioumy and Tada, 2005; Baioumy and Lehmann, 2017). The organic-rich, highly oil-prone Duwi Formation is the primary source rock for discovered oil in the Gulf of Suez Basin (El Diasty and Peters, 2014; El Diasty et al., 2015, 2020).

3. Experimental methodology

3.1. Set-up experiments

The generation of thermogenic hydrocarbons from kerogen in source rocks, both in laboratory pyrolysis experiments and in geological basins, can be explained by three slightly overlapping stages (Erdmann and Horsfield, 2006; Sanei, 2020). These stages are (1) kerogen decomposition or cracking into a highly polar bitumen and gas; (2) bitumen cracking to produce oil and gas based on the specific kerogen type; and (3) oil cracking to gas and a carbon-rich residue.

To identify the maximum point of bitumen generation (end of stage 1) before oil expulsion, six initial pyrolysis experiments were carried out under low-pressure hydrous conditions, with 15 ml of water added to the reactor vessel, and temperatures of 300, 310, 320, 330, 340, and 350 °C for 6 h. Based on the results, the maximum point of bitumen generation was inferred to occur at 320 °C (6 h), while bitumen started to crack to oil at 330 °C (6 h). This conclusion was based on the absence of floating oil on the water surface in the reactor vessel at room temperature following pyrolysis at 320 °C.

3.2. Pyrolysis vessel and experimental procedure

A whole-rock sample was used for each pyrolysis experiment instead of isolated kerogen to mimic kerogen-mineral interactions during the maturation of source rocks (Eglinton et al., 1986; Carr et al., 2009). Four grams (ca. 0.77 g TOC) of the crushed, non-extracted rock sample (2–5 mm size) were used. This size range (2–5 mm) possibly enhances petroleum generation from the source rock compared to that expelled from larger masses in geological basins. Therefore, the term “oil yield” used in this study does not necessarily reflect the oil amount generated from source rocks in geological basins. The pyrolysis experiments were conducted using a 25 ml Hastalloy cylindrical pressure vessel, rated up to 1400 bar at 420 °C, connected to an Autoclave Engineers pressure gauge and rupture disc rated to 950 bar (Fig. 1), following the experimental technique outlined by Uguna et al. (2012a, 2015). For all experiments, the accuracy of the monitored temperature was ±1 °C. Results from duplicate runs for the anhydrous and 500-bar experiments at 350 °C for 24 h indicate that experimental error for calculated gas yields is ≤ 2%, while error for calculated bitumen and oil yields is ≤ 5% (Supplementary file). This is consistent with experimental error reported in previous studies employing the same experimental approach as this work (e.g., Carr et al., 2009).

Based on the initial experiments, the Duwi shale samples were pyrolysed under three conditions: anhydrous (no added water), low-pressure hydrous (110–160 bar), and high water-pressure (500, 700, and 900 bar) conditions. The experiments were conducted at 320 °C (end of bitumen generation) and 350 °C (oil-window generation) for 6 and 24 h, respectively. For low-pressure hydrous experiments, the

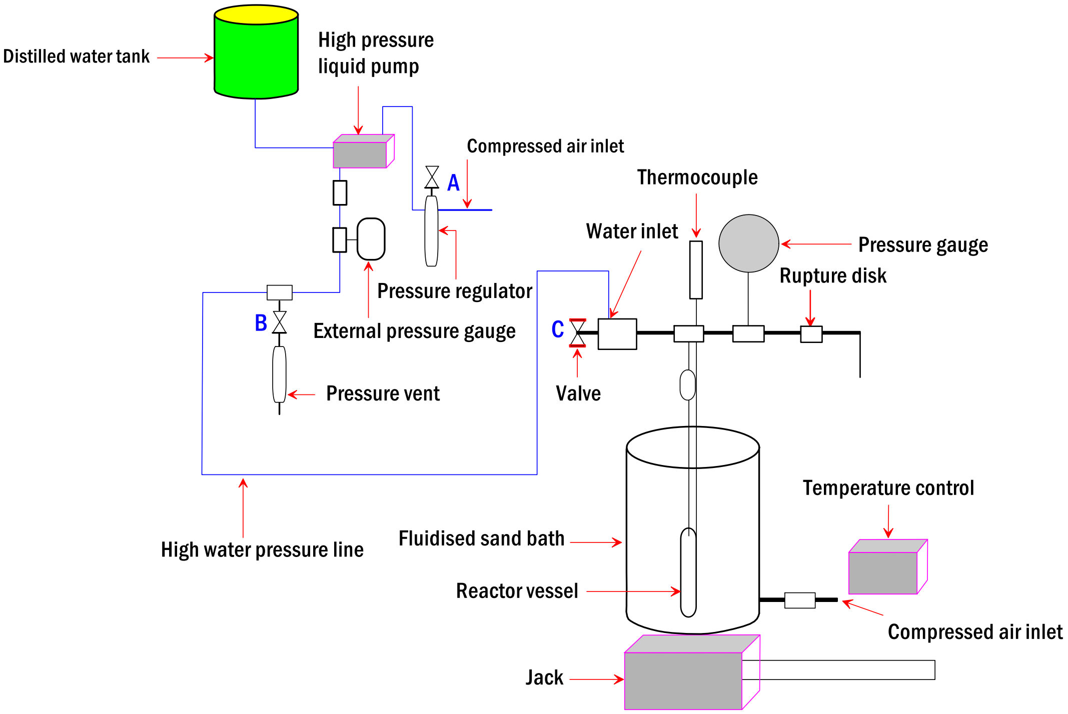


Fig. 1. Schematic diagram of pyrolysis equipment used in this study.

reactor vessel was filled with 15 ml of distilled water. The pressure was produced by the vapour pressure of the added water and the generation of gases from the cracking of organic matter, giving a final pressure of 110 bar at 320 °C and 160 bar at 350 °C. In contrast, for high water-pressure experiments (500–900 bar), 20 ml of distilled water was added to the vessel, which was not enough to produce the desired pressure; therefore, extra water was pumped into the reactor via an air-driven liquid pump (Fig. 1). Herein, the term hydrous pyrolysis is used to refer to pyrolysis experiments conducted in the presence of water, including low-pressure hydrous (110–160 bar) and high water-pressure (500, 700, and 900 bar) experiments. Anhydrous experiments were conducted to examine the effect of water on hydrocarbon generation during thermal maturation by comparing their results with the low-pressure hydrous pyrolysis experiments. Hydrous pyrolysis experiments in this study were conducted using distilled water. Further research is required to understand how using saline water in high water-pressure pyrolysis experiments may affect hydrocarbon generation under different pressure conditions.

Hydrostatic pressure in geological basins increases at a rate of ~100 bar/km (e.g., Pruess, 2005). Petroleum generation in these basins (hydrostatically pressured) typically occurs at pressures ranging from 200 to 500 bar and a depth interval of 2–5 km, assuming an average geothermal gradient of 30 °C/km to reach the temperature required for petroleum generation (i.e., 60–200 °C; Peters and Cassa, 1994). Consequently, the pressure (up to 500 bar) used in this study is analogous to that in geological basins during petroleum generation, corresponding to depths up to 5 km. On the other hand, experiments at 700–900 bar resemble burial depths of 7–9 km, which are beyond typical petroleum generation. These high pressures were used to investigate whether trends from lower-pressure experiments are continuous through high pressures. In addition, petroleum generation can occur at pressures up to 900 bar or higher in overpressured basins or those with lower geothermal gradients. For instance, in the Central Graben in the North Sea, Jurassic reservoirs can exhibit overpressures of up to 600 bar, with a hydrostatic pressure of 400 bar at a depth of 4 km. Consequently, the total pore pressure can reach ~1,000 bar in Jurassic source rocks (Uguna et al., 2016b). Another example is the Gulf of Mexico Basin, where pressure gradients in overpressured zones range from 158 to 226 bar/km (Burke et al., 2012). On the other hand, the experimental temperatures are significantly higher than those required for petroleum generation in geological basins, as hydrocarbon generation in geological basins typically occurs at temperatures <250 °C. This is because the reaction in the laboratory is required to occur within shorter duration, while under natural conditions, the process takes millions of years due to slower reaction rates at lower temperatures.

3.3. Gas analysis

After each pyrolysis experiment, the generated gaseous compounds were released and collected from the reactor vessel using a gas-tight syringe and then transferred to a gas bag after recording the volume of the collected gas. The generated gases were immediately analysed for hydrocarbon (C_1–C_5) and non-hydrocarbon gases using a Clarus 580 gas chromatograph (GC) equipped with a flame ionisation detector (FID) and a thermal conductivity detector (TCD), operating at 200 °C. The analysis of hydrocarbon gases was achieved by injecting 100 μl (split ratio 10:1) onto the FID at 250 °C, and the separation was achieved utilising an Rt-Alumina Bond/KCl Plot fused silica column (30 m × 0.32 mm × 5 μm). Helium was used as the carrier gas, and the instrument oven was heated at 10 °C/min from 60 (13 min hold) to 180 °C (10 min hold). Quantitative calculation of individual hydrocarbon (C_1–C_5) gas yields was achieved in relation to a separately injected (C_1–C_5) external gas standard. Analysis of non-hydrocarbon gases (H_2S, H_2, CO_2, and CO) was achieved by injecting 500 μl onto the TCD, and the separation was conducted using a Haysep N6 packed column (60–80, 7_ × 1/8_sulfinert) with argon as carrier gas. The instrument oven was heated from 60 °C (13 min hold) to 160 °C (2 min hold) at 10 °C/min. The yields of H_2S, H_2, CO_2, and CO were calculated in relation to their individual gas standards, which were injected separately as part of an external gas standard mixture.

3.4. Recovery of expelled oil, generated bitumen, and pyrolysed rock

After analysing the generated gas, the reactor vessel was disassembled. For 320 °C (6 h) experiments (where no oil was produced), the water in the vessel was carefully decanted. On the other hand, before decanting water from the 350 °C (24 h) experiments, the expelled floating oil on the water was collected by a spatula and recovered through rinsing with cold dichloromethane (DCM). Any oil adhering to the sides of the reactor walls or on the surface of the pyrolysed rock was also recovered by rinsing with cold DCM. All these three products were collectively described as expelled oil. The recovered expelled oil was then transferred to a pre-weighed glass vial, allowed to dry, and oil weight was recorded.

The pyrolysed rock was then dried in an oven at 45 °C for 24 h, and the weight of the dried sample was recorded. The bitumen and retained oil within the rock sample, collectively referred to as bitumen, were then recovered from the rock sample. Approximately 1.2 g of the dried rock was crushed and Soxhlet-extracted with 200 ml of methanol/DCM mixture (7:93 v/v) for 48 h at 40 °C. Rotary evaporation was used to separate the bitumen from the solvent. The extracted bitumen was then transferred to a pre-weighed vial and dried in a fume cupboard to ensure complete solvent removal. The weight of the extracted bitumen was recorded, and these values were used to calculate bitumen yields (mg/g TOC).

3.5. Rock-Eval pyrolysis

The extracted rock residues were analysed using Rock-Eval pyrolysis to determine the remaining hydrocarbon generative potential of each pyrolysed sample; therefore, the impact of pressure on hydrocarbon generation could be inferred, supporting the calculated oil, gas, and bitumen yield data. Rock-Eval analysis was conducted on ~60 mg of the pyrolysed extracted residues, applying the Basic/Bulk Rock method following the procedure of Behar et al. (2001). The analysis was conducted at the British Geological Survey (BGS), Nottingham, UK.

3.6. Sulphur analysis

The pyrolysed rock residues were analysed for total sulphur content (TS wt.%) using a LECO S628 instrument. Approximately 100–150 mg of the pulverised rock sample was weighed into a ceramic combustion boat and combusted in oxygen at 1350 °C. The sulphur oxidises to sulphur dioxide, which is then detected using infrared cells. Before analysis, 15 blanks were run, and the instrument was calibrated using 0.25 g of 502–677 coal standard (~1.14 wt.% sulphur). In addition, the initial rock sample was subjected to the kerogen isolation procedure (Traverse, 2007), and the total sulphur content was measured for both the initial rock sample and the isolated kerogen. Moreover, ~20–50 mg of each oil sample was transferred to a ceramic combustion boat by a spatula and analysed for sulphur content using the same instrument.

4. Results

4.1. Initial rock sample

The Rock-Eval pyrolysis and elemental analysis results for the initial non-extracted Duwi shale sample are presented in Table 1. The rock sample is thermally immature based on a T_{max} of 411 °C. The TOC and S_2 values are 19.16 wt.% and 138.75 mg HC/g rock, respectively, reflecting excellent organic richness and hydrocarbon generation potential (Peters and Cassa, 1994). The kerogen is Type-I oil-prone with an HI of 724 mg

Table 1

Elemental analysis and Rock-Eval pyrolysis results for the Duwi Formation initial non-extracted shale sample used in this study.

TOC	S_1	S_2	S_3	T_{max}	HI	OI	PI	TS	TS*
19.16	4.53	138.75	3.87	411	724	20	0.03	4.06	9.52

TOC = Total organic carbon (wt.%); S_1 = Free volatile hydrocarbons (mg HC/g rock); S_2 = hydrocarbons cracked from kerogen during pyrolysis (mg HC/g rock); S_3 = Carbon dioxide yield (mg CO_2/g rock); T_{max} = Oven temperature at maximum S_2 peak (°C); HI: Hydrogen index = $S_2 \times 100$/TOC (mg HC/g TOC); OI: Oxygen index = $S_3 \times 100$/TOC (mg CO_2/g TOC); PI = Production index = $S_1/(S_1 + S_2)$; TS = Total sulphur (wt.%) of the initial sample; TS* = Total sulphur (wt.%) of the isolated kerogen.

HC/g TOC (e.g., Peters and Cassa, 1994). However, the sample is enriched in sulphur, with a total sulphur content of 4.06 and 9.52 wt.% for the initial rock sample and isolated kerogen, respectively (Table 1). The high TOC value of the shale sample is attributed to the prevalent anoxic depositional environment, high palaeo-productivity rates, and low sedimentation rates (Makled et al., 2014).

4.2. Pyrolysis at 320 °C for 6 h

4.2.1. Gas yields

Table 2 presents the total hydrocarbon (C_1–C_5) gas yields (mg/g of initial rock TOC) generated by pyrolysis experiments at 320 °C for 6 h. The maximum total hydrocarbon (C_1–C_5) gas yield was obtained under anhydrous conditions (2.72 mg/g TOC; Table 2; Fig. 2a). Under low-pressure hydrous pyrolysis conditions (110 bar), the C_1–C_5 gas yield slightly decreased to 2.36 mg/g TOC (Table 2). Then, the gas yield systematically dropped with increasing water pressure, reaching a minimum value of 0.67 mg/g TOC at 900 bar (Table 2; Fig. 2a). Individual gas yields (Fig. 3a) indicate that alkene concentrations, particularly ethene and pentene, significantly dropped with increasing water pressure at 320 °C. Their yields were higher under both anhydrous and low-pressure hydrous conditions (110 bar), but they dropped significantly and became negligible at higher pressure (Table 2; Fig. 3a).

At 320 °C, gas generated from the anhydrous experiment displayed the lowest dryness ratio [$100 \times C_1 / (\Sigma C_1–C_5) = 58\%$], and the gas dryness increased slightly to 61% under low-pressure hydrous conditions (Table 2). The dryness of the generated gas generally increased as water pressure increased to 500–900 bar, varying from 67% to 70% (Table 2).

Individual yields of non-hydrocarbon gases are presented in Table 2. These gases follow the same trend as hydrocarbon gases, with maximum generation under anhydrous and low-pressure hydrous conditions and a general decrease in concentrations as water pressure increases (Table 2). Yields of H_2S and H_2 were most affected, showing a significant drop as pressure increased. Carbon dioxide is the dominant generated gas, except for the anhydrous experiment, where a considerable amount of H_2S was generated (Table 2). A significant decrease (~60%) in H_2S was observed for the low-pressure hydrous experiment (110 bar) compared to the anhydrous run, while the yields of all other non-hydrocarbon gases were similar under both experimental conditions. The pyrolysed residues have similar total sulphur contents for low-pressure hydrous and high water-pressure experiments (Table 3).

4.2.2. Bitumen yields

The extracted bitumen and expelled oil yields (mg/g of initial rock TOC) for the pyrolysis experiments are presented in Table 4 and Fig. 4a. Oil generation did not commence at 320 °C (6 h), and only bitumen was generated. The lowest bitumen yield was obtained under anhydrous conditions at 320 °C (505 mg/g TOC; Table 4; Fig. 4a). The bitumen yield reached a maximum value (579 mg/g TOC) under low-pressure hydrous conditions (110 bar), which is attributed to the promotional effect of water on bitumen generation (e.g., Lewan, 1997; Behar et al., 2003). When the water pressure increased to 500 bar, ~12% reduction in the generated bitumen was observed compared to the 110-bar experiment, with a bitumen yield similar to that obtained from the anhydrous experiment (507 mg/g TOC; Table 4). At 700 and 900 bar, bitumen yields increased slightly to 534 and 559 mg/g TOC, respectively, in comparison with the yield at 500 bar. Overall, the bitumen yield results (Table 4) show that more bitumen was generated in the presence of water at 110 bar compared to anhydrous conditions, while bitumen yields obtained at higher water pressures (500–900 bar) were generally lower than those at 110 bar. These results agree with previously published data (e.g., Uguna et al., 2012a, 2012b).

4.2.3. Rock-Eval pyrolysis

Table 5 shows the TOC and Rock-Eval pyrolysis results for extracted rock residues after each pyrolysis experiment. At 320 °C, the highest TOC and S_2 values were obtained from rock residues pyrolysed under anhydrous conditions (15.21 wt.% and 81.50 mg HC/g rock, respectively; Table 5). Under low-pressure hydrous conditions (110 bar), S_2 reached a minimum value (63.55 mg HC/g rock), indicating more remaining hydrocarbon generation potential under anhydrous conditions. S_2 values then increased with increasing pressure to 500–900 bar, ranging from 72.41 to 75.89 mg HC/g rock (Table 5), reflecting more remaining hydrocarbon generation potential at higher pressures compared to low pressure (110 bar). This is consistent with lower HI values at 110 bar (509 mg HC/g TOC) compared to those at high water-pressure conditions (Table 5). However, HI values do not display a consistent trend for high water-pressure experiments (500–900 bar). Similarly, hydrous pyrolysis at 320 °C resulted in residual TOC values that exhibited no significant change as pressure increased, ranging from 12.18 to 13.00 wt.% (Table 5). T_{max} values are similar under all experimental conditions, ranging from 426 to 427 °C (Table 5), and were not influenced by increasing pressure.

4.3. Pyrolysis at 350 °C for 24 h

4.3.1. Gas yields

Pyrolysis at 350 °C for 24 h generally produced higher individual and total gas yields (hydrocarbon and non-hydrocarbon gases) than the 320 °C, 6 h experiments (Table 2). Like experiments at 320 °C for 6 h, the maximum total (C_1–C_5) hydrocarbon gas yield was obtained under anhydrous conditions at 350 °C (21.67 mg/g TOC; Table 2; Fig. 2b). Unlike the 320 °C hydrous pyrolysis experiments, where the maximum total hydrocarbon gas yield was obtained at 110 bar, the maximum yield under hydrous conditions at 350 °C occurred at 500 bar (20.60 mg/g TOC; Table 2; Fig. 2b). With increasing water pressure at 350 °C, the hydrocarbon (C_1–C_5) gas yields decreased but less significantly than 320 °C experiments (Table 2), as the effect of pressure on gas generation becomes less significant with increasing temperature. Again, the concentrations of unsaturated alkenes dropped significantly with increasing water pressure (Table 2; Fig. 3b).

The gases generated from 350 °C, 24 h experiments were generally less dry compared to those from corresponding 320 °C experiments (Table 2) because more alkenes and heavier hydrocarbon gases were generated at 350 °C. With increasing maturity, the generated gases become more enriched in methane (drier); however, this trend is less evident in Type-I and Type-II kerogens compared to Type-III kerogen (Whiticar, 1994). Methane concentrations in gases generated by lab pyrolysis experiments are typically lower than those in natural gases impacted by fractionation processes that occur after hydrocarbon expulsion from source rocks (Price and Schoell, 1995). The anhydrous

Table 2

Hydrocarbon (C_1–C_5) and non-hydrocarbon gas yields (mg/g TOC of initial rock TOC) for the Duwi shale pyrolysis experiments at 320 and 350 °C for 6 and 24 h, respectively.

Experiment	Water pressure (bar)	Hydrocarbon gases (mg/g TOC)											Non-hydrocarbon gases (mg/g TOC)			
		Methane CH_4	Ethane C_2H_6	Ethene C_2H_4	Propane C_3H_8	Propene C_3H_6	Butane C_4H_{10}	Butene C_4H_8	Pentane C_5H_{12}	Pentene C_5H_{10}	$\sum C_1$–C_5	Gas dryness	H_2	H_2S	CO_2	CO
320 °C, 6 h	Anhydrous	1.57	0.38	0.01	0.23	0.15	0.12	0.14	0.06	0.06	2.72	58	2.88	16.64	14.07	0.01
	110	1.44	0.38	0.01	0.18	0.08	0.09	0.08	0.05	0.06	2.36	61	2.08	6.64	13.48	0.00
	500	0.54	0.13	<0.01	0.06	0.01	0.03	0.01	0.02	0.01	0.80	67	0.07	0.02	3.08	0.00
	700	0.52	0.11	<0.01	0.06	<0.01	0.03	0.01	0.01	<0.01	0.75	70	0.06	0.00	3.03	0.00
	900	0.46	0.10	<0.01	0.05	<0.01	0.03	<0.01	0.01	<0.01	0.67	69	0.07	0.00	1.89	0.00
350 °C, 24 h	Anhydrous	9.79	5.27	0.01	3.71	0.39	1.54	0.31	0.57	0.10	21.67	45	8.13	22.75	22.24	0.02
	160	8.04	3.63	0.01	1.78	0.31	0.80	0.28	0.32	0.15	15.32	52	10.43	6.07	24.80	0.00
	500	10.59	4.76	<0.01	2.67	0.11	1.55	0.15	0.68	0.09	20.60	51	2.87	5.36	22.56	0.00
	700	9.66	4.50	<0.01	2.58	0.07	1.63	0.11	1.00	0.09	19.64	49	2.30	6.23	22.68	0.00
	900	9.30	4.14	<0.01	2.22	0.05	1.33	0.08	0.74	0.06	17.93	52	1.85	5.80	21.68	0.00

Gas dryness = 100 × C_1 / (ΣC_1–C_5).

experiment showed the lowest dryness ratio (45%; Table 2), reflecting greater methane enrichment under hydrous conditions, in line with the results obtained at 320 °C. Unlike the 320 °C experiments, gas dryness showed no significant trend with increasing water pressure for low- and high water-pressure experiments at 350 °C, varying between 49% and 52% (Table 2).

Non-hydrocarbon gases follow the same trend for gases generated at 320 °C, with carbon dioxide being the most dominant gas apart from the anhydrous experiment, where similar quantities of H_2S and CO_2 were generated. Like hydrocarbon gases, increasing water pressure at 350 °C caused a less significant reduction in non-hydrocarbon gas yields, except for H_2 concentrations, which dropped by ~82% at 900 bar compared to the 160-bar experiment (Table 2). As observed at 320 °C, there is a considerable decrease in H_2S yield of 73% at 160 bar compared to higher concentrations from the anhydrous experiment (Table 2). However, the pyrolysed residues from different experiments display similar total sulphur content (Table 3). While the maximum total (C_1–C_5) yield of hydrocarbon gases was obtained at 500 bar, non-hydrocarbon gases reached their maximum yields under anhydrous and low-pressure hydrous conditions at 350 °C (Table 2).

4.3.2. *Bitumen and oil yields*

Hydrous pyrolysis at 350 °C for 24 h resulted in oil generation. The maximum yield of oil was obtained at 500 bar (209 mg/g TOC; Table 4; Fig. 4b), which then decreased systematically with increasing pressure, with a minimum oil yield of 59 mg/g TOC at 900 bar (Table 4; Fig. 4b). The decrease in oil yield was 25% and 72% at 700 and 900 bar, respectively, when compared to the yield at 500 bar. In contrast, bitumen yields increased significantly with increasing water pressure, with the lowest bitumen yield at 160 bar (358 mg/g TOC, Table 4) and the highest at 900 bar (555 mg/g TOC, Table 4). Unlike pyrolysis at 320 °C, the bitumen yield from the anhydrous experiment at 350 °C (648 mg/g TOC; Table 4; Fig. 4b) is generally higher than that for low-pressure hydrous and high water-pressure experiments. Additionally, bitumen yields at 350 °C are lower than corresponding yields at 320 °C, except for the anhydrous run, as bitumen started to crack to oil and gas at 350 °C. Furthermore, the total bitumen plus oil yield from hydrous pyrolysis at 350 °C reached a maximum value (639 mg/g TOC) at 500 bar due to maximum oil generation before decreasing with increasing pressure to 700 bar (Table 4). A slight increase in the total bitumen plus oil yield at 900 bar resulted from retention of more bitumen and oil in the rock (high bitumen yield). The generated oils are generally enriched in sulphur, with total sulphur (TS) contents varying from 4.68 to 15.94 wt.% (Table 3; Fig. 5). Although oils produced at 160–700 bar have similar TS values, the TS content nearly tripled at 900 bar (Fig. 5).

4.3.3. *Rock-Eval pyrolysis*

The TOC, S_2, and HI values for extracted pyrolysed residues at 350 °C for 24 h are lower than those from the corresponding 320 °C (6 h) experiments (Table 5). This reduction in the remaining source rock potential is attributed to the main phase of oil and gas generation occurring at 350 °C. On average, HI and S_2 values at 350 °C were reduced by ~72% and ~85%, respectively, compared to their values at 320 °C, as significant amounts of petroleum were generated.

The highest residual TOC and S_2 values were obtained at 160 bar (9.00 wt.% and 13.61 mg HC/g rock, respectively; Table 5) and then under anhydrous conditions (8.30 wt.% and 12.89 mg HC/g rock, respectively; Table 5). In contrast, high water-pressure experiments showed lower values, ranging from 4.58 to 5.82 wt.% for TOC and 7.18–9.53 mg HC/g rock for S_2. However, no obvious trend for residual TOC and S_2 was observed with increasing pressure for high water-pressure experiments (Table 5). Like the 320 °C results, HI values at 350 °C display no consistent trend with S_2 values as pressure increases.

The relationship between HI and S_2 values with increasing pressure and experiment duration is complex (Uguna et al., 2015). High S_2 and TOC values at 350 °C (160 bar) may have resulted from the presence of

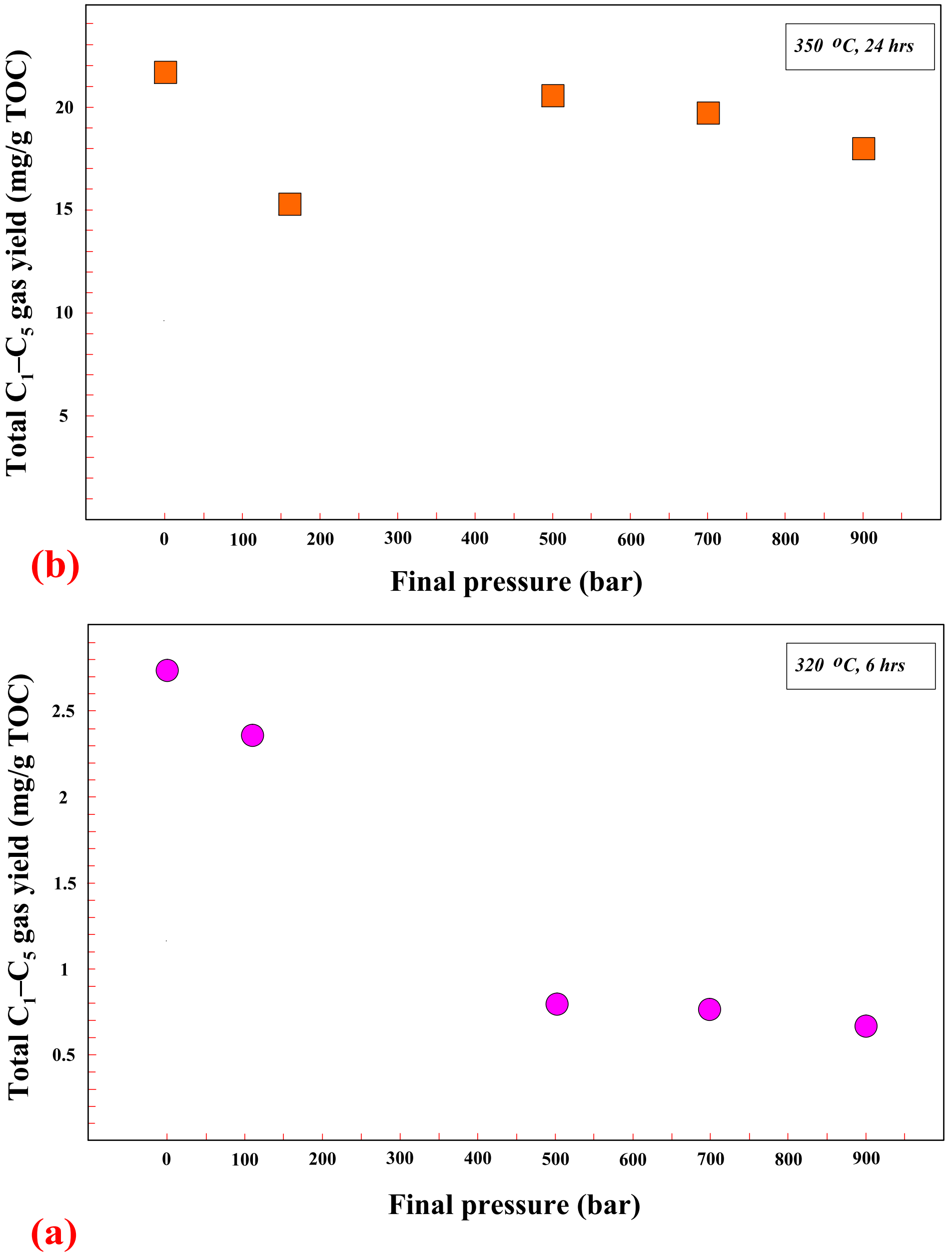


Fig. 2. Total hydrocarbon (C_1–C_5) gas yields (mg/g TOC of initial rock TOC) for pyrolysis experiments on the Duwi shale at (a) 320 °C for 6 h and (b) 350 °C for 24 h.

solid bitumen, residual secondary organic matter retained within the source rock, which formed as kerogen/bitumen undergoes thermal cracking to generate oil and gas. This solid bitumen contributes to the S_2 peak, as it can be partially or mostly insoluble in organic solvents such as dichloromethane, which was used to extract free bitumen from the pyrolysed rock. In contrast, high water-pressure conditions inhibit the formation of solid bitumen by retarding bitumen conversion to oil and, to a lesser extent, gas (Uguna et al., 2016b). While organic geochemists use the term pyrobitumen to describe secondary organic matter retained in source rocks, solid bitumen and pyrobitumen are the corresponding terms in organic petrography (Mastalerz et al., 2018). In addition to insolubility in organic solvents, petrographic observations are required to characterise a substance as pyrobitumen. Solid bitumen is formed due to kerogen-to-oil cracking in the oil window, while primary pyrobitumen results from secondary oil-to-gas cracking at higher maturity (gas window) (e.g., Mastalerz et al., 2018; Sanei, 2020). Therefore, this study uses the term solid bitumen to refer to secondary residual organic matter retained in the rock sample after pyrolysis experiments, as it is a broader term that can also encompass pyrobitumen when optical anisotropy is combined with insolubility. For more information about pyrobitumen versus solid bitumen terminology, the reader is referred to Mastalerz et al. (2018) and Sanei (2020).

T_{max} values at 350 °C (ranging from 444 to 447 °C) are higher than those for 320 °C experiments (426–427 °C) due to increasing thermal maturity from the immature to peak mature oil window (Peters and Cassa, 1994). Again, T_{max} values were not impacted by increasing experimental pressure. T_{max} is rarely useful as a maturity indicator for oil-prone Type-I kerogen because, unlike other kerogen types, it displays little or no change throughout the oil window (Espitalié et al., 1985; Huizinga et al., 1988; Peters and Cassa, 1994), suggesting that the chemical structure of Type-I kerogen is more homogeneous than that of Type-II and Type-III kerogens (Spigolon et al., 2015). Although vitrinite reflectance was not used to assess post-pyrolysis maturity in the current study, Peters et al. (2018) reported that high concentrations of liptinite-rich kerogen suppress vitrinite reflectance in artificial rock mixtures containing both vitrinite- and liptinite-rich kerogen. This suppression

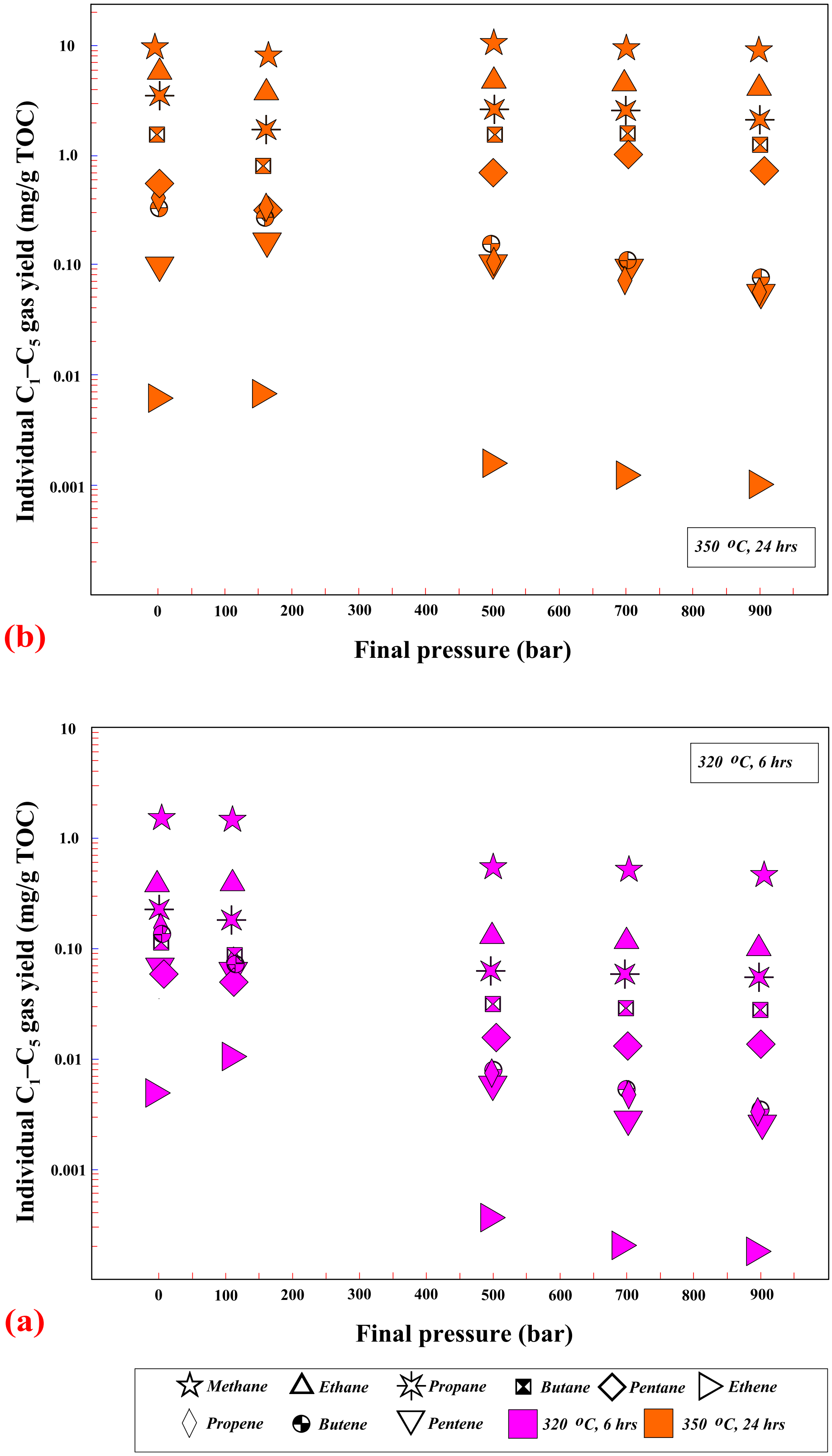


Fig. 3. Individual hydrocarbon (C_1–C_5) gas yields (mg/g TOC of initial rock TOC) for pyrolysis experiments on the Duwi shale at (a) 320 °C for 6 h and (b) 350 °C for 24 h.

was likely due to free radicals from bitumen and volatile products generated during maturation of liptinite-rich kerogen, which slow aromatisation reactions in vitrinite. However, the exact chemical mechanism is unclear. Additionally, Type-I kerogen typically has a narrow maturity range, with activation energy for major decomposition reactions ~50–55 kcal/mol, whereas Type-II kerogen displays broader and more complex reactivity, resulting in a wider maturity range for hydrocarbon generation due to structural and compositional differences

(Burnham et al., 2018).

Table 3
Total sulphur content (TS, wt.%) of the pyrolysed rock residues and expelled oil samples compared to the yield of the generated H_2S gas.

Experiment	Water pressure (bar)	H_2S (mg/g TOC)	S wt.% in pyrolysed residue	S wt.% in generated oils
320 °C, 6 h	Anhydrous	16.64	3.19	–
	110	6.64	2.91	–
	500	0.02	2.87	–
	700	0	2.74	–
	900	0	2.86	–
350 °C, 24 h	Anhydrous	22.75	2.26	–
	160	6.07	1.86	6.98
	500	5.36	2.04	4.68
	700	6.23	2.01	5.93
	900	5.80	2.13	15.94

5. Discussion

5.1. Effect of pressure on bitumen generation

Pyrolysis set-up experiments for the Duwi shale sample suggest that kerogen conversion into bitumen and gas reached a maximum at 320 °C for 6 h, marking the end of the bitumen generation stage. In contrast, pyrolysis at 350 °C for 24 h included the main stage of bitumen cracking to oil and gas. Therefore, only the pyrolysis experiments conducted at 320 °C for 6 h are discussed in this section, since at 350 °C, the generated bitumen was cracked to oil and gas.

At 320 °C, the lowest bitumen yield was obtained under anhydrous conditions (505 mg/g TOC) before reaching a maximum value (579 mg/g TOC) under low-pressure hydrous (110 bar) conditions. This is consistent with minimal residual S_2 values at 110 bar (63.55 mg HC/g rock), while maximum S_2 occurred under anhydrous conditions (81.50

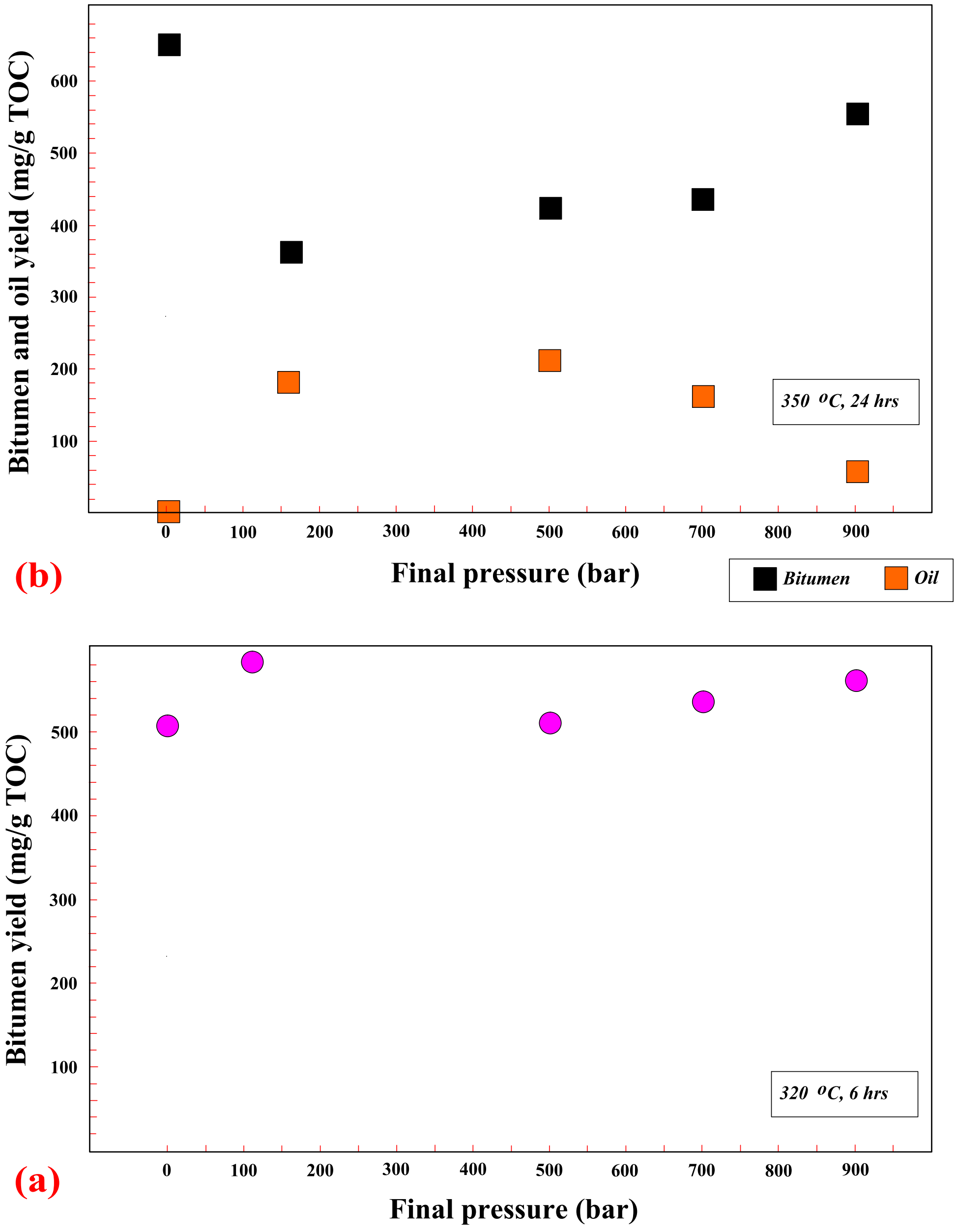


Fig. 4. Bitumen and oil yields (mg/g TOC of initial rock TOC) for pyrolysis experiments on the Duwi shale at (a) 320 °C for 6 h and (b) 350 °C for 24 h.

Table 4
Expelled oil and extracted bitumen yields (mg/g TOC of initial rock TOC) for the Duwi shale sample pyrolysis experiments at 320 and 350 °C for 6 and 24 h, respectively.

Experiment	Water pressure (bar)	Expelled oil (mg/g TOC)	Extracted bitumen (mg/g TOC)	Bitumen plus oil (mg/g TOC)
320 °C, 6 h	Anhydrous	0	505	505
	110	0	579	579
	500	0	507	507
	700	0	534	534
	900	0	559	559
350 °C, 24 h	Anhydrous	0	648	648
	160	175	358	533
	500	209	430	639
	700	157	436	594
	900	59	555	614

mg HC/g rock; Table 5). The significant increase in bitumen yield when experimental conditions changed from anhydrous to low-pressure hydrous is attributed to hydrogen in the added water that enhanced bitumen generation from kerogen. Several authors (e.g., Lewan, 1997; Behar et al., 2003; Carr et al., 2009) reported a similar increase in bitumen yield with changing pyrolysis experimental conditions from anhydrous to low-pressure hydrous. Carr et al. (2009) referred to this as the "chemical effect" of water, which involves hydrogen transfer from water to kerogen, facilitating bitumen generation from kerogen (Hoering, 1984; Lewan, 1997; Carr et al., 2009). This promotional effect of water on bitumen generation at 320 °C is not obvious for gas generation under the same experimental conditions (Section 5.3; Table 2).

The "chemical effect" of water discussed here is based on experiments with distilled water. More research is required to understand how water salinity affects bitumen generation before the oil window stage. Previous work investigated the influence of saline vs. distilled water on hydrocarbon yields during the main oil generation stage. For instance, Lewan (1997) observed that using a 5% NaCl solution during hydrous pyrolysis slightly increased expelled oil yields, while Wang et al. (2011) noted that natural seawater increased total gas yields compared to distilled water. Li et al. (2023) reported that saline formation water increases hydrocarbon yields at temperatures of 325–375 °C, likely by increasing water reactivity and enhancing kerogen decomposition. In contrast, He et al. (2018) reported lower gas yields with increasing salt concentrations in hydrous pyrolysis experiments. Hackley et al. (2025) compared the results of pyrolysis experiments using distilled water and brine solutions on oil shale from the Salt Range Formation. The results of four brine experiments were inconclusive, with no consistent differences observed in the geochemical and reflectance values of the pyrolysis product residues. This was attributed to either analytical error or using a

Table 5
TOC and Rock-Eval pyrolysis results for residual extracted Duwi shale samples pyrolysed at 320 and 350 °C for 6 and 24 h, respectively.

Experiment	Water pressure (bar)	TOC	S_1	S_2	S_3	T_{max}	HI	OI	PI
320 °C, 6 h	Anhydrous	15.21	0.34	81.50	1.41	426	536	9	0.00
	110	12.49	0.14	63.55	0.84	427	509	7	0.00
	500	12.18	0.27	72.41	0.70	427	594	6	0.00
	700	13.00	0.28	75.89	0.87	427	584	7	0.00
	900	12.97	0.13	75.04	0.73	426	579	6	0.00
350 °C, 24 h	Anhydrous	8.30	0.10	12.89	0.50	447	155	6	0.01
	160	9.00	0.14	13.61	0.59	446	151	7	0.01
	500	5.82	0.06	9.53	0.44	444	164	8	0.01
	700	4.58	0.07	7.18	0.48	444	157	10	0.01
	900	5.32	0.09	8.21	0.54	445	154	10	0.01

TOC = Total organic carbon (wt.%); S_1 = Free volatile hydrocarbons (mg HC/g rock); S_2 = hydrocarbons cracked from kerogen during pyrolysis (mg HC/g rock); S_3 = Carbon dioxide yield (mg CO_2/g rock); T_{max} = Oven temperature at maximum S_2 peak (°C); HI: Hydrogen index = $S_2 \times 100/TOC$ (mg HC/g TOC); OI: Oxygen index = $S_3 \times 100/TOC$ (mg CO_2/g TOC); PI = Production index = $S_1/(S_1 + S_2)$.

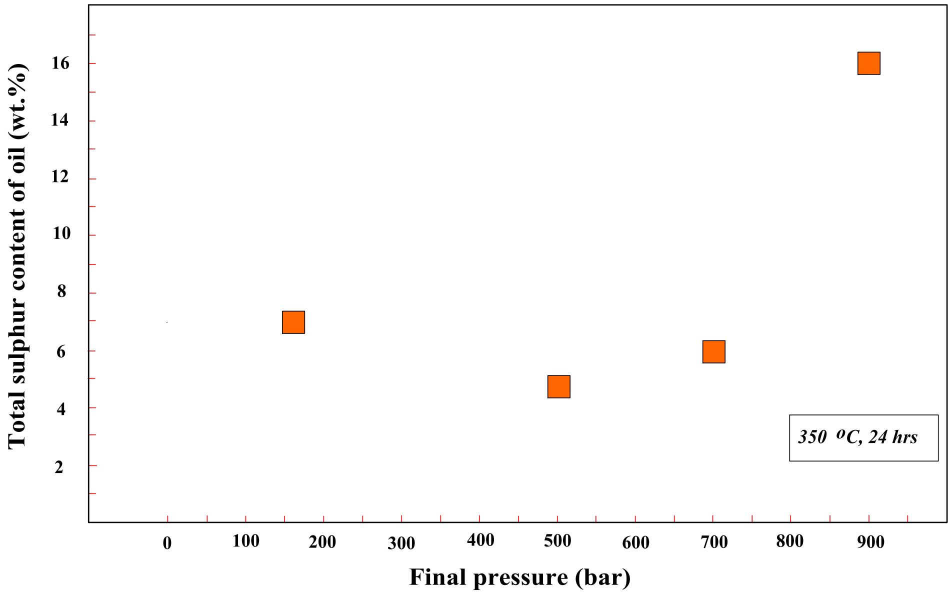


Fig. 5. Variation in total sulphur content (wt.%) for generated oil from pyrolysis experiments at 350 °C for 24 h.

lower salinity brine solution.

At 500 bar, the extracted bitumen yield was ∼12% lower than that at 110 bar, suggesting that higher pressure inhibits kerogen-to-bitumen conversion. However, bitumen yields increased by ∼5% and ∼10% when pressure increased from 500 bar to 700 and 900 bar, respectively (Table 4), possibly due to experimental error or sample heterogeneity. Although the samples for pyrolysis experiments were as homogeneous as possible, evidence indicates that vertical heterogeneity exists in the Duwi Formation. For example, organic petrography confirms that oil shales from the Duwi Formation at El Nakheil mine are heterogeneous. Fine and coarse lamination couplets were observed, resulting from variable mixing between organic matter and minerals. This coupling typically occurs when coarse particles of shell debris and planktonic foraminifera accumulate in layers within a fine-grained organic-rich matrix, reflecting possible cyclic changes in surface plankton productivity. Field observations confirmed the occurrence of such lamination with no evidence of bioturbation (Abou El-Anwar et al., 2024). Overall, lower bitumen yields observed at high pressures (500–900 bar) compared to 110 bar suggest that high water pressure retards bitumen generation (Table 4). This is further supported by higher S_2 and HI values (remaining hydrocarbon generation potential) obtained for high water-pressure (500–900 bar) rock residues compared to the 110-bar residue at 320 °C (Table 5), suggesting that high water pressure generally retards the conversion of kerogen to bitumen in the source rock. The lowest S_2 value (63.55 mg HC/g TOC) was displayed by the low-pressure hydrous (110 bar) pyrolysed extracted rock residue compared to the anhydrous and high water-pressure experiments (Table 5). In summary, pyrolysis results at 320 °C for 6 h indicate that bitumen generation was promoted by adding water under low-pressure hydrous compared to anhydrous conditions, while high water pressure retarded bitumen generation.

5.2. *Effect of pressure on oil generation*

The oil expelled during pyrolysis at 350 °C reached a maximum at 500 bar (209 mg/g TOC) before decreasing consistently with increasing water pressure to 700 bar and 900 bar (Table 4). The drop in oil yield was more significant at 900 bar, with a 72% reduction compared to its value at maximum oil generation at 500 bar. This indicates that high water pressure retarded bitumen-to-oil conversion or oil expulsion from source rocks enriched in Type-I kerogen. This is confirmed by extracted bitumen yields for hydrous experiments at 350 °C, where the highest yield (555 mg/g TOC; Table 4) was at 900 bar, indicating that more bitumen or oil was retained in the rock at higher pressure. In contrast, the lower bitumen yield (430 mg/g TOC; Table 4) at 500 bar was due to maximum oil generation. Overall, the opposite trend for bitumen and oil yields from high water-pressure experiments (500–900 bar) at 350 °C indicates that high pressure retards oil generation (Table 4; Fig. 4b). Anhydrous conditions at 350 °C did not favour oil generation and expulsion because of the absence of water, resulting in the highest bitumen yield (648 mg/g TOC; Table 4; Fig. 4b) compared to low-pressure hydrous and high water-pressure runs. In addition, the anhydrous experiment showed high S_2 (12.89 mg HC/g TOC) and residual TOC (8.30 wt.%; Table 5) compared to high water-pressure experiments due to the formation of more solid bitumen by crosslinking reactions under anhydrous conditions (e.g., Lewan, 1997).

Although oil generation was substantially retarded as pressure increased from 500 to 900 bar at 350 °C, there was no corresponding systematic increase in residual S_2 and HI values (Table 5). This could be a result of the high reactivity of kerogen within the source rock, where the retardation effect of pressure was considerable in the conversion of bitumen to oil but not significant in the kerogen conversion to bitumen. As a result, the residual hydrocarbon potential of the pyrolysed rock was not affected at 350 °C. This agrees with previously published data based on hydrous pyrolysis of Monterey shale at 350 °C and water pressure up to 900 bar (Uguna et al., 2016b). In geological basins, the amount of generated petroleum and maturation of source rock are controlled by the interaction between several parameters, including bitumen, source rock or kerogen type, mineral composition, reactant phase, and pressure (Uguna et al., 2013). S_2 was higher under anhydrous conditions at 350 °C, as such conditions do not favour oil generation and expulsion because of the absence of water. In addition, the formation of cross-linked solid bitumen is more likely under anhydrous conditions (e.g., Lewan, 1997), contributing to higher S_2 values. This solid bitumen is absent at higher pressure (700–900 bar), as high water-pressure conditions retard bitumen conversion to oil and inhibit the formation of solid bitumen (Uguna et al., 2015). Pyrolysis at 500 bar at 350 °C resulted in maximum oil and gas generation, with residual rock S_2 and TOC values lower than that obtained from pyrolysis at 160 bar (Table 5). In addition, the residual rock TOC and S_2 values were greater at 160 bar than at high water pressure (500–900 bar), possibly due to solid bitumen formation resulting from bitumen cracking within the source rock to oil and lighter bitumen. On the other hand, the lower oil yield at 160 bar compared to 500 bar (Table 5, Fig. 4b) may be due to enhanced oil generation at 500 bar, cracking of generated oil within the source rock into gas at 160 bar, or the loss of lighter hydrocarbons from bitumen and oil at 160 bar during product recovery.

The increase in bitumen yields caused by the retardation of oil generation with increasing water pressure should be combined with a reduction in residual rock TOC values (e.g., Uguna et al., 2016b), as high pressure retards bitumen conversion to oil and gas and prevents the formation of solid bitumen. This is reflected in the lower residual rock TOC values obtained between 500 and 900 bar compared to anhydrous conditions and 160 bar (Table 5), which suggests that solid bitumen formation was retarded at high pressures. For the anhydrous and 160-bar experiments at 350 °C, residual TOC likely reached minimum values like those observed at high water pressures before increasing again. This is because the anhydrous and 160-bar experiments probably proceeded at a faster rate than the high water-pressure runs, which were retarded by pressure. Similar findings were reported by (Uguna et al., 2016b) based on hydrous pyrolysis of Kimmeridge Clay (Type-II kerogen) at 350 °C for 24 h.

The significant retardation effect of pressure on oil generation and expulsion reported here for the Duwi shale is consistent with results obtained from source rock samples of Monterey shale and Kimmeridge Clay (Uguna et al., 2016b). This is because high pressure retards bitumen-to-oil conversion, and the presence of pressurised water inhibits the expulsion of oil from the rock, resulting in direct cracking of the generated bitumen and retained oil within the rock into gas, with catalytic clay minerals promoting gas generation. Therefore, greater gas yields were obtained at 500 to 900 bar at 350 °C, as will be discussed in Section 5.3.

The sulphur content of oil is a bulk parameter that reflects its quality and origin (Peters et al., 2005). This parameter measures both bound and free sulphur in the oil sample. The latter represents elemental sulphur dissolved in oil, whereas bound sulphur includes sulphur in organic compounds within crude oil (Dembicki, 2017). Sulphur content is commonly inversely related to API gravity. Sulphur tends to concentrate in the heavier fractions of oil, particularly the asphaltene fraction. As a result, high-sulphur oils are enriched in asphaltenes, which, along with the high density of sulphur atoms, contribute to their low API gravity (Waples, 1985).

Previous high water-pressure pyrolysis experiments did not investigate the impact of pressure on bulk properties (e.g., sulphur content) of the generated oil. The high sulphur content of the generated oils (4.68–15.94 wt.%; Table 3) is linked to the initial kerogen type, which has a total sulphur content of 9.52 wt.% (Table 1). Spigolon et al. (2015) reported that oil generated by hydrous pyrolysis of a Type-I kerogen source rock is more sulphur-rich than oil expelled from source rocks in geological basins. This could be due to shorter distances (centimetres) of migration in laboratory settings compared to natural conditions in geological basins, which may exaggerate sulphur contents of the generated oils (Spigolon et al., 2015). The significant change in sulphur content with increasing pressure from 700 to 900 bar could be due to the effect of pressure. Low-maturity oils contain more sulphur than mature oils because of thermal cracking of sulphur compounds in mature oils, while these compounds remain largely unaffected in low-maturity oils. Therefore, the high sulphur content of the 900-bar oil sample could be due to pressure that retards thermal cracking of the generated oil, allowing more sulphur compounds to be retained. This suggests that high pressure in geological basins can result in oil highly enriched in sulphur if the parent kerogen in the source rock is sulphur-rich. Uguna et al. (2016a) reported combination reactions during oil cracking under high water pressure, resulting in more asphaltene content. Although analytical error in the sulphur measurement reported here cannot be ruled out, these results are consistent with other geochemical parameters, such as higher asphaltene content of oil generated under high water pressures (Khairy et al., unpublished data). These observations align with studies that reported sulphur enrichment in oils from overpressured reservoirs. For instance, Jurassic Smackover oils from the northern Gulf of Mexico are enriched in sulphur (up to 3.7 wt.%; Kennicutt et al., 1992). The Puguang Gas Field in Sichuan Basin, China, is known for high-sulphur gas and oil, facilitated by overpressure and thick anhydrite cap rocks (Ma et al., 2024). Ping et al. (2020) proposed a formation mechanism for heavy, non-biodegraded oil in overpressured basins, involving the precipitation and retention of polar compounds from previously charged high-maturity oil due to intense pressure release during uplift. However, pressure reduction was not applied in the current experiments, as constant pressure was maintained throughout each run.

5.3. Effect of pressure on gas generation

Maximum (C_1–C_5) gas generation was achieved under anhydrous conditions at both 320 and 350 °C (Table 2). This was due to the absence of water and the availability of enough space in the reactor vessel to accommodate the volume expansion required for gas generation from the direct conversion of kerogen to bitumen as well as the cracking of bitumen into gas. On the other hand, hydrous pyrolysis at 320 and 350 °C resulted in gas yields maximising at low-pressure hydrous (110 bar) and 500 bar, respectively, with a systematic decrease as water pressure increased (Table 2; Fig. 2). This reflects the retardation effect of pressure on gas generation and is consistent with previously published data (Carr et al., 2009; Uguna et al., 2012a, 2012b). The most significant reduction in gas yield occurred as the pressure increased from 110 to 500 bar and beyond at 320 °C (Table 2). Under low-pressure hydrous conditions (110 bar), a water-vapour mixture exists in the vessel, and the available free vapour space can easily accommodate more quantities of the generated gases. Conversely, there is no available vapour space at 500 bar and above, where the reactor is completely filled with water, and therefore gas generation was retarded. The retardation effect on gas generation is more significant when compared to that on bitumen generation, consistent with previously reported data (Uguna et al., 2012a, 2015). This could be related to the difference in volume expansion needed to accommodate the generated gases and bitumen. Gases have a higher volume and lower density than bitumen. Therefore, gases require more energy than bitumen to displace the surrounding water at high pressure. Consequently, pressure has a more pronounced retardation effect on gas generation (Uguna et al., 2012a, 2015). This may explain why sample heterogeneity could impact bitumen generation more than gas generation, as the former is less retarded with increasing water pressure.

Alkenes were most impacted by increasing pressure (Fig. 3) at both 320 and 350 °C. This may be related to the hydrogenation of alkenes into alkanes, as hydrogen is transferred from water to kerogen and/or the suppression of alkene generation at high pressure, where reaction pathways that produce alkenes are inhibited by high pressure. Another explanation could be that high water pressure favours the addition of free radicals to alkenes to produce branched short-chain alkanes. The significant reduction in alkene concentrations as pressure increases might explain the absence of alkene gases in natural gas generated in geological basins under water pressure conditions.

At 320 °C, gas from the anhydrous experiment showed the lowest dryness ratio (58%), which increased slightly to 61% under low-pressure hydrous conditions (Table 2). As water pressure increased to 500–900 bar, dryness ratios increased further, ranging from 67% to 70% (Table 2). This is due to less generation of heavy hydrocarbon gases at higher pressure, and the generated gas becomes more depleted in alkenes. In contrast, at 350 °C, generated gas is less dry, and gas dryness was not affected by increasing pressure (Table 2). This is likely due to bitumen cracking to oil at 350 °C, resulting in the generation of wet heavier gases.

The decrease in total (C_1–C_5) gas yields was more obvious at 320 °C (Fig. 2). The total gas yield at 350 °C showed only a 13% reduction when the pressure increased from 500 to 900 bar compared to a 72% drop in gas yield with increasing pressure from 110 to 900 bar at 320 °C (Table 2). This could be due to the dominant impact of temperature over pressure at 350 °C. Therefore, high pressure, up to 900 bar, was not sufficient to substantially retard gas generation from the Duwi shale at 350 °C. Since gases have a lower viscosity than oil, they can escape from the rock more easily. Thus, pressure has not significantly impacted gas generation, while oil expulsion was retarded because of its higher viscosity. This is consistent with previously published data which indicated that high pressure has less retardation impact on gas generation and a significant impact on oil generation and expulsion (Uguna et al., 2012b, 2016b).

Uguna et al. (2013) reported that gas yields and vitrinite reflectance values were higher for pyrolysis experiments using whole rock samples than those using isolated partially matured source rock, isolated bitumen, or a mixture of both. This indicates that interactions between source rock/kerogen, bitumen, and the mineral composition of the rock facilitate both gas generation and source rock maturation. High temperatures promote clay-mineral catalytic effects and provide an additional mechanism for gas generation through clay-mineral and kerogen/bitumen interactions (e.g., He et al., 2022). Previous studies from the Duwi Formation confirmed the enrichment of clay minerals such as montmorillonite and kaolinite. A strong positive correlation was reported between SiO_2 and Al_2O_3, revealing that most Al_2O_3 is present in clay minerals (Abou El-Anwar et al., 2024). These catalytic effects of clay minerals also enhance oil cracking, especially at high temperatures (He et al., 2022). At high pressures, the retardation of oil generation and expulsion led to the retention of oil and bitumen in the reacted rock, which could be directly cracked into gas and gasoline when clay minerals are present. Therefore, in geological basins, an oil-prone source rock could be a shale gas reservoir (Uguna et al., 2016b). Additionally, the retardation effect of pressure is influenced by sample reactivity, with the effect being less pronounced for highly reactive source rocks (i.e., rock samples enriched in sulphur).

The yields of non-hydrocarbon gases were also lower as water pressure increased, with maximum yields obtained under anhydrous and low-pressure hydrous conditions at both 320 and 350 °C. Generally, the reduction of non-hydrocarbon gas yields was more significant at 320 °C (Table 2).

The yields of H_2S decreased by 60% and 73% at 320 and 350 °C, respectively, going from anhydrous to low-pressure hydrous conditions. However, total sulphur contents are similar for residues pyrolysed under different experimental conditions (Table 3), suggesting that changes in H_2S concentrations are due to its solubility in water at room temperature rather than a pressure retardation effect. At 320 °C, less H_2S was generated compared to 350 °C. Therefore, most of the generated H_2S from high water-pressure pyrolysis (500–900 bar) at 320 °C dissolved in water, resulting in negligible H_2S yields (Table 2). In contrast, the water became saturated with sulphur in the 350 °C experiments due to the generation of more H_2S, with H_2S yields varying from 5.36 to 6.23 mg/g

TOC in the 500–900 bar experiments. At 350 °C, some of the generated H_2S gas at high pressure could also be retained in the oil phase in addition to water, providing another explanation of sulphur enrichment in oil generated at 900 bar.

Similar CO_2 yields were obtained from anhydrous and low-pressure hydrous (110 bar) experiments at 320 °C (Table 2). The decrease in CO_2 yields at high pressure at 320 °C may be a consequence of solubility in water and/or a pressure retardation effect. At 350 °C, the CO_2 yields are similar for all experiments, except for the 160-bar experiment, which is slightly higher (Table 2). The reduced effect of pressure or water on CO_2 yields at 350 °C is due to temperature becoming dominant. In addition, carbonate minerals contribute to the generation of CO_2, and probably more CO_2 was generated at 160 bar and higher water pressure. Therefore, the water became over-saturated with CO_2, resulting in more CO_2 in the gas component.

5.4. Comparisons of high water-pressure pyrolysis of Type-I, -II, and -III kerogen source rocks

With increasing maturity, TOC could be decreased by 12–20 wt.% for Type-III kerogen and up to 70 and 50 wt.% for Type-I and Type-II kerogen, respectively (Daly and Edman, 1987). In this study, the reduction in TOC for extracted residues pyrolysed at 350 °C under different experimental conditions is in the range of 53–76% compared to the initial sample. Pyrolysis at 350 °C for 24 h and pressures up to 900 bar resulted in a decrease in TOC by 63–83% for Kimmeridge Clay (Type-II kerogen) and 55–57% for Monterey shale (Type-IIS kerogen) samples (Table 6; Uguna et al., 2016b).

At 350 °C, the 13% reduction in gas yield at 900 bar compared to maximum gas generation at 500 bar for the Duwi Formation Type-I kerogen is significantly lower than reductions for other kerogen types reported in previous studies that applied the same experimental approach (Table 6). For example, reductions in gas yields at 900 bar compared to maximum yields at ~180 bar were reported at 46% for Type-II kerogen (Kimmeridge Clay), 56% for Type-IIS kerogen (Monterey shale), and between 54% and 57% for Type-III kerogen (Longannet and Svalbard coals) (Uguna et al., 2012a, 2016b).

At 350 °C, the 72% reduction in oil yield at 900 bar reported here for Type-I kerogen from the Duwi Formation is greater than that reported for Type-II kerogen from Kimmeridge Clay (61%) and Type-IIS from Monterey shale (33%; Table 6). Moreover, at 350 °C, maximum oil and gas generation for the investigated sample (Type-I kerogen) occurred at 500 bar, while maximum generation occurred at 180 bar for Kimmeridge Clay and Monterey shale samples (Uguna et al., 2016b). However, pyrolysis of these two samples at 380 °C for 24 h resulted in maximum oil and gas generation at 500 bar (Uguna et al., 2016b). Interestingly, a reverse relationship can be observed between the reduction in oil yield and gas generation at 900 bar during pyrolysis of different rock samples at 350 °C for 24 h (Table 6). For example, pyrolysis of the Duwi shale (Type-I kerogen) resulted in the highest reduction in oil yield at 900 bar (72%), while gas generation was less affected, with only a 13% reduction in gas yield at 900 bar compared to maximum gas generation at 500 bar. In contrast, Monterey shale showed the lowest reduction in oil yield at 900 bar (33%) combined with a significant decrease in gas yield (56%) compared to maximum gas generation at 180 bar. This suggests that retained oil in the pyrolysed rock significantly contributes to gas generation at high pressures in the presence of clay minerals. It also indicates that Type-I kerogen Duwi Formation could be a potential shale gas reservoir in the Red Sea Basin, Egypt, if other key parameters for shale gas systems are present.

5.5. Implications for petroleum systems

This study improves the current understanding of the process of hydrocarbon generation from source rocks in geological basins, particularly in overpressured basins. The outcomes of this study indicate that pressure, temperature, and time collectively exert significant control on petroleum generation from source rocks. While the utilised pyrolysis technique operates at higher temperatures to simulate long-term petroleum generation in geological basins, source rocks under natural basin conditions are impacted by much lower temperatures, with similar or higher pressures in overpressured basins. This suggests that the retardation effect of pressure on hydrocarbon generation and expulsion may be more pronounced in geological settings than in experimental conditions.

This study reveals that high water pressure systematically retards hydrocarbon generation and expulsion. High water pressure retards oil, gas, and bitumen generation, with more effect of pressure on oil generation. The retardation effect of pressure on gas generation was more evident at lower temperatures (320 °C), suggesting a similar impact of pressure in geological basins with low geothermal gradients or in overpressured basins, where pressure could be more dominant. The significant reduction of alkenes during pyrolysis experiments explains why alkene gases are absent in natural gas generated in geological basins under water pressure conditions.

For Type-I kerogen-rich source rocks, high water pressure retards the conversion of bitumen to oil and inhibits the subsequent oil expulsion. This results in higher bitumen and oil retention in the source rock and increases the potential for secondary cracking of retained oil and bitumen to gas, facilitated by catalytic clay minerals. Unexpelled petroleum can also enhance the hydrocarbon potential of the source rock in the gas window, explaining how oil-prone source rocks can be unconventional shale gas reservoirs under natural conditions in geological basins if other key parameters are present. This highlights the role of pressure in controlling hydrocarbon generation and accumulation in geological basins. In addition, high water-pressure conditions may enhance the sulphur content of generated oils when the parent kerogen is enriched in sulphur. This is likely because high pressure inhibits thermal cracking of generated oils, allowing the retention of sulphur compounds. However, longer migration distances under natural conditions might also result in lower sulphur content in oil expelled from source rocks in geological basins. These insights are critical for understanding petroleum systems in geological basins. Retarded oil expulsion and enhanced gas generation at high pressures closely replicate

Table 6
Comparison between hydrous (low- and high-pressure) pyrolysis results of the Duwi shale (this study) and those of Monterey shale, Kimmeridge Clay, Svalbard, and Longannet rock samples (Uguna et al., 2012a, 2016b).

Rock Sample	Kerogen Type	Initial TOC wt.%	Pressure of maximum gas and oil generation	Reduction in gas yield at 900 bar compared to maximum generation	Reduction in oil yield at 900 bar compared to maximum generation	Reduction in TOC compared to the initial sample
Monterey shale	IIS	13.18	180 bar	**56%**	**33%**	**55–57**
Kimmeridge Clay	II	30.40	180 bar	**46%**	**61%**	**63–83%**
Duwi shale (this study)	I	19.16	500 bar	**13%**	**72%**	**53–76%**
Longannet coal	III	69.90	175 bar (gas only)	**57%**	**Not generated**	**ND**
Svalbard coal	III	78.50	175 bar (gas only)	**54%**	**Not generated**	**ND**

conditions in overpressured basins. Under such conditions, oil expulsion decreases significantly, while unconventional gas resources and high-sulphur oils could be more common than previously thought.

In Egypt, the Duwi Formation emerges as a significant focus for exploration in the under-explored Red Sea Basin. Although successful exploration has been elusive, the Egyptian Red Sea remains an area of high promise, and more work is required to understand its petroleum systems (e.g., Dolson, 2020). Challenges include navigating the deep-water column, managing abnormally high pressures and temperatures, and overcoming poor seismic imaging due to the thick Miocene evaporite cover (Noureldin et al., 2025). It is generally believed that the northern part of the Red Sea is a continuation of the Gulf of Suez petroleum system; however, offshore drilled wells in the Egyptian Red Sea (only 12 wells at the time of this writing) did not encounter the Duwi Formation or any pre-Miocene strata (Gordon et al., 2010), possibly due to off-structure drilling (Noureldin et al., 2025). This study emphasises the potential of the Duwi Formation not only as an oil source but also as a candidate for unconventional gas exploration. Under high-pressure conditions, this formation may retain more unexpelled bitumen and oil, increasing the likelihood of gas generation at optimum thermal maturity.

6. Conclusions

An immature Type-I oil shale sample from the Duwi Formation, Eastern Desert, Egypt, was pyrolysed under anhydrous, low-pressure hydrous (110–160 bar), and high water-pressure (500–900 bar) conditions at 320 °C (end of bitumen generation) and 350 °C (oil-generation window) for 6 and 24 h, respectively. The aims were to examine the effect of high water pressure on hydrocarbon generation from source rocks enriched in Type-I kerogen and to investigate whether these findings are consistent with that previously observed in rocks enriched in Type-II and Type-III kerogens.

Pyrolysis at 320 °C for 6 h showed that bitumen generation was promoted in the presence of water under low-pressure hydrous compared to anhydrous conditions, while high water pressure retarded it. High water pressure also retarded oil generation at 350 °C, with maximum generation at 500 bar before dropping by 72% at 900 bar. High water pressure retarded bitumen-to-oil conversion or oil expulsion from the rock, as confirmed by lower bitumen yields at 500 bar and higher yields at 900 bar, reflecting the retention of more bitumen or oil in the rock sample at higher pressures. At 350 °C, the retardation effect of pressure on oil generation from the Duwi Formation Type-I kerogen is more significant than that previously reported for Type-II and Type-IIS kerogens. The retained oil in the rock at 900 bar could be directly cracked into gas in the presence of clay minerals. This may explain why gas generation from the investigated Type-I kerogen rock sample was less affected by water pressure compared to Type-II, Type-IIS, and Type-III rock samples pyrolysed under the same conditions at 350 °C for 24 h.

Maximum hydrocarbon gas generation occurred under anhydrous conditions at 320 and 350 °C, while pyrolysis in the presence of water at these temperatures produced maximum gas yields at 110 and 500 bar, respectively. As water pressure increased, hydrocarbon gas yields decreased systematically, especially for alkenes, reflecting the retardation effect of high pressure on hydrocarbon gas generation. The decrease was more pronounced at 320 °C because of the dominant effect of pressure over temperature, and the retardation effect on gas generation was more significant than that on bitumen generation.

The generated oil at 900 bar is more enriched in sulphur than oil from lower-pressure experiments. This could be due to (1) pressure retarding thermal cracking of the generated oil, which allows more sulphur compounds to be retained; (2) combination reactions during oil cracking under high water pressure that result in more asphaltene and sulphur content; and (3) retention of some generated H_2S as sulphur at 900 bar in the oil phase in addition to its solubility in water.

The results of this study indicate that high pressure in geological basins impacts petroleum generation from Type-I kerogen source rocks. While high pressure reduces the efficiency of conventional oil expulsion, it enhances the potential for gas systems and unconventional gas resources. These findings contribute to a better understanding of the petroleum systems of the under-explored Egyptian sector of the Red Sea Basin. The Duwi Formation should not only be regarded as a source of oil but also as a potential candidate for unconventional gas exploration, particularly in overpressured areas of the basin. Under such conditions, this formation may retain more unexpelled bitumen and oil, increasing the likelihood of gas generation at optimum thermal maturity.

The pressure effect may be more pronounced in overpressured basins or in basins with low geothermal gradients. Additionally, temperatures in geological basins are much lower than experimental temperatures used in this study. Therefore, the impact of pressure on hydrocarbon generation will be more significant in geological basins than reported in this study. While the elevated experimental temperatures used in this study accelerate reactions that naturally occur over millions of years in geological basins, they do not substantially affect the calculated hydrocarbon yields. Thus, the relative effects of pressure on hydrocarbon generation observed in this study remain applicable to natural conditions in geological basins and may be more significant in overpressured basins.

CRediT authorship contribution statement

Ahmed Khairy: Writing – review & editing, Writing – original draft, Validation, Software, Methodology, Investigation, Conceptualization. **Clement N. Uguna:** Writing – review & editing, Validation, Supervision, Methodology, Conceptualization. **Christopher H. Vane:** Writing – review & editing, Supervision. **Waleed Sh. El Diasty:** Writing – review & editing, Supervision. **Kenneth E. Peters:** Writing – review & editing, Supervision. **Colin E. Snape:** Supervision. **Sherif Farouk:** Resources. **Will Meredith:** Writing – review & editing, Supervision, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Funding for Rock-Eval pyrolysis was provided by the British Geological Survey (BGS) NC programme (Organic Geochemistry Facility), reference NE4699S, with permission for publication granted by the Director of the BGS. Financial support for this study was also provided by the Egyptian Ministry of Higher Education and Scientific Research, through the Egyptian Bureau for Cultural and Educational Affairs in London. The authors thank the editor-in-chief, Prof. Deolinda Flores, Dr. George Siavalas, Shell Global Solutions International, and an anonymous reviewer for their insightful reviews and constructive comments, which improved the quality of this manuscript.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.coal.2025.104708.

Data availability

Data will be made available on request.

References

Abou El-Anwar, E., Salman, S., Makled, W., Mousa, D., Gentzis, T., Shazly, T.F., 2024. Depositional mechanism of Duwi Formation organic-rich rocks in anoxic Campanian-early Maastrichtian condensed sections in the Qusseir–Safaga region in Eastern Desert of Egypt and their economic importance. Mar. Pet. Geol. 163, 106759.

Agwu, O.E., Akpabio, J.U., Ekpenyong, M.E., Inyang, U.G., Asuquo, D.E., Eyoh, I.J., Adeoye, O.S., 2021. A comprehensive review of laboratory, field and modelling studies on drilling mud rheology in high temperature high pressure (HTHP) conditions. J. Nat. Gas Sci. Eng. 94, 104046.

Baioumy, H., Lehmann, B., 2017. Anomalous enrichment of redox-sensitive trace elements in the marine black shales from the Duwi Formation, Egypt: Evidence for the late Cretaceous Tethys anoxia. J. Afr. Earth Sci. 133, 7–14.

Baioumy, H., Tada, R., 2005. Origin of Late Cretaceous phosphorites in Egypt. Cretac. Res. 26, 261–275.

Barakat, M.A., Abd El-Gawad, E.A., Gaber, M.A.W., Lotfy, M.A., Abd El Ghany, A.A., 2019. Mineralogical and geochemical studies of oil shale deposits in the Cretaceous/Paleogene succession at Quseir Area, Egypt. Egypt. J. Pet. 28, 11–19.

Behar, F., Beaumont, V., Penteado, H.D.B., 2001. Rock-Eval 6 technology: Performances and developments. Oil Gas Sci. Technol. 56, 111–134.

Behar, F., Lewan, M.D., Lorant, F., Vandenbroucke, M., 2003. Comparison of artificial maturation of lignite in hydrous and nonhydrous conditions. Org. Geochem. 34, 575–600.

Burke, L.A., Kinney, S.A., Dubiel, R.F., Pitman, J.K., 2012. Regional map of the 0.70 psi/ft pressure gradient and development of the regional geopressure-gradient model for the onshore and offshore Gulf of Mexico basin, USA. GCAGS J. 1, 97–106.

Burnham, A.K., Pomerantz, A.E., Gelin, F., 2018. Oil, bitumen, and other confusing concepts: What do lab experiments really tell us? AAPG Bull. 102, 653–669.

Carr, A.D., Snape, C.E., Meredith, W., Uguna, C., Scotchman, I.C., Davis, R.C., 2009. The effect of water pressure on hydrocarbon generation reactions: some inferences from laboratory experiments. Pet. Geosci. 15, 17–26.

Chevron, 2024. Chevron starts production at Anchor with industry-first deepwater technology. https://www.chevron.com/newsroom/2024/q3/chevron-starts-production-at-anchor-with-industry-first-deepwater-technology.

Dalla Torre, M., Ferreiro Mählmann, R., Ernst, W.G., 1997. Experimental study on the pressure dependence of vitrinite maturation. Geochim. Cosmochim. Acta 61, 2921–2928.

Daly, A.R., Edman, J.D., 1987. Loss of organic carbon from source rocks during thermal maturation (abstract). AAPG Bull. 71, 546.

Dembicki, H., 2017. Practical Petroleum Geochemistry for Exploration and Production. Elsevier, p. 331.

Dolson, J., 2020. The petroleum geology of Egypt and history of exploration. In: Hamimi, Z., El-Barkooky, A., Martínez Frías, J., Fritz, H., Abd El-Rahman, Y. (Eds.), The Geology of Egypt. Springer, pp. 635–658.

Dominé, F., 1991. High pressure pyrolysis of *n*-hexane, 2,4-dimethylpentane and 1-phenylbutane. Is pressure an important geochemical parameter? Org. Geochem. 17, 619–634.

Eglinton, T.I., Rowland, S.J., Curtis, C.D., Douglas, A.G., 1986. Kerogen-mineral reactions at raised temperatures in the presence of water. Org. Geochem. 10, 1041–1052.

El Beialy, S.Y., 1995. Campanian-Maastrichtian palynomorphs from the Duwi (Phosphate) Formation of the Hamrawein and Umm El Hueitat mines, Red Sea Coast, Egypt. Rev. Palaeobot. Palynol. 85, 303–317.

El Diasty, W.Sh., Peters, K.E., 2014. Genetic classification of oil families in the central and southern sectors of the Gulf of Suez, Egypt. J. Pet. Geol. 37, 105–126.

El Diasty, W.Sh., El Beialy, S.Y., Mostafa, A.R., Abo Ghonaim, A.A., Peters, K.E., 2015. Crude oil geochemistry and source rock potential of the Upper Cretaceous–Eocene succession in the Belayim oilfields, Central Gulf of Suez, Egypt. J. Pet. Geol. 38, 193–215.

El Diasty, W.Sh., El Beialy, S.Y., Mostafa, A.R., Abo Ghonaim, A.A., Peters, K.E., 2020. Chemometric differentiation of oil families and their potential source rocks in the Gulf of Suez. Nat. Resour. Res. 29, 2063–2102.

El-Kammar, A., 2017. Oil shale resources in Egypt: the present status and future vision. Arab. J. Geosci. 10, 439.

Erdmann, M., Horsfield, B., 2006. Enhanced late gas generation potential of petroleum source rocks via recombination reactions: Evidence from the Norwegian North Sea. Geochim. Cosmochim. Acta 70, 3943–3956.

Espitalié, J., Deroo, G., Marquis, F., 1985. La pyrolyse Rock-Eval et ses applications. Deuxième partie. Rev. de l`Institut français du Pétrole 40, 755–784.

Falcon, R., Braun, C., Klaus, K., Shinde, S., Wu, G., Rodriguez, I., 2024. Anchor Project: Best practices and lessons from detailed design through fabrication of the Anchor FPU. In: Offshore Technology Conference. https://doi.org/10.4043/35076-MS.

Freund, H., Clouse, J.A., Otten, G.A., 1993. Effect of pressure on the kinetics of kerogen pyrolysis. Energy Fuel 7, 1088–1094.

Gordon, G., Hansen, B., Scott, J., Hirst, C., Graham, R., Grow, T., Spedding, A., Fairhead, S., Fullarton, L., Griffin, D., 2010. The hydrocarbon prospectivity of the Egyptian North Red Sea basin. Geol. Soc. London, Petrol. Geol. Conf. Series 7, 783–789.

Hackley, P.C., Jubb, A.M., Smith, P.L., McAleer, R.J., Valentine, B.J., Hatcherian, J.J., Botterell, P.J., Birdwell, J.E., 2022. Evaluating aromatization of solid bitumen generated in the presence and absence of water: Implications for solid bitumen reflectance as a thermal proxy. Int. J. Coal Geol. 258, 104016.

Hackley, P.C., Valentine, B.J., McAleer, R., Hatcherian, J.J., Nedzweckas, J.L., McDevitt, B., Khan, I., 2025. Evaluation of solid bitumen created from marine oil shale bituminite under hydrous and anhydrous pyrolysis conditions. J. Anal. Appl. Pyrolysis 186, 106881.

Hao, F., Sun, Y., Li, S., Zhang, Q., 1995. Overpressure retardation of organic-matter maturation and petroleum generation: A case study from the Yinggehai and Qiongdongnan basins, South China Sea. AAPG Bull. 79, 551–562.

Hao, F., Zou, H., Gong, Z., Yang, S., Zeng, Z., 2007. Hierarchies of overpressure retardation of organic matter maturation: Case studies from petroleum basins in China. AAPG Bull. 91, 1467–1498.

He, S., Middleton, M., Kaiko, A., Jiang, C., Li, M., 2002. Two case studies of thermal maturity and thermal modelling within the overpressured Jurassic rocks of the Barrow Sub-basin, North West Shelf of Australia. Mar. Pet. Geol. 19, 143–159.

He, K., Zhang, S., Mi, J., Zhang, W., 2018. Pyrolysis involving *n*-hexadecane, water and minerals: Insight into the mechanisms and isotope fractionation for water-hydrocarbon reaction. J. Anal. Appl. Pyrolysis 130, 198–208.

He, M., Wang, Z., Moldowan, M.J., Peters, K., 2022. Insights into catalytic effects of clay minerals on hydrocarbon composition of generated liquid products during oil cracking from laboratory pyrolysis experiments. Org. Geochem. 163, 104331.

Hill, R.J., Jenden, P.D., Tang, Y.C., Teerman, S.C., Kaplan, I.R., 1994. Influence of pressure on pyrolysis of coal. In: Mukhopadhyay, P.K., Dow, W.G. (Eds.), Vitrinite Reflectance as a Maturity Parameter: Applications and Limitations. American Chemical Society Symposium Series, pp. 161–193.

Hoering, T.C., 1984. Thermal reactions of kerogen with added water, heavy water and pure organic substances. Org. Geochem. 5, 267–278.

Huang, W.L., 1996. Experimental study of vitrinite maturation: effects of temperature, time, pressure, water, and hydrogen index. Org. Geochem. 24 (2), 233–241.

Huijun, L., Tairan, W., Zongjin, M., Wencai, Z., 2004. Pressure retardation of organic maturation in clastic reservoirs: a case study from the Banqiao Sag, Eastern China. Mar. Pet. Geol. 21, 1083–1093.

Huizinga, B., Aizenshtat, Z., Peters, K., 1988. Programmed pyrolysis-gas chromatography of artificially matured Green River kerogen. Energy Fuel 2, 74–81.

Kennicutt, M.C., McDonald, T.J., Comet, P.A., Denoux, G.J., Brooks, J.M., 1992. The origins of petroleum in the northern Gulf of Mexico. Geochim. Cosmochim. Acta 56, 1259–1280.

Khorasani, G.K., Michelsen, J.K., 1994. The effects of overpressure, lithology, chemistry and heating rate on vitrinite reflectance evolution, and its relationship with oil generation. APPEA J. 34, 418–436.

Knauss, K.G., Copenhaver, S.A., Braun, L., Burnham, A.K.R., 1997. Hydrous pyrolysis of New Albany and Phosphoria Shales: production kinetics of carboxylic acids and light hydrocarbons and interactions between the inorganic and organic chemical systems. Org. Geochem. 27, 477–496.

Landais, P., Michels, R., Elie, M., 1994. Are time and temperature the only constraints to the simulation of organic matter maturation? Org. Geochem. 22, 617–630.

Lewan, M.D., 1993. Laboratory Simulation of Petroleum Formation. In: Engel, M.H., Macko, S.A. (Eds.), Organic Geochemistry: Principles and Applications. Springer, US, Boston, MA, pp. 419–442.

Lewan, M.D., 1997. Experiments on the role of water in petroleum formation. Geochim. Cosmochim. Acta 61, 3691–3723.

Lewan, M.D., Winters, J.C., McDonald, J.H., 1979. Generation of oil-like pyrolyzates from organic-rich shales. Science 203, 897–899.

Li, S., Guo, X., Zheng, L., Han, Y., 2023. Semi-closed hydrous pyrolysis of type I source rock using formation water: Implications for biomarker behaviour under supercritical conditions. Mar. Pet. Geol. 158, 106510.

Ma, Y., Cai, X., Li, M., Li, H., Zhu, D., Qiu, N., Pang, X., Zeng, D., Kang, Z., Ma, A., Shi, K., Zhang, J., 2024. Research advances on the mechanisms of reservoir formation and hydrocarbon accumulation and the oil and gas development methods of deep and ultra-deep marine carbonates. Pet. Explor. Dev. 51, 795–812.

Makled, W.A., Mostafa, T.F., Maky, A.B.F., 2014. Mechanism of Late Campanian–Early Maastrichtian oil shale deposition and its sequence stratigraphy implications inferred from the palynological and geochemical analysis. Egypt. J. Pet. 23, 427–444.

Mastalerz, M., Drobniak, A., Stankiewicz, A.B., 2018. Origin, properties, and implications of solid bitumen in source-rock reservoirs: A review. Int. J. Coal Geol. 195, 14–36.

McTavish, R.A., 1998. The role of overpressure in the retardation of organic matter maturation. J. Pet. Geol. 21, 153–186.

Michels, R., Landais, P., Philp, R.P., Torkelson, B.E., 1994. Effects of pressure on organic matter maturation during confined pyrolysis of Woodford kerogen. Energy Fuel 8, 741–754.

Michels, R., Landais, P., Torkelson, B.E., Philp, R.P., 1995. Effects of effluents and water pressure on oil generation during confined pyrolysis and high-pressure hydrous pyrolysis. Geochim. Cosmochim. Acta 59, 1589–1604.

Monthioux, M., Landais, P., Monin, J.-C., 1985. Comparison between natural and artificial maturation series of humic coals from the Mahakam Delta, Indonesia. Org. Geochem. 8, 275–292.

Monthioux, M., Landais, P., Durand, B., 1986. Comparison between extracts from natural and artificial maturation series of Mahakam Delta coals. Org. Geochem. 10, 299–311.

Noureldin, A.M., Hassan, M., Farouk, M., Mabrouk, W.M., Radwan, A.E., Metwally, A., 2025. Hydrocarbon potential in the Northern Egyptian Red Sea: insights from geophysical datasets and analysis of onshore marginal outcrop analogues and subsurface sequences. Sci. Rep. 15, 1198.

Peters, K.E., Cassa, M.R., 1994. Applied source rock geochemistry. In: Magoon, L.B., Dow, W.G. (Eds.), The Petroleum System – From Source to Trap, vol. 60. AAPG Memoir, pp. 93–120.

Peters, K.E., Walters, C.C., Moldowan, J.M., 2005. The Biomarker Guide, Second edition. Cambridge University Press, Cambridge, p. 1155.

Peters, K.E., Hackley, P.C., Thomas, J.J., Pomerantz, A.E., 2018. Suppression of vitrinite reflectance by bitumen generated from liptinite during hydrous pyrolysis of artificial source rock. Org. Geochem. 125, 220–228.

Pickel, W., Kus, J., Flores, D., Kalaitzidis, S., Christanis, K., Cardott, B.J., Misz-Kennan, M., Rodrigues, S., Hentschel, A., Hamor-Vido, M., Crosdale, P., Wagner, N., ICCP, 2017. Classification of liptinite – ICCP System 1994. Int. J. Coal Geol. 169, 40–61.

Ping, H., Li, C., Chen, H., George, S.C., Gong, S., 2020. Overpressure release: Fluid inclusion evidence for a new mechanism for the formation of heavy oil. Geology 48, 803–807.

Porter, K.G., Robbins, E.I., 1981. Zooplankton fecal pellets link fossil fuel and phosphate deposits. Science 212, 931–933.

Price, L.C., Schoell, M., 1995. Constraints on the origins of hydrocarbon gas from compositions of gases at their site of origin. Nature 378, 368–371.

Price, L.C., Wenger, L.M., 1992. The influence of pressure on petroleum generation and maturation as suggested by aqueous pyrolysis. Org. Geochem. 19, 141–159.

Pruess, K., 2005. Numerical studies of fluid leakage from a geologic disposal reservoir for CO_2 show self-limiting feedback between fluid flow and heat transfer. Geophys. Res. Lett. 32 (14), L14404. https://doi.org/10.1029/2005GL023250.

Reuters, 2024. Chevron delivers industry first in ultra-high pressure oil field. https://www.reuters.com/business/energy/chevron-delivers-industry-first-ultra-high-pressure-oil-field-2024-08-12/.

Sanei, H., 2020. Genesis of solid bitumen. Sci. Rep. 10, 15595.

Sauer, S., White, R.D., Varnado, M., Wilhelmi, J., 2024. Anchor Project: Processes, lessons and challenges from developing 20K subsea equipment. Offshore Technol. Conferen. https://doi.org/10.4043/35256-MS.

Shuai, Y., Peng, P., Zou, Y., 2006. Influence of pressure on stable carbon isotope ratio and production yield of coal-derived methane. Fuel 85, 860–866.

Spigolon, A.L.D., Lewan, M.D., de Barros Penteado, H.L., Coutinho, L.F.C., Mendonça Filho, J.G., 2015. Evaluation of the petroleum composition and quality with increasing thermal maturity as simulated by hydrous pyrolysis: A case study using a Brazilian source rock with Type I kerogen. Org. Geochem. 83-84, 27–53.

Stainforth, J.G., 2009. Practical kinetic modeling of petroleum generation and expulsion. Mar. Pet. Geol. 26, 552–572.

Tahoun, S.S., Mohamed, O., 2020. Distribution of peridiniacean dinoflagellate cysts from cores of organic rich shales of the Duwi and Dakhla formations of Egypt. J. Afr. Earth Sci. 170, 103892.

Tao, W., Zou, Y.-R., Carr, A., Liu, J., Peng, P., 2010. Study of the influence of pressure on enhanced gaseous hydrocarbon yield under high pressure–high temperature coal pyrolysis. Fuel 89, 3590–3597.

Tissot, B.P., Welte, D.H., 1984. Petroleum Formation and Occurrence, Second edition. Springer-Verlag, Berlin, p. 699.

Traverse, A., 2007. Paleopalynology, Second edition. Springer, Dordrecht, p. 813.

Uguna, C.N., Carr, A.D., Snape, C.E., Meredith, W., Castro-Díaz, M., 2012a. A laboratory pyrolysis study to investigate the effect of water pressure on hydrocarbon generation and maturation of coals in geological basins. Org. Geochem. 52, 103–113.

Uguna, C.N., Snape, C.E., Meredith, W., Carr, A.D., Scotchman, I.C., Davis, R.C., 2012b. Retardation of hydrocarbon generation and maturation by water pressure in geologic basins: An experimental investigation. In: Peters, K.E., Curry, D.J., Kacewicz, M. (Eds.), Basin Modelling: New Horizons in Research and Applications, vol. 4. AAPG Hedberg Series, pp. 19–37.

Uguna, C.N., Azri, M.H., Snape, C.E., Meredith, W., Carr, A.D., 2013. A hydrous pyrolysis study to ascertain how gas yields and the extent of maturation for a partially matured source rock and bitumen in isolation compared to their whole source rock. J. Anal. Appl. Pyrolysis 103, 268–277.

Uguna, C.N., Carr, A.D., Snape, C.E., Meredith, W., 2015. High pressure water pyrolysis of coal to evaluate the role of pressure on hydrocarbon generation and source rock maturation at high maturities under geological conditions. Org. Geochem. 78, 44–51.

Uguna, C.N., Carr, A.D., Snape, C.E., Meredith, W., 2016a. 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. Org. Geochem. 97, 61–73.

Uguna, C.N., Carr, A.D., Snape, C.E., Meredith, W., Scotchman, I.C., Murray, A., Vane, C. H., 2016b. Impact of high water pressure on oil generation and maturation in Kimmeridge Clay and Monterey source rocks: Implications for petroleum retention and gas generation in shale gas systems. Mar. Pet. Geol. 73, 72–85.

Wang, C., Du, J., Wang, W., Xie, H., Chen, G., Duan, Y., Zhou, X., 2006. Experimental study to confirm the existence of hydrocarbon under high pressure and temperature of deep lithosphere. Chin. Sci. Bull. 51, 1633–1638.

Wang, X., Liu, W., Xu, Y., Zheng, J., 2011. Influences of water media on the hydrogen isotopic composition of natural gas/methane in the processes of gaseous hydrocarbon generation and evolution. Sci. China Earth Sci. 54, 1318–1325.

Waples, D.W., 1985. Geochemistry in Petroleum Exploration: Boston. International Human Resources and Development Corporation, p. 232.

Whiticar, M.J., 1994. Correlation of natural gases with their sources. In: Magoon, L.B., Dow, W.G. (Eds.), The Petroleum System–From Source to Trap, vol. 60. AAPG Memoir, pp. 261–283.

Zou, Y-R., Peng, P., 2001. Overpressure retardation of organic-matter maturation: a kinetic model and its application. Mar. Pet. Geol. 18 (6), 707–713.