Reconsideration of the pre-1970 model for the timing of oil expulsion from source rocks

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Abstract

The current model for oil expulsion occurring at 120-150°C by anhydrous pyrolysis is inconsistent with both the total organic carbon (TOC) content of subsurface source rocks and the chemical attributes of shallow oils. New data from North Sea Upper Jurassic source-rock samples show no decline in TOC between 120 and 150°C, which is a key prediction by the current model for oil expulsion. Instead, it is proposed here that oil expulsion occurs mainly at around 30°C at depths <1 km, similar to models advocated prior to 1970. Expulsion is suggested to be facilitated by CO_2 gas generated from decomposing organic matter. Migration out of the source rock and into nearby high-permeable pathways occurs in the direction towards decreasing overburden/rock pressure via horizontal fractures that originate from swelling of load-bearing organic laminae. The thermally immature (heavy) oil is then converted to light oil within reservoirs by hydrogenation at 60-70°C. Hydrogen gas is common in subsurface fluids and is released by coalification of organic matter in mudstones in amounts sufficient to hydrogenate the reservoired heavy oil volumes. In this model, most heavy oil accumulations are interpreted as immature rather than the products of low-temperature biodegradation or partial evaporation of mature oil.

1. Introduction

The problem of when, how, and where hydrocarbons are generated in sedimentary basins has been debated throughout most of the 20th century. Prior to 1970, most geologists believed that oil was expelled from organic-rich mudstones early in their burial history in an immature state (Van Tuyl and Parker, 1947; Hedberg, 1964; Dott and Reynold, 1969), and that the resins and asphaltene non-hydrocarbons (NSOs) were converted to paraffinic hydrocarbons in reservoir rocks during burial (Banks, 1934; McNab et al., 1952). It was also believed that most hydrocarbons formed at temperatures well below 100°C (Hedberg, 1964).

This early timing of oil expulsion from source rocks was based on observations made by field geologists who were involved in the discovery of most of the worlds giant oil fields, including most of the major North American accumulations (Wilson, 2005). It was recognized that early-formed traps commonly contain oil while those formed later often did not (Scholten, 1959; Banks, 1966). The oil was believed to migrate laterally into reservoirs from local source rocks (Van Tuyl and Parker, 1941; Gester, 1947; Hedberg, et al., 1947; Hedberg, 1964; Dott and Reynolds, 1969), which meant that early structuring and trap formation was considered critical (Hedberg, 1954; Weeks, 1958; Scholten, 1959; Banks 1966).

Early oil expulsion and the role of local source rocks was documented by Hedberg et al. (1947) in their classic study of the shallow Tertiary Greater Oficina basins in eastern Venezuela, where oil in the individual lenticular sands varies in gravity, colour, gas content, wax content, sulphur, and other characteristics, including gravities that range from less than 10° to 57°API. These differences could, according to Weeks (1956), only be explained by different source materials for the oil. Likewise, Teas and Miller (1933) concluded that, in the Gutoskey lenticular sand zone of the Raccoon Bend field in Texas, expulsion was completed prior to 600 m of burial, suggesting that the 14° to 34° API oil variability (and other differences) was due to differences in local source rock material (see also Wilson, 1990 for a review on early oil expulsion).

These early oil explorers were not able to develop a viable explanation for how viscous bituminous oil was transported out of source rocks and into reservoirs (Erdman, 1965; Hedberg 1964). In addition, artificial thermal maturation of these immature oils in laboratory experiments always led to the precipitation of significant amounts of (pyro)-bitumen, which is normally not observed in reservoirs containing light oil (Connan et al., 1975; Rogers et al., 1974). These two deficiencies in the pre-1970 model paved the way for a new and mainly laboratory-based ~~(~~geo~~)~~chemical compromise model (Hunt, 1979) for generation of hydrocarbons within source rocks, typically between 50 and 130°C and peaking at around 90°C, from which today’s model (Mackenzie and Quigley, 1988; Pepper and Corvie, 1995) was developed. Since the late 1980s, geochemists and geologists have assumed that in most sedimentary basins, hydrocarbons are generated within organic-rich mudstones at temperatures higher than 100°C and expelled in a mature and light state at temperatures ranging between 120 and 150°C (Mackenzie and Quigley, 1988). Heavy oil accumulations (Meyer et al., 2007) are generally thought to be the residue of these light oils where most of the paraffins with less than 30 carbon atoms have been removed by bacteria at reservoir temperatures < 70°C (Evans et al., 1971; Milner et al., 1977; Head et al. 2003).

Today's model for generation and expulsion of oil (referred to here as the high-temperature model) is based on laboratory analysis. During high-temperature (> 400°C), anhydrous pyrolysis of source rock samples 10 to 80% of the organic carbon is converted to hydrocarbons (Tissot et al., 1971; 1974; Ishiwatari et al., 1977; Quigley and Mackenzie, 1988; Baskin, 1997). Whereas the Rock-Eval results (Ishiwatari et al., 1977) have been extensively compared between laboratories (Price and McNeil, 1997), the theoretical predictions have not been sufficiently corroborated with subsurface observations (e.g., Price and McNeil, 1997). Notably, it has not been shown that the total amount of organic carbon (TOC) decreases in source rocks as implied by the laboratory-based model (Peters and Cassa, 1994).

This paper highlights some subsurface observations that conflict with the high-temperature model. A TOC dataset from Norwegian North Sea marine (Type II) source rocks (Figure 1) and published data from pooled oil are more consistent with the earlier models (e.g., Hedberg, 1964).

2. Objections to today's model for generation and expulsion of oil

Figure 1 shows TOC analyses of 871 samples from the Upper Jurassic Draupne Formation source rock (Kimmeridge Clay Formation equivalent in the Norwegian North Sea) at burial depths of 3.5 to 4.5 km, roughly corresponding to 120-150°C. The median curve for TOC fluctuates around 5% throughout the whole interval and does not decline within the predicted oil expulsion window (Okiongbo et al., 2005; Okiongbo, 2011). Publications describing TOC variation with depth in source rocks refer to North Sea data, although with only 13 samples within the predicted oil expulsion window between 3.5-4.5 km burial depth

(Okiongbo et al., 2005; Okiongbo, 2011). Although too limited to test the model, these earlier data also show no reduction in TOC with depth.

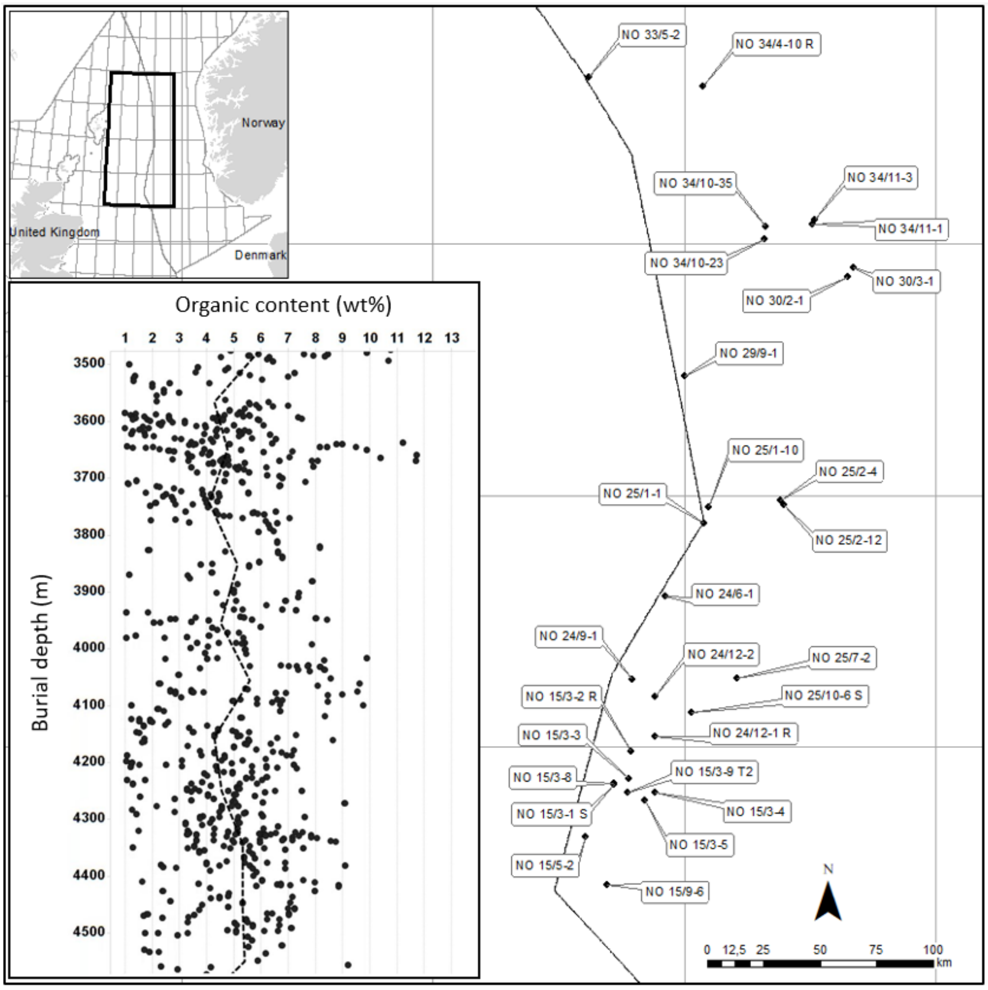

Figure 1. TOC of 871 source-rock samples from 28 wells in the Draupne Formation. The range of depth corresponds with the 120–150 °C oil-expulsion window of the high-temperature expulsion model, but the median (P50) TOC (calculated for every 100 metres) fluctuates around 5% (stippled line) and shows no trend of decrease with depth. Samples with < 1% TOC are defined as non-source rocks (Hunt, 1995) and are excluded from the plot. TOC is a measure of non-reactive organic matter + reactive organic matter + the C_{15+} (S1) fraction. In rock-eval pyrolysis (T> 400 °C) the reactive fraction (~50%) is converted to oil and most of it is predicted to be expelled from source rocks between 120 °C and 150 °C.

Hence, TOC data from North Sea source rocks conflict with the high-temperature model for the timing of oil expulsion. This is especially significant because samples of similar North

Sea source rocks were used in the laboratory studies that established the high-temperature model (Cooles et al., 1986; Pepper and Corvi, 1995; Hunt, 1995).

The high-temperature model can be upheld if the original TOC was higher and exactly compensated for the expelled organic carbon as suggested by Okiongbo et al. (2005, p. 2497-2498): “Total organic carbon ranges from 3.44% to 9.8%, mainly between 4% and 9% (Table 1). Because petroleum generation and expulsion reduce the TOC content of oil-prone source rocks by around one-half, the original TOC contents of the most mature samples would have been around 9-12%.” Although possible, this is unlikely, considering the large number of TOC data presented in Figure 1.

The early oil expulsion advocated her is supported in a study of 215 wells in the Norwegian sector of the North Sea, in which oil inclusions trapped at the detrital grain boundary by quartz cement attach to the grain surfaces at temperatures of 70-80°C (Walderhaug, 2022) suggesting that the oil columns were present at these temperatures. Oil inclusions are often also present in carbonate cement precipitated before quartz cementation started. Walderhaug (2022) concluded that temperatures of oil expulsion from North Sea (Draupne) source rocks are not higher than 90 – 100°C, and that they could be much less.

Additionally, several other observations are incompatible with the high-temperature expulsion model, although entirely consistent with the pre-1970 model:

1. The Athabasca heavy oil and bitumen in Western Canada are optically active (Montgomery et al, 1974; George et al., 1977), but their ability to rotate polarized light decreases with increasing thermal maturation and becomes close to zero at 65°C (Tissot and Welte, 1984). This suggests that a significant proportion of the oil must have been expelled well below 65°C.
2. Many of the biomarkers (chemical “bio-fossils”) used by organic geochemists to determine oil maturity (Farrimond et al., 1998) were discovered and calibrated during the 1970s and early 1980s, when most geochemists believed that oil was expelled from source rocks at temperatures between 50 and 130°C (Hunt, 1979). These biomarkers are still in use (Hunt, 1995; Farrimond et al., 1998), even though oil is now predicted to be expelled from source rocks at temperatures > 120°C, where most of these biomarkers are useless (Tissot and Welte, 1984). Notably, $\beta\beta$-hopene,

which is common in heavy oil and bitumen (Tissot and Welte, 1984), does not survive far into the catagenesis stage (Tissot and Welte, 1984), and temperatures higher than 50-70°C, suggesting that fluids that contain $\beta\beta$-hopene cannot have experienced temperatures much above 70°C.

3. Most oils with API < 25° are believed to be the remnants of in-reservoir bacterial degradation of lighter crude oils (e.g., Hunt, 1995; Head et al. 2003; Nadeau et al., 2005). However, the presence of living microorganisms capable of degrading oil in subsurface reservoirs has never been documented (Head et al., 2003) and therefore in-reservoir biodegradation should consequently be regarded as highly speculative.
4. Bacteria are considered to operate at, or close to the oil water-contact, and to feed on n-alkanes with < 30 carbons via molecular diffusion through the heavier asphaltene with oil that accumulates in the lower part of the column (Head et al., 2010). However, the physical model (Larter et al., 2003; Huang and Larter, 2005; Larter et al., 2006) ignores gravitational segregation due to buoyancy, which would cause the lighter oil molecules to concentrate in the upper part of the column (Hirschberg, 1998). Also, electrical forces that cause the polar asphaltenes (concentrated at lower parts of the oil column) to repel the non-polar alkanes (Hirschberg, 1998) are ignored. Hence, the assumption that the biodegradation process itself produces the compositional gradients in heavy oil fields (Larter et al., 2003) is not justified.
5. Light oil is shown to be converted to heavy oil by bacteria under laboratory conditions (Jobson et al., 1972). However, when these heavy, laboratory-biodegraded oils are subsequently heated to temperatures > 400°C, light paraffinic oil is not produced (Jobson et al., 1972; Hunt, 1979). Conversely, heavy oils found in reservoirs in nature generate light, crude-like oils upon high-temperature pyrolysis (Hunt, 1979; Cannon, 1974). These observations are consistent with interpreting major heavy oil accumulations as oil that has never been heated to temperatures > 70°C, rather than as biodegraded light oil.
6. According to Mayer et al. (2007) the average concentration of non-hydrocarbon asphaltenes and resins (NSOs) in light oil is 10.9% (131 basins, 8148 accumulations) and increases to 35.6% (74 basins, 774 deposits) for heavy oil and 49.2% (50 basins,

305 deposits) for bitumen. If heavy oil is a residue where hydrocarbon molecules with < 30 carbon atoms have been eliminated by bacteria (Head et al., 2003), the initial volume of oil should be reduced by 3-5 times. Hence, unless oil is continuously supplied, a thick zone of residual oil below a current oil-water contact should be expected, but this is not commonly observed.

7. The average vanadium content in heavy oil and bitumen is more than ten times greater than in light oils (Meyer et al. 2007). Vanadium is present in a chlorophyll derivate (porphyrin) and cannot therefore be re-introduced to the oil after burial. As such, if the concentration of vanadium in heavy oils is due to selective removal of the light paraffins, the initial volume of oil must have been more than ten times larger, which is very unlikely (Meyer et a., 2007) since it would mean that some 90% of the expelled oil has been “eaten” by the bacteria.
8. The average uranium content in bitumen is approximately 1000 ppb, which is about a thousand times more than in light oils with API between 30 and 40° (Bell, 1960). This suggests that bitumen cannot be the remains of degraded light oil (Bell, 1960) since uranium cannot be re-introduced to pooled oil by any known process.
9. The high-temperature model rests on gas chromatography of heated rock samples where molecules with < 40 carbons evaporate (Ishiwatari et al., 1977; Hunt, 1995). The hetero-atomic (NSO) resin and asphaltene macromolecules, which makes up 35.6-49.2% of heavy oil and bitumen, respectively (Meyer et al., 2007). The asphaltenes in heavy oil or bitumen are reported to have a molecular weight of 1000-10,000 amu (Hirschberg, 1988), and thus approximately 60 - 600 carbon atoms in the molecular structure. However, the high-molecular weight C_{40+} non-hydrocarbons and hydrocarbons are not detected in standard gas chromatography of oil samples or pyrolysis of rock samples because they do not evaporate. Hence, the high-molecular oil fraction has been methodologically ignored since the invention of Rock-Eval pyrolysis and gas chromatography (Ishiwatari et al., 1977).
10. Van Tuyl and Parker (1941, p. 156) stated that kerogen buried to depths > 2 km is unable to generate petroleum unless exposed to temperatures well above those normally encountered at depths where economic oil accumulations occur. This

statement was later supported by Hedberg (1964), who reported that TOC has decreased significantly in source rocks close to thick magmatic intrusions.

The only chemical data that conflict with the pre-1970 model are those obtained under artificial high-temperature laboratory conditions; thermal cracking of immature oil (Rogers et al., 1974; Evans et al., 1971; Connan et al., 1974; Hunt, 1979) and non-isothermal (> 400 °C) Rock-Eval pyrolysis of source-rock samples (Ishiwatari et al. 1977; Quigley and Mackenzie, 1988; Hunt, 1995).

The use of non-isothermal Rock- Eval pyrolysis (Ishiwatari et al. 1977) was initially meant to be a screening tool for well-site geologists (Hunt, 1979). Its use for prediction was criticised because the fraction of hydrocarbons generated from non-isothermal Rock-Eval pyrolysis varies as a function of sample size and heating rate (Dominé et al., 1988; Schneider, 1993; Price and McNeil, 1997). Schneider (1993, p. 686) concluded that “in non-isothermal thermogravimetry the computed 'kinetic parameters' are valid for the weight loss in the used conditions only and they are neither related to the reaction mechanism, nor can be used for predicting the course of the reaction in other conditions” and that “From the point of view of chemical kinetics they are neither attributable to a determined reaction mechanism nor can they be used for predictions.”

However, thermal breakdown of organic matter in close contact with magmatic intrusions has been confirmed in recent publications (Moneral et al., 2009; Spacapan et al., 2018). Spacapan et al. (2018) showed that TOC is reduced by more than 50% in the Vaca Muerta marine (Type II) source rock in the immediate vicinity of intrusions. This is the same reduction in TOC typically observed in Rock-Eval pyrolysis of marine source rock, suggesting that Rock-Eval pyrolysis is merely replicating what happens under extreme condition in nature, thus substantiating the conclusions by Van Tuyl and Parker (1941) and Hedberg (1964).

The pre-1970 model was eventually abandoned because no viable physical explanation for early oil expulsion was apparent and there was no known chemical model for in-reservoir generation of hydrocarbons. In the following section, however, solutions to both these issues are proposed, and the implications are addressed.

3. CO_2-gas-driven expulsion of bituminous oil from source rocks

The main difficulty in explaining early oil expulsion stems from the belief that the high viscosity of heavy oil (API° between 10 and 25) and extra heavy oil/bitumen (API°< 10) would prevent their expulsion from source rocks and subsequent transport to reservoirs (Erdmann, 1965). How could oil with a viscosity 10-10,000 times greater than conventional crude oil (Meyer et al., 2007) flow even very short distances? However, the present viscosity of pooled oil may not be representative of its physical state during expulsion and migration because the viscosity of the expelling oil is likely to be reduced by the presence of the CO_2 and CH_4 gases that are generated from organic matter early in the burial history (Tissot and Welte, 1984). CO_2 gas is injected to enhance oil production from reservoirs (Abedini et al., 2014) because it can reduce oil viscosity by up to three orders of magnitude (Zhou, 2018; Behzadfa and Hatzikirakos, 2014) due to the development of CO_2 gas bubbles. This causes the volume of the CO_2-oil mixture to increase by some 30% at confining pressures of 30bar and 70/100 bar (Abedini et al., 2014). The solubility of CO_2 in oil increases with increasing API° (Zhang, et al., 2010), possibly causing preferential enrichment in low-molecular-weight oil.

CO_2 gas also causes solid organic matter to swell by a few percent (Tesson and Firoozabadi, 2019). The net effect of increased CO_2-gas in oil is therefore a significant volume expansion of the millimetre to sub-millimetre thin organic lamina. This lifts the overburden and forms tensional fractures (Mandl and Harkness, 1987). The fractures will initially grow as an extension of the sub-horizontal organic laminae (Mandl and Harkness, 1987), but will then be redirected toward a strictly horizontal orientation and perpendicular to the vertical rock stress. This is the only direction fractures can propagate without increasing the local rocks stress, which would arrest the fracture growth. If fractures remain bed-parallel, they will stop growing within a few metres, since the supply of oil from a single organic lamina is limited. However, by remaining horizontal, the fractures will cut through other laminae which will serve to rejuvenate the fracture with pressurised oil. The fractures are therefore predicted to be able to grow horizontally within the source rock and possibly into and through adjacent mudstones. The sizes of the fracture openings are undetermined, but a report of pollens being derived from the same source rock as the reservoir oil suggests that the fracture openings can be a few tens to 100μm in diameter (Jiang, 1988) which is also enough to accommodate the 50-200 nm self-associated particles of asphaltenes and resins that are common constituents in heavy oil (Meyer et al., 2007; Zhao and Shaw, 2007).

The rate of oil expulsion from source rocks for any given oil should be controlled by the overburden lateral pressure gradient and the fracture permeability. For a fracture opening of 10 and 100μm, the rock horizontal permeability will be 10^{-15}m^2 (1mD) and 10^{-12}m^2 (1D), respectively. With a surface topography of 0.1° and the oil viscosity is set to 0.01 Pa·s, which is close to the average for conventional crude oil (Meyer et al., 2007), the lateral flux will be $6\cdot10$ m^1 and $6\cdot10^4$ m^3/m^2 cross section in one million years. It translates to a total flux of oil through a cross section area of 10^4 m^2 (10 mx1000 m) of $6\cdot10^5$ and $6\cdot10^8$ m^3 per million years, respectively, which is substantial.

If the fractures encounter a highly permeable reservoir rock, the oil pressure would change from lithostatic to hydrostatic, causing the CO_2-gas bubbles (dispersed in the oil as in foam) to expand, thus resulting in the CO_2-oil mixture becoming more buoyant and less viscous. Hence, the oil will migrate updip along permeable beds until it is trapped. If the oil is not trapped during updip migration, a sealing asphaltene tar mat might form where the reservoir is subaerially exposed, and the lighter components are lost by evaporation or bacterial degradation (Hunt, 1995). After pooling in a subsurface reservoir, the oil will lose most of its gases (CO_2, CH_4, C_2H_6, C_3H_8, H_2S, N_2) by diffusion and go through both chemical and structural changes that increase its viscosity (Mehrotra and Svrcek, 1988; Lesueur, 2009). Notably, both heavy oil and bitumen contain radioactive elements (Bell, 1960). Irradiation by gamma-rays is known to break C-H bonds and generate free radicals. This results in cross-linking and polymerization, increasing the average molecular weight of the non-hydrocarbons (NSOs) and aromatics (i.e., unsaturated hydrocarbons) and resulting in increased oil viscosity after pooling (Mouazen et al., 2013).

The mobilizing effect of CO_2 vanishes when CO_2 gas liquifies at pressures higher than 70-100 bar and temperatures less than 50°C (Abedini et al., 2014). Since organic matter is defined as a viscoelastic fluid (Schneider, 1993) and because CO_2 is generated within the load bearing organic matter, the CO_2 gas will experience a pressure equal to the overburden pressure between 70 and 100 bar at 350 to 500 m burial. At greater depths of burial, CO_2 gas becomes a liquid (supercritical), and the CO_2-oil mixture shrinks to a volume less than the original fluid (Abedini et al., 2014) causing viscosity to increase. Peak expulsion is therefore predicted to take place between 200 and 500 m of burial (assuming minor water depth).

The idea that CO_2 might mobilize oil in source rocks was recognized by Momper (1978), although he did not discuss the importance of CO_2 being in a gas phase. Also, Momper (1978) concluded that peak oil generation post-dates generation of CO_2, such that little or no CO_2 is available during oil expulsion.

4. In-reservoir maturation of oil by external supply of hydrogen

In-reservoir maturation of oil due to increased temperature, as described by Milner et al. (1977) must involve addition of hydrogen (Evans et al., 1971) because hydrogen-to-carbon ratios of reservoir oils tend to increase with burial depth (Pratt, 1934; Evans et al., 1971; Connan et al., 1974, Tissot and Welte, 1984; Hunt, 1995). The only viable source of hydrogen during artificial thermal maturation of oil is asphaltene and aromatic molecules, which dehydrogenate and precipitate as coke and bitumen (Connan et al. 1974). Typically, > 20% of the oil precipitates as coke and bitumen in laboratory experiments (Hendersen and Weber, 1965; Rogers et al, 1972, Connan et al., 1974), but large amounts of bitumen are not commonly observed in reservoir core samples (Evans et al., 1971; Connan et al., 1974), suggesting that in-reservoir maturation is not a realistic process.

If, however, a few grams of hydrogen are added for every kilogram of immature oil, as is commonly done in oil refineries, the asphaltene and aromatics are hydrogenated/hydrocracked and converted to paraffinic hydrocarbons (Rollmann, 1976; Korre et al., 1994; Ancheyta, et al. 2005; Shan et al., 2017). Hence, if hydrogen were supplied to pooled oil in the subsurface, as suggested by Pratt (1934), immature heavy oil could be converted to light oil without precipitation of significant bitumen. Subsurface hydrogen, however, is not normally measured (Hunt, 1979), although it is a common constituent in subsurface fluids (Hunt, 1979; 1995; Zgonnik, 2020). Indeed, Hunt (1972) estimates that there is approximately 30 times more hydrogen in sedimentary basins than in the pooled petroleum of those basins.

Some of the hydrogen in the subsurface might originate from the mantle (Zgonnik, 2020), although a significant proportion is likely to have been generated from coalification of organic matter in mudstones (Hunt, 1972; Hunt, 1979), which would result in a reduction in the hydrogen-carbon ratio with depth. The hydrogen-carbon ratio of organic matter in source rock at the beginning and at the end of today's oil expulsion window (120 -150°C) is typically 1.3 and 0.7, respectively (Baskin, 1997; Behar and Vandenbroucke, 1987), which translates to a hydrogen loss of more than 4% by weight (relative to organic carbon). This reduction in hydrogen in source rock organic matter is generally attributed to the expulsion of hydrocarbons, since these have a higher hydrogen-carbon ratio than organic matter (Baskin, 1997; Hunt, 1995).

However, as shown in Figure 1, the amount of organic carbon does not decrease within the conventionally accepted 120-150°C oil window, indicating that little carbon or hydrocarbons have left the source rock within this window. This implies that most of the hydrogen leaves the organic matter as elemental hydrogen (H_2). If every kilogram of organic carbon generates approximately 40 g hydrogen, a source rock with 5% organic carbon will produce 2000 g of H_2 per ton of rock within the 120-150°C oil window. Therefore, because of low solubility of hydrogen in water (Wieber and Gaddy, 1934), oil (Cai, et al., 2001), and organic matter (Ji et al., 2013), > 90% of the hydrogen generated from a good source rock must be released as free gas.

5. Discussion

5.1 Hydrogen generation from organic matter

The average amount of organic carbon in mudstones is around 1% (Hunt, 1972). Assuming a TOC weight loss of 2% by release of hydrogen, every ton of mudstone will generate around 200 g hydrogen. Thus, every km^3 of mudstone can produce $\sim 5 \times 10^{11}$ g hydrogen, which is enough to convert 2×10^8 ton (1.5 billion barrels) of low-quality naphthenic oil to high-quality paraffinic oil. Even if only 10% of the hydrogen is consumed, this still a large number.

The hydrogen solubility in *heavy oil* at 100 bar and 50°C is < 0.2 g/kg (Cai, et al., 2001), which is > ten times less than the amount of hydrogen required to convert 1 kg heavy oil to light oil (Ancheyta, et al. 2005). Most of the hydrogen must therefore be supplied from the water phase after accumulation. The solubility of hydrogen in *water* at 100 bar and 50°C is 0.2 g/kg (Wiebe and Gaddy, 1934). Most of the hydrogen required to convert naphthenic heavy oil to light paraffinic oil is therefore likely to be supplied by the water phase. This might explain why the hydrogen concentration in formation water is reported to decrease close to oil accumulations (Zgonnik, 2020).

5.2 How and why hydrogen is produced from kerogen during burial

The decline in H/C ration (Baskin, 1997) and the constant organic carbon content of kerogen within the predicted oil window can be understood from the chemical changes during burial. Hydrogen is expected to be generated when the aliphatic chains ($-CH_2-$) attached to aromatics in the kerogen biopolymer (Berner, 1980) are broken during burial and incorporated into the growing aromatic structure of kerogen (Campbell et al., 1980; Behar and Vandenbrouke, 1987; Vandenbrouke and Largeau, 2007; Fusetti et al., 2010).

This interpretation is supported by the study by Clough et al. (2015) comparing medium- and high-maturity kerogens, which showed that the length of the aliphatic fraction decreases with increased maturation while the aromatic fraction increases in a way that organic carbons are preserved within the kerogen (Clough et al., 2015, Fig. 4). However, in high-temperature artificial maturation experiments, aromatization of aliphatic chains appears to be overridden by formation of alkanes (by hydrogenation of alkyls) with < 40 carbons, which therefore evaporate, and leave the reaction site. This explains why the overall quantity of hydrocarbons generated in pyrolysis decreases with decreasing heating rates. If extrapolated to subsurface conditions, no oil would form at a heating rate less than 3.1°C/million years, comparable to a sedimentation rate of 100 m/million years (Lewan, 1998). At heating rates of 10°C/million years a few % hydrocarbons are estimated to form from the kerogen (Lewan, 1998).

This above analysis supports the statement by Schneider (1993), who appears to have been unaware of the TOC conflict (Figure 1), that high-temperature non-isothermal artificial heating of kerogen is not replicating natural process and is valid only for the experimental conditions.

5.3 Implications of the in-reservoir hydrogenation model

If supply of hydrogen dissolved in the water phase is rate limiting, it might explain why young, rapidly subsiding oil accumulations are less mature than older, slower subsiding oil accumulations at similar temperatures (Barton, 1934, McNab et al., 1952). Consequently, the disputed time-dependent (kinetic) explanation for generation of hydrocarbons (Dominé et al., 1988; Schneider, 1993; Price and McNeil, 1997) can probably be replaced by an approach assuming thermodynamic equilibrium in pooled oils, with the molecular composition of the hydrocarbons in most cases is controlled by the rate at which hydrogen is supplied to the reservoir.

If that is the case, the size of the oil accumulation also matters. The transport-rate-limited model for supply of hydrogen predicts that exceptionally large oil accumulations mature at a slower rate than smaller accumulations. The super-giant heavy oil (API < 22°) Cantarell field in Mexico, where the reservoir temperature is 115°C (Nadeau et al., 2005), might be an example of a size-related retardation of maturation by restricted supply of hydrogen. Insufficient supply of hydrogen might also explain why some oils have not been cracked to gas at reservoir temperatures > 200°C (Dominé et al., 1988; Waples, 2000; Zhu et al., 2018). Also, lack of an external supply of hydrogen might be the reason why oil and biomolecules trapped in mineral cements are reported to have endured for > 2 billion years at > 280°C and probably as high as 350°C (George et al., 2008).

Variation in supply of hydrogen to the oil within a reservoir might also explain the origin of enigmatic tar mats (Wilhelms and Larter, 1994). If some fraction of the oil is heated in the absence of supply of hydrogen the immature oil is expected to evolve on a path toward bitumen, like the hydrogen-starved bitumen formed during artificial heating of immature oil (Hendersen and Weber, 1965). Once formed, bituminous tar mats are likely to resist hydrogenation (and conversion to paraffinic oil) since the hydrogen solubility is lower in bitumen than in light oil (Ji et al., 2013; Cai, et al., 2001) which means that the supplied hydrogen is expected to be preferentially dissolved in and consumed by the maturing light oil phase.

Although the presence of hydrogen in subsurface fluids was recognized during the 1970s (Hunt, 1972; 1979), extra supply of hydrogen was not considered necessary to explain the quality of reservoir oil (Hawkes, 1972) since most of the hydrocarbons were assumed to have been generated within the source rocks prior to expulsion (Hunt, 1979).

5.4 The effect of free hydrogen on the type of organic matter as source for oil

The supply of hydrogen during burial might explain why terrestrial (Type III) organic matter, despite its higher content of non-hydrocarbon structures and low hydrogen-carbon ratio compared with marine (Type II) organic matter (Behar and Vandenbroucke, 1987), might also be an important source for high-quality liquid hydrocarbons in deeply buried reservoirs.

The presence of hydrogen is expected to be important for shale oil plays where the non-expelled oil is targeted (Hill et al., 2007). Abundant in-situ supply of hydrogen (from organic matter) might explain why oil appears to be cracked at much lower thermal maturation levels than predicted by today's high-temperature model (Hill et al., 2007).

5.5 The effect of free hydrogen on vitrinite reflectance (R_o)

The presence of molecular hydrogen in subsurface fluids is also likely to affect the thermal evolution of organic macerals (e.g., spores/vitrinite) and might therefore jeopardize the use of vitrinite reflectance, R_o, measurements as a proxy for thermal stress (Hunt, 1995) and for calibration of basin-modelling programs (Cooles et al., 1986). The ability to reflect light stems from flat light-reflecting polyaromatic sheets developed by the dehydrogenation of twisted (non-reflecting) cycloalkanes (Tissot and Welte, 1984 1984). The presence of hydrogen will impede or even reverse development of light-reflecting (flat) aromatic structures (Korre et al., 1994). Variation in the supply of hydrogen might therefore explain why R_o differs in sandstones, mudstones, and limestones from the same stratigraphic section (Price and Baker, 1985). Abundant in-situ generated hydrogen gas might therefore explain why vitrinite reflectance of samples from source rocks are significantly suppressed (Fang and Jianyu, 1992) as illustrated by the difference between the vitrinite reflectance of 0.6% in source rocks at 120°C (Cooles et al., 1986) compared with vitrinite reflectance of 1.2% in reservoir rocks at 120°C, where the supply of hydrogen is expected to be less (Hunt, 1979). Lastly, variation in the supply of hydrogen might also explain why R_o differs in sandstones, mudstones, and limestones from the same stratigraphic section (Price and Baker, 1985).

5.6 Implication of CO_2-driven expulsion

According to the proposed model for oil expulsion from source rocks, expulsion efficiency should be related to the amount of CO_2 generated early in the burial history. Freshwater organic matter is assumed to generate the most oil per kilogram of organic carbon (Baskin, 1997; Q&M, 1988), but generates by far the least amount of CO_2 (Tissot and Welte, 1984) and should therefore be the least efficient oil source rock. Marine algal (Type II) and terrestrial land plant (Type III) source rocks are known to lose approximately 25% and 50%

weight, respectively, due to the generation of CO_2 and H_2O during the first few hundred meters of burial (Tissot and Welte, 1984).

Except for the first 30 m (Smith, 1952a, b; 1954), there are no reliable source-rock data covering the upper 1.5 km of the sedimentary section (Cordell, 1972; Tissot and Welte, 1984; Hunt, 1995), which makes it impossible to document or test the shallow oil expulsion model from TOC data. Also, reduction in TOC is likely to be dominated by loss of CO_2. The volume of expelled oil is therefore uncertain and is likely to remain so. However, Hunt (1995) noticed that about 40-60% of fresh organic matter is soluble in acids, bases, and organic solvents, compared with < 20% of the organic matter in lithified rocks. Thus, the fraction of the oil mobilized by CO_2 gas, is likely to be < 20-40% of the original organic matter.

The CO_2-gas-flushing model also suggests that oil might not be expelled from source rocks deposited at *water depths* > 1000 m, since CO_2 will be liquified above 100 bars. The presence of methane gas will cause volume expansion of organic matter and oil (Bazyleva et al., 2013) resulting in horizontal fractures, but without significant reduction of oil viscosity, since methane affects oil viscosity much less than CO_2 (Bazyleva et al., 2013). Hence, some later and high-temperature oil expulsion cannot be excluded. However, a viable mechanism for oil expulsion is yet to be described.

5.7 Today's and the revised pre-1970-model compared

A comparison between today's and the revised pre-1970 oil model is shown in Figure 2. The global reservoir database used by Nadeau et al. (2005) shows that most basins have both oil and gas that are trapped in reservoir at temperatures less than 120 °C. This seems to indicate both oil and gas are being generated together and therefore are genetically connected. However, as argued by Bjørkum (2022) most of the gas, which contains mainly methane, is generated from dispersed organic matter in mudstones throughout most of the burial history implying that generation of oil and gas are decoupled.

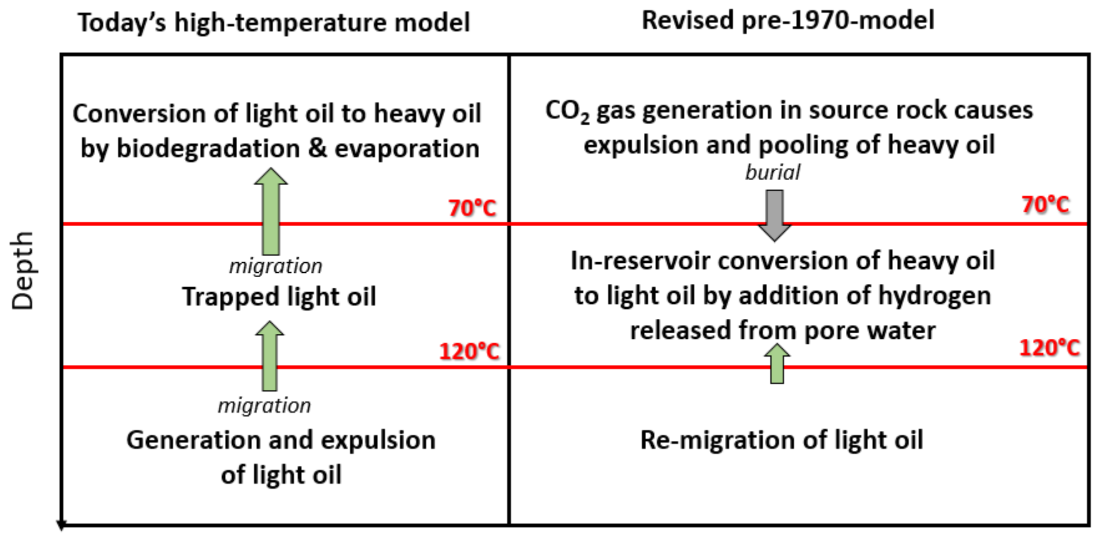

Figure 2. Todays-high-temperature model for generation, expulsion and biodegradation is compared with the revised pre-1970 model of early expulsion and in-reservoir maturation of oil. Note that both models point at the 70 °C and 120 °C isotherms as critical temperature thresholds, but for different reasons. The 120 °C re-migration isotherm is taken from Nadeau et al. (2005).

6. Concluding remarks

Data from North Sea source rocks between 3.5 and 4.5 km burial depth, corresponding to 120-150 °C, show that the amount of organic carbon (TOC) does not decline within the 120-150 °C oil expulsion window as predicted by today's high-temperature model for the generation and expulsion of oil. To the author's knowledge, this predicted decline in TOC has also not been documented elsewhere. Furthermore, pooled oils have chemical and physical attributes that conflict with the high-temperature model, but are more consistent with the pre-1970 models wherein most oil is expelled at shallow depths and low temperatures.

Most of the reduction in the H/C ratio of organic matter during burial results from loss of hydrogen, as shown by the lack of decrease in TOC as the H/C ratio decreases in the predicted oil generation and expulsion window (120 to 150°C). Hence, artificial high-temperature pyrolysis of organic matter, like Rock-Eval, does not replicate normal processes within the source rock, but rather produces synthetic oils like in refineries

Chemical data from heavy oil accumulations show that they have not experienced temperatures much higher than 70°C, indicating that most heavy oil was not formed by biodegradation of light oil.

In this paper, the shallow/early oil-expulsion model advocated prior to 1970, is revitalized and improved. It is argued that oil expulsion from source rocks is propelled by CO_2 gas generated within source rocks early in the burial history. CO_2 gas causes organic lamina to swell, creating horizontal fractures through which the oil is expelled. Oil then migrates out of the source rock in the direction of lower overburden pressure until it enters carrier beds that transport it to reservoir traps or to the Earth's surface.

The model presented here for early timing of expulsion of oil and lateral migration via horizontal fractures into nearby traps lends support to the pre-1970 model by providing possible explanations to some of its unresolved issues and implies that many of the enigmas associated with today's high-temperature model (Wilson, 1990; Wilson, 2005) can be resolved, notably the long-distance sub-horizontal (up to 400 km) secondary oil migration required to explain the major accumulations in Eastern Venezuela and Western Canada (Hunt, 1995). The new expulsion model explains how most of these low-temperature oil accumulations may be locally sourced. It also follows that some, approximately 1/3, of the pooled oil is buried and upgraded to conventional light oil by the combined effect of higher temperature (> 70°C) and external supply of hydrogen. However, oil is likely to leak from traps via hydro-fractures (Engelder and Leftwich, 1997) at temperatures > 120°C (Bjørkum and Nadeau, 1998), which explains why most oil is produced from reservoirs with temperatures < 120°C (Hedberg, 1964; Nadeau et al., 2005).

A comparison between today's and the revised pre-1970 oil model is shown in Figure 2.

Hydrogen is produced from dispersed organic matter in mudstones and source rocks by thermally driven coalification of organic matter which preserves the carbon atoms. Most of the generated hydrogen is dissolved in the formation water. Presence of hydrogen gas will supress aromatization of cycloalkanes in solid organic matter and therefore its ability to reflect light, which explains why vitrinite reflectance is lower in source rocks compared to reservoir rocks at similar burial depths.

In the proposed model, immature oil is converted to mature (paraffinic) oil within the reservoir starting at temperatures of around 70°C. Precipitation of bitumen is prevented because hydrogen generated from coalification of organic matter in mudstones and source rocks is supplied to the pooled oil, where it is consumed in the conversion of non-hydrocarbons (asphaltenes and resins) to paraffinic hydrocarbons as in refineries. Since hydrogen is supplied to the pooled oil, the original composition of source material for the reservoir oil, either marine or terrestrial, may not be critical for oil quality at temperatures > 70-100 °C unless the supply of hydrogen is limited.

The molecular composition of the reservoir oil at any given temperature will be influenced by the rate at which hydrogen is supplied by the water phase, either by diffusion or flow of water, which might be the rate-limiting process. Large oil accumulations should therefore mature at slower rates than smaller accumulations. Hence, todays-time-temperature concept (Hunt, 1995), which assumes that chemical reactions are very slow, is challenged by a model assuming a state of thermodynamic equilibrium where the rate of transformation is controlled by external supply of necessary reactants (H_2). Insufficient supply of hydrogen might therefore explain the origin of tar mats.

The main implication for oil exploration arising from the proposed low-temperature expulsion model is that both low- and high-quality oils can be found in basins where source rocks have not experienced temperatures > 120°C, which according to today's high-temperature expulsion model represents the minimum temperature for significant expulsion of oil. This greatly extends the petroleum envelope into areas where source rocks are currently considered immature and non-prospective.

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