Origin, transport, accumulation of methane in sedimentary basins revisited

By
Per Arne Bjørkum

Professor emeritus at University of Stavanger

email: pab1952@gmail.com

Abstract

The current widely accepted models for generation of methane by thermal cracking of oil and by bacterial fermentation have several serious inconsistencies. Experiments show that high-temperature pyrolysis of liquid (C_{6+}) hydrocarbons does not produce methane even if hydrogen is added to the feed, and condensate, which is generally assumed to be the direct precursor to methane, generally amounts to only a few percent of produced oil. The bacterial origin for methane generation at low temperatures is also flawed because the pores in mudrocks are too small relative to the dimensions of bacteria, making their proliferation unfeasible. Furthermore, it is well known that most of the methane in sedimentary basins is dissolved in the formation water, with only about 1% of the total occurring as free gas in conventional reservoirs, and today's models for generation of methane cannot account for such enormous volumes.

Two alternative models are advocated here: (1) high-temperature (>100-120°C) "thermic" methane -generation from alkylated aromatics in the organic matter dispersed in mudstones and (2) "CO_2" methane formation by reaction of CO_2 and H_2 produced from decomposing organic matter, which occurs from low to high temperatures (throughout most of the burial history). These processes can generate enough methane to saturate formation water using only a few percent of the organic carbon in mudstones.

Large accumulations of methane-rich gas in shale-dominated siliciclastic basins, like the Gulf of Mexico or North Sea, can be explained as the products of exsolution from upward-moving formation water. In most basins, the water-pressure profile typically increases from hydrostatic above 2-3 km depth to approach the hydrofracturing isobar (pore pressure between 1.8 and 2 times hydrostatic) at around 3-3.5 km. In this situation, most of the vertical water flow takes place via hydraulic fractures that have originated in highly overpressured high-permeability rock (sandstone) underlying the hydrofracturing isobar. It takes millions to tens of millions of years to form a significant accumulation by this means, but if the hydraulic fractures originate in previous gas accumulations, the time required can be reduced by two orders of magnitude.

For the subordinate proportion of methane formed in source rocks, as opposed to the main proportion formed in normal mudrocks, the gas resides in an entirely different pore system than the oil. Most of the free gas is contained in the inorganic pores, whereas the oil is confined within the kerogen.

Introduction

Current models for the origin of methane in sedimentary basins have several obvious inconsistencies, so it is necessary to question fundamental assumptions and consider alternative mechanisms that can better explain the facts. According to the widely accepted thermal cracking model, most methane in petroleum reservoirs is assumed to be formed at subsurface temperatures of 100-200°C, thus referred to here as "thermic methane" (Hunt, 1984; Mango and Jarvie, 2009), either directly from kerogen or by thermal cracking of oil in source rocks or reservoirs (Quigley and Mackenzie, 1988a, b; Mango and Jarvie, 2009). However, this theory has been criticised for lacking experimental support (Mango, 1997). Non-associated gas accumulations typically contain > 80% methane (Rice and Threlkeld, 1990; Hunt, 1995; Mango, 1997), whereas pyrolysis of immature kerogen produces gas with 10-60% methane in the C_1-C_4 fraction (Mango, 1997, and references therein). It is assumed that more than 50% of the reservoir gas is formed by cracking of oil (Rooney et al., 1995; Hantschel and Kauerauf; 2009, Figure 4.13; Hunt, 1995, s. 236) and that the C_{2+} hydrocarbons are thermally broken down to methane at temperatures >150°C either in source rocks or in reservoirs (McNab et al., 1952; Landes, 1967; Hunt, 1972; Stahl, 1974; Tissot and Welte, 1984; Horsfiled et al., 1992; Hunt, 1995; Allen and Allen, 2013). However, when C8 to C12 alkanes are heated to temperatures >500°C, although some propane and butane are formed, neither methane nor ethane is produced, even if hydrogen is added to the feed (Weitkamp, 1975; Mohanty et al., 1990; Sie (1993a). Sie (1993a) concluded that there is "almost zero production of C_1 and C_2 in hydrocracking» (p. 408), while Jackson et al. (1995) stated that "n-alkane cracking gives too little methane to be a significant source for natural gas in the earth" (p. 423). Ethane is exceptionally stable and expected to have a half-life of several billion years under reasonable geological conditions, suggesting that conversion of ethane to methane is extremely slow, if it occurs at all (McNeil and McBent (1996, and reference therein). In fact, all normal paraffins with <6 carbons are very stable (Weitkamp, 1975).

Also, if methane is the product of cracked hydrocarbons, methane precursors (condensate C_2-C_4) should be more abundant than methane. However, condensate makes up only a few percent of produced gases (Tong, et al., 2018). Lastly, < 5% of crude oil is produced from reservoirs at temperatures >120°C (Hedberg, 1964; Nadeau et al., 2005; Angulo and Vargas, 2022), suggesting that most oil accumulations are never exposed to the temperatures required to form methane according to current theory.

A mechanistic model for the origin thermic methane

This section outlines the widely accepted thermal cracking model of methane generation at high temperatures (100-120°C) from methylated aromatics in source-rock kerogen and oil (Figure 1; Savage et al., 1989; Smith and Savage, 1991; McNeil and McBent, 1996, Mango, 1997, Savage, 2000. Mango, 2001; Lorant and Béhar; 2002).

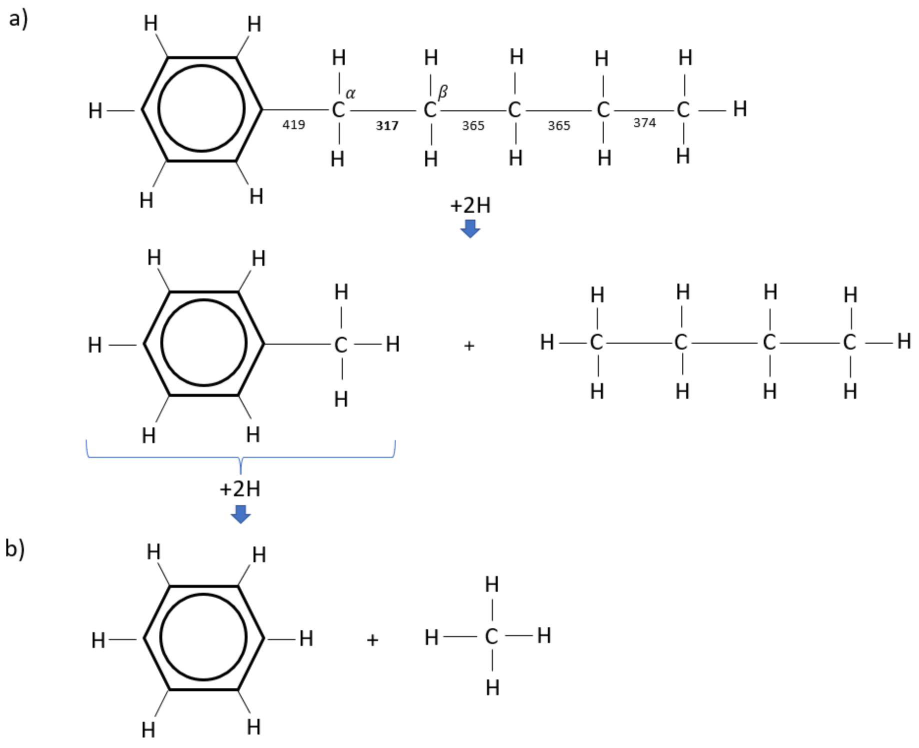

Figure 1
a) The weakest bond in an alkyl-benzen is the bond between second α and third β carbon in the alkyl chain. Therefore, this bond will be most frequently broken to create methylated benzene by i*pso*-addition of H. b) Methylated benzene is demethylated by hydrogenation to form benzene and methane (Fusetti et al., 2010). Adapted from Savage (2000).

Organic matter and oil contain a certain fraction of alkylated aromatics, that is aromatic structures with methylene (-CH_2-) in the alkyl chains attached to one or more of the carbons in the six-ring structure. Since the C- C bond between the second and third carbon, as measured from the ring structure, is the weakest (Fig 1), this bond it mostly frequently broken (often referred to as to as β-session) during burial. Thus, methyl groups are generated during burial, which explains why *mature* kerogen consists mainly of single-carbon methyl groups attached to aromatics (Redding et al., 1980; Hunt, 1995, p. 209; Clough et al., 2015).

The methyl can be released to form methane (Smith and Savage, 1993; Hunt, 1995, pp. 207-209; McNeil and MeBent, 1996; Al Darouich et al., 2006, Craddock et al., 2015) via *ipso*- addition of hydrogen (Fusetti et al., 2010). Liberation of methyl will take place at different temperatures because the aryl-methyl C-C bond (i.e., the first and second C-C) is influenced the number of rings in the aromatic structure and by the position in the aromatic structure (Smith and Savange, 1991; 1993). Hence, peak generation of methane is predicted to take place mainly between 100 and 200°C.

Methane will form when a methyl combines with one hydrogen atom (see below) through a free radical reaction (Bell and Kistakowsky, 1962):

$$\cdot CH_3 + H\cdot \text{->} CH_4 \qquad (1)$$

This reaction can take place within the organic matter or in the water phase, meaning that some of the methane is predicted to form within the water phase. Hydrogen is generated from fusing/condensation of aromatics (Campbell et al.1980; Fusetti et al., 2000: Lorant and Béhar, 2002) and when n-alkyl radicals or n-alkanes, which have a H/C ration greater 2, are converted to aromatics with a H/C ratio < 1 (Shi et al., 2017; Clough et al., 2015). Generation of methane from alkylated aromatics is not expected to become significant until the kerogen biopolymer dealkylates and evolves toward an aromatic stage, which according to the measure H/C ratio (Baskin, 1997 and references therein) appears to be around 120°C, that is, at the beginning of the oil window, as defined by Quigley and Mackenzie (1988a, b).

The source material for thermic methane

The largest deficiency with today's model for generation of methane is probably that it aims at explaining the origin of reservoir methane, which constitutes only about 1% of the total amount of methane in sedimentary basins, most of which is dissolved in formation waters (Buckley, 1958; Hunt, 1995; Mango, 2001). Although the thermal cracking model of McNeil and McBent (1996) explains preferential generation of methane over ethane and propane, Mango (1997) demonstrated that there is not enough methylated aromatics in source rocks and oils to account for the total amount of methane in sedimentary basins and therefore concluded that "The source of methane in natural gas needs additional study" (Mango, 1997, p. 436).

The solution is to include the organic matter in all mudstones as initially suggested in the early 1930s (Hunt, 1979. p. 9). Mudstones contain on average 1% organic carbon (Hunt, 1972), equivalent to 10 kg of organic carbon per ton of rock. The organic carbon in mudstones is mostly derived from terrestrial organic matter (Hunt,1995) and is estimated to be 100 times larger than the organic carbon in the organic-rich mudstones providing the source rocks for oil (Vandenbrouke and Largeau, 2007). In addition, there is an average of around 0.3% organic carbon in sandstones and carbonates (Hunt, 1972).

The solubility of hydrocarbons in water decreases exponentially with the number of carbon atoms up to 12 (Ferguson et al., 2009). The solubility of C_{5+} is < 1/100 that of ethane (Pereda et al., 2009). Thus, even though most mudstones contain a few hundred grams of C_{5+} hydrocarbons (Hunt, 1977), hydrocarbons with five or more carbon atoms will not dissolve in the formation water. Hence, the water phase serves as a physical filter for hydrocarbons.

While pyrolysis of *immature* kerogen generates wet gas with 10-60% methane in the C_1-C_4 fraction (Mango, 1997), pyrolysis of *mature* kerogen generates dry gas, that is > 90% methane in the C_1-C_4 fraction (Harwood, 1977; Redding et al., 1980; Hill, et al., 2007).

Approximately 5% of the organic carbon is converted to methane (Redding et al., 1980; Harwood, 1997; Hill et al., 2007). Thus, each ton of mudstones can produce ~0.7 kg of methane (~ 1 m^3). Assuming a rock porosity of 10% and a rock density of 2.5 ton/m^3, every ton of rock will contain ~ 0.04 m^3 water. The solubility of methane in formation water of sea water salinity at 1000 bar and 150°C is slightly less than 10 kg (~14 m^3) per m^3 water (Duan et al., 1992). Thus, most pore waters at great depth and high temperatures are likely to be nearly saturated with methane.

Methane derived from CO_2

Up to 20% of methane is assumed (Hunt, 1995) to be generated early in the burial history from CO_2 and hydrogen according to the following reaction (Hunt, 1995, p. 189):

$$CO_2 + 4H_2 <=> CH_4 + 2H_2O \qquad (2)$$

The reaction is assumed to be mediated by bacteria (Claypool and Kaplan, 1974; Fuex, 1977; Rice and Claypool, 1981; Hunt, 1995). However, generation of methane from CO_2 and H_2 by reaction (2) is exothermic up to 600°C (Schaaf et al., 2017) and is therefore not dependent on bacterial mediation. Small amounts of ethane (C_2H_6) are also formed from CO_2 and H_2. That reaction is exothermic up to 400°C (Schaaf et al., 2017), which means that a small amount of ethane also forms together with the methane from reaction (2).

CO_2 and H_2 are derived from decomposing organic matter by the following (irreversible) exothermic reaction (Berner, 1980, p. 82):

$$CH_2O + 2H_2O -> CO_2 + 8H \qquad (3)$$

where CH_2O represents the organic compound.

Therefore, methane and some ethane might continue to form from CO_2 and H_2 at temperatures higher than the temperature of 70°C at which bacteria are *assumed* to become inactive (Claypool and Kaplan, 1974; Fuex, 1977; Rice and Claypool, 1981). It means that the amount of CO2 derived methane might be greater than commonly believed.

In generating methane from CO_2 and H_2, bacteria are currently presumed to release H_2 and to use enzymes to catalyse the process (Claypool and Kaplan, 1974; Fuex, 1977; Rice and Claypool, 1981). However, Zobell (1946) showed that the number of bacteria in marine mud decreases from 63 million per gram of mud in the upper 5 cm, to <400 at 180-185 cm depth. Bacteria are typically 1-10 µm in length (Momper, 1978), while mudstones are dominated by clay particles <2 µm (Vogt et al., 2002), suggesting that the pores in mudstones are too small for bacteria to thrive.

Rice and Claypool, (1981), therefore raised the question of whether bacteria can function in *compacted* shales, but nevertheless maintained that they would thrive down to 1-2 km. On the other hand, Stahl (1974, p.134) stated "biogenic alteration of organic matter is predominant during the first few feet of sedimentary burial".

The light carbon isotopic composition of shallow methane has been suggested to result from bacterial fractionation (Claypool and Kaplan, 1974; Fuex, 1977; Rice and Claypool, 1981). However, Sackett (1968) concluded that bacterial fractionation is not required because low temperatures will in any case produce the observed isotopic fractionation between CO_2 and methane (Whiticar, 1999).

If 10% of the carbon content of average mudstone is converted to methane from CO_2, one ton of mudstone will generate 1.4 kg of methane. Assuming a rock porosity of 20% and an average water pressure of 100 bar, less than 10% of the methane will dissolve in the formation water, with the result that free gas will form. CO_2 has a solubility in water many times greater than methane, however, and is therefore unlikely to be present as a discrete gas phase (Bando et al., 2003).

Significant amounts of methane migrate towards the surface via molecular diffusion in water (Smith et al., 1971; Hunt, 1995). Smith et al. (1971) showed that a gas accumulation of 200 bcf ($2{,}8 \times 10^8 m^3$)

at slightly less than 2 km depth with an area of 100 km^2 will be emptied within <80 million years if no further gas is supplied. However, Smith et al. (1971) did not consider that methane is continuously generated in the overburden. This gas will serve as a diffusional barrier for the underlying trapped gas, thus significantly increasing the gas residence time in shallow reservoirs. It also means that a significant portion of the methane formed in mudstones from CO_2 and H_2 will be lost since most of the CO_2 is produced early in the burial history (Tissot and Welte, 1984) suggesting that methane from methylated aromatics is the main source for methane. Even so, a significant fraction of the shallow West Siberian Cenomanian dry gas accumulations (Schaefer et al., 1999; Littke et al., 1999), might be derived from CO_2 and H_2.

Methane that migrates to the surface via molecular diffusion within the water phase (where the bacteria reside) is likely to be oxidized to CO_2 in the ~ 1m thick bacterial sulphate reduction zone present in submarine mudstones (Berner, 1980, Figure 6-12). Therefore, the flux of methane at the surface of sedimentary basins is not a good measure of vertical methane flux.

Accumulation of methane gas

For dissolved methane to form gas accumulations, it must be released from the water. It has been shown that uplift and pressure reduction can result in exsolution of large amounts of gas (Masters, 1979; Schaefer et al., 1999; Law, 2002), but no universal quantitative model has been presented for how large methane accumulations might form by exsolution from formation water in a subsiding sedimentary basin. Although it is well established that open fractures exist in the deeper highly overpressured part of sedimentary basins (Mandl and Harkness, 1987; Engelder and Leftwich, 1997, and references therein), there is also no universal model presently available for the quantitative roles of fracture flow vs. matrix flow as subsidence progresses.

Engelder and Leftwich (1997) provide data that can be used to determine the relative importance of fracture vs. matrix water flow. They showed that pore water pressure in south Texas oil and gas fields was close to hydrostatic down to 2-3 km, but then increased greatly along a “pressure ramp” to approach the overburden gradient (1.8-2.0 times hydrostatic pressure) at around 3-3.5 km.

At the deep end of the pressure ramp, the calculated hydraulic gradients are typically reduced by four to five times (Engelder and Leftwich, 1997). Since the flux of fluid immediately below and above the hydrofracturing isobar is approximately the same, Darcy’s equation demands that the rock permeability below the hydrofracturing isobar must have increased by four to five times. The only universal phenomenon that can explain this increase in permeability is an increase in open fractures. Such fractures are expected to form close to maximum overpressure in high-permeability rock (Mandl and Harkness, 1987) hereafter referred to as "sandstone" (Mandl and Harkness, 1987).

The fractures are predicted to originate in sandstone [Mandl and Harkness, 1987) and propagate though (tight) mudstones until they hit a new sandstone. It important to notice that generation of hydraulic fractures does not increase the flux of water across the hydrofracturing isobar. The vertical flux of water through any given horizontal surface, matrix plus fracture flow, is determined by thermally-driven, pressure-insensitive porosity-loss rates (Bjørkum, 1996; Bjørkum and Nadeau, 1998; Nadeau et al., 2005) in the underlying rocks.

The pore pressure within hydro-fractured sandstones is predicted to stay high and be close to the fracturing pressure for as long as water is expelled from the underlying rocks, that is, if the porosity in the underlying rock is greater than zero. This implies that once a facture is generated, the thermally-driven pressure-insensitive porosity-reducing mineral reactions will proceed and pump the water upward, with the result that the fracture water flow will be continuous and long-lasting, and not episodic and short-lived (< 100 years) as assumed by Roberts and Nunn (1995, and references therein).

If methane-saturated pore water flows upwards through hydraulic fractures (Figure 2), methane gas will be released as the water pressure and temperature decrease, according to the methane solubility data of Duan et al. (1992).

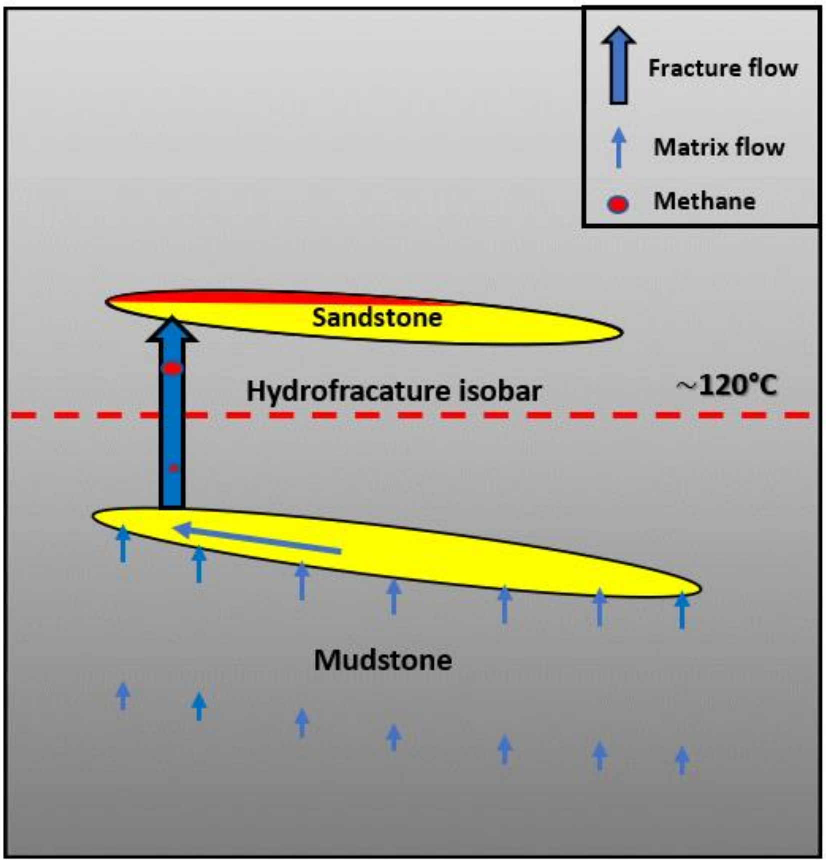

Figure 2
Water containing molecularly dissolved methane are expelled from highly overpressure sandstones through a hydraulic fracture that cut through mudstones until it is arrested when it hits a high-permeable sandstone situated above the hydrofracturing isobar. A significant fraction of methane is predicted to exsolved due to drop in pressure and temperature and a gas accumulation might form. If the lower sandstone contains free gas, the vertical flux of gas might increase by two orders of magnitude.

The following hypothetical example demonstrates that compactionally-driven upward flow of geologically reasonable volumes of pore water can release significant amounts of methane. Each 1 m^3 of methane-saturated water moving from 1000 bar and 150°C upward to 400 bar and 90°C will release ~5 m^3 of methane (Duan et al., 1992). From such movement, it will take $4x10^8$ m^3 water to form a methane accumulation of $2x10^9$ m^3 that is, a volume ten times the average gas fields sizes (Smith et al., 1971). This volume of water ($4x10^8$ m^3) can be provided by a porosity reduction of 4% in 10^{10} m^3 of mudstone (comparable to 100 m thickness of mudstone with an aerial extend of 100 km^2). If we assume that it takes 10 million years to reduce the porosity by 4%, the flux into the receiving reservoir will be 40 m^3 water per year, or ~0.1 m^3 gas per day.

To form a methane accumulation the size of the North Sea Troll Field (1.25 10^{12} m^3 = 44.6 Tcf), the volume of water must be 800 times larger than in the above calculation. This can be supplied by compaction of an underlying thickness of 4 km of mudstone with an aerial extent of 2000 km^2 (an aera three times the Troll Field (Horstad and Larter, 1997).

Alternatively, the gas might be sourced from previous gas accumulations that have transcended the hydrofracturing isobar. Then gas will accumulate in the receiving reservoir at a rate two orders of magnitude greater (several hundred kg methane per m^3 fluid) than if the gas was supplied with the water phase as described above (a few kg per m^3 fluid). Rapid remigration is consistent with the exponential decline in producing gas (and oil) field beneath the 120°C isobar (Nadeau et al., 2005; Figure 8) which is assumed to coincide with the hydrofracturing isobar (Bjørkum and Nadeau, 1998; Nadeau et al., 2005; Angulo and Vargas, 2022). Nadeau et al. (2005) showed that > 90% of the gas and >n 95% of the conventional oil are located at temperature < 120°C.

Thick and geologically fast subsiding basins, such as evinced the Gulf of Mexico, are more likely to have been through more remigration events than slowly subsiding basins. As a result, rapidly subsiding basins are expected to contain more gas in the gas accumulation zone at $T < 120°C$ (Nadeau et al. 2005; Angulo and Vargas, 2022) than in most slowly subsiding and thinner basins.

The residence time above the hydrofracturing isobar is critical since reservoirs can only retain a significant amount of gas while located above the hydrofracturing isobar. Any gas accumulated at greater depths would tend to be among the first fluids released along fractures. The time above the hydrofracturing isobar is lowest in rapidly subsiding basins, but less time might to be more than compensated by the anticipated increased number of remigration events and larger volumes of mudstones relative to cases of slower subsidence.

The hydrofracturing-water-flow model for transport of methane presented here might also explain why most hydrocarbon gas accumulations contain helium (Barry et al., 2016). Helium is present in trace amounts in pore water (Zartman et al., 1961), but its concentration will increase in gas accumulations by up to 100 times (Zartman et al., 1961) due to gas-stripping (Barry et al., 2016). A quantitative model for accumulation of helium has been difficult to establish since large volumes of water are required (Barry et al., 2016) and today's model for gas migration assumes that migration of the gas as a separate phase. The model for transport of methane as molecularly dissolved in water (in a ratio of approximately 1/100) presented in this paper provides the volume of water necessary to explain the presence of helium in many gas accumulations.

Implications for shale gas

Unconventional gas is currently produced form organic rich shales. Empirical data also suggest the TOC in the source rock must be 2% or higher for kerogen of medium to high maturity to form economic amounts of free gas (Montgomery et al., 2005; Jarvie et al., 2007). There are a few STP m^3 of gas per ton rock (Jarvie, 2007). Therefore, the in-situ volumes of pressurized gas are on the order of a few tens of dm^3 per m^3 rock, which is close to the volume of mudstone pores (Jarvie, 2007). Hence, most of the gas is likely to be confined to inorganic pores.

The production of unconventional gas decreases rapidly after the first year, after which the rate of gas production continues for many years with little decline and with close to constant gas/water ratio (Jarvie, 2012; 2015). This differs from the production of gas from conventional gas reservoirs where the gas/water ratio declines during production. (Jarvie, 2012; 2015) and other attempts to predict the shale gas production profile from first principles have not been successful (Kuske et al., 2019; Orozco et al., 2020). However, if we accept that most of the gas is produced from the mudstone, the shale gas production profile can be understood as reflecting the increased connectivity of initially isolated gas pockets due to reduced pressure from production.

The fate of the free gas in source rocks/shales is unclear, but at near-zero porosity, most of the in-situ gas must have escaped or been incorporated into the kerogen structure (Mango, 2013). At temperatures higher than 700°C (only likely to be achieved in subduction zones), reaction 1 will be reversed (Schaaf et al., 2017), implying that remaining methane will react with water and produce CO_2 and H_2.

Unconventional oil is also produced from source rocks (Jarvie, 2012). According to Bjørkum (2021), this oil comes from expulsion of immature oil at depths less than 1km. There are typically slightly more than $\sim$0.1 kg oil per kg organic carbon in source rocks from which oil is produced (Jarvie, 2012), which means that a source rock with 3% TOC (30 kg organic carbon per ton rock) will contain $\sim$3 kg oil per ton rock. Hence, all in-situ oil might be confined to the kerogen.

The remaining oil is not likely to invade the mudstone nano-pores because of short-range repulsive electrical forces (Cordell, 1973; Buckley et al, 1989; Basu and Sharma, 1996) between negatively charged oil/water interphase and negatively charged mineral surfaces in mudstone pores, in addition to the curvature forces (Cordell, 193). Calculation of the entry pressure, p_c, for oil into mudstone nanopores must include the electrical forces as described by the augmented Laplace-Young equation (Basu and Sharma, 1996):

$$p_c = \frac{2\sigma}{r} + p_{electrical} \qquad (4)$$

where σ is the curvature interfacial force, r the interface curvature radius, and $p_{electrical}$ the electrical repulsive pressure (Basu and Sharma, 1996).

Since the oil is produced from hydraulically induced vertical fractures, most of the oil is likely to be produced from organic lamiae with a lateral extent comparable to the distance between the vertical fractures.

Therefore, production of oil and gas from organic-rich mudstones probably does not involve a complex, and to date unsolved three-phase (PVT) problem (Kuske et al., 2019), but rather a two-phase gas problem (gas and water) and a “one”-phase oil problem (kerogen and oil).

For in-situ separation of gas and oil, gas production rates will be controlled by the permeability of the mudstone, while oil production rates will be sensitive to both permeability and the lateral continuity of the organic lamina. The mudstone oil saturation and relative permeability (Kuske et al., 2019) are thus irrelevant. Faulting might disrupt the lateral continuity of organic lamina, with resulting decline in oil production near major fault zones.

The in-situ separation of oil and gas can also explain why in “Huff’n Puff” gas injection (Orozco et al., 2020) results in a doubling of oil recovery (from 10 to 20%), while most of the injected gas remains in the ground. Attempts to model the experience from first principles have not been successful (Orozco et al., 2020). If we assume that the oil is confined to the organic laminae and that most of the injected gas invades the organic laminae (because there is no capillary entry pressure), invasion of gas will substitute for and mobilize some of the oil adsorbed on the organic matter.

The fate of liquid hydrocarbons retained in sources rocks is unclear since hydrocarbons with <7 carbons are highly stable (Wietkamp, 1975). The answer might have been found by Lewan (1985), who noticed that the residual carbon increased during aqueous pyrolysis of immature kerogen at temperatures >350°C while the oil fraction decreased (Lewan, 1985), suggesting that the oil fraction is ingested by the kerogen. This possibility appears to have been anticipated by McCoy (1924), who stated that the oil must squeezed out beds before the “the liquid oil in source beds has been solidified to kerogen” (p. 1023).

Discussion

The fact that artificial heating of immature kerogen generates wet gas while artificial heating of mature kerogen generates dry gas calls for an explanation. The answer appears to reside in the role of time involved in pyrolysis of kerogen. The overall quantity of hydrocarbons (oil and gas) generated in artificial heating of immature kerogen decreases significantly with decreasing heating rate (Campbell and Evans, 1979; Evans and Smith, 1979; Lewan and Ruble, 2002). Below a heating rate of 120°C/hr, the oil yield is approximately proportional to the log of the heating rate (Evans and Smith, 1979). If extrapolated to subsurface conditions and heating rates less than 3.1°C/million years, comparable to a sedimentation rate of ~100m/million years, no hydrocarbons would form (Lewan, 1998). At heating rates of 10°C/million years, a few % of the kerogen is predicted to form hydrocarbons, suggesting that most source rocks are not expected to lose noticeable amounts of organic carbon within the oil generation window of 120-150°C (Quigley and Mackenzie, 1988a, b).

These observations are contrary to expectation, since conversion of kerogen to hydrocarbons is a kinetically controlled process, such that more time should result in the formation of more hydrocarbons (Hunt, 1995). However, the predictions by Lewan (1998) have been given some support by Bjørkum (2021) who showed that TOC does not decline in North Sea Draupne source rock in the predicted oil generation and expulsion window.

These conflicting observations can be understood from the different chemical structural changes of kerogen during burial and in short-lived artificial high-temperature experiments. When the aliphatic chains ($-CH_2-$) attached to aromatics in the kerogen biopolymer (Berner, 1980; Vandenbrouke and Largeau, 2007) are broken during burial, they are incorporated into the growing aromatic (-CH-) structure of kerogen (Campbell et al., 1980; Béhar and Vandenbrouke, 1987; Vandenbrouke and Largeau, 2007; Fusetti et al., 2010; Clough et al. (2015). Hence, during burial, kerogen is dehydrogenated, and organic carbon is preserved. Clustering and ordering of aromatic ring structures towards graphite (CH_0) is a kinetically impeded crystallisation process requiring geological timescales (Grew, 1974; Beyssac et al, 2002; 2003), which explains why kerogen is not aromatized in short-lived laboratory experiments.

Also, due to high temperatures (> 400°C), most of the artificially generated C6-C30 hydrocarbons will evaporate (to form pyrolysate) and are therefore prevented being incorporated into aromatic structures. Hence, the amount of organic carbon declines during pyrolysis of immature kerogen. Due to the high temperatures, some of the C6+ hydrocarbons crack to form propane and butane, which might explain why pyrolysis of immature kerogen generates wet gas while mature dealkylated kerogen produces mainly methane (Campbell et al., 1980; Mango, 1997 and references therein).

Hydrogen is also produced during pyrolysis of immature kerogen. On a mol basis, H_2 is the major gaseous pyrolysis product (Campbell et al., 1980). However, the amount of H_2 generated decreases with decreasing heating rates, probably due the greater time available for hydrocracking the artificially generated C6+ hydrocarbons.

Since ∼ 5% of organic carbon is converted to methane (Redding et al., 1980; Harwood, 1977; Hill, et al., 2007), only a small fraction of the remaining hydrogen is used form methane. Thus, most of the remaining hydrogen is expelled from kerogen as H_2 if kerogen reaches the graphite stage at approximately 700°C (Landis, 1971).

It has been difficult to explain why methane, which has the highest H/C ratio of all hydrocarbons is generated form kerogen with a lower H/C ratio (< 0,8) than during generation of liquid hydrocarbons (Hunt, 1995; Baskin, 1997). However, if methane is formed from methylated aromatics, the H/C ratio of the kerogen at the time of methane generation is not relevant.

All organic matter contains alkylated aromatics (Vandenbrouke and Largeau, 2007), which implies that all type organic matter will generate methane (Harwood, 1977). Organic matter from land plants (Type III), which dominates in mudstones (Hunt, 1995), has a higher fraction of alkylated aromatics than organic matter stemming from marine lifeforms which has more alkylated aromatics than freshwater (Type I) organic matter (Béhar and Vandenbrouke, 1987).

Even though Type III organic matter in mudstones is expected to be the source for most of the methane in sedimentary basins (Hunt, 1995), methane produced directly form source rocks is generated from marine (Type II) organic matter (Jarvie, 2015).

The models for generation of early and late methane presented in this communication explains the origin off conventional non-associated dry gas accumulations. Most of the wet reservoir gas (< 10% C1 in the C1-C4 gas fraction) is predicted to stem from contact with oil. If sufficient dry gas enters an oil reservoir to form a gas cap, it will be enriched in C3 and C4 hydrocarbons due to gas-stripping.

Most geologist would probably contend that the absence of oil shows in cores indicates the lack of any previous oil column in the rocks. This might not be true, however, because a gas phase in contact with oil will result in spontaneous formation of a thin oil film at the gas-water interphase (Øren et al., 1992; Øren et al., 1994). This continuous oil film will serve as a drainage channel for the oil towards the oil leg. Hence, no oil shows might be present in the cores where the oil has been.

However, if gas has been in contact with oil, it is predicted to be wet (< 10% C1 in the C1-C4 gas fraction) due to gas stripping. Some of the C3 and C4 hydrocarbons are likely to have originated from in-reservoir hydrogenation (hydrocraking) of C6+ hydrocarbons where the required H_2 is supplied (Bjørkum, 2021) from decomposition of organic matter in mudstones during burial (Hunt, 1995). For a given oil, the wetness of the gas will depend on the pressure, temperature, and the volume of free gas relative to volume of oil, as well as the thermal maturity of the oil. If oil inclusions can be documented in mineral cements, it is probably safe to conclude that the reservoir has had an oil column.

Conclusions

The total amount of methane in sedimentary basins is estimated to be 100 times larger than in conventional reservoirs. Most methane is dissolved in the pore water. The origin of the methane dissolved in the pore water is not accounted for in today's models for the generation of methane.

Two mechanisms are proposed that can together explain the large volumes of methane. Most is generated from the organic matter dispersed in mudstones, but some methane is formed by reaction of the CO_2 and H_2 released from decomposition of organic matter during most of the burial history.

To explain the origin of free methane in mature conventional reservoirs, approximately one percent of the methane dissolved in pore water methane must be exsolved from the formation water by the decrease in pressure and temperature during upward flow through fractures.

It has been shown that large amounts of water saturated with dissolved methane, generated in mudstones, might flow vertically through hydraulic fractures originated in high-permeability rocks below the hydrofracturing isobar at around the 120°C isotherm. Given optimal geological settings, significant gas accumulation might form above the hydrofracturing isobar from methane released from water due to lower pressures in a few tens of millions of years. However, if hydro-fractures originate in previous gas accumulations (situated *below* the hydrofracturing isobar), a new gas accumulation might form in less than one million years.

Basins with the largest volumes of mudstones are expected to contain the most convention gas. Rapidly subsiding basins might give rise to the largest gas accumulations due to the possibility of multiple remigration episodes.

The model for gas generation might also shed light on the challenges facing shale-gas production. It is argued that most of the gas is the inorganic pores, while the oil is confined to the organic matter. This results in a two-phase problem for the gas and a one-phase problem for the oil. It implies that oil production will be sensitive to the permeability and continuity of organic laminae whereas, gas production should be sensitive to the mudstone permeability.

Acknowledgement

The author thanks Olav Walderhaug and Rune Mjøs for fruitful discussions. The manuscript has benefitted significantly from suggestions form Stephen N. Ehrenberg and Paul H. Nadeau.

References

Al Darouich, T., A. Béhar, F., and C. Largeau, 2006, Thermal cracking of the light aromatic fraction of Safaniya crude oil – experimental study and compositional modelling of molecule classes, Organic Geochemistry, v. 37, pp. 1130-1154. https://doi.org/10.1016/j.orggeochem.2006.04.003

Allen, P.A., and J. R. Allen, 2013, Basin analysis – principles and application to petroleum play assessment, Third edition, Oxford, 619p.

Angulo, A., and C.A. Vargas, 2022, Global distribution of the hydrocarbon Golden Zone, Marine and Petroleum Geology, v. 144, 105832. https://doi.org/10.1016/j.marpetgeo.2022.105832

Baker, D. R., and G. e. Claypool, 1970, Effects of incipient metamorphism on organic matter in mudrock, American Association of Petroleum Geologists Bulletin, v. 54, pp. 456-468. https://doi.org/10.1306/5D25C9AF-16C1-11D7-8645000102C1865D

Barry, P.H., M. Lawson, W.P. Meurer, O. Warr, J.C. Mabry, D.J., Byrne, and C. J. Ballentine, 2016, Noble gas solubility models of hydrocarbon charge mechanism in Sleipner Vest gas field, Geochimica et Cosmochimica Acta, v. 194, pp. 291-309. https://doi.org/10.1016/j.gca.2016.08.021

Baskin, D. K., 1997, Atomic H/C Ratio of Kerogen as an Estimate of Thermal Maturity and Organic Matter Conversion, American Association of Petroleum Geologists Bulletin, v. 81, No. 9, p. 1437–1450. https://doi.org/10.1306/3B05BB14-172A-11D7-8645000102C1865D

Basu, S. H. and M. M. Sharma, 1996, Measurement of critical disjoining pressure for dewetting of solid surfaces, Journal of Colloidal and Interface Science, v. 181, p. 443-455. https://doi.org/10.1006/jcis.1996.0401

Béhar, F., Vandenbrouke, M, 1987, Chemical modelling of kerogens, Organic Geochemistry, v. 11, pp. 15-24. https://doi.org/10.1016/0146-6380(87)90047-7

Béhar, F., M. Vandenbroucke, Y. Tang, F. Marquis, and J. Espitalie, 1997, Thermal cracking of kerogen in open and closed systems: determination of kinetic parameters and stoichiometric coefficient for oil and gas generation, Organic Geochemistry, v. 26. pp. 321- 339. https://doi.org/10.1016/S0146-6380(97)00014-4

Bell, J. A. and G.B. Kistakowsky, 1962, The Reactions of Methylene. VI. The Addition of Methylene to Hydrogen and Methane, Journal of the American Chemical Society v. 84, pp. 3417–3425. https://pubs.acs.org/doi/pdf/10.1021/ja00877a001

Berner, R.A., 1980, Early diagenesis – A theoretical Approach, Princeton Series in Geochemistry, Princeton University Press, 241p.

Beyssac, O., Goffé, B., Chopin, C., and J. N. Rouzaud, 2002, Raman spectra of carbonaceous material in metasediments: a new geothermometer, Journal of Metamorphic Geology., v. 20, pp. 859-871. https://doi.org/10.1046/j.1525-1314.2002.00408.x

Beyssac, O., Brunet, F., Pettet, J-P., Goffé, B., and J.N. Rouzaud, 2003, Experimental study of microtextural and structural transformation of carbonaceous material under pressure and temperature, European Journal of Mineralogy, v. 15, pp. 937-951. https://doi.org/10.1127/0935-1221/2003/0015-0937

Bjørkum, P.A., 2021, Timing of oil expulsion from source rocks and a revitalization of the pre-1970 model**,** eartharxiv.org. https://doi.org/10.31223/X5CW49

Bjørkum, P.A. and Nadeau, P.H., 1998**,** Temperature controlled porosity/permeability reduction, fluid migration, and petroleum exploration in sedimentary basins. Australian Petroleum Production and Exploration Association Journal, v. 38, pp. 453-464. https://www.publish.csiro.au/aj/AJ97022

Bolonin, M.D. and V.I Slavin, 1998. Abnormally high formation pressures in petroleum regions of Russian and other countries of the C.I.S, *in* Law, B.E. G.F. Ulminshek, and V.I. Slavin, eds., Abnormal pressures in hydrocarbon environments, American Association of Petroleum Geologists Memoir 70, pp. 115-121. https://archives.datapages.com/data/specpubs/memoir70/m70ch07/m70ch07.htm

Buckley, S. E., 1958, Distribution of dissolved hydrocarbons in subsurface waters, in: L. G. Weeks, ed., Habitat of oil: A symposium, American Association of Petroleum Geology Special Volumes, pp. 580-882. https://archives.datapages.com/data/specpubs/basinar2/data/a125/a125/0001/0850/0850.htm

Buckley, J.S., K. Takamura, and N.R. Morrow, 1989, Influence of electrical surface charges on the wetting properties of crude oils. SPE Reservoir Engineering, SPE-16964-PA, p. 332-340. https://doi.org/10.2118/16964-PA

Buseck, P.R. and O. Beyssac, 2014, From organic matter to graphite: graphitization, Elements, v. 10, pp. 421-426. https://doi.org/10.2113/gselements.10.6.421

Campbell, J.H. and R.A. Evans, R.A., 1979, Oil shale resorting: a correlation of selected infrared absorbance bands with process heating rates and oil yield, In Situ, v. 3, pp. 33-51. https://www.osti.gov/biblio/6709625

Campbell, J.H., G.J. Koskinas, G. Gallegos, and M. Gregg, 1980, Gas evolution during shale pyrolysis. 1, Nonisothermal rate measurements, Fuel, v. 59, pp. 718-726. https://doi.org/10.1016/0016-2361(80)90027-7

Claypool, G. E., and I. R. Kaplan, 1974, The origin and distribution of methane in marine sediments, Natural Gases in Marine Sediments, pp. 99-139. https://link.springer.com/chapter/10.1007/978-1-4684-2757-8_8

Clayton, C. 1991, Carbon isotope fractionation during natural gas generation from kerogen, Marine and Petroleum Geology. v. 8, pp. 232- 240. https://doi.org/10.1016/0264-8172(91)90010-X

Clough, A., J.L. Sigle, D. Jacobi, J. Sheremata, and J.L. White, 2015, Characterization of kerogen and source rock maturation using solid-state NMR spectroscopy, Energy Fuel, v. 29, pp. 6370-6382. https://pubs.acs.org/doi/full/10.1021/acs.energyfuels.5b01669?casa_token=hi5X7Fd_SrkAAAAA%3A8B9J51YwCwRsPHzg-I65eGbbKDzKlHvxTdRjMfkw0P9DRGGIOJConGSVtdn1_FRyfC5LYAZQamgiITPu

Cordell, R. J. 1973, Colloidal soap as proposed primary migration medium for hydrocarbons, **American Association of Petroleum Geologists** Bulletin, v. 57, pp. 1618-1643. https://doi.org/10.1306/83D9101A-16C7-11D7-8645000102C1865D

Craddock, P., T. Van Le Doan, K. Bake, M. Polyakov, A.M. Charsky, and A. E., Pomerantz, 2015, Evolution of kerogen and bitumen during thermal maturation via semi-open pyrolysis investigated by infrared spectroscopy, Energy and Fuel, v. 29, pp. 2197-2210. https://pubs.acs.org/doi/full/10.1021/ef5027532?casa_token=1rzHlnL1Y7AAAAAA%3AUU2JwUfNcqq-PwZw-eLrFcBc_Yo7rsAjICrfjYN3bOo7tV9pp1bz8XDAQzmTJq5QZ_GwJ8SNGfMay4XV

Duan, Z. Møller, N. Greenberg, J., H. Weare, 1992, The prediction of methane solubility in natural waters to high ionic strength from 0 to 250°C and from 0 to 1600 bar, Geochemica et Cosmochimica Acta, v. 56, pp. 1451-1460. https://doi.org/10.1016/0016-7037(92)90215-5

Engender, T. and J. Leftwich, 1997, A pore-pressure limit in overpressured South Texas oil and gas fields, *in* R.C. Surdam, ed., Seals, traps, and the petroleum system, American Association of Petroleum Geologists Memoir 67, pp. 255-267. https://archives.datapages.com/data/specpubs/mem67/ch15/ch15.htm

Evans, C.R, M.A. Rogers, and N.J.L. Bailey, 1971, Evolution and alternation of petroleum in Western Western Canada, Chemical Geology, v. 8, pp. 147-170. https://doi.org/10.1016/0009-2541(71)90002-7

Ferguson, A. L., P.G. Debenedetti, and A.Z., Pangaiotopoulos, 2009, Solubility and molecular conformation of *n*-alkane chains in water, Journal of Physical Chemistry, v. 113, pp. 6405-6414. https://pubs.acs.org/doi/full/10.1021/jp811229q?casa_token=tZB51licQGsAAAAA%3Aa67e99vUjn5dTiaSZghqa-aRp_rLoUG17QLHN-0B8omjtwIVQHfuY5X4uXDkOudOQiD57-we4QSvsMAF

Fuex, A. N., 1977, The use of stable carbon isotope in hydrocarbon exploration, Journal of Geochemical Exploration, v. 7, pp. 155-188. https://doi.org/10.1016/0375-6742(77)90080-2

Fusetti, L., Béhar, F., Bounaceur, P.M. Marguaire, K. Grice, and S. Derenne, 2010, New insight into secondary gas generation from thermal cracking of oil: Methylated monoaromatics. A kinetic study using 1,2,4 trimethylbenzene. Part I: A mechanistic kinetic model, Organic Geochemistry, v. 41, pp. 146-167. https://doi.org/10.1016/j.orggeochem.2009.10.013

Galimov, E.M., 2006, Isotope organic geochemistry, Organic Geochemistry, v. 37, pp. 1200-1262. https://doi.org/10.1016/j.orggeochem.2006.04.009

Grew, E.S., 1974, Carbonaceous material in some metamorphic rock of New England and other areas, Journal of Geology, v. 82, pp. 50-73. https://www.journals.uchicago.edu/doi/abs/10.1086/627936

Hantschel, A.I. and T. Kauerauf, 2009, Fundamentals of Basin and Petroleum Systems Modelling, Springer-Verlag Berlin Heidelberg, 476p.

Harwood, R. J. 1977, Oil and gas generation by laboratory pyrolysis of kerogen, American Association of Petroleum Geologists Bulletin, v. 61, pp. 2082–2102. https://doi.org/10.1306/C1EA47CA-16C9-11D7-8645000102C1865D

Hauser, A., F. AlHumaidan, H. Al-Rabiah, and M. A., and H. Halabi, 2014, Study on thermal cracking of Kuwaiti oil (vacuum residue) and its SARA fraction by NMR spectroscopy, Energy Fuels, v. 28, pp. 4321- 4332. https://pubs.acs.org/doi/full/10.1021/ef401476j?casa_token=Oy_4D2lYUZwAAAAA%3AsGkxpE07hUo_GSSBYfgKVBdGshMinMKz2qyP3DEajDM3LTja9fHT3Qc3urGZLudfYF2iAc-zIdcxFg95

Hedberg, H. D., 1964, Geologic aspects of origin of petroleum: American Association of Petroleum Geologists Bulletin, v. 48, no. 11, pp. 1755-1803. https://doi.org/10.1306/BC743DB7-16BE-11D7-8645000102C1865D

Hill, R.J., E. Zhang, B.J. Katz, and Y. Tang, 2007; Modelling of gas generation from Barnett shale, Fort Worth Basin, Texas, American Association of Petroleum Geologists Bulletin, v. 4, pp. 501- 521. https://doi.org/10.1306/12060606063

Hunt, J.M. 1961, Distribution of hydrocarbons in sedimentary rocks, Geochemica et Cosmochimica Acta, v. 22, pp. 37-49. https://doi.org/10.1016/0016-7037(61)90071-0

Hunt, J.M. 1972; Distribution of carbon in crust of earth, 1972, AAPG, v. 56, pp. 2273-2277. https://doi.org/10.1306/819A4206-16C5-11D7-8645000102C1865D

Hunt, J. M, 1977, Distribution of carbon as hydrocarbons and asphaltic compounds in sedimentary rocks, American Association of Petroleum Geologists Bulletin v. 61, pp. 100-104. https://www.osti.gov/biblio/7122211

Hunt, J. M., 1979, Petroleum Geochemistry and Geology, 1st ed., W. H. Freeman, San Francisco, 617p.

Hunt, J.M., 1984, Generation and migration of light hydrocarbons, Science, v. 226, pp. 1265-1270. https://www.science.org/doi/abs/10.1126/science.226.4680.1265

Hunt, J. M., 1995, Petroleum Geochemistry and Geology, 2nd ed., W. H. Freeman, San Francisco, 743p.

Horstad, I. and S. R. Larter, 1997, Petroleum migration, alteration, and remigration within Troll Field, Norwegian Sea, v. 81, pp. 222-248. https://doi.org/10.1306/522B42F3-1727-11D7-8645000102C1865D

Inan, S., 2000, Gaseous hydrocarbons generated during pyrolysis of petroleum source rocks using unconventional grain-size: implications for natural gas composition, Organic Geochemistry, v. 31, pp. 1409-1418. https://doi.org/10.1016/S0146-6380(00)00070-X

Jackson, K. J., A.K. Burnham, R.L. Braun, and K. G. Knauss, 1995, Temperature and pressure dependence of n-hexadecane cracking, Organic Geochemistry, v. 23, pp. 941-953. https://doi.org/10.1016/0146-6380(95)00068-2

Jarvie, D. M., 2012, Shale resrources systems for oil and gas: Part 2 – shale oil-resource systems, *in* J. A., Breyer, ed., Shale reservoirs - Gigant resources for the 21st century, American Association of Petroleum Geologists Memoir 97, pp. 89-119. https://archives.datapages.com/data/specpubs/memoir97/CHAPTER01P2/CHAPTER01P2.HTM?q=%2BtextStrip%3Aclassifying+textStrip%3Apore+textStrip%3Asystems

Jarvie, D. M, 2015, Geolocical asessment of unconventional shale gas resrevoir systems, Fudnamentals of Gas Shale Reservoirs, Firsdt edition, R. Rezaee, ed., pp. 87-69. https://doi.org/10.1002/9781119039228.ch3

Jarvie, D. M., R. J. Hill, T.E. Ruble, and R.M. Pollastro, 2007, Unconventional shale-gas systems: The Mississippian Bernett Shale of north-central Texas as a model for thermogeneic shale gas assesment, AAPG Bulletin, v. 91, pp. 475-499. https://doi.org/10.1306/12190606068

Kuske, S., B. Horsfield, J. Jweda, G. E., Micahel, and Y. Song, 2019, Geochemical factors controlling the phase behaviour of Eagle Ford shale petroleum fluids, American Association of Petroleum Geologists Bulletin, v. 103, pp. 835-870. https://doi.org/10.1306/09051817227

Landes, K.K., 1967; Eometamorphism, and oil and gas in time and space, American Association of Petroleum Geologists Bulletin, v. 51, pp. 828-841. https://doi.org/10.1306/5D25C0F1-16C1-11D7-8645000102C1865D

Law, B. E., 2002, Basin-centered gas systems, American Association of Petroleum Geologists Bulletin, v. 86, pp. 1891-1919. https://doi.org/10.1306/61EEDDB4-173E-11D7-8645000102C1865D

Masters, J.A., 1979, Deep basin gas, Western Canada, American Association of Petroleum Geologists Bulletin, v. 63, pp. 152-181. https://doi.org/10.1306/C1EA55CB-16C9-11D7-8645000102C1865D

Lewan, M. D., 1985, Evaluation of petroleum generation by hydrous pyrolysis experimentation, Philosophical Transactions of the Royal Society of London, A 315, pp. 123 – 135. https://doi.org/10.1098/rsta.1985.0033

Lewan, M. D., 1988, Reply to the comments by A. K. Burnham on "Experiments on the role of water in petroleum formation", Geochimica et Cosmochimica Acta, v. 62, pp. 2211-2216. https://doi.org/10.1016/S0016-7037(98)00150-1

Lewan, M.D., and T.E. Ruble, 2002. Comparison of petroleum generation kinetics by isothermal hydrous and non-isothermal open-system pyrolysis, Organic Geochemistry, v. 33, pp. 1457–1475. https://doi.org/10.1016/S0146-6380(02)00182-1

Littke, R., B. Cramer, P. Gerling, N. V. Lopatin, H. S. Poelchau, R. G. Schaefer, and D. H. Welte, 1999, Gas generation and accumulation in the West Siberian Basin, American Association of Petroleum Geologists Bulletin, v. 83, pp. 1320–1336. https://doi.org/10.1306/E4FD4233-1732-11D7-8645000102C1865D

Lorant, F. and F. Béhar, 2002, Late generation of methane from mature kerogens, Energy, v. 16, pp. 412-427. https://pubs.acs.org/doi/full/10.1021/ef010126x?casa_token=a9PI58Dfd_oAAAAA%3AO7MMAmzkpfh60sOJCnxt6oJwKk44cueoqJs5QRN6aSX6TV7r5mgdgPkWleKrbQQWrAlTe5itqDUkdAY9#

Mandl, G. and R.M. Harkness, 1987, Hydrocarbon migration by hydraulic fracturing, *in* M. E. Jones and R.M. F. Preston, eds., Deformation of sediments and sedimentary rocks, Geological Society of London Special Publications, v. 29, pp. 1005-1018. https://doi.org/10.1144/GSL.SP.1987.029.01.04

Mango, F. D., 1997, The light hydrocarbons in petroleum: a critical review, Organic Geochemistry, v. 26, pp. 417-440. https://doi.org/10.1016/S0146-6380(97)00031-4

Mango, F.D., 2001, Methane concentration in natural gas: the genetic implications, Organic Geochemistry, v. 32, pp. 1283-1287. https://doi.org/10.1016/S0146-6380(01)00099-7

Mango, F. D., 2013, Methane and carbon at equilibrium in source rock, Geochemical Transactions, v. 14, pp. 1-9. https://geochemicaltransactions.biomedcentral.com/articles/10.1186/1467-4866-14-5

Mango, F. D., and D.M. Jarvie, 2009, Low-temperature gas from marine shales, Geochemical Transactions, v. 10, pp. 4-11. https://geochemicaltransactions.biomedcentral.com/articles/10.1186/1467-4866-10-3

McCoy, A. W., 1924, A brief outline of some oil-accumulation problems, American Association of Petroleum Geologists Bulletin, v. 10, pp. 1015-1034. https://doi.org/10.1306/3D93274F-16B1-11D7-8645000102C1865D

McNab, J.G., P.V. Smith Jr., and R. L. Betts, 1952, The Evolution of Petroleum, Industrial and Engineering Chemistry, v. 44. pp. 2556- 2563. https://pubs.acs.org/doi/pdf/10.1021/ie50515a029

McNeil, R.I. and W.O. BeMent, W.O., 1996, Thermal stability of hydrocarbons: laboratory criteria and field examples, Energy Fuel, v. 10, pp. 60-67. https://pubs.acs.org/doi/full/10.1021/ef9501399?casa_token=QsLvNm_11QcAAAAA%3Avp9lndGwVh2S5sIsu6TWxwVGvpOF5i2NFl4KthAi8tAlyVPuEPOR9L8GeKcQwkAqn2mC40NC-qaAvAIp

Mohanty, S., D., Kunzru, and D.N. Saraf, 1980, Hydrocracking: a review: Feul, v. 69, pp.1467-1473. https://doi.org/10.1016/0016-2361(90)90192-S

Montgomery, S.L., D.M. Jarvie, K.A. Bowker, and R.M. Pollastro, 2005, Mississippian Barnett shale Forth Worth basin, north-central Texas: Gas-shale play with multi-trillion cubic foot potential. **American Association of Petroleum Geologists** Bulletin, v. 89, pp. 155-175. https://doi.org/10.1306/09170404042

Morgan , T. J. and R. Kandiyoti, 2014, Pyrolysis of coals and biomass: analysis of thermal breakdown and its products, Chemical Review. V. 114, pp. 1547-1607. https://pubs.acs.org/doi/full/10.1021/cr400194p

Nadeau, P. H., P.A. Bjørkum, and O. Walderhaug, 2005, Petroleum system analysis: impact of shale diagenesis on reservoir fluid pressure, hydrocarbon migration, and biodegradation risks, in Doré, A. G. and B.A. Vining, eds., Petroleum Geology: North-West Europe and Global Perspectives - Proceedings of the 6th Petroleum Geology Conference, London, Geological Society of London, pp. 1267-1274. https://doi.org/10.1144/006126

Orozco, D., A. Fragoso, K. Selvan, G. Noble, and R. Aquilera, 2020, Eagle Ford huff 'n' puff gas-injection pilot: comparison of reservoir-simulation, material balance, and real performance of the pilot well, SPE Reservoir Evaluation and Engineering, SPE-191575-PA, v. 20, pp. 247-260. https://doi.org/10.2118/191575-PA

Pelet, R., F. Béhar, and J.C. Monin, 1985, Resins and asphaltenes in generation and migration of petroleum, Advances in Organic Geochemistry, vol. 10. pp. 481-498. https://doi.org/10.1016/0146-6380(86)90048-3

Pereda, S., J.A. Awan, A.H. Mohammadi, A.H., A. Valtz, C. Coquelet, E.A. Brignole, and D. Richon, 2009. Solubility of hydrocarbons in water: experimental measurements and modelling using a group contribution with association equation of state (GCA-EoS), Fluid Phase Equilibria, v. 275, pp. 52-59. https://doi.org/10.1016/j.fluid.2008.09.008

Pratt, W. E., 1934, Hydrogenation and the origin of oil, Part II. Origin and evolution of petroleum: Group 3. Variation in physical properties, in Problems of Petroleum Geology**,** in W.E. Wrather and F. H. Lahee, eds., American Association of Petroleum Geologists, pp. 235-245. https://archives.datapages.com/data/specpubs/methodo1/data/a069/a069/0001/0200/0235.htm

Quigley, T.M. and A. S. Mackenzie 1988a, The temperature of oil and gas formation in the sub-surface, Nature, v. 333, pp. 549-552. https://www.nature.com/articles/333549a0

Quigley, T.M. and A.S. Mackenzie, 1988b, Principles of Geochemical Prospect Appraisal, American Association of Petroleum Geologists, v. 72, pp. 399-415. https://doi.org/10.1306/703C8EA2-1707-11D7-8645000102C1865D

Rice, D.D. and G.E Claypool,, 1981, Generation, accumulation, and resource potential of biogenic gas, American Association of Petroleum Geologists Bulletin, v. 65, pp. 5-25. https://doi.org/10.1306/2F919765-16CE-11D7-8645000102C1865D

Roberts, S.J. and J. A. Nunn, 1995, Episodic fluid flow expulsion from geopressured sediments, Marine and Petroleum Geology, v. 12, pp. 195-202. https://doi.org/10.1016/0264-8172(95)92839-O

Rooney, M.A., G.E. Claypool, and H.M. Chung, 1995, Modelling thermogenic gas generation using carbon isotope ratios of natural gas hydrocarbons, Chemical Geology, v. 126, pp. 219-232. https://doi.org/10.1016/0009-2541(95)00119-0

Rouzaud, J.N and A. Oberlin, 1989, Structure, microstructure, and optical properties of anthracene and saccharose-based carbon. Carbon, v. 27, pp. 517-529. https://doi.org/10.1016/0008-6223(89)90002-X

Sackett, W.M., 1968, Carbon isotopic composition of natural methane occurrences, American Association of Petroleum Geologists Bulletin. V. 52, pp. 853-857. https://doi.org/10.1306/5D25C469-16C1-11D7-8645000102C1865D

Savage, P.E. 2000, Mechanisms and kinetics models for hydrocarbon pyrolysis, Journal of Analytical and Applied Pyrolysis, v. 54, pp. 109-126. https://doi.org/10.1016/S0165-2370(99)00084-4

Savage, P.E., G. Jacobs, and M. Javanmardian, 1989, Autocatalysis and aryl-alkyl bond cleavage in 1-dodecylpyrene. Journal of the American Institute of Chemical Engineering, v. 28, pp. 645-654. https://pubs.acs.org/doi/pdf/10.1021/ie00090a001

Schaefer, R.G., Y.I. Galushkin, A. Kolloff, R. Littke, 1999, Reaction kinetics of gas generation in selected source rocks of the West Siberian Basin: implications for the mass balance of early-thermogenic methane, Chemical Geology, v. 156, pp. 41-65. https://doi.org/10.1016/S0009-2541(98)00177-6

Schaaf, T., J. Grüing, M.R. Schuster, T. Rothenfluh, and A. Orth. 2017, Methanation of CO2 – storage renewable energy in gas distribution system, Energy, Sustainability and Society, pp. 1-15. https://energsustainsoc.biomedcentral.com/articles/10.1186/s13705-014-0029-1

Shi, J., Y. Ma, S. Li, and L. Zhang, 2017, Characterization of thermal bitumen structure as the pyrolysis intermediate of Longkou oil shale, Energy Fuels, v. 31, pp. 10535-10544. https://pubs.acs.org/doi/full/10.1021/acs.energyfuels.7b01542?casa_token=AqzGh_Lp_qMAAAAA%3AJmBJD-s0gZUYiKQSklJ36BX1irBa8AG21UC_fUjyiHv58RX5DNhwmgMKNntTqizdsw5zXHt7TYlBR0H2

Sie, S. T., 1993a, Acid-catalyzed cracking of paraffinic hydrocarbons, 3. Evidence for protonated cyclopropane mechanism from hydrocracking/hydroisomerization experiments, Industrial and Engineering Chemistry Research, v. 32, pp. 403-408. https://pubs.acs.org/doi/pdf/10.1021/ie00015a002

Sie, S.T, 1993b, Acid-catalyzed cracking of paraffinic hydrocarbons. 2. Evidence for the protonated cyclopropane Mechanism from catalytic cracking experiments, Industrial and Engineering Chemistry Research, v. 32, pp. 397-402. https://pubs.acs.org/doi/pdf/10.1021/ie00015a001

Smith, J.E., J. G., Erdmann, and D.A. Morris, 1971, Migration, accumulation, and retention of petroleum in the Earth, in English world petroleum Congress, proceedings, Geological and exploration: London, Applied Science Publisher, v. 2. pp. 13-26. https://onepetro.org/WPCONGRESS/proceedings-abstract/WPC08/All-WPC08/WPC-14102/199064

Smith, C.M., and P.E., Savage, 1991, Reaction of polycyclic alkyl aromatics: **S**tructure and reactivity, Journal of the American Institute of Chemical Engineering, v. 37, pp. 1613-1624. https://doi.org/10.1002/aic.690371104

Smith, C.M, and P.E., Savage, 1993, reactions of polycyclic alkylaromatics: 5. Pyrolysis of methyantracenes. Journal of the American Institute of Chemical Engineering, v. 39, pp. 1355-1368. https://doi.org/10.1002/aic.690390812

Silverman, S. R. and S. Epstein 1958, Carbon isotopic composition of petroleum and other sedimentary organic materials, American Association of Petroleum Geologists Bulletin, v. 42, pp. 998-1012. https://doi.org/10.1306/0BDA5AEC-16BD-11D7-8645000102C1865D

Stahl, W, 1974, Carbon isotope fractionations in natural gases, Nature, v. 251, pp. 134-135. https://www.nature.com/articles/251134a0

Tang, Y., P.D. Jenden, A. Nigrini, and S. Teerman, Modelling early methane generation in coal, Energy & Fuels, v. 10, pp. 659-671. https://pubs.acs.org/doi/full/10.1021/ef950153l?casa_token=JexmcsOZJGMAAAAA%3A-HUm_0klaeL_n4CoWywtQLrFNUdHLb2H045Rv1GSbba5JlAZw-6hOtIpbBNL68qraGhr51O3Ii-EyPeI

Tong, X., G. Zhang, Z. Wang, Z. Wen, Z. Tian, H. Wang, F. Ma, and Y. Wu, 2018, Distribution and potential of global oil and gas resources, Petroleum Exploration Development, v. 45, pp.779–789. https://doi.org/10.1016/S1876-3804(18)30081-8

Tissot, B.P and D.H. Welte, 1984, Petroleum Formation and Occurrence, 699 p.

Vandenbroucke, M. and C. Largeau, 2007, Kerogen origin, evolution and structure, Organic Geochemistry, v. 38, pp. 719-833. https://doi.org/10.1016/j.orggeochem.2007.01.001

Vogt, C., J. Lauterjung, and R. X. Fisher, 2002 Investigation of the clay fraction (<2µm) of the clay minerals society reference clays, Clays and Clay Minerals, v. 50, pp. 388-400. https://pubs.geoscienceworld.org/ccm/article-abstract/50/3/388/48221/INVESTIGATION-OF-THE-CLAY-FRACTION-lt-2-m-OF-THE

Weitkamp, J, 1975, The influence of chain Length in hydrocracking and hydroisomerization of *n*-Alkanes, ACS Symposium Series, American Chemical Society, v. 20, pp. 1-27. https://pubs.acs.org/doi/abs/10.1021/bk-1975-0020.ch001

Whiticar, M.J., 1999, Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane, Chemical Geology, v. 161, pp. 291-314. https://doi.org/10.1016/S0009-2541(99)00092-3

Wiebe, R, and V.L. Goddy, 1934, The solubility of hydrogen in water at 0, 50, 75 and 100° from 25 to 1000 atmosphere, Journal of the American Chemical Society, v. 56, pp. 76-79. https://pubs.acs.org/doi/pdf/10.1021/ja01316a02

Zartman, R.E., G.J., Wasserburg, and J. H. Reynolds, 1961, Helium, argon, and carbon natural gases, Journal of Geophysical research, v. 66, pp. 277-306. https://doi.org/10.1029/JZ066i001p00277

Zgonnik, V., 2020, The Occurrence and geoscience of natural hydrogen: A comprehensive review: Earth-Science Reviews, v. 203, pp. 1-51. https://doi.org/10.1016/j.earscirev.2020.103140

Zobell, C.E., 1946, Studies on redox potential of marine sediments**,** American Association of Petroleum Geologists Bulletin, v. 30, pp. 447-513. https://doi.org/10.1306/3D933808-16B1-11D7-8645000102C1865D

Zumberge, J., F. Ferworn, and S. Brown, 2012, Isotopic reversal ('rollover') in shale gas from Mississippian Bernett and Fayettevile formations, Marine and Petroleum Geology, v. 31, pp. 43-52. https://doi.org/10.1016/j.marpetgeo.2011.06.009

Øren, P.E., J. Billiotte, and W.V. Pinczewski, 1992, Mobilization of waterflood residual oil by gas injection for water-wet conditions. SPE Formation Evaluation, SPE-20185-PA, v.7, pp. 70-78. https://doi.org/10.2118/20185-PA

Øren, P. E., J. Billiotte, and W.V. Pinczewski, 1994, Pore-scale network modelling of waterflood residual oil recovery by immiscible gas flooding, Improved Oil Recovery Symposium, SPE-27814-MS, pp. 346-359. https://doi.org/10.2118/27814-MS