Chapter 23

Unconventional Hydrocarbons: Oil Shales, Heavy Oil, Tar Sands, Shale Oil, Shale Gas and Gas Hydrates

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For many decades conventional oil which could be produced at low cost was present in abundance. A low oil price gave no incentive to look for other types of resources. It is now clear, however, that we are gradually running out of new sedimentary basins to explore and that the reserves of conventional oil which can be produced cheaply are limited.

This is the reason why many of the major oil companies now invest in what is often called unconventional hydrocarbons. There are large reserves of these and the main types are oil shales, heavy oil, tar sand, shale oil and shale gas. Production of hydrocarbons from these sources occurs mainly in onshore basins and may be challenging environmentally.

Gas hydrates may also become an important source of hydrocarbons but the development of methods to produce from such accumulations is still at an early stage.

The reserves of unconventional hydrocarbons are very large, probably larger than those of conventional oil. We will therefore not run out of fossil hydrocarbons for a long time but the prices will be higher because these sources are more difficult to produce, particularly if strict environmental standards should be met.

23.1 Heavy Oil and Tar Sands

Heavy oil seeping out on the surface has been known for a long time and this was easy to exploit for use in small quantities. Even after drilling for oil became successful (in 1857 in Pennsylvania), mining for heavy oil continued in many parts of the world including Germany. In southern California (Ventura and Los Angeles basins) oil was mined from the early 1860s to the 1890s because the heavy oil there would not flow to the wells (Fig. 23.1).

Tar sands are sandstone reservoirs which have been filled with oil at shallow depth <2 km (<70–80°C) so that the oil has become biodegraded. Reservoir rocks which have been buried more deeply and then uplifted before the oil migration may be sterilised at higher temperatures and are less likely to be biodegraded.

When the sandstone has not been buried to more than about 2 km depth the sand will remain mostly uncemented as loose sand because of a lack of quartz cement.

Tar sand contains asphaltic oil rich in asphaltenes and resins. It has a high content of aromatics and naphthenes compared to paraffins, and a high content of nitrogen, sulphur and oxygen (NSO). Most of the hydrocarbon molecules have more that 60 carbon atoms and the boiling point and viscosity are therefore very high.

The viscosity of the biodegraded oil is very low and the oil must be heated so that the viscosity is reduced before it can be produced by drilling wells. There are transitions between reservoirs with heavy oil and nearly solid bitumen. Heating can be achieved by soaking the reservoir with injected steam so that the heat of condensation to water helps to heat the oil. This is called cyclic steam injection when the steam is injected in the production well and left to soak for a few weeks before production starts when the oil is warmer. The steam may also be injected in a nearby well and driven towards the production well. Much of the energy is

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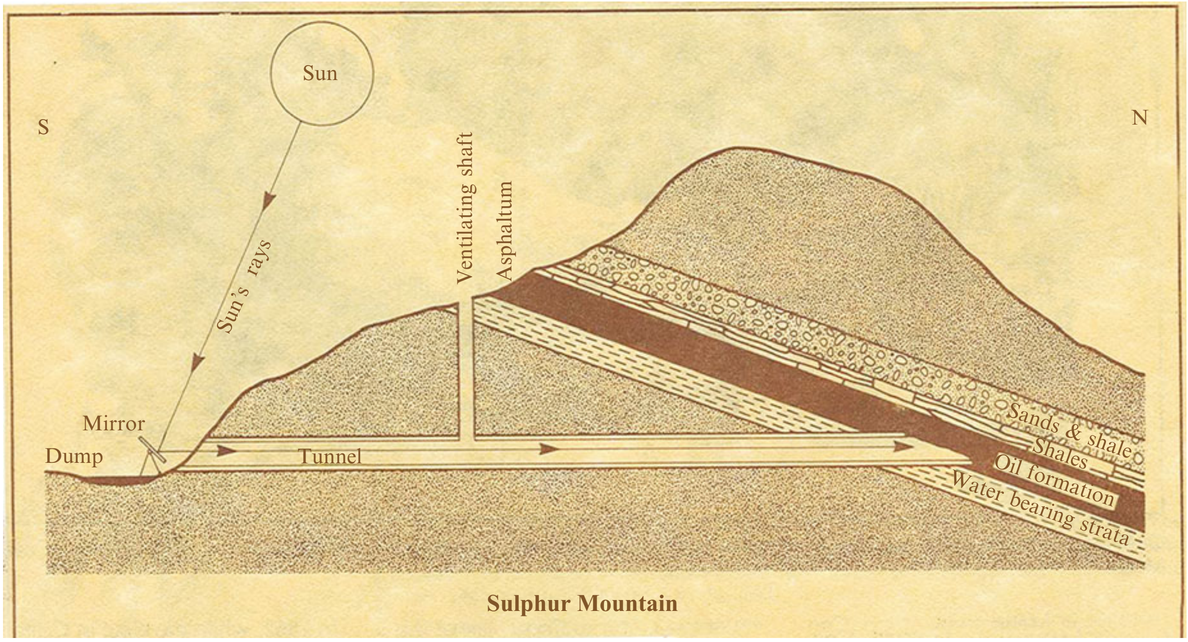

Fig. 23.1 Mining for heavy oil in the Sulfur Mountain near Santa Paula, South California (from 1860 to 1890). Mine tunnels could be 6–700 m long and a mirror was used to light the tunnel and the sunlight would contribute to the heating of the heavy oil so that it could flow. See the Oil Museum in Santa Paula (http://www.oilmuseum.net/)

used to heat the water in the reservoir and it is important to reduce the inflow of water from adjacent rocks. One method includes freezing the ground at a distance from the well to avoid the flow of water towards the well. It is also possible to burn some of the oil in the subsurface to provide heat to heat the oil.

It has also been proposed to heat the oil electrically, possibly powered by a nuclear reactor to reduce the CO_2 emissions from burning oil to produce heat.

The tar sands in Alberta, Canada (Athabasca) are of Middle Cretaceous age (Aptian, 100 million years).

The main reservoir rock is the McMurray Formation, a sandstone representing fluvial to tidal environments, and it is important to find thick sequences of sand with few clay layers. The oil was generated from older source rocks during the Laramide folding of the Rocky Mountains to the west and migrated into the Athabasca sands during the Cretaceous when these fluival sandstone were still at a relatively shallow depth. Starting in the Eocene (50 million years) the sand was uplifted and most of the overburden eroded. The oil was then biodegraded by bacteria. These tar sands contain 1.7 trillion bbl (270×10^9 m^3) of bitumen in-place, comparable in magnitude to the world's total proven reserves of conventional *petroleum*. There are currently large mining operations at Athabasca (Fig. 23.2). At surface temperatures, which are low in northern Canada, this tar sand is rather hard (Fig. 23.3) because of the high viscosity of the oil. The oil must be separated from the sand using hot water (Fig. 23.4). The oil (tar) is very viscous and may be denser than water (API <10).

Tar sand is produced by *in situ* mining where the sand is excavated with heavy equipment (Fig. 23.1) The separation of tar from the sand requires very large amounts of water. About 350,000 m^3 of hot water is used yearly in the treatment of the Athabasca tar sand.

There are very large volumes of heavy oil and tar in sandstone reservoirs which cannot be produced at normal surface temperatures. In Alberta alone this may represent 1–2 trillion barrels. Heavy oil with API gravity between 10–20 has viscosities exceeding 10,000 centipoise (cP) while bitumen with API gravity below 10 may be very hard and solid with viscosity exceeding 1 mill cP. Heating the tar to 200–300°C the viscosity becomes very much reduced so that it can flow to a well, The heating may occur by soaking the reservoir with steam for several weeks before production starts. This is called CSS (Cyclic Steam Stimulation).

Fig. 23.2 Athabasca tar sand. The oil-impregnated sand is mined and the heavy oil is separated from the sand with hot water

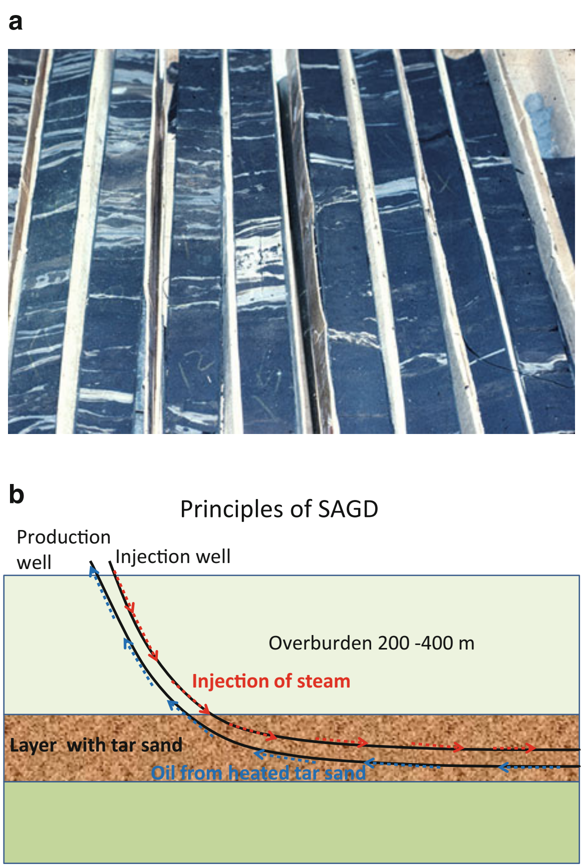

Fig. 23.3 (**a**) Cores from the Athabasca tar sand. The oil sand is highly viscous, almost solid, but will flow at high temperatures. Dark intervals are loose sand mostly with more than 30% porosity, filled with biodegraded heavy oil. *Grey layers* are thins shales which will reduce the vertical mobility of the heated oil during production, illustrated in (**b**)

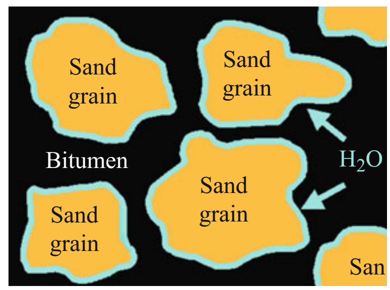

Fig. 23.4 Schematic representation of tar sand. The oil may also stick more closely to the grain surfaces, so the system is more oil-wet

Another method mostly used in Alberta is called SAGD (Steam Assisted Gravity Drainage). Here two horizontal wells are drilled into the reservoir with tar sand. Steam is injected into the upper well to heat up the tar so that it becomes viscous enough to be produced from the lower well. The tar (bitumen) must generally be heated to 200°C for the viscosity to be reduced to about 10 cP. Water and air is then injected to displace the steam further into the sandtone reservoir. Each m^3 of oil produced may require from 2-10 GJ of energy.

When cheap gas is used as energy for the heating process it may be profitable to produce oil even if there should be a negative energy balance.

As the steam condenses to water it gives off heat in the reservoir. A recovery between 40–60% may be expected.

The produced oil will also contain some water and clay which must be removed before the oil can be processed. The water is then re-injected or used for the generation of steam, to reduce the use of new freshwater.

It is also possible to produce oil and sand from wells and then separate the sand out as is done when mining the tar sand.

Another method is to pump air down boreholes and burn some of the oil to produce heat.

Fluvial sandstones like the lower Cretaceous McMurray Fm of the Athabasca Tar sand in Alberta represent a very complex reservoir with respect to migration and filling of hydrocarbons. Each channel sand may represent a small trap which will be first filled with early mature oil from the source rock. As the oil becomes more mature and less dense it may displace the first oil to arrive and finally gas may migrate in and displace most of the oil into shallower structures. This is a good example of fill and spill in a series of rather small compartments.

Fluvial channels which are abandoned by channel avulsion are filled with clay and mud and they may represent clay plugs which are barriers for fluid flow and sometimes seals in these reservoirs (Fustic et al. 2012). When oil and gas has migrated into shallow sandstones like the McMurray Fm where the temperatures are below 80°C, bacteria are present.

The sand will be loose and indurated due to little or no quartz cement and the temperatures will also be low enough for biodegradation at a high rate. Most of the biodegradation occurs near the oil/water contact and since new oil/water contacts may develop during migration there may be complex zones of biodegradation. The highest viscosity oil is usually found near the base of the oil column where the biodegradation has been most intense (Jones et al. 2008). The OWC contact may however have changed during the fill and spill, resulting in more than one intensively biodegraded zone. Variations in the oil viscosity within the reservoir play an important role in the planning of production.

Only about 20% is close enough to the surface to be economically mined and the rest must be heated in place.

A cubic metre of oil, mined from the tar sands, needs 2–4.5 m^3 of water.

Oil may be extracted by steam-assisted gravity drainage (SAGD) (Fig. 23.3b). Two parallel horizontal wells are drilled so that one is about 5 m below the other. Steam is injected in the shallowest well and the heated, less viscous, oil is drained into the lower well where it is produced. The steam will remain near the top due to its low density but will sink when condensed to water. The shales will reduce the vertical permeability and the drainage, but the heating will cause some fracturing which may allow more vertical flow. This method requires rather thick and homogeneous sand. Steam can also be injected into one well for a few weeks until the oil is heated and then produced from the same well. This is called cyclic steam stimulation (CSS).

Large amounts of energy and water are required to produce the steam for this method. If petroleum is burned to produce the heat, high emissions of CO_2 will result not only from when the oil is burnt as fuel but also from producing it. The steam may be mixed with solvents (gas) and this may reduce the amount of heat (steam) required. Much of the water used to produce steam can be recovered and used again.

For each 3 bbl of oil produced one barrel is burned to produce the steam required for the production. 50–70 kg of CO_2 is typically produced and emitted for earch barrel of oil produced mainly due to the production of steam. This heavy oil should also be mixed with gas during the refining and a supply of gas is therefore important.

Heating the oil with electricity has also been proposed and hydroelectric or nuclear power would reduce the CO_2 emissions.

173 billion bbl (27.5×10^9 m^3) of crude bitumen, which is 10% of the total bitumen in place in Alberta, has been considered to be, economically recoverable using current technology at oil prices above 60–100 USD/barrel. In recent years the price of gas has dropped due to shale gas. Heating the oil with steam produced by gas is now more economical than using oil. In some cases there may a negative energy balance so that the energy from gas exceeds the energy in the produced oil.

The environmental problems associated with oil production from tar sand are considerable and very large amounts of water are required both for the production of steam for subsurface operations and for the processing of loose sand excavated from surface pits. As a result the release of CO_2 is higher by 20–25% than with normal petroleum production if the CO_2 is not captured and sequestrated.

In Venezuela there are also very large reserves of heavy oil and tar sand such as the Orinoco tar sand. While the average surface temperature in Northern

Alberta is only slightly above 0°C the surface temperature in Venezuela is much higher (>20°C) and the oil therefore needs less heating to reduce its viscosity.

Much of the oil in Venezuela is heavy oil and it occurs in a foreland basin in front of the Cordilleran Mountains in a similar plate tectonic position to the heavy oil in Alberta. Also the oil in the Middle East is located in a similar foreland basin but here the reservoirs have not been uplifted so close to the surface and are therefore in most cases not so biodegraded.

It is possible to make an emulsion between bitumen and water which has low viscosity and which can flow in pipelines and be burned directly to produce electric power. The heavy oil and bitumen is rather rich in sulphur which should be removed to avoid pollution. It can also be mixed with gas so that it can be used to produce normal oil products.

There are other important tar sand deposits in the USA (Utah) and Africa (Congo and Madagascar).

Tar sand has only recently been included in data on world oil reserves and as a result Canada has become one of the nations with the highest oil reserves.

23.2 Oil Shales

Oil shales are source rocks, usually mudstones and shales, with a high organic content (TOC), which have not been buried deeply enough to become sufficiently mature for most of the hydrocarbons to be generated. Although they may contain some hydrocarbons they must be heated in an oven (pyrolysis) to 400–500°C so that most of the petroleum can be generated from the remaining kerogen.

Oil shales must therefore be mined near the surface in quarries and then heated in large ovens so that the petroleum can be distilled off.

Source rocks may be uplifted close to the surface after deeper burial; it is the temperature history that determines how much of the kerogen is altered to oil and gas.

Some source rocks may have been buried to more than 5–6 km (160–170°C) and they have then generated and expelled most of the hydrocarbons, but some oil and particularly gas may remain. The Upper Cambrian alum shale which is found in the Oslo region is a good example of a rich source rock which has been buried to at least 200°C (5–7 km) and lost most of its hydrocarbons during the Caledonian folding in the late Silurian and early Devonian. In Sweden the Upper Cambrian alum shales have not been buried so deeply and therefore contain more oil which can be distilled off by pyrolysis at 400–500°C.

In the Baltic region the lowermost Ordovician shales are even less mature so that more of the kerogen remains and in Estonia this shale is mined for oil on a large scale. Here the reserves are very large (0.6×10^9 sm^3 oil equivalents – o.e).

Oil shales are used in electric power generation and provide 60% of Estonia's stationary energy. It is also used for oil production and refining. The waste is 70–80 Mt. of semi-coke and the mounds exceed 100 m in height. The waste is very fine grained and is alkaline with significant concentrations of sulphides and heavy metals.

On a global basis oil shales represent a reserve almost as large as conventional oil. Reserves of oil which can be produced from oil shale are difficult to estimate but they may total close to 5 trillion barrels (800×10^9 sm^3). This is about equivalent to the estimated world reserves of conventional oil and gas (480 sm^3 o.e.). More than 80% of the well known reserves are located in the US but there are probably other regions with oil shales which have not been recorded and evaluated.

The Green River Shale in Colorado, Utah and Wyoming is a gigantic source of hydrocarbons. This organic-rich mudstone was deposited in very large lakes during the Eocene and the organic matter was mostly freshwater algae (Fig. 23.5a, b).

In Australia there are also very large reserves of oil shale and they have been used for oil production already in the latter part of the 19th Century when more than 100,000 tonnes of shale were processed.

In areas including Queensland and South Australia there are Cenozoic shales or mudstones deposited in freshwater associated with coal deposits but there are also older (Permian) oil shales. Strict environmental restrictions on oil shale mining have been imposed here, particularly because of the association with The Great Barrier Reef.

Also in other parts of the world oil shales may represent large potential oil reserves but they may not be produced with the present technology.

Oil shales must however be mined and heated in ovens (pyrolysis) to generate the petroleum and the energy for the heating is taken from the burning of the

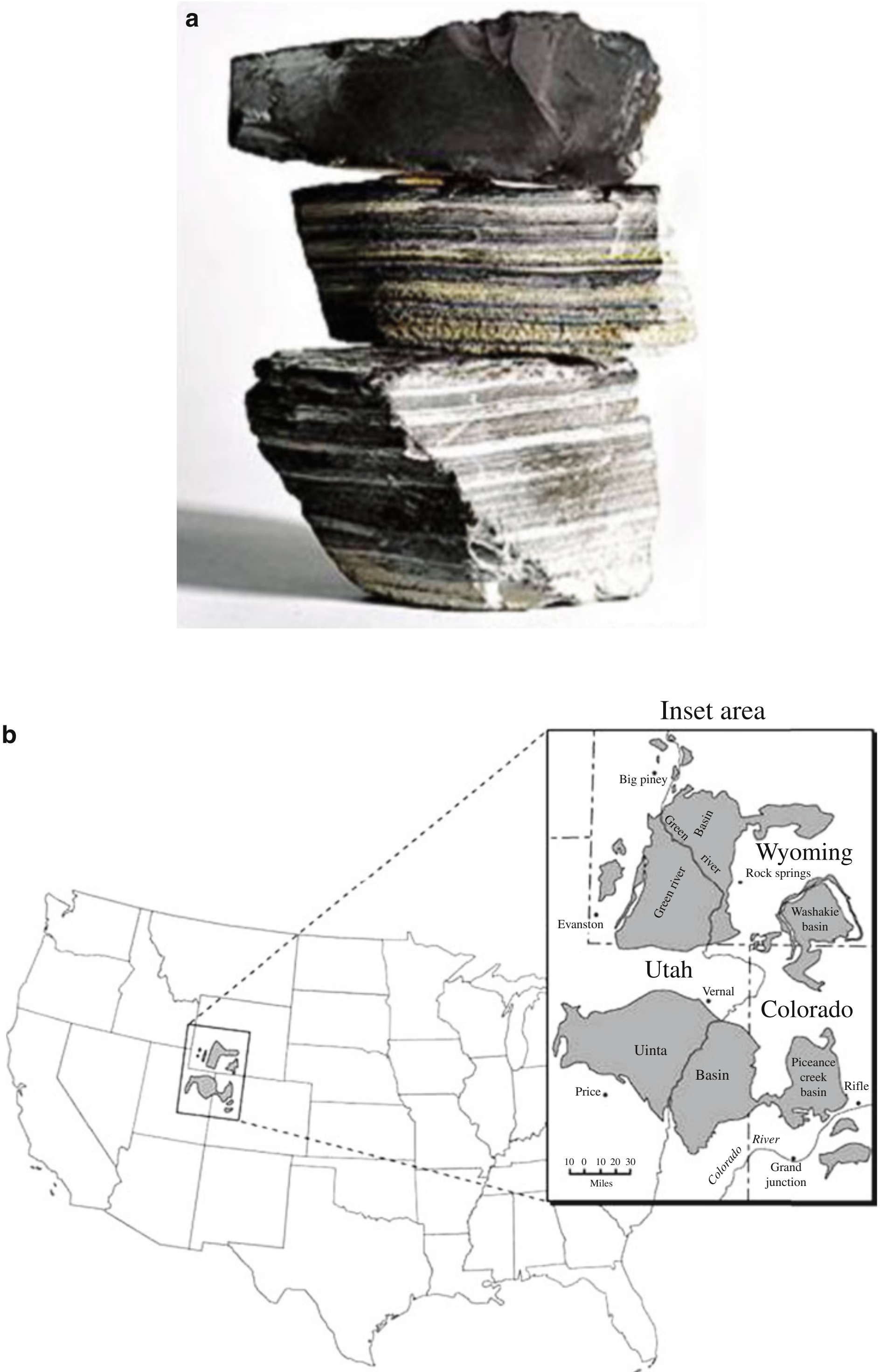

Fig. 23.5 (**a**) Green River Shale. This shale has a high content of organic carbon from algae and contains mostly Type I kerogen. It is far from mature and the shale must be mined and heated to 400–500°C to form oil by pyrolysis. (**b**) The Green River oil shale was deposited in shallow lakes and is of Tertiary (Eocene) age. This shale is very extensive in Utah, Wyoming and Colorado (adapted from Smith 1980)

oil shales. The release of CO_2 is therefore high also during production. Oil shales may only contain 5–10% organic matter and the volume of waste will then be 10–20 times the oil produced. The waste consists of coke and also smectite formed in the heating process and is very difficult to store. It is also rich in heavy metals, including vanadium and uranium which are typical of black shales.

Production of oil from oil shales requires very large amounts of water, so in dry areas the water supply may be a limiting factor. There are therefore considerable environmental problems linked to the exploitation of oil shales as a major source of oil.

Attempts has also been made to heat the shale in the ground so that the environmental problems related to water supply and storage of waste is reduced.

By establishing an underground barrier by freezing the ground using refrigerated fluid a "freeze wall" is established. The purpose is to prevent the hydrocarbons from escaping and groundwater from entering into the area which is heated.

Some source rocks may have enough permeability to serve as reservoir rocks too. The Miocene Monterey Formation in California is an organic-rich diatomaceous source rock, which is also a reservoir rock. Oil can in this case be produced because of tectonic fracturing which has enhanced the permeability. Source rocks may also be interbedded with thin sandstones or limestones and then only a very short migration is required.

23.3 Coal Bed Methane (CBM)

Coal and kerogen rock with a high content of plant material (Type III kerogen) are the main source rocks for gas which will migrate to a reservoir rock or up to the surface. Relatively large quantities of gas (methane) will, however, be retained in the coal because its micro-porous structure provides a very large surface area for adsorbed gas. This can be exploited by drilling into the coal. Commercial production of methane from coal is common in the US. Near the surface gas can leak off from coal but where coal is buried a few hundred metres much of the gas is still retained in the coals and can be produced by drilling. Coal has very low permeability and the flow of gas to the wells depends on thin fractures (cleats) developed during uplift. The gas produced from coal is normally very pure methane with low sulphur content and is referred to as sweet gas. Wyoming has very large reserves of coal bed methane in the Powder River, Bighorn, Wind River and Green River basins. These are Cretaceous and Tertiary coals which have been buried more deeply and then uplifted. Gas may be produced from these coals down to depths of 1.5–2 km (5,000 ft). The reserves of CBM are large in the USA (20×10^{12} m^3) and Canada also has major reserves.

Methane is constantly being formed by bacteria at shallow depth and it may be argued that this is at least to some extent a renewable resource but the rate of accumulation is slow compared to our consumption. Artificial growth of algae may produce some oil and gas and consume CO_2.

23.4 Shale Gas and Shale Oil

Organic-rich shales which have been buried to depths where most of the oil and gas has been generated and expelled may nevertheless contain considerable amounts of gas. The gas remaining in these shales is present in very small pores and may also be partly adsorbed on remaining organic matter or its residue (coke) and on clay minerals. The shales have been uplifted and may therefore have small extensional fractures, but they must be hydrofractured by water injection to increase the permeability.

Barnett Shale is tight shale of Mississippian age in Texas, containing at least 2.5 trillion cubic feet of gas. It is referred to as a tight gas reservoir. Much of the gas is in urban areas such as the Dallas-Forth Worth area.

The permeability of the shale matrix is generally very low but there may be thin silty layers and also fractures that increase the effective permeability. Hydraulic fracturing can be carried out to further increase the permeability, and horizontal drilling also helps to produce more gas. The Woodford Shale (Devonian) in Oklahoma can be almost 100 m thick.

Devonian tight gas shales include the Middle Devonian Marcellus Shales in the Appalachians. These are now mostly at 1–2 km depth but have previously been buried much deeper (5–6 km or more).

Shale gas is estimated to account for 50% of the gas produced in North America by 2020.

Higher gas prices will also result in increased interest in shale gas in other parts of the world.

The occurrence of gas in onshore shales has been well known in many European countries but very little has been produced so far.

In the UK Lower Carboniferous shales and coal were buried deeply in front of the Variscian metamorphic front in the south of England and adjacent parts of the North Sea basin. The Carboniferous Bowland Shale in NW England has been regarded as a potential target for shale gas production in Britain. Also in parts of Northern England and Scotland have Upper Palaeozoic sediments been buried deep enough to generate significant gas. At 4–5 km burial depth gas is generated from primary oil. The shales are then so hard and indurated that they can sustaina fracture network produced by natural fracturing during uplift and during fracking.

In the Liassic and Kimmeridge clays (shales) there are potential source rocks for both thermal gas and biogenic gas. They are immature in many areas and may not be hard enough for effective fracturing. When developed as carbonate-cemented shales they become brittle but the fractures may then become cemented up.

The total reserves of shale gas is very difficult to estimate due to uncertainty about gas prices and the energy policy of each country.

There are considerable reserves of shale gas which can be produced in Europe. Most countries have however introduced strong restrictions on the development of shale gas. In many countries such as Germany and France many of the potential areas for such production are rather densely populated and there are strong environmental concerns about pollution of groundwater etc. In Germany, Poland and France there are shales of Jurassic, Permian and Carboniferous age which could be produced, but it is uncertain to what extent they will be produced. Much of these resources are in densely populated areas with strict environmental restrictions, and France has banned fracking. Also in Spain, Romania and Bulgaria there are large reserves in terms of shale gas.

Shale gas represents very large reserves of hydrocarbons which can be used directly as gas, but can also be converted to diesel fuels for cars and trucks. This gas can also be mixed with heavy oil and tar sand to make regular petrol. Production of gas from shales requires much water for fracturing, and produced water may also create environmental problems.

Shale Oil is produced from source rocks, mostly shales, which have not been buried as deeply as those with mostly gas and have only reached the oil window. Oil is then produced by fracturing in the same way as for gas. Shale oil may be found in the same formations and sedimentary basins as shale gas but where the maximum burial depth (temperature) has been lower.

Until about 10 years ago it was not considered possible to produce oils from shales. In recent years oil production from shales has increased rapidly particularly in the US, increasing their domestic production and reducing their import.

The fact that it is now possible to produce oil from shale has changed petroleum geology and the distribution of reserves. Conventional oil is limited to reservoirs rocks with sufficient quality and a structural trap. Shale oil may be found in very extensive layers of shale which have had a maximum burial temperature corresponding to the oil window.

The late Cretaceous Eagle Ford Formation of South Texas has since 2008 developed into a major oil producer. This is a 100 m thick transgressive organic-rich black shale with some carbonate layers and siltstones. This makes it a good producer in many areas. The Eagle Ford shale was deposited on top of the Woodbine sandstone and overlain by the Austin Chalk.

The Bakken Formation (late Devonian) in the Willistone basin is found subcropping in much of North Dakota, Montana and Saskatchewan but is not exposed. It is black shale deposited as organic-rich mud with layers of dolomite. The average porosity is about 5% and the permeability is very low (0.04 mD) but due to new fracturing technology production rates have increased very significantly and the reserves have recently been estimated to about 24 billion bbl.

23.5 Gas Hydrates (Clathrates)

Gas hydrates are crystalline solids almost like ice, consisting of gas (mostly methane) surrounded by water. Most common is methane clathrate which is water molecules bonded by hydrogen and with gas

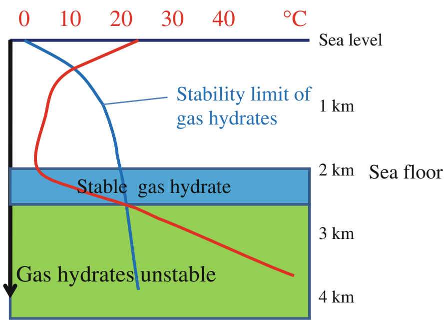

Fig. 23.6 Stability of gas hydrates. Gas hydrates are stable at high pressure and low temperatures and are therefore found beneath the deeper part of the continental slopes. As the temperatures in the sedimentary basins increase with depth, gas hydrates become unstable

trapped within its structure. It is stable at high pressures and low temperatures (Fig. 23.6). It therefore typically occurs on the slopes and below the seafloor in deep oceans. At about 2.0 km water depth (20 MPa water pressure) the temperature must not exceed about 18°C and at 0.5 km below the seafloor (2.5 km depth – 25 MPa pressure) the temperature must be below 20°C. The temperature near the seafloor is usually less than 2–3°C but the geothermal gradients may be about 30°C/km and it is therefore clear that gas hydrates can only exist a few hundred metres below the seafloor (Fig. 23.7).

When gas hydrates dissolve (melt) one volume of gas hydrate produces 160 volumes of gas. The source of the methane is mostly biogenic, from organic rich sediments, but gas hydrates may also fill the pores in sand beds. During the glaciations gas hydrates were more widespread than now and occurred also beneath the seafloor in basins like the North Sea (Fig. 23.7). Gas hydrates are potentially a very important source of gas.

Production of methane from sediments with gas hydrates may become possible from sand beds cemented with gas hydrates. It is however difficult to predict how economic it would be to produce from gas hydrates.

23.6 Summary

Unconventional oil and gas as discussed above represent very large energy reserves which are much greater than conventional oil. The environmental problems associated with producing these reserves are however great, particularly for oil shale and tar sand.

There is a need for new research to develop methods which can minimise both the local environmental impact and the release of CO_2 into the atmosphere.

When burning hydrocarbons to produce energy the carbon dioxide can be separated out and stored in the subsurface to prevent emissions to the atmosphere, see chapter 24.

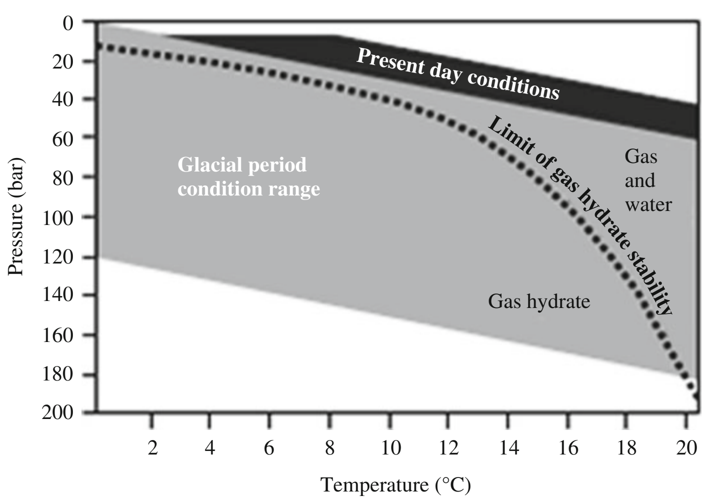

Fig. 23.7 During glacial periods, gas hydrates formed in basins like the North Sea due to the low surface temperatures in front of the ice (from Fichler et al. 2005)

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