

Green Energy and Technology



Carlo Giavarini
Keith Hester



Gas Hydrates

Immense Energy Potential and
Environmental Challenges



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and Environmental Challenges

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Foreword

The scientific community has known and studied gas hydrates for decades. However, most people do not know of this “strange” material so common on the Earth. At the international level, it seems that a text is missing for non-experts in gas hydrates. This book aims to fill this gap, in the simplest way possible, by explaining in a strictly scientific manner what gas hydrates are and highlighting the important energy and environmental aspects related to them. Are gas hydrates a huge source of energy or an environmental challenge to humanity, or both?

Our ambition is to make the main issues and implications of gas hydrates accessible to a general technical audience, while providing enough detail to be useful for the practicing scientist or engineer. In large part, the various chapters have been designed so they can be read independently of each other, without compromising overall understanding. The use of equations, formulas, and complicated graphs has been limited as much as possible. Non-technical readers may gloss over some of the more specific discussions without losing the overall message presented. For the experts, some parts may seem elementary. However, it is hoped that this does not jeopardize the general idea of the work.

The field of gas hydrates is fascinating and covers virtually all disciplines ranging from chemistry to geology to biology. From the engineering of energy production and transportation to environmental science and climatology, gas hydrates present difficult challenges and exciting possibilities.

For more in-depth specific knowledge of the various scientific and engineering aspects related to gas hydrates, we direct the reader to now classic works on gas hydrates by authors such as E. D. Sloan, Y. Makogon, M. Max, J. Carrol, T. Collett, B. Dillon, J. S. Gudmunsson, and others. These texts will be frequently cited in the various chapters of this book.

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Abbreviations

ANG	Adsorbed natural gas
bbl	Barrel
BP	Before present
CNG	Compressed natural gas
DEG	Diethylene glycol
DOE	US Department of Energy
DSC	Differential scanning calorimetry
EO	Ethylene oxide
EPICA	European project for ice coring in Antarctica
FPSO	Floating Production, Storage, and Offloading
GHSZ	Gas hydrate stability zone
GRIP	Greenland ice core project
GTL	Gas-to-liquids
GTW	Gas to wire
H	Hydrate
I (or) Ih	Hexagonal ice
ICGH	International Conference on Gas Hydrates
IFP	French Petroleum Institute
IGCC	Integrated gasification combined cycle
IODP	Integrated ocean drilling program
IPCC	Intergovernmental panel on climate change
IPEV	French Polar Institute Paul-Emile Victor
JAPEX	Japan Petroleum Exploration Co
JIP	Joint industry project
JNOC	Japanese national oil company
KHI	Kinetic hydrate inhibitor
LDHI	Low-dosage hydrate inhibitor
LNG	Liquefied natural gas
L _w	Liquid water
MDSC	Modulated differential scanning calorimetry
MEG	Monoethylene glycol

MES	Mitsui Engineering and Shipbuildings Co.
MeOH	Methanol
MM	Thousand
MMbpd	Million barrels per day
MMcm	Million cubic meters
Mscf	Thousand standard cubic feet
mol%	Mole percent
n	Hydration number
NGH	Natural gas hydrate
NGHP	National gas hydrate program of India
NMR	Nuclear magnetic resonance
OECD	Organization for Economic Co-operation and Development
P	Pressure
P-T	Pressure-Temperature
PNRA	Italian National Antarctic Research Program
PVCap	Polyvinylcaprolactam
PVP	Polyvinyl pyrrolidone
Q ₁	Lower quadruple point
Q ₂	Upper quadruple point
ROV	Remotely operated vehicle
sI	Type-I or Structure I gas hydrate
sII	Type-II or Structure II gas hydrate
sH	Type-H or Structure H gas hydrate
SEM	Scanning electron microscopy
STP	Standard temperature and pressure
T	Temperature
T-x	Temperature-composition
TCM	Trillion cubic meters
THF	Tetrahydrofuran
TMO	Trimethylene oxide
toe	Tons of oil equivalent
USGS	US Geological Survey
v	Vapor
wt%	Weight percent

Introduction

In 1996, off the coast of California, in the Monterey Bay Canyon, a special remote operated vehicle comes to rest on the ocean floor at over 900 m depth. A controlled amount of methane is injected into the 4°C water and bottom sediments. Within seconds, this mixture of gas and water formed into a solid mass, bright white, and fluffy. In this way, it was experimentally confirmed that methane hydrate formation was not only possible in marine waters but extremely easy and rapid, provided the presence of suitable pressure and temperature conditions.

In November 2000, a fishing trawler off the coast of Vancouver, Canada, pulled up a large block of yellow-stained *ice*. Almost immediately, the catch began to bubble and fizz. The crew had inadvertently discovered a large seafloor deposit of methane hydrate. If a sailor had lit a match, there could have been disaster as the gas hydrates they brought on board were releasing large quantities of hydrocarbon gas as they bubbled away.

The discovery of gas hydrates dates back to 1810. Sir Humphry Davy is given credit for the discovery of hydrates formed from chlorine. These compounds were largely treated as a scientific curiosity until the third decade of the last century, when a connection between hydrates and blockages in oil and gas pipelines was established.

Naturally occurring hydrates were first discovered in the 1960s by Yuri Makogon, where the Russians produced gas from hydrates in the Siberian permafrost. Since that discovery, subsequent research has led to the discovery of vast deposits of hydrates in nature, both in the permafrost and the continental shelves of the World's oceans.

Will gas hydrates become a significant source of energy? Despite the recent acceleration of activities to develop reliable production techniques, it seems unlikely that we will see significant global production within the next 10 to 15 years. However, in certain parts of the world (e.g. Japan and India) with limited resources of conventional energy sources, it is possible that methane hydrates may become an important source of natural gas in the near future.

The recognition that enormous quantities of methane in gas hydrates exist (and have existed) in the subsurface has led to a reconsideration of past climatic events

in the Earth's history. Researchers have hypothesized that former catastrophic releases of methane could have been related with disturbance of gas hydrate deposits. This concern has led environmentalists to consider the current potential of gas hydrates to be involved in future large-scale climate change events.

Undoubtedly, many environmental concerns associated with gas hydrates need to be resolved. For example, the stability of submarine slopes containing hydrates needs to be better understood. A large scale disturbance, such as an earthquake or increasing sea temperatures, could lead to massive release of methane, a potent greenhouse gas, from their icy cages into the atmosphere.

Chapter 1

The Evolution of Energy Sources

1.1 Conventional Fossil Fuels

Coal, oil, and natural gas have served as the traditional energy sources for mankind and have played an enormous role in the development of our modern society. Coal originally displaced wood as the World's major energy supplier, helping spark the Industrial Revolution in the latter part of the eighteenth century. The age of petroleum began in 1859 starting with the first oil well drilled by Colonel Edwin Drake in Titusville, Pennsylvania. Since that time, oil and refined petroleum products have evolved to power transportation over land, sea, and air [2]. It is worth mentioning that the transportation sector relies on oil for 97–98% of its energy and consumes over 50% of the World's oil. Natural gas usage lagged behind oil but is now continually increasing as transportation issues associated with moving a gas versus a liquid are being (at least partially) solved through pipelines and liquefaction techniques.

Despite the decline of coal usage compared to oil and gas, coal reserves far exceed conventional oil and gas and remain an important energy source. This can be seen in Table 1.1, which gives energy consumption by different sources over the last 25 years. Figure 1.1 shows the relative importance of different energy sources over the last century. For comparison purposes, all energy usage has been converted to tons of oil equivalent (toe). Thus, for example, a ton of oil equivalent is about 1,200 m³ of natural gas.

1.1.1 Crude Oil

Figure 1.2 shows the evolution of oil demand in the period 2006–2010, fluctuating around 86 million barrels/day (MMbpd), or about 4.3 billion tons/year. In contrast to Organization for Economic Co-operation and Development (OECD) member nations, non-OECD countries are steadily increasing their consumption of crude

Table 1.1 Worldwide energy consumption (in millions of toe)

	1985	1990	1995	2000	2005	2008	% in 2008
Crude oil	2,793	3,172	3,283	3,612	3,892	3,929	34.6
Natural Gas	1,492	1,781	1,914	2,178	2,508	2,768	24.4
Coal	2,089	2,246	2,239	2,247	2,884	3,324	29.3
Nuclear	335	453	526	585	627	620	5.4
Hydro-Geo	448	490	562	601	658	718	6.3
Total	7,157	8,142	8,524	9,223	10,569	11,359	100.0

Source: BP Statistical Review

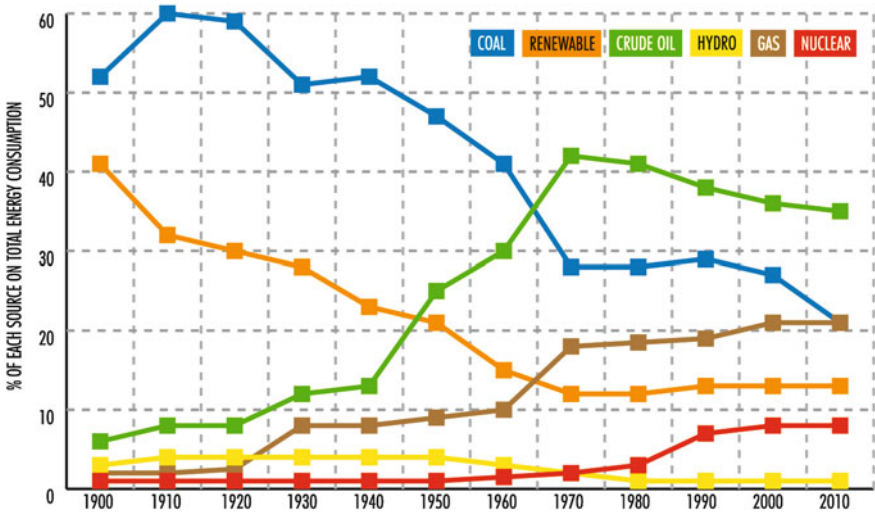


Fig. 1.1 The relative importance of different energy sources in the twentieth century (IEA Data Processing and Aeneas by IIASA-WEC)

oil. China is now a major energy consuming nation, responsible of about one-third of new growth in oil demand.

The future of oil will be likely more influenced by geo-political attitudes than exhaustion of resources. As the Stone Age did not end due to lack of stones, the Age of Oil will likely not end due to lack of the raw material, but for other reasons.

Current estimates of conventional oil (over 160 billion tons) could supply 40 years of demand, at current rates of consumption. One should note that 30 years ago, estimated reserves and “Peak Oil” could then only ensure consumption for three decades or so. In fact, the amount of current new discoveries (though more limited on scale than previous ones) and improved production techniques with higher extraction efficiencies contribute to the continually positive increases in oil reserves. Figure 1.3 shows the estimate from the French Institute of Petroleum, which is similar for other oil companies. Production is expected to reach its peak around 2035 and begin to slowly decline. The increasing forward

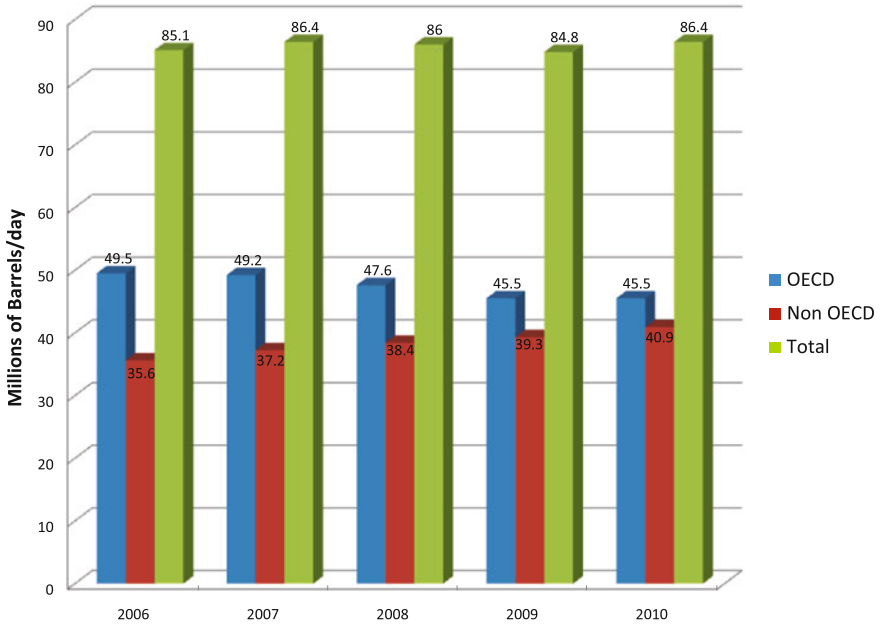


Fig. 1.2 Total oil demand for OECD and non-OECD nations (Source: Hydrocarbon Process, January 2011)

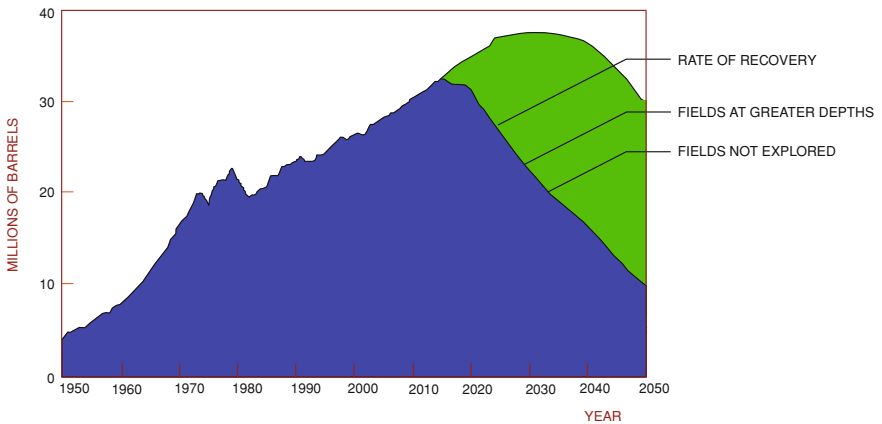


Fig. 1.3 Evolution of oil production. IFP forecast through 2050

estimates of peak oil production is attributed to discovery of new reserves and advancement in oil drilling technology (increase in achievable drilling depths, better drilling techniques, and enhanced oil recovery capabilities, from ~35% to over 50%).

Table 1.2 Typical compositions of dry and wet gases (mol%)

Components	Dry gas	Wet gas
<i>Hydrocarbons</i>		
Methane	70–99	50–92
Ethane	1–10	5–15
Propane	Trace-5	2–14
Butane	Trace-2	1–10
Pentane	Trace-1	Trace-5
<i>Non hydrocarbons</i>		
Nitrogen	Trace-15	Trace-10
CO ₂	Trace-1	Trace-14
H ₂ S	0-Trace	0–6
Helium	0–5	0

* The values here should be considered as averages. There may be gas reservoirs with significantly higher content of individual species, e.g., H₂S

The largest known reserves are held by countries such as Saudi Arabia (nearly 40 billion tons), followed by Iran (just under 20 billion tons), Iraq, Kuwait, UEA, Venezuela, and Russia. While countries such as Norway, Nigeria, and Libya (along with Russia) do not have the largest reserves, they are among the largest worldwide exporters. As we will see later, other petroleum sources, such as oil sands and extra-heavy oils, are moving closer to being considered conventional and the international distribution of known petroleum reserves could see a marked increase.

Oil prices (reported in barrels, equivalent to 159 l) fluctuate greatly depending on events and the International economy. As a historical note for the reader, the use of barrels stems from the first containers used to transport oil: they were wooden barrels originally used to transport whiskey. While the physical metal barrels used today have a greater volume, the barrel unit was standardized at 42 US gallons for commercial and fiscal purposes. To convert between barrels and tons, you can multiply barrels by 0.14 taking into account an average crude oil specific gravity of about 0.85.

1.1.2 Natural Gas

The term *natural gas* is usually reserved for gas from subsurface sediments that is rich in methane, but often contains higher hydrocarbons (primarily ethane and propane). It can also contain higher hydrocarbons and various amounts of acid gases such as carbon dioxide and hydrogen sulfide.

Natural gas is defined as a *wet gas* if it contains relatively significant amounts of higher hydrocarbons compared to methane. The definition of a *sour gas* is one that contains sulfur compounds, particularly hydrogen sulfide. Otherwise, it is known as *sweet gas*. Table 1.2 gives typical ranges for parameters defining the quality of a

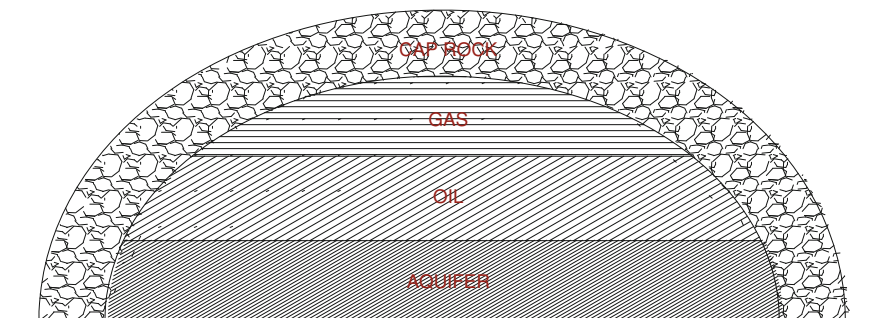


Fig. 1.4 Schematic of a field with associated natural gas

natural gas and their effect on the price it is traded for. A sweet gas typically will sell for a higher price than a sour gas as less processing is needed from raw to final product. Natural gas is often associated with oil production and present in the upper layer of a petroleum deposit (Fig. 1.4).

Conventional natural gas reserves are substantial (about 190 trillion cubic meters, or 160 billion toe), accounting for over 60 years at current rates of consumption. Non-conventional reserves are becoming increasingly important (e.g., shale gas and coal bed methane). This could be especially true as natural gas consumption is steadily increasing and anticipated to surpass oil with 10–20 years. The most prevalent deposits are in Russia ($\sim 50,000 \text{ MM m}^3$), Iran, Qatar, Saudi Arabia, UAE, USA, and Algeria. Russia is the World's largest producer, followed by the USA.

The success of natural gas comes from the fact that it can be easily purified and transformed into an almost pure methane product. Methane, which contains only one atom of carbon with four atoms of hydrogen, is the cleanest burning fossil fuel. It is currently the main source for deriving hydrogen gas and will be for the foreseeable future.

Contrasting the simple clean burning nature of methane, because it is a gas, transportation and storage are significantly more complex compared to liquid petroleum products. The relative ease of liquid oil transportation allows access to different markets over the lifetime of producing a well. With natural gas, dedicated infrastructure must be in place, such as a pipeline or liquefied natural gas (LNG) plant, to ensure the gas can reach the market. This is usually stipulated in the contract terms and certain guarantees and certainty is needed before such an economic investment can be made. Much of the proven natural gas reserves are considered *stranded*, meaning they are difficult to reach or far from current markets and not large enough to justify an investment in a pipeline or LNG plant.

Beyond traditional means of transporting natural gas, new technologies are being developed. These include high pressure transportation, gas-to-liquids (GTL) conversion, and in the form of gas hydrates. As further detailed in [Chap. 9](#), these technologies seem particularly well suited for stranded gas fields (Fig. 1.5).