Green Energy and Technology

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# Gas Hydrates

## Immense Energy Potential and Environmental Challenges

Springer

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ISSN 1865-3529
e-ISSN 1865-3537
ISBN 978-0-85729-955-0
e-ISBN 978-0-85729-956-7
DOI 10.1007/978-0-85729-956-7
Springer London Dordrecht Heidelberg New York

British Library Cataloguing in Publication Data
A catalogue record for this book is available from the British Library

*Cover design:* eStudio Calamar, Berlin/Figueres

Printed on acid-free paper

Springer is part of Springer Science+Business Media (www.springer.com)

# 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.

# Contents

# 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 $m^3$ 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

C. Giavarini and K. Hester, *Gas Hydrates*, Green Energy and Technology,
DOI: 10.1007/978-0-85729-956-7_1,

**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

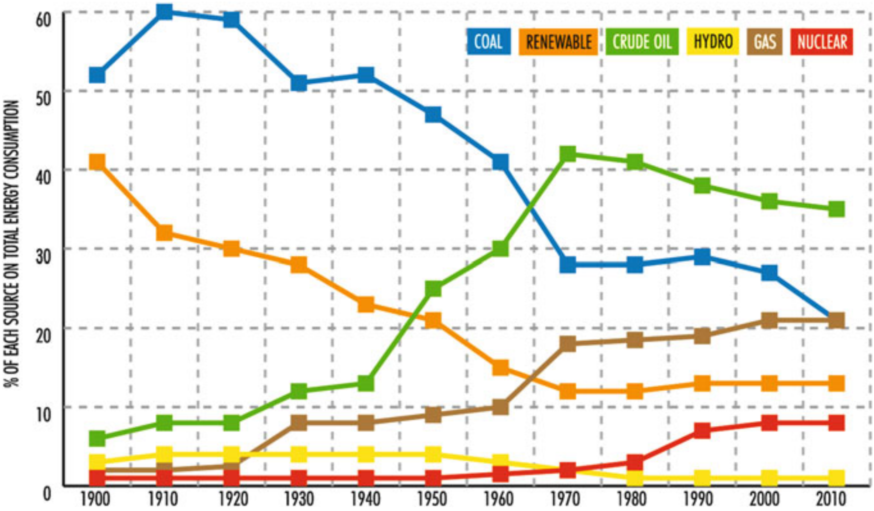

**Fig. 1.1** The relative importance of different energy sources in the twentieth century (IEA Data Processing and Aeneas by IIASA-WEC)

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 billon 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

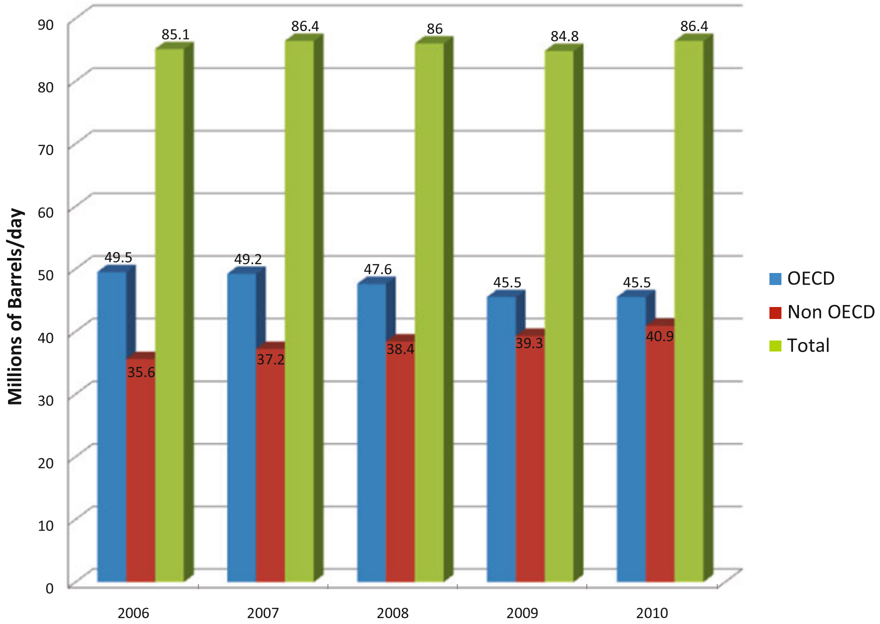

**Fig. 1.2** Total oil demand for OECD and non-OECD nations (Source: Hydrocarbon Process, January 2011)

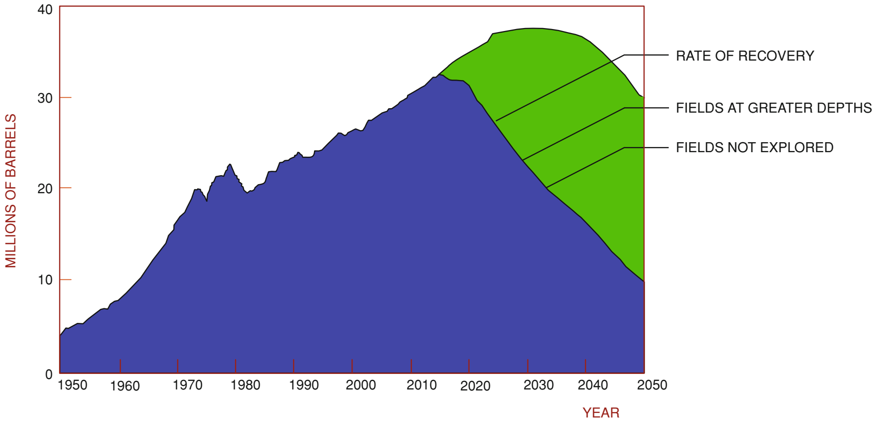

**Fig. 1.3** Evolution of oil production. IFP forecast through 2050

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 |
|---|---|---|
| *Hydrocarbons* | | |
| 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 |
| *Non hydrocarbons* | | |
| Nitrogen | Trace-15 | Trace-10 |
| $CO_2$ | Trace-1 | Trace-14 |
| $H_2S$ | 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., $H_2S$

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

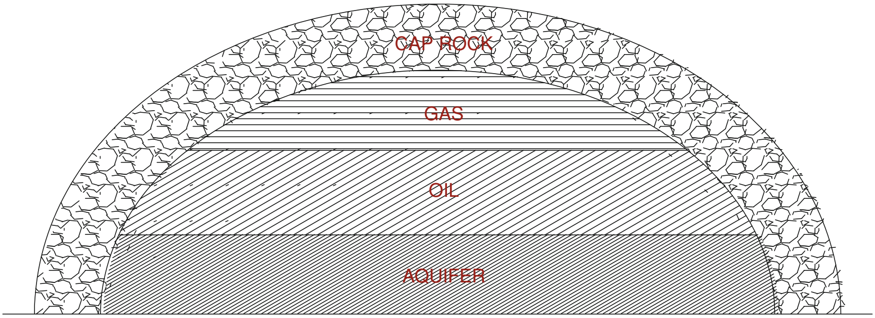

**Fig. 1.4** Schematic of a field with associated natural gas

natural gas and their effect on the price it is traded for. A sweet gas typically will sale 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 increasing 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 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).