



On the future of energy: the de-carbonisation of Methane

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As well known, we are presently facing a novel phenomenon, coined by Eugene Stoermer and popularized by the Nobel Laureate Paul Crutzen, namely the emergence of a manmade Anthropogenic Era. For the first time, human activities may strongly influence the future of the earth's climate. The development of low-carbon techniques to produce hydrogen from fossils could be of great importance during the transition to a long-term sustainable energy system.

In this framework, at the Institute for Advanced Sustainability Studies (IASS) in Potsdam, a new alternative technology for methane decarbonisation based on liquid metal technology has been proposed. An ambitious programme was set up in collaboration with the Karlsruhe Institute of Technology (KIT) and carried out successfully over a period of three years. The project was awarded the Innovation Prize of the German Gas Industry Association in Berlin in December 2018. Future CO₂-free Methane de-carbonisation based on liquid metal technology may become a further development of our experimental activities in China and elsewhere.

In this paper we discuss natural gas utilisation options in view of reducing CO₂ emissions. Three methods (Figure 1) are here compared: (a) conventional process with CO₂ emitted in the atmosphere; (b) geo-engineering attempts to compensate for CO₂ emissions; and (c) methane cracking without CO₂ emissions.

Since 1750 about one million million tons, 1000 Gtons, of CO₂ have been injected into the atmosphere. From about 6 GtC/y in the early nineties, we are now at 9.5 GtC/y. By 2020 and at the present rate of increase, the CO₂ will reach twice the 1990 rate # 12 GtC, a factor 2 over 30 years.

The average lifetime of large amounts of anthropogenic CO₂ is # 30 kyr. As a comparison, the nuclear lifetime of Plutonium (Pu-239) is 26 kyr. The surviving fossil carbon will be of about 10-15% after 10,000 years and about 7% after 100,000 years: in practice it will last forever. At such rates, it is indeed urgent for emissions not be freely emitted indefinitely and some future CO₂ curbing mechanism is unavoidable.

Geo-engineering technologies may be used in order to provide for CO₂ mitigation. But, as noted by the Royal Society (2009), the safest and most predictable method of moderating climate change is to take early and effective action to reduce greenhouse gas emissions. No geo-engineering method can provide an easy or readily acceptable alternative solution to the problem of climate change. Geo-engineering methods could however potentially be useful in the future to augment continuing efforts to mitigate climate change by reducing emissions and thus should be subject to more detailed research and analysis.

Underground storage of CO₂ was initially studied by Herzog *et al.* [1]. Carbon capture and sequestration (CCS) is seriously being considered: the CO₂ is injected down into the earth or ocean bottom. This method is already used by the oil industry, but at the level of few million tons/y. Several billion US\$ have already been spent by the USA, and similar incentives have been given elsewhere. However, CCS is not applicable to all sources of CO₂.

Sequestration is not elimination, and eventually CO₂ will have to come back into the atmosphere, after dissipation of the greenhouse effect and after thousands of years of accumulation!

Safety considerations are especially important. The degradation processes of the sealed wells and their behaviour over a long timeframe (millennia) are difficult to predict. Provided the likelihood of leaks from a CO₂ reservoir is similar to that of hydrocarbon reservoirs during production, leaks (> 10 t/day) are expected to occur at about 10⁻³ per reservoir x year. But we need CO₂ wells under pressure for >10³ years and therefore accidental leaks are frequent. The expanded CO₂, if promptly emitted, will be very cold and hence remain close to the surface of the escaping area.

Although not toxic, above some % CO₂ acts as a powerful brain vein dilatator. In a few minutes, unconsciousness occurs at 15% of relative concentration and immediate death at 30%. Deaths start being

observed already at 9%. In 1986 at Lake Nyos a volcanic CO₂ leak of 2.4 x 10⁵ ton killed all the 1746 people + animals < 15 km from the source.

In order to ensure 550 ppm by 2100 with the option “Business as usual” – according to IPCC – we must accumulate CSS with # 2 x 10¹² ton.

Another alternative may be Aerosol SO₂ cooling. If there were a way to continuously inject SO₂ into the lower stratosphere at a level of # 1/1000 of the CO₂ emissions, it would produce large, compensatory global cooling.

Worldwide SO₂ emissions have increased from about 10 million tons of Sulfur per year (Mt S/y) to a peak of 65-70 Mt S/y in the early 1980s and have been declining to about 55 Mt S/y as of 2000. The main advantage of these non-CO₂ effects is that the weight of the material to be captured is of the order of millions of tons, and not billions of tons as in the case of CO₂.

Let us assume that we will put SO₂ into the lower stratosphere (16-22 km) over the Equator at a daily rate equal to 5 Mt/yr (1 Pinatubo eruption every 4 years) or 10 Mt/yr (1 Pinatubo every 2 years) for 20 years, or at 68°N at a daily rate equal to 3 Mt/yr for 20 years (Figure 2).

Volcanic eruptions inject mostly SO₂ but it is preferable to produce H₂S that would oxidize and form H₂SO₄ droplets with water. However, H₂S is toxic and flammable. Using airplanes would not be costly, especially with existing military planes, but there are still questions about whether desirable aerosols could be created. No means have been studied so far on how to inject aerosol precursors (gases). Rough estimates show it would cost a few billion dollars to build a system, a few billion dollars per year to operate it and less than a decade to implement.

However, eventual schemes perceived to work will lessen the incentives to mitigate greenhouse gas emissions. Even if it works, whose hand will be on the thermostat? How could the world agree on an optimal climate? Who has the moral right to advertently modify the global climate?

In the past 2000 years there have been three major high altitude natural eruptions: Eldgjá, Iceland in the year 939, Lakagígur (Laki), Iceland (14.7 km³ of lava) in the years 1783-84 and Novarupta (Katmai), Alaska in the year 1912.

Quoting Reference [3] the 1783 flood was not sufficient in Egypt. The Nile failed to rise again in 1784 and the death toll was very high. The famine continued, and the streets of Cairo, previously full of beggars, were now deserted: all had perished or escaped from the city. By January 1785, 1/6 of the population of Egypt had either died or left the country.

The beginning of the French revolution was also strongly influenced by the famine related to the Laki eruption. Famine devastated India as the monsoon failed in summer 1783. There was also the Great Famine in Japan in 1783-1787, which was exacerbated locally by the Mount Asama eruption of 1783.

Returning to the present, we have suggested using a new procedure, fossil Methane de-carburization. Methane cracking or Methane de-carburization is a proven process based on the splitting of the Methane molecule into its atomic components, Carbon and Hydrogen. As an alternative without CO₂ emissions we have investigated the experimental feasibility aspects of *the spontaneous, thermal dissociation of NG*:



Hydrogen becomes the final form of energy. The total absence of CO₂ is the main reason for its development. The black carbon produced can either be sequestered or sold on the market as a material commodity, for instance reducing costs by marketing the carbon as a filler or construction material.

At IASS-KIT we have evaluated and carried out at laboratory scale this novel methane decarbonisation process, successfully overcoming the obstacles, in view of its possible industrial implementation. The preferred option, in analogy with most of the previous studies, is based on molten metals, as carbon separation seems more achievable due to the large density difference between the liquid metal and the carbon.

As early as 1930, Tyrer had proposed and patented a process for producing hydrogen from methane or methane-containing gases using molten iron (1200-1300°C). Many authors have pursued the technology since then.

In our opinion, a future progressive industrialization of molten media to host the methane-cracking reactions is promising, although a major change is required because of the large amounts of black carbon produced.

The present (table top) project we have completed is based on the implementation of a *liquid metal technology* for the production of H₂ from NG without CO₂ emissions. The main features have been the following: bubble

formation in ceramic sponges and a liquid metal bath; compatible liquid metals, such as Lead or Tin; high temperatures (approximately 1200°C); and compatible with Hydrogen production (Figure 4).

A crucial choice is the possible presence of catalysts in the reaction. Significant effort had been previously devoted to providing catalysts to the reaction in order to achieve a viable implementation also below 1000°C. The industrial implementation in the case of catalysed reactions is limited by the deactivation of the catalyst and by its lifetime and cost. The deactivation of the catalyst is a process f.i. resulting from the formation of coke on the surface of the catalyst during its operation. Solutions with no catalyst are hereby preferred (Figure 3).

Several aspects have been carefully analysed: the formation of Carbides or Hydrides in liquid metal; the removal of Carbon plugging of the structural materials; separation of pure H₂ from the remaining hydrocarbons and carbon; and recovery of Carbon particles from the liquid metal.

Methane pyrolysis can be compared to the standard *Methane Steam reforming* MSR. Industrial Hydrogen generation is now 1.9 x 10¹¹ Nm³/y, # 5% of the Oil production (84 MBOL/d). MSR is producing commercial H₂ with CO₂ starting from NG with 700-1100°C and efficiencies of 70-80%.

Hydrogen yields have been studied as a function of temperature at 50 mln/min and 200 mln/min (Figure 5) pure methane volume flow rate for two different packed bed designs: cylindrical rings (porosity 84 vol-%) from the current study and quartz glass fragments (porosity 76 vol-%) published earlier in Geißler *et al.* and *equilibrium hydrogen yields* as a function of temperature at 1 bar, 1.5 bar and 2 bar (dashed lines).

The technical feasibility of methane decomposition in a liquid metal bubble column reactor has been successfully demonstrated (Figures 6 and 7). The maximum hydrogen yield of 78% was obtained at 1175°C. No major differences in terms of hydrogen yield were found between experiments.

Diluting the methane feed gas with nitrogen in the range of 0-90 vol-%, revealed no significant influence on the resulting hydrogen yield in the investigated temperature range.

During the present experiments, no clogging issues due to solid carbon deposition on reactor walls or other parts occurred. The produced carbon mainly accumulated above the liquid metal interface in powder form with particle sizes in the range of 15-20 µm.

Disassembling the reactor after 15 days of operation, only a thin carbon layer, around 10 µm in thickness, was found.

The present production of black carbon is # 6 million tons/y. The industrialisation of the NG de-carbonisation is considering the additional accumulation of much larger amounts of black carbon.

<i>CH₄</i>	<i>Dheat</i>	<i>Black C</i>	<i>2 x H₂</i>
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The direct combustion of NG will produce 890 kJ/mol. Instead, the combustion of the resulting H₂ is 572.2 kJ/2mol H₂. The product's theoretical efficiency is then 64%. Black carbon represents 394 kJ/mol C. Its final mass is 75%.

The endothermic contribution of the transformation in Black C and 2H₂ is 76 kJ/CH₄ mol, i.e. 8.5% of the CH₄. This contribution may be produced with additional CH₄ and a small CO₂ contribution or from H₂ with some reduction in efficiency.

However, Hydrogen is a gas and its transformation into a general-purpose final product is extremely expensive: there is need for a liquid fuel: methanol has been chosen.

Methanol freezes at -97.6°C, boils at 64.6°C, and has a density of 0.791 at 20°C. It is a convenient, safe liquid easily obtained from existing coal or natural gas sources via classic methods developed and practiced since the 1920s. Roughly 8% of the fuel used in the Chinese transportation system is methanol. China is now the largest producer of methanol in the world.

Methanol can also be readily converted into many other chemicals like ethylene, propylene and others. Methanol not only represents a convenient, safe way to store and transport energy, but together with its derived product dimethyl ether (DME), is an excellent fuel.

Therefore it could replace oil both as a fuel and chemical raw material, mitigating the dangers of global warming without costly new infrastructures.

Let us assume that we recover CO₂ as a chemical material (Figure 8), recycling it from a conventional source of concentrated CO₂ waste, removed by the recovery of the CO₂ conversion of the previous application (two for one). We can combine it with Hydrogen, for instance produced with black carbon, and without CO₂ from the de-carburation of NG.

CO₂ and hydrogen can produce Methanol and water, a liquid substitute of Gasoline in all distant transport applications.

If Methanol or its substitute were burnt in a concentrated source, its CO₂ could be indefinitely recycled. Otherwise CO₂ may be re-emitted, returning it to the atmosphere.

Finally, we should be aware that an important new development is expanding the availability of NG. In 2000 Shale gas provided only 1% of U.S. natural gas production; by 2010 it was over 20% and the U.S. government predicts that by 2035 46% of the United States' natural gas supply will come from shale gas.

Methane hydrate (the so-called *Burning Ice*) is the most abundant natural form of clathrate, a chemical substance in which molecules of water form an open solid lattice that encloses, without chemical bonding, appropriately-sized molecules of methane (Figure 9).

Future supply options (Figure 8) are nuclear and solar energies for Hydrogen and the capture from the atmosphere for CO₂. At high pressure methane clathrates remain stable up to 18°C. One litre of methane clathrate contains as much as 168 litres of methane gas.

According to either of the above methods, the NG from the bottom of the ocean or permafrost can be directly extracted liberating the clathrates and bringing them to the surface. The methane hydrates in sediments in part of U.S. territory alone could supply the present U.S. natural gas needs for > 103 years.

In conclusion: can we foresee a new age of fossil-generated abundance? Our new method of Hydrogen production associated with the very large resources of newly discovered NG – eventually converted into Methanol, whenever a fuel is required in the liquid form – would permit to continue the safe supply of an already widely available fossil fuel at low cost, eliminating the ordinary environmental drawbacks of an ordinary NG combustion.

In view of the well-known, serious environmental concerns, the technology of methane de-carburation and no CO₂ emissions could become one of the primary energy sources during the decades to come.

The energy innovation process is generally characterised by long lead times, often decades, to achieve substantial markets, due to the scale of investments needed and the technological and regulatory inertia inherent in existing energy systems.

Public intervention to support energy innovation is thus both necessary and justified.

References.

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