

FEATURE 5 October 2016

The reaction that would give us clean fossil fuels forever

Crack natural gas into its constituent atoms and you can burn it without producing CO_2 – giving us green energy without all the pain of renewables



Jack Hudson

By **Jon Cartwright**

SCARRED landscapes, billowing smoke, seabirds writhing in liquorice gloop: there's no denying fossil fuels have an image problem. That's before we even start to factor in the grave risk continuing to burn them poses to Earth's climate. But what's the alternative? Nuclear is expensive, renewables are unreliable, and we are a long way from making batteries that could power our fuel-hungry lifestyles. Realistically, we are going to be reliant on fossil fuels for a while yet.

What we need is a way to exploit them without emitting any planet-warming carbon dioxide. Alberto Abánades thinks he has the answer. He isn't a PR man for the fossil fuel industry, and nor does he have anything to do with various schemes to capture and bury carbon emissions after the event. He and his research team think they have cracked the problem using chemistry alone. By simply changing the way we liberate the energy trapped inside natural gas molecules, we can have all the benefits of fossil fuels

– and none of the guilt. Too good to be true?

It's easy to see why we love fossil fuels. For a start, they are cheap and abundant. Discoveries of new resources and extraction techniques such as fracking mean reports of “peak oil” always seem exaggerated. They are reliable, too – you can shovel coal or pipe gas into a power station when the sky is cloudy or the wind's not blowing. And they can be portable – simply fill a car tank with petrol and you are good to go.

We have tried to kick our fossil addiction before. During the oil crisis of the 1970s, all the talk was of hydrogen. The gas ticks a lot of boxes as a fuel: it is non-toxic and the most abundant element in the universe. It is clean, burning in air to create water vapour that falls harmlessly back to Earth as rain. It is energy-dense – you could drive the 600-odd kilometres from London to Edinburgh, or San Francisco to Los Angeles on a single tank. And it can be burned in power plants, even competing cost-wisely with fossil fuels once carbon taxes are taken into account.

In practice, things aren't so simple. Being light and tiny, hydrogen has an annoying ability to wiggle through any material designed to contain it. Like petrol, it is flammable, yet burns with a near-invisible flame. Above all, it isn't abundant where and how we want it.

On Earth, hydrogen isn't a free agent. It is only found bound up in compounds such as water. Pure hydrogen can be generated by splitting water molecules using electrolysis, but that takes a lot of energy. Or you can extract hydrogen from coal or natural gas by heating them with steam, but that generates copious amounts of carbon dioxide.

So it came as little surprise when, in 2009, then US energy secretary Steven Chu, a Nobel prizewinning physicist, ditched funding for research into hydrogen-powered vehicles. Last year, Elon Musk, CEO of electric-vehicle manufacturer Tesla, summed up many sceptical opinions when he labelled hydrogen an “incredibly dumb” alternative fuel.

Perhaps, though, we haven't been thinking about it in the right way. Natural gas is essentially methane, a molecule of one carbon atom and four hydrogen atoms. Rather than reacting natural gas with steam to liberate the hydrogen, Abánades, who is now at the Technical University of Madrid, and his team developed a deceptively simple plan. You “crack” the methane into its constituent atoms – pure, clean hydrogen, plus inert atomic carbon, or soot.

If it were that simple, it would already have been done. Breaking carbon-hydrogen bonds takes a lot of energy. They only start to crack spontaneously at temperatures above 550 °C or so; normally, temperatures over 800 °C are needed. But there is a bigger problem: the soot. This scuppered an early attempt to make methane cracking industrially viable: it coated the nickel-iron-cobalt catalyst used by chemists at the petroleum company Universal Oil Products to improve the reaction rate at lower temperatures. Their solution was to burn off the carbon – making carbon dioxide.

It's been the same lament with methane cracking ever since. Soot clogs things up and the whole process grinds to a standstill. It's inevitable: the carbon has to go somewhere.

In his 20 years as an engineer, Abánades has worked on various types of energy

generation, including nuclear and solar. His old group leader, Carlo Rubbia, first put him on to methane cracking in 2008. Rubbia had shared the Nobel prize for physics in 1984 for his part in finding the particles that govern nuclear decay, but, in his late seventies, he had long since turned his focus to energy innovation. “Professor Rubbia has always said to me, don’t do what others do,” says Abánades.

Bubble bath

Trawling back through the literature, they soon found something someone hadn’t done. Back in 1999, Meyer Steinberg, a chemical engineer at Brookhaven National Laboratory in New York, and a veteran of the Manhattan Project to make a nuclear fission bomb, had proposed performing methane cracking in a heat bath made of molten metal. The idea, apparently never acted upon, was that the molten metal would improve heat transfer and allow the soot to float to the surface, avoiding clogging.

Abánades and Rubbia were then based at the Institute for Advanced Sustainability Studies in Potsdam, Germany. On the other side of the country, at the Karlsruhe Institute of Technology, was perhaps the best molten metal laboratory in Europe. By 2012 the two groups were collaborating on a 30-month fast-track project to see whether they could, well, crack methane cracking.

After two years of trial and error, they had what they thought was a viable reactor design: a vessel about the height and diameter of a hockey stick lined with quartz glass and stainless steel and filled with molten tin. Its external foil insulation made it look rather like a domestic hot water tank but it worked: they bubbled methane in at the bottom while raising the temperature of the tin up to 1000 °C, until hydrogen gas spouted continuously from the top.

But the real test was what it looked like inside. After two weeks, Abánades and colleagues switched off the reactor and peered in. Soot had indeed formed, but it had all floated neatly to the tin’s surface, where it could be scraped away like the slag in an ore refinery. “We could even have operated the reactor for a couple more days,” says Abánades. Last year, repeating the experiment at 1200 °C, the team managed to convert nearly 80 per cent of the methane they pumped in into hydrogen (*International Journal of Hydrogen Energy*, vol 41, p 8159).

The notion that hydrogen can be continuously generated from methane, without directly producing any greenhouse gases, is enough to turn the heads of those in the field. “These are serious people,” says Eric Croiset, a chemical engineer at the University of Waterloo in Canada, who performed a review of the state of methane cracking five years ago. “I wouldn’t distrust their results.”

We haven’t reached the promised land yet, though. To heat their reactor, Abánades’s team resorted to electricity from the wall socket – not necessarily the green option. A renewable source of heat, such as a solar concentrator, might do the trick, says Stéphane Abanades (no relation) at the French solar innovation lab PROMES, although there’s a risk that when the sun sets or goes behind a cloud, the molten tin could solidify, damaging the reactor. “Supplying solar energy to such a reactor may not be an easy task,” he says.

Alberto Abánades hopes that a future reactor could simply burn a little of the hydrogen it generates, perhaps 15 per cent of the total yield. This approach would generate

similar low levels of carbon dioxide as hydrogen produced by wind-powered electrolysis of water, but would be cheaper, more reliable and more scalable, according to his team's preliminary analysis, performed in collaboration with RWTH Aachen University in Germany.

That still leaves the question of the soot. Scaling up methane cracking to terawatt-scale production – a reasonable extrapolation for a global hydrogen economy – would create a mountain of soot several cubic kilometres in volume every year. That is far less problematic than the carbon dioxide generated by directly burning fossil fuels, but still not an amount you can brush under the carpet.

Abánades is confident a cheap and abundant supply of pure black carbon will find its uses, given the element is already in demand for nanotechnology, steel production and as a filling for car tyres. "A new market could be opened up," he says. But first the carbon produced has to be of a higher quality. The methane cracking team believes its carbon is about 90 per cent pure, and could be improved either by tinkering with the reactor's chemistry or by purifying the carbon further down the line.



Clean hydrogen could transform our energy and crop production

Nicolas Loran/Getty

Is it full steam ahead for the hydrogen economy? Perhaps, especially as other bits of the puzzle seem to be coming together. For example, chemists are tinkering with ways to convert hydrogen into fuels that are easier to handle, such as methanol (see "Booze cruise"). That might sound convoluted, but Abánades points out that oil is just as useless when freshly drilled from the ground. "Do we actually use crude oil? No, we transform it into gasoline. Hydrogen could be similar," he says.

Spurred on by cheaper hydrogen technology and the current range limitations of batteries, Toyota, Hyundai and Honda have all recently put cars powered by hydrogen fuel cells back on sale. Last year the European Union launched the Hydrogen Mobility

Europe project, aiming to create a network of hydrogen refuelling stations across Europe. The UK government is providing small subsidies for fleets of hydrogen-powered vehicles. Croiset believes electric and hydrogen cars could address different markets, perhaps electric for inner city travel and hydrogen for longer distance commuting. "You will buy the vehicle that suits your needs," he says.

Others are less keen on the incentives that producing hydrogen-based fuels from natural gas create. The technology could commit us to more fossil-fuel infrastructure in the future, distracting from efforts to pursue renewable alternatives, warns climate scientist Ilissa Ocko from the Environmental Defense Fund, a New York-based non-profit that campaigns on global warming. What's more, the pipelines used to transport natural gas are known to leak a considerable amount of methane, a far more potent greenhouse gas than carbon dioxide. "Unless these leaks are plugged, it's possible that the warming from leaked methane will offset the climate benefits from methane cracking in the near-term," she says.

Abánades agrees that climate impact should be the deciding factor on which technologies to pursue. But in energy innovation, he says, it is tempting to view those working on different technologies as enemies, and it is easy to become tarnished by an association with fossil fuels. In the absence of a renewable silver-bullet, anything that limits the impact of fossil fuels has to be a good thing, he says. "Emissions should be stopped now, and that could be done through methane cracking. If they aren't, when it comes to controlling global warming, we will be too late."

Booze cruise

It is inherently difficult to compress flighty hydrogen gas into a fuel tank. The problem evaporates if you first convert it into a liquid alcohol, such as methanol. Aside from being easy to store, methanol can be used in regular internal combustion engines - where it can even perform better than petrol.

Compared with methane, methanol contains just an extra oxygen atom, but it is tricky to make from natural gas. It is much easier to create by combining hydrogen with carbon dioxide. The combustion of methanol in an engine releases carbon dioxide into the atmosphere, but if you use atmospheric carbon dioxide in the first place, the overall process is carbon-neutral. Eric Croiset at the University of Waterloo in Canada is hoping to work with a company to build a proto-plant that generates methanol in this way.

There are other options. In 2014, scientists at the Swiss Federal Institute of Technology in Lausanne reported a straightforward process for converting hydrogen into formic acid that can be fed into fuel cells, the battery-like power systems that drive hydrogen vehicles. The process is also reversible, so formic acid could be an alternative way to squirrel away hydrogen when regular storage is impractical.

The reaction that feeds the world

Should the futuristic hydrogen economy fail to materialise (see main story), hydrogen from methane cracking has a market ready and waiting: ammonium fertiliser. The Haber-Bosch process, which converts hydrogen and nitrogen into ammonia, generates most of the ammonium fertiliser used in agriculture. The reaction has been credited with fuelling the 20th century's population boom. It is so ubiquitous that it is part of you: over 80 per cent of the nitrogen that finds its way into the average person's tissue is thought to be as a result of the Haber-Bosch process.

Currently over 95 per cent of hydrogen production comes from traditional fossil-fuelled processes, mostly blasting natural gas with steam. In 2007 alone, the fertiliser industry generated a little short of 500 million tonnes of carbon dioxide, nearly 1 per cent of total global emissions. Re-supplying the Haber-Bosch process with methane-cracked hydrogen could drastically shrink this carbon footprint. With the world population expected to exceed 10 billion by the end of this century, that would be a significant step on its own.

This article appeared in print under the headline "Going clean"

Jon Cartwright is a freelance journalist based in Bristol, UK

Magazine issue 3094, published 8 October 2016