The *Ineos Insight*, carrying US shale gas, approaches port in Scotland in September 2016.

JEFF J MITCHELL/GETTY

THE GREAT GAS GOLD RUSH

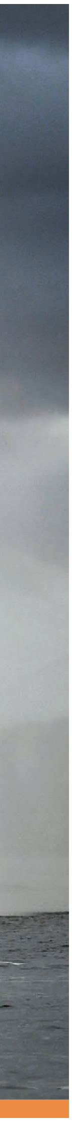
Cheap and abundant shale gas is changing how the chemical industry makes the ingredients of modern life. Chemists want to ensure that it's change for the better.

BY MARK PEPLOW

As the *Ineos Intrepid* cruised slowly through the sapphire waters of Norway's Frierfjord, chaperone tugboats sprayed jets into the sky to herald her arrival. In giant refrigerated tanks below decks, the ship carried 27,500 cubic metres of liquid ethane — enough to fill 11 Olympic swimming pools. *Intrepid* also brought a message, painted in giant capital letters along her side: "SHALE GAS FOR PROGRESS".

The vessel's arrival in March 2016 brought the first ever shipment of shale gas from the United States to Europe — and marked the start of a burgeoning business. More of these 180-metre-long 'Dragon'-class vessels have followed in her wake, forming a 'virtual pipeline' for ethane across the Atlantic Ocean. This gas, which is extracted from the ground through the hydraulic fracturing of shale deposits, isn't destined to fuel power stations or domestic stoves. Instead, it will be transformed into the chemical building blocks needed to make a panoply of products, including plastics, clothes, adhesives and medicines.

Intrepid's voyage is a striking demonstration of how cheap US shale gas is reshaping the chemical industry and changing the origin of



countless manufactured objects. For decades, the industry's raw ingredients have mostly come from crude oil. Chemical plants break down long hydrocarbon molecules in crude to produce a smorgasbord of smaller molecules, such as ethene, propene and benzene — all important precursors to polymers.

But shale gas, which is composed mainly of methane, ethane and propane, is turning that pathway on its head. The abundance of the gas has slashed the costs of these molecules. As a result, some are now usurping large hydrocarbons as the preferred starting point for industrial synthesis.

This shift from oil to gas brings enormous opportunities. According to the American Chemistry Council, a trade group based in Washington DC, the shale boom has attracted about US$160 billion in investment from the US chemical industry since 2011, and will help to create half a million jobs in plastics manufacturing over the coming decade[1]. But it also poses huge challenges. Some of the main techniques that are used to turn the components of shale gas into more valuable compounds — processes generally known as upgrading — are decades-old, dirty and energy-intensive. And they rarely produce the same mix of chemicals as conventional oil-based routes, which means that some relatively minor, yet valuable, chemicals such as butadiene, an ingredient of synthetic rubber, are becoming scarcer.

These challenges are driving an intensive research effort, spanning industry and academia, to develop catalysts and reactors that can transmute small hydrocarbons in cleaner, cheaper and more efficient ways.

Translating that research into commercial production will depend on the finely balanced economics of a changeable market. It will also require a reliable supply of gas. The US Energy Information Administration predicts that natural-gas extraction in the United States will continue to grow until at least 2040, but that might be too optimistic (see *Nature* **516,** 28–30; 2014). Meanwhile, concerns that fracking can contaminate groundwater — along with the broader climate implications of extracting fossil fuels — continue to dog the technology. If the glut does persist, however, it could usher in technologies that would form the foundations of a much more sustainable chemical industry. "We could totally redesign our chemical plants," says Bert Weckhuysen, a chemist at Utrecht University in the Netherlands.

THE ETHANE REVOLUTION

Shale gas is extracted from kilometres below ground, and typically contains about 70–95% methane, less than 15% ethane and less than 5% propane. After traces of oil, water and other impurities are cleaned out, the gas is chilled so that ethane and propane can be separated in liquid form, leaving methane behind.

Although ethane makes up a small proportion of shale gas, it has so far had the biggest impact on the chemical industry. That's because chemists can easily use it to make ethene, also known as ethylene. Ethene is used to make various types of polyethylene and the precursors to other plastics, such as polyvinyl chloride (PVC) and polystyrene. So voracious is the world's appetite for these plastics that the chemical industry produces roughly 150 million tonnes of ethene every year, more than any other chemical building block.

> "WE COULD TOTALLY REDESIGN OUR CHEMICAL PLANTS."

Most processes in the chemical industry use catalysts. But ethene can be produced simply by steam cracking ethane or larger hydrocarbons. First developed in the 1920s, steam cracking is a blunt, energy-intensive process that requires little more than water and 850 °C temperatures. "You basically just heat the snot out of it," says Jeffrey Plotkin, an industry analyst at IHS Markit in New York City. "The heart and soul of the thing is this gigantic furnace, that's where all the chemistry happens."

The boom in shale-gas-derived ethane has driven the chemical industry to invest nearly $45 billion in extra steam-cracking capacity[2]. But the transition to this feedstock is also creating a headache. When steam crackers are fed with mixtures of long hydrocarbons from crude oil, they make an array of useful by-products. But when they are supplied with ethane, the output is almost entirely ethene. "So there is a shortage of other building blocks," says Weckhuysen.

One of those building blocks is propene, arguably the second most important product of the chemical industry after ethene. Propene is turned into polypropylene, a plastic used in packaging and textiles, along with other polymer ingredients such as acrylic acid. But by one estimate, propene production by US steam crackers dropped by almost half between 2005 and 2014, even as global demand rose (see 'Dwindling supply').

To combat the shortfall, the industry is rolling out alternative ways to make propene. One of the leading routes starts with the shale-gas component propane. A combination of heat and a catalyst to remove two hydrogen atoms can be used to turn it into propene.

The conversion is becoming more profitable: more than 20 of these propane-dehydrogenation units are already operating worldwide, and at least 40 more have been ordered since 2011. But Weckhuysen says that there is much scope to improve the process, which tends to chew up catalysts quickly, requires a time-consuming and costly catalyst-regeneration step, and can use harsh reagents.

THE METHANE QUESTION

Although ethane and propane are already making waves as commercial feedstocks, the big prize for chemists is to upgrade the most abundant component of shale gas: methane.

Most of the world's methane is currently burnt as fuel, its lowest-value application. The gas can also be used as a chemical feedstock, but it contains strong carbon–hydrogen bonds that are difficult to break in a controlled way. When methane is converted into other molecules, it is done mainly through an inefficient sledgehammer of a process called steam reforming. First commercialized in the 1930s, this involves smashing methane and water together at up to 1,100 °C, over a metal catalyst. It produces an extremely useful mixture of carbon monoxide and hydrogen called syngas — and also emits several hundred million tonnes of carbon dioxide per year, accounting for roughly 3% of all industrial emissions[3].

Syngas is the world's principal source of hydrogen, much of which goes to make the ammonia in fertilizer. Syngas can also be used to produce longer hydrocarbons, such as basic components of diesel and waxes.

Such upgrading is typically done through a technique called the Fisher–Tropsch (FT) process, which uses cobalt or iron catalysts and heat to create daisy-chains of carbon atoms. FT was developed in Germany in the 1920s to make petrol and a wide range of other hydrocarbons from syngas derived from coal.

Producing transport fuels in this way is generally more expensive than refining oil. There are just six large-scale FT plants in the world, made economical only thanks to their proximity to huge coal or gas fields and the mind-boggling scale of the plants themselves: the world's largest, in Qatar, cost $19 billion to build and munches through 45 million cubic metres of methane every day, on a par with the natural-gas consumption of Belgium.

But the shale boom has prompted chemical engineers to take a fresh look at the FT process. Shale-gas wells typically don't produce enough gas to support a conventional FT plant, so research teams and companies have been developing smaller reactors that can process modest gas flows. One of those is Velocys, based in Houston, Texas, which developed a 5-metre-long reactor that can convert syngas into substances such as naphtha, diesel and wax. Its reactor technology is being used in Oklahoma City in the first commercial mini-FT plant in the United States. The plant, which is owned by ENVIA Energy, started production earlier this year.

Temperature control is a big challenge for the FT process: the reaction kicks in at about

180 °C, then generates huge amounts of heat. If not carefully controlled, it will run away with itself, turning carbon atoms into useless soot. To address this, Velocys's reactor contains corrugated layers of channels that are alternately stuffed with catalyst or filled with water. This keeps the reaction running at a steady 200 °C, so that the reactor can use an efficient catalyst without risking a runaway reaction. "It allows you to pack a lot of reaction in a very small space," says Neville Hargreaves, business-development director for Velocys in Oxford, UK.

The reactor in Oklahoma City pulls methane from a landfill site, an activity that comes with renewable-energy credits. But Hargreaves thinks companies could ultimately profit by tapping remote and relatively small natural-gas reserves that are unlikely to get a pipeline. Another potential target is unwanted gas from oil wells, which is often simply burnt off. Such 'flaring' puts about 350 million tonnes of CO_2 into the atmosphere every year. According to the World Bank, it carries enough energy to meet Africa's entire current electricity requirements.

THE DIRECT ROUTE

The high temperatures involved in producing syngas will always make it a costly way to create complex chemicals — as well as a major source of CO_2 emissions. Researchers have spent decades looking for ways to convert methane directly to methanol or other products, cutting syngas out of the route altogether. The shale boom has given this effort fresh urgency, along with a burst of investment in research and development in both academia and industry.

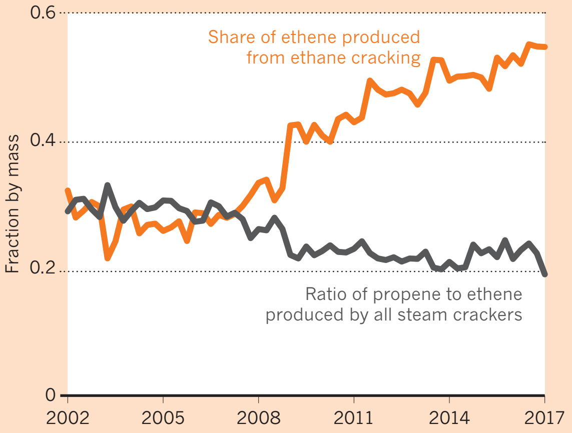
Turning methane into methanol — itself a key precursor to a wide range of other compounds — involves adding only a single oxygen atom. But first, one of methane's strong carbon–hydrogen bonds must be broken, and the high temperatures or strong oxidants needed to do that can set the molecule on a one-way journey down a thermodynamic roller coaster with a messy end. Methanol sits on a brief crest about halfway down, but it is all too easy to race downhill as the reaction goes too far, producing a mixture of other molecules, including formaldehyde, formic acid or carbon monoxide.

In 2005, however, a team led by Robert Schoonheydt at the University of Leuven in Belgium, found[4] that copper seeded onto a porous material called a zeolite could unite oxygen and methane to make methanol at less than 200 °C. Crucially, the methanol became trapped in the zeolite's pores, preventing further reactions. But extracting methanol from the pores and reactivating the catalyst would have proved expensive and impracticable in a commercial setting.

Since then, research groups have developed a range of copper–zeolyte catalysts that are more industry-friendly. Others have focused on completely redesigning chemical reactors. The European Union-funded project Adaptable Reactors for Resource- and Energy-Efficient Methane Valorisation, for example, aims to build small reactors that use renewable electricity, rather than heat generated from fossil fuels, to turn methane into compounds such as ethene and methanol. One approach uses microwaves to generate intense hotspots in the catalyst, lowering the heating requirements for the incoming gas.

DWINDLING SUPPLY

As steam crackers in the United States increasingly make ethene from ethane, rather than oil, they produce a smaller range of other chemicals, such as propene.



SOURCE: S&P GLOBAL PLATTS

Another approach to direct methane upgrading aims to couple pairs of the molecule together to make ethene. Since 2015, Siluria Technologies, a start-up in San Francisco, California, has been running a demonstration plant for this process in La Porte, Texas. It relies on a catalyst made of metal-oxide nanowires that collectively offer a surface area of about 200 square metres per gram of catalyst, hundreds of times more than a bulk catalyst could offer.

The company builds its catalysts in a unique way, based on a technique[5] developed by co-founder Angela Belcher, a materials scientist at the Massachusetts Institute of Technology in Cambridge. First, viruses are genetically engineered to express proteins that bind to dissolved metal ions. The ions form orderly arrangements as they stick to the surface of the virus. When the biological template is burned away, it leaves behind a highly stable, crystalline nanowire.

Rahul Iyer, Siluria's vice-president of corporate development, says that the process is cost-competitive with steam cracking ethane, and produces far fewer CO_2 emissions than steam reforming methane. Siluria has already licensed the technology to some chemical companies, and expects the first commercial facilities to be operating in 2019.

Plotkin says that Siluria is currently in the lead in the race to commercialize direct methane upgrading, and is backed by multimillion-dollar investments from big players in the industry. "People are keeping a watchful eye on it," he says.

GAS THAT'S GREENER

The shale-gas boom is credited with spurring a major renaissance in the US chemical industry, which has invested heavily in chemical plants and other infrastructure, as well as research and development. Enthusiasm for shale-gas upgrading has fostered major collaborations between academia and industry.

Translating laboratory results into commercial production is an ongoing challenge, although the trend towards small, modular reactors is helping to make it less daunting. The chemical industry is notoriously conservative: if a process succeeds in the lab but fails at commercial scale, tonnes of catalyst can be wasted and a plant shut down for months. "Industry will not take the risk unless they are sure it will work," says Weckhuysen.

Despite these challenges, he is optimistic that gas upgrading could have a huge impact — not only on the chemical industry's processes, but also on its environmental footprint. Some of the reactor technologies being developed to feed on shale gas could be adapted to use bio-based feedstocks, such as methane from landfills, as Velocys has found. Meanwhile, shortages in some compounds caused by the shift to shale gas could improve the economic case for starting with ethanol from crops, or lignin from wood[6]. There has already been movement along these lines. In 2013, for example, French tyre-maker Michelin and partners launched a €52-million (US$61-million) project to make butadiene from bioethanol.

But for now, US shale ethane continues its relentless march around the world. More chemical companies are commissioning ships to transport the gas to destinations in Europe, Brazil and India. By 2022, according to one estimate, about 8 million tonnes of ethane will flow through these virtual pipelines each year. They will carry this revolution in the US chemical industry to the rest of the globe — both its challenges and its opportunities. ■

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