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Renewable fuels

Harnessing hydrogen

Esteban Chornet and Stefan Czernik

Biomass can produce clean fuels and could be a vital, renewable energy source for the future. The demonstration of hydrogen production from biomass-derived molecules marks progress towards this goal.

ossil-fuel stocks are a limited resource and, as the world's governments struggle to agree on a strategy to combat pollution and greenhouse-gas emissions, the search for clean, renewable energy sources has never been more intense. On page 964 of this issue, Cortright *et al.*¹ provide experimental evidence that simple biomassderived molecules, such as glucose and glycerol, can be treated to produce hydrogen with reasonable efficiency. The authors suggest that, with some additional effort, their technique could also be technologically and commercially viable.

Cortright et al. demonstrate that glucose (the sugar used as an energy source in both

plants and animals) and glycerol (derived from fats) can be reformed in the aqueous phase in the presence of a platinum-based catalyst to produce $\rm H_2$. The conversion takes place at moderate temperatures, around 225–265 °C, and at pressures of 27–54 bar — conditions that prevent steam formation and ensure that the reaction sequence takes place in the aqueous phase.

The authors propose that the mechanism of hydrogen production involves the rupture and rearrangement of the biomolecules' C–C and C–O bonds on the platinum catalyst, leading to the formation of intermediates. These can then produce H₂ by reacting with the abundant water present —

glucose was used at a water–carbon molar ratio of 165, but the authors indicate that ratios as low as 15 are possible. Simple hydrocarbons and carbon dioxide are also formed. The amount of gaseous $\rm H_2$ produced as a proportion of the reaction products ranges from 36–50% for glucose to 51–75% for glycerol; and carbon conversion to gaseous products is 50–84% for glucose and 83–99% for glycerol. A yield of up to 80 g of $\rm H_2$ per kilogram of catalyst per hour is possible.

Cortright et al. claim that their approach represents a significant departure from traditional high-temperature, steam-reforming technologies. Even though these can be carried out at atmospheric pressure, they require temperatures of around 800 °C to be effective with steam-carbon molar ratios typically of 5 and even lower². Alcohols offer a lower-temperature option; vapour-phase steam reforming of those can be effectively carried out at temperatures of around 300 °C (ref. 3).

But does the proof of concept reported by Cortright $et~al.^1$ hold the promise of an aqueous-phase technology for producing H_2 fuel from renewable biomass? To answer that question requires an interlinking of science, engineering and the economics of H_2 production.

Today's benchmark in $\rm H_2$ production is provided by catalytic steam-reforming technology that uses simple hydrocarbons (such as methane and liquid petroleum gases) as feedstocks, and catalysts that are variations of well established nickel-based preparations and whose robustness guarantees operation over thousands of hours. The

Oceanography

Crossing the highway

The powerful current of the Gulf Stream is like a highway, carrying warm tropical waters from the Caribbean to Europe. The current is known to meander and to shed rotating rings of water on both sides. However, its interaction with the surrounding water tends to be limited to the outer edges of the current, especially along the well defined northern wall of the Gulf Stream.

But satellite images presented by Xiaofeng Li and his colleagues in Geophysical Research Letters show a parcel of cold water from a region

NOAA-10 October 4, 2001 00.39 OTC

known as the Middle Atlantic Bight breaching the northern boundary of the Gulf Stream, and traversing the full width of the current (*Geophys. Res. Lett.* **29**, 10.1029/ 2002GL015378; 2002).

The left panel of the picture, taken at 7:08 a.m. on 3 October 2001, shows the penetration of cold water as a green tongue that extends into the main current just east of Cape Hatteras, where the Gulf Stream leaves the American East Coast and veers off into the North Atlantic Ocean. The right panel shows the fate of the intrusion about 24 hours later: the cold tongue has been swept along with the current while extending southeastwards.

In early October 2001, strong and persistent winds from northerly directions blowing along the shore

north of Cape Hatteras piled up cold water from the Middle Atlantic Bight in the corner formed by the coastline and the Gulf Stream's north wall. Under less extraordinary wind conditions, long streaks of the relatively cold shelf water are slowly mixed into the Gulf Stream along its northwestern edge. But after three days of wind speeds exceeding 12.8 m s⁻¹ — conditions unique for early autumn in the 11-year period from 1991 to 2001 — the cold coastal water broke into the main Gulf Stream and eventually crossed it.

Li and colleagues say they are not aware of any other reports of such a breaching event. After all, crossing a busy highway is rarely attempted and is even less often successful.

Heike Langenberg

NOAA/NESDIS COAST WATCH PROGRAM

conversion takes place in fractions of a second, resulting in H_2 productivities of, typically, $200\,g$ of H_2 per kilogram of catalyst per hour². Productivity at this level means that the production costs of H_2 (expressed as the cost in US dollars per joule of calorific value contained in the molecule) are two to three times higher than for natural gas^{4,5}. However, taking into account the transportation and distribution costs of natural gas, and how pure you want the H_2 to be, the comparative cost of H_2 production can vary.

Biomass, the product of photosynthesis, could become a feedstock of choice for H₂ production, even in the absence of environmental premiums. At present, two strategies are being intensively pursued. The first is fractionation, which leads to the isolation and depolymerization of constitutive biomass fractions. An advantage of this approach is that the production of marketable goods (such as chemicals and fibres) can be integrated with the conversion of particular residual fractions to H2, as well as to other biofuels or to bioenergy6. In fact, in the absence of subsidies or carbon credits (through which countries can trade off carbon-producing industry against carbon-absorbing activities, such as the planting of crops), co-products from biomass are necessary to make bioenergy or biofuels economically viable⁷.

The second approach is through biosyntheses that produce H₂ directly. This requires photosynthesis to be conducted, as in algae, either with the removal of oxygen (to avoid poisoning the natural hydrogenases), or with oxygen-tolerant hydrogenases, which would need genetic engineering⁸. Alternatively, certain wet biomass fractions can be fermented by hydrogen-producing microorganisms in anaerobic environments where methanogenic pathways are suppressed⁹. Efforts in all of these directions are being pursued actively in academic and industrial laboratories.

Realistically, the introduction of a clean fuel such as H₂ is most likely to be achieved if the production technology can be integrated within the existing infrastructure used for natural-gas reforming. To use biomass as the source of H₂, several objectives must be achieved. To begin with, reaction and reactor productivities must match those achieved in hydrocarbon reforming. According to the results of Cortright et al.1, this is almost achieved with glycerol as substrate, but in the case of sugars as substrate much lower water-sugar ratios for aqueous-phase reforming will need to be used. Heat inputs to balance the endothermic reforming reaction must also be equivalent to those used in hydrocarbon reforming. In steam reforming, a steamcarbon molar ratio of between 3 and 5 is normally used, so for aqueous-phase reforming, an energy-equivalent liquid-watercarbon molar ratio of between 7.5 and 12.5 is needed, at an operating temperature of 260 °C.

Practical feedstocks should be chosen, such as sugar-containing hydrolysates (and not just high-purity, model sugars) or glycerol-containing liquors derived from residual fats with minimum purification. These feedstocks should preferably be obtained from high-productivity biomass crops, with little or no use of synthetic fertilizers. The biomass should also be able to yield co-products that will improve the economics of the process. Crops such as sugar cane (in tropical climates), as well as switchgrass and hybrid poplar (in temperate climates), might well be suitable.

Biofuels are becoming a viable component of tomorrow's energy mix. If the appropriate feedstocks are considered, biomass refineries seem uniquely suited to providing a variety of products — food, fibres and chemicals as well as biofuels — to satisfy society's needs in a sustainable manner.

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Cognitive neuroscience

The molecules of forgetfulness

Alcino J. Silva and Sheena A. Josselyn

Not everything that we learn is useful, so the brain needs a mechanism to prevent itself being burdened by unhelpful details. The molecular details of this mechanism are now being uncovered.

tudies of the molecular and cellular foundations of cognitive processes have come of age with the development of techniques that allow genes to be over-expressed, deleted or modified in mice. These altered animals have been studied from a variety of aspects simultaneously by molecular biologists, neurophysiologists and psychologists. The result is the birth of a field that is unravelling the basis of learning, remembering¹, and now — as a paper in this issue shows — forgetting. On page 970, Genoux and colleagues² report that an enzyme known as protein phosphatase 1 (PP1) actively suppresses memories in mice, both during and after a learning exercise.

Like other biological processes, memory is regulated by yin-and-yang-like interactions between molecules with opposing functions — in this case, protein phosphatases and kinases, which respectively remove and add phosphate groups on target proteins, thereby altering their properties.

To examine the role of these interactions in forming and maintaining memories, Genoux *et al.*² generated mice that express a natural inhibitor of PP1, called inhibitor 1. When phosphorylated, this protein binds to PP1 and prevents it from working. The authors regulated the expression of inhibitor 1 in mice by using the reverse tetracycline transactivator system³: simply feeding the mice a tetracycline-like compound switches

on the gene encoding the inhibitor, enabling PP1 activity to be blocked at will.

To test the animals' memory, the authors trained them in an object-recognition task that takes advantage of the natural propensity of mice and other rodents to investigate new objects more avidly than familiar ones. Their memory for objects depends on the hippocampus — a brain structure that shows robust expression of the inhibitor.

The authors' initial results help to explain one of the earliest discoveries of modern experimental psychology. In landmark experiments published in 1885, Hermann Ebbinghaus⁴ showed that distributing training into several sessions results in stronger memories than equivalent amounts of training crammed into a single session (students take note!). Genoux et al. now find that massed training triggers more PP1 activity than distributed training. Remarkably, when the authors switched on inhibitor 1 specifically during massed training, blocking the PP1 activity, this type of training became as effective as distributed training. So PP1 apparently suppresses memory formation during massed training — but how?

One of PP1's targets is a gene-transcription factor called CREB, which becomes inactive when dephosphorylated by PP1. When phosphorylated, CREB directs the transcription of genes with specific CREB-binding DNA sequences in their control regions⁵, and so is needed for proteins to be