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Hydrogen: the green energy carrier of the future?

Hydrogen may be the fuel of the future, but how can we produce it sustainably? **Karin Willquist** explains.

Hydrogen has been called 'the energy carrier of the future' – because it can be oxidised in a fuel cell to generate electricity, for example to power cars, without releasing carbon dioxide (CO_2), and it can be produced in remote places without an electricity infrastructure. In contrast to available resources such as natural gas and gasoline, hydrogen has to be produced, making it an *energy carrier* and not a fuel.

An energy system in which hydrogen is used to deliver energy – a *hydrogen economy* – was proposed by John Bockris in 1970; in 1977, an international hydrogen implementing agreement was established to work towards it[w1].

Hydrogen is mainly used now as a chemical reagent rather than an energy carrier, but there is no doubt that it has the potential to transform our transport and energy systems. However, realising its potential is not easy. Most fuels currently in use are liquids, solids or gases with high energy per volume (energy density). Hydrogen, in contrast, has a low energy density: at a given pressure, burning one litre of hydrogen produces one third of the energy that burning a litre of methane does. This poses problems of storage, distribution and use that are being addressed by scientists (Schlapbach & Züttel, 2001)[w2]. A more fundamental challenge, however, is that of producing hydrogen in a sustainable manner. This is what I shall focus on here.

Ways to produce hydrogen

Hydrogen is an abundant element on Earth's surface, normally linked to carbon in carbohydrates (in plants) or to oxygen in water (H_2O). Hydrogen gas (H_2), in contrast, exists only in small quantities on Earth. One of the challenges for sustainable hydrogen production is releasing H_2 from its bonds with carbon and oxygen.

Currently, H_2 is produced mainly from fossil fuels (e.g. natural gas) by steam reforming: heating the fuels to high temperatures with water[w2]:

- Biochemistry
- Environmental science
- Biology
- Organic chemistry
- Hydrogen economy
- Energy
- Ages 14-19

Following the publication of Jeremy Rifkin's book on the hydrogen economy (2002), this topic is frequently addressed in media as a real possibility for the near future. Another common issue surrounding hydrogen is its supposed role as a clean energy source. In this article, Karen Willquist offers a thorough overview of the issues involved in hydrogen production and of the ongoing research – including her own work – into sustainable ways to achieve this goal.

Given the author's clear approach, the article is particularly suitable for science teachers and upper-secondary-school students (ages 14-19) wishing to deepen their knowledge of this complex topic. Furthermore, both teachers and students will benefit from the many resources listed.

The article would be relevant for lessons on biochemistry (respiration, fermentation and photosynthesis), physics (fuel cells, thermodynamics: energy and efficiency), environmental science (energy resources, fossil fuels and renewable resources), biology (algae, bacteria, cyanobacteria and Archaea) and organic chemistry (hydrocarbons and steam reforming). It could also provide valuable background reading before a visit to a power plant or research laboratory working on fuel cells or hydrogen production, use or storage.

The article could be used to initiate a discussion on the difference between energy resources and energy carriers; the problems of hydrogen use and storage; and possible scenarios for the transition from our hydrocarbon economy to a hydrogen economy.

Suitable comprehension questions include:

1. Which of the following apply to respiration, to dark fermentation, or to both?
   a) The presence of glucose
   b) The presence of oxygen
   c) The absence of oxygen
2. Which of the following *is not* a process involved in converting acetate into hydrogen?
   a) Dark fermentation
   b) The use of electricity in a microbial fuel cell
   c) The hythane process

Giulia Realdon, Italy

REVIEW

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (1)$$
$$CO + H_2O \rightarrow CO_2 + H_2 \quad (2)$$

However, this method relies on fossil fuels and releases CO_2, causing the same emission problems as burning fossil fuels. Steam reforming is only sustainable if renewable hydrocarbons such as biogas are used, because the CO_2 released has previously been absorbed in the production of the hydrocarbons.

H_2 can also be produced by electrolysis[w2], whereby electricity is used to split H_2O into H_2 and oxygen:

$$2H_2O \rightarrow 2H_2 + O_2 \quad (3)$$

This method can be sustainable if the electricity is from renewable resources such as wind, wave or solar power. H_2 can thus be used to store energy on windy days when the windmills produce more electricity than can be consumed.

Interestingly, H_2O splitting occurs naturally in the oceans, because microscopic algae and cyanobacteria use solar energy to split water in a process called biophotolysis (Equation 3). However, the rate of H_2 production is extremely slow.

Efforts have been made to increase the production rate under controlled conditions using modified micro-organisms, but the processes are still too slow and expensive to be a realistic source of H_2 any time soon (Hallenbeck & Ghosh, 2009).

Finally, *biohydrogen* can be produced from crops and from industrial,

Figure 1: *C. saccharolyticus* bacteria under the electron microscope

forestry and agricultural waste, using bacteria. Like us, these bacteria oxidise plant material as a source of energy, but unlike us, they live in anaerobic environments (lacking oxygen). In aerobic respiration, we use O_2 to oxidise sugars, e.g.

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6\,H_2O \qquad (4)$$

In contrast, to oxidise the substrate as far as possible and thus optimise their energy gain, these anaerobic bacteria reduce protons, released during substrate oxidation, to H_2 (Equation 6, below).

Hot bugs

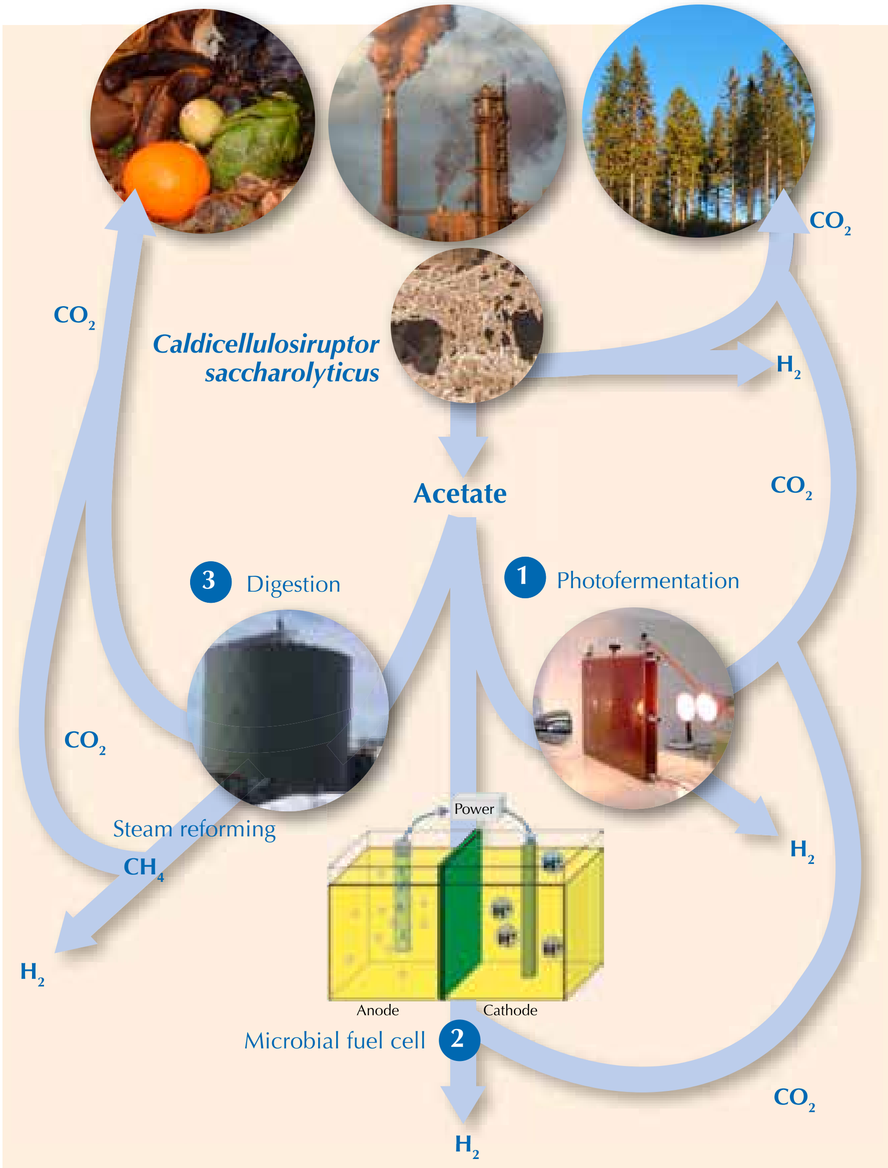
During my PhD, I investigated the hydrogen-producing abilities of one of these bacteria, *Caldicellulosiruptor saccharolyticus* (Figure 1, page 13), which lives in hot springs: anaerobic environments at 70 °C, with low levels of available carbohydrates. This bacterium is of particular interest because it is twice as efficient as most bacteria used for H_2 production.

Unlike humans, *C. saccharolyticus* gains energy from a wide spectrum of plant building blocks: not only glucose, but also, for example, xylose (Willquist et al., 2010). This allows the bacteria to produce H_2 from waste such as that produced during potato, sugar and carrot processing, as well as from industrial waste from pulp and paper production, or agricultural waste such as straw.

This is a promising start, but even *C. saccharolyticus* releases only 33% of the potential H_2 that could be released from the substrate. Equation 5 shows the potential complete oxidation of glucose, releasing $12H_2$ per molecule of glucose. Equation 6 shows the dark fermentation performed by *C. saccharolyticus*, which releases only $4H_2$ (33%) per molecule of glucose. The rest of the energy is released as acetate (CH_3COOH).

Total conversion of glucose to H_2:

$$C_6H_{12}O_6 + 6H_2O \rightarrow 12H_2 + 6CO_2 \qquad (5)$$



Images courtesy of Holger / pixelio.de (waste), Michael Cavén (paper factory), Keith Bryant (trees), Marcel Verhaart (C. saccharolyticus), Jakub Cebicki (photobioreactor), Gokce Avcioglu, METU Biohydrogen Research Lab, Turkey (anaerobic digestion reactor) and Karin Willquist (microbial fuel cell)

Figure 2: Biohydrogen production from waste. Waste is degraded and oxidised to H_2 and acetate by *C. saccharolyticus*. Acetate is converted to methane (CH_4) by anaerobic digestion (3), or to H_2 either by a microbial fuel cell (2) or by photofermentation (1). The CO_2 produced is taken up by the substrate, which results in a CO_2-neutral process

Dark fermentation:

$$C_6H_{12}O_6 + 2H_2O \rightarrow 4H_2 + 2CO_2 + 2CH_3COOH \qquad (6)$$

To release the rest of the H_2 from the acetate requires external energy. Alternatively, methane (CH_4) – which can be steam reformed to release H_2 (Equations 1 and 2) – can be generated from acetate. Luckily, there are three promising ways of doing this (Figure 2).

1. Using sunlight to convert acetate to H_2 with photofermentative bacteria (Equation 7)[w3]. However, like algal H_2 production, this process is currently too slow and expensive to be commercially viable in the near future (Hallenbeck & Ghosh, 2009).

$$2CH_3COOH + 4H_2O \rightarrow 8H_2 + 4CO_2 \qquad (7)$$

2. Using electricity to push the reaction of acetate to H_2 in a microbial fuel cell with a mixture of bacterial species (Equation 7)[w4]. This is an elegant concept, but its application is currently limited by low production rates (Hallenbeck & Gush,

2009). (To learn how to build your own microbial fuel cell, see Madden, 2010.)

3. Using methane producers (Archaea) to digest the acetate, generating methane (Equation 8). The combination of dark fermentation (Equation 6) and methane production is known as the hythane process (*hy*drogen me*thane*), and can convert approximately 90% of the original substrate to H_2 and methane.

$$CH_3COOH \rightarrow CH_4 + CO_2 \qquad (8)$$

The methane can then be steam reformed, releasing H_2.

To put the hythane process into perspective: if four people in a house eat 10 kg potato products each in one month, their waste could fuel 0.5% of their monthly domestic energy requirement (3500 kWh), provided that the H_2 produced is used directly (to avoid energy losses) and that the house is equipped with a heat and power fuel cell[w5]. More hydrogen could of course be generated from other waste – 0.5% is just from potatoes.

This is a rough estimate of the *potential* of the hythane process, based on a) 30% energy loss in the production of H_2 and CH_4 (hythane) and b) 30% in then steam reforming CH_4 to H_2. The steam-reforming step (b) is used in the production of hydrogen from natural gas, and is a well developed commercial technique. The production of hythane (a), however, is not yet that efficient, although research is ongoing to improve the efficiency to reach 70% (as in the example) and thus make the production of biohydrogen competitive with the steam reforming of fossil fuels for producing hydrogen.

Although there has been some recent progress[w6] (see box, right), it is too early to give a reliable time estimate for when sustainable H_2 production could play a significant part in supplying us with energy. However, as poet Mark Strand once said, "The future is always beginning now."

Image courtesy of Felix O; image source: Flickr

One of London's buses powered by hydrogen fuel cells

Image courtesy of Bull-Doser; image source: Wikimedia Commons

The Hyundai ix35 FCEV, powered by a hydrogen fuel cell

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Research into hydrogen storage and production

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ESRF

Storing hydrogen safely and efficiently is one of the main technological challenges to adopting hydrogen as an energy carrier. The Institut Laue-Langevin (ILL)[w7] has firmly established itself in frontier research into the hydrogen economy, using neutron diffraction to monitor hydrogenation and dehydrogenation reactions in potential hydrogen storage materials. To find out more, visit the ILL website[w7].

The powerful X-ray beams of the European Synchrotron Radiation Facility (ESRF)[w8] have recently probed the complex mechanisms by which hydrogen is produced by enzymes called hydrogenases. Most of these enzymes work under anaerobic conditions and are, in fact, inhibited by the presence of oxygen. Hydrogenases that remain active under aerobic conditions, therefore, are of great interest for technologies such as enzymatic fuel cells and the light-driven production of hydrogen. A German team of scientists has recently solved the crystalline structure of one of these enzymes (Fritsch et al., 2011) – perhaps a step towards a hydrogen economy?

Both ILL and ESRF are members of EIROforum[w9], the publisher of *Science in School*.

Image courtesy of David Berkowitz; image source: Flickr

Portable Fuels mobile phone charger from Powertrekk. Just add some water, and after a few minutes you have a battery for your mobile phone

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Microbial Cell Factories is an open-access journal, so the article is freely available.

Web references

w1 – To learn more about the hydrogen implementing agreement of the International Energy Agency, see: http://ieahia.org

w2 –To learn more about hydrogen prospects, see Joseph Romm's analysis on the Environmentalists for Nuclear Energy website (www.ecolo.org; under 'documents') or via the direct link: http://tinyurl.com/77dhx8x

See also Joan Ogden's peer-reviewed analysis *Hydrogen as an Energy Carrier: Outlook for 2010, 2030 and 2050* on the website of the University of California: http://escholarship.org/uc/item/9563t9tc

w3 – For a video about how hydrogen is released from potato biomass using sunlight, see: www.biohydrogen.nl/hyvolution

w4 – To learn more about microbial fuel cells, see: www.microbialfuelcell.org

w5 – To find out more about heat and power fuel cells, see: www.fchea.org/index.php?id=57

w6 – To read about recent progress on a biohydrogen fuel station in Taiwan, see the Focus Taiwan website (http://focustaiwan.tw) or use the direct link: http://tinyurl.com/7jao2tp

w7 – ILL is an international research centre at the leading edge of neutron science and technology, based in Grenoble, France. To learn more, see: www.ill.eu

For more information on ILL's research into the hydrogen economy, see the ILL website or use the direct URL: http://tinyurl.com/illhydrogen

w8 – Situated on the same campus as ILL, in Grenoble, France, ESRF operates the most powerful synchrotron radiation source in Europe. To learn more, see: www.esrf.eu

For more information on ESRF's research into hydrogen storage, see the ESRF website or use the direct URL: http://tinyurl.com/87bnj4c

w9 – To find out more about EIROforum, see: www.eiroforum.org

Resources

If you enjoyed this article, you may like to browse the other chemistry-related articles in *Science in School*. See: www.scienceinschool.org/chemistry

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Chemical engineer Karin Willquist obtained her PhD on biohydrogen production from Lund University, Sweden. Her research interests include microbial physiology, process optimisation and outreach activities. She works at Lund University, using computer simulations to improve the hythane process. She also organises courses on bioenergy for a multi-disciplinary bioenergy research platform (LUBiofuels) at Lund University. She is in the process of writing a book on bioenergy for high-school students.

To learn how to use this code, see page 57.