Artificial Photosynthesis

For the conversion of sunlight to fuel

ROBIN PURCHASE, HUIB DE VRIEND EN HUUB DE GROOT
EDITORS: PAULIEN HARMSEN EN HARRIËTTE BOS

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About this publication

This publication is intended for anyone with an interest in global developments in the field of renewable energy. It describes the potential of artificial photosynthesis, which could make a substantial contribution to our future energy supply.

We wish to thank the Royal Society of Chemistry (RSC) in the UK for giving us permission to use their publication on solar fuels, which appeared in January 2012. Some of the illustrations in this publication are reproduced from the RSC publication.

About BioSolar Cells

BioSolar Cells is a five-year Dutch research programme, which seeks to contribute to research and innovation in the field of photosynthesis aimed at the sustainable production of food, renewable energy and raw materials for the chemicals industry. Nine knowledge centres and thirty-eight companies, ranging from multinationals to small technology firms, are working together to unravel the fundamental principles of photosynthesis: the natural process by which energy from sunlight is captured and stored as chemical energy in the form of sugars. Within the BioSolar Cells project, knowledge about the photosynthesis process is utilized in plants, algae, bacteria and artificial systems that mimic the natural process. The BioSolar Cells project aims to provide the knowledge and technology needed for innovation.
The various research programme partners contribute knowledge and technology from a wide range of disciplines, including chemistry, physics, genomics, physiology, nanotechnology, biotechnology and ICT. Part of the research programme is devoted to education and social debate.

BioSolar Cells has a budget of 43 million euros and is funded by the Ministry of Economic Affairs, universities, companies and the Netherlands Organization for Scientific Research (NWO). The programme is supported by Stichting Topconsortium voor Kennis- en Innovatie Biobased Economy (the Top Consortium Foundation for the Knowledge and Innovation Biobased Economy) (TKI-BBE). More information about the programme is available from www.biosolarcells.nl/en/home.

Foreword

The Netherlands consumes almost 18 billion litres of fossil fuels per year. That produces a vast amount of CO_2, a greenhouse gas that is known to contribute to global warming. In order to limit climate change, we will have to recycle $CO_{2,}$ which can only be achieved with fuel. The fuel market is the only one that is large enough to absorb the large volumes of CO_2 exhaust. However, the potential production volume of biofuels is not large enough to offer a meaningful contribution the supply of renewable fuel.

One of the very few other options we have is to harness solar energy and store it in fuels in a CO_2-neutral way. This is an area of technological expansion that is often referred to with concepts such as 'the artificial leaf', 'artificial photosynthesis' or 'solar fuel'. These concepts all stand for the same principle: production of fuel from sunlight such as hydrogen, a completely CO_2-free fuel, or carbon-based fuels that recycle CO_2 from the air.

In all scenarios for sustainable energy supply solar energy is key. Scientists are working hard to develop solar fuel, also in our BioSolar Cells consortium. That is a development the public is not yet very familiar with. This publication aims to inform a wider audience about the principles and opportunities of solar fuel on a scientific solid basis and in a non-technical way.

If we want to create a sustainable future we will have to change production systems, not only in industrial production processes but also in our own living environment. These will be changes we all will have to deal with and we all can benefit from.

I am convinced that the technology will offer solutions, and we can obtain a great deal in solar fuels. In the end there will be questions such as: how do we apply these technologies? How can solar fuels be integrated in our economic system, where are we going to produce them, and who is going to benefit from them? What are possibilities for co-production or cascading for the bio-based economy, where evolution of nature and industry go hand in hand? What kind of drawbacks and risks can we expect?

These are questions that will keep our minds busy for a long time and cannot be answered overnight. I sincerely hope that this publication offers a tool for further reflection and debate about the do’s and the don’ts, aiming for sustainable economic systems and social structures.

Huub de Groot, BioSolar Cells Scientific Director

Contents

1 Why we need renewable energy

In 2015 the world population reached 7.2 billion. The United Nations Food and Agriculture Organisation predicts that growth will continue and that in 2050 the population will have reached 9 billion [1]. Emerging economies will drive global energy markets. As prosperity continues to grow, we will arrive at a point where the demand for energy and food outstrips supply. The tendencies in the west of reducing energy consumption and consuming less meat do help to some extent, but are not enough: in the future we are going to have to produce more food and make more use of sustainable forms of energy.

According to estimates by the International Energy Agency, the world's oil reserves will decline by 40-60 % in the next twenty years [2]. This decline in oil can be compensated by other fossil fuels, such as natural gas and coal, and by uranium. Current developments in the exploitation of shale gas seem to have given us access to huge reserves of natural gas at a low price. Our coal reserves will continue to last for a long time, and uranium reserves are still plentiful. But burning fossil fuels leads to emissions of large quantities of carbon dioxide (CO_2). This is one of the major greenhouse gases causing global warming, which in turn is leading to climate change and a rise in sea levels. These developments are adversely affecting biodiversity, precipitation patterns, fresh water supply, agriculture and food supply, and the safety of those living in low-lying coastal areas. This makes sustainable, low carbon energy supplies one of the most pressing challenges facing society.

To combat climate change, we need not only different policies, but also scientists and engineers who can help us make more efficient use of fossil energy sources and can develop new, sustainable forms of energy generation.

The goal of this booklet is to raise awareness of the concept of artificial photosynthesis and its potential to become an additional and significant new option in our longer-term energy future.

2 Solar fuels

2.1 Introduction

“With the help of the sun we could solve our energy problem. Every thirty minutes the Earth absorbs enough sunlight to supply the whole world a year long with energy. Every thirty minutes! This is where our challenge is. We have to use this potential. This is where we can use the forces of nature to our advantage.” This statement, made by Willem Alexander, King of the Netherlands, at a seminar in Dresden in 2011 is very true. The sun's potential as a renewable energy source is vast. If we can develop systems to use solar energy to produce fuels on a large scale, this will transform our future energy options.

We already use solar energy in many different ways. We produce electricity using photovoltaic solar panels, we install solar collectors on our roofs to heat our water and in countries such as Spain we build large installations that concentrate sunlight using mirrors. Solar energy is also used to cultivate plants and algae, from which food and biofuels are produced. However, the focus of this publication is artificial photosynthesis. Other methods of obtaining energy from sunlight are described in the appendix.

Currently, only 8 % of the energy we use globally is from renewable sources (principally hydroelectricity). 87 % of the fuel for transport, electricity generation and heating comes from fossil sources: coal, oil and gas. Those fossil resources also serve as important raw materials for industry. In the European Union, only 0.7 % of the electricity that we use is generated from sunlight. Although that percentage could be boosted by installing more and better solar panels, new ways of producing liquid and gaseous fuels using sunlight are needed, because no more than a third of the energy we use is in the form of electricity.

2.2 Converting sunlight into fuel: three methods

A fuel is a molecule that has energy concentrated and stored in a chemical form, which can be released when needed. The state of the art in solar concentration and storage is photosynthesis. Fossil fuels are the result of photosynthesis, and biomass contributes an estimated 10% of the global primary energy mix. Photosynthesis is the chemical process by which plants, algae and some bacteria store energy from the sun in the form of carbohydrates. These carbohydrates act as fuels: they are either used by the plant for growth and maintenance, or eaten by plant-eating animals, or, after an organism has died, slowly converted and concentrated at high temperatures and pressures underground into fossil fuels with high energy density. Photosynthesis is thus the ultimate source of all fuel we use today. The raw materials needed for photosynthesis are water and CO_2. The oxygen formed by the process is to a significant extent a waste product for the plants and microorganisms concerned. However, it is billions of years of photosynthesis that has given people and other animals the oxygen that they breathe.

Both yield and densification are important considerations in the development of solar fuels. While the strength of plants is that they use the self-sustaining, low-input, technically simple and economically efficient paths of agriculture and horticulture, and biofuels produced by high-yielding plants offer dense energy carriers, natural photosynthesis in plants is not very efficient in terms of the overall yield, the amount of solar energy that is ultimately stored. This limits the range of application of primary and secondary biofuels in recycling CO_2 for fighting global warming. Most field crops convert no more than 0.5 to 1 % of the solar energy they are exposed to into chemical energy (carbohydrates). Even the most efficient plants convert only about 2 %. Algae and cyanobacteria are more efficient: they can potentially utilize 5–10 % of solar energy. In the field of artificial photosynthesis, an efficiency of 18-20 % appears attainable in practice and the theoretical limit is roughly 40 %. Alternatively, various thermochemical processes can be considered.

The three basic approaches to converting sunlight into fuel are outlined below.

2.2.1 Photosynthesis in plants, bacteria and algae

Plants, bacteria and algae[1] convert solar energy into carbohydrates and oil (see figure 1). However, plants are not suitable for large-scale use as solar fuel, because they use a complex network of biochemical reactions to convert CO_2 into the end product (see intermezzo 1 on photosynthesis on page 13), meaning that their efficiency and production volume are too low to make a major contribution to energy supply. Efficiency is not generally limited by the amount of sunlight available, but by other environmental factors, such as the availability of CO_2, water and nutrients.

Certain modified algae and photosynthetic bacteria constantly release fuel into the medium in which they live. The advantage of that from a production viewpoint is that it is not necessary to harvest the whole organism. However, a significant portion of the

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[1] *More information about the production of fuel and other substances at cellular level using microorganisms, please refer to another publication in this series: 'Micro-algae: the green gold of the future?*

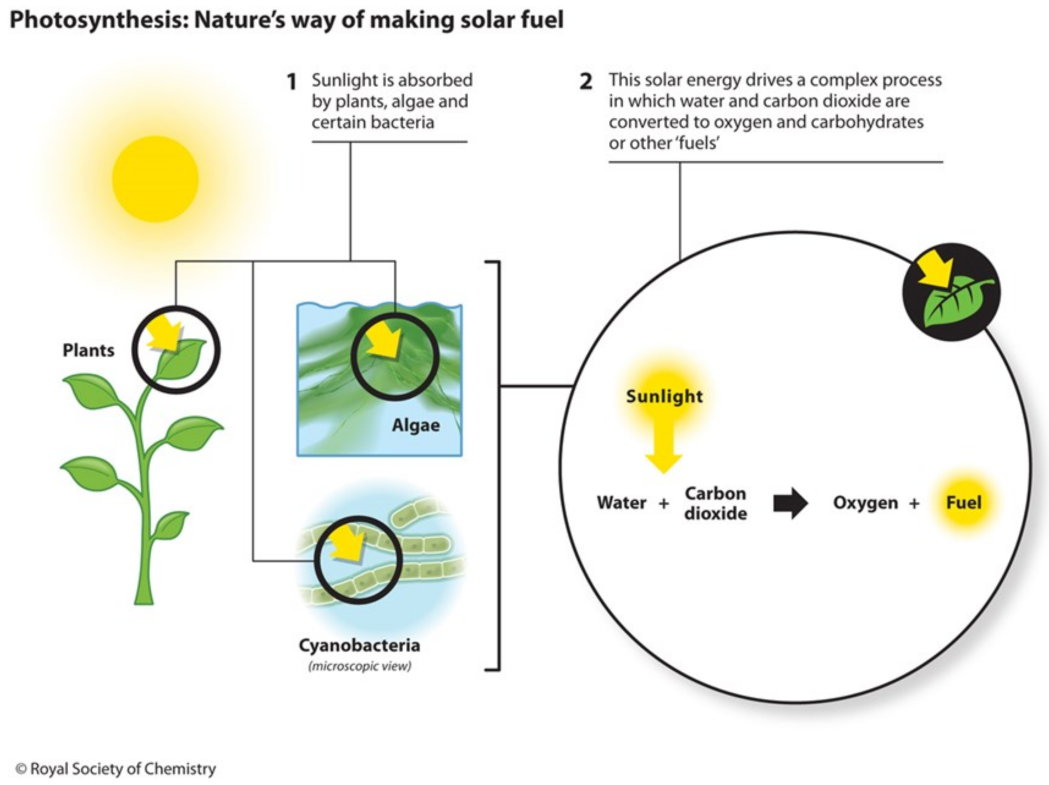


Figure 1: Photosynthesis: nature's way of making solar fuels. Source: Royal Society of Chemistry.

solar energy is used to maintain the metabolism of the cell itself and the organisms utilize only half of the solar spectrum.

2.2.2 Artificial photosynthesis

In artificial photosynthesis (the 'artificial leaf'), sunlight is converted directly into solar fuel, without making use of biomass as in the production of biofuels from plants, and without involving an electricity network, as in electrolysis using power from photovoltaic cells.

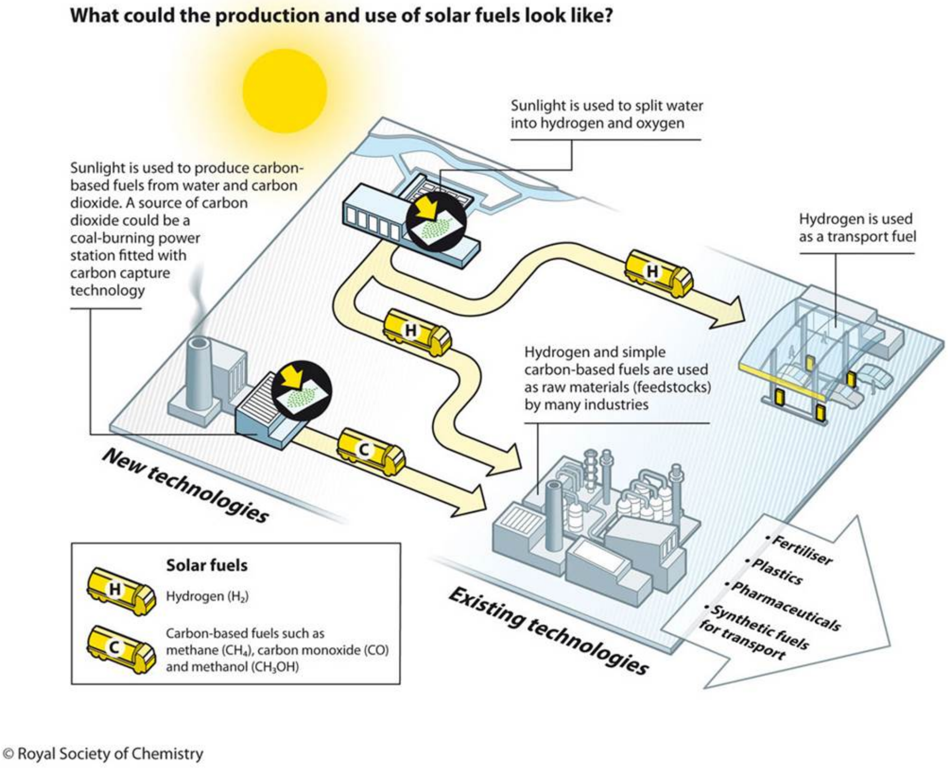
2.2.3 Thermochemical routes

The third way of converting solar energy into fuel is to take a very different route based on a thermochemical process, in which photosynthesis plays no part.

Thermochemical conversion involves using sunlight to heat materials to very high temperatures, at which they react with steam or CO_2 to produce carbon monoxide (CO) or hydrogen (H_2).

2.3 About this publication

The BioSolar Cells research programme researches the conversion of sunlight into fuel by means of photosynthesis. The three methods outlined in the previous subsection differ not only in their chemical and biological complexity, but also in their inherent efficiency. Of the three methods, artificial photosynthesis has by far the highest potential efficiency. It is a chemical process that imitates natural photosynthesis at the molecular level. Sunlight is used to convert water and CO_2 into oxygen and hydrocarbons or hydrogen (figure 2). Because of its high efficiency, artificial photosynthesis has the potential to provide an alternative to fossil fuels.



What could the production and use of solar fuels look like?

Sunlight is used to split water into hydrogen and oxygen

Sunlight is used to produce carbon-based fuels from water and carbon dioxide. A source of carbon dioxide could be a coal-burning power station fitted with carbon capture technology

Hydrogen is used as a transport fuel

Hydrogen and simple carbon-based fuels are used as raw materials (feedstocks) by many industries

© Royal Society of Chemistry

Figure 2: The production of solar fuels. Source: Royal Society of Chemistry

This publication in the Green Raw Materials series is intended to increase awareness of the concept of artificial photosynthesis for the production of fuels. In the following section, the concept of artificial photosynthesis is examined in more detail. Section 4 is devoted to research activities and section 5 considers the contribution that solar fuels might make to our future energy supply. The booklet ends by summarizing the opportunities that exist in the field of solar fuels for the Netherlands and Europe.

Intermezzo 1: The four stages of photosynthesis

Photosynthesis involves four steps: light harvesting, charge separation, water splitting, and fuel production [3].

Light harvesting

Light harvesting involves the absorption and concentration of electromagnetic radiation by antenna molecules (mainly chlorophyll, but also carotene). These molecules are packed together in protein complexes or organelles and serve to concentrate the captured energy in 'reaction centres'.

Charge separation

In the reaction centre at the heart of photosystem II, charge separation takes place: a chlorophyll molecule expels a negatively charged electron, leaving a positively charged 'hole'. In this way, energy from sunlight is used to separate positive and negative charges from each other.

Water splitting

In the third stage, multiple positive charges are collected and used to split water molecules into hydrogen-ions and oxygen. The water splitting is performed in a separate compartment away from the charge separation stage: far enough to prevent loss of charge upon arrival of the next photon, and close enough to allow for efficient buildup of charge for catalysis.

Fuel production

Electrons from the charge separation step are transferred via cytochrome b_6f and small mobile electron carriers to another protein complex, photosystem I. In photosystem I, more energy is added using photons from sunlight and the electrons are then used in a chemical reaction that ultimately produces carbohydrates.

The chemical reactions by which water is split and fuel is produced are as follows:

1. Water (H_2O) is split into oxygen, hydrogen ions and electrons:

$$2H_2O \xrightarrow{4h\nu} O_2 + 4H^+ + 4e^-$$

2. Carbohydrates (H_2CO) are produced from carbon dioxide (CO_2) and the hydrogen ions and electrons released by water splitting:

$$CO_2 + 4H^+ + 4e^- \xrightarrow{4h\nu} (H_2CO) + H_2O$$

Those two half-reactions combine to make the complete photosynthesis reaction:

$$CO_2 + H_2O \xrightarrow{8hv} (H_2CO) + O_2$$

The reactions described above are powered by light. Each half-reaction requires four photons (indicated by '4*hv*' above the reaction arrows). Four electrons are transferred and eight photons are used, two photons per electron. The photosynthesis reaction is therefore proportional to the number of absorbed photons.

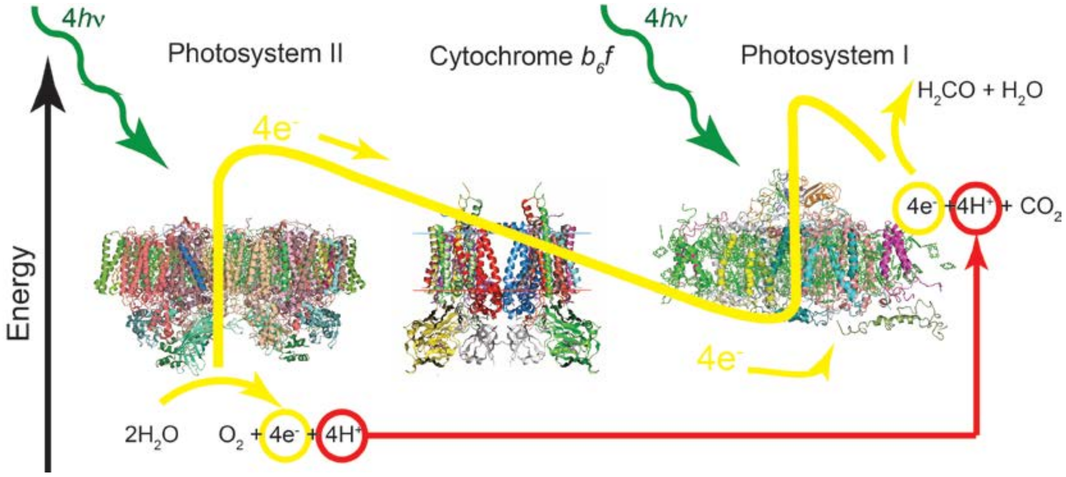


Figure 3:A schematic diagram of natural photosynthesis. Natural photosynthesis is engineered for direct conversion of CO_2 *from the air with 10-12 photons per* CO_2 *for the highest chemical yield. The photosynthetic antenna molecules absorb light (green wavy lines). This energy is used to separate the charges in the reaction centre of photosystem II. The positive charges are used to split water in the oxygen-producing photosystem II. Negative charges are passed via cytochrome* b_6f *to photosystem I, where sunlight is used to increase the energy of the electrons, so that they can be used for the production of carbohydrates. The yellow line gives the approximate energy of the electrons. The photochemical conversion volume is kept small so that charges are separated but never further apart than necessary to avoid unproductive thermodynamic work. Within this small volume the time scales, length scales and energy scales of the conversion cascade are optimised, responsive matrices with quantum coherent kinetic control (see intermezzo 2) provide synergy benefits for high yield,* CO_2 *is collected from the air, and solid fuel is concentrated into a thermodynamic sink that avoids possible back pressure while delivering starch, a dense concentrated carbon based primary energy carrier.*

3 Artificial photosynthesis

3.1 Introduction

Artificial photosynthesis involves four stages, making it very similar to natural photosynthesis (see also intermezzo 1) [3]:

1. Light harvesting: the collection of light particles (photons) by antenna molecules and the concentration of the collected energy in a reaction centre.
2. Charge separation: at the reaction centre, the collected sunlight is used to separate positive ('holes') and negative (electrons) charges from each other.
3. Water splitting: positive charges are directly injected into catalytic centres where they are used to split water into hydrogen ions (protons) and oxygen.
4. Fuel production: electrons from step 2 are given more energy from new photons and subsequently combined with the hydrogen ions and possibly CO_2 to produce either hydrogen or a carbon-based fuel. [4]

The chemical processes involved in the production of hydrogen (see figure 4) are simpler than those involved in the production of carbon-based fuels. Four protons and four electrons, released by splitting water with four photons, go to create two hydrogen molecules using the energy from a further four photons:

$$4H^+ + 4e^- \xrightarrow{4h\upsilon} 2H_2$$

Hydrogen is an attractive carbon-free energy carrier, which may play a lead role in future renewable energy technology. The drawback of hydrogen is that it is a highly explosive gas, while the existing energy infrastructure is based on liquids.

The carbon-based fuels that may be produced by means of artificial photosynthesis are not complex molecules like carbohydrates, but simpler molecules such as methane, methanol and carbon monoxide. The processes by which these fuels are produced are more complex than those involved in the production of hydrogen, because in many cases more than four electrons and protons and more than eight photons play a role in the reaction. The storage of energy in carbon-based fuels represents a major scientific challenge. However, carbon-based fuels have the advantage that many are liquid and could therefore be integrated into the existing energy infrastructure relatively easily.

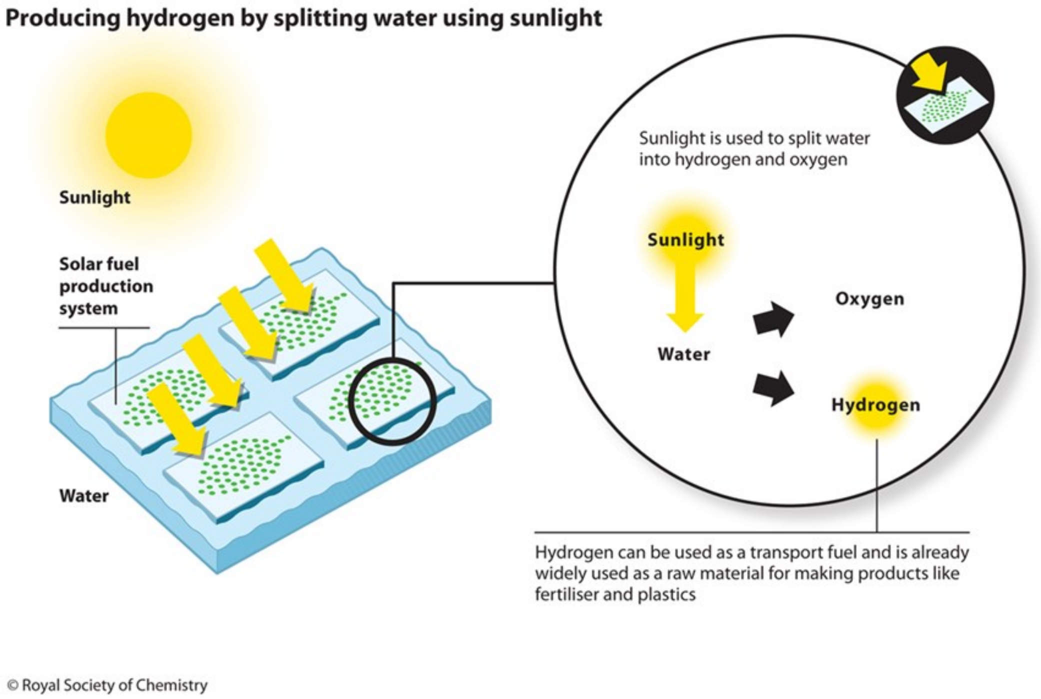


Figure 4: Producing hydrogen by splitting water using sunlight. Source: Royal Society of Chemistry.

3.2 What is sunlight?

The sun emits light across a broad wavelength spectrum, from ultraviolet (UV), to visible to infrared (IR) light. This light is made up of large numbers of light particles called photons, each of which carries a certain amount of energy. The amount of energy per particle depends on the wavelength or the colour of the light. UV photons carry more energy than IR photons (see figure 5).

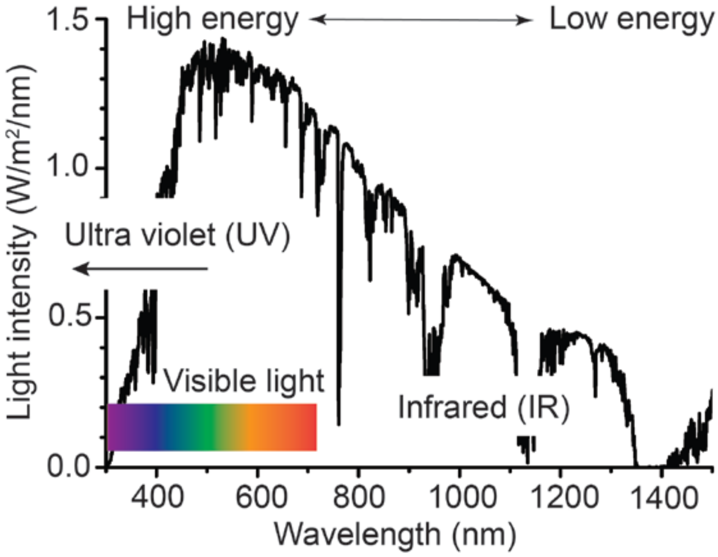


Figure 5: The solar spectrum. The black line shows the so-called 'AM1.5 spectrum': the intensity of the sunlight that reaches the earth, given the oblique angle of incidence and an air density of 1.5 times atmospheric density. The wavelengths of visible light are represented by the rainbow of colours. Infrared light is shown to the right of visible light, and ultraviolet light to the left (part of it being off the graph). Higher energy and shorter wavelengths are to the left, while lower energy and longer wavelengths are to the right.

A useful unit for measuring the large number of light particles in sunlight is the 'mole': 1 mole of photons is 6.022 10^{23} light particles. Each square metre of the earth's surface is struck by an average of between 10 and 120 moles of photons per day, depending on the location and time of year. Across the whole spectrum, the average daily photon flux in the Netherlands is roughly 40 mole/m^2.

3.3 Absorption of sunlight

Most materials absorb light only in a particular wavelength range and therefore in a particular energy range. Lower-energy photons are not absorbed, and the energy surplus associated with higher energy photons is lost in the form of heat.

Figure 6 illustrates how the photosynthetic apparatus in the leaves of plants absorbs light with a wavelength of less than 700 nanometres (nm). This is the photosynthetically active radiation (PAR) part of the spectrum. From the illustration, it can be seen that plants use only half of the incoming photons. They use the visible part of the spectrum, but not the IR part.

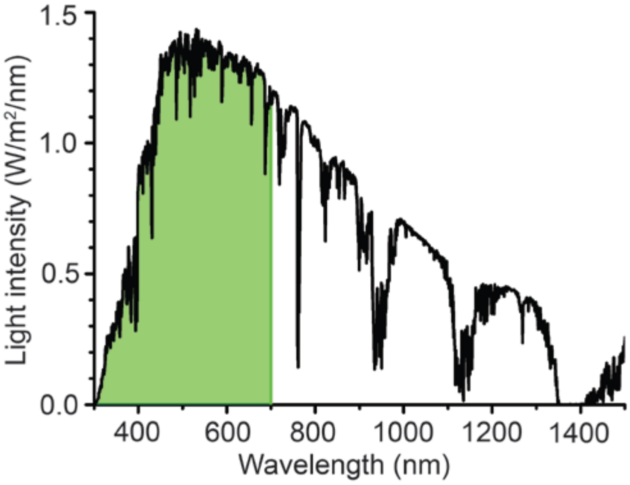


Figure 6: Photosynthetically active radiation (PAR) is light with a wavelength of between 400 and 700 nm, which organisms can use for photosynthesis. PAR makes up roughly 50 % of all light reaching the earth. The Daily Light Integral (DLI) is the number of moles photons in the relevant wavelength range that strike an area of 1 m^2 *per day.*

Silicon photovoltaic cells, on the other hand, absorb light with wavelengths less than 1100 nm, and therefore use photons from a wider band of the spectrum. The cut-off wavelength at which light is absorbed determines the potential difference of the electrons produced by the charge separation processes. For the 700 nm cut-off used by photosynthesis, the potential difference is 1.8 V, in contrast the 1100 nm cut-off of silicon photovoltaic cells yields electrons with a potential difference of 1.1 V. In other words, although silicon photovoltaic cells use more of the photons in the sunlight, they produce lower-energy electrons.

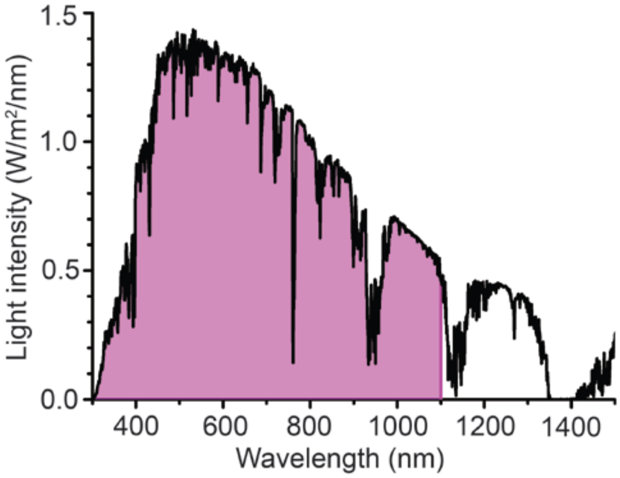


Figure 7: Sunlight absorbed by a solar cell. The magenta-shaded area indicates the approximate portion of the solar spectrum that is used by a silicon solar cell

3.4 Photosystems in tandem

In nature, the two stages that collect light for the production of fuel compete with each other for the same photons (see intermezzo 1 on photosynthesis). The red and infrared photons (those with wavelengths of more than 700 nm) are not used. In fuel production, it is better to capture as many of the incoming photons as possible, so that optimal use is made of the available sunlight.

That could be achieved by getting one of the two photosystems to absorb the visible part of the spectrum, and the other photosystem to absorb the infrared part. In this way, the proportion of the available photons that is absorbed subsequently used for energy conversion is maximized. With that aim in mind, scientists are studying tandem systems that incorporate two light absorbers with different cut-off wavelengths and consequently make optimal use of the captured light.

A schematic figure of a tandem artificial photosynthesis device and its associated light-absorbing properties is shown in figure 8. The energy levels and other chemical properties of the photosystems have to be chosen in such a way that, over the two stages, the incoming photon flux is (almost) entirely utilized in the conversion to fuel [5], because that results in the highest energy efficiency.

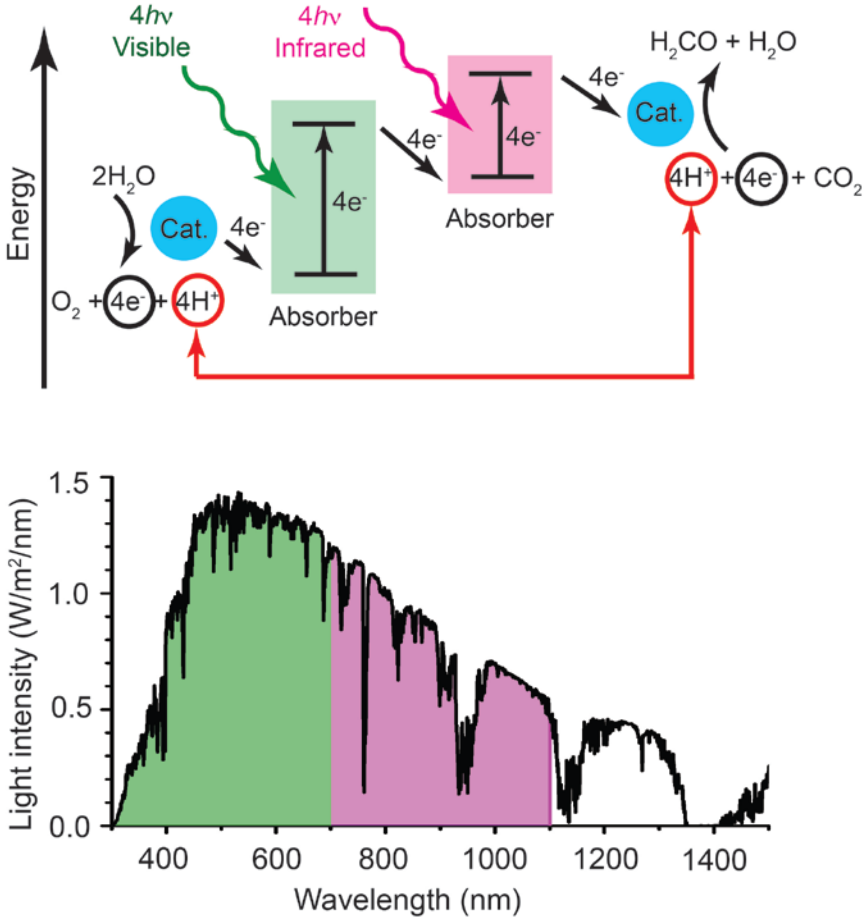


Figure 8: A tandem system for artificial photosynthesis (top) and utilization of the incoming photon flux. The tandem is in balance when each of the two halves collects a similar number of photons. Optimum utilization of the sunlight is achieved with cut-off wavelengths of about 700 and 1100 nm, as illustrated in the bottom chart.

3.5 The energy budget for artificial photosynthesis

Electrons generated from the absorption of light with a wavelength of up to 700 nm can bridge an electrochemical potential difference of up to 1.8 volts (V); those from light with a wavelength of up to 1100 nm can bridge a potential difference of 1.1 V. An electron's potential difference is a measure of how much energy it carries.

Consequently, a tandem artificial photosynthetic device with two photosystems that have cut off wavelengths of 700 and 1100 nm, respectively, yields a total of up to 2.9 V. (Compared with the 3.6 V energy budget of natural photosynthesis.) So 2.9 V is the energy budget available for breaking down the chemical bonds in water and forming the new bonds that hold together oxygen and fuel. In a system that produces hydrogen, the following functions need to be performed with the available potential budget:

- Water splitting. The standard redox potential for water splitting is 1.23 V, but in practice that potential is insufficient for the reaction to take place. For thermodynamic reasons, a further 0.25 V is needed to generate heat, so that the required potential is 1.48 V.
- An extra 0.5 V is required to prevent light reactions from running backwards.
- Catalysts rarely get reactions to run at the minimum required potential; they have overpotential associated with them. Water splitting is a complex reaction that takes place in four steps, and the catalytic overpotential required with existing technology is roughly 0.4 V.
- For hydrogen production, the overpotential is roughly 0.2 V.
- Hydrogen ions need to be transported, at the cost of a further 0.2 V.
- Finally, the hydrogen gas that is produced has to be compressed for storage. This takes at least 0.2 V, depending on the pressure required. In a standalone system, this energy also has to come from the available energy budget.

The figures presented above are estimates obtained by the computer modelling of artificial photosynthesis systems. From the sum of the required potentials (2.98 V) it can be seen that performing the reaction with the available 2.9-volt energy budget is very difficult in practice. Moreover, only 1.23 V will ultimately be used for the storage of energy in the chemical bonds of hydrogen.

The difference between the potential used for storage and the total potential required by the system is attributable to the use of energy to stabilize and compress the fuel and to ensure that the tandem system does not go into reverse and expel photons instead of storing them. The challenge is even greater when carbon-based fuels are concerned, because a further 0.5 V or so of over-potential is needed on the production side to reduce CO_2. Energy is also needed to concentrate CO_2 from the atmosphere. The main challenge facing artificial photosynthesis researchers is therefore to achieve a high level of efficiency through synergy in the chemical process of capturing light and converting it into hydrogen or carbon-based fuel. If the different steps can be integrated in a single organic or inorganic membrane to obtain synergy benefits, it should be possible for the process to operate within the available energy budget.

In this way, solar energy can be immediately concentrated and potential losses in the chemical conversion chain can be minimised by careful management of the various stages of the reaction. Direct conversion based on such a model could have a chemical efficiency as high as 80 to 90 %. That would boost the energy efficiency of a sunlight-to-hydrogen process to more than 30 %. This is the potential of artificial photosynthesis.

3.6 The responsive matrix

The working principles of natural photosynthesis act as a blueprint for artificial photosynthesis. One of the most intriguing aspects of nature's success is the use of 'responsive matrices': the various components (antennas, charge separators, multi-electron catalysts for water splitting and fuel production) are pre-programmed by their protein environment for optimal operation in their given function, and the entire photosynthetic process is driven forward with minimal losses.

For example, chlorophyll takes on a number of different roles in plant photosynthesis: it acts as a light harvester, it dissipates excess excitation energy under high light levels and acts as a charge separator. There are negligible structural differences between the chlorophylls performing these different functions. Instead, these differences are caused by the protein matrix subtly altering the local environment of the pigment, which in turn alters its properties.

One of the matrix's functions is to inject electrical charge from the reaction centre directly into a manganese oxide catalyst that splits water, without using an electric conductor in between. Without this direct injection, the electrical charges would disperse and subsequently require re-concentration, resulting in additional potential and efficiency losses.

The matrix also stabilizes and regulates the catalyst centre and slows down the photosynthesis reaction to achieve synergy between charge separation, catalysis and heat emission. Proper control of the catalytic centre enables the oxygen-oxygen bond to be formed immediately before releasing the oxygen gas. In this way, any heat that has been generated in the process is used optimally for both oxygen formation and release. If the oxygen-oxygen bond is formed too early, then more heat needs to be generated to liberate the oxygen, thus reducing the efficiency of the overall process. In this way, the losses associated with the first three points described in subsection 3.5 (heat generation, preventing recombination, and stabilisation of catalytic intermediates) are combined in natural photosynthesis, and can therefore be covered by the same over-potential. It is one of nature's clever tricks, which is not yet fully understood, for optimising the conversion of sunlight into fuel.

Embedding the photosynthetic components into a responsive matrix has enabled nature to construct a self-assembling, self-repairing system from a limited set of materials that operates with a high efficiency. How nature performs this feat is not yet well understood, but much progress has been made in the understanding of how this matrix works with the help of ultrafast spectroscopy, high-resolution solid-state NMR and quantum-mechanical modelling. In recent years, there has been a growing body of evidence to suggest that coupling with vibrational modes plays a key role in the functioning of the responsive matrix. (See Intermezzo 2 Quantum coherence in photosynthesis.) Scientists now believe that it is possible to create an artificial system with its own 'responsive matrix' that is capable of mimicking nature's tricks.

Intermezzo 2: Quantum coherence in photosynthesis

The responsive matrix uses molecular-scale vibrations to control energy exchange with the environment and to guide reactions. The protein environment influences the performance of the individual components and generates vibrations that create quantum-mechanical instabilities so that the desired chemical reactions can take place with minimal losses.

The principle of the responsive matrix is illustrated in figure 9 [6]. Two quantum states |r> (reactant) and |p> (product) are depicted as a red and a green line, respectively. |r> and |p> have a close spatial relationship that enables them to connect, they may be two energy levels in a chlorophyll oligomer or a catalyst complex, for example. If one of the states is occupied and there is an energetic difference between the two (as shown in figure 9A), the connection is suppressed and the occupied state is stable. The two pure states are then (non-interacting) quantum eigenstates.

If vibrations generated by the environment cause |r> and |p> to fluctuate in energy over time and to regularly cross, something extraordinary happens when |r> and |p> are at the same energy and the fluctuations are more rapid than the response time (dephasing time) of the quantum mechanical system: |r> and |p> become coupled by means of one of the vibrations in the environment (Figure 9B). The result is a quantum mechanical instability, leading to a mixed state and chemical conversion. The vibration of the atoms triggers a complex quantum rotation of the electronic wave function, so that the reactant |r> is gradually converted to the pure product state |p> (figure 9C). The reaction is by no means complete after a single oscillation; however, if the electronic motion is synchronous with the vibration and there is no interference, the chemical reaction can progress a little further every time that |r> and |p> are at the same energy. The process is consequently quite slow, but has the desired result and it costs very little energy.

A notable feature of the responsive matrix is that the interaction between the vibration and the movement of the electrons to produce the desired quantum rotation is actually self-regulating, because the movement of the electrons within the molecules adapts to the movement of the atoms. It ensures that the electron movement is neither too fast nor too slow, but synchronous with the quantum processes by which chemical bonds are broken and formed between the atoms. It is a manifestation of what is known as the quantum Goldilocks effect. This effect is named after the English fairy tale about a girl who tries out various items in the house of the three bears in search of items that are ‘just right’ (porridge that is not too hot or too cold, beds that are not too hard or too soft, etc.) Like the heroine of the fairy tale, the responsive matrix naturally selects a perfectly suitable vibration and perfectly suitable atom and electron motions. Thus a channel is opened, enabling chemical reactions to take place by quantum evolution from |r> to |p>. The responsive matrix selects the most efficient quantum process, *i.e.* that which is neither too complex nor too simple and is appropriate for the reaction channel.

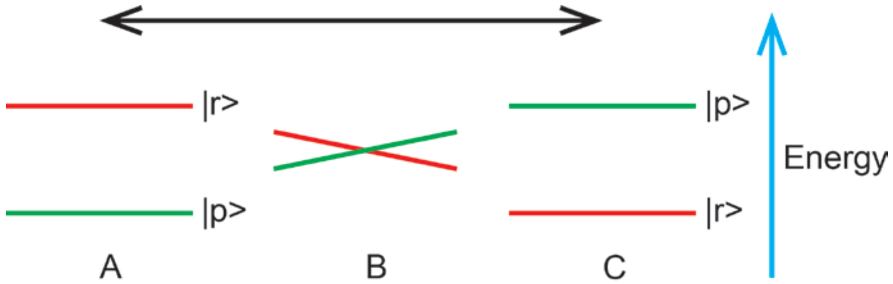


Figure 9: The principle of the responsive matrix for the conversion of a quantum chemical reactant state |r> into a product state |p> by means of coupling to a molecular vibration. In A, at the start of the vibration (indicated by the double-headed arrow at the top of the figure), the states are energetically well separated and the system is in state |r>. Both |r> and |p> are pure quantum eigenstates. The molecular vibration brings the two states periodically together (B) so that they overlap and become quantum mechanically unstable. State |p> is then mixed into state |r>. After half a period of the vibration (C), the energy levels of |r> and |p> are exchanged. If the vibration of the atoms in the matrix is synchronous with the quantum conversion process between the two levels, a number of periods of the vibration A-B-C-B-A will bring about the conversion of the chemically pure reactant |r> into the chemically pure product |p>.

3.7 Approaches to artificial photosynthesis

There are a number of different approaches that can be taken to artificial photosynthesis. All approaches involve the four basic steps of light harvesting, charge separation, water splitting, and fuel production. Here we have divided up the different approaches according to the types of materials used: molecular, inorganic, hybrid and semi-synthetic.

3.7.1 Molecular systems

Molecular catalysts are often developed following bio-mimetic approaches. Studies of energy conversion and storage in efficient natural enzymes provide inspiration for the development of the complex chemistry by mimicking enzymatic catalytic functions.

Entirely molecular systems are difficult to develop, but they have a number of advantages. Molecular systems offer the advantage of enabling a modular approach. Individual components for light harvesting, charge separation, water oxidation and fuel production can be made and investigated separately to maximise performance before being integrated into an appropriate architecture. Another advantage is that organic molecules have a well-defined structure that can be deliberately modified to improve a given property. Molecular systems are also readily studied using various analytical techniques that give both structural and kinetic information. Processes can therefore be followed and understood at a very detailed level.

This molecular assembly approach is elegant, but in the absence of a viable spontaneous assembly strategy, the large amount of synthesis involved renders it impractical [7]. Furthermore, most molecules tend to degrade quickly under extended exposure to sunlight. With a better understanding of responsive matrices (see section 3.6), which can control molecular reactivity and enable a system to self-assemble and self-repair, these molecular systems may become the champions.

3.7.2 Inorganic systems

Photovoltaic cells (made of semiconductors) can absorb sunlight and separate electrical charges. Semiconductors are therefore obvious candidates for use in artificial photosynthesis. Semiconductors with appropriate electronic properties can provide enough electrochemical potential to split water and produce fuel at the surface. Semiconductor materials are also stable under prolonged exposure to sunlight. However, many semiconductor materials with the right electronic properties to split water either absorb only ultraviolet light, which is only a small part of the solar spectrum, or require more than two photons per electron to absorb the whole spectrum. Moreover, semiconductor materials are rigid, making it difficult to generate the vibrations needed to control the reactions.

Despite the appealing simplicity of having a single material that performs all the necessary tasks, from absorption and charge separation to catalysis, no material capable of doing so has yet been discovered [7]. However, nanotechnology could make it possible to have the various functions performed by specific nanostructures.

3.7.3 Molecular-inorganic hybrids

An attractive solution is to combine the best properties of organic and inorganic materials. A semiconductor or an organic pigment molecule on a semiconductor surface absorbs the light; charge separation then takes place within the semiconductor and the charge is injected directly into optimized molecular catalysts attached to the surface. This is a promising approach, which has yielded a number of experimental devices. However, the designs produced so far have proved too expensive or too inefficient to warrant scaling up to commercial level.

3.7.4 Semi-synthetic systems

An interesting new approach is a hybrid of biological and artificial components. For instance, a biological component that harvests light and splits water could be modified chemically or by synthetic biology and tethered to a suitable scaffold. This complex could then be linked to a hydrogen-producing enzyme or a catalyst, similarly optimized by chemical or biochemical synthesis. Alternatively, chlorophyll molecules could be modified and combined with semi-artificial components. The advantage of such an approach is that biological components can be very efficient (nature has been performing photosynthesis for three billion years). This approach is still in its infancy, so it is not yet clear whether biological components can be made sufficiently robust by chemical modification to operate outside their natural environments, or whether they can be extracted on a commercially viable basis. However, even if this approach never yields commercially viable systems, the knowledge acquired may be extremely valuable.

4 Research and outlook

4.1 Requirements for artificial photosynthesis

In the previous section, various possible systems for artificial photosynthesis were introduced. A number of the systems are still in their infancy, but in various areas considerable progress has already been made (see also subsection 4.2). Generally speaking, to be a viable source of renewable energy, an artificial photosynthesis system needs to be efficient, robust and cost-effective. A number of existing systems fulfil two of those requirements, but none yet fulfils all three.

4.1.1 Efficient

A tandem system with cut-off wavelengths of 700 and 1100 nm makes optimal use of incoming photons and drives water splitting and fuel production with two photons per electron. The challenge then remains to optimize the yield of the forward chemical reactions into useful products and avoiding wasteful recombination of the charges generated by the photons after they have been absorbed. This is a delicate balance and nature does this very effectively, with an efficiency (the so-called ‘quantum efficiency’) in excess of 90 % at low light intensities. The higher the quantum efficiency, the less material and surface area is needed. The latest generation of solar cells achieves high internal quantum efficiency, but in this respect, there is still a lot of room for improvement in artificial photosynthesis. At the moment, there are only a few very expensive systems that work with a quantum efficiency of more than 25 %, corresponding to an energy efficiency of more than 10 %.

4.1.2 Durable

Any artificial photosynthesis system will need to be durable so that it can convert a lot of energy in its lifetime relative to the energy required to install and maintain it. This is a significant challenge because many materials degrade quickly when exposed to sunlight or corrode when exposed to oxygen or water.

There are two possible solutions. One is to build systems of very robust materials, like the coated semiconductors that are used in photovoltaic cells. The other is to devise a system that can repair itself when it is damaged. Nature takes this latter approach: the essential components of the photosystems in plants are regularly replaced. Some experimental systems mimic this. This self-repairing approach has the advantage that the system can then potentially also be self-assembling, making the system simpler and cheaper to build.

4.1.3 Cost-effective

Any artificial photosynthesis system must be cost effective to be commercially viable. Artificial photosynthesis must compete with other technologies for the production of hydrogen (and other fuels). This means that as little material as possible should be used in its construction and rare and expensive materials must be avoided.

A recent report for the Fuel Cells and Hydrogen Joint Undertaking gave expected costs for the production of hydrogen of €2.60 - 3.30 per kg and €4.40 per kilogram at the pump for large-scale (400 kg per day) production of renewable hydrogen with electrolysis technologies [8]. Those figures are consistent with the hydrogen cost projected by the US NREL, namely $3.10 to $3.70 per kg [9]. To make artificial photosynthesis as cheap as possible, these systems may ultimately be made locally from plastics using three-dimensional printing technologies.

4.2 Research into artificial photosynthesis

Research into artificial photosynthesis is highly interdisciplinary. Challenges of a physical, chemical, biological and technical nature need to be overcome. Expertise from subdisciplines within chemistry, such as photochemistry, electrochemistry, materials chemistry, catalysis, organic chemistry and chemical biology is very important.

4.2.1 Research in the Netherlands: BioSolar Cells

As mentioned earlier, the major research initiative on solar fuels in The Netherlands is the BioSolar Cells program. This public private partnership was established in 2010. The program is funded by FOM/ALW/NWO, the Dutch ministry of Economic Affairs, many companies and a number of Dutch Universities and Research Organisations. The BioSolar Cells program has three themes: artificial photosynthesis, photosynthesis in cellular systems, and photosynthesis in plants. These three research themes are underpinned by a fourth theme: education and societal debate, where educational modules are developed to equip and inspire future researchers, policy makers and industrialists; and the societal consequences of new solar-to-fuel conversion technologies are debated. Since this booklet is about artificial photosynthesis, only the research on artificial photosynthesis is described here. For information on other research within BioSolar Cells, the reader is directed to www.biosolarcells.nl

Although many scientists all over the world are working to find an efficient, durable and cost-effective method for artificial photosynthesis, no system has yet been devised that is suitable for practical application. The BioSolar Cells programme therefore takes a broad approach, embracing research into all of the methods described in subsection 3.7.

Molecular systems

Various molecular catalysts have been developed, for both water oxidation and hydrogen ion reduction, including some that contain no rare metals. They now need to be modified to meet all the requirements applicable to an artificial photosynthesis system, particularly the reaction speed and the longevity of the catalysts (which, like the catalyst in a car's catalytic converter, need to remain in use for years). A number of molecular pigment molecules have been discovered as well, which are suitable for capturing sunlight. In solution, one such pigment molecule has already been successfully tested in combination with a molecular water oxidation catalyst. When a solution of the molecules in water was exposed to light, oxygen was spontaneously formed. The next step is to anchor the molecules to a surface in improving their utility and efficiency.

Inorganic systems

Another part of the programme involves the fabrication of special semiconductors. By manipulating the semiconductor at the nanoscale, it is possible to increase its surface area, for example, enabling more of the catalyst to be bonded to it. The charge separation process can also be improved modifying the aspect ratio of the material at the nanoscale so that charges do not need to travel so far before participating in a catalytic reaction.

A variety of nanomaterials have been developed and are currently being bonded with catalysts to make them suitable for water splitting. The first solar fuel cell has been made using specially treated bismuth vanadate (a paint pigment that can capture light and is very good at separating charges), a small solar cell, platinum and a cobalt-phosphate catalyst [10]. Powered by light, the assembly produces hydrogen from water with an efficiency of about 5 %. Details of the research have recently been published in the leading scientific journal *Nature Communications* [11].

Molecular-inorganic hybrids

With the goal of producing a more effective system, intensive collaboration is taking place between the various research fields, with a view to combining the various components. Molecular catalysts have been bonded to inorganic photoactive semiconductor surfaces, for example, with the aim of accelerating the catalytic reactions.

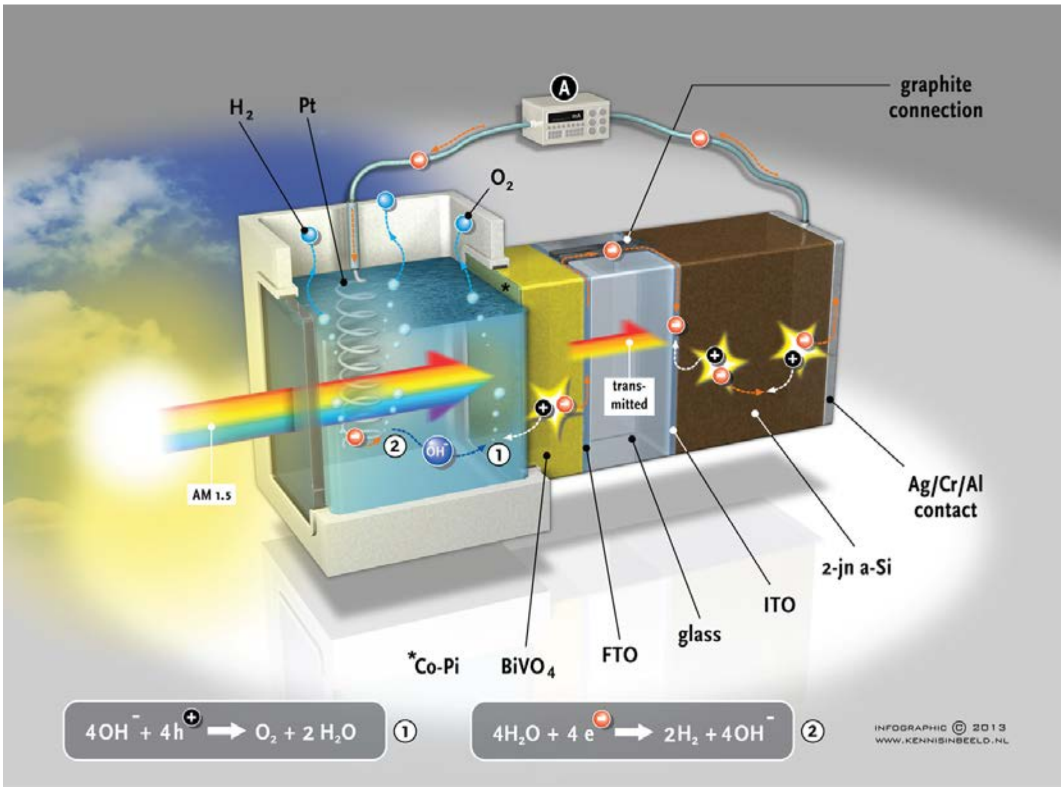


Figure 10: BioSolar Cells scientists are working to achieve scientific breakthroughs. The figure is an infographic of an artificial leaf that converts sunlight into hydrogen with an efficiency of roughly 5 %.

Semi-synthetic systems

A bio-hybrid system is also under development, which uses an enzyme to convert CO_2 from the air into methanol. If the reaction can also be powered by light, it will provide a way of directly producing a carbon-based fuel by means of artificial photosynthesis.

For the verification of experimental data and improved understanding of how the systems work, spectroscopic and theoretical research is very important. The molecules and materials are literally and figuratively illuminated in various ways to obtain insight into their structure and how they work, both individually and in combination with other components. Computer calculations are providing information about how the catalytic reactions are induced by the coupling of molecular vibrations and the movement of electrons (see section 3.6 and intermezzo 2), and about the associated energy requirements, so that certain adaptations to the components can be made to improve the performance of the system as a whole. In the near future, the work is expected to lead to at least two artificial leaves that use sunlight to split water into oxygen and hydrogen, with the highest possible efficiency and robustness and at the lowest possible cost.

4.2.2 Research in Europe

As part of the EU's Seventh Framework Programme (FP7), various research projects involving solar-powered hydrogen production by means of water splitting have been completed, including SOLHYDROMICS [12], SOLAR-H2 [13], NANOPEC [14] and H2OSPLIT [15]. The European Science Foundation (ESF) has recently concluded the EuroSolarFuels Eurocores programme [16]. This programme is the first coherent fundamental research initiative to focus on solar fuels, with funding from scientific organizations in the member states.

In 1994, the Swedish Consortium for Artificial Photosynthesis was started. This consortium carries out integrated, basic research with the goal to produce fuel from solar energy and water. It is a bottom-up initiative by university-based scientists. Like the Dutch BioSolar Cells consortium both natural and artificial photosynthesis is studied. The vision is to develop novel routes for hydrogen production from solar energy and water.

The European Energy Research Alliance has launched the Joint Programme Advanced Materials & Processes for Energy Applications (AMPEA) to promote fundamental research into new, complex and nanostructured materials. Artificial photosynthesis is the first energy research sub-field organised within AMPEA [17]. The joint programme began at the end of 2011 and to date more than 40 European scientific institutions participate.

4.2.3 Research in the US

In 2010, the Department of Energy created the Energy Innovation Hubs, and among them, a Joint Centre for Artificial Photosynthesis (JCAP) was established between the California Institute of Technology and the Lawrence Berkeley National Laboratory in California [18]. In 2012, the Solar Fuels Institute (SOFI), based at Northwestern University, was launched [19]. This institute is a research consortium of universities, government labs, and industry united around the goal of developing and commercialising a liquid solar fuel within 10 years.

4.2.4 Research in Asia

There are ambitious programs in South Korea, China and Japan. The Korean Centre for Artificial Photosynthesis (KCAP) was launched at Sogang University in 2009 [20]. The centre has collaboration agreements with a number of research centres and companies.

China has recently established the Institute for Clean Energy, which forms part of the Chinese Academy Institute of Chemical Physics in Dalian [21]. In 2007, the Japanese government launched its World Premier International Research Centre Initiative. The most recent initiative is creation of the International Institute for Carbon-neutral Energy Research in Kyushu [22].

Japanese automotive companies are also engaged in artificial photosynthesis research and development. There is an active research programme in artificial photosynthesis at Toyota Central R&D Labs [23], and in late March 2012 Honda began construction of a second station to produce hydrogen from sunlight and water in the prefecture of Saitama [24].

5 The contribution of artificial photosynthesis to our future energy supply

5.1 Introduction

The development of artificial photosynthesis is still in a laboratory phase and much remains to be accomplished before commercial application is possible. Nevertheless, artificial photosynthesis has the potential to be an attractive and sustainable alternative to fossil fuels. Furthermore, artificial photosynthesis can contribute to transformation of the energy infrastructure as a whole. This section describes how solar fuels can contribute to our energy supply in the future.

5.2 Energy storage and transportation

Like the wind, the sun is not a constant energy source. Sometimes the sun shines, sometimes the sky is overcast, and at night no solar energy is available for capture. As long as solar energy's share of overall energy consumption remains small (0.13 % in 2013 in the Netherlands [25]), the difference between the demand for energy and the variable supply from solar sources can easily be accommodated by conventional power plants. However, if solar energy is ever to be a substantial component of the energy mix, other ways need to be found of absorbing fluctuations in the supply. A continuous energy supply when little or no sunlight is available depends on new technology for the storage and transportation of solar energy.

In the production of solar fuels, solar energy is directly stored locally in the form of chemical bonds in concentrated fuels that can be transported by pipeline, road, rail or ship. Artificial photosynthesis can also be combined with fuel cells, in which fuel (often hydrogen) and oxygen are converted into electricity and heat. The resulting systems can provide buildings and small communities with energy. The solar fuel production and storage concept is illustrated in figure 11.

An example of the concept is the EnTranCe pilot project in Groningen, where a trial set-up for a future energy system has been created, consisting of nine fuel cells [26]. At the moment, the set-up uses natural gas, a fossil fuel, but in the future it will also be able to run on hydrogen produced from solar energy.

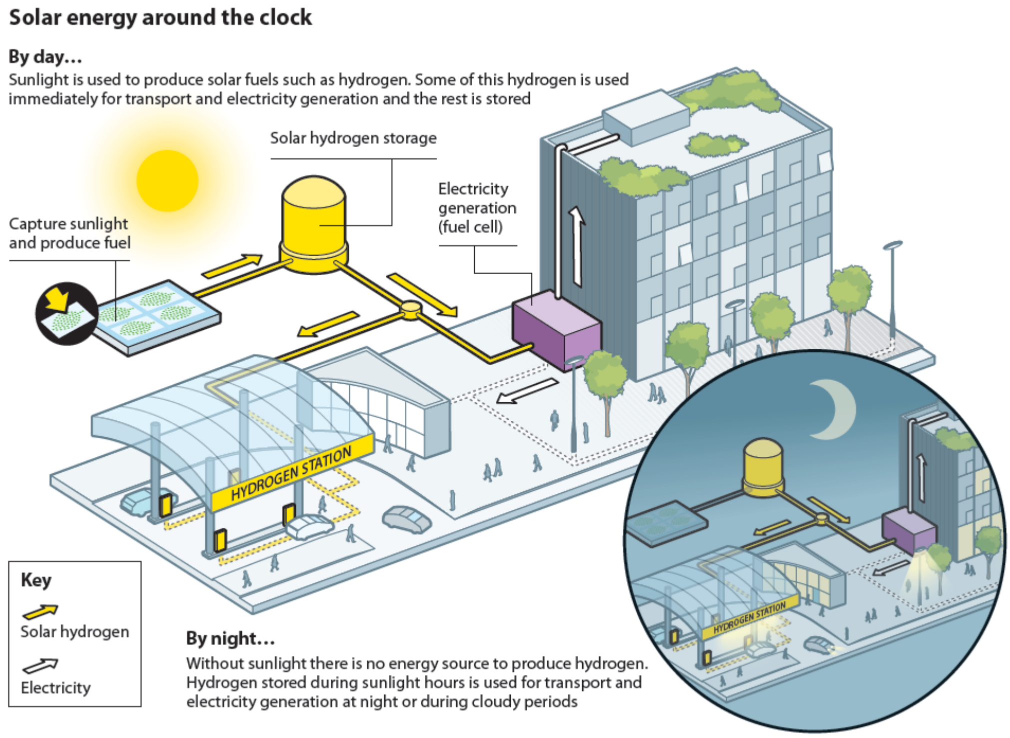


Figure 11: Solar energy around the clock. Source: Royal Society of Chemistry.

5.3 New business models for energy generation

More and more homes across Europe nowadays have solar panels fitted to their roofs, enabling the homeowners to produce some or all of their own electricity. Indeed, people with a large enough area of solar panelling can actually supply power to the public grid and earn money from it. In such cases, the consumer is also a supplier of energy: a 'producing consumer' or 'prosumer'. However, electricity is not easily stored and the scope for consumers to be true prosumers is consequently limited. Artificial photosynthesis systems do not have the same drawback as photovoltaic systems, because their product is not electricity but fuel, which can be stored and used for energy at any time. Artificial photosynthesis systems therefore provide owners with much more flexibility in terms of what they do with the energy they produce and their ability to respond to fluctuations in supply and demand.

The cost of solar fuels could be brought down if local producers join forces to protect their interests [27] and to organize distribution of their energy surpluses [28]. That might lead to energy companies adopting a new role: instead of acting as energy producers, they might become energy distributors, acting as agents for the prosumers.

Another great advantage of artificial photosynthesis is that solar energy is relatively evenly distributed around the world (in contrast to fossil fuels). If artificial photosynthesis enters worldwide use, then people in poor countries will have access to the necessary energy resources to improve their standard of living.

5.4 Renewable transport fuels

Globally, more than 60 % of the available oil is used for transport [29]. In Europe, roughly a third of all energy use is transport-related [30]. In the 2009 Renewable Energy Directive (RED, 2009/28/EU) and other documents, the European Union has set itself the target of meeting a fifth of its energy needs from renewable sources by 2020. In the transport sector, that objective has been translated into a alternative fuels strategy [31] and a draft directive on the rollout of an alternative fuels infrastructure [32]. The strategy focuses on alternatives to oil that result in low CO_2 emissions, consisting of a mix of LPG, natural gas, electricity, liquid biofuels and hydrogen. Although artificial photosynthesis is not currently referred to in the policy documents, they could readily be accommodated in a renewable energy mix for transport. Solar fuels are not only suitable for use in the propulsion of light vehicles, such as passenger cars, but also in aviation and shipping, where other technologies, such as electrical energy, are harder to utilize.

Hydrogen produced from solar energy can be used as a propulsion fuel in cars. In April 2013, Hyundai introduced the first hydrogen-powered car to the Netherlands (the ix35). This car has an electric motor and a fuel cell, which converts hydrogen and oxygen into water and electricity. Several other car manufacturers have released limited editions of hydrogen-powered cars, including Honda's FCX Clarity and BMW's Hydrogen 7 (which has a combustion engine). General Motors, Daimler Ford, Nissan and Toyota are all working to develop affordable fuel cell-powered cars.

Fuel-cell grade hydrogen is currently produced by an energy-intensive process. One of the great challenges for hydrogen-powered cars is therefore finding alternative ways of producing hydrogen. Could sunlight be the answer? On average, the earth's surface is struck by between 10 and 120 moles of photons per square metre per day. Is that enough to power a car? Earlier in this document, we demonstrated that four moles of photons are needed to produce one mole of hydrogen. That implies that up to 2.5 to

30 moles of hydrogen per square metre per day could be produced, which equates to 5 to 60 grams. The Honda Clarity requires roughly 500 grams of hydrogen per day, for example [33, 34]. Therefore, in a sunny location, roughly 10 to 20 square metres of artificial photosynthesis would be needed to fuel a car: roughly the area of a garage roof.

Other challenges also remain to be overcome, including the creation of a hydrogen distribution network, the safe storage of hydrogen and the improvement of fuel cell technology. Nevertheless, the ability to produce hydrogen using sunlight would be a major step forward on the road to hydrogen becoming a viable transport fuel.

5.5 Use and recycling of CO_2

Increasing emissions of carbon dioxide from the combustion of fossil fuels have been identified as the dominant factor behind global warming. One possible solution to that problem is the storage of CO_2. Various proposals have therefore been made for capturing CO_2 and storing it underground. However, CO_2 storage represents a serious technological challenge, and considerable progress could be made by regarding CO_2 not as waste but as a raw material for the production of renewable fuel.

In Iceland, a plant has already been built, where CO_2 from the steam generated by geothermal power plants is used to produce methanol. According to a recent review by a group of British chemists, the biggest obstacle to basing industrial processes on CO_2 is the large amount of energy required to reduce CO_2 molecules (the high potential involved). Research groups in countries such as Germany and the Netherlands are working on technologies to increase the energy-efficiency of the process. Sunlight could well be the ideal energy source for the reduction of CO_2 and thus the production of carbon-based fuels (see also figure 2 on page 12). We have already seen that in the Netherlands an average of 40 moles of photons per square metre strikes the earth's surface per day. We have also demonstrated that in a natural or artificial photosynthesis reaction, CO_2 can be converted using two photons per electron. The table on the next page shows the potential tonnage of CO_2 that could be converted per square kilometre per day by means of various CO_2 conversion reactions, in comparison with hydrogen. Carbon-based fuels that might be produced include formic acid, carbon monoxide (which when mixed with hydrogen constitutes syngas), formalin, methanol and methane (natural gas).

Reaction	Redox potential at pH 7 (V)	CO_2 conversion potential (tons per km^2 per day)	Fuel production potential (tons per km^2 per day)
$2H^+ + 2e^- \rightarrow H_2$	-0.4	-	20
$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$	-0.61	440	460
$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	-0.53	440	280
$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O$	-0.48	220	150
$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	-0.38	147	107
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	-0.24	110	40

5.6 Fuel production that does not compete with food production

In the short term, the use of biofuels is regarded as one of the most important means of realizing Europe's renewable transport fuel targets. However, this strategy is the subject of debate because of the role of the 'first-generation biofuels', which are made from agricultural products, such as sugar, starch and vegetable oil. Fuel production from such products implies the use of agricultural land and crops that can also be used for the production of food[2]. The EU strategy for alternative fuels has therefore introduced support for the 'second generation' of biofuels, which are made from lignocellulose (the inedible, fibrous parts of plants), organic waste, algae and microorganisms, whose production does not compete with the production of food. However, the demand for fuel is huge in comparison with agricultural production, and there is considerable demand for raw materials from agriculture, both in food production and for non-food applications. A new source of fuel that does not tie up large amounts of agricultural land is therefore very desirable.

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[2] *Various aspects of the food versus fuel debate are summarized at http://www.biosolarcells.nl/maatschappij/food-versus-fuel.html*

6 Conclusions

Technology for converting solar energy into fuel can help to close cycles and is suitable for large-scale or small-scale use. Developments in the field of conventional solar panels have shown that commercial renewable energy activities can develop quickly once they become economically viable. The Netherlands and the European Union have the scientific and industrial infrastructure needed to take the lead in the field of artificial photosynthesis.

Around the world, scientists and engineers are working on ways of making hydrogen and carbon-based fuels using water, carbon dioxide and sunlight. Such fuels offer the attractive prospect of enabling solar energy to be stored and transported, so that energy from the sun is available anywhere in the world whenever it is needed. Artificial photosynthesis can not only meet our need for sustainable transport fuel, but also serve as an alternative to the fossil raw materials used in industry.

Within the BioSolar Cells programme, work is being done to unravel the fundamental principles of photosynthesis and then apply this knowledge not only in improving natural photosynthesis, but also to mimic it in a device. The aim is, amongst others, to develop two prototype artificial leaves, which will be able to split water into hydrogen and oxygen. After this, the research results will be translated into commercially viable systems. The active involvement of thirty-eight partners from industry is expected to lead to the results of the BioSolar Cells programme finding rapid application and playing a major role in the Biobased Economy, first and foremost in Europe, but also beyond. A sustainable supply of resources by capturing solar energy is the single most important enabling factor for any form of a biobased economy coming into existence. It is surprising that biobased economy programs invest in research on downstream conversion technology but provide very limited funds for the resource side, where the competition will be between land use and efficiency. One of the key challenges is the creation of sufficient critical mass within industry to enable further development of the technology and to attract the funding needed to continue building on the results of the first five years of research. Molecular structures are now available, which can capture light and split water, and there is a semiconductor system capable of storing energy from sunlight in hydrogen with an efficiency of roughly 5 %. In addition, systems for converting CO_2 are under development. In a number of countries, the next stage of the innovation process has begun: researchers and their industrial partners are developing concrete applications on a scale of about 100 m^2, as precursors to the more general application of artificial photosynthesis.

References

1. FAO, *How to feed the world in 2050*, 2009, FAO.
2. International energy agency, *World energy outlook*, 2011, International energy agency.
3. Cogdell, R.J., et al., *Artificial photosynthesis – solar fuels: current status and future prospects.* Biofuels, 2010. **1**(6): p. 861-876.
4. Ball, P. *Reinventing the leaf*. Nature News 1999; Available from: http://www.nature.com/news/1999/991004/full/news991007-3.html.
5. Blankenship, R.E., et al., *Comparing Photosynthetic and Photovoltaic Efficiencies and Recognizing the Potential for Improvement.* Science, 2011. **332**(6031): p. 805-809.
6. Purchase, R.L. and H.J.M. de Groot, *Biosolar cells: global artificial photosynthesis needs responsive matrices with quantum coherent kinetic control for high yield.* Interface Focus, 2015.
7. Concepcion, J.J., et al., *Chemical approaches to artificial photosynthesis.* Proc Natl Acad Sci U S A, 2012. **109**(39): p. 15560-4.
8. Bertuccioli, L., et al., *Development of Water Electrolysis in the European Union*, 2014, Fuel Cells and Hydrogen Joint Undertaking.
9. NREL. *Hydrogen producation cost analysis*. 11 November 2014]; Available from: http://www.nrel.gov/hydrogen/production_cost_analysis.html.
10. Kanan, M.W. and D.G. Nocera, *In Situ Formation of an Oxygen-Evolving Catalyst in Neutral Water Containing Phosphate and Co2+.* Science, 2008. **321**(5892): p. 1072-1075.
11. Abdi, F.F., et al., *Efficient solar water splitting by enhanced charge separation in a bismuth vanadate-silicon tandem photoelectrode.* Nature Communications, 2013. **4**.
12. Saracco, G., *SOLHYDROMICS*, 2013.
13. *SOLARH2*, 2013.
14. *NANOPEC*. 8 December 2014]; Available from: http://nanopec.epfl.ch/.
15. *H2OSPLIT*.
16. *EuroSolarFuels*. 8 December 2014]; Available from: http://www.esf.org/index.php?id=6397.
17. Thapper, A., et al., *Artificial Photosynthesis for Solar Fuels – an Evolving Research Field within AMPEA, a Joint Programme of the European Energy Research Alliance.* Green, 2013. **3**(1): p. 43-57.
18. *JCAP*. 8 December 2014]; Available from: http://solarfuelshub.org/.
19. *SOFI*. 8 December 2014]; Available from: http://www.solar-fuels.org/.
20. *KCAP*. 8 December 2014]; Available from: http://www.k-cap.or.kr/e_index.html.
21. *Dalian National Laboratory for Clean Energy*. 8 December 2014]; Available from: http://www.dnl.org.cn/index_en.php.
22. *International institure for carbon-neutral energy research, kyushu universtiy*. 8 December 2014]; Available from: http://i2cner.kyushu-u.ac.jp/en/.
23. *Toyota CRDL Succeeds in World's First Artificial Photosynthesis Using only Water and CO2*. 8 December 2014]; Available from: http://www.japanfs.org/en/news/archives/news_id031515.html.
24. *Honda opens solar hydrogen station in Japan's Saitama Prefecture*. 8 December 2014]; Available

from: http://green.autoblog.com/2012/04/08/honda-opens-solar-hydrogen-station-in-japans-saitama-prefecture/.

25. statisteik, C.B.v.d., *Hernieuwbare Energie in Nederland 2013*, 2013.
26. *EnTranCe*. 8 December 2014]; Available from: http://www.hanze.nl/home/Onderzoek/Kennisportal/Kenniscentra/Energie+Kennis+Centrum/Energy-academy-europe/entrance.htm.
27. de Groot, H.J.M. *The agricultural knowledge model will change the world*. Bio Based Press 2013 8 December 2014]; Available from: http://www.biobasedpress.eu/2013/02/the-agricultural-knowledge-model-will-change-the-world/.
28. de Groot, H.J.M. *artificial photosynthesis is going to be the backbone of energy supply*. Bio Based Press 2013 8 December 2014]; Available from: http://www.biobasedpress.eu/2013/01/huub-de-groot-artificial-photosynthesis-is-going-to-be-the-backbone-of-energy-supply/.
29. International energy agency, *Key World Energy Statistics*, 2014, International energy agency.
30. Agency, E.E. *Final energy consumption by sector*. 8 December 2014]; Available from: http://www.eea.europa.eu/data-and-maps/indicators/final-energy-consumption-by-sector-5/assessment.
31. Commission, E., *COMMUNICATION FROM THE COMMISSION TO THE EUROPEAN PARLIAMENT, THE COUNCIL, THE EUROPEAN ECONOMIC AND SOCIAL COMMITTEE AND THE COMMITTEE OF THE REGIONS Clean Power for Transport: A European alternative fuels strategy*, 2013.
32. Commission, E., *Proposal for a DIRECTIVE OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL on the deployment of alternative fuels infrastructure* 2013.
33. *Honda FCX Clarity*. 8 December 2014]; Available from: http://en.wikipedia.org/wiki/Honda_FCX_Clarity.
34. *Thuis waterstof tanken*. 8 December 2014]; Available from: http://www.waterstofautos.nl/archives/297.
35. EurObserver, *Photovoltaic Barometer*, 2014.
36. Parisi, M.L., S. Maranghi, and R. Basosi, *The evolution of the dye sensitized solar cells from Grätzel prototype to up-scaled solar applications: A life cycle assessment approach.* Renewable and Sustainable Energy Reviews, 2014. **39**: p. 124-138.
37. Ludin, N.A., et al., *Review on the development of natural dye photosensitizer for dye-sensitized solar cells.* Renewable and Sustainable Energy Reviews, 2014. **31**: p. 386-396.
38. Janssen, R.A. and J. Nelson, *Factors limiting device efficiency in organic photovoltaics.* Adv Mater, 2013. **25**(13): p. 1847-58.
39. Friedman, D.J., *Progress and challenges for next-generation high-efficiency multijunction solar cells.* Current Opinion in Solid State and Materials Science, 2010. **14**(6): p. 131-138.
40. Luque, A., *Will we exceed 50% efficiency in photovoltaics?* Journal of Applied Physics, 2011. **110**(3): p. 031301.
41. *GemaSolar*. 8 December 2014]; Available from: http://www.torresolenergy.com/TORRESOL/gemasolar-plant/en.
42. Counci, E.A.S.A., *Concentrating solar power: its potential contribution to a sustainable energy future*, European Academies Science Advisory Counci.
43. *Plant-e*. 8 December 2014]; Available from: http://plant-e.com/.

44. microbiology, A.s.f. *Bacteria Use Hydrogen, Carbon Dioxide to Produce Electricity*. 2013 8 December 2014]; Available from: http://www.asm.org/index.php/newsroom/92-news-room/press-releases/91683-bacteria-use-hydrogen-carbon-dioxide-to-produce-electricity.
45. MacKay, D.J.C., *Sustainable Energy - without the hot air*2009, Cambridge, UK: UIT.
46. Zondag, H. *Zouthydraten als kachel*. 2009 8 December 2014]; Available from: https://http://www.ecn.nl/nl/nieuws/newsletter-nl/archief-2009/maart-april-2009/seizoensopslag-van-warmte/.
47. Wolkers, H., et al., *Microalgae: the green gold of the future?* Groene grondstoffen, ed. P. Harmsen and H. Bos2011, Wageningen: Wageningen UR.
48. World Bank. *Electric power transmission and distribution losses (% of output)*. 2014 8 December 2014]; Available from: http://data.worldbank.org/indicator/EG.ELC.LOSS.ZS.

Appendix: Other methods of converting solar energy

Energy is already being extracted from sunlight using various methods, which are described below.

1. Electricity and heat from sunlight

Photovoltaic (PV) cells
In the Netherlands and other European countries, the most widely used solar energy technology is the photovoltaic cell. Solar panels are rapidly being installed on the roofs of private homes, public buildings and business premises. In Germany, France, Italy and elsewhere, complete fields of solar panels can be seen. One example is the Gabardan Solar Park in the French department of Landes: a facility with a capacity of 67.5 MW. By the end of 2013, the total installed PV generating capacity in the twenty-seven countries of the European Union was 79 GW. Germany (36 GW) and Italy (18 GW) are the leaders in the field of PV. EurObserver predicts that, by 2030, solar panels will account for a generating capacity of 480 GW (15 % or the European Union's electricity) [35].

Present-day PV technology is based largely on the use of crystalline silicon. However, other PV technologies are used for particular applications. For example, there are photovoltaic cells in the form of thin films, made by applying multiple layers of photovoltaic material to a flexible substrate. Such 'thin film PV' is used in advanced installations integrated into buildings and charging systems for electric cars. In thin film PV, it is also possible to make use of organic molecules that can convert sunlight into electricity. Such 'dye-sensitized solar cells' are made using straightforward conventional printing techniques, meaning that they are cheap to produce [36, 37]. Analysts expect that, by 2020, the countries of the European Union will have more than 22GW of thin film PV capacity installed.

There are also organic photovoltaic cells, which use conductive organic polymers or small organic molecules to absorb light and split charges [38].

So-called multi-junction photovoltaic cells (cells made up of numerous layers) or tandem cells have multiple photovoltaic cells made from different chemical compounds. Each compound is designed to respond to sunlight of a different wavelength, so that the overall efficiency of the cell is increased. At present, the best-performing laboratory examples of conventional single-layer photovoltaic technology achieve an efficiency of 25 %, whereas the prototype multi-layer cells can achieve

43 %. Multi-layer photovoltaic cells with efficiencies of 30 % are already commercially available. However, the high efficiencies are associated with a high degree of complexity and consequently high production costs. To date, they have been used only for special applications, such as space exploration, where a high performance-to-weight ratio is very important and cost is less of an issue. On earth, multi-layer photovoltaic cells are used mainly in installations where the sunlight is concentrated on the solar cells using lenses (Concentrated Photovoltaics, or CPV). Such systems can now achieve efficiencies of more than 44 % [39, 40].

Concentrated Solar Power (CSP)

Another approach used for large-scale electricity generation is to create a large array of mirrors and lenses to concentrate sunlight on a small surface to heat oil or melt salt. The heat stored in this way can subsequently be used to generate electricity, also at times when no sunlight is available. A recently realized example is the Gemasolar plant in Spain, which has a capacity of 20 MW and works by storing heat in molten salt [41].

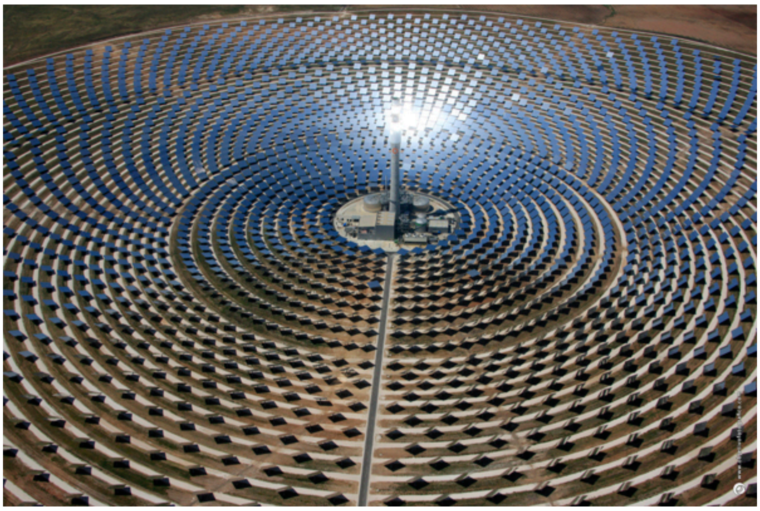

Figure 12: The Gemasolar plant in Spain. Source: http://www.torresolenergy.com/TORRESOL/gemasolar-plant/en

The European Union expects that, by 2020, CSP will account for roughly 0.5 % of total electricity production. In a recent report, the European Academies Science Advisory Council highlighted the potential for concentrated solar power as part of the electricity networks in Southern Europe, North Africa and the Middle East [42].

Other forms of solar energy

Various electricity generation technologies that make use of solar energy are currently under development but are not yet in commercial use. One involves the use of microorganisms to break down organic material from the root zone of living plants: a technology being developed by the Wageningen-based company Plant-E [43]. Work is also being done with bacteria capable of generating electricity from hydrogen and carbon dioxide [44], and with solar fuels for use in electrochemical fuel cells.

Solar heat

The simplest technology for utilizing solar heat involves panels in which water is heated for use in the home or in business premises as hot tap water of as a spatial heating medium [45]. There are also systems in which solar energy in the form of heat is stored in a material, which is connected to a heat pump. The Dutch Energy Research Centre (ECN) has developed a method for the storage of heat in hydrate, an inorganic salt that is capable of incorporating water molecules into its crystal structure [46].

Such systems can provide a home or an entire neighbourhood with heat around the clock and can even store heat during the summer, for spatial heating in the winter.

2. Biomass and side streams

Crop plants use natural photosynthesis to capture solar energy and store it in the form of chemical energy (sugars or oils). In most cases, however, the efficiency of the process does not exceed 0.5 %. Algae are already widely used for the production of food ingredients (e.g. proteins, unsaturated fatty acids and pigments) and cosmetics. They can also serve as a source of biofuel in the form of oil [47]. Algae can grow in saltwater and extract nutrients from side streams. Their cultivation does not therefore compete with food production by adding to the demand for (scarce) fresh water or land.

Biofuels are made by harvesting and processing plants or algae. It is also possible to use industrial or household waste. Vegetable oils extracted from seeds by crushing can be refined directly into biodiesel. Biomass and side streams can be directly combusted, e.g. in conventional coal-fired power plants (co-firing), or used as nutrients for microorganisms, which convert the organic material in bio-ethanol or another liquid fuel. Bio-ethanol can be mixed with conventional petrol. At present, most bio-ethanol is made from sugar and starch (sugar cane and maize).

Because first-generation biofuels are made from agricultural products, their production can compete with food production. The second generation of biofuels will therefore be made using enzymes that are capable of breaking down the inedible parts of plants (made up of cellulose and lignin) to form sugars, which can then be converted into bio-ethanol. In principle, biofuels made in that way create less competition for land that could be used for food production, but the production scale is small in relation to the total demand for energy.

3. Energy storage

Because sunlight is not available at all times, most of the existing generating techniques that make use of solar energy need to be allied with energy storage systems. A temporary surplus of electricity produced by photovoltaic cells or wind farms can be stored in batteries or used to pump water into an elevated storage facility, from which is can later be allowed to flow, generating electricity. In 2013, elevated storage facilities accounted for 99 % of the world's electricity storage capacity. The efficiency of the method is between 70 and 80 %. Naturally, the technique is appropriate mainly for places where the topography provides significant differences in elevation. That is not the case in the Netherlands, but it is possible to work around that problem by transporting temporary electricity surpluses abroad, e.g. to Norway.

Batteries should be seen mainly as an energy storage solution for small-scale, independent electricity networks (off grid). One advantage of a battery is that it can be located anywhere. The main drawbacks with batteries are their limited storage capacity and their short working life, which means that they require replacement after a few years, or even a few months. Various companies are working to develop better batteries based on alternative materials.

A temporary energy surplus can also be used to split water into hydrogen and oxygen by electrolysis. . A fundamental weakness of this approach is the use of electricity as an intermediate between the electrons concentrated in chemical bonds in the raw starting material and the bound electrons in the product at the end of the process. This disregards the synergy benefits of artificial photosynthesis that result from separating electric charges just enough to prevent wasteful charge recombination. Since conventional solar panels are used instead of a tandem, the process involves the loss of 25 to 30 % of the available energy. In addition, it struggles with the intermittency of solar power, and is inefficient with regard to the use of large amounts of electrocatalytic materials to operate at low current density. Finally, energy from photovoltaic solar panels is generally supplied to the grid in the first instance, enabling it to be stored when the supply of energy exceeds the demand. That involves the electricity being transformed to a high voltage for transmission and subsequently transformed back to a low voltage: processes which result in further energy losses of between 4 and 7 % in West European countries and 15 % or more in most developing countries [48].

Colophon

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For the conversion of sunlight into fuel

Robin Purchase, Huib de Vriend, Huub de Groot
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Biophysical Organic Chemistry/Solid State NMR
Leiden Institute of Chemistry
P.O. Box 9502
2300 RA Leiden
The Netherlands

Wageningen UR Food & Biobased Research
Bornse Weilanden 9
Postbus 17
6700 AA Wageningen
The Netherlands

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