Solar Fuels: Vision and Concepts

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Abstract The world needs new, environmentally friendly and renewable fuels to allow an exchange from fossil fuels. The fuel must be made from cheap and ‘endless’ resources that are available everywhere. The new research area on solar fuels, which are made from solar energy and water, aims to meet this demand. The paper discusses why we need a solar fuel and why electricity is not enough; it proposes solar energy as the major renewable energy source to feed from. The present research strategies, involving direct, semi-direct and indirect approaches to produce solar fuels, are overviewed.

Keywords Solar fuels · Artificial photosynthesis · Renewable fuels · Solar energy · Photobiological hydrogen

INTRODUCTION

The global energy supply amounted to ca. 140 000 TWh in 2009 and is dominated to ca. 80% by fossil energy (Fig. 1) [International Energy Agency (IEA) 2008, 2009, 2010]. It is expected that this will at least double around the year 2050 (Fig. 1; Lewis and Nocera 2006) when the world population will be ca. 10 thousand million people. In contrast to today, future energy carriers should be free or neutral with respect to release of CO₂ and there are strong incitements for development of renewable energy systems. There is no lack of renewable energy on the planet, not even with respect to the huge future global energy consumption. The most abundant renewable resource is solar energy but this is still used in only small amounts. Therefore, many call for heavy development and investments in solar energy research. This is reflected in the varied research on solar cells for electricity production and different technologies exist from an industrial scale (silicon solar cells) to early research stages (for

example organic solar cells and tandem solar cells). However, in addition to electricity generation, the development of renewable fuels is a vital interest.

FUELS AND ELECTRICITY

How is all this energy used? An important dividing factor is how much of this energy is used as electricity and how much is used as a fuel (or maybe better—as a stored form of energy). On a global scale ca. 17% of the supplied energy is used as electricity. The rest, an amazing 83% are used in some other way (Fig. 1; IEA 2008, 2009, 2010). It is used as fuel or being fossil fuels used as raw materials to produce plastic, reduce N₂ to fertilizer etc. The fraction of electricity grows and IEA estimates the growth to 2.5% per year on average. In 2030 this would result in ca. 22% of the total energy production being used as electricity. At the same time, the total energy use also increases; and in TWh numbers much more. Thus, it can be concluded that electricity is not everything that matters. All visions for future energy systems changes must take this into account. Not only electricity must be produced—at least four times larger amounts of fuel need to be found. In a sustainable and CO₂ neutral energy economy this must come from other than fossil energy sources. In addition, these energy sources must everywhere be renewable and environmentally friendly. Here, the perspective of solar fuels as important future energy carriers and the best way to store solar energy makes them a theme that quickly moves up on the global research agenda.

SOLAR FUELS: ARTIFICIAL PHOTOSYNTHESIS

The term ‘solar fuel’ has become established in the last 10 years. The research is often named ‘artificial

Fig. 1 *Bottom* total energy used in the world in 2009. 80% of this energy came from fossil resources. This energy use is expected to double to 2050 (white box; Lewis and Nocera 2006). *Middle* the division between use of energy for electricity or for other purposes. *Top* total solar irradiation on the planet per hour amounts to almost the same amount of energy as the entire world uses in a year

photosynthesis', 'solar-hydrogen research', 'the artificial leaf', 'photobiological hydrogen production' or something analogous. The introduction of solar fuels on a very large scale is motivated by concerns about global warming, energy security for all nations and decreased availability of oil and gas. It is also driven by recent advances in a range of scientific fields that make scientists convinced that solar fuels are possible to produce in an efficient and cheap way in a not too distant future. An important driving force is that it is vital that the energy can be stored for long times to be used for what and when we want. A solar fuel is always made using solar energy as the only energy source. The idea is to harvest the energy that comes when the sun shines, convert it and store it as a fuel. This is the vision and major driving force behind solar fuels.

Huge amounts of solar energy are available everywhere and are often abundant where population is dense. Even in northern countries there is abundant solar energy in the summer when the days are long. If this abundant solar energy could be converted into a storable energy carrier (fuel), solar energy could become an important energy source also in northern countries. The same issues are relevant also on a much shorter time scale. Often the energy consumption is highest in the morning and in the afternoon/early evenings while the sun shines brightest in the middle of the day. It does not shine at all in the night even though much energy is used also then. Thus, storage of the energy from the sun would be critical to balance this situation. A convenient way would be in the form of a fuel.

There are additional advantages with a large scale use of solar fuels. Development of solar fuels can be seen as the real chance for many third world countries to catch up with the energy consumption and the thereby connected advantages of the richer countries. Given the limited and unevenly spread fossil reserves there is little chance for thousands of millions of people to increase their living standard since this is too closely connected to the use of fossil energy. It is costly and there is not enough of fossil energy available. A powerful way to change this is to explore the potential of solar energy which is a resource available everywhere. This demands not only solar electricity from solar cells but also solar fuels for storage, transport and many other purposes.

The raw material for the (storage) fuel is an equally important key aspect. The desirable raw material must be essentially inexhaustible, cheap and widely available. Most scientists target water as the raw material and this is the only really sound option. Processes in which water is split (oxidized) into its constituents by solar energy can become large contributors to shift away from fossil fuels on a global scale. Thus, solar fuels research gathers scientists with the aim to provide a fuel based on solar energy and water. Both resources are essentially endless and fairly evenly spread over the entire planet. An additional advantage is that such a fuel would be CO₂ lean—a huge advantage over fossil fuels.

The target fuel is the third important issue. Many scientists target hydrogen as the solar fuel. When water is

used as starting material this is natural from scientific reasons. However, the transition to a hydrogen based economy is not easy. The hydrogen technologies have their own hurdles to overcome and technological issues to tackle before hydrogen can become a world wide fuel. An alternative is to use CO₂ itself as a second raw material (together with water) to create a carbon based solar fuel. This might have lower technological problems on a shorter term but will not remove CO₂ from the energy cycle. In addition, the science involved is most likely more difficult than for hydrogen production.

Research on solar fuels constitutes a novel, diverse field that aims to answer these demands and challenges. The field is evolving quickly around the world. The development of technologies for direct solar to fuel conversion requires revolutionary scientific breakthroughs in several areas of fundamental science.

RENEWABLE ENERGY, SOLAR ENERGY

There is no lack of renewable energy on planet earth! Some resources, like solar energy, are available everywhere while others, like wave energy, are restricted in spread. The largest is solar energy and there falls similar amounts of solar energy on the planet in 1 h as the yearly human energy consumption (Fig. 1). Much solar energy falls on for example the oceans and high mountains and can probably not be used but attempts to calculate how much of the solar influx that can be ‘useful’ in future energy systems indicate that there is more accessible solar energy to use than mankind can ever find use for, certainly much more than ever discussed for use in 2050 or 2100.

The use of solar energy in today’s energy system is very small, also in locations where the solar influx is high. This reflects in part shortcomings in the available technologies but depends to a large extent also on the price of fossil fuels. At today’s price picture the fossil fuels are simply difficult to beat. This will however change in the near future due to raising demand and simultaneous lower availability of oil and natural gas. It is also likely that the concerns for CO₂ release from fossil fuels will drive up the prices. It is difficult to predict when the costs of fossil fuels will meet the costs of solar based systems. However, it will happen soon enough—it is therefore necessary to develop today the solar technologies of tomorrow.

METHODS TO PRODUCE A SOLAR FUEL

The development of solar fuels follows a few scientific and technological pathways. These contain similar elements (solar energy, energy conversion, cheap raw materials) but

also critical differences. One useful distinction is to separate *direct* and *indirect* processes. A second useful distinction is between processes in *molecular* and *non-molecular* systems. Figures 2 and 3 depict a range of research strategies that are currently in focus for the research efforts and separate them after these principles.

Indirect Processes for Solar Fuel Production

In *indirect processes* the energy in the fuel produced originates in solar energy but the connection between the energy source and the fuel is not direct. Instead, the solar energy is first converted and stored as an intermediate before being converted to the desired fuel. The intermediate can in itself be valuable but it is not directly useful as a versatile fuel. It can therefore not exchange for fossil fuels, instead the intermediate is further transformed to the desired fuel. Figure 2 shows two very important indirect pathways to achieve a solar fuel.

Photovoltaics and Electrolyzer

The use of photovoltaics is an important option. Here, electricity is first produced in a solar cell. Then, the electricity is used as the energy source in an electrolyser where water is split into H₂ and oxygen. These systems can be built and work well. The general drawback is the detour around electricity that results in loss of already converted and gained energy (in this case in the form of electricity) when the fuel is made. Many commercial electrolyzers work with efficiencies of ca. 60% of the input energy appearing in the form of hydrogen. Improvements are likely (better electrolyzers exist) but there will be a significant loss in the extra step. The very promising system described by Reece et al. (2011) falls in this category. Here the solar cell is used to drive, not a normal electrolyser, but instead two catalytic systems able to oxidize water and reduce protons to hydrogen.

Biomass

Another indirect process is to grow a tree, plant or photosynthetic microorganism, which is rich in wood, a fibre, a biological oil or something else that can serve as a fuel or as raw material to make a fuel (Fig. 2). The organism is then harvested to produce the fuel. Typical industrial examples of this is to cut down a tree to produce wood, wood chips, char coal or something else to burn; to ferment the carbohydrates in sugarcane, grapes or corn to produce alcohol or to make a motor fuel from rape seed. However, in all systems based on harvesting biomass, the critical limitation what concerns energy efficiency is the detour around the life of the organism. Only a very small fraction

Fig. 2 Top hydrogen, fatty acids, alcohols or other potential fuels can be formed and secreted from photosynthetic microorganisms, in particular cyanobacteria and green algae. This is well described as a semi-direct process as the cell is used as a catalyst for production of

the fuel that to a large extent is derived from stored intermediates in the cell. Bottom two well known indirect processes for solar fuels and their general drawbacks

of the solar energy is converted into the biomass. Typical yields for the conversion into biomass energy falls in the range of 0.1–2% of the solar energy that falls on the field where the tree or the crop is grown. Much of the ‘lost’ energy is used to sustain life while other large losses originate from inefficient solar energy absorption since plants are green (not black) etc. (Gust et al. 2008). In case a secondary process like alcohol fermentation and distillation is involved the overall yield is even lower.

All processes involving biomass are indirect and inefficient with respect to solar energy conversion into the fuel. They work, the quantity is very large but the efficiencies will never be high enough to allow for a conceptual change from the fossil fuel based economy on a global scale.

Extra Systems Costs

The extra steps in the indirect processes will inevitably bring extra costs to the system. This is not analyzed in depth for most systems but the combined installation of both solar cells and electrolyzers, or both biomass production units and biomass converting plants seems

unnecessary if an alternative can be developed where only one apparatus or unit is necessary. Ideas along these lines are the direct processes for solar fuels production.

Direct Processes for Solar Fuel Production

Direct processes have the potential to become more efficient than the *indirect processes*. They can become cheaper since they do not make use of unnecessary steps or machines. In addition, they are not dependent on already valuable intermediate products like electricity or a photo-synthetically produced biomaterial. Instead the process has the sole role to harvest solar energy and convert this into a fuel. An important factor is that some of the indirect processes discussed above work on a large scale while there is no direct process that works on any technological scale. Instead, the development of direct processes is connected to heavy research initiatives in several fields.

The larger potential in the direct processes make them nevertheless attractive future technologies. The strategies to develop direct processes fall in three categories described in Fig. 3.

Fig. 3 Three direct processes for solar fuels and their general advantages. Artificial photosynthesis can be made in both molecular systems and non-molecular systems. A third option is to split water at

a metal oxide surface at very high temperatures in a system where thermo-chemical cycles are utilized

Artificial Photosynthesis

In one category, we find attempts to develop what is often called artificial photosynthesis. The vision is to make light driven catalysts that can oxidize (split) water directly. The fuel will utilize the highly reducing electrons achieved by the oxidation of water. Artificial photosynthesis therefore also involves development of catalysts that can catalyze reaction of those electrons with a suitable substrate. The fuel can be hydrogen. This is often the target since the electrons need only to be reacted with protons. It can also be a carbon based fuel, for example an alcohol, which might be easier to use but is probably more difficult to make. An essential aspect is that the catalysts should be made from earth abundant metals like Co, Mn, Fe, Ni while scarce elements like Ru, Pd, Re etc. are not available in amounts enough to allow development of a process of a scale enough to exchange for the use of fossil fuels.

Molecular and Non-Molecular Processes

The light driven catalyst can be molecular or non-molecular (Fig. 3). The physical limitations are equal and the scientific problems are of equal magnitude since development of catalysts that can assist the light driven oxidation of water is the main research problem. The capture of solar energy and the formation of hydrogen are easier to achieve. Systems combining the two reactions (light driven water

oxidation and hydrogen formation) have the highest potential with respect to solar energy to fuel conversion of all systems envisioned today.

The catalysts and maybe the entire system for artificial photosynthesis can be entirely molecular in nature. (Magnuson et al. 2009; see also articles in Chem. Soc. Reviews 2009 and in Hammarström et al. 2009, which are special issues to a large extent dealing with molecular processes). This is difficult to achieve and the essential element is that the catalysts are molecules. They can be varied through small, deliberate synthetic modifications to improve and fine tune their properties. They are also amenable to studies with high level molecular or kinetic spectroscopy. Thereby the catalytic process can be followed and understood to a very detailed level (see for example Ott et al. 2010). This is a clear advantage in the development of these methods.

In non-molecular systems the light driven catalysis occurs on metal surfaces, semiconductors or nano-structured carbon based materials while the catalysts involved for water splitting are often cores of metal oxides, sometimes doped with other metals (Cook et al. 2010; Walter et al. 2010; see also articles in Hammarström and Hammes-Schiffer 2009). A disadvantage is that many systems are based on catalysts made from scarce and expensive metals; a severe limitation. Another disadvantage when compared to the molecular systems is that it is much more difficult to study the mechanism for the reactions involved. An important advantage is that many non-molecular systems

are seemingly sturdier against degradation and inactivation while most molecular systems studied to date are unstable and easily brake during illumination. It is not obvious that this situation will always prevail when more functional systems have been better characterized.

A rapid development involves ideas where molecular and non-molecular systems are mixed. Here, the solar energy capture system is semi-conductor based or made from some other nano-technology while the chemistry is carried out by linked molecular catalysts. These catalysts are then made from abundant materials like (Co, Fe, Mn or Ni) similar to the ‘purely’ molecular systems described above. It is not unlikely that these mixed systems will become dominant in research and maybe technology since they combine advantages from both fields.

Thermochemical Cycles

A totally different technology is the employment of thermal processes for solar fuels production (Chueh et al. 2010; Pagliaro et al. 2010), which involve generation of very high temperatures in closed environments to split water into its constituents directly. This results in a solar fuel when the high temperature is achieved in a reaction vessel in a solar tower by concentration of solar energy in a heliostat. However, the high temperature can also be achieved from nuclear energy. In this case the result is not a solar fuel. Therefore, these thermal processes should be distinguished from the solar fuels processes described above. The technology represents interesting engineering and physical science and is very demanding technically involving very high temperatures and huge systems like heliostats. They are mainly suitable to very sunny locations.

Semi-Direct Photobiological Processes

Photobiological solar fuels production is another approach, which is perhaps best defined as semi-direct (Fig. 2). Here, a photosynthetic microorganism harvests the solar energy and uses this to produce a fuel in high yield, as a dominating product (Melis 2007; Lindblad and Jeffries 2009; Hemschemeier and Happe 2011). This is then secreted from the organism. The fuel can then be formed continuously in a vessel called a photo-bioreactor and collected directly from the reactor vessel. The fuel production does not demand the harvest of the entire organism. Therefore this is a process where maintaining life and growing the organism only uses a part of the supplied solar energy. The efficiency of such a photo-biological process can be much higher than of a system where the biomass is harvested. It is however lower than what can be achieved by artificial photosynthesis. This is because a significant fraction of the solar energy is used to maintain life-processes. In addition,

photosynthetic organisms cannot use as much of the solar spectrum as a synthetic system which essentially can be made black while most organisms are green.

Different types of fuels can be anticipated from photobiological processes in photosynthetic microorganisms. Some cyanobacteria and green algae combine efficient water oxidizing photosynthesis with the capacity to produce hydrogen. Thus, hydrogen is a natural product in both cyanobacteria and green algae and can be collected as a solar fuel in these organisms. Other targets fuels involve oils, alcohols and other natural substances that are suitable for fuel and that can be secreted from the organism (Fig. 2). In these approaches scientists will use a photosynthetic organism to drive inserted new metabolic pathways to produce the fuel directly. The metabolic pathway will be inserted into an existing organism by synthetic biology. The science involves reasonable foreseeable efforts in strain selection, molecular biology, biochemistry and metabolic engineering and might be quite close to breakthroughs.

Two types of photosynthetic organisms dominate photobiological solar fuels research at present. One is green algae, *Chlamydomonas* sp. and others, which can be forced to produce hydrogen or valuable oil products under certain circumstances. The other are different cyanobacteria that already in nature possess the metabolic machinery to produce hydrogen (Melis 2007; Lindblad and Jeffries 2009; Hemschemeier and Happe 2011). Both systems have limitations and advantages and demand similar developments using molecular biology, metabolic engineering and synthetic biology approaches. At present it is impossible to judge which system will have the largest potential.

It is a matter of choice if these methods for hydrogen (or another fuel) formation in photosynthetic microorganisms shall be called a direct or indirect pathway for solar fuel production. Probably the best definition is that the use of the entire cell machinery in a photosynthetic cell as the catalyst makes this process something in between. It can therefore be called a semi-direct process.

CONCLUSIONS

There are several strategies to produce solar fuels from solar energy and water. Several indirect processes already work but are all connected to unnecessary limitations resulting in lower yield in different steps in addition to extra costs in the technical design. The photobiological processes where photosynthetic microorganisms are used can become quite efficient and it is highly likely that some approaches to both hydrogen and carbon based fuels will be available on a reasonable commercial basis within a rather short time frame. The direct processes for artificial

photosynthesis (and the thermal solar fuels processes) all have a longer time before successful and efficient processes have been reached. However, they also have the option to become very efficient and potentially cost effective. This demands strong and dedicated research from researchers in many fields, combining skills, methodology and knowledge from chemistry, physics, biology, biochemistry and engineering in a way that has seldom been accomplished before.

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