Appraisal of bio-hydrogen production schemes

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ABSTRACT:

Work is ongoing on several schemes of biological hydrogen production. At one end is the genetic modification of biological systems (such as algae or cyanobacteria) to produce hydrogen from photosynthesis, instead of the energy-rich compounds (such as $NADPH_2$) normally constituting the endpoint of the transformations through the photosystems. A second route is to collect and use the biomass produced by normal plant growth processes in a separate step that produces hydrogen. This may be done similar to biogas production by fermentation, where the endpoint is methane (plus CO_2 and minor constituents). Hydrogen could be the outcome of a secondary process starting from methane, involving any of the conventional methods of hydrogen production from natural gas. An alternative to fermentation is gasification of the biomass, followed by a shift-reaction leading to hydrogen. I compare advantages and disadvantages of these three routes, notably factors such as system efficiency, cost and environmental impacts, and also compare them to liquid biofuels.

KEYWORDS : *biofuels, fermentation, gasification, photoproduction of hydrogen, life-cycle assessment.*

1. Introduction

Biomass currently accounts for about 14 % of the global energy use (including food energy). Roughly 60% of this is for direct combustion and a few percent is for more advanced uses, such as creating liquid or gaseous fuels. Table 1 gives an overview of the current situation. Although more than 99% of the standing biomass crop is on land, the production at sea is actually as large as that on land. The table shows that biomass production on land could be greatly increased with more intense farming practices (in those parts of the world not yet employing them) and particularly with increased irrigation. How much that would be feasible depends on how much water can be made available in a sustainable way. The difference between harvest yields and the food ending up in our stomachs indicates a large potential for diverting more biomass in the form of residues and waste products to energy uses, without jeopardising food provision to an increasing world population. Many bio-energy schemes allow energy to be extracted and subsequently nutrients and soil conditioning straw (or similar products) returned to the fields, i.e. not distracting from current uses of residues. Furthermore, much biomass which is currently used for burning in inefficient stoves and burners could be available for quality energy uses, if more efficient ways of providing space and cooking heat are implemented.

Table 1. Year 2000 global average biomass growth, harvest and use in W/cap., based on data and estimates from [1, 2]:

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Biomass growth (biomass added = net primary production, gross estimate)	20000 W/cap.
Biomass growth on land (new biomass added, gross estimate)	9000 W/cap.
Hypothetical biomass growth on land with full irrigation and fertilising	24000 W/cap.
Harvested biomass for food production	1135 W/cap.
Food energy (reaching end user, incl. food from range animals and fish)	135 W/cap.
Biomass used as fuelwood	216 W/cap.
Wood use for construction, furniture, paper, etc.	89 W/cap.
Residues used for soil conditioning, farm and industrial uses, estimated	. 300 W/cap.
Biomass growth reduction (forest removal, altered land use, estimated)	45 W/cap.
Waste utilised for energy (reporting countries only)	4 W/cap.
Biogas production	3 W/cap.
Liquid biofuel production	2 W/cap.

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The following is a discussion of the options for using biomass in the energy sector, by a range of different technologies, which will be assessed for efficiency, cost and environmental impacts, including views on sustainability in general. Bio-hydrogen is compared with conventional energy uses of biomass, for combustion or for producing liquid biofuels. In particular, liquid biofuels constitute the obvious competitors to bio-hydrogen in the transportation sector.

2. Biomass combustion

Direct combustion of biomass is the largest present biomass use in the energy sector. It is polluting, especially in small boilers and intermittent operation, and cannot be considered an ecologically acceptable solution in the long range. Further discussion of efficiencies and environmental impacts may be found in Chapter 4 of ref. [1].

3. Liquid biofuels

Traditional production of liquid biofuels have been by fermentation (using yeast and bacteria to produce ethanol) or by wood gasification followed by a shift reaction on the synthesis gas (yielding e.g. methanol). The efficiency of these schemes have traditionally been 40-45%, but could reach 50-65% with use of new catalysts and in the ethanol case advanced zeolite or membrane techniques to replace distillation for water removal. Recent progress has indicated scope for bringing the price of liquid biofuels from residues down from the present cost of nearly twice that of diesel oil. The production from food material, such as the Brazilian ethanol made from sugar has, as a result of experience and scale of production, reached prices similar to or even lower than those of conventional fuels [3]. In the US, where ethanol has been used as a minor additive to gasoline, the view is that production from grain will not become competitive, but that production from cellulosic residues may have that potential [4]. A project carried out with the Danish company Novozymes indicates prospects for a cost of 4.0-4.5 euro-cents per litre of ethanol produced from cellulosic corn stover by a new enzymatic process for degrading cellulose to simple sugar molecules ready for fermentation [5].

A range of potentially low-cost biofuels are the bio-diesels, i.e. fuels that may replace conventional diesel fuel and hence avoid much of the infrastructure cost normally associated with the introduction of a new fuel (e.g. in the transportation sector). Features of these fuels are discussed in a separate contribution [6].

The key usage area for liquid biofuels is as a replacement for oil products in the transportation sector. There are some negative environmental effects associated with using each of the liquid biofuels in combustion engines. In addition to releasing un-burnt hydrocarbons, there would be CO releases and NO_x releases from the reactions between biofuel and the constituents of air. Typically, CO emissions are smaller than for conventional diesel fuel, and NO_x emissions larger [6]. For methanol, concern has been expressed over the toxicity of fumes. A recent review concludes that there are still insufficient studies to pinpoint the precise magnitude of the problem, as far as genetic damage is concerned [7]. The cost of methanol production from woody biomass by conventional black liquor (a residue from paper pulp mills) gasification is estimated as 182 euro/ton or 0.29 euro per equivalent litre of gasoline fuel [8]. This is more than three times higher than the current cost of production from natural gas [9]. Conversion efficiencies run from 43 to 65%, being highest for forest residues or black liquor as the primary material.

4. Biogas fermentation

Traditional fermentation plants producing biogas are in routine use, ranging from farm-size plants to large municipal plants. As feedstock they use manure, agricultural residues, urban sewage and waste from households, and the output gas is typically 64% methane [1]. The biomass conversion process is accomplished by a large number of different agents, from the microbes decomposing and hydrolysing plant material, over the acidophilic bacteria dissolving the biomass in aquatic solution, and to the strictly anaerobic methane bacteria responsible for the gas formation. Operating a biogas plant for a period of some months usually makes the bacterial composition stabilise in a way suitable for obtaining high conversion efficiency (typically above 60%, the theoretical limit being near 100%), and it is found important not to vary the feedstock compositions abruptly, if optimal operation is to be maintained. Operating temperatures for the bacterial processes are only slightly above ambient temperatures, e.g. in the mesophilic region around 30°C.

A straightforward (but not necessarily economically optimal) route to produce hydrogen rather than methane would be to subject the methane generated to conventional steam reforming. The ensuing biomass-to-hydrogen conversion efficiency would in practice be about 45%. This scheme could be operated with present technology and thus forms a reference case for assessing proposed alternative hydrogen production routes.

A direct method for hydrogen production by fermentation is to select bacteria that produce hydrogen selectively. Candidates would include *Clostridium* and *Rhodobacter* species. The best reactor operating temperatures are often in the thermophilic interval or slightly above (50-80°C). Typical yields are 2 mol of H_2 per mol of glucose [2], corresponding to 17% conversion efficiency. The theoretical maximum efficiency is around 35%, but there are also acetic or butanoic acids formed, which could be used to produce methane and thus additional energy, although not necessarily additional hydrogen. Operation of this type of hydrogen-producing plant would require pure feedstock biomass (here sugar), because of the specific bacteria needed for hydrogen production, and because con-

tamination can cause decreased yields. Even the hydrogen produced has this negative effect and must therefore be removed continually [2].

It is seen that the efficiency of direct hydrogen formation by fermentation almost certainly has lower conversion efficiency than first producing methane and then hydrogen by reformation. Again, this does not rule out economic advantages, because the one-step process may be less expensive to implement [10].

For comparison to other ways of using solar energy (such as photovoltaic conversion), the hydrogen production efficiency quoted above have to be compounded with the efficiency of converting solar energy to glucose, being on average for cultivated crops about 0.6%, for the biosphere as a whole 0.2%, and for a hypothetical theoretically ideal system above 10% [1].

Overall energy balancing requires consideration of energy use for transportation of feedstock and for cleaning and eventually transporting hydrogen. To this comes in-plant energy use for stirring and gas cleaning. For most likely sources of biomass for this purpose, the greenhouse gas emissions may be considered neutral (i.e. balancing earlier sequestration), but emissions of pollutants need to be considered. Emissions of SO_2 are lower, but those of NO_x higher than for conventional fossil fuels. On the positive side is the creation of residues highly suited as fertilisers (better than industrial fertilisers and better than biomass that has not been going through the gaseous fuel production process).

5. Biomass gasification

Gasification occurs through the thermal decomposition of biomass with the help of an oxidant such as pure oxygen or oxygen enriched air to yield a combustible gas such as synthesis gas (syngas) rich in carbon monoxide and hydrogen. The synthesis gas is post-treated, by steam reforming or partial oxidation, to convert the hydrocarbons produced by gasification into hydrogen and carbon monoxide. The carbon monoxide is then put through the shift process to obtain a higher fraction of hydrogen, by carbon dioxide-removal and methanation [11] or by pressure swing adsorption (PSA). The theoretical efficiency of this process is well above 50%. Small-scale EU-funded experimental projects indicate efficiency in the range of 60-75% [11]. However, the data from different studies show large variations concerning practical efficiencies and cost. Assessment of this technology should therefore be regarded as preliminary.

The basic gasification of biomass (such as e.g. wood scrap) is a well-known process, taking place in pyrolysis (oxygen supply far below what is required for complete combustion, the fraction called "equivalence ratio") or fluidised-bed type of reactors. Conditions such as operating temperature determine whether hydrogen is consumed or produced in the process. Hydrogen evolvement is largest for near-zero equivalence ratios, but the energy conversion efficiency is highest at an equivalence ratio around 0.25 [1]. The hydrogen fraction (in this case typically some 30%) must be separated for most fuel-cell applications, as well as for long-distance pipeline-transmission.

In the pyrolysis-type application, gas production is low and most energy is in the oily substances that must be subsequently reformed in order to produce significant amounts of hydrogen [10]. Typical operating temperatures are around 850°C. An overall energy conversion efficiency of around 50% is attainable, with considerable variations. Alternative concepts use membranes to separate the gases produced, and many reactor types use catalysts to help the processes to proceed in the desired direction, notably at a lower temperature (down to some 500°C).

Environmental concerns include disposal of associated tars and ashes, particularly for the fluidised bed reactors, where these substances must be separated from the flue gas stream (in contrast to the pyrolysis plants, where most tar and ash deposits at the bottom of the reactor). Concerns over biomass transportation are similar to those mentioned above for fermentation, and a positive fertiliser effect can also in many cases be derived from the gasification residues. Biomass ash has also the potential to be used as a clarifying agent in water treatment, as a wastewater adsorbent, as a liquid waste adsorbent, as a hazardous waste solidification agent, as a lightweight fill for roadways, parking areas, and structures, as asphalt mineral filler, or as a mine spoil amendment [12].

6. Direct biological hydrogen production

The photosynthetic production of hydrogen employs micro-organisms such as cyanobacteria, which have been genetically modified to produce pure hydrogen rather than the metabolically relevant substances (notably $NADPH_2$). The conversion efficiency from sunlight to hydrogen is very small, usually under 0.1%, indicating the need for very large collection areas. The current thinking favours ocean locations of the bio-reactors. They have to float on the surface (due to rapidly decreasing solar radiation as function of depth), and they have to be closed entities with a transparent surface (e.g. glass), in order than the hydrogen produced is retained and in order for sunlight to reach the bacteria. Because hydrogen build-up hinders further production, there further has to be a continuous removal of the hydrogen produced, by pipelines to e.g. a shore location, where gas treatment and purification can take place, as illustrated in Figure 1 [2]. These requirements make it little likely that equipment cost can be kept so low that the very low efficiency can be tolerated.

A further problem is that if the bacteria are modified to produce maximum hydrogen, their own growth and reproduction is quenched. There presumable has to be made a compromise between the requirements of the organism and the amount of hydrogen produced for export, so that replacement of organisms (produced at some central bio-factory) does not have to be made at frequent intervals. The implication of this is probably an overall efficiency lower than 0.05%.

In a life-cycle assessment of bio-hydrogen produced by photosynthesis, the impacts from equipment manufacture are likely substantial. To this one should add the risks involved in production of large amounts of genetically modified organisms. In conventional agriculture, it is claimed that such negative impacts can be limited, because of slow spreading of genetically modified organisms to new locations (by wind or by vectors such as insects, birds or other animals). In the case of ocean bio-hydrogen farming, the unavoidable breaking of some of the glass- or transparent plastic-covered panels will allow the genetically modified organisms to spread over the ocean involved and ultimately the entire biosphere. A quantitative discussion of such risks is difficult, but the negative cost prospects of the bio-hydrogen scheme probably rule out any practical use anyway.

7. Life-cycle analysis

Because the fermentation route from biomass to hydrogen is the most well established one, I shall briefly state the life-cycle impacts of this scheme. Use of life-cycle assessment to establish the viability of the various hydrogen production schemes is in any case the proper way to compare alternatives that are of a different nature with possibly different types of impacts [1].

The life-cycle costs quoted in Table 2 are derived from a study of a Danish biogas plant [1], but with appropriate scaling for hydrogen production of a different efficiency and with slightly different side

products. The negative figure for methane is due to current loss of methane from silos where manure is conventionally stored for extended periods. With the introduction of biogas plants (whether for methane or hydrogen production), this negative impact is largely avoided. Due to the high greenhouse warming impact of methane, this feature dominates the total life-cycle costs and makes bio-hydrogen an attractive option despite direct costs likely above current hydrogen cost. This conclusion rests on the European valuation of global warming costs, set forth in [1].

Table 2. Life-cycle impacts from a hypothetical hydrogen production plant based on biomass fermentation. Impacts are given in physical units and with an estimated monetised value according to the methods set out in [1]. The impacts are per MJ of hydrogen produced and the monetary unit is euro (ε).

Environmental impacts	Impact type: emissions (g/MJ)	Uncer-tainty	Monetised value ε cents/MJ	Uncertainty ranges and scope
From fossil energy currently used in plant construction and operation:				
CO_2 equiv. (leading to greenhouse effect)				
Plant and truck construction:	9	Large	0.2	0.15–0.3
Transportation of feedstock/residues	33	Large	0.9	0.5–2
Methane leaks (incurred minus avoided)	−106	Medium	−2.9	−2 to −5
SO_2 (leading to acid rain and aerosols)	0.09	Large	0.02	regional
NO_x (possibly aerosols and health impacts)	0.13	Large	0.4	regional
particulates (lung diseases)	0.01	Large	0.00	regional
Land use			NQ	
Social impacts				
Occupational health damage	*Cases per PJ:*			
(manuf. & operation): death	0.6	Large	0.02	local
major injury	0.8	Large	0.12	local
minor injury	0.3	Medium	0.00	local
reduced span of life	2.0	Medium	0.62	local
Economic impacts				
Direct costs			1.5–6	
Resource use (energy pay-back time given)	2.7 y	Large	NQ	
Labour requirements (manufacture)	17 person y/MW	Large	NQ	
Import fraction (for Denmark)	0.1	Large	NQ	
Benefits from energy sold			2-5	
Other impacts				
Supply security (variability in wind is high, entry based on plant availability)	High		NQ	
Robustness (up-front investment binds, entry based on technical reliability)	High		NQ	
Global issues (non-exploiting)	Compatible		NQ	
Decentralisation & choice (plant size)	Good		NQ	
Institution building (monopolistic management)	Modest		NQ	

8. Summarising remarks

A number of processes allow biomass to be transformed into liquid fuels such as bio-diesel, ethanol or methanol, or into gaseous fuels such as methane or hydrogen. I have discussed generic examples of these processes for overall efficiency of conversion from solar energy to fuel, and identified some of the technical processes required for establishing industrial size plants for large-scale gaseous fuel production. Also reliability and environmental impacts are found to be important issues.

One hydrogen pathway uses algae and bacteria that have been genetically modified to produce hydrogen directly instead of the conventional biological energy carriers. Problems include intermittent production, low efficiency and difficulty in constructing hydrogen collection and transport channels of low cost. The maximum value obtained for short periods of time (some 30 minutes), low irradiation (50 W/m2) and in a pure argon atmosphere, is 1% for Anabaena variabilis [13]. Over 24 hours in outdoor ambient solar radiation condition, the efficiency has been found to be 0.05% or lower [14]. Intense solar radiation typically leads to reduced efficiency, and growth of the culture over several days also may lead to decreased efficiency. Further genetic manipulation may improve these numbers, but sustained efficiencies over 1% are unlikely to emerge. This means that growth management should have extremely low cost in order for the hydrogen production cost to become acceptable. This points to ocean growth as the most likely technology choice, as illustrated in Figure 1. Costly items include algae production, frames for collecting hydrogen (and keep the algae at shallow depths) and pipelines to transport it to the shore, where a purification step must be added.
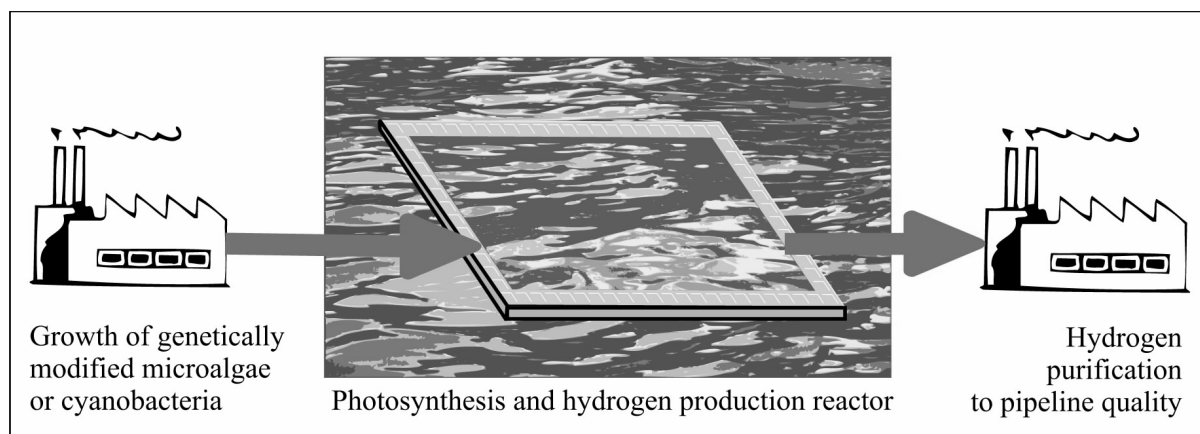

Growth of genetically modified microalgae or cyanobacteria

Photosynthesis and hydrogen production reactor

Hydrogen purification to pipeline quality

Figure 1. Schematic outline of the production set-up for photobiological hydrogen production using aquatic algae or bacteria [2].

A second pathway uses plant material such as agricultural residues in a fermentation process leading to biogas from which the desired fuels can be isolated. This technology is established and in widespread use for waste treatment, but often with the energy produced only for on site use, which often implies less than maximum energy yields. A production set-up is illustrated in Figure 2.

Thirdly, high-temperature gasification supplies a crude gas, which may be transformed into hydrogen by a second reaction step. This pathway may ultimately offer the highest overall efficiency and lowest cost. The production set-up is similar to that shown in Figure 2, except that the biogas reactor

is replaced by a gasification chamber. Gas cleaning and pollution scrubbing equipment is often integrated with the gasifier [2].

The fermentation and gasification routes are both influenced by the average photosynthetic efficiencies of 0.2% (global average) to some 2% (fertilised species of high biomass yield), and the processes leading from biomass to hydrogen will typically have efficiencies around 50% under industrial conditions, implying overall efficiencies of up to 1%. Again, transportation of biomass from the point of production to the hydrogen plant is an important cost issue that has to be handled by optimising transport distances and correspondingly plant sizes. Finally, a purification stage is required in order for the hydrogen to reach pipeline quality.
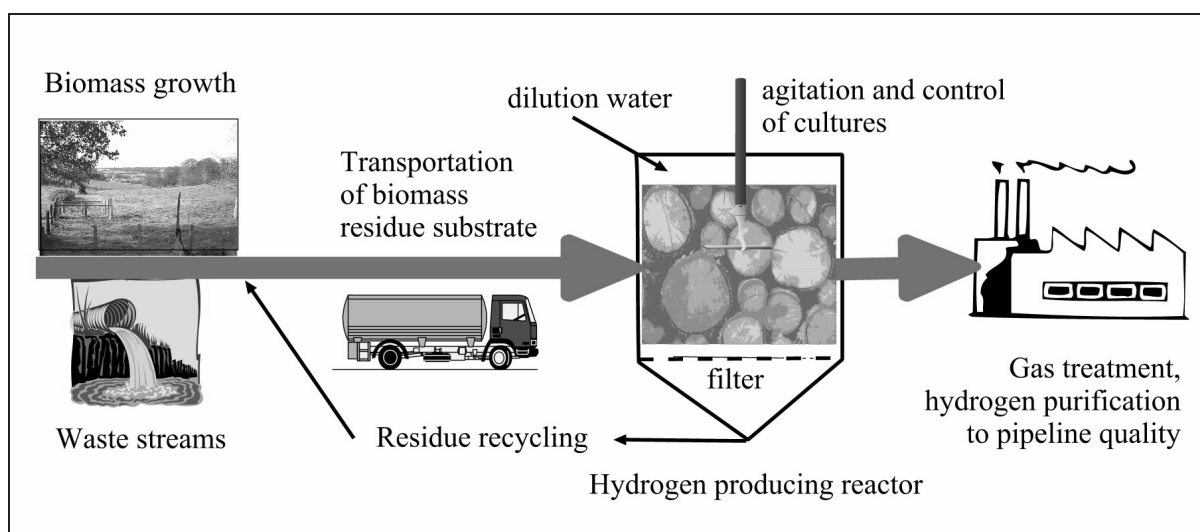

Figure 2. Schematic layout of hydrogen production by direct fermentation [2].

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