Gaseous fuels from biomass (with S. Njakou and D. Blumberga)

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Abstract

A number of processes allow biomass to be transformed into gaseous fuels such as methane or hydrogen. A range of such processes is analysed for overall efficiency of conversion from solar energy to fuel, and the technical processes required for establishing industrial size plants for large-scale gaseous fuel production are identified. Also reliability and environmental impacts will be discussed. One pathway uses algae and bacteria that have been genetically modified to produce hydrogen directly instead of the conventional biological energy carriers. Problems are intermittent production, low efficiency and difficulty in constructing hydrogen collection and transport channels of low cost. 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. Finally, high-temperature gasification supplies a crude gas, which may be transformed into hydrogen by a second reaction step. This pathway may offer the highest overall efficiency.

Keywords: *biofuels, fermentation, gasification, photosynthesis, biological hydrogen production.*

1. Introduction

Biomass has the potential to accelerate the realisation of hydrogen as major fuel of future. Since biomass is renewable and consumes atmospheric CO_2 during growth, it can have a small net greenhouse warming effect compared to fossil fuels. However, hydrogen from biomass has major challenges. The technologies for hydrogen production from biomass analysed here include: fermentation, gasification, and direct biophotolysis, for which we give a short overview of the current technology status. A life cycle analysis (LCA) for CO_2 and other environmental impacts is performed for the fermentation pathway. The paper concludes by summarizing the strength and weakness of each of the three options.

2. 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 hydrogen production 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.

One method is to select bacteria that produce hydrogen directly. 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 contamination 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 [3].

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).

3. 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 [4] 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% [4]. 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 [3]. 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 uses 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 [5].

4. 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 [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.

5. Life-cycle analysis

Because the fermentation route from biomass to hydrogen is the most well established one, we 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 1 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].

6. Conclusions

From the survey described above, the following conclusions can be drawn:

- Thermochemical H_2-production (gasification and pyrolysis) has medium/high efficiency and is still in the development phase.

- Direct H_2-production by fermentation has relatively low efficiency and is not fully developed, while hydrogen production from methane is an established low/medium-efficiency technology that can use methane from biogas as well as from natural gas.

- Direct biophotolysis processes have extremely low efficiency and are as yet far from any practical implementation.

- The LCA results generally support the view that hydrogen production from biomass have impacts that may be kept low compared to fossil-fuel based hydrogen production pathways.

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Table 1. 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) [6].

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 (less with large size)	Good		NQ	
Institution building (collection management)	Modest		NQ	