Introduction: the perspectives of biological methane and hydrogen production

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1.1 The need for CO_2-neutral energy production

Our energy requirements are almost fully provided for by carbon-containing fossil sources such as oil, coal and natural gas, which have been formed during many millions of years from plant biomass. The rapid consumption of these fossil resources causes an accelerated release of the bound carbon as CO_2. The resulting increase of the CO_2 concentration in the earth's atmosphere is generally acknowledged as the major cause of global warming and associated climate change. Furthermore, the depletion of fossil resources will cause a shortage of energy carriers in the long term. The Intergovernmental Panel on Climate Change (IPCC) recommends a reduction of global CO_2 emissions by more than 50% in order to stabilise the CO_2 level in the atmosphere at 550 parts per million volume (ppmv) to curb negative climate effects. In the framework of the Kyoto Agreements –to which currently 106 countries have subscribed [1]– a number of industrialised nations have committed themselves to reduce their joint CO_2 emission by 5% in 2010 relative to the level in 1990. Recent estimates show however that CO_2 emissions are still increasing and that even these moderate targets will not be met without more drastic measures [2].

CO_2 emissions from fossil fuel use can be reduced by enhanced efficiency of electricity production and by more efficient energy use in industry and for transportation. Another option is to substitute fossil fuels with a high CO_2 emission per unit of energy with other (fossil) fuels with lower emissions, for example, substituting natural gas instead of coal to generate electricity. These measures receive broad attention but have so far been insufficient. A more radical approach is the use of renewable energy produced from sunlight, wind, hydropower and biomass. These sources are all directly or indirectly based on solar energy so that no CO_2 is added to the atmosphere ("CO_2-neutral"). The surface of our planet receives 3.8 million exajoules (EJ)[1] of solar energy per year [3], while current global energy use is approximately 400 EJ –equivalent to just 0.01% of solar energy supply– with an anticipated growth to 850 - 1100 EJ in 2050 [4]. Although the yearly supply of solar energy greatly exceeds our energy needs, making this energy available in a suitable form thus far poses technological and –largely– economic obstacles. At present approximately 85% of the world's energy requirement is provided by fossil sources, 7% by nuclear energy and 8% by renewable sources, primarily through the use of wood as a fuel and hydropower [4].

A large-scale transition to renewable energy is not feasible in the short term, because renewable energy production using current technology is not competitive with fossil based energy production. The current production costs for electricity from various renewable sources in the European Union are [5]:

- 0.30 - 0.80 Euro per kilowatt hour (Euro/kWh) for photovoltaic solar cells (PV);
- 0.04 - 0.25 Euro/kWh for hydropower;
- 0.07 - 0.19 Euro/kWh for biomass; and
- 0.04 - 0.08 Euro/kWh for wind turbines.

These costs can be compared with current contract prices for electricity from fossil fuels that range between 0.03 - 0.05 Euro/kWh [6]. Likewise, the costs of renewable transport fuels are at present much higher than for their fossil counterparts. Fuel ethanol from starch crops such as corn is produced today at a cost of approxim-

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[1] 1 Exajoule (EJ, 10^{18} Joule) is equivalent to 172 million barrels of oil or 33 million tonnes of coal or 28,500 million m3 of natural gas. 1 Petajoule (PJ) is 10^{15} Joule, 1 Terajoule (TJ) 10^{12} Joule, 1 Gigajoule (GJ) 10^{9} Joule, 1 Megajoule (MJ) 10^{6} Joule. 1 kilowatt hour (kWh) equals 3.6 MJ.

ately 16 Euro per gigajoule (GJ) which is more than twice the cost of gasoline of 7 Euro/GJ [7]. The above shows that with currently available technology the cost of renewable energy is at least two to three times higher than for fossil energy. The costs of renewable energy production do, however, show a clear downward trend over the past decades due to technological improvements. This trend will no doubt continue through R&D and "learning effects" from implementation of renewable energy systems. In the short and medium term, however, financial incentives from governments are required in the form of "feed-in tariffs" and fiscal stimulation as is already happening in many countries [5]. Furthermore, supranational policies such as the recent European Commission directive for introduction of biofuels in the transport sector and the CO_2-emissions trading system (starting in 2005) will stimulate the introduction of renewable energy.

In the longer term, cost-effective technology is required for large-scale renewable energy production. The current energy requirement in The Netherlands is 3,000 petajoules (PJ) per year with an expected growth to 3,400 PJ in 2020 [8]. The target of the Netherlands' government for 2020 is a 10% contribution from renewable energy sources, equivalent to 340 PJ avoided use of fossil fuels. More than half of this amount (180 PJ) will have to be provided by biomass (including organic residues). On a global scale the use of renewables in 2050 may amount to approximately 30% (280 - 335 EJ) of total energy use according to recent Shell scenarios [4]. Most of this amount will be provided by "green" electricity generated by wind turbines, hydropower, PV and combustion and gasification of biomass and in the form of gaseous and liquid fuels produced from biomass.

1.2 Renewable energy production and the hydrogen economy

The future energy economy will have an important role for hydrogen (H_2) as a clean, CO_2-neutral energy source for use in fuel cell vehicles and for decentralised electricity generation in stationary fuel cell systems. In fuel cells, hydrogen can be converted to electricity very efficiently, producing only water as a waste product, thus drastically reducing CO_2, NO_x, particulate and other emissions that accompany the use of fossil fuels. A crucial feature of fuel cell technology is that highly efficient electricity generation is feasible at all system scales in contrast to other technologies which show a strong drop in efficiency with diminishing scale. This allows the application of fuel cells in vehicles and in decentralised electricity production for industry, for public distribution at the city district level and even for individual residences as outlined in Chapter 3 of this publication. Hydrogen could already become an important energy source in the next decade or two, at first in the transportation sector (fuel cell vehicles) and later on for decentralised electricity generation [9]. Broad implementation requires the development of cost effective fuel cell technology, hydrogen storage systems and related infrastructure.

Initially, hydrogen will primarily be produced through electrolysis or from fossil fuels in small-scale "reformers" or in large-scale, centralised plants e.g. through "steam-reforming" of natural gas ($CH_4 + 2\ H_2O \rightarrow 4H_2 + CO_2$). Large-scale production will allow recovery of the CO_2 for use in greenhouses to stimulate plant growth or for storage in chemical form (e.g. as carbonates) or in underground reservoirs. Production of hydrogen from fossil fuels with CO_2 capture is one of the elements in the "clean fossil" strategy, aimed at limiting the negative climate effects of fossil fuels use. This approach will play an important role in the transitional phase to a fully renewable energy economy. It also includes energy saving measures and the development of highly efficient conversion technology such as fuel cells for the use of natural gas and other fossil fuels that will continue to play an important role into the foreseeable future [4].

Although the use of hydrogen produced from fossil sources will lead to a substantial reduction of emissions, the energy efficiency of the production-to-end-use chain (natural gas → hydrogen → electricity) is limited. This is due to energy losses in the H_2 production phase with concomitant CO_2 capture. In the long run, hydrogen would preferably be produced from renewable sources such as the electrolysis of water with renewable electricity, or by means of biomass gasification or (photo)biological hydrogen production. With large-scale implementation of renewable energy production, hydrogen can be a clean carrier of energy for storage and transport. Off-peak electricity from renewable sources such as hydropower can be converted through electrolysis into hydrogen for storage and transport in liquid or gaseous form to end-users, where it can be re-converted to electricity in high-efficiency fuel cells. Because of this interchangeable nature, hydrogen and electricity are expected to become the principal clean energy carriers in a future renewable energy economy [10]. The development of hydrogen technology has a high priority in the European Union (6th Framework Program), the U.S.A. and Japan. Industries (car manufacturers and utility companies) and governments are investing in the development of fuel cells, hydrogen storage systems and infrastructure. In these programs, safety issues and societal aspects associated with the implementation of hydrogen as an energy carrier will receive considerable attention.

1.3 The role of biomass and biotechnological processes for renewable energy production

All renewable energy sources are ultimately based on solar energy that is made available to us through photovoltaic cells, wind energy or stored as chemical energy in biomass. The latter will play a major role as a feedstock for sustainable production of electricity as well as gaseous and liquid biofuels. A distinction can be made between the use of dry biomass (such as wood) and the use of wet biomass sources such as the organic fraction of domestic waste, agro-industrial wastes and slurries, and wastewater.

Dry biomass should be used preferentially for thermal conversion processes that require a low water content such as green electricity generation (via combustion or gasification) or the production of renewable diesel fuel through gasification, followed by Fischer-Tropsch synthesis [11]. Wet biomass and residues are less suitable for thermal conversion because transport and drying require a considerable amount of energy, which leads to a limited or even negative overall CO_2 reduction. The available amount of wet biomass and residues is however considerable, so that their use as feedstock for renewable energy production is certainly worth while. Biotechnological conversion processes are particularly useful for this application because they are catalysed by microorganisms in an aqueous environment at low temperature and pressure. Furthermore these techniques are well suited for decentralised energy production in small-scale installations in locations where biomass or wastes are available, thus avoiding energy expenditure and costs for transport. The general expectation is that biotechnological processes will play a substantial role in the production of renewable gaseous and liquid biofuels including methane, hydrogen, bioethanol and ABE (Acetone-Butanol-Ethanol) [12,13].

1.4 Biotechnological production of bio-methane and bio-hydrogen

This publication provides an overview of the state-of-the-art and perspectives of microbiological production of methane and hydrogen from biomass and/or sunlight. The final products are designated *bio-methane* (biological methane) and *bio-hydrogen* (biological hydrogen) respectively.

Methane production through anaerobic digestion of wastewater and residues (including sewage sludge, manure and the organic fraction of municipal waste) is already broadly applied. In this process, hydrogen is an intermediary product that is, however, not available because it is rapidly taken up and converted into methane by methane-producing microorganisms. In biological hydrogen production processes, hydrogen formation and consumption are uncoupled, so that hydrogen is available as the final product. These processes are still in the R&D phase and substantial research is required to enable commercialisation of the technology. Several processes are currently under development, ranging from biomass fermentations to photobiological processes through which hydrogen can be produced directly from sunlight. Table 1 gives an overview of biological hydrogen production processes, that are being explored in fundamental and applied research.

A related field is the development of efficient and cheap hydrogen catalysts based on the catalytic

TABLE 1 *Overview of currently known biological hydrogen production processes [16]*

Process		General reaction	Microorganisms used
1 Direct Biophotolysis		$2\ H_2O$ + light $\rightarrow 2\ H_2 + O_2$	Microalgae
2 Photo-fermentations		$CH_3COOH + 2\ H_2O$ + light $\rightarrow 4\ H_2 + 2\ CO_2$	Purple bacteria, Microalgae
3 Indirect biophotolysis	a	$6\ H_2O + 6\ CO_2$ + light $\rightarrow C_6H_{12}O_6 + 6\ O_2$	Microalgae,
	b	$C_6H_{12}O_6 + 2\ H_2O \rightarrow 4\ H_2 + 2\ CH_3COOH + 2\ CO_2$	Cyanobacteria
	c	$2\ CH_3COOH + 4\ H_2O$ + light $\rightarrow 8\ H_2 + 4\ CO_2$	
		Overall reaction: $12\ H_2O$ + light $\rightarrow 12\ H_2 + 6\ O_2$	
4 Water Gas Shift Reaction		$CO + H_2O \rightarrow CO_2 + H_2$	Fermentative bacteria, Photosynthetic bacteria
5 Two-Phase H_2 + CH_4 Fermentations	a	$C_6H_{12}O_6 + 2\ H_2O \rightarrow 4\ H_2 + 2\ CH_3COOH + 2\ CO_2$	Fermentative bacteria +
	b	$2\ CH_3COOH \rightarrow 2\ CH_4 + 2\ CO_2$	Methanogenic bacteria
6 High-yield Dark Fermentations		$C_6H_{12}O_6 + 6\ H_2O \rightarrow 12\ H_2 + 6\ CO_2$	Fermentative bacteria

site of natural hydrogen production enzymes (hydrogenases) [14, 19]. In recent years, the structure of the active site of these enzymes has been unravelled. The catalytic sites consist of inorganic elements mainly nickel, iron and sulphur. This knowledge provides an opportunity for the production of cheap, synthetic hydrogen catalysts to replace the expensive precious metal based catalysts that are used today for the interconversion of hydrogen and electricity in fuel cells and electrolysers. In 2001, the first stable and active "bio-mimetic" catalyst was synthesised [17]. Another approach is the use of purified hydrogenase enzymes as a component in hydrogen electrodes. Research has already shown that an enzyme-based hydrogen electrode can be constructed with good stability and equal catalytic activity as a platinum based electrode [18]. This field lies outside the scope of this publication. It is clear however that this line of development can make a valuable contribution to a future hydrogen economy, through the intelligent exploitation of natural systems. An excellent review of the status and prospects of this field can be found in Cammack, et al., 2001 [19].

Both bio-hydrogen production and anaerobic digestion produce CO_2-neutral, gaseous biofuels from biomass and residues and can therefore be competing technologies [14]. For efficient utilisation of the available feedstock it is important to select the most profitable route for further development and implementation. This depends on many factors including the overall energy efficiency (biomass → energy carriers → electricity), integration in the energy infrastructure, environmental impact (including the overall CO_2-reduction), production costs and the perspectives of further technological development.

Considering the first step, the conversion of biomass into hydrogen or methane, the energy conversion efficiency of bio-hydrogen production is higher than for bio-methane[2]. This would favour bio-hydrogen production, especially when hydrogen is the preferred energy carrier for electricity generation in low temperature Proton Exchange Membrane (PEM) fuel cells. Bio-hydrogen can be used directly in these cells, while methane requires reforming which will reduce the amount of generated electricity. "Green" bio-methane on the other hand has the advantage that it can be

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[2] Calculated for Higher Heating Value (HHV) 1 mole of glucose ($C_6H_{12}O_6$) yields either 12 moles of H_2 (HHV: 3.4 MJ/mole glucose converted) or 3 moles of CH_4 (2.7 MJ/mole glucose converted). For Lower Heating Value (LHV) the difference is smaller i.e. 1 mole of glucose yields 2.8 MJ of H_2 versus 2.3 MJ of CH_4. For bio-hydrogen production this requires complete conversion of the organic feedstock to H_2. This can be realised in a two-stage process, as discussed in Chapter 5.

applied in the existing natural gas infrastructure, while a substantial market demand for hydrogen will only arise in 20 years or more. A further potential advantage of (bio-)hydrogen is the possibility for CO_2 capture in the production phase as an additional, "bonus" opportunity to reduce overall CO_2-emissions. As outlined in Chapters 4 to 6, the production costs of bio-methane and the (projected) costs of bio-hydrogen are within a range of 10-20 Euro/GJ, which is quite similar to liquid biofuels such as bioethanol and Fischer-Tropsch diesel. With the current insights therefore both routes can contribute to a sustainable energy economy.

Although bio-methane production through anaerobic digestion is already commercially applied, further technological development and process improvement is required, as addressed in Chapter 4. This requirement is much larger for the various bio-hydrogen processes which are generally developed for laboratory scale or pilot project scale level. There are several arguments for co-operation between the two fields. Bio-hydrogen and bio-methane production are closely related processes through the interaction of microbial hydrogen and methane metabolism on both the physiological and process level where various species of microorganisms co-operate. Hydrogen is an intermediary product in the decomposition route of organic material to methane. For example, research has shown that methane productivity in anaerobic digestion processes can be greatly enhanced via addition of hydrogen-producing species of microorganisms [15]. Other shared R&D themes concern optimisation of feedstock pretreatment and hydrolysis (a bottleneck in both routes), process and reactor development, and product gas processing and conditioning for use in fuel cells. Furthermore, short term development of combined bio-hydrogen and bio-methane production processes may fit well in the transition phase towards a renewable/hydrogen economy (see Chapter 5). Finally, the introduction of renewable energy and the long-term development of a hydrogen economy require optimal use and gradual modification of existing structures. The introduction of bio-hydrogen can thus possibly be realised via a transition trajectory employing the technological know-how in the field of bio-methane production and the existing gas infrastructure.

1.5 The contents of this publication

Chapter 2 consists of a Dutch language translation of this general introduction. Chapter 3 addresses the background for the potential role of bio-methane and bio-hydrogen in the energy economy as a function of future energy end-use technology, infrastructure and energy policy. Chapters 4 to 6 provide in-depth reviews of bio-methane and bio-hydrogen production technology. These chapters successively address:

- Methane production through anaerobic digestion (Chapter 4),
- Biological hydrogen production via (dark) fermentation (Chapter 5), and
- Photobiological hydrogen production (Chapter 6).

The authors are researchers with active involvement in the field, affiliated with various R&D groups in The Netherlands. They co-operate in The Netherlands Biohydrogen Network. For an overview of current projects, publications and other information the reader is referred to the Internet platform www.biohydrogen.nl. Chapters 4 to 6 provide a review of the current status and a technological and scientific perspective on the field. Also addressed are the potential contribution to sustainable energy production, economics and the international status of development. For each field major R&D themes are indicated. In Chapters 7 and 8 summaries are provided in English and Dutch respectively.

The role of bio-methane and bio-hydrogen in the future energy economy

The potential of bio-methane and bio-hydrogen production is not only decided by the characteristics and costs of the production process, but also by their integration into the overall energy infrastructure. For insight in this issue, A. de Groot of the Energy research Centre of The Netherlands, Unit Clean Fossil Fuels, analyses the integral "production to end-use chain" and the influence of the future energy infrastructure and energy policy on the application of bio-methane and bio-hydrogen in Chapter 3.

Relatively small-scale production systems in locations where feedstocks are available are most likely for both processes. As discussed in Chapter 3, the gas is either used directly at the point of production (*"stand-alone system"*) or supplied to an existing gas transport network for use at another location (*"grid-connected production system"*). In a "stand-alone system" the produced gas is converted to electricity on site for delivery to the public electrical power grid. Recovered heat may be used internally or externally if a heat distribution network is available, e.g. for district heating. Such "stand-alone" applications are widely employed in biogas plants and landfill gas production sites. An alternative is to use an (existing) pipeline network for the distribution of produced gas to end-use locations. This gas network then functions as a buffer for matching energy supply and demand.

Chapter 3 further illustrates that different energy carriers may become dominant in the future depending on the employed scenario, the influence of governmental energy policy, and the quality requirements for energy carriers as dictated by the (future) end-use technologies and infrastructure. It is evident that fuel cells will play an important role for the use of both bio-methane and bio-hydrogen because of their highly efficient energy conversion and near-zero emissions. For the generation of electricity from methane, however, many efficient alternative technologies are available that are steadily being improved. For hydrogen utilisation fuel cell technology is crucial, because the added value of hydrogen as a fuel can only be realised through its (final) conversion in fuel cells, as outlined in Chapter 3. For distribution of (upgraded) bio-methane, the existing natural gas infrastructure and technology is available or –alternatively– on-site conversion into electricity for delivery to the electrical grid. For bio-hydrogen production systems the advantages of hydrogen distribution to the end-user (instead of electricity) are much greater, due to the highly efficient, CO_2-free electricity generation in small-scale fuel cell systems. Chapter 3 concludes that the most favourable option is to distribute the produced bio-hydrogen via a transport network on local, regional or wider scale.

Production of bio-methane by anaerobic digestion

The technological state of the art and perspectives of anaerobic digestion are reviewed in Chapter 4, a contribution from T.Z.D. de Mes, A.J.M. Stams and G. Zeeman, Lettinga Associates Foundation (LeAF) and Wageningen University, and J.H. Reith, Energy research Centre of The Netherlands ECN, Unit Biomass.

Anaerobic microbial degradation of biomass or "anaerobic digestion" is a process in which microorganisms degrade organic matter to methane and CO_2 in the absence of oxygen. The process can be divided in several phases in which consortia of various species of microorganisms work closely together. The first phase, the degradation of complex organic compounds to simple molecules, hydrolysis, is the rate limiting step in the overall process of anaerobic digestion. The hydrolysis stage is followed by a phase where organic acids are formed (with hydrogen as an additional intermediate product). In a final phase organic acids and hydrogen are converted into methane.

In general, residues and wastes are used as feedstock for anaerobic digestion, varying from wastewater to more concentrated wastes such as manure, sewage sludge, agro-industrial residues and the organic fraction of municipal solid waste. The anaerobic digestion systems developed for these different substrates are presented in Chapter 4.
Worldwide, the Upflow Anaerobic Sludge Bed (UASB) system is most frequently applied for industrial wastewater treatment. In tropical regions the UASB is also increasingly applied for treatment of municipal wastewater. A recent development, highlighted in Chapter 4, is the application of anaerobic digestion in Decentral Sanitation and Reuse (DeSaR) concepts. This concept aims for separate collection of concentrated and diluted domestic waste(water) followed by anaerobic digestion of the concentrated streams for recovery of energy and nutrients.

The final product of anaerobic digestion is ‘biogas’ which mainly consists of methane (55-75 vol%) and CO_2 (25-45 vol%). The amount of bio-methane produced depends on the substrate used. The organic fraction of domestic waste generally yields 100-200 m^3 of biogas per tonne while animal manure typically yields 10-20 m^3 of biogas per tonne. As outlined in Chapter 4, the amount of biogas produced from manure can be increased significantly by enriching the substrate ("co-digestion") with other residues such as animal wastes, thus improving economic feasibility. Biogas can be used for production of heat, co-generation of heat and electricity (CHP), or for upgrading to natural gas or transportation fuel quality. Most widely applied is the utilisation of biogas in gas engines for production of electricity and recoverable heat. Gas turbines may be used for larger capacities e.g. in landfill gas production sites. For the future, fuel cells offer a good perspective for electricity generation from biogas because of the high conversion efficiency and the absence of emissions. Currently, fuel cells are being tested in digesters at pilot-plant scale, with promising results. In 2000, the average production costs of biogas in the European Union ranged from 10-20 Euro per GJ, while the costs of electricity from biogas amounted to 0.10-0.20 Euro per kWh. These costs show a clear downward trend over the past decades, which is expected to continue. The current capacity of anaerobic digestion systems in Europe is approximately 1,500 MW. The potential for 2010 in Europe is estimated at 5,300-6,300 MW and worldwide at up to 20,000 MW. Restrictions on landfill disposal of organic waste (as foreseen in the European Union) and incentives for renewable energy production will undoubtedly stimulate this development.

Anaerobic wastewater treatment plants produce a small amount of sludge which is stable and can be easily de-watered. In addition to biogas, anaerobic digestion of more concentrated streams such as manure and solid bio-wastes produces an amount of organic residue ("digestate") that is enriched in nutrients (N, P, K). After de-watering, these residues can be marketed as compost or "mineral concentrates" as fertiliser substitute for agriculture, thus enabling full recovery of nutrients. Wastewater effluents require post-treatment. As discussed in Chapter 4 the treatment of residual products and sales of digestate are important factors for economic feasibility of biogas plants treating manure or solid wastes, in addition to "gate fees" and the revenues from energy sales. In the longer term the main competitor for anaerobic digestion of solid bio-wastes is composting, which is an energy consuming process. As discussed in Chapter 4, the costs of anaerobic digestion are decreasing gradually, and as a result the technology is increasingly competitive with composting.

Chapter 4 identifies as the most important areas for further development of the anaerobic digestion technology: increase of biogas yields via co-digestion, improvement of feedstock hydrolysis, and reduction of investments and operational costs by technological improvements. Furthermore, cost-effective technologies need to be developed for the treatment of digestates and effluent post-treatment.

Production of bio-hydrogen via (dark) fermentation

Chapter 5 is a contribution by T. de Vrije and P.A.M. Claassen, Agrotechnological Research Institute ATO bv. In this chapter the state of the art and perspectives of biological hydrogen production from biomass by means of (dark) fermentation are reviewed.

In contrast to anaerobic methane digestion (in which the intermediate product hydrogen is converted into methane) the final product of the process is hydrogen. An important distinction with anaerobic methane digestion (where methane is produced as a result of co-operative actions of different microorganisms) is that in hydrogen fermentations only hydrogen producing microorganisms are active. Another essential difference is that complex organic compounds in the feedstock are converted to simple molecules not during the digestion process, but rather in a separate process preceding the fermentation. This pretreatment and hydrolysis process is performed by means of physical/chemical methods (e.g. extrusion) and/or treatment with (industrial) enzymes. The resulting organic compounds are converted into hydrogen, acetic acid and CO_2 by microorganisms.

As discussed in Chapter 5 many species of microorganisms are capable of producing hydrogen, which in nature is taken up immediately by hydrogen-consuming microorganisms. Therefore development of a bio-hydrogen production process requires uncoupling of the action of hydrogen producers and hydrogen consumers, as well as optimisation of the amount of hydrogen produced per unit of feedstock. To this end hyperthermophilic microorganisms with an optimum cultivation temperature of 70^0 C and higher have been selected with a high hydrogen yield. Production of bio-hydrogen via dark fermentation is still in the research and development phase. On laboratory scale the process has been successfully tested by ATO, as discussed in Chapter 5. In these tests a variety of substrates have been used including Miscanthus, sweet sorghum, steam-potato peels and vegetable, fruit and yard waste. In 2002 and 2003 TNO – Environment, Energy and Process Innovation, in co-operation with ATO, successfully tested hyperthermophilic H_2 fermentation for prolonged periods at pilot scale in a 400 liter bioreactor.

The final products of the (dark) fermentation are hydrogen and acetic acid. The latter can be further converted in a second reactor into hydrogen (and CO_2) by photosynthetic bacteria with the aid of absorbed light energy in a process called photofermentation. The latter process is discussed in detail in Chapter 6. The two-stage bioprocess, comprising a dark fermentation followed by a photofermentation, is a focal point in the current bio-hydrogen research in The Netherlands. A preliminary design and cost estimate for a small-scale, two-stage bio-hydrogen production process with a hydrogen production capacity of 425 Nm^3/hour (from 1 metric tonne of biomass/hour) is presented in Chapter 5. The economic evaluation indicates that bio-hydrogen could be produced at a cost of 19 Euro/GJ. Based on the potentially available feedstock in The Netherlands (mainly residues) it is estimated that sufficient bio-hydrogen could be produced to provide 9% of the Dutch households with electricity.

The two-stage bioprocess with hydrogen as the sole final product shows potential for sustainable hydrogen production. Further development is however required, particularly for the photofermentation stage. As discussed in Chapter 5, the development of a bioprocess for the production of hydrogen through dark fermentation followed by a second stage for the conversion of acetic acid into methane, is also possible. Such a bioprocess for combined production of bio-hydrogen and bio-methane could well fit into a transition application. The combination of dark hydrogen fermentation and methane production seems technically feasible in the near term, whereas a longer development trajectory is anticipated for the two-stage "hydrogen-only" process.

Several issues for further development are identified in Chapter 5. A major challenge is to optimise feedstock pretreatment, especially the mobilisation of fermentable substrates from lignocellulosic biomass. The available physical/chemical and enzymatic pre-treatment methods need to be optimised with respect to efficiency, cost and energy consumption. Another major R&D issue is to enhance hydrogen production rates by increasing the concentration of active biomass and improving the efficiency of hydrogen separation. The latter is required because the rate of fermentative hydrogen production is inhibited by the hydrogen produced.

Photobiological hydrogen production

Chapter 6 reviews the status of and outlook for photobiological hydrogen production. This chapter is written by I. Akkerman, The New Delta vof, M. Janssen and R.H. Wijffels, Wageningen University, J.M.S. Rocha, University of Coimbra, and J.H. Reith, Energy research Centre of The Netherlands ECN, Unit Biomass.

Sunlight is the driving force for photobiological hydrogen production. As outlined in Chapter 6, two types of processes are being developed.

Biophotolysis

A variety of microalgae and cyanobacteria are able to split water into hydrogen and oxygen with the aid of absorbed light energy. A bottleneck in this "direct biophotolysis" process is that the enzyme responsible for hydrogen production (hydrogenase) is inhibited by the oxygen produced. As a consequence, the photochemical efficiency[3] of

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[3] Photochemical efficiency is defined as the fraction of the light energy that is stored in the produced hydrogen.

this process is thus far much lower (<1% on solar light) than theoretically possible (10%). Several process variants are under development in which the inhibition of hydrogen production is prevented by separating the hydrogen from the oxygen production phase in space or time ("indirect biophotolysis").

Photofermentation

Photofermentations are processes in which organic compounds, like acetic acid, are converted into hydrogen and CO_2 with sunlight by bacteria. This process takes place under anaerobic conditions and can be combined with the dark hydrogen fermentation described in Chapter 5. In the dark hydrogen fermentation acetic acid is one of the end products. A photofermentation can be employed as the second stage in a two-stage biohydrogen production process, where the organic substrate is completely converted into hydrogen and CO_2.

The main bottleneck for practical application of photobiological hydrogen production is the required scaling-up of the system. A large surface area is needed to collect light. Construction of a photobioreactor with a large surface/volume ratio for direct absorption of sunlight is expensive. A possible alternative is the utilisation of solar collectors. Again, a drawback of these collector systems are the high production costs with the currently available technology. Although many types of photobioreactors have been designed, there is currently only one type of photobioreactor realised in practice that could be used for biological hydrogen production. The IGV (Institut für Getreideverarbeitung GmbH, Germany) constructed a tubular reactor with a ground surface area of 1.2 hectare at a total investment of 8 million Euro or 660 Euro/m^2. In Chapter 6 this system is compared to a 3 hectare roof structure equipped with photovoltaic cells with investment costs of 580 Euro/m^2. For the bio-hydrogen production system conversion of hydrogen into electricity at 50% efficiency in a fuel cell was assumed. The comparison shows that both the investment costs per m^2 and the overall efficiency (sunlight to electricity) of the photovoltaic and the photobiological system are comparable.

The energy potential of photobiological hydrogen production is assessed in Chapter 6 on the basis of the amount of sunlight received. At maximum light conversion efficiency (10%) a 1,000 hectare photobioreactor system in The Netherlands could produce 21,300 tons of hydrogen per year, equivalent to 3 PJ. A system of the same size in the south of Spain or in the desert of Australia could produce 4.6 PJ and 5.3 PJ of hydrogen energy per year respectively due to the higher solar irradiance in these areas. The estimate shows that the potential energy production of a photobiological system per hectare is 10-fold higher than for energy crops, such as Miscanthus which would yield approximately 0.3 PJ of energy on a 1,000 hectare surface. An additional advantage of the photobiological system is that it produces clean hydrogen (with 10-20% CO_2) that can be transported easily and used directly in fuel cells.

Preliminary cost estimates in the literature indicate that photobiological hydrogen could be produced in large-scale systems (100 ha and more) at a cost of 10-15 Euro/GJ. These estimates are based on preliminary data and favourable assumptions, and indicate the major directions for further development. Chapter 6 concludes that the development of low-cost photobioreactors and optimisation of photosynthetic light conversion efficiency are the major R&D issues in this field.

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