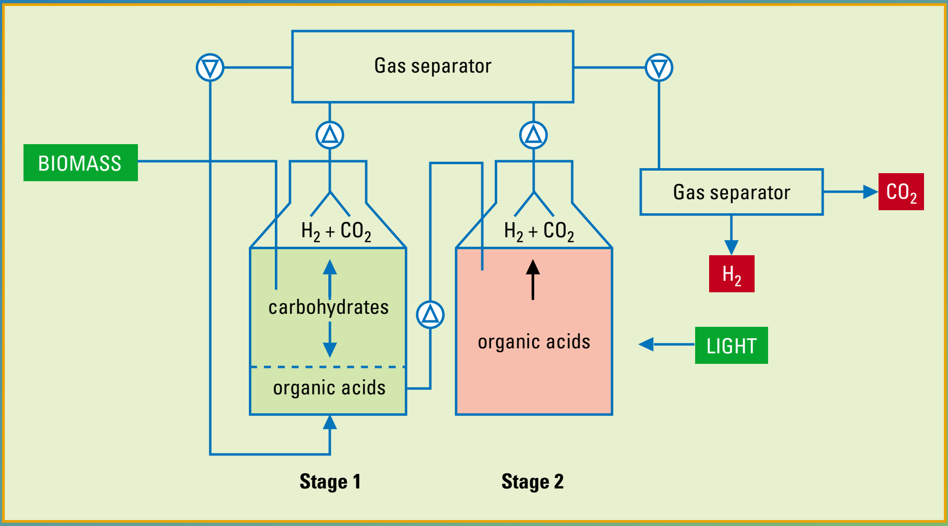
Bio-methane & Bio-hydrogen



Status and perspectives of biological methane and hydrogen production

Edited by J.H. Reith, R.H. Wijffels and H. Barten

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Front cover illustration:
Outline of bioprocess for production of hydrogen from biomass in a 2 stage fermentation. Stage 1 is for heterotrophic fermentation of carbohydrates to hydrogen, carbon dioxide and organic acids. In stage 2 the photoheterotrophic fermentation of organic acids to hydrogen and carbon dioxide takes place. Source: ATO B.V. See chapter 5 of this publication.

Back cover illustration:
UASB reactor for anaerobic wastewater treatment producing methane at Cerestar, Sas van Gent, The Netherlands. Photo by courtesy of Biothane Systems International.

This book is a publication of the *Dutch Biological Hydrogen Foundation,* c/o Energy research Centre of The Netherlands ECN, Unit Biomass, attn. J.H. Reith, secretary, P.O. Box 1, 1755 ZG Petten, The Netherlands. Tel. +31-(0)224-564371; e-mail: reith@ecn.nl. Website: http://www.biohydrogen.nl. The publication was realised with funding from the programme NECST (New Energy Conversion Systems and Technologies) executed by Novem on behalf of the Ministry of Economic Affairs, under contract number 249.402-0180 and 249-01-03-11-0003. *Novem, the Netherlands Agency for Energy and the Environment,* contributes to sustainable development both on a national and international level through stimulation of the application of sustainable energy in all sectors of society and technological innovations in the field of energy generation and utilisation. Websites: http://www.novem.nl and http://www.novem.org.

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Foreword

In 2020, a 10% share of the energy demand in The Netherlands will have to be provided for by renewable energy sources. This target is a consequence of decisions to realise an extensive reduction of the global CO_2 emissions, particularly in the industrialised nations. The objective is to stabilise the CO_2 level in the atmosphere in order to limit further negative climate effects.

Given the current situation it is logical to aim at energy saving and more efficient conversion of fossil fuels. In addition, "CO_2-free" operation is required. The objective of this "clean fossil" strategy is to enable utilisation of fossil fuels in a societally responsible manner.

A substantial contribution of renewable energy sources (solar, wind, hydropower, biomass and geothermal energy) to the energy economy is expected in the long term. This requires development of an integrated energy system comprising innovative and highly efficient energy conversion technologies. This enormous challenge calls for a creative approach, while a concomitant modification of the current energy structures is expected.

This publication, commissioned by the *Netherlands Agency for Energy and the Environment (Novem)*, reviews the status and perspectives of research and development (R&D) in the field of biological production of methane and hydrogen from biomass and/or sunlight. The expertise and developed techniques in this field can contribute to the targets for CO_2-free energy generation from renewable sources.

The authors of the chapters in this publication are prominent researchers working in various R&D groups in the Netherlands. These researchers are active in closely related research areas and co-operate in the *Netherlands Biohydrogen Network*, a platform for knowledge exchange and R&D collaboration and for active participation in the *International Energy Agency (IEA) Hydrogen Program* (Website http://www.eere/energy.gov/hydrogenandfuelcells/iea). Furthermore, the Network intends to function as an "expertise centre" for the market sector and governments. An overview of ongoing projects, publications and other information is provided on the Internet platform
http://www.biohydrogen.nl.

This collection of essays thus provides a thorough review of the field from a technological and scientific perspective and it gives insight into the available expertise in The Netherlands.

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Voorwoord

In 2020 moet 10% van de Nederlandse energiebehoefte worden geleverd door duurzame energiebronnen. Dit is een uitvloeisel van besluiten om op wereldschaal een zeer omvangrijke reductie van de CO_2 emissies te realiseren, met name in de geïndustrialiseerde landen. Het doel is het CO_2 gehalte in de atmosfeer niet verder te laten stijgen en daarmee verdere negatieve klimaateffecten te beperken.

Vanuit de huidige realiteit is het logisch om in te zetten op energiebesparing en hogere efficiency bij conversie van fossiele energiedragers. Het is daarbij dus ook nodig om dit CO_2 vrij te doen. Via dit "schoon-fossiel" gebruik kan de inzet van fossiele energiebronnen op maatschappelijk verantwoorde wijze plaatsvinden.

Op de langere termijn wordt verwacht dat hernieuwbare energiebronnen (zon, wind, water, biomassa en geothermische energie) een substantieel aandeel in de energiebehoefte zullen leveren. Dit vereist de ontwikkeling van een samenstel van innovatieve en efficiënte energieconversietechnologieën. Dit is een enorme uitdaging die om een creatieve benadering vraagt waarin naar verwachting ook de huidige energiestructuren zullen veranderen.

Deze publicatie, samengesteld in opdracht van *Novem*, laat de status en perspectieven zien van onderzoek en ontwikkeling op het gebied van biologische productie van methaan en waterstof uit biomassa en/of zonlicht. De kennis en ontwikkelde technieken op dit gebied kunnen bijdragen aan de doelstellingen ten aanzien van CO_2 vrije opwekking met behulp van hernieuwbare energiebronnen.

De auteurs van de hoofdstukken in deze publicatie zijn vooraanstaande onderzoekers verbonden aan Nederlandse onderzoeksgroepen. Deze onderzoekers zijn actief in aanpalende researchgebieden en werken samen in de *Nederlandse Contactgroep Biologische Waterstofproductie (Netherlands Biohydrogen Network)* die als platform fungeert voor kennisuitwisseling en samenwerking, onder meer in het kader van het *International Energy Agency (IEA) Hydrogen Program.* (Website: http://www.eere/energy.gov/hydrogenandfuelcells/iea).
Daarnaast beoogt het platform een functie als expertisecentrum voor de marktsector en overheden. Het Internet platform www.biohydrogen.nl biedt een overzicht van lopende projecten, publicaties en andere informatie.

Deze bundel levert dan ook een gedegen overzicht vanuit technisch en wetenschappelijk perspectief én inzicht in de in Nederland beschikbare expertise.

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1

Introduction: the perspectives of biological methane and hydrogen production

J.H. Reith, R.H. Wijffels and H. Barten

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		$2\ H_2O + \text{light} \rightarrow 2\ H_2 + O_2$	Microalgae
2 Photo-fermentations		$CH_3COOH + 2\ H_2O + \text{light} \rightarrow 4\ H_2 + 2\ CO_2$	Purple bacteria, Microalgae
3 Indirect biophotolysis	a	$6\ H_2O + 6\ CO_2 + \text{light} \rightarrow C_6H_{12}O_6 + 6\ O_2$	Microalgae,
	b	$C_6H_{12}O_6 + 2\ H_2O \rightarrow 4\ H_2 + 2\ CH_3COOH + 2\ CO_2$	Cyanobacteria
	c	$2\ CH_3COOH + 4\ H_2O + \text{light} \rightarrow 8\ H_2 + 4\ CO_2$	
		Overall reaction: $12\ H_2O + \text{light} \rightarrow 12\ H_2 + 6\ O_2$	
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 micro-organisms 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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2

Inleiding: de perspectieven van biologische methaan en waterstof productie

J.H. Reith, R.H. Wijffels en H. Barten

2.1 De noodzaak van CO_2-neutrale energieproductie

Onze energiebehoefte wordt vrijwel geheel gedekt uit fossiele bronnen als olie, steenkool en aardgas die in vele miljoenen jaren zijn gevormd uit plantaardige biomassa. Door het snelle verbruik van de fossiele voorraden komt de daarin gebonden koolstof in versneld tempo vrij. De resulterende stijging van het CO_2 gehalte van de atmosfeer wordt algemeen gezien als een van de belangrijkste oorzaken van de opwarming van de aarde en de daaraan gekoppelde klimaatsveranderingen. Daarnaast zal op lange termijn een tekort aan fossiele energiedragers ontstaan. Teneinde het CO_2 gehalte in de atmosfeer te stabiliseren op het niveau van 550 parts per million volume (ppmv) en verdere negatieve klimaatseffecten te beperken, beveelt het Intergovernmental Panel on Climate Change (IPCC) een wereldwijde reductie aan van de CO_2 emissies met meer dan 50%. In het kader van de Kyoto Akkoorden –waaraan inmiddels 106 landen deelnemen [1]– heeft een aantal geïndustrialiseerde landen zich gecommitteerd aan een reductie van de gezamenlijke CO_2 emissies van 5 % in 2010 ten opzichte van het niveau van 1990. Recente ramingen tonen echter dat de CO_2 emissies nog steeds toenemen en dat zelfs deze bescheiden doelstelling niet gehaald zal worden zonder ingrijpende maatregelen [2].

Een reductie van de CO_2 emissies veroorzaakt door (fossiel) energiegebruik kan worden bereikt door het verhogen van de energie-efficiency in de energieproductiesector, de industrie en het transport, en door vervanging van fossiele brandstoffen met een relatief hoge CO_2 uitstoot per eenheid energie door andere (eveneens fossiele) brandstoffen met een lagere CO_2 uitstoot, zoals de vervanging van kolen door aardgas voor elektriciteitsproductie. Deze maatregelen krijgen veel aandacht, maar leveren tot dusver nog onvoldoende resultaat. Een meer radicale oplossing is het gebruik van hernieuwbare energiebronnen, zoals zon, wind, waterkracht en biomassa. Deze energiebronnen zijn alle direct of indirect gebaseerd op zonlicht, zodat geen CO_2 wordt toegevoegd aan de atmosfeer ("CO_2 neutraal") en de voorraden in principe oneindig zijn. De oppervlakte van onze planeet ontvangt jaarlijks 3,8 miljoen exajoules (EJ)[1] aan zonlichtenergie, terwijl het huidige wereldenergieverbruik ca. 400 EJ bedraagt –ofwel slechts 0,01 % van de zonlichtinstraling –met een verwachte groei naar 850 à 1100 EJ in 2050 [3,4]. Hoewel de jaarlijkse toevoer van zonne-energie ruim voldoende is om volledig in onze energiebehoefte te voorzien, vormt het beschikbaar maken van deze energie in een bruikbare vorm vooralsnog een technisch en – vooral – economisch obstakel. Op dit moment wordt ongeveer 85% van de energiebehoefte op wereldschaal gedekt uit fossiele bronnen, 7% door kernenergie en 8% uit hernieuwbare bronnen, voornamelijk door gebruik van hout als brandstof en waterkracht [4]. Een volledige overgang naar hernieuwbare energiebronnen is op korte termijn niet mogelijk omdat hernieuwbare energieproductie met de nu beschikbare technologie (nog) niet concurrerend is met energieproductie uit fossiele bronnen. Zo bedragen de huidige kosten voor elektriciteitsproductie in de Europese Unie [5] voor verschillende hernieuwbare bronnen:

- 0,30 - 0,80 Euro/kilowattuur (Euro/kWh) voor fotovoltaïsche zonnecellen (PV);
- 0,04 - 0,25 Euro/kWh voor waterkrachtcentrales;

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[1] 1 Exajoule (EJ; 10^{18} J) komt overeen met ca. 172 miljoen vaten aardolie of 33 miljoen ton steenkool of 28.500 miljoen m3 aardgas. 1 Petajoule (PJ) is 10^{15} J, 1 Terajoule (TJ) 10^{12} Joule, 1 Gigajoule (GJ) 10^{9} Joule, 1 Megajoule (MJ) 10^{6} Joule. 1 kilowattuur (kWh) komt overeen met 3,6 MJ.

- 0,07 - 0,19 Euro/kWh voor biomassa; en
- 0,04 - 0,08 Euro/kWh voor windturbines.

Deze prijzen kunnen worden vergeleken met de contractprijzen voor elektriciteit geproduceerd uit fossiele brandstoffen die 0,03 - 0,05 Euro/kWh bedragen [6]. Ook voor hernieuwbare transportbrandstoffen bestaan nog grote prijsverschillen met de gangbare fossiele alternatieven. Zo wordt ethanol (dat benzine kan vervangen) uit zetmeelhoudende gewassen zoals maïs geproduceerd voor een kostprijs van ca. 16 Euro per gigajoule (GJ), terwijl benzine ca. 7 Euro/GJ kost [7]. Hieruit blijkt dat hernieuwbare energiedragers bij de huidige stand van de techniek minimaal twee tot drie maal duurder zijn dan hun fossiele tegenhangers. De kosten van hernieuwbare energieproductie vertonen echter een duidelijke daling in de tijd als gevolg van technische ontwikkelingen. Door voortzetting van de R&D en de "leereffecten" bij implementatie van hernieuwbare energietechnologie zal deze tendens zich naar verwachting voortzetten. Voor de korte en middellange termijn is echter financiële stimulering door overheden vereist via onder meer terugleververgoedingen en fiscale maatregelen, zoals reeds het geval is in veel landen [5]. Ook supranationaal beleid zoals het recent ingezette beleid in de Europese Unie voor de introductie van biobrandstoffen in de transportsector en de handel in CO_2 emissierechten (voorzien vanaf 2005) zullen de introductie van duurzame energie stimuleren.

Uiteindelijk zullen wij technologie beschikbaar dienen te hebben om op grote schaal hernieuwbare energiedragers te produceren. Het huidige energieverbruik in Nederland bedraagt ca. 3.000 petajoules (PJ) per jaar met een verwachte groei naar 3.400 PJ in 2020 [8]. De doelstelling van de Nederlandse overheid is dat 10% van de energiebehoefte wordt gedekt uit hernieuwbare bronnen in 2010. Dit komt neer op 340 PJ aan vermeden inzet van fossiele brandstoffen, waaraan de inzet van biomassa (inclusief organische reststromen) meer dan de helft (180 PJ) zal moeten bijdragen [8]. Op wereldschaal zal de inzet van hernieuwbare energiedragers in 2050 volgens recente Shell scenario's ca. 30% van het totale energieverbruik bedragen (280 - 335 EJ) [4]. Voor het overgrote deel zal het hierbij gaan om "groene" elektriciteit opgewekt met windturbines, waterkrachtcentrales, PV, en via verbranding en vergassing van biomassa, en om gasvormige en vloeibare brandstoffen geproduceerd uit biomassa.

2.2 Hernieuwbare energieproductie en de waterstofeconomie

In de toekomstige energiehuishouding wordt een belangrijke rol voorzien voor waterstof (H_2) als schone, CO_2-neutrale brandstof voor gebruik in brandstofcelvoertuigen en voor decentrale elektriciteitsopwekking in stationaire brandstofcelsystemen. In dit verband wordt vaak gesproken van een "waterstofeconomie". Waterstof kan in brandstofcellen zeer efficiënt worden omgezet in elektriciteit (en warmte), waarbij (vrijwel) uitsluitend water vrijkomt als restproduct, zodat een drastische reductie kan worden gerealiseerd van de emissies van CO_2, NO_x, roet etc. die gepaard gaan met het gebruik van fossiele brandstoffen. Een cruciale eigenschap van brandstofcellen is dat elektriciteitsproductie ook in (zeer) kleinschalige systemen met hoog rendement plaatsvindt, dit in tegenstelling tot andere technieken waarvan de efficiency sterk daalt bij afnemende schaal. Dit maakt het mogelijk brandstofcellen toe te passen in voertuigen en voor gedecentraliseerde productie van elektriciteit in de industrie, op wijkniveau en zelfs in individuele huishoudens. In Hoofdstuk 3 van deze publicatie wordt hierop uitvoerig ingegaan. Waterstof kan al op een termijn van 10 tot 20 jaar een belangrijke energiedrager worden, in eerste instantie in het wegtransport (brandstofcelvoertuigen) en op langere termijn voor (decentrale) elektriciteitsproductie [9]. Brede toepassing vereist ontwikkeling van goedkope brandstofceltechnologie, waterstofopslagsystemen en infrastructuur.

In de komende decennia zal waterstof vooral worden geproduceerd via elektrolyse of uit fossiele energiedragers in kleinschalige "reformers" of in grootschalige, centrale installaties via bijv. stoom "reforming" van aardgas ($CH_4 + 2\ H_2O \rightarrow 4H_2 + CO_2$). Bij grootschalige productie is het mogelijk de CO_2 af te vangen voor gebruik in kassen t.b.v. versterking van de plantengroei, of opslag in chemische vorm (bijv. als carbonaten) of in ondergrondse reservoirs. De productie van waterstof uit fossiele grondstoffen is één van de elementen in de "schoon fossiele" strategie waardoor de negatieve klimaatseffecten van fossiele energiedragers kunnen worden beperkt. Deze strategie zal in de overgangsfase naar een hernieuwbare energiehuishouding een belangrijke rol spelen en omvat ook energiebesparing en de ontwikkeling van efficiëntere conversietechnieken, waaronder brandstofcellen, voor inzet van aardgas en andere fossiele brandstoffen die in de voorzienbare toekomst een belangrijke rol zullen blijven spelen [4].

Hoewel het gebruik van waterstof geproduceerd uit fossiele brandstoffen tot een belangrijke reductie leidt van emissies, is het energetisch rendement van de gehele keten van productie tot en met eindgebruik (aardgas → waterstof → elektriciteit) beperkt. Dit wordt veroorzaakt door de energieverliezen die optreden bij de H_2 productie en de daaraan gekoppelde afvangst en opslag van CO_2 (zie Hoofdstuk 3). Op langere termijn zal waterstof dan ook bij voorkeur dienen te worden geproduceerd met behulp van hernieuwbare energiebronnen waaronder de elektrolyse van water met duurzaam opgewekte elektriciteit, thermische vergassing van biomassa en (foto)biologische waterstofproductie. Bij grootschalige inzet van hernieuwbare energiebronnen kan waterstof een belangrijke rol spelen als schone, intermediaire energiedrager voor opslag en transport. Elektriciteit uit duurzame bronnen zoals bijv. waterkracht kan via elektrolyse worden gebruikt voor de productie van waterstof, die kan worden opgeslagen en naar de eindgebruikers getransporteerd in vloeibare vorm of via een (gas)transportnet en met hoog rendement in brandstofcellen weer worden omgezet in elektriciteit. Door deze onderlinge uitwisselbaarheid worden waterstof en elektriciteit als de belangrijkste schone energiedragers gezien voor de toekomstige energiehuishouding [10]. De ontwikkeling van waterstoftechnologie heeft hoge prioriteit in de Europese Unie (6e Kader Programma), de Verenigde Staten en Japan. Bedrijven (automobielindustrie en energiebedrijven) en overheden investeren in de ontwikkeling van brandstofcellen, waterstofopslagsystemen en infrastructuur. In deze programma's wordt tevens aandacht besteed aan veiligheid en de maatschappelijke aspecten van toepassing van waterstof als energiedrager [10].

2.3 De rol van biomassa en biotechnologische processen voor hernieuwbare energieproductie

Alle hernieuwbare energiebronnen zijn afgeleid van zonne-energie, die tot onze beschikking komt via fotovoltaïsche zonnecellen (PV), windenergie of opgeslagen als chemische energie in biomassa. De laatste zal een belangrijke rol gaan spelen als grondstof voor duurzame productie van elektriciteit en gasvormige en vloeibare biobrandstoffen.
Bij gebruik van biomassa kan een onderscheid gemaakt worden tussen het gebruik van droge biomassa (zoals hout) en het gebruik van natte biomassastromen, zoals groente- en fruitafval, agro-industriële reststromen en afvalwater. Droge biomassa zal bij voorkeur worden ingezet voor thermische processen die een laag watergehalte vereisen zoals de productie van "groene" elektriciteit (door verbranding of vergassing) of de productie van hernieuwbare dieselbrandstof via vergassing, gevolgd door Fischer-Tropsch synthese [11]. Natte biomassa en reststromen zijn hiervoor minder geschikt omdat het transport en het verwijderen van water uit deze stromen veel energie kosten, waardoor de netto CO_2 reductie beperkt of zelfs negatief is. De beschikbare hoeveelheid natte biomassa(rest)stromen en residuen is echter zo groot dat het de moeite waard is deze stromen in te zetten voor duurzame energieproductie. Biotechnologische processen zijn hiervoor bij uitstek geschikt omdat deze worden gekatalyseerd door micro-organismen en plaatsvinden in waterig milieu bij lage temperatuur en druk. Daarnaast lenen deze technieken zich goed voor decentrale energieproductie in relatief kleinschalige installaties op locaties waar grondstoffen beschikbaar zijn, zodat energiegebruik en kosten van transport kunnen worden beperkt. In het algemeen wordt verwacht dat biotechnologische processen een substantieel aandeel zullen leveren aan de productie van hernieuwbare gasvormige en vloeibare brandstoffen zoals methaan, waterstof, ethanol en ABE (Aceton-Butanol-Ethanol) [12, 13].

2.4 Biotechnologische productie van bio-methaan en bio-waterstof

Deze publicatie geeft een overzicht van de state-of-the-art en de toekomstperspectieven van de microbiologische productie van methaan en waterstof uit biomassa al dan niet met behulp van zonlicht. De eindproducten van deze processen worden aangeduid met de termen *bio-methaan* (biologische methaan) en *bio-waterstof* (biologische waterstof). Methaanproductie via anaërobe vergisting van afvalwater en reststromen zoals zuiveringsslib, mest, en de organische fractie van huisvuil wordt reeds veel toegepast. Bij dit proces is waterstof een tussenproduct dat echter niet vrij beschikbaar komt omdat het door micro-organismen direct wordt opgenomen en omgezet in methaan. Bij biologische waterstofproductie is waterstof het eindproduct. Deze processen verkeren nog in de R&D fase en veel onderzoek is nog nodig voor de commerciële implementatie van de technologie, waarvan verschillende varianten bestaan. Naast de productie van bio-waterstof uit biomassa en reststromen is het mogelijk om met behulp van fotobiologische processen direct waterstof te maken uit zonlicht. Tabel 1 geeft een overzicht van alle bekende microbiologische waterstofproductieprocessen die momenteel onderwerp zijn van fundamenteel en toepassingsgericht onderzoek [16].

Een verwant gebied is de ontwikkeling van efficiënte waterstofkatalysatoren gebaseerd op het katalytische centrum van natuurlijke waterstofproductie enzymen (hydrogenasen) [14,19]. In de afgelopen jaren is de structuur van het actieve centrum van deze enzymen opgehelderd. De katalytische centra zijn opgebouwd uit anorganische elementen met name nikkel, ijzer en zwavel. Deze kennis opent de weg naar de productie van goedkope, synthetische waterstofkatalysatoren ter vervanging van de kostbare edelmetaal katalysatoren die momenteel worden toegepast in brandstofcellen en elektrolyse systemen. In 2001 is de eerste stabiele en actieve "bio-mimetische" katalysator gesynthetiseerd [17]. Een alternatieve benadering is het gebruik van gezuiverde hydrogenase enzymen als component van waterstofelektroden. Uit onderzoek is reeds gebleken dat stabiele enzym-waterstofelektroden kunnen worden geproduceerd, met een activiteit die identiek is met die van een platina-elektrode [18]. Deze ontwikkeling valt buiten het bestek van deze publicatie. Het is echter duidelijk dat ook deze ontwikkelingslijn

TABLE 1 *Overzicht van op dit moment bekende biologische waterstofproductieprocessen[16]*

Proces		Algemene reactie	Gebruikte microorganismen
1 Directe Biofotolyse		$2\ H_2O$ + licht → $2\ H_2 + O_2$	Microalgen, Cyanobacteriën
2 Fotofermentaties		$CH_3COOH + 2\ H_2O$ + licht → $4\ H_2 + 2\ CO_2$	Purperbacteriën, Microalgen
3 Indirecte biofotolyse	a	$6\ H_2O + 6\ CO_2$ + licht → $C_6H_{12}O_6 + 6\ O_2$	Microalgen Cyanobacteriën
	b	$C_6H_{12}O_6 + 2\ H_2O \rightarrow 4\ H_2 + 2\ CH_3COOH + 2\ CO_2$	
	c	$2\ CH_3COOH + 4\ H_2O$ + licht → $8\ H_2 + 4\ CO_2$	
		Overall reactie: $12\ H_2O$ + licht → $12\ H_2 + 6\ O_2$	
4 Water Gas Shift Reactie		$CO + H_2O \rightarrow CO_2 + H_2$	Fermentatieve bacteriën, Fotosynthetische bacteriën
5 Twee fasen fermentaties	a	$C_6H_{12}O_6 + 2\ H_2O \rightarrow 4\ H_2 + 2\ CH_3COOH +2\ CO_2$	
	b	$2\ CH_3COOH \rightarrow 2\ CH_4 + 2\ CO_2$	Fermentatieve bacteriën + Methanogene bacteriën
6 Hoog rendement donkerfermentaties		$C_6H_{12}O_6 + 6\ H_2O \rightarrow 12\ H_2 + 6\ CO_2$	Fermentatieve bacteriën

een waardevolle bijdrage kan leveren aan een toekomstige waterstofeconomie via intelligente exploitatie van natuurlijke systemen. Een uitstekend overzicht van de status en perspectieven op dit gebied is te vinden in Cammack, et al., 2001 [19].

Zowel biologische waterstofproductie als methaangisting produceren CO_2-neutrale, gasvormige energiedragers uit reststromen en kunnen daarmee concurrerende technieken zijn [14]. Omdat de beschikbare grondstoffen zo efficiënt mogelijk moeten worden benut is het van belang bij de verdere ontwikkeling en implementatie de meest voordelige route te kiezen. Dit is afhankelijk van vele factoren waaronder het energetisch rendement (biomassa → energiedragers → elektriciteit), de integratie van de energiedragers in de infrastructuur, milieu effecten (waaronder de netto reductie van CO_2 emissies), productiekosten en de perspectieven van verdere techniekontwikkeling. Een beschouwing van de eerste stap, de omzetting van biomassa in waterstof of methaan, leert dat het energetisch rendement van biowaterstof productie hoger ligt dan voor de productie van bio-methaan[2]. Dit is een pluspunt voor bio-waterstof productie, zeker ingeval een voorkeur bestaat voor waterstof als brandstof voor lage temperatuur Proton Exchange Membrane (PEM) brandstofcellen. Bio-waterstof kan direct worden gebruikt in deze cellen, terwijl methaan hiervoor "reforming" dient te ondergaan waardoor de elektriciteitsproductie afneemt. "Groene" bio-methaan heeft daarentegen het voordeel dat het in de bestaande infrastructuur kan worden toegepast terwijl voor waterstof pas op langere termijn een substantiële afzetmarkt zal ontstaan. Een verder potentieel voordeel van (bio)waterstof is de mogelijkheid van CO_2 afvangst in de productiefase waardoor de CO_2-emissies extra kunnen worden gereduceerd. Zoals toegelicht in Hoofdstuk 4 tot en met 6 liggen de productiekosten van biomethaan en de (geprojecteerde) kosten van biowaterstof in eenzelfde bandbreedte t.w. 10-20 Euro/GJ. Dit is vergelijkbaar met vloeibare biobrandstoffen zoals bioethanol en Fischer-Tropsch diesel. Bij de huidige inzichten lijken beide routes dan ook een bijdrage te kunnen leveren aan een duurzame energiehuishouding.

Hoewel methaanproductie door anaërobe vergisting reeds commercieel wordt toegepast zijn ook voor deze techniek nog verdere ontwikkeling en procesverbeteringen gewenst, zoals toegelicht in Hoofdstuk 4. Dit geldt in veel sterkere mate voor de verschillende varianten van biologische waterstofproductie waarvan de ontwikkeling zich nog op laboratorium schaal of (kleine) pilot schaal bevindt. Er zijn goede argumenten voor een versterking van de samenwerking tussen beide werkgebieden. Biologische waterstof en methaan productie zijn verwante processen door de interactie van het microbieel waterstof en methaan metabolisme op zowel fysiologisch als procesniveau waar verschillende soorten micro-organismen nauw samenwerken. Waterstof is een intermediair product in de afbraakroute van organisch materiaal naar methaan. Zo is uit onderzoek gebleken dat de productiviteit van methaangisting sterk kan worden verbeterd door bijmenging van waterstofproducerende micro-organismen [15]. Andere gemeenschappelijke onderzoeksthema's betreffen de optimale ontsluiting van grondstoffen (voor beide routes een obstakel), proces- en reactorontwikkeling, en de opwerking en conditionering van het productgas voor gebruik in brandstofcellen. Daarnaast kan de ontwikkeling van gecombineerde bio-waterstof en bio-methaan productieprocessen goed passen in de overgangsfase naar een duurzame waterstof economie (zie Hoofdstuk 5). Tenslotte vereist de introductie van hernieuwbare energie en de lange-termijn ontwikkeling van de waterstofeconomie optimaal gebruik en geleidelijke aanpassing van bestaande structuren. De introductie van bio-waterstof kan mogelijk plaatsvinden langs een transitietraject waarbij gebruik wordt gemaakt van de technologische know-how op het gebied van bio-methaan productie en de bestaande gasinfrastructuur.

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[2] Op basis van de 'Higher Heating Value' (HHV) levert 1 mol glucose ($C_6H_{12}O_6$) ofwel 12 mol H_2 (HHV: 3,4 MJ/mol omgezette glucose) of 3 mol CH_4 (2,7 MJ/mol omgezette glucose). Voor de 'Lower Heating Value' is het verschil kleiner: 1 mol glucose levert 2,8 MJ H_2 ofwel 2,3 MJ CH_4. Voor biologische waterstofproductie is hiervoor een volledige omzetting van organisch materiaal naar H_2 vereist. Dit kan worden gerealiseerd in een twee-traps proces, zoals wordt toegelicht in Hoofdstuk 5.

2.5 De inhoud van deze publicatie

In Hoofdstuk 3 wordt het kader geschetst voor de potentiële rol van bio-methaan en bio-waterstof in de energiehuishouding en de invloeden daarop van de ontwikkeling van eindgebruikstechnologie en infrastructuur, en het energiebeleid. De Hoofdstukken 4 t/m 6 gaan uitvoerig in op de technieken voor bio-methaan en bio-waterstof productie. Achtereenvolgens worden belicht:

- Methaanproductie via anaërobe vergisting (Hoofdstuk 4),
- Biologische waterstofproductie via (donker) fermentatie (Hoofdstuk 5), en
- Fotobiologische waterstofproductie (Hoofdstuk 6).

De auteurs zijn onderzoekers die nauw betrokken zijn bij lopend onderzoek en daarnaast samenwerken in de *Nederlandse Contactgroep Biologische Waterstofproductie (Netherlands Biohydrogen Network)*. Voor een overzicht van lopende projecten, publicaties en andere informatie verwijzen wij de lezer naar het Internet platform http://www.biohydrogen.nl. De Hoofdstukken 4 tot en met 6 geven een gedegen overzicht van de status en perspectieven van de verschillende processen vanuit een technisch en wetenschappelijk perspectief. Tevens wordt ingegaan op de potentiële bijdrage aan de energiehuishouding, economische aspecten en de internationale status van het onderzoek en worden voor elk gebied de belangrijkste R&D richtingen aangegeven. In de Hoofdstukken 7 en 8 zijn Engelstalige en Nederlandse samenvattingen van de essays opgenomen.

De rol van bio-methaan en bio-waterstof in de (toekomstige) energiehuishouding

Het potentieel van bio-methaan en bio-waterstofproductie wordt niet alleen bepaald door de kenmerken van het productieproces maar tevens door de integratie in de infrastructuur. Om hierin inzicht te krijgen analyseert A. de Groot van het Energieonderzoek Centrum Nederland, Unit Schoon Fossiel, in Hoofdstuk 3 de integrale keten "van productie tot en met eindgebruik" en de invloed van de toekomstige energie-infrastructuur en het energiebeleid op de toepassing van bio-methaan en bio-waterstof.

Voor beide processen zijn relatief kleinschalige productiesystemen, op locaties waar grondstoffen beschikbaar zijn, het meest aangewezen. Zoals besproken in Hoofdstuk 3, wordt het geproduceerde gas ofwel direct gebruikt (*"stand-alone systeem"*) of geleverd aan een transportnet voor gebruik op andere locaties (*"netwerk gekoppeld systeem"*). In het eerste geval wordt het gas ter plaatse omgezet in elektriciteit voor levering aan het openbare net. Warmte wordt intern benut of extern als een transportnetwerk beschikbaar is voor bijv. stadsverwarming. Dit "stand-alone" principe wordt veel toegepast in anaërobe vergistingsinstallaties en stortgas productielocaties. Een alternatief is het gebruik van een (bestaand) transportnet voor distributie van het gas naar de eindgebruikers. Het transportnet fungeert dan als buffer voor het afstemmen van energieproductie en energieafname.

Hoofdstuk 3 illustreert dat verschillende typen energiedragers in de toekomst belangrijk kunnen worden afhankelijk van het gebruikte scenario, het energiebeleid van de overheid, en de eisen die (toekomstige) eindgebruikstechnieken en infrastructuur stellen aan de kwaliteit van de energiedragers. Brandstofcellen zullen voor zowel methaan als waterstof een belangrijke rol gaan spelen door hun hoge efficiëntie en de (vrijwel) emissievrije eindconversie naar elektriciteit. Voor elektriciteitsproductie uit methaan echter zijn vele andere efficiënte technieken beschikbaar die voortdurend worden geoptimaliseerd. Voor toepassing van waterstof daarentegen is brandstofceltechnologie een cruciale voorwaarde, omdat de meerwaarde van waterstof als brandstof uitsluitend via de conversie in brandstofcellen kan worden gerealiseerd, zoals toegelicht in Hoofdstuk 3. Voor distributie van bio-methaan kan gebruik worden gemaakt van de bestaande, uitgebreide aardgasinfrastructuur na opwerking tot aardgaskwaliteit. Een alternatief is opwekking van elektriciteit voor levering aan het net. Voor bio-waterstof productiesystemen is distributie van waterstof naar de eindgebruiker (in plaats van elektriciteit) veel aantrekkelijker vanwege de efficiënte, CO_2-vrije elektriciteitsopwekking in kleinschalige brandstofcelsystemen. Hoofdstuk 3 concludeert dan ook dat distributie van bio-waterstof via een transportnet op locale, regionale of grotere schaal de voorkeur heeft.

Productie van bio-methaan via anaërobe vergisting

De status en vooruitzichten van de anaërobe vergistingstechnologie voor productie van bio-methaan worden belicht in Hoofdstuk 4, een bijdrage van T.Z.D. de Mes, A.J.M. Stams en G. Zeeman, Lettinga Associates Foundation (LeAF) en de Wageningen Universiteit, en J.H. Reith, Energieonderzoek Centrum Nederland ECN, Unit Biomassa.

Anaërobe microbiële afbraak van biomassa of "anaërobe vergisting" is een proces waarin micro-organismen in zuurstofloze omstandigheden organisch materiaal afbreken tot methaan en CO_2. Dit proces omvat een aantal fasen waarin verschillende groepen micro-organismen nauw samenwerken. De eerste stap, de afbraak van complexe organische verbindingen tot eenvoudige moleculen, hydrolyse, is de snelheidsbeperkende stap voor het gehele vergistingsproces. Daarna volgt een fase van zuurvorming (met waterstof als additioneel tussenproduct) en een fase waarin de organische zuren en waterstof worden omgezet in methaan.

De grondstoffen voor anaërobe vergisting zijn in het algemeen rest- en afvalstromen. Deze kunnen sterk verdund zijn zoals huishoudelijk en industrieel afvalwater tot relatief geconcentreerd zoals mest, zuiveringsslib en de organische fractie van huisvuil. De voor deze verschillende typen grondstoffen ontwikkelde anaërobe vergistingssystemen worden gepresenteerd in Hoofdstuk 4. Wereldwijd wordt het Upflow Anaerobic Sludge Bed (UASB) systeem het meest toegepast voor de zuivering van industrieel afvalwater. In de tropen wordt de UASB techniek in toenemende mate ook ingezet voor de behandeling van huishoudelijk afvalwater. Een recente ontwikkeling, die wordt belicht in Hoofdstuk 4, is de toepassing van anaërobe vergisting als onderdeel van Decentrale Sanitatie en Hergebruik (DeSaH) concepten. Dit concept richt zich op gescheiden inzameling van geconcentreerde en verdunde huishoudelijke afval(water)stromen, gevolgd door anaërobe vergisting van de geconcentreerde fractie voor de terugwinning van energie en nutriënten.

Het eindproduct van vergisting is "biogas" dat bestaat uit voornamelijk methaan (55-75 vol%) en CO_2 (25-45 vol%). De hoeveelheid geproduceerde bio-methaan is afhankelijk van de gebruikte grondstof. Uit de organische fractie van huisvuil kan bijvoorbeeld tussen 100 en 200 m^3 biogas per ton afval geproduceerd worden en uit mest 10 à 20 m^3 per ton. Zoals toegelicht in Hoofdstuk 4, kan de biogasproductie uit mest aanzienlijk worden verhoogd door het bijmengen van andere reststromen zoals dierlijk afval ("co-vergisting"), waardoor de economische haalbaarheid verbetert. Biogas kan worden ingezet voor de productie van warmte, gecombineerde opwekking van warmte en elektriciteit (W/K) of voor opwaardering tot aardgas- of transportbrandstofkwaliteit. Het gebruik van biogas in gasmotoren voor productie van elektriciteit en warmte wordt het meest toegepast. Voor grootschalige installaties (zoals stortgas productielocaties) kunnen gasturbines een geschikt alternatief zijn. Voor de toekomst biedt het gebruik van brandstofcellen een aantrekkelijk perspectief, vanwege het hoge rendement en de afwezigheid van emissies. Vergistingsinstallaties uitgerust met brandstofcellen zijn in gebruik of worden beproefd op pilot-schaal, met veelbelovende resultaten. In 2000 bedroegen de productiekosten van biogas in de Europese Unie 10-20 Euro per GJ. De kosten van elektriciteit uit biogas bedroegen 0,1-0,2 Euro per kWh. De productiekosten vertonen een neerwaartse trend die naar verwachting zal worden voortgezet. De huidige capaciteit van anaërobe vergistingssystemen in Europa bedraagt ca. 1.500 MW. Het potentieel voor 2010 in Europa wordt geraamd op 5.300 - 6.300 MW en tot 20.000 MW op wereldschaal. Invoering van stortverboden voor organisch afval (zoals voorzien in de Europese Unie) en financiële stimulering van duurzame energieproductie zullen deze ontwikkeling ongetwijfeld stimuleren.

Bij anaërobe behandeling van afvalwater wordt een geringe hoeveelheid slib gevormd, dat stabiel is en goed ontwaterbaar. Bij vergisting van mest en vast afval resulteert naast biogas een organisch residu ("digestaat") met een hoge concentratie nutriënten (N, P, K). Dit materiaal kan na droging worden afgezet als "mineralen concentraat" of compost als vervanger van kunstmest. Hierdoor is volledige terugwinning van nutriënten mogelijk. De resterende afvalwaterstroom dient een nazuivering te ondergaan. Zoals toegelicht in Hoofdstuk 4 vormen de behandeling van nevenproducten en de afzet van digestaat belangrijke factoren voor de economische rentabiliteit bij vergisting van mest en vast afval, naast "poorttarieven" en de opbrengsten uit energieverkoop. De belangrijkste concurrent voor verwerking van vast afval is compostering dat in tegenstelling tot anaërobe vergisting echter geen energie oplevert maar energie kost. De kosten van anaërobe vergisting dalen gestaag en zijn in toenemende mate concurrerend met de kosten van compostering.

In Hoofdstuk 4 worden als de belangrijkste gebieden voor verdere ontwikkeling van de anaërobe vergistingstechnologie geïdentificeerd: verhoging van de biogasopbrengst door co-vergisting verbetering van de ontsluiting (hydrolyse) van grondstoffen, en het reduceren van investeringen en operationele kosten door technologische verbeteringen. Daarnaast dienen kosteneffectieve technieken te worden ontwikkeld voor de behandeling van digestaten en water(na)zuivering.

Produktie van bio-waterstof met behulp van (donker)fermentatie

Hoofdstuk 5 is een bijdrage van T. de Vrije en P.A.M. Claassen, Agrotechnologisch Onderzoeksinstituut ATO BV, die gewijd is aan de status en perspectieven van biologische waterstofproductie uit biomassa via (donker)fermentatie.

In tegenstelling tot anaërobe methaangisting (waar de gevormde waterstof verder wordt omgezet in methaan) is dit proces gericht op de productie van uitsluitend waterstof als eindproduct. Een belangrijk verschil met anaërobe methaangisting (waar verschillende typen micro-organismen nauw samenwerken) is dat in waterstoffermentaties uitsluitend waterstofproducerende micro-organismen actief zijn. Een ander essentieel verschil is dat de complexe verbindingen in de grondstof niet in het proces zelf maar voorafgaand aan het fermentatieproces worden afgebroken tot eenvoudige moleculen met behulp van fysisch/chemische methoden (zoals extrusie) en/of behandeling met (industriële) enzymen. Deze organische verbindingen worden vervolgens door micro-organismen via fermentatie omgezet in waterstof, azijnzuur en CO_2. Zoals toegelicht in Hoofdstuk 5, zijn vele soorten micro-organismen in staat tot productie van waterstof, die in de natuur direct wordt opgenomen door waterstof consumerende micro-organismen. De ontwikkeling van een bio-waterstof productieproces vereist derhalve ontkoppeling van de acties van waterstof producenten en -consumenten, naast optimalisatie van de waterstofproductie per eenheid grondstof. Hiertoe zijn hyperthermofiele micro-organismen geselecteerd met een optimale kweektemperatuur van 70 ^{0}C en hoger, en een hoge waterstofproductiviteit.

De productie van bio-waterstof via donkerfermentatie verkeert nog in de R&D fase. Zoals toegelicht in Hoofdstuk 5 is op laboratorium schaal het proces door ATO met succes getest voor verschillende typen grondstoffen zoals Miscanthus, Sweet Sorghum, aardappelstoomschillen en Groente Fruit en Tuin afval (GFT). In 2002/2003 heeft TNO Milieu, Energie en Procesinnovatie in samenwerking met ATO, de hyperthermofiele waterstoffermentatie met succes getest gedurende langere perioden in een 400 liter bioreactor.

De eindproducten van de (donker)fermentatie zijn waterstof en azijnzuur. Het azijnzuur kan in een tweede reactor worden omgezet in waterstof (en CO_2) door fotosynthetische bacteriën met behulp van (zon)lichtenergie in een zgn. "fotofermentatie". Dit laatste proces wordt uitvoerig besproken in Hoofdstuk 6. Een twee-traps bioproces bestaande uit een donkerfermentatie gevolgd door een fotofermentatie staat centraal in de lopende bio-waterstof R&D in Nederland. In Hoofdstuk 5 wordt een kostenraming gepresenteerd voor een kleinschalig twee-traps bio-waterstof productiesysteem met een productiecapaciteit van 425 Nm^3 waterstof/uur (uit 1 ton biomassa/uur). Volgens deze raming zou waterstof met dit proces kunnen worden geproduceerd voor een prijs van 19 Euro/GJ. Een raming van het energiepotentieel (op basis van de in Nederland potentieel beschikbare grondstoffen, met name reststromen) geeft aan dat ca. 9% van de Nederlandse huishoudens via dit proces zou kunnen worden voorzien van elektriciteit.

Het ontwikkelde twee-traps proces voor de productie van uitsluitend bio-waterstof biedt perspectief voor de langere termijn. Zoals besproken in Hoofdstuk 5 is ook de ontwikkeling denkbaar van een proces dat in de eerste stap waterstof produceert via donker fermenatatie, gevolgd door een tweede stap voor de omzetting van azijnzuur in methaan. Zo'n bioproces voor gecombineerde productie van bio-waterstof en bio-methaan kan een rol spelen in de overgangsfase naar een waterstof economie. De combinatie van waterstof fermentatie en methaan productie is naar verwachting op kortere termijn te realiseren dan een proces voor de productie van uitsluitend waterstof.

In Hoofdstuk 5 worden verschillende onderwerpen geïdentificeerd voor verdere ontwikkeling. Een belangrijke uitdaging is de optimalisatie van grondstof voorbehandeling, met name het mobiliseren van fermenteerbaar substraat uit lignocellulose. De beschikbare voorbehandelingsmethoden dienen te worden geoptimaliseerd m.b.t. efficiency, kosten en energiegebruik. Een tweede onderzoeksthema is het vergroten van de waterstof productiesnelheid door verhoging van de concentratie micro-organismen in de reactor en het tegengaan van (eind)productremming door effectieve afvangst van de geproduceerde waterstof.

Fotobiologische waterstofproductie

Hoofdstuk 6 is gewijd aan fotobiologische waterstofproductieprocessen die gebruik maken van zonlicht. Dit hoofdstuk is een bijdrage van I. Akkerman, De Nieuwe Delta vof, M. Janssen en R.H. Wijffels, Wageningen Universiteit, J.M.S. Rocha, University of Coimbra, en J.H. Reith Energieonderzoek Centrum Nederland ECN, Unit Biomassa.

Zonlicht is de drijvende kracht voor fotobiologische waterstofproductie. Zoals toegelicht in Hoofdstuk 6 zijn er twee typen processen in ontwikkeling.

Biofotolyse

Verscheidene soorten micro-algen en cyanobacteriën zijn in staat met behulp van geabsorbeerde lichtenergie water te splitsen in waterstof en zuurstof. Een obstakel bij deze "directe biofotolyse" is dat het enzym hydrogenase dat waterstof produceert wordt geremd door de geproduceerde zuurstof. Als gevolg hiervan zijn de bereikte fotochemische efficiënties[3] tot dusver lager (tot 1% op zonlicht) dan de theoretisch haalbare fotochemische efficiëntie (10%). Er zijn verschillende procesvarianten in ontwikkeling waarbij de remming van de waterstofproductiesnelheid wordt voorkomen door een scheiding aan te brengen in plaats of tijd van de fasen van resp. waterstof- en zuurstofproductie ("indirecte biofotolyse").

Fotofermentatie

Fotofermentaties zijn processen waarbij bacteriën organische stoffen, zoals azijnzuur, omzetten in bio-waterstof en CO_2 met behulp van zonlicht. Dit proces vindt plaats onder zuurstofloze condities en is uitstekend te combineren met de in Hoofdstuk 5 beschreven (donker) waterstoffermentaties waarbij azijnzuur een van de eindproducten is. De fotofermentatie vormt dan de tweede stap in een twee-traps bio-waterstofproces, waardoor de aangeboden organische stof volledig kan worden omgezet in waterstof en CO_2.

Het grootste obstakel voor praktijktoepassing van fotobiologische waterstofproductie is de benodigde opschaling van het systeem. Een groot oppervlak is nodig om licht op te vangen. Constructie van een fotobioreactor met een grote oppervlakte/volume verhouding voor directe absorptie van zonlicht is kostbaar. Een alternatief is het gebruik van zonlichtcollectoren, die echter bij de huidige stand van de techniek eveneens kostbaar zijn. Hoewel er verschillende fotobioreactor ontwerpen ontwikkeld zijn, is er slechts één fotobioreactor in bedrijf die gebruikt zou kunnen worden voor bio-waterstofproductie. Het IGV (Institut für Getreideverarbeitung GmbH, Duitsland) heeft een reactor bestaande uit buizen gebouwd met 1,2 ha grondoppervlak en investeringskosten van 660 Euro per m^2. In Hoofdstuk 6 wordt dit systeem vergeleken met een dakconstructie voorzien van fotovoltaïsche zonnecellen met investeringskosten van 580 Euro/m^2. Voor het fotobiologische systeem werd uitgegaan van omzetting van de gepro-

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[3] Fotochemische efficiëntie is de fractie van de zonlicht energie vastgelegd in waterstof.

duceerde waterstof in elektriciteit in een brandstofcel met 50% rendement. De vergelijking toont dat zowel de investeringskosten per m^2 als het overall conversierendement (van zonlicht naar elektriciteit) voor het fotobiologische en het fotovoltaïsche systeem vergelijkbaar zijn.

In Hoofdstuk 6 wordt de potentiële waterstofproductie geraamd met behulp van gegevens over de zonlichtinstraling. Bij maximale fotochemische efficiëntie (10%) zou een fotobioreactorsysteem in Nederland met een oppervlak van 1.000 hectare 21.300 ton waterstof per jaar kunnen produceren ofwel 3 PJ. Een systeem van gelijke grootte zou in het zuiden van Spanje en in de woestijn van Australië respectievelijk 4,6 PJ en 5,3 PJ aan waterstof kunnen produceren vanwege de hogere zonlichtintensiteit. De raming laat zien dat de potentiële energieopbrengst van fotobiologische waterstofproductie per oppervlakte-eenheid tien maal zo hoog is als voor energiegewassen zoals het snelgroeiende Miscanthus die ongeveer 0,3 PJ per jaar bedraagt op een oppervlak van 1.000 ha. Een bijkomend voordeel is dat de geproduceerde waterstof (met 10-20 vol% CO_2) eenvoudig kan worden getransporteerd en direct kan worden ingezet in brandstofcellen.

Globale kostenramingen uit de literatuur geven aan dat fotobiologische waterstof op grotere schaal geproduceerd zou kunnen worden voor 10-15 Euro/GJ. Deze ramingen zijn gebaseerd op voorlopige gegevens en gunstige aannames, en geven daarmee vooral de belangrijkste richtingen aan voor verdere ontwikkeling. Hoofdstuk 6 concludeert dat de ontwikkeling van goedkope fotobioreactoren en de optimalisatie van de fotochemische efficiëntie de belangrijkste onderzoeksdoelstellingen zijn.

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3

Methane and hydrogen: on the role of end-use technologies in shaping the infrastructure

A. de Groot[1]

Abstract

In Chapters 4 to 6 the status and potential of microbiological technologies for producing methane ('biogas') and hydrogen from (wet) biomass streams and sunlight is reviewed. To evaluate the potential of these processes the projected efficiencies and costs are considered. However, the evaluation of the technical and economical feasibility should not only take into account the costs of producing the energy carrier. The profitability of bio-methane and bio-hydrogen production also depends on the ways by which these products can be utilised for generation of electricity and heat, as a transport fuel etc. What are the costs for producing 1 GJ of heat and/or electricity or to drive a vehicle over a certain distance? How favourable do the emissions compare with competing technologies? To address these issues, the full 'production to end-use' chain for the two energy carriers (hydrogen and methane) should be included in the evaluation. In this chapter the focus is therefore on the ways that methane and hydrogen can be utilised. Biogas and biologically produced hydrogen will be referred to as 'bio-methane' and 'bio-hydrogen' respectively. Based on an evaluation of the role of end-use technologies, infrastructure requirements and energy policy the implications for bio-methane and biohydrogen will be evaluated.

3.1 Introduction: Evaluation of the full 'production to end-use' chain

Bio-methane and bio-hydrogen production methods are inherently extensive processes i.e. requiring relatively large process volumes. Furthermore the feedstock (wet biomass or bio-waste) cannot be easily transported over large distances. Based on these two characteristics relatively small-scale production systems, located where bio-wastes or other biomass sources are available, are most likely. This leads to two possible configurations for the 'production to end-use chain'. Either the gas is used directly at the point of production or the gas is supplied to an existing grid for use at another location. The first type of system is indicated as 'stand-alone system' and the second as 'grid-connected production systems'.

- In the stand-alone case the 'production to end-use' chain is integrated. The produced gas is converted on site into the required form of energy: power and/or heat (Figure 1). This type of system is at present widely applied for conversion of bio-methane (biogas or landfill gas) into electricity and heat by means of gas engine /generator units. For wide spread applications of the technology stand-alone operation has a number of limitations. Energy demand and biomass streams may not be available at the same location. Furthermore a load (or demand) following stand-alone system requires either flexibility in the production capacity, storage capacity for the energy carrier or integration with other systems supplying the actual load following characteristics.
- An alternative option that enables load following of the final energy demand without adding the extra cost of storage or flexible production capacity is to connect both the production and the end-use stages to a grid system for transport of methane (i.e. natural gas) or hydrogen. The 'production to end-use' chain in a grid-connected system consists of production and end-use as well as transport and distribution of hydrogen or methane. The infrastructure fulfils the function of matching energy demand and supply. As indicated in Figure 2, the production and end-use system can be at different locations when a gas infrastructure is used.

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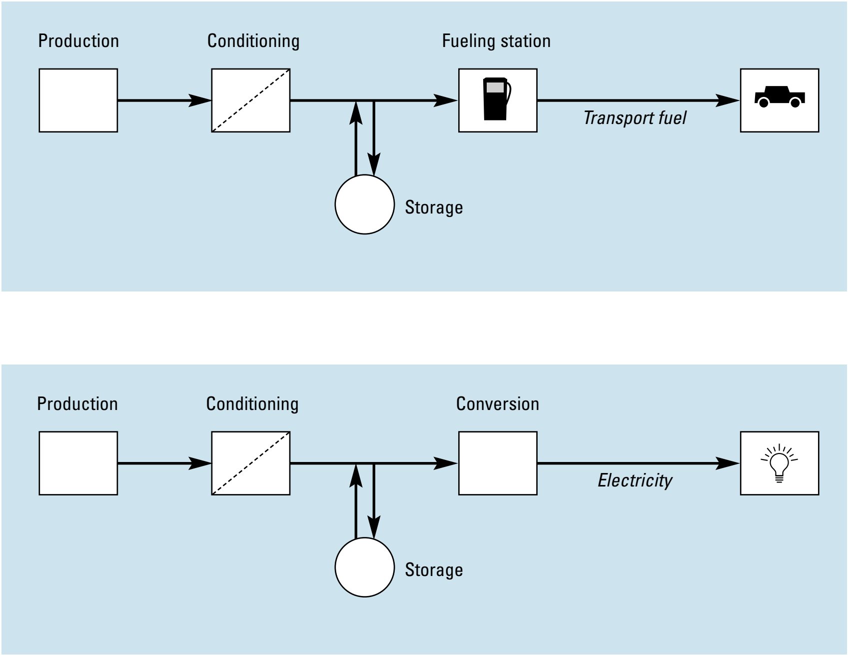


Figure 1: Production of bio-methane or bio-hydrogen for transportation or for stationary application in a stand-alone system (production and end-use on-site)

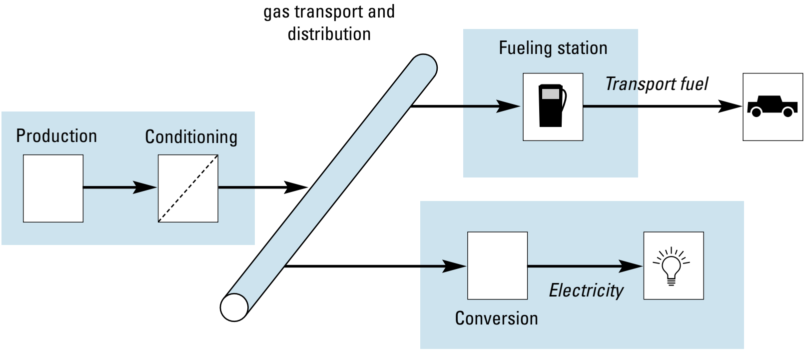


Figure 2: Separating production of bio-methane or bio-hydrogen and their end-use for transportation or for stationary application by means of infrastructure.

Approach

The feasibility of (bio)hydrogen or (bio)methane production processes does not only depend on the characteristics of the production process itself. For example, producing hydrogen for transport applications will only be feasible if hydrogen is used more widely as a transport fuel. Only then will there be cars driving on hydrogen, a refuelling infrastructure for supply of hydrogen to the cars, etc. In this chapter the integral chain from production to end-use is evaluated. The availability of an attractive production process of bio-hydrogen in itself is not sufficient.

Because the opportunities for bio-methane and bio-hydrogen depend on the available end-use technologies and infrastructure as well, this chapter addresses the playing field for the production technologies for these energy carriers.

- In Section 2 the emergence of future energy carriers is addressed. Conclusions from a recent Shell scenario study are used to illustrate that different energy carriers become dominant in different scenarios and that end-use technologies are essential for the emergence of specific energy carriers. For bio-hydrogen it is evidently relevant to determine whether a future hydrogen infrastructure is likely. Bio-methane on the other hand could benefit from the existing natural gas infrastructure.
- In Section 3 the final energy demand in the Netherlands is considered. Final energy demand determines which end-use technologies are required. Subsequently end-use technologies for stationary and transport applications using hydrogen and methane are discussed.
- Although technology is an important driver, energy policy will have a substantial influence on the emergence of specific energy carriers and technologies as well. It is therefore important to assess what the influence of energy policy will be. In Section 4 the implications of three policy scenarios for the (future) use of methane and hydrogen are evaluated.
- Section 5 provides an integration of the information from the preceding sections and addresses the implications for bio-methane and bio-hydrogen.

3.2. Future energy carriers and infrastructure

3.2.1 The choice of energy carrier

In the global energy system, two trends are apparent. The first is the ever-growing consumption of energy. The second is 'decarbonisation'. Figure 3 illustrates this second trend: the decreasing carbon content (per unit consumed primary energy) in global energy use over the last 150 years. The gradual introduction of fuels with an increasingly lower carbon content per unit of energy (wood > coal > oil > natural gas) results in a continuous decarbonisation of the global fuel mix. The replacement of one primary source by another (coal → oil → natural gas) also corresponds to a gradual increase of the hydrogen/carbon ratio in the last century [1].

How will this trend continue into the 21st century? Natural gas is expected to play an increasingly important role in the energy system. A further increase of the hydrogen/carbon ratio beyond 4 (corresponding to methane) is only possible by introducing hydrogen as an energy carrier. Although it is clear that both hydrogen and methane will probably be important energy carriers in the coming century, it is not clear how their use will develop compared to other energy carriers.

Recently, Shell has published a new long-term strategic study: ‘Energy needs, choices and possibilities’ [3] in which two scenarios for the first half of the 21st century are explored.

- In the scenario *'The Spirit Of The Coming Age'* the development is more or less driven by the benefits of the technology. The central element is the drive (or driving force) that results from the benefits of the end-use technology to the consumers (efficiency, versatility and flexibility of end-use). In this scenario the fuel cell creates the demand for the energy carriers it requires and natural gas and hydrogen are the most important energy carriers.
- In the scenario *‘Dynamics As Usual’* the choices and developments are to a larger extent controlled by the (negative) impacts of the energy system on society. The choices shaping the energy system are made as reactions to threats or limitations (resource scarcity, environment, etc.)

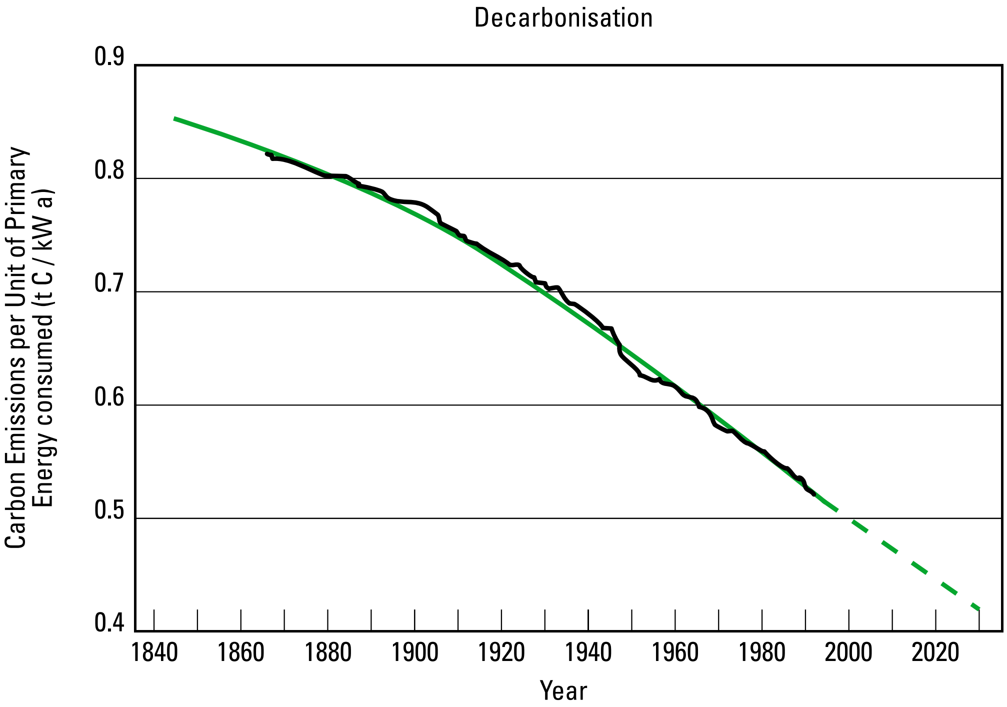


Figure 3: Decarbonisation of the global energy consumption. Adapted from [2]

instead of searching for optimum solutions. As a result other energy carriers and sources emerge in 2050 in this scenario. In *'Dynamics as Usual'* electricity (including electricity from renewable sources) and bio-fuels for transportation become important energy carriers.

The two scenarios show the uncertainty in the roles of future energy carriers and consequently the uncertainty for conversion technologies because every primary source and energy carrier requires specific technologies. Figure 4 illustrates that many different technologies may exist for the production and utilisation of a specific energy carrier. Figure 4 more or less defines the 'field' on which processes such as the biological production of methane or hydrogen will play a role. The relevance of assessing which technologies or energy carriers will emerge is evident: it defines the playing field for bio-hydrogen and bio-methane. On the other hand the scenario *'Spirit of the Coming Age'* shows that specific technologies can be the driver for a choice of sources and energy carriers as well.

3.2.2 Natural gas or hydrogen infrastructure

The economic lifetime of the energy infrastructure is around 50 years [4]. Therefore the infrastructure that will be put in place in the coming years will still be operational in 2050. This illustrates that it takes a long time to put an infrastructure in place and that infrastructure which is created today should take into account future needs. Although it is impossible to predict which energy carriers and technologies will be leading in 20 or 50 years, the benefits and barriers for specific energy carriers and the corresponding technologies can be assessed. In this chapter the opportunities for the energy carriers hydrogen and methane are discussed. As shown, these opportunities depend on the end-use technologies which develop and on the infrastructure for energy carriers which becomes available.

Methane and hydrogen are in some aspects very similar. The ease and efficiency with which they can be converted to heat or electricity is comparable and both are relatively clean fuels (although hydrogen much more so than methane or natural

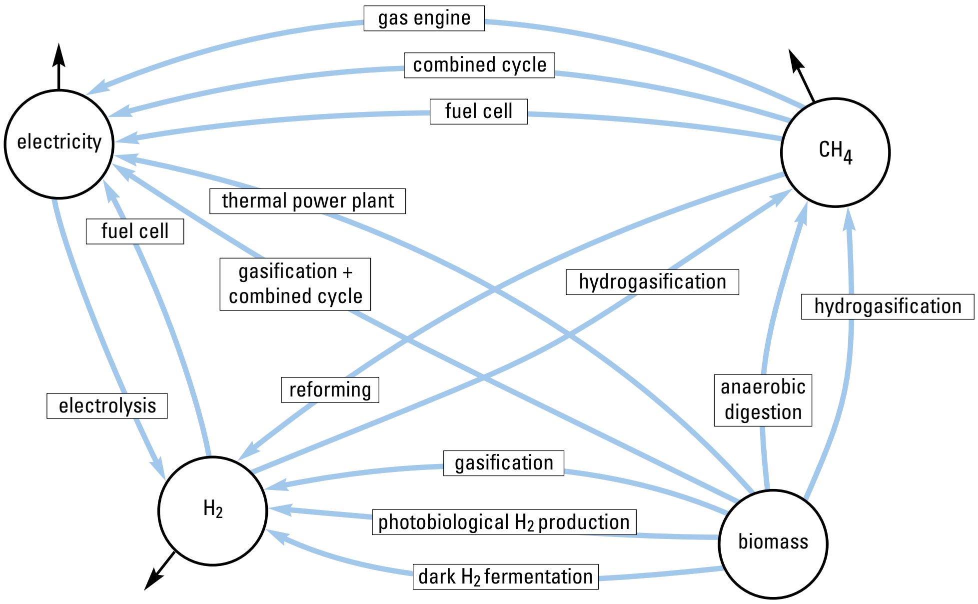


Figure 4: Possible routes from biomass to secondary energy carriers.

gas). Fuel cells, one of the most important emerging technologies, can operate both on methane and on hydrogen. The main difference is that methane in the form of natural gas is a primary energy carrier whereas hydrogen is an intermediate produced from primary sources. Secondly for natural gas a considerable infrastructure is in place today.

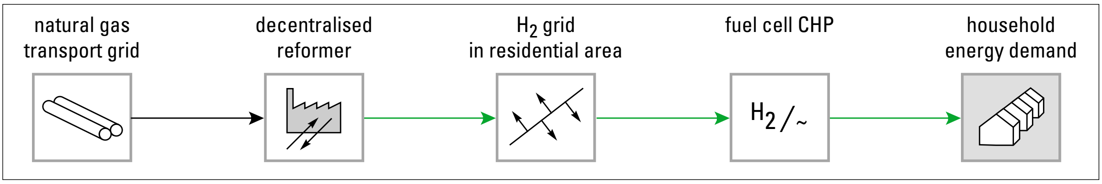
There are several uncertain factors considering the infrastructure. The first aspect is whether an infrastructure will be available. A second aspect is the requirements infrastructure imposes on the gas quality. Purification and conditioning of bio-methane and bio-hydrogen poses no technical obstacles because a range of commercial technologies is available to meet the required quality standards. Purification and further conditioning of biogas (and landfill gas) to natural gas or vehicle fuel standards is a common practice today (see Chapter 4). However, the cost of purification may play an important role.

In The Netherlands natural gas is already the most important energy carrier for stationary applications. It provides approximately half of the current primary energy consumption in The Netherlands. Gas penetration in the Dutch households is 97% and more than half the electricity produced in The Netherlands originates from natural gas [5]. In this chapter the natural gas infrastructure will be considered as the infrastructure which will be used for bio-methane. An implicit assumption is that methane from biomass will not justify a separate infrastructure in addition to the existing natural gas network. In that sense, the infrastructure for bio-methane is already in place. Transportation through the existing infrastructure defines the quality standards and consequently the required conditioning of bio-methane. ‘Raw’ biogas is a mixture of methane and carbon dioxide saturated with water vapour. It may further contain sulphides and ammonia. There are different reasons for limitations to the quality of the biogas. Corrosion for example limits the moisture and sulphur content. The biogas should also be free from poisonous components that cause a hazard in case of gas leaks or uncontrolled discharge from an appliance. The most important issue for the gas companies is that the appliances (boilers, furnaces etc.) are designed for a specific gas quality defined by the Wobbe index [6], in which the higher heating value is the most important parameter. If the biogas or substitute natural gas (SNG) consists of more or less the same components, the Wobbe index is the most important limitation. If components are present which do not occur in the current natural gas, other limitations may occur. Hydrogen for example may have an effect on leakages in the distribution network and leads to distinct combustion properties. For substitute natural gas additional requirements will therefore be applicable with regard to the allowable hydrogen concentration.

Hydrogen does not have any significance as an energy carrier in today's energy system. Limited hydrogen infrastructure exists for industrial applications, but it is in no way comparable to the natural gas infrastructure. In contrast to the natural gas infrastructure, where a new gas has to use an existing infrastructure, the conditions for gas transport through a hydrogen network cannot be defined beforehand. However, the fuel cell as the proposed end-use technology, sets rigorous restrictions on the allowable limits for a large number of components in the gas. Especially CO and sulphur are tolerated only in very small amounts, dependent on fuel cell type. For current state-of-the-art Proton Exchange Membrane (PEM) fuel cells for example the CO concentration in the fuel should be below 10-20 ppm. Other components that have been found to deteriorate the cells' performance include NH_3 and sulphur components that de-activate the catalyst. Putting in place a hydrogen infrastructure is a major challenge. The question is which driving forces exist for such a development. In the next section a short overview of the main drivers will be presented.

3.2.3 Drivers for creating a hydrogen infrastructure

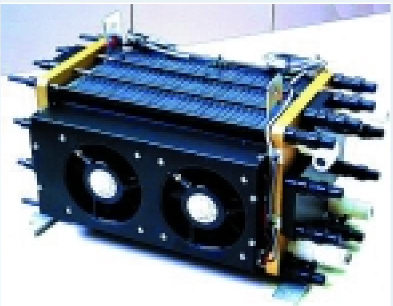
Today, hydrogen is used mainly in the petrochemical industry and in industry as a feedstock, but not as an energy carrier. The introduction of hydrogen as an energy carrier requires development of the application (end-use) as well as the supply side. The supply of hydrogen incorporates production facilities and the infrastructure for transport & distribution and storage (if required). This whole technical infrastructure from production to end-use has to be created simultaneously. Such a development will require high investments.



Production to end-use chain for hydrogen for fuel cells.

Demonstrations

There are no current activities that focus specifically on the ‘production to end use’ chain. A number of demonstrations, however, focus on elements of this chain. Large-scale production of hydrogen from fossil fuels is an industrial practice and on a small scale it is being demonstrated for transport chains (see below). An example of a hydrogen fuelled fuel cell demonstration is the co-operation of the Hamburg electricity company HEW and gas company HGW who are operating and demonstrating two phosphoric acid fuel cells (PAFC) in an urban environment [7]. The fuel cells deliver electricity and heat to the Lyserstrasse in Hamburg Bahrenfeld. The first system is natural gas fuelled. The second operates on hydrogen. The hydrogen is trucked-in as liquid hydrogen. The latter project focuses on demonstrating hydrogen in an actual urban environment.



This will only come about if strong drivers exist for introducing hydrogen as an energy carrier. Very dissimilar drivers can be identified for introducing such an infrastructure:

- The highly efficient and ultra-clean way in which hydrogen can be used to produce electricity in PEM fuel cells;
- The potential of hydrogen as a clean transport fuel;
- Use of hydrogen to store energy from intermittent renewable sources;
- Application as energy carrier for the global transport of renewable energy;
- Use of hydrogen as intermediate energy carrier for efficient and CO_2-free use of fossil fuels.

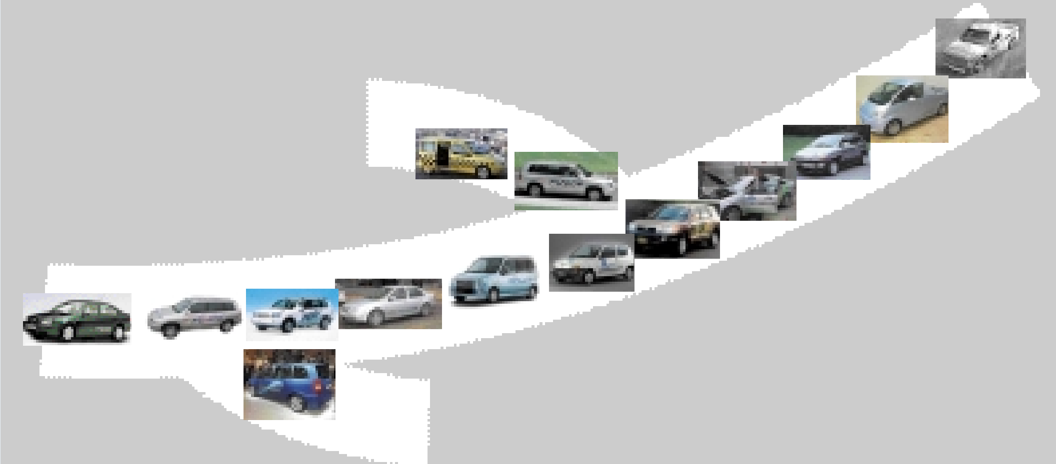
These drivers will be reviewed separately below.

Hydrogen: the fuel for fuel cells

The highest small-scale conversion efficiency from gas to electricity can be achieved by using hydrogen as a fuel for (PEM) fuel cells. However, hydrogen is not available as a primary fuel: it has to be produced from another primary source of energy. Using hydrogen from renewable sources has its own rationale and will be discussed below. Alternatively, hydrogen for fuel cells can be obtained by production from fossil fuels by means of reforming technology.

Current activities

Transport on hydrogen has a long history of interest. Already in the 1970's several automobile manufacturers including General Motors and BMW worked on hydrogen as a transportation fuel. Since the beginning 1990's hydrogen is in the focus of attention due to the developments achieved in the area of the fuel cell. Protagonist is the Canadian developer Ballard. Prototype hydrogen vehicles based on standard type cars have been introduced by a large number of automobile producers: Daimler-Chrysler, GM, Volkswagen, Mazda, Honda and Ford. Almost all other car manufacturers participate in fuel cell projects.



Test models of fuel cell vehicles presented in 2001 by the major car manufacturers

The lack of a refuelling infrastructure limits the scope of projects with passenger cars. One of the objectives of the California Fuel Cell Partnership, an alliance of automobile industries, oil companies and governmental organisations, is to demonstrate the viability of alternative fuelling infrastructure for fuel cell vehicles. The most important demonstration programmes currently focus on busses. In several places, e.g. Vancouver, Chicago and Palm Springs, operating experience has been collected using hydrogen busses. A very large project, which is in the initial phase, is the European CUTE project (Clean Urban Transport for Europe). In this project 30 busses will be operated in 10 European cities (3 busses each). The busses will be delivered by Daimler-Chrysler using Ballard fuel cell technology.

In the product to end-use chain illustrated here, the efficiency of the chain may be higher than for the direct conversion (natural gas → electricity) because of the high efficiency of the fuel cell. The high efficiency of the final-conversion is thus the driver for the system. By producing hydrogen in a centralised plant for a large number of fuel cells the cost of hydrogen decreases. If the scale of hydrogen production becomes too large, the infrastructure required for hydrogen distribution becomes a limitation.

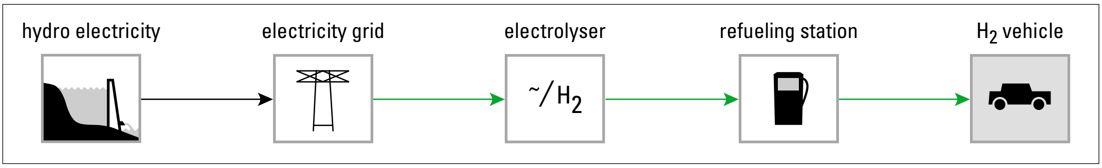
Driving on hydrogen

Although there is a lot to be gained in terms of emission reduction by improving the current gasoline and diesel engines and introducing natural gas vehicles (section 3), increasingly higher standards are closing the gap for fuel cell vehicles. In particular the complete elimination of local emissions is a strong driver for hydrogen vehicles. Main obstacles at present are the cost of the fuel cell stack and above all the storage requirements. The storage issue is a larger problem with small compact cars than with trucks or busses. The most viable introduction route therefore is by using vans and/or busses, which can use gaseous hydrogen storage tanks.

Creating the infrastructure for refuelling is another issue. Apart from the less stringent requirements with respect to the volume of the hydrogen storage, vans and busses in many cases operate in a fleet, making it easier to refuel them from one central point. Hydrogen for the refuelling stations can be produced from fossil fuels or using electrolysis. The first option is interesting to demonstrate because fossil fuels are expected to be the primary energy source from which hydrogen will be produced for large-scale introduction as a vehicle fuel. The merit of the electrolysis route lies in the role it will play in integrating renewable energy into the system.

Storing renewable energy using hydrogen

Most renewable sources deliver energy in the form of electricity: photovoltaic systems, hydro, wind



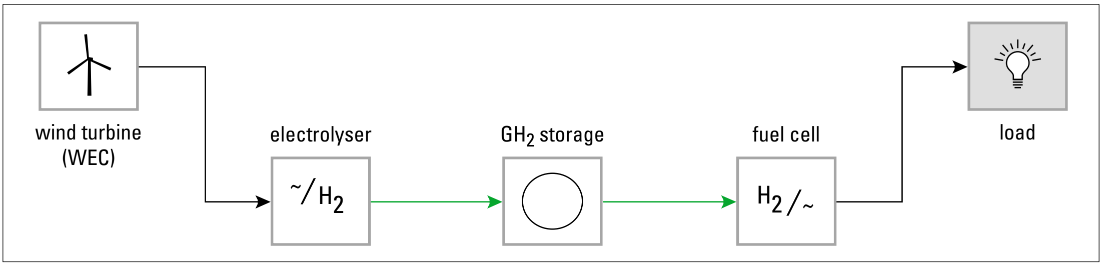
An emission free route for transportation

Current activities

Storage of renewable energy has been demonstrated in a number of cases [8]. The most extensive of these projects is the solar-hydrogen project in Bavaria, Germany. The Solar-Wasserstoff-Bayern (SWB) hydrogen project, which ran from 1986 to 1999, aimed at testing, on an industrial demonstration scale, major technologies of the hydrogen cycle utilising electric power from photovoltaic solar energy. Among others, the facility includes photovoltaic solar generators, water electrolysers, catalytic and advanced conventional heating boilers, a catalytically heated absorption-type refrigeration unit, fuel cell plants for stationary and mobile application, an automated liquid hydrogen (LH_2) filling station for test vehicles, and a gaseous hydrogen (GH_2) filling station. Other projects in which renewables/hydrogen systems are demonstrated include the Phoebus project, an autonomous solar electricity supply to the central library building of the Research Centre Jülich, and the Schatz solar hydrogen project.
An interesting project, that represents a new phase in demonstration of the potential of renewables/hydrogen systems, is a Norsk Hydro project which aims at using wind turbines and a hydrogen system to supply energy to an island off the Norwegian coast [9]. Very favourable wind conditions and the remote location are two factors that could make this option viable. Hydrogen produced by electrolysis from the surplus wind energy will be used to supply electricity when wind resources are low and to fuel a number of vans.

turbines. Electricity is a suitable energy carrier, because it can be used directly in many applications (e.g. for television or communication equipment) while it can be converted easily into other required forms of energy for final use such as heat or mechanical work.

Electricity has one major drawback: it is difficult to store while renewable sources from which it is generated (solar energy, wind power) are intermittently available. For storing small quantities of



Storage of renewable energy in a stand-alone renewable power system

Current activities

Two large programmes have been carried out which aim at assessing the potential of hydrogen as an intermediate carrier for renewable energy. The first is the Euro-Quebec Hydro Hydrogen Pilot Project [10]. This project has evaluated the possibilities to transport hydro-energy from Quebec (Canada) to Europe in the form of hydrogen. Focus has been technical (e.g. liquefaction and transport of LH_2) as well as economical and regulatory.

Vision of hydrogen economy based on renewables. New Energy and Industrial Technology Development Organization (NEDO), Japan.

The second is the Japanese WE-Net program. This program aims at the construction of a world wide energy network (WE-NET) for supply, transportation and utilisation of renewable energy using hydrogen [NEDO; 11]. The program extends over 28 years (1993 to 2020) and aims at development of technologies for all aspects: efficient production of hydrogen (electrolysis), liquefaction, transport, storage and utilisation (fuel cells, H_2/turbine) electricity the use of batteries, flywheels or supercapacitors can be considered. To store large amounts of energy, the required energy densities can only be achieved by converting the electricity into some form of chemical energy. The most basic manner in which electricity can be converted into chemical energy is by producing hydrogen through electrolysis. Hydrogen can therefore be used to store renewable energy when supply exceeds demand. When the direct supply of renewable energy is insufficient, the stored hydrogen can be used to produce electricity.

The role of hydrogen for large-scale import of renewable energy

The potential of renewable energy in Europe is limited. To reach for example a 50% share of renewables, Europe will have to import renewable energy from other parts of the world, with the additional reason that renewable energy is available at much lower costs elsewhere. If the source of renewable energy is biomass, hydrogen is not the preferred energy carrier: bio-fuels or methanol will be much easier to transport. However, in many cases (solar, wind, hydro) renewable energy will be available in the form of electricity. The choice is between transport as electricity or in the form of chemical energy. In the latter case, hydrogen is again the most logical choice.

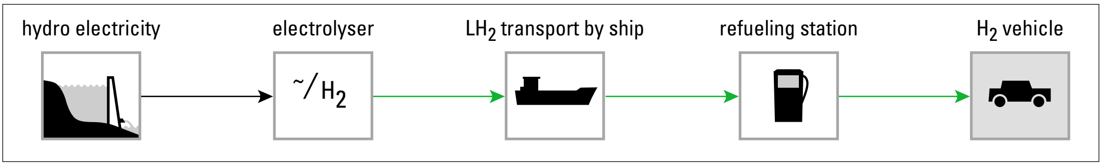
Hydrogen and CO_2 capture and sequestration

Reduction of CO_2 emissions is achieved by increasing the efficiency of the energy system and by enlarging the share of renewable energy. However, to achieve the emission reductions agreed upon as a consequence of the Kyoto Protocol, capture and sequestration of CO_2 may probably play a role as well.

Hydrogen enters into the picture through the ‘equation’:

fossil fuels - CO_2 = hydrogen

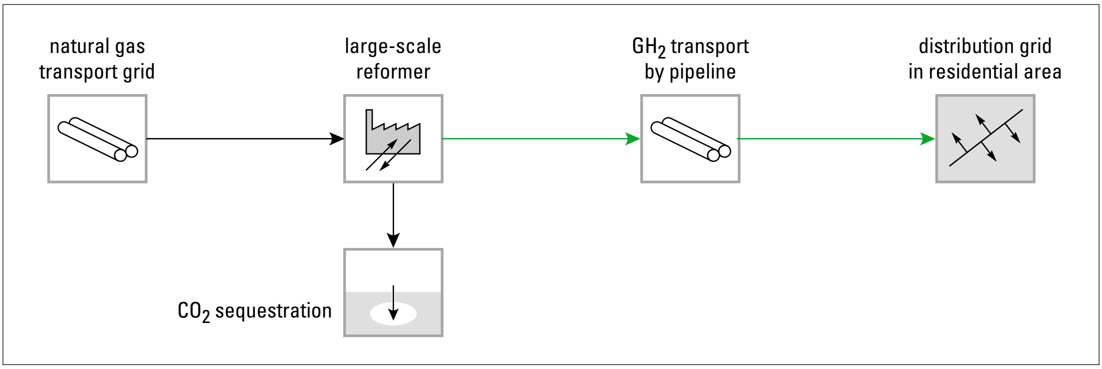
CO_2 capture is most cost-efficient if it takes place where sizeable concentrated CO_2 flows occur. A logical starting point for CO_2 capture can therefore be found in industrial processes where large quantities of CO_2 - rich gas are produced (e.g. in hydrogen production for the petrochemical industry) and in power plants. CO_2 separation from the flue gas flow of a power plant (post-combustion) is possible using current technologies but the efficiency of the power plant decreases by 10 to 20% depending on the primary fuel (natural gas, coal). The energy penalty for CO_2 capture can be reduced considerably by producing syngas and removal of CO_2 from the syngas flow, where it is available in a much higher concentration than in the flue gas. The end product of this pre-combustion



Long distance transport of hydro-based energy in the form of LH_2 by bulk tanker

Current activities

There are no integrated systems demonstrations in the area of hydrogen production with CO_2 capture and sequestration. There is however a number of ongoing pilot projects on CO_2 sequestration [12]. Statoil (Norway) is sequestering vast amounts of CO_2 in an 800 meters deep underseas sandstone formation. The CO_2 is separated from the natural gas produced in the North Sea. The Sleiper Vest project is in operation for more than 3 years. Other pilot projects, which are underway or being planned are aimed at enhanced oil recovery (EOR) by injecting CO_2. Both Pan Canadian Resources and BP-Amoco are preparing EOR projects. Pilot plants for injecting CO_2 to recover methane from coal beds (coal bed methane production) are underway in New Mexico (USA) and in the Alberta Basin (Canada). Technologies for more efficient hydrogen production with CO_2 capture are part of the Carbon Capture Project (CCP) co-ordinated by the American Department of Energy (DoE) in which all major oil companies participate.



The role of hydrogen in CO_2 *sequestration*

route is a hydrogen-rich gas. This gas (or pure hydrogen that can be produced from it) can subsequently be used to generate electricity in a turbine or fuel cell.

3.3 End-use technologies

3.3.1 Final energy demand

The starting point for an overview of the end-use technology should of course be the final energy demand. In this chapter only the required amount of energy is considered. A more detailed analysis should also look into aspects related to quality and time of demand (variation in demand over the day, over the year) etc. The analysis is based on the final energy demand in The Netherlands. It would however not be very different if the European energy demand would be used as a starting point. In Figure 5 the total energy demand for The Netherlands is shown for the different sectors [13,14]. The shaded bars indicate the final energy consumption in 1990. The open bars are extrapolated values for 2050 based on scenarios from the Dutch Central Planning Bureau (CPB) in co-operation with RIVM and ECN [13].

The final energy use differs from the use of primary energy as a result of the conversion efficiency. In the distribution of final use industry is dominant, while this is not as strong as for primary energy consumption. In particular, the non-energetic use of oil and gas in industry and the low efficiency of other sectors (e.g. transport) result in a more even distribution of primary energy use compared with final energy use[1]. If the non-energetic use of oil and gas is not considered[2] energy demand consists of the three following ‘energy functions’:

- Heat;
- Electricity;
- Transport.

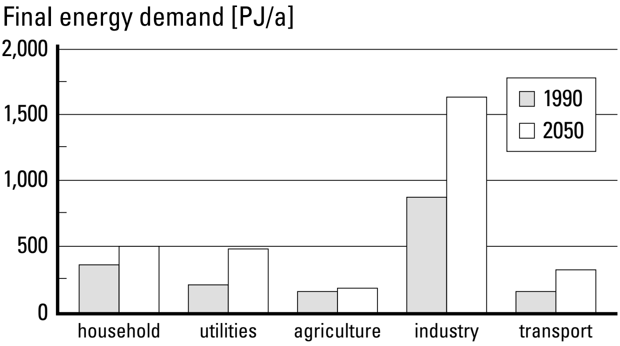


Figure 5: Final energy consumption for The Netherlands in 1990 and 2050 [13]

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[1] Although primary energy use is a better indicator for the 'importance' of a sector, the amount of final energy use is the relevant figure for evaluating end-use technologies.

[2] As there is no final conversion, there is no role for an end-use technology.

Electricity and heat are the energy functions for stationary energy supply. Transportation is the energy function for mobile applications. Both will be considered separately.

3.3.1.1 Final energy demand for stationary applications

End-use for stationary applications excluding non-energetic use of gas and oil is shown in Figure 6. Again the energy demand for 1990 and for 2050 is shown [13]. The energy demand in the form of heat and electricity are shown separately. The ratio between the heat demand and electricity demand for example in households in 1990 was equal to 5 (see Figure 6). The projected energy consumption in households in 2050 is characterised mainly by a large increase in electricity consumption (currently increasing by 3% each year) and a reduction of the heat demand for space heating. Hot water (tap water) demand grows much slower. Nonetheless, the data in figure 6 show that heat demand in households and in other sectors is expected to exceed electricity demand. This is an important observation because it indicates that reducing emissions and primary energy use in households and other sectors (excluding transport) will not only require efficient production of electricity but also more efficient ways of providing heat.

3.3.1.2 Final energy demand for transport applications

The final energy demand for transport in The Netherlands and the projections for 2050 are shown in Figure 7. The most important feature in the diagram is the dominance of final energy demand for passenger vehicles in the current situation and in the projection for 2050.

3.3.2 End-use technologies for stationary applications

3.3.2.1 End-use technologies for methane and natural gas

Current natural gas utilisation technologies in The Netherlands include:

- gas fired boiler power plants (efficiency 40…45%)
- steam and gas (STAG) power plants units (55…60%)
- industrial steam boilers (approx. 95%)
- back pressure turbines for combined heat and power (efficiency depends heavily on heat-to-power ratio)
- natural gas (domestic) heaters (85…95%)

Some of the more recent developments for stationary applications include gas engines for combined heat and power generation, micro gas turbines and fuel cell systems.

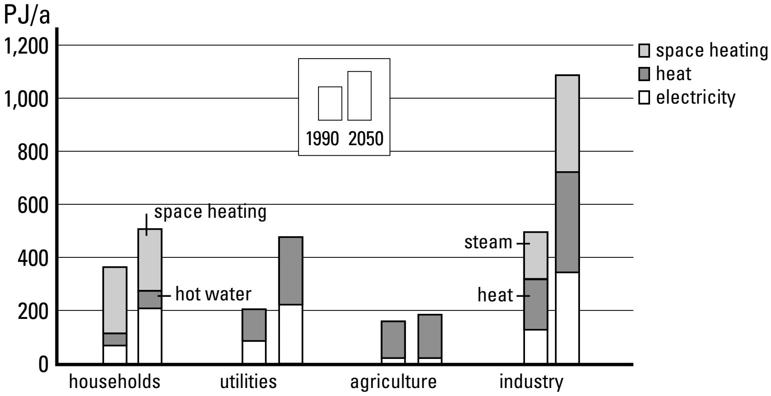

Figure 6: End-use stationary energy supply (excluding non-energetic use) in The Netherlands.

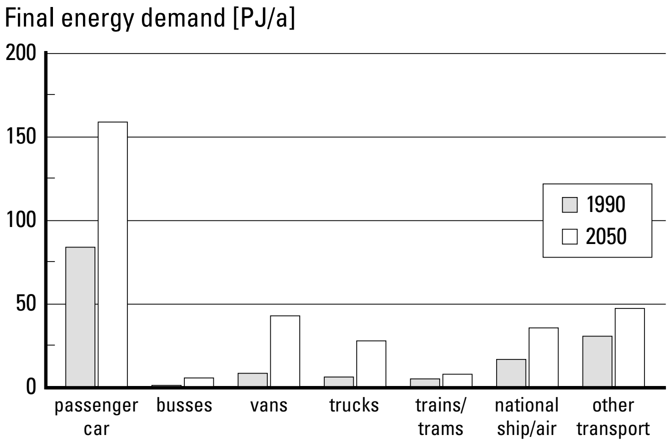

Figure 7: End-use energy demand for transport application in The Netherlands.

Gas engines

Internal combustion engines (ICE) are a long established technology for mobile applications. For stationary applications internal combustion engines running on natural gas can be used as combined heat and power units (CHP). Currently 4000 gas engines of this type, with electrical power ranging from 200 to 1000 kW, are installed in The Netherlands. The main applications are in agriculture or horticulture, utility and residential buildings and swimming pools. For mobile applications the costs of such engines have been reduced very substantially by the enormous series which are produced. However, the typical lifetime for which these engines are developed is 5000 hours while a much longer lifetime is required for stationary applications. As a result of the design modification to enhance the lifetime the costs for stationary internal combustion engines become much higher than for mobile applications. The most important advantage of the gas engine as a CHP unit is the maturity of the technology. The electrical efficiency which can be achieved using a gas engine depends strongly on the capacity: for engine sizes < 5kW the electrical efficiencies range between 20 and 25%. This increases to 35…40% for the very large engines (2 MW). Heat can be recovered directly from the cooling system of the engine leading to a high total efficiency for the CHP systems (85…95 %). Disadvantages of the gas engine, apart from the limited efficiency of the smaller engines, include the environmental impact: emissions and noise production. Two types of emissions are particularly relevant. NO_x emissions are high (80 – 450 g/GJ [15]). Although NO_x reduction technologies are available, there is a cost and efficiency penalty involved with their application. The emission of methane is a problem because methane is a known greenhouse gas[3]. Typically 1…2% of the methane in a gas engine will not be converted and is emitted to the atmosphere.

Micro-turbines

Fairly recent is the development of micro-gas turbines[4]. Before 1990 gas turbine power ranged from approximately 5 to 100 MW. Gas turbine technology for stationary applications has profited immensely from the aerospace application of gas turbines as jet engines and the vast development that was achieved in this area. Initially gas turbines for stationary application were modified gas turbines from the aerospace industry (‘aeroderivatives’). In a later stage gas turbines were developed specifically for stationary applications. More strict emission regulations favour the use of gas turbines over reciprocating engines. The continuous combustion process and high air factor are beneficial in reducing emissions. The high volume production of turbochargers for the automobile industry has made available a cheap range of rotating equipment in the specific 10-100 kW

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[3] The Global Warming Potential (GWP) of methane over a 100-year period is 21-fold the GWP of CO_2

[4] In general the term ‘micro turbine’ refers to the 25-500 kW range. The qualification ‘mini turbine’ is used for turbines ranging between 500 kW to 5 MW capacity.

TABLE 1. *Major fuel cell types.*

Type of fuel cell (FC)	Alkaline (AFC)	Proton Exchange Membrane (PEMFC)	Phosphoric Acid (PAFC)	Molten Carbonate (MCFC)	Solid Oxide (SOFC)
operating temperature	60 - 80 °C	60 – 90 °C	190 °C	600-700 °C	800-1000 °C
electrical efficiency[1]	50 – 60%	50 – 60%	40 - 50%	50 – 60%	50 –60%
temperature of waste heat	Low	Low	Medium	High	very high
requirement precious metal (e.g. Pt) catalyst	Not strictly necessary	Yes	Yes	No	No
Directly used fuel	H_2	H_2	H_2	H_2, CO, CH_4 (natural gas)	H_2, CO, CH_4 (natural gas)
Requires near-complete removal of	S, CO, CO_2	S, CO, NH_3	S, (CO)	S	S

[1] The electrical efficiency depends on several conditions:
- the applied fuel (reformed natural gas, syngas, pure hydrogen)
- the applied oxidant (air, pure oxygen)
- fuel utilisation factor (= fraction of the fuel actually converted in the FC)
- use of waste heat for electricity generation or reforming

range. Companies such as Capstone and AlliedSignal have successfully adapted these components to develop micro-gas turbines. The use of recuperators has significantly increased the efficiency of the micro-turbine cycle. The efficiency of a simple cycle (without recuperator) for a 100 kW gas turbine ranges from 15 to 20%. Using a recuperator increases the efficiency to 30% and higher. Future efficiency improvements are possible, for example by developing new ceramic materials that allow for higher temperatures at the turbine inlet.

Fuel cells

Fuel cell technology is one of the technologies that could strongly influence the infrastructure. An overview of major fuel cell types is presented in Box 1 and in Table 1.

For natural gas two separate types of systems should be distinguished. Low temperature fuel cells (PAFC and PEMFC) are capable of converting directly only hydrogen. Natural gas has to be converted to hydrogen first by reforming. Because of the sensitivity of the low temperature fuel cells to CO (in particular the PEMFC), the complexity of the fuel processing step from natural gas to H_2 gives rise to considerable losses and reduces the efficiency of the overall process. High temperature fuel cells do not suffer this drawback because of their ability to convert CO and CH_4.

BOX 1: General characteristics of different types of fuel cells

Fuel cells convert fuel into electricity and heat in a direct electrochemical reaction. There is a number of different types of fuel cells with widely varying characteristics. Therefore, first an overview will be given of the general characteristics of the different fuel cell types:

- Alkaline fuel cells **(AFC)** use concentrated KOH as the electrolyte. The matrix in which the electrolyte is retained is usually asbestos. Electrocatalysts vary (Ni, Ag, metal oxides, and noble metals) and the operating temperature ranges from 120 to 250 °C. Alkaline fuel cells have been used in the space program (Apollo and Space Shuttle) since the 1960's. The efficiency of the AFC is the highest of all types of fuel cells. However, the AFC is intolerant to CO_2 in either fuel or oxidant flow. This makes it an unlikely candidate for large-scale stationary application.
- Proton exchange membrane fuel cells **(PEMFC)** use a polymer membrane as the electrolyte which acts as a proton conductor. The catalyst is typically platinum with loadings about 0.2…0.4 mg/cm^2. If the hydrogen feed contains CO, Pt-Ru alloys are an alternative for platinum. Operating temperature is typically between 60 and 80 °C and the operating pressure between 1 and 3 bar. The most important characteristic of the PEMFC is its suitability for mobile applications. As a result, interest in the development exceeds that of all other types of fuel cells. The PEMFC is capable of converting only hydrogen directly in the cell. Natural gas fuelled systems therefore require a fuel processing unit which converts the natural gas into a hydrogen rich mixture. The fuel cell is very sensitive to CO, which currently has to be reduced to approximately 10 ppm in the fuel processor to prevent poisoning.
- Phosphoric acid fuel cells **(PAFC),** use concentrated phosphoric acid (~100%) as the electrolyte. The acid is retained in a matrix used (usually SiC). The electro-catalyst in both the anode and cathode is platinum on carbon black. The operating temperature lies between 150-220 °C. For stationary applications the PAFC has a number of distinct advantages over the PEMFC. The tolerance to CO is much higher (1…2%) and the operating temperature is sufficiently high to produce steam instead of hot water.
- In molten carbonate fuel cells **(MCFC)** the electrolyte is composed of a mixture of alkali (Li, Na, K) carbonates. The state-of-the-art matrix that holds the electrolyte is made of LiAlO2. Operating temperatures are between 600-700 °C where the carbonates form a highly conductive molten salt, with carbonate ions providing ionic conduction. At such high operating temperatures non-noble metals (e.g. Ni) have sufficient catalytic activity. Furthermore, the high temperature makes it possible to convert other fuel component (CO, CH_4) in the fuel cell. Using natural gas directly as a fuel eliminates the need for an external reforming and can improve the heat management in the fuel cell. The main problem is the extreme corrosiveness of the electrolyte that seriously limits lifetime of the stacks.
- Solid oxide fuel cells use a solid, ceramic electrolyte material. Commonly used in the state-of-the-art fuel cells is Y2O3-stabilized ZrO2 (YSZ). The cell operates at 900-1000 °C because the electrolyte is a good conductor of oxygen ions at this temperature. In contrast to the other types of fuel cells, which all consist of a large number of flat cells which are built into a stack to achieve the required power, the state-of-the-art SOFC is of the tubular type. One of the main problems of the SOFC is the mechanical integrity of the stack at high temperature. Matching the thermal expansion coefficients of the different components and sealing are the major issues. These problems are much more difficult to solve for the flat-plate type of cell than for the tubular which Siemens-Westinghouse, market leader in SOFC's, has chosen to develop. Another approach followed by other developers is to try to reduce the working temperature by developing materials and stacks which have good electrochemical properties at much lower temperatures (500-700 °C). Operating at this temperature is expected to enable the use of flat-plate cells, for which a considerably higher efficiency is expected [Bossel, 1990].

- **Low temperature fuel cell systems**

The PAFC is currently the furthest developed fuel cell system. Electrical efficiencies for low temperature fuel cell systems (natural gas to electricity) range between 35 and 45%. The 40…45% efficiency range is achieved currently by a series of commercial units manufactured by the company ONSI in the USA. Approximately 150 PAFC units have been sold to date by ONSI. However, a very significant improvement of the efficiency of this system is not foreseen and the investment costs are not expected to diminish much below the current level. The PAFC is therefore not expected to become a competitor for widespread application in power generation.

The potential for the PEMFC lies in its use for transport application. For the stationary applications cost reduction becomes possible if this type of fuel cell finds broad use for transport applications and is expected to make the technology competitive. Efficiencies for natural gas fuelled systems are not expected to exceed the 35…45% range. The predicted efficiency of PEMFC systems on natural gas is lower than for PAFC systems because the fuel processing in the latter is simpler (CO tolerance). In addition a higher degree of heat integration between the PAFC and the fuel processor is possible due to the higher temperature at which the PAFC operates. Currently predicted efficiencies for PEMFC on natural gas are approximately 35%. But improvements in both fuel cell and fuel processing technologies are expected to increase this efficiency.

- **High temperature fuel cell systems**

Higher efficiencies are attainable with high temperature fuel cells. This is mainly due to the elimination of the fuel processing unit or, if natural gas is reformed directly prior to the fuel cell, the possibility to utilise heat from the fuel cell for the reforming process. Small-scale systems, for example CHP systems in the range 110 kW, operate at atmospheric conditions with a typical projected efficiency of 45%. Larger scale systems (>100kW) seem very suitable for integration with gas turbines. In these systems, so called 'hybrid fuel cell systems', a fuel cell and a gas turbine are combined. The heat that is produced in the fuel cell and the unspent fuel from the fuel cell are utilised in the gas turbine cycle to produce power. Projected efficiencies for these systems are 70% and even higher [16]. The SOFC seems to be the most likely candidate for hybrid systems [17], although studies on hybrid MCFC systems have predicted similar efficiencies [18]. Siemens-Westinghouse expects to achieve 70% efficiency with the pressurised 1 MW SOFC system they are currently developing.

3.3.2.2 End-use technologies for hydrogen

The most important characteristic of hydrogen as a fuel lies in its end-use. The absence of emissions and the high attainable conversion efficiency are the two most important reasons for considering the use of hydrogen as an energy carrier. In particular for stationary energy systems the efficiency of the final conversion is an important quality of the technology. Therefore the hydrogen internal combustion engine is not considered here (see section 3.2.3). The discussion focuses on two hydrogen technologies with zero emissions and a high efficiency: fuel cells and the H_2/O_2 turbine.

Fuel cells

The low temperature fuel cell, in particular the PEM fuel cell, seems the most logical choice for hydrogen conversion. A hydrogen fuelled fuel cell system is both simple and efficient. The efficiency of a fuel cell is proportional to:

- the cell voltage;
- the fuel utilisation.

Fuel cells are typically operated at a cell voltage ranging between 0.6 and 0.8 V. For pure hydrogen the cell voltage will lie on the upper end of this range, because the losses which occur in the fuel cell and which limit the cell voltage will be lowest. This is partly due to the higher hydrogen concentration in the fuel compared with reformed natural gas and partly to the fact that the hydrogen concentration does not decrease along the cell as is the case in a natural gas fuelled system. As a result of these declining fuel concentrations the fuel utilisation (the converted fraction of the fuel) in natural gas fuelled cells is limited to 80…85%. When hydrogen is used the fuel utilisation can be increased to (almost) 100%. The combined effect of a higher cell voltage and complete fuel utilisation leads to a 20…30% higher efficiency for fuel cells operating on hydrogen.

In principle the hydrogen based fuel cell system is very simple. It consists of the fuel cell, a blower for the air supply to the cell, control systems for air and fuel and a converter/controller for transforming DC electricity to AC. The heating value of the fuel that is not converted into electricity can be recovered in the form of heat (60 - 80 °C). Taking into account both its inherent characteristics and those of competing technologies, the hydrogen fed fuel cell will mainly find its application as a *decentralised* power generator.

H_2/O_2 turbines

A fuel cell operating on hydrogen is nearly completely modular and is therefore especially suited for decentralised power generation. For centralised electricity generation the H_2/O_2 turbine is an option which can reach similar efficiencies. In Japan the development of such a turbine is part of the WE-Net program (section 3.2.3). Turbines operating on H_2/air have two disadvantages: limited efficiency and NO_x production. By using an H_2/O_2 cycle an efficiency above 60% is attainable [19] while at the same time the process is free of any emissions. The turbine is essentially a steam turbine. Except for the first stages, the system can be based on established steam turbine technology. The very high operating temperatures make this technology effective only for large-scale power plants [20]. The main technical challenges are the development of a combustor for H_2 and O_2 at very high temperatures and the development of turbine blades for the first stage at 1700 °C.

3.3.3 End-use technologies for transport application

3.3.3.1 Technologies based on current transport fuels and their future potential

Widespread use of fuel cell vehicles will lead to very substantial reductions of emissions. (See Table 2; section 3.4.1). However, the fuel cell is not the only technology that can be put into action to reach this goal. In general the following future drive-train options exist:

- Improved internal combustion engines (ICE)
- Electrical vehicles with battery and internal combustion engine (ICE hybrid)
- Natural gas vehicles using an internal combustion engine (NGV)
- Fuel cell vehicles, which can be either on-board reforming (logistic fuels, methanol) or hydrogen fuelled.

Besides systems for natural gas and hydrogen, end-use technologies for logistic fuels (gasoline, diesel) are discussed because these are likely to remain the reference system for a long time. The methanol route falls outside the scope of this chapter. For the other fuels the end-use technologies will be discussed. Whether the fuels are from mineral origin or derived from biomass (bio-fuels) is not relevant for the end-use technology.

The reference for either natural gas or hydrogen fuelled vehicles are vehicles using gasoline or diesel. Considerable advances in engine technology are foreseen for both gasoline and diesel engines. Technical improvements for gasoline engines with an impact on efficiency include direct injection and valve timing. Further reduction of NO_x emissions can be achieved for example by improving catalytic NO_x converters.

The largest improvements, both in efficiency and in reduction of emissions, can be obtained by using the hybrid concept. In this concept the drive for the automobile is electrical. The electricity is delivered by a battery system that is charged by the operation of the engine until it is fully loaded. This type of drive train has several advantages:

- the engine operates at its optimum working point (efficiency, emissions);
- there is no idle-operation: the engine is turned off as soon as the battery is charged;
- the energy which is released by breaking can be recovered.

Technical improvements in diesel engines are expected to keep the diesel engine ahead of the gasoline engine in terms of efficiency. The diesel engine has the potential to conquer a larger share of the market at the expense of the gasoline engine [21]. Technical improvements include direct injection to improve efficiency and application of particle filters, catalysts for NO_x removal, and exhaust gas recycle for emission reduction. Many ‘well-to-wheel’ studies indicate that the hybrid diesel engine is the main competitor for alternative drives when it comes to drive-cycle efficiency.

Reforming gasoline on-board to produce hydrogen for a fuel cell is an option as well. Reforming logistic fuels such as gasoline and diesel is however not straightforward. The low H/C ratio and corresponding tendency to form carbon and the high temperature required to convert the components in the fuel to syngas make the development of a compact, light and efficient fuel processing unit for logistic fuels a difficult task. Furthermore, the relatively high CO/H_2 ratio of the syngas leads to a larger number of steps for purifying the hydrogen to the quality required by the fuel cell. As a result efficiency and emission reduction are limited [22]. An extensive MIT study [23] states that improved internal combustion engine-hybrid concepts are expected to outperform vehicles with on-board reforming of logistic fuels on all counts. The attractiveness of the concept of on-board reforming seems to lie mainly in the possible role in a transition toward fuel cells for automotive applications and relies on a faster development of the fuel cell than of the infrastructure.

3.3.3.2 End-use technologies for methane and natural gas

Natural gas is in itself a cleaner fuel than gasoline and diesel. The substitution of logistic fuels by natural gas with a much lower carbon ratio (kg carbon/MJ) already leads to a substantial reduction of CO_2 emissions. Furthermore the use of a gaseous fuel which easily achieves complete mixing, strongly reduces the emissions of non-methane organic components. A two-year demonstration program in California, CleanFleet [24], showed that in particular the ozone forming potential (OFP) of the exhaust of NGV was 90-95% lower than that of gasoline exhaust. NO_x levels in the exhaust of gas engines are not automatically lower than for gasoline or diesel, although appropriate measures are possible to reduce the NO_x.

A complicating factor is the substantial trade-off between emissions and efficiency. Current technology, with operation near stochiometric point, can easily meet United States ULEV standards and Tier 2 standards However, near-stoichiometric operation is in conflict with the requirements for a higher efficiency. Potential improvements for gas engines for vehicles have been evaluated in a DoE project [25]. Operating at near-stoichiometric conditions limits the increase in efficiency relative to (current) gasoline engines to less than 10%. Much larger efficiency advantages are deemed possible using lean-burn technology and high compression ratios. Using lean burn spark ignition can increase the efficiency up to 20% above gasoline engines. Even higher improvements can be obtained by lean burn compression ignition (30-35%).

3.3.3.3 End-use technologies for hydrogen

Hydrogen for fuel cells

Converting fuel to power on a kW scale with an efficiency reaching 50 to 60% is a unique characteristic of the hydrogen fuel cell. This represents an efficiency that is more than double the achievable efficiency with state-of-the-art internal combustion engines (based on the total driving cycle). This type of performance can be achieved by the Proton Exchange Membrane Fuel cell (PEMFC). The other two qualities that make this type the ideal fuel cell for transport applications are the high energy density and the low operating temperature. The high conversion efficiency of fuel cells on hydrogen is counterbalanced by two disadvantages of the fuel:

(a) the efficiency of the full cycle (production of hydrogen to utilisation in the vehicle);

(b) the low energy density per unit volume of hydrogen makes it difficult to store the quantity of fuel required for a reasonable driving range on-board.

ad a) Hydrogen can be produced either from fossil fuels or from renewables. The conversion efficiency for the production of hydrogen from a primary fossil energy source (natural gas, coal) is limited. Kolke states that it costs 30% more energy to deliver hydrogen to the vehicle than gasoline [26]. Therefore the efficiency of hydrogen utilisation on-board should be at least 30% higher than in an advanced gasoline engine. Production of hydrogen using renewables is not an option in the current energy system: renewable energy can be used much more effectively by direct replacement of fossil fuels used in electricity production.

ad b) Storage of hydrogen aboard a vehicle can be achieved using state-of-the-art technology only in two manners: in the form of liquid hydrogen (LH_2) or in the form of compressed, gaseous hydrogen (GH_2).

- Liquid hydrogen is stored at extremely low temperature (-253 °C at 2 bar) and has a relatively high per weight and volumetric storage density, comparable to gasoline. However, much energy is required to liquefy hydrogen. The energy consumption in the liquefaction corresponds to approximately 1/3 of the heating value of the hydrogen[5] [27]. A second disadvantage of LH_2 storage on board is that heat leaks from the environment cause slow evaporation of the liquid hydrogen. The 'boil-off' is in the order of magnitude of 1% of the maximum tank capacity per day.
- Compressed hydrogen at 300 bar is delivered in steel cylinders. However, the weight penalty for using steel cylinders is too high for transport applications. This has led to development of new types of storage vessels for hydrogen: for example fibre-wrapped aluminium vessels and composite materials. In particular this last type has the potential to strongly reduce the weight and volume of the storage. Storage systems are being developed for even higher pressures (700 bar).

Other techniques for hydrogen storage which are under development, such as storage in metal hydrides and nano-tubes, are not realistic options today but may become important in the future.

Hydrogen for combustion engines

The use of hydrogen as a fuel for internal combustion engines potentially increases the efficiency of these engines (compared to gasoline) by an average of 20% [28]. The specific power of an internal combustion engine on gaseous hydrogen however decreases by up to 40% due to the lower heating value of the stoichiometric mixture of hydrogen and air compared to gasoline/air mixtures. Emissions of hydrogen fuelled internal combustion engines can be much lower than for gasoline. The emissions of NO_x in hydrogen engines are typically one order of magnitude smaller than emissions from comparable gasoline engines [28]. The NO_x emissions can be reduced by using excess air or by using techniques such as water injection or exhaust gas recycle.

Pre-ignition and back-firing are important engine design issues which need to be eliminated in the currently available spark-ignition engines to obtain an efficient and trouble-free engine running on hydrogen [29]. The use of liquid hydrogen as a fuel alleviates the problems of engine design. Compression ignition (CI) engines show more promise [30] because of the higher efficiencies and better possibilities for NO_x control. The efficiency of the hydrogen internal combustion engines however will not come close to the efficiency expected for fuel cells on hydrogen. This is true even if substantial improvements can be obtained from the specific development of internal combustion engines for hydrogen. Using internal combustion engines for hydrogen only aggravates the real issues for transport on hydrogen: storage requirements and the efficiency of the full cycle (production of hydrogen to utilisation in the vehicle).

3.4 Policy drivers

3.4.1 Objectives for the energy policy

The technical drivers for (bio)hydrogen and (bio)methane discussed in the previous section are important considerations in the selection of energy carriers and conversion routes. How easy can hydrogen or natural gas be converted into electricity, what is the expected efficiency of the conversion and how far can emissions be reduced? However, the choice of energy carriers is also determined by non-technical factors. In the strongly simplified treatment in this section, these will be indicated as the 'policy drivers'. The approach is to identify the main objectives in the energy policy. Subsequently, the consequences of making each of these objectives leading in the energy policy for the energy carriers are considered. By assessing whether the energy carrier fits in each of those strategies its 'robustness' can be determined.

First the general aspects on which the energy policy focuses will be reviewed. Although the European and Dutch energy policy may be different in its nuances, on the level of the higher objectives these policies are similar and converging as a result of the growing European influence on national energy policy.

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[5] If the primary energy use is considered, taking into account the efficiency of electricity production, the ratio becomes even worse.

Efficiency

Economic growth and energy use are linked. To achieve economic growth while curbing the use of energy therefore requires using energy with a higher efficiency: doing more with less energy. The Dutch government has created a large number of instruments for energy-efficiency [31, 32]. Among others:

- Benchmarking is an important tool for improving the energy efficiency in industry;
- For residential areas the methodology based on the "Energy Performance Coefficient" (EPN/EPL) regulates minimum energy efficiency requirements for newly constructed buildings;
- Fiscal regulations promote the sales of energy efficient cars and appliances such as refrigerators.

Increasing efficiency is considered important from an economic point of view, but also based on geo-political (decreased reliance on foreign sources) and sustainability (resource depletion).

Renewable energy

The Dutch policy on renewable energy aims at a 10% share of renewable energy (RE) in 2020. Initially the share of RE will expand by an increasing use of biomass & waste. After 2010 the growing share of renewables will be covered mainly by off-shore wind [33]. Studies for Europe on renewable energy potential show that offshore wind will be the most important source on European scale as well [34]. Hydro and solar energy are thought to have a limited potential for Europe and even less for The Netherlands. For the large shares of renewable energy which are foreseen for the longer-term future (2050), The Netherlands and Europe will probably become importers of renewable energy.

Emission reduction

As a consequence of the Kyoto protocol, Europe has agreed to substantially reduce its greenhouse gas emissions in 2020. With the 1990 emissions as a reference, Europe has agreed to an 8% emission reduction. For The Netherlands this translates to an emission reduction target of 6%. Not only CO_2 emissions have to decrease. Other emissions like NO_x, particulate matter, NH_3 and CO are harmful as well. Table 2 gives the indicative reduction targets for 2030 for the most important substances.

TABLE 2. *Indicative reduction targets (relative to 1990) for The Netherlands for 2030 [36]*

CO_2	70 - 100	Mton	40 – 60%
NO_x	70 - 120	Kton	80 – 90%
VOC*	50 - 120	Kton	75 – 90%
Particulates	5 - 10	Kton	85 – 95%
NH_3	30 - 55	Kton	75 – 85%

* Volatile Organic Compounds

In general it can be said that the technologies with the purpose to increase efficiency, increasing the share of renewables and reducing CO_2 emissions will automatically lead to a reduction of 'other emissions' [35]. Therefore these other emissions are not considered separately, with the exception of emissions as a result of transport. In the most recent National Environmental Plan (NMP4), the Department of the Environment (VROM) concludes:

> *After 30 years of environmental policy NO_x, particulate matter and smog remain a problem because the reduction achieved by industry is largely cancelled out by the increase of emissions as a result of traffic due to the increase in mobility.*

The quote illustrates the need for a strong emphasis on reducing other emissions. Table 3 summarises the emissions as a result of mobility in The Netherlands for the most relevant pollutants [37]. As a reference, the total emissions for stationary applications are given. VHC (volatile hydrocarbons), NO_x and particulate matter (PM) are the main problems, CO emissions can be reduced to acceptable levels using current technology [26]. Diesel engines are of greater concern due to the much higher NO_x emissions than the modern gasoline engine with three-way catalyst. For Europe regulations on emissions are based on centralised standards (EURO). For the different categories of vehicles (passenger cars, heavy goods vehicles, urban transit busses and light-duty vehicles) different sets of standards and timeframes will be used. For all types substantial reductions of emissions will be required over the coming decade.

TABLE 3 *Emissions as a result of transport in The Netherlands (10^6 kg/yr, source CBS)*

	CO_2	NO_x	CO	SO_2	particulate matter	NMVOC*
Highways	10,700	92.4	100.1	1.9	3	17.3
Urban	9,700	43.1	220.1	1.7	3.5	72.1
Rural	8,000	45.1	77.4	1.2	2.3	17.7
Total road transport	28,400	180.6	397.6	4.8	8.8	107.1
Other mobile sources	6,400	102.6	40.2	18.4	8.5	12.6
Total mobile sources	34,800	283.2	437.8	23.2	17.3	119.7
Stationary sources	146,200	147	249	84	23	173

*NMVOC: Non-Methane Volatile Organic Compounds

3.4.2 Energy carriers in three policy scenarios

In policy emphasis may change (and often does). As a result of such a change in policy, a technology may become less or more competitive. It is not only interesting to know how an end-use technology or an energy carrier fits into a specific scenario. It is also important to see how a technology will fit into different scenarios. A technology that fits into a broad range of scenarios is called a *robust* technology. Evidently developing robust technology reduces the risk of developing the 'wrong' technology. To assess the robustness of the hydrogen and methane technology, they are considered against three policy 'scenarios'.

- *Clean and efficient:* Focus of the energy policy is on immediate problems: increasing efficiency to reduce import dependency and economic considerations and to reduce local emissions, particularly in urban areas;
- *CO_2 free:* In excess of the above, the government adheres strictly to the Kyoto Protocol and its possible successors leading to a policy focus on reduction of CO_2 emissions and other green house gasses;
- *Renewable:* The government commits itself to increasing the share of Renewable Energy (RE) considerably. The amount of renewables in this scenario is assumed to be large enough to require adaptation of the energy infrastructure.

Is an infrastructure for hydrogen or methane required in each of these scenarios? Each scenario provides the limitations for the choice of end-use technologies and the corresponding choice of energy carrier. Again the final energy demand from the previous section is taken as a starting point. We consider how heat and electricity for stationary applications can be generated using a hydrogen or natural gas infrastructure in each of the scenarios. In addition the options for transport using hydrogen or methane are considered for each of the scenarios.

3.4.3 Stationary energy demand in three scenarios

Efficient and clean electricity and heat

Natural gas fits very well in a policy that proposes to increase the efficiency of the energy supply system. State-of-the-art gas-fired power plants are combined steam and gas (STAG) units which reach efficiencies in the range of 55-60%. Although even higher efficiencies might be obtained in the future, a further increase of the efficiency of power generation is likely to come from the development of hybrid fuel cell systems (see section 3.3.2.1). Although the efficiencies for large-scale systems (>100 MW) might be slightly higher because of the higher efficiency of rotating equipment and heat recovery, medium scale systems (2…20 MW) have the advantages of lower investments (risk) and flexibility. The development of hybrid fuel cell systems can reinforce the trend towards decentralised power.

Hydrogen as a fuel for centralised power generation in a system based on fossil fuels does not have any advantages over the direct utilisation of fossil fuels. The conversion of fossil fuels to hydrogen by reforming or gasification results in energy losses. Because for large-scale electricity production the use of hydrogen does not lead to a higher efficiency, these losses are not compensated. The chain efficiency of the conversion of fossil fuel to electricity is therefore lower if hydrogen is used as an intermediate. However, for decentralised generation (micro combined heat and power) the efficiency on hydrogen is substantially higher than for natural gas. For this application the total efficiency of the 'production to end-use' chain could therefore become competitive with the use of natural gas.

At present heat is mostly generated by burning natural gas in a hot water or steam boiler. The most important option to provide the heat directly from fossil fuels in a more efficient manner is to generate heat and power combined. Power plants generally do not utilise the heat which is produced and the efficiency is therefore far below 100%. Combined heat and power generation can be more efficient than using natural gas boilers or heaters for heat production and separate electricity production. Although the total efficiency of the separate components (boiler and electricity production) may be higher than that of the combined heat and power system, the latter system may be more efficient because the loss of the heat in centralised electricity production is avoided.

In 1998 the electricity demand in The Netherlands was met for more than half by combined heat and power (CHP) generation [5]. This high contribution is due in part to the emphasis put on CHP in the Dutch energy policy and in part to the large share of natural gas in the Dutch fuel mix. Currently in horticulture and utility buildings gas engines are being used. Other types of micro units for combined heat and power using natural gas are being developed. Higher efficiencies will be possible using fuel cell systems. One of the main candidates for micro-CHP is the solid oxide fuel cell (SOFC). Atmospheric natural gas fuelled small-scale (1-5 kW) systems are expected to achieve electrical efficiencies of 40-45%. Combined heat and power is considered the most important fossil based technology to provide the heat demand more efficiently.

Combusting hydrogen to produce heat is inefficient. Although the efficiency of the process itself may be high (hydrogen in, heat out), the losses which occur during hydrogen production have to be taken into account. If the hydrogen for example has been produced by reforming of natural gas with an efficiency which is typically < 80%, the direct route of combusting natural gas to produce heat has a much higher efficiency. A high efficiency in producing heat from hydrogen can therefore only be achieved by using combined heat and power and can only be a competitor for the natural gas route if the combined efficiency of hydrogen production and hydrogen utilisation exceeds the efficiency of the direct conversion of natural gas.

CO_2 free electricity and heat

Distributed (decentralised) production of electricity (for example in micro-CHP systems) using natural gas is not possible in combination with capture and sequestration of CO_2. However, more centralised production of CO_2 free electricity using natural gas offers many possibilities. The use of end-of-pipe technologies for separation of CO_2 from the flue gasses of power plants is technically feasible but the penalties in terms of efficiency for separating and compressing CO_2 for sequestration are steep. Fuel cell technology, in particular the SOFC, may offer more efficient methods of separating CO_2 [39] because it is able to convert (the largest part of) the fuel without diluting the flue gas with nitrogen. The attractiveness of this concept is the combination of high efficiency hybrid technology and the high concentration in which CO_2 is available for capture. Evidently, due to the need to capture CO_2 in a more or less centralised manner, the CO_2 free route will not require an extensive natural gas or methane infrastructure. Electricity as an energy carrier becomes more important in this case.

Other routes to separating CO_2 with a smaller efficiency penalty than end-of-pipe technology lie in removing CO_2 from syngas which is obtained by (steam)reforming of natural gas or coal gasification followed by steam reforming. In the resulting syngas CO_2 is present at much higher partial pressures than in flue gas while the total mass flows are much smaller. Therefore capture of CO_2 from syngas is much more efficient. The syngas can be used in a gas turbine or STAG unit or in a fuel cell power plant. However, purifying the syngas to hydrogen, which is only a small step further, has the important benefit that it can be converted into electricity in a fuel cell at high efficiency. This offers a distinct advantage to using hydrogen for CO_2 free production of electricity for distributed power supply.

Heat can only be transported over a limited distance and is therefore always produced near the end-user. On the other hand capture and sequestration of CO_2 requires a certain scale. For CO_2 free production of heat, natural gas is not an appropriate energy carrier, because it does not seem feasible to capture CO_2 for all separate end-use appliances (boilers, etc). The most important competition to supplying CO_2 free heat comes from the combination of a heat pump using CO_2 free electricity.

Hydrogen offers more potential. Fossil fuels can be used to produce hydrogen. The CO_2 'by-product' can be separated and sequestered. The hydrogen can be distributed to produce heat at the required location. As indicated previously however, heat production using hydrogen is only efficient by means of combined heat and power generation.

Renewable electricity and heat

Biomass could also be a renewable source of hydrogen or methane. Thermal conversion processes (gasification, pyrolysis) can be used to produce syngas. From syngas either hydrogen or methane/substitute natural gas can be produced. It is not likely at first sight that a methane/substitute natural gas infrastructure would be feasible for bio-methane only.

Electricity produced from renewable sources (photovoltaic systems, wind turbines, etc.) should be used directly as much as possible, i.e. without using an intermediate energy carrier such as hydrogen or methane. Additional conversion steps will only increase the losses in the chain. Two factors might make the use of an intermediate energy carrier necessary: if renewable energy is transported over long distances and to match the difference in supply and demand by storing energy or peak-shaving. In these cases, hydrogen is the logical choice for an intermediate because it can be produced from electricity and (re)converted into electricity easily. Hydrogen could play a role in large-scale import from areas that are attractive for 'harvesting' renewable energy (high solar radiation intensity, favourable wind regime) as considered for example in the Japanese WE-Net program. Storage or buffering of hydrogen serves to provide electricity in times with a low supply of renewable energy. The key technology in both cases is the highly efficient production of electricity from hydrogen.

Renewable heat production using methane is only possible using substitute natural gas (SNG). This is a methane-rich mixture that is produced from biomass, for example by digestion (bio-methane) or by hydro-gasification [40]. Using this type of gas for centralised electricity production does not seem feasible, because the direct conversion from biomass to electricity is more attractive. But SNG does seem attractive for distributed use, for example in CHP systems. The long-term issue is if sufficient 'green gas' can be produced to warrant maintaining a full methane/natural gas-infrastructure.

Hydrogen can be used to produce renewable heat quite well, on condition again that it is used in a CHP system. Sources of hydrogen for heat production in the renewable system are the same as for electricity production: large scale import of renewable energy using hydrogen and hydrogen as an intermediate for buffering or peak-shaving. The main competition for renewable heat production is the use of heat pumps using renewable electricity and solar thermal systems.

3.4.4 The choice of transport fuel in three scenarios

Efficient and clean transport

Emissions (NO_x, VOC, particulate matter) are the main concerns for policy makers and car manufacturers. For Europe the current and future EURO standards are the decisive factor in determining what technology will be used for new vehicles. In a study on commercial fleet vehicles (light-duty trucks, heavy-duty trucks, busses), ECN compares using fuel cells to reduce emissions to the use of advanced concepts based on internal combustion engines (improved diesel, hybrid-diesel, NGV) [41]. The study concludes that until 2010, emission reduction using fuel cells leads to higher costs than advanced internal combustion engine concepts. For emission reductions beyond EURO IV the fuel cell may become the more attractive technology. For this type of high emission reduction only the hybrid diesel system is an alternative. Other types, for example CNG and LPG vehicles, will not likely be capable of required reduction in emissions. For the hybrid system, with substantial cost for the battery system, the fuel cell system is expected to be able to compete on cost in the long run. In a similar type of study for passenger cars, the German environmental agency UBA concludes, that for the time being improvements of the internal combustion engine (ICE) will be more cost effective in reducing emissions [26]. Natural gas vehicles can offer much cleaner transportation in the short term at limited additional cost. Using hydrogen as a fuel (and a fuel cell as the drive train) will lead to unequalled reduction of emissions but cannot compete on investment cost with the internal combustion engine.

To compare the total efficiency of different types of vehicles using different fuels, it is necessary to take into account both the efficiency of fuel production from the primary energy source (well-to-tank efficiency) and the efficiency with which the fuel is used in the vehicle (tank-to-wheel efficiency). The efficiency for the total cycle is therefore indicated as the well-to-wheel efficiency. Evidently hydrogen and natural gas are very different in this aspect. The well-to-tank efficiency for natural gas is very high, the losses occur mainly in the vehicle. For hydrogen a substantial part of the losses occurs in the hydrogen production stage limiting the well-to-tank efficiency but the tank-to-well efficiency for a hydrogen fuel cell vehicle is the highest. However, even though a large number of well-to-wheel studies are available, it is not very simple to compare the different technologies. The studies show a wide margin in their predictions, due to the differences in assessments how far each technology will develop and what the consequences are for efficiency and emissions. The complicating factor is that for all technologies (gasoline, diesel, NG-ICE, fuel cells) substantial improvements in efficiency are expected, which makes the comparison of future options very difficult. The efficiency of natural gas as a transportation fuel is not clear. The MIT study [23] estimates that hybrid CNG vehicles will be the most efficient (well-to-wheel) of all options available in 2020. On the other hand, the current NGV will not be able to compete with the expected performance of the improved gasoline or diesel engines on efficiency.

Hydrogen fuel cell vehicles initially will use hydrogen from fossil sources as hydrogen from renewable sources will be extremely costly [34]. The well-to-wheel efficiency is only high if hydrogen can be produced and delivered with a sufficiently high efficiency. According to a study by GM, ANL, BP, Exxon and Shell [42], hydrogen fuel cell vehicles offer the highest well-to-wheel efficiency. However, hybrid systems are in the same range and in other studies achieve higher efficiencies than hydrogen fuel cell vehicles.

Transport based on CO_2 free energy carriers

Natural gas vehicles have a low CO_2 emission because of efficiency and in particular as a result of the low C/H ratio of the primary fuel. However, for a CO_2 free transport strategy natural gas vehicles are not an option: CO_2 reduction using capture and sequestration is not feasible for distributed mobile sources. The use of biomass based fuels, which does fit in the CO_2 free strategy as well, is treated under ‘renewables’.

Hydrogen production with CO_2 capture and sequestration on the other hand fits very well in a CO_2 free transport strategy. The production of hydrogen from fossil fuels can be achieved most economically by reforming natural gas: this is the standard technology for industrial hydrogen production today. In the reforming based hydrogen process, the intermediate (syngas) is a mixture of mainly CO_2 and H_2. Removing CO_2 from the reforming process is therefore possible at a relatively low efficiency penalty, in comparison to for example removing CO_2 by end-of-pipe technologies in a power plant. Furthermore the scale at which the hydrogen is produced is appropriate for CO_2 capture and sequestration as well: both in centralised hydrogen plants and in on-site production of hydrogen at the refuelling station the scale is large enough to separate CO_2. This makes the hydrogen transport option especially attractive in a CO_2 free strategy. Storage on-board is the main issue that would limit application of hydrogen as a transportation fuel under this strategy.

Transport based on renewables

There are not many competing technologies for hydrogen in a CO_2 free strategy. This is because the cost of hydrogen from fossil fuels is expected to be substantially lower than hydrogen from renewables. However, in a renewable system, the hydrogen will have to come from renewables as well, the cost will be much higher and consequently a larger number of renewable routes become competitors. In particular for transport, renewable routes leading to liquid fuels are considered, for example bioethanol produced from lignocellulose by fermentation or synthetic diesel produced from biomass-derived syngas by Fischer-Tropsch synthesis. Although use of substitute natural gas (SNG) from biomass for transportation purposes is conceivable, it does not seem to have advantage over the liquid fuel routes. The use of liquid biomass based fuels eliminates complicated on-board storage schemes. Transport on hydrogen fits very well in a renewable energy system. Hydrogen production from renewables on large scale or small scale in combination with peak shaving (as discussed in section 3.4.3) are two options to achieve this.

3.5 Conclusions: the future role of methane and hydrogen as energy carriers and the implications for bio-methane and bio-hydrogen

3.5.1 Introduction

In the preceding sections several factors that influence the (future) role of methane and hydrogen as energy carriers were evaluated. These include the final energy demand and the available end-use technologies, the need for an infrastructure covering all elements of the production to end-use chain, and the robustness of the energy carrier in an environment that is subject to changes in energy policy. This section attempts to integrate the information from the preceding sections and to evaluate the implications for bio-methane and bio-hydrogen.

3.5.2 The role of end-use technologies

The required end-use technology is characterised by a high efficiency that is also more or less scale-independent, making it particularly attractive for decentralised applications. Furthermore it is a clean technology producing low or negligible amounts of harmful emissions. It is clear that fuel cells meet these requirements for both methane and hydrogen provided that the manufacturing costs can be reduced to a competitive level.

For the conversion of methane into electricity and heat a range of technologies and technology combinations such as steam and gas turbine (STAG) units are available. Large-scale ‘state-of-the-art' installations already show good electrical and overall energetic efficiency. Furthermore, systems for smaller scale, decentralised applications –such as micro turbines– are being developed. The inevitable thermal NO_x emissions can be reduced by commercial catalytic or non-catalytic methods. Based on the limited experience with methane use in fuel cells it can, however, be expected that the use of fuel cells will improve the conversion efficiency and the economic feasibility of (especially) smaller scale systems. In addition, end-of-pipe NO_x removal is not required due to the negligible NO_x emissions of the fuel cell. The use of fuel cells for methane conversion thus offers economic and environmental advantages. It is however not critical for the use of methane as an energy carrier because of the availability of efficient alternative technologies.

In contrast, the use of hydrogen as an energy carrier is inextricably linked to efficient and clean final conversion in fuel cells. Other technologies, such as internal combustion engines or turbines, do not have the high efficiency and low emissions that can be attained in fuel cells, particularly in small-scale stationary and transport applications. If the full chain from production to end-use is considered, these end-use technologies do not compensate for the energy losses in the beginning of the chain i.e. in the phase of hydrogen production e.g. by reforming of natural gas. The broad implementation of fuel cell technology is therefore crucial for the success of hydrogen as a clean and versatile energy carrier.

As outlined above, the use of fuel cells for methane conversion is advantageous because of improved conversion efficiency and economic feasibility, while it is essential for the effective use of hydrogen as an energy carrier. Methane and hydrogen require different fuel cell types. Methane can be used in Phosphoric Acid Fuel Cells (PAFC) after reforming or directly in high-temperature Solid Oxide Fuel Cells (SOFC), which are both suitable for stationary applications. On the longer term the low temperature Proton Exchange Membrane Fuel Cell (PEMFC) is a logical choice for hydrogen use in vehicles and in distributed mini- or micro-Combined Heat and Power (CHP) systems. It is in these small-scale, mobile or stationary applications that the advantages of hydrogen can be fully exploited. In PEM fuel cell vehicles energy losses and cooling requirements are limited due to the low operational temperature. In residential micro-CHP systems the PEM cell has a superior overall efficiency, because the low temperature heat produced by the cell can be used for water and space heating.

For biologically produced methane and hydrogen this implies that the fuel specifications posed by the respective fuel cell types must be met. At the current state of fuel cell development the presence of contaminants such as sulphur (in H_2S or S-compounds), carbon monoxide (CO) and halogens are most critical, depending on the fuel cell type. Bio-methane ('biogas') is mainly composed of methane (55-75 vol%) and carbon dioxide (25-45 vol%), saturated with water vapour. It usually contains sulphides (mainly H_2S) and NH_3 in low concentrations dependent on feedstock composition and operational factors. Trace amounts may be present of hydrogen, carbon monoxide, and halogenated compounds. A range of commercial technologies is in use today to remove impurities that have a negative impact on the conversion of bio-methane to electricity and heat and for upgrading biogas to natural gas or vehicle fuel standards. The conditioning of bio-methane to fuel cell standards therefore poses no technological obstacle. Biologically produced hydrogen is primarily composed of hydrogen (70 - 90 vol%) and CO_2 (10 - 30 vol%) saturated with water vapour. At present it is not clear whether contaminants such as sulphides may be present in bio-hydrogen because the technology is still under development and conclusive data on this issue are not yet available. It can be expected however that the presence of contaminants in bio-hydrogen may also be influenced by feedstock composition and process operation. In any case they can be removed with available technology. Bio-methane application in PAFC's or SOFC's requires near complete removal of sulphides. The use of bio-hydrogen in the currently available PEM fuel cells similarly requires deep removal of sulphides and NH_3 in order to prevent detrimental effects on the cells' performance. Removal of CO_2 from bio-methane and bio-hydrogen (both with a relatively high CO_2 concentration) may be recommended in order to increase the energy contents of the fuel and to enable sequestration of the recovered CO_2.

3.5.3 The role of infrastructure requirements

The deployment of an energy carrier requires the availability of an infrastructure for production, transport and final conversion. Furthermore, the infrastructure should be able to match demand and supply, either by storage of the energy carrier or by modifying production and/or demand. For methane such an infrastructure is available in the form of the natural gas distribution network. To enable the use of the natural gas infrastructure, bio-methane must be conditioned to comparable properties as the natural gas because the end-use appliances are tuned to this quality. The upgrading of bio-methane (biogas or landfill gas) to natural gas standards or transport fuel specifications and delivery via the existing infrastructure is a common practice. It mainly involves the removal of nitrogen and sulphur compounds, CO_2, water and impurities such as halogenated compounds followed by pressurising the gas and delivery. The alternative is to use stand-alone systems where the bio-methane is converted into heat and/or electricity on site. In this case purification is required as well, depending on the applied technology. For gas engine CHP systems (which are mostly used) particulates should be removed and the sulphur content should be reduced to < 1000 ppm. Use in fuel cells at least requires near-complete removal of sulphides.

In the case of hydrogen distribution, the desired quality will be determined mainly by the fuel cell based end-use technology, which requires high purity hydrogen. Conditioning in this case consists mainly of purification. As discussed before, the advantages offered by hydrogen as an energy carrier can be exploited fully through its final conversion in PEM fuel cells in vehicles or small-scale CHP systems at the level of individual buildings or districts. In the latter, useful application of the low temperature heat produced by the cell for water or space heating is possible. On district level a heat distribution network is required for maximum overall efficiency. This emphasis on highly decentralised end-use implies that for optimal use of hydrogen a distribution system is required. The feasibility of hydrogen use in stand-alone systems (i.e. end-use where it is produced) appears to be limited to systems for remote locations, because hydrogen storage is difficult due to the low energy density (kJ/kg and kJ/m^3). In contrast to natural gas however no infrastructure for hydrogen transport is available today. The addition of hydrogen to the natural gas grid is thus far regarded as technically and/or economically unfeasible. It should be noted here that hydrogen distribution networks could be of a much smaller scale than for natural gas. The optimum size depends on the scale of hydrogen production and the distribution area to be covered. In fact, the feasibility of decentralised production (e.g. by electrolysis or biological processes) coupled to smaller scale distribution systems, is one of the outstanding features of hydrogen. The drivers for creating a hydrogen infrastructure are very diverse. They include the reduction of local emissions through the use of hydrogen as a transport fuel, the potential role of hydrogen in capturing and sequestering CO_2 and the use of hydrogen as an intermediate storage and transport medium for renewable energy. Creating a suitable infrastructure is, however, a great challenge partly because the drivers for its realisation are so diverse.

3.5.4 The role of energy policy

Uncertainty with respect to the energy policy over a longer period is another reason why far-reaching changes in the infrastructure are difficult to achieve. By comparing the role of methane and hydrogen as energy carriers in three different scenarios the 'robustness' of the energy carrier can be evaluated, as outlined in section 3.4, where three scenarios with the primary drivers: ‘Efficiency’, ‘CO_2 free’ and ‘Renewable’ were evaluated. Both methane/natural gas and hydrogen fit well in the scenario where ‘Efficiency’ is the primary driver, although hydrogen has the weakness in this scenario that a suitable infrastructure will be more difficult to achieve with only this driver.

Distribution of methane and/or natural gas by means of a dense distribution grid to the end-user and the use of methane and/or natural gas as a transport fuel do not fit very well in the other two scenarios with 'CO_2 reduction' and 'Renewable' as the primary drivers. In these scenarios electricity or hydrogen are more likely energy carriers for distribution. Natural gas and bio-methane in these scenarios will more probably be used for electricity production, while hydrogen has a definite role as a transport fuel. In the 'Renewable' scenario the competition with electricity as the final energy carrier for distribution becomes tougher for hydrogen because of the much higher production costs of hydrogen from renewables as compared to the costs of hydrogen produced from fossil fuels with CO_2 sequestration. As shown both energy carriers have their weaknesses and strengths. These can be used to compare them and try to answer the question: "methane or hydrogen?" However, the recent Shell scenario *'Spirit of the coming age'* shows that this might not be the proper question, because both natural gas and hydrogen emerge as important future energy carriers in this scenario.

3.5.5 Implications for bio-methane and bio-hydrogen

The analysis in this chapter can also be used to identify strategies in which the strong points of both energy carriers can be exploited. For the distribution and application of bio-methane the natural gas infrastructure is available, although the final energy carrier delivered to the end-user may be electricity or hydrogen. If conditioning of bio-methane to natural gas standards is not feasible, e.g. for economic reasons, the stand-alone option remains where methane is used at the site of production for the generation of electricity and heat. For hydrogen, which is more difficult to store, much larger advantages are obtained by connecting the production process to a hydrogen grid or an alternative distribution system. Hydrogen is the more attractive energy carrier for distribution to the end user because of the high and scale-independent efficiency of its final conversion in the fuel cell. The most favourable option for bio-hydrogen production systems is therefore to deliver the produced hydrogen to a hydrogen distribution network on local, regional or larger scale.

3.6 Abbreviations

AFC	Alkaline Fuel Cell
CHP	Combined Heat and Power generation
CI	Compression ignition
CNG	Compressed natural gas
EOR	Enhanced Oil Recovery
GH_2	Gaseous Hydrogen
LH_2	Liquefied Hydrogen
LPG	Liquefied Propane Gas
MCFC	Molten Carbonate Fuel Cell
NG	Natural gas
NGV	Natural Gas Vehicle
NMVOC	Non-Methane Volatile Organic Compounds
OFP	Ozone Forming Potential
PAFC	Phosphoric Acid Fuel Cell
PEMFC	Proton Exchange Membrane Fuel Cell
PM	particulate matter
RE	Renewable Energy
SNG	substitute natural gas
SOFC	Solid Oxide Fuel Cell
STAG	Steam and Gas Turbine
VHC	volatile hydrocarbons
VOC	volatile organic compounds

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4

Methane production by anaerobic digestion of wastewater and solid wastes

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Abstract

Anaerobic digestion is an established technology for the treatment of wastes and wastewater. The final product is biogas: a mixture of methane (55-75 vol%) and carbon dioxide (25-45 vol%) that can be used for heating, upgrading to natural gas quality or co-generation of electricity and heat. Digestion installations are technologically simple with low energy and space requirements. Anaerobic treatment systems are divided into 'high-rate' systems involving biomass retention and 'low-rate' systems without biomass retention. High-rate systems are characterised by a relatively short hydraulic retention time but long sludge retention time and can be used to treat many types of wastewater. Low-rate systems are generally used to digest slurries and solid wastes and are characterised by a long hydraulic retention time, equal to the sludge retention time. The biogas yield varies with the type and concentration of the feedstock and process conditions. For the organic fraction of municipal solid waste and animal manure biogas yields of 80-200 m^3 per tonne and 2-45 m^3 per m^3 are reported, respectively. Co-digestion is an important factor for improving reactor efficiency and economic feasibility. In The Netherlands co-digestion is only allowed for a limited range of substrates, due to legislation on the use of digested substrate in agriculture. Maximising the sale of all usable co-products will improve the economic merits of anaerobic treatment. Furthermore, financial incentives for renewable energy production will enhance the competitiveness of anaerobic digestion versus aerobic composting. Anaerobic digestion systems currently operational in Europe have a total capacity of 1,500 MW, while the potential deployment in 2010 is estimated at 5,300-6,300 MW. Worldwide a capacity up to 20,000 MW could be realised by 2010. Environmental pressures to improve waste management and production of sustainable energy as well as improving the technology's economics will contribute to broader application.

4.1 Introduction

Anaerobic conversion of organic materials and pollutants is an established technology for environmental protection through the treatment of wastes and wastewater. The end product is biogas –a mixture of methane and carbon dioxide–, which is a useful, renewable energy source. Anaerobic digestion is a technologically simple process, with a low energy requirement, used to convert organic material from a wide range of wastewater types, solid wastes and biomass into methane. A much wider application of the technology is desirable in the current endeavours towards sustainable development and renewable energy production. In the 1980's several projects were initiated in The Netherlands to produce biogas from wastes. Many projects were terminated due to insufficient economic viability. Currently, the production of methane from wastes is receiving renewed attention as it can potentially reduce CO_2 emissions via the production of renewable energy and limit the emission of the greenhouse gas methane from especially animal manure. This trend is supported by the growing market demand for 'green' energy and by the substantial optimisation of anaerobic digestion technologies in the past decades, especially the development of modern 'high rate' and co-digestion systems.

The aim of this chapter is to review and evaluate the various anaerobic digestion technologies to establish their potential for methane production, aimed at broadening the range of waste streams

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used for biogas production. The principles of anaerobic digestion are outlined in Section 4.2. In Section 4.3 anaerobic digestion technologies and their application for specific waste streams are discussed. An overview of solid wastes and wastewater streams available for anaerobic digestion in The Netherlands is presented in Section 4.4. In Section 4.5 the utilisation of biogas as a renewable energy source is highlighted, including the current and potential share of bio-methane in The Netherlands. The economics of anaerobic digestion are discussed in Section 4.6. The status of international developments is presented in Section 4.7. Conclusions and perspectives for further development are presented in Section 4.8.

4.2 Basic principles of anaerobic digestion

4.2.1 Principle of the process

Anaerobic microbiological decomposition is a process in which micro-organisms derive energy and grow by metabolising organic material in an oxygen-free environment resulting in the production of methane (CH_4). The anaerobic digestion process can be subdivided into the following four phases, each requiring its own characteristic group of micro-organisms:

- Hydrolysis: conversion of non-soluble biopolymers to soluble organic compounds
- Acidogenesis: conversion of soluble organic compounds to volatile fatty acids (VFA) and CO_2
- Acetogenesis: conversion of volatile fatty acids to acetate and H_2
- Methanogenesis: conversion of acetate and CO_2 plus H_2 to methane gas

A simplified schematic representation of anaerobic degradation of organic matter is given as Figure 1. The acidogenic bacteria excrete enzymes for hydrolysis and convert soluble organics to volatile fatty acids and alcohols. Volatile fatty acids and alcohols are then converted by acetogenic bacteria into acetic acid or hydrogen and carbon dioxide. Methanogenic bacteria then use acetic acid or hydrogen and carbon dioxide to produce methane.

For stable digestion to proceed it is vital that various biological conversions remain sufficiently coupled during the process, to prevent the accumulation of intermediate compounds. For example, an accumulation of volatile fatty acids will result in a decrease of pH under which conditions methanogenesis cannot occur anymore, which

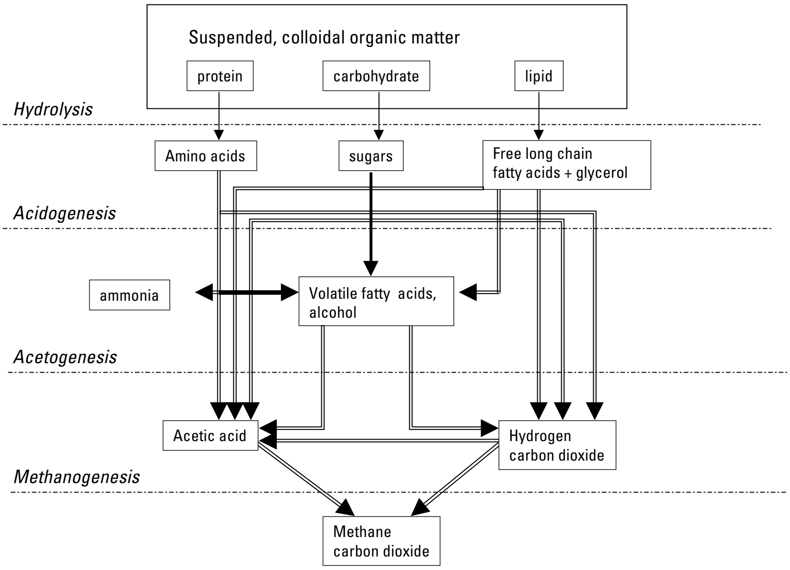


Figure 1. Simplified schematic representation of the anaerobic degradation process [1].

results in a further decrease of pH. If hydrogen pressure becomes too high, further reduced volatile fatty acids are formed, which again results in a decrease of pH.

4.2.2 Environmental factors affecting anaerobic digestion

As anaerobic digestion is a biological process, it is strongly influenced by environmental factors. Temperature, pH and alkalinity and toxicity are primary control factors.

Controlled digestion is divided in psychrophilic (10-20 °C), mesophilic (20-40 °C), or thermophilic (50-60 °C) digestion. As bacterial growth and conversion processes are slower under low temperature conditions, psychrophilic digestion requires a long retention time, resulting in large reactor volumes. Mesophilic digestion requires less reactor volume. Thermophilic digestion is especially suited when the waste(water) is discharged at a high temperature or when pathogen removal is an important issue. During thermophilic treatment high loading rates can be applied. Anaerobic digestion can occur at temperatures as low as 0°C, but the rate of methane production increases with increasing temperature until a relative maximum is reached at 35 to 37° C [2]. At this temperature range mesophilic organisms are involved. The relation between energy requirement and biogas yield will further determine the choice of temperature. At higher temperatures, thermophilic bacteria replace mesophilic bacteria and a maximum methanogenic activity occurs at about 55°C or higher.

The first steps of anaerobic digestion can occur at a wide range of pH values, while methanogenesis only proceeds when the pH is neutral [2]. For pH values outside the range 6.5 - 7.5, the rate of methane production is lower. A sufficient amount of hydrogen carbonate (frequently denoted as bicarbonate alkalinity) in the solution is important to maintain the optimal pH range required for methanogenesis.

Several compounds exhibit a toxic effect at excessive concentrations such as VFA's, ammonia, cations such as Na^+, K^+ and Ca^{++}, heavy metals, sulphide and xenobiotics, which adversely affect methanogenesis.

4.2.3 Methane production potential

The Chemical Oxygen Demand (COD) is used to quantify the amount of organic matter in waste streams and predict the potential for biogas production. The oxygen equivalent of organic matter that can be oxidised, is measured using a strong chemical oxidising agent in an acidic medium.

During anaerobic digestion the biodegradable COD present in organic material is preserved in the end products, namely methane and the newly formed bacterial mass.

In case an organic compound ($C_nH_aO_bN_d$) is completely biodegradable and would be completely converted by the anaerobic organism (sludge yield is assumed to be zero) into CH_4, CO_2 and NH_3, the theoretical amount of the gases produced can be calculated according to the Buswell equation (1):

$$C_nH_aO_bN_d + (n-a/4 - b/2 + 3d/4)\ H_2O \rightarrow$$
$$(n/2 + a/8 - b/4 - 3d/8)\ CH_4 +$$
$$(n/2 - a/8 + b/4 + 3d/8)\ CO_2 + dNH_3 \quad \text{(equation 1)}$$

The quantity of CO_2 present in the biogas generally is significantly lower than follows from the Buswell equation. This is because of a relatively high solubility of CO_2 in water and part of the CO_2 may become chemically bound in the water phase.

Another widely used parameter of organic pollution is the Biological Oxygen Demand (BOD). This method involves the measurement of dissolved oxygen used by aerobic microorganisms in biochemical oxidation of organic matter during 5 days at 20 °C.

A very useful parameter to evaluate substrates for anaerobic digestion is the anaerobic biodegradability and hydrolysis constant [3]. The total anaerobic biodegradability is measured by the total amount of methane produced during a retention time of at least 50 days.

The gas yield depends on factors such as digestibility of the organic matter, digestion kinetics, the retention time in the digester and the digestion temperature. By controlling conditions such as temperature, humidity, microbial activity and waste properties, the process can be optimised.

4.2.4 Requirements for anaerobic digestion

Unlike aerobic wastewater treatment systems, the loading rate of anaerobic reactors is not limited by the supply of a reagent, but by the processing capacity of the microorganisms. Therefore, it is important that a sufficiently large bacterial mass is retained in the reactor. For low rate systems the latter is achieved by applying a sufficiently long retention time. For high rate systems the retention of biomass is increased in comparison with the retention of the liquid. The following conditions are essential for high rate anaerobic reactors [2]:

- A high concentration of anaerobic bacterial sludge must be retained under high organic (>10 kg/m^3/day) and high hydraulic (>10 m^3/m^3/day) loading conditions.
- Maximum contact must occur between the incoming feedstock and the bacterial mass.
- Also minimal transport problems should be experienced with respect to substrate compounds, intermediate and end products.

The base for design of anaerobic digestion systems is the slowest step during digestion, which is usually the conversion of biodegradable non-dissolved organic solids into soluble compounds. This process is described as hydrolysis, and is temperature dependent.

Sludge Retention Time (SRT) is an important parameter. When too short, methanogenesis will not occur [4], and the reactor will acidify as a result. An SRT of at least 15 days is necessary to ensure both methanogenesis, sufficient hydrolysis and acidification of lipids at 25 °C [4]. At lower temperature the SRT should be longer, as the growth rate of methanogens and the hydrolysis constant decrease with temperature. To ensure the same effluent standards, the SRT should be increased. In completely mixed systems, the SRT is equal to the HRT, while in systems with inbuilt sludge retention, the SRT is higher than the HRT. For the particular Upflow Anaerobic Sludge Bed (UASB) system, the required reactor volume ensuring a sufficient SRT is calculated according to equation 2. This equation is applied for wastewater with a high concentration of suspended solids, and for systems that are not hydraulically limited [5]:

$$HRT = \left(\frac{COD_{SSin}}{X}\right) * R * (1-H) * SRT \qquad \text{(equation 2)}$$

in which:
COD_{SSin} = COD of suspended solids in the influent (g/l)
X = sludge concentration in the reactor (g VSS/l); (1 g VSS=1.4 g COD)
R = fraction of the COD_{SS} removed
H = fraction of the removed COD_{SS}, which is hydrolysed at the imposed SRT

4.2.5 Advantages and disadvantages of anaerobic treatment

Advantages of anaerobic treatment are numerous and can be summarised as follows [1,6]:

- provision of energy source through methane recovery;
- anaerobic treatment processes generally consume little energy. At ambient temperature the energy requirements are in the range 0.05-0.1 kWh/m^3 (0.18-0.36 MJ/m^3), depending on the need for pumping and recycling effluent;
- reduction of solids to be handled; excess sludge production on the basis of biodegradable COD in anaerobic treatment is significantly lower compared to aerobic processes;
- facilitation of sludge dewatering;
- raw waste stabilisation;
- relatively odour free end-product;
- almost complete retention of the fertiliser nutrients nitrogen (N), phosphate (P) and potassium (K);
- modern anaerobic treatment processes can handle very high loads, exceeding values of 30 g COD/l/day at ca. 30 °C and up to 50 g COD/l/day at ca. 40 °C for medium strength mainly soluble wastewater;
- anaerobic sludge can be preserved for prolonged periods without any feeding;
- the construction costs are relatively low;
- the space requirements of anaerobic treatment are lower than conventional systems.

During anaerobic treatment biodegradable compounds are effectively removed, leaving a number of reduced compounds in the effluent, as well as ammonium, organic N-compounds, sulphide, organic P-compounds and pathogens. Depending on the further use a complementary treatment step is needed.

The disadvantages of anaerobic treatment are summarised below [1]:

- the high sensitivity of methanogenic bacteria to a large number of chemical compounds. In many cases anaerobic organisms are capable of adapting to these compounds;
- the first start-up of an installation without the presence of proper seed sludge can be time-consuming due to the low growth yield of anaerobic bacteria;
- when treating waste (water) containing sulphurous compounds, the anaerobic treatment can be accompanied by odour due to the formation of sulphide. An effective solution to this problem is to employ a micro-aerophilic post-treatment step, to convert sulphide to elemental sulphur.

4.3 The technology of anaerobic digestion

Anaerobic treatment is divided in 'low rate' systems, in which long hydraulic retention times are applied, and 'high rate' systems, in which hydraulic retention time is relatively short. Low rate systems are mainly used for waste streams such as slurries and solid waste, which require a long time for sufficient anaerobic degradation. High rate systems are mainly used for wastewater. The retention time of sludge in a low rate system is equal to the hydraulic retention time. In high rate systems however, the sludge retention time should be much higher than the hydraulic retention time. In essence, all high-rate processes have a mechanism either to retain bacterial sludge mass in the reactor or to separate bacterial sludge from the effluent and return it to the reactor. High rate systems are divided in two categories:

1) systems with fixed bacterial films on solid surfaces;
2) systems with a suspended bacterial mass where retention is achieved through external or internal settling.

Examples of low rate systems are: Batch, Accumulation, Plug flow and Continuously Stirred Tank Reactor (CSTR) systems. Examples of high rate systems are: Contact Process, Anaerobic Filter, Fluidised Bed and Upflow Anaerobic Sludge Bed (UASB) / Expanded Granular Sludge Bed (EGSB) [7].

4.3.1 Systems for treatment of solid waste and slurries

Systems used to digest solid waste are classified according to the percentage of Total Solids (TS) in the waste stream [8]:

15-25%	low solids anaerobic digestion: wet fermentation;
>30%	high solids anaerobic digestion: dry fermentation.

Figure 2 shows a schematic overview of digestion systems for slurries and solid wastes. Examples of existing plants are also shown, the processes of which are discussed later in detail.

During wet fermentation, slurry is digested; so the techniques for digestion of solid waste during wet fermentation and the digestion of slurries are comparable. Most digesters comprise a single reactor vessel (one phase system), but it is also possible to split microbial digestion into two phases, which can be operated in separate reactor vessels. Many types of reactors have been developed, based on the processes described above for the treatment of different types of wastes. They can be broadly categorised as low-solids, high-solids and multi-stage systems.

Plants used to treat organic solid waste are listed in Appendix I. This highlights the development of the technology and only includes plants processing more than 2,500 tonnes of slurry or solid waste per year. Appendix I includes wet fermentation and dry fermentation principles, both are discussed in the following sections and the techniques most commonly used are explained.

4.3.1.1 Wet fermentation systems

The most common form of low-solids reactor is the Continuously Stirred Tank Reactor (CSTR). Feed is introduced into the reactor, which is stirred continuously to ensure complete mixing of the reactor contents. At the same time an equal quantity of effluent is removed from the reactor. Retention time within the reactor can be varied according to the nature of the feedstock and process temperature applied, which is typically in the range of 2 - 4 weeks. Such systems have a low operating expenditure [8].

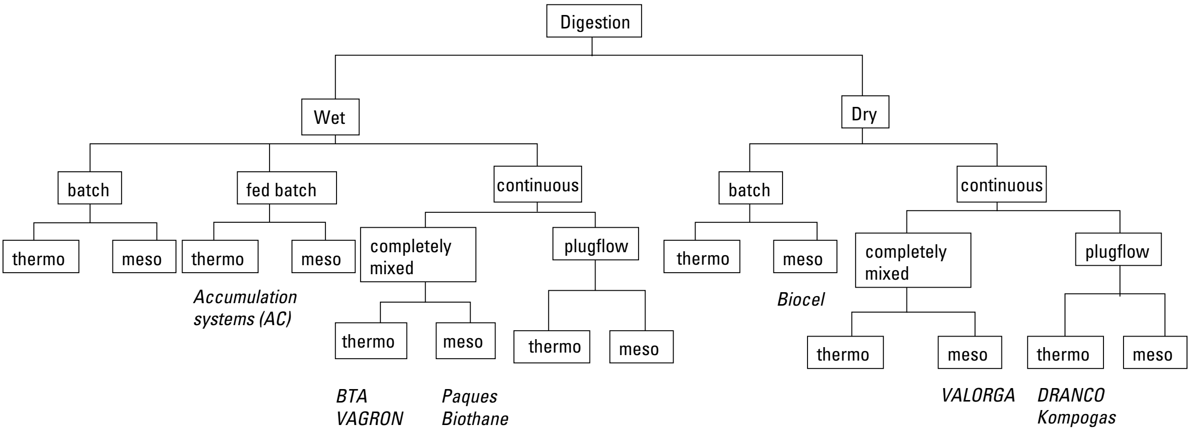


Figure 2. Schematic overview of digestion systems for slurries and solid waste. Commercial plants are indicated in italics.

The CSTR is generally used for treatment of slurries with a TS percentage of approximately 2-10%. The influent concentration range applicable for CSTR's is determined by:

- gas yield in relation to the energy requirement for heating;
- possibility of mixing the reactor content.

CSTR systems are applied in practice for treating animal manure, sewage sludge, household waste, agricultural wastes, faeces, urine and kitchen waste or mixtures of these substrates.

Mixing creates a homogeneous substrate, preventing stratification and formation of a surface crust, and ensures solids remain in suspension. Bacteria, substrates and liquid consequently have an equal retention time resulting in SRT is equal to HRT.

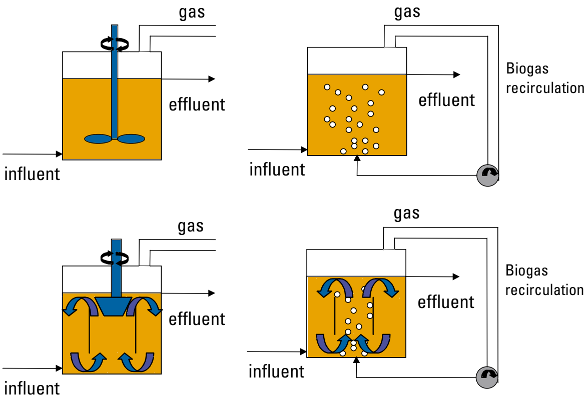


Figure 3. Schematic diagram of a CSTR system, mechanically stirred (top) and stirred by biogas recirculation (bottom) [10].

Digester volume ranges from around 100 m^3 to several thousand cubic metres, often with retention times of 10-20 days, resulting in daily capacities of 6 m^3 to 400 m^3 [9]. Examples of CSTR digesters with different mixing and heating systems are shown in Figure 3.

Plug-flow digesters use slurries, e.g. almost undiluted manure and have a total suspended solids concentration of 10-12% TS [11]. The basic digester design is a long trough (Figure 4), often built below ground level with a gas tight but expandable cover. At low TS concentration problems with floating and settling layers can appear [12]. This problem can be solved using vertical mixing inside the pipe. In this particular process, anaerobic stages such as hydrolysis and methanogenesis are separated over the length of the pipe. At first, hydrolysis mainly occurs, whereas later in the process methanogenesis takes place at full velocity. Using this system, the SRT is equal to the HRT. These systems are frequently used to treat slurries with a high fraction of suspended solids, as the hydrolysis of particulate matter is rate-limiting [3] hence only low loading rates can be applied.

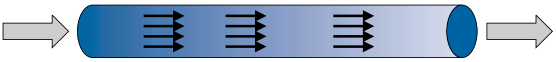


Figure 4. Schematic diagram of a plug flow digester.

In a batch system (Figure 5) the digester is filled at the start of the process. A disadvantage of the system is that a separate influent tank and effluent tank are needed. Batch systems are used as high-solids systems resulting in an equal SRT and HRT. It is advisable to leave approximately 15% of the contents to speed up the start-up of the process. In a batch system, treating mainly suspended solids, the different processes like hydrolysis, acidification and methanogenesis will not occur at the same rate. At first, time is needed to bring the suspended solids into a soluble form before it can be converted further to methane. The balance between the different processes at the start-up will depend on the percentage of inoculum applied. For solid waste digestion, liquid recirculation is applied to ensure sufficient contact between bacterial biomass and substrate.

Instead of a separate storage tank for the effluent, a combination of digestion and storage can be achieved in one tank. An **Accumulation System (AC)** is continuously fed and characterised by an increasing effective reactor volume with time. The reactor is almost completely emptied leaving 10-15% as inoculum. This system is the simplest system for on-site application of slurry digestion. A further facility, to normal storage consists of equipment for collection and use of the produced biogas and equipment is needed to optimise the process temperature, such as isolation and/or heating. The use of an AC-system is suitable when long-term storage is required. This type of system is mainly used on farms for the storage/digestion of manure, and is also used to digest faeces and urine in DeSaR (Decentralised Sanitation and Re-Use) systems [13]. The AC-system has also been tested on a small scale for solid manure digestion at thermophilic conditions for on-site energy production.

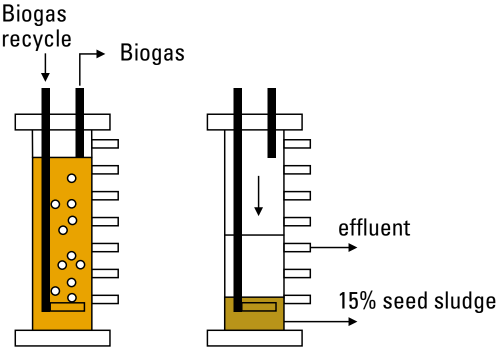


Figure 5. Schematic diagram of a batch reactor.

Wet digestion also has been carried out in a number of commercial and pilot-scale plants:

- AVECON or Waasa process, Vaasa, Finland [14], [15];
- VAGRON, Groningen, The Netherlands [16] named CiTech in Appendix I;
- Bigadan process, Denmark and Sweden [17], [18].

There are four **AVECON process** plants in Europe (one under construction), that can treat 3,000 - 85,000 tonnes per annum. The process can be operated at both thermophilic and mesophilic temperatures; the plant at Vaasa operates both systems in parallel. The thermophilic process has a retention time of 10 days compared to 20 days in the mesophilic process. The process has been tested on a number of waste types including a mixture of mechanically separated municipal solid waste/sewage sludge and operates in a solids range of 10-15%. The reactor is a single vessel, which is sub-divided internally to provide a pre-digestion chamber. Pumping biogas through the base of the reactor carries out mixing. The operational performance indicates that gas production is in the range 100-150 m^3/tonne of bio-waste added, with a volume reduction of 60%, weight reduction 50-60% and a 20-30% internal consumption of biogas. Aerobic composting, dependent on waste quality, can be used for post-treatment of the digested material.

At the **VAGRON plant** in Groningen (see Figure 11) the organic residual fraction is separated mechanically from the municipal solid waste stream and digested. At VAGRON, the temperature in the fermentation tanks is approximately 55 °C, resulting in thermophilic fermentation. The washed Organic Waste Fraction (OWF) remains in the tank for approximately 18 days, during which time approximately 60% of the organic material is converted into methane producing a total of 125 m^3 of biogas per tonne OWF.

The Krüger company developed the **Bigadan Process** in Denmark. The system is used to treat a mixture of livestock manure, organic industrial waste and household waste. This way of digesting is called co-digestion. More than 20 plants are in operation in Denmark. In Kristianstad in Sweden, the same process is used, operating since 1996. The digester is fed with manure, organic household waste and industrial waste. The industrial waste includes gastrointestinal waste from abattoirs and bio-sludge from a distillery, as well as potato and carrot waste. The solid waste is automatically fed into a coarse shredder and cut into pieces of approximately 80 mm. After a magnetic separator has removed metals, a fine shredder cuts the waste into 10 mm pieces before being mixed with manure and bio-sludge. The mixture is transported to a primary mixing tank. After homogenisation, the biomass is pumped into two pasteurisation tanks at 70 °C. Via a heat exchanger the slurry enters a stirred digester, which operates at 38 °C with a hydraulic retention time of 20-24 days. The daily amount of biomass digested is approximately 200 tonnes producing 8,000-9,000 Nm^3 biogas/day. The total yearly input is approximately 70,000 tonnes corresponding to approximately 20,000 MWh/year. Approximately 10% of the biogas is used for operation of the plant.

4.3.1.2 Dry fermentation systems

High-solids anaerobic digestion systems have been developed to digest solid wastes (particularly municipal solid waste or MSW) at solids contents of 30% or above. High-solids systems enable the reactor size to be reduced, require less process water and have lower heating costs. A number of commercial and pilot scale plants have been developed including:

- the Valorga process [15], [19], [20];
- the Dranco process [15], [20], [21];
- the Kompogas process [15], [20];
- the Biocel process [15], [22], [23].

The **Valorga system,** a semi-continuous one-step process, was developed in France. The installation at Amiens combines four mesophilic high-solids reactors with the incineration of residues and non-digested matter. Mixing within the reactor is carried out by reverse circulation under pressure of a small proportion of biogas. In the installation in Tilburg, before entering the anaerobic step, the separately collected VFY waste is screened and then crushed to decrease particle size to below 80 mm. After crushing, the waste is intensively mixed with part of the excess process water and heated by steam injection. The biogas produced has a methane content of 55-60%. The biogas can be purified to a methane content of 97% which is then fed into the gas network (Tilburg plant), used to produce steam for an industrial process (Amiens) or for heating and electricity production (Engelskirchen). The specific methane yield is between 220 - 250 m^3/tonne of total volatile solids (TVS) fed to the digester or between 80 - 160 m^3/tonne of waste fed, depending on waste characteristics. The process operates at solids contents typically ca. 30% with residence times between 18-25 days. The waste is diluted in order to keep the TS content of the mixture at approximately 30%.

The **Dranco (Dry Anaerobic Composting) system** was developed in Gent, Belgium. The system operates at high solids content and thermophilic temperatures. Feed is introduced daily at the top of the reactor, and digested material is removed from the base at the same time. Part of the digested material is recycled and serves as inoculation material, while the remainder is de-watered to produce organic compost material. There is no mixing within the reactor, other than that brought about by downward plug-flow movement of the waste. The total solids content of the digester depends on the waste material source but is in the range 15 - 40%. Reactor retention time is between 15 - 30 days, the operating temperature is in the range 50 - 58 °C and the biogas yield is between 100 - 200 m^3 / tonne of waste feedstock.

The **Kompogas system** is a high-solids thermophilic digestion system developed in Switzerland. The reaction vessel is a horizontal cylinder into which feed is introduced daily. Movement of material through the digester is in a horizontal plug-flow manner with digested material being removed from the far end of the reactor after approximately 20 days. An agitator within the reaction vessel mixes the material intermittently. The digested material is de-watered, with some of the press water being used as an inoculum source and the remainder being sent to an anaerobic wastewater treatment facility that also produces biogas.

The **Biocel process** is a high-solids batch process operated at mesophilic temperatures. Wastes are mixed with inoculum before being sealed into unstirred batch reactors. Wastes are kept within the digestion vessel until biogas production ceases. Leachate produced during the digestion process is heated and recirculated through the waste. A full-scale plant at Lelystad in The Netherlands commenced operation in September 1997. It processes 50,000 tonnes per year of Source Separated organic fraction of Municipal Solid Waste (SS-MSW) yielding energy and compost. The retention time is approximately 21 days [23].

4.3.1.3 Two-phase digestion systems

The idea of two- and multi-stage systems is that the overall conversion process of the waste stream to biogas is mediated by a sequence of biochemical reactions which do not necessarily share the same optimal environmental conditions [20]. The principle involves separation of digestion, hydrolysis and acidogenesis from the acetogenesis and methanogenesis phases. Optimising these reactions separately in different stages or reactors leads to a larger overall reaction rate and biogas yield [24]. Concentrated slurries and waste with a high lipid concentration should preferably be treated in a one-stage digester for two reasons. (1) Lipids will not be hydrolysed in the absence of methanogenic activity. (2) The possible decrease of the lipid-water interface in the first stage of a two-stage sludge digester can result in a longer SRT in the second stage [25]. Moreover hydrolysis and acidification of proteins and carbohydrates are not promoted by acidogenic conditions [4].

There are two kinds of two-phase digestion systems, one in which the different stages are separated, based on a wet fermentation, and one based on dry fermentation, in which only the percolate experiences a second methanogenic stage. The first system operates on dilute materials, with a total solids content of less than 10%. Unlike conventional low-solids digestion systems, which operate within a single reaction vessel, multiphase liquid systems separate the digestion process into two or more stages, each taking place in a separate reaction vessel. Systems include:

- The BTA-process [15];
- The BRV process [15], [20].

The **BTA-process** was developed in Germany as a three-phase liquid system for digestion of the organic fraction of MSW [15]. The waste is mixed with recycled process water before entering an acidification reactor. In this vessel, soluble organic material such as sugars and starch are rapidly converted into organic acids. The waste is then dewatered, and the liquid portion fed into a fixed-film methane reactor. The solids, containing polysaccharides such as cellulose are then mixed with more process water and fed into a hydrolysis reactor, where hydrolysis and acidification of the more resistant fibres takes place. After hydrolysis, waste is once more de-watered, the liquid effluent is fed into the methane reactor, and the solid fraction is removed and used as compost. Effluent from the methane reactor is used as process water to slurry incoming wastes.

The **BRV system** was developed in Switzerland and is an aerobic/anaerobic conversion system. The anaerobic phase is the Kompogas system, described earlier [15].

There is also a system, which consists of a dry fermentation stage followed by a liquid methanogenic stage. A number of different systems have been developed that use this configuration and they have been described as 'leach-bed' or percolation systems. Again a number of systems have been described but most apply the same principle. An example is the **Biothane-AN system** [15], in which solid wastes are placed batch-wise (at a high-solids concentration) into a reaction vessel. Process water is percolated through the waste, hydrolysis takes place and the resultant percolate is fed into a methane reactor. Effluent from the methane reactor is then recirculated through the hydrolysis vessel to generate further percolate. Normally, a series of batch hydrolysis vessels will feed a single methane reactor, to ensure a constant supply of percolate to the methane reactor.

4.3.2 Systems for wastewater treatment

High Rate Anaerobic Treatment systems (Figure 6, 7, 8), like the UASB (Upflow Anaerobic Sludge Bed) reactor, Anaerobic Filter and the Contact Process, are unfit for the digestion of concentrated slurries but suitable for diluted and concentrated wastewater and can be part of a multi-stage system. The sludge retention time is longer than the hydraulic retention time, as the sludge is retained in the reactor by using internal settler systems or external settlers with sludge recycling or fixation of biomass on support material. In single-phase high rate systems, all anaerobic stages take place at the same time.

High rate systems are most suitable for waste streams with a low suspended solids content. Different types, used world-wide for the treatment of wastewater are [1], [26]:

- Contact process; Biobulk-system by Biothane [27];
- Upflow Anaerobic Sludge Bed (UASB);
- Anaerobic Fixed Film Reactor (AFFR);
- Fixed film Fluidised Bed system;
- Expanded Granular Sludge Bed (EGSB);
- Hybrid systems;
- Anaerobic Filter (AF).

Biobulk is a conventional anaerobic contact process, with sludge recirculation, applicable for

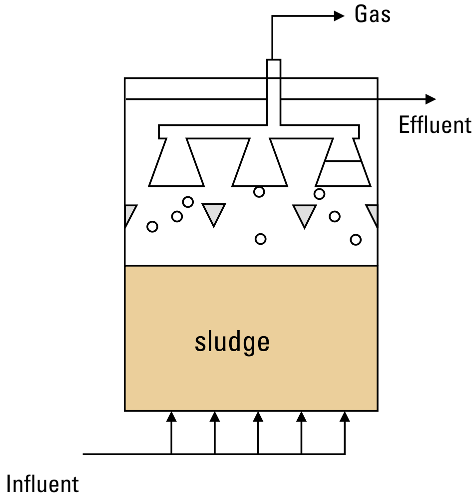


Figure 6. Schematic diagram of a UASB.

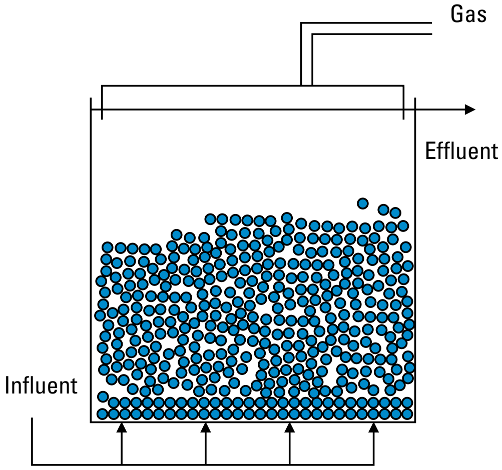


Figure 7. Schematic diagram of an Anaerobic Filter (AF).

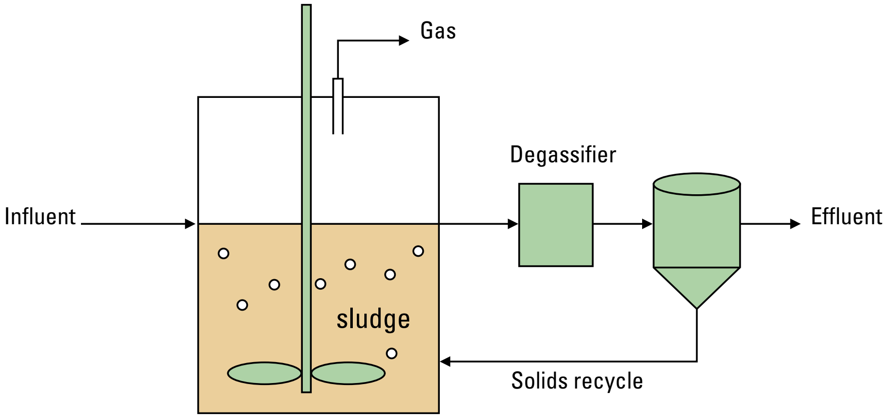


Figure 8. Schematic diagram of an Anaerobic Contact (AC) process.

Figure 9. UASB reactor at Cerestar, Sas van Gent, The Netherlands. Photo by courtesy of Biothane Systems International.

waste streams containing high strength COD / BOD concentrations and fats, oils and grease concentrations higher than 150 mg/l. Biobulk is a 'medium loaded' system with volumetric loading of 2-5 kg/COD/m^3/day.

The Biobulk Continuously Stirred Tank Reactor (CSTR) has specially-designed mixing capability to ensure the wastewater is in constant contact with the biomass.

The process is applied in ice cream plants and other food processing facilities which discharge effluents high in biodegradable fats and oils. Removal efficiencies with this technology have been found to consistently average above 90% with respect to COD and BOD and close to 75% with respect to the organic fraction of TSS.

The **Upflow Anaerobic Sludge Bed (UASB)** concept was developed in the late 1960's at Wageningen University in The Netherlands. The Dutch beet sugar firm, CSM, developed the basic technology for wastewater treatment in several sugar factories. Companies such as Paques and Biothane carried out further development of the system on a commercial basis (Figure 9).

The key to the commercialisation step was the design and engineering of simple but efficient internal topworks (settler) to effectively degasify the biomass and ensure its retention in the reactor vessel. Wastewater enters the bottom of the reactor vessel through an inlet distribution system and passes upward through a dense anaerobic sludge bed. Soluble COD is then converted to biogas, which is rich in methane and an upward circulation of water, establishing well-settleable sludge. The specially constructed settler sections allow an effective degasification so sludge particles devoid of attached gas bubbles, sink to the bottom establishing a return downward circulation (see also Figure 6).

Upward flow of gas-containing sludge through the blanket combined with return downward flow of degassed sludge creates continuous convection. This ensures effective contact of sludge and wastewater without the need for any energy consuming mechanical or hydraulic agitation within the reactor. The unique design of the reactor allows a highly active biomass concentration in relation to soluble organic solids passing through the sludge bed and is responsible for the very high loading rate (short hydraulic retention time), which can be readily achieved. When the UASB is applied for wastewater containing suspended solids (like sewage), flocculent sludge will grow rather than granular sludge [1]. Flocculent sludge can also result in sufficient sludge retention for removal of organic material.

A successful version of this concept is the **Internal Circulation (IC) reactor,** characterised by biogas separation in two stages in a reactor with a high height/diameter ratio and gas-driven internal effluent circulation (Figure 10). The IC system can process high upflow liquid and gas velocities, which enables treatment of low strength effluents at short hydraulic retention times, and treatment of high strength effluents at high volumetric loading rate. In recent years IC technology has been successfully applied at full scale on a variety of industrial wastewater types [28].

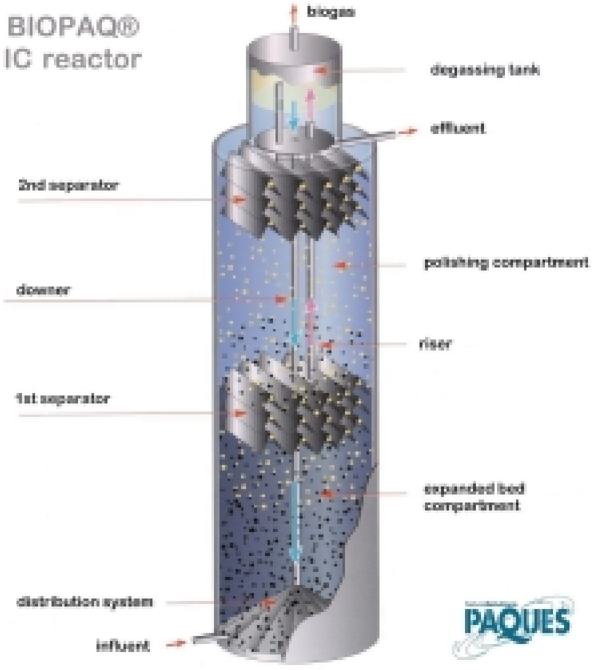


Figure 10. Schematic diagram of Internal Circulation (IC) reactor. Courtesy of Paques Biosystems B.V.

The **Expanded Granular Sludge Bed (EGSB)** process incorporates the sludge granulation concept of UASB's. The main improvement of the EGSB system, trademarked 'Biobed' (by the company Biothane), compared to other types of anaerobic fluidised or expanded bed technologies is the elimination of carrier material as a mechanism for biomass retention within the reactor. This process is therefore perceived either as an ultra high rate UASB or a modified conventional fluidised bed. Applications for Biobed include wastewater from breweries, chemical plants, fermentation industries and pharmaceutical industries. This system is designed to operate at high COD loading; it is very space efficient, requiring a smaller footprint size than a UASB system.

Anaerobic Fixed Film Reactors (AFFR) contain a mixed population of bacteria immobilised on the surfaces of support medium, and have been successfully applied in the treatment of high-strength effluent treatment [29].

The **hybrid system** was developed to overcome the problems in UASB and AF systems. In an AF reactor, the presence of dead zones and channelling in the lower part of the filter generally occurs. In UASB systems sludge washout may be a problem when the wastewater contains large fractions of suspended solids. The hybrid system combines both the fixed bed system (at the top of the reactor) with the UASB system. The filter zone in the hybrid reactor has as well a physical role for biomass retention as biological activity contributing to COD reduction [30].

4.4 Waste streams

The various types of waste streams which can be digested for the recovery of energy in the form of methane, can be divided as follows:

1. Solid wastes:

- domestic wastes, such as separately collected Vegetable, Fruit and Yard waste (VFY);
- organic residual fraction after mechanical separation of integral collected household waste (grey waste);
- agricultural wastes (crop residues);
- manure.

Figure 11. Vagron plant (Groningen) for separation and digestion of the organic fraction of MSW. Photo by courtesy of Vagron BV.

2. Waste slurries:

- liquid manure;
- sewage sludge;
- urine and faeces;
- industrial waste (e.g. fat-, slaughterhouse and fish wastes).

3. Wastewater:

- industrial wastewater (especially from the food and beverage industry);
- domestic wastewater (sewage).

4.4.1 Vegetable, Fruit and Yard waste and organic residual of Municipal Solid Waste

Vegetable, Fruit and Yard (VFY) waste is the organic fraction of domestic solid waste and contains the following components [31]:

- leaves, peels and remains of vegetables, fruits, potatoes;
- all food remains;
- egg-shells, cheese-rinds;
- shells of nuts;
- coffee-filters, tea-leaves and tea-bags;
- cut flowers, indoor plants (without clod), grass, straw and leaves;
- small lop waste and plant material from gardens (no soil);
- manure of pets, pigeons, rabbits (no cat's box grit).

In The Netherlands, VFY waste is mainly composted, but there are two installations in which VFY waste is digested, one in Tilburg (Valorga) and one in Lelystad (Biocel). Grey waste is treated in Groningen (Vagron; Figure 11).

A second plant has been constructed in Heerenveen and is now in the start-up phase. A comparison of the three plants based on measurements from practice is given in Figure 12. The methane content in the biogas is 55-70% [15]. The highest amount of biogas per tonne biowaste is produced in the Vagron plant, operated at thermophilic conditions. The other plants are operated under mesophilic conditions. Moreover the organic waste fraction is collected in a different manner. The organic fraction treated in the Valorga plant contains a low amount of yard waste. Valorga and Biocel are both dry fermentation processes, the main differences being that the Valorga system employs mixing using reverse circulation of the biogas, while in the Biocel process only leachate circulation is employed. Moreover Biocel is a batch system while Valorga is a continuous system. The retention time in the Biocel is approximately 21 days, in the Vagron and Valorga plant approximately 18 days. A more detailed scheme of the Vagron plant is given in Appendix III.

4.4.2 Agricultural wastes

Agricultural wastes contain remains of the process such as cut flowers, bulbs, verge grass, potatoes, chicory, ensilaged weed etc. This type of waste is suitable for re-use after fermentation, as the type of waste collected is 'cleaner' than ordinary VFY [34].

4.4.3 Manure and liquid manure

In The Netherlands approx. 35 on-farm manure digestion installations were in operation in the period 1978 to 1993. In 1993, only four installations still remain operational [31]. In 1995, the only central digester, a medium scale demonstra-

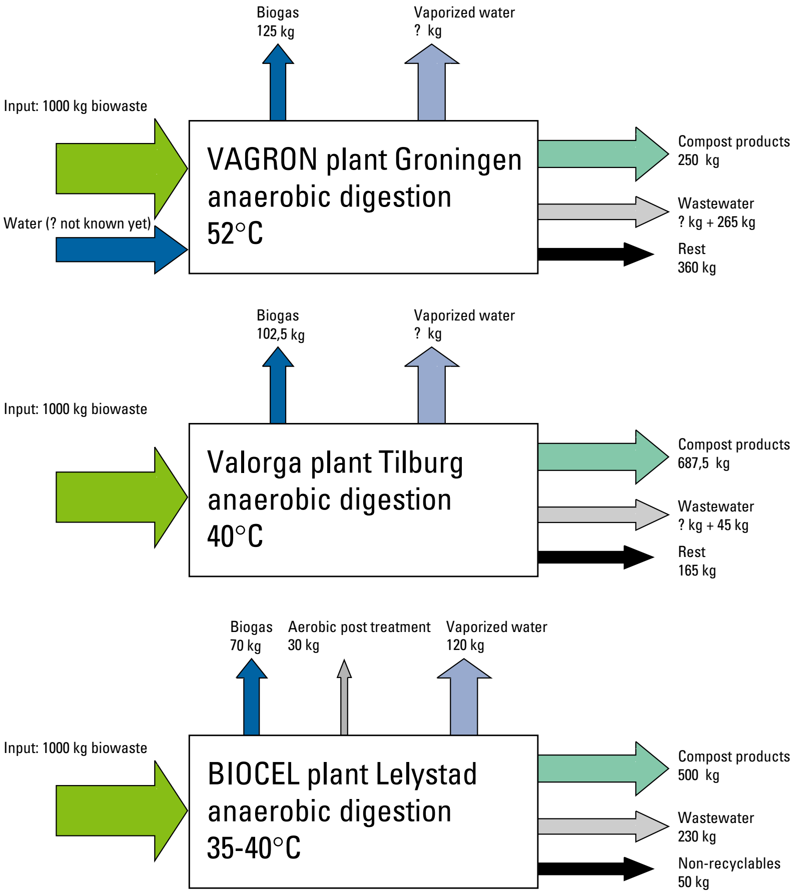


Figure 12. Mass-balances for the three operating digestion plants on the organic fraction of Municipal Solid Waste. Data Vagron from [33], data Valorga from [32], Biocel scheme adapted from [23].

Figure 13. Biogas plant for manure digestion Praktijkcentrum Sterksel, The Netherlands. Photo by courtesy of www.energieprojecten.com.

TABLE 1. *Typical composition of the influent pig and dairy cattle manure in The Netherlands and in Switzerland (All values are given in kg/m^3) [7].*

	The Netherlands Dairy Cattle	**Switzerland Dairy Cattle**	**Switzerland Pig**
Total Solids	85.4	83	43
Volatile Solids	74.7	73	74
NH_4^+-N	2.2	1.5	1.9
Total COD	101	-	-
Dissolved COD	27.6	-	-
VFA (COD)	11.1	2.6	7.4
pH	7.5	7.4	7.2

tion plant at Daersum was closed down. The full-scale plant, named PROMEST in Helmond where 600,000 tonnes animal manure was processed per year was also closed in the same period. The PROMEST processing plant consisted of anaerobic digestion followed by separation of liquid /solids and treatment of the liquid, in order to produce clean water and granulated fertilisers. Until recently manure digestion was not taken in operation in The Netherlands. Farm scale digesters became too expensive and labour intensive and farmers were not willing to pay for manure processing in the central digesters. In summary the reasons are [35]:

- Low return for biogas and electricity (low prices);
- Strict regulation for the application of co-digestion. Co-digestion can increase the gas yield per m^3 reactor content per day, but legislation prevented the application of digested co-substrates on agricultural fields [36];
- Insufficient collaboration effort between the agricultural sector, energy sector and the waste sector to introduce this technique.

The situation has improved since 1997 due to the following development [35]:
- Increased price for disposal of organic waste due to the ban on organic matter landfill;
- Higher prices for renewable energy;
- The need for selective manure distribution due to stronger manure legislation;
- Lower capital/investments costs due to lower interest rates and fiscal incentives;

Digestion of manure is economically efficient when mixed with other organic waste streams, like VFY waste, left-over feed, roadside grass, old frying fat etc. This technique is called co-digestion and widely used in Denmark. In Denmark a specific biogas production of ca. 37 m^3 per tonne of biomass is achieved using co-digestion, while only using manure approximately 20 m^3 per tonne biomass is produced. At the Research Institute for Animal Husbandry in Lelystad (The Netherlands) a study has been conducted on the feasibility of anaerobic manure digestion for individual Dutch dairy and pig farms. The most important conclusion of the report is that manure digestion can be economically viable given a sufficiently large farm and economic feasibility is dependent on the market value of electricity. The reduction of CO_2 emission is also emphasised. Given these trends, manure digestion will become an increasingly interesting option in the coming years. At present several demonstration plants are operational in The Netherlands, which apply co-digestion, limited to plant materials, for example at a dairy farm in Nij Bosma Zathe, in Leeuwarden and at a pig farm in Sterksel, Brabant (see Figure 13). The volume of the digester is dependent on the concentration of the manure. A higher concentration ensures less volume is needed to apply the same hydraulic retention time and biogas production. The concentration of manure is dependent on the method used to clean out stables. A typical composition of pig and dairy cattle manure in The Netherlands and Switzerland is shown in Table 1. Concentrations have been increased as a result of reduction in 'spilling' water. The biodegradability can also vary with the kind of manure. The biodegradability of dairy manure is much lower due to the very efficient digestive track of ruminants. In digestion of pig-slurry about 40% of the COD will be converted to methane-COD [37], while in the digestion of cow slurry this is approximately 25% [7]. The methane content of the biogas varies between 55-70% [38]. An overview of initiatives in The Netherlands for manure digestion is given as Appendix IV.

4.4.4 Sewage sludge

Sewage sludge contains primary sludge as a result of a pre-settling stage of sewage and secondary sludge as a result of sludge growth during aerobic wastewater treatment. To stabilise sludge before further treatment, anaerobic digestion is commonly used. In The Netherlands in 2001 approximately 100 one-step digesters were in operation [39]. The average process conditions are summarised in Table 2. From a theoretical point of view approximately 50 large sewage treatment plants (capacity higher than 50,000 p.e.) in The Netherlands could improve efficiency if anaerobic digestion was applied [39]. Typical values for the amount of total solids in the influent are 4% to 6% [40]. Due to a high number of one-step digestion installations in the Netherlands not performing at optimum conditions with respect to biogas production, Royal Haskoning B.V. performed research to optimise these conditions [40]. One of the conclusions was that process factors such as retention time, loading rate and mixing have a larger influence on the degradation of organic material than temperature. Optimisation of these factors can lead to an increase in biogas production of approximately 25%.

The dry matter of sludge contains approximately 70% organic matter. During digestion this can be reduced to approximately 45%. As a result of this reduction and the increased de-waterability

TABLE 2. *Typical process parameters of sludge digestion installation in The Netherlands, minimum, maximum and average value [40].*

Parameter	Minimum value	Maximum value	Average
Digester Volume (m^3)	450	26,464	3,963
Temperature (°C)	30	35	33
HRT (days)	11	77	31
Influent Dry matter (kg/day)	512	55,000	6,641
Influent Organic matter (kg/day)	255	41,250	4,581
Loading (kg dry matter/m^3/day)	0.53	4.66	1.52
Removed (kg dry matter/m^3/day)	0.10	1.40	0.54
Gas production (m^3 CH_4/day)	74	13,000	1,216
Gas production (m^3 CH_4/kg dry matter input)	0.116	2.063	0.682

the final sludge volume after de-watering is decreased. The digestion of aerobic biomass (secondary sludge) is limited due to slow dying and lysis of aerobic microbial cells. In The Netherlands the further treatment, after digestion, is mainly dewatering and incineration of the solid fraction. The latter represents the largest cost in the treatment of domestic sewage. Digested sewage sludge cannot be used in agriculture as a result of heavy metals pollution.

4.4.5 Industrial waste slurry and wastewater

Industrial wastewater is heterogeneous, both in composition and volume. Effluents from the Food & Beverage (F&B) industry contain the highest concentration of organic compounds [41]. Anaerobic wastewater treatment is widely applied in this branch of industry as in the Pulp and Paper industry, as is shown in Table 3 and Figure 14.

TABLE 3. *World-wide application of high rate anaerobic systems adapted from a vendor's database [26].*

Application	Number of plants
Breweries and beverages	304
Distilleries and fermentation	206
Chemical	61
Pulp and paper	130
Food	371
Landfill leachate	20
Undefined/unknown	70
Total in database	**1,162**

Food and Beverage industry

The most important Food and Beverage industries can be summarised [41]:

- Slaughterhouses and meat-processing
- Dairy
- Fish-processing
- Starch-processing
- Sugar
- Edible oil
- Beverages and distilleries
- Fruit and vegetable processing
- Coffee processing

As each process involves different compounds and the majority of these industries do not operate continuously over a 24 hour period each waste-water characteristic shown below will vary with time:

1. Volume (varying from 0.1-175 m^3/tonne product);
2. BOD/COD concentration and ratio (BOD 30-40 g/l; COD 70-80 g/l);
3. pH (in the range 3-12);
4. Temperature (10-100 °C);
5. Concentration of nutrients, chemicals, detergents.

If the wastewater does not contain a large percentage of suspended solids, a high rate system is usually applied. Otherwise removal of solids in a primary treatment system can be applied. These solids can be treated, e.g. to produce animal feed or fertiliser, or can be digested separately or, in the worst case, incinerated. When solids are not removed in advance, the HRT should be increased so a sufficient SRT is provided [5].

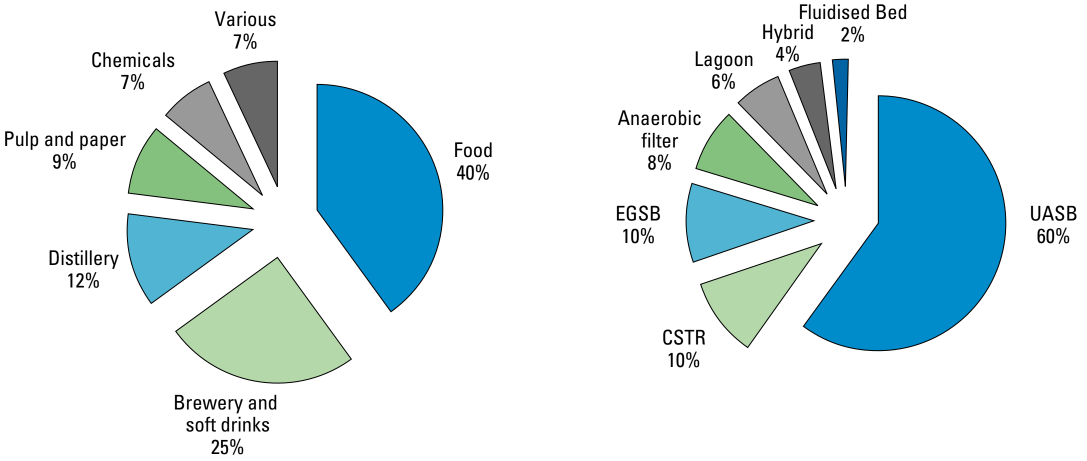


Figure 14. Industries using Anaerobic Digestion for wastewater pre-treatment and types of AD systems used for industrial wastewater pre-treatment plants [42].

An overview of the characterisation and anaerobic biodegradability of different industrial wastewater streams is given as Appendix II.

4.4.6 Domestic wastewater

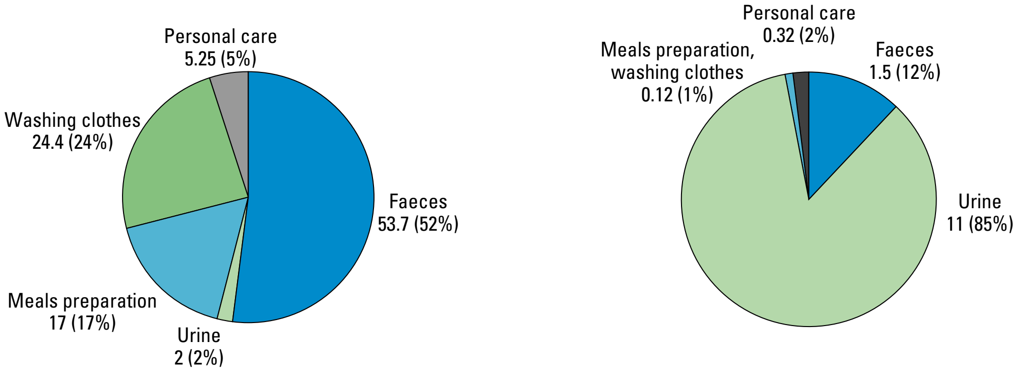
Domestic wastewater is composed of different flows, which can be discharged separately or combined:

1. **Black water:** Wastewater from flushing the toilet contains faeces, urine and cleansing materials. Black water contains a high number of pathogens. The concentration of this waste stream is dependent on the amount of flushing water used. In 'conventional' European and northern American toilets about 10 litres per flush is used. Poor-flush toilets use 2-5 litres per flush and modern vacuum toilets only use ca. 1 litre per flush.
2. **Grey water:** Wastewater from in-house usage such as bathing, washing and cleansing does not contain excreta and therefore less pathogens and little nutrients (N, P, K). Volumes and concentration are strongly dependent on water consumption patterns and waste handling.
3. **Combined wastewater:** Both black and grey water combined with urban run-off water, such as rain and drain water.

Combined wastewater is too diluted in western countries to be treated anaerobically; it would take more energy to heat the wastewater than the amount of methane formed. Treatment at low temperatures is possible but long HRT's are necessary, in order to provide sufficient SRT for hydrolysis and methanogenesis. Recently, new technologies for treatment of raw domestic sewage at low

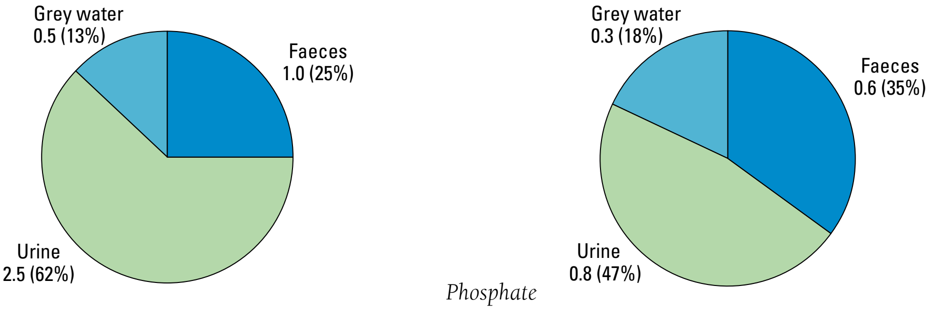
TABLE 4. *Composition of raw sewage in various cities in the world. The sewage is mainly of domestic origin [44]*

Characteristic	**Pedregal, Brazil**	**Cali, Colombia**	**Bennekom, The Netherlands**	**Accra, Ghana**
Total Suspended Solids (TSS mg/l)	429	215	160	980
Volatile Suspended Solids (VSS mg/l)	252	107	70	769
BOD (mg/l)	368	95	230	879
COD (mg/l)	727	267	525	1546
Total Nitrogen (mg N/l)	44	24	75	93
Total Phosphorus	11	1.3	18	16
Alkalinity	388	120	350	491



COD *Nitrogen*

Figure 15. Organic matter (g COD) and Nitrogen (g) produced in domestic wastewater per person per day [45].



Potassium *Phosphate*

Figure 16. Potassium (g) and phosphate (g) produced in domestic sewage per person per day [45].

temperatures have been developed and tested on pilot scale [30], [43]. In developing countries anaerobic treatment of domestic sewage is an appropriate technology as temperatures are favourable. Several full-scale UASB systems are applied in South America, India, and recently Ghana (West Africa). The composition of sewage is given in Table 4. The maximum anaerobic biodegradability of domestic sewage is 74% [30]

Wastewater quality and quantity

A large fraction of domestic wastewater components, viz. organics, nitrogen, phosphorus, potassium and pathogens are produced in small volumes, viz. as faeces plus urine. The latter is shown in Figures 15 and 16. The diagrams show that 85% nitrogen, 2% organic matter, 46% phosphorus and 62% potassium present in domestic wastewater originates from the urine, while 11.5% nitrogen, 52% organic matter, 35% phosphorus and 25% potassium originates from faeces. The mean production of faeces plus urine amounts to 1.5 l per person per day. This volume contains 96.5% nitrogen, 54% organic matter, 81% phosphorus (when no phosphorus is used in washing powders) and 97% potassium produced per person per day. Moreover, faeces contain the largest amount of pathogens. All these compounds are diluted with clean water when flushing toilets and moreover when shower and bath water, washing water and kitchen water are added, before entering the sewer. In the sewer rainwater is also added. Finally a large volume of water is transported to the wastewater treatment system, where the different compounds should be removed, consuming a large amount of energy when conventional aerobic treatment is applied. The former clearly shows that separation of toilet wastewater (black water) can prevent the pollution of other wastewater streams (grey water) with organics, nutrients and other salts and pathogens.

The section Environmental Technology of Wageningen University researches the separate collection, transport and treatment of black and grey water. The concept will be demonstrated in 2005. In Germany the concept is already applied in practice at a few locations, for example in a new housing estate in Lübeck.

4.5 Utilisation of biogas as a renewable energy source

4.5.1 Introduction

Biogas or landfill gas is primarily composed of methane (55-75 vol%), and carbon dioxide (25-45 vol%) with smaller amounts of H_2S (0-1.5 vol%) and NH_3 (0-0.05 vol%). The gas mixture is saturated with water vapour and may contain dust particles and trace amounts of H_2, N_2, CO and halogenated compounds depending on the feedstock and process conditions [46]. The fuel value of biogas containing 55-75 vol % methane ranges between 22–30 MJ/Nm^3 (Higher Heating Value) and 19-26 MJ/Nm^3 (Lower Heating Value) respectively.

Biogas can be utilised for the production of heat, co-generation of electricity and heat (CHP) or for upgrading to natural gas or fuel gas quality. A part of the biogas energy is utilised on site to provide for the internal energy requirement of the plant (digester heating, pumps, mixers etc.).

The amount of energy used for plant operation ranges between 20 and 50% of the total biogas energy contents depending on climate and technical specifications. For systems treating solid biowastes internal energy use is around 20%. In [47] a biogas plant in Germany is described treating 26,000 tonnes of fruit and vegetable wastes and 4,000 tonnes of park wastes per year. The plant produces 2.8 Million Nm^3 of biogas per year (60 vol% methane) with a total energy content of 16,650 MWh. The biogas is converted in a CHP system into electricity (35%) and heat (50%) with 15% energy loss. The energy balance indicates that the plant consumes 23% of the energy content of the total biogas production. The electricity surplus for export to the grid amounts to 3,510 MWh/year or 21% of the biogas energy content [47].

In the remaining part of this section techniques for utilisation and upgrading of biogas and landfill gas are described, including the required purification processes. For reviews the reader is referred to [46], [48], [49].

4.5.2 Generation of heat and combined heat and power generation (CHP)

Heat production in gas heater systems

Heat production in gas heater/boiler systems does not require a high gas quality [46]. Reduction of the H_2S content to below 1,000 ppm is recommended to prevent corrosion. Furthermore it is advisable to condense the water vapour in the gas to prevent interference with the gas nozzles. Removal of water will also remove a substantial amount of the H_2S [46].

Gas engine and gas turbine CHP systems

The utilisation of biogas in internal combustion engines ('gas engines') is a long established technology. Engine sizes range from 45 kWe in small plants to several MWe in large biogas plants or landfill sites. Mostly used in large-scale applications are diesel engines rebuilt to spark ignited gas engines or dual fuel engines with 8-10% diesel injection [46]. Small-scale CHP systems (< 45 kWe) reach an electrical efficiency of 29% (spark ignition) and 31% (dual fuel engine). Larger engines can reach an electrical efficiency of 38% [46]. Up to 50% of the biogas energy content is converted to heat which can partly be recovered from the exhaust gas (high temperature heat) and the cooling water and oil cooling (lower temperature heat) [48], [49]. Energy losses are about 15%. Utilisation of biogas in gas engines may require removal of H_2S, NH_3 and particles depending on manufacturers' specifications (see Table 5).

Gas engine CHP systems have a higher electrical efficiency than gas turbine CHP systems and lower specific investment costs. Maintenance costs for gas engines are higher than for turbines. The use of gas turbines in CHP systems may be more economical in applications with a large, constant high value heat requirement (> 110 °C) or in large installations of several MWe's capacity [49]. A restriction of gas turbines is the limited flexibility with varying gas flows because a reduced gas inflow leads to a decreased efficiency [48].

Fuel cell CHP systems

Fuel cells make use of direct electrochemical conversion of the fuel with oxygen to generate electricity and heat with near-zero emissions. The fuel (methane in the case of biogas) is converted to hydrogen by the action of a catalyst or high temperature steam reforming. The H_2 is then electrochemically converted to electricity and heat. Water and CO_2 are the main by-products. The potential electrical efficiency is > 50% while the thermal efficiency is approx. 35%. For utilisation of biogas two fuel cell types are most relevant for the near future. Phosphoric acid fuel cells (PAFC) are at present applied in a number of 200 kW to 2 MW power plants operating on natural gas with a practical electrical efficiency of 41% [46]. The PAFC operates at approx. 200 °C which allows usable heat recovery. Utilisation of biogas in a PAFC requires near-complete removal of sulphides and halogenated compounds [46], [50]. In Japan a 200 kWe PAFC is used in a brewery for conversion of biogas from wastewater effluent [51]. Before entering the fuel cell the biogas is purified in a pre-treatment section composed of a desulphuriser, an ammonia/salt removing unit, a buffer tank and a gas analyser. Impurities are adequately removed while at the same time CO_2 is removed from the gas. The overall conversion efficiency (electricity + heat) is 80% [51]. Solid Oxide Fuel Cells (SOFC) operate at temperatures > 900 °C. The SOFC has a relatively high tolerance for impurities, although it also requires near-complete removal of sulphides and halogens. The high operating temperature allows direct methane conversion and recovery of high temperature heat. The attainable electrical efficiency on natural gas is > 40%. In The Netherlands the utilisation of biogas from animal manure in an SOFC system is currently being explored at farm scale [52].

The utilisation of biogas in fuel cells is an important strategy to enhance the efficiency of electricity generation. A substantial cost reduction of fuel cells is however required for large-scale application. The conversion of fermentation gases in fuel cells is being explored in ‘BFCNet’: ‘Network on Biomass Fermentation Towards Usage in Fuel Cells’ [53]. The objectives of BFCNet include R&D and demonstration, and the development of standards on EU level.

4.5.3 Upgrading of biogas and landfill gas to natural gas and vehicle fuel quality

Upgrading of biogas and landfill gas to natural gas standards and delivery to the (local) natural gas network is a common practice. In The Netherlands 45% of the produced landfill gas was upgraded to natural gas quality in 1995 [48]. Landfill gas is the final product from biodegradation of organic materials present in landfill sites and consists mainly of methane (50-60 vol%) and carbon dioxide (40-45 vol%). It further contains sulphur (0-200 mg/m^3) and chlorinated and fluorinated hydrocarbons. The Higher Heating Value is 20-24 MJ/m^3 [48]. To reach natural gas quality the landfill gas undergoes extensive dewatering, removal of sulphur components in a bed charged with impregnated active carbon or iron oxide, and removal of halogens by absorption in an active carbon bed. Further upgrading involves changing the composition of the gas by separating the main components methane and carbon dioxide in a high calorific (methane rich) and a low calorific (methane poor) gas flow in order to attain a calorific value and 'Wobbe index' similar to natural gas. Upgrading technologies include chemical absorption, Pressure Swing Adsorption and membrane separation. Before delivery to the grid the gas must be free from solid and fluid components and it must be pressurised [48]. Upgrading of biogas from controlled digestion makes use of similar technology.

Upgrading of biogas to transport fuel quality is common practice in several European countries (including Sweden, the Czech Republic, France), the USA and New Zealand. World wide 23 facilities for production and upgrading of biogas to transport fuel standards were in operation in 1999 [46]. Sweden produces an amount of biogas of 1,35 TWh/year primarily in sewage treatment plants and also in landfill sites and industrial wastewater treatment plants. Approximately 100 GWh/year (10 Million m^3) are currently used as vehicle fuel. Based on experiences gained from projects with municipal fleets of busses and taxis, the Swedish program now aims for commercial expansion of vehicle fleets and infrastructure for (upgraded) biogas refuelling stations [54]. Upgraded biogas can be used in existing engines and vehicles suitable for natural gas. At present approx. 1.5 million natural gas fuelled vehicles are in use world wide. Sulphur, water and particles must be removed to prevent corrosion and mechanical engine damage. Carbon dioxide must be removed to reach a required methane content

TABLE 5. *Indicative gas quality requirements for various applications. Sources: [46], [48], [49].*

Component:	**H_2S**	**CO_2**	**Halogens (Cl, F; landfill gas)**	**Dust particles**	**H_2O**
Utilisation:					
Gas heater/boiler	< 1000 ppm 1)				Removal advisable
Gas engine		Minimum LHV 3) 13-21 MJ/m^3	Cl and F3) 60-80 mg/m^3		Humidity 3) < 70-80%
- per 10 kWh (LHV) input3)	< 1150 – 2000 mg			< 50 mg/m^3	
- per m^3 of biogas3)	< 700-1200 mg/m^3			< 30 mg/m^3	
Fuel cells					
- Phosphoric Acid Fuel Cell	< 10 ppm4		Near-complete removal required	Removal required	
- Solid Oxide Fuel Cel	< 10 ppm4)				
Vehicle fuel 5)	Max. 23 mg/Nm^3	Max. 3 vol%	Removal required		Max. 32 mg/Nm^3
Natural gas quality6)	Sulphur < 5mg/m^3 7)		Cl < 5mg/ m^3	Removal required	Dew point at –10°C

1) removal required if input limits are exceeded
2) data provided by Jenbacher (2002) per 10 kWh (LHV) gas input for gas engines ranging between 300-3000 kW; data were calculated per m^3 biogas assuming 60 vol% methane. The maximum allowable NH_3 concentration is 55 mg/10 kWh [49]. If an NO_x (and CO) catalyst is used to purify the engines' exhaust gases, near-complete removal of halogens from the biogas is required.
3) according to ref. [48].
4) preferably lower i.e. < 1 ppm.
5) specifications for transport fuel used in Sweden. From ref. [46].
6) natural gas composition in The Netherlands. From ref. [48].
7) removal (to about 5 vol%) required to attain suitable combustion value and Wobbe index.

of 96 - 97 vol%. The gas is compressed and stored at a pressure of 250 bar for distribution, using the same technology as for compressed natural gas [46].

Demands for the removal of components differ depending on the biogas application. Indicative quality requirements for several applications are summarised in Table 5.

4.5.4 Purification technologies

Raw biogas should be treated to prevent corrosion of installed equipment or to achieve adequate quality standards for use as a natural gas substitute or transport fuel. An overview of available techniques for biogas treatment is provided in Table 6.

4.6 The economics of anaerobic digestion

4.6.1 Introduction

In assessing the economic viability of biogas programs, it is useful to distinguish between three main areas of application:

1) Anaerobic treatment of household waste(water)
   a) DeSaR (Decentralised Sanitation and Reuse); including community-on-site anaerobic treatment of domestic waste(water) and organic household waste
   b) central digestion of the organic fraction of household waste
      i) source separated at the household

TABLE 6. *Overview of techniques used for biogas treatment [55].*

Compound removed	Technique	Principle
Water/Dust	Demister	Physical
	Cyclone separator	"
	Moisture trap	"
	Water trap	"
	Cooling in combination with demister	"
	Absorption to silica	"
	Glycol drying unit	"
H_2S	Air oxygen dosing[1)]	Biological
	$FeCl_3$ dosing to digester slurry	Chemical
	Adsorption to Fe_2O_3 pellets	Physical-chemical
	Absorption with caustic solution	"
	Absorption with iron solution	"
	Absorption closed loop systems	"
	Membrane separation	Physical
	Biological filters	Biological
	Activated carbon filtration	Physical-chemical
	Molecular sieves	Physical
CO_2	Pressure swing adsorption	Physical-chemical
	Membrane separation	Physical
	Absorption techniques	Physical-chemical

1) The H_2S content can be reduced by adding a small amount of air at the end of the digestion process.

        ii) mechanically separated
    c) digestion of sewage sludge at a central sewage treatment plant
2) Anaerobic digestion of manure
    a) on-farm digestion for energy production
    b) central digestion for energy production
    c) central digestion and further processing (recovery/removal of nutrients from the liquid phase)
3) Anaerobic treatment of industrial wastewater and waste

In this section mainly 1b, central digestion of the organic fraction of household waste, and 2, anaerobic digestion of manure, are discussed. In each case, the economic feasibility of individual facilities depends largely on whether output in the form of gas (for cooking, lighting, heating and electricity generation) and solid and liquid by-products (for use as fertiliser/soil conditioner, fishpond or animal feed) can substitute for fuels, fertilisers or feeds, previously purchased. For example, a plant has a good chance of being economically viable when farmers or communities previously paid substantial percentages of their incomes for fuels (e.g. gas, kerosene, coal), fertilisers (e.g., nitrates or urea) or soil conditioners. The economics may also be attractive in farming and industry, where considerable cost is experienced in disposing manure, solid wastes and effluents. In these cases, the output can be sold or used to reduce energy and disposal costs, repaying the original capital investment. In cases when the community is charged for treatment of wastes the digestion process may be of great financial importance. When the products do not generate income or reduce cash outflow the economic viability of a biogas plant decreases. For example when cooking fuels such as wood or dung can be collected at zero cost or where the cost of commercial fuel is so low that the market for biogas is limited. Technical, social and economic factors, government support, institutional arrangements, and the general level of commercial activity in the construction of biogas plants and related equipment are highly interrelated [56]. This section focuses on the economic aspects of anaerobic digestion of manure and solid organic wastes, which are currently undergoing new developments and rapid expansion.

4.6.2 Anaerobic digestion of manure

The Danish Biogas Programme [57] is an excellent example of what can be achieved through an ambitious and consistent government policy and is therefore discussed in some detail here. In Denmark 20 centralised biogas plants are operational for treatment of animal manure [58], [59], [60]. The plants mostly employ thermophilic co-digestion (52-53 °C) with approx. 25% organic wastes mainly from food processing industries. These include animal wastes such as intestinal contents (27%), fat and flotation sludge from food or fodder processing (53%) and wastes from fruit & vegetable processing, dairies and other industries. In the biogas plants manure and organic waste are mixed and digested for 12-25 days. The biogas is utilised for combined heat and power generation. Heat is usually distributed in district heating systems, while electricity is sold to the power grid. The digestate is returned to the farms for use as fertiliser. In 1998 a total of 1 Million tonnes of manure (slurry) were treated in centralised biogas plants and 325,000 tonnes of other wastes, yielding a total of 50.1 Million m^3 biogas at an average gas yield of 37 m^3 per m^3 of biomass [59]. Whereas the normal yield is 20 m^3 of biogas per m^3 of manure slurry, co-digestion thus adds considerably to biogas production and economic feasibility. Techno-economic data for 6 centralised biogas plants in Denmark [59] are summarised in Table 7.

The development of centralised biogas plants in Denmark was made possible in a framework of governmental renewable energy policy, economic incentives and legislative pushes. The latter include the obligation for a 6-9 month manure storage capacity, restrictions on manure application on land and on landfilling of organic wastes. Economic incentives include government investment grants, low interest rate long-term loans (20 years), energy tax exemptions and subsidies on electricity produced from biogas (DKK 0.27 or Euro 0.04 /kWh in 1998; [58]). Another important factor is that heat sales are possible through widely available district heating networks for 6-9 months per year. The plants are operated mostly by co-operatives involving farmers, municipalities and/or private organisations.

The investment costs for the 6 plants in Table 7 (including digesters, storage, transport vehicles and CHP units) range between Euro 870–1,265 /m^3 digester capacity (average: Euro 1,070/m^3) and Euro 48 - 87/tonne processing capacity (average: Euro 65/tonne). This value is low as compared to e.g. a recently built manure processing biogas plant in The Netherlands (25,000 tonnes/year; Euro 160/tonne). The larger scale of the plants (70,000-140,000 tonnes/year) and limited investments for wastewater treatment possibly causes the lower specific investments of the Danish plants. The digested slurry of the Danish plants is returned to the farmers as organic fertiliser, while for the Dutch plant further processing is applied.

The net energy production of the six plants in Table 7 (producing a total of 23.5 million Nm^3 of biogas/year) is estimated at 29,900 MWhe electricity/year and 170 TJ heat/year. The total investment costs per kWe electricity (estimated from Table 7) is around Euro 9,000/kWe. This is however an overestimation because the plants produce heat as well. The total biogas production in centralised plants in Denmark [59] is approx. 50 million Nm^3/ year with an estimated electricity generation of 63,600 MWhe/year and 360,000 TJ /year of heat.

In 1998 most of the operational Danish plants produced an income at or above the break-even level [58]. The income consists of energy sales and gate fees minus operating costs. The total treatment costs (manure and additional wastes) for transport and anaerobic digestion are around Euro 8/m^3 with an income of Euro 7/m^3 from energy sales [60]. Approximately half of the income for energy sales is derived from subsidies (exemption of energy taxation, refunding system). The net treatment costs are Euro 1.4/m^3 [60]. Economic feasibility depends on the co-digestion of food processing wastes, both through the enhanced biogas production and gate fees charged for industrial wastes of Euro 7-13 m^3. According to [60] this is highly competitive –under Danish conditions– with incineration including waste deposit tax (Euro 54-74/tonne) and composting (Euro 40-50/tonne).

TABLE 7. *Techno-economic data for 6 centralised biogas plants in Denmark. Based on [59].*

	Plant location	Lemvig	Thorso	Arhus	Studsgaard[1]	Blabjerg	Nysted
	Units						
Year of operation start-up	--	1992	1994	1995	1996	1996	1998
Animal manure	Tonne/day	362	230	346	230	222	180
Other organic wastes	Tonne/day	75	31	46	36	87	31
Biogas production	Million Nm^3/yr	5.4	2.9	3.8	5.7	3.1	2.6
Biogas production	Nm^3/tonne	38	34	30	65	31	38
Total digester capacity	m^3	7600	4650	8500	6000	5000	5000
Process temperature	Degrees Celsius	52.5	53	38 / 52	52	53.5	38
Gas storage capacity	m^3	5000	2790	370	170	4000	2500
Utilisation of biogas	--	CHP	CHP	CHP	CHP	CHP	CHP/ Boiler
Total energy production biogas2)	GJ/year	100,980	54,230	71,060	106,590	57,970	48,620
Electricity production2)	MWh/year	6,872	3,691	4,836	7,254	3,945	3,309
Heat production2)	GJ/year	38,877	20,879	27,358	41,037	22,318	18,719
Investment costs	Million DKK	55.2	29.1	54.2	55.7	44.1	43.7
Cost index (2000=394) 3)	--	358	368	381	381	381	390
Investment in Euro 2000 (calculated) 4)	Million Euro	8.0	4.1	7.4	7.6	6.0	5.8
Investments per m^3 digester capacity 5)	Euro/m^3	1054	883	869	1265	1202	1164
Investments per tonne capacity 5)	Euro/tonne	56	48	57	87	59	84

1) The Studsgaard plant applies 2.5 hours heating at 60°C prior to digestion.
2) Estimated; assuming 55 vol% methane in biogas (19 MJ/Nm^3, Lower Heating Value); 30 % internal use in the biogas plant; CHP conversion efficiency to electricity 35% and to heat 55%, respectively.
3) Chemical Engineering Plant Cost Index.
4) Recalculated to Euro 2000, using cost indices and exchange rate of 1 DKK = 0.1318 Euro.
5) Including digesters, storage, transport vehicles and CHP units [59].

Manure digestion in The Netherlands. In The Netherlands anaerobic digestion of manure is gaining renewed attention. The largest fraction of produced animal manure is directly recycled as fertiliser. A surplus of 15 million tonnes/year is available for anaerobic digestion [61]. Several small-scale and larger scale biogas plants have started operation in 2001 and 2002 [61]. See Appendix IV for an overview of recent initiatives. A stimulus for this development is the active involvement of utility companies since the end of the 1990's due to the relatively high market price for natural gas and the interest in producing renewable energy.

In The Netherlands the economic benefit of a manure digester can only be achieved with a very high biogas production. In a study on the possibilities of manure co-digestion, it was estimated that the capacity of an installation should be 200 m^3 per day, with a biogas yield of 80 m^3 per tonne of biomass. This can only be achieved when energy rich additives are added such as Fuller's earth or fish-oil sludge [62]. Up till now however, only limited use is made of co-digestion (e.g. with verge grass) to enhance biogas production and economic feasibility. This is mainly caused by incompatible environmental regulations and restrictions on the use of digestates as fertiliser [61], which evidently slows down the development of new plants. There is considerable activity from the side of producers to modify regulations in favour of co-digestion. The attainable electricity production from anaerobic digestion of the total surplus of animal manure in The Netherlands (15 Million tonnes) is estimated at 1,100 GWh (389,000 households). Furthermore a volume of 4 Million tonnes of agricultural wastes is available for co-digestion, which could generate an additional 470 GWh of electricity, for 159,000 households [61].

A regional installation for anaerobic digestion and further processing of pig manure is operational in Elsendorp, The Netherlands since 2001. This installation processes 25,000 tonnes of pig manure per year and produces 1.6 Million kWh of electricity (sufficient for 500 households), 7,500 tonnes of mineral concentrates for use as substitute fertiliser and 17,500 tonnes of clean water. The gate fee for manure is Euro 16-18/m^3, which is similar to alternative manure treatment options [61]. Biogas plant 'De Scharlebelt' at Nijverdal started operation in 2002 [63]. This plant has a capacity of 25,000 tonnes/year (70 tonnes/day) and makes use of thermophilic (50 °C) co-digestion of pig manure and verge grass. The total digester capacity is 1,500 m^3. The total investment costs were Euro 4 Million (or Euro 160/tonne processing capacity and Euro 6,700/kWe) including storage, CHP unit (600 kWe) and membrane filtration units for effluent post treatment and production of mineral concentrates. The digestate is mechanically separated into a 'humus' fraction and a liquid fraction, which is processed further by means of ultrafiltration and reverse osmosis to produce mineral concentrates and clean water. The biogas is used for the process and the generation of 3 Million kWh of electricity per year (1,000 households). In [64] the investment costs per kWe for biogas plants producing (only) electricity from animal wastes is estimated at Euro 4,400–6,600/kWe (recalculated to Euro 2000) for a 1 MW_e plant.

The cost of biogas produced in small-scale (80 m^3) manure digesting systems on farm level in The Netherlands is estimated at Euro 19/GJ based on data in [38]. Through the use of larger scale systems and economic optimisation a cost reduction to approx. Euro 9/GJ is considered feasible. Calculations based on data from the USA [65] even suggest a possible future biogas cost of Euro 5/GJ for large-scale farms.

4.6.3 Anaerobic digestion of solid biowastes

The main competitors for anaerobic digestion of solid wastes are landfilling and composting. Due to legislation landfilling is already restricted in some countries. Since the European Union is striving towards a substantial reduction of landfilling in the near future[1], composting remains as the main competitor on the longer term. Organic residues from agricultural industry, nowadays used as animal feed, could become available for anaerobic digestion in the future.

Composting is a widely used technique, offering a route for recycling organic matter and nutrients from the organic fraction of municipal solid waste and other biowastes. Composting is however an energy consuming process (approximately 30-35 kWh is consumed per tonne of input waste), while anaerobic digestion is a net energy producing process (100-150 kWh per tonne of input waste) [14]. This evidently makes anaerobic digestion the preferred processing route because it produces renewable energy (biogas) while nutrients are preserved for recycling as well. In a 1994 IEA study [66] the economics of municipal solid waste treatment in The Netherlands by composting and anaerobic digestion were compared based on a 1992 study by Haskoning. The analysis showed somewhat higher treatment costs for anaerobic digestion (Euro 80-35/tonne for a capacity range of 20,000-120,000 tonne/year) than for composting (Euro 60-30/tonne). The study concludes that co-digestion with animal manure could lead to significantly lower costs and that the cost difference between composting and anaerobic digestion is very sensitive to the value of the produced electricity [66]. This illustrates the significance of financial incentives for renewable energy production as a tool for enhancing the competitiveness of biogas plants. Similar cost estimates are provided in [67] for anaerobic digestion of source separated organic fraction of municipal waste (SS-MSW) and mixed waste (MW; separated at the plant) in North America. The capital cost of an SS-MSW facility varies between US \$ 635 and \$ 245/tonne of design capacity for plants between 10,000 and 100,000 tonnes/year. The capital cost of mixed waste facilities is higher because of the need for a sorting system and ranges between \$ 690 and \$ 265/tonne. The projected, net annual costs (incl. capital and operating costs, labour and revenues from the sale of biogas

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[1] In the proposed EC Landfill Directive the targets for landfilling (relative to the 1993 situation) are reductions to 50% (2005) and 25% (2010) respectively.

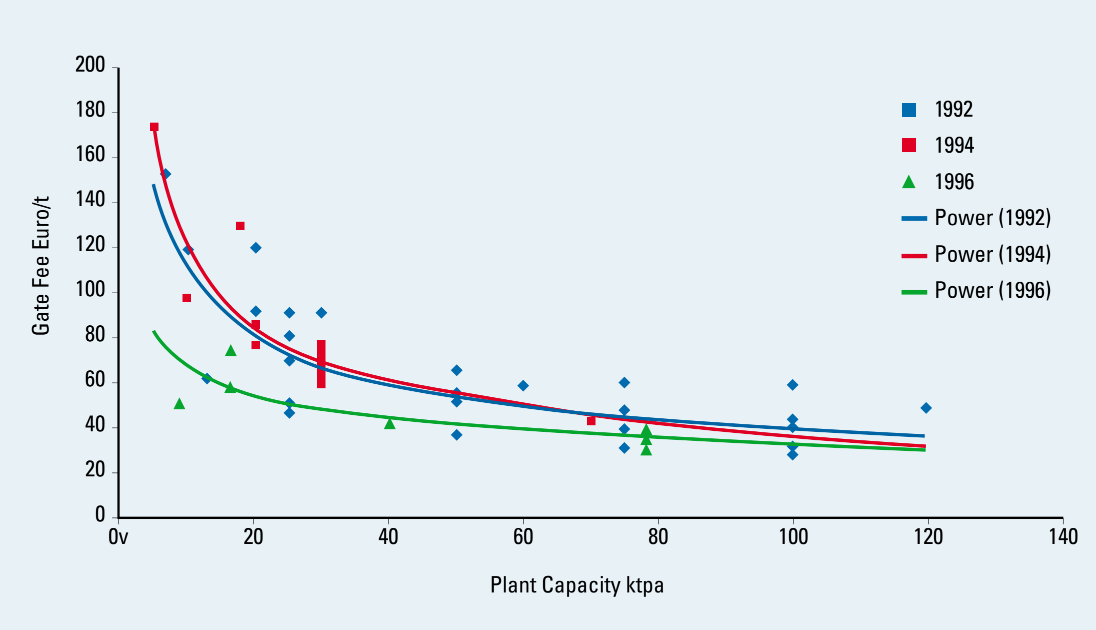

Figure 17. Trends in treatment costs for anaerobic digestion of MSW and biowastes in Europe (ktpa = kilo tonne per year) [42].

and cured digestate for soil conditioning) range between $ 107 and $ 46/tonne for SS-MSW plants and $ 135 - $ 63/tonne for MW plants in the 10,000 to 100,000 ton/year capacity range [67]. The higher costs of anaerobic treatment in comparison to aerobic composting of solid waste are subscribed to the cost of the required water treatment in anaerobic digestion plants in [68]. The latter reference describes a model, consisting of two layered economic and technical sub-models. The results of model calculations indicate that full anaerobic treatment is indeed higher in costs than aerobic composting. Lowest costs are achieved at combined anaerobic/aerobic treatment. Such combined treatment systems are more competitive though the net gas yield will be somewhat lower. Only drastic increases in energy prices or eco-tax would move the system with minimum costs to more anaerobic conversion.

In [47] a detailed techno-economic evaluation is given for an anaerobic digestion system in Germany, processing 26,000 tonnes of fruit and vegetable waste and 4,000 tonnes of green wastes from parks. The biogas is converted in a CHP system to electricity and heat, which is partly used for the process, and an electricity surplus for export to the grid (3,510 MWh/year). The total investment of the plant (including CHP) is 13,2 Million Euro (or Euro 440/tonne processing capacity). The gross treatment costs were estimated at Euro 80/tonne and net at Euro 72/tonne including sales of electricity. According to the study these treatment costs are competitive in the German market compared to modern composting systems [47]. The investments are similar for anaerobic digestion plants for source separated organic waste (SS-MSW) and agro-wastes in The Netherlands which were estimated at Euro 300/tonne capacity (excluding CHP) in the range between 25,000 to 100,000 tonne/year [69]. Assuming a 30% share of CHP in the investment costs the total installed costs (including CHP) would be around Euro 400/tonne processing capacity. The average costs for anaerobic treatment of source separated organic fraction of municipal waste in various systems (Biocel, Valorga, Dranco) were estimated at Euro 75/ tonne excluding energy sales [69]. In The Netherlands the composting costs are mainly dependent on the type of material, especially the dry matter concentration. For verge grass for example the costs of composting are on the order of Euro 50/tonne, while the composting costs for woody materials may be somewhat lower i.e. Euro 25-40/tonne. Comparison with the data provided above shows that the costs of anaerobic digestion are still somewhat higher than for composting.

The trends in treatment cost in Europe per tonne of MSW and biowaste for different scales are shown in Figure 17. The figure clearly shows that the costs of anaerobic digestion are increasingly competitive with composting.

Overlooking the international situation there are clear differences between countries in anaerobic digestion plant costs as was shown in [70]. The cost of biogas (per GJ) is highest for Austria and Switzerland, while Germany and Italy are cheapest [70]. The difference between these cheaper plants and more expensive ones has been reduced, due to higher gas yields from the latter.

Economic impacts of digestate utilisation and effluent disposal

The disposal and/or re-use of digestates and liquid effluents originating from anaerobic digestion processes is an important economic issue for all biogas programs. Deposition of liquid and other organic wastes in landfills will be phased out in the near future in the EU. Evidently the recovery and re-use of nutrients (N,P,K) is an important advantage of anaerobic digestion in addition to the recovery of energy because it contributes indirectly to a reduction of greenhouse gas emissions (especially CO_2 and N_2O). In plants treating solid biowastes and/or manure, the solid fraction is in many cases mechanically separated from the process liquor and matured into a compost product. The market value of these compost type products as a soil conditioner or fertiliser depends on the compliance with the governing quality standards especially with respect to the concentration of heavy metals, but also on the guarantee of a pathogen and seed free product. For digestates from the mechanically separated organic fraction of MSW (separation at the plant) the heavy metal content is a critical issue [66]. Digestates from the organic fraction of source separated MSW can comply with the quality standards much more easily.

The digested slurry from manure (co-)digestion may be recycled as fertiliser without much treatment, as is the case in the Danish biogas plants [59]. The digestate is sufficiently sanitised in the thermophilic digestion and care is taken that individual farmers receive a balanced amount of nutrients. Alternatively, the solid fraction of manure digestates may be recovered as a compost-type product while the remaining nutrients are recovered in the form of re-usable mineral concentrates by means of membrane or other technology, as is the case in the new manure processing biogas plants in The Netherlands [62], [63]. In this approach an acceptable water quality for discharge or even re-use is achieved, but investment and maintenance costs will increase considerably. Latter systems are mainly attractive for processing of excess manure, which cannot be used in the direct environment of the farm. Dry minerals can be transported over larger distances. In all processing plants the remaining liquid effluents must be disposed off. Discharge to external (communal or other) wastewater treatment plants may involve considerable costs for transport and treatment charges, depending on the effluent quality [71]. In many cases pre-treatment is required to reduce especially BOD, COD, VFA and nitrogen/ammonia levels prior to disposal. To reduce these costs an on-site effluent post-treatment system may be advantageous. Commonly used techniques include aeration, de-nitrification and reverse osmosis [71].

The role of financial incentives for renewable energy production

As discussed above, financial incentives in the context of renewable energy production play an important role for enhancing the competitiveness of biogas plants, particularly versus composting. A recent overview [72] on the status and promotion of renewable energy in the EU countries provides the following information relevant for biogas plants. The average investment costs for biogas plants for electricity generation have been reduced from Euro 7,000–8,000/kWe (in 1990) to Euro 3,000-5,000/kWe (2000). The investment costs for electricity production from landfill gas have remained constant (Euro 1,000/kWe) over the period 1980-2000. The costs for electricity produced from biogas (2000) range between Euro 0.1 and 0.22/kWh, while electricity from landfill gas is produced for Euro 0.04 - 0.07/kWh. The review also provides an overview of promotion strategies in the EU [72]. These strategies include 'voluntary approaches' such as 'green electricity tariffs' paid by consumers and 'green labels'. Furthermore a number of regulatory, price driven strategies are in place in the EU either 'investment focused' (tax rebates and incentives) or 'generation based'. A widely used form of the latter is the 'feed-in tariff', which is the price per unit of electricity that a utility or supplier has to pay for renewable electricity to private generators ('producers'). In 2000 the highest feed-in tariffs for electricity from biogas and landfill gas were in force in Austria (up to Euro 0.12/kWh), Germany (up to Euro 0.1/kWh), Denmark (Euro 0.08/kWh) and Greece (Euro 0.06/kWh) [72]. As discussed before the biogas program in Denmark has been successful through a combination of legislative measures and financial incentives (tax exemp-tion, investment subsidies). Similarly, the rapid expansion of biogas plants for (especially) manure digestion in Germany in recent years has been greatly stimulated by financial incentives that are guaranteed for long periods (20 years).

4.6.4 Conclusions

From this section the following conclusions can be drawn. Small-scale decentralised biogas plants (e.g on a farm level) can be economically feasible through savings on energy costs and sales of surplus electricity. Larger-scale centralised biogas plants for (co-)digestion of manure (with or without further processing) and/or bio-wastes and municipal solid waste require gate fees for economic viability and depend to a larger extent on sales of energy and other products, such as mineral concentrates or digestates for use as fertiliser. Therefore, in the foreseeable future, gate fees will remain an important element for economic feasibility of larger scale centralised biogas plants. Economic feasibility of larger biogas plants can be optimised through continued technology development including the enhancement of biogas production (co-digestion, pre-treatment) and a reduction of capital investments and operating costs. The past decades have already seen substantial improvements in these two fields. Important elements for enhancing overall economic feasibility for solid waste and manure processing units with anaerobic treatment as the core-technology, are the development of cost effective technologies for effluent post treatment and recovery of mineral concentrates. The combined anaerobic treatment/ aerobic composting of solid waste could be applied to reduce the cost of additional water treatment.

Treatment of wastes in biogas plants is nearing competitiveness towards composting, which will strongly increase renewable energy production. On the short and medium term legislative and financial incentives are an important driver for economic feasibility of biogas plants of all scales. Several measures are already in place including the reduction of landfill deposition and financial incentives in the context of renewable energy policy. Continuation and broadening of support for biogas plants is logical because anaerobic digestion clearly offers advantages over composting, landfilling and incineration in the form of renewable energy production, reduction of greenhouse gas emissions and the possibility for full re-use of nutrients.

It is evident that government programs aimed at increasing the share of renewable energy and greenhouse gas reduction will have an important impact on the expansion of anaerobic digestion.

4.7 International status of anaerobic digestion

Worldwide, more than 125 anaerobic digestion plants are in operation using municipal solid waste or organic industrial waste as their principal feedstock. Their total annual processing capacity is over five Million tonnes, with a potential of generating 600 MW of electricity [42]. Throughout the world, more than 1,300 vendor-supplied systems are in operation or under construction for the treatment of sewage sludge [42]. More than 2,000 anaerobic systems are also in operation for the treatment of industrial wastewater and landfill leachates [26]. Anaerobic digestion systems currently operational in Europe have a total capacity of 1,500 MW, while the potential for 2010 is estimated at 5,300-6,300 MW. Worldwide installed capacity could reach up to 20,000 MW by 2010 [64,77] (Figure 18).

Deployment rates are the highest in Asia, due to governmental programs in China an India including the construction of millions of small-scale digesters. A rapid expansion of anaerobic diges-

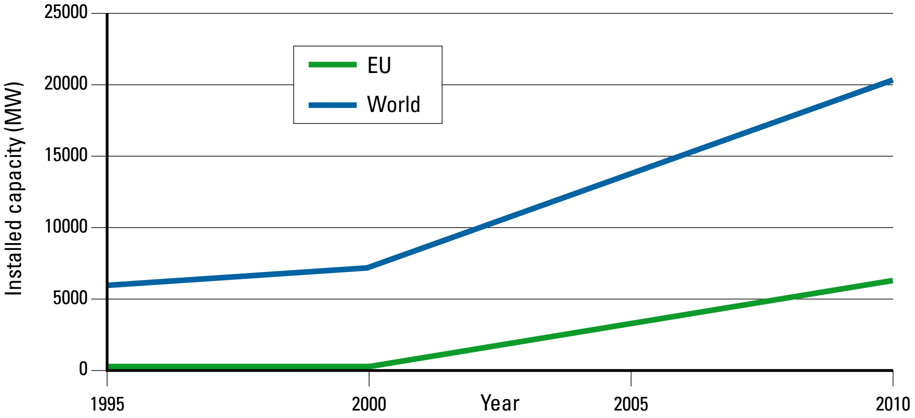

Figure 18. Deployment of anaerobic digestion and estimate of future potential. Adapted from [64, 77].

tion is expected, especially in developing countries, where there is a demand for low cost, reliable plants, which can be locally manufactured [64].

Although anaerobic digestion is a proven technique for a variety of waste streams, there are some barriers to expanded and commercialised biogas production. The most important barriers to overcome are listed in a study on viable energy production and waste recycling from anaerobic digestion of manure and other biomass materials [73]:

- Energy prices and access to energy markets
- Poor data on economics
- Low energy yield
- Bad reputation due to unsuccessful plants
- Lack of information about environmental, agricultural and other non-energy advantages
- Lack of co-operation between relevant sectors/parties
- Legal obstacles

In The Netherlands most renewable energy is derived from incineration of organic waste, while only 9% originates from controlled anaerobic digestion (Table 8 and Figure 19). Not all substrates are suitable for digestion, for example, only the organic part of MSW is suitable, and the digestion of large amounts of wood is also not possible. There are

TABLE 8. *Total amount of energy produced from biomass in The Netherlands in 1998. The number of installations was approx. 1,170. [74].*

			Unit
Consumed by installations	Electric power	518	MW
	Heat	18,665	MW
Avoided amount of primary fossil fuel	Waste incineration	23.3	PJ
	Wood incineration	9.3	PJ
	Landfill gas	2.1	PJ
	Anaerobic Digestion	*3.6*	*PJ*
	Total	38.3	PJ
Delivered as	Electricity	2,743	GWh
	Natural gas	1.9	PJ
	Heat	12.0	PJ
Avoided CO_2 emission		2,451	Ktonne

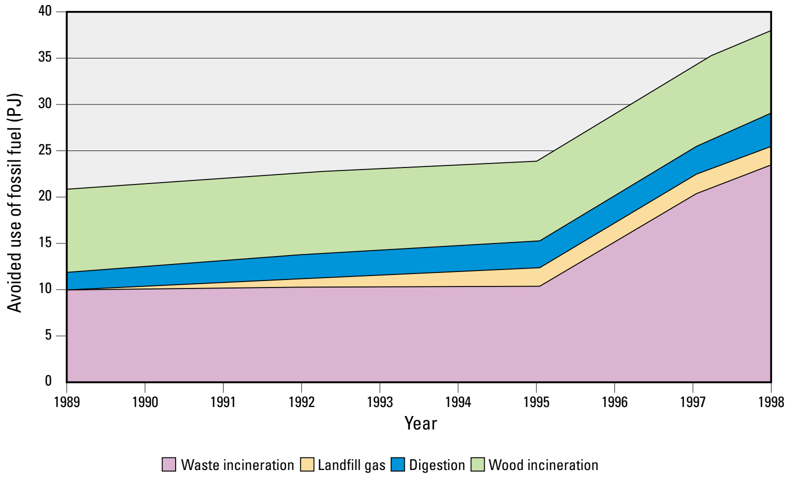

Figure 19. Total amount of energy produced from biomass in The Netherlands over the years 1989-1998 [74].

TABLE 9. *Gas production and energy generation from anaerobic digestion in The Netherlands in 1996 [74].*

Number of installations		**Ca. 225**
Used by installations	Electrical power	21 MW
	Heat	42 MW
Gas production	Total	280 million m^3
	Sewage treatment	191 million m^3
	Industry	78 million m^3
	Manure	5 million m^3
	VFY	5 million m^3
Delivered as	Electricity	106 GWh
	Heat	0.8 PJ
	Natural gas	1.2 PJ
Saved primary energy		3.1 PJ
Avoided CO_2 emission		141 ktonne

sources, which undergo a less favourable treatment in terms of energy consumption, for which controlled anaerobic digestion would be an option. Nowadays most of organic municipal waste (VFY) is composted. Part of the domestic sewage sludge is incinerated without prior digestion. The amount of energy generation from waste is increasing over the years, but the amount contributed by anaerobic digestion remains approximately the same (Figure 19).

Only 2% of biogas produced originates from VFY, as there are only two large plants digesting separated VFY and only one plant (Vagron, Groningen) that treats the organic fraction of MSW in The Netherlands (Figure 20). A second plant (located in Heerenveen) for treating the organic fraction of MSW is currently commencing operation. The contribution of manure digestion is thus far very low (approximately 2%) but is expected to increase in the near future. A combination of these types of waste streams (co-digestion) can lead to higher biogas production [62]. As The Netherlands produces a large amount of manure (Table 10) co-digestion would be a promising technique.

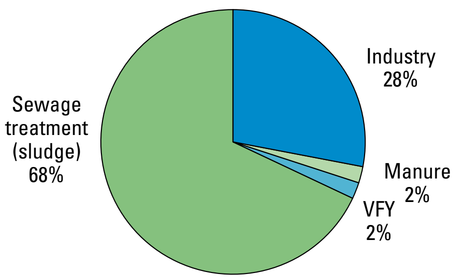

Figure 20. Contribution of different substrates to biogas production (280 million m^3) in The Netherlands in 1996.

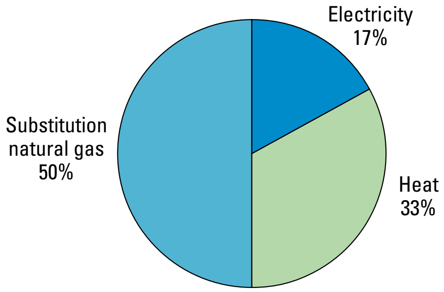

Figure 21. Utilisation of the biogas produced in The Netherlands in 1996 [74].

TABLE 10. *Total manure production in The Netherlands in the period 1994-2000 [75].*

Year	Total produced manure (organic matter). Excluding meadow manure. In kg*1,000
1994	4,208,739
1995	4,263,720
1996	4,206,780
1997	4,125,636
1998	4,075,187
1999	4,039,965
2000	3,906,441

The realisation of 'centralised' treatment facilities will require additional infrastructure, as manure has to be collected from the farm and returned after treatment to the farm for use as fertiliser. In order to prevent the spreading of disease, treatment should include the removal of pathogens by e.g. thermophilic treatment.

Potential feedstocks for anaerobic digestion in The Netherlands are summarised in Table 11. At the moment of the 1,457,000 tonnes of VFY produced each year in The Netherlands, approximately 102,000 tonne is digested and 1,355,000 tonne is treated by other means. Anaerobic treatment of the latter amount could produce 15-23 MW of electricity assuming that one tonne of biowaste can produce approximately 100-150 kWh. Based on the VAGRON process, operating at 52°C, the amount of potential electricity production is 18 MW, accounting for heat loss, electrical conversion and consumption by the plant.

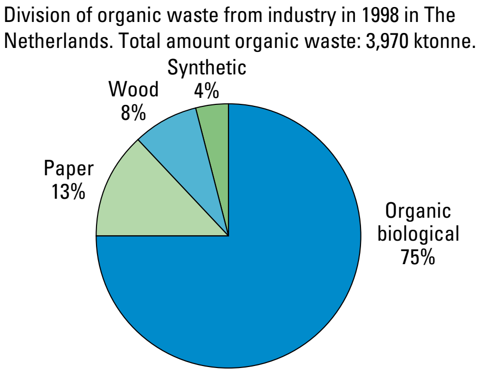

Figure 22. Organic solid waste from industry in The Netherlands in 1998.

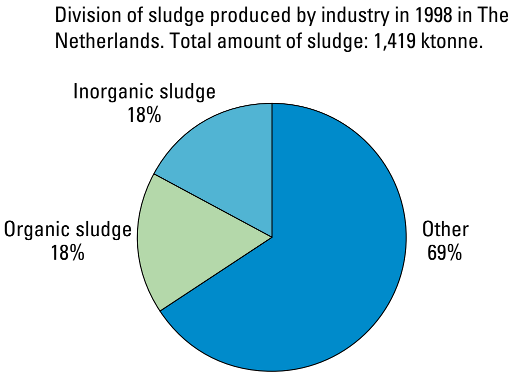

Figure 23. Produced water treatment sludge from industry in The Netherlands in 1998.

TABLE 11. *Possible sources for anaerobic digestion for the generation of methane in The Netherlands [62], updated with values (*) for 2000 [75]*

Source	**Waste stream**	**Production (tonne/year)**	**Dry matter (%)**	**Ash content (%)**
Municipal waste	VFY	*1,457,000	30	35
Market gardening	Stalks/leaf	231,500	15	10
	Withdrawn vegetables	51,000	6.5	9
	Tomato-stalks	45,000	15	19
	Withdrawn fruit	21,000	12	5
	Withdrawn ornamental plants	485	10	10
	Cabbage leaf	100,000	18	11
	Chicory waste	87,500	20	10
	Roadside grass	600,000	50	20
Maintenance greenery	Waste	150,000	12	5
Maintenance ditches/canals	Organic waste	110,000	9	10
Flavour industry	Slurry from onion oil	11,500	9	15
	Filter bed	4,000	50	
Onion processing industry	Sorting waste	60,000	13	5
Vegetable proc. Industry Fruit	Organic biological	*4,806,000		
proc. Industry	Activated sludge	*3,000		
Pulp and paper Industry	(primary) sludge	*330,000	40	15
Slaughterhouses	sludge grease catcher	10,000	5	
	flotation sludge	*44,000	5	
	slaughter waste/blood/hair	*617,000		
	unborn manure	95,000		
	purification sludge	*8,000	100	
Dairy industry	organic biological	*129,000		
	purification sludge	*1,000	15	
Fish proc. Industry	organic biological	*31,000	100	
	Fuller's earth	15,000	100	28
Oil and grease industry	Purification sludge	*20,000		
Starch and fodder industry	Organic biological	*2,674,000		
Trade/services/etc.	OSS-waste 1)	290,000	20	
Catering/homes/etc.	Swill 2)	107,800	5-7	
Other industrial treatment plants	Purification sludge	1,600,000		
TOTAL		**14,194,300**		

1) organic fraction of office, shops and services waste, like canteen waste
2) organic waste of catering industry and kitchens of homes, barracks, etc

Another potential source for anaerobic digestion is solid waste from industry. In the Food and Beverage industry, producing most organic waste, solid organic waste streams or slurries are mostly used as fodder. The amount of organic waste from industry can be seen in Figure 22 and Figure 23.

4.8 Conclusions and perspectives for further development

Anaerobic digestion is a proven technique and at present applied to a variety of waste (water) streams but world wide application is still limited and a large potential energy source is being neglected. Moreover some potential sources, which are now treated otherwise, are an excellent substrate for anaerobic treatment and could contribute to renewable energy production rather than consuming energy during treatment.

Although The Netherlands is a leading country in the application of anaerobic treatment of industrial and agricultural wastewater, the anaerobic digestion of slurries and solid waste for energy production is scarcely applied. In other European countries like Germany, Austria, Switzerland and Denmark hundreds of installations are currently in operation, showing that technical obstacles and barriers have been overcome. The limited application of anaerobic digestion for energy production from slurries and solid wastes in The Netherlands can, amongst others, be contributed to relatively low natural gas prices. An important difference is moreover the widespread application of co-digestion in other European countries, which significantly improves the economic efficiency of an anaerobic digestion system by increasing the gas production per m^3 reactor content. In The Netherlands, co-digestion is thus far restricted due to legislation. Nowadays a limited range of substrates, mainly plant material, is allowed for co-digestion. However the addition of high-energy substrates like lipids, slaughterhouse wastes or fish-wastes, to manure digesters could substantially increase the gas yield and therefore the economical feasibility of manure digestion. Where co-digestion is applied on a larger scale a large sustainable energy potential becomes available.

Small-scale decentralised biogas plants (e.g. on a farm level) can be economically feasible through savings on energy costs and sales of surplus electricity. Larger-scale centralised biogas plants for (co-) digestion of manure (with or without further processing) and/or bio-wastes and municipal solid waste require gate fees for economic viability and depend to a larger extent on sales of energy and other products, such as mineral concentrates or digestates for use as fertiliser. Maximising the sale of all usable co-products will thus influence the economic merits of an anaerobic treatment system. In the foreseeable future, gate fees will remain an important element for economic feasibility of larger scale biogas plants. Economic feasibility can be optimised through continued technology development including the enhancement of biogas production (co-digestion, pre-treatment) and a reduction of capital investments and operating costs.
In the short and medium term legislative and financial incentives are an important driver for economic feasibility of biogas plants. Besides this, legislation can contribute to a formal consideration of the true cost of various energy options. Several measures are already in place including the reduction of landfill deposition and financial incentives in the context of renewable energy policy. The government now stimulates anaerobic digestion of slurries, as it provides 'green energy'. Another aspect, especially related to the application of controlled anaerobic digestion of animal manure, is the reduction of spontaneous methane emissions that occur during storage of raw manure. In The Netherlands, a large governmental program aimed at the prevention emission of non-CO_2 greenhouse gases such as CH_4 stimulates (among others) the application of animal manure digestion.

The trend in treatment costs in Europe per tonne of MSW and biowaste for different scales shows that the costs of anaerobic digestion are increasingly competitive with composting. Important elements for enhancing overall economic feasibility of solid waste and manure processing units with anaerobic treatment as the core-technology, are the development of cost effective technologies for effluent post treatment and recovery of mineral concentrates. Combined anaerobic treatment/ aerobic composting of solid wastes could be applied to reduce the cost of additional water treatment, though lower gas yields will be the result.

The development of anaerobic conversion techniques has shown that more and more substrates, which originally were not considered for anaerobic treatment, are anaerobically digested today. Diluted, low temperature streams or wastewater with high temperatures and wastewater with toxic and/or xenobiotic components appear to be suitable for anaerobic treatment and lead to stable end products. Anaerobic treatment is a proven technique from an environmental and economic viewpoint. The technology is relatively new, and in many countries application is still in an initial phase. It is of utmost importance to establish demonstration projects in many parts of the world to show the environmental and economic benefits and provide the necessary confidence in the technique. Once demonstrated, anaerobic treatment will become its own advertisement.

The application of anaerobic treatment of domestic sewage is so far limited to tropical countries. Large UASB systems are being applied for this purpose in Asia and South America. Recently the first UASB system for domestic sewage in Africa was installed in Ghana. In low and medium temperature regions the technique is not applied in practice. New developments in high rate anaerobic treatment systems can lead to wider application of anaerobic treatment of conventionally collected domestic sewage even at low temperatures. The strong dilution of domestic sewage in the present collection and transport system of domestic sewage is one of the main difficulties, especially at low temperature conditions. Considering the composition and concentration of the various waste steams produced in the household, illustrates the possibilities of applying new sanitation concepts to enable reuse of energy, water and fertiliser values. Nearly three billion people in the world do not have effective sanitation at their disposal. The central sanitation systems developed in the industrial world are too expensive and too complex to be used world wide. In November 2000, the technical expert consultation on *'Appropriate and Innovative Wastewater Management for Small Communities in EMR countries'*, organised by the World Health Organisation (WHO) in Amman, Jordan concluded that: 'Decentralised Sanitation and Reuse (DeSaR) is the only achievable and environmentally friendly option for countries in the Middle East region.'

The DeSaR concept [76] focuses on the separate collection, transportation and decentralised processing of concentrated domestic waste streams (faeces plus urine or 'night soil' and kitchen waste) and the diluted wastewater streams ('grey water'). Faeces, urine and kitchen waste contain potential energy, which can be recovered by anaerobic digestion, and -in addition- nutrients which can be recovered for use as agricultural fertiliser. Here lies an important key that, with the implementation of DeSaR will allow the energy and nutrient cycle to be closed. The introduction of DeSaR means the transition to a new paradigm. This transition can only become successful when stimulated by governments via for example demonstration projects in new housing estates or large buildings.

4.9 Abbreviations

AF	Anaerobic Filter
AFFR	Anaerobic Fixed Film Reactor
AC	Accumulation reactor
BOD	Biological Oxygen Demand (mg O_2/l)
COD	Chemical Oxygen Demand (mg O_2/l)
CSTR	Continuously Stirred Tank Reactor
DeSaR	Decentralised Sanitation and Re-use
EGSB	Expanded Granular Sludge Bed
F&B	Food and Beverage
FOG	Fat, Oil and Grease (mg/l)
HRT	Hydraulic Retention Time (hours or days)
IC	Internal Circulation reactor
MSW	Municipal Solid Waste
OSS-waste	Organic fraction of Office, Shops and Services waste
OWF	Organic Waste Fraction
p.e.	population equivalent
P&P	Pulp and Paper
RDF	Refuse Derived Fuel
SRT	Sludge Retention Time (hours or days)
SS-MSW	Source Separated Municipal Solid Waste
STP	Sewage Treatment Plant
TS	Total Solids (mg/l) or (%)
TSS	Total suspended solids (mg/l)
TVS	Total Volatile Solids (mg/l)

UASB	Upflow Anaerobic Sludge Bed
VFA	Volatile Fatty Acids (mg/l)
VFY	Vegetable, Fruit and Yard Waste
VS	Volatile Solids (mg/l) or (%)
VSS	Volatile Suspended Solids (mg/l)

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Appendix I Operating anaerobic digestion plants of commercial scale.

All plants have a processing capacity > 2,500 t.p.a. (tonnes/year). MSBW = Municipal Solid Biodegradable Waste; OIW = Organic Industrial Waste; Biosolids = sewage sludge.

Country	Location	Feedstock	System	Scale t.p.a.	Date
Austria	Bergheim-Siggerwiesen	MSBW	Dranco	20,000	1993
	Böheimkirchen	Biowaste, Agricultural	Arge Biogas	5,000	1996
	Eferding	OIW	Entec	7,500	1984
	Feldbach	MSBW	AAT	11,000	1998
	Frastanz	OIW	Entec	17,000	1985
	Graz	MSBW	Dranco		1990
	Hirsdorf	Biowaste, Agricultural	Entec		1994
	Hollabrunn	OIW	Entec	11,000	1983
	Kainsdorf	Biowaste, Agricultural, OIW	Entec	14,000	1995
	Koblach	MSBW	AAT	15,000	1993
	Leesternau	Biowaste	Kompogas	8,000	1997
	Lustenau	Biowaste	Kompogas	10,000	1996
	Mayerhofen	Biowaste, Agricultural	Arge Biogas	2,500	1997
	Roppen	Biowaste	Kompogas	10,000	2001
	Salzburg	OIW, Biosolids	AAT	160,000	1999
	Wels	Biowaste	LINDE	15,000	1996
	Westerwesede	Agricultural, OIW	Entec	5,000	1986
Belgium	Brecht	Biowaste	Dranco	20,000	1992
	Brecht	Biowaste	Dranco	35,000	1999
	Gent	MSBW	AAT	182,000	1999
Canada	Newmarket	Biowaste, OIW	BTA	150,000	2000
Denmark	Arhus	Biowaste, Agricultural, OIW	C.G. Jensen	125,000	1995
	Blaabjerg	Agricultural, OIW	BWSC/Bioscan	113,000	1996
	Blåhøj	Agricultural, OIW	NIRAS	30,000	1997
	Davinde	Agricultural, OIW	Krüger	10,000	1988
	Fangel	Agricultural, OIW	Krüger	53,000	1989
	Filskov	Agricultural, OIW	NIRAS	27,000	1995
	Grindsted	Biowaste, Biosolids	Krüger	40,000	1997
	Hashøj	Agricultural, OIW	Krüger	53,000	1994
	Hodsager	Agricultural, OIW	NIRAS	17,500	1993
	Lemvig	Agricultural, OIW	BWSC	144,000	1992
	Lintrup	Agricultural, OIW	Krüger/Bioscan	190,000	1990
	Nysted	Biowaste, Agricultural, OIW	Krüger	100,000	1998
	Revinge	Agricultural, OIW	Bioscan	15,300	1989
	Ribe	Agricultural, OIW	Krüger	147,000	1990
	Sinding	Biowaste, Agricultural, OIW	Herning Municipal	45,000	1988
	Snertinge	Agricultural, OIW	NIRAS	43,000	1996
	Studsgård	Biowaste, Agricultural, OIW	Herning Municipal	130,000	1996
	Thorsø	Agricultural, OIW	BWSC	110,000	1994
	Vaast-Fjellard	Biowaste, Agricultural, OIW	NIRAS	55,000	1997
	Vegger	Agricultural, OIW	JYSK Biogas	19,000	1986
	Vester Hjermitslev	Agricultural, OIW	Krüger	17,000	1984

Country	Location	Feedstock	System	Scale t.p.a.	Date
Finland	Vaasa	MSBW	Waasa/Wabio	15,000	1994
France	Amiens	MSBW	Valorga	85,000	1988
Germany	Alzey	Biowaste	Kompogas	24,000	2000
	Baden-Baden	Biowaste, Biosolids	BTA	5,000	1993
	Bassum	Grey waste	Dranco	16,500	1997
	Behringen	Agricultural, OIW	LINDE	23,000	1996
	Bottrop	Biowaste	Wabio	6,500	1995
	Braunschweig	Biowaste	Kompogas	20,000	1997
	Buchen	Grey waste	ISKA	20,000	2001
	Dietrichsdorf-Volkenschwand	Biowaste, OIW	BTA	17,000	1995
	Ellert	Biowaste	Entec	5,000	1997
	Engelskirchen	Biowaste	Valorga	35,000	1998
	Erkheim	Biowaste, OIW	BTA	11,000	1997
	Finsterwald	Biowaste, Agricultural	Schwartung UHDE	90,000	1995
	Frankfurt	Biowaste	Kompogas	15,000	2000
	Freiburg	Biowaste	Valorga	36,000	1999
	Fürstenwalde	Biowaste, OIW	LINDE	85,000	1998
	Ganderkesee	Biowaste	ANM	3,000	1995
	Gröden-Schraden	Agricultural, OIW	Haase Energietechnic	110,000	1995
	Groß Mühlingen	Biowaste, Agricultural, OIW	DSD	42,000	1996
	Groß Pankow	Agricultural, OIW	Alusteel/NNR	7,700	1994
	Heppenheim	Biowaste, OIW	LINDE	33,000	1999
	Herten	Biowaste	IMK	18,000	1998
	Himmelkron	Agricultural, OIW	AAT	2,800	1995
	Herschfelde	OIW	AAT	3,600	1997
	Kahlenburg	MSBW	Wehrle/Biopercolat	20,000	2001
	Karlsruhe	Biowaste	BTA	800	1996
	Kaufbeuren	Biowaste, OIW	BTA	2,500	1992
	Kempten	Biowaste	Kompogas	10,000	1995
	Kirchstockach	Biowaste	BTA	25,000	1997
	Lemgo	Biowaste, OIW	LINDE	38,000	2000
	Michaelisdonn	Agricultural, OIW	Krüger	35,000	1995
	München	Biosolids, OIW	Schwarting UHDE	86,400	1987
	München/Eitting	Biowaste	Kompogas	24,000	1997
	Münster	Biowaste	BTA/Roediger	20,000	1997
	Neukirchen	Agricultural, Biowaste	AAT	55,000	1998
	Nordhausen	Biowaste	Haase	16,000	1999
	Oldenburg	Agricultural, OIW	Krüger	20,000	1992
	Pastitz/Rügen	Agricultural, OIW	Bioplan	100,000	1997
	Radeberg	Biosolids, Biowaste, OIW	LINDE	56,000	1999
	Regensburg	Biowaste	TBW/Biocomp	12,000	1996
	Roding	Biowaste	AAT	7,000	1996
	Sagard/Island Rügen	Biowaste, Agricultural, OIW	LINDE	48,000	1996
	Schwabach	Biowaste	BTA/ATU	12,000	1996
	Schwanebeck	Biowaste, Agricultural	Haase	50,000	1999
	Simmern	Biowaste	Kompogas	10,000	1997
	Wadern-Lockweiler	Biowaste, OIW	BTA	20,000	1998
	Wittmund	Agricultural, OIW	Krüger	120,000	1996
	Zobes	Biowaste, Agricultural, OIW	DSD	20,000	1986

Country	Location	Feedstock	System	Scale t.p.a.	Date
Indonesia	Bogor	OIW	Dranco		1986
Italy	Bastia/Brettona	Agricultural, OIW	RPA	30,000	1982
	Bellaria	MSBW	Ionics Italbia	4,000	1988
	Marsciano	Agricultural, OIW	SPI	300,000	1988
	Thiene	Agricultural, OIW	KIKlos	60,000	1990
Japan	Kagoshima	Biowaste, Agricultural	Dranco		1998
Netherlands	Breda	Niowaste	Paques	10,000	1992
	Breda	OIW	Paques	25,000	1987
	Groningen	Grey waste	CiTec	85,000	1999
	Lelystad	Biowaste	Heidemij, Biocel	35,000	1997
	Tilburg	Biowaste	Valorga	52,000	1994
Spain	La Coruña	OIW	AAT	34,000	1993
Sweden	Borås	MSBW	YIT/VMT	9,000	1995
	Helsingborg	Agricultural, OIW	NSR	20,000	1996
	Kalmar	Agricultural, OIW	VBB Viak/Läckeby	25,000	1998
	Kil	MSBW	CiTec	3,000	1998
	Kristianstad	MSBW, Agricultural, OIW	Krüger	73,000	1997
	Laholm	Agricultural, OIW	Krüger	37,000	1992
	Linköping	Agricultural, OIW	Purac	105,000	1997
	Uppsala	MSBW, Agricultural, OIW	VBB Viak/Läckeby	30,000	1997
	Vanersborg	MSBW	YIT/VMT	20,000	2000
Switzerland	Aarberg	Biowaste	Dranco	11,000	1997
	Baar	Biowaste	LINDE	6,000	1994
	Bachenbülach	Biowaste, Yard	Kompogas	10,000	1994
	Frauenfeld	Biowaste, OIW	Rom-OPUR	15,000	1999
	Geneva	Biowaste	Valorga	10,000	2000
	Muhen	Agricultural, OIW	LINDE	5,000	1986
	Niederuzwil	Biowaste	Kompogas	13,000	1997
	Otelfingen	Biowaste	Kompogas	12,000	1996
	Rümlang	Biowaste, Yard	Kompogas	8,500	1992
	Samstagern	Biowaste, Yard	Kompogas	10,000	1995
	Villeneuve	Biowaste	Dranco	10,000	1999
	Volketswil	Biowaste, Yard	Kompogas	10,000	2000
	Vuiteboeuf	Agricultural, OIW	LINDE	6,900	1986
	Wädenswil	OIW	Entec	5,000	1997
Ukraine	Zaporozhstol	Agricultural, OIW	Krüger	12,000	1992
USA	Greenboro, NC	Yard wastes	DEES	30,000	2000
	Moorfield, WV	Biowaste/Agricultural/Biosolids	Enviro-control	3,000	1996
	Princeton, NC	Agricultural, OIW	DEES	3,500	1999

Appendix II Characteristics of various types of industrial wastewater [41].

Branch of industry	**Raw wastewater characteristics**		**(max) Anaerobic degradability**	**Reference**
	BOD_5 (mg/l)	COD (mg/l)	(m^3 CH_4/kg COD removed)	
Food & Beverage				
Slaughterhouses				
Meat	450-1500		IWACO 1991	
	500-1500		IWACO 1991	
	490-650	1500-2200		Sayed 1987
"low strength"	1100	1440	82.7% of CODtot inf.	Nunez and Martinez 1999
"medium strength"	1400	2500	82.7% of CODtot inf.	Nunez and Martinez 1999
"high strength"	2400	4200	82.7% of CODtot inf.	Nunez and Martinez 1999
Poultry	250-3700			IWACO 1991
	350-500			IWACO 1991
	370-620			Middelbrooks 1979
	1000-2100	1500-3500		Eremektar, Cokgor et al. 1999
meat processing	100-300			IWACO 1991
	1300			IWACO 1991
		1880		Campos, Foresti et al. 1986
Dairy				
Dairy products	300-10000			IWACO 1991
	480-2500			IWACO 1991
		52000	0.36	Hickey and Owens 1981
		12000-35000	0.27-0.3	Li, Sutton et al. 1982
		2200-10000	0.1-0.395	Boening and Larsen 1982
		3560-4250	0.08-0.29	Viraraghavan, Kikkeri et al 1990
cheese whey	12000	20000	0.55	Yilmazer and Yenigun 1999
egg processing	3000-3200	5000-6900		Middlebrooks 1979
	150			IWACO 1991
	1400-3000			IWACO 1991
Fish				
Fish processing	350-3500			IWACO 1991
	5000			IWACO 1991
		20000-53600		Veiga, Mendez et al. 1992
	3000-4200	4800-6400		Nair 1990
	84-32700			Middlebrooks, 1979
		1830-12230	75-80% of CODtot inf.	Palenzuela 1983
		18500-55200	75-95% of CODtot inf.	Soto, Mendez et al. 1991
Tuna		29500	72-76% of CODtot inf.	Punal and Lema 1999
mussel cooking		18500	86-95% of CODtot inf.	Punal and Lema 1999
Pulp & Paper				
Pulping				
Thermo mechanical pulping		1000-4500	67-87% of CODtot inf.	Sierra-Alvarez 1999
Chemo-thermo mechanical pulping	6000-13000		Sierra-Alvarez 1999	
Chemical		5000-6000	85-90% of CODtot inf.	Kroiss, Svardal et al. 1985
paper making	1500	3000		Hulshoff-Pol and Lettinga 1986

Appendix II (continued) Characteristics of various types of industrial wastewater.

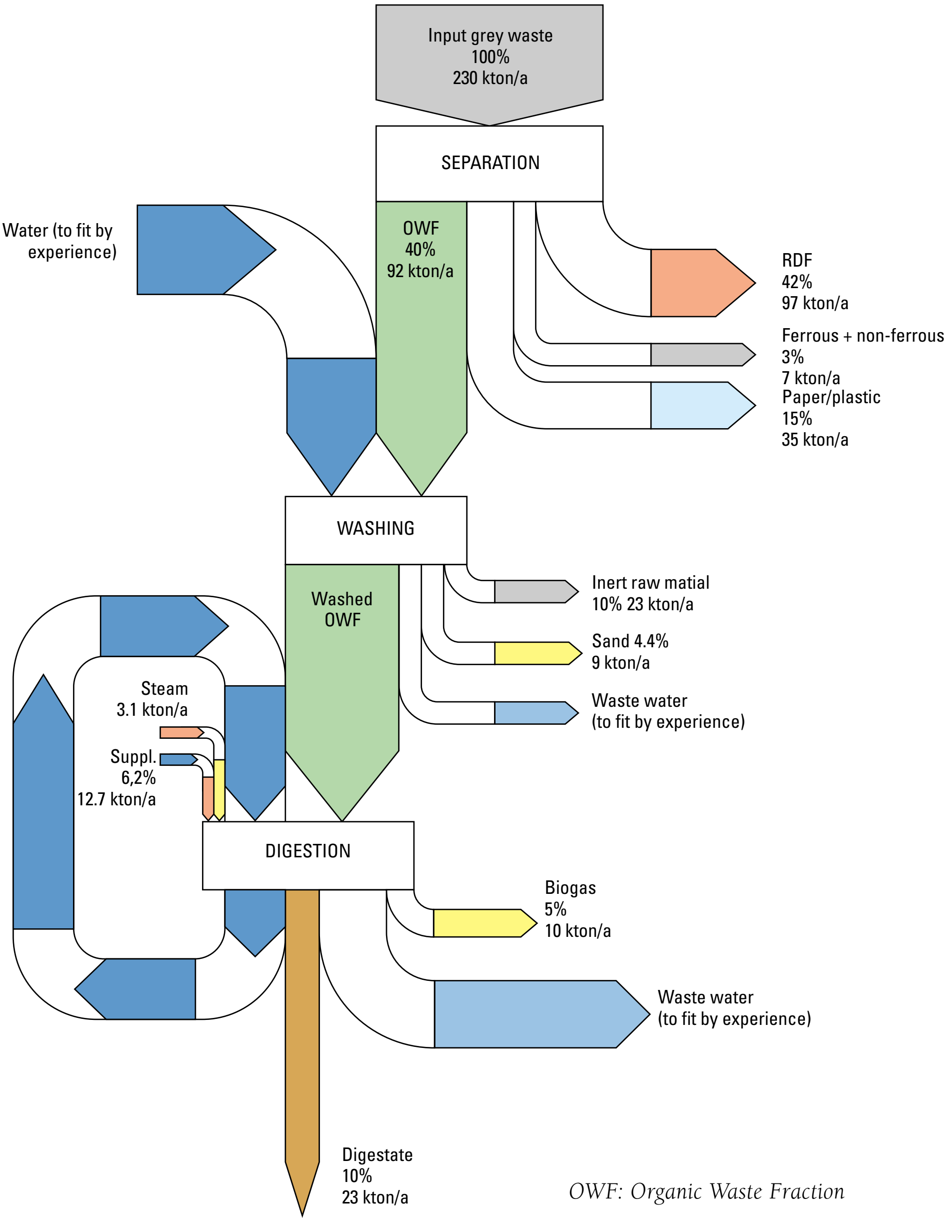
Branch of industry	Raw wastewater characteristics		(max) Anaerobic degradability	Reference
	BOD$_5$ (mg/l)	COD (mg/l)	(m^3 CH$_4$/kg COD removed)	
Grain & Starch				
Grain	240-500			IWACO 1991
	225-14600			Middlebrooks, 1979
Maize	5700-11900	5300-24900		Krings, Donnerhack et al. 1992
	8100			IWACO 1991
Patatoes	4900	5700		Krings et al 1992
	500-1500			IWACO 1991
Wheat	18600-37500	21700-52500		Krings et al 1992
	4700			IWACO 1991
Sugar				
	250			IWACO 1991
	930			IWACO 1991
	15-1900	60-4400		Barnes, Forster et al. 1984
		480-9000	0.33	Chen, Li et al. 1982
	4000-6000	6000-10000		Austermann Haun, Meyer et al. 1999
Edible oil and Grease				
	100-2000			IWACO 1991
	500-5000			IWACO 1991
	500-6700			Middlebrooks, 1979
	31300-31800	69700-72000	75-80% of CODtot inf.	Tsonis and Grigoropoulos 1988
Beverages/Distilleries				
Soft drink	180-370			IWACO 1991
	380-660			Middlebrooks, 1979
	500	1400	89%COD/96% BOD removal	Craveiro, Soares et al. 1986
		6000	0.41	Hickey and Owens 1981
Breweries	750			IWACO 1991
	750-3000			IWACO 1991
	1600			Middlebrooks, 1979
	1500	2500	92%COD/99% BOD removal	Craveiro et al. 1986
	1500	2300		Austermann-Haun et al 1999
Distilleries	100			IWACO 1991
	15000			IWACO 1991
	480-9000			Middlebrooks, 1979
	19800-25000	45000-65000		Costa, Rocha et al. 1986
		8700-9500	0.348	Frostell 1982
		12000-20000		Austermann-Haun et al 1999
Fruit/Vegetable processing				
Fruit/Vegetable processing	1900			IWACO 1991
Vegetables	200-800			IWACO 1991
Potato		5000	80% of CODtot infl.	Zoutberg and Eker 1999
Coffee	1250			IWACO 1991
		9400-15000		Calzada, Rolz et al. 1986
	3000	4000		Hajipakkos 1982

Appendix III Energy and mass balance of the VAGRON installation treating grey waste

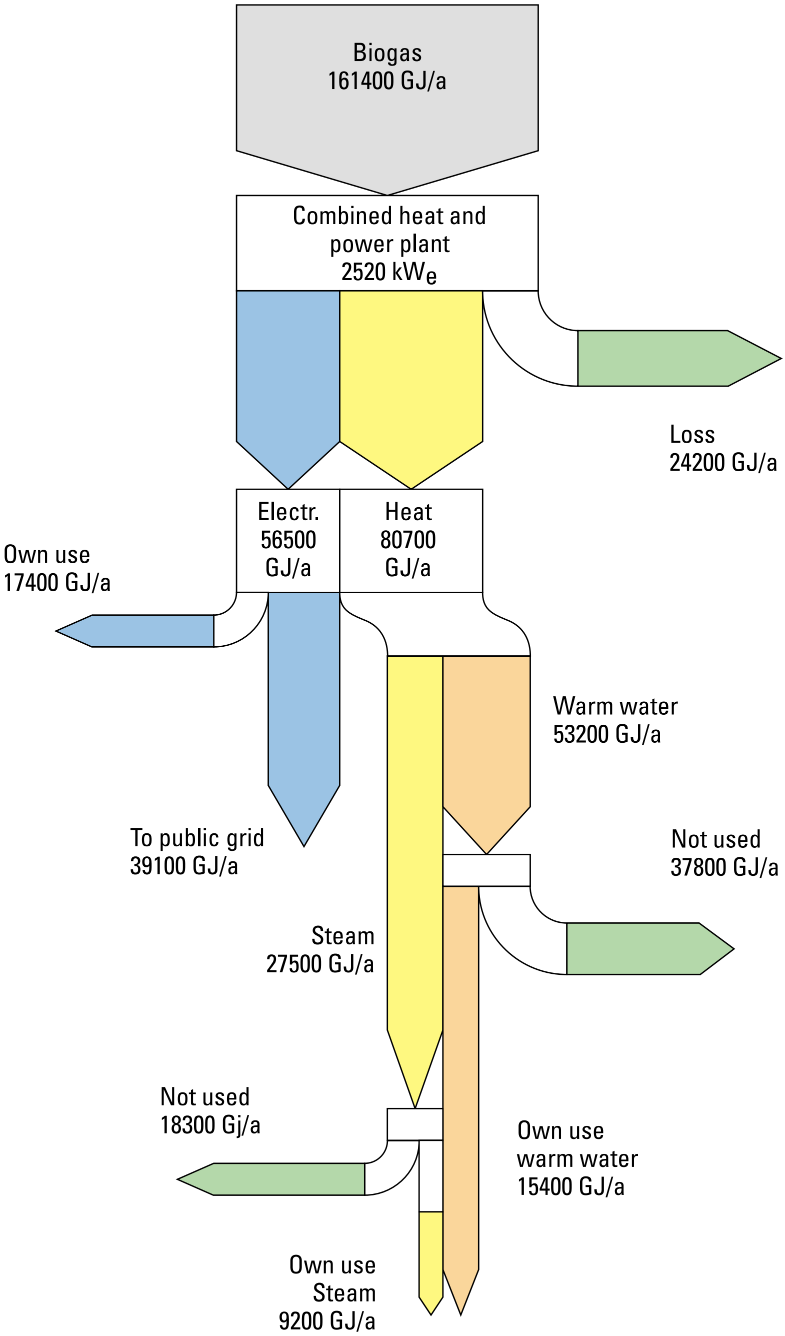
Adapted from the Vagron website
http://www.vagron.nl/html/nl/massa.htm.

Separating waste results in the reuse of more than 50% of the incoming waste stream. Only about 42% of the waste is incinerated.

A total of 2.5 MWe of electric energy is produced, about one third of which is used internally. The remainder is supplied to the public electricity network. About 3.6 MWh of thermal energy is produced, which is used to heat process water and create steam. In total, the conversion of bio-methane into energy (electricity + heat) achieves an energy yield of 85%.



OWF: Organic Waste Fraction


Biogas
161400 GJ/a
Combined heat and power plant
2520 kW$_e$
Loss
24200 GJ/a
Electr.
56500
GJ/a
Heat
80700
GJ/a
Own use
17400 GJ/a
Warm water
53200 GJ/a
To public grid
39100 GJ/a
Not used
37800 GJ/a
Steam
27500 GJ/a
Not used
18300 Gj/a
Own use
warm water
15400 GJ/a
Own use
Steam
9200 GJ/a

Appendix IV Operational manure digesters in The Netherlands [61,63].

Location	Description of project	Capacity	Start-up date
Elsendorp	Regional digestion of 25,000 tonnes of pig manure per year. The installation produces 1,600 GWh of electricity/yr, 7,500 tonnes of mineral concentrates and 17,500 tonnes of clean water. Supplier: Biorek Agro B.V.	1,600 GWhe / year	September 2001
Goutum	Farm-scale digester at Praktijkcentrum Nije Bosma Zathe. Capacity: 900 m^3 cattle manure /year (+ 900 planned). Co-digestion with green maize. Supplier: Biogas Nederland BV		February 2001
Nijverdal	Regional, thermophilic (co)digestion of 22,000/3,000 tonne pig manure / roadside grass at "De Scharlebelt". Biogas is used for Combined Heat and Power production. Composting of solid fraction of digestate. The liquid fraction is processed by ultra filtration and reverse osmosis to produce mineral concentrates and clean water. Supplier: Wolter & Dros Biowatt B.V.	600 kWe CHP – unit	February 2002
Miste	Farm-scale co-digestion of 1,000 m^3/year pig and chicken manure with green maize, cabbage and fodder beets. J. Leemkuil. Supplier: WISA.		January 2001
Sterksel	Digester at testing farm for pigs (Praktijkcentrum Sterksel). Capacity 4,500 m^3/year pig manure. Biogas is used in 37 kWe CHP unit. Supplier: Ecogas international B.V.	37 kW CHP unit	January 2002

5

Dark hydrogen fermentations

T. de Vrije and P.A.M. Claassen [1]

Abstract

The production of hydrogen is a ubiquitous, natural phenomenon under anoxic or anaerobic conditions. A wide variety of bacteria, in swamps, sewage, hot springs, the rumen of cattle etc. is able to convert organic matter to hydrogen, CO_2 and metabolites like acetic acid, lactate, ethanol and alanine. In general, these bacteria live in the close vicinity of other bacteria which consume these metabolites, including hydrogen, producing their own endproducts like methane and CO_2. In this way, a stable ecosystem is formed where potential feedback inhibition of the hydrogen producers by hydrogen, is annulled by the action of the hydrogen consumers.

In view of the design of a bioprocess for the production of hydrogen from biomass, extreme thermophilic anaerobic bacteria have been selected because of their high yield with respect to hydrogen production. The yield is reported to be approximately 83-100% of the maximal theoretical value of 4 mol hydrogen/mol glucose, in contrast to the strict anaerobic *Clostridia* which produce hydrogen with an approximate yield of 2 mol/mol and the facultative anaerobes which show a H_2 yield of less than 2. Besides optimal H_2 molar yields, high hydrogen production rates are needed. Product formation appeared to be dependent on cell densities. Thermophiles usually grow to low densities and, therefore production rates are expected to be low. High production rates are reported for *Clostridia* and *Enterobacter* of maximal 23 and 58 mmol/L.h, respectively. Hydrogen fermentations by co- and mixed cultures showed production rates of approximately 30-50 mmol/L.h.

5.1 Introduction

This Chapter focusses on the microbial production of hydrogen from biomass by fermentation. In anoxic or anaerobic environments, hydrogen is commonly produced during microbial breakdown of organic compounds. In case organic compounds are the sole carbon and energy source providing metabolic energy, the process is termed ‘dark’ hydrogen fermentation. When light is required to provide additional energy, the process belongs to the category of photobiological processes (discussed in Chapter 6). In this Chapter, several features of dark hydrogen fermentation are presented and discussed to provide an insight in the state of the art and the presently recognized bottlenecks and R&D challenges associated with the first design of an envisaged production plant for hydrogen from biomass.

An overview of basic hydrogen fermentation processes and hydrogen producing micro-organisms is provided in sections 5.2 and 5.3. In section 5.4 the capacity to utilize various substrates is discussed. The design of a bioprocess for hydrogen from biomass and potential process improvements are dicussed in section 5.5. This section is followed by a description of the economical consequences of this bioprocess in section 5.6. In section 5.7 the current (inter)national developments and programs are summarized. This Chapter is concluded by section 5.8 in which the conclusions and perspectives are presented.

5.2 Physiology of dark hydrogen fermentation

Dark hydrogen production is a ubiquitous phenomenon under anoxic or anaerobic conditions (i.e. no oxygen present as an electron acceptor). A wide variety of bacteria use the reduction of protons to hydrogen to dispose of reducing equivalents which result from primary metabolism. In

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other words: when bacteria grow on organic substrates (heterotrophic growth), these substrates are degraded by oxidation to provide for building blocks and metabolic energy for growth. This oxidation generates electrons which need to be disposed of for maintaining electrical neutrality. In aerobic environments, oxygen is reduced and water is the product. In anaerobic or anoxic environments, other compounds need to act as electron acceptor, e.g. protons, which are reduced to molecular hydrogen (H_2). Other examples of alternative electron acceptors in anaerobic environments are nitrate with nitrogen gas (N_2) as the product or sulfate with dihydrogensulfide (H_2S) as the reduced product. Even organic compounds can act as electron acceptors as e.g. in the microbial production of butanol which is done through the reduction of butyric acid. The capacity to reduce other electron acceptors than oxygen requires the presence of a specific enzyme system in the micro-organisms: hydrogen producing bacteria possess hydrogenase enzymes; nitrate reducing bacteria possess an elaborate set of enzymes catalyzing the stepwise reduction of nitrate to nitrogen etc.

Even though many organic compounds enable the production of hydrogen during dark fermentation, estimations of potential yields are mostly based on hexose conversions. The theoretical yield per mole of glucose is described in the following reaction [1, 2]:

$$C_6H_{12}O_6 + 4H_2O \rightarrow$$
$$2CH_3COO^- + 2HCO_3^- + 4H^+ + 4H_2$$

$$\Delta G'_0 = -206 \text{ kJ.mol}^{-1}$$

A maximum of 4 moles of H_2 per mole of glucose can be produced concurrently with the production of energy (206 kJ per mole of glucose) which is sufficient to support microbial growth. The remainder of the hydrogen in the hexose is conserved in the byproduct acetate, and under non-ideal circumstances, more reduced products like ethanol, lactate or alanine. The complete oxidation of glucose to H_2 and CO_2 yields a stoichiometry of 12 mole H_2 per mole of glucose but in this case no metabolic energy is obtained. The yield of hydrogen during dark fermentation is severely affected by the partial pressure of the product. At high H_2 partial pressures a metabolic shift to production of more reduced products, like lactate [3] or alanine [4] occurs, thereby decreasing the yield of H_2.

Having established that microbial hydrogen production is a ubiquitous phenomenon, it must be surprising that no hydrogen bubbles are coming out of organic waste piles or the sewer. The underlying reason is the fact that, in natural environments, microbial activity is governed by an ecological niche. This niche is the resultant of many contributing factors including the presence and quality of available organic matter, presence of minerals, temperature, light, pH, salinity, redox potential, synergistic or antagonistic activity of microbial populations etc. The ecological niche governs the activity of certain microbial populations and thus the concentration and variety of the final products, i.e. CO_2, water, hydrogen, nitrate, CH_4 etc. No hydrogen is bubbling out of the sewer since in nature there are numerous other bacteria, which readily consume hydrogen as a source of reducing power. When the aim is to produce hydrogen from organic matter, a specific environment needs to be created in which hydrogen producing microorganisms flourish and others perish (Fig. 1).

5.3 Hydrogen producing micro-organisms

In reviews by Kosaric and Lyng [5] and Nandi and Sengupta [6] extensive lists of heterotrophic bacteria known to produce hydrogen have been published. An update is listed in this chapter.

5.3.1. Strict anaerobes

5.3.1.1. *Clostridia*

Many anaerobes produce hydrogen from hexoses in acetic acid, butyric acid and acetone-butanol-ethanol fermentations. The highest maximal yield of 4 mole H_2 from 1 mole of glucose is produced in acetic acid fermentations. The production of other, more reduced organic acids and/or alcohols lowers the yield of H_2. For instance the conversion of one mole of glucose into butyrate is accompanied by the production of only 2 moles of H_2. Usually a mixture of products is produced by

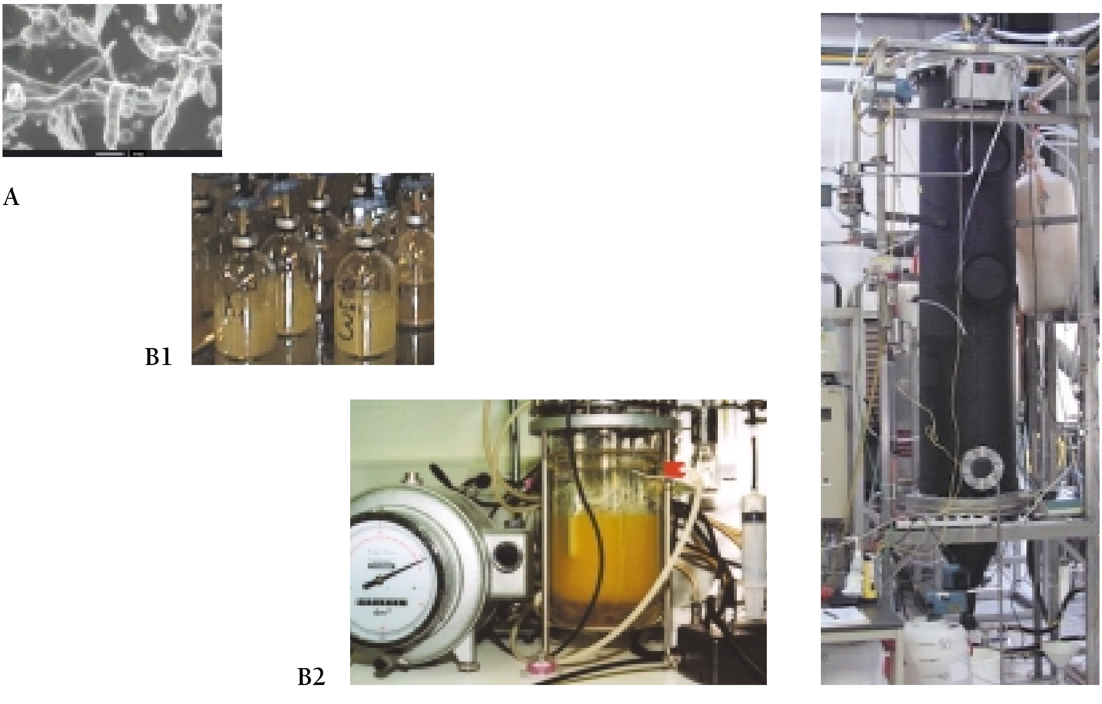

Figure 1. Growth of Caldicellulosiruptor saccharolyticus (A) on sucrose in flasks (B1) and under controlled conditions in fermentors (B2, B3). Photo of the fermentor (B3) by courtesy of TNO Environment, Energy and Process Innovation, Apeldoorn, The Netherlands.

Clostridia and the available H_2 from glucose is determined by the butyrate/acetate ratio.

C. butyricum, C. welchii, C. pasteurianum, C. beijerincki, newly isolated *Clostridium* spp. and mixtures of *Clostridia* have been used in studies dedicated to produce high amounts of hydrogen. Taguchi and collegues isolated various new *Clostridia* strains. A growing culture of *C. beijerincki* AM21B isolated from termites yielded 1.8 to 2.0 mole H_2 on glucose [7]. The strain could also utilize a large number of other carbohydrates, such as xylose, arabinose, galactose, cellobiose, sucrose, and fructose with efficiencies from 15.7 to 19.0 mmol/g of substrate in batch fermentations of 24 h [8]. H_2 was also produced from starch with equal efficiencies, but sustained production was not achieved and production ceased before the exhaustion of carbohydrates in the medium. Another ***Clostridium*** sp., strain no. 2, also isolated from termites, produced H_2 more efficiently from xylose and arabinose (13.7 and 14.6 mmol/g or 2.1 and 2.2 mol/mol) than from glucose (11.1 mmol/g or 2.0 mol/mol) [9]. These results suggest that both *Clostridia* spp. can be used for the production of H_2 from both cellulose and hemicellulose present in plant biomass. The hydrolysis of biomass for the production of a fermentable substrate can either be done during fermentation, in a simultaneous saccharification and fermentation process, or in a separate process preceding fermentation. Using *Clostridium* sp. strain no.2 it was found that the simultaneous saccharification of xylan with a crude xylanase preparation and hydrogen fermentation of the resulting hydrolysate by strain no. 2 could proceed in a single fermentor [10]. However, simultaneous conversion was less efficient than the independent conversion of the hydrolysate. Furthermore, hydrolysis of a cellulose preparation (Avicel) with a commercial cellulase preparation and hydrogen fermentation of the hydrolysate by strain no. 2 could not proceed in one flask because the conditions required for the enzyme activity and the growth of strain no. 2 differed significantly. Another approach is using *Clostridia* strains which are known to produce cellulase or xylanase activity. At present, no strains are available that are able to hydrolyse both glucans and xylans. Taguchi et al. [11] isolated a novel strain, *Clostridium* sp. strain X53 from wild termites, which produced xylanase in a batch culture and converted xylan to hydrogen. In comparison to xylose, the kinetics of hydrogen production from xylan were not significantly different, but the total yield from xylan was lower than from xylose. *Clostridia* have also been used in continuous hydrogen fermentations on glucose [12, 13, 14, 15, 16]. For *Clostridium* sp. strain no. 2 it has been shown that the maximal H_2 production rate and the molar yield were comparable in batch and continuous fermentations. Continuous H_2 production by fermentation of a continuously produced hydrolysate of cellulose in an aqueous two-phase system (polyethylene glycol and dextran) has been studied. The H_2 production rate and the H_2 yield were higher with Avicel hydrolysate compared to glucose. Since the H_2 yield on Avicel is higher than the theoretical maximum the presence of hydrolyzed dextran in the Avicel hydrolysate was suggested [17]. In continuous fermentations maximal H_2 production rates of 20.4 and 21.7 mmol/L.h have been measured [13, 15] at low yields of 1.4 mole H_2 per mole glucose. Higher yields, 2.4 mol/mol were accompanied by lower H_2 production rates of 7 mmol/L.h [15]. On xylose similar results were obtained, maximal H_2 production rates of 21.0 mmol/L.h have been measured at yields of 1.7 H_2 mol/mol xylose. Hydrogen has also been produced from *N*-acetyl-D-glucosamine and chitin waste products. In batch fermentations by the chitinolytic bacterium *C. paraputrificum* M-21 a H_2 yield of 2.2 mol/mol *N*-acetyl-D-glucosamine has been obtained at production rates of 31 mmol/L.h [18, 19]. The ability of *Clostridia* to produce H_2 looks very promising. Hydrogen yields and production rates can still be improved by optimizing process conditions.

5.3.1.2. Rumen bacteria

Other strict anaerobic bacteria producing hydrogen are rumen bacteria. *Ruminococcus albus* has long been known to produce H_2 together with other products like acetate, ethanol, formate and CO_2 from carbohydrates. In a continuous culture a H_2 yield of 2.4 mol/mol glucose was reported by Innotti et al. [20]. Since then production of H_2 by *R. albus* was not studied further.

5.3.1.3. Thermophiles

The hyperthermophile *Pyrococcus furiosus,* an archaebacterium, produces H_2, organic acids and CO_2 from carbohydrates [21, 22, 23]. Hydrogen production efficiencies were not evaluated. From characterization studies of utilized substrates and produced products many extreme- and hyperthermophiles are known to produce hydrogen from carbohydrates (reviewed by [24]). Cellulolytic thermophiles and extreme and hyperthermophilic bacteria producing hydrogen are e.g. species of *Anaerocellum, Caldicellulosiruptor, Clostridium, Dictyoglomus, Fervidobacterium, Spirocheta, Thermotoga and Thermoanaerobacter.* Schröder et al. [25] reported on batch fermentations at 80 °C with *Thermotoga maritima*. A H_2 yield on glucose of 4 mol/mol was obtained which is equal to the maximal theoretical value. However, glucose consumption was low (1.6 mM) and low cell densities (1.4 x 10^8 per mL) were reached. Maximal hydrogen production rates of approximately 10 mmol/L.h were measured. Similar stoichiometries as for *T. maritima* were obtained for two moderate thermophiles, *Acetothermus paucivorans* and *Acetomicrobium flavidum,* grown at 60 °C [26, 27]. Recently, results on growth and hydrogen production by two other extreme thermophiles during sugar fermentation have been published [28]. In cultures of *Caldicellulosiruptor saccharolyticus* grown on sucrose at 70 °C and *Thermotoga elfii* grown on glucose at 65 °C stoichiometries of 3.3 mole H_2 per mole hexose were obtained which is 83% of the theoretical maximum. Maximal hydrogen production rates of 8.4 and 2.7 mmol/L.h, respectively, were measured. These results show that higher hydrogen yields on hexose can be reached by extreme and hyper-themophiles compared to mesophilic facultative and strict anaerobes.

5.3.1.4. Methanogens

Methanogens are characterized by the presence of hydrogenase, which is usually involved in the oxidation of H_2 coupled to CH_4 production and CO_2

reduction. However, under conditions of inhibition of CH_4 formation Bott et al. [29] reported production of H_2 and CO_2 in stoichiometric amounts from CO and H_2O by a strain of *Methanosarcina barkeri,* the so-called water-gas shift reaction.

5.3.2. Facultative anaerobes

Facultative anaerobes are resistant to oxygen. These bacteria have the advantage of rapidly consuming oxygen thereby restoring anaerobic conditions immediately in reactors. Strict anaerobes are very sensitive to oxygen and often do not survive low oxygen concentrations.

5.3.2.1. *Enterobacter*

Enterobacter as well as other members of the *Enterobacteriaceae* can have several beneficial properties favourable for H_2 production. In addition to high growth rates and utilization of a wide range of carbon sources, H_2 production by *Enterobacter* is not inhibited by high H_2 pressures [30]. However, the H_2 yield on glucose is normally lower compared to that of e.g. *Clostridia.* Tanisho et al. [31] isolated strain ***E. aerogenes*** E.82005 from leaves of *Mirabilis jalapa.* Under batch cultivation a hydrogen production rate of 21 mmol/L.h was obtained over a period of 23 h. The H_2 yield was 1.0 mol/mol glucose. In a continuous fermentation hydrogen was produced during 42 days using the same strain and molasses as the substrate. The average H_2 production rate was approximately 17 mmol/L.h. The average H_2 yield on sucrose was 1.5 mole. In contrast to batch fermentations lactate was the major product and butyrate and acetic acid were produced in lower amounts [32]. Although production by *Enterobacter* is not inhibited by high H_2 pressures flushing the culture medium with argon enhanced the H_2 yield to 1.6 mole per mole glucose. It was suggested that the removal of CO_2 was responsible for the yield improvement [33]. Yokoi et al. [34] isolated an aciduric *E. aerogenes,* strain HO-39, which was able to grow and produce hydrogen at low pH of 4.5. In a continuous culture without pH control hydrogen was produced at a rate of approximately 5 mmol/L.h for 26 days with a yield of 0.8 on glucose. To enhance H_2 production rates mutants of *E. aerogenes* and *E. cloacae* were developed. The mutants are blocked in the production of other metabolites, alcohols and organic acids, which normally decreases hydrogen production. In an *E. aerogenes* double mutant which produced lower amounts of ethanol and butanediol but comparable amounts of organic acids the hydrogen production and yield were 2 times higher compared to the wild type [35]. Kumar and Das [36] have isolated *E. cloacae* IIT-BT 08 strain from leaf extracts which was capable to grow and produce hydrogen by using different carbon sources. In batch fermentations the maximum H_2 yield was 2.2 mol/mol glucose and 6.0 and 5.4 on sucrose and cellobiose, respectively. The maximum H_2 production rate measured was 35 mmol/L.h on sucrose as substrate. The same approach as for *E. aerogenes* has been used to develop mutants with enhanced H_2 production [37]. In batch fermentations a double mutant produced less ethanol and butanediol, and lower yields of lactate and butyrate were obtained. The yield of acetate was similar as the wild type strain. The block in formation pathways of alcohols and organic acids was accompanied by a 1.5 times increased H_2 yield on glucose, i.e. 3.4 mole per mole glucose. Continuous fermentations were performed with *E. aerogenes* wild types and a double mutant [38]. Due to self-flocculation, cells were retained in the reactor even at high dilution rates. Maximum production rates of 58 mmol/L.h at a dilution rate of 0.67 h^{-1} were reached for the double mutant, which was nearly 2 times higher compared to the wild type. The molar H_2 yield on glucose was maintained at 1.1. In a packed column with spongy material an *E. aerogenes* wild type strain produced hydrogen on a starch hydrolysate with a yield of 1.5 mol/mol glucose at a dilution rate of 0.1 h^{-1} [39].

5.3.2.2. *E. coli*

E. coli has been shown to be capable of producing H_2 and CO_2 from formate in the absence of oxygen [40, 72]. The catalytic activity, called formate hydrogen lyase, was shown to be a membrane-bound multi-enzyme complex, consisting of a formate dehydrogenase and a hydrogenase [73]. Sustained lysis of formate required blocking of other anaerobic reductases [74]. Production of hydrogen from carbohydrates was also reported [40]. Inconsistency exists on the pathway leading to H_2 production, either via formate or without formate as an intermediate [40, 41]. The molar H_2 yield on glucose by growing *E. coli* was 0.9 [41, 42] or 1.2 by immobilized cells.

5.3.2.3. *Citrobacter*

A *Citrobacter* species, *Citrobacter* sp. Y19 isolated from sludge digesters, has been shown to produce hydrogen from CO and H_2O by the water-gas shift reaction under anaerobic conditions [43, 44]. H_2 production was observed in serum-bottles and during continuous operations. In the latter case H_2 production rates of approximately 15 mmol/L.h have been observed. Equimolar amounts of H_2 were produced from the consumed CO, but the conversion efficiency of CO, which was about 20%, was relatively low. This was attributed to short retention times of CO.

5.3.3. Aerobes

5.3.3.1 *Alcaligenes*

A. eutrophus has been shown to grow heterotrophically on gluconate and fructose, and when exposed to anaerobic conditions produced hydrogen [45]. It contains a soluble NAD-reducing hydrogenase [46].

5.3.3.2 *Bacillus*

A hydrogen-producing *B. licheniformis* was isolated from cattle dung [47]. It produced 0.5 mol H_2/mol glucose [48]. Immobilized cells had an average H_2 yield of 1.5 mole per mole glucose and cells were stable during 60 days.

5.3.4. Co- and mixed cultures

Yokoi et al. [49, 50] reported on a co-culture in a continuous fermentation of *Clostridium butyricum* and *Enterobacter aerogenes* in which the higher H_2 yield of the strict anaerobe and the oxygen consumption by the facultative anaerobe were combined. This resulted in fermentations with no need for an expensive reducing agent since the presence of *E. aerogenes* was sufficient to rapidly restore anaerobic conditions in the fermentor upon short oxygen exposures. A continuous fermentation by immobilized mixed cells on porous glass beads and starch as the substrate showed a H_2 production rate of approximately 50 mmol/L.h and a H_2 yield of 2.6 on glucose at dilution rates of 1 h^{-1}.
Microflora for mixed cultures have been isolated from various sources, such as fermented soybean meal or sludges from anaerobic digesters of municipal sewage or organic waste and sludge from kitchen waste water. These microflora often contain unwanted bacteria such as methanogens which consume the produced hydrogen and convert it to methane. Enrichment cultures of the microflora are prepared by forced aeration of the sludge or by heat treatment which inhibits the activity of the hydrogen consumers while the spore forming anaerobic bacteria survive. Additionally, in continuous fermentations higher dilution rates are used to wash out the slow growing methanogens and select for the acid producing bacteria. In industrial applications the use of mixed cultures for hydrogen production from organic wastes might be more advantageous because pure cultures can easily become contaminated with H_2 consuming bacteria. The first reports published on hydrogen production during wastewater treatment showed inhibited methane production but low H_2 yields and lack of stability [51, 52]. Ueno et al. [53] have found that the anaerobic microflora in sludge compost converted cellulose to hydrogen with high efficiency of 2.4 mol/mol hexose in batch experiments at 60 °C. Furthermore, stable hydrogen production for 190 days from industrial wastewater from a sugar factory by the same microflora in a chemostat culture was reported [54]. Hydrogen yield on hexose was similar as in the batch culture and a H_2 production rate of 1.4 mmol/L.h at a HRT of 3 days was obtained. The maximal removal efficiency of carbohydrates was approximately 97% and also other organic compounds were converted. The hydrogen producers in the thermophilic microflora were identified. Sixty-eight strains were isolated and classified in 9 distinct groups and it was suggested that hydrogen production from cellulose is performed by a consortium of several species of microorganisms [55]. *Thermoanaerobacterium thermosaccharolyticum* was the dominant strain in the enrichment cultures. A patent has been issued [56] claiming a process for stable H_2 production at high efficiency by anaerobic bacteria from sludge compost under anaerobic conditions in combination with treatment of wastewater. Other recent work utilized sewage sludge to convert glucose and sucrose into hydrogen in continuous cultures at 35 °C [57, 58]. At retention times of 6 to 8 hours a molar H_2 yield of 1.7 and 3.4 on glucose

and sucrose, respectively, was obtained at production rates of approximately 26 to 29 mmol/L.h over a two-week period. Kinetic models were developed to describe and predict the results and based on this it was suggested that product formation was essentially a linear function of biomass concentration. Results on mixed cultures from digester sludge have been reported by Lay [59, 60]. Conditions were varied according to central composite design methodology in order to model and optimize the anaerobic digested sludge converting starch and cellulose to hydrogen. Mizuno et al. [61] improved the H_2 yield on glucose by mixed cultures isolated from fermented soybean meal through sparging the medium in a continuous stirred-tank reactor with N_2. During an 8 week period of continuous operation stable H_2 production rates of approximately 8 mmol/L.h were obtained. Noike and Mizuno [62] reported on hydrogen fermentations of organic waste, such as bean curd manufacturing waste, rice and wheat bran by the same mixed culture in batch reactors. The H_2 yield varied from 1.7 to 2.5 mol/mol hexose and the carbohydrates were used as the main source while soluble protein was hardly degraded.

To summarize, the highest H_2 yields on hexose have been obtained by hydrogen producing extreme thermophilic anaerobic bacteria (Table 1). The yields were approximately 83-100% of the maximal theoretical value of 4 mol/mol. More research is needed to confirm these results and to determine whether this is a general property of thermophilic bacteria. The strict anaerobic *Clostridia* produce hydrogen with higher yields, approximately 2 mol/mol, than facultative anaerobes which show a H_2 yield of less than 2. However, higher molar yields of more than 3 have been obtained in mutants of *Enterobacter* which are blocked in biosynthetic pathways leading to organic acid and alcohol production. In mixed cultures molar H_2 yields of around 2 are obtained, which reflects the dominant presence of *Clostridia* in enriched cultures. Besides optimal H_2 molar yields, high hydrogen production rates are needed. Product formation appears to be dependent on cell density. Thermophiles usually grow to low densities and, therefore production rates are expected to be low. High production rates are reported for *Clostridia* and *Enterobacter* of maximal 23 and 58 mmol/L.h, respectively. Hydrogen fermentations by co- and mixed cultures showed production rates of approximately 30-50 mmol/L.h.

5.4. Feedstocks for dark hydrogen fermentation

In this section two aspects of the feedstock for this type of hydrogen production are discussed. The first concerns the range of organic compounds which can be utilised. The second concerns the quality of the feedstocks which can be used for dark hydrogen fermentation.

With respect to the range of potential substrates which can be utilised by the broad range of hydrogen producing bacteria it can be stated that, at present, it is vast and open for further exploration. From a thermodynamic point of view, the conversion of carbohydrates to hydrogen and organic acids is preferred because it yields the highest amount of hydrogen per mole of substrate. These carbohydrates can be monosaccharides but may also be polymers such as starch, cellulose or xylan, as discussed in section 3. Besides carbohydrates (Fig. 2) also formate and peptides have, until now, been studied as substrates for dark hydrogen production.

From our own work with extreme thermophilic bacteria, it has recently become clear that amino acids can also be oxidised to hydrogen by certain strains. It is not clear whether specific amino acids, entering bacterial metabolism at the level of pyruvate are selected or whether this phenomenon is more general. Furthermore, we have observed that growth of hydrogen producers on certain saccharides is not always associated with reduction of protons to hydrogen but limited to reduction of other electron acceptors which were, allegedly, used for analytical reasons, e.g. like thiosulfate being reduced to the easily detected H_2S in the study of Ravot [63].

Finally, to add to the confusion, there is the fact that there have not (yet) been many studies on dark hydrogen production. This, together with the large number of hydrogen producing microbial species, allows the suggestion that most carbohydrates are a suitable feedstock for dark hydrogen fermentation. Proteins, peptides and amino acids are probably less suitable for dark

TABLE 1. Hydrogen yields and production rates by microorganisms as reported in the literature.

microorganism	**conditions**				**substrate**	**H_2 yield mol/mol monosaccharide**	**H_2 production rate (maximal) mmol/h.L**	**source**
	culture	**D, h^{-1}**	**pH**	**T, ºC**				
Strict anaerobes								
Clostridia								
Clostridium sp. no 2	batch		6.0	36	glucose	2.0	23.9	[9]
	batch		6.0	36	xylose	2.1	21.7	
C. paraputrificum M-21	batch		uncontrolled	37	GlcNAc[1]	2.5	31.0	[18, 19]
C. butyricum LMG1213tl	continuous	0.222	5.8	36	glucose	1.5	21.7	[13]
Clostridium sp. no 2	continuous	0.18	6.0	36	glucose	2.4	7.1	[15]
	continuous	1.16	6.0	36	glucose	1.4	20.4	
	continuous	0.96	6.0	36	xylose	1.7	21.0	
Thermophiles								
Thermotoga maritima	batch		uncontrolled	80	glucose	4.0	10	[25]
Thermotoga elfii	batch		7.4	65	glucose	3.3	2.7	[28]
Caldicellulosiruptor saccharolyticus	batch		7.0	70	sucrose	3.3	8.4	[28]
Facultative anaerobes								
Enterobacter								
E. aerogenes E.82005	batch		6.0	38	glucose	1.0	21	[30, 31]
E. cloacae IIT-BT 08 wt	batch		uncontrolled	36	glucose	2.2		[36, 37]
	batch		uncontrolled	36	sucrose	3.0	35	
E. cloacae IIT-BT 08 m DM_{11}	batch		uncontrolled	36	glucose	3.4		
E. aerogenes E.82005	continuous	0.32	6.0	38	molasses	0.7	20	[9]
E. aerogenes HU-101 wt	continuous	0.67	uncontrolled	37	glucose	0.6	31	[38]
E. aerogenes HU-101 m AY-2	continuous	0.67	uncontrolled	37	glucose	1.1	58	
Co-culture								
C. butyricum IFO13949 + *E. aerogenes* HO-39	continuous	1.0	5.2	36	starch	2.6	53	[49, 50]
		HRT, h						
Mixed cultures from:								
- sludge compost	continuous	12	6.8	60	waste water sugar factory	2.5	8.3	[54]
- sewage sludge	continuous	6	5.7	35	glucose	1.7	29.6	[57]
	continuous	8	6.7	35	sucrose	1.7	26.2	[58]
- fermented soybean meal	continuous	8.5	6.0	35	glucose	1.4	8	[61]

[1] GlcNAc=*N*-acetyl-D-glucosamine

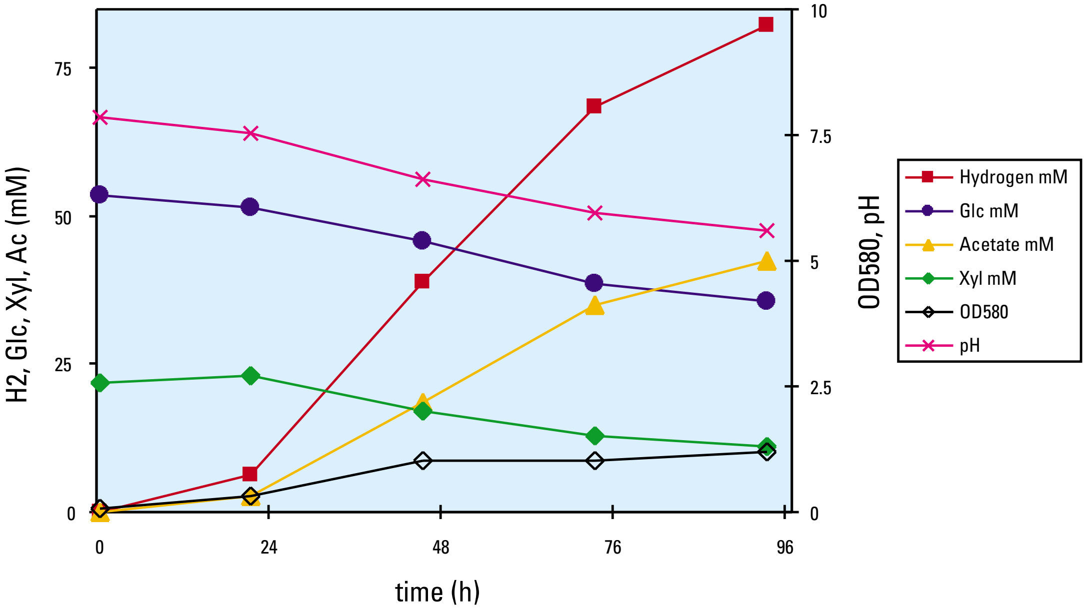

Figure 2. Simultaneous consumption of glucose and xylose during growth of Thermotoga elfii on Miscanthus hydrolysate at 65 °C. (from: de Vrije et al., 2002 [75])

hydrogen production whereas biopolymers like lipids will be unsuited.

This great potential of dark hydrogen fermentation, i.e. the vast range of potential organic substrates, has also been recognized by other workers in the field. Noike and Mizuno [62] and Yu et al. [78] refer to several forms of organic waste streams ranging from solid wastes like rice straw to waste water from a sugar factory and a rice winery, which have been successfully used for dark hydrogen production. Besides the organic substrates, CO in syngas has been used as feedstock for biological H_2 production. Syngas or fuel gas is a mixture of (mainly) CO and H_2, which can be produced cheaply and on a large scale by thermochemical gasification of coal or wood. A wide range of anaerobic micro-organisms are capable of CO oxidation with concomitant H_2 production in a biological variant of the water-gas shift reaction [29, 77]. These organisms could serve as a biological alternative for chemical catalysts to remove CO from H_2 rich gases, and produce H_2 linked to CO oxydation. CO uptake has been shown to occur at very high rates. The process could be used for fuel gas conditioning and upgrading, both by CO removal and H_2 production. A technological challenge is to enhance CO mass transfer which is the rate limiting step in the process.

At this point the second aspect of the feedstock, i.e. the quality, enters the discussion. Even though there have been reports on dark hydrogen fermentation using solid organic waste, this phenomenon has also been denied. Besides this contrast which is probably due to different species being involved, there is the even more basic discussion concerning the configuration of the feedstock on the molecular level. As stated above and shown in section 3 several hydrogen producers are able to convert biopolymers like starch, cellulose and xylan to hydrogen and organic acids (Fig. 3).

This is very convenient, because pretreatment of biomass is then only, eventually, needed from the process technological point of view e.g. for improving rheological properties. However, apart from the more easily degradable feedstocks such as starch and cellulose, the main components of future feedstocks will, most probably, to a large extent be derived from lignocellulosic raw materials. Lignocellulose is a biopolymer consisting of

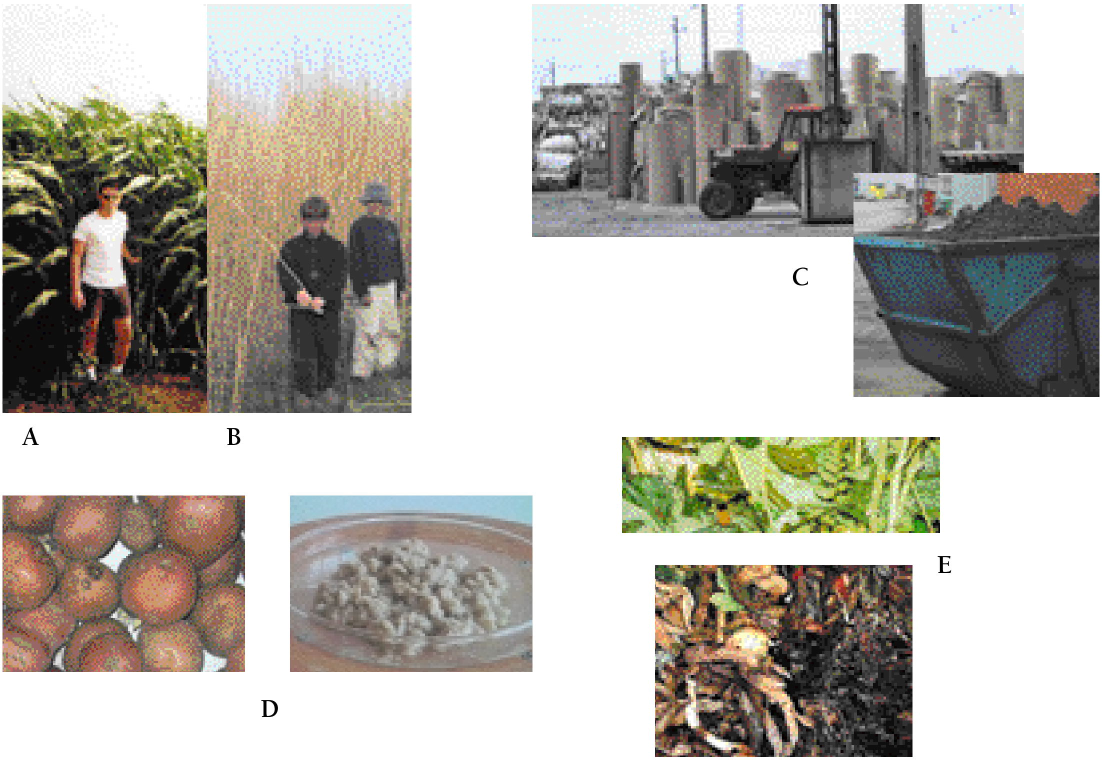

Figure 3. Feedstocks which have been successfully used for hydrogen production by extreme thermophiles (A. Sweet Sorghum, B. Miscanthus, C. paper sludge, D. potato steam peels, E. domestic organic waste).

tightly bound lignin, cellulose and hemicellulose. Whereas cellulose and hemicellulose can be feedstocks for hydrogen fermentation, lignin is not degraded under anaerobic conditions. Moreover, lignin strongly hampers the utilisation of cellulose and hemicellulose because a) the bonding in lignocellulose resists mobilisation and b) chemically degraded lignin is often inhibitory to microbial growth.

These parameters need to be studied in view of producing cheap feedstocks for dark hydrogen fermentation from lignocellulosic biomass residues

Figure 4. Chopped Miscanthus before (Left) and after extrusion in combination with a sodium hydroxide treatment (Right). The pretreatment removed 77% of the lignin.

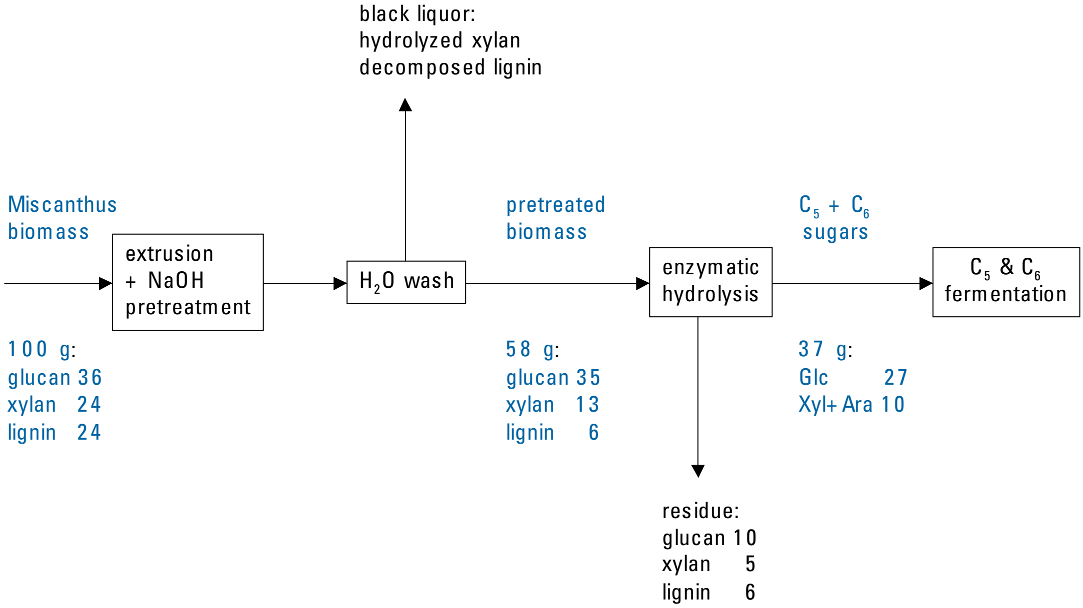

Figure 5. Flowsheet of pretreatment (extrusion combined with sodium hydroxide) and enzymatic hydrolysis of Miscanthus. Pretreatment and enzymatic hydrolysis results in fermentable sugars and (non)fermentable sidestreams. (from: de Vrije et al., 2002 [75])

and/or energy crops. It seems obvious that producing cheap feedstocks will require the development of cost effective pretreatment methods with a low energy demand (Fig. 4).

This constraint in dark hydrogen fermentation is also studied in our own hydrogen projects which focus on the whole chain of events for hydrogen production from biomass. The approach for successful pretreatment is to use a combination of physical and (bio)chemical methods for mobilisation of saccharides for fermentation, while simultaneously preserving the nonfermentable components for further valorisation, e.g. lignin as a biofuel (Fig. 5).

5.5. Bioprocesses for hydrogen from biomass

5.5.1. Current process development

The physiology of dark hydrogen fermentation explains, thisfar, that hydrogen production is a common microbial asset and that for obtaining this hydrogen as the final product, only a specific environment needs to be created in which hydrogen producing bacteria flourish and others perish. However, as outlined above, dark hydrogen fermentation is an incomplete oxidation. This means that organic matter is not completely oxidised to CO_2 but to intermediate compounds, like acetic acid or lactate. Further oxidation of these products in the dark, to hydrogen and CO_2, is thermodynamically very unfavourable. Thus, dark hydrogen fermentation delivers, besides very pure hydrogen, other, reduced carbonaceous products which need to be utilised for making a sound balance when considering energy production from organic matter. As can be read in the chapters dealing with methane production (Chapter 4) and photobiological hydrogen production (Chapter 6) these intermediate products can be further metabolised to methane or converted to hydrogen in the presence of light, respectively.
Our approach is to counter one of the physiological drawbacks of dark hydrogen fermentation, i.e. the incomplete oxidation, by coupling the process to a subsequent fermentation (Fig. 6).
In this way the chemical energy present in the initial organic matter remains preserved as much as possible. This also applies to situations where the yield of hydrogen is lower than theoretically

expected. Theoretically, 1 mole of glucose is converted to 4 moles of hydrogen, 2 moles of acetic acid and 2 moles of CO_2. As can be read in section 3 of this chapter, there are several microbial conversions where the yield is less than 4 moles of hydrogen. Other workers in the field [64] strongly adhere to attaining this theoretical maximum. Even though our present projects aim at reaching a yield of 4 moles of hydrogen in the dark fermentation, it is our conviction that the whole chain should be considered here. The substrate range of phototrophic bacteria in a subsequent fermentation is fairly wide. This means that a lower hydrogen production during dark fermentation is compensated by a higher hydrogen production in e.g. a consecutive photobiological fermentation. Thus, in the end, the same amount of hydrogen will be produced. When the dark hydrogen fermentation is followed by a methane fermentation, there may be less room for negotiation, although acetic acid is amongst the favorite substrates for methane production (Fig. 7).

Several approaches can be considered to increase hydrogen yields in the dark fermentation. The optimisation of methane and photobiological fermentations, is discussed in Chapters 3 and 5, respectively.

Metabolic engineering of hydrogen producing micro-organisms to minimise production of other more reduced products by blocking their biosynthetic pathways will provide higher yields [35, 37, 38]. Additionally, higher hydrogen yields will most probably be achieved by limiting cell growth through nutrient limitations, thereby enhancing catabolic processes. High cell densities are needed to maximize hydrogen production rates. Therefore, major improvements are expected in systems with biomass retention, e.g. by immobilized cells [79], under nutrient limitations operating in a continuous mode.

As another potential improvement the production of hydrogen at high temperatures by extreme and hyper-thermophiles could be considered [65]. At increased temperatures hydrogen production

5.5.2. Process optimisation

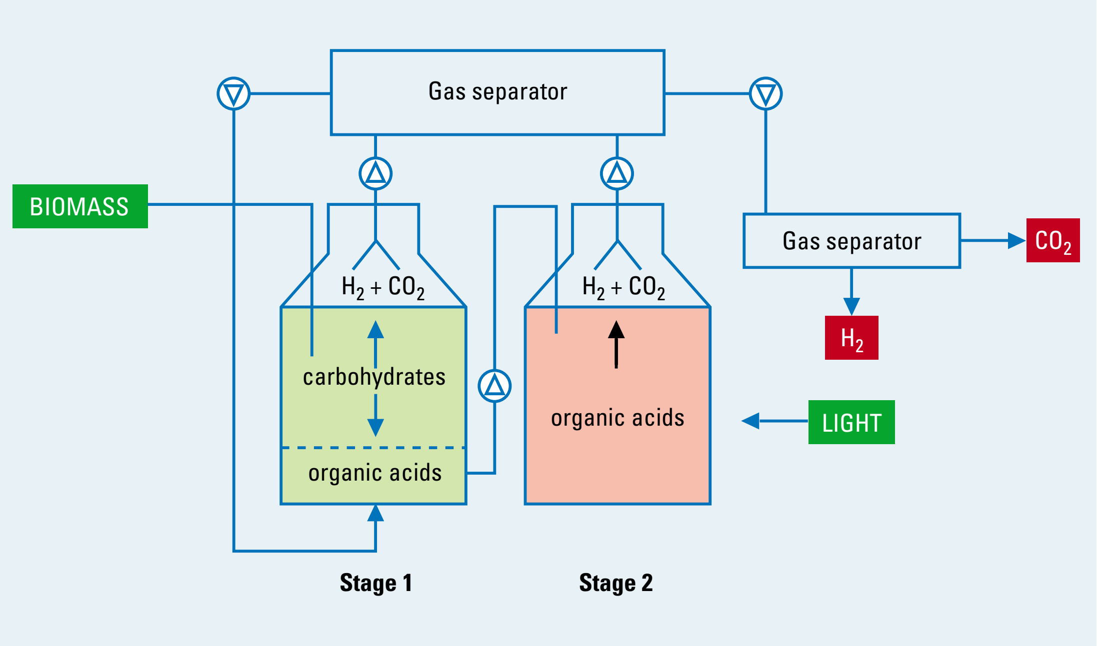

Figure 6. Outline of the bioprocess for production of hydrogen from biomass in a 2 stage fermentation. Stage 1 is for heterotrophic fermentation of carbohydrates to hydrogen, carbon dioxide and organic acids. In stage 2 the photoheterotrophic fermentation of organic acids to hydrogen and carbon dioxide takes place.

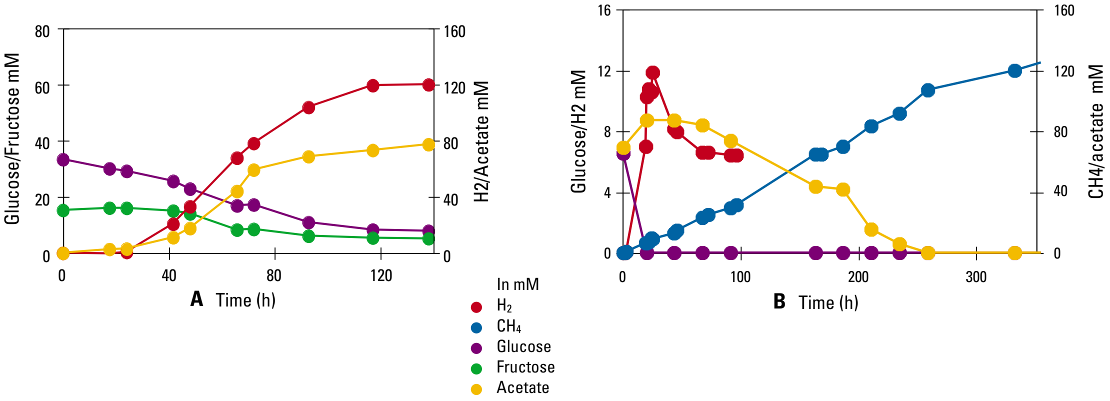

Figure 7. Results from a bioprocess for production of hydrogen and methane from domestic organic waste in a 2 stage bioprocess. In stage 1 hydrogen and acetic acid are produced during growth of Thermotoga elfii on domestic organic waste hydrolysate (A). In stage 2 the methanogenic fermentation of acetic acid to methane takes place (B). (from: Claassen et al., 2002 [76])

becomes more exergonic [66]. *Pyrococcus furiosus* hydrogenase showed a dramatic increase in H_2 evolution activity above 80° C which may be partly due to a decreased affinity of the enzyme for H_2 [67]. Therefore, extreme- and hyper-thermophiles show a better resistance to high hydrogen partial pressures [68] which otherwise cause a metabolic shift to production of more reduced lactate or alanine instead of acetate. This could be one of the reasons that extreme- and hyper-thermophiles produce hydrogen with an efficiency of almost the theoretical maximum. Another advantage of fermentations at extreme temperatures is that the process is less sensitive to contaminations by e.g. hydrogen consumers, thus establishing a specific environment enabling maximum evolution of hydrogen. In spite of the higher tolerance for hydrogen in thermophiles, this product may still impose feed-back inhibition. Therefore, the design of a highly efficient hydrogen removal step is needed to further augment productivity [80, 81].

5.6. Economics for hydrogen from biomass

Here data are presented which were collected during a Kiem-EET study (Nov 1998–Feb 2000) performed by ATO (co-ordinator), WU-Laboratory for Microbiology, WU-Department Agrotechnology and Food Sciences, TNO-MEP and Paques Biosystems [69] and financially supported by the Dutch Ministries of Economic Affairs (EZ), Education, Culture and Science (OCenW), and Housing, Spatial Planning and the Environment (VROM) via the Economy, Ecology, Technology Programme (EET) and the Ministry of Agriculture, Nature Management and Fisheries.

As stated above, dark hydrogen fermentation is an incomplete oxidation, yielding not only hydrogen and CO_2, but also organic acids like acetic acid. For an economically sound process, the reduced carbonaceous compounds need to be converted too; either in a photo-bioreactor to H_2 and CO_2 or in a methane reactor to CH_4 and CO_2. If the dark hydrogen fermentation is not followed by further conversion, the H_2 yield will not warrant economic feasibility. Therefore, the costs of hydrogen production were estimated from a first design of a complete bioprocess for hydrogen from biomass, consisting of an extruder for preparing fermentable feedstock, a thermo-bioreactor (95 m^3) for

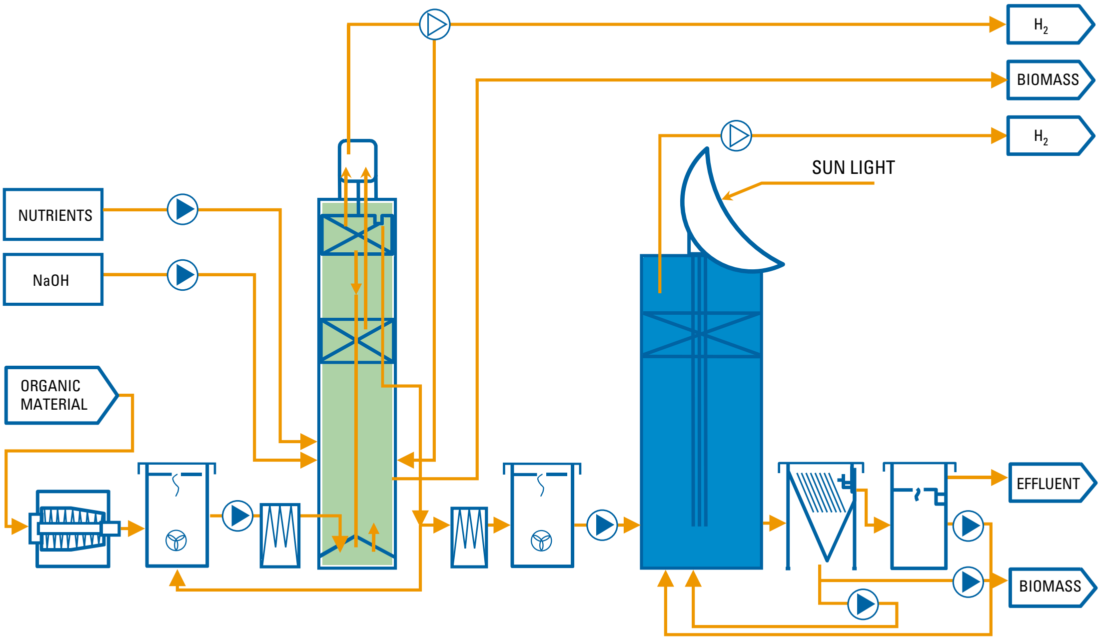

Figure 8. First design of a bioprocess for the conversion of biomass to hydrogen in a thermo-bioreactor, followed by a photo-bioreactor (adapted by ATO from the conceptual design by Paques Biosystems B.V.).

dark hydrogen fermentation and a photobioreactor (300 m^3) equipped with a sunlight collector, for the conversion of acetic acid to hydrogen and CO_2 (Fig. 8).

The estimate is based on the use of extreme thermophilic bacteria for the dark hydrogen fermentation since only these have been shown, until now, to achieve the theoretical production of 4 moles of hydrogen per mole of glucose consumed. The conversion efficiency in the thermo-bioreactor was assumed to be 80%. The same efficiency was assumed for the consecutive photo-bioreactor where acetate from the effluent of the thermo-bioreactor was converted to hydrogen at a ratio of 4 moles hydrogen per mole of acetate.

Hydrogen produced in the thermo-bioreactor was recovered using gas stripping and this hydrogen was further purified to specifications for fuel cell application using pressure swing adsorption.

The size of the plant was set at a production capacity of 425 Nm^3 H_2/hour (39 kg H_2/hour), aiming at relatively small scale systems, fed by locally produced feedstock. As feedstock a common lignocellulosic substrate was chosen consisting of 65% (w/w dry matter) (hemi)cellulose of which 65% becomes available for fermentation after pretreatment in the extruder. On this basis it was calculated that 1000 kg biomass (dry weight)/hour is required to produce 425 m^3 H_2/hour.

The contribution of the investment costs and energy demand of the separate steps to the production costs of hydrogen from biomass is shown in Tables 2 and 3. As the current costs of biomass range from low to even negative, being very volatile in view of future demands, no value was included for the acquisition of the feedstock. The same accounts for the mobilisation of fermentable substrates from the feedstock. This is a potential cost factor which is dependent on intrinsic feedstock properties and applied pretreatment and hydrolysis schemes and therefore impossible to consider under a common denominator.

The data shown in Tables 2 and 3 result in an estimated overall cost of EURO 2.74/kg H_2, equiva-

TABLE 2. *First estimate of investment costs for equipment required for a hydrogen from lignocellulosic biomass production process for production of 425 m*^{3} *H_2 /h or 312 tonne H_2 /year, and the contribution to the H_2 production costs.*

Item	**Investment costs (EURO)**	**Annual capital costs (EURO)**	**Costs/kg H_2 (EURO)**
Extruder	1,045,455	156,818	0.50
Bioreactors, pumps etc.	1,295,455	194,318	0.62
Sunlight collector	811,064	121,660	0.39
Equipment for H_2 recovery from thermo-bioreactor	403,182	60,509	0.20
Equipment for H_2 recovery from photobioreactor	196,803	29,520	0.10
Total:	3,751,959	562,825	1.81

TABLE 3. *First estimate of energy consumption and costs for a hydrogen from lignocellulosic biomass production process for production of 425 m*^{3} *H_2 /h or 312 tonne H_2 /year. Assumed electricity costs 0.068 EURO / kWh.*

Item	**Energy consumption (GJ/h)**	**Energy costs/year (EURO)**	**Costs/kg H_2 (EURO)**
Extruder	0.547	82,879	0.26
Bioreactors	0.842	127,576	0.41
Recovery of H_2 from thermo-bioreactor	0.225	34,030	0.11
Recovery of H_2 from photobioreactor	0.281	42,545	0.14
H_2 Purification	0.010	1,515	0.01
Total:	1.90	288,545	0.93

lent to 0.25 EURO/Nm^3 H_2 or 19.2 EURO/GJ (based on upper combustion value). This final cost estimation is based on acquisition of biomass at zero value, zero hydrolysis costs and excludes personnel costs and costs for civil works, all potential cost factors. On the other hand, process units have been considered separately, thus precluding the opportunity to couple technical devices and energy requiring and energy yielding process units. For comparative purposes, present production costs for hydrogen produced in small scale production plants based on alternative technologies are presented in Table 4. Except for the technologies where natural gas or conventional electricity is used for the production of hydrogen, these production methods are without net CO_2 emission.

In the bioprocess for hydrogen from biomass, CO_2 is one of the products. However, since this CO_2 is derived from biomass, no net emission occurs and thus this process is considered as CO_2 neutral. Besides CO_2, formed in a ratio of 1 : 2 (CO_2 : H_2 v/v), no other volatile products are expected from the dark fermentation. So, besides being CO_2 neutral, another advantage of this bioprocess is the production of pure product streams.

Besides the final cost of the produced hydrogen, the energy balance of this bioprocess has been considered. The production of 425 m^3 H_2/h is equivalent to an energy production of 5.4 GJ/h, based on the upper combustion value of 12.74 MJ/Nm^3. The electricity requirement in this design is estimated at 1.9 GJe/h. These observations show the weak points in the first design which are now being studied in new projects.

First of all the yield in terms of hydrogen is addressed. The yield is inherently related to the mobilisation of fermentable feedstock which can

TABLE 4. *Comparison of H_2 production costs and net CO_2 emissions in small-scale production plants with capacities in the range 100 – 1000 Nm^3 H_2 /h.*

Technology1)	**Production costs (EURO/Nm^3 H_2)**	**CO_2-emission (kg/Nm^3 H_2)**
Steam-reforming of natural gas	0.32	0.8
Electrolysis with conventional electricity	0.23	1.8
Electrolysis with CO_2-lean electricity 2)	0.27-0.36	0
2-stage bioprocess for hydrogen from biomass (this estimate)	0.25	0
Steam-reforming of bio-methane	0.32	0
Electrolysis with electricity from wind turbines	0.25	0
Electrolysis with electricity from photovoltaic cells	2.95	0

1) *Data for alternative technologies were provided by TNO Environment, Energy and Process Innovation (personal communication).*

2) *Here CO_2 is sequestered in e.g. aquifers, rendering this process CO_2 neutral.*

TABLE 5. *Estimated energy potential of a bioprocess for hydrogen from biomass in The Netherlands.*

		Units
Available biomass for biohydrogen production1)	2,650	ktonne d.w./year
Total bio-H_2 production (39 kg H_2 /tonne biomass)2)	103	ktonne / year
Total energy content of Bio-H_2 produced3)	14.7	PJ
Potential number of Bio-H_2 plants 2)	330	
Total electricity production 4)	7.4	PJe / year
Electricity production per bio-H_2 plant	22,294	GJe / year
Electricity consumption per household; 3380 kWh/yr5)	12.2	GJe / year
Number of households per Bio-H_2 plant	1830	
Total number of households with Bio-H_2 electricity	600,000	

1) *50 % of total available biomass (5.3 Mtonne/a according to Faaij et al. [71])*

2) *For a plant producing 39 kg H_2 /hour from 1 tonne (d.w.) of biomass.*

3) *Based on upper combustion value: 142.7 GJ/tonne H_2*

4) *Fuel cell with 50% conversion efficiency*

5) *Ref: http://www.energie.nl/*

6) *Total number of households is 6.86 million Ref: http://www.energie.nl/*

be converted to hydrogen. Besides increasing the efficiency of mobilisation, e.g. from 65% to 85%, also other feedstocks besides lignocellulosic feedstocks, e.g. energy crops (Sweet Sorghum) or starchy wastes (potato steam peels) are now under consideration. Secondly, the energy requirement of the bioprocess is addressed. By a new reactor design the energy demand has become significantly decreased [81]. A new, but certainly necessary strategy, is the utilisation of the residual biomass for the production of energy in a non-fermentative way. It seems feasible to generate sufficient energy from the residues to prevent the addition of external electricity from the grid.

An indication of the energy potential of the bioprocess for The Netherlands is provided in Table 5. The estimate is based on data provided by Faaij et al (1997) [71] for the total biomass availability (5.3 Mtonne/yr) in The Netherlands. It is assumed that 50% of the total amount of biomass (2,650 ktonne/y) is available for biohydrogen production (103 ktonne H_2/y) and that the energy requi rement of the bioprocess is fully covered by thermochemical conversion of residual non-fermented biomass. It is further assumed that the produced hydrogen is converted to electricity in fuel cells at 50% efficiency. As the total number of households is 6.86 million [2000; ref http://www.energie.nl/], the coverage with respect to electricity demand is 9% of all households. If the biomass availability increases, e.g. due to a decreased demand in the animal feed industry, the coverage increases accordingly. Finally, fuel cells generate heat besides electricity. This aspect has not yet been introduced in the calculations presented here because at present its quantification is unsure.

5.7. International status of development

The potential of biological hydrogen production is recognized worldwide. At the recent international conference Biohydrogen 2002, with 150 participating researchers from around the world, the status and progress in fundamental microbiological/biochemical research and technological R&D in the field of both photobiological and dark fermentative hydrogen production was reviewed [82]. Biohydrogen 2002 shows that the international attention and R&D efforts in the field of dark fermentative hydrogen production from biowastes and wastewater are rapidly increasing. At present, The Netherlands is leading in research on application of thermophilic bacteria for hydrogen production in projects supported by national governmental organisations as well as the European Union. The targeted feedstocks include biowastes (potato-processing residues, organic fraction of municipal solid wastes, paper sludge) as well as energy crops such as Miscanthus and Sweet Sorghum. In some countries R&D focuses primarily on mesophilic H_2 fermentations. In Japan H_2 fermentation R&D has included feedstocks such as bean manufacturing waste ('okara'), rice bran, wheat bran, apple and potato peels, palm oil mill effluent and tofu waste water. Additional R&D takes place in China (rice winery wastewater) and in Hungary (in co-operation with The Netherlands) on H_2 fermentation of paper sludge hydrolysate. A relatively new focus in the field is the development of combined two-stage H_2 and CH_4 fermentation systems e.g in The Netherlands and Japan. A major technical prerequisite for efficient H_2 fermentations is the maintenance of low H_2 partial pressures through continuous removal of H_2 from the fermentation broth. At the Biohydrogen 2002 conference several recent developments were presented including the use of membranes, which indicates that this obstacle can be overcome with continued development [82]. The development of dark hydrogen fermentations also benefits from the rapid progress in the field of fundamental hydrogenase research that includes the recent elucidation of the structure of the catalytic sites and basic physiological research.

In order to accelerate the technological development and to generate critical mass for the development of a hydrogen based economy international knowledge exchange and co-operation are required. The IEA Hydrogen Program supports collaborative activities for the advancement of hydrogen technologies in various tasks focusing on hydrogen production and storage technologies and infrastructural integration [83]. Work on dark hydrogen fermentations is included in Task 15, 'Photobiological hydrogen production' that has recently been extended. The objectives of the European COST Action 841 'Biological and Biochemical Diversity of Hydrogen Metabolism' are to enhance the understanding of the basic molecular and physiological aspects of biological hydrogen metabolism as an indispensable basis for fundamental and applied research [84]. The European Union further supports the European Thematic Network on Hydrogen: HyNet [85].

In the USA the activities for the transition to a hydrogen economy are combined in the 'Hydrogen, Fuel Cells & Infrastructure Technologies Program' supported by the Department of Energy [86]. In November 2002 the 'National Hydrogen Energy Roadmap' was presented in which biological hydrogen production is seen as one of the options for renewable hydrogen production on the longer term.

Increasingly, expert groups of various disciplines throughout Europe, Canada, Asia and, to a smaller extent, the USA are focussing on the biological production and application of hydrogen, as well as the societal impacts of implementation. The insight that hydrogen needs to be produced from renewable sources in the future is recognised at the level of the European Commission and described in reports like 'Future Needs and Challenges for Non-Nuclear Energy Research in the European Union' (2002). The future role of hydrogen as a clean fuel for fuel cells producing near-zero emissions and as an intermediate energy carrier for storage and transport of renewable energy is increasingly recognized in Europe. The EU will therefore intensify the R&D in the field of hydrogen and related technologies. Several Expression of Interests related to biological hydrogen production and supported by more than 30 workers in the field have been submitted to the European Commission in June 2002. This may form the basis for continuation and expansion of bio-hydrogen development in Europe. Finally, the combination of fermentation processes with the use of product gas in fuel cells is particularly relevant for the future application of bio-hydrogen. This topic is being explored in 'BFCNet': 'Network on Biomass Fermentation Towards Usage in Fuel Cells' [87]. The objectives of BFCNet include joint research and demonstration and the development of standards on EU level.

It is clear from the above that biological hydrogen production through fermentation of biowastes is receiving increased attention. Furthermore, the potential of (renewable) hydrogen is increasingly recognized internationally, which provides a stimulus for the further development of biological hydrogen production.

5.8. Conclusions and perspectives for further development

5.8.1. Brief conclusions

- Dark hydrogen fermentation is a natural phenomenon but is, in natural environments often obscured due to rapid consumption of hydrogen by other species.
- The capacity to ferment organic compounds to hydrogen is widespread amongst micro-organisms. There are great differences in yields and production rates.
- Dark hydrogen fermentation can be done with almost all carbohydrates. The production of fermentable feedstocks from lignocellulosic material requires further investigation and technology development.
- The realization of a bioprocess for hydrogen requires two consecutive steps for complete utilisation of the chemical energy in the substrate. In the first step hydrogen is produced by dark hydrogen fermentation. In the second step the effluent is converted to either hydrogen or methane. Solutions for obtaining high yields and high production rates in the dark fermentation phase are envisaged.
- For an economically feasible hydrogen from biomass production process, a two stage fermentation is required for complete conversion of sugars to hydrogen.

A tentative cost estimate for hydrogen from biomass in a first design shows a cost for hydrogen which is favourable as compared to other sustainable hydrogen production processes. The energy demand of the bioprocess should be covered by utilisation of the non-fermentable residual biomass.

5.8.2. R&D challenges and perspectives

The mobilisation of fermentable feedstocks from biomass is an important R&D issue for every fermentative biofuel process, including the hydrogen from biomass process described here. This technological obstacle can be tackled by further development and optimisation of pretreatment techniques, aiming at an increase in efficiency of the current 65% to 85%. Improved mobilisation of fermentable substrate will increase the yield of hydrogen from biomass and hence the overall energy efficiency of the bioprocess. Here it is important to realise that some pretreatment techniques are more suitable for pretreatment of a specific biomass type than others. When different biomass types are considered, e.g. steam explosion or other techniques may be more adequate. In general, pretreatment is followed by, presently very expensive or environmentally undesirable, (bio)chemical hydrolysis. Even though many hydrogen producing micro-organisms are able to directly convert (hemi)cellulose to hydrogen, this conversion may be rate-limiting or impair proper process performance. Therefore, this topic has to be considered too in further optimisation.

In addition, it is very important that new techniques are developed for the utilisation of non-fermentable biomass fractions, such as lignin, for energy production (Supercritical Water Gasification) or other product (composites) applications. For the designed 2-stage bioprocess, the volumetric H_2 productivity in the thermophilic fermentation step must be increased at least 10-fold in order to meet the production capacity of 425 m^3 H_2 /h. This can be done by conventional methods such as optimisation of culture conditions, biomass retention, or selection of highly productive species or strains from the broad range of available hydrogen producing micro-organisms.

The productivity of the photobiological fermentation step should be increased by at least a factor 15 through optimization of sunlight conversion efficiency. In this case the main improvement has to come from technological improvements of sunlight collection and light transfer systems, and photobioreactor development. The reader is referred to Chapter 5 ‘Photobiological hydrogen production’ for a discussion of these topics. To support the profitable utilisation of the effluent of the thermo-bioreactor, the conversion to methane should be considered here as well. It is obvious that during the night, sunlight is lacking. Instead of storing the effluent, methane production might act as a substitute. When this option turns out favourable, the advantages of a partial photofermentation supplemented with a methane fermentation have to be weighed against a complete replacement of the photofermentation step. This issue needs to be evaluated together with the progress in the field of the application of methane in fuel cells and the utilisation of H_2/CH_4 mixtures as new energy carriers.

At the current stage of development, the estimated investment costs of the bioprocess and, especially, the energy requirement are substantial. This is mostly due to the fact that this bioprocess has been the first designed hydrogen from biomass process. Several components in the design have already been abandoned to improve process technology and reduce energy consumption. Also, the utilisation of the residual biomass has not been considered thusfar. It has become clear that application of the residue for energy production will significantly contribute to a sound energy balance. Furthermore, the biomass pretreatment, the two consecutive fermentations, and the H_2 recovery have been considered separately. It is expected that process integration of the separate units will enable substantial reduction of both the investment costs and the energy consumption. Finally, other products from the bioprocess such as new, thermostable proteins from the dark fermentation, new secondary metabolites (including vitamins) from the photobiological fermentation, and even clean carbon dioxide produced on site, may find their own application and thus contribute to making the bioprocess even more economically viable.

5.9. References

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6

Photobiological hydrogen production: Photochemical efficiency and bioreactor design

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Abstract

Photobiological production of hydrogen can be performed by photoautotrophic and photoheterotrophic microorganisms. In this chapter the photosystems of both processes are described.

In photoautotrophic hydrogen production solar energy captured by the photosystem is used to produce hydrogen and oxygen from water (biophotolysis of water). The main drawback of the process is that hydrogen and oxygen are produced simultaneously, which causes oxygen inhibition of the hydrogen producing enzymes. The few efficiencies reported for the conversion of light energy into hydrogen energy are low: less than 1.5 % on a full solar spectrum basis. The efficiency can be increased to 3 - 10% by the immediate removal of the produced oxygen. Alternatives are being developed which prevent oxygen inhibition through temporal or spatial separation of the hydrogen and oxygen evolution stages.

Photoheterotrophic hydrogen production uses captured solar energy and organic compounds as substrates. The maximum photochemical efficiency of photoheterotrophic hydrogen production can be calculated theoretically, and is approximately 10% (on full solar spectrum basis). With use of the theoretical photochemical efficiency and climatic data on sunlight irradiance, the theoretical maximum hydrogen production for a given location can be estimated. The potential hydrogen production on a surface of 1000 hectares in The Netherlands is estimated at 3 PJ per year, which is 10-fold higher than for woody energy crops. Data on H_2 yields and photochemical efficiencies from experiments reported in the literature are summarised. Photochemical efficiencies, mostly based on indoor experiments with the use of artificial light, can reach 10% or even more but only at low light intensities, with associated low H_2 production rates. According to preliminary economic evaluations in the literature photobiohydrogen could potentially be produced at a cost of US $ 10-15/GJ. The development of low cost photobioreactors and the optimisation of photosynthetic efficiency are major R&D challenges. Some reflections on possible photobioreactors lead to two types of (modified) photobioreactors that might be successful for large-scale biological hydrogen production.

6.1 Introduction

Biological hydrogen production from residual organic substrates with phototrophic microorganisms, in connection with wastewater treatment, is a promising option.

Photobiological production of hydrogen can be performed by photoautotrophic or photoheterotrophic organisms. The basic principles are outlined in section 6.2 of this Chapter.

The photosystems of both kinds of microorganisms, which are responsible for the capture and conversion of sunlight energy, are described in section 6.3.

Section 6.4 deals with the photochemical efficiency of photobiological hydrogen production processes. With use of the theoretical photochemical efficiency and the climatological data on sunlight irradiance at a certain location at a certain moment in the year, the theoretical maximum hydrogen production can be estimated. Data on H_2 yields and photochemical efficiency from experiments reported in literature are summarized.

Section 6.5 discusses the development of photobioreactors for large-scale biological hydrogen production. In section 6.6 economic aspects are discussed. The international status of development is highlighted in section 6.7. Conclusions and perspectives for further development are presented in section 6.8.

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6.2 Basic principles of photobiological hydrogen production

Microalgae and cyanobacteria are photoautotrophic organisms because they can use light as the energy source and carbon dioxide as sole carbon source. Some bacteria are termed photoheterotrophic microorganisms because in spite of their ability of using light as the energy source, they need organic carbon as the carbon source.

Photoautotrophic H_2 production

Microalgae and cyanobacteria are able to use sunlight to metabolise carbon dioxide (CO_2) into energy-rich organic compounds $[C_n(H_2O)_n]$, with water (H_2O) as an additional substrate.
Normal photoautotrophic microalgal growth follows route A:

Route A: $CO_2 + H_2O$ + "light energy" =>
$[C_n(H_2O)_n] + O_2$ [Equation 1]

Under anaerobic conditions, microalgae can produce H_2, by water photolysis, using light as the energy source. The catalyst is a hydrogenase, an enzyme that is extremely sensitive to oxygen, a by-product of photosynthesis (route B):

Route B: $4H_2O$ + "light energy" =>
$2O_2 + 4H_2$ ($\Delta G^0 = +1498$ kJ) [Equation 2]

Photoheterotrophic production of H_2

The ability of N_2 fixation by photoheterotrophic bacteria or (heterocystous) cyanobacteria is catalysed by the nitrogenase enzyme. The nitrogenase enzyme also catalyses the evolution of H_2, particularly in the absence of N_2. The overall energy consuming reaction is:

$N_2 + 8H^+ + 8e- + 16ATP$ =>
$2NH_3 + H_2 + 16ADP + 16P_i$ [Equation 3]

The conversion of the organic substrate (acetate in the example below) into hydrogen demands energy, and this is obtained from light.

$C_2H_4O_{2liq} + 2H_2O_{liq}$ + "light energy" =>
$2CO_{2gas} + 4H_{2gas}$($\Delta G^0 = +75.2$ kJ) [Equation 4]

The nitrogenase enzyme is also highly sensitive to oxygen, and inhibited by ammonium ions. This explains why bioreactors must usually operate under anaerobic conditions free of N_2, with illumination and limiting concentrations of nitrogen sources.

6.3 Photosynthesis

6.3.1 The photosystem

Photoautotrophic organisms such as microalgae and cyanobacteria, and photoheterotrophic bacteria, have the capacity to absorb light energy (photons) and to store it as chemical energy via the formation of chemical bonds. The basic unit of the photosynthetic apparatus is the photosystem. In this system, light energy, i.e. photons, is absorbed by carotenoid and chlorophyll pigments of the photosystem antenna complex.

A photosystem consists of an "antenna complex" of tens to hundreds of pigment molecules (cartenoids and chlorophyll a and b in the case of green algae) that absorb light and a "reaction center" consisting of a strongly specialised molecule (P680 in the PS II system in the case of green algea) that transforms light energy into chemical energy.
A light particle (a photon) hits one of the antennae pigments. The pigment gets into an excitated condition and can transfer the excitation energy to the following antenna molecule with a lower excitation energy: the photons fall into a so-called energy hole. The excitation energy is finally used to lift the reaction center into an excitated condition.
In the reaction center, the excitation energy is used to transmit one electron from one chemical compound (donor) towards the other compound (acceptor). In the reaction center actually separation of charge occurs: the excitation energy is stored into an energy-rich chemical bond.
During the transport of the energy from a photon towards the reaction center, some energy loss always occurs (heat loss by excitation transfer). This is the price to be paid for storage of light energy. There is sufficient energy left to induce a charge separation that produces fuel for the cell (energy available for storage). Like other examples in nature, the chemical energy storage by the cells is to satisfy their own biological activity require-

ments; however, this ability of the cells can be exploited for energy production.

6.3.2 The photosystem of green algae; direct biophotolysis

In oxygenic photosynthesis, two photosystems, photosystem I (PS I) and photosystem II (PS II), operate in series. The reaction center of PS II shows the strongest absorption at 680 nm and is called P680. Practically this means that the excitation energy of every photon with a wavelength smaller than 680 nm (i.e. higher energy), absorbed by the antenna pigments, can be transferred to the reaction center.

The PS I reaction center, P700, absorbs most strongly at 700 nm. PS II generates a strong oxidant capable of liberating electrons from water. The reductant delivers the reducing equivalents via a series of electron carriers and the cytochrome b_6f complex to the oxidised reaction center of PS I. The light energy absorbed by PS I is not only used to oxidize the reaction center, but also to produce a strong reductant capable of reducing oxidised nicotinamide adenine dinucleotide phosphate ($NADP^+$) to NADPH.

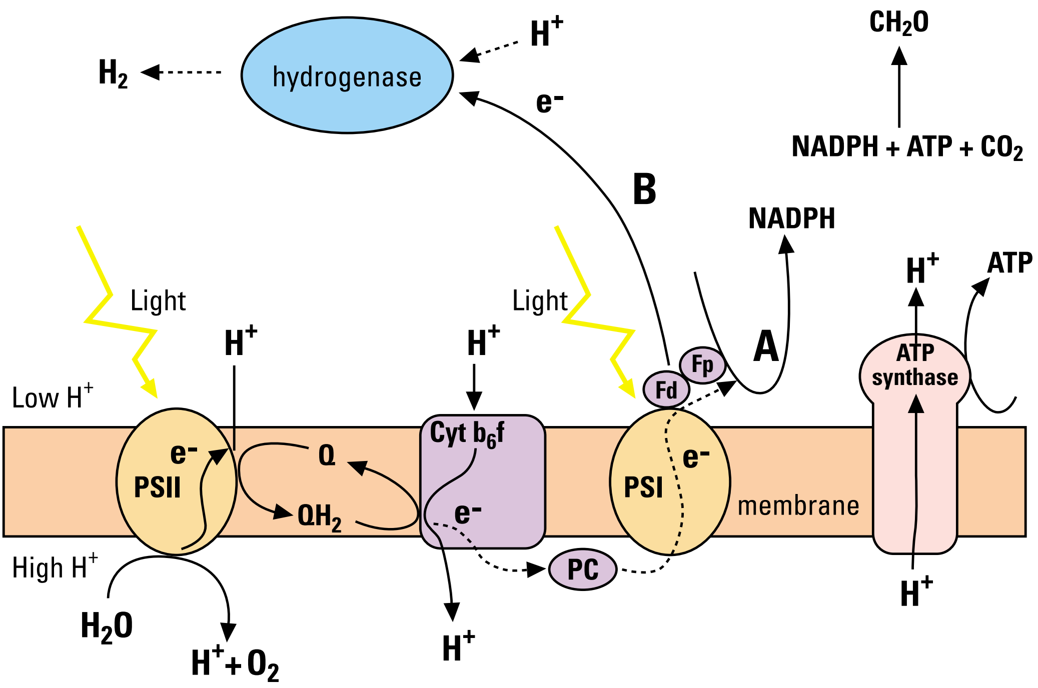

Figure 1. The site of the 'light reactions': the thylakoid membrane, linear electron transport and production of adenosine triphosphate (ATP) via a proton driving force.

In Figure 1, the structure of the photosynthetic machinery is shown in more detail. Both photosystems are inserted in the lipid bi-layer of the so-called thylakoid membranes. The thylakoid membranes enclose an inner space called the lumen. The strong oxidant formed after excitation of the PS II reaction center induces the splitting of water into oxygen, electrons and protons. The protons are left in the lumen. In a continuous process, electrons are used to reduce the reaction center, and, after renewed excitations, they are transported to plastoquinone (PQ). Protons are picked up from the surrounding medium (stroma) producing fully reduced plastoquinone (PQH_2). This membrane-soluble protein diffuses to the cytochrome b_6f complex. Via the cytochrome complex, electrons are transferred to the water-soluble electron carrier plastocyanin (PC). A special mechanism inside this complex allows for additional pumping of protons across the lipid bilayer (Figure 1). Via the lumen, plastocyanin diffuses to PS I, which acts as an oxidant after light-induced excitation. One by one, the electrons released by plastocyanin reduce the reaction center, and, after renewed light-induced excitations, they are transported to the electron carrier ferredoxin (Fd). Finally, NADP⁺ is reduced to NADPH via the action of ferredoxin-NADP reductase (Fp). The proton gradient across the thylakoid membrane drives adenosine triphosphate (ATP) production via the action of ATP synthase

In eukaryotic microalgae, the thylakoid membranes are found in the chloroplast. In prokaryotic cyanobacteria, the site of photosynthesis is the plasma membrane or membranes derived from it. The energy and reducing power derived as ATP and NADPH is used to fix carbon dioxide via the action of ribulose-biphosphate carboxylase (Rubisco) in the Calvin cycle. The carbon reduction reactions take place in the aqueous region of the chloroplast, the stroma, or in the cytoplasma (cyanobacteria). The product of the Calvin cycle is phosphoglyceraldehyde (triose P) and this is the building block for synthesis of fats, fatty acids, amino acids and carboxylic acids. In addition, triose P is the starting point for synthesis of hexose P, followed by carbohydrate synthesis. Carbohydrates (e.g. starch) are stored and used later as energy source (respiration) and building blocks.

Route A: During normal oxygenic photosynthesis (green algae, but also cyanobacteria or blue-green algae and higher plants) the electrons of the ferrodoxin are transposed to the chemical compound NADP⁺. NADPH and ATP are now used to fix carbon dioxide (CO_2) as carbohydrates [$C_n(H_2O)_n$].

Route B: Under special conditions (anaerobic, very low P_{H2}, light), the electrons that are placed on the ferrodoxin can be used to reduce protons to hydrogen (H_2). This reaction is catalysed by the hydrogenase enzyme and does not require any extra energy in the form of ATP. This mechanism can be considered as the photobiological electrolysis of water. The hydrogenase enzyme, however, is extremely sensitive to oxygen.

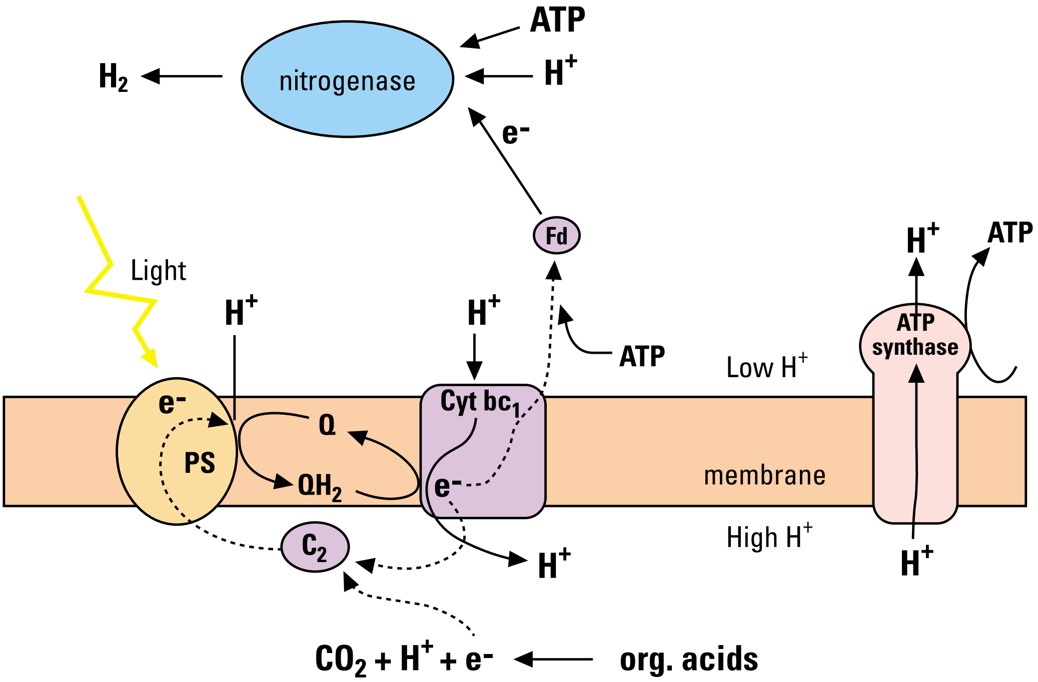

Figure 2. Photofermentation by purple bacteria.

6.3.3 The photosystem of purple bacteria; photofermentation

The photosynthetic device of purple bacteria is simpler, it consists of only one photosystem (PS), Figure 2. This photosystem is also fixed in the intracellular membrane. The photosystem itself is not powerful enough to split water. Under anaerobic circumstances, however, these bacteria are able to use simple organic acids, like acetic acid, or even dihydrogensulfide as electron donor.

The electrons that are liberated from the organic carbon (for example acetate) or H_2S are pumped around through a large number of electron carriers (amongst which are Q and C_2). During the electron transport, protons are pumped through the membrane (*e.g.* in the cytochrome bc_1 protein complex). A proton gradient is developed (high and low H^+), and the ATP synthase enzyme uses this to generate ATP. The extra energy in the form of ATP can be used to transport the electrons further to the electron acceptor ferredoxin (Fd). Under nitrogen-limited circumstances, these electrons can be used, using extra "ATP energy", by the nitrogenase enzyme, to reduce molecular nitrogen into ammonium.

When molecular nitrogen is not present, this enzyme can, again with the help of extra energy in the form of ATP, reduce protons into hydrogen gas (H_2), with the electrons derived from the ferredoxin (Fd). It has been shown that, in this way, many organic acids can be transformed into hydrogen gas (H_2) and carbon dioxide (CO_2).

The nitrogenase enzyme is also sensitive to oxygen (O_2). In this case, it is no problem because no oxygen is produced during the process (anoxygenic photosynthesis).

6.3.4 Comparison of the photoautotrophic and the photoheterotrophic process

The photoautotrophic process is very attractive because it produces energy (H_2) out of cheap and generally available sources, namely water and sunlight, and with no CO_2 produced.

The most important problem connected to the photoautotrophic production is the fact that the enzymes that produce hydrogen (hydrogenases) are strongly inhibited by oxygen, while during the hydrogen production process oxygen is simultaneously produced.

Several studies concentrate on ways to overcome this problem [1,2]. In the future, genetic engineering might produce modified strains with increased O_2 tolerances [3,4].

Increased gas transfer could reduce the O_2 tensions, but this requires quite a high degassing velocity, that it is not feasible practically. Regenerable oxygen absorbers have been used, but are considered impractical for scale-up. Irreversible oxygen absorbers can be used, like carbohydrates or other organic substrates, for respiration. When this substrate would have to be produced in the same process (for instance by the algae), it would reduce the overall solar efficiency by half because as many photons are needed for its production, as for H_2 production.

So far no direct biophotolysis process has advanced beyond laboratory experimentation [1]. Apart from this, the process would produce a mixture of H_2 and O_2, which requires careful handling and separation.

Alternative processes, are the ones in which the photosynthetic water splitting and the H_2 evolving reactions are separated in either time or place, the so called indirect photobiolysis process. In this case, the O_2 inhibition is no longer a problem. The heterocystous cyanobacteria are an example of this system. Heterocysts are specialised cells in which the nitrogenase is protected from O_2 inhibition, and that are provided with substrates from the vegetative cells. Solar conversion efficiencies are generally low (0.2-0.3% outdoors) [1].

In another type of process [5,6,7] the green alga ***Chlamydomonas reinhardtii*** is alternated from a phase of photosynthetic O_2 evolution and carbon accumulation to a phase of H_2 production and consumption of metabolites. The latter phase is enforced by sulphur (S) deprivation. There is much discussion on whether this is truly a separation of the two reactions, or that the stress situation in which the culture is put by S deprivation causes all the O_2 produced to be consumed for energy production. In the U.S.A. researcher A. Melis has started a company working with the this process, but is not producing hydrogen on a commercial scale yet [8].

The nitrogenase enzyme that is used by the photoheterotrophic microorganisms and the heterocystous cells of cyanobacteria to produce H_2, is also sensitive to oxygen (O_2). In this case, it is not a problem because no oxygen is produced during the process (anoxygenic photosynthesis). Another advantage is that the hydrogen production continues while the fermentation liquid is supersaturated with hydrogen gas (H_2). A disadvantage of the process is, that the nitrogenase enzyme requires extra energy in the form of ATP. This reduces the photochemical efficiency if the ATP has to be derived from light energy.

The efficiency of transforming, for instance, a waste into accessible substrate and again into hydrogen, has to be taken into account, or, alternatively, the energy requirement for growing energy-crops.

H_2 production from organic substrates would be bioenergetically more favourable than from water. However, photochemical efficiencies are low [1]. The reason for this would be that these bacteria saturate at even lower light intensities than microalgae. The photoheterotrophic bacteria can use a wider part of the solar spectrum (higher wavelengths), but with associated lower energies.

The features, disadvantages and advantages of the photoautotrophic and the photoheterotrophic H_2 production process are summarized in Table 1.

6.4 Photochemical efficiency

Three important variables are used to evaluate the photobiological hydrogen production process: the efficiency with which light energy is used to produce energy in the form of hydrogen, the so-called photochemical efficiency (PE), the hydrogen production yield, and the yield coefficient of hydrogen produced relative to the carbon source consumed. Because we assume that the carbon source will be organic waste, and because the hydrogen yield is related to the PE, we concentrate here on the photochemical efficiency. The

TABLE 1. *Comparison of the photoautotrophic and photoheterotrophic H_2 production process*

	Photoautotrophic H_2 production: biophotolysis of water		Photoheterotrophic H_2 production: photofermentation of organic acids
Reaction	$4H_2O_{liq}$ + "light energy" => $2O_{2\,gas} + 4H_{2\,gas}$		$C_2H_4O_{2liq}$[1] + 2 H_2O_{liq} + "light energy" => 2 $CO_{2\,gas}$ + 4 $H_{2\,gas}$
	Direct biophotolysis	Indirect biophotolysis[2]	
Enzyme	hydrogenase	hydrogenase	nitrogenase
ATP requirement for enzymatic reaction	no	no	yes
O_2 inhibition	yes	yes	yes
O_2 evolution during H_2 production phase	yes	no[2]	no
Substrate	water	overall: water[2]	organic substrates, usually organic acids such as acetate.
Net CO_2 production	no	no[2]	yes; from organic substrates[3]
Product gas composition	$H_2 + O_2$	$H_2 + CO_2$	$H_2 + CO_2$

1) acetic acid, as example.

2) indirect biophotolysis involves temporal or spatial separation of the photosynthetic O_2 evolution and anaerobic H_2 production stages, thus preventing O_2 inhibition. The process steps are coupled through CO_2 fixation/evolution. In the **first stage CO2 is fixed and stored as carbohydrates through photosynthesis; the carbohydrates are fermented to** H_2 and CO_2 in the anaerobic H_2 production stage.

3) since the CO_2 ultimately derives from biomass, there is no net CO_2 emission to the atmosphere, apart from the CO_2 emitted as a consequence of energy use for producing the original biomass.

definition we use in this chapter is:

$$\text{efficiency (\%)} = \frac{H_2 \text{ production rate x } H_2 \text{ energy content}}{\text{absorbed light energy per unit time}} \qquad \text{[Equation 5]}$$

For the energy calculations in this chapter we will use the upper combustion value (or gross calorific value) of 0.29 MJ/mole H_2.

6.4.1 Yields and photochemical efficiencies of photoautotrophic microorganisms

There are few data on experimentally determined photochemical efficiencies for photoautotrophic hydrogen production. Data found by Greenbaum [9] are presented in Table 2. The efficiencies are based on PAR (Photosynthetic Active Radiation). This means that based on the total solar spectrum they would be 0.43 times the value. (See section 4.2 on theoretical photochemical efficiency). They would thus vary from 3 to 10%. The efficiencies were calculated for a period of illumination after a dark period. However, it is important to observe that the oxygen produced in the reactor is immediately replaced by the helium gas, in a construction that does not seem very feasible for scale-up. A conversion efficiency was estimated for the cyanobacterium *Synechococcus* sp. Miami BG043511 of 3.5% based on PAR [10], which would be around 1.5% based on a total solar energy basis. In contrast, the photochemical efficiency

TABLE 2. *Energy conversion efficiencies of green algae for hydrogen production [9].*
The efficiency is calculated as in equation 5, but with the lower combustion value for H_2 *(0.23 MJ/mole).*
This results in 15 % lower efficiencies.

Alga	**Absorbed light**	**Light on**	**H_2**	**Efficiency (PAR)**
	µW/cm²	*no.**	*nmol/h*	*%‡*
Scenedesmus D_3	5.1	1	126	16
		2	181	23
C. reinhardtii (sup)	2.2	1	44	13
		2	54	16
		3	61	18
		4	64	19
		5	71	21
		6	71	21
		7	61	18
C. reinhardtii (UTEX 90)	8.4	1	78	6
		2	104	8
		3	104	8
C. moewusii	9.1	1	337	24
		2	309	22
		3	253	18

*The entries in this column correspond to the ordinal number of successive periods of illumination. The light was on for either a 3- or 4-h period, after an equal period of darkness.

‡ Conversion efficiency based on absorbed photosynthetically active radiation (PAR). Based on repeated measurements and calibrations, it is estimated that the experimental error in these measurements is, at most, ± 15%. The efficiencies were computed for the rates of hydrogen evolution at the end of the period of illumination when the algae were in a steady (or nearly steady) state.

for *A. cylindrica* for outdoor hydrogen production was 0.2% [11].

Photochemical efficiencies for photoautotrophic hydrogen production are only 3-10%, when the oxygen is totally and immediately removed. In other processes it is about 1-2%. As long as ways to overcome the oxygen inhibition have not been found, the photoautotrophic process is impractical for application in research dedicated to photobioreactor design and process optimisation studies. When solutions to the oxygen inhibition might be found in the future, many outcomes of the research would be also applicable for the photoautotrophic process. Therefore we continue to focus on the photoheterotrophic process only.

6.4.2 Theoretical photochemical efficiency of photoheterotrophic bacteria

With the help of data (if available) on quantum yields (number of moles of light photons needed to produce 1 mole of hydrogen), one can calculate the theoretical photochemical efficiency (PE): the efficiency with which light energy is needed to produce H_2 energy. With the help of data on solar irradiance, the maximal hydrogen production/m^2 at a certain geographical location can be estimated. As discussed above, we choose to do this for photoheterotrophic bacteria. Similar calculations of photochemical efficiencies could be made for photoautotrophic organisms. However, in this case there is more uncertainty concerning the value of the basic data needed. Moreover, the theoretical photochemical efficiency is of limited meaning, because, in practice, oxygen inhibition occurs. Experimental data on photochemical efficiencies, however, if applicable, can be used to estimate maximal hydrogen production rates in a similar way as described below.

The photosynthetic efficiency (PE) is defined as energy stored as biomass produced per unit of light energy absorbed. The light energy absorbed can be based on the PAR range, the Photosynthetically Active Radiation (400 to 700 nm for green algae, and 400-950 nm for purple bacteria) or on the full solar irradiance (all wavelengths). Biomass yield (as protein or dry weight) on light energy can be used as a measure for efficiency. Because the intended product is energy (in the form of H_2) and the limiting factor is light, the efficiency is best expressed on the basis of the energy produced per unit of light energy absorbed.

The efficiency by which the light energy (of, for instance, the sun) can be transformed into hydrogen gas energy, is dependent on the part of the energy that is absorbed by the antenna system of the organism, the energy loss during the several steps of excitation and electron transfers that follow. This efficiency can be calculated as described below.

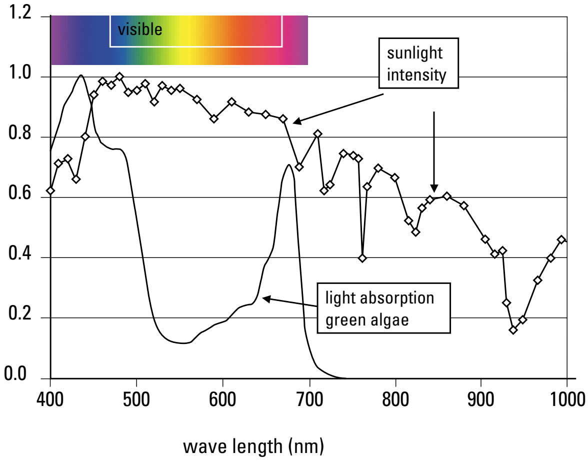

Figure 3. Sunlight and light absorption by green algae

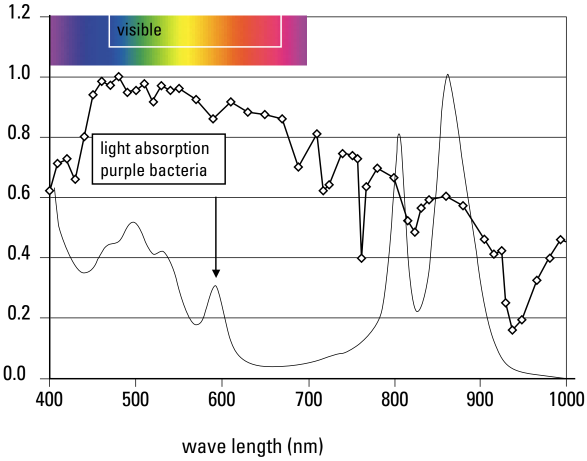

Figure 4. Sunlight and light absorption by purple bacteria

Figure 3 shows the light absorption spectrum of green algae (solid line) compared to the sunlight spectrum (dotted line). The X-axis represents the wavelength, with the visible part indicated by the shaded bar, and the relative light intensity shown on the Y-axis. Part of the sunlight energy from the spectrum is not absorbed by the green algae. For this reason, the efficiency of transformation of sunlight energy into hydrogen energy can never be 100%.

Figure 4 shows the light absorption spectrum of purple bacteria (solid line) compared to the sunlight (dotted line) spectrum. The X-axis represents the wavelength, with the visible part indicated by the shaded bar, and the relative light intensity shown on the Y-axis. Again the efficiency of light absorption is not 100%.

It is important to note that these photoheterotrophic organisms also absorb light energy from the non-visible part of the spectrum.

In Figure 5 the energy content of 1 mole of photons at two wavelengths (522 and 860 nm, location of the absorption peaks of purple non-sulphur bacteria) is calculated. Göbel [12] determined the number of photons required to produce one ATP in photophosphorylation of ***Rhodopseudomonas species***, as 1.5 photons per ATP, at 860 nm. Miyake [13] estimated from this that the total reaction (4 ATP) and electron elevations required 11 photons per molecule H_2 at 860 nm. Analogous calculations (by ourselves) show that 14 - 15.8 photons are required per molecule H_2 at 522 nm. The energy of 1 mole of photons depends on the wavelength, and is 0.229 MJ and

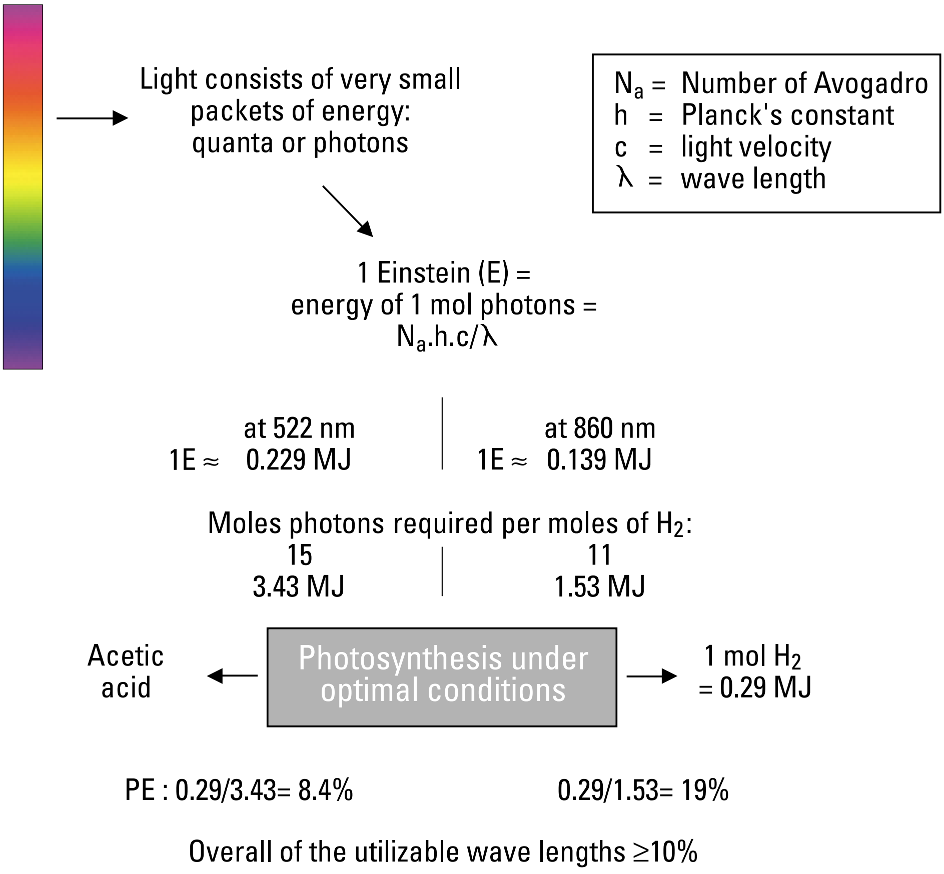

Figure 5. Photochemical efficiency of purple bacteria

0.139 MJ at 522 and 860 nm respectively.

The photofermentation efficiency (PE) can be calculated as the ratio between energy gained in the form of hydrogen gas, and the energy needed in the form of photons. The energy content of 1 mole of hydrogen is 0.29 MJ (upper combustion value). Therefore the PE is 8.4% and 19% at 522 nm and 860 nm wavelength respectively (Figure 5). The quantum yield at other wavelengths of the absorption spectrum is not known. However data on quantum yields of other organisms have shown that the quantum yield is only little lower at wavelengths other than the absorption maximums. So the PE will accordingly be somewhat lower at other near-by wavelengths of the absorption spectrum. The overall PE over the whole of utilisable wavelengths of the absorption spectrum of the purple bacteria, is therefore, considering the relation with wavelength, estimated to be at least 10%. It should be noted that the energy content of the substrate and the energy fixed inside the biomass are neglected in the calculations. It is assumed that all energy required for the reaction and electron transport is derived from the light energy, and that the production of the substrate (requiring energy) is done elsewhere (for instance by making use of waste products).

6.4.3 Maximum hydrogen production with sunlight as light source

Sunlight is the ultimate energy source for microalgae. In Figure 6 the relative light intensity of sunlight at ground level (data from [14] is shown).

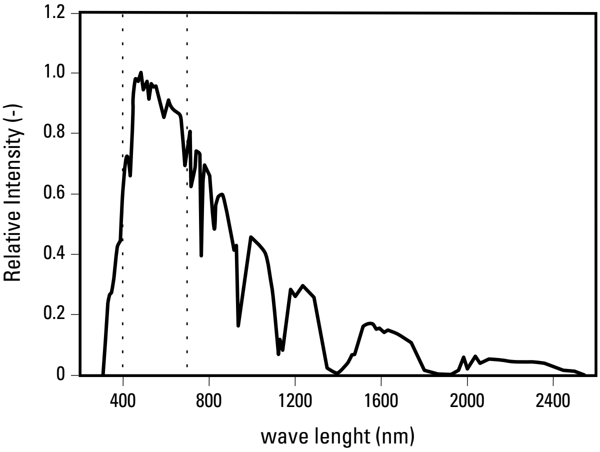

Figure 6. Relative intensity on energy basis of sunlight at ground level [14].

Although the wavelength range of solar radiation is very broad, only radiation between 400 and 700 nm can be used by microalgae (Figure 3). This part of the solar spectrum is called 'Photosynthetic Active Radiation' (PAR) and is enclosed with dotted lines (Figure 3). On an energy basis, 43% of the solar radiation is in the PAR region [15].

For purple bacteria this PAR region is 400-950 nm (Figure 4). On an energy basis 65.8% of the solar radiation is in this PAR region (own calculations based on Figure 6 data).

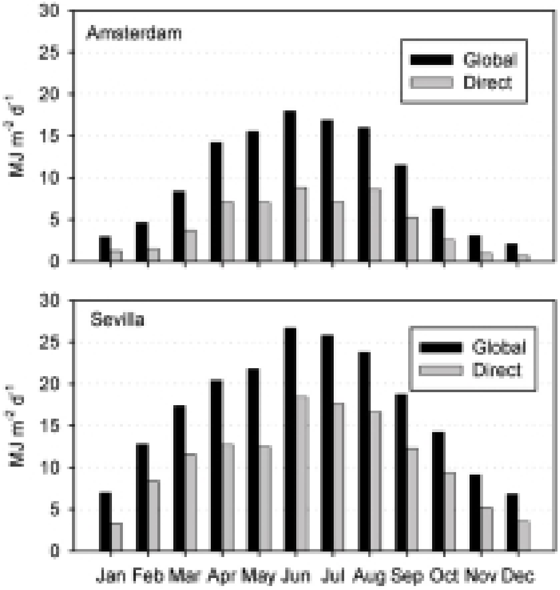

Figure 7. Horizontal global and direct daily irradiance on ground level in: Amsterdam 52°21'N and Sevilla 37°22'N in 1996 and 1997 according to The European Database of Daylight and Solar Radiation [16].

The magnitude of solar radiation is dependent on the geographical position on Earth and the climatic conditions at that position. As an illustration the irradiance [16] on a horizontal surface at two different geographical locations, Amsterdam and Sevilla is shown in Figure 7. Global irradiance is the sum of the direct beam irradiance and the diffuse irradiance. The diffuse irradiance is caused by the scattering of light by small aerosols in the atmosphere and water droplets (clouds). In June, the monthly average global irradiance in Amsterdam is 18.0 MJ m^{-2} d^{-1}, which is 68% of that in Sevilla, 26.6 MJ m^{-2} d^{-1}. In Sevilla much more than half of the global radiation (69% in June) reaches ground level as direct beams. In Amsterdam this is less than half (49% in June) because of more days with overcast skies.

In Figure 8 the maximal H_2 production is calculated on the basis of the different sunlight intensities at two different locations (Amsterdam and Sevilla). The maximal intensity in July of 25.78 MJ m^{-2} d^{-1} in Sevilla, corresponds with 257.8 GJ ha^{-1} d^{-1}. Given the fact that only a part, 65.8% of this light is in the 400-950 nm region, and the theoretical photochemical efficiency is 10%, the yield is 0.12 t H_2 $ha^{-1}d^{-1}$. For Amsterdam, in July, this would be 0.078 t H_2 $ha^{-1}d^{-1}$ (corresponding with 850 Nm^3 H_2 $ha^{-1}d^{-1}$).

6.4.4 Yields and efficiencies of photoheterotrophic bacteria in practice

The performance of photosynthetic bacteria with respect to biological hydrogen production must be evaluated on the basis of several parameters. One of them is the yield coefficient of H_2 produced relative to the carbon source consumed. Another important parameter is the efficiency of light conversion, taking into account the H_2 production rate and the H_2 energy content, as well as the absorbed light. Although sunlight is cheap (in outdoor experiments), the costs of large areas to capture sufficient light can be very high. Both yield coefficients and light efficiencies are not very abundant in the literature.

A search in recent literature enabled us to select the papers from which it was possible to get enough information to calculate the values of those parameters. The calculated values of yields and efficiencies were compared to the ones presented by the authors, when available, which also allowed us to validate our calculations, and these are shown in Table 3. The complete table, including data on reactor type, operations, and medium was published in [17], accompanied by a detailed evaluation of all calculations, assumptions and quality of available data.

The lab-scale experiments reported in Table 3 involved photofermentation with phototrophic bacteria in artificial culture media, with malate or lactate. References to complex media, such as residual wastewater, were not included.

The hydrogen yield, as the number of moles of H_2 produced per mole of carbon source consumed, or as a percentage of the maximum value theoretically possible is not very often shown by the authors. Although we can only talk about yields when related to well defined carbon sources, which are not the most important ones from a practical point of view, it seems that high yields can be achieved and this thus will not be a bottleneck in H_2 production.

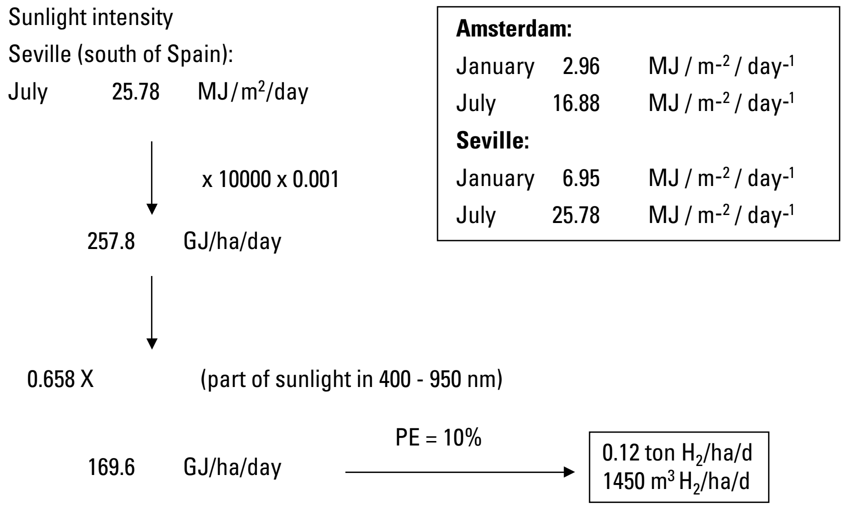

Figure 8. Comparison of H_2 production at locations with different solar irradiance (Amsterdam and Sevilla as examples).

TABLE 3. *Hydrogen production rate, yields and efficiencies of photoheterotrophic bacteria (S: carbon source).*

Strain	I_{energy}	H_2 (ml ml$^{-1}_{cult}$ h^{-1})$^{(1)}$	Yield (H_2/S)(%)	Efficiency of light (%)$^{\#}$	Ref.
Rhodobacter sphaeroides RV	155 W m^{-2}	0.131	56$^{(b)}$	2.7$^{(b)}$	[18]
Rhodobacter sphaeroides RV$^{(2)}$	65 W m^{-2} (850 nm)	0.054 (0.6 mmol m^{-3}s^{-1})		3.7$^{(b)}$	[19]
Rhodobacter sphaeroides S	10 klux (35 W m^{-2})	0.019	38$^{(b)}$	8.7$^{(b)}$	[20]
		0.013$^{(3)}$	28$^{(b)}$	5.9$^{(b)}$	
		0.004$^{(4)}$	8$^{(b)}$	1.9$^{(b)}$	
		0.011$^{(5)}$		4.8$^{(b)}$	
Rhodobacter sphaeroides O.U. 001 *(DSM 5648)*	200 W m^{-2}	0.020$^{(6)}$	-	1.1$^{(b)}$	[21]
	"	0.002$^{(7)}$	12$^{(b)}$	0.1$^{(b)}$	
	"	0.004$^{(8)}$	27$^{(b)}$	0.2$^{(b)}$	
Rhodobacter sphaeroides O.U. 001	200 W m^{-2}	0.006	-	0.2$^{(b)}$	[22]
Rhodobacter sphaeroides RV	5000 lux (45 W m^{-2})	0.107	43$^{(b)}$	11.3$^{(b)}$	[23]
Rhodopseudomonas sp.	10000 lux		75$^{(a)}$ -67$^{(b)}$	(3.4$^{(c)}$/1.9$^{(d)}$)$^{(b)(*)}$	[24]
Rhodospirillum Rubrum	300 W m^{-2}	0.065	65$^{(b)}$	2.8$^{(b)}$	[25]
MO006 *Rhodospirillaceae (?)*	10000 lux	11.6 ml h^{-1} (highest rate)	≈ 80$^{(b)}$	(5.1$^{(c)}$/2.8$^{(d)}$)$^{(b)(*)}$	[26]
Rhodovulum sp. NKPB160471R(marine)	1800 W m^{-2}	27 μmol ml^{-1} h^{-1}		2$^{(a)}$-2.1$^{(b)}$	[27]
	13 W m^{-2}	2.4 μmol ml^{-1} h^{-1}		26$^{(a)(b)}$	
and its H-l uptake H_2-ase mutant	1800 W m^{-2}	34 μmol ml^{-1} h^{-1}		3$^{(a)\ -2}$.7$^{(b)}$	
	13 W m^{-2}	3.2 μmol ml^{-1} h^{-1}		35$^{(a)(b)}$	
Rhodobacter sphaeroides RV	720 W m^{-2}(1st)	0.235 (1st)$^{(9)}$	13$^{(b)}$	0.9$^{(a)(b)}$(1st)	[28,29]
	223 W m^{-2}(2nd)	0.210 (2nd)	11$^{(b)}$	2.5$^{(a)}$-2.6$^{(b)}$(2nd)	
	72 W m^{-2} (3rd)	0.090 (3rd)	5$^{(b)}$	3.3$^{(a)}$-3.4$^{(b)}$(3rd)	
	22 Wm^{-2}(4th)	0.025 (4th)	1$^{(b)}$	3.2$^{(a)}$-3.1$^{(b)}$(4th)	

TABLE 3. (continued) *Hydrogen production rate, yields and efficiencies of photoheterotrophic bacteria (S: carbon source).*

Strain	I_{energy}	H_2 (ml ml^{-1}_{cult} h^{-1})(1)	Yield (H_2/S)(%)	Efficiency of light (%)#	Ref.
Rhodopseudomonas palustris R-1	434 W m^{-2}		- (10) 0.5(a) (12)	0.3(a)(b) (11)	[30]
Rhodobacter sphaeroides RV	Max 1 kW m^{-2} Integral: (13) (14) 6- 7 kWh m^{-2}		12(b)	2.2(a) -(2- 2.4) (b)	
	Max 1 kW m^{-2} Integral: (14) (15) 7 kWh m^{-2}		7(b)	1.1(a) -1.3(b)	[31]
Rhodobacter sphaeroides RV	330 W m^{-2}	75 μmol ml^{-1}	42(a) (b)	0.4(b) (*)	[32]
Rhodobacter capsulatus ST410	6600 lux (66 W m^{-2})	0.1(16)	73(a) (b)	4.8(b) (*)	[33]
		2.5 ml ml^{-1} (17)	84(a) –83(b)		
Rhodobacter sphaeroides RV	3000 lux	1.4- 1.6 (3) (11^{-1} d^{-1})	(50- 70)(a) -7(b)	(2.5(c) /1.4(d))(b)(*)	[34]
Rhodospirillum Rubrum	10000 lux	0.048 (3)	10(b)	(4.0(c) /2.2(d))(b)(*)	[35]
Rhodospirillum Rubrum	400 W m^{-2}	0.18	80(b)	4.4(b)	[36]
Rhodobacter Sphaeroides	50 W m^{-2}	1.45 l $m^{-2}h^{-1}$		7.9(a)-9.3(b)	[37]
	1000 W m^{-2}	7.9 1 m^{-2} h^{-1}		2.1(a) -2.5(b)	
Rhodobacter sphaeroides O.U. 001	4000 lux	0.014	7(b)	(1.1(c) /0.6(d))(b)(*)	[38]
Rhodobacter marinus	135 μE $m^{-2}s^{-1}$			(18)	[39]
Rhodobacter sphaeroides RV	300 Wm^{-2}	7812 (ml m^{-2} h^{-1})	(62-73)(a)-47(b)	9.2(a)(19)-8.3(b)	[40,41]
Rhodobacter Capsulatus	250 W m^{-2}	0.080 (3)	30(a) –28(b)	1.3(b)	[42]

Annotations to Table 3:

- (a) given by authors;
- (b) calculated by ourselves;
- (c) 100 lux = 1 Wm^{-2}, according to Ooshima et al. (1998), ref [33];
- (d) 55.5 lux = 1 Wm^{-2}, according to Nakada et al. (1996), ref [43];
- (*) values calculated for efficiencies are not very accurate because (i) lux and different conversions to Wm^{-2} can be used, according to the kind of light source and sensor used, or (ii) the irradiation area was roughly estimated.

Comments to Table 3:

- # efficiency is calculated according to equation 5
- (1) this is the default unit for hydrogen production rate, when other is not indicated;
- (2) mutant P3, UV irradiation;
- (3) nitrogen source was ammonium salt;
- (4) carbon source was acetate;
- (5) carbon source was a mixture of acetate and propionate;
- (6) semi-continuous, L-malic acid 7.5 mM, sodium glutamate 10 mM;
- (7) batch, L-malic acid 7.5 mM, sodium glutamate 10 mM;
- (8) batch, L-malic acid 30 mM, sodium glutamate 2 mM;
- (9) a batch photobioreactor with 4 flat compartments, see text;
- (10) carbon source was a mixture of acetate, propionate, butyrate and ethanol;
- (11) efficiency of light conversion to H_2 for the long-term (66 days);
- (12) efficiency of light conversion to H_2 in the latter stage (8 days);
- (13) sun light;
- (14) light irradiation over a period of 12 h expressed in an integral way, by energy per unit of area;
- (15) halogen lamps;
- (16) with DL-malate 30 mM;
- (17) with acetate 30 mM;
- (18) the use of cells immobilised onto light-diffusing optical fibres did not enable the calculation of illuminated area and, consequently, the light efficiency;
- (19) highest value.

The light efficiency is also not often referred to by authors, first because there is more than one definition and second because it is not easy to present a value with certainty. All the values of light efficiency presented in Table 3 (which includes all the references we found with the necessary parameters available), both directly from literature and calculated by ourselves, were obtained using the same expression (eq. 5 from paragraph 4):
efficiency (%) = H_2 production rate x H_2 energy content / absorbed light energy per unit time

Although this definition of light efficiency is the most generally accepted one, each term of the equation can have associated errors:

- (i) H_2 production rate, as a productivity, is correct for continuous cultures but in batch cultures is a function of time;
- (ii) H_2 energy content, as combustion enthalpy of H_2, can be expressed as a net or gross calorific value (resp. 10.8 J ml^{-1}, and 12.7 J ml^{-1} at 0 °C and 1 atm). The efficiencies in our overview (Table 3) are calculated using the gross combustion enthalpy.
- (iii) the absorbed light energy has not been used, but the measured light intensity (per time unit) instead.

The energy content of the organic substrate and of the biomass is neglected in the calculations.

Our calculations of light efficiency could reproduce the values presented by the authors in most cases, and some differences could be attributed to differences in calculation [17]. Reasonable efficiencies were obtained at low light intensities (7-9% at 50 W m^{-2}, and 26-35% at 13 W m^{-2}) but the associated H_2 production rates were too low to be interesting from a practical point of view. The main bottleneck of biological hydrogen production seems not to be the H_2 yield itself but light efficiency. This will determine the costs of photobioreactors and their operation.

The calculation of the theoretical photochemical efficiency was made for sunlight as light source. Only one of experiments referred in Table 3 was done with sunlight as light source, all others used artificial light sources.
If the assumption can be made that the number of photons needed to produce 1 mole of hydrogen, does not depend very much on the wavelength (in the utilizable spectrum of wavelengths) and it is assumed that all available light is absorbed in the bioreactor, the efficiencies found in Table 3 (with different kinds of artificial light) can be compared to the theoretical efficiency as calculated above (approximately 10 % or more).
Efficiencies of about 10% or higher are reported in the previously presented Table 2, but as mentioned before, mostly at the lower light intensities, with generally associated lower H_2 production rates.

6.4.5 Energy potential

Based on our calculations, an indication of the energy potential of photoheterotrophic H_2 production can be obtained. The maximum yield that we calculated for the month of June in Amsterdam was 0.078 tonnes of H_2 ha^{-1} day^{-1}or 11.1 GJ ha^{-1} day^{-1}. Assuming an average sunlight intensity of 75% of the maximum value over the year, a photobioreactorsystem with a surface of 1,000 hectares would yield an amount of 21,300 tonnes of H_2 or 3 PJ per year (1 PJ= 10^{15} J). For a 1,000 ha system in Seville, assuming an average light intensity of 75% of July irradiance, the energy production would amount to 4.6 PJ per year, and in the desert of Australia (with 75% of November sunlight intensity) to 5.3 PJ per year. These estimates are comparable to projections in the literature (recalculated to a 1,000 ha system surface) of 5.8 PJ/year for an indirect microalgal biophotolysis system [44] and 7.3 PJ/ year for a direct algal biophotolysis system [45]. All estimates –including our own– are based on favourable assumptions with regard to light conversion efficiency and productivity. Considerable R&D is required to realize the potential in practical systems. For comparison, the current total energy consumption in The Netherlands is approx. 3,000 PJ/year (data for 2000; [46]) with an estimated growth to 3,400 PJ in 2020. The Dutch government aims for a share of renewable energy of approx. 10% or 340 PJ/year in 2020 from various sources including wind turbines, photovoltaics and biomass. According to our estimate, to meet 1 % of this target (3.4 PJ) by photobiological hydrogen production would require a total production surface of approx. 1,150 ha, which could be divided over several locations. This compares favourably with the potential primary energy production of energy crops such as *Miscanthus* or short rotation poplar which is on the order of 0.3 PJ/year for a 1000 ha surface. The potential energy yield of photobiological H_2 production per ha is thus 10-fold higher than these alternatives. An additional benefit is that the energy becomes available in the form of clean H_2 (with 10-20 vol% CO_2) which can be transported easily and used directly in fuel cells with high efficiency.

6.5 Photobioreactors

6.5.1 Bioreactor requirements

A reactor for photobiological hydrogen production has to meet several conditions.

Since the hydrogen gas has to be collected, a prerequisite of the photobioreactor is for it to be an enclosed system. It has to be possible to maintain a monoculture for an extended time (it must be practical to sterilize the reactor). Preferably sunlight is the energy source.

The productivity of a photobioreactor is light limited, and a high surface to volume ratio is a prerequisite for a photobioreactor. The photochemical efficiencies are low (theoretically a maximum of 10%, and in laboratory experiments 10% and sometimes more, see above), and tend to decrease at higher light intensities (the effect of light saturation, photons cannot all be used for reaction energy but are dissipated as heat energy). This means that in order to create an efficient biological process, it is important to dilute the light and distribute it as much as possible over the reactor volume, and/or mix the culture at a high rate, so that cells are light exposed only for a short period.

Janssen [47] reviewed three types of photobioreactors: vertical column reactors (air-lift loop reactor and bubble column), flat panel reactors, and tubular reactors. He looked at the light gradients and the mixing- induced light/dark cycles, photosynthetic efficiency (PE), and scalability.

Depending on the reactor type and the way it is operated, cells are exposed for a certain period at the irradiated surface, or in a dark part of the reactor. The (mixing-induced) light/dark cycles, when they are in the range of micro- or milliseconds, can enhance photosynthetic efficiency (PE), approaching the PE at low light intensities. When the cycles have durations of several seconds to tens of seconds, there is no improvement and even a decrease in PE has been reported.

The depth (and volume) of the photic zone depends on the dimensions and operations of the reactor, algal concentration, and the specific absorption coefficient of the algae, (and the wavelength of the incoming light). On the basis of model calculations and/or empirical data, several reactor types were compared. The results (for biomass production of photoautotrophs) are shown in Table 4.

Flat panel reactors show a high photochemical efficiency or biomass yield on light energy, while biomass density is also high.

Tubular reactors in theory should show better efficiencies because of the shorter average light/dark cycles. This is not supported by the data in Table 4, probably due to other factors.

The analysis of typical examples of microalgal cultivations in enclosed (outdoor) photobioreactors showed that the photosynthetic efficiency and productivity is determined by the light regime inside the reactors [47]. In addition, only oxygen accumulation and shear stress limit productivity in certain designs [47].

The comparison of the bioreactors described above referred to processes with microalgae, diatoms or cyanobacteria. Though photoheterotrophic bacteria differ for instance in photochemical efficiency, absorption coefficient and size, the relative difference in performance of the reactor types, might be extrapolated to the case of photoheterotrophic bacteria. The light regime, including mixing induced light/dark cycles, is assumed to be much more determining than biological factors.

TABLE 4. *Enclosed photobioreactors; Photosynthetic efficiency (PE) and biomass yield on light energy (Ydw,E). After [47].*

Photobioreactor type	**PE or Ydw,E** $^{(1)\ (2)}$ **(% or g dw mol^{-1})**	**Reference** **(microorganism)**
Bubble column and air-lift column reactors: - internal draught tube - split cilinder	0.84 ($Y_{dw,E}$) $^{(3)}$	[48] *(Phaeodactylum tricornutum)*
air-lift column	0.82 ($Y_{dw,E}$)	[49] *(Phaeodactylum tricornutum)*
flat panel a) vertical b) tilted	a) 1.48 ($Y_{dw,E}$) ≈ 16 (PE) b) 10 – 20 (PE)	a) [50] b) [51] *(Spirulina platensis)*
tubular reactor	0.60 ($Y_{dw,E}$); 6.5 (PE) $^{(4)}$	[52] *(Spirulina platensis)*
tubular reactor diameter 2.5 cm diameter 5.3 cm	a) 0.48 - 0.63 ($Y_{dw,E}$) $^{(5)}$ b) 0.68 - 0.95 ($Y_{dw,E}$) $^{(5)}$	[53] *(Phaeodactylum tricornutum)*

1. daily irradiance values in MJ m^{-2} d^{-1} were divided by 12 x 3600 s, assuming a day length of 12 h, multiplied with 0.429, the fraction PAR in the solar spectrum [15], and multiplied with 4.57, mol photons MJ^{-1} [15].
2. monthly averages of daily solar irradiance on a vertical cylindrical surface in the same period of the year were obtained from the European Database of Daylight and Solar Radiation, www.satel-light.com [16].
3. based on a linear growth phase with a productivity of about 0.49 g L^{-1} d^{-1} observed in an outdoor batch culture in three different reactor types.
4. before calculating PE and $Y_{dw,e,}$ irradiance data were corrected for transmittivity tubes [52].
5. calculated by Janssen [47].

Considering the findings that flat panel reactors and tubular reactors (at least in theory) show highest efficiencies, it is worthwhile to look further into these two types of reactors, and their possibilities to be scaled up for practical purposes.

6.5.2 Flat panel reactors

Flat panel reactors consist of a rectangular transparent box with a depth of only 1 to 5 cm. The height and width can be varied to some extent, but in practice only panels with a height and width both smaller than 1 m have been studied.

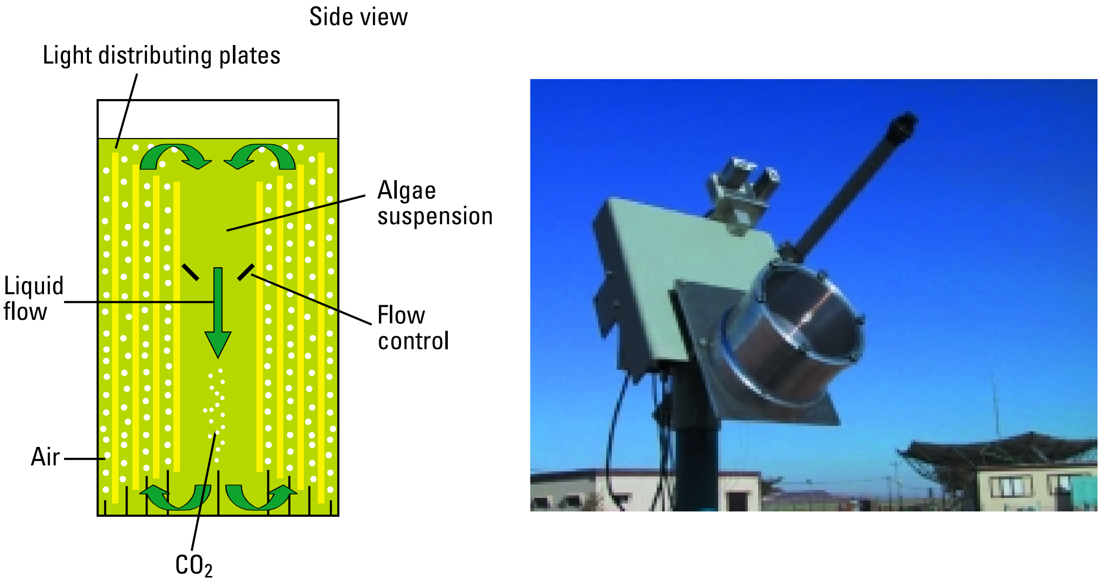

Figure 9. The design of the large-scale flat-plate photobioreactor (left) and prototype of a sunlight collector (right)

The photobioreactors are mixed with gas introduced via a perforated tube at the bottom of the reactor. In order to create a high degree of turbulence, 3 to 4 litre of air per litre of reactor volume per minute has to be provided.
Usually the panels are illuminated from one side by direct sunlight and the panels are placed vertically, or inclined towards the sun. Light/dark cycles are short in these reactors, and this is probably the key factor leading to the high PE.
A disadvantage of these systems is that the power consumption of aeration (or mixing with another gas) is high, although mixing is always necessary in any reactor.

We believe it is very attractive to separate light collection from biological cultivation. Solar beam irradiation in 'clear-sky' areas can be collected and concentrated into optical fibres with lenses or parabolic mirrors. Via the fibres light can be guided into a large-scale photobioreactor. Presently, this is quite a costly solution, but when production costs of lenses, mirrors, solar tracking devices and optical fibres decrease because of increasing scale of demand, this cultivation technique can be generally applicable. The recent innovation of dual-axis tracking solar fiber-optic mini-dish concentrators may contribute to this development [54].

In Figure 9, the design of the large-scale flat-plate photobioreactors suggested by Janssen [47] and by [55] is shown. In addition, a prototype of the sunlight collector is shown that will be connected to the reactor and provide the light energy.
The large-scale flat plate reactor is a rectangular air-lift photobioreactor with a large number of light re-distributing plates fixed a few centimetres from each other. Mixing will be provided by air (or gas) injected between adjacent plates and the culture liquid will rise in between. Only the space between the two most inner plates is not aerated and will act as a downcomer.
Many scaled up versions of photobioreactors in fact consist of a manifold repetition of the smaller photobioreactor units, with its practical implications. Since our scaled up reactor consists of only one unit, it is still practical to sterilize it and only one control unit is needed.

6.5.3 Tubular reactors

Tubular photobioreactors consist of long transparent tubes with diameters ranging from 3 to 6 cm, and lengths ranging from 10 to 100 m. The culture liquid is pumped through these tubes by means of mechanical or air-lift pumps. The tubes can be positioned in many different ways: in a horizontal plane as straight tubes with a small or large number of U-bends; vertical, coiled as a cylinder or a cone; in a vertical plane, positioned in a fence-like structure using U-bends or connected by manifolds; horizontal or inclined, parallel tubes connected by manifolds; in addition, horizontal tubes can be placed on different reflective surfaces with a certain distance between the tubes. Although tubular reactor design is very diverse, the predominant effect of the specific designs on the light regime is a difference in the photon flux density incident on the reactor surface (PFD_{in}). The shape of the light gradient in the tubes is similar in most designs. Also with respect to liquid mixing, i.e. L/D cycling, the circumstances in most designs are similar.

The length of the tubes is limited because of accumulation of gas (demonstrated for oxygen, and probably applicable for hydrogen), though this might not be so important for nitrogenase based processes, since they may be less inhibited by H_2. The way to scale up is to connect a number of tubes via manifolds. This approach was chosen by the Institut Für Getreideverarbeitung GmbH in Germany, in a reactor consisting of 25,000 glass tubes, divided in 20 units of 35 m^3 and in total 12,000 m^2 ground surface. It is used for production of the alga *Chlorella* sp.

6.6 Economics

6.6.1 Biohydrogen production costs

Only a limited number of economic analyses of photobiohydrogen production have been performed. Benemann [44] provided a preliminary cost estimate for a 200 ha indirect microalgal biophotolysis system comprising 140 ha open ponds and 14 ha of photobioreactors. The assumed plant capacity was 280,000 Nm^3 H_2 /day equivalent to 3,600 GJ/day or 1.2 million GJ/yr (at 90% plant capacity). The total capital costs for the system were estimated at US $ 43 million, the annual operating costs at US $ 12 million/year. The total H_2 production costs were estimated at US $ 10/GJ. In this analysis, the capital costs were almost 90 % of total costs at a 25% annual capital charge. The costs of the algal ponds were estimated at US $ 6/m^2. The photobioreactors with assumed costs of US $ 100/m^2 were the major capital and operating cost factors, while the costs of gas handling were a significant cost factor as well.

Tredici et al. [45] performed a preliminary cost analysis for a large scale (>100 ha) single stage algal or cyanobacterial biophotolysis process in a near-horizontal tubular reactor (NHTR) system. The authors state that the presented analysis is initial and highly conceptual and that the main objective was to determine if the proposed photobioreactor design could meet the cost requirements for H_2 production through single stage biophotolysis. The NHTR photobioreactor offers advantageous features for biophotolytic H_2 production due to the internal gas exchange and the possibility for effective water spray cooling The analysis was based on favourable assumptions including 10% solar energy conversion efficiency (PE). The costs of the NHTR were projected at US $ 50/m^2, as a maximum allowable cost target. The analysis did not include costs for gas handling and assumed a relatively low annual capital charge (17%). The capital fixed costs amounted to approx. 80% of total costs, with the tubular material for the NHTR as the largest single cost. The H_2 production costs were estimated at US $ 15/GJ.
The projected H_2 production costs for the photobiological processes discussed above are comparable to the costs projected for H_2 produced in a two-stage biological hydrogen production process from biomass residues, which is discussed in Chapter 5 of this publication. For this system - comprising a thermophilic dark fermentation stage followed by a photoheterotrophic fermentation stage - the H_2 production costs are projected at Euro 19/GJ (see Chapter 5).

The available economic analyses indicate that photobiohydrogen could be produced at a cost of US $ 10-20/GJ. According to [56] this is a reasonable maximal cost target for renewable H_2 fuel. The available estimates are based on favourable assumptions and are highly preliminary and incomplete. They are intended primarily to identify the major cost drivers for photobiological H_2 production and the targets and R&D issues for future development. From the performed analyses it is clear that the development of low cost photobioreactors and the optimisation of photosynthetic efficiency are the major R&D challenges.

6.6.2 Comparison of photobiological hydrogen production to photovoltaics

Although many different designs of photobioreactors have been developed, only few large-scale photobioreactors are in operation today. Currently there is one large-scale closed photobioreactor in use that could be employed for hydrogen production. This reactor was already briefly described in section 3. After long-term investigation by the IGV (Institut für Getreideverarbeitung GmbH, Germany) the German company Preussag initiated the construction of a closed tubular photobioreactor system in Klötze (Germany) of 12,000 m^2 ground surface (1.2 ha) with an investment cost of Euro 8 million. The investments per unit of ground surface are Euro 660/m^{-2}. It should be noted that this photobioreactor design seems too sophisticated for the process of photobiological hydrogen production and there is space for simplification, which could lower the investment costs. We assume that H_2 can be produced in this reactor with an efficiency of at least 7 % (on a full solar spectrum basis) and converted to electricity (at an assumed electrical efficiency of 50%), which would lead to an overall conversion efficiency of sunlight-to-electricity of 3.5 %.

With these data we can compare the photobiological H_2 production system to the 'state-of-the-art' of photovoltaic cells. During the 'Floriade' Exhibition held in 2002 in The Netherlands, a roof of photovoltaic cells was constructed with a surface of 30,000 m^2 (3 ha). This roof is estimated to produce 1.2 million kWh of electricity yr^{-1}. Using average irradiance data for this geographical location (Amsterdam) we calculated a solar conversion efficiency to electricity of 4 %. The investment costs of the solar roof are Euro 17.5 million or Euro 580 m^{-2}. This shows that both the capital costs per m^2 and the overall conversion efficiency (sun light to electricity) are similar for the photobioreactor system and the photovoltaics system. It should be noted that the PV roof is most probably not fully optimised to maximise the capture of sunlight. Comparing these numbers however it seems reasonable to say that the costs of electricity produced through photobiological hydrogen production are on a similar level as photovoltaic electricity production.

6.7 International status

Photobiological hydrogen production has been the subject of basic and applied research for several decades.

In the USA research on photobiological hydrogen production has mainly been focussed on photoautotrophic processes, either direct or indirect photobiolysis, performed by microalgae and cyanobacteria. The R&D on direct biophotolytic processes has thusfar not evolved beyond the laboratory stage. The recent work on temporally separated indirect biophotolysis through S-deprivation can accelerate the development of microalgal biohydrogen production processes. Another promising development in this field is the R&D on microalgal and bacterial mutants with truncated antennae in the USA and Japan. The use of organisms with reduced antenna sizes leads to an enhancement of photosynthetic light conversion efficiency and thus productivity in photobioreactors. In Japan there is more attention for photoheterotrophic processes. The Japanese RITE programme has stimulated research in this field with much attention for research on the involved enzymes.

Only in recent years research on biological hydrogen production has become important in Europe, with a relatively strong focus on photoheterotrophic H_2 production as well as dark fermentations in programs such as the EU Biohydrogen project [57]. Several initiatives for co-operation in both fundamental and applied R&D in the field are being undertaken in the context of the EU 6th Framework Programme (2002 - 2006), in which the development of hydrogen technologies will have a prominent position. On a global scale the IEA co-ordinates international co-operation and knowledge exchange in the field of biological hydrogen production through the IEA Hydrogen Program, Task 15, Photobiological Hydrogen Production, which has recently been extended to

2004 [58]. Current member countries are Japan, Norway, Sweden, the USA, Canada and The Netherlands, while the UK, Hungary, Mexico and Portugal are considering active membership. The objective of Task 15 is to advance the basic and early-stage applied science in photobiohydrogen R&D to allow an evaluation of the potential of the technology.

6.8 Conclusions and perspectives for further development

The few data found on PE of the photoautotrophic hydrogen production support the theory that oxygen inhibition leads to low PE's of only a few %. The theoretical photochemical efficiency of the photoheterotrophic process is low, 10%, the efficiencies found in literature generally are even lower.

When the PE would be maximal (calculated as 10%) at all light intensities, still a large surface would be needed to reach a reasonable hydrogen production volume. In The Netherlands 330 hectares would be needed for the production of 1 PJ (10^{15}J) of hydrogen per year. In southern Spain the required surface would be 220 hectares, due to the higher average solar irradiance.

The potential for renewable energy production is limited, but certainly not negligible. Furthermore the energy production potential per hectare is approx. 10-fold higher than for alternative energy crops while the output consists of clean H_2 (with 10-20 vol% CO_2) that can be applied directly in fuel cells. However, calculations have been done with favourable assumptions that are doubtfully met in practice. To make photobiological hydrogen production a sustainable energy carrier of significance, the conversion of solar energy into chemical energy must be optimised. This can be achieved by working at three fields at the same time: the biomolecular field, for instance by finding a solution for the oxygen inhibition of hydrogenases (in photoautotrophic organisms), the optimisation of light collection and the photobioreactor design. The productivity of photobioreactors is determined by the light regime inside the reactors. Optimising the reactors in this respect, and optimising the reactor surface are crucial for making photobiological hydrogen production successful.

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7

Summaries of chapters 3 - 6

7.1 Methane and hydrogen: on the role of end-use technologies in shaping the infrastructure

A. de Groot

To evaluate the status and potential of microbiological technologies for producing methane (‘biogas’) and hydrogen from (wet) biomass streams and sunlight, the projected efficiencies and costs are considered in Chapters 4 to 6 of this publication. However, an evaluation of the technical and economical feasibility should not only take into account the costs of producing the energy carrier. The profitability of bio-methane and bio-hydrogen production also depends on the ways by which these products can be utilised for generation of electricity and heat, as a transport fuel, etc. What are the costs for producing 1 GJ of heat and/or electricity or to drive a vehicle over a certain distance? How favourable do the emissions compare with competing technologies? To address these issues, the full ‘production to end-use’ chain for the two energy carriers (hydrogen and methane) should be included in the evaluation. In Chapter 3 the focus is therefore on the ways that methane and hydrogen can be utilised. Biogas and biologically produced hydrogen will be referred to as ‘bio-methane’ and ‘bio-hydrogen’ respectively.

Bio-methane and bio-hydrogen production methods are inherently extensive processes i.e. requiring relatively large process volumes. Furthermore the feedstock (wet biomass or bio-waste) cannot be easily transported over large distances. Based on these two characteristics relatively small-scale production systems, located where bio-wastes or other biomass sources are available, are most likely. This leads to two possible configurations for the ‘production to end-use chain’. Either the gas is used directly at the point of production (‘*stand-alone system'*) or the gas is supplied to an existing grid for use at another location (*'grid-connected production system'*).

- In a 'stand-alone system' the ‘production to end-use’ chain is integrated. The produced gas is converted on-site into the required form of energy: power and/or heat. This type of system is at present widely applied for conversion of bio-methane (biogas or landfill gas) into electricity and heat by means of gas engine/generator units. Limitations are that energy demand and biomass streams may not be available at the same location. Furthermore a load (or demand) following stand-alone system requires either flexibility in the production capacity, storage capacity for the energy carrier or integration with other systems supplying the actual load following characteristics.
- An alternative option that enables load following of the final energy demand without adding the extra cost of storage or flexible production capacity is to connect both the production and the end-use stages to a grid system for transport of methane (i.e. natural gas) or hydrogen. The ‘production to end-use’ chain in a grid-connected system consists of production and end-use as well as transport and distribution of hydrogen or methane. The infrastructure fulfils the function of matching energy demand and supply. The production and end-use system can be at different locations when a gas infrastructure is used.

In particular the second type of application, where the system producing bio-hydrogen or bio-methane is linked to the infrastructure, requires that not only the technology, but the role this technology can play in the larger energy infrastructure is evaluated. Chapter 3 addresses the ‘playing field’ for the production technologies for bio-methane and bio-hydrogen. The emergence of future energy carriers is addressed. Conclusions from a recent Shell scenario study are used to illustrate that different energy carriers become dominant in different scenarios and that end-use technologies are essential for the emergence of specific energy carriers. For bio-hydrogen it is evidently relevant to determine whether a future hydrogen infrastructure is likely. Bio-methane on the other hand could benefit from the existing natural gas infrastructure. Moreover, it is important to understand how the infrastructure and the end-use technologies will impose requirements with respect to purification and conditioning of the energy carriers methane and hydrogen.

End-use technologies play a key role. The final energy demand in The Netherlands is considered because final energy demand determines which end-use technologies are required. Subsequently, end-use technologies for stationary and transport applications using hydrogen and methane are considered. The discussion shows that fuel cells may play an important role. But this role is different for methane and hydrogen. For methane the fuel cell is one of many technologies. For hydrogen as an energy carrier the development of cost-effective fuel cell technology is both the critical component and (one of) the main reasons to use hydrogen.

Although technology is an important driver, energy policy will have a substantial influence on the emergence of specific energy carriers and technologies as well. It is therefore important to assess what the influence of energy policy will be. The implications of three policy scenarios for the (future) use of methane and hydrogen are evaluated, with the emphasis on ‘efficiency’, ‘CO_2 emission reduction’ and ‘renewables’ respectively. The possible role of hydrogen and methane/natural gas for both transport and stationary applications is considered.

The analysis can also be used to identify strategies in which the strong points of both energy carriers can be exploited. For the distribution and application of bio-methane the natural gas infrastructure is available, although the final energy carrier delivered to the end-user may be electricity or hydrogen. If conditioning of bio-methane to natural gas standards is not feasible, e.g. for economic reasons, the stand-alone option remains where methane is used at the site of production for the generation of electricity and heat. For hydrogen, which is more difficult to store, much larger advantages are obtained by connecting the production process to a hydrogen grid or an alternative distribution system. Hydrogen is the more attractive energy carrier for distribution to the end user because of the high and scale-independent efficiency of its final conversion in fuel cells. The most favourable option for bio-hydrogen production systems is therefore to deliver the produced hydrogen to a hydrogen distribution network on local, regional or larger scale.

7.2 Methane production by anaerobic digestion of wastewater and solid wastes

T.Z.D. de Mes, A.J.M. Stams, J.H. Reith and G. Zeeman

Biogas production and utilisation

Anaerobic digestion is an established technology for the treatment of wastes and wastewater. Anaerobic digestion systems are technologically simple with low energy and space requirements and produce a low amount of sludge that is stable and can be easily de-watered. The final product of anaerobic digestion is biogas: a mixture of methane (55-75 vol.%) and carbon dioxide (25-45 vol.%) with a fuel value ranging between 22 and 30 MJ/Nm^3 (Higher Heating Value). The amount of methane that can be produced from a specific waste stream depends on the concentration of digestable organic matter and on the applied system and operational conditions. For example, the biogas yield from the organic fraction of municipal solid waste generally ranges between 100 and 200 m^3 per tonne and for liquid manure between 10 and 20 m^3 per tonne. Anaerobic digestion systems currently operational in Europe have a total capacity of approx. 1,500 MW, while the potential for 2010 is estimated at 5,300-6,300 MW. The worldwide potential for 2010 is estimated at up to 20,000 MW.

Biogas can be utilised for the production of heat, co-generation of heat and electricity (CHP) and for upgrading to natural gas or fuel gas quality. A part of the biogas energy is utilised on-site to provide for the internal energy requirement of the plant (digester heating, pumps, mixers etc.). The amount of energy used for plant operation ranges between 20 and 50% of the total biogas energy contents depending on climate and technical specifications. The utilisation of biogas in gas engines is a long established technology. Electrical conversion efficiency varies from 29-38%, depending on the size of the engine, while up to 50% of the biogas energy content is converted to heat which can partly be recovered. In large-scale plants (e.g. landfill gas production sites) gas turbines may be used.

The utilisation of biogas in fuel cells is an important strategy to enhance the efficiency of electricity generation. Fuel cells make use of direct electrochemical conversion of the fuel with oxygen to generate electricity and heat with near-zero emissions. The potential electrical efficiency is greater than 50% while approx. 35% of the fuel energy is converted into heat. An anaerobic wastewater treatment plant equipped with a fuel cell system has been realised in Japan. Recent pilot-scale experiments in The Netherlands with a fuel cell for electricity generation from biogas produced in a farm-scale manure digestion system have shown promising results. A substantial cost reduction of fuel cell systems is however required for broad implementation. The current costs for biogas production in Europe range between 10 and 20 Euro/GJ. The costs of electricity generated from biogas range between 0.1 and 0.22 Euro/kWh, while electricity from landfill gas is produced for 0.04 - 0.07 Euro/kWh (data for 2000). Whereas the production cost of electricity from landfill gas has not changed much in the past decades, the cost of electricity from controlled biogas production plants has dropped considerably. It is expected that this trend will continue through further technology development.

Types of anaerobic digestion systems

Anaerobic digestion systems are divided in: low rate systems with long retention times, mainly applied for slurries and solid wastes, and high rate systems with relatively short hydraulic retention times and a mechanism to retain the sludge mass in the reactor, applied for wastewater treatment. Low rate systems are divided in 'wet' and 'dry' fermentation. Both can be batch or continuously operated. High rate systems are divided into systems with fixed bacterial films on solid surfaces and systems with a suspended bacterial mass where retention is achieved through external or internal settling. Digestion systems can operate at different temperature ranges; those usually applied are mesophilic (20-40 °C) and thermophilic (50-60 °C). Psychrophilic digestion is referred to when the system is operated at ambient temperatures below 20 °C. The choice of temperature is determined by the relationship between energy requirement and biogas yield. Moreover, the need to reduce pathogens will encourage the application of thermophilic digestion, while low temperature manure digestion in accumulation (fed-batch) systems is stimulated when long storage periods in winter are compulsory.

Application for wastewater treatment

Anaerobic treatment is applicable for a wide range of users, from industry to farming, waste-treating companies, water boards and individual farms or households. The technology is widely applied in industry, especially in the food and beverage and pulp and paper industry, particularly for wastewater treatment. The *Upflow Anaerobic Sludge Bed (UASB)* reactor is the most frequently applied anaerobic wastewater treatment system. In tropical regions this technique is also increasingly used for the treatment of domestic sewage. The low temperature in combination with the strong dilution of domestic sewage is thus far the main obstacle for the application of anaerobic domestic sewage treatment in temperate climates. New techniques are however under development. The latest development in The Netherlands and worldwide is to apply anaerobic digestion as part of a *Decentralised Sanitation and Re-use (DeSaR)* concept. The *DeSaR* concept focuses on the separate collection, transportation and decentralised processing of concentrated domestic waste streams and the diluted wastewater streams (‘grey water’). The concentrated streams contain potential energy, which can be recovered by anaerobic digestion and, in addition, nutrients which can be recovered for use as agricultural fertiliser.

Anaerobic digestion of manure

While the anaerobic treatment of wastewater is a measure for reducing the pollution load *and* for the production of energy, anaerobic digestion of animal manure should mainly be considered as an energy and nutrients recovery technique. Projects initiated in the 1980's in The Netherlands for manure digestion failed due to low biogas yields and energy recovery, and relatively low energy prices. Recently, anaerobic digestion of animal manure is re-introduced, stimulated by 'green energy' incentives and subsidies for reduction of greenhouse gas emissions. When manure digestion is combined with post-treatment techniques for recovery (or removal) of nutrients from the liquid fraction, solutions for the environmental problems caused by manure surpluses can be generated. In this case a part of the produced biogas energy has to be used for the post-treatment processes. For manure processing plants, gate fees and sales of mineral concentrates as fertiliser will, next to energy sales, become important elements for economic feasibility.

The biogas yield can be improved by technological innovations such as co-digestion, in which an energy-rich additive is added to the feedstock. Currently, in The Netherlands only a limited range of co-substrates, mainly plant materials, are allowed for co-digestion with animal manure. In Denmark 20 centralised biogas plants are operational for treatment of animal manure. These plants mostly employ thermophilic co-digestion (52 - 53 °C) with approx. 25% organic wastes mainly from food processing industries. These include animal wastes such as intestinal contents (27%), fat and flotation sludge from food or fodder processing (53%) and wastes from fruit & vegetable processing, dairies and other industries. The experience in Denmark shows that the biogas yield per tonne can be doubled through co-digestion, with a positive effect on economics.

Anaerobic digestion of solid bio-wastes

The economic feasibility of anaerobic digestion of the organic fraction of municipal solid waste (MSW) is determined by 'gate fees', and the sales of energy and digestates as compost. The main competitors for anaerobic digestion of solid wastes are landfill deposition and composting. In The Netherlands and other countries where landfill deposition of non-stabilised material is increasingly restricted, composting remains the main competitor on the longer term. Composting is a widely used technique for recycling of organic matter and nutrients from bio-wastes. Composting is however an energy consuming process (approximately 30-35 kWh is consumed per tonne of waste input), while anaerobic digestion is a net energy producing process (100-150 kWh per tonne of input waste). On the other hand, composting results in a dry, hygienically safe end-product, while the digestate remaining after anaerobic digestion requires de-watering and drying. Though the costs for anaerobic digestion of MSW and bio-waste are increasingly competitive with composting, somewhat higher treatment costs are still in effect for anaerobic digestion (Euro 80-35 /tonne for a capacity range of 20,000 - 120,000 tonne/year) as compared to composting (Euro 60-30 /tonne). Water treatment is a major cost factor in anaerobic digestion of solid waste. Combined anaerobic treatment/ aerobic composting of solid wastes could be applied to reduce the cost of additional water treatment, though lower gas yields will be the result.

Perspectives and issues for further development

Although anaerobic digestion is a mature technology, the implementation rate is relatively slow. In The Netherlands biogas is so far mainly produced from sewage sludge and industrial wastewater and hardly from animal manure and Vegetable Fruit and Yard waste (i.e. source separated organic fraction of MSW). The reasons for the thus far limited application of anaerobic digestion include: relatively low energy prices and limited access to energy markets, poor economic data, low energy yield, bad reputation due to unsuccessful plants, lack of information about environmental advantages, lack of co-operation between relevant sectors/parties and legal obstacles. On the short and medium term legislative and financial incentives are an important driver for economic feasibility of biogas plants of all scales. Several measures are already in place including the restriction of landfill deposition and financial incentives in the context of renewable energy policy. Continuation and broadening of support for biogas plants and anaerobic wastewater treatment systems is a sound policy. These techniques clearly offer advantages over aerobic wastewater treatment, composting, landfill deposition and incineration in the form of renewable energy production, reduction of greenhouse gas emissions and the possibility for full reuse of nutrients. It is evident that government programs aimed at increasing the share of renewable energy and greenhouse gas reduction will have an important impact on the expansion of anaerobic digestion.

Key technical areas for development are: biogas yield optimisation (co-digestion, pre-treatment), reduction of capital investments and operating costs through continued technological development, and modular design. Important elements for enhancing overall economic feasibility for solid waste and manure processing units with anaerobic treatment as the core-technology, are the development of cost effective technologies for effluent post-treatment and recovery of mineral concentrates. Non-technical areas for development include the establishment of demonstration plants in order to obtain reliable cost and environmental impact data and improvement of knowledge about the technology amongst the financial community, planning agencies and international development banks. A rapid expansion of the application of anaerobic digestion is expected, especially in developing countries where a demand exists for low-cost, reliable treatment plants.

7.3 Dark hydrogen fermentations

T. de Vrije and P.A.M. Claassen

The production of hydrogen from biomass as sole carbon and energy source i.e. dark hydrogen fermentation, is a ubiquitous, natural phenomenon under anoxic or anaerobic conditions. A wide variety of bacteria, in swamps, sewage, hot springs, the rumen of cattle etc. is able to convert organic matter to hydrogen, and carbonaceous products like CO_2 and acetic acid, lactate, ethanol and alanine. In general, these bacteria live in the close vicinity of other bacteria, mainly methanogenic bacteria, which consume these metabolites, including hydrogen, producing their own end-products like methane and CO_2. In this way, a stable ecosystem is formed where potential feedback inhibition of the hydrogen producers by hydrogen is annulled by the action of the hydrogen consumers. Since hydrogen, in nature, is consumed as soon as it is being formed, no net production of hydrogen is observed.

In view of the design of a bioprocess for the production of hydrogen from biomass, several prerequisites have to be met. The first prerequisite is, obviously, the uncoupling of hydrogen production from hydrogen consumption. This goal can be achieved by designing a two-step bioprocess consisting of two consecutive fermentations. In the first fermentation the applied conditions should favour dark hydrogen production and suppress hydrogen consumption. In the second fermentation, the carbonaceous end-products of dark hydrogen fermentation are used as substrate for further bioconversion, preferably to hydrogen using a photobiological fermentation. This Chapter discusses the prerequisites which are encountered when establishing an optimised dark hydrogen fermentation as part of a bioprocess for biological production of hydrogen from biomass.

As mentioned above, a wide variety of bacteria is able to convert organic matter to hydrogen and other products under anaerobic conditions. From this vast variety, extreme thermophilic anaerobic bacteria have been selected because of their high yield with respect to hydrogen production. The yield is reported to be approximately 83-100% of the maximal theoretical value of 4 mol hydrogen/mol glucose, in contrast to the strict anaerobic *Clostridia* which produce hydrogen with an approximate yield of 2 mol/mol and the facultative anaerobes which show a H_2 yield of less than 2. However, besides optimal H_2 molar yields, high hydrogen production rates are needed as well. Product formation is among others dependent on cell densities which are usually low in cultures of thermophilic bacteria. Therefore, the increase of the hydrogen production rate is an important challenge when optimising dark hydrogen fermentation. Furthermore, since dark hydrogen fermentation is inhibited by its end product at, on the average 10-20 kPa, removal of hydrogen is another challenge for optimal hydrogen production.
The second prerequisite for optimisation of dark

hydrogen fermentation is the utilisation of biomass. From literature and our own experiments, several types of biomass have been shown to be suited for fermentation to hydrogen. However, biomass requires pretreatment and hydrolysis, both from a physiological point of view and from a process technological point of view. The first consideration arises from the availability of fermentable substrate, the second is based on e.g. rheological properties. The conversion of biomass to a suitable fermentation feedstock is a crucial challenge which is shared with other fermentative biofuel production processes each having their own specific needs but all having the common denominator of pretreatment and hydrolysis for mobilisation of fermentable substrate. Besides the conversion to fermentable feedstock, it is also of prime importance to devise a strategy for a profitable utilisation of the residual biomass which can not be fermented. The optimisation of dark hydrogen fermentation can not be executed without addressing the constraints or potentialities of the complete biomass on offer.

In short: dark hydrogen fermentation is the first step in achieving biological hydrogen production; optimisation of dark hydrogen fermentation is dependent on increasing hydrogen productivity and availability of fermentable feedstock.

For an economically sound bioprocess for hydrogen production, the end-products of dark hydrogen fermentation have to be utilised as well. As discussed previously, we have therefore designed a bioprocess consisting of two consecutive fermentations: the first is the dark hydrogen fermentation described above; the second is a photofermentation described in Chapter 6 of this publication. In this photofermentation the end-products of the dark hydrogen fermentation are completely oxidised to H_2 and CO_2. In this way, the total yield of the bioprocess will increase to 12 mol hydrogen/mol glucose as compared to 4 mol/mol in the dark fermentation only. Besides this bioprocess, aimed at the production of hydrogen only, the design of a bioprocess for the production of hydrogen, followed by the conversion of the products of the dark hydrogen fermentation to methane, is conceivable also. This bioprocess would fit into a transition application since the combination of dark hydrogen fermentation and methane production seems feasible at the short term. However, in view of the future hydrogen economy, a bioprocess optimised for hydrogen production is favoured.

A complete bioprocess including biomass pretreatment has been designed, assuming a feasible (but not yet realised) production rate of 425 Nm^3 H_2/h using 1,000 kg dry biomass/h, removing hydrogen in the dark fermentation to the required low partial pressure and delivering hydrogen at fuel cell specifications. A first estimation of the hydrogen production costs has been done. In this calculation, cost for biomass, hydrolysis, personnel, civil works etc. have been omitted as well as profits from process integration, utilisation of residues or products. From these assumptions, the final production cost of hydrogen amounts to 2.74 Euro/kg H_2 or 19.2 Euro/GJ (based on upper combustion value). This is comparable to alternative technologies for CO_2 neutral H_2 production at a similar scale. The energy potential of biological hydrogen production in The Netherlands can be estimated from the approximate availability of organic feedstocks ranging from agro- and food industries to domestic waste. On the basis of this available feedstock, the contribution of the bioprocess to the electricity demand of Dutch households could amount to over 9%. This is an interesting amount but it has to be taken into account that in this case all available organic feedstock in The Netherlands is used for hydrogen production, leaving none for the production of other biofuels such as ethanol. On the other hand, many organic waste streams are currently treated by composting which is an energy consuming process. Alternatively, wastes are deposited in landfills, or discharged to surface waters. This puts a considerable burden on the environment in the form of methane emissions to the atmosphere and a deterioration of water quality. The use of these waste streams for bio-hydrogen production will increase the production of renewable, CO_2 neutral energy and, at the same time, reduce environmental problems. It is therefore evident that biological hydrogen production systems have a large potential for commercial application as waste-to-energy systems.

Future commercial application can be realised in the form of relatively small scale systems, operated by waste processing companies on a regional or local level or by industrial companies (e.g. agro- and food industries) with organic waste streams. It is expected that utility companies will take a share in future exploitation as well. The end-products could be either hydrogen, or electricity and heat, produced in fuel cells, depending on the local energy requirements and available infrastructure. For companies treating their own wastes, the generation of electricity and heat for the production process is an attractive option. For regional systems, the production of hydrogen may be a better option.

The potential for biological hydrogen production is recognised world-wide. The recent international conference *BioHydrogen 2002* drew 150 participants from around the world. The conference was devoted to both photobiological hydrogen production and fermentative hydrogen production in the dark. The attention for dark hydrogen fermentation increases world-wide.
At present, The Netherlands is leading in the research on the application of thermophilic bacteria for hydrogen production, due to the support from the Dutch Economy, Ecology and Technology Programme (E.E.T.), the EU programmes and Novem.

Increasingly, expert groups of various disciplines throughout Europe, Canada, Asia and, to a smaller extent, the USA are focussing on the biological production and application of hydrogen and concomitant implementation in society. However, this work seems fragmented as it is carried out individually and therefore these efforts seem to lack the coherence in the Dutch projects.

To conclude: The biological production of hydrogen is an environmentally friendly process. Furthermore the bioprocess delivers the cleanest hydrogen with an elegant and simple technology and is suitable even for small-scale application, thus having a high chance of becoming an economically feasible technology. The proof of principle has been delivered but, due to the limitation of the current projects, the required integration for demonstration and full economic evaluation has not been accomplished. The greatest obstacles for further development are the mobilisation of fermentable feedstock from cheap lignocellulosic biomass and the development of a cost-effective photofermentation. The first obstacle, applicable to lignocellulosic biomass, is shared with other emerging biofuel technologies thus benefiting from extensive critical mass in research and the second obstacle may be tackled by replacement by methane fermentation.

7.4 Photobiological hydrogen production: Photochemical efficiency and photobioreactor design

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Light energy is the driving force for photobiological hydrogen production. Energy from absorbed solar irradiance is converted into chemical energy stored in hydrogen in biocatalytic processes. In order to generate large amounts of hydrogen as an energy carrier it is essential to capture solar light (for which a large surface area is needed) and to convert this energy with high efficiency into hydrogen. The basic biological principle through which solar energy is stored is photosynthesis. The basic principles and processes for photobiological hydrogen production that are under development are outlined below.

Direct and indirect biophotolysis

Direct biophotolysis is the simplest photobiological hydrogen generating process. Several species of microalgae and cyanobacteria can be applied to perform the reaction:

$$2\ H_2O + \text{light} \rightarrow 2\ H_2 + O_2$$

In this process the water splitting reaction of oxygenic photosynthesis is coupled with the action of a hydrogen-evolving enzyme (hydrogenase). Both microalgae and cyanobacteria are able to use the visible part of the solar spectrum in the wavelength range 400-700 nm. Direct biophotolysis is an attractive process because it produces H_2 from cheap and widely available sources namely water and sunlight. The main drawback of the process is that hydrogen and oxygen are produced simultaneously, which causes oxygen inhibition of the hydrogen producing enzymes. The few efficiencies reported on the conversion of light energy into hydrogen energy are low: less than 1.5% on a full solar spectrum basis. The efficiency can be increased to 3 - 10%, by the immediate removal of the produced oxygen. Several options, including genetic modification, to overcome oxygen inhibition are under investigation, but not yet applicable in practice.

Indirect biophotolytic processes are being developed which separate the oxygen and hydrogen evolution stages in either space or time thus preventing O_2 inhibition. A well-studied indirect biophotolysis process employing spatial separation is based on green microalgae. In the first stage (consisting of open ponds) microalgae reduce CO_2 through photosynthesis into carbohydrates. In this phase O_2 is generated as a by-product of photosynthesis. In a second, anaerobic phase in closed (photo)bioreactors the stored carbohydrates are first converted into acetic acid in the dark. This step is followed by conversion of the acetate in a photobioreactor with the aid of sunlight into H_2 and CO_2. The algal cells can then be recycled to the open growth ponds. The reactions in the various steps are:

$$6\ H_2O + 6\ CO_2 + \text{light} \rightarrow C_6H_{12}O_6 + 6\ O_2$$

$$C_6H_{12}O_6 + 2\ H_2O \rightarrow 4\ H_2 + 2\ CH_3COOH + 2\ CO_2$$

$$2\ CH_3COOH + 4\ H_2O + \text{light} \rightarrow 8\ H_2 + 4\ CO_2$$

The 'overall' reaction is: $12\ H_2O + \text{light} \rightarrow 12\ H_2 + 6\ O_2$

A recent development of a process employing temporal separation is based on alternating the green microalga *Chlamydomonas reinhardtii* between a phase of photosynthetic O_2 evolution and carbohydrate storage and a phase of H_2 production in which metabolites are consumed. The H_2 production phase is enforced by sulphur (S) deprivation of the growth medium.

Photofermentations

In photofermentations phototrophic bacteria are grown heterotrophically and used to convert organic substrates like organic acids or alcohols (from biomass) into hydrogen and carbon dioxide according to the reaction:

$$2\ CH_3COOH + 4\ H_2O + \text{light} \rightarrow 8\ H_2 + 4\ CO_2$$

The microorganisms that can be applied in such a process are purple bacteria that produce hydrogen mainly due to the nitrogenase enzyme present in the cells. The nitrogenase is used by the organisms for nitrogen fixation i.e. reduction of N_2 from the air to NH_3 which is a nitrogen source required for growth. The nitrogenase enzyme also catalyses the evolution of H_2, particularly in the absence of N_2. The nitrogenase enzyme is also sensitive to oxygen (O_2). In this case, however, this is not a problem because no oxygen is produced during the process (anoxygenic photosynthesis). A disadvantage of the process is, that the nitrogenase enzyme requires extra metabolic energy in the form of ATP, which somewhat lowers the H_2 yield per unit absorbed light.

Photoheterotrophic bacteria are able to use light between 400 and 950 nm. It can be calculated that under ideal circumstances 10 % of the solar energy can be stored as hydrogen gas by these bacteria. In this scenario the energy content of the organic acid is neglected. It should be noted that the gas produced in this process is a clean product consisting of only hydrogen (80-90 vol%) and carbon dioxide (10-20 vol%).

Photofermentations are mostly applied in 2-stage processes as the second step following a dark fermentation process. Suitable substrates for the process are organic compounds originating from diluted waste products (e.g. molasses; industrial residues) or biomass hydrolysates. In the first step the sugars are converted to hydrogen and acetate (dark fermentation). The acetate can be further converted into hydrogen using a phototrophic fermentation step.

Energy potential

With data on irradiance levels (sunlight intensity) the potential energy production in the form of H_2 can be estimated. Assuming an average sunlight intensity of 75% of the maximum value over the year and a 10% photosynthetic conversion efficiency a photobioreactor system with a surface of 1,000 hectares in The Netherlands could yield an amount of 21,300 tonnes of H_2 or 3 PJ per year (1 PJ= 10^{15} J). For a 1,000 ha system located in Spain the energy production could amount to 4.6 PJ per year, and in the desert of Australia to 5.3 PJ per year, due to the higher solar irradiance in these regions. Considerable R&D is required to realise this potential in practical systems. The Dutch government aims for a 10% share of renewable energy or 340 PJ/year in 2020 from various sources including wind turbines and biomass. According to our estimate the contribution to this target of a 1,000 ha photobiological H_2 production system in The Netherlands would be less than 1 % (3 PJ/y). Although this amount of energy may not seem impressive it compares favourably with the primary energy production of energy crops such as ***Miscanthus*** or short rotation poplar which is on the order of 0.3 PJ/year for a 1,000 ha surface. The potential energy yield per hectare of photobiological H_2 production is thus 10-fold higher than these alternatives. With the additional benefit that the energy becomes available in the form of clean H_2 (with 10-20 vol% CO_2) that can be transported easily and used directly in fuel cells with high efficiency.

Economics

Economic analyses from literature indicate that photobiohydrogen can be produced at a cost of 10-15 Euro/GJ. The available estimates are, however, based on favourable assumptions and are highly preliminary. They are intended primarily to identify the major cost drivers for photobiological H_2 production and the targets and R&D issues for development. It is clear that the development of low-cost photobioreactors and the optimisation of photosynthetic efficiency are the major R&D challenges.

Although many different designs of photobioreactors have been developed, only few large-scale photobioreactors are in operation today. Currently there is one large-scale closed photobioreactor in use that could be employed for hydrogen production. The IGV (Institut für Getreideverarbeitung GmbH, Germany) constructed a closed tubular photobioreactor system of 12,000 m^2 ground surface (1.2 ha) with an investment cost of 8 million Euro. The investments per unit of ground surface are 660 Euro/m^{-2}. We assume that H_2 can be produced in this reactor with an efficiency of at least 7 % (on a full solar spectrum basis) and converted to electricity (at an assumed efficiency of 50%), which would lead to an overall conversion efficiency of sunlight-to-electricity of 3.5 %.

With these data we can compare the photobiological H_2 production system to the 'state-of-the-art' of photovoltaic cells. During the 'Floriade' Exhibition held in 2002 in The Netherlands, a roof of photovoltaic cells was constructed with a surface of 30,000 m^2 (3 ha). This roof is estimated to produce 1.2 million kWh of electricity yr^{-1}. Using average irradiance data for this geographical location (Amsterdam) we calculated a solar conversion efficiency to electricity of 4%. The investment costs of the solar roof are 17.5 million Euro or 580 Euro/m^{-2}. This shows that both the capital costs per m^2 and the overall conversion efficiency (sun light to electricity) are similar for the photobioreactor system and the photovoltaic system. Comparing these numbers it seems reasonable to say that the costs of electricity produced through photobiological hydrogen production are on a similar level as photovoltaic electricity production.

International status

Photobiological hydrogen production has been the subject of basic and applied research for several decades. In the USA research on photobiological hydrogen production has mainly been focussed on photoautotrophic processes, either direct or indirect photobiolysis, performed by microalgae and cyanobacteria. The R&D on direct biophotolytic processes has thus far not evolved beyond the laboratory stage. The recent work on temporally separated indirect biophotolysis through S-deprivation can accelerate the development of microalgal biohydrogen production processes. Another promising development in the field is the R&D on microalgal and bacterial mutants with truncated antennae in the USA and Japan. The use of organisms with reduced antenna sizes leads to an enhancement of photosynthetic light conversion efficiency and thus productivity in photobioreactors. In Japan there is more attention for photoheterotrophic processes. The

Japanese RITE programme has stimulated research in this field with much attention for research on the enzymes involved. Only in recent years research on biological hydrogen production has become important in Europe, with a relatively strong focus on photoheterotrophic H_2 production as well as dark fermentation in programs such as the EU Biohydrogen project. Several initiatives for co-operation in both fundamental and applied R&D in the field are being undertaken in the context of the EU 6th Framework Programme (2002 - 2006), in which the development of hydrogen technologies will have a prominent position. On a global scale the International Energy Agency co-ordinates international co-operation and knowledge exchange in the field of biological hydrogen production through the IEA Hydrogen Program, Task 15, Photobiological Hydrogen Production, which has recently been extended until 2004. Current member countries are Japan, Norway, Sweden, the USA, Canada and The Netherlands, while the UK, Hungary, Mexico and Portugal are considering active membership.

Perspectives and R&D issues

In order to make photobiologically produced hydrogen a sustainable energy carrier of significance, the conversion of solar energy into chemical energy must be optimised. This can be achieved by working in three fields at the same time: the biomolecular field, for instance by finding a solution for the oxygen inhibition of hydrogenases through increased oxygen tolerance, the optimisation of light collection and transfer, and the photobioreactor design. The development of low cost photobioreactors and the optimisation of photosynthetic efficiency and productivity are major R&D challenges.

8

Samenvattingen van hoofdstukken 3 - 6

8.1 Methaan en waterstof: de betekenis van eindgebruikstechnieken voor de vormgeving van de infrastructuur

A. de Groot

Voor een evaluatie van het potentieel van microbiologische technieken voor de productie van methaan en waterstof uit (natte) biomassastromen en zonlicht worden in de Hoofdstukken 4 t/m 6 de geprojecteerde rendementen en productiekosten in beschouwing genomen. Het profijt van biomethaan en bio-waterstofproductie is echter evenzeer afhankelijk van de wijze(n) waarop deze energiedragers kunnen worden ingezet voor de productie van elektriciteit en warmte, als transportbrandstof enz. Wat zijn de kosten voor de productie van 1 GJ warmte of elektriciteit, of voor het aandrijven van een voertuig over een bepaalde afstand? Hoe verhouden de emissies zich tot concurrerende technologieën? Voor een antwoord op deze vragen, dient de integrale keten 'van productie tot en met eindgebruik' van de energiedragers in de evaluatie te worden meegenomen. Hoofdstuk 3 richt zich daarom met name op de wijzen waarop methaan en waterstof kunnen worden ingezet als energiedragers.

Biologische methaan- en waterstofproductie zijn van nature extensieve processen die relatief grote procesvolumes vereisen. Daarnaast kunnen de benodigde grondstoffen (natte biomassa of reststromen) niet eenvoudig worden getransporteerd. Op basis van deze twee kenmerken zijn relatief kleinschalige productiesystemen - op locaties waar reststromen of andere biomassabronnen beschikbaar zijn - het meest waarschijnlijk. Dit leidt tot twee mogelijke configuraties voor de 'productie t/m eindgebruik' keten: het productgas (CH_4 of H_2) wordt ofwel direct gebruikt bij het productiesysteem (*'stand-alone systeem'*) of het gas wordt toegevoerd aan een bestaand transportnet voor gebruik op een andere locatie (*'netwerk gekoppeld systeem'*).

In een *'stand-alone systeem'* is de 'productie t/m eindgebruik' keten geïntegreerd. Het geproduceerde gas wordt ter plaatse omgezet in de gewenste energiedrager(s): elektriciteit en/of warmte. Dit type systeem wordt reeds veel toegepast voor de conversie van bio-methaan (biogas of stortgas) in elektriciteit en warmte in gasmotoren. Een beperking van 'stand-alone' systemen is dat de energievraag en de biomassagrondstoffen mogelijk niet op dezelfde locatie voorhanden zijn. Een belasting- (of energievraag-) volgend 'stand-alone' systeem vereist een flexibele productiecapaciteit, opslagmogelijkheden voor de energiedragers, of integratie met andere systemen die het volgen van de energievraag mogelijk maken. Deze voorzieningen werken kostenverhogend. Een alternatieve optie die het volgen van de uiteindelijke energieafname mogelijk maakt zonder extra kosten voor opslag of variabele productiecapaciteit, is het verbinden van de productie- en eindgebruiksfasen via een transportnet voor methaan (i.c. het aardgasnet) of waterstof. In zo'n *'netwerk gekoppeld systeem'* omvat de 'productie t/m eindgebruik' keten zowel de fasen van productie en eindgebruik als transport en distributie. In het systeem vervult de infrastructuur de functie van het op elkaar afstemmen van energievraag en -productie. Door gebruik van een gas-infrastructuur kunnen productie en eindgebruik op verschillende locaties zijn gesitueerd.

Met name het tweede geval, waar het bio-methaan of bio-waterstofproductiesysteem is verbonden met de (gas)infrastructuur, vereist dat niet alleen de technologie zelf maar ook de rol die de technologie kan spelen in de bredere energie-infrastructuur wordt geëvalueerd. Dit 'speelveld' voor bio-methaan en bio-waterstofproductietechnieken staat centraal in Hoofdstuk 3, waarin de opkomst en potentiële rol van toekomstige energiedragers wordt geëvalueerd. Aan de hand van de uitkomsten van een recente Shell scenario studie wordt geïllustreerd dat verschillende typen energiedragers in verschillende scenario's dominant worden en dat eindgebruikstechnieken essentieel zijn voor de opkomst van specifieke energiedragers. Voor bio-waterstof is het van evident belang te bepalen of een toekomstige waterstofinfrastructuur waarschijnlijk is, terwijl bio-methaan zou kunnen profiteren van de bestaande aardgasinfrastructuur. Bovendien is het van belang inzicht te krijgen in de eisen die de infrastructuur en de eindgebruikstechnieken (zullen) stellen aan de kwaliteit en conditionering van de energiedragers methaan en waterstof. Eindgebruikstechnieken spelen een sleutelrol. Het finale energiegebruik in Nederland wordt in beschouwing genomen, omdat dit eindgebruik bepalend is voor de vereiste eindgebruikstechnologieën. Vervolgens worden de eindgebruikstechnieken voor stationaire en mobiele toepassingen van methaan en waterstof beschouwd. Die evaluatie laat zien dat brandstofcellen voor zowel methaan als waterstof een belangrijke rol kunnen spelen door hun hoge efficiëntie en de emissievrije eindconversie. Voor methaan inzet is de brandstofcel echter één van de vele mogelijke technieken. Voor toepassing van waterstof daarentegen is de ontwikkeling van kosteneffectieve brandstofceltechnologie zowel een cruciale factor als één van de belangrijkste redenen voor het gebruik van waterstof als energiedrager.

Hoewel de technologie een belangrijke 'driver' is, zal ook het energiebeleid grote invloed hebben op de opkomst van specifieke energiedragers en eindgebruikstechnologie. Het is daarom van belang de potentiële invloed van het energiebeleid op de toekomstige ontwikkeling in kaart te brengen. De implicaties van drie beleidsscenario's voor het (toekomstig) gebruik van methaan (en aardgas) en waterstof, voor zowel stationaire- als mobiele toepassingen, worden geëvalueerd. In deze scenario's ligt de nadruk op respectievelijk 'efficiency', CO_2-emissiereductie' en 'hernieuwbare energie'.

De analyse kan ook worden gebruikt om strategieën te evalueren, waarin de sterke punten van methaan en waterstof als energiedrager ten volle kunnen worden benut. Voor distributie en toepassing van bio-methaan kan gebruik worden gemaakt van de aardgasinfrastructuur, hoewel de finale energiedrager geleverd aan de eindgebruiker elektriciteit of waterstof zou kunnen zijn. Als de conditionering van bio-methaan tot aardgaskwaliteit niet haalbaar is - bijvoorbeeld om economische redenen - rest nog de 'stand-alone' optie, waarin de bio-methaan ter plaatse wordt gebruikt voor het opwekken van elektriciteit en warmte. Voor waterstof, dat lastiger kan worden opgeslagen, kunnen veel grotere voordelen worden behaald door het productieproces te koppelen aan een waterstoftransportnet of een ander type distributiesysteem. Waterstof is een aantrekkelijke energiedrager voor transport naar de eindgebruiker vanwege de hoge, schaalonafhankelijke efficiency van de conversie naar elektriciteit in brandstofcellen. De meest gunstige optie voor bio-waterstofproductiesystemen is derhalve de geproduceerde waterstof af te zetten via een distributienetwerk op locale, regionale of grotere schaal.

8.2 Methaanproductie door toepassing van anaërobe vergisting van afvalwater en vast afval

T.Z.D. de Mes, A.J.M. Stams, J.H. Reith en G. Zeeman

Productie en toepassing van biogas

Anaërobe vergisting is een in de praktijk bewezen techniek, toegepast voor de behandeling van afval en afvalwater. Vergistingssystemen zijn technologisch eenvoudig, verbruiken weinig energie en nemen weinig ruimte in beslag. Vergeleken met de gangbare aërobe waterzuivering wordt een geringe hoeveelheid slib geproduceerd dat tevens stabiel is en goed kan worden ontwaterd. Het eindproduct van anaërobe vergisting is biogas, een mengsel van methaan (55-75 vol%) en kooldioxide (25-45 vol%) met een energie-inhoud van 22-30 MJ/Nm^3 (Bovenste Verbrandingswaarde). De productie van methaan uit een specifieke afval-stroom is afhankelijk van de concentratie vergistbaar organisch materiaal, het type vergistingssysteem en de procescondities. De biogasopbrengst uit de organische fractie van huisvuil varieert over het algemeen tussen de 100 en 200 m^3 per ton, die uit drijfmest tussen 10 en 20 m^3 per ton. De thans in Europa operationele vergistingssystemen hebben een totale capaciteit van ca. 1.500 MW. Het potentieel in Europa voor 2010 wordt geraamd op 5.300-6.300 MW en dat op wereldschaal op 20.000 MW.

Biogas kan worden ingezet voor de productie van warmte, gecombineerde opwekking van warmte en elektriciteit (W/K) of worden opgewaardeerd tot aardgas- of transportbrandstof kwaliteit. Een deel van de biogas energie wordt intern gebruikt om te voorzien in de energiebehoefte van de installatie (verwarming van de vergister, pompen, menginstallaties enz.). De hoeveelheid energie die gebruikt wordt voor interne doeleinden varieert van 20-50% van de totale biogasproductie, afhankelijk van klimatologische condities en technische specificaties.

Het gebruik van biogas in gasmotoren is een reeds lang toegepaste technologie. De efficiëntie van elektriciteitsproductie varieert van 29-38%, afhankelijk van het vermogen van de motor, terwijl tot 50% van de energie omgezet wordt in warmte die gedeeltelijk kan worden teruggewonnen. In zeer grootschalige installaties, zoals bij de winning van stortgas, kunnen gasturbines worden toegepast. De inzet van biogas in brandstofcellen is een belangrijke strategie voor het verhogen van het rendement van de elektriciteitsproductie en het terugdringen van emissies. Brandstofcellen maken gebruik van directe elektrochemische omzetting van de brandstof met zuurstof voor het, vrijwel emissieloos, opwekken van elektriciteit en warmte. De potentiële efficiëntie voor elektriciteitsproductie is meer dan 50%, terwijl ca. 35% in warmte wordt omgezet. Een anaërobe waterzuiveringsinstallatie uitgerust met brandstofcellen is reeds gerealiseerd in Japan. Recent in Nederland uitgevoerde pilot-schaal experimenten met elektriciteitsopwekking uit biogas, geproduceerd in een mestvergistingsinstallatie, met behulp van een brandstofcel hebben veelbelovende resultaten opgeleverd. Voor bredere implementatie van brandstofcellen is echter nog een substantiële kostenreductie vereist.

De huidige kosten van biogasproductie in Europa bedragen 10-20 Euro/GJ. De kosten van elektriciteit geproduceerd uit biogas bedragen 0,1-0,22 Euro/kWh, tegen 0,04-0,07 Euro/kWh voor elektriciteit uit stortgas (data 2000). De kosten van elektriciteitsproductie uit stortgas liggen reeds langere tijd op vrijwel hetzelfde niveau. Daarentegen zijn de productiekosten van elektriciteitsproductie via gecontroleerde anaërobe vergisting gedurende de afgelopen decennia substantieel gedaald. De verwachting is dat deze trend zich, bij voortgaande techniekontwikkeling, zal voortzetten.

Typen vergistingssystemen

Anaërobe vergistingssystemen kunnen worden onderverdeeld in laag- en hoogbelaste systemen. Laagbelaste systemen worden gekenmerkt door lange verblijftijden en worden meestal toegepast voor de behandeling van slurries en vast afval. Hoogbelaste systemen hebben een relatief korte hydraulische verblijftijd en een mechanisme om slib in de reactor achter te houden en worden toegepast voor behandeling van afvalwater. Laagbelaste systemen kunnen onderverdeeld worden in natte en droge vergistingssystemen. Beide kunnen zowel ladingsgewijs als continu worden bedreven. Hoogbelaste systemen zijn onderverdeeld in systemen met gefixeerde bacteriële films op vaste oppervlakken en systemen met een gesuspendeerde bacteriële massa, waarbij slibretentie bereikt wordt door externe of interne bezinking. Alle vergistingssystemen kunnen werken bij verschillende temperaturen; mesofiele (20-40 °C) en thermofiele (50-60 °C) vergisting worden het meest veelvuldig toegepast. Psychrofiele vergisting vindt plaats bij omgevingstemperaturen beneden de 20 °C. De keuze voor de temperatuur wordt mede bepaald door de relatie tussen de energievraag voor opwarming van de vergister en de biogas opbrengst. Als pathogenen reductie van belang is, kan toepassing van thermofiele vergisting interessant worden, terwijl lage temperatuur mestvergisting in accumulatie ('fed-batch') systemen aantrekkelijk wordt bij verplichte, lange mestopslag periodes gedurende de winter.

Toepassing voor afvalwaterbehandeling

Anaërobe vergisting is toepasbaar voor verschillende gebruikersgroepen: van industrieën tot boerenbedrijven, afvalverwerkingsbedrijven, waterbeheerders en zelfs individuele huishoudens. De technologie wordt veelvuldig toegepast in de industrie, in het bijzonder in de voedingsmiddelen- en drankenindustrie en de pulp- en papierindustrie. De *Upflow Anaerobic Sludge Bed (UASB)* reactor is wereldwijd het meest frequent toegepaste anaërobe waterbehandelingssysteem. In de tropen wordt deze techniek in toenemende mate ook toegepast voor de behandeling van huishoudelijk afvalwater. De lage temperatuur in combinatie met de sterke verdunning is tot nu toe het grootste obstakel voor toepassing van anaërobe behandeling van rioolwater in gematigde klimaten. Nieuwe technieken zijn in ontwikkeling. De laatste ontwikkeling in Nederland en wereldwijd is de toepassing van anaërobe vergisting als onderdeel van een *DeSaH (Decentrale Sanitatie en Hergebruik)* concept. Het *DeSaH* concept richt zich op de gescheiden inzameling, transport en decentrale behandeling van geconcentreerde (faeces en urine, keukenafval) en verdunde (grijswater) huishoudelijk afval(water) stromen. De geconcentreerde stroom bevat potentiële energie, die kan worden terugwonnen door toepassing van anaërobe vergisting; bovendien kunnen nutriënten worden terugwonnen voor gebruik als meststof in de landbouw. De technologie toegepast voor de vergisting van dierlijke mest kan tevens toegepast worden voor vergisting van menselijk fysiologisch afval.

Anaërobe vergisting van mest

Terwijl anaërobe behandeling van afvalwater een methode is voor reductie van de vervuilingslast én voor de productie van energie, moet de anaërobe vergisting van dierlijke mest vooral worden beschouwd als een techniek voor het terugwinnen van energie en nutriënten. Projecten voor de vergisting van dierlijke mest, geïnitieerd in Nederland in de 1980'er jaren zijn mislukt als gevolg van lage gasopbrengsten en beperkte efficiëntie van energieopwekking, en relatief lage energieprijzen. Recent is de toepassing van mestvergisting weer geïntroduceerd, mede gestimuleerd door groene energie toeslagen en subsidies voor reductie van emissies van niet CO_2 broeikasgassen. Als mestvergisting wordt gecombineerd met nabehandelingtechnieken voor de terugwinning (of verwijdering) van nutriënten uit de vloeistof fractie, kunnen oplossingen worden gegenereerd voor het mestoverschotten probleem. In dat geval wordt een deel van het geproduceerde biogas gebruikt voor de nabehandelingprocessen. Voor mestverwerkingbedrijven vormen poorttarieven en verkoop van minerale concentraten belangrijke elementen voor economische haalbaarheid, naast de opbrengsten uit energieverkoop.

De biogasopbrengst kan worden verhoogd door technische innovaties zoals covergisting, waarbij een energierijk substraat wordt toegevoegd. Op dit moment mogen in Nederland slechts een beperkt aantal substraten, voornamelijk plantaardige materialen, worden toegevoegd aan mestvergistingsinstallaties. In Denemarken zijn ca. 20 centrale vergistingsinstallaties in bedrijf voor behandeling van dierlijke mest. Bij deze installaties wordt over het algemeen thermofiele (52-53 °) covergisting met ca. 25% organisch afval toegepast. Deze afvallen bestaan uit dierlijke resten, zoals darminhoud (27%), vet en flotatie slib van levensmiddelen- en diervoedingbedrijven (53%) en afvallen van groente- en fruitverwerking, zuivelbedrijven en andere industrieën. De ervaring in Denemarken leert dat de biogasproductie per m^3 mest door covergisting kan worden verdubbeld.

Anaërobe vergisting van vast organisch afval

De haalbaarheid van de anaërobe behandeling van de organische fractie van huishoudelijk vast afval (HVA) wordt bepaald door poorttarieven, en de productie en afzet van energie en goede kwaliteit compost. De belangrijkste concurrenten van vergisting van organisch vast afval zijn storten en composteren. In Nederland (en andere landen) waar storten van niet gestabiliseerd organisch afval in toenemende mate wordt beperkt, blijft compostering over als belangrijkste concurrerende techniek. Compostering wordt algemeen toegepast en biedt een methode voor recycling van organische stof en nutriënten uit de organische fractie van HVA en andere bio-afvallen. Compostering is echter een energie consumerende techniek (ca. 30-35 kWh per ton afval). Daarentegen resulteert compostering in een droog, hygiënisch veilig product, terwijl na anaërobe vergisting een nat product resteert dat ontwatering en droging behoeft. Hoewel de kosten voor anaërobe vergisting van HVA en bioafval in toenemende mate competitief zijn met compostering, zijn de kosten voor anaërobe vergisting nog steeds enigszins hoger, (80-35 Euro/ton afval voor een capaciteit van 20.000-120.000 ton/jaar) in vergelijking met compostering (60-30 Euro/ton). Waterbehandeling vormt een belangrijke kostenpost bij de anaërobe behandeling van vast organisch afval. Toepassing van anaërobe vergisting in combinatie met compostering zal deze kosten reduceren, maar tegelijkertijd de biogasproductie verlagen.

Perspectieven en aandachtspunten voor verdere ontwikkeling

Hoewel anaërobe vergisting kan worden beschouwd als een bewezen techniek, is de snelheid waarmee het proces in de praktijk wordt ingevoerd, met name voor vergisting van dierlijke mest en vast afval, relatief laag. In Nederland wordt anaërobe vergisting tot nu toe voornamelijk toegepast op rioolwaterzuiveringsslib en (nog) nauwelijks op dierlijke mest en GFT (aan de bron gescheiden organische fractie van Huishoudelijk Vast Afval). Anaërobe zuivering van industrieel afvalwater kent daarentegen wel een ruime toepassing. De redenen voor de tot dusver beperkte toepassing van anaërobe vergisting zijn divers: relatief lage energieprijzen en beperkte toegang tot energiemarkten, slechte economische resultaten, lage energieopbrengsten, slechte reputatie als gevolg van niet succesvolle installaties, gebrek aan informatie over milieuvoordelen, gebrek aan samenwerking tussen relevante sectoren/partijen en wettelijke obstakels. Op korte en middenlange termijn kunnen wettelijke en financiële maatregelen de economische haalbaarheid van anaërobe vergisting versterken. Verschillende maatregelen zijn al van kracht, waaronder de restricties op het storten van onbehandeld organisch afval en financiële vergoedingen in het kader van duurzaam energiebeleid. Voortzetting en uitbreiding van dit beleid is gewenst. Anaërobe technieken bieden duidelijke voordelen boven aërobe waterbehandeling, compostering, stort en verbranding in de vorm van duurzame energieproductie, reductie van broeikasgas emissies en de mogelijkheid tot volledige terugwinning en hergebruik van nutriënten. Overheidsprogramma's op het gebied van hernieuwbare energieproductie en reductie van emissies van broeikasgassen zullen een belangrijke stimulans vormen voor de toepassing van anaërobe vergisting.

Optimalisatie van de biogasproductie (covergisting, voorbehandeling), reductie van investeringen en operationele kosten door technische verbeteringen, en het ontwerpen van modulaire eenheden zijn belangrijke technische aspecten voor verdere ontwikkeling. De ontwikkeling van kosteneffectieve technieken voor effluent nabehandeling en terugwinning van nutriënten kunnen de economische haalbaarheid van vast afval- en mestverwerkinginstallaties, met anaërobe zuivering als de centrale technologie, aanzienlijk verbeteren. Daarnaast zijn verscheidene niet-technische aspecten van belang, zoals de bouw van demonstratie installaties voor het verkrijgen van betrouwbare gegevens over de kosten en milieueffecten, en het verbeteren van de kennis over de technologie in de financiële sector en bij (inter)nationale planning- en ontwikkelingsorganisaties. Met name in ontwikkelingslanden waar een grote vraag bestaat naar goedkope en betrouwbare afval(water)behandelingssystemen, valt een snelle uitbreiding van de toepassing van anaërobe zuivering/vergisting te verwachten.

8.3 Waterstof fermentaties

T. de Vrije en P.A.M. Claassen

De productie van waterstof uit biomassa als enige koolstof en energiebron, de zogenaamde 'donker fermentatie', is een natuurlijk verschijnsel dat optreedt in ecosystemen waarin geen of zeer weinig zuurstof aanwezig is. Diverse bacteriën die voorkomen in moerassen, riolering, heetwaterbronnen, ingewanden van runderen etc. kunnen organische substraten omzetten in waterstof en koolstofhoudende producten zoals azijnzuur, melkzuur, ethanol, alanine en CO_2. Deze bacteriën leven in het algemeen in de dichte nabijheid van andere, methanogene bacteriën die de eindproducten van de waterstofproducenten consumeren en omzetten in hun eigen eindproducten, t.w. methaan en CO_2. Op deze manier ontstaat een stabiel ecosysteem waarin de mogelijke remming van de waterstofproducenten door waterstof wordt voorkomen. Aangezien de waterstof direct na productie wordt geconsumeerd, komt er in natuurlijke systemen geen waterstof vrij.

Voor het ontwerpen van een bioproces voor de productie van waterstof uit biomassa moet aan een aantal randvoorwaarden worden voldaan. De eerste is het ontkoppelen van de waterstofproductie van de waterstofconsumptie. Dit kan bewerkstelligd worden door een twee-traps bioproces te ontwerpen dat uit twee opeenvolgende fermentaties bestaat. In de eerste fermentatie worden de condities zodanig gekozen dat de waterstofproductie bevoordeeld wordt en de waterstofconsumptie onderdrukt. In de tweede fermentatie worden de koolstofhoudende eindproducten van de waterstof fermentatie verder gefermenteerd, bij voorkeur tot waterstof, in een fotobiologische fermentatie.

In Hoofdstuk 5 worden de randvoorwaarden behandeld voor een optimale waterstof fermentatie, als onderdeel van een bioproces voor de productie van waterstof uit biomassa. Zoals eerder vermeld is een groot scala bacteriën in staat onder anaërobe condities organisch materiaal om te zetten in waterstof en andere producten. Hieruit zijn extreem thermofiele anaërobe bacteriën geselecteerd vanwege de hoge opbrengst aan waterstof. Deze opbrengst is bijna 83-100% van het theoretische maximum van 4 mol waterstof/mol glucose, terwijl de strikt anaërobe *Clostridia* ongeveer 2 mol/mol en de facultatief anaërobe bacteriën minder dan 2 mol waterstof/mol glucose produceren. Naast optimale waterstof opbrengst is echter ook de waterstof productiesnelheid van belang. Deze productiesnelheid is o.a. afhankelijk van de celdichtheid die in het algemeen laag is in kweken van thermofiele bacteriën. Dientengevolge vormt het verhogen van de productiesnelheid een grote uitdaging bij het optimaliseren van waterstof fermentaties. Hiernaast vormt het verwijderen van de gevormde waterstof, die bij een partiaal druk van gemiddeld 10-20 kPa tot remming van de productie snelheid leidt, een tweede uitdaging.

De tweede randvoorwaarde voor een functioneel bioproces voor waterstof productie is de geschiktheid van het substraat. Uit literatuur onderzoek en onze eigen experimenten zijn reeds verschillende substraten geschikt gebleken voor waterstof fermentatie. Echter, zowel vanuit fysiologisch als procestechnologisch oogpunt, is het noodzakelijk biomassa voor te behandelen en te hydrolyseren. Ten eerste is dit nodig voor het beschikbaar maken van het substraat, ten tweede voor de verbetering van bijv. rheologische parameters. De conversie van biomassa tot geschikt fermentatie substraat is een cruciale uitdaging die gedeeld wordt met andere fermentatieve biobrandstof productie processen, met ieder weer hun eigen speciale eisen. Naast de conversie tot fermenteerbaar substraat is het zaak een strategie te definiëren voor profijtelijk gebruik van het residu dat niet gefermenteerd kan worden. Een optimaal bioproces voor waterstofproductie kan niet uitgevoerd worden zonder aandacht te besteden aan de beperkingen of mogelijkheden die de aanwezige biomassa biedt.
Samengevat: Waterstof fermentatie met biomassa als enige koolstof- en energiebron is de eerste stap in een bioproces voor waterstof productie; het optimaliseren van deze waterstof fermentatie wordt bepaald door het verhogen van de waterstof productiesnelheid en de beschikbaarheid van fermenteerbaar substraat.

Voor een kosteneffectief bioproces voor waterstof productie moeten de eindproducten van de eerste fermentatie ook in beschouwing worden genomen. Zoals eerder vermeld hebben we daarom een bioproces ontworpen dat uit twee opeenvolgende fermentaties bestaat: de eerste is de waterstof fermentatie die hierboven beschreven is; de tweede is de fotofermentatie die in Hoofdstuk 6 van deze publicatie beschreven wordt. In de fotofermentatie worden de eindproducten van de waterstof fermentatie volledig omgezet in H_2 en CO_2. Zodoende zal de totale opbrengst van het bioproces toenemen tot 12 mol waterstof/mol glucose, in plaats van 4 mol/mol in de waterstof fermentatie alleen. Naast dit bioproces dat uitsluitend gericht is op waterstof productie, is een bioproces denkbaar waarin na de waterstof fermentatie tot 4 mol/mol glucose, de koolstofhoudende eindproducten verder worden omgezet in methaan en CO_2. Een dergelijk bioproces zou een tijdelijke toepassing kunnen vinden aangezien de combinatie van waterstof en methaan op korte termijn een haalbare kaart lijkt. Met het oog op de toekomstige waterstof economie geniet de ontwikkeling van een bioproces voor uitsluitend waterstof productie echter de voorkeur.

Een volledig bioproces, inclusief biomassa voorbehandeling, is ontworpen na aanname van een haalbare (maar nog niet gerealiseerde) productie snelheid van 425 Nm^3 H_2/u. In het ontwerp is gebruik gemaakt van 1.000 kg droge biomassa/u, en rekening gehouden met de verwijdering van waterstof tot de lage vereiste partiaal druk. De uiteindelijke waterstof voldeed aan de specificatie voor toepassing in een brandstofcel. Op basis hiervan is een eerste schatting van de waterstof productiekosten gemaakt. In deze berekening zijn geen kosten opgenomen voor de biomassa, personeel, civiele werken etc., en ook niet voor mogelijke revenuen voortkomend uit integratie van procesunits of exploitatie van residuen of bijproducten. Op basis hiervan zijn de productiekosten geschat op 2,74 Euro/kg H_2 ofwel 19,2 Euro/GJ (gebaseerd op hogere verbrandingswaarde). Dit bedrag is vergelijkbaar met andere alternatieve technologieën voor CO_2 neutrale, kleinschalige productie van waterstof. Het energiepotentieel van een waterstof bioproces in Nederland kan afgeleid worden uit de beschikbaarheid van organisch materiaal dat afkomstig kan zijn van de agro- en voedingsmiddelen industrie of huishoudelijk afval. Hierop gebaseerd is een bijdrage van het bioproces aan de electriciteitsbehoefte van Nederlandse huishoudens tot meer dan 9% haalbaar. Dit is een interessante hoeveelheid maar er moet rekening gehouden worden met het feit dat in dit geval al het beschikbare organisch materiaal in Nederland gebruikt wordt voor waterstof productie en dat er niets over is voor de productie van andere biobrandstoffen zoals ethanol. Op het moment worden vele organische reststromen gecomposteerd in een energievragend proces. Hiernaast worden afvalstromen gestort of geloosd op het oppervlaktewater. Beide gevallen belasten het milieu in de vorm van methaan emissie of vervuiling van het oppervlaktewater. Het aanwenden van deze afvalstromen voor biowaterstof productie zal de productie van CO_2-neutrale energie vergroten en gelijktijdig milieu problemen voorkómen. Het is dientengevolge duidelijk dat een bioproces voor de productie van waterstof een aanzienlijke bijdrage kan leveren aan de conversie van afval tot energie.

De toekomstige commerciële toepassingen zullen kunnen bestaan uit betrekkelijk kleinschalige systemen bij locale of regionale afvalverwerkende industrieën of bij industrieën uit de agro- of voedingsmiddelen sector. Nutsbedrijven zullen naar verwachting eveneens participeren in de toekomstige exploitatie. De eindproducten kunnen ofwel waterstof, ofwel elektriciteit en warmte zijn, afhankelijk van de locale energiebehoeften en de beschikbare infrastructuur. Voor industrieën die hun eigen reststromen verwijderen of valoriseren lijkt de productie van elektriciteit en warmte voor hun eigen productie proces een aantrekkelijke optie. In het geval van regionale toepassing, lijkt de productie van waterstof een beter alternatief.

Het potentieel voor biologische waterstof productie wordt wereldwijd erkend. Bij het recentelijk gehouden internationale congres ***BioHydrogen 2002***, waren 150 deelnemers uit alle werelddelen aanwezig. Het congres was gewijd aan zowel fotobiologische waterstof productie als aan waterstof fermentatie met organische koolstofverbindingen als enige koolstof- en energiebron. De belangstelling voor deze laatste fermentaties neemt overal ter wereld toe.
Op het moment is Nederland koploper op het gebied van research naar de toepassing van thermofiele bacteriën voor waterstof productie, met name door financiële ondersteuning uit het Economie, Ecologie en Technologie Programma (E.E.T.), het 5de kaderprogramma van de EU en Novem.
Experts in diverse research disciplines in Europa, Canada, Azië en, in mindere mate, de USA raken in steeds toenemende mate geïnteresseerd in biowaterstof productie, toepassingen van waterstof en maatschappelijke implementatie. Dit werk is evenwel gefragmenteerd en wordt individueel uitgevoerd zodat het de samenhang zoals in de Nederlandse projecten aanwezig mist.

Concluderend: productie van biowaterstof is een milieuvriendelijk proces. Dit bioproces levert de schoonste waterstof op op basis van een elegante en simpele technologie en is zelfs geschikt voor kleinschalige toepassing zodat de kans op succesvolle toepassing groot is. De 'proof-of-principle' is geleverd maar vanwege de beperkingen van de huidige projecten, is de voor demonstratie vereiste procesintegratie en volledige economische evaluatie nog niet voltooid. De grootste obstakels voor verdere ontwikkeling zijn de mobilisatie van fermenteerbaar substraat uit goedkope lignocellulose houdende biomassa, en de ontwikkeling van een kosteneffectieve fotofermentatie. Het eerste obstakel dat geldt bij gebruik van lignocellulose, wordt gedeeld met andere nieuwe biobrandstof productie processen en zal zo zijn voordeel halen uit de uitgebreide kritische massa voor desbetreffend onderzoek; de tweede hindernis zou genomen kunnen worden door het vervangen van de fotofermentatie door een methaan fermentatie.

8.4 Fotobiologische waterstof productie; Fotochemische efficiëntie en fotobioreactor ontwerp

I. Akkerman, M. Janssen, J.M.S. Rocha, J.H. Reith en R.H. Wijffels

Zonlicht is de drijvende kracht achter fotobiologische waterstof productie. Zonne-energie wordt met behulp van biokatalytische processen omgezet in chemische energie in de vorm van waterstof. Om grote hoeveelheden waterstof als energiedrager te kunnen produceren is het belangrijk om zonlicht in te vangen (waar een groot oppervlak voor nodig is) en deze energie met hoge efficiëntie om te zetten in waterstof. Het biologische principe waarmee zonne-energie wordt opgeslagen is fotosynthese. De basisprincipes en de ontwikkelde processen worden hieronder beschreven.

Directe and indirecte biofotolyse

Directe biofotolyse is het eenvoudigste fotobiologische waterstof productie proces. Verscheidene soorten microalgen en cyanobacteriën kunnen deze reactie uitvoeren:

$$2\ H_2O + \text{licht} \rightarrow 2\ H_2 + O_2$$

In dit proces wordt water gesplitst. De reactie wordt gekatalyseerd door het waterstofproducerende enzym hydrogenase. Zowel microalgen als cyanobacteriën kunnen zonlicht uit het zichtbare deel van het zonnespectrum in het golflengtegebied 400-700 nm benutten. 'Directe biofotolyse' is een aantrekkelijk proces omdat het H_2 produceert uit goedkope en ruim voorhanden zijnde bronnen, namelijk water en zonlicht. Het grote nadeel van dit proces is dat waterstof en zuurstof tegelijk gevormd worden, waardoor zuurstofinhibitie van de waterstofproducerende enzymen optreedt. In de literatuur is een beperkt aantal efficiënties van de omzetting van lichtenergie in waterstofenergie vermeld. Deze efficiënties zijn tot dusver laag: minder dan 1,5% op totaal spectrum basis. De efficiëntie kan worden verhoogd tot 3-10% wanneer de zuurstof onmiddellijk wordt verwijderd. Verschillende technieken, waaronder genetische modificatie van organismen, zijn in onderzoek om het probleem van zuurstof inhibitie te ondervangen. Deze technieken worden nog niet toegepast in de praktijk.

Indirecte biofotolyse is een proces waarbij de productie van zuurstof en waterstof gescheiden worden in plaats of tijd, waardoor het probleem van zuurstofinhibitie wordt voorkómen. Een voorbeeld is een proces gebaseerd op groenalgen, waarin de waterstof en zuurstof productie ruimtelijk van elkaar gescheiden zijn. In de eerste fase (open vijvers) vormen microalgen koolhydraten door reductie van CO_2 met behulp van lichtenergie. Zuurstof wordt hierbij gevormd als bijproduct van de fotosynthese. In een tweede, anaërobe fase (gesloten bioreactoren) worden, in het donker, de opgeslagen koolhydraten eerst omgezet in azijnzuur. Daarna wordt het azijnzuur omgezet in H_2 en CO_2 in een fotobioreactor met behulp van zonlicht. De algencellen kunnen gerecycled worden door ze weer in de open vijvers te brengen. De opeenvolgende reacties zijn:

$$6\ H_2O + 6\ CO_2 + \text{licht} \rightarrow C_6H_{12}O_6 + 6\ O_2$$

$$C_6H_{12}O_6 + 2\ H_2O \rightarrow 4\ H_2 + 2\ CH_3COOH + 2\ CO_2$$

$$2\ CH_3COOH + 4\ H_2O + \text{licht} \rightarrow 8\ H_2 + 4\ CO_2$$

De 'overall' reactie is:
$12\ H_2O + \text{licht} \rightarrow 12\ H_2 + 6\ O_2$

Recent is een proces ontwikkeld gebaseerd op scheiding in tijd van de O_2 en H_2 productiefasen. De groenalg ***Chlamydomonas reinhardtii*** wordt afwisselend in een fase van fotosynthese, dus O_2 ontwikkeling en opslag van koolhydraten, en een fase van consumptie van metabolieten en H_2 productie, gebracht. De H_2 productie fase wordt opgeroepen door beperking van de zwavel (S) toevoer in het voedingsmedium.

Fotofermentaties

Fotofermentaties zijn processen waarin fototrofe bacteriën organische substraten zoals organische zuren of alcoholen omzetten in waterstof (H_2) en kooldioxide (CO_2) met behulp van licht:

$$2\ CH_3COOH + 4\ H_2O + \text{light} \rightarrow 8\ H_2 + 4\ CO_2$$

Purperbacteriën kunnen worden toegepast in een dergelijk proces, omdat zij waterstof kunnen produceren met behulp van het nitrogenase enzym dat aanwezig is in de cel. Nitrogenase wordt door de organismen gebruikt voor stikstoffixatie: de reductie van stikstof (N_2) uit de lucht tot ammoniak (NH_3) wat de stikstof beschikbaar maakt voor groei. Het nitrogenase enzym katalyseert ook de productie van H_2, in het bijzonder in afwezigheid van N_2. Het nitrogenase enzym is ook gevoelig voor zuurstof, maar aangezien bij dit proces geen zuurstof wordt gevormd (anoxygene fotosynthese), is dit geen probleem. Een nadeel van dit proces is wel, dat het nitrogenase enzym extra metabole energie in de vorm van ATP vraagt, waardoor de H_2 opbrengst per hoeveelheid geabsorbeerde lichtenergie enigszins verlaagd wordt.

Fototrofe bacteriën kunnen licht met golflengten tussen 400 en 950 nm benutten. Berekeningen tonen aan dat deze bacteriën onder ideale omstandigheden 10% van de zonne-energie kunnen opslaan in waterstofgas. In deze berekening is de energie inhoud van het organisch zuur niet meegerekend. Het gas dat in het proces wordt gevormd, is een schoon product dat alleen uit waterstof (80-90 vol%) en kooldioxide (10-20 vol%) bestaat. Fotofermentaties worden meestal uitgevoerd als tweede fase in twee-traps processen na een donker fermentatie proces. Geschikte substraten zijn organische stoffen uit verdunde residuen (zoals melasse) of gehydrolyseerde biomassa. In de eerste fase worden de koolhydraten omgezet in waterstof en acetaat (donkerfermentatie). Het acetaat kan vervolgens verder omgezet worden in waterstof via een fotofermentatie fase.

Energiepotentieel

De potentiële energieproductie in de vorm van waterstof kan berekend worden met behulp van gegevens over de zonlichtintensiteit. Aannemende dat de jaargemiddelde zonlichtintensiteit 75% van de maximale waarde is en uitgaande van een maximale fotochemische efficiëntie van 10%, zal een fotobioreactorsysteem in Nederland met een oppervlak van 1.000 hectare 21.300 ton H_2 met een energie-inhoud van 3 PJ per jaar kunnen produceren. (1 PJ= 10^{15} J). Een 1.000 hectare groot systeem in zuid Spanje en in de woestijn van Australië zouden respectievelijk 4,6 PJ en 5,3 PJ per jaar kunnen produceren, vanwege de hogere zonlichtintensiteit in deze gebieden.

De Nederlandse regering streeft naar een aandeel duurzame energie van 10% ofwel ca. 340 PJ/jaar in 2020 vanuit verschillende bronnen, waaronder windmolens, zonnecellen en biomassa. Volgens onze raming zou de bijdrage van een 1.000 hectare groot fotobiologisch H_2 productiesysteem aan deze doelstelling ca. 1% (3 PJ/jaar) kunnen bedragen. Hoewel deze potentiële bijdrage niet indrukwekkend lijkt is hij 10-maal groter dan de potentiële primaire energieproductie van energiegewassen als het snelgroeiende gewas ***Miscanthus*** welke ongeveer 0,3 PJ/jaar bedraagt op een oppervlak van 1.000 ha. Een bijkomend voordeel van fotobiologische waterstofproductie is dat de energie vrijkomt in de vorm van schone H_2 (met 10-20 vol% CO_2) die eenvoudig kan worden getransporteerd en direct en efficiënt kan worden toegepast in brandstofcellen.

Economie

Kosten en baten analyses uit de literatuur geven aan dat fotobiologische waterstof geproduceerd kan worden tegen kosten van 10-15 Euro/GJ. Deze kostenramingen zijn gebaseerd op gunstige aannames en voorlopige cijfers. Ze zijn vooral bedoeld om de belangrijkste kostenposten voor fotobiologische waterstof productie, en de aandachtspunten voor optimalisatie te identificeren. Het is duidelijk dat de ontwikkeling van goedkope fotobioreactoren en de optimalisatie van de fotosynthetische efficiëntie de belangrijkste onderzoeksdoelstellingen zijn.

Hoewel er veel verschillende ontwerpen van fotobioreactoren zijn ontwikkeld, zijn er slechts enkele grootschalige fotobioreactoren in bedrijf. Er is één grootschalige gesloten fotobioreactor in bedrijf die geschikt zou kunnen zijn voor waterstofproductie. Het IGV (Institut für Getreideverarbeitung GmbH, Duitsland) heeft een gesloten buizenreactor gebouwd van 12.000 m^2 grondoppervlak (1,2 ha). De investeringskosten bedroegen 8 miljoen Euro, ofwel 660 Euro per m^2.

Als we ervan uitgaan dat H_2 geproduceerd kan worden met een efficiëntie van minstens 7% (totaalspectrum basis) en in een brandstofcel omgezet wordt in elektriciteit met een efficiëntie van 50%, resulteert dit in een overall omzettingsefficiëntie van zonlicht naar elektriciteit van 3,5%. Met deze gegevens kunnen we fotobiologische H_2 productie vergelijken met de 'state of the art' van zonnecellen. Tijdens de 'Floriade' tentoonstelling in 2002 in Nederland, werd een dak geconstrueerd van zonnecellen met een oppervlakte van 30.000 m^2 (3 hectare). Geschat werd dat dit dak 1,2 miljoen kWh elektriciteit per jaar produceert. Uitgaande van gemiddelde zonlichtintensiteiten voor dit gebied (Amsterdam) berekenen we het rendement van de conversie van zonlicht naar elektriciteit op 4%. De investeringskosten van het zonnecellendak bedroegen 17,5 miljoen Euro ofwel 580 Euro per m^2. Hieruit kan worden geconcludeerd dat zowel de kosten per m^2 als de overall efficiëntie (van zonlicht naar elektriciteit) van vergelijkbare orde van grootte zijn voor het zonnecellen systeem en het fotobiologische systeem.

Internationale status

Fotobiologische waterstof productie is al enkele decennia het onderwerp van fundamenteel en toegepast onderzoek. In de VS is het onderzoek vooral gericht op het fotoautotrofe proces, zowel directe als indirecte biofotolyse, met behulp van microalgen en cyanobacteriën. De R&D naar direct biofotolytische processen verkeert nog goeddeels op laboratoriumschaal. Het recente werk aan de in tijd gescheiden indirecte biofotolyse door zwavel deprivatie kan de ontwikkeling van biowaterstof productie op basis van microalgen een nieuwe impuls geven. Een interessante ontwikkeling in de VS en Japan, is de R&D naar mutanten van microalgen en bacteriën met verkleinde 'antennesystemen' voor de invang van licht. Het gebruik van deze organismen verhoogt de fotosynthetische efficiëntie en derhalve de productiviteit in fotobioreactoren.

In Japan is meer aandacht voor fotoheterotrofe processen. Het Japanse RITE-programma heeft onderzoek op dit terrein gestimuleerd met veel aandacht voor onderzoek naar de betrokken enzymen. De nadruk in het huidige Europese onderzoek ligt op fotoheterotrofe H_2 productie en donker fermentaties in programma's zoals het EU Biohydrogen project. Verscheidene initiatieven voor samenwerking in zowel fundamentele als toegepaste R&D op dit terrein zijn genomen in het EU 6e kader Programma (2002 - 2006), waarin de ontwikkeling van waterstof technologie een belangrijke plaats heeft. Op wereldschaal coördineert het International Energy Agency (IEA) de samenwerking en kennisuitwisseling op het gebied van biologische waterstof productie door middel van het IEA Hydrogen Program, Task 15, Photobiological Hydrogen Production, welke recent is verlengd tot 2004. De huidige deelnemende landen zijn Japan, Noorwegen, Zweden, de VS, Canada en Nederland. Hongarije, Mexico en Portugal overwegen deelname aan Annex 15.

Conclusies en perspectieven

Om fotobiologisch geproduceerde waterstof tot een belangrijke duurzame energiedrager te kunnen maken dient de conversie van zonne-energie naar chemische energie te worden geoptimaliseerd. Dit kan worden nagestreefd door werk op drie gebieden t.w.: het biomoleculaire gebied, bijvoorbeeld door een oplossing te vinden voor de zuurstofinhibitie van de hydrogenase enzymen via verhoogde zuurstoftolerantie, de optimalisatie van lichtinvangst en transport, en het ontwerp van de fotobioreactor. De ontwikkeling van voordelige fotobioreactoren en de optimalisatie van de fotosynthetische efficiëntie zijn de belangrijkste R&D uitdagingen.

Bio-methane & Bio-hydrogen

This publication provides an overview of the state of the art and perspectives of microbiological processes for production of the renewable gaseous biofuels methane and hydrogen from biomass and/or sunlight. These processes for production of "bio-methane" and "bio-hydrogen" are expected to play an important role in a future energy infrastructure based on renewables along with other biomass processes, wind energy, photovoltaics and hydropower. The extensive information in this publication is intended for all those who are interested in new energy options to meet our future energy needs, especially replacing fossil energy carriers. The contents may especially be of interest for energy experts in industry and the utility sector, policymakers with an interest in (renewable) energy production and for researchers and students.

The core of this publication consists of four reviews written by researchers with active involvement in the field, affiliated with various R&D groups in the Netherlands. These chapters consecutively address the influence of infrastructure and energy policy on the role of bio-methane and bio-hydrogen in the future energy infrastructure, and the state of the art and perspectives of methane production through anaerobic digestion, biological hydrogen production via (dark) fermentation and photobiological hydrogen production. The essays provide a thorough review from a technological and scientific perspective and address the potential contribution to sustainable energy production, economics and the international status of development.
It furthermore provides insight into the available expertise in the Netherlands.

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