STUDY ON HYDROGEN FROM RENEWABLE RESOURCES IN THE EU

FINAL REPORT

A joint report by

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FCH JU Notice

The Fuel Cells and Hydrogen Joint Undertaking (FCH JU) is a unique public private partnership supporting research, technological development and demonstration (RTD) activities in fuel cell and hydrogen energy technologies in Europe. Its aim is to accelerate the market introduction of these technologies, realising their potential as an instrument in achieving a carbon-lean energy system.

Fuel cells, as an efficient conversion technology, and hydrogen, as a clean energy carrier, have a great potential to help fight carbon dioxide emissions, to reduce dependence on hydrocarbons and to contribute to economic growth. The objective of the FCH JU is to bring these benefits to Europeans through a concentrated effort from all sectors.

The three members of the FCH JU are the European Commission, fuel cell and hydrogen industries represented by the NEW Industry Grouping and the research community represented by Research Grouping N.ERGHY.

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ACRONYMS AND ABBREVIATIONS

AER	Absorption Enhanced Reforming
(aq)	aqueous
AnD	Anaerobic fermentation
AR	Assessment Report
ATR	Auto-thermal reforming
BMBF	Federal Ministry of Education and Research, Germany
°C	Degree Celsius
CAGR	Compound Annual Growth Rate
CAPEX	Capital Expenditure
CGH_2	Compressed gaseous hydrogen
CNG	Compressed Natural Gas
CSP	Concentrated Solar Power
DoE	US Department of Energy
EC	European Commission
EPFL	Ecole Polytechnique Fédérale de Lausanne
FAME	Fatty acid methyl ester
FC	Fuel Cell
FCEV	Fuel Cell Electric Vehicle
FCH JU	Fuel Cells and Hydrogen Joint Undertaking
FET	Future and Emerging Technologies Programme, European Commission
FICFB	Fast Indirect Circulating Fluidised Bed
(g)	gaseous
GHG	Greenhouse Gas
GT	Gas Turbine
GWP	Global warming potential
H2020	Horizon 2020 EU Research Framework
H_2	Hydrogen
HHV	Higher heating value
HT	High Temperature
HyF	Thermophilic hydrogen fermentation
HyS	Hybrid sulphur cycle
IA	Innovation Action
IEA	International Energy Agency
IPCC	Intergovernmental Panel on Climate Change
KIT	Karlsruhe Institute for Technology
(l)	liquid

LBST	Ludwig-Bölkow-Systemtechnik GmbH
LCA	Life-Cycle-Assessment
LHV	Lower Heating Value
LNG	Liquid Natural Gas
MSW	Municipal solid waste
N	Nitrogen
NG	Natural Gas
NREL	US National Renewable Energy Laboratory
OPEX	Operating Expenditure
PEC	Photo-Electrochemical Cell
PEM	Proton-Exchange-Membrane
PGM	Platinum group metals
PhF	Photo fermentation reactor
PM	Particulate Matter
PSA	Pressure-Swing Adsorption
PV	Photovoltaic
R&D	Research and Development
RIA	Research Innovation Action
SCWG	Supercritical Water gasification of biomass
SI	Specialization Index
SMR	Steam Methane Reforming
SRF	Short rotation forestry
StH	Solar-to-Hydrogen conversion
ThF	Thermal Fermentation reactor
TRL	Technology Readiness Level
UNECE	United Nations Economic Commission for Europe (UNECE)
Vol.	Volume
WE	Water electrolysis
WIPO	World Intellectual Property Organization
WtT	Well-to-Tank
WtW	Well-to-Wheel
yr	Year

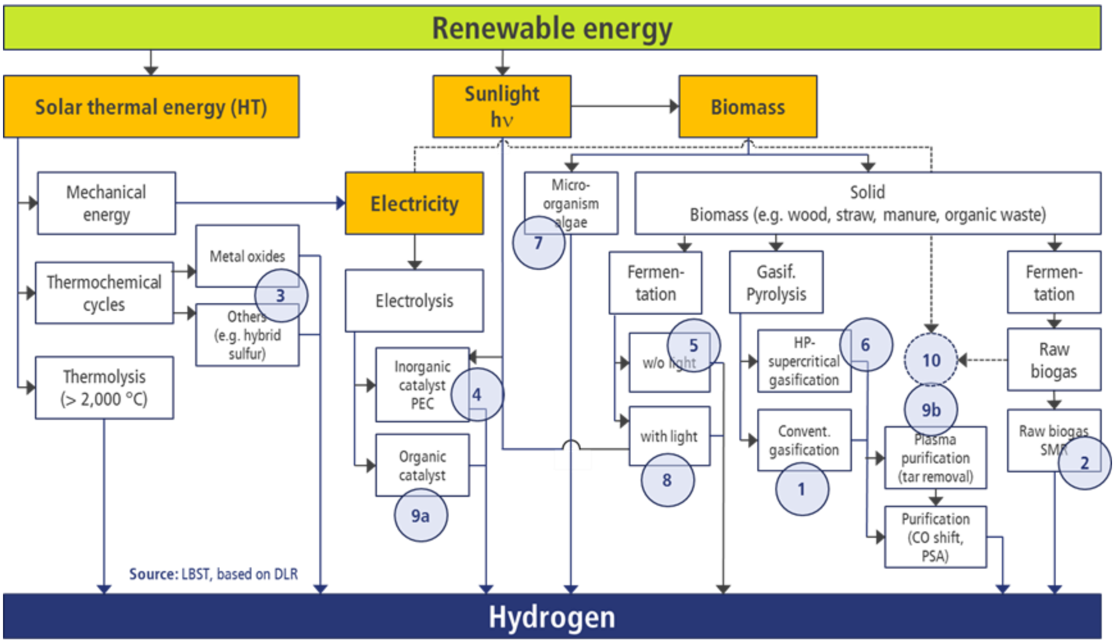
EXECUTIVE SUMMARY

Hydrogen can be produced from a broad range of renewable energy sources, acting as a unique energy hub providing low or zero emission energy to all energy consuming sectors. Technically and efficiently producing hydrogen from renewable sources is a key enabler for these developments.

Traditionally, hydrogen has been produced from fossil sources by steam methane reforming of natural gas. At present, the technology of choice to produce renewable 'green' hydrogen is water electrolysis using renewable electricity. FCH JU has been supporting research and development of electrolyser technology and application projects, aiming to increase the energy efficiency of electrolytic hydrogen production from renewable sources and to reduce costs.

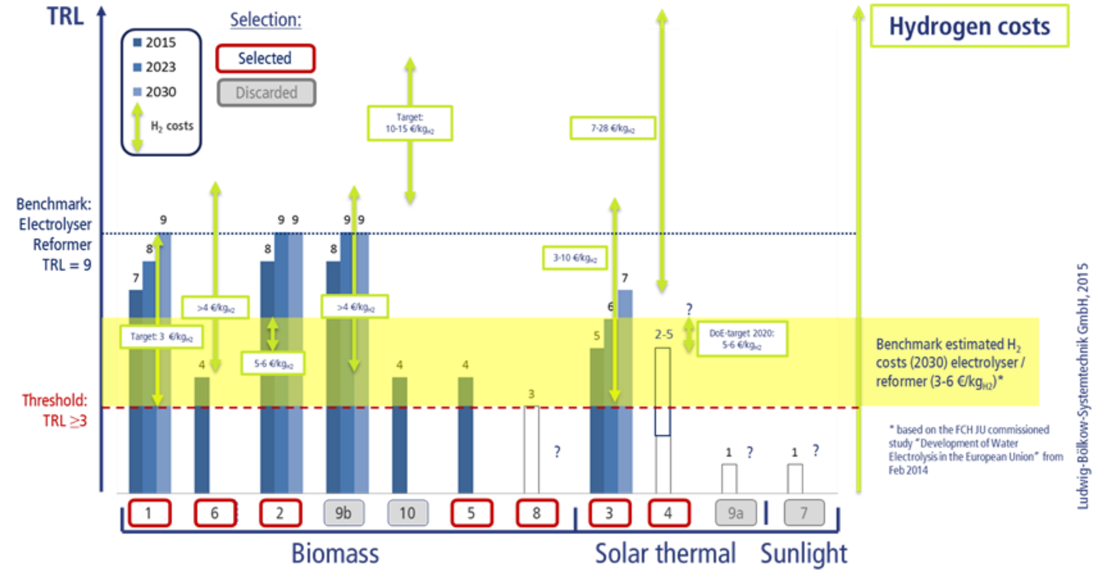
This study complements these activities by focusing on renewable hydrogen generation other than electrolysis. In this report, these alternative hydrogen generation technologies are described, characterized by their technical capabilities, maturity, and economic performance, and assessed for their future potential.

A methodology has been devised to first identify and structure a set of relevant green hydrogen pathways (eleven pathways depicted in the figure below), analyse them at a level of detail allowing a selection of those technologies which fit into and promise early commercialization in the framework of FCH 2 JU's funding program. These originally proposed eleven pathways use solar thermal energy, sunlight or biomass as major energy input.



Originally proposed eleven Green Hydrogen Pathways

The selection process was based on a set of key performance indicators and criteria agreed among the study team as well as representatives of the project's bodies, i.e. the FCH JU, the European Commission (DG RTD, DG-ENER) and the project Steering Committee. Additionally, a bibliometric research was undertaken to measure the intensity of research and patenting for each pathway in Europe as compared to other regions. The result of this first assessment round is shown in the figure below.



TRL and cost based evaluation of originally proposed Green Hydrogen Pathways

The figure showcases the expected Technology Readiness Level TRL (FCH JU requested a TRL ≥ 3 as major criterion) of the 11 technologies assessed and benchmark them against hydrogen production costs of water electrolysis using renewable electricity (≈4-6 €/kg$_{H2}$) and steam methane reforming[1] (≈3-5 €/kg$_{H2}$). The selected hydrogen production technologies clearly represent pathways applying process technologies which as of today have already proven (near to) commercial viability (pathways (1) and (2)) or which have already undergone extensive research in past or ongoing programs in Europe or internationally providing evidence of their general promise for early commercialization (i.e. target costs being within the benchmark range).

Pathways which have also shown a sound potential for commercialization but have not been selected are plasma technology based. The decision was based on the fact that these pathways do not target hydrogen as primary product but instead depend on the potential market value of their primary product or service, be it to dispose of critical waste or to produce other high value products such as speciality graphite. These pathways are advised to search for funding from other EU programs.

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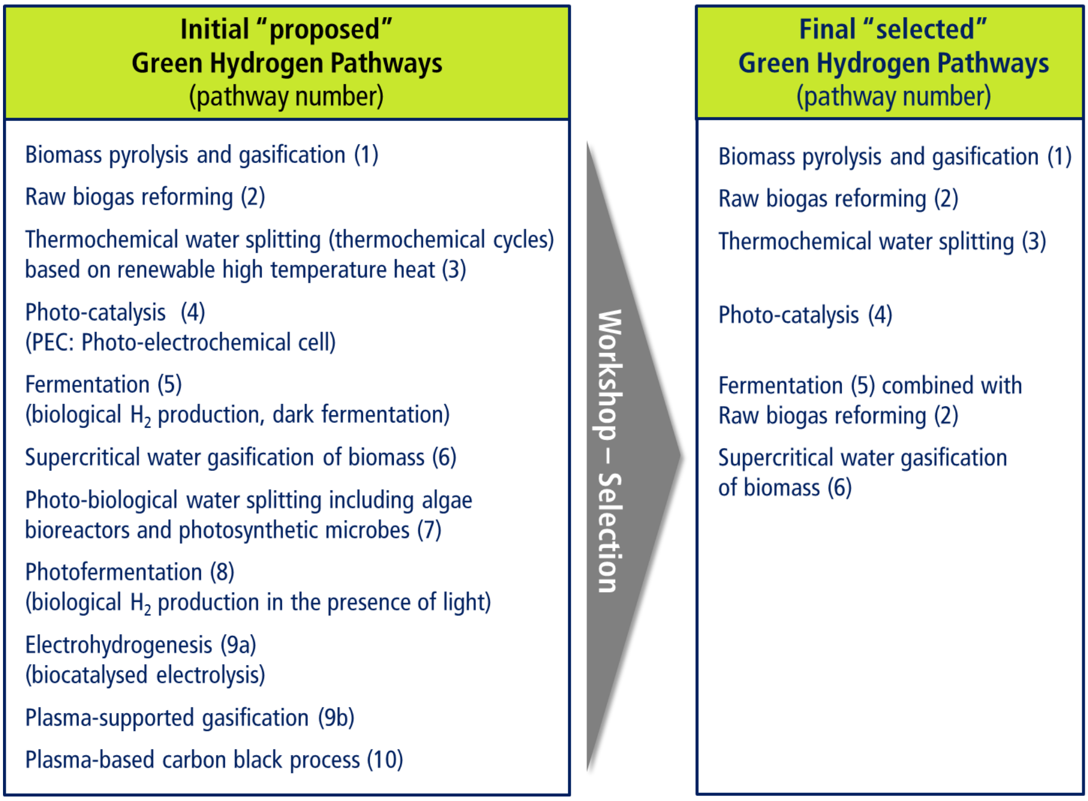
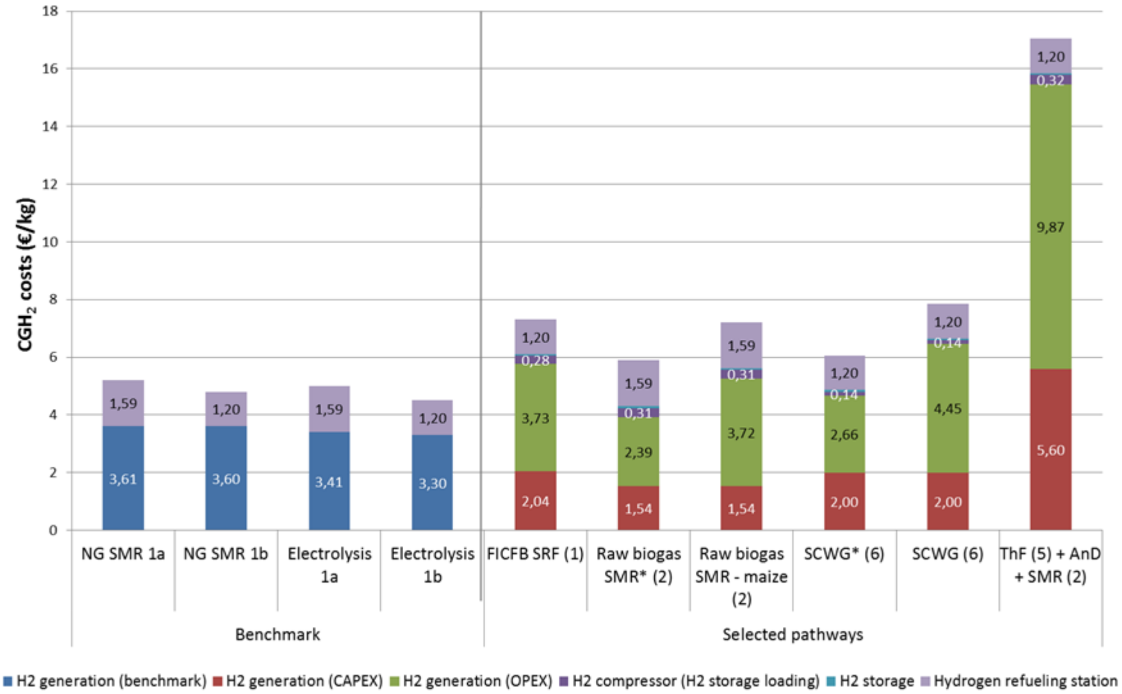
[1] Steam methane reforming is deliberately used as a benchmark, even though it is does not produce 'green' hydrogen.



Selection of six out eleven originally proposed Green Hydrogen Pathways

In the second part of this study, the six selected pathways then undergo a detailed techno-economic analysis, identifying a set of technical, economic, or other gaps which are translated into a structured list of development goals that may enter upcoming FCH 2 JU calls for funding.

The detailed analysis has focused on hydrogen production costs, energy use (being an indicator for the sustainable use of renewable energies), and greenhouse gas emissions as major criteria, all benchmarked against water electrolysis using renewable electricity and steam reforming of methane. The year 2030 was chosen as a time horizon as it clearly represents the market relevant perspective of the technologies selected. As can be seen from the figure below, hydrogen production costs of all but one local hydrogen production pathways lie within the same ballpark as the benchmarks. The outlier is the combination of dark fermentation of wet biomass (5) with anaerobic digestion (2) which is posed to provide hydrogen at more than three times the benchmark costs (for details see chapter 5.3.1).

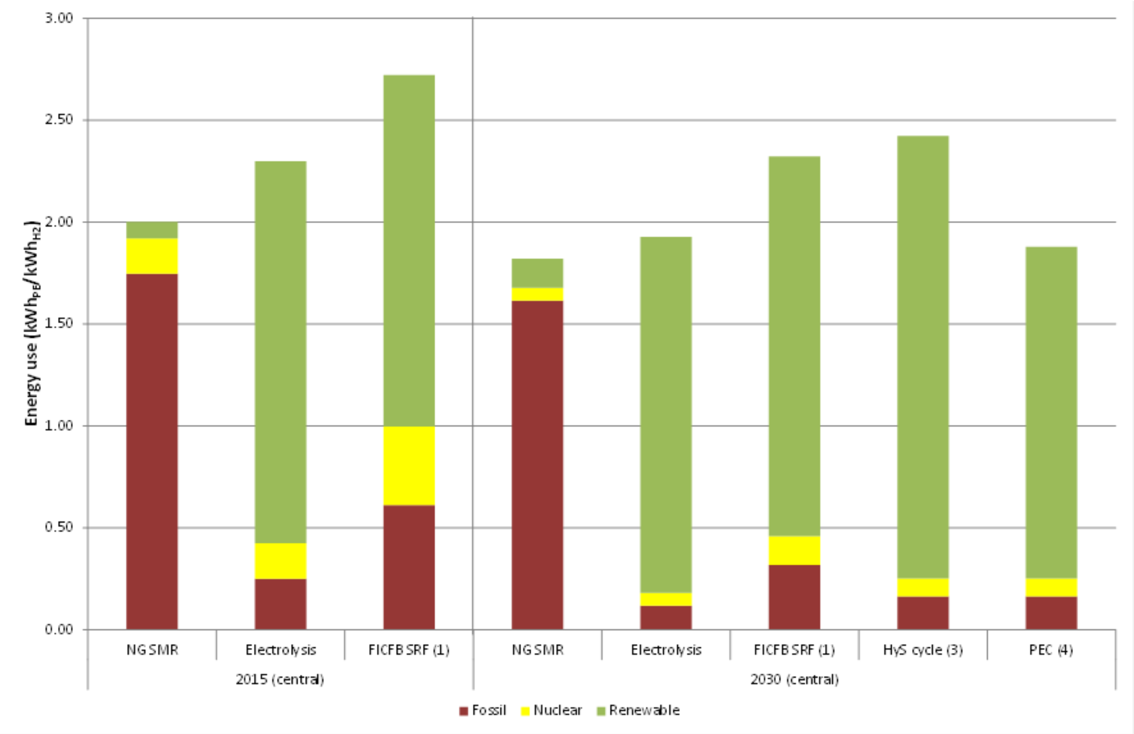


* including revenue for bio-waste/sewage sludge treatment

From left to right: NG SMR = Natural Gas Steam Methane Reforming; FICFB SRF = Fast Indirect Circulating Fluidised Bed Short Rotation Forestry; SCWG = Supercritical Water Gasification; ThF = Thermal Fermentation Reactor; AnD = Anaerobic Fermentation; SMR = Steam Methane Reforming

Well-to-tank local specific hydrogen production costs for selected green hydrogen pathways (time horizon: 2030)

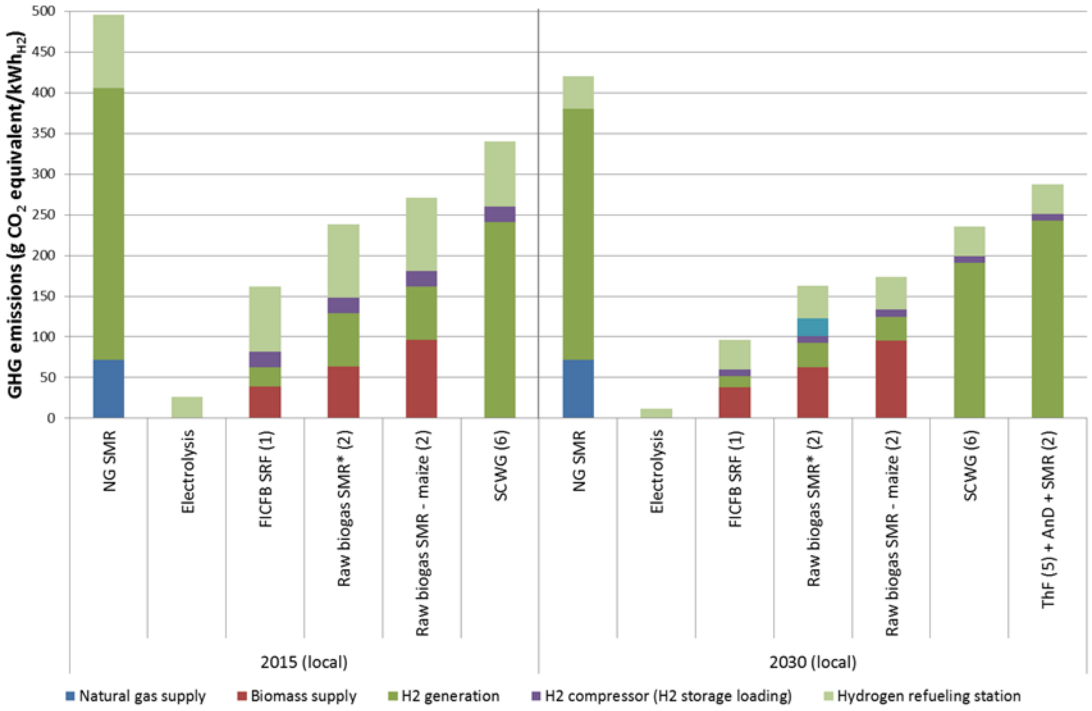
Concerning specific primary energy use, all pathways at all scales (local, semi-central and central) are within the range of the benchmark consumption, the only exception being the combination of dark fermentation of wet biomass (5) with anaerobic digestion (2) pathway for local hydrogen production with about triple the specific energy use than the benchmark (for more details refer to chapter 5.3). However, for local production scale, also all other green hydrogen pathways are still somewhat more primary energy intense than the benchmark.



No data from existing demonstration plants are available for the thermochemical water splitting (HyS cycle) (3) and the photo-catalysis (PEC) (4) pathways for 2015

Well-to-tank central specific primary energy use for hydrogen production for selected green hydrogen pathways (time horizon: 2030)

Concerning specific greenhouse gas emissions, it is rather striking to observe, that except for the sulphur-based solar thermochemical water splitting (3) and the PEC (4) pathways all other, i.e. the biomass based pathways generate significant emission levels when compared to water electrolysis, being positioned somewhere between renewable electricity based water electrolysis and fossil energy based steam methane reforming (see figure below). The reason lies in the specific emissions related to biomass provision and conditioning. Only the solar energy based pathways offer similar GHG reduction potentials to hydrogen from water electrolysis. In perspective, the fossil energy share of the pathways biomass gasification and pyrolysis (1), raw biogas reforming (2), and supercritical water gasification (6), which we have assumed for this study can be further reduced in the future. The reason is that auxiliary electricity from EU's electricity mix and external heat provided by natural gas can progressively be substituted by electricity and heat from renewable energy sources, i.e. renewable electricity or biomass, even though not to the level of hydrogen electrolysis from green electricity.



* including revenue for bio-waste/sewage sludge treatment

Well-to-tank local specific GHG emissions for hydrogen production for selected green hydrogen pathways (time horizon: 2030)

The results of the gaps analysis reflect these detailed findings and are graphically condensed in the table and figure below.

The table presents the gaps analysis summary benchmarking the key performance indicators (KPI) of the six selected pathways against water electrolysis (WE) and steam methane reforming (SMR) for the reference year 2030.

For the benchmark the following important assumptions need to be understood:

- The main feedstock of the six selected green hydrogen pathways is 100% renewable energy to allow for a like-for-like comparison of renewable based hydrogen pathways.
- The summary table contains analysis results for idealized assumptions and do not reflect real plant operation, for which assumptions can vary for all processes involved, with regional or site specific conditions to be taken into consideration (e.g. grid mix, varying energy prices, solar irradiation, availability of land etc.).
- Cost data for the benchmark technologies (WE, SMR in 2030) have been taken from [E4Tech & EE 2014]. In contrast to the cost data for the six

selected green hydrogen pathways assumed for this study, [E4Tech & EE 2014] also applied other than 100% renewable energy sources, e.g. electricity costs for WE in [E4Tech & EE 2014] are based on market prices for industrial customers in Germany in 2030.

Summary of gaps analysis – Comparison of key performance indicators (KPIs) of selected pathways to benchmark technologies

Green Hydrogen Pathway (GHyP) / Key Performance Indicator (KPI)	Biomass gasification and pyrolysis (1)	Steam reforming of raw biogas (2)	Thermochemical water splitting (3)	Photo-Catalysis (PEC: Photo-electrochemical cell) (4)	Supercritical water gasification of biomass (6)	Combined dark fermentation (5) and anaerobic digestion with downstream (2)
TRL	0	0	-	--	--	---
Feedstock availability compared to WE	-	-	0	0	-	-
H_2 costs	-	-	-	-	-	--
GHG compared to WE	-	-	0	0	--	--
GHG compared to SMR	++	+	++	++	+	0
Land use compared to WE	--	--	++	0	--	--
Land use compared to WE when using biomass residue	++	++	n. a.	n. a.	++	++
Waste to energy	++	++	n. a.	n. a.	++	++

++	much better than benchmark (SMR and water electrolysis)
+	better than benchmark (SMR and water electrolysis)
0	similar performance as benchmark
-	worse than benchmark
--	much worse than benchmark

WE: water electrolysis using renewable electricity (solar); SMR: steam methane reforming; n. a.: not applicable

The graph below indicates a development path and roadmap for green hydrogen pathway technologies, showing the selected six pathways along a staged path in the following four development dimensions:

(a) development period (2015…2030),

(b) TRL on the way to commercialization (1…9),

(c) GHG-emissions (in g_{CO2}/kWh_{H2}), and

(d) primary energy input (solar, biomass based).

The graph represents best case data, e.g. for the pathways raw biogas reforming (2) and supercritical water gasification (6) revenues for bio-waste treatment have been considered in this figure. For water electrolysis and natural gas steam reforming also best case data[2] are presented in this graph.

For the six selected pathways, fossil based auxiliary can be substituted by renewable energies in the long-term. This would lower the GHG-emissions, especially for the pathway of supercritical water gasification of biomass (6), combined dark fermentation (5) and anaerobic digestions with SMR (2) and raw biogas reforming (2).

In this graph the raw biogas reforming (2) and biomass pyrolysis and gasification (1) processes stand out as being closest to commercialization. Yet, if considering the other evaluation dimensions such as greenhouse gas emissions, hydrogen production costs, biomass diversity (dry and wet biomass, waste or sewage sludge etc.), or the potential process scale, also other technologies such as the sulphur-based solar thermochemical water splitting (3) and PEC (4) pathways hold some promise.

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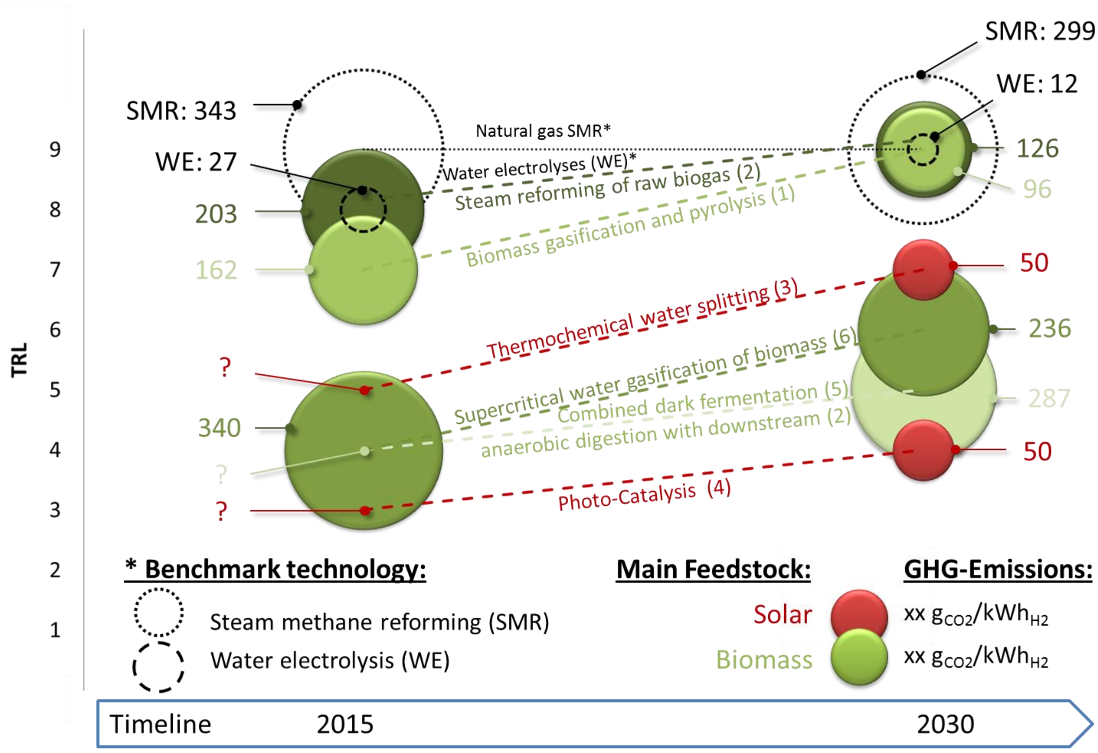
[2] Lowest GHG-emission of benchmark technologies have been assumed by 2030 for local H_2 production via water electrolysis and central H_2 production via natural gas SMR.



For 2015 no GHG-emission data are available for the thermochemical water splitting (3), photo-catalysis (4) and combined dark fermentation (5) and anaerobic digestion with downstream (2) pathways.

Staged Green Hydrogen Pathway development roadmap from 2015 to 2030

The results of the gaps analysis have been translated into a structured input for the preparation of upcoming FCH 2 JU calls for proposals. For all pathways, remaining technical or economic challenges have been pinpointed and recommendations provided as input for further and more detailed discussion with the FCH 2 JU stakeholders to develop corresponding call texts. Further detailed information is given in chapter 6.

1 Introduction

Hydrogen holds a strong potential for becoming a dominant energy carrier in all energy sectors:

- It is currently being introduced as a transportation fuel for fuel cell electric vehicles including cars, buses, and trucks.
- Fuel cell electric drives are well suited for material handling and logistics vehicles (forklifts, airport logistics etc.) as well as for other special purpose vehicles.
- Hydrogen fuel cell technology can be used in stationary applications e.g. in combined heat and power (CHP) plants or in fuel cell electric generators for uninterrupted power supply.
- It is an important feedstock for industry.
- It can be blended with natural gas with the potential to eventually substitute it in many applications.

Hydrogen can, in particular, be produced from a broad range of renewable energy sources, acting as a unique energy hub providing low or zero emission energy to all energy consuming sectors. Technically and efficiently producing hydrogen from renewable sources is essential for enabling these developments.

At present, electrolysis is the technology of choice for converting renewable electricity into hydrogen. Several large scale electrolyser plants are being piloted in international projects, most of them in Europe. FCH JU has been supporting research and development of electrolyser technology and application projects, aiming to increase the energy efficiency of electrolytic hydrogen production from renewable sources and to reduce costs. In a previous study, the state of the art for electrolysers specifically in view of their expected large scale commercialization has been examined and areas for future FCH JU calls have been identified.

This study complements these activities by focusing on renewable hydrogen generation other than electrolysis. In this report, these alternative hydrogen generation technologies are described, characterized by their technical capabilities, maturity, and economic performance, and assessed for their future potential. Based on the overall assessment, the most relevant technologies will then be subject to a more detailed techno-economic analysis.

The approach chosen to achieve these assessment goals is depicted in Figure 1.

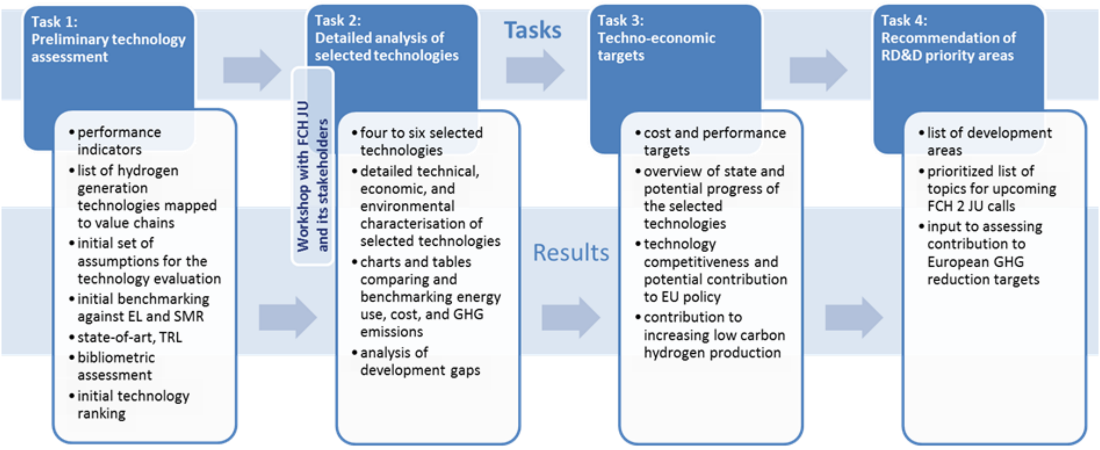


Figure 1: Assessment approach for the analysis of green hydrogen pathways other than electrolysis

The first part of this report essentially covers Task 1 and the subsequent technology selection process. Chapter 2 structures the hydrogen production pathways and presents them in detail. Chapter 3 complements the analysis in chapter 2 with the findings from a bibliometric analysis, comprising information on scientific publications as well as on patenting activity in Europe and worldwide in the fields relevant to the green hydrogen pathways studied here. Chapter 4 provides the information on the six pathways eventually studied in further detail, presenting the methodology and criteria for the pathway selection.

Part 2 of this report covers the detailed analysis of the selected pathways. Chapter 5 documents the findings from the detailed techno-economic analysis, following a key performance indicator list. The results provide the basis for the analysis of technology and development (chapter 6), identifying actions required to move the technologies towards commercial viability in the framework of FCH 2 JU, i.e. by 2023. In chapter 7, the findings of the gaps analysis are used to suggest key elements for further specific research and funding needs to progress the six pathways within the coming FCH 2 JU calls, specifically identifying priorities for research and innovation actions (RIAs) and innovation actions (IAs).

2 Green Hydrogen Pathways identified

2.1 Methodology

The ambition of this task was to identify those alternative green hydrogen pathways with the best chance to arrive at a commercial state-of-development within the duration of the FCH-JU Phase II program, i.e. by about 2020.

For that purpose, the suggested Green Hydrogen Pathways are broadly characterised by the following criteria:

- Technology Readiness Level (TRL) (1-9) (see Table 1),
- Production capacity of a typical installation,
- Feedstock (biomass / solar thermal / sunlight).

Definition of *green hydrogen*

The title of the Green Hydrogen Pathway study reflects the understanding of FCH JU to only analyse hydrogen production pathways using renewable energy input. In the case of green hydrogen produced by water electrolysis, the electricity is assumed to be solely based on renewable electricity, i.e. also excluding CO_2-free electricity such as nuclear energy. In the case of green hydrogen from other sources, which is less specific concerning the energy source, this study follows the definition by the EU Renewable Energy Directive (RED) which reads as follows:

…'energy from renewable sources' means energy from renewable non-fossil sources, namely wind, solar, aerothermal, geothermal, hydrothermal and ocean energy, hydropower, biomass, landfill gas, sewage treatment plant gas and biogases…

…'Biomass' means the biodegradable fraction of products, waste and residues from biological origin from agriculture (including vegetal and animal substances), forestry and related industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal waste… [RED 2009]

Technology Readiness Level (TRL)

The classification of the TRL has originally been developed for the NASA space program to principally classify the state of technology development. For its application here it should be noted that the TRL definition by NASA does not reflect any market or commercialisation readiness.

For the purpose of this study, FCH JU has defined a minimum TRL threshold of 3, i.e. technologies under scrutiny should have a TRL above 3. However, for completeness, we also list processes with lower TRL including a brief description.

Table 1: Technology Readiness Level (TRL) as defined by NASA

TRL	Description
1	Basic principles observed
2	Technology concept formulated
3	Experimental proof of concept
4	Technology validated in lab
5	Technology validated in relevant environment (industrially relevant environment in the case of key enabling technologies)
6	Technology demonstrated in relevant environment (industrially relevant environment in the case of key enabling technologies)
7	System prototype demonstration in operational environment
8	System complete and qualified
9	Actual system proven in operational environment (competitive manufacturing in the case of key enabling technologies; or in space)

Source: [FCH 2 JU 2014]

Production capacity

To compare the pathways from the perspective of process scale, FCH JU had suggested to characterise any of the given pathways by plant size and hence, regional applicability. This criterion also allows to later benchmark the green hydrogen pathways against the electrolysis based pathways which had been assessed for the same settings. Three hydrogen production value chain scales had been defined by FCH JU:

Table 2: Production scales and regional applicability of value chains

Type	H_2 production quantity
Local	0.2…4 t/day (e.g. onsite a hydrogen refuelling station)
Semi-central	4…20 t/day
Central	>20 t/day

Feedstock

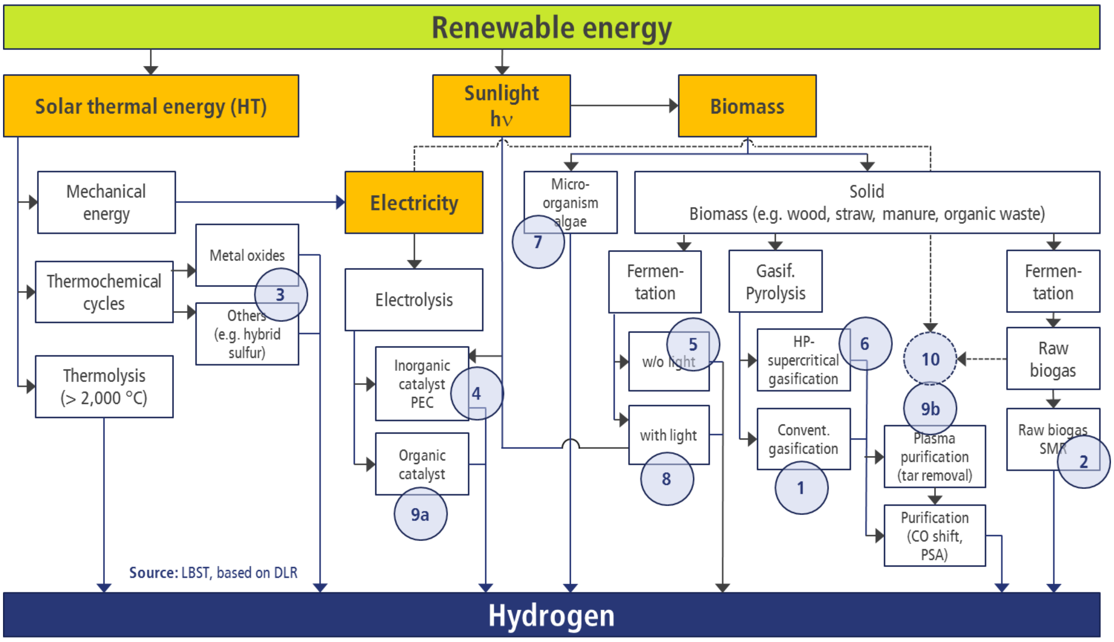
Renewable energy sources for Green Hydrogen Pathways discussed are biomass and solar energy. We further differentiate solar energy using processes into those using solar thermal heat and those directly using sunlight i.e. photonic energy.

Table 3 summarises the Green Hydrogen Pathways identified, also indicating the corresponding TRL, applicability, and main source of feedstock.

Table 3: Matrix of Green Hydrogen Pathways for the three value chains

No.	Green Hydrogen Pathway	TRL 2015	TRL 2023	TRL 2030	Applicability Local	Applicability Semi-central	Applicability Central	Feedstock Biomass	Feedstock Solar thermal	Feedstock Sunlight
1	Biomass pyrolysis and gasification	7	8	9		X	X	X		
2	Raw biogas reforming	8	9	9	X			X		
3	Thermochemical water splitting (thermochemical cycles) based on renewable high temperature heat	5	6	7	X	X	X		X	
4	Photo-catalysis (PEC: Photo-electrochemical cell)	3			X	X	X		X	
5	Fermentation (biological H_2 production, dark fermentation)	4			X	X		X		
6	Supercritical water gasification of biomass	4			X	X	X	X		
7	Photo-biological water splitting including algae bioreactors and photosynthetic microbes	1								X
8	Photofermentation (biological H_2 production in the presence of light)	1			X	X		X		
9a	Electrohydrogenesis (biocatalysed electrolysis)	1							X	
9b	Plasma-supported gasification	8	9	9		X	X	X		
10	Plasma-based carbon black process	4				X		X		

Figure 2 shows the pathways analysed in an overview chart including relevant sub-processes, pathway numbering corresponding to Table 3.



Source: LBST, based on DLR

Figure 2: Overview – Green Hydrogen Pathway

Additional criteria have been defined for a more detailed assessment. A set of criteria has been developed to better understand the pathways from a technical, environmental, and economic perspective. Accordingly, in this chapter each process description of a pathway is structured as follows:

- Process description
- Resource use
- Output
- Waste emissions
- Relevant projects
- Relevant stakeholders
- Preliminary assessment for further discussion and down-selection, see chapter 4.

2.2 Biomass Pyrolysis and Gasification (1)

a) Process description

Solid lignocellulosic biomass such as wood chips and straw is used as feedstock for biomass pyrolysis and gasification. In the first step the feedstock is converted to coke, methanol, and primary gases via pyrolysis. In the next step the methanol and primary gases are converted to a gas mixture mainly consisting of CO, H_2, CO_2, and CH_4 via gasification (some manufacture call this step 'reforming'). The two steps pyrolysis and gasification can be carried out in one reactor or in separate reactors.

It has to be distinguished between directly heated gasifiers and indirectly heated gasifiers:

- Directly heated gasifier: Either oxygen (in oxygen blown gasifier) or air (in air blown gasifier) is used as gasification agent. No external heat is required. The heat for the endothermal pyrolysis and gasification reactions is supplied by exothermal reactions inside the gasification reactor.
- Indirectly heated gasifier: Water (as steam) is used as gasification agent. External heat is required to meet the heat requirement for the endothermal pyrolysis and gasification reactions.

If air is used as gasification agent a high share of nitrogen (N_2) will be found in the product gas stream leading to a low hydrogen recovery in the downstream pressure swing adsorption (PSA) plant. Therefore, pure oxygen or steam has to be used as gasification agent if pure hydrogen is the desired final product. Air blown gasifiers generally are used for stationary electricity and heat generation where the product gas leaving the gasifier is directly fed into a gas engine, gas turbine, or (high temperature) fuel cell. The use of pure oxygen requires an air separation plant, which is not required in indirectly heated gasifiers using water (as steam) as a gasification agent.

Indirectly heated gasifiers provide a synthesis gas with higher hydrogen content than directly heated gasifiers leading to the highest hydrogen recovery after CO shift conversion[3] in the downstream PSA plant. The challenging issue is the introduction of the heat into the gasification reactor. In case of the process developed by Battelle Columbus Laboratory (BCL), now called "Rentech-SilvaGas Biomass Gasification Process", and the gasification plant in Güssing from 'Güssing Renewable Energy GmbH', hot sand is used as heat carrier.

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[3] The CO shift conversion or water-gas shift reaction (WGSR) denotes the reaction of carbon monoxide and water vapor to form carbon dioxide and hydrogen: $CO + H_2O \leftrightarrow CO_2 + H_2$

The "Rentech-SilvaGas Biomass Gasification Process" is based on an indirectly heated "Fast Internally Circulating Fluidized Bed" (FICFB) gasifier using water as a gasification agent. This type of gasifier had been successfully operated in Burlington, Vermont (USA) for over two years in a project for the Department of Energy (DoE) and in cooperation with the National Renewable Energy Laboratory (NREL) and the Battelle Columbus Laboratory [Rentech 2014].

The gasification plant in Güssing, Austria also employs an FICFB gasifier and uses water as gasification agent. The fluidized bed is divided into two zones, a gasification and a combustion zone. Between the two zones a circulating loop of bed material acts as heat carrier.

The Güssing gasification plant has been in operation since 2002 with more than 58,000 operating hours so far. Until now, the synthesis gas leaving the gasifier is mainly used for electricity and heat generation, a smaller part is used for experiments, e.g. further processing hydrogen to synthetic methane. To provide pure hydrogen of high quality, the synthesis gas leaving the gasifier needs to be purified via CO shift and PSA using commercially available technology. The gasification technology is close to commercialisation.

Biomass pyrolysis and gasification processes are adoptable to local, semi-central, and central hydrogen production.

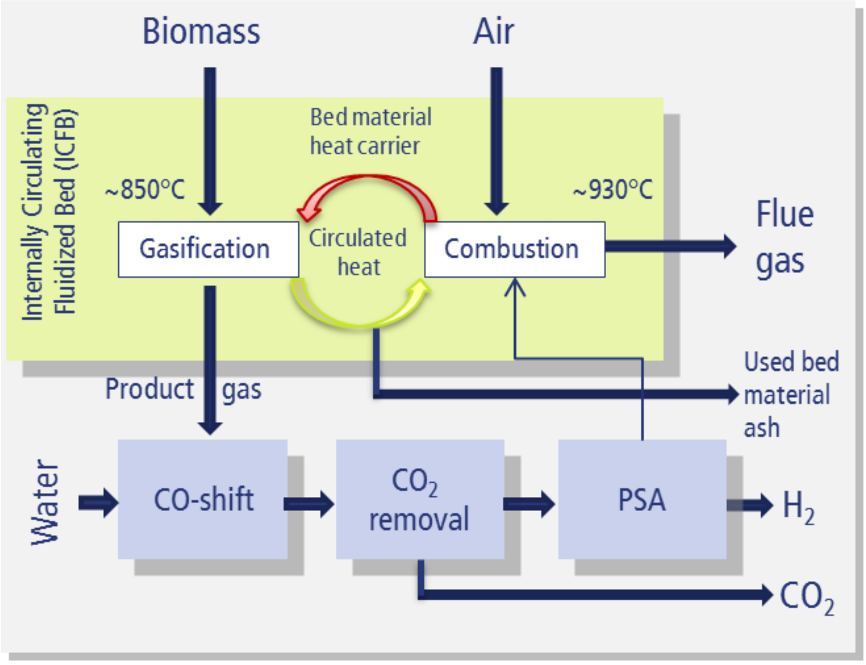

Figure 3: **Basic process diagram of a biomass gasification plant**

Major energy and material inputs to the process are:

- Solid biomass as feedstock,
- Electricity, primarily for the compression of syngas for the PSA; a smaller share is also needed to transport the feedstock into the reactor
- oxygen or water as a gasification agent, and
- fatty acid methyl esters (FAME) used as a washing agent for tar removal.

b) Resource use

No critical resources[4] are used.

c) Output

The main output product is hydrogen at a purity level of 99.8% which is produced with high efficiency.

d) Waste emissions

The following waste products[5] from a typical gasifier plant need to be considered and taken care of:

- Used bed material
- Ash
- Flue gas

Flue gas can partly be used for combustion; otherwise it is emitted. Ash should be circulated to improve the soils while used bed materials must be deposited.

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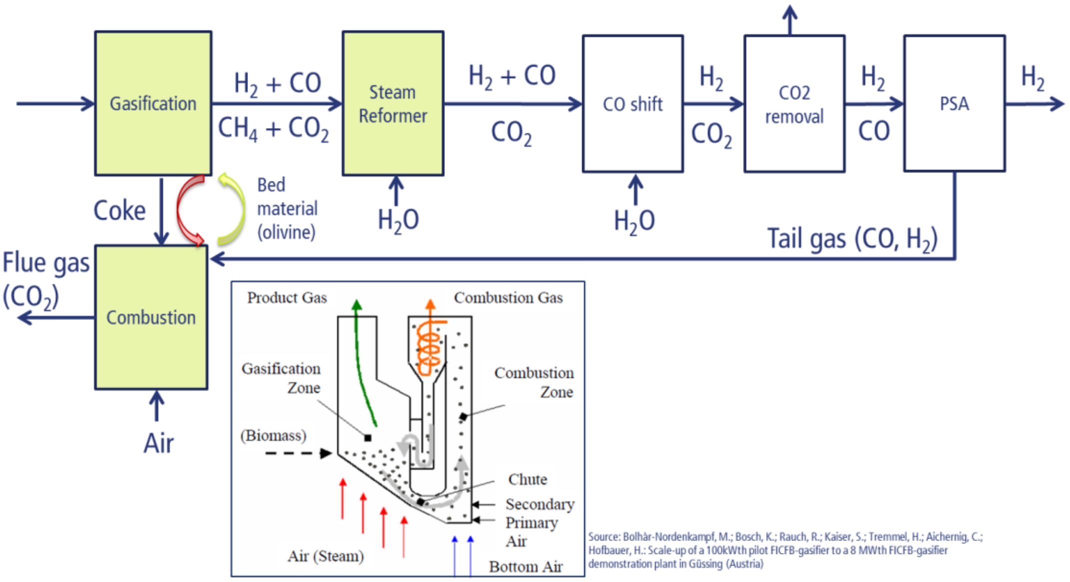
[4] 'Critical resources' are those with globally limited availability such as platinum group metals (PGM) or rare earth oxides (REO).

[5] The emitted biomass-derived CO_2 is carbon-neutral and hence not listed here.



Source: Bolhàr-Nordenkampf, M.; Bosch, K.; Rauch, R.; Kaiser, S.; Tremmel, H.; Aichernig, C.; Hofbauer, H.: Scale-up of a 100kWth pilot FICFB-gasifier to a 8 MWth FICFB-gasifier demonstration plant in Güssing (Austria)

Figure 4: Detailed view to the process flow and of a process reaction chamber

e) Relevant Projects

- In 2014, Güssing Renewable Energy and Edison Power Co. Ltd. signed a licence agreement for exclusive rights on their FICFB gasification technology for Japan. Within this partnership a first demonstration plant is under construction (2014/2015), which is intended to transfer know-how to Edison Power Co. Ltd. and to demonstrate the reliability of the technology to potential public and private customers in Japan. The first commercial plant with a power output of 1 MW_{el} will be constructed in Ibaragi, Japan, in 2015.
- The Zentrum für Sonnenenergie- und Wasserstoff-Forschung (ZSW) Baden-Württemberg in Germany has developed the so-called „Absorption Enhanced Reforming“ (AER) process which has also been tested at the biomass gasification plant in Güssing in Austria. In the AER process, biomass is gasified with steam and the resulting CO_2 is directly separated via a limestone-based, chemically active bed material that is used as a CO_2 absorption agent. The AER process produces a synthesis gas with a high hydrogen content which can be processed further into pure hydrogen via downstream CO-shift and pressure swing adsorption (PSA).
- BioH2-4Refineries: Within the Austrian Funding Scheme “Energies 2020” the concept is integrated into the process environment of a refinery with the aim to reduce the carbon footprint of the refinery by means of biomass produced hydrogen.

- UNIfHY is a 3 year collaborative research project (FP7) started in September 2012 with a total budget of €3.3M (€2.2M EC Grant, €1.1M own funding from project partners). The UNIfHY consortium includes 7 partners (4 from industry, 3 from research) from 4 European Member States (France, Germany, Italy, and the Netherlands). In detail, the project aims at the development of a steam gasification process coupled to a syngas purification plant in order to produce pure hydrogen from biomass. Secondary targets are to increase the process well-to-tank efficiency and contribute to a sustainable energy portfolio in general, exploiting results obtained from past EU R&D projects on hot gas catalytic conditioning. The project is based on well-proven and reliable plant components as well as on well-established processes (UNIQUE coupled gasification and hot gas cleaning and conditioning system, water-gas shift system, and PSA). Thus, the UNIfHY concept is targeting reliability targets of up to 20 years durability at an availability of >95%. The overall scope of UNIfHY is the integration of these components to obtain a continuous process for pure hydrogen production from biomass (description based on http://www.unifhy.eu/).

f) Relevant Stakeholders

The following non-exhaustive list of key stakeholders contains representatives from industry and research:

- Güssing Renewable Energy GmbH, Austria [AER]
- Renewable Power Technologies Umwelt Technik GmbH (Reptoec), Austria [BioH2_4Refineries, AER]
- Technical University of Vienna, Austria [BioH2_4Refineries, AER]
- OMV, Austria [BioH2_4Refineries]
- Zentrum für Sonnenenergie- und Wasserstoff-Forschung (ZSW), Renewable Fuels and Processes department Stuttgart, Germany [AER]
- Rentech, USA
- Pall Filter Systems GmbH Werk Schumacher, Germany [UnifHy]
- CIRPS (Inter-university Research Centre for Sustainable Development based at "Sapienza" University of Rome), Italy [UnifHy]
- Engineering, Procurement & Construction (EPC), Germany [UnifHy]
- HyGear, The Netherlands [UnifHy]
- University of Strassbourg (Unistra), France [UnifHy]

- ENEA, Italy
- Air Liquide, France

g) Assessment

The biomass gasification has been developed from demonstration to pilot scale for many years. First pilot plants for industrial applications are currently under development. Large scale demonstration units for industrial customers could follow in the coming years. The TRL for this pathway is estimated up to level 7. Depending on interest in and support for the erection of demonstration units in Europe, TRL 9 should be reached within the next 10-15 years. The biomass gasification process is applicable for local, semi-central and central hydrogen production

Hydrogen production from biomass gasification has the following strengths:

- High maturity of the biomass gasification process (e.g. many years of successful operation, in Güssing, Austria)
- Actual target applications for industrial customers under development, e.g. use of biomass-derived H_2 in refineries (counts towards biofuels target)

Major challenges include:

- Consistent quality of biomass required for a stable gasification process
- Feedstock impact on product gas quality (e.g. tar content)
- Feedstock availability (biomass)

2.3 Raw Biogas Reforming (2)

a) Process description

Hydrogen production from natural gas via steam reforming of methane is a fully mature technology and can also be applied to biogas. If crude biogas (without CO_2 removal) is used as feedstock, the different gas composition can influence the performance of the steam reforming process. To avoid this, the conventional method is to remove CO_2 from the raw biogas stream by pressure swing adsorption (PSA) to feed the steam reformer with pure methane.

As indicated above, raw biogas reforming plants do not necessarily require natural gas grade input. This is an advantage, if the steam methane reformer (SMR) is co-located with the biogas plant because the upgrading stage via PSA can be omitted (see Figure 5).However, if the SMR is not located at the site of the biogas plant, upgrading of the raw biogas to natural gas (removal of CO_2) is required before injecting the methane (CH_4) into the natural gas grid.

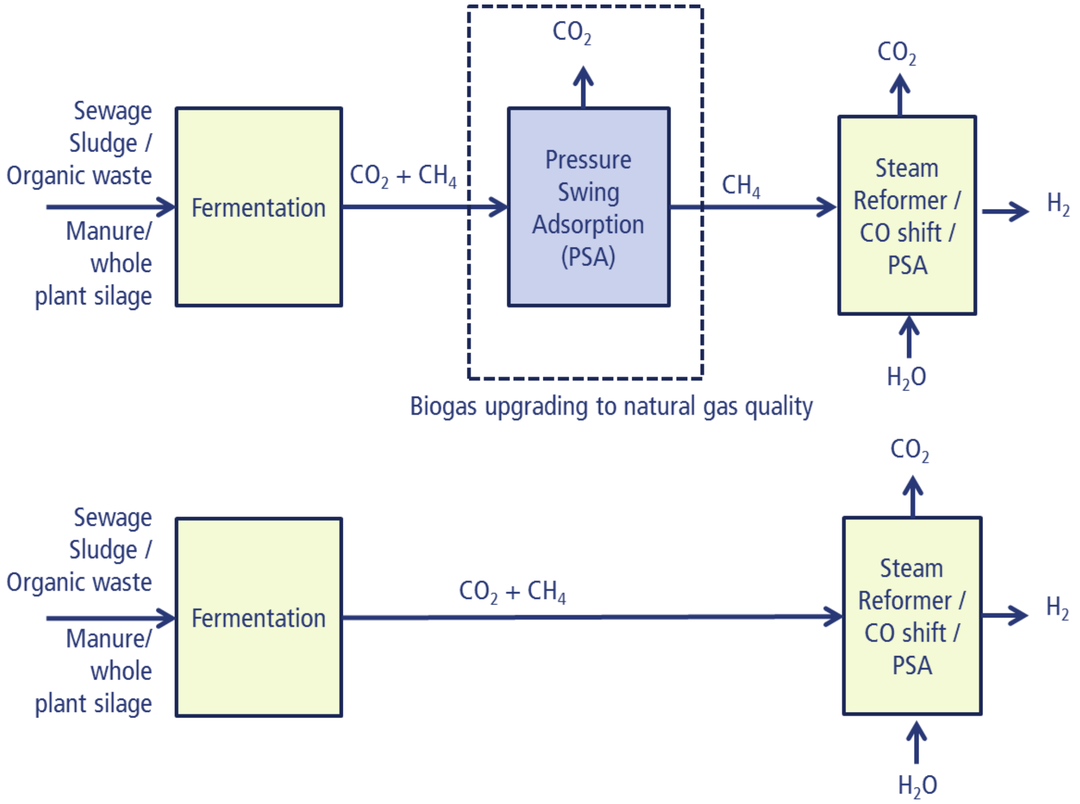


Figure 5: **Upper diagram: raw biogas is purified in a PSAand pure methane gas is fed into the steam reformer;**
Lower diagram: direct reforming of biogas

The mining university Freiberg has investigated the influence of the gas composition on the efficiency and operating conditions of a conventional steam reforming process with the goal to avoid adding a separate CO_2-removal step via PSA.

For that purpose, a small steam reforming plant has been operated with both natural gas and biogas feeds. The tests have been carried out with different biogas compositions, i.e. different CO_2 content of the biogas. The results are summarised in Table 4.

Table 4: **Syngas composition of steam reformer and CO-shift reactor with natural gas (middle column) or biogas (right columns) as input gas [Nitzsche et al. 2007]**

Gas composition after	Input natural gas				Input biogas (50% CO_2)			
	H_2	CO	CO_2	CH_4	H_2	CO	CO_2	CH_4
Reforming	71.8%	3.6%	22.7%	0.4%	64.8%	3.9%	31%	0.3%
CO-shift	74%	0.9%	23.9%	0.5%	64.1%	1.1%	33.8%	0.4%

The full process flow is shown in Figure 6. These analysis results confirm that the steam reforming plant can principally be operated with raw biogas without an initial purging step. However, it is expected that the hydrogen recovery at the downstream PSA plant is slightly lower in case of biogas due to the lower hydrogen content of the feed gas.

The main reason for the lower H_2 content is the higher CO_2 content introduced by the feedstock, which does however not pose any challenges as the CO_2 in the product gas can easily be removed from the gas stream via PSA.

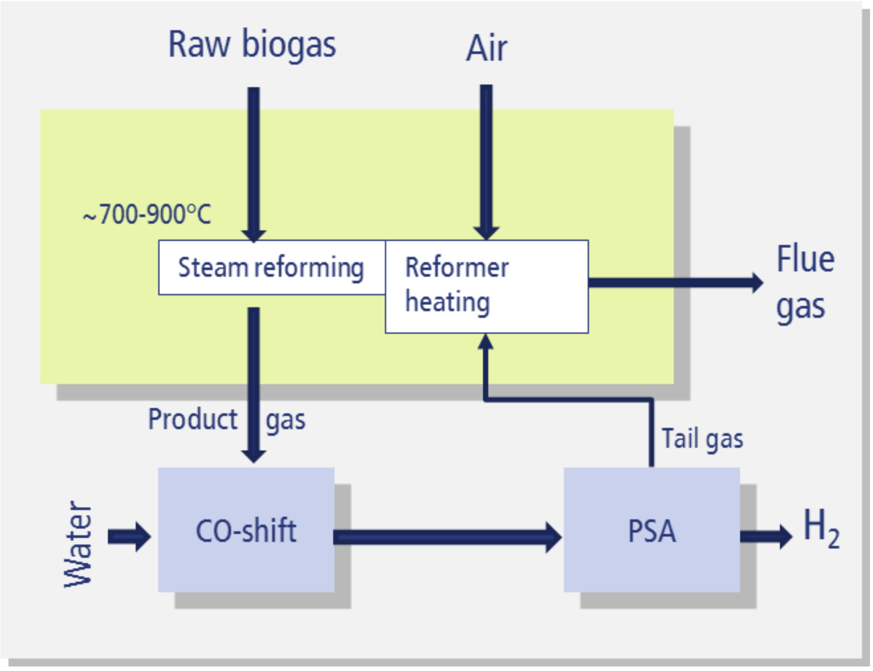


Figure 6: **Process flow chart of hydrogen production via steam reforming and raw biogas as input**

Material and energy input to the reforming process are:

- raw biogas
- electricity
- air

Biogas is the main input; electricity is primarily needed for the compression of the syngas; air is needed for the combustion of the tail gas for reactor heating

b) Resource use

No critical resources[6] are used.

c) Output

Primary output is syngas which is upgraded to pure hydrogen (H_2).

d) Waste emissions

Flue gas

e) Relevant Projects

The tests of input gas quality and output gas emissions as described above have been performed during the years prior to 2007. Cooperation partners involved in the activity were Technische Universität Bergakademie Freiberg, Institut für Wärmetechnik und Thermodynamik, and Institut für Agrartechnik Bornim e.V., Potsdam.

A reformer prototype has been developed and presented at the Hannover Fair 2007. Field tests had been announced in the same year, but to our information none have been carried out.

f) Relevant Stakeholders

Relevant stakeholders from research with experience in this pathway are:

- ⇒ Institut für Agrartechnik Bornim e.V., Potsdam, Germany
- Technische Universität Bergakademie Freiberg, Germany
- University of Stuttgart, Institute of Thermodynamics and Thermal Engineering, Stuttgart, Germany

g) Assessment

Experienced stakeholders from research have demonstrated that the direct gasification of raw biomass without prior stripping of the carbon dioxide via PSA is possible in principle with almost zero energy losses. It can therefore be concluded that this biogas based pathway is in principle ready for commercial implementation, representing a TRL of 8. However, no further activities have been reported since 2007, probably caused by a lack of interest from industry. Reasons for the missing interest may include that biogas from fermentation is preferably and more economically used elsewhere, typically being cleaned and fed directly into the

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[6] 'Critical resources' are those with globally limited availability such as platinum group metals (PGM) or rare earth oxides (REO).

natural gas grid or being directly applied locally for combined electricity and heat production. The raw biomass gasification pathway is adaptable for local, semi-central, and central hydrogen production.

The technology is characterised by the following strengths:

- ⇒ mature technology
- ⇒ suitable for decentralized hydrogen production, e.g. in a robust containerised solution to supply hydrogen to existing fuelling stations where biogas and electricity are readily available

However, the steam reforming of biogas suffers from similar challenges as those of compact small scale natural gas steam reformers:

- ⇒ the need of further cost reduction e.g. by series production, as today most SMR plants are of large scale,
- ⇒ the reduction of plant footprint for onsite H_2 production at hydrogen refuelling stations, and
- ⇒ the high specific operating & maintenance costs as compared to e.g. electrolysers.

It is another way of hydrogen production from biomass resources complementary to pathway (1).

2.4 Thermochemical Water Splitting (3)

a) Process description

The key process along this hydrogen pathway comprises the oxidation of a metal oxide (MO) or an oxidable fluid (e.g. iodine-sulphur) by a reaction with water:

$$H_2O + MO \rightarrow H_2 + MO_2$$

The oxidation process takes place at lower temperatures while the recycling of the metal oxide takes place at higher temperatures by stripping off one oxygen atom from the metal oxide (see Figure 7):

$$MO_2 \rightarrow MO + \frac{1}{2} O_2$$

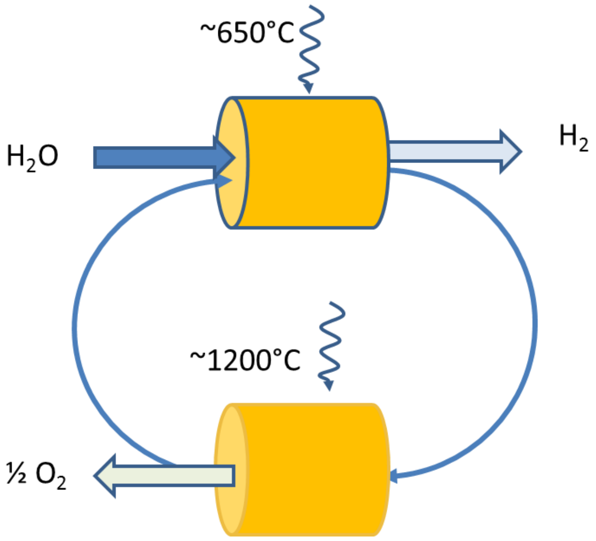

Figure 7: **Principle of hydrogen production by thermochemical water splitting. The orange cylinders stand for the reaction chamber with the metal oxide inside.**

The way heat is supplied to the reactor determines whether this process runs on conventional or renewable primary energy supply. In the context of this renewable hydrogen focused study, solar energy from a concentrating solar receiver is the second key component providing the required high temperature heat.

Figure 8 shows a flow diagram of thermochemical hydrogen production from solar energy. The first process step is the heat supply, consisting of a concentrating solar power plant providing high temperature heat. This part of technology has already been developed for commercial operation, though still being at the beginning of market introduction. Worldwide, about 750 MW of solar tower capacity have been installed – most of it in the U.S. – with plans to increase the capacity to about 1,900 MW by 2018.

A second solar concentrating technology applies parabolic trough solar receivers and has already gained a much larger market share with almost 5 GW installed worldwide, almost half of it in Spain. However, as 2-dimensional parabolic trough concepts are operated at much lower process temperatures in the range of 400-500°C, they cannot be applied for thermochemical water splitting plants, as these require high temperatures of up to 1,800°C. These temperature levels can typically only be provided by 3-dimensional concentrating solar towers or small scale parabolic dishes.

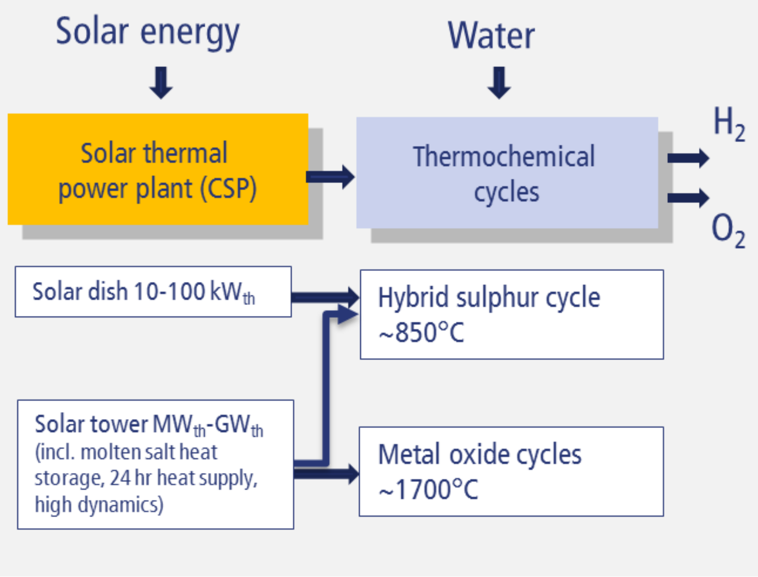

Figure 8: **Process flow diagram of renewable hydrogen production using thermochemical cycles.**

The second process step in Figure 7 symbolizes the chemical reaction chamber. Even though several hundred processes from one-step reactions up to multi-step reactions have been identified, basically two typical pathways are distinguished in the literature:

High temperature cycles operating at about 1,600-1,800°C, including various metal oxide cycles such as:

- CeO_2/CeO-cycle
- Fe_3O_4/FeO-cycle
- MnO/Mn_3O_4-cycle
- ZnO/Zn-cycle

Metal oxide cycles are in general quite simple, mostly involving one or two-step reactions.

Low temperature cycles at about 850-950°C, including various forms of liquid cycles such as:

- Sulphur-iodine-cycle
- Hybrid sulphur-cycle

These cycles involve two, three, or even more single process steps.

The Sandia sulphur-iodine-cycle operates at between 850 and 950°C and involves the following three single process steps:

(1) $H_2SO_4 \rightarrow H_2O + SO_2 + \frac{1}{2}O_2$

(2) $SO_2 + 2\ H_2O + I2 \rightarrow H_2SO_4 + 2\ HI$

(3) $2\ HI \rightarrow H_2 + I_2$

The first two reactions are coupled by exchanging SO_2 und H_2SO_4, while the second and third reactions are coupled by the exchange of HI and I_2.

The hybrid sulphur cycle is a mixed two step cycle involving a first thermochemical reaction at about 850°C

(1) $H_2SO_{4(aq)} \rightarrow H_2O_{(g)} + SO_{2(g)} + \frac{1}{2}O_{2(g)}$,

and a second thermoelectric reaction at 80-120°C

(2) $SO_{2(aq)} + 2\ H_2O_{(l)} \rightarrow H_2SO_{4(aq)} + H_{2(g)}$.

Inputs to the process are:

- Solar heat
- Water
- Electricity (which is generated from part of the input heat)

b) Resource use

- Metals depending on the technology, e.g. Cerium (high temperature cycle)
- Steel (for the construction of the CSP-plant)
- Concrete (for the construction of the CSP plant)
- Catalyst materials
- Sulphur (low temperature cycle)

As solar based energy conversion generally needs huge aperture areas, material consumption for construction is considerably larger than for fuels based energy conversion. Correspondingly, construction materials play a larger role and are explicitly mentioned here.

Also the dissipation of metals and catalysts during recycling processes requires a regular replacement and needs to be accounted for.

c) Output

- H_2
- O_2

As the key process is the splitting of water, per ton of hydrogen about 9 t of oxygen are produced.

d) Waste emissions

No waste except for material degradation and replacement.

e) Relevant Projects

Europe

- HycycleS (FP7, 2008-2011): Materials and components for hydrogen production by sulphur based thermochemical cycles
  (see http://hycycles.eu/)

  > *"HycycleS aimed at the qualification and enhancement of materials and components for key steps of thermochemical cycles for solar or nuclear hydrogen generation. The focus of HycycleS was the decomposition of sulphuric acid which is the central step of the sulphur based family of those processes, especially the hybrid sulphur cycle and the sulphur-iodine cycle. Emphasis was put on materials and components for sulphuric acid evaporation, decomposition, and sulphur dioxide separation. The final aim was to bring thermochemical water splitting closer to realisation by improving the efficiency, stability, practicability, and costs of the key components involved and by elaborating detailed engineering solutions. The project took into account the activities currently performed in the US, Japan, and Australia. Therefore key partners from those countries, Westinghouse, JAEA, and CSIRO, were involved. HycycleS activities were also strongly linked with international initiatives on hydrogen production under the aegis of IPHE, IEA, INERI, and Gen IV."*

  (Quoted from http://cordis.europa.eu/project/rcn/85748_en.html)

- ARMOS (FP7, 2011-2016): (see at http://erc.europa.eu/projects-and-results/erc-funded-projects/armos?retain-filters=1)
  This project focussed mainly on the production of a liquid fuel from H_2 and CO_2.

- Hydrosol_3D (FP7, 2010 – 2012) (see at http://www.hydrosol_3d.org)

> *"HYDROSOL-3D aimed at the preparation of a demonstration of a CO_2-free hydrogen production and provision process and related technology, using two-step thermochemical water splitting cycles by concentrated solar radiation. This process has been developed in the frame of EU co-financed projects within FP5 and FP6. From the initial idea over the proof of principle and over several steps of improvement - that have awarded to project HYDROSOL the EU "2006 Descartes Prize for Collaborative Scientific Research" - the technology has recently reached the status of a pilot plant demonstration in a 100 kW scale showing that hydrogen production via thermochemical water splitting is possible on a solar tower under realistic conditions. The present project focuses on the next step towards commercialisation carrying out all activities necessary to prepare the erection of a 1 MW solar demonstration plant. HYDROSOL-3D concerns the pre-design and design of the whole plant including the solar hydrogen reactor and all necessary upstream and downstream units needed to feed in the reactants and separate and bottle the products. Two alternative options will be analyzed: adapting the hydrogen production plant to an already available solar facility or developing a new, completely optimised hydrogen production/solar plant. The most promising option will be analysed in detail, establishing the complete plant layout and defining and sizing all necessary components. Validation of pre-design components and process strategies by experiments (in laboratory, solar furnace, solar simulator and solar tower facilities) and a detailed techno-economic analysis covering market introduction will complement the project. The HYDROSOL-3D consortium has been built accordingly bringing together the experience and knowledge elaborated in all the R&D work carried out up to the current status of HYDROSOL projects, with industrial leaders and innovative SME's capable to bring the technology to maturity and to the market."*

(Quoted from http://cordis.europa.eu/project/rcn/75098_en.html)

- Hydrosol Plant (FP7, 2014-2017):
  (see at http://cordis.europa.eu/project/rcn/111501_en.html)

> *"The HYDROSOL-PLANT project is expected to develop, verify and operate all of the tools required to scale up solar H_2O splitting to*

the pilot (750 kW_{th}) scale. The work will be based on the successful HYDROSOL series projects and mainly on the outcome of the current FCH-JU co-funded project, HYDROSOL-3D, dedicated to the provision of all main design specifications of such a pilot plant. HYDROSOL-PLANT comes thus as the natural continuation of such an effort for CO_2-free hydrogen production in real scale. The main objectives of HYDROSOL-PLANT are to:
- Define all key components and aspects necessary for the erection and operation of a 750 kW_{th} solar plant for H_2O splitting (heliostat field, solar reactors, overall process monitoring and control, feedstock conditioning, etc.)
- Develop tailored heliostat field technology (field layout, aiming strategies, monitoring and control software) that enables accurate temperature control of the solar reactors.
- Scale-up the HYDROSOL reactor while advancing the state-of-the-art (redox materials, monolithic honeycomb fabrication and functionalization) for optimum hydrogen yield.
- Design the overall chemical process, covering reactants and products conditioning, heat exchange/recovery, use of excess/waste heat, monitoring and control.
- Construct a solar hydrogen production demonstration plant in the 750 kW_{th} range to verify the developed technologies for solar H_2O splitting.
- Operate the plant and demonstrate hydrogen production and storage on site (at levels > 3 kg/week).
- Perform a detailed techno-economic study for the commercial exploitation of the solar process."

(Quoted from http://cordis.europa.eu/project/rcn/111501_en.html).

- Sol2Hy2 (FP7, 2013-2016):

  "The FCH JU strategy has identified hydrogen production by water decomposition pathways powered by renewables such as solar energy to be a major component for sustainable and carbon-free hydrogen supply. Solar-powered thermo-chemical cycles are capable to directly transfer concentrated sunlight into chemical energy by a series of chemical and electrochemical reactions, and of these cycles, hybrid-sulphur (HyS) cycle was identified as the most promising one.
  The challenges in HyS remain mostly in dealing with materials

> *(electrolyser, concentrator, acid decomposer/cracker and plant components) and with the whole process flowsheet optimization, tailored to specific solar input and plant site location. With recent technology level at large-scale hydrogen production concepts hydrogen costs are unlikely to go below 3.0-3.5 €/kg. For smaller scale plant, the costs of hydrogen might be substantially higher. The present proposal focuses on applied, bottle-necks solving, materials research and development and demonstration of the relevant-scale key components of the solar-powered, CO_2-free hybrid water splitting cycles, complemented by their advanced modeling and process simulation including conditions and site-specific technical-economical assessment optimization, quantification and benchmarking. For the short-term integration of solar-power sources with new Outotec Open Cycle will be performed. Simplified structure, extra revenues from acid sales and highly efficient co-use of the existing plants may drop hydrogen costs by about 50-75% vs. traditional process designs.*
>
> *Besides providing key materials and process solutions, for the first time the whole production chain and flowsheet will be connected with multi-objective design and optimization algorithms ultimately leading to hydrogen plants and technology "green concepts" commercialization.*
>
> *The consortium consists of key materials suppliers and process development SME and industry, RTD performers and a university."*

(Quoted from http://cordis.europa.eu/project/rcn/108795_en.html)

North America:

- Integrated Solar Thermochemical Reaction System for the High Efficiency Production of Electricity (IEA SolarPACES[7] 2012-2015)
  The DoE-Funded Project with partners from USA worldwide is the only project for the development of a dish based solar thermochemical reactor though in combination with steam reforming of natural gas.
- STCH –Solar Thermochemical Hydrogen (IEA SolarPACES, long-term activity since 2004)

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[7] The IEA-financed network on Concentrating Solar Power Plants, CSP, published under Task II, Solar Chemistry Research, ongoing international research activities. The research work for the current term 2012-2017 lists six activities. This project is listed under activity 1, Solar Fuels. [IEA SolarPACES 2015]

This DoE funded long-term project with US-partners has the primary target to achieve Solar-to-Hydrogen-Conversion-Efficiency (StH-Efficiency) greater 26% at hydrogen production cost of less than 3.70 USD/gallon by 2020, with an ultimate goal below 2 USD/gallon.

Asia, Australia

- In Asia, important international project cooperations exist between Japanese and Korean Researchers (Joint project of Niigata University and Korea Institute of Energy Research on the "Solar demonstration of Water-Splitting Reactor using Ceramic Foam Device") and between Japan and Australia with the focus to import carbon free fuels from Australia – either from solar energy or from coal liquefaction [Cho et al. 2014].

f) Relevant Stakeholders

Europe

- Paul Scherrer Institute, Villigen, Switzerland (ZnO/Zn cycle and carbothermic ZnO/Zn cycle)
- Deutsches Zentrum für Luft- und Raumfahrt (DLR), Germany (MnO/Mn_3O_4 cycle, FeO-Fe_3O_4/Fe_2O_3 cycle, Zn/ZnO cycle and combinations, and hybrid sulfur cycle) [Agrafiotis et al. 2010], [DLR 2014]
- CNRS, France
- CIEMAT, France

North America

- Sandia National Laboratories, USA (CeO_2/CeO cycle) [Siegel et al. 2011]
- Savannah River National Laboratory (SRNL), USA (hybrid sulfur cycle)
- National Renewable Energy Laboratory (NREL), USA
- Westinghouse
- Diver Solar LLC, Albuquerque, NM, USA
- Bucknell University

Asia, Australia

- Korea Institute of Energy Research, Daejeon
- Tokyo University
- Hiroshima University

- Niigata University
- CSIRO, Australia

g) Assessment

The hydrogen production via thermochemical water splitting is estimated to be at TRL 5. As the technical problems and how to solve them are well understood, advancing the TRL primarily depends on future engagement. At present, European institutes are among the leading groups as European research was continuously financed over the last decades. According to expert interviews, with high probability the TRL may increase to 7-8 until 2030. Under optimistic conditions with sufficient financing TRL 9 could be reached by 2030.

The technology has following strengths:

- use of solar thermal energy as main feedstock,
- solar thermal power plants including thermal storage enable a 24 hour operation and thus hydrogen production from solar energy,
- solar thermal power plants are well suited for a cooperation with e.g. North Africa addressing energy security as well as capacity building; both topics gain high attention in the European Agenda.

Major remaining challenges comprise:

- cycle stabilisation and increase of the lifetime of the thermochemical cycles ; materials must endure extreme heat and corrosive and reactive environments; high temperatures aggravate these problems; materials with improved physical and chemical stability, thermal compatibility, efficient heat transfer, and fast kinetics are required
- substitution of expensive and rare materials (e.g. cerium, PGM) by cheaper high temperature resistant materials (e.g. perovskite-structures) with adequate properties
- further cost reduction of the solar fields, balance of plant and operation and maintenance
- applicability restricted to regions with high direct solar irradiation; requiring hydrogen export concepts for more universal approaches

2.5 Photo-catalysis (Photo-electrochemical cells – PEC) (4)

a) Process description

The conventional way of producing hydrogen from solar energy comprises two single process steps. First, electricity is generated via photovoltaic cells. Secondly, the electricity drives an electrolyser which splits water into oxygen and hydrogen.

Photo-electrochemical cells (PEC) combine photovoltaic electricity generation and electrolysis in a single process. A photo-electrochemical cell has similarities to a photovoltaic cell (PV). Basically, a PV-cell separates electrons and holes in the semiconductor material. The electric current via external loads recycles the electrons. The PEC-device separates anode and cathode via an electrolyte in between them. It consumes the free electrons at the solar irradiated cathode by the formation of neutral hydrogen molecules from positive protons (H^+), which are attracted by the cathode during the water splitting process. Negative oxygen ions (usually bound in negatively charged OH^- ions) are attracted by the anode where they are transformed in neutral oxygen molecules by stripping off their surplus electrons at the anode. A current recycles the electrons back to the anode. The major difference of PV-cells and PEC-devices is that anode and cathode are separated by an electrolyte.

Basically, four different technological realisations have been investigated in the literature:

- Type I: Nanoparticulates consisting of hematite (Fe2O3) and thin catalyst layers which are mixed in a single compartment with colloidal suspension. The whole cell is encapsulated while the mixed oxygen/hydrogen gas is removed through a pipe.
- Type II: Nanoparticulates consisting of hematite (Fe2O3) and thin catalyst layers which are mixed in a dual compartment with colloidal suspension. The compartments are doubled, alternating rows collecting hydrogen and oxygen, respectively.
- Type III: Planar PEC-array, as explained above.
- Type IV: Planar high efficiency PEC arrays which are irradiated by concentrated solar light (enhancement by a factor of 10 or more).

Each of these types has its advantages and disadvantages, which are shortly explained below.

Figure 9 and Figure 10 show the basic principle of a Type III and Type I/II photo-electrochemical devices, respectively. In this Type III example (Figure 9) the anode is irradiated. Type IV reactors are similar with the difference that the incoming solar radiation is concentrated to higher power density requiring high power anode materials (e.g. GaAs-compounds). The absorbed energy shifts the valence electrons into the conduction band leaving holes in the valence band. These holes are neutralised with electrons from the decomposition of the negative OH^--radicals into oxygen molecules and water. The surplus electrons in the conduction band move to the cathode. At the cathode, water molecules are dissociated into hydrogen molecules and OH^--radicals by consuming the electrons which are supplied by the electric current once anode and cathode are connected. The OH- -radicals move through the electrolyte to the anode where they are decomposed as already explained.

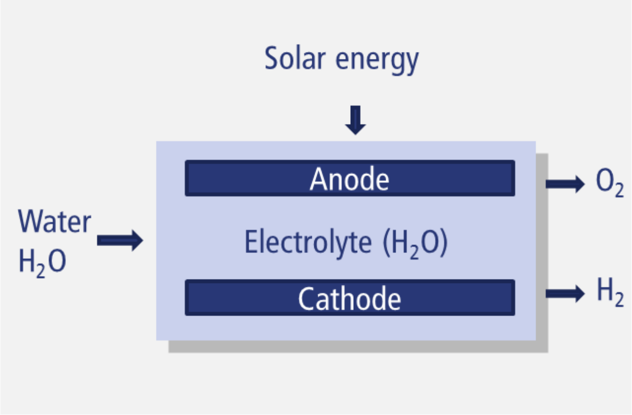

Figure 9: **Schematic view of a Type III (planar) photo-electrochemical device for hydrogen production from solar energy**

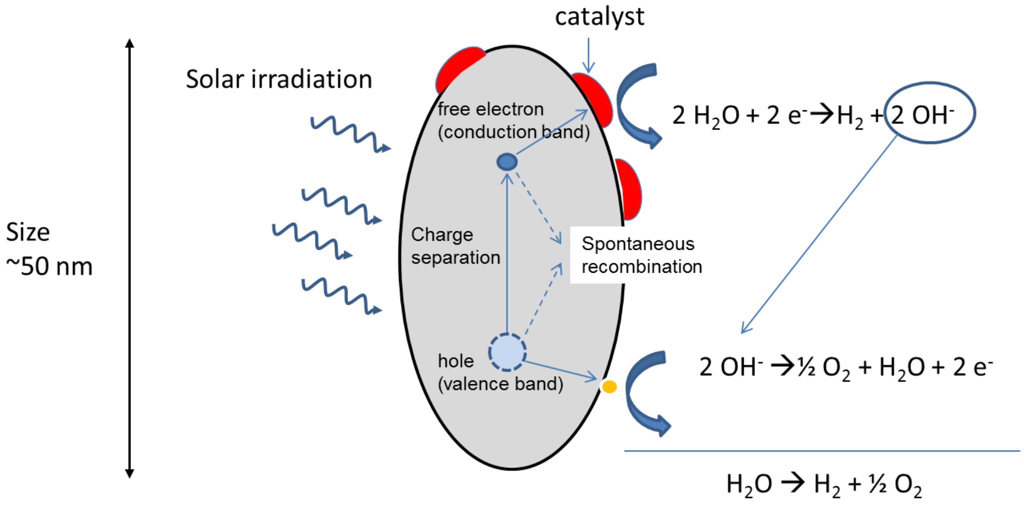

Figure 10: **Schematic view of a Type I or Type II nanoparticulate photo-electrochemical device for hydrogen production from solar energy. The nanoparticulates are suspended in the electrolyte (drawing after [Chou et al.])**

Inputs to the process are:

- Solar photons which provide the required energy
- Water (electrolyte) serving as “fuel” for the hydrogen production.

b) Resource use

- Nano-particles (e.g. hematite) for Type I and Type II
- Catalyst materials (predominantly platinum group metals)
- Rare elements (e.g. GaAs, GaInP) for Type IV
- Large land area required

Similar to thermochemical hydrogen production (pathway No. 3), the hydrogen production from solar energy and water requires huge land area, large amounts of construction material and some chemical elements with special electrochemical properties. As these degrade over time, such materials are relevant in an LCA-analysis to be compared with the fuels throughput in combustion plants.

c) Output

- H_2
- O_2

As the key process is the splitting of water, per ton of hydrogen about 9 t of oxygen are produced.

d) Waste emissions

No waste emissions. A major advantage of solar based hydrogen production pathways is their environmentally sound operation which – except for land use and possible emissions during materials production – renders them very "clean".

e) Relevant Projects

PEC – devices are the ultimate vision of solar hydrogen production already from the beginning. Therefore scientific interest has always been high. This resulted in a long history of learning processes. Here, we focus on recent European research activities.

- NanoPEC (FP7, 2009-2011)
  http://nanopec.epfl.ch/

  > *"Project goals were:*
  > *(1) the development of 1 cm² test device (nanostructured) with >10% solar-to-hydrogen-(StH-)conversion and 10% maximum performance decay over the first 5,000 hours.*
  > *(2) the develop 100 cm² test device with sustained 7% StH efficiency and similar stability, to be used as performance standard well beyond existing*
  > *(3) Production cost less than 5€/kg* H_2
  >
  > *According to project reports these goals were achieved as follows: .*
  > *(1) fully,*
  >
  > *(2) 64 cm² with 6% STH efficiency and more than 3 years operation with hematite without substantial degradation*
  > *(3) at 20 years and 8 hours/day cost of 7 €/kg* H_2 *are calculated."*

  (Quoted from Report Summary:
  http://energycenter.epfl.ch/files/content/sites/energy-center/files/projets/docs/Nanopec_report_summary.pdf
  http://cordis.europa.eu/project/rcn/89410_en.html)

  However, the deeper investigation – which was also confirmed by expert interviews- exhibited that the long term operation stability was – and still is – a very critical issue which within this project could not be solved, though important progress was achieved.

- PHOCS (FP7, 2012-2015)
  http://www.phocs.eu/project/abstract.html

PHOCS intends to combine the visible-light absorption properties of organics, together with the enhanced charge transport capabilities of inorganic semiconductors in order to build a hybrid photoelectrode for hydrogen generation. Final goal of the research is the realization of a novel photoelectrochemical system for hydrogen production, based on hybrid organic/inorganic and organic/liquid interfaces. Key is the development of photogenerated hydrogen by organic catalytic systems (PHOCS) The final goal is to build and operate a 10x10 cm² device with 1% StH conversion efficiency as a first step of more complex devices.

- FOPS (Fundamentals of Photocatalytic Splitting of Water (ERC-funded, 2014-2019)
  http://erc.europa.eu/projects-and-results/erc-funded-projects/fops?retain-filters=1 and http://cordis.europa.eu/project/rcn/109646_en.html

This ongoing project focusses on gaining deeper insights into materials; the project description describes the problem as follows:

> *“Remarkably, insights into how water is bound to the catalyst and into the dynamics of the photodissociation reaction, have been scarce up to now, due to the lack of suitable techniques to interrogate water at the interface. The aim of this proposal is to provide these insights by looking at specifically the molecules at the interface, before, during and after their photo-reaction. With the surface sensitive spectroscopic technique sum-frequency generation (SFG) we can determine binding motifs of the ~monolayer of water at the interface, quantify the heterogeneity of the water molecules at the interface and follow changes in water molecular structure and dynamics at the interface during the reaction. The structure of interfacial water will be studied using steady-state SFG; the dynamics of the water photodissociation will be investigated using pump-SFG probe spectroscopy. At variable delay times after the pump pulse the probe pulses will interrogate the interface and detect the reaction intermediates and products. Thanks to recent developments of SFG it should now be possible to determine the structure of water at the TiO2 interface and to unravel the dynamics of the photodissocation process. These insights will allow us to relate the interfacial TiO2-water structure and dynamics to reactivity of the photocatalyst, and to bridge the gap between the fundamentals of the process at the molecular level to the efficiency of the*

> *photocatalys. The results will be essential for developing cheaper and more efficient photocatalysts for the production of hydrogen."*

- PEC-DEMO (FCH JU-Project, 2014-2016)
  http://pecdemo.epfl.ch/

  > *"The PECDEMO project seeks to develop a hybrid photoelectrochemical-photovoltaic tandem device for light-driven water splitting with an active area of $\leq 50\ cm^2$ and a solar-to-hydrogen efficiency of 8–10% while maintaining stability for more than 1,000 h.*
  > *Highly innovative approaches will be used to tackle the challenges of designing and constructing prototype modules for photoelectrochemical hydrogen production. These innovations will enable the researchers to go substantially beyond the state-of-the-art in four critical areas:*
  > *(1) stable and efficient metal oxide photoelectrodes,*
  > *(2) optimized tandem cell designs,*
  > *(3) scale-up, and*
  > *(4) techno-economic and life-cycle assessments. "*

  (quoted with slight adaptations from the project description at the website.)

- PHOTOCATH2ODE (FP7, 2012-2017)
  http://cordis.europa.eu/project/rcn/104489_en.html

  > *"The objective of this project is to design an operating photocathode based on Earth abundant elements for PEC H2 production, answering therefore the sustainability and cost issues. The novelty relies on the approach gathering organic and hybrid photovoltaics with artificial photosynthesis to design new materials and architectures."*

  (quoted with slight adaptations from the project description at the website.)

- ArtipHyction (FCH-JU-Project, 2012-2015)
  (http://www.artiphyction.org/partners.aspx and
  http://www.fch-ju.eu/sites/default/files/FCH%20Review%20day%202012%20-%20project%20ArtipHyction.pdf

  > *The project tries to synthetically imitate the natural photosynthesis process. James Barber, one of the key players of ArtipHyction, elucidated Photosystem II (PSII), the enzyme that governs this process. In photosynthesis,* H_2 *is used to reduce* CO_2 *and give rise*

> *to the various organic compounds needed by the organisms or even oily compounds which can be used as fuels. However, a specific enzyme, hydrogenase, may lead to non-negligible* H_2 *formation even within natural systems.*
>
> *Building on the pioneering work performed in a FET project based on natural enzymes (Solhydromics, FP7-Energy-2008-FET) and the convergence of the work of the physics, materials scientists, chemical engineers and chemists involved in the project, an artificial device will be developed to convert sun energy into H2 with close to 10% efficiency by water splitting at ambient temperature, including:*
>
> *i. an electrode exposed to sunlight carrying a PSII-like chemical mimic deposited upon a suitable transparent electronconductive porous electrode material (e.g. ITO, FTO);*
>
> *ii.a membrane enabling transport of protons via a pulsated thin water gap;*
>
> *iii.an external wire for electron conduction between electrodes;*
>
> *iv.a cathode carrying an hydrogenase-enzyme mimic over a porous electron-conducting support in order to recombine protons and electrons into pure molecular hydrogen at the opposite side of the membrane.*
>
> *A tandem system of sensitizers will be developed at opposite sides of the membrane in order to capture light at different wavelengths so as to boost the electrons potential at the anode for water splitting purposes and to inject electrons at a sufficiently high potential for effective* H_2 *evolution at the cathode. Along with this, the achievement of the highest transparence level of the membrane and the electrodes will be a clear focus of the R&D work. A proof of concept prototype of about 100 W (3 g/h* H_2 *equivalent) will be assembled and tested by the end of the project for a projected lifetime of >10,000 h.*

Project description quoted from the project website. Unfortunately, there was no literature available which could confirm the achievement of the project results. Interviewed experts doubted at least the proposed lifetime goal.

f) Relevant Stakeholders

- Delft University of Technology, The Netherlands, http://www.tudelft.nl/en/current/latest-news/article/detail/tu-delft-verbetert-productie-vanwaterstof-uit-zonlicht/(Roel Van de Krol)
- Department of Chemical System Engineering, School of Engineering, The University of Tokyo, Tokyo, Japan
- EPFL Lausanne, Micheal Graetzel, CH,
- Fritz-Haber-Institute of the Max-Planck-Society, Theory Department, Berlin, Germany
- Hawaii Natural Energy Institute, School of Ocean and Earth Science and Technology University of Hawaii at Manoa, Honolulu, Hawaii 96822, USA (E. Miller, R. Rocheleau), see http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/30535x.pdf (Miller 2001)
- Helmholtz Zentrum Berlin, Germany, http://www.helmholtz-berlin.de/pubbin/news_seite?nid=13764&sprache=de&typoid=1 (van de Krol)
- Helmholtz-Gesellschaft (Prof. J. de Kol)
- Max-Planck Institute of Colloids and Interfaces, Department of Colloid Chemistry, Research Campus Golm, Postdam, Germany
- National Renewable Energy Laboratory (NREL), USA (http://techportal.eere.energy.gov/technology.do/techID=1076)
- Research Institute of Photocatalysis, State Key Laboratory Breeding Base of Photocatalysis, Fuzhou University, Fuzhou, China
- University of Stuttgart, Institute for Materials Science (Prof. Dr. Anke Weidenkaff)

g) Assessment

The current TRL for this technology has been estimated by relevant stakeholders in interviews at between 2 and 5. Estimated hydrogen production costs in the literature range from 7 to almost 30 € per kg_{H2}. The U.S. Department of Energy (DoE) has set a 2020 target of 5-6 US$ per kg_{H2}.

Among the hydrogen production technologies surveyed, PEC shows the widest range of TRL and hydrogen production cost estimates. The technology of hydrogen production in a PEC, using only sunlight and water offers one of the most interesting (and challenging) pathways for hydrogen production as – theoretically or visionary – it finally might be only slightly more complex than pure PV at only marginally higher cost. The PEC technology could produce hydrogen for all three value chains defined her: local, semi-central and central.

PEC does not offer any footprint specific improvements when compared to conventional PV/electrolysis. StH-efficiency is claimed to be about 12%. (see https://techportal.eere.energy.gov/technology.do/techID=1204). However, the motivation and vision is that production cost might be only slightly larger than for PV modules but lower than for the combination of PV modules and electrolysers.

The US-DoE-goal is to reach a conversion efficiency of more than 10% at more than 1,000 hours of successful operation
(see http://techportal.eere.energy.gov/technology.do/techID=1076).

According to the experts interviewed, European research has shown incremental improvements over the last subsequent projects. The present PEC-Demo project is focusing on the achievement of high conversion efficiencies from a large scale module (>50 cm²). Once that has been achieved, the research focus will be tuned towards long-term stability of the core materials. Although this is not a trivial task, one interviewee confirmed that the steps necessary for optimizing the material and improving the catalysts are theoretically well understood. Other sources claimed that the improvement of materials follows a trial-and-error approach with unpredictable outcome. However, the latter sources also believe huge progress could be obtained once adequate material combinations have been identified; otherwise, only slow and small improvements may be possible.

The major strengths of PEC based hydrogen generation pathways are:

- the option for diversifying the energy base by using solar energy
- the advantage of a low temperature process (20-60°C) compared to the thermochemical process
- high scalability to build plants at virtually all scales

The major challenges are:

- large area required (typical for solar based energy conversion processes)
- required increase of stability and lifetime
- increase of the stable process efficiency during long term operation
- discovery / development of suitable materials

- optimisation of reactor design
- overall cost reduction (i.e. concentrator, semiconductor material)

2.6 Fermentation (5)

a) Process description

Fermentation is the transformation of biomass by bacteria under dark or lighted conditions. The dark fermentation process offers a variety of substrates as main feedstock, ranging from sugar-rich to complex biomass including lignocellulosic biomass, sewage and food or animal waste. Pre-treatment may be required to convert the cellulose in the feedstock into polysaccharides and glucose.

Each mole of glucose contains twelve moles of hydrogen. Under dark fermentation conditions the theoretical maximum hydrogen extraction is four moles of hydrogen per mole of glucose while eight moles of hydrogen are still bound in the co-produced two moles of acetate.

The photo fermentation process requires acetate as input. The theoretical maximum hydrogen extraction is four moles of hydrogen per mole of acetate.

In summary, the dark fermentation process is a first step which produces hydrogen and acetate as co-product. Photofermentation might be seen as a second step which converts additional hydrogen from the co-produced acetate. The combination of both processes has a theoretical maximum yield of twelve moles of hydrogen per mole of glucose.

However, the hydrogen which after dark fermentation is still bound in the acetate can also be extracted by a conventional biomass fermentation process. Hence, although the combination of dark and photo fermentation has a theoretically high yield, a more practical approach with reasonable cost and conversion rates is the combination of dark fermentation with conventional fermentation.

Photo fermentation is still discussed in more detail in pathway (8) below. The further discussion of this chapter concentrates on hydrogen production by dark fermentation.

The process temperature of dark fermentation varies from ambient temperature to 80°C. Pre-treatment (e.g. Saccharification and comminution) improves the fermentation rate of the biomass. Major products are H_2 and organic acids, which should be transferred into a second process for complete conversion as already described above.

Advantages and disadvantages of various hydrogen producing fermentation processes are discussed in [Hallerbeck et al. 2010]. Pawar and van Niel of Applied

Microbiology of Lund University Sweden give an overview of thermophilic biohydrogen production and some optimization features [Pawar et al. 2013].

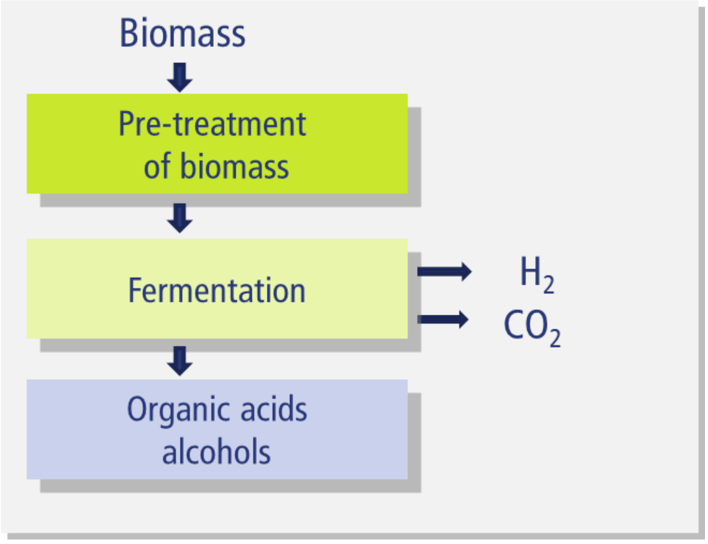

Figure 11: **Schematic view of the fermentation pathway (in the absence of light) for hydrogen production**

Besides the simplicity of the reactor a specific advantage of dark fermentation is the variety of possible feedstock. Depending on the sort of bacteria the substrate can consist of sugar-rich or complex biomass including lignocellulosic biomass or organic acids like in waste or sewage.

Fermentation processes can be classified in mesophilic (ambient temperature) and thermophilic (> 60°C) H_2 production. The thermophilic process shows higher H_2 yield (nearly the theoretical 4 mol of H_2 per mol of glucose) and fewer by-products. In fermentation with extreme thermophilic bacteria (> 70°C) the substrate does not have to be sterilized (otherwise typically at 120°C, 1 atm pressure), which is a clear advantage for industrial scale production. Mesophilic fermentation needs sterilized pretreatment to prevent competing processes.

b) Resource use

- Heat and chemicals for pre-treatment
- Heat for fermentation
- Mechanical energy for stirred tank reactor

c) Output

- H_2
- Organic acids for further conversion

- Other organic products depending on bacteria consortia

d) Waste emissions

- Organic acids in case they are not fed into a second conversion process
- CO_2

e) Relevant Projects

The following projects have been carried out or are under way.

Europe

- BIOHYDROGEN (FP5, 2000 - 2002) (www.biohydrogen.nl/biohydrogen)

  Main objective: production of hydrogen from energy crops and wastes employing (hyper)thermophilic and photoheterotrophic microorganisms.

  Research was done in the field of processing the raw material and in screening microorganisms to optimize the fermentation processes.

- HyVolution (FP6, 2006-2010) (http://www.biohydrogen.nl/hyvolution/24295/5/0/20)

  Non-thermal production of pure hydrogen from biomass.

  The aim of the project was to deliver prototypes of process modules with high H_2 production efficiency. Reactor design was an important technological objective. Costs of the two-step process could be estimated. Process design was successful, but cost evaluation has shown that photo fermentation will not be suitable for industrial application because of high investment and maintenance costs.

- HyTime (FCH JU, 2012 -2014) (www.hy-time.eu)

  Low temperature hydrogen production from 2nd generation biomass

  The objective of the project was the increase the productivity of hydrogen production via fermentation of 2nd generation biomass and the development of a dedicated prototype installation. Dark fermentation was combined with anaerobic digestion to valorise the waste products.

  A final report has not been published until now. In the mid-term report [HyTIME 2013] no specific bottlenecks to fulfil the project targets have been identified (e.g. increase of hydrogen production rate, design of a hydrogen production system).

- BWP I (2000 – 2003) and BWP II (2003-2006) (Dutch EET programme)

Objective: evaluation of dark and photo fermentation

The projects have "covered the whole chain of pretreatment of biomass to fermentation and up-grading of the produced gas and a techno-economic evaluation. The first techno-economic evaluation, based on thermo-fermentation followed by photofermentation using potato steam peels as biomass, showed that production costs for H_2 would amount to €3.10/kg_{H2}. The techno-economic evaluation was done assuming that present seemingly feasible targets for thermophilic and photoheterotrophic fermentation will have been met in the future" (quoted from [BWP II 2007]).

- **University of Regensburg, Germany**

  At the University of Regensburg a dark fermentation process has been developed using extremely thermophilic bacteria working at 80 C and on a wide range of substrates. A pilot plant with a 30 m³ reactor is in the planning phase. It will be constructed in Norway to convert food waste. Waste treatment credits instead of feedstock costs improve the economy o the planned reactor [Thomm 2015].

Asia

- In Taiwan the research group headed by Prof. Lin at the Feng Chia University and the Green Energy Development Center (GEDC) is active in the field of bio-hydrogen research. The GEDC has built a 400 litre dark fermentation pilot plant at the Feng Chia campus in December, 2007.

  Ongoing projects are working on hydrogen/methane production via food fermentation (dark fermentation - combination with "conventional" anaerobic digestion for simultaneously H_2 and CH_4 production). Production reactors with 50 m³ (CH_4) and 2 m³ (H_2) have been built in a food industry plant to verify the technology for commercialization. [GEDC 2015]

North America

- A further leading player in the field of bio hydrogen production is the working group around Prof. Hallenbeck at the University of Montreal in Canada. [Hallenbeck et al. 2010]

f) Relevant Stakeholders

Stakeholders are found in all world regions:

- National Renewable Energy Laboratory (NREL), USA
- Hyperthermics in Ørsta, Norway, http://www.hyperthermics.com/

- Hyperthermics in Regensburg, Germany, http://www.bioregio-regensburg.de/index2.php?mid=1211&fid=75
- University of Regensburg, Institute of microbiology, Prof. Thomm, Germany
- Green Energy Development Center, Department of Environmental Engineering and Science, Feng Chia University, Prof. Chiu-Yue Lin, Taichung, Taiwan http://www.greenenergy.fcu.edu.tw
- University of Birmingham, School of Biosciences, Institute of Microbiology and Infection, Prof. Lynne Macaskie, Edgbaston, Birmingham, UK http://www.birmingham.ac.uk/research/activity/bio-hydrogen/index.aspx
- DLO-FBR Stichting Dienst Landbouwkundig Onderzoek, Institute Food and Biobased research, NL, www.wageningenur.nl; see for example http://www.wageningenur.nl/en/Expertise-Services/Research-Institutes/food-biobased-research/Expertise-areas/Biobased-chemicals/show/Producing-hydrogen-from-biomass.htm
- Université de Montréal, Département de microbiologie et immunologie. Prof. P. Hallenbeck
- University of Duisburg-Essen, Faculty of Engineering Sciences (Building Sciences), Department of Urban Water and Waste Management
- Lund University, Sweden, Department of Chemical Engineering

g) Assessment

The dark fermentation process can work with a variety of substrates as main feedstock, ranging from sugar-rich or complex biomass to lignocellulosic biomass or sewage and food waste. Other advantages include the inherent waste disposal capability and the simple reactor technology.

Interest of the European industry on the dark fermentation process has recently increased. The current TRL is 4.

Major challenges of hydrogen production via fermentation are:

- the high yield in combination with high productivity
- the combination with a simple second fermentation process for conversion of the organic acids by-products improving the overall efficiency of biomass conversion

2.7 Supercritical Water Gasification of Biomass (6)

a) Process description

Supercritical water gasification of biomass and other hydrocarbon-containing streams uses water under supercritical conditions. Further to the solid, liquid and gaseous phases, water becomes supercritical beyond the critical point, i.e. beyond a temperature of 374°C and a pressure of 22.1 MPa (see Figure 12). Under such conditions, water is neither liquid nor gaseous, but the characteristics (density, viscosity, etc.) vary between liquid and gaseous depending on the temperature-pressure conditions. Conditions can be selected that lead to a viscosity similar to superheated steam and thus much lower than for a liquid, which enables high reaction rates. Furthermore, supercritical water is highly miscible with many organic compounds and gases, supporting reactions of them. On the other hand, it is a poor solvent for ions such as inorganic salts. Sulphur and nitrogen contained in the biomass input remain in the liquid phase at the exit of the process leading to clean product gases.

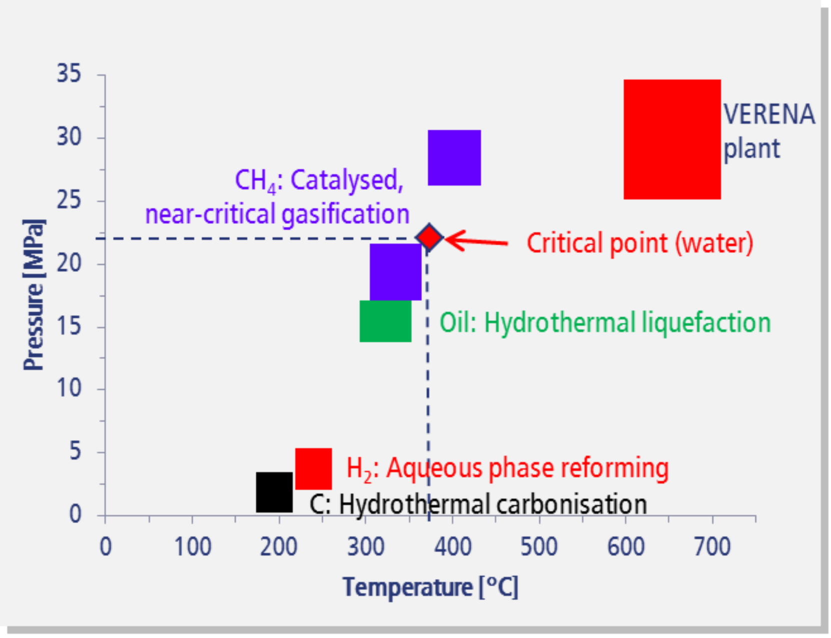

Figure 12: **Temperature and pressure conditions of supercritical water gasification relative to other gasification and reformation processes**

As an example, the following is the idealized chemical reaction of cellulose in supercritical water gasification:

$$C_6H_{10}O_5 + 7\,H_2O \rightarrow 6\,CO_2 + 12\,H_2$$

Typically, methane is also produced in the reaction together with small amounts of carbon monoxide, higher hydrocarbons such as ethane and gaseous nitrogen. A typical gas composition after CO_2 removal is 70% hydrogen, 27% methane, 1% carbon monoxide, 2% higher hydrocarbons. Carbon dioxide can easily be washed out using conventional water scrubbers. Methane can be separated using pressure swing adsorption (PSA); the tail gas can be used to provide input heat to the process.

Tar and char production (among others on reactor walls) in supercritical water gasification can be an issue, depending on gasification conditions and feedstock.

The wet biomass input to the process, which may have an organic content as low as a few percent by weight, is pressurized by a pump. Compressing a liquid, in this case water, requires very low energy input compared to the pressurization of gases. As the entire process is under high pressure the product gas exits at high pressure, avoiding the need for energy intensive gas pressurization, e.g. for bottling the gas or filling it into gas trailers.

After pressurization, the liquid feed is then heated in a heat exchanger transferring heat from the outgoing liquid to the feed. Additionally, heat is provided by a burner combusting PSA tail gas and typically natural gas. After the gasification reaction, the products exit through the heat exchanger and enter two phase separators, one at high pressure separating the product gases, and one at low pressure separating lean gas that is fed to the heater together with the PSA tail gas. Liquid effluents still contain certain amounts and qualities of hydrocarbons, depending on the feedstock, and thus need to be disposed of properly.

Suitable feedstocks are wet biomass and organic wastes, including food industry residues, sewage sludge, etc. In recent years, interest has increased in the gasification of algae.

The effects of different kinds of catalysts in supercritical water gasification have been analysed by research groups. However, the process does not require heterogeneous catalysts. This is an advantage as sulphur, chlorine, and other components, which are commonly contained in biomass and organic wastes, can poison the catalysts applied in other technologies.

b) Relevant Projects

The VERENA[8] pilot plant was built by the Karlsruhe Institute of Technology (KIT), Germany, and started operation in 2002. Based on experimental results at laboratory scale, the VERENA pilot plant was designed to have a total throughput of

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[8] Versuchsanlage zur Energetischen Nutzung Agrarwirtschaftlicher Stoffe – Experimental plant for the energetic use of agricultural materials

100 kg per hour (max. solids content 20%). The reactor volume is 35 litres. The plant has been designed for a working pressure of up to 35 MPa and a maximum temperature of 700°C.

Project ETAMAX, KIT (project co-funded by: Federal Ministry of Education and Research (BMBF): direct production of methane from fermenting mud with precious metal catalysts in supercritical water.

Project PHYKON, KIT (project co-funded by FNR Fachagentur Nachwachsende Rohstoffe): within the scope of the project PHYKON an installation engineering and process engineering is developed with which microalgae can be converted by hydrothermal conversion under high pressure into the storable energy sources hydrogen (H_2) and methane (CH_4). The by-products of the conversion (CO_2, nutrients, waters, heat) can directly be used for the cultivation of microalgae.

BWP II project “Hydrogen from Biomass”, Netherlands, 2003-2006:

- Increased understanding of metabolism in hydrogen producing bacteria
- Reforming of non-fermentables at supercritical water conditions
- Development of bioreactors and up-scaling of the fermentations
- Gas treatment and application of biohydrogen

c) Relevant Stakeholders

- Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany
- Biomass Technology Group (BTG), Enschede, Netherlands
- SPARQLE International, Hengelo, Netherlands
- Ecole Polytechnique Fédérale de Lausanne (EPFL), ENAC-ISTE, Lausanne, Switzerland
- General Energy Research Department, Laboratory for Energy and Materials Cycles, Paul Scherrer Institut (PSI), Villigen, Switzerland
- State Key Laboratory of Multiphase Flow in Power Engineering (SKLMF), Xi’an Jiaotong University, Xi’an, People’s Republic of China
- Hawaii Natural Energy Institute, University of Hawaii at Manoa, Honolulu, United States of America
- Department of Chemical Engineering, University of Michigan, Ann Arbor, United States of America

d) Assessment

The most advanced installation of supercritical water gasification is the VERENA pilot plant with a throughput of 100 kg per hour (max. solids content 20%) operated by KIT. This represents a TRL of 4.

It is difficult to predict the TRL development over the coming years as there are no obvious industrial stakeholders investing in this technology. Commercial installations would need a wet biomass throughput of 5 t/h, i.e. 50 times the VERENA installation or higher. This makes it a central hydrogen production technology with production rates above 2 t/day; a 5 t/h wet biomass installation using sewage sludge would produce around 670 t of hydrogen per year.

The technology has the following strengths:

- it is applicable to biomass with high water content,
- it is a continuous process, which allows decomposition of organic matter at high rates,
- it is energy efficient as liquids are compressed (rather than gases), and as heat is exchanged between input and output,
- the process allows for a nearly complete conversion to hydrogen, methane and carbon dioxide at relatively low temperatures of 600-700°C,
- the gases are free of sulphur and nitrogen compounds, which remain in the liquid phase,
- the product gas mainly consists of hydrogen and methane (after simple CO_2 removal) and is generated at high pressure avoiding the need for energy intensive gas pressurization, e.g. for bottling the gas or filling it to gas trailers.

Major challenges include:

- the process requires high pressures, and thus high-pressure equipment (heat exchanger, reactor etc.) with associated investment costs and operation & maintenance requirements,
- an economic analysis of a 5 t $t_{wet\_Biomass}$/h (wet biomass) installation using sewage sludge results in hydrogen costs that would only be commercially viable if free-of-charge waste streams would be used [Gasafi 2008].

According to [Gasafi et al. 2008] CAPEX is estimated at 14.1 million € for a 5 $t_{wet\_Biomass}$/h, plant producing 670 t/a of hydrogen. 36-44% of total hydrogen production costs are OPEX (operation & maintenance, auxiliary fuel: natural gas). Resulting hydrogen generation costs are 35 €/GJ excluding feedstock costs (or rather assuming feedstock to be free-of-charge waste streams). The commercial case can be improved by assuming that waste streams are used as input, the disposal of which is associated to relevant costs, which would represent an income here.

2.8 Photo-biological Water Splitting (7)

a) Process description

Photobiological water splitting uses microorganisms to convert solar energy into hydrogen. Microorganisms, such as green microalgae or cyanobacteria, absorb sunlight to split water through direct photolysis routes.

Thus far, only cyanobacteria and green algae, e.g. the unicellular green algae "Chlamydomonas Reinhardtii", have been identified to have the ability of photobiological water splitting. The fundamental process is based on photosynthesis (see Figure 13):

In living plant cells sunlight splits water into oxygen, protons and electrons in photosystem II (PS II)[9], which then move, in simplified words, to photo system I (PS I), and onwards to CO_2 fixation, i.e. biomass generation, in the cell with the help of an enzyme called hydrogenase. Under sulphur deficiency, the algae switch to hydrogen production.

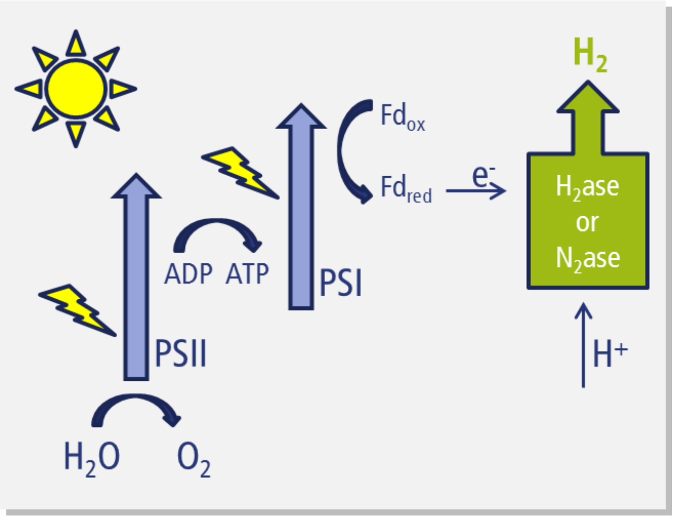

Figure 13: Photobiological water splitting (PSI/PSII – photo system I/II)

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[9] Photosystems are functional and structural units of protein complexes involved in photosynthesis that together carry out the primary photochemistry of photosynthesis. PS I and PS II are two different types of reaction centres.

There are two options to use photosynthesis for hydrogen production:

Option 1: Green algal and cyanobacterial photosynthesis capabilities generate oxygen (O_2) and hydrogen (H_2) ions. A hydrogenase enzyme converts hydrogen ions into H_2 gas.

Option 2: Cyanobacteria use direct photolysis to split water, and then employ a nitrogenase enzyme (instead of a hydrogenase as in option 1) to produce hydrogen in the absence of nitrogen, requiring additional inputs of adenosine triphosphate (ATP; used in cells for intracellular energy transfer).

Option 1 has two sub options, either optimising microbes for hydrogen production, notably using biotechnological methods, or developing technical processes mimicking the biochemical reactions of the microbes without using living cells (see also photo-catalysis in section 2.5). Both of these approaches are being followed by research.

b) Relevant Projects

- CyanoFactory (FP7, 2012 –2015)

  Main objective: Design, construction and demonstration of solar biofuel production using novel (photo)synthetic cell factories,

  The project has 10 partners from Germany, Italy, Portugal, Slovenia, Spain, Sweden, and the United Kingdom. The project was coordinated by Uppsala University, Sweden.

  CyanoFactory aims at applying synthetic biology principles towards a cell factory notion in microbial biotechnology. The vision is to build on recent progress in synthetic biology and develop novel photosynthetic cyanobacteria as chassis to be used as self-sustained cell factories in generating solar hydrogen. To reach the goal, a combination of basic and applied R&D is needed; basic research to design and construct the cyanobacterial cells efficiently evolving H_2, and applied research to design and construct advanced photobioreactors.

- TOHPN: Towards the optimization of hydrogen production by nitrogenase, (European Research Council/IDEAS Program-Starting Grant, 2008 –2014)

  The research project was carried out by principal investigator L. M. Rubio Herrero of Universidad Politecnia de Madrid, Spain.

  The three major components of the research were:

  - in vitro evolution of nitrogenase, in which new nitrogenase variants were generated by metagenomic gene shuffling and random

  mutagenesis, and selection of those with increased hydrogen production activity;
  - development of a genetic system to select for hydrogen over-producers; and
  - a biochemical element designed to understand the biochemical requisites for efficient hydrogen production by the molybdenum nitrogenase as a basis for its re-engineering.

- ArtipHyction (FCH-JU-Project 2012-2015) (http://www.artiphyction.org/partners.aspx

  The project had 8 partners from France, Greece, Italy, Spain, and Switzerland. The project was coordinated by Politecnico di Torino, Italy.

  The project builds on the results of the SOLHYDROMICS project (see below). Its objectives were:

  - improved and novel nano-structured materials for photo-activated processes comprising photo catalysts, photo anodes interfaced with liquid or new polymer electrolytes
  - chemical systems for highly efficient low temperature water splitting using solar radiation
  - demonstration of solar to hydrogen efficiency > 5% with a perspective of >10,000 h lifetime
  - small to medium scale applications ranging from 100 W for domestic use (ca. 3 g/h H_2 equivalent) to 100 kW (ca. 3 kg/h H_2 equivalent) for commercial use.

- SOLARH2: European Solar-Fuel Initiative – Renewable Hydrogen from Sun and Water. Science Linking Molecular Biomimetics and Genetics,
  (FP7, 2008 –2012)

  The project had 12 partners from Finland, France, Germany, Hungary, Netherlands, Spain, Sweden, and Switzerland. The project was coordinated by Uppsala University, Sweden.

  The project aimed at

  - contributing to the development of the knowledge base necessary to advance towards the design, synthesis and characterisation of bio-mimetic compounds able to convert solar radiation into a usable fuel like hydrogen.

  - developing a bio-mimetic complex based on a Ru-center as photo-active system and a Mn-ensemble as redox-active catalyst to mimic solar radiation capture and photosynthetic water oxidation, and an iron based hydrogenase mimic to achieve hydrogen generation.
  - demonstrating photobiological hydrogen production by cyanobacteria and green algae in medium scale laboratory bio-reactors and further improve the best suited organisms using molecular biology and metabolic engineering techniques.

- SOLHYDROMICS: Nanodesigned electrochemical converter of solar energy into hydrogen hosting natural enzymes or their mimics (FP7, 2009 –2012)

  The project had seven partners from Belgium, Germany, Italy, Switzerland, and the United Kingdom. The project was coordinated by Politecnico di Torino, Italy.

  Building on the cooperation of physicists, materials scientists, biochemists and biologists involved, the aim of the project was to develop an artificial device to convert sun energy into H_2 with the potential of achieving 10% efficiency by water splitting at ambient temperature, including:

  - an electrode exposed to sunlight carrying PSII or a PSII-like chemical mimic deposited upon a suitable electrode;
  - a membrane enabling transport of both electrons and protons via e.g. carbon nanotubes or TiO_2 connecting the two electrodes and ion-exchange resins like e.g. Nafion, respectively;
  - a cathode carrying the hydrogenase enzyme or an artificial hydrogenase catalyst in order to recombine protons and electrons into pure molecular hydrogen at the opposite side of the membrane.

- **H_2 design cells** (network project, BMBF – Federal Ministry of Education and Research, Germany, 2005-2011)

  The project had six partners from Germany.

  The major aim of the project was the combination of the natural process of photosynthesis with the reduction of protons by the enzyme hydrogenase (H_2ase). The processes have never been optimally synchronized for a most efficient H_2 production:

  - construction of a cyanobacterium-based „design cell" which uses electrons from water-splitting photosynthesis primarily for H_2 production instead of CO_2 fixation

  - development of low-cost photobioreactors, suitable for scale up and mass production.

c) Relevant Stakeholders

- Ruhr-Universität Bochum, AG Photobiotechnologie, Department of Plant Biochemistry; and Institute of Energy Technology, Chair of Energy Systems and Energy Economics, Bochum, Germany
- National Renewable Energy Laboratory, Golden, United States of America
- Uppsala University, Photochemistry and Molecular Science, Sweden
- Commissariat à l'Energie Atomique et aux Energies Alternatives (CEA), Life Science Division/iRTSV/Laboratory of Chemistry and Biology of Metals-LCBM, SolHyCat Research Group (a research unit co-operated by CEA, CNRS and Université Joseph Fourier, Grenoble), Grenoble, France; and Matter Science Division/IRAMIS/ Service for Physical Chemistry of Surfaces and Interfaces-SPCSI

d) Assessment

Photo-biological hydrogen production is still in the phase of fundamental research, representing a TRL of 1.

Research in photo-biological hydrogen production is closely linked to an increasing understanding of the detailed functioning of the photosynthetic processes. In broader terms, a large number of research groups world-wide is working in this field. However, specific work on photo-biological hydrogen production is carried out by a limited number of researchers.

The approach has the following strengths:

- it has the largest possible hydrogen production potential based on solar radiation and water as only inputs required
- photosynthesis is fundamental to life on earth

Major challenges include:

- hydrogenase is very sensitive to oxygen, which is a by-product of the process; consequently, the process is stable only for short periods of time, currently below two minutes
- so far, conversion rates are low in the order of below 1% solar-to-hydrogen, due to the low light-saturation of photosynthesis
- the competition of hydrogen production with CO_2 fixation

- hydrogen and oxygen are produced as a mixture and need to be separated

Current research focuses on:

- identification and characterization of microorganisms for potential use,
- optimisation of microbes using microbiological methods,
- improving oxygen tolerance,
- increasing solar-to-hydrogen efficiency,
- developing photobioreactor designs,
- developing synthetic mimics of natural enzymes,
- solar converter systems hosting natural enzymes or their mimics,
- developing combined systems (photofermentative systems; see section 2.9).

2.9 Photofermentation (8)

a) Process description

Photofermentation is the fermentative conversion of organic substrate to hydrogen by a diverse group of photosynthetic bacteria. Conversion occurs in a series of biochemical reactions involving three steps similar to anaerobic conversion. The last step is methanation. If hydrogen is the desired product, a two-stage process is applied. Photofermentation differs from dark fermentation because it only proceeds in the presence of light. Unlike biophotolysis (or photobiological water splitting, see below) in which hydrogen is produced from water, photofermentation produces hydrogen from organic substrates.

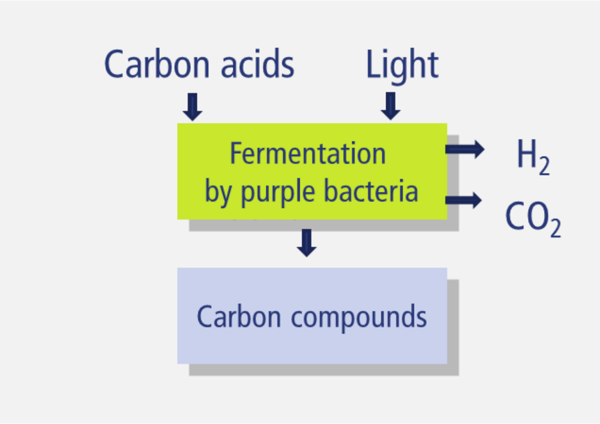

Figure 14: **Schematic of the photofermentation process for hydrogen production**

For example, photo-fermentation with certain Rhodobacter sphaeroides can be used to convert small molecular fatty acids into hydrogen. Rhodobacter sphaeroides are a species of purple bacteria, a group of bacteria that can obtain energy through photosynthesis.

One of the main challenges is huge demand of surface area of the bioreactor, resulting from the need for sunlight and the limited conversion efficiency of the photofermentation process. Another challenge is the management and control of the operating temperature as temperatures below < 20°C are not suitable for the bacteria [BWP II 2007].

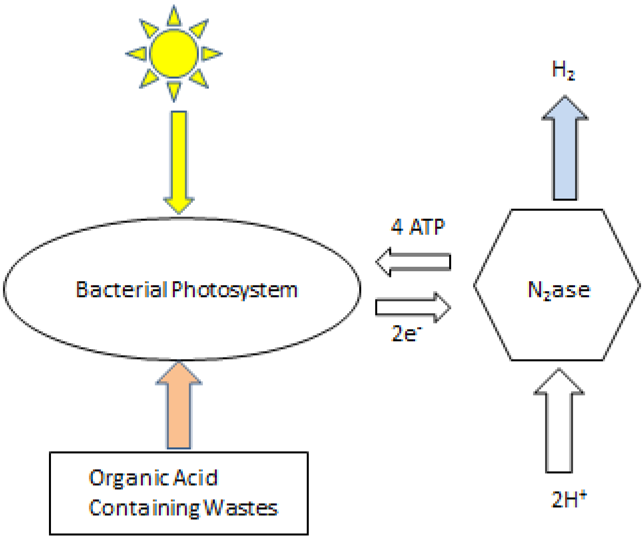

Figure 15: **Process description of photofermentation (after [Hallenbeck et Benemann 2002])**

In [Yongzhen et al. 2007] a two-stage process has been described. At first dark fermentation has been applied to convert sucrose into fatty acids. The photo-fermentation process has been applied to convert the fatty acids into hydrogen.

At the University of Birmingham the research group around Prof. L. Macaskie and Dr. Mark Redwood works with a combination of dark and photo fermentation. In the Integrated Biohydrogen Refinery (IBHR) process described in [Redwood et al. 2012] H_2 is produced via three steps:

1) hot compressed water hydrolysis to pre-treat the biomass,
2) electrofermentation (dark fermentation with separation of volatile fatty acids),
3) photofermentation of the acids by purple bacteria. The production is at a laboratory scale.

Another leading player in the field of bio hydrogen production is the University of Montreal in Canada. Working group around Prof. Hallenbeck also researches on the field of a single stage photofermentative hydrogen production from glucose [Abo-Hashesh et al. 2011].

b) Relevant Projects

The following project are relevant for both pathways, photo fermentation (8) and dark fermentation (5):

- BIOHYDROGEN (FP5, 2000 - 2002)
  (www.biohydrogen.nl/biohydrogen)

  Main objective: production of hydrogen from energy crops and wastes employing (hyper)thermophilic and photoheterotrophic microorganisms.

  Research was done in the field of processing the raw material and in screening microorganisms to optimize the fermentation processes.

- HyVolution (FP6, 2006-2010)
  (http://www.biohydrogen.nl/hyvolution/24295/5/0/20)

  Non-thermal production of pure hydrogen from biomass.

  The aim of the project was to deliver prototypes of process modules with high H2 production efficiency. Reactor design was an important technological objective. Costs of the two-step process could be estimated. Process design was successful, but cost evaluation has shown that photo fermentation will not be suitable for industrial application because of high investment and maintenance costs.

- BWP I (2000 – 2003) and BWP II (2003-2006) (Dutch EET programme)

  Objective: evaluation of dark and photo fermentation

  The projects have “covered the whole chain of pretreatment of biomass to fermentation and up-grading of the produced gas and a techno-economic evaluation. The first techno-economic evaluation, based on thermofermentation followed by photofermentation using potato steam peels as biomass, showed that production costs for H_2 would amount to €3.10/kg_{H2}. The techno-economic evaluation was done assuming that present seemingly feasible targets for thermophilic and photoheterotrophic fermentation will have been met in the future” (quoted from [BWP II 2007]).

c) Relevant Stakeholders

- University of Birmingham, School of Biosciences, Institute of Microbiology and Infection, Prof. Lynne Macaskie, Edgbaston, Birmingham, UK http://www.birmingham.ac.uk/research/activity/bio-hydrogen/index.aspx
- DLO-FBR Stichting Dienst Landbouwkundig Onderzoek, Institute Food and Biobased research, NL, www.wageningenur.nl
  see for example http://www.wageningenur.nl/en/Expertise-Services/Research-Institutes/food-biobased-research/Expertise-areas/Biobased-chemicals/show/Producing-hydrogen-from-biomass.htm
- Université de Montréal, Département de microbiologie et immunologie. Prof. P. Hallenbeck

d) Assessment

Photosynthetic efficiencies – which describe the conversion of solar energy into hydrogen – are rather low[10], even under ideal conditions, as photosynthetic bacteria are optimized for low-light conditions. According to [Hallenbeck et Benemann 2002] major bottlenecks of photo fermentation are:

- the use of the nitrogenase-enzyme with its inherent high energy demand,
- low solar conversion efficiencies, and
- the requirement for elaborate photo-bioreactors, covering large areas.

Hallenbeck and Benemann concluded in 2002: "After extensive R&D research on this system in Japan under the RITE (Research on Innovative Technologies for the Earth) program, it was dropped from further study. In conclusion, the rates and efficiencies of hydrogen production by these systems fall far short of even plausible economic feasibility."

A recent check of RITE projects indicated that today RITE is not involved in corresponding projects. Instead its major activities concerning the hydrogen energy vector are addressed to membrane development for hydrogen separation. Nevertheless, worldwide research in the field continues. In the following, the HyVolution project is analysed in more detail.

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[10] In the literature, often a very high H_2-yield of the substrate is quoted, sometimes approaching even 100%; however, these yields refers only to the extraction efficiency of the produced hydrogen gas in relation to the hydrogen which was bound in the input biomass.

Analysis of HyVolution project results:

TRL-level: According to the report, the two laboratory scale plants with 60-100 litres of bioreactor volume worked for about 6 months in an outdoor environment, with a planar reactor in Germany (Aachen) and a tubular reactor in Turkey (Ankara). This justifies a TRL level of at least 3 ("experimental proof of concept") and maybe 4 ("technology validated in lab") but certainly less than 5 ("technology validated in industrially relevant environment").

Technical Parameters: Based on the experimental results of these two reactors in combination with the first step of a dark fermenter, the HyVolution project also included a techno-economic analysis of an upscaled reactor. Table 5 summarizes the basic technical results of this techno-economic analysis.

Table 5: Summary of experimental results of HyVolution project and their upscaling within a techno-economic analysis [Claassen 2011]; (a) Data are taken from the reference; (b) calculation based on these data; PHF=photo fermentation reactor

Parameter	Tubular PHF	Planar PHF
Size (m²) (a)	1,300,000	2,000,000
Hydrogen production (kg_{H2}/hr) (a)	60	60
Operating hours (THF) h/yr (a)	8000	8000
Operating hours (PHF) h/yr (a)	3330	3330
Hydrogen production (t_{H2}/yr) (b)	480 (278 due to PHF)	480 (278 due to PHF)
H_2-yield (kWh_{H2}/m²/yr) (b)	12.3	8
H_2-yield (MJ_{H2}/yr) (b)	44.3	28.8

According to the performed experiments, the overall yield of hydrogen extraction from glucose amounted 50%, of which 21% are due to the first process step of dark thermophilic fermentation (THF) and 29% to photo fermentation (PHF). If the hydrogen production from the first dark fermentation step (THF) is subtracted the StH conversion of photo fermentation results in 4.6 – 7.1 kWh_{H2}/m²/yr for planar and tubular reactors, respectively. Assuming a solar irradiation of about 1,000 and 2,000 kWh/m²/yr in Aachen and Ankara, respectively, results in a StH-yield of between 0.36 and 0.44 %.

A comparison with conventional PV (electricity production of about 140 kWh_{el}/m²/yr in Germany) and subsequent electrolysis at 65% efficiency of the electrolyser results in hydrogen conversion of 90 kWh_{H2}/m²/yr, which is a factor of 13-20 larger than from photo fermentation. The differences to StH production rates from PEC or TEC, which are also area consuming technologies, are similarly large.

Economical Parameters: Table 6 summarizes the results of the techno-economic study performed in the project and addressed to calculate hydrogen cost of an upscaled plant with 60 kg/h hydrogen production capacity.

Table 6: Calculated investment for the plant with four components: Raw materials preparation, dark fermentation bioreactor, photo fermentation bioreactor and hydrogen upgrading. The data are taken from [Claassen 2011]

Parameter	Tubular PHF	Planar PHF
CAPEX PHF-bioreactor (€)	91,000,000	332,000,000
CAPEX all other components (€)	24,600,000	24,600,000
Total spec. hydrogen cost (€/kg_{H2})	55-60	385-390
share of PHF- cost	82.8 %	Not published
share of THF- cost	10.3 %	Not published
Spec. hydrogen for THF-plant without PHF-step	21	21

In the project description at beginning in 2004 hydrogen production costs of the conceptual design were estimated to amount 29 €/GJ_{H2} (4 €/kg_{H2}) with a possible cost reduction perspective to 10 €/GJ_{H2} (1.21 €/kg_{H2}) until 2020.

In order to meet the cost target of 1.21 €/kg_{H2}, envisaged for 2020, the total CAPEX of the whole plant should not exceed 5.3 million €, which is a factor of 20 below the cost calculation and still a factor of five below the cost calculated for the dark fermentation plant alone without PHF. A planar reactor design is even farther away from any realistic number.

This example illustrates the above cited statement by [Hallenbeck et Benemann 2002] on the low efficiency and large cost expectations being connected with this technology.

In the present context, the cost goal would be achieved much easier with the dark fermentation process alone simply skipping the photo fermentation process step. This would also reduce the plant size considerably though the material requirement would increase by a factor of 2.4 due to the lower hydrogen extraction yield.

Organic acids produced from dark fermentation are treated much cheaper by conventional biogas production. This offers two additional options; either using the biogas for electricity/heat production or converting it in a steam reformer to increase the hydrogen yield of the full process further.

2.10 Electrohydrogenesis (9a)

a) Process description

Microbial electrolysis cells (MEC) are a variation of microbial fuel cells, in which a microbial culture decomposes organic matter, supplying protons and transferring electrons to the anode. These travel to the cathode and combine with oxygen and the protons to produce water and a low voltage. In an MEC, a small external voltage is applied to produce hydrogen gas instead of water at the cathode. The bacteria used in the anodic compartment can reduce different compounds including organic material from waste water (see Figure 16 below). In theory, an MEC using acetate as a feedstock needs 0.114 V to produce H_2 at the cathode; in practice around 0.25 V must be applied. In comparison, water electrolysis (WE) systems theoretically require 1.23 V, and in practice usually require 1.6-2.0 V.

Inputs/feedstocks to be used in this process (also called ‘bio-catalysed electrolysis”) include organic matter (e.g. acetic acid from upstream dark fermentation, or aquatic plants such as reed, sweetgrass, cordgrass, rice, tomatoes, lupines, or algae.) and electricity.

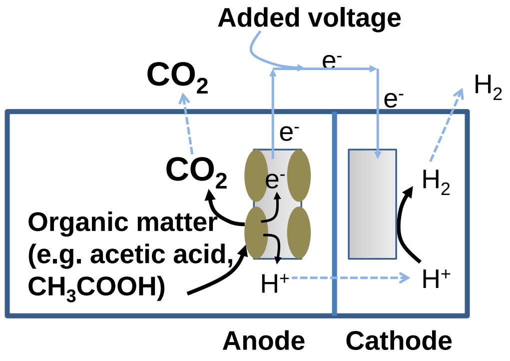

Figure 16: Schematic of the electrohydrogenesis process for hydrogen production (figure based on USDRIVE, Hydrogen Production Technical Team Roadmap, June 2013, p. 81)

b) Relevant Projects

No relevant projects were identified.

c) Relevant Stakeholders

- Department of Civil and Environmental Engineering, Logan Lab, Penn State University, United States of America

- Wageningen UR (University & Research Centre), Wageningen, the Netherlands
- Wetsus Centre of Excellence for Sustainable Water Technology, Leeurwarden, the Netherlands

d) Assessment

Electrohydrogenesis is still in the phase of fundamental research, representing a TRL of 1.

The approach has the following strengths:

- the process can used a large variety of feedstocks including waste waters, and only requires little electricity,
- feedstocks that are not suitable for fermentative hydrogen production can be used.

Major challenges include:

- lack of identified species and consortia,
- lack of knowledge on the effects of different conditions on H_2 production,
- limited availability of molecular biology tools for strain optimisation,
- biological system performance needs to be evaluated in view of production rates, total yields, and reactor performance,
- new materials need to be developed including durable cathodes and non-noble catalysts,
- designing commercial reactors from the current laboratory scale,
- many different feedstocks can be used, however, suitable low-cost and abundant feedstocks need to be identified,
- systems should be suitable for using (volatile) renewable electricity,
- separation of evolving CO_2 and H_2.

Current research focuses on:

- discovering/identifying microorganism strains with improved characteristics,
- identifying optimal growth conditions (e.g. pH, temperature, feedstock loading etc.),
- modifying known organisms to improve their characteristics.

2.11 Plasma-supported Gasification (9b)

a) Process description:

Plasma supported gasification originally was developed for waste removal. A gasifier is fed with wet waste, having a typical water content of 20 %, and heated by a plasma torch able to generate temperatures of up to several thousand degrees Celsius. Complex chemical bindings are cracked under these conditions. The resulting output is syngas with a large share of carbon monoxide, hydrogen, and inert gases, and liquid slag with about 20% of feedstock weight and 5% of feedstock volume. After cooling, the slag forms black glassy rocks like obsidian which can be used as construction material or mixed with concrete or asphalt. Depending on the feedstock quality, most of the hazardous components contained in the waste become inert by their confinement into the glassy slag.

Though originally designed for gasification of hazardous waste, the process can also be used for gasification of municipal slag or even biomass.

Figure 17 shows the basic process steps involved. Municipal waste or biomass is fed into the gasifier which is heated by an electrically ignited plasma torch. The gasification process is driven by oxygen from input air. The energy rich syngas usually feeds a gas turbine to produce electricity. However, in the present context, carbon monoxide will be converted by CO-shift to hydrogen in order to increase the hydrogen yield.

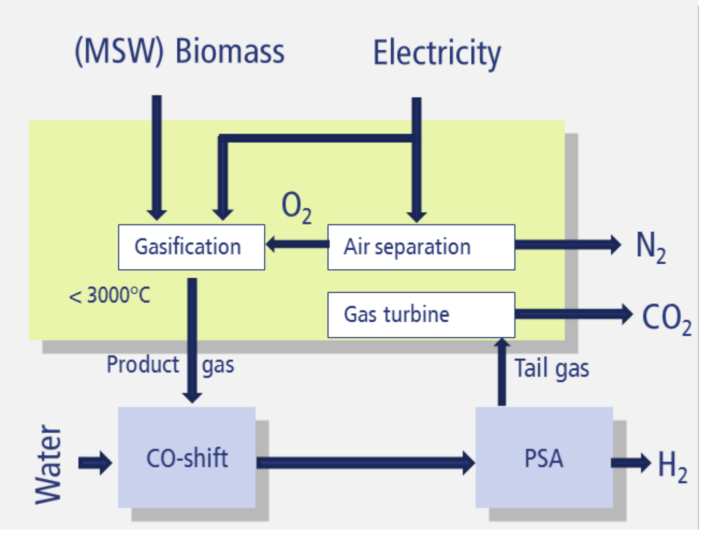

Figure 17: **Schematic of the plasma gasification process with the conversion of the resulting syngas into hydrogen**

Inputs to the process are:

- Toxic waste, municipal waste or biomass
- Water
- Coke (~2-3 mass-%)

b) Resource use

No critical resources[11] are used.

Small amounts of coke as fossil resource input for the process are needed.

c) Output

- Synthetic gas, mainly CO, CO_2 and H_2.
- Slag (e.g. useable as aggregate for concrete products)

d) Waste emissions

- Assuming that particulates are recycled back into the gasifier, only about 5%-vol. of the material introduced into the plasma gasification plant, needs to the sent to landfill
- Air pollutant emissions from combustion process

e) Relevant Projects

Europe

- Tees Valley Renewable Energy Facility project, UK (2012-2016).

  Air Products ordered two Westinghouse Plasma Corp (WPC) plasma gasification plants, each with 350,000 t per year capacity and solid municipal waste (SMW) as feedstock. The first plant operates since 2014, producing 50 MW electricity in a combined cycle. Up to now it is the largest waste-to-energy plant in UK. The construction of the second plasma gasification plant at Tees Valley was started in January 2015. Instead of feeding a combined cycle conventional turbine, the syngas will be optimised for hydrogen production (via steam reforming) and feed an AFC fuel cell with 50 MW power output. Though owned by Air Products, this plant will be operated by Waste2tricity.
- National Grid Bio-SNG demonstration project, APP, UK (2014-2016)

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[11] 'Critical resources' are those with globally limited availability such as platinum group metals (PGM) or rare earth oxides (REO).

In this project Advanced Plasma Power (APP) will demonstrate in an existing 'Gasplasma' demonstration plant in Swindon the production of bio-substitute natural gas ("Bio-SNG") from waste. The demonstration plant should be operated from July 2015 until March 2016.

North America

- GeoPlasma St. Lucie Waste-to-Energy-Project, Florida

  The U.S.-based company Energy Resources Group (ERG) ordered a plasma gasification plant from InEnTec, with a consumption of 600 t MSW per day and 25 MW electricity production which was installed in St. Lucie, Florida. The project became operational in 2013.

- Canadian Waste-to-Energy-Project

  APP, a European competitor to the Calgary based Westinghouse Plasma Corporation (WPC) and U.S.-based InEnTec., received a first order for a Canadian Waste-to-Energy-Project (9th June 2014). According to company news this project for a 20 MW Waste-to-Energy plasma gasification plant in the order of 20 million pounds is their first order for a full-scale commercial facility. The project in the port of Hamilton, Ontario, is designed to process up to 170,000 t of waste annually and to feed the resulting electricity into the grid. The technology was developed by APP and is named GasPlasma®.

Asia

- **Mihama Mikata-Project, Japan** (2002)

  This was the world's first commercial scale plasma gasification project, according to WPC.

- **Biomass gasification project Kaidi, China** (2012)

  In 2012, the WPC-Technology was ordered by the company Kaidi, Wuhan, to demonstrate the conversion of biomass to liquid fuels.

f) Relevant Stakeholders

Europe

- Advanced Plasma Power Ltd, (APP), Swindon, Wilts, UK
- Europlasma in France
- Siemens in Germany

North America

- Westinghouse Plasma Corp. (WPC), Calgary, Alberta, CDA
- AlterNRG, Calgary, Alberta, CDA
- Integrated Environmental Technologies (InEnTec), USA
- Solena Fuels, Washington, D.C., USA (Biomass gasification with subsequent liquefaction).

g) Assessment

One process of plasma supported gasification of municipal solid waste (MSW) to syngas has been developed by Westinghouse in North America. The process was originally developed for waste disposal and syngas / energy production. Another process has been developed in Europe by Advanced Plasma Power (APP).

The TRL for the production of hydrogen via plasma supported gasification of biomass as main feedstock is rated at a level of 8.

Strength of the process:

- Almost commercially developed technology, more than 10 years' experiences
- Municipal solid waste (MSW) can be uses as feedstock (yielding revenues for waste removal)

Major challenges include:

- economics of biomass as feedstock: current processes are optimized for waste as feedstock (revenue from waste disposal vs. biomass feedstock costs)
- availability of biomass
- dynamics of the process plant (cold start: 1 week; warm start: 1 day) requires permanent input of feedstock

2.12 Plasma-based Carbon Black Process (10)

a) Process description

By pyrolysis of hydrocarbon feedstocks (e.g. natural gas, heavy fuel oil, biomass) two valuable products are obtained, hydrogen and carbon black. The pyrolysis process uses a plasma torch mounted in a high temperature reactor. The plasma torch supplies the necessary energy via radiation and convection from the produced plasma gas to pyrolyse the hydrocarbon feedstock.

The decomposition of methane occurs in the following reaction:

$$CH_4 \rightarrow C + 2\,H_2\,; \qquad \Delta H = +\,75\ kJ/mol$$

Methane is produced from biomass via gasification process.

The plasma torch is equipped with a magnetic coil, which enables the arch to rotate at predetermined speed. The energy content (LHV) of 1 mole CH_4 is about 802 kJ, the energy content of the produced hydrogen is 484 kJ. Therefore, the minimum natural gas utilization that can be reached theoretically is 1.66 kWh_{NG}/kWh_{H2}. The by-product carbon black is not used as an energy source. The actually realized Kvaerner process reaches about 1.72 kWh_{NG}/kWh_{H2}.

The process reaches an efficiency of about 48% including electricity (0.347 kW_{el}) but without counting the energy needed for electricity generation and without any credit for the produced carbon black and export steam (0.19 kW_{th}).

The obtained hydrogen purity from the process without additional purification steps is 98% when operated on natural gas. The thermal efficiency of the plasma generator is 97%- 98%. The specific electricity consumption of the hydrogen production process is 1.1 kWh/Nm^3_{H2}. The conversion rate of the hydrocarbon feedstock is almost 100%.

Figure 18 shows the process flow: conventional biomass must be converted into methane which is the input for the plasma process. The heat is coupled into the reaction chamber by microwaves. The cold plasma at about 800°C decomposes methane into solid carbon, which can be extracted at the bottom of the reaction chamber, and into gaseous hydrogen, which can be extracted at the top of the reaction chamber.

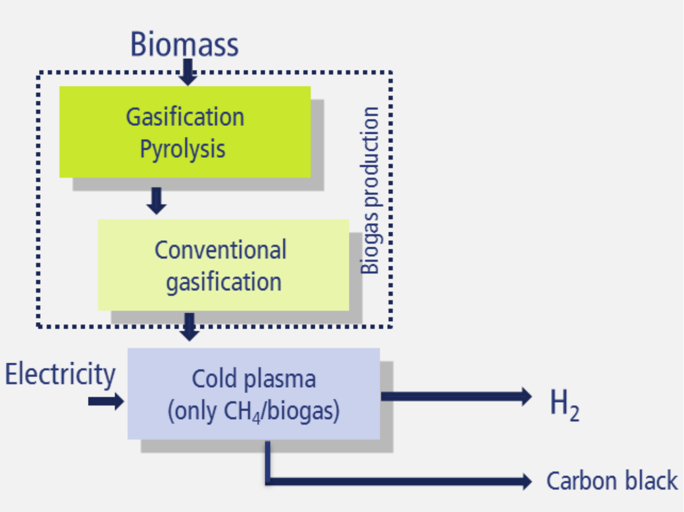

Figure 18: **Plasma process to produce hydrogen and carbon black from methane gas**

Inputs to the process are:

- Methane or purged biogas
- Electricity

b) Resource use

- Steel
- Copper
- No critical resources[12] are used.

c) Output

- Carbon (solid)
- Hydrogen (mixed with fine carbon dust particles)

d) Waste emissions

- No waste emissions

e) Relevant Projects

Europe

- Gassmark, Norway

North America

- Atlantic Hydrogen (AHI) has signed an $800,000 contribution agreement with Alberta Innovates – Energy and Environment Solutions (AI-EES) in support of the development of the first AHI CarbonSaver® field-demonstration plant. (May 2014) The AI-EES funds will be used for process validation, thermal optimization, and component modularization at the Bayside CarbonSaver field demonstration plant in Saint John, NB. The contribution will cover roughly one third of the total costs of these activities to the end of 2014.

  "Through meetings and discussions, we've learned that the interest Alberta organizations show in the CarbonSaver technology is a reflection of the vision of AI-EES to adapt innovative technologies that maximize the value of Alberta's natural resources while protecting the environment," says David Wagner, president and CEO of AHI. "AI-EES' contribution to the

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[12] 'Critical resources' are those with globally limited availability such as platinum group metals (PGM) or rare earth oxides (REO).

> development of CarbonSaver's low-emission technology will help reduce greenhouse gas emissions from processing and refining oil sands crude."
>
> Construction at AHI's Bayside site is almost complete. The plant is scheduled to be commissioned by June 2014. The rest of 2014 will be spent optimizing the current reactor design and preparing for larger scale production in 2015.
>
> By supporting AHI, AI-EES hopes to have low-CO_2 hydrogen produced by the CarbonSaver contribute to reducing the greenhouse gas intensity of upgrading and refining oil sands crude.

f) Relevant Stakeholders

Europe

- SINTEF
- GasPlas

North America

- Atlantic Hydrogen Inc. (AHI)
- Idaho National Laboratory

Asia

- LNG Technology Research Center, Korea Gas Corporation

g) Assessment

The process has been developed for the production carbon black from methane.

The TRL of this technology is rated at 4.

Major strengths are:

- High scalability
- Semi-central application targeted (e.g. H_2 refuelling stations)
- High dynamics of cold plasma generators (use of electricity)

Major challenges include:

- Costs and lifetime of the plasma system
- Carbon collection system (separation of the fine carbon particulate matter from the gas stream)

3 Bibliometric Anaylsis of the identified pathways

A bibliometric data analysis for each technology under scrutiny has been performed, reviewing research activity in terms of number of scientific publications and patents over the past 8 years. The results of this analysis help the project team identify which technologies are subject to the most development and innovation efforts in the relevant world regions and assess the level of maturity of the different processes (by spotting where R&D is gaining/losing traction).

3.1 Methodology

Publications

- The Publications/scientific papers were searched through Google scholar,
- The searches were based on keyword sets for each technology. The keyword generated for each technology are based on a large list of words provided by LBST, a number of leading projects on the fields,
- The results are shown at global level (no geographical differentiation),
- Classified by year of publication,
- A list of the 10 most cited publications have been developed for each technology (see annex), presenting the leading research groups (from either industry/academia),

Patents

- The Patents were retrieved from the PatStat database using the tool ESPACENET online tool, with a worldwide data base including more than 90 countries,
- Searches were based on keyword sets for each technology.
- Patents are classified by patent family. Therefore, we avoid double counting patents registered in different countries (patent offices) that refer to the same invention.
- Geography:
  - Sorted by priority country (the country where the patent was first registered),
  - Countries grouped in regions 7 regions; the focus has been put on Europe, North America, Asia,

- Time line:
    - Classified by ‘priority year’,
    - Although patents were filtered for the period 2007 to 2015, the results are shown from 2006 until 2012. Time from patent registration (priority year) to publication varies widely (typically 1-2, and up to 12 years); in average 1.3 years. As a result, absolute values for 2014 and 2013 are significantly lower than for previous years and, therefore, not shown.

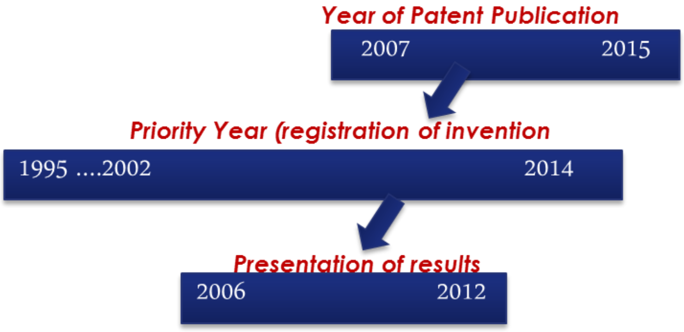


Figure 19: Time scope for patents search and presentation

- Results: The results of the bibliometric research for patents are based on 3 indicators:
    - Total number of patents registered for the period observed (2006 to 2014),
    - Compound annual growth rate (CAGR) for the period 2006 to 2012,
    - Smart specialization index*,

***Specialization index (SI)**: We have calculated the specialization index (SI) as research intensity of a given region in a given research area (e.g. biogas reforming) relative to the research intensity of a reference entity (in this case, the world) in the same research area:

$$SI = (\frac{XS}{XT})/(\frac{NS}{NT})$$

where:

X_S = # of patents from region X in a given research area (e.g. EU patents in biogas reforming);

X_T = # of patents from region X in a reference set of patents (e.g. total EU patents);

N_S = # of patents from reference region in a given research area (e.g. global patents in biogas reforming);

N_T = # of patents from reference region in a reference set of Patents (e.g. total global patents).

A specialization index >1 indicates that the region in question is more specialized vs. the global average.

However, it should be noted that regions with low patenting activity, with a shorter industrial history, or a more narrow technology base will tend to show higher SI values in areas where they are active; as a result, Asian SI values may generally trend higher than for Europe or North America.

Total patent activity by country and region has been extracted from the World Intellectual Property Organization (WIPO).

3.2 Results

Regarding the publication of scientific papers from a worldwide perspective, we can observe a continuous increase throughout the years (figure x). Technologies can be grouped in 4 main clusters, based on the total number of publication and growth rates, as displayed in the graph. Biomass gasification and thermochemical water splitting of biomass perform the largest activity, indicating the high interest from the research community and the increasing maturity rates in these two pathways. Technologies like biogas reforming ad plasma-supported gasification, on the other hand, display very little activity, indicating in this case that these technologies are quite mature.

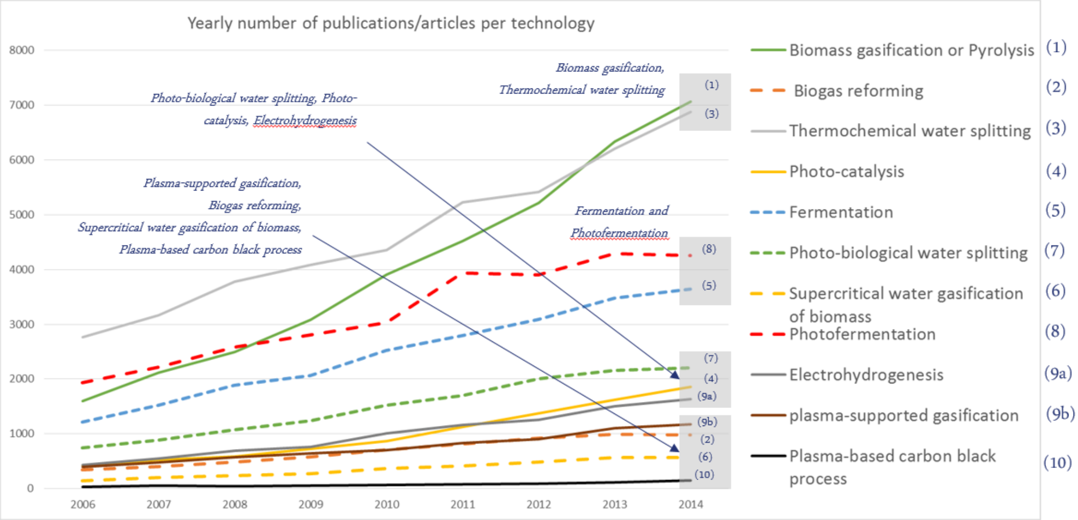


Figure 20: Publications by Technology (worldwide)

For patent activity, we have looked not only into global annual activity (Figure 21), but also into the specialization index in the region, the accumulated number of patent throughout the period, and the compound annual growth rate (Figure 22).

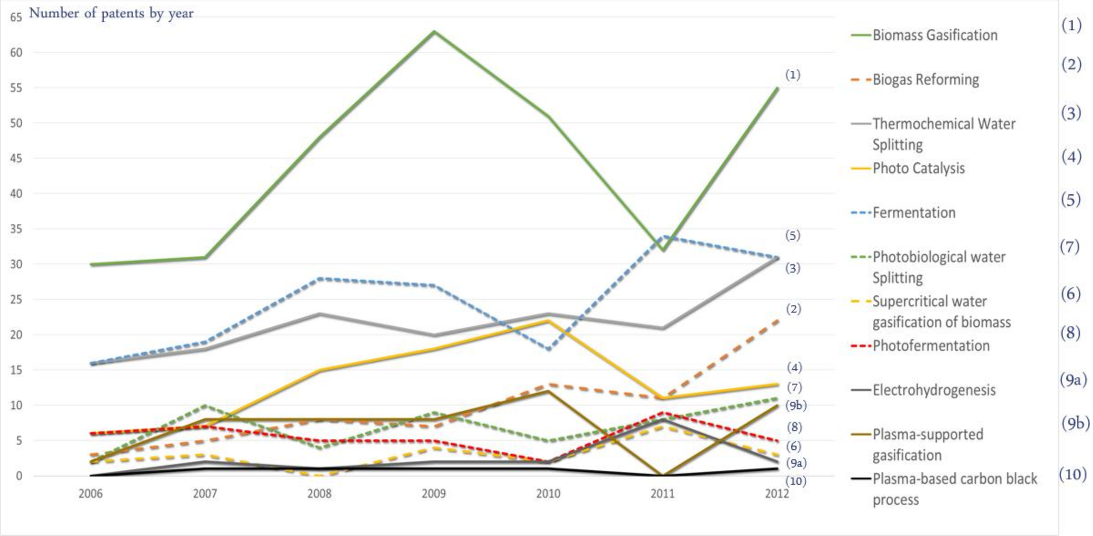
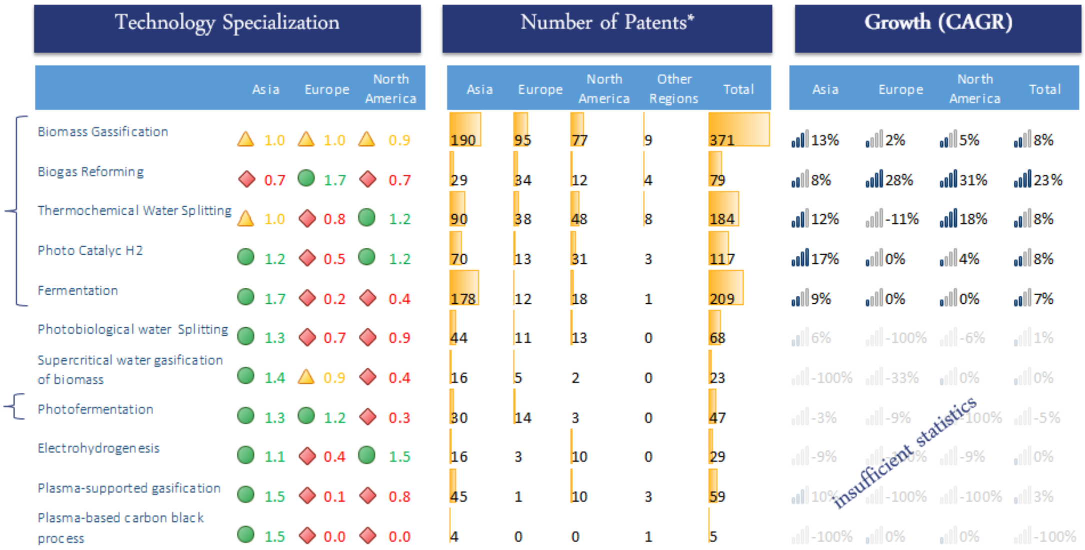


Figure 21: Patent Activity by Technology (worldwide)



	Technology Specialization			Number of Patents*					Growth (CAGR)			
	Asia	Europe	North America	Asia	Europe	North America	Other Regions	Total	Asia	Europe	North America	Total
Biomass Gassification	△ 1.0	△ 1.0	△ 0.9	190	95	77	9	371	13%	2%	5%	8%
Biogas Reforming	◆ 0.7	● 1.7	◆ 0.7	29	34	12	4	79	8%	28%	31%	23%
Thermochemical Water Splitting	△ 1.0	◆ 0.8	● 1.2	90	38	48	8	184	12%	-11%	18%	8%
Photo Catalyc H2	● 1.2	◆ 0.5	● 1.2	70	13	31	3	117	17%	0%	4%	8%
Fermentation	● 1.7	◆ 0.2	◆ 0.4	178	12	18	1	209	9%	0%	0%	7%
Photobiological water Splitting	● 1.3	◆ 0.7	◆ 0.9	44	11	13	0	68	6%	-100%	-6%	1%
Supercritical water gasification of biomass	● 1.4	△ 0.9	◆ 0.4	16	5	2	0	23	-100%	-33%	0%	0%
Photofermentation	● 1.3	● 1.2	◆ 0.3	30	14	3	0	47	-3%	-9%	-100%	-5%
Electrohydrogenesis	● 1.1	◆ 0.4	● 1.5	16	3	10	0	29	-9%	-100%	-9%	0%
Plasma-supported gasification	● 1.5	◆ 0.1	◆ 0.8	45	1	10	3	59	10%	-100%	-100%	3%
Plasma-based carbon black process	● 1.5	◆ 0.0	◆ 0.0	4	0	0	1	5	-100%	0%	0%	-100%

Figure 22: Technology Overview by Region (period 2006-2012)

We are not able to derive strong conclusions for all technologies given the relatively small numbers of patents.

Looking at the total number of patents, biomass gasification clearly stands out from the rest of technologies. Furthermore, similar specialization index in all regions reflects a high level of competition.

Biogas reforming presents the strongest CAGR, especially in Europe; Europe is also more specialized on this pathway than North America and Asia.

Activity on thermochemical water splitting is also quite high, with comparable specialization index among regions and presenting strong growth in the North America, given by a strong push in the last years.

A detailed assessment per technology can be found in section 3.4.

It is important to note that there is little differentiation between Europe and North America (in terms of number of patents and specialization index). Generally, one can observe higher number of patents in Asia, being likely caused by different patenting strategies. Also patent quality may differ systematically between countries.

3.3 Conclusions

Strongest international activity is found on:

- Biomass gasification
- Thermochemical water splitting
- Fermentation and photofermentation
- Photo-catalysis
- Biogas reforming

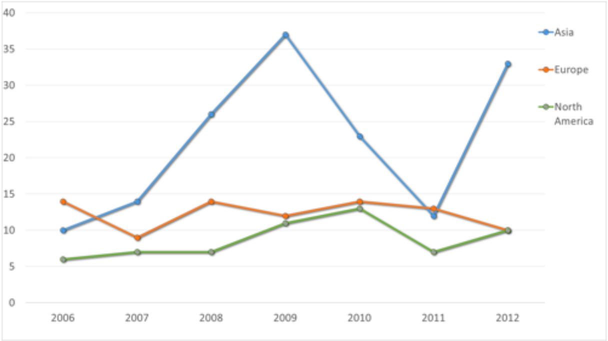
The results in patent and publication search are largely consistent, presenting similar top technologies; showing that more mature technologies tend to show less publications (e.g. biogas reforming, plasma-supported gasification); exhibiting strong patent and publication activity in biomass gasification, and displaying a small number of patents in several technologies (due to their low Technology Readiness Levels).

Regarding the regions, we observe the following:

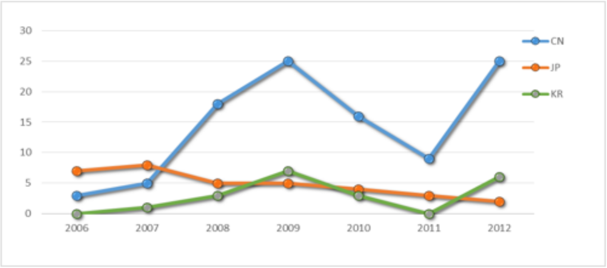
- Europe
  - High specialization in biogas reforming with a significant growth in recent years. Also specialized in photofermentation.
  - Very little activity in plasma-based processes
  - Patenting activity generally limited except for biomass gasification, biogas reforming and thermochemical water splitting.
- North America
  - Specialization in thermochemical water splitting, photo-catalysis and electrohydrogenesis.

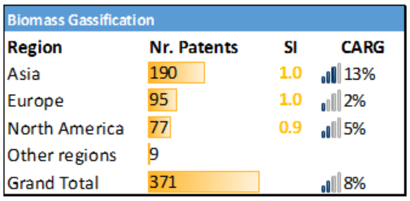
- Asia
  - Specialized in all technologies expect biogas reforming and thermochemical water splitting.
  - Strong growth in plasma supported production. Only region active in carbon black process.

3.4 Individual technology analysis and conclusions



Zoom into the leading region





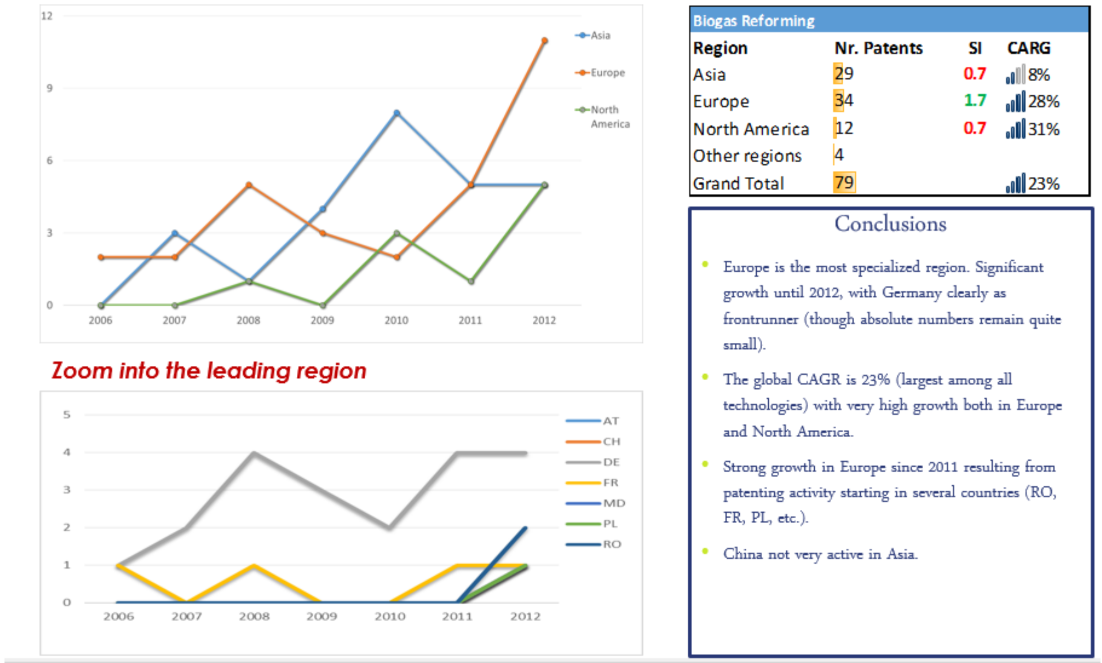
Biomass Gassification

Region	Nr. Patents	SI	CARG
Asia	190	1.0	13%
Europe	95	1.0	2%
North America	77	0.9	5%
Other regions	9		
Grand Total	371		8%

Conclusions

- Technology with the highest patent numbers of all technologies under scrutiny.
- No significant difference among regions on specialization.
- The global CAGR is 8%, with Asia showing the highest growth rate.
- Asian results distorted by Chinese numbers on the high side.
- Japan has a steady decrease while US and Europe remain relatively constant
- Rebound effect after 2011 in Asia and to a lesser extent North America.

Figure 23: **Biomass Pyrolysis and Gasification (1)**

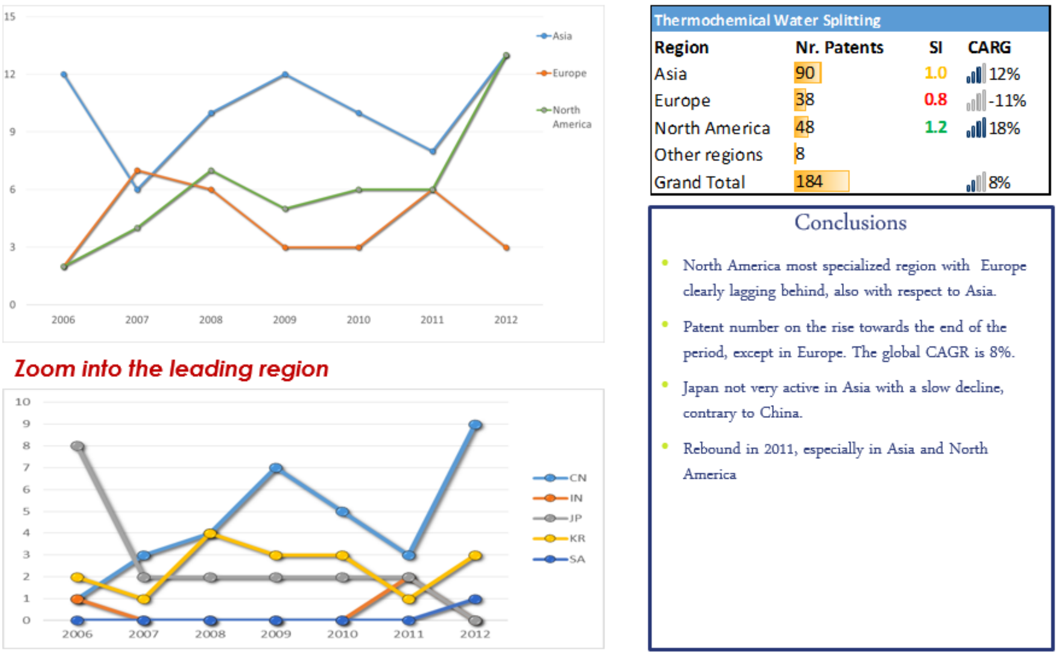


Biogas Reforming			
Region	**Nr. Patents**	**SI**	**CARG**
Asia	29	0.7	8%
Europe	34	1.7	28%
North America	12	0.7	31%
Other regions	4		
Grand Total	79		23%

Conclusions

- Europe is the most specialized region. Significant growth until 2012, with Germany clearly as frontrunner (though absolute numbers remain quite small).
- The global CAGR is 23% (largest among all technologies) with very high growth both in Europe and North America.
- Strong growth in Europe since 2011 resulting from patenting activity starting in several countries (RO, FR, PL, etc.).
- China not very active in Asia.

Figure 24: **Biogas Reforming (2)**

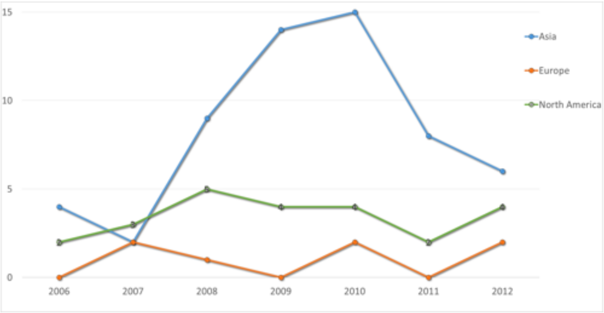


Thermochemical Water Splitting			
Region	**Nr. Patents**	**SI**	**CARG**
Asia	90	1.0	12%
Europe	38	0.8	-11%
North America	48	1.2	18%
Other regions	8		
Grand Total	184		8%

Conclusions

- North America most specialized region with Europe clearly lagging behind, also with respect to Asia.
- Patent number on the rise towards the end of the period, except in Europe. The global CAGR is 8%.
- Japan not very active in Asia with a slow decline, contrary to China.
- Rebound in 2011, especially in Asia and North America

Figure 25: **Thermochemical water splitting based on renewable high temperature heat (3)**



Zoom into the leading region

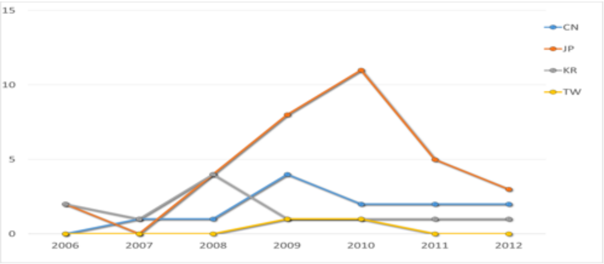
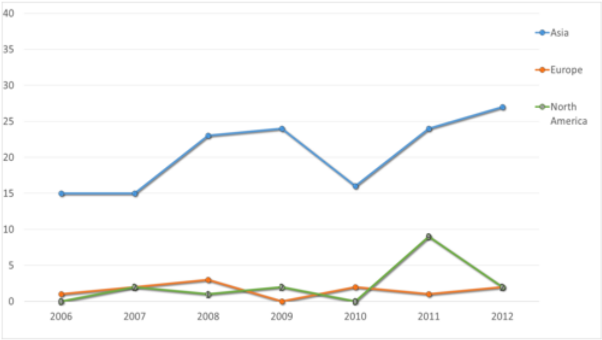


Photo Catalyc H2			
Region	**Nr. Patents**	**SI**	**CARG**
Asia	70	1.2	17%
Europe	13	0.5	0%
North America	31	1.2	4%
Other regions	3		
Grand Total	117		8%

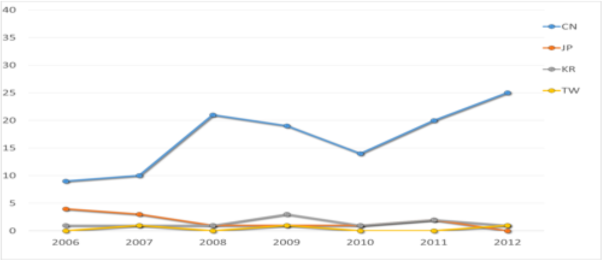
Conclusions

- Strongest growth in Asia until 2010 followed by a steady decline ever since, directly related to patenting activity in Japan.
- Patenting activity globally declining after 2010 with a small rebound in 2011 in Europe and North America.
- Europe lagging behind on both growth rate and specialization index.

Figure 26: **Photo-catalysis (4)**



Zoom into the leading region

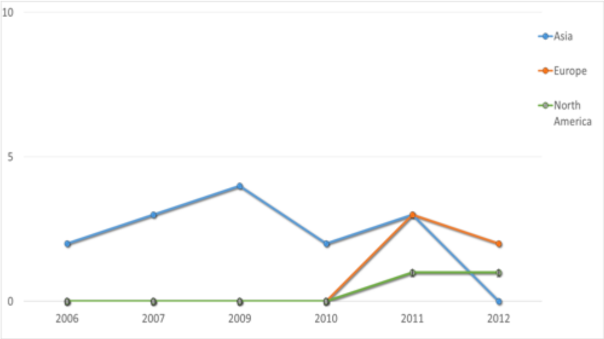


Fermentation			
Region	**Nr. Patents**	**SI**	**CARG**
Asia	178	1.7	9%
Europe	12	0.2	0%
North America	18	0.4	0%
Other regions	1		
Grand Total	209		7%

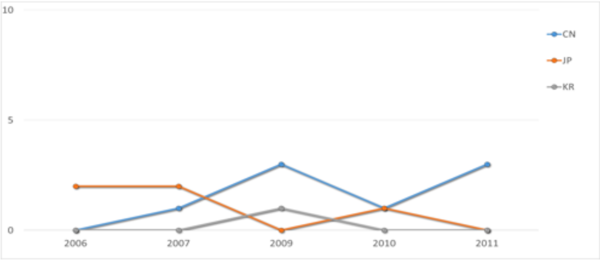
Conclusions

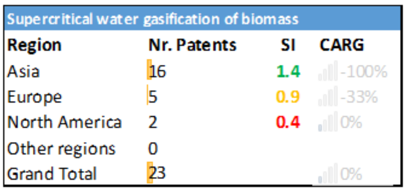
- Asia, more specifically China clearly leading.
- With the exception of a peak in 2011 in North America, patenting activities are very limited globally outside of China.
- Specialization index very low both in Europe and North America.

Figure 27: **Fermentation (5)**



Zoom into the leading region





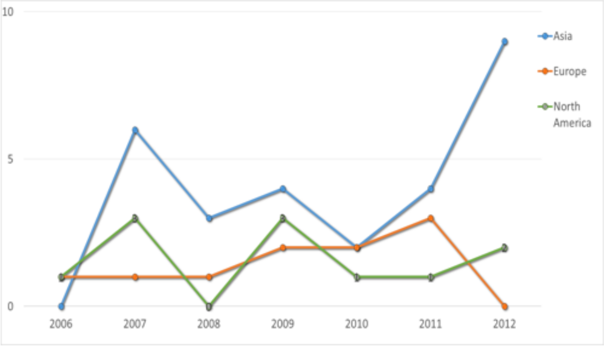
Supercritical water gasification of biomass

Region	Nr. Patents	SI	CARG
Asia	16	1.4	-100%
Europe	5	0.9	-33%
North America	2	0.4	0%
Other regions	0		
Grand Total	23		0%

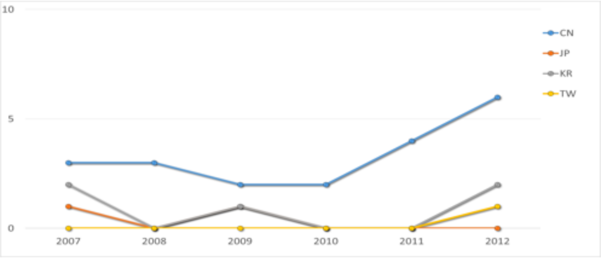
Conclusions

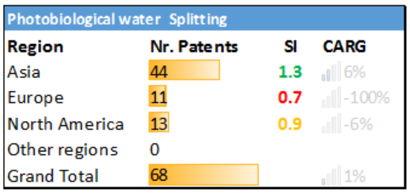
- Overall very few patents identified. It may be explained by the fact that most of the activities in this field were included in category "Biomass gasification".
- Activity in North America and Europe only starts in 2010.

Figure 28: Supercritical water gasification of biomass (6)



Zoom into the leading region





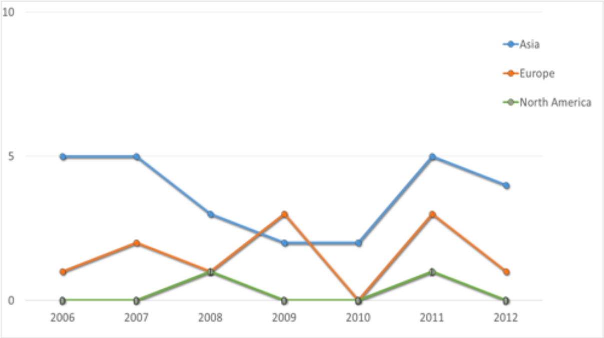
Photobiological water Splitting

Region	Nr. Patents	SI	CARG
Asia	44	1.3	6%
Europe	11	0.7	-100%
North America	13	0.9	-6%
Other regions	0		
Grand Total	68		1%

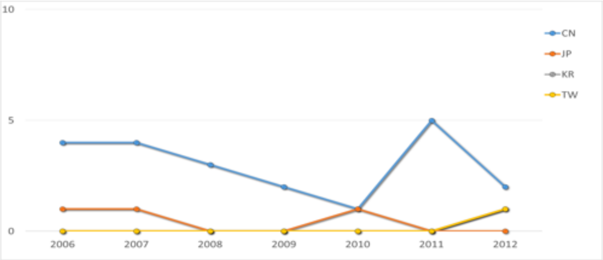
Conclusions

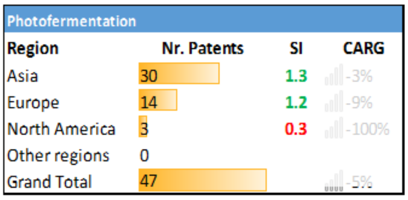
- Asia experimenting a strong growth since 2010 and leading on total number of patents, as well as on specialization.
- Activities in Europe and North America are low and remain mostly constant throughout the time observed.
- China is leading the activity in Asia.
- We can observe interest raising in Asia in 2012, with Korea and Taiwan registering patents after a long period of inactivity.

Figure 29: Photobiological water splitting (7)



Zoom into the leading region





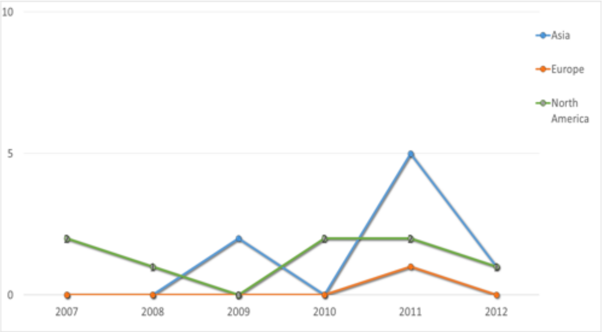
Photofermentation

Region	Nr. Patents	SI	CARG
Asia	30	1.3	-3%
Europe	14	1.2	-9%
North America	3	0.3	-100%
Other regions	0		
Grand Total	47		-5%

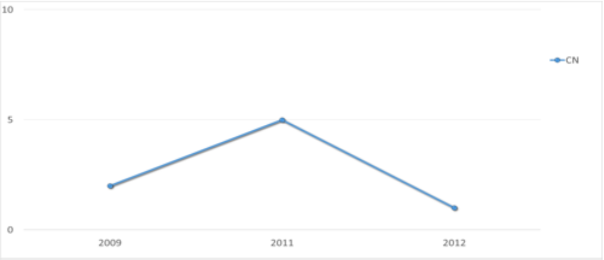
Conclusions

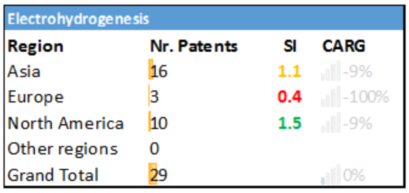
- Negative growth in all regions. Patenting activity globally declining until 2010, where we observe a rebound
- Specialization index is higher for Asia and Europe, when considering the whole time period.
- North America lagging behind on both growth rate and specialization index.

Figure 30: Photofermentation (8)



Zoom into the leading region





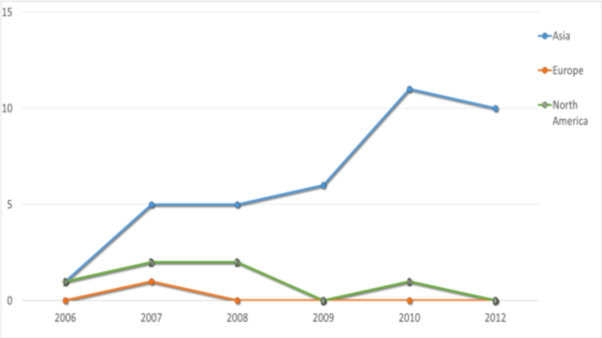
Electrohydrogenesis

Region	Nr. Patents	SI	CARG
Asia	16	1.1	-9%
Europe	3	0.4	-100%
North America	10	1.5	-9%
Other regions	0		
Grand Total	29		0%

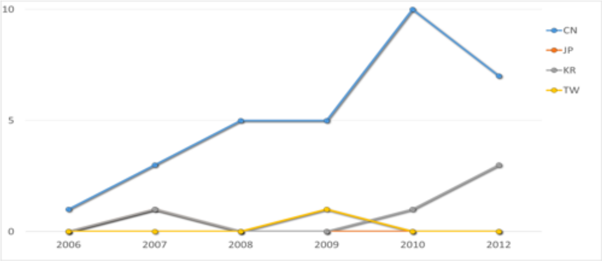
Conclusions

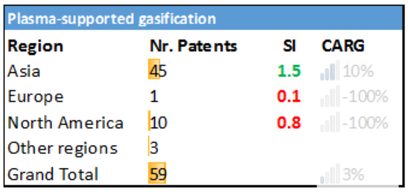
- Overall very few patents identified.
- North America and China accumulated most of the activity in this field.
- We observe and decreasing tendency in all regions from 2011.

Figure 31: Electrohydrogenesis (9a)



Zoom into the leading region





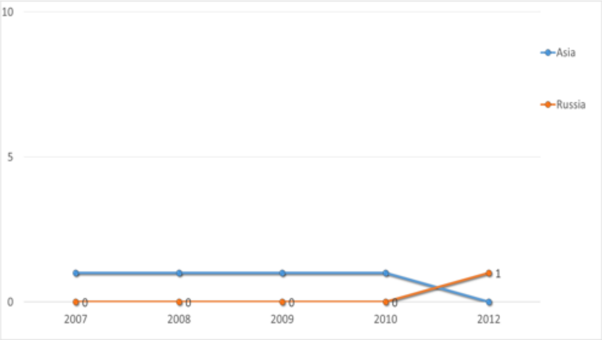
Plasma-supported gasification

Region	Nr. Patents	SI	CARG
Asia	45	1.5	10%
Europe	1	0.1	-100%
North America	10	0.8	-100%
Other regions	3		
Grand Total	59		3%

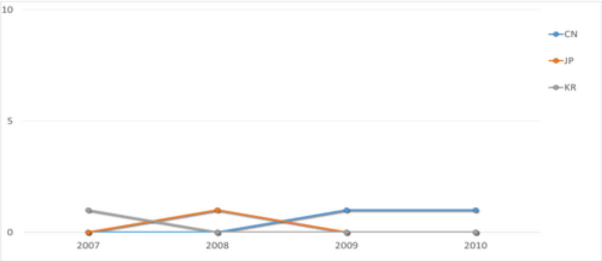
Conclusions

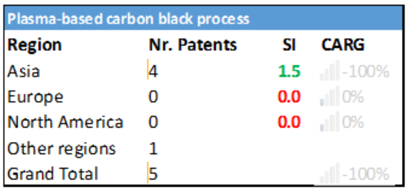
- Asia, led by China is the most active region on patents registration.
- There is a clear growth tendency in Asia that do not correspond to the low activity in North America and Europe.
-

Figure 32: Plasma-supported gasification (9b)



Zoom into the leading region





Plasma-based carbon black process

Region	Nr. Patents	SI	CARG
Asia	4	1.5	-100%
Europe	0	0.0	0%
North America	0	0.0	0%
Other regions	1		
Grand Total	5		-100%

Conclusions

- Almost no patent activity identified for this technology.

Figure 33: Plasma-based carbon black process (10)

4 Selection of six green hydrogen pathways for hydrogen production

During a one day workshop in Brussels with FCH JU and its stakeholders all green hydrogen pathways screened in this study and their specific performance indicators have been scrutinized one by one. Based on the results of the initial assessment as documented in sections 2 and 3, six technologies have been selected for a detailed assessment with specific focus on a techno-economic analysis and on environmental impact criteria. This detailed analysis will then lead to an identification of specific areas requiring targeted further research and development for each of the six selected pathways.

4.1 Summary

Figure 34 summarises TRLs and their expected development as well as specific hydrogen production costs for the selected pathways over time, grouped by the main feedstock (biomass, solar thermal, and sunlight), where the blue bars summarise estimated TRL for the years 2015, 2023 and 2030, and green arrows indicate first estimates of hydrogen production costs[13] until 2030.

Values for hydrogen production by water electrolysis (WE) and by the steam reforming of natural gas (SME) are shown as a benchmark[14].

---

[13] Hydrogen cost estimates in this figure are based on literature or expert input as documented in chapter 2, specific hydrogen cost analyses are made in the subsequent detailed analysis.

[14] Benchmark data based on L. Bertuccioli et al., Development of Water Electrolysis in the European Union, Final Report, Fuel Cells and Hydrogen Joint Undertaking, 7 Feb 2014

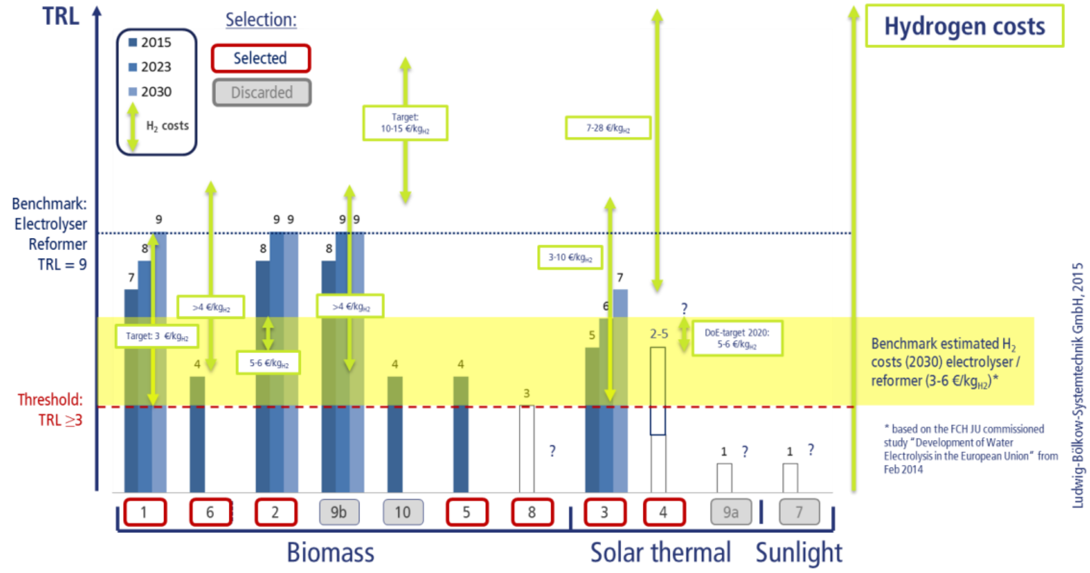


Figure 34: **Summary of TRL and cost estimates of Green Hydrogen pathways; pathway numbers with red frames denote selected pathways**

4.2 Selected Pathways

Six technologies have been selected for a more detailed analysis in a workshop with FCH JU and its stakeholders on 12 March, 2015 in Brussels. Pathway numbers with red frames denote selected pathways in Figure 34[15]. The following Green Hydrogen Pathways have been selected for Phase 2:

Biomass Pyrolysis and Gasification (1)

This pathway has reached high maturity. The scale-up and build-up of larger demonstration plants in the next years could lead to an increase of the TRL to 9. Biomass gasification processes are adoptable to local, semi-central, and central hydrogen production. First hydrogen cost estimates indicate that these could be competitive to water electrolysis and SMR.

Raw Biogas Reforming (2)

Raw biogas reforming is also a very mature technology. Hydrogen production from raw biogas as feedstock could be commercially available for local and semi-central applications, e.g. at fuelling stations in the next years.

---

[15] Pathways 2 and 5 are combined into one for the subsequent analysis.

The potential to integrate this technology into existing fuelling stations is one of the major advantages. Green hydrogen could be produced from local biogas plants or from (bio)methane produced remotely and injected into the natural gas grid.

Thermochemical Water Splitting (3)

This pathway with a current TRL of 5 could reach a TRL of 7-8 until 2030. At present, European institutes are among the leading groups internationally, as European research into hydrogen production from solar thermal energy has received continuous funding over the last decades. European and international activities for demonstration plants could potentially increase the TRL to a level of 9 by 2030, e.g. by large scale demonstration activities in Australia. Hydrogen production costs via thermochemical water splitting could be at a competitive level to WE and SMR by 2030.

Photo-catalysis (PEC: Photo-electrochemical cell) (4)

Even though the PEC process offers a more long-term solution with currently a wide TRL bandwidth of 2 to 5, it presents an interesting wildcard for hydrogen production from solar energy. The photo-electrochemical cell is a scalable technology and has demonstrated a sufficient advancement in the recent years in EC funded projects and thus a potential for significant TRL improvement. The technology is pursued by European and international players from industry and research. PEC technology can generally produce hydrogen in local, semi-central, and central settings and has a chance to reach hydrogen production costs levels comparable to WE and SMR by 2030.

Supercritical water gasification of biomass (6)

This technology is the only pathway providing for the use of wet biomass and organic wastes as main feedstock, offering a diversification of hydrogen production by using food industry residues, sewage sludge, etc. Notably, it can also be used for the gasification of algae. The process supplies clean product gas, as e.g. sulphur or nitrogen remain in the liquid phase. Though the current TRL is estimated at 4, industrial interest in Europe has increased in the last years, particularly in the Netherlands. However, so far industry focus has not been on the production of hydrogen but on the production of combustible gas in general. First pilot plants exist. The process provides hydrogen at high pressure. Hydrogen costs can potentially reach those of WE and SMR by 2030.

Fermentation (in the absence of light) (5) combined with raw biogas reforming (2)

The dark fermentation process can work with a variety of substrates as main feedstock, ranging from sugar-rich or complex biomass to lignocellulosic biomass or sewage and food waste. Other advantages include the inherent waste disposal capability and the simple reactor technology.

For the selected hydrogen production pathway, the residue of the dark fermentation is fed into a 'conventional' biogas plant to generate biogas (which mainly consists of methane and CO_2). The biogas is then fed into a steam reforming plant to generate hydrogen (raw biogas reforming). This process step of raw biogas reforming has a high maturity.

Interest of the European industry on the dark fermentation process has recently increased. The current TRL is 4.

4.3 Pathways not selected

The following pathways have not been selected for further analysis:

Plasma-supported gasification (9b)

This process has been developed and optimized for waste disposal. The high temperature process is using municipal solid waste (MSW) as feedstock. Even with a TRL of 9 and the fact that it has been commercially developed in North America (Westinghouse) the process is not optimized for biomass as feedstock.

Although the adaption of this technology for using biomass as main feedstock and to produce pure hydrogen offers a path towards a green hydrogen production, industry interest and support is limited according to [Gorodetsky 2015].

The plasma supported gasification process is a large scale application for central production of syngas or hydrogen. The dynamics of the process plant (cold start: 1 week; warm start: 1 day) requires a permanent supply and input of the feedstock. Thus, availability and cost of biomass feedstock are crucial in potential applications for green hydrogen production.

Plasma-based carbon black process (10)

The plasma-based carbon black process has been developed to produce high quality carbon black from methane as main feedstock. Here, hydrogen is only a by-product and contains very fine carbon particles. As a consequence, the resulting hydrogen purity is not sufficient for the use in fuel cells, and the efficient separation of the carbon from the gas stream represents one of the major challenges. However, the major driver for the further development of this technology is the provision of products for industry, e.g. carbon black, and not to optimise the process for high quality and quantity hydrogen. Other issues are the high cost and the limited lifetime of the plasma system. TRL is estimated at 4. In Europe, industrial interest to adapt and optimise this technology for hydrogen production is limited. The bibliometric analysis has shown that between 2006 and 2012 no patents and only a few publications have been made worldwide.

Electrohydrogenesis (biocatalysed electrolysis) (9a)

The process of electrohydrogenesis is still in the phase of fundamental research. The TRL is 1 and thus under the defined threshold of TRL>3. Several fundamental R&D issues remain.

Photo-biological water splitting including algae bioreactors and photosynthetic microbes (7)

The photo-biological hydrogen production is also still in the phase of fundamental research with a TRL of 1. Several fundamental R&D issues have to be addressed before possibly reaching the required selection threshold of TRL>3.

5 Detailed assessment of the six selected pathways

5.1 Assumptions and methodology

Where possible, assumptions taken in the FCH JU Report on the Development of Water Electrolysis in the European Union [E4tech & EE 2014] have been used in this study as well in order to provide for comparability.

5.1.1 Cost assumptions

The discount rate on capital cost has been assumed to be 7%, consistent with the assumption taken for hydrogen production from wind energy in [E4tech & EE 2014].

For many processes auxiliary electricity for equipment such as screw conveyors, compressors, pumps, air blowers, agitators and control systems is required. Some processes need natural gas for heat supply. Analogous to the report by [E4tech & EE 2014] the natural gas price has been assumed to be 0.040 € per kWh based on the lower heating value (LHV). For consumers with an electricity consumption of up to 2,000 MWh per year an electricity price of 0.166 € per kWh has been assumed as indicated in [E4tech & EE 2014]. For consumers with an electricity consumption above 2,000 MWh per year an electricity price of 0.139 € per kWh has been assumed based on [DBFZ 2014].

The final hydrogen fuel costs do not include taxes.

5.1.2 Efficiency method

For the calculation of the energy requirements the so-called “efficiency method” has been used similar to the procedure adopted by international organizations (IEA, EUROSTAT, UNECE).

In this method the efficiency of electricity generation from nuclear power is based on the heat released by nuclear fission which leads to an efficiency of about 33%.

In the case of electricity generation from hydropower and other renewable energy sources which cannot be measured in terms of a calorific value (wind, solar energy) the energy input is assumed to be equivalent to the electricity generated which leads to an efficiency of 100%.

The efficiency of electricity generation from geothermal energy sources is assumed to be 10%.

5.1.3 GHG emissions

Greenhouse gases considered in this study are carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O)[16]. The global warming potential of the various greenhouse gases is expressed in CO_2 equivalents. Table 7 shows the global warming potential for a period of 100 years according to the Fourth and Fifth Assessment Reports of the Intergovernmental Panel on Climate Change (IPCC).

Table 7: Global warming potential (GWP) of various GHGs [IPCC 2007], [IPCC 2013]

	AR4* g CO_2 equivalents/g	**AR5* (used in this study) g CO_2 equivalents/g**
CO_2	1	1
CH_4	25	30
N_2O	298	265

* AR - Assessment Report

Several international research institutions (e.g. Argonne National Laboratory in its 'GREET 2014' tool) have already started to use the values of the latest (fifth) IPCC report, i.e. a GWP of 30 g_{CO2eq}/g_{CH4} and 265 g_{CO2eq}/g_{N2O} [IPCC 2013]. These are also used in the present study.

In the evaluation, only CO_2 generated by the combustion of fossil fuels is considered. The combustion of biomass is defined to be CO_2 neutral: the amount of CO_2 emitted during the combustion of biomass is the same as the amount of CO_2 which was taken from the atmosphere by the plants during their growth.

Analogous to [JEC 2014], the energy requirements and GHG emissions resulting from the construction and decommissioning of manufacturing plants and vehicles are not considered here.

5.1.4 Benchmark of hydrogen production costs

For the benchmarking against hydrogen production costs via water electrolysis (WE) and steam methane reforming (SMR) data and assumptions have been taken from [E4Tech & EE 2014].

For the different applicability cases for hydrogen production (*local*, *semi-central* and *central)* specific use cases have been selected from [E4Tech & EE 2014] (see Table 8).

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[16] Other greenhouse gases are CFCs, HFCs, and SF6, which are, however, not relevant in this context.

Table 8: Selected benchmark data, taken from [E4Tech & EE 2014]

Applicability cases for H_2 production	Selected use case in the [E4Tech & EE 2014] study for benchmark	Key assumptions and results of the [E4Tech & EE 2014] study*
Local production (0.2-4 t_{H2}/day)	1a: Small car HRS	1 MW_e onsite WE (0.4 t_{H2}/day) H_2 generation costs WE: 3.41 €/kg_{H2} H_2 generation costs SMR: 3.61 €/kg_{H2} HRS costs:1.59 €/kg_{H2} *Total costs WE: 5.00 €/kg_{H2}* *Total costs SMR: 5.20 €/kg_{H2}*
	1b: Large car HRS	5 MW_e onsite WE (2 t_{H2}/day) H_2 generation costs WE: 3.30 €/kg_{H2} H_2 generation costs SMR: 3.60 €/kg_{H2} HRS costs:1.20 €/kg_{H2} *Total costs WE: 4.50 €/kg_{H2}* *Total costs SMR: 4.80 €/kg_{H2}*
Semi-central production (4-20 t_{H2}/day)	1d: distributed from central electrolyser	20 MW_e onsite WE (8 t_{H2}/day) H_2 generation costs WE: 3.30 €/kg_{H2} H_2 generation costs SMR: 2.80 €/kg_{H2} H_2 distribution via truck: 0.81 €/kg_{H2} HRS costs:1.59 €/kg_{H2} *Total costs WE: 5.70 €/kg_{H2}* *Total costs SMR: 5.20 €/kg_{H2}*
Central production (>20 t_{H2}/day)	2b: industrial H_2	100 MW_e onsite WE (960 t_{H2}/day) H_2 generation costs WE: 1.17 €/kgH2 H_2 generation costs SMR: 0.91 €/kgH2 H_2 compressor: 0.09 €/kg_{H2} H_2 storage: 0.27 €/kg_{H2} H_2 transport (pipeline): 0.44 €/kg_{H2} HRS costs:1.59 €/kg_{H2} *Total costs WE: 4.10 €/kg_{H2}* *Total costs SMR: 3.30 €/kg_{H2}*

WE : Water electrolysis, SMR: Steam methane reforming
* Data for grid-connected water electrolysis in Germany, 2030

The following cost reductions for electrolysers until 2030 are estimated in [E4Tech & EE 2014]:

- Current investment costs (2012) for alkaline electrolysers are expected to fall from 1,000-1,100 to 370-800 €/kW by 2030
- Investment costs of PEM electrolysers are estimated to be reduced from 1,860-2,320 €/kW to 250-1,270 €/kW by 2030.

The estimated energy prices (in Germany) for industrial customers are:

- Electricity 2030: 66 €/MWh
- Gas price: 42 €/MWh

5.2 Pathway characterisation and analysis of the six selected pathways

5.2.1 Biomass gasification and pyrolysis (1)

a) Process description

Solid lignocellulosic biomass such as wood chips and straw is used as feedstock. In the first step, the feedstock is converted to coke, methanol, and primary gases via pyrolysis. In the next step, methanol and primary gases are converted to a gas mixture mainly consisting of CO, H_2, CO_2, and CH_4 via gasification (dubbed 'reforming' by some manfacturers). The two steps pyrolysis and gasification can be carried out in one single reactor or in separate reactors.

It has to be distinguished between directly heated gasifiers and indirectly heated gasifiers:

- **Directly heated gasifier**: Oxygen (oxygen blown gasifier) or air (air blown gasifier) is used as a gasification agent. No external heat is required. The heat for the endothermal pyrolysis and gasification reactions is supplied by exothermal reactions inside the gasification reactor.
- **Indirectly heated gasifier**: Water (as steam) is used as gasification agent. External heat is required to meet the heat requirement for the the endothermal pyrolysis and gasification reactions.

If air is used as gasification agent a high share of nitrogen (N_2) will be left in the product gas stream with the consequence of a lower hydrogen recovery in the downstream pressure swing adsorption (PSA) plant. Therefore, pure oxygen or water is typically used as gasification agent if pure hydrogen e.g. for fuel cell vehicles is the desired final product. Air blown gasifiers generally are used for stationary electricity and heat generation where the product gas leaving the gasifier is directly fed into a gas engine, gas turbine or (high temperature) fuel cell. The use of pure oxygen requires an air separation plant. Indirectly heated gasifiers do not require an air separation plant as water (as steam) is used as gasification agent.

Indirectly heated gasifiers provide a synthesis gas with higher hydrogen content than directly heated gasifiers leading to the highest hydrogen recovery following the CO shift in the downstream PSA plant. A challenge is the introduction of the heat into the gasification reactor. In the reactors originally developed by Battelle Columbus Laboratory (BCL), now called "Rentech-SilvaGas Biomass Gasification Process", and the gasification plant in Güssing by 'Güssing Renewable Energy GmbH', hot sand is used as heat carrier.

The gasifier from 'Güssing Renewable Energy GmbH' employs a 'Fast Internally Circulating Fluidized Bed' (FICFB) gasifier and has been selected as representative for this pathway for further analysis.

b) Pathway description

Wood chips from short rotation forestry are used as feedstock. On average, the wood chips are transported to the H_2 plant via truck over a distance of 50 km. Three process scales have been chosen, one gasification plant with a hydrogen output of 3 MW_{LHV} (90 kg_{H2}/h), one gasification plant with a hydrogen output of 9 MW_{LHV} (270 kg_{H2}/h) and one gasification plant with a hydrogen output of 33 MW_{LHV} (~ 1 t/h). The technical and economic data for the gasification plant have been taken from [DBFZ et al. 2014] and [Rauch 2015].

Table 9 shows the economic data assumed for the production of hydrogen via gasification of wood chips.

Table 9: **Technical and economic data for the production of hydrogen via gasification of wood chips**

	Unit	3 $MW_{H2, LHV}$	9 $MW_{H2, LHV}$	33 $MW_{H2, LHV}$
Input				
Wood chips	MW	6.59	17.5	50
Electricity	MW	0.12	0.31	5.6
FAME	MW	0.09	0.24	0.89
Output				
Hydrogen	MW	3.00	9.00	33.33
Economic data				
CAPEX	M€	14.6	32	100
O&M, repair, insurance, overhead	-	6.75% of CAPEX/yr	6.75% of CAPEX/yr	3% of CAPEX/yr
Lifetime	yr	20	20	20
Equivalent full load period	h/yr	7,500 h/yr	7,500 h/yr	7,500 h/yr
Applicability	-	local	semi-central	central

Fatty acid methyl ester (FAME) is used for tar removal from the product gas stream leaving the CO shift reactor.

The costs for the wood chips have been assumed to be 90 € per t of dry substance. The LHV of wood chips is about 18.5 MJ per kg of dry substance. The cost of FAME has been assumed to be about 1 € per l (27 €/GJ). In line with [E4tech & EE 2014] the electricity price for industrial customers in Germany with an electricity consumption of 500 to 2,000 MWh per year is assumed to be about 0.166 €/kWh. The electricity consumption of the 3 MW_{H2} plant is about 900 MWh per year, 2300 MWh per year for the 9 MW_{H2} plant and 42,000 MWh per year for the 33 MW_{H2} plant. Hence, the price for electricity has been assumed to be 0.166 € per kWh for the two smaller gasification plants and 0.139 €/kWh for the 33 MW_{H2} plant (based on [DBFZ et al. 2014]).

Figure 35 shows a schematic drawingof a biomass gasification process for hydrogen production based on the FICFB gasifier.

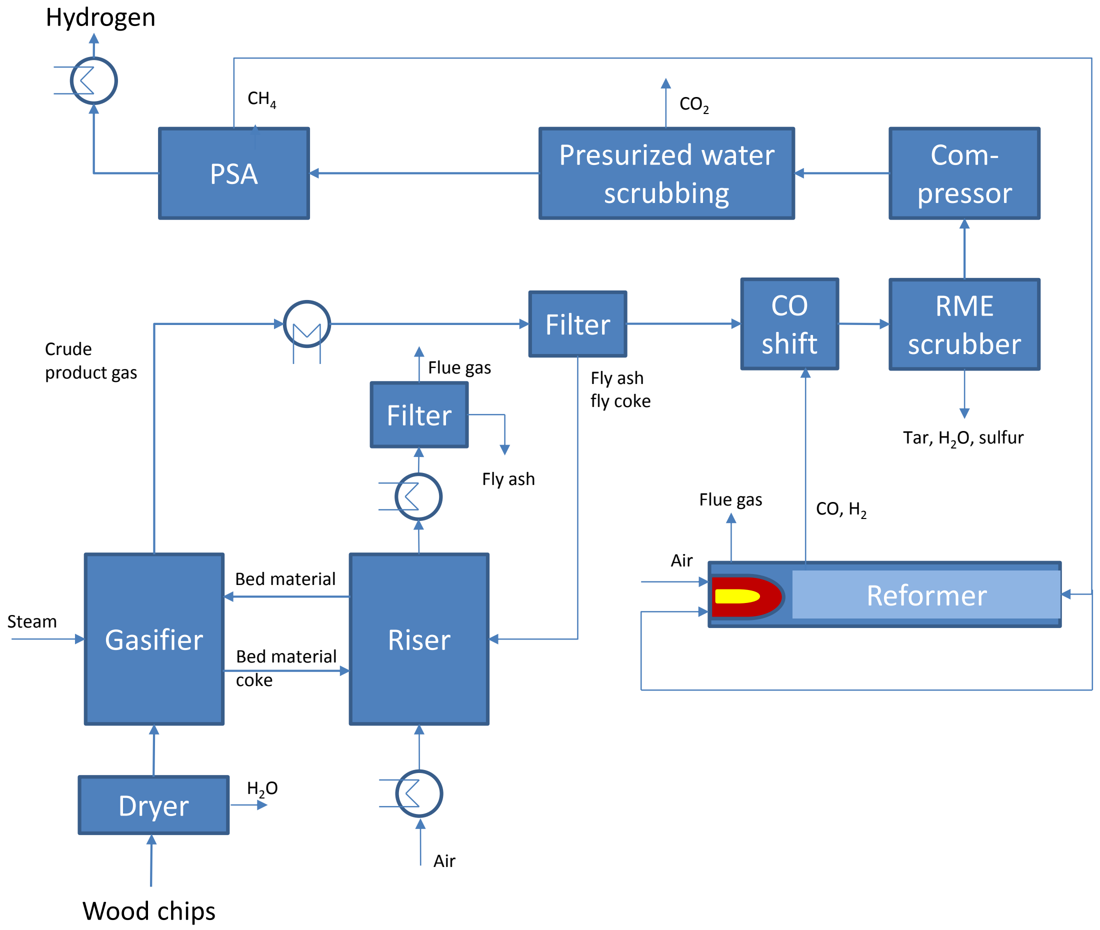

Figure 35: **Schematic of biomass gasification process for hydrogen production based on the FICFB gasifier based on [DBFZ et al. 2014]**

In a first stage, hydrogen is compressed from 0.8 MPa (outlet of the PSA of the 3 and 9 MW_{H2} plant) or 2 MPa (outlet of the PSA of the 33 MW_{H2} plant) to 6.4 MPa and stored in a buffer storage (12 hours of full load hydrogen production capacity) onsite the H_2 plant.

Buried underground tubes have been used for hydrogen storage for which the CAPEX has been derived from [Jauslin Stebler 2009]. CAPEX for the underground tubes used for the storage of natural gas as installed in Etziken in Switzerland, comprising 12 single tubes of 320 m length each, has been indicated at 17.4 million

CHF. Their geometric volume is 6,760 m³. At an exchange rate of 0.65 €/CHF the CAPEX then amounts to about 11.3 Million € or 2,950 € per m of tube length. The lifetime of the storage arrangement has been assumed at 30 years.

The costs for hydrogen distribution and dispensing have been taken from [E4tech & EE 2014].

In case of the 3 MW_{H2} plant (2.2 t/d) a large car refuelling station is located onsite the H_2 plant (similar to case 1b in [E4tech & EE 2014]). In case of the 9 MW_{H2} or 6.5 t/d plant the hydrogen is distributed to small car hydrogen refuelling stations (400 kg/d) via tube trailer (similar to case 1d in [E4tech & EE 2014]). In case of the 33 MW_{H2} (24 t/d) plant the hydrogen is distributed to small car refuelling stations (400 k/d) via pipeline (similar to 2b in [E4tech & EE 2014]).

Table 10: H_2 storage and distribution (€/kg_{H2})

	3 MW_{H2} (local)	9 MW_{H2} (semi-central)	33 MW_{H2} (central)
H_2 compression loading H_2 storage	0.28	0.22	0.11
H_2 storage	0.06	0.06	0.06
H_2 distribution*	-	0.81 (truck)	0.44 (pipeline)
Refuelling station*	1.20	1.59	1.59

*taken from [E4tech & EE 2014], page 9-10 in Appendix 5

c) Results

Figure 36 shows the costs for hydrogen produced by biomass gasification 'well-to-tank' benchmarked against hydrogen produced from steam methane reforming (SMR) and water electrolysis (WE) for the time horizon 2030.

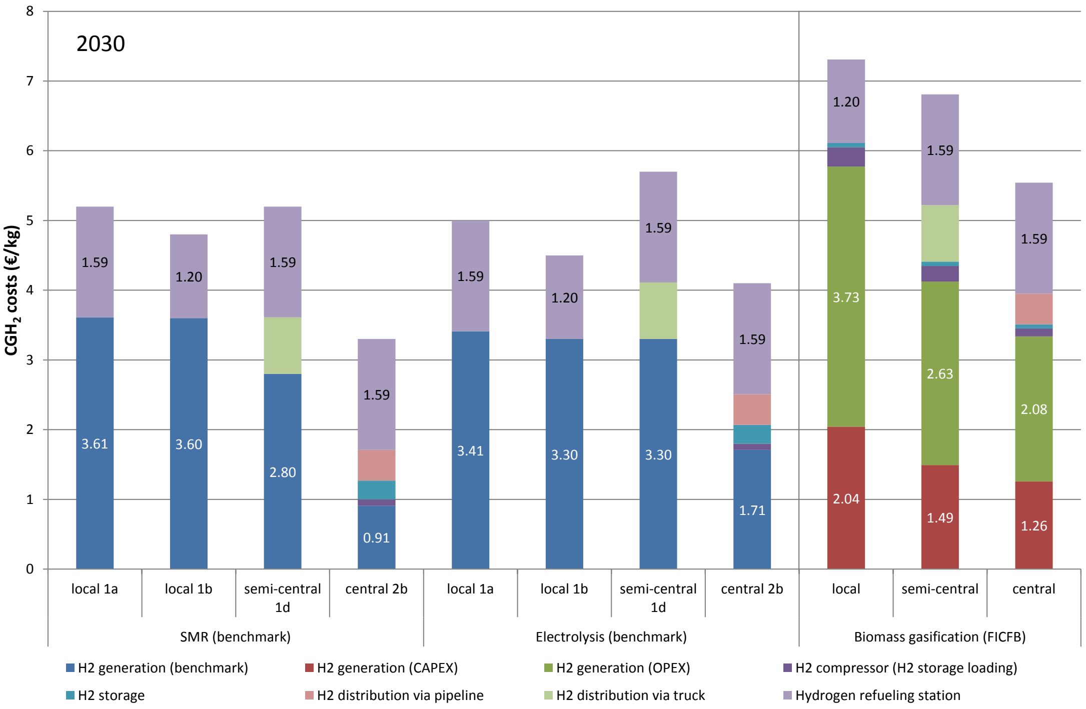

Figure 36: **Costs of hydrogen from biomass gasification 'well-to-tank' benchmarked against hydrogen from SMR and water electrolysis**

Operating costs (OPEX) for hydrogen generation include feedstock costs, electricity costs, costs for chemicals, labour costs, and costs of maintenance and repair.

5.2.2 Raw biogas reforming (2)

a) Process description

In [Nietzsche et al. 2007] the steam reforming of desulfurized biogas (which consists of a mixture of CH_4, CO_2, and traces of O_2) replacing natural gas as feedstock (which typically has a high methane content of more than 80%) has been assessed.

The following reactions occur if natural gas is used as feedstock:

$$C_nH_m + n\ H_2O \rightarrow n\ CO + (n + m/2)\ H_2$$

$$CH_4 + H_2O \rightarrow CO + 3\ H_2$$

$$CH_4 + 2\ H_2O \rightarrow CO_2 + 4\ H_2$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

If biogas is used additional reactions occur:

$$CH_4 + CO_2 \rightarrow 2\ CO + 2\ H_2$$

$$CH_4 + 3\ CO_2 \rightarrow 4\ CO + 2\ H_2O$$

$$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$$

In real SMR plants it could be demonstrated that the steam reforming of biogas is possible without significant changes in methane conversion. In a specific case, the CO_2 content behind the CO shift has increased from 23.9% to about 33.8% when substituting natural gas with biogas and the hydrogen content has decreased from 74% to about 64%. It was concluded that the slightly lower H_2 content has only a minor influence on the H_2 recovery of a downstream pressure swing adsorption plant (not assessed in [Nietzsche et al. 2007]).

b) Pathway description

Fermentable biomass such as maize, manure, and organic waste from households is converted to biogas in a biogas plant. The raw biogas is converted to hydrogen via steam reforming.

Figure 37 shows a schematic for the production of hydrogen via steam reforming of raw biogas including the biogas plant.

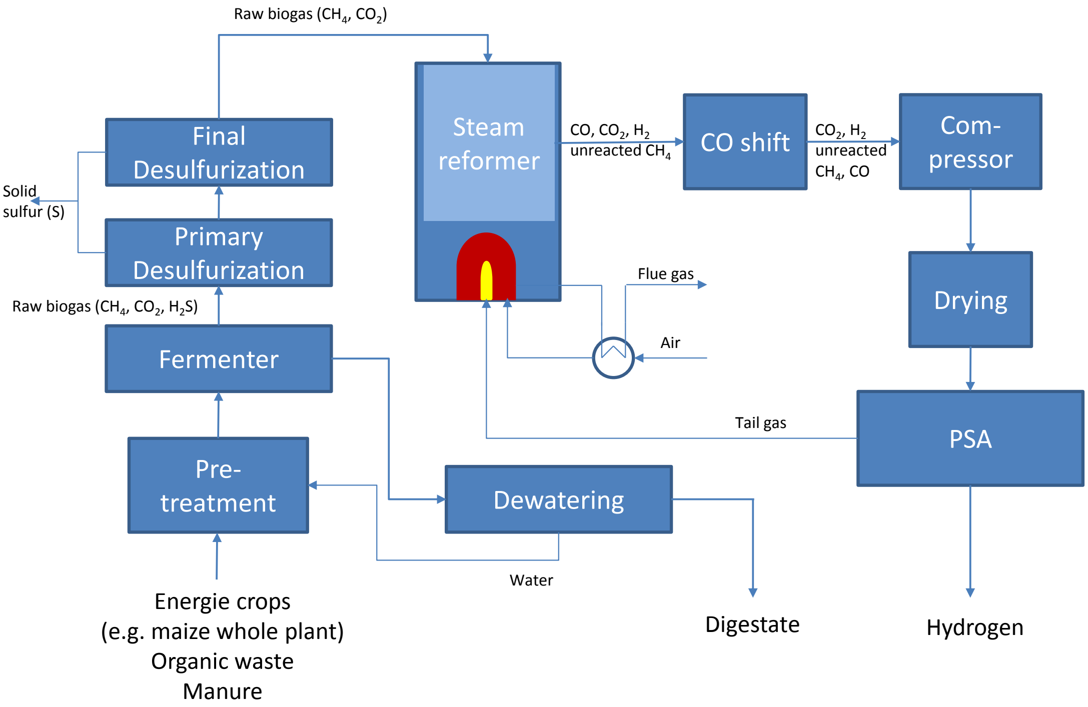

Figure 37: **Schematic of raw gas biogas steam reforming based on [DBFZ 2014]**

Table 11 shows the technical and economic data for the production of hydrogen via steam reforming of raw biogas including the biogas plant. The technical and economic data for the larger plant (6 MW_{H2} based on the lower heating value) have been taken from [DBFZ 2014].

For the smaller plant it has been assumed that a small steam reforming plant (2 units, each 100 Nm^3_{H2} per hour or 0.3 MW_{H2}) has been installed onsite a biogas plant which uses maize whole plant silage as feedstock. The technical and economic data for the steam reforming plant have been taken from [H2Gen 2007] and [de Wit 2015][17]. The investment for this plant is about 275 € per m^3 of fermenter volume including biomass pre-treatment etc. [Eder & Schulz 2006]. About 3,000 m^3 of fermenter volume are required per 1,250 kW of gross biogas production per hour [FNR 2008] (assuming the use of a 500 kW_{El} CHP plant with an efficiency of 40%). The heat requirement for the fermenter has been taken from [DBFZ 2009] (53 Nm^3 of biogas per 534 Nm^3 of biogas leaving the fermenter), the electricity requirement has been taken from [FNR 2008].

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[17] CAPEX for SMR (200 Nm^3/h) in 2015 = 2.0 million € (for natural gas system); for raw biogas reforming it is estimated that the SMR CAPEX is 20% higher than for natural gas reforming; expected cost reduction for SMR component until 2030 = 50%

Table 11: **Technical and economic data for the production of hydrogen via steam reforming of raw biogas including raw biogas generation in 2030**

	Unit	0.6 MW_{H2}	6 MW_{H2}
Input			
Maize whole plant silage	MW	1.45	10
Organic waste	MW	-	4.93
Cattle manure	MW	-	0.14
Electricity	MW	0.10	0.43
Output			
Hydrogen	MW	0.60	6.00
Economic data			
CAPEX	M€	1.9	21.3
O&M	-	6.75% of CAPEX/yr	6.75% of CAPEX/yr
Lifetime	yr	15	15
Equivalent full load period	h/yr	7,500	7,500
Applicability	-	local	semi-central

Table 12 shows the costs for the feedstock used by the biogas plants. Two cases have been assessed. Analogous to [DBFZ 2014], in case 1 negative costs for the organic waste have been assumed. In case 2 the costs for organic waste have been set to zero.

Table 12: **Feedstock costs**

Feedstock	Unit	Case 1	Case 2
Maize whole plant silage	€/t_{moist}	35	35
	€/t_{dry}	101.4	101.4
	€/kWh_{LHV}	0.0228	0.0228
	€/GJ_{LHV}	6.3	6.3
Organic waste	€/t_{moist}	-35*	0
	€/t_{dry}	-87.4	0
	€/kWh_{LHV}	-0.0268	0
	€/GJ_{LHV}	-7.5	0
Cattle manure	€/t_{moist}	0	0
	€/t_{dry}	0	0
	€/kWh_{LHV}	0	0
	€/GJ_{LHV}	0	0

* Negative values: revenue for waste treatment

In case of the larger plant (6 MW_{H2}) the hydrogen is compressed from 0.8 MPa (H_2-pressure at the outlet of the PSA) to 6.4 MPa and stored in a buffer storage (12 hours of full load hydrogen production capacity) onsite the H_2 plant.

As for biomass gasification buried underground tubes have been used for hydrogen storage at the same specifications based on [Jauslin Stebler 2009]. The costs for hydrogen distribution and dispensing are based on [E4tech & EE 2014].

In case of the 0.6 MW_{H2} plant (0.4 t/d) a small car refuelling station (400 kg/d) is located onsite the H_2 plant (similar to case 1a in [E4tech & EE 2014]) and in case of the 6 MW_{H2} (4.3 t/d) the hydrogen is distributed to small car hydrogen refuelling stations (400 kg/d) via tube trailer (similar to case 1d in [E4tech & EE 2014]).

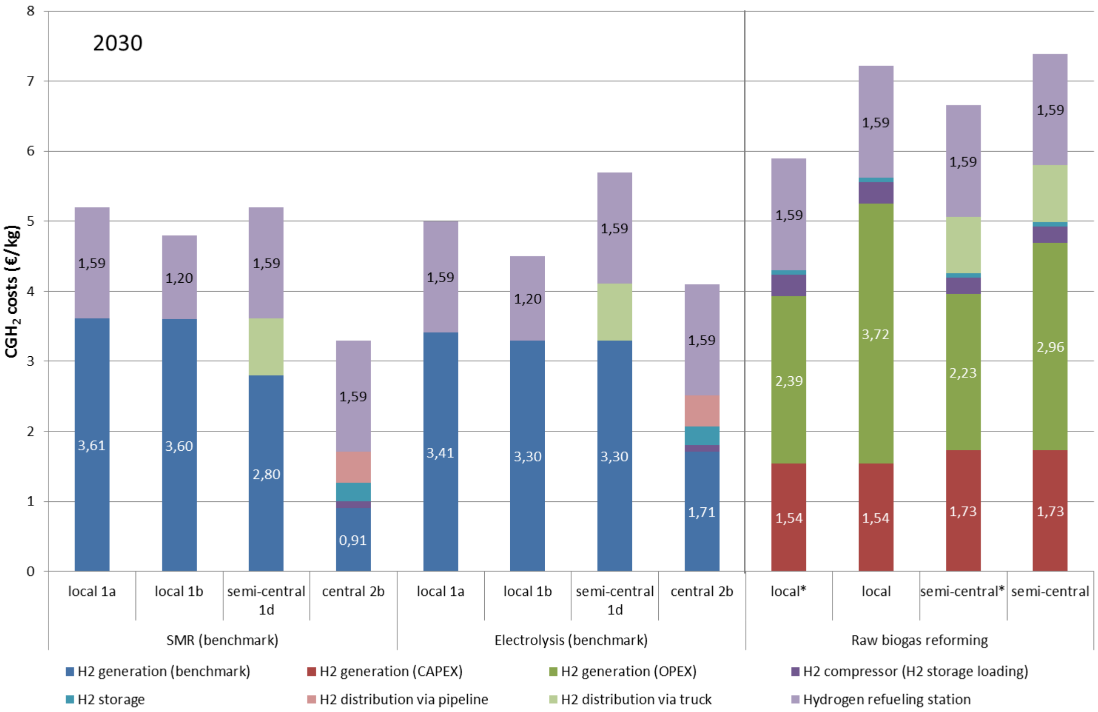
Table 13: H_2 storage and distribution (€/kg_{H2})

	0.6 MW_{H2} (local)	6 MW_{H2} (semi-central)
H_2 compression loading H_2 storage	0.31	0.23
H2 storage	0.06	0.06
Distribution*	-	0.81 (truck)
Refuelling station*	1.59	1.59

*taken from [E4tech & EE 2014], page 9-10 in Appendix 5

c) Results

Figure 38 shows the hydrogen production costs from raw biogas reforming 'well-to-tank' benchmarked against hydrogen costs from steam methane reforming (SMR) and water electrolysis (WE).



* including revenue for bio-waste/sewage sludge treatment

Figure 38: Costs of hydrogen from raw biogas reforming ‘well-to-tank’ benchmarked against hydrogen from SMR and water electrolysis

Operating costs (OPEX) for hydrogen generation include feedstock costs, electricity costs, costs for chemicals, labour costs, and costs of maintenance and repair.

5.2.3 Thermochemical Water Splitting (3)

a) Process description

For this assessment the hybrid sulfur cycle (also called 'Westinghouse Sulfur Cycle' or 'Ispra Mark 11 cycle') has been selected. The hybrid sulfur cycle is a combination of thermal decomposition of H_2SO_4 and electrolysis of SO_2.

The first step of this process is the thermal decomposition at 800-900°C:

$$H_2SO_4 \rightarrow SO_3 + H_2O$$

$$SO_3 \rightarrow SO_2 + 0.5\ O_2$$

The second step is the electrolysis at 80-120°C:

$$SO_2 + 2\ H_2O \rightarrow H_2SO_4 + H_2$$

The resulting net reaction is:

$$H_2O \rightarrow H_2 + 0.5\ O_2$$

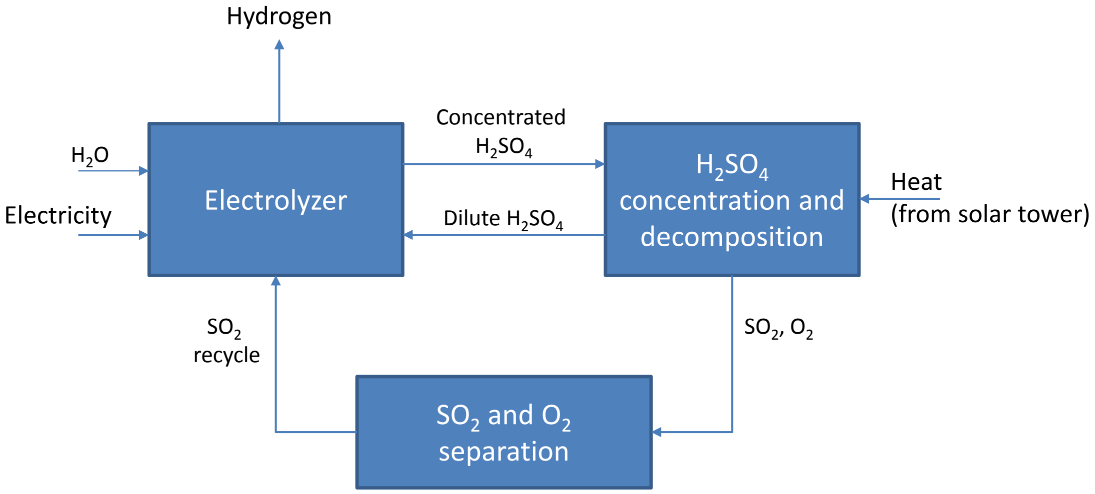


Figure 39: **Hydrogen production via a hybrid sulphur cycle**

b) Pathway description

Today, the heat supply is estimated to account for around 60% of the direct investments for the production of hydrogen from solar heat via the hybrid sulphur cycle [Sattler 2015]. According to [IEA 2014] the investment costs for solar thermal power plants could follow a 10% learning rate (i.e. diminish by 10% for each doubling of the cumulative capacity) in the next decades.

The technical and economic data for the production of hydrogen from solar heat via the hybrid sulphur cycle in the year 2030 are based on [Graf et al. 2008]. In [Graf et al. 2008] the costs of solar heat supply are expected to fall to a share of ~ 36% of the direct investments (see Figure 40). The specific investment cost for the solar equipment (heliostats, tower, receiver, and land) is expected to be reduced to ~290 €/kW$_{th}$.

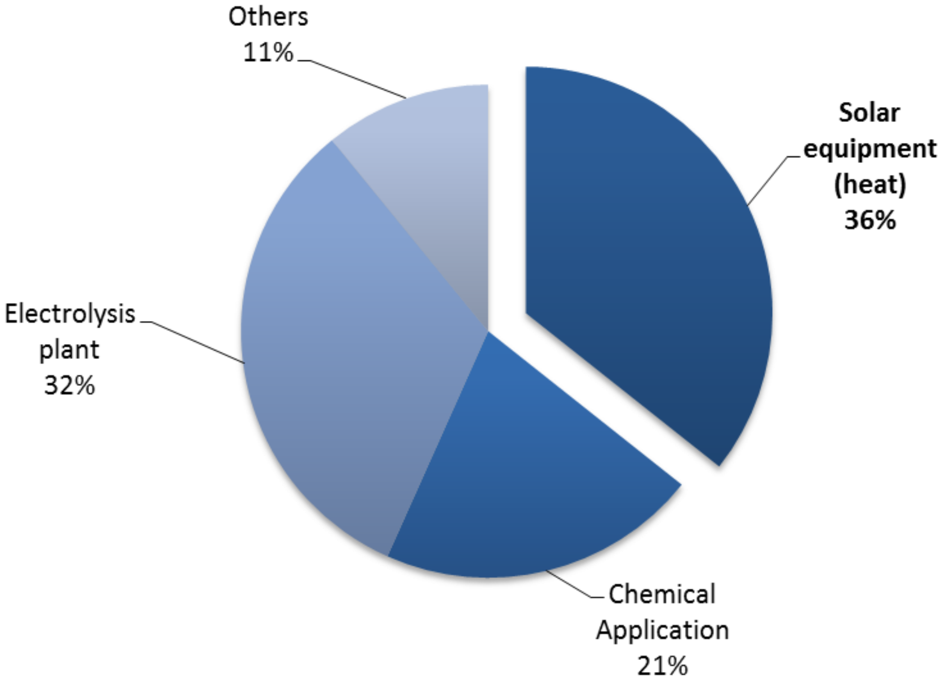


Figure 40: **Direct investments for hydrogen generation from solar energy via the hybrid sulphur cycle in an optimised 50 MW$_{th}$ solar thermal energy plant in 2030 [Graf et al. 2008]**

The annually averaged heat supply from a solar tower amounts to 50 MW_{th}[18]. The average hydrogen output amounts to 432.1 kg per hour (14.4 $MW_{H2,LHV}$), if electricity is supplied by a separate electricity generation plant, based on a solar tower plant. According to [SRNL 2005] the electricity requirement amounts to about 0.45 kWh per kWh of hydrogen (LHV).

Table 14 shows detailed CAPEX calculations for hydrogen generation from solar energy via the hybrid sulphur cycle including the solar tower for the supply of the required high temperature and including the separate power station.

Table 14: CAPEX for optimised hydrogen generation from solar energy via hybrid sulphur cycle in the year 2030

Component	50 MW_{th} plant (€) [Graf et al. 2008]	50 MW_{th} plant (€) [Quantius 2007]	290 MW_{th} plant (€) [Quantius 2007]
Solar equipment			
Heliostats	38,251,000	38,251,000	229,478,000
Tower	3,700,000	3,700,000	57,882,000
Receiver	5,200,000	7,420,000	44,520,000
Land	2,200,000	1,100,000	5,000,000
Total	**49,351,000**	**50,471,000**	**336,880,000**
Chemical application			
Heat exchanger	16,800,000	5,385,282	17,852,798
Cooling	8,200,000	6,304,000	18,134,724
Separation	1,700,000	4,196,310	15,994,071
Pumps		348,690	803,190
Compressor, others	2,400,000	14,642,756	110,242,302
Total	**29,100,000**	**30,877,038**	**163,027,085**
Tanks			
Sulphuric acid		9,619,048	53,866,667
Sulphur dioxide		19,238,095	106,194,286
Total		**28,857,143**	**160,060,953**
Electrolysis plant			
Electricity generation	6,300,000	34,307,937	282,383,175
Electrolyser	38,500,000	13,315,161	60,628,395
Total	**44,800,000**	**47,623,098**	**343,011,570**
Other			
Buildings	**1,800,000**	**10,926,573**	**92,759,511**
Pumps, piping, connection	**13,300,000**		
Total direct investment		**168,754,852**	**1,095,739,119**
Safety surcharge	13,600,000	16,875,485	109,573,912
Sulphuric acid	20,000	9,561,390	53,853,586
Total indirect investment	**16,620,000**	**26,436,875**	**163,427,498**
Total capital investment (CAPEX)	**151,971,000**	**195,191,727**	**1,259,166,617**
Specific investment (CAPEX)	10,552 €/kW_{H2}	13,553 €/kW_{H2}	15,074 €/kW_{H2}

---

[18] Average heat supply of 50 MW_{th} → peak heat generation capacity of the receiver of ~170 MW_{th}).

The specific investment for the 290 MW_{th} plant is higher than that for the 50 MW_{th} plant. Therefore, the economic data for the 50 MW_{th} plant based [Graf et al. 2008] have been selected.

In [S&L 2003] the number of staff for the plant operation is indicated with 67 persons for the 555 MW_{th} plant. For this analysis, the required staff number has been downscaled to 170 MW_{th}, the peak heat generation capacity of the receiver, using a scaling exponent of 0.25. In [Quantius 2007], annual insurance costs have been indicated with 2% and costs for maintenance and repair with 4% of the total capital investment.

Using the hydrogen energy content of 33.33 kWh/kg_{LHV} yields the technical and economic data in Table 15.

Table 15: Input and output data for the production of hydrogen from solar energy via the hybrid sulphur cycle

	Unit	Value
Input		
Average Heat(from solar tower)	MW	50
Water	kg/h	3,892
Electricity (from solar tower)	MW	6.44 (included in CAPEX)
Output		
Hydrogen	MW	14.4
Economic data		
CAPEX	million €	152
Lifetime	yr	20
Staff	persons	15
O&M	Million €/yr	9.9
Equivalent full load period*	h/yr	8,760

* Capacity is based on average capacity within a year

The hydrogen product is compressed from 2 MPa (H_2 pressure at the outlet H_2 plant) to 6.4 MPa and stored in a buffer storage (12 hours of full load hydrogen production capacity) onsite the H_2 plant.

Like in the biomass gasification analysis buried underground tubes have been assumed for hydrogen storage at the same specifications based on [Jauslin Stebler 2009]. The costs for hydrogen distribution and dispensing have been taken from [E4tech & EE 2014].

During unloading of the hydrogen storage the hydrogen is compressed from 3.6 MPa (average pressure between 2 and 6.4 MPa) to a pressure of 8 MPa for injection into a long distance pipeline. The hydrogen is transported via this pipeline to the consumers over a distance of 2,000 km. To compensate for the pressure drop electrically driven compressors have been installed for every 125 km.

According to [Krieg 2012] the CAPEX per km of pipeline including compressor stations can be calculated by

$$C = 0.0022 \cdot D^2 + 0.86 \cdot D + 247.5$$

where

C CAPEX in €/m

D Pipeline diameter in mm

Annual costs for maintenance and repair amount to 5% of the CAPEX [Krieg 2012]. For the transport of hydrogen from the H_2 plant to the consumers in central Europe a pipeline diameter of 44 inch (1,219 mm) has been chosen. Furthermore, it has been assumed that a large number of 14.4 MW_{H2} units are connected with the long distance pipeline.

Table 16: Long distance pipeline

	Unit	
Maximum throughput	Nm^3/h	5,440,000
	GW_{H2}	16.3
	$t\ H_2/d$	11,600
Diameter	mm (inch)	1,219 (44)
Distance between compressors	km	125
CAPEX	€/km	4,566
	million €	9,132
Electricity consumption total	kWh/kWh_{H2}	0,07
Maintenance and repair	-	5% of investment/yr

Hydrogen distribution and dispensing costs have been taken from [E4tech & EE 2014]. The hydrogen is distributed via a local hydrogen pipeline grid to the small hydrogen refuelling stations (400 kg/d) (case 2b in [E4tech & EE 2014]).

Table 17: H_2 storage, transport and distribution (€/kg_{H2})

Step	Value
H_2 compression loading H_2 storage	0.12
H_2 storage	0.05
H_2 compression for injection into long distance pipeline	0.08
Long distance pipeline including compressors (2,000 km)	0.63
Distribution via local pipeline grid*	0.44
Refuelling station*	1.59

*taken from [E4tech & EE 2014], page 9-10 in Appendix 5

c) Results

Figure 41 shows the hydrogen production costs from thermochemical cycles (hybrid sulphur cycle) 'well-to-tank' and benchmarked against hydrogen produced from steam methane reforming (SMR) and water electrolysis (WE).

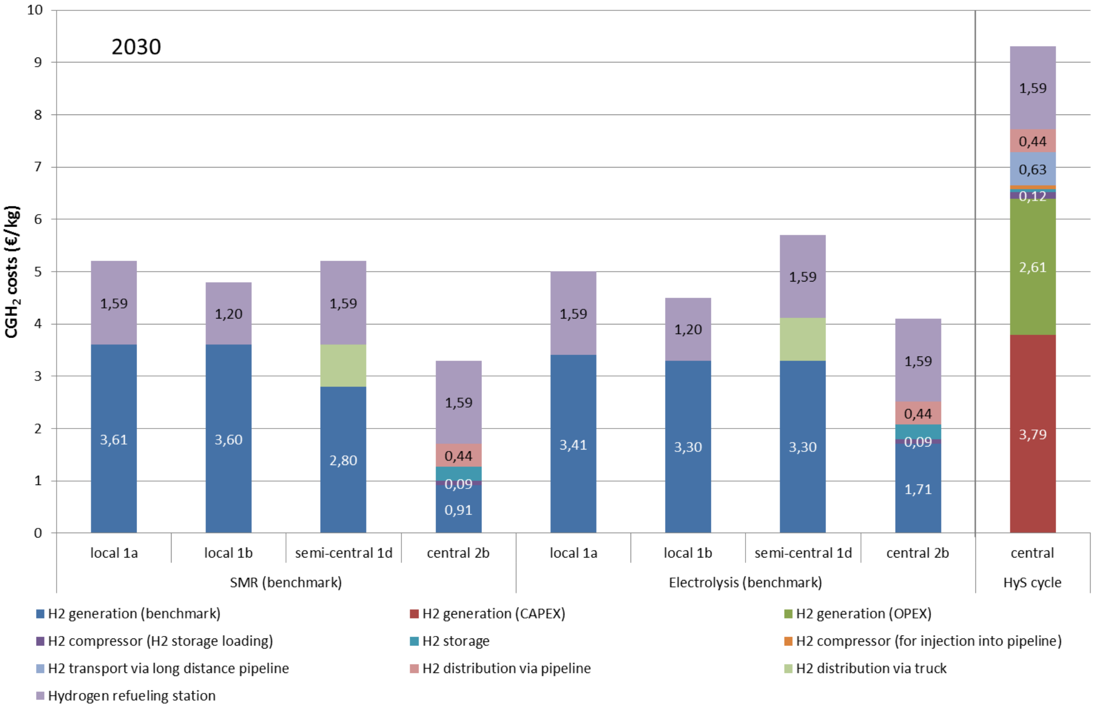


Figure 41: Costs of hydrogen from thermochemical cycle (hybrid sulphur cycle) 'well-to-tank' compared to hydrogen from SMR and water electrolysis

Operating costs (OPEX) for hydrogen generation include costs of maintenance and repair costs, labour and water. Major costs drivers are maintenance and repair and insurance costs.

Different to [Graf et al. 2008] no by-product credits for sold oxygen was considered. Oxygen has a quite limited market and selling it as a by-product will only be possible in selected cases.

5.2.4 Photo-catalysis (PEC: Photo-electrochemical cell) (4)

a) Process description

Photo-electrochemical cells (PEC) combine photovoltaic electricity generation and electrolysis into a single process.

In [DT 2009] four different systems for hydrogen generation via PEC have been assessed:

- **Type 1:** Single horizontal water bed with colloidal suspension of PEC nanoparticles
- **Type 2:** Dual horizontal water beds with colloidal suspension of PEC nanoparticles, each bed carrying out a half reaction
- **Type 3:** Fixed planar array tilted toward the sun at the angle of the latitude
- **Type 4:** Steered solar concentrator and tracker system, focusing solar flux on PEC planar element receivers pressurized to approximately 300 psi (2.1 MPa)

The type 1 PEC system is a basic single bed colloidal suspension reactor and consists of a suspension of photo-active nanoparticles in a shallow pool or bed of electrolyte. The exact composition and fabrication techniques for the nanoparticles are not well understood as the full functionality of the postulated nanoparticles has not been demonstrated at lab-scale, let alone in a complete system [DT 2009].

The type 2 PEC system uses nanoparticles like the type 1 PEC system. The exact material system is not known.

The type 3 and type 4 PEC systems use photovoltaic (PV) cells to generate electricity for the electrolysis step.

b) Pathway description

The type 3 PEC system has been selected for the assessment in this study, because it is believed to use the most mature technology.

The required land area for the production of 1 t of hydrogen per day amounts to 241,758 m² and the capture, or net (= active), area amounts to about 53,845 m². The capacity factor is about 0.9 which lead to an equivalent full load period of about 8,000 h/yr.

Table 18 shows the CAPEX of a type 3 PEC system with a capacity of 1 t of hydrogen per day (1,389 kW_{H2} based on the LHV). For the conversion from US$ to € an exchange rate of 0.719 €/US$[19] has been assumed.

Table 18: **CAPEX for hydrogen generation via photoelectrochemical cells (PEC type 3) for a module with a capacity of 1 t H_2/d**

Component	US$	€
Reactor subassembly		
PECs	8,238,271	5,923,317
Make-up water pump	213	153
Water manifold piping	45,053	32,393
Water collection piping	52,394	37,671
Water column collection piping	6,563	4,719
Water final collection piping	851	612
Reactor subassembly total	**8,343,345**	**5,998,865**
Gas processing subassembly		
Compressor	759,481	546,067
Condenser	16,607	11,940
Intercooler 1	17,894	12,866
Intercooler 2	18,495	13,298
Manifold piping	45,053	32,393
Collection piping	52,394	37,671
Column collection piping	6,563	4,719
Final collection piping	851	612
Gas processing subassembly total	**917,338**	**659,566**
Control system		
PLC	3,000	2,157
Control room building	17,527	12,602
Control room wiring panel	3,000	2,157
Computer and monitor	1,500	1,079
Labview software	4,299	3,091
Water level controllers	134,615	96,788
Pressure sensors	6,210	4,465
Hydrogen area sensors	136,800	98,359
Hydrogen flow meter	5,500	3,955
Instrument wiring	451	324
Power wiring	225	162
Conduit	6,735	4,842
Control system total	**319,862**	**229,981**
Direct capital cost	**9,580,545**	**6,888,412**
Installation costs		
Piping installation	30,843	22,176
Panel installation	1,076,898	774,290
Reactor subassembly install	64	46
Gas processing subassembly install	243,743	175,251
Control system install	95,959	68,995
Installation cost total	**1,447,507**	**1,040,758**
Costs with installation	**11,028,052**	**7,929,169**

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[19] average exchange rate in 2009, the study year

It has been assumed that the plant consists of 100 single units, each with a capacity of 1 t hydrogen per day, leading to a total hydrogen production capacity of 100 t per day (139 MW_{H2} based on the LHV). The staff requirement is about 169 persons for a system with a capacity of 100 t/d [DT 2009].

It is reported that the PECs have to be replaced every 10 years. Hence, the cost of PEC replacement has been added to the cost of maintenance and repair.

Table 19: Input and output data for the production of hydrogen from solar energy via PEC

	Unit	Value
Input		
Solar insulation	MW	1,660
Electricity (auxiliaries)	MW	38
Water	kg/h	37,530
Output		
Hydrogen	MW	139
Economic data		
CAPEX	million €	793
Lifetime	yr	20
Staff	persons	169
Maintenance and repair (except PECs)	million €/yr	3.4
Replacement of PECs	million €/yr	67.0
Equivalent full load period	h/yr	7,884

The electricity is assumed to be supplied by a photovoltaic (PV) power plant which is located onsite the PEC plant.

In [DT 2009] it has been assumed that the plant is installed at a location with a solar insolation of 2,431 kWh per year on surface inclined at 35° latitude. Therefore, for this study the plant is assumed to be located in the South e.g. Spain or Morocco.

The hydrogen product is compressed from 0.1 MPa (H_2 pressure at the outlet H_2 plant) to 6.4 MPa and stored in a buffer storage (12 hours of full load hydrogen production capacity) onsite the H_2 plant.

As for other pathways buried underground tubes have been used for hydrogen storage with specifications based on [Jauslin Stebler 2009]. The costs for hydrogen distribution and dispensing have been taken from [E4tech & EE 2014].

During unloading of the hydrogen storage the hydrogen is compressed from 3.6 MPa (average pressure between 2 and 6.4 MPa) to a pressure of 8 MPa for injection into a long distance pipeline. The hydrogen is transported via this pipeline to the consumers over a distance of 2,000 km. To compensate the pressure drop electrically driven compressors have been installed for every 125 km.

For the transport of hydrogen from the H_2 plant to the consumers in central Europa a pipeline diameter of 44 inch (1,219 mm) has been assumed. Further, it has been assumed that 119 H_2 plants of 139 MW_{H2} each are connected with the long distance pipeline (being identical to the pipeline in chapter 5.2.3).

The costs for hydrogen distribution and dispensing have been taken from [E4tech & EE 2014]. The hydrogen is distributed via a local hydrogen pipeline grid to small hydrogen refuelling stations (400 kg/d) (case 2b in [E4tech & EE 2014]).

Table 20: H_2 storage, transport and distribution (€/kg_{H2})

Step	Value
H_2 compression loading H_2 storage	0.07
H_2 storage	0.06
H_2 compression for injection into long distance pipeline	0.05
Long distance pipeline including compressors (2,000 km)	0.63
Distribution via local pipeline grid*	0.44
Refuelling station*	1.59

*taken from [E4tech & EE 2014], page 9-10 in Appendix 5

c) Results

Figure 42 shows the hydrogen production costs from photoelectrochemical cells (PEC) ‘well-to-tank’ compared to the production costs of hydrogen from steam methane reforming (SMR) and water electrolysis (WE).

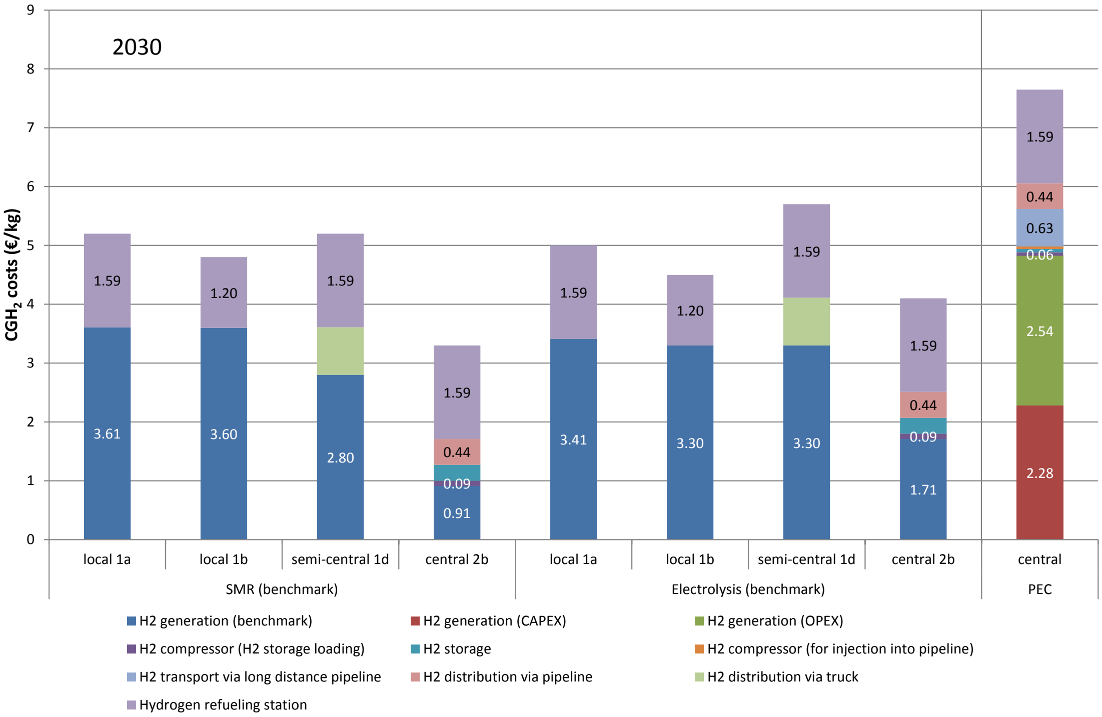


Figure 42: **Costs of hydrogen from PEC ‘well-to-tank’ compared to hydrogen from SMR and water electrolysis**

Operating costs (OPEX) for hydrogen generation include electricity costs, labour costs, and costs of maintenance and repair.

5.2.5 Supercritical water gasification of biomass (6)

a) Process description

The process of supercritical water gasification of biomass is carried out at operating conditions above the critical point of water (22.1 MPa, 374°C). A biomass/water slurry or organically contaminated aqueous waste is brought to a pressure of 25-40 MPa and heated to 650°C for a short period. A mixture of gases with high hydrogen content is generated. The product gas stream is cooled by the biomass/water mixture input via a heat exchanger and subsequently sent to a scrubbing plant to separate the CO_2 from the product gas stream. Further processing of the product gas stream leads to pure hydrogen.

The process was realized by the Karlsruhe Institute of Technology (KIT) in the VERENA pilot plant. To achieve practical experience and results, the VERENA pilot plant (‘Experimental plant for the energetic use of agricultural materials’) with a total throughput of 100 kg per hour (max. solids content 20%) has been built and operated. The plant has been designed for a working pressure of up to 35 MPa and a maximum temperature of 700°C.

Figure 43 shows a schematic of a super critical gasification plant as described in [FZK 2008].

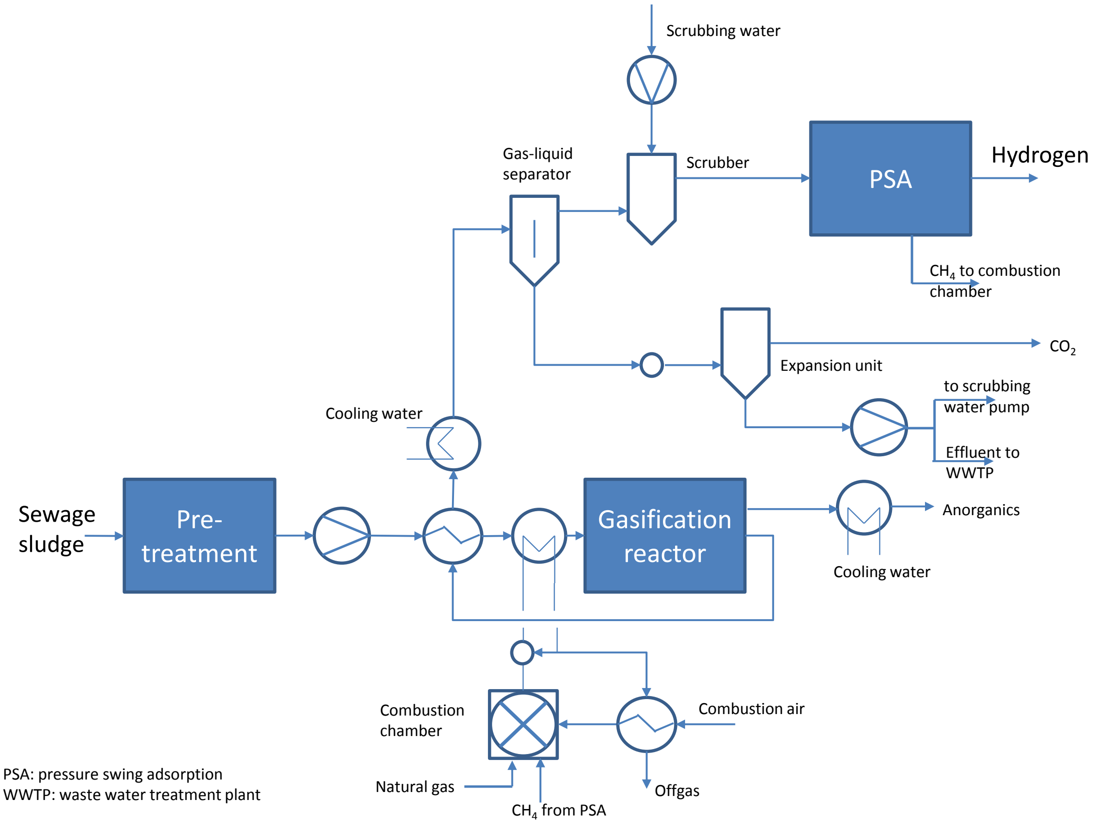


Figure 43: Schematic of a supercritical water gasification plant

b) Pathway discription

In [FZK 2008] a plant for the supercritical water gasification of sewage sludge with a capacity of 5 t of moist sewage sludge input has been assessed. The dry matter content of the sewage sludge amounts to 20%, thereof 75% organic substance. According to [ECN 2015] the lower heating value (LHV) of sewage sludge is about 25.86 MJ per kg of dry organic substance.

Table 21 shows the CAPEX of the supercritical water gasification plant as described in [FZK 2008].

Table 21: CAPEX for a supercritical water gasification plant

Component	€
Feeding (conveyor, stirrer, crusher vessel)	103,000
High pressure pump	82,000
Pre-heater	784,000
Reactor pre-heater	301,000
Burner	598,000
Air pre-heater	20,000
Product cooler	151,000
Cooling unit for ashes (cooling screw)	277,000
Reactor	50,000
Gas-liquid separator	66,000
Scrubber	81,000
PSA	362,000
Effluent pump	10,000
Scrubbing water pump	30,000
Purchased equipment costs (PEC)	**2,915,000**
Direct costs	
Purchased Equipment	1,136,850
Installation (piping)	903,650
Installation (instrumentation and controls)	378,950
Electrical systems	291,500
Land	174,900
Buildings	1,136,850
Service facilities	1,603,250
Total direct costs	**5.625.950**
Indirect costs	
Engineering and supervision	932,800
Construction expenses	991,100
Contingency	1,569,728
Total indirect costs	**3.493.628**
Fixed capital investment (FCI)	**12,034,578**
Other outlays	
First commissioning	842,420
Working capital	941,156
Pre-financing	378,950
CAPEC Total	**14,197,104**

Table 22 shows the technical and economic data assumed for the production of hydrogen via supercritical gasification of sewage sludge.

Table 22: Technical and economic data for the production of hydrogen via supercritical water gasification of sewage sludge

	Unit	Value
Input		
Sewage sludge	MW	5.39
Electricity	MW	0.541
Natural gas	MW	1.69

Output		
Hydrogen	MW	2.80
Economic data		
CAPEX	million €	14.2
Lifetime	yr	20
Labor	€/yr	762,120
Administration, repairs, sales, marketing	-	15% of labor costs
Variable operating costs	€/yr	962,766
Equivalent full load period	h/yr	8,000

Analogous to [DBFZ 2014] negative values for the cost of organic waste have been assumed for the applicability case “local*” and has been set to zero in the applicability case “local”.

The hydrogen produced is compressed from 2 MPa (H_2 pressure at the outlet of the PSA) to 6.4 MPa and stored in a buffer storage (12 hours of full load hydrogen production capacity) onsite the H_2 plant.

As for other pathways, buried underground tubes have been used for hydrogen storage with specifications based on [Jauslin Stebler 2009]. The costs for hydrogen distribution and dispensing have been taken from [E4tech & EE 2014].

A large vehicle refuelling station is located onsite the H_2 plant (similar to case 1b in [E4tech & EE 2014]).

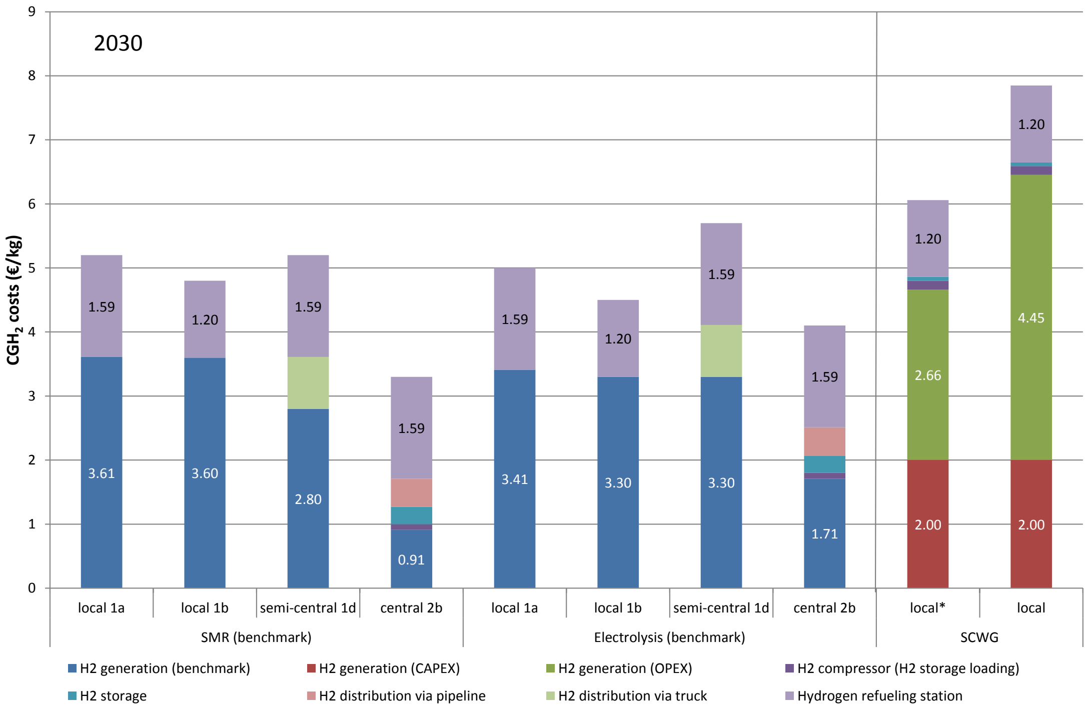
Table 23: H_2 storage and distribution costs (€/kg_{H2})

	2.8 MW_{H2} (local)
H_2 compression loading H_2 storage	0.14
H2 storage	0.06
Refuelling station*	1.20

*taken from [E4tech & EE 2014], page 9-10 in Appendix 5

c) Results

Figure 44 shows the hydrogen production costs from supercritical water gasification (SCWG) 'well-to-tank' and benchmarked against hydrogen from steam methane reforming (SMR) and water electrolysis (WE).



* including revenue for bio-waste/sewage sludge treatment (= negative value for the cost of organic waste)

Figure 44: **Costs of hydrogen from supercritical water gasification (SCWG) 'well-to-tank' benchmarked against hydrogen from SMR and water electrolysis**

Operating costs (OPEX) for hydrogen generation include feedstock costs, natural gas costs, electricity costs, labour costs, and costs of maintenance and repair.

5.2.6 Dark fermentation + raw gas reforming (5 + 2)

a) Process description

Fermentable biomass is converted to hydrogen via dark fermentation, also dubbed 'fermentation in the absence of light' or 'thermophilic hydrogen fermentation' (HyF). The residue (organic acids e.g. acetic acid) is converted to biogas via anaerobic digestion whereas the biogas is sent to a steam methane reforming plant. Therefore, this pathway can be considered as a combination of pathway (5) and pathway (2).

The core process of this two-step process for the production of hydrogen and methane, glucose is converted in the following reactions:

Dark fermentation:

$$C_6H_{12}O_6 + 2\ H_2O \rightarrow 4\ H_2 + 2\ CO_2 + 2\ C_2H_4O_2$$

Anaerobic digestion:

$$2\ C_2H_4O_2 \rightarrow 2\ CH_4 + 2\ CO_2$$

Overall reaction:

$$C_6H_{12}O_6 + 2\ H_2O \rightarrow 4\ H_2 + 2\ CH_4 + 4\ CO_2$$

The theoretical hydrogen yield would be 4 moles of hydrogen per mole of glucose or about 0.38 MJ of hydrogen per MJ of glucose (LHV). In practice the yield is much lower, about 2 moles of hydrogen per mole of glucose. The inserted biomass generally comprises a mixture of starch, lignocellulose, proteins and ash.

b) Pathway description

[Ljunggren et al. 2010] carried out a techno-economic analysis of a two-step biological process producing hydrogen and methane. Next to dark fermentation the plant also comprises pre-treatment (before) and anaerobic digestion and gas upgrading (after).

In the pre-treatment step, saccharification is carried out to extract the sugars from the lignin and the proteins. The gas upgrading is carried out by scrubbing with diethanolamine (DEA). The methane from the anaerobic digestion is sent to the dark fermentation step for stripping of the fermentation medium to enhance the fermentation process. As a result, the plant generates a mixture of hydrogen and methane. For the supply of pure hydrogen the two gases have to be separated. In this study the methane is further processed in a steam methane reforming plant to generate additional hydrogen.

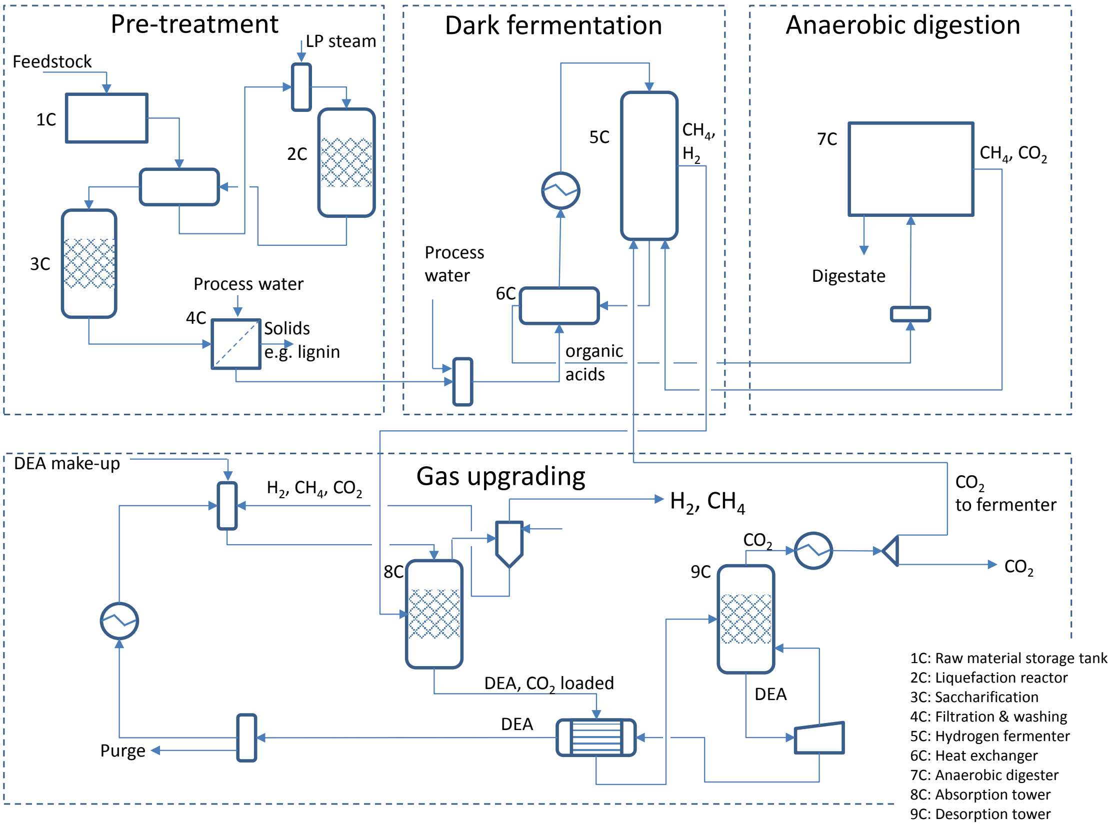


Figure 45: **Schematic of a two-step biological process producing hydrogen and methane**

In this specific study, potato steam peels have been used as feedstock. Three plant layouts for different goals have been assessed:

- High productivity (HP)
- High yield (HY)
- Low yield and low productivity (LL)

Table 24 shows the input and output data for the combined hydrogen and methane production via a two-step biological process consisting of dark fermentation and anaerobic digestion.

Table 24: Input and output data for the production of hydrogen and methane via dark fermentation and anaerobic digestion

	Unit	HP	HY	LL
Inputs				
Feedstock	t_{moist}/h	13.4	12.6	13.8
Enzymes	kg/h			
Diethanolamine (DEA)	kg/h			
Yeast extract	kg/h	68	143	3*
Na and K phosphate buffers	kg/h			
Sodium hydrogen carbonate ($NaHCO_3$)	kg/h			
Ammonium chloride	kg/h			
Ammonium molybdate	kg/h			
Cobalt chloride	kg/h			
Nickel chloride	kg/h			
Enzymes	kg/h			
Electricity**	kW	33.6	152.32	72.96
Heat	kW	987	2,173	1,170
Outputs				
H_2	kg/h	8.9	21.2	10.8
CH_4	kg/h	122.1	92.2	117.5
Ligneous residue	kg/h			

*Traced back from cost data (100.1 €/GJ, thereof 29% for nutrients and 11% for yeast extract; 2 MW product gas; 9 € per kg of yeast extract)

**for agitators with a power consumption of 20 W per m³ of fermenter volume;

The potato steam peals which are used as feedstock consist of starch, lignocellulose, protein and ash. The dry matter content is indicated at 13.4%. From the composition of the potato steam peals the lower heating value (LHV) of the feedstock has been calculated.

Table 25: Properties of potato steam peals

	LHV (MJ/kg)	Composition	LHV (MJ/kg)
Starch	13.0*	34.0%	
Lignocellulose	18.5**	38.7%	
Protein	15.5*	16.8%	
Ash		10.5%	
Total dry substance		100%	14.18

*[INRA 2009];

**[Kaltschmitt 2001] (assumed to be the same as for wood)

The cost for the potato steam peals has been indicated with 75 € per t of starch [Ljunggren et al. 2010] leading to about 25.5 € per t of total dry biomass.

The variants ‘high productivity’ and ‘high yield” require very high inputs of nutrients leading to very high hydrogen and methane costs. Therefore, in this study the variant ‘low yield and low productivity’ has been selected.

Separation of hydrogen and methane has not been considered in the layout of the plant in [Ljunggren et al. 2010]. Therefore, an additional separation step e.g. a pressure swing adsorption plant (PSA) has been added for this study to separate methane and hydrogen.

For the assessment in this study a consecutive steam methane reforming plant has been added to produce additional hydrogen from methane. As a result, the output of the final product decreases from about 2 MW (sum of H_2 and CH_4) to about 1.5 MW (sum of H_2 from dark fermentation and H_2 from steam reforming of the methane). The CAPEX for the SMR plant has been added to the CAPEX of the two-step biological process described in [Ljunggren et al. 2010].

It has furthermore been assumed that the net heat requirement (e.g. low pressure steam for the liquefaction reactor) of the plant is met by a natural gas boiler with a thermal efficiency of 90%.

Table 26: **Technical and economic data for the production of hydrogen via dark fermentation and anaerobic fermentation with downstream raw biogas SMR**

	Unit	Value
Input		
Potato steam peals	MW	7.29
Electricity	MW	0.179
Natural gas	MW	1.300
Yeast extract	kg/h	3
Other nutrients	kg/h	286
Output		
Hydrogen	MW	1.486
thereof from dark fermentation step	MW	0.360
Economic data		
CAPEX	million €	18.2
Lifetime	yr	15
Labor	€/yr	150,000
Maintenance, insurance	-	3% of CAPEX/yr

The hydrogen is compressed from 0.8 MPa (H_2 pressure at the outlet of the PSA) to 6.4 MPa and stored in a buffer storage (12 hours of full load hydrogen production capacity) onsite the H_2 plant.

As for other pathways buried underground tubes have been used for hydrogen storage with specifications based on [Jauslin Stebler 2009]. Hydrogen distribution and dispensing costs have been taken from [E4tech & EE 2014].

A large car refuelling station is located onsite the H_2 plant (similar to case 1b in [E4tech & EE 2014]).

Table 27: **H_2 storage and distribution (€/kg_{H2})**

	2.8 MW_{H2} (local)
H_2 compression loading H_2 storage	0.32
H2 storage	0.06
Refuelling station*	1.20

*taken from [E4tech & EE 2014], page 9-10 in Appendix 5

c) Results

Figure 46 show the costs for hydrogen from combined dark fermentation, anaerobic digestion and raw gas reforming 'well-to-tank' compared to hydrogen from steam methane reforming (SMR) and water electrolysis.

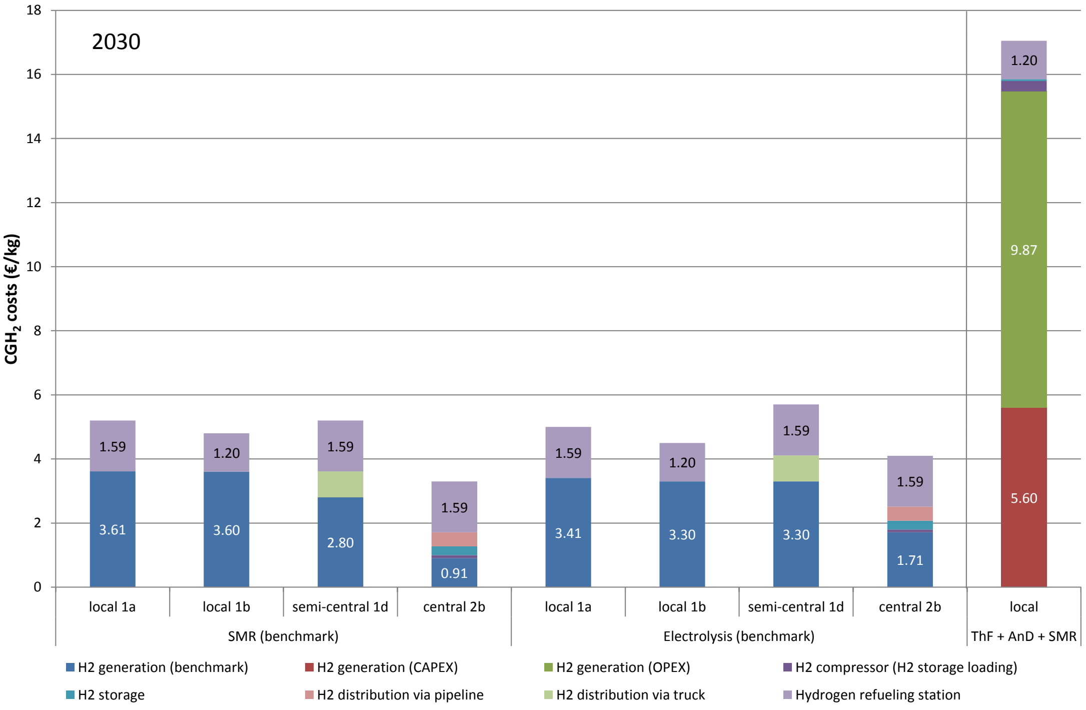


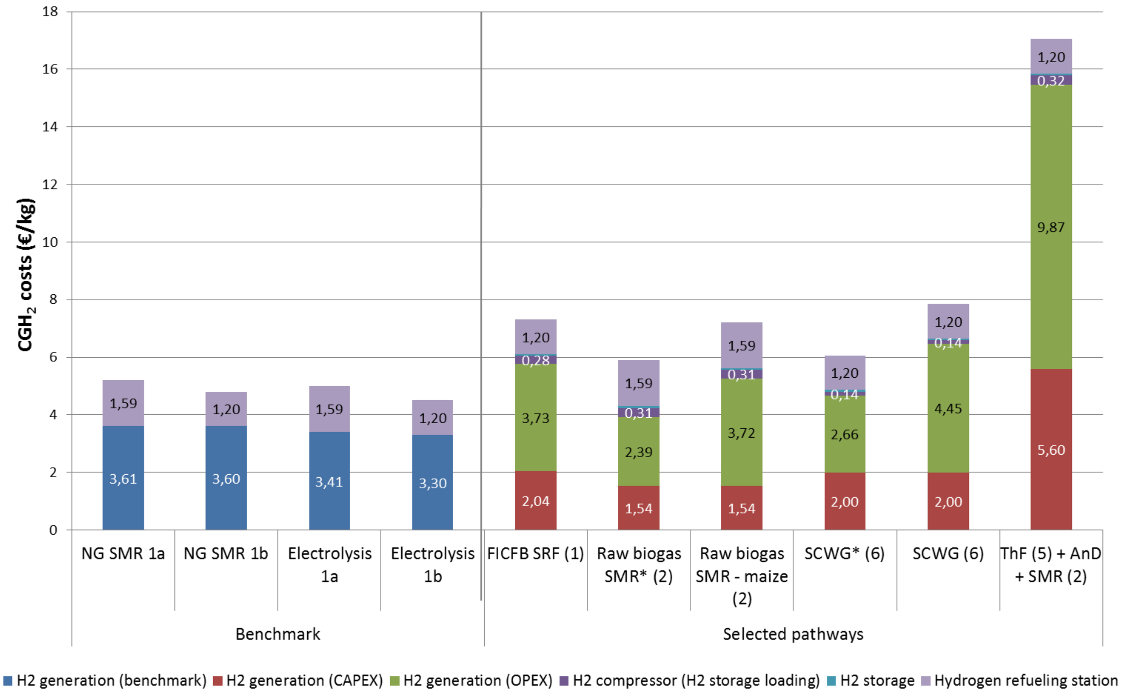
Figure 46: **Costs of hydrogen from combined dark fermentation, anaerobic digestion and raw gas reforming 'well-to-tank' compared to hydrogen from SMR and water electrolysis**

Operating costs (OPEX) for hydrogen generation include feedstock costs, electricity costs, natural gas costs, costs for chemicals and nutrients, labour costs, and costs of maintenance and repair.

5.3 Pathway analysis – summary

5.3.1 Costs

The processes for hydrogen generation scrutinized here, are grouped by process scale. Figure 47 comprises hydrogen production costs for the local processes with a capacity of 0.2 to 4 t of hydrogen per day. They are biomass gasification in a fast indirect circulating fluidised bed (FICFB) gasifier, raw biogas steam methane reforming, supercritical water gasification (SCWG), and dark fermentation (Thf) combined with anaerobic digestion (AnD) with downstream raw biogas steam methane reforming (SMR). These costs are benchmarked against the hydrogen production costs from natural gas SMR and water electrolysis using renewable electricity.



* including revenue for bio-waste/sewage sludge treatment

Figure 47: Costs of CGH_2 supply 'well-to-tank' for local hydrogen production

Operating costs (OPEX) include feedstock costs, costs for electricity, natural gas, chemicals, and other operating costs such as labour, maintenance and repair.

The supply of hydrogen via combined dark fermentation and anaerobic digestion with downstream SMR leads to the highest costs of final fuel. The low efficiency of this process leads to high feedstock costs and high costs for natural gas and electricity.

In addition, semi-central hydrogen production pathways with a capacity of 4 to 20 t of hydrogen per day have been considered for hydrogen generation via biomass gasification in a fast indirect circulating fluidised bed (FICFB) gasifier and raw biogas steam methane reforming. Figure 48 shows the costs for the supply of compressed gaseous hydrogen (CGH_2) for these pathways benchmarked against the natural gas SMR and water electrolysis using renewable electricity.

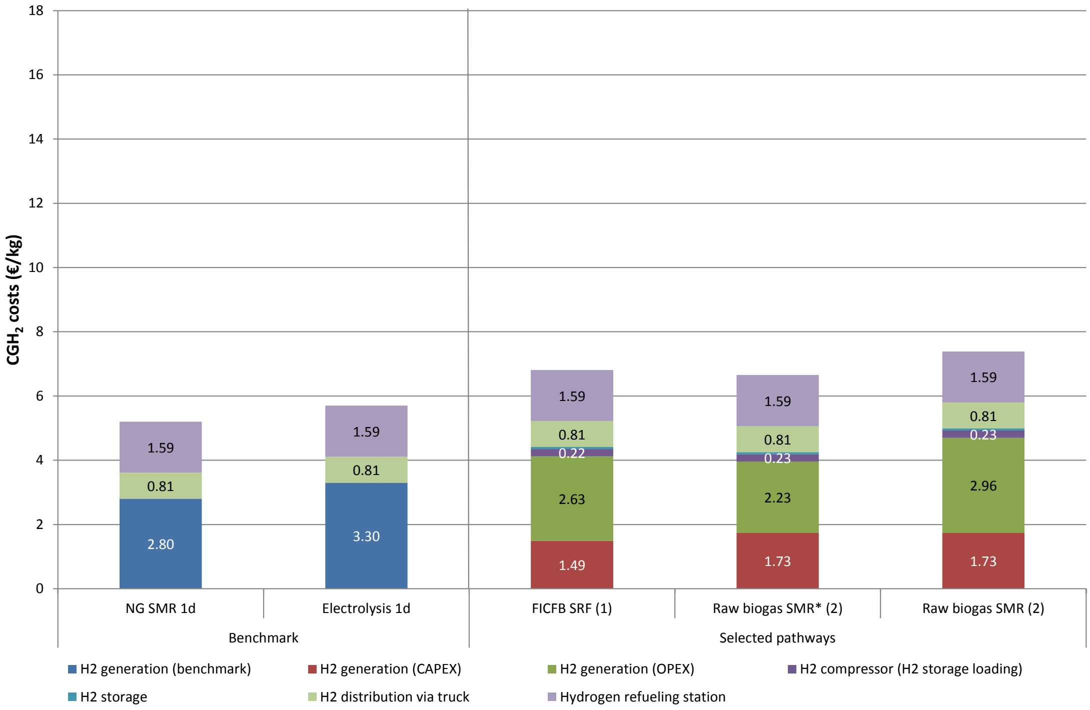


Figure 48: **Costs of CGH_2 supply 'well-to-tank' for semi-central hydrogen production**

Both biomass gasification and raw gas reforming are understood as mature technologies. The costs for the supply of CGH_2 are only slightly higher than those for the benchmark pathways. However, the potential for biomass is limited and competing use (e.g. for heat and electricity generation) have to be taken into account. Strong demand of biomass would lead to an increase of the biomass cost leading to higher overall costs of CGH_2 supply.

The third group of hydrogen production pathways comprises the central pathways, for which the hydrogen production costs are shown in Figure 49. These processes comprise biomass gasification in a fast indirect circulating fluidised bed (FICFB) gasifier, the hybrid sulphur cycle (HyS), and the photo-electrochemical cells (PEC) with a capacity of more than 20 t of hydrogen per day. The hydrogen production costs are benchmarked against natural gas SMR and water electrolysis using renewable electricity.

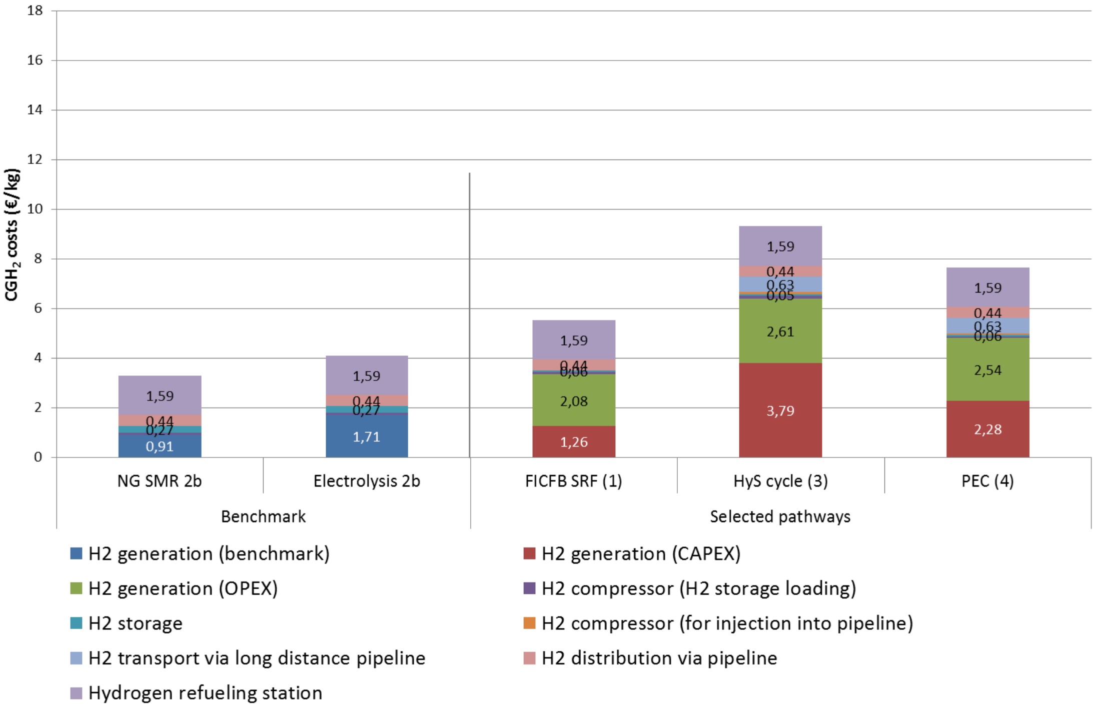


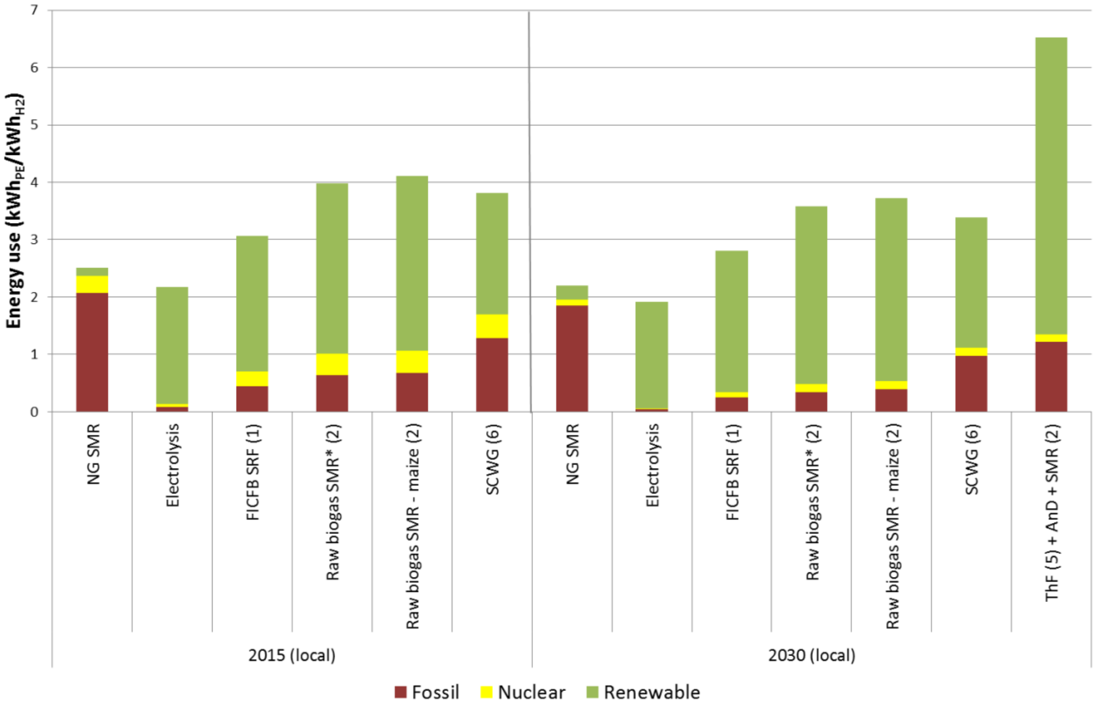
Figure 49: **Costs of CGH_2 supply 'well-to-tank' for central hydrogen production**

The supply of CGH_2 via the hybrid sulphur cycle results in the highest overall hydrogen costs. One reason are the relatively high annual costs for maintenance and insurance, which are indicated to be 6% of the CAPEX in combination with a relatively high CAPEX. However, both the sulphur hybrid cycle (which compared to other thermochemical cycles is the technology where reliable operation over many years is most likely), while PEC have not yet been operated over an extended period. Therefore, the cost goals are accompanied by high uncertainty.

5.3.2 Energy use

The figures for energy use presented in this study include the energy bound in the final fuel.

Figure 50 shows the specific energy use for the local hydrogen pathways (0.2 to 4 t of hydrogen per day) and benchmarks it against the one of natural gas SMR and water electrolysis using renewable electricity.



* including revenue for bio-waste/sewage sludge treatment

Figure 50: **Primary energy for the supply and use of CGH_2 for local hydrogen production**

In case of supercritical water gasification of sewage sludge the main fraction of the non-renewable energy input results from the combustion of natural gas for heat supply and the high amount of auxiliary electricity used in the process. This could be potentially substituted by biomass.

The demand of external heat and electricity for the combined dark fermentation (Thf) and anaerobic digestion (AnD) with downstream raw biogas steam methane reforming (SMR) is high, which results in a comparatively high input of non-renewable energy sources.

Figure 51 shows the specific energy use for the semi-central hydrogen pathways (4 to 20 t of hydrogen per day) benchmarked against SMR and WE using renewable electricity.

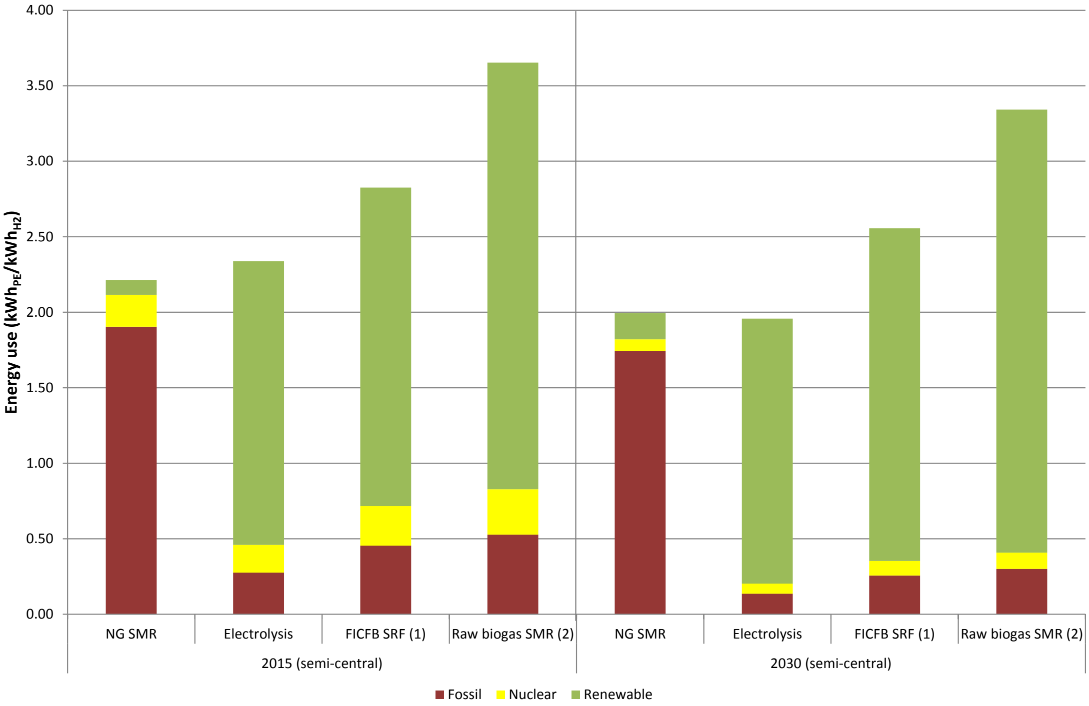


Figure 51: **Primary energy for the supply and use of CGH_2 for semi-central hydrogen production**

Figure 52 shows the specific energy use for the central hydrogen pathways (above 20 t of hydrogen per day) benchmarked against SMR and WE using renewable electricity.

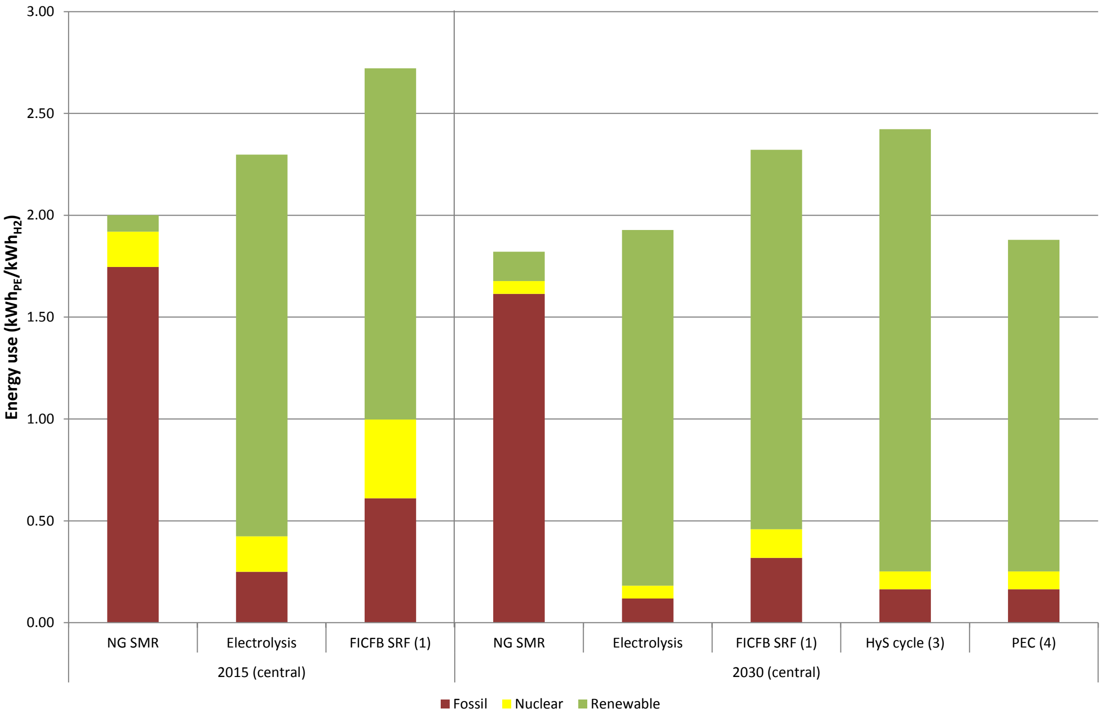


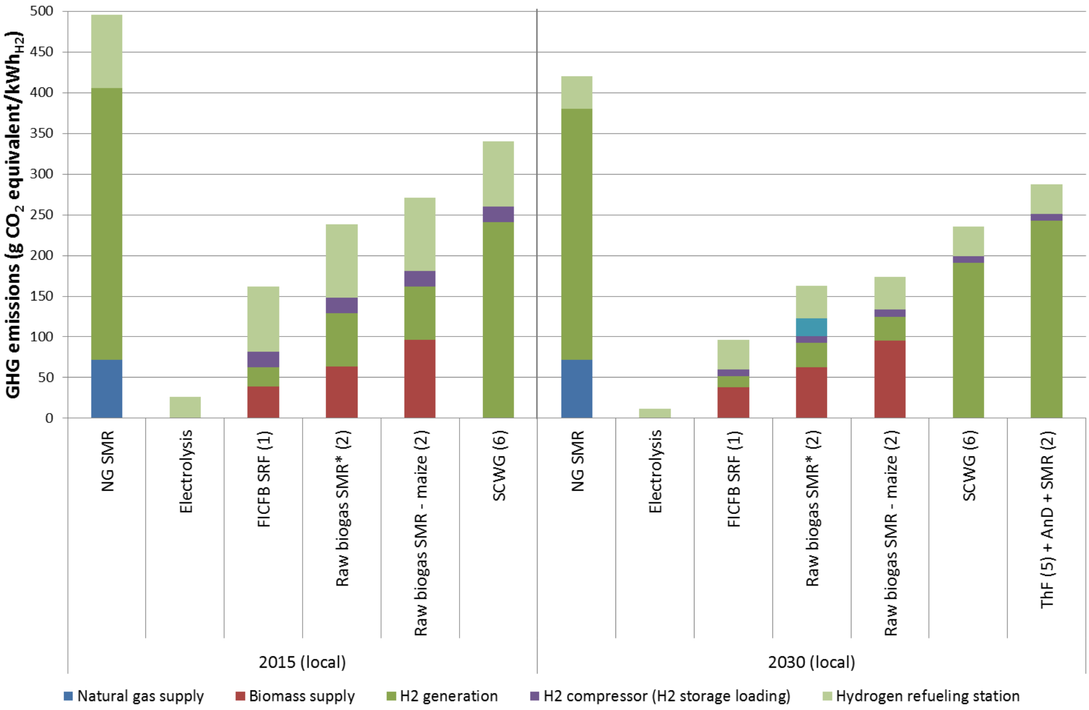
Figure 52: **Primary energy for the supply and use of CGH_2 for central hydrogen production**

The large FICFB gasifier is characterized by a relatively high electricity demand, correspondingly leading to a higher input of fossil energy.

In case of the hybrid sulphur cycle and the PEC the definition of 'energy input' is uncertain as compared with e.g. for electricity from wind or geothermal energy. In case of a hybrid cycle the renewable energy demand is based on the heat released by the receiver and hence is defined as 100%. For the case of PEC a hybrid efficiency is defined based on the combination of PV and electrolyser components. Then the efficiency combines a PV efficiency of 100% with the electrolysis efficiency of 70%, giving a gross 70% efficiency.

5.3.3 GHG emissions

Figure 53 shows the specific greenhouse gas emissions for the local hydrogen pathways (0.2 to 4 t of hydrogen per day) benchmarked against SMR and WE using renewable electricity.



* including revenue for bio-waste/sewage sludge treatment

Figure 53: **GHG emissions 'well-to-tank' for local hydrogen production**

In 2030, the overall GHG emissions decrease for all pathways due to the higher renewable share in the EU electricity mix and the resulting lower GHG emissions from electricity.

The GHG emissions from short rotation forestry (SRF) for the supply of wood chips and the GHG emissions from the supply of maize whole plant silage include soil N_2O emissions, GHG emissions from fertilizer supply, and GHG emissions from the use of diesel for farming machines.

In case of maize whole plant, the feedstock supply contributes to a high share of total GHG emissions for the supply of CGH_2. If green waste (e.g. from mowing along streets) is used instead of maize (whole plant) for biogas generation the GHG emissions from the supply of CGH_2 via raw gas steam methane reforming (SMR) decrease from 271 g CO_2 equivalent per kWh of CGH_2 in 2015 to about 174 g CO_2

equivalent per kWh of hydrogen and from 174 g CO_2 equivalent in 2030 to about 78 g CO_2 equivalent per kWh of CGH_2.

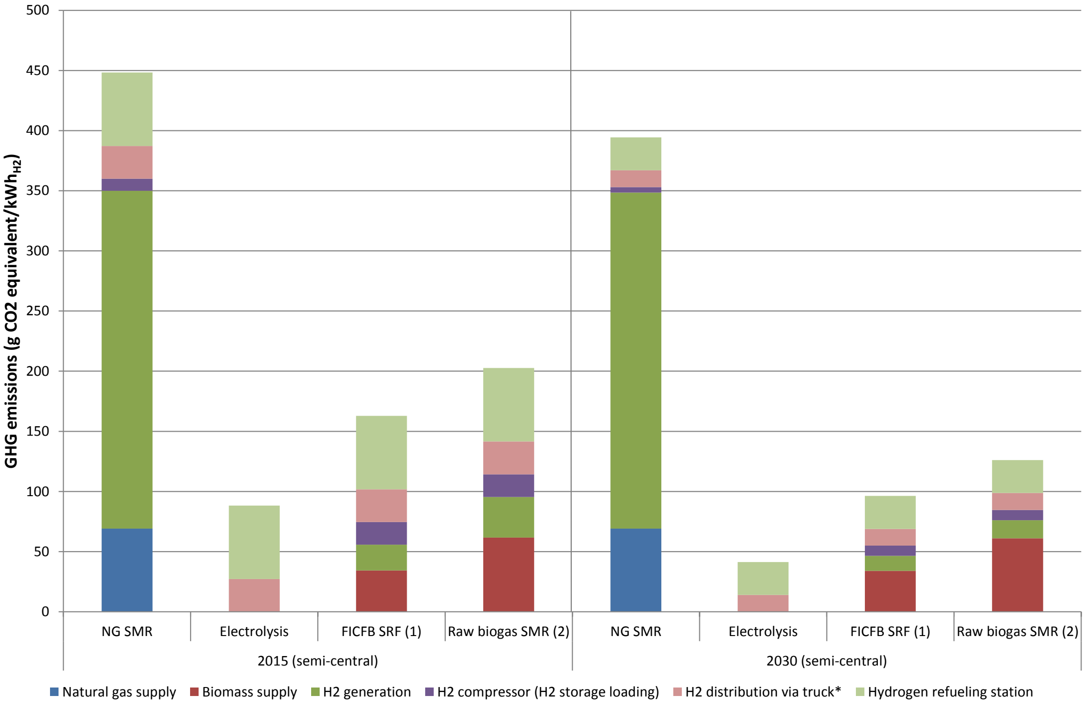
In case of supercritical water gasification of sewage sludge the main fraction of the GHG emissions results from the combustion of natural gas for heat supply and the high amount of auxiliary electricity used in the process. This could be potentially substituted by biomass.

Combined dark fermentation (Thf) and anaerobic digestion (AnD) with downstream raw biogas steam methane reforming (SMR) requires a comparatively high external input of heat and electricity resulting in high overall GHG emissions.

For CGH_2 via water electrolysis (benchmark) renewable electricity has been applied to feed the electrolyser whereas the electricity for secondary hydrogen compression and pre-cooling has been obtained from the EU electricity mix in 2015 and 2030, resulting in GHG emissions at the refuelling station step.

In case of CGH_2 from natural gas steam reforming (benchmark) the supply and use of natural gas contributes the main fraction of the overall GHG emission for this pathway.

Figure 54 shows the specific greenhouse gas emissions for the semi-central hydrogen pathways (4 to 20 t of hydrogen per day) and benchmarks them against those of natural gas SMR and water electrolysis using renewable electricity.



* including trailer refuelling

Figure 54: **GHG emissions 'well-to-tank' for semi-central hydrogen production**

In case of semi-central hydrogen production the hydrogen is transported to the hydrogen refuelling station via a diesel fuelled 40 t truck over a distance of 50 km (one way). The net payload of the CGH_2 trailer (maximum pressure about 50 MPa) is about 965 kg of hydrogen.

Figure 55 shows the specific greenhouse gas emissions for the central hydrogen pathways (above 20 t of hydrogen per day) benchmarked against those of natural gas SMR and water electrolysis using renewable electricity.

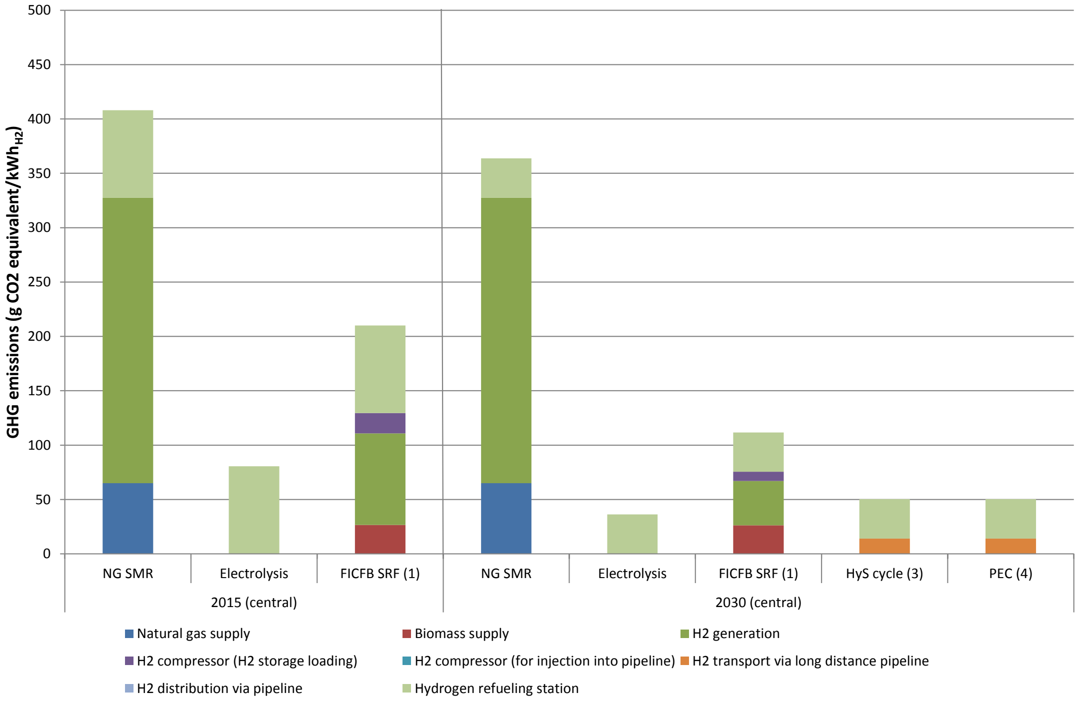


Figure 55: **GHG emissions 'well-to-tank' for central hydrogen production**

Hydrogen from the hybrid sulphur cycle (HyS) and from the photo-electrochemical cells (PEC) shows low overall GHG emissions similar to conventional water electrolysis levels if renewable electricity is applied. The GHG emissions only originate from the electricity supply to the electrically driven compressors for the long distance pipeline and the refuelling station, based on an EU electricity mix in 2030.

For hydrogen from large central biomass gasification the electricity requirement of the H_2 plant is relatively high (higher than for the smaller ones) leading to relatively high overall GHG emissions in 2015.

6 Gaps analysis of the six selected pathways

6.1 Summary

In this chapter the technology gaps and improvements needed for the six selected pathways to achieve competitiveness are analysed in detail.

Figure 56 shows the TRL of the selected pathways in 2015 and their expected development until 2030. Biomass based pathways are illustrated in green and solar energy pathways in red. Bubble sizes indicate the corresponding value chain (i.e. local, semi-central and central).

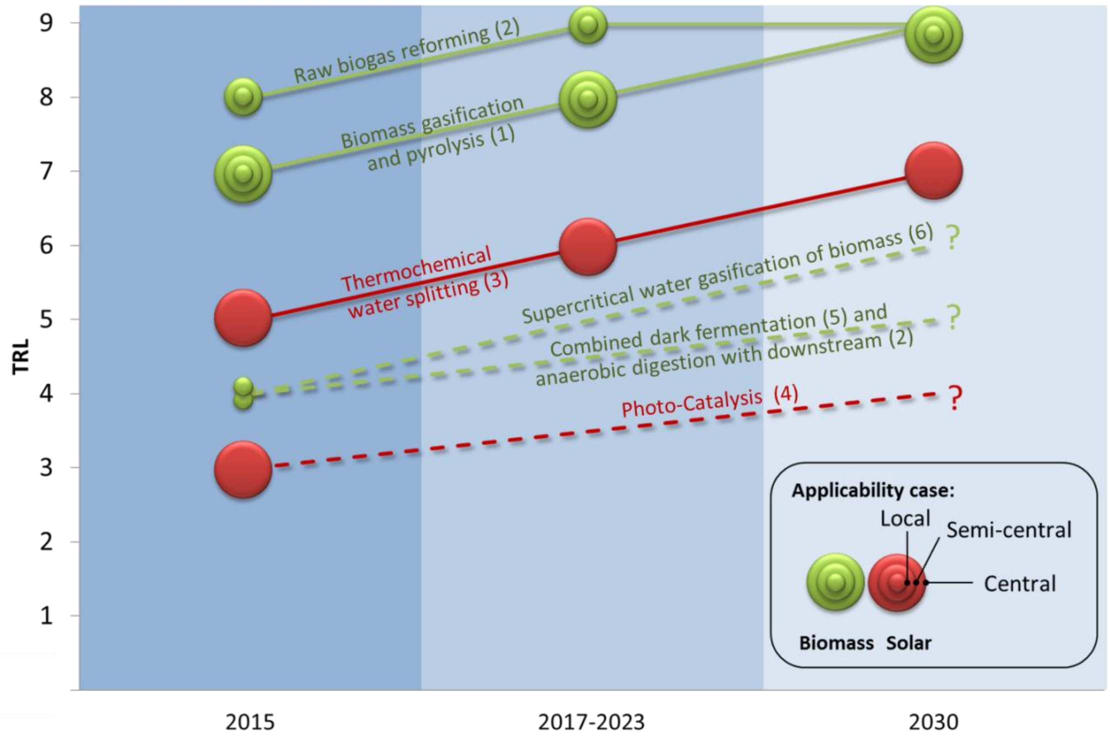


Figure 56: **Expected TRL of the six selected pathways until 2030 and their applicability cases**

The pathways biomass gasification and pyrolysis (1) (applicable for local, semi-central and central H_2 production) and raw biogas reforming (2) (local and semi-central H_2 production) show high maturity levels already today and are expected to reach a TRL comparable to water electrolysis and steam methane reforming by 2030.

Thermochemical water splitting (3) currently has a lower TRL but could reach a level of at least 7 by 2030. Due to the need of direct solar irradiation of solar thermal power plants demonstration and commercial plants have to be installed in Southern

Europe or in North Africa. As a result, the hydrogen has to be transported via pipeline to users in other parts in Europe.

The other pathways photo-catalysis (4), supercritical water gasification (6) and the combination of dark fermentation (5) with raw gas reforming (2) currently have lower TRL, lacking demonstration plants and larger scale hydrogen production experience.

Figure 57 shows the GHG-emissions associated with each pathway for 2015 and 2030. Bubbles sizes indicate the calculated GHG-emissions in g_{CO2}/kWh_{H2}. By 2030 solar energy based pathways could provide H_2 at very low GHG-emission levels. GHG-emissions for the solar energy based pathways result from the long-distance transport of the H_2. The graph also shows corresponding values for the water electrolysis (WE) and natural gas steam methane reforming (SMR) benchmarks.

The figure shows best case data, for the pathways raw biogas reforming (2) and supercritical water gasification (6). For water electrolysis and natural gas steam reforming also best case data[20] are presented in this graph.

For the six selected pathways, fossil based auxiliary energy may substituted by renewable energies in the long term. This would lower the GHG-emissions, especially for the pathway of supercritical water gasification of biomass (6), combined dark fermentation (5) and anaerobic digestions with SMR (2), and raw biogas reforming (2).

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[20] Lowest GHG-emission of benchmark technologies have been assumed by 2030 for local H_2 production via water electrolysis and central H_2 production via natural gas SMR.

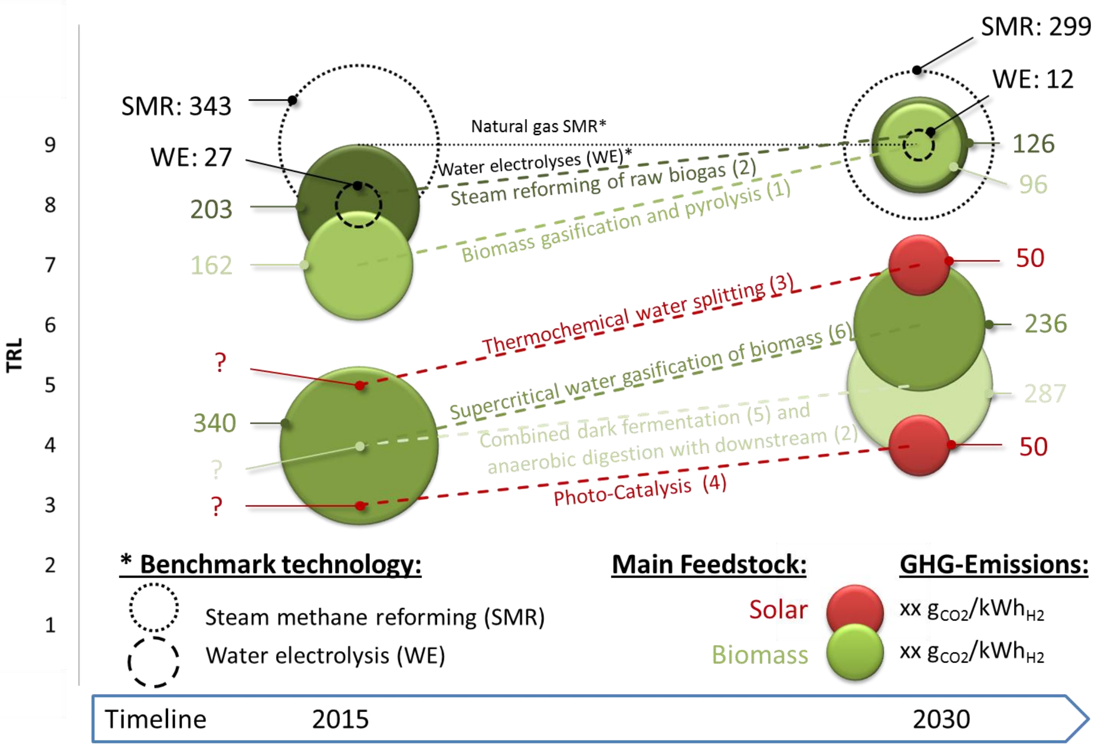

Figure 57: Development of TRL and GHG-emissions of the selected pathways and benchmark technologies between 2015 and 2030

Table 28 and Table 29 present the gaps analysis summary benchmarking the key performance indicators (KPI) of the six selected pathways against water electrolysis (WE) and steam methane reforming (SMR) for the reference year 2030.

For the benchmark the following important assumptions need to be understood:

- The main feedstock of the six selected green hydrogen pathways is 100% renewable energy to allow for a like-for-like comparison of renewable based hydrogen pathways.
- The summary table contains analysis results for idealized assumptions. Hence, the results do not reflect real plant operation. For real world operating conditions the process assumptions for all processes can vary, as regional or site specific conditions need to be taken into consideration (e.g. grid mix, varying energy prices, solar irradiation, availability of land etc.).
- Cost data for the benchmark technologies (WE, SMR in 2030) have been taken from [E4Tech & EE 2014]. In contrast to the cost data for the six selected green hydrogen pathways assumed for this study, [E4Tech & EE 2014] also applied other than 100% renewable energy sources, e.g. electricity costs for WE in [E4Tech & EE 2014] are based on market prices for industrial customers in Germany in 2030.

Table 28: **Summary of gaps analysis – Comparison of key performance indicators (KPIs) of selected pathways to benchmark technologies**

Green Hydrogen Pathway (GHyP) / Key Performance Indicator (KPI)	Biomass gasification and pyrolysis (1)	Steam reforming of raw biogas (2)	Thermochemical water splitting (3)	Photo-Catalysis (PEC: Photo-electrochemical cell) (4)	Supercritical water gasification of biomass (6)	Combined dark fermentation (5) and anaerobic digestion with downstream (2)
TRL	0	0	-	--	--	---
Feedstock availability compared to WE	-	-	0	0	-	-
H_2 costs	-	-	-	-	-	--
GHG compared to WE	-	-	0	0	--	--
GHG compared to SMR	++	+	++	++	+	0
Land use compared to WE	--	--	++	0	--	--
Land use compared to WE when using biomass residue	++	++	n. a.	n. a.	++	++
Waste to energy	++	++	n. a.	n. a.	++	++

++	much better than benchmark (SMR and water electrolysis)
+	better than benchmark (SMR and water electrolysis)
0	similar to benchmark
-	worse than benchmark
--	much worse than benchmark

WE: water electrolysis using renewable electricity (solar); SMR: steam methane reforming; n. a.: not applicable

Table 29: Summary of gaps analysis – Comparison of key performance data of selected pathways to benchmark technologies

Green Hydrogen Pathway (GHyP) / Key Performance Indicator (KPI)	Biomass gasification and pyrolysis (1)	Steam reforming of raw biogas (2)	Thermochemical water splitting (3)	Photo-Catalysis (PEC: Photo-electrochemical cell) (4)	Supercritical water gasification of biomass (6)	Combined dark fermentation (5) and anaerobic digestion with downstream (2)	Benchmark WE	Bechmark SMR
Potential Production Capacity (t_{H2}/d)								
Local (0.2-4)	2.2	0.4			2	1	**0.4 / 2**	**0.4 / 2**
Semi-Central (4-20)	6.5	4.3					**8**	**8**
Central(>20)	24		104	100			**960**	**960**
TRL								
2015	7	8	5	2-5	4	4	**8-9**	**9**
2023	8	8	6				**9**	**9**
2030	9	9	7				**9**	**9**
Feedstock	**Solid biomass**	**Wet biomass**	**Solar**	**Solar**	**Wet biomass**	**Waste biomass**	**Renewable electricity**	**Natural gas**
Feedstock availability	Limited	Limited	High	High	Limited	Limited	**High**	
H_2 generation cost (ex plant)	(€/kg_{H2})	(€/kg_{H2})	(€/kg_{H2})	(€/kg_{H2})	(€/kg_{H2})	(€/kg_{H2})		
Local	5.8	3.9*/5.3			4.7*/6.5	15.5		
Semi-Central	4.1	4.0*/4.7						
Central	3.3		6.4	4.8				
CGH_2 costs 2030 (€/kg_{H2})	(€/kg_{H2})	(€/kg_{H2})	(€/kg_{H2})	(€/kg_{H2})	(€/kg_{H2})	(€/kg_{H2})	(€/kg_{H2})	(€/kg_{H2})
Local	7.3	5.9*/7.2			6.1*/7.8	17.0	**5.0/4.5**	**5.2/4.8**
Semi-Central	6.8	6.7*/7.4					**5.7**	**5.2**
Central	5.5		9.3	7.6			**4.1**	**3.3**
GHG 2030 [g_{GHG}/kWh_{H2}]								
Local	96	163/174**			236	287	**12**	**349**
Semi-Central	96	126					**41**	**325**
Central	112		50	50			**36**	**299**
Land use [kWh_{H2}/(m^2*yr)]* **								
Local	1.9	2.5			n.a.	n.a.	**42**	**n.a.**
Semi-Central	2.1	2.5					**42**	**n.a.**
Central	2.7		111.6	45.3			**42**	**n.a.**
Lifetime (years)	20	15	20	20	20	15	**30**	**30**

* including revenue for bio-waste treatment

** maize only

***if only energy crops are used

Feedstock availability: In principle, the availability potential of all types of biomass is limited compared to wind power and solar energy. As a result, all pathways based on biomass as major feedstock suffer from a limited availability. Even though, biomass diversification (wet biomass, dry biomass, waste, etc.) is generally useful, but does not change the overall picture. Furthermore, biomass cultivation is characterized by environmental impacts (topics are e.g. water contamination and biodiversity), which need to be considered. On the other hand, biomass pathways offer the advantage to use waste streams allowing to close open material loops.

Hydrogen costs: In general, hydrogen costs for all green hydrogen pathways assessed in this study prove to be higher than those for the benchmark technologies, even for the 2030 perspective. However, hydrogen production from steam methane reforming does not represent a ‘green’ pathway and is thus not strictly comparable. It should also be kept in mind that natural gas costs posed to rise in the medium- to long-term.

At the same time, also increasing biomass prices with growing biomass supply shortages will have a negative impact on the cost to produce green biomass-derived hydrogen. In the short-term, i.e. with ample biomass waste, the replacement of conventional biomass by bio-waste or sewage sludge can reduce hydrogen production costs due to additional revenue streams. With growing competition, also this cost advantage is posed to decrease over time.

GHG emissions: Hydrogen production from supercritical water gasification (6) and from combined dark fermentation and anaerobic digestion with downstream steam methane reforming (pathway 5+2) results in higher greenhouse gas emissions than from the other pathways due to significant quantities of natural gas required for auxiliary heat supply if realized in the short-term.

In perspective, the fossil energy share of the pathways biomass gasification (1) and pyrolysis, raw biogas reforming (2), and supercritical water gasification (6), which we have assumed for this study can be further reduced in the future. The reason is that auxiliary electricity from EU’s electricity mix and external heat provided by natural gas can progressively be substituted by electricity and heat from renewable energy sources, i.e. renewable electricity or biomass.

Land use: The specific hydrogen yield per m^2 of land area for hydrogen production from solar energy (water electrolysis using electricity from solar energy, thermochemical cycle using solar heat (3), photo-electrochemical cells (4)) is at least by a factor of 20 higher than that for hydrogen production from energy crops such as wood chips from short rotation forestry (1) or from maize (whole plant) via biogas (2). No land use is associated with the use of waste biomass.

6.2 Biomass gasification and pyrolysis (1)

Table 30 shows the key performance indicators for the supply of hydrogen from biomass gasification via fast indirect circulating fluidised bed (FICFB) gasifiers as benchmarked against natural gas steam reforming and water electrolysis.

Table 30: Key performance indicators (KPI) for biomass gasification or pyrolysis (1) – 2030

	Unit	**SMR**	**Electro-lysis**	**local (3 MW_{H2})**	**semi-central (9 MW_{H2})**	**central (33 MW_{H2})**
TRL						
2015			8-9	7	7	7
2023				8	8	8
2030				9	9	9
Feedstock/ Energy source		NG	Renewable electricity	Wood chips		
Feedstock availability			high	limited	Limited	limited
Costs						
CAPEX	€/kW_{H2}		600-800	4,867	3,556	3,000
	€/(kWh_{H2}/yr)			0.65	0.47	0.40
	€/kWh_{H2}			0.061	0.045	0.038
OPEX	€/kWh_{H2}			0.112	0.079	0.062
thereof feedstock	€/kWh_{H2}			0.038	0.034	0.026
H_2 costs ex H_2 plant	€/kWh_{H2}			0.173	0.124	0.100
	€/GJ_{H2}			48.1	34.4	27.8
	€/kg_{H2}			5.8	4.1	3.3
CGH_2 costs pathway	€/kWh_{H2}	0.099-0.156	0.123-0.171	0.219	0.204	0.166
	€/GJ_{H2}	27.5-43.3	34.2-47.5	60.9	56.8	46.2
	€/kg_{H2}	3.3-5.2	4.1-5.7	7.3	6.8	5.5
Lifetime (H_2 plant)			30	>20	>20	>20
Environment						
Area specific yield	kWh_{H2}/(m²*yr)	n. a.	42.2*	1.9**	2.1**	2.7**
GHG emissions	g/kWh_{H2}	299-349	12-41	96	96	112
	g/MJ_{H2}	83-97	3-11	27	27	31
Other issues				Biodiversity		

* Electricity from PV in Germany (solar irradiation: 1,200 kWh per m² an year); efficiency PV panel: 20%; PR = 0.80; ratio PV panel/land area = 0.33; electricity consumption electrolysis: 50 kWh/kg_{H2};

** Wood chips from short rotation forestry: 8 t dry substance per ha and year

Technology readiness / commercialisation perspective

- Biomass gasification has been successfully demonstrated in Güssing in Austria (TRL 7).
- Until 2030 the TRL should be comparable to water electrolysis (WE) and steam methane reforming (SMR), i.e. TRL 9.
- **Identified gap:** Missing experience from larger demonstration plants for the production of hydrogen via biomass gasification.
- **Potential target:** Setting up integrated (including CO shift and PSA) demonstration units of biomass gasification plants until 2020.

  Example:

  - In the next 2-3 years build-up of larger demonstration units for crude oil refineries (e.g. up to 24 t_{H2}/d)
  - In the next 2-3 years erection of local (~2 t_{H2}/d) and semi-central (~6 t_{H2}/d) demonstration plants for the supply of hydrogen vehicles.

Feedstock

The potential European as well as worldwide availability of sustainable biomass is limited in the medium to long term, even though the capability to use bio-waste as feedstock is a short-term advantage of this pathway. Biomass gasification plants require feedstock with a defined quality.

- **Identified gap:** Availability of biomass with well-defined homogeneity and consistently high levels of quality and sustainability.
- **Potential target:** Develop plant concepts for flexible feedstock input. Example: experiments with scrap wood in the next 2-3 years.

Costs

CAPEX is much higher than for the benchmark technologies. However, as biomass gasifiers operate at higher equivalent full load hours, the resulting hydrogen costs of biomass reforming are only slightly above the costs of WE.

⇒ **Identified gaps**: High OPEX
Feedstock costs (biomass) are estimated at ~20-30% of the H_2 costs (ex H_2 plant).

  - Major cost drivers of the OPEX are the biomass feedstock costs. Thus, any increase of biomass costs would lead to an increase of hydrogen production costs. An increasing demand for sustainable quality feedstock is expected to increase its market price.

  - Further cost drivers are electricity and O&M costs.

- **Potential targets:**
  - Increase flexibility and tolerance of the biomass gasifier to use variable feedstock biomass with lower quality.
  - Reduction of the auxiliary electricity use (especially for the central plant which consumes approx. 0.17 MJ per MJ of hydrogen)
  - Reduction of O&M costs (especially for the local and semi-central plant).
  - Increase of gasifier efficiency to reduce biomass demand (small plants).

6.3 Steam reforming of raw biogas (2)

Table 31 shows the key performance indicators for the supply of hydrogen from steam methane reforming of raw biogas benchmarked against natural gas steam reforming and water electrolysis.

Table 31: Key performance indicators (KPI) for steam reforming of raw biogas (2)

	Unit	SMR	Electrolysis	local (0.6 MW_{H2})	semi-central (6 MW_{H2})
TRL					
2015			8-9	8	8
2023				9	9
2030				9	9
Feedstock/Energy source		NG	Renewable Electricity	Maize	Maize, bio-waste, manure
Feedstock availability			High	limited	limited
Costs					
CAPEX	€/kW_{H2}		600-800	3,148	3,550
	€/(kWh_{H2}/yr)			0.42	0.47
	€/kWh_{H2}			0.046	0.052
OPEX	€/kWh_{H2}			0.072-0.112	0.067-0.089**
thereof feedstock	€/kWh_{H2}			0.015-0.055	0.016-0.038**
H_2 costs ex H_2 plant	€/kWh_{H2}			0.118-0.158	0.119-0.141**
	€/GJ_{H2}			32.8-43.8	33.0-39.1**
	€/kg_{H2}			3.9-5.3	4.0-4.7**
CGH_2 costs pathway	€/kWh_{H2}	0.099-0.156	0.123-0.171	0.177-0.217	0.200-0.222**
	€/GJ_{H2}	27.5-43.3	34.2-47.5	49.1-60.1	55.5-61.6**
	€/kg_{H2}	3.3-5.2	4.1-5.7	5.9-7.2	6.7-7.4**
Lifetime (H_2 plant)			30	15	15
Environment					
Area specific yield	$kWh_{H2}/m^{2}*yr)$	n. a.	42.2*	2.5***	n. a.
GHG emissions	g/kWh_{H2}	299-349	12-41	163-174	126
	g/MJ_{H2}	83-97	3-11	45-48	35
Other issues				Biodiversity, agrochemicals	

* Electricity from PV in Germany (solar irradiation: 1,200 kWh per m² an year); efficiency PV panel: 20%; PR = 0.80; ratio PV panel/land area = 0.33; electricity consumption electrolysis: 50 kWh/kg_{H2};

** lower value: including revenue for bio-waste treatment;

*** Maize whole plant yield: 44 t fresh substance per year; dry matter content: 35%; thereof organic matter: 96%; Storage losses: 12%; gross CH_4 yield: 312 Nm³ per t of dry organic substance; Biogas for fermenter heating: approx. 10% of the gross biogas yield; Biogas requirement SMR plant: 1.45 kWh of biogas per kWh of H_2

Technology readiness / commercialisation perspective

- **Identified gap**: Missing experience from small, compact, and reliable steam reformers for biomass/biogas for local hydrogen production

  Example: onsite small biogas plants, onsite small hydrogen refuelling stations, ~100 – 450 kg_{H2}/d range (maximum 20 to 90 cars/d).

- **Potential target**: Build-up of small scale compact pilot and demonstration reformers:
  - Until 2017: Installation of steam reformers onsite biogas plants in combination with small hydrogen refuelling stations at locations nearby motorways.
  - Until 2020: Installation of steam reformers onsite biogas plants in combination with small hydrogen refuelling stations in rural regions.

Feedstock

The availability/potential of sustainable biogas/biomass is limited in Europe and worldwide.

Costs

High OPEX: Feedstock accounts for ~30% of CAPEX and cannot be significantly reduced (intensive maize cultivation has negative impacts on environment, more sustainable cultivation of energy crops e.g. crop rotation systems including flowering plants probably leads to higher costs). In case of rising demand, the price for waste biomass will increase.

- **Identified gap**: High CAPEX

⇒ **Potential target**: Cost reduction of compact small scale steam reforming plants

Example: 50% cost reduction until 2020 via series production.

Plant size

⇒ **Identified gap**: Relatively large plant footprint for onsite H_2 production.

Figure 58 shows the actual footprint of small compact natural gas reformers for H_2 production. The data are based on commercially available SMRs for onsite H2 production and should serve as benchmark for small compact biogas reformer.

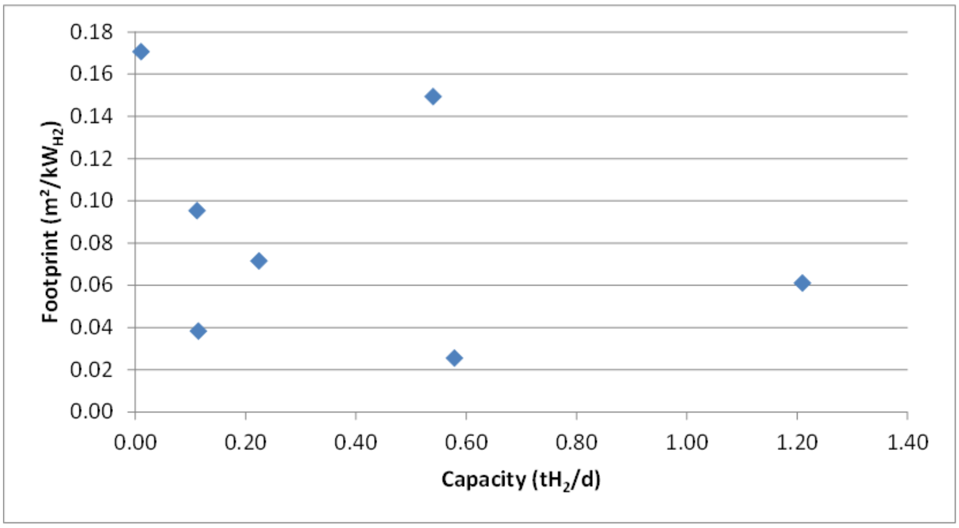

Figure 58: **Commercial SMRs for onsite H_2 generation (today)**

⇒ **Potential target:** Build-up of small scale & compact pilot and demonstration reformers until 2020.

6.4 Thermochemical water splitting (3)

Table 32 shows the key performance indicators for the supply of hydrogen from a thermochemical cycle based on the hybrid sulphur cycle benchmarked against natural gas steam reforming and water electrolysis.

Table 32: Key performance indicators (KPI) for thermochemical water splitting (3)

	Unit	SMR	Electrolysis	Central
TRL				
2015			8-9	5
2023				6
2030				7
Energy source		NG	Renewable Electricity	Renewable heat
Energy source availability			high	high
Costs				
CAPEX	€/kW$_{H2}$		600-800	10,552
	€/(kWh$_{H2}$/yr)			1.20
	€/kWh$_{H2}$			0.114
OPEX	€/kWh$_{H2}$			0.078
thereof feedstock	€/kWh$_{H2}$			0 (solar)
H_2 costs ex H_2 plant	€/kWh$_{H2}$			0.192
	€/GJ$_{H2}$			53.5
	€/kg$_{H2}$			6.4
CGH_2 costs pathway	€/kWh$_{H2}$	0.099-0.156	0.123-0.171	0.279
	€/GJ$_{H2}$	27.5-43.3	34.2-47.5	77.6
	€/kg$_{H2}$	3.3-5.2	4.1-5.7	9.3
Lifetime (H_2 plant)			30	20
Environment				
Area specific yield	kWh$_{H2}$/m²*yr)	n. a.	42.2*	112**
GHG emissions	g/kWh$_{H2}$	299-349	12-41	50
	g/MJ$_{H2}$	83-97	3-11	14

* Electricity from photovoltaic in Germany (solar irradiation: 1,200 kWh per m² an year);
efficiency PV panel: 20%; PR = 0.80; ratio PV panel/land area = 0.33;
electricity consumption electrolysis: 50 kWh/kg$_{H2}$;
**Solar irradiation: 3,000 kWh per m² and year

Technology readiness / commercialisation perspective

⇒ **Identified gap**: Missing experience with larger demonstration plants.

⇒ **Potential target**: Build-up of demonstration plants and scale-up of hydrogen production in order to improve TRL and to strengthen European position.

Example: Target application: central hydrogen production

Build-up of demonstration plants in Southern Europe and Morocco until 2020.

Example: U.S. target: 2017, 200 MW$_{th}$ producing 11,000 t of H_2 per year.

Feedstock

- ⇒ **Identified gap**: Direct solar irradiation is required; thus, the technology is only applicable to southern Europe / North Africa.
- ⇒ **Potential target**: Develop cross-border production and logistics concepts.
  Example: Target application: central hydrogen production;
  build-up of demonstration plants in e.g. Morocco until 2020.

Costs

High CAPEX (especially the solar field) and OPEX are major key cost drivers.

- ⇒ **Identified gaps:** Limited lifetime of the thermochemical cycles. High O&M costs (~4% of investment per year).
- **Potential targets**: Increase plant and component lifetime, e.g. by the stabilisation of cycles, by solving the problem of corrosion, and by using high temperature resistant materials.
  DoE cost target for solar driven thermochemical cycles [US Drive 2013]
    - for 2015 US$$_{2009}$ 14.80/gge$_{H2}$ (10.5 €/kg$_{H2}$)
    - for 2020 US$$_{2009}$ 3.7 gge$_{H2}$ (2.6 €/kg$_{H2}$)

6.5 Photo-Catalysis (PEC: Photo-electrochemical cell) (4)

Table 33 shows the key performance indicators for the supply of hydrogen from photo-electrochemical cells (PEC, Type 3) benchmarked against natural gas steam reforming and water electrolysis.

Table 33: Key performance indicators (KPI) for PEC (4)

	Unit	SMR	Electrolysis	Central
TRL				
2015			8-9	2-5
2023				
2030				
Energy source		NG	Renewable Electricity	Renewable heat
Energy source availability			high	high
Costs				
CAPEX	€/kW$_{H2}$		600-800	5710
	€/(kWh$_{H2}$/yr)			0.72
	€/kWh$_{H2}$			0.068
OPEX	€/kWh$_{H2}$			0.076
thereof feedstock	€/kWh$_{H2}$			0 (solar)
H_2 costs ex H_2 plant	€/kWh$_{H2}$			0.145
	€/GJ$_{H2}$			40.3
	€/kg$_{H2}$			4.84
CGH_2 costs pathway	€/kWh$_{H2}$	0.099-0.156	0.123-0.171	0.229
	€/GJ$_{H2}$	27.5-43.3	34.2-47.5	63.7
	€/kg$_{H2}$	3.3-5.2	4.1-5.7	7.6
Lifetime (H_2 plant)			30	20
Environment				
Area specific yield	kWh$_{H2}$/m^2*yr)	n. a.	42.2*	45.3**
GHG emissions	g/kWh$_{H2}$	299-349	12-41	50
	g/MJ$_{H2}$	83-97	3-11	14

* Electricity from PV in Germany (solar irradiation: 1,200 kWh per m^2 an year); efficiency PV panel: 20%; PR = 0.80; ratio PV panel/land area = 0.33; electricity consumption electrolysis: 50 kWh/kg$_{H2}$;
**Solar irradiation: 2,400 kWh per m^2 and year

Technology readiness / commercialisation

- ⇒ **Identified gap:** Missing demonstration of hydrogen production and scaled-up pilot plants.
- ⇒ **Potential target:** Example: Target application: central hydrogen production Build-up of demonstration plants in e.g. Morocco until 2020.

Costs

Material costs of PEC semiconductors have a major influence on the efficiency and PEC Cell lifetime. Table 34 shows the relation between PEC cell costs per m^2, the efficiency and lifetime of the cells.

Table 34: PEC cell, type 3, costs and effect on efficiency and lifetime ([DT 2009]; assumed average exchange rate = 0.719 €/US$)

PEC Cell Costs	Efficiency	PEC Cell Lifetime
58 €/m²	5%	5 years
110 €/m²	**10%**	**10 years**
144 €/m²	15%	20 years

Another cost driver is the structure and the packaging of the PEC cell as well as the BOP costs, including controls and sensors.

⇒ **Identified gap**: High CAPEX and high OPEX due to PEC replacement costs. The PEC lifetime of 10 years leads to high annual O&M costs of around ~9% of CAPEX .

⇒ **Potential target**: CAPEX/OPEX reduction.

Potential R&D topics include:

- increase of stability and lifetime (material and design),
- reduce the problem of corrosion of PEC materials,
- increase of efficiency,
- development of suitable materials,
- optimisation of reactor design,
- cost reduction (i.e. concentrator, semiconductor material),
- identification and development of optimised materials, integrated devices, and reactor configurations.

The disadvantage of PECs is that piping over the entire solar array is required to feed water to and remove hydrogen from the system. In contrast to PEC, an electrolysis plant is separate from the PV electricity generation and can independently be optimized towards higher current densities.

We have applied PEC cost data from [DT 2009], which may be regarded as optimistic.

- DoE cost target for photoelectrode system [US Drive 2013]
  - for 2015 $US\$_{2009}$ 17.30/gge_{H2} (12.3 €/kg_{H2})
  - for 2020 $US\$_{2009}$ 5.70 gge_{H2} (4.0 €/kg_{H2})
  - Comparison: H_2 costs production costs (plant gate), type 3, central, based on [DT 2009]: 4.84 €/kgH_2 (3.5 US$/$kg_{H2}$ for an exchange rate of 0.719 €/$US\$_{2009}$)

6.6 Supercritical water gasification of biomass (6)

Table 35 shows the key performance indicators for the supply of hydrogen from supercritical water gasification of biomass, in particular being able to process wet biomass (e.g. sewage sludge), benchmarked against natural gas steam reforming and water electrolysis.

Table 35: Key performance indicators (KPI) for supercritical water gasification of wet biomass (6)

	Unit	SMR	Electrolysis	Local
TRL				
2015				4
2023				
2030				
Feedstock		NG	Renewable Electricity	Wet biomass
Feedstock availability			high	medium
Costs				
CAPEX	€/kW$_{H2}$		600-800	5093
	€/(kWh$_{H2}$/yr)			0.64
	€/kWh$_{H2}$			0.060
OPEX	€/kWh$_{H2}$			0.080-0.133**
thereof feedstock	€/kWh$_{H2}$			-0.054-0**
H_2 costs ex H_2 plant	€/kWh$_{H2}$			0.140-0.194
	€/GJ$_{H2}$			38.9-38.9
	€/kg$_{H2}$			4.7-6.5
CGH_2 costs pathway	€/kWh$_{H2}$	0.099-0.156	0.123-0.171	0.182-0.235
	€/GJ$_{H2}$	27.5-43.3	34.2-47.5	50.5-65.4
	€/kg$_{H2}$	3.3-5.2	4.1-5.7	6.1-7.8
Lifetime (H_2 plant)				20
Environment				
Area specific yield	kWh$_{H2}$/m²*yr)	n. a.	42.2*	n. a.
GHG emissions	g/kWh$_{H2}$	299-349	12-41	236
	g/MJ$_{H2}$	83-97	3-11	65

* Electricity from PV in Germany (solar irradiation: 1,200 kWh per m² an year); efficiency PV panel: 20%; PR = 0.80; ratio PV panel/land area = 0.33; electricity consumption electrolysis: 50 kWh/kg$_{H2}$;
** lower value: including revenue for sewage sludge treatment

Technology readiness / commercialisation perspective

- ⇒ **Identified gap**: Missing demonstration of hydrogen production and of larger scale pilot plants.
- ⇒ **Potential target**: Build-up of demonstration plants and scale-up of hydrogen production in order to improve TRL.

Example: Target application: local and semi-central hydrogen production: Build-up of integrated demonstration plants (incl. CO shift and PSA) until 2020.

Costs

⇒ **Identified gap:** High CAPEX because of required high-pressure equipment (heat exchanger, reactor etc.) with associated investment costs and operation & maintenance requirements.

⇒ **Identified gap**: High OPEX.
An economic analysis of a 5 t of wet sewage sludge per hour (1 t dry substance/h) installation using sewage sludge arrives at the conclusion that hydrogen costs would only become commercially viable for free-of-charge waste streams.

⇒ **Potential target:** Reduce CAPEX and OPEX.

7 Recommendation of RD&D priorities

7.1 Introduction

The objective of the chapter is to

- identify priorities for research and innovation actions (RIAs) and innovation actions (IAs) under the FCH 2 JU using the results of the detailed analysis of the selected pathways, and
- develop call topic content for implementation in FCH 2 JU calls for proposals addressing these priorities.

Keeping in mind that the H2020 calls for proposals need to be challenge based, and following the structure used for call topics, this effort comprised

- developing a sharable synthetic overview of the six selected pathways,
- identifying their specific challenges and
- defining the scope of work and expected impact in terms of targets linked to the specific challenges.

Template for pathway overview and proposed topic content

To that end, a template structure for the presentation of each pathway overview and the proposed call topic content has been developed. In order to facilitate an easier use, part 1 of each template includes a concise summary of the results of the analyses in previous chapters.

Template structure:

Part 1 – Pathway overview

- Basic description of pathway
    - Basic description of process
    - Basic description of benefit
    - [If applicable, condition for being more competitive than other process using same feedstock]
    - Basic assessment of development stage

- Technologies
    - Presentation of the most relevant technologies, including justification
    - Recent activities and current state of development and performance
    - Potential costs and impact
- Current development objective
    - Most needed type of activity
    - Summary of specific overall development objective

Part 2 – Proposed call topic content

- Specific challenges
    - List of the specific challenges to be addressed
- Scope
    - Type of action
    - Technologies covered
    - Specific challenges to be addressed in priority
    - Activities to be carried out for addressing the specific challenges
- Impact
    - Minimum performance targets related to the specific challenges that proposal should target

Methodology for identification of specific challenges

For each technology, technical characteristics that may impact viability and competitiveness from the following list were considered (see chapters 2, 5, and 6):

- Hydrogen yield
- Thermal efficiency
- Plant capacity
- Plant lifetime
- Maintenance requirements
- System integration
- Reaction rate
- Use of rare or costly materials

- Plant footprint
- Feedstock flexibility
- Operating flexibility

The most relevant ones with regard to moving the reviewed technology forward were selected and the associated most important specific challenges identified.

Note: potential approaches for addressing the challenges are indicated for an illustrative purpose only – these should not be considered as being recommended approaches.

Scope

Considering the state of development and the type of difficulties to be overcome, this section indicates the type of action that should be considered, the technologies on which to focus efforts, and challenges to be addressed in priority.

Impact

This section describes the expected impact of the actions in terms of technical targets which are related to the challenges that need to be addressed, also taking into consideration the type of action (RIA or IA).

7.2 Biomass gasification and pyrolysis (1)

7.2.1 Pathway overview

Basic description

The biomass pyrolysis and gasification process[21] allows to convert solid lignocellulosic biomass such as wood chips (from waste wood or short rotation forestry) and straw into a gas mixture mainly consisting of CO, H_2, CO_2, and CH_4 (syngas), from which hydrogen is produced through further chemical reactions (reforming, CO water shift) and purification[22].

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[21] Pyrolysis is a thermochemical decomposition of organic material at elevated temperatures in the absence of oxygen (or any other gasification agent) leading to pyrolysis gases, pyrolysis oils, and coke. Gasification is a process that converts organic or fossil fuel based carbonaceous materials into a syngas which consists of carbon monoxide, hydrogen, carbon dioxide, and small amounts of gaseous hydrocarbons. This is achieved by reacting the material at high temperatures (>700 °C), without combustion, with a controlled amount of oxygen and/or steam.

[22] Black liquor, a combustible waste product generated in large quantities from the pulp and paper industry is also a feedstock that may be used to produce hydrogen by gasification.

This pathway allows to efficiently convert locally available lignocellulosic biomass into high value energy in the form of hydrogen.

While biomass gasification has already been successfully implemented in full scale units operating in an industrially relevant environment, the demonstration of pure hydrogen production through this process is just in its infancy.

Technology review summary

Indirectly heated gasifiers using water as the gasification agent are the most suitable ones for the production of hydrogen, as they avoid the introduction of nitrogen that would result from the use of air and also maximize the hydrogen yield (kg of H_2 per kg of feedstock).

Combustion heat is applied indirectly to the feedstock via a heat carrier (allothermal design), e.g. by means of a fast internally circulating fluidized bed (FICFB).

This type of process has been applied in Güssing, Austria, since 2002, with more than 58,000 hours of operation so far. Use of a CO_2 absorbing bed material, allowing more hydrogen to be produced by displacement of a chemical reaction equilibrium, has also been successfully tested in the Güssing facility. The construction of a unit processing 4 MW_{th} (i.e. 0.8 to 1 t/h) of biomass input using the above process is projected for 2015 at Ibaragi, Japan.

The presence of nitrogen in the syngas can also be avoided by using oxygen as the gasifying agent, in which case combustion heat can be applied directly (autothermal design). Furthermore water and oxygen may be used in combination as gasifying agents.

The on-going EC funded UnifHy project aims at developing and demonstrating an optimized biomass gasification process for the production of hydrogen using a 1 MW_{th} fluidized bed steam/oxygen gasifier processing 190 kg_{dry}/h of biomass. Catalytic hot gas cleaning (for breakdown of tar) is integrated to the gasification reactor.

As the production of hydrogen by water electrolysis also generates oxygen, production of hydrogen by biomass gasification with oxygen as a gasifying agent in combination with water electrolysis presents synergies that remain to be investigated.

Cost and impact potential

The production costs of hydrogen using biomass gasification with the FICFB process is projected to be between 5.8 and 3.3 €/kg_{H2} depending on the type of facility (local, semi-central or central), see chapter 5.2.1.

When the hydrogen is used in fuel cell electric vehicles (FCEV), the well-to-wheel energy use per km of this pathway is 2 to 3 times lower than that of 2nd generation biofuels (produced from the same feedstock), further motivating the deployment of FCEVs in order to make the most out of this widely available lignocellulosic biomass feedstock.

Current development objectives

Biomass gasification processes that are suitable for H_2 production are close to commercial implementation. However, for materialization of the pathway's potential, **continued research and innovation activities are required for techno-economical optimisation of the total system through improvements that will lower investment costs, increase feedstock flexibility, lower ancillary energy consumption, maximise hydrogen yield, and reduce maintenance requirements**.

New process approaches need to be validated at pilot plant scale before they are implemented in full scale demonstration activities.

7.2.2 Specific challenges

In order to achieve the above mentioned development goals, the following challenges need to be addressed:

Process integration

Challenge: further integrate the total process and reduce size (more capacity with less equipment)

Potential approaches: simplify process; combine function in single piece of equipment; increase operating pressure (also decreasing pressure drop); combine gasification process with production of hydrogen by water electrolysis

Feedstock flexibility

Challenge: increase flexibility with regards to type (wood chips from short rotation forestry, waste wood) and quality (tar generation, sulphur content, ash content…) of feedstock

Potential approaches: feedstock behaviour modelling

Lifetime and maintenance requirements

Challenge: deal with the unwanted tar formation and, more generally, prevent slagging, fouling, and bed sintering/agglomeration (leading also to corrosion and abrasion)

Potential approaches: catalytic hot gas cleaning (also increasing yield); hot gas quenching and downstream clean-up

Challenge: lifetime of catalysts (e.g. for tar destruction)

Hydrogen yield

Challenge: maximise conversion rate of feedstock to H_2

Potential approaches: shift equilibrium e.g. through Absorption Enhanced Reforming, which also cracks tar; optimize oxygen/steam ratio

Overall energy efficiency

Challenge: minimise heat losses

Potential approaches: avoid process steps requiring the product to be cooled down (e.g. quenching); thermal integration

Challenge: minimise pressure drop

Potential approaches: use of structured bed material; increase of operating pressure

Recycling of bottom ash (slag)

Challenge: establish and ensure fitness for purpose of bottom ash, ideally as fertilizing ingredient, for return to close-by soil in order to maintain local nutrient balance

Potential approach: determination of maximum allowable concentration of detrimental trace elements in the feedstock for use of bottom ash in land applications

7.2.3 Scope

Proposals should cover Research and Innovation actions (RIAs) or Innovation Actions (IAs) targeting the improvement and techno-economic optimisation of lignocellulosic biomass gasification for the production of pure hydrogen, considering the whole system.

These may address either allothermal processes (indirect heating) using steam as gasifying agent, or autothermal processes (direct heating) using oxygen as gasifying agent, possibly applying steam.

In the latter case, the oxygen needed should be assumed to be the by-product of hydrogen production by water electrolysis, and technical synergies between both hydrogen production systems should be studied.

Proposals should address feedstock flexibility as well as at least three other technical challenges among those listed above.

Proposals may nonetheless address the optimisation of the process for a single type of feedstock produced in large quantities from an already established and perennial activity, such as wood-dust, thistle (cardoon), or black liquor.

Before implementation in full scale units, new technical solutions should be developed and validated at pilot scale, in order to achieve a TRL of 5.

RIA proposals should combine different scientific means so as to achieve their objectives as effectively as possible, such as system and process modelling, experimental investigations, sub-system or system testing and qualification to pre-defined criteria as well as sub-system or system instrumentation for detailed monitoring.

An objective of IA proposals should be plant capacity scale up in order to prove economy of scale. Reliable and continuous operation should be demonstrated with close monitoring of performance and analysis of deviations. Furthermore proposals should include techno-economic analysis.

7.2.4 Impact

RIA activities should provide a clear step forward towards potential hydrogen production costs of 5 €/kg as projected for 2030.

IA proposals should aim at the demonstration in industrial environments, i.e. in a continuously operated full scale unit targeting at least the following characteristics:

- H_2 production capacity: > 1 t/d
- Feedstock flexibility: use of at least 2 different types of feedstock, or flexibility with regards to varying feedstock characteristics in the case of a plant dedicated to one type of feedstock
- Mean time between significant(1) maintenance (MTBM): > 6 months
- Overall LHV efficiency (based on H_2 production only): > 49%(2)
- Project CAPEX costs: 9.0 M€/(t/d)(3)

(1) requiring more than 24 hours of shut down; (2) based on Task 2 projections + 10%; (3) including engineering, based on Task 2 + 20% to account for extra IA demonstration costs

For RIA proposals, targets regarding the demonstrated performance should exceed the above targets where these relate to the challenges specifically addressed.

7.3 Raw biogas reforming (2)

7.3.1 Pathway overview

Basic description

Biogas is produced from anaerobic fermentation of organic material such as organic waste, municipal waste, manure, or whole plant silage. It is mainly composed of methane and CO_2, a CO_2 content of 50% being typical.

The conventional process for producing hydrogen from biogas is to first upgrade the biogas to biomethane (through CO_2 removal), from which, with addition of steam, hydrogen is produced by steam methane reforming (SMR), being a very mature process.

However, it is also possible to produce hydrogen by directly reforming the raw biogas without prior removal of the CO_2. CO_2 present in the feed as well as that generated by the reforming process is subsequently removed in one step (by pressure swing adsorption - PSA) downstream of the reforming unit.

Although eliminating the raw biogas upgrade step results in a slightly lower hydrogen yield due the higher CO_2 content in the hydrogen/CO_2 mixture downstream of the reforming unit, this approach is expected to reduce the total hydrogen production costs from biogas with regards to the conventional process through a reduction of total CAPEX.

7.3.2 Technology review summary

The impact of the amount of CO_2 in the biogas on the H_2 yield has already been experimentally investigated and shown to be acceptable. Raw biogas reforming as such therefore does not pose major technical challenges. A 10 kg_{H2}/d raw biogas reforming pilot unit is currently being tested in Albi in France (Vabhyogaz project).

An alternative to steam reforming also providing a relatively high hydrogen yield (thanks to a H_2/CO ratio in the syngas of approx. 3.5) is auto-thermal reforming (ATR), a process which is simpler, more compact, and which provides greater operational flexibility than steam reforming. ATR, combining partial oxidation and steam reforming in the same reactor, requires the provision of pure oxygen, which could be made available as a by-product of H_2 production by electrolysis. The production of hydrogen by autothermal reforming of raw biogas in combination with water electrolysis promises synergies that remain to be investigated.

Cost and impact potential

The hydrogen production costs by reforming of raw biogas, are projected to be between 5.3 and 3.9 €/kg depending on the type of facility (local, semi-central) and the value of the waste feedstock used to produce the biogas (zero or even negative), see chapter 6.3.

When the hydrogen produced is used in fuel cell electric vehicles (FCEV), the well-to-wheel energy use per km of this pathway is 1.5 to 2 times lower than that of CNG vehicles running on biomethane, further motivating the deployment of FCEVs in order to efficiently take advantage of very common waste materials for fuelling mobility.

Current development objectives

Reforming technology is mature and commercially available. However, process optimization is required for processing raw biogas rather than methane.

Furthermore, in view of the very large number of small biogas production facilities running on farm waste products, **engineering efforts need to focus on providing small (e.g. 0.5 t_{H2}/d), highly integrated packages for efficient autonomous local production of hydrogen from biogas with minimal supervision and maintenance needs and wide tolerance to biogas quality variations**.

7.3.3 Specific challenges

In order to achieve the above mentioned development goal, the following challenges need to be addressed:

Process integration

Challenge: further integrate the total process and reduce size (more capacity with less equipment)

Potential approaches: simplify process, combine functions in single piece of equipment; increase operating pressure; use simpler ATR (in combination with production of hydrogen by water electrolysis)

Maintenance requirements

Challenge: provide autonomous operation with minimal maintenance requirements

Potential approaches: use simpler self-regulating process such as ATR (in combination with hydrogen production by electrolysis)

Overall energy efficiency

Challenge: minimise heat losses and compression losses despite large fraction of CO_2 acting as ballast

7.3.4 Scope

Proposals should cover Innovation Actions (IAs) targeting techno-economic optimisation of raw biogas reforming for the autonomous production of pure hydrogen considering the total system.

The process considered may be either steam methane reforming or auto-thermal reforming.

In the latter case, the oxygen needed should be assumed to be the by-product of hydrogen production by water electrolysis, and technical synergies between both hydrogen production systems should be studied.

Proposals should address the three technical challenges listed above.

Before implementation in field tested units, new technical solutions affecting the chemical conversion process should be developed and validated at pilot scale.

Proposals should demonstrate continuous and autonomous operation in an existing biogas production facility with close monitoring of performance and analysis of deviations.

A techno-economic analysis evaluating to what extent the pathway provides an advantage over the conventional process (biogas upgrade to bio-methane followed by steam reforming) should be performed.

7.3.5 Impact

Proposals should target the demonstration of full scale units with the following minimum characteristics:

- H_2 production capacity: 0.5 t_{H2}/d compact unit
- Overall LHV efficiency (based on H_2 production only): < 44%$^{(1)}$
- Project CAPEX costs: < 5.1 M€/(t_{H2}/d)$^{(2)}$
- Meantime between maintenance: < 6 months
- Design lifetime: 20 years

(1) based on Task 2 projection +10% to account for extra close-to-commercialisation IA demonstration unit costs; (2) including engineering based on Task 2 projections + 10%

7.4 Thermochemical water splitting using concentrated solar power (3)

7.4.1 Pathway overview

Basic description

Solar thermochemical pathways use only water, heat from concentrated sunlight, and chemicals being recycled. Only hydrogen and oxygen are produced, with water and solar thermal energy as primary inputs. Hydrogen production through solar thermochemical processes is still at a relatively early stage of development, requiring additional fundamental and applied R&D. With the rapid development of concentrated solar power in the last decade and its cost decrease, hydrogen from solar thermochemical cycle processes is now at the focus of research globally since its long-term cost reduction potential is significant, comparable to other solar-based hydrogen production pathways.

Technology summary review

Hydrogen production through thermochemical water splitting can be mainly classified in two pathways:

High-temperature cycles, operating at temperatures between 1,200-1,800°C, including various metal oxides combinations. These cycles are characterised by achieving the highest theoretical efficiencies. However, many of them are based on rare-earth metals that could complicate their large-scale commercialization and require very high-temperatures, leading to corrosion and material degradation challenges not yet fully solved.

“Low-temperature” cycles, operating at about 850-950°C, including various forms of liquid cycles. Within this category, the sulphur-based cycles are the most developed and understood. In particular, the hybrid-sulphur cycle has been identified as the most promising route due to the relative low temperature needed, the high thermochemical efficiency of the process, and the use of commonly used chemicals, such as sulphuric acid.

Projects currently funded by the European Commission are focusing on both technological routes. The projects of the Hydrosol series have focused its efforts on exploring several metal oxides combinations in a ceramic-based thermal reactor installed in an existing research facility (concentrated solar power plant in Almeria). As very high temperatures and a very stable solar input are needed, the existing facility (optimized for power production) is far from optimal, leading to low efficiencies and yields. However, quasi-continuous operation has been established by the use of a two-chamber solar reactor and the perspectives to improve the technology are very encouraging.

The project Sol2Hy2, on the other hand, is focusing on developing a full hybrid sulphur cycle plant. In the first phase, an “open” cycle (Outotec® Open Cycle) has been used, using various sources of SO_2 from chemical and metallurgical plants. This approach allows fast, scalable build-up of smaller scale hydrogen production plants without affecting acid production.

Cost and impact potential

Since thermochemical cycles require very high temperatures, the use of solar energy as a source is only viable through the use of large sunlight collection areas. This leads to associated costs due to land and construction material costs (solar collectors, concrete, metal, etc.). Therefore, the main challenge for this technology is to achieve high conversion efficiency levels that keep overall footprint related costs as low as possible. In the long-term, the goal is to reach solar-to-hydrogen efficiencies in the range of 20 to 25% (HHV), which could allow to reach cost targets in the order of 3-5 €/kg_{H2}. This represents a significant challenge, considering that current projects show low efficiencies (the Hydrosol 3D project reports up to only 4%) and cannot yet demonstrate long-term stable operation.

Current development objectives

The success of solar thermochemical hydrogen production is contingent on developing suitable reactive materials, on incorporating these materials into an efficient solar thermochemical reactor, and on integrating the reactor into a cost-effective solar collection and concentration system.

For the most advanced technologies (most promising cycles compatible with high production capacities), such as the *hybrid-sulphur cycle (HyS)* or high-temperature *metal oxides cycles*, R&D efforts are being directed at reactor design and system-level challenges. The challenges and efforts that need to be addressed in order to unlock the commercial viability of this technology can be classified in two groups:

- **Material development and design associated with the chemical cycle**. This includes the heat exchange/recovery system, the reactant materials and conditioning products used in the reactor, the monitoring and control processes, the acid decomposer, and the sulphur dioxide electrolyser (specifically for the hybrid ones).
- **Specific solar plant design, tailor made for hydrogen production and continuous operation**. Accurately controlling the temperature at the solar receiver and reactor is the key to increase production yields and reduce heat

losses. A specific layout of the heliostats/solar dishes, a dedicated solar tower and tailor-made control system software will be required to optimize H_2 production yield and system efficiency, allowing for stable temperatures needed in the reactor.

In addition to addressing these major challenges, research should continue to prioritize the identification and characterization of the most promising thermochemical cycles and associated reactive materials. The DoE has identified 25 cycles having a potential solar-to-hydrogen efficiency greater than 25%. Techno-economic studies will be necessary in order to characterise these materials that could provide cycle stabilisation, endure corrosion, and achieve fast kinetics. However, this more fundamental research should be out of the scope of the FCH 2 JU program. Other funding programs, such as the NMP (Nanotechnologies, Advanced Materials and Production) and Energy themes within the Horizon 2020 or national research programs should continue with its support of the characterization of new materials.

7.4.2 Specific challenges

In order to achieve the above mentioned development goals, the following challenges need to be addressed:

Thermal efficiency

The conversion of solar-derived heat into chemical energy is a strong function of both the thermodynamic behaviour of the reactive material and the reactor in which the thermochemical cycle is implemented. A thermochemical reactor efficiency of at least 36% (heat to chemical energy in the reactor) should be achieved, allowing to reach overall system efficiencies (solar to hydrogen) above 20% in the longer term.

The regulation of pressure in the decomposer, the exact operating temperature and the concentration of material (e.g. acid concentration) are some of the aspects that will determine the optimal efficiency for a given set of reactive materials.

Efficiency gains in the upstream components (solar collection and concentration), although small (given the maturity of this technology), can also be achieved, for instance by limiting the number of components in the optical pathway (reflectors, windows). These gains can help to relax the thermal efficiency requirement for the reactor.

Material lifetime and degradation

The short lifetime of catalysts and reactant materials is a key issue due to degradation from high temperature exposure.

For the hybrid technologies, where a sulphur dioxide based electrolyser is used, the use of catalyst and membrane materials that allow low-voltage/high efficiency operations has been identified as one of the main solutions to alleviate the problem.

Material sustainability and cost

The current use of platinum group materials (PGM) and cerium based catalysts poses another challenge, as these materials are scarce and their costs are high. Hence, identifying material substitutes that allow to keep a low degradation of the electrolyser cell performance (for the case of hybrid systems) should be a key research objective.

Hydrogen yield

Reactors in a solar concentrated thermochemical plant must endure daily cycling from low to high temperatures resulting from the solar day/night cycles as well as from weather effects (e.g. passing clouds). One option is to decrease reactor cycling by storing thermal energy in salts or other materials (e.g. ceramics) to enable continuous hydrogen production. Another more promising option would be to decouple the two chemical cycles from the solar collection. In this case, a sunlight receiver compartment with ceramic particles could absorb heat at very high temperatures to then exchange heat into the reactor, creating a heat storage buffer.

For the hybrid-sulphur cycle, decoupling is already achieved by transforming all solar heat into sulphuric acid. In this case, sulphuric acid is stored easily (chemical storage), allowing a continuous operation of the sulphur dioxide electrolyser, independent of the solar conditions. Hence, for this technology this specific challenge is already solved.

In addition to the use of storage/back-up systems, the control of solar collectors, along with a tailor-made layout for hydrogen production will also be needed to operate the reactor at optimal conditions and to avoid a batch operation mode, leading to a more continuous operation and maximization of hydrogen yield. To solve this challenge, solar plants optimized for hydrogen production will have to be built, integrating hydrogen-production-oriented solar towers, which allow temperature operations in the range of 1,200-1,800°C (specifically for the case of metal oxide cycles).

7.4.3 Scope

Proposals should cover Research and Innovation Actions (RIAs) targeting the improvement of system design, optimization of the thermochemical reactor and aiming at continuous operation by using a specifically designed concentrated solar power plant for hydrogen production.

Proposals should address technologies that are either based on hybrid-sulphur cycles (HyS) or metal oxide combinations, building on existing optimized designs already developed in Europe and providing continuity to past or ongoing research and demonstration projects, in particular the HYDROSOL plant and the Sol2H2 projects. Since these two projects are working on two rather different processes, each with its specific challenges, we recommend to derive two funding topics, addressing different areas of research.

Given the state of development of these projects and the interest of industry, we recommend to first focus on HyS (2016) and to target the improvement of metal oxide combinations at a later state (2017-2018), once the ongoing work will have delivered more results.

Given the difficulties of working at very high temperatures and under real operating (weather) condition, proposals should aim to validate and demonstrate the technology in pilot plants, specifically designed for hydrogen production (solar collector system tailored to hydrogen production, not power production).

The proposals should aim to improve system efficiency and increase plant lifetime by the validation of operating configurations both at the reactor level and the solar collection system that could prove the continuous production of hydrogen.

In case of technology 1 (hybrid-sulphur cycle), specific activities should target the development and operation of industrial-scale sulphur dioxide electrolysers and sulphuric acid decomposers, using catalyst materials that promise long life time without major degradation.

In case of technology 2 (metal oxides cycle), specific activities should target to enhance the stability of the reactant materials, proving long-term stability, and drawing recommendations of optimal metal oxide combinations to minimize degradation at high temperatures. Additionally, a solar receiver that helps decoupling the chemical reactions from the collection of solar heat at very high temperatures (above 1,200°C) should be designed and developed (e.g. ceramic particle receiver and exchanger).

Proposals should assess the sustainability and viability of technology (LCA of GHG and water use) for future applications in remote areas with high irradiation sources (e.g. North Africa).

7.4.4 Impact

Proposals addressing the described technology should carefully justify the current state-of-the-art and the potential evolution of the technology until 2025-2030, considering the ongoing research activities/project in Europe and the option for this technology to be commercially viable by 2030, with production costs in the range of 6-7 €/kg_{H2}.

The project should lead to the following results:

- Validated continuous operation of the plant for at least one year ensuring 10% “solar-to-hydrogen” energy efficiency
- Control software to manage the solar array based on the thermochemical reactor specifications
- An industrial-size sulphur dioxide electrolyser and acid decomposer developed with demonstrated durable catalyst materials (5,000 h without major degradation) (technology 1)
- Demonstration of metal oxide combinations used under real operating conditions and continuously operating with acceptable lifetime and stability (technology 2)
- Test of new concepts for solar heat storage/exchange at high temperatures that allow to decouple the chemical reaction for hydrogen production from the solar heat collection

7.5 Photo-electrochemical (PEC) hydrogen production (4)

7.5.1 Pathway overview

Basic description

Photo-electrochemical (PEC) hydrogen production is a solar-driven water-splitting process that converts solar energy directly into chemical energy in the form of hydrogen. PEC relies on materials that couple photon absorption with water-splitting catalysis and hydrogen fuel formation. There are similarities between a PEC cell and a photovoltaic (PV) cell, the main difference being that in a PEC device the anode and cathode are separated by an electrolyte.

PEC hydrogen production offers the potential to efficiently convert solar energy into hydrogen at low operating temperatures (20-60°C) using low cost thin-film (similar to the semiconductors used in the PV industry) and/or particle-based materials.

PEC technology offers one of the most interesting (and challenging) pathways for hydrogen production as it offers the theoretical prospect of being only slightly more complex than pure PV technology at only marginally higher cost. The PEC technology is flexible to produce hydrogen in local, semi-central, and central applications. PEC does not offer any footprint specific improvements when compared to conventional PV plus electrolysis, nor is the solar-to-hydrogen efficiency expected to be higher. The motivation and vision is that hydrogen production costs using PEC technology may eventually be lower than those resulting from the combination of PV modules and electrolysers.

A disadvantage of PECs is that piping over the entire solar array is required to feed water to and remove hydrogen from the system. Also, in contrast to PEC technology, performing hydrogen generation in a separate electrolysis plant allows production to be independently optimized towards higher current densities.

Technology summary review

PEC hydrogen production processes can be classified into two main reactor configurations:

- Photo-electrode panel reactors
- Photo-catalyst particle reactors

Since the photo-electrode panel reactor is based on semiconductor materials and design concepts used by the photovoltaic industry, it has received more research attention until now and presents a more mature development stage, with theoretical device efficiencies ranging from 4% to 18%.

Within this technology, the semiconductor device is immersed in an aqueous environment. Thus, corrosion and device durability are major issues, obliging to address efficiency and lifetime in parallel. Recently developed devices have proven operation of more than 1,000 hours, but the highest efficiencies demonstrated were in the range of 4% for lab-scale devices with a size of about 10cm^2. Current tandem configurations help to increase efficiency through wider light-absorption bands, however, such combinations of materials also limit power density. The discovery of new active materials with optimal properties seems to be a key factor for the future success of the technology.

On the other hand, photo-catalyst particle reactor systems offer a theoretically higher cost reduction potential due to the elimination of panel and panel-mount infrastructure (which in the case of the photovoltaic industry, represents the highest share of the PV-system costs). However, the challenge of in-situ hydrogen/oxygen separation has not yet been solved and new reactor concepts need to be developed.

Cost and impact potential

The long-term target for the PEC hydrogen production pathway is to reach efficiencies comparable to those of PV combined with electrolysis using cost-competitive materials. Hence, research should aim to achieve solar-to-hydrogen efficiencies in the range of at least 10% to 12% while ensuring device stability and minimum degradation for a period of at least 10 years. Those conditions could lead to hydrogen production costs in the range of 4-5 €/kg$_{H2}$ by 2030.

Current development objectives

Both technologies (photo-electrode and photo-catalyst reactors) require a strong research focus. However, the photo-catalyst particle reactor, given its early development stage both concerning the device concept and the lack of understanding of material properties, should continue to be addressed by fundamental research through Horizon 2020 and other research programs (e.g. European Research Council). For the time being, the FCH 2 JU program should focus on photo-electrode panel-devices. R&D efforts should focus on materials development, along with reactor design and engineering. The work should be directed to improve the device efficiency and durability, while increasing systems size and decreasing its costs.

7.5.2 Specific challenges

In order to achieve the above mentioned development goals, the following challenges need to be addressed:

Efficiency

Due to the relatively low efficiency of solar hydrogen production pathways, large scale PEC hydrogen production will demand vast areas for collecting the necessary solar power, potentially leading to significant capital costs. Additionally, it will require large amounts of non-active materials associated to the panel reactor (aluminium, glass, pipes to collect the hydrogen generated, etc.) and high installation costs (cabling, piping, mount-structures, etc.). Therefore, maximizing conversion efficiency to reduce the overall footprint remains critical to cost reduction.

Process efficiency is limited by light absorption, charge separation, and charge transport in the bulk. Tandem configurations of materials need to be designed to provide an appropriate light-absorption bandgap (between 1.6 and 2.2 V), maximizing the electron transport through the electrolyte and effectively favouring photo-electrochemical water-splitting half reactions.

Material lifetime and degradation

Up to date, the semiconductor corrosion at the interface with the electrolyte represents the biggest challenge of this technology. Durable materials that can offer stability and longer lifetime only yield low energy efficiency. Materials that can provide high light-absorbing efficiency are very sensitive to corrosion. Finding the ideal set of materials to address this dual challenge simultaneously seems out of reach for the time being. However, other alternative solutions can be found like modifying the surface of the active material through coatings or dispersions, helping to protect and stabilize the interface.

In that respect, research facilitating the understanding of corrosion mechanisms will help to develop systems and designs to enhance durability.

Maximized efficiency with affordable materials

The cost of hydrogen produced is mostly driven by the costs of the PEC semiconductor material as this has a direct effect on overall system costs (footprint, auxiliary materials, etc.). High-efficiency materials based on crystalline III-V semiconductors have been developed, following similar efforts in concentrated PV technology. These materials can help reaching efficiency and durability objectives, but generally have very high costs, restricting their use to particular applications (e.g. space). Like in PV, solar concentration systems may help optimizing the use of the material and reducing the system footprint and thus overall costs. On the other hand, lower-efficiency materials such as thin-film materials offer attractive costs and simplified production methods; however, the efficiencies offered are significantly lower leading to a high overall system footprint and costs. Finding the right balance between semiconductor efficiency and implication on system costs therefore is of high priority.

For known material configurations, a 10-12% efficiency should be set as the short-term goal while developers should aim at device efficiencies as high as 20% if new materials will be discovered.

Device design and integration

Beyond the challenges of corrosion and efficiencies, the design and fabrication of a device that can be scaled for commercial uses (practical dimension) still remain a key area for improvement. Some of the engineering challenges associated with large-area PEC devices are proton diffusion, resistive losses in the electrolyte, and H_2/O_2 separation.

Auxiliary materials, such as the interconnection system between anode and cathode and the protective layer (e.g. flexi glass) also have an important impact on device integrity and durability. Innovative concepts for gas separation and collection, innovative flexible and transparent materials that allow light transmission and gas retention, as well as structures and materials that support low-concentration could be instrumental to the success of the PEC technology, in order to allow for high yields and reduced costs.

The focus should be put on the integration of device design, addressing efficiency and durability simultaneously while targeting larger device areas. Cell areas above 50 cm^2 will more easily facilitate multiple cells to be interconnected for durable and larger modules.

For that purpose, optimized materials and device configurations for high light-absorption, improved charge transport, and interfacial catalyst configurations should be targeted.

7.5.3 Scope

Since the design of device prototypes is closely interlinked with the photo-active and auxiliary materials used, addressing fundamental research on materials in parallel with applied engineering research on device design and integration seems necessary to develop optimized systems that can reach hydrogen production cost targets. However, fundamental research on materials should be kept out of the proposals.

Instead, proposals should cover **Research and Innovation Actions (RIAs)** targeting the **testing of materials in innovative device designs, addressing the challenge of efficiency and durability, and demonstrating integrity in scalable cell areas**. The proposals should also cover the **construction and test of prototype devices** (integration and assembly of multiple cell modules), designed to the new material configuration. The identification and test of new materials is out of the scope of the FCH 2 JU proposals. The materials to be tested should have been already discovered and should already present promising efficiencies and low-degradation results.

Proposals should aim to:

- Design a PEC device that can reach efficiencies above state-of-the-art with limited degradation, making use of earth-abundant and sustainable photo-sensitive materials which can allow large-scale commercialization
- Validate stable operation over 1,000 h in real operating conditions, after solar simulated lab scale tests
- Design a device with practical dimensions that is scalable, allowing interconnecting several devices into a module for achieving a system scaled to a size in the range of few kWs (indicative device area: 50 cm^2)

- Design and implement innovative system-level components such as innovative hydrogen collection and extraction systems

A techno-economic analysis of the whole system should be performed, with cost characterisation for all system components, allowing for benchmark against competing hydrogen production solutions.

7.5.4 Impact

RIA activities should provide a clear step forward towards concepts and materials that could lead to stable devices and cost goals in the order of 4-5 €/kg$_{H2}$, as projected for 2030. The proposal should lead to the following results:

- Validate in-field operation of the PEC device for over 1,000 h with stable performance, reaching a solar-to-hydrogen system efficiency of the PEC device of above 10%
- Characterisation of new materials that can lead to higher conversion efficiencies
- Device concept scalable to the multi kW range
- Development of a module prototype and of a complete system capable to produce, collect and extract hydrogen, tested for a period of over 1,000 h under real operating conditions
- Strong cooperation between material scientists and device engineers within the project allowing for a fast transfer of knowledge between material properties and optimized system concepts

7.6 Supercritical water gasification of biomass (6)

7.6.1 Pathway overview

Basic description

Super critical water gasification of biomass consists in exposing biomass with a high water content, such as sewage sludge, manure, or wine trester, to a pressure and temperature beyond the point at which water becomes supercritical. At this state, water is highly miscible with organic compounds, allowing high rate co-reactions as a result of the elevated temperature, with production of a gas mixture containing mainly CO_2, H_2, and CH_4, from which hydrogen is readily extracted directly at high pressure.

In addition, unwanted biomass contaminants such as sulphur and nitrogen remain in the liquid phase, eliminating the need to remove them from the gas. Furthermore, the recuperation of phosphorus, an essential non-renewable ingredient for fertilizers, is facilitated.

While the application of heat is required at least in part from an external energy source, the overall energy efficiency significantly exceeds the one of other biomass conversion routes as soon as the moisture content of the feedstock exceeds 30% (weight). Moreover, biomass conversion takes place within minutes, in contrast to anaerobic fermentation which requires a residence time counted in weeks.

This method of converting wet organic waste into high value energy for mobility therefore offers an attractive potential alternative to disposal or anaerobic fermentation.

Continuous operation of the gasification process has already been successfully demonstrated at small scale in a pilot unit.

Technology review summary

The above mentioned pilot plant (VERENA), operated by KTI starting in 2002, was designed for a total biomass (max. solid content of 20%) of 100 kg of wet (20% dry substance) biomass per hour. It included a 35 l volume reactor designed for a pressure of up to 35 MPa and a maximum temperature of 700°C.

A specific phenomenon that needs to be dealt with is salt precipitation, due to the rapid decrease of solubility of salts when water becomes supercritical. In the VERENA plant, the reactor acts both as reactor and salt separator, through spatial control of temperature.

Corrosion and plugging issues remain to be overcome for enabling commercial operation.

Cost and impact potential

The cost of production of hydrogen by supercritical water gasification of biomass is projected to be below 5 €/kg$_{H2}$ for a local production unit, based on a negative value of the biomass (sewage sludge). Cost is sensitive to ancillary energy consumption (now estimated to reach ¾ of H_2 output energy content) and energy cost.

If hydrogen becomes a commonly used energy carrier, this production pathway, if successfully developed, shows prospects of providing a competitive solution for utilizing wet biomass waste. However, the process competes with raw biogas reforming where also wet biomass is used in the upstream anaerobic digestion to generate biogas for the SMR (pathway 2).

Current development objective

The process presents distinct advantages, even though a number of technical issues still need to be solved. **Therefore, development efforts need to focus on identifying and validating solutions addressing these issues while scaling up to full size hydrogen production capacity**.

7.6.2 Specific challenges

In order to achieve the above mentioned development goal, the following challenges need to be addressed:

Production capacity

Challenge: increase capacity of a 35 MPa, 700°C reactor

Thermal efficiency

Challenge: minimise ancillary energy consumption

Potential approaches: thermal integration; reduction of operating temperature (with help of catalysts)…

Lifetime and maintenance requirements

Challenge: improve corrosion resistance

Challenge: avoid plugging (biomass slurry and precipitation of salts)

Challenge: avoid formation of coke

Potential approach: quick heating of biomass

7.6.3 Scope

Proposals should cover Research and Innovation Actions (RIAs) targeting the development and validation of technical solutions providing the capacity, thermal efficiency, lifetime, and low maintenance operation required for commercial implementation of supercritical water gasification of biomass.

Proposals should address the three technical challenges listed above.

Different scientific means should be combined in order to address the challenges as effectively as possible, such as system and process modelling, experimental investigations, sub-system or system testing and qualification to pre-defined criteria, and sub-system or system instrumentation for detailed monitoring.

Before implementation in full scale field tested units, new technical solutions affecting the chemical conversion process should be developed and validated at pilot scale. Construction and operation of an integrated pilot H_2 plant is required.

A techno-economic analysis of the implementation of the process for the conversion of the targeted biomass waste product should be performed.

7.6.4 Impact

Activities should provide a clear step forward towards a potential H_2 production cost of 5 €/kg_{H2}.

Demonstration of full scale units may be included and should target at least the following:

- H_2 production capacity: > 0.5 t_{H2}/d
- Ancillary energy consumption : < 60% of H_2 LHV energy output$^{(1)}$
- Meantime between significant$^{(2)}$ maintenance: < 6 months
- Project CAPEX cost: < 9.1 M€/(t_{H2}/d)$^{(3)}$

(1) based on Task 2 projections -25%; (2) requiring more than 24 hours of shut down; (3) including engineering, based on Task 2 projections +30%, to account for extra RIA pilot unit costs

7.7 Dark fermentation (5) + raw gas reforming (2)

7.7.1 Pathway overview

Basic description

Dark fermentation allows the direct production of hydrogen from a variety of substrates as main feedstock, ranging from sugar-rich to complex biomass including lignocellulosic biomass, sewage, and food or animal waste, with some pretreatment.

The fermentation process implements specific bacteria and conditions for hydrogen to be generated instead of methane. The process produces acetates which, with the remaining substrate, can be subjected to conventional (anaerobic) fermentation in a second step for the further high yield production of synthetic methane.

Besides the simplicity of the reactor, a specific advantage of dark fermentation is the variety of possible feedstocks. Nonetheless, 2nd generation biomass (grass, straw, residues from food-industry) requires tailor made pretreatment procedures for transformation (of cellulose and starch) into simpler sugar forms (saccharification).

Further research is needed for optimizing pre-treatment and significantly increasing productivity of the fermentation process while maintaining production stability.

Technology review summary

Most efforts focus on thermophylic fermentation, i.e. implementing thermophylic bacteria thriving at temperatures higher than 60°C.

The on-going EC FP7 funded HyTime project, targets the design of a pilot unit capable of producing more than 1 kg_{H2}/day from 2nd generation biomass, with construction of a 50 l bioreactor capable of producing 50 g_{H2}/d. Satisfactory results that could potentially be further improved have been achieved. Identifying conditions for the use of 2nd generation feedstock under non-sterile conditions, a significant advantage for industrial application, is under investigation.

Projected cost and pathway impact

The projected costs of hydrogen production by associating dark fermentation together with biogas reforming are very high, due to the equipment costs and energy consumption e.g. for pre-treatment of the biomass (saccharification).

Current development objective

Development efforts are still focussed on identifying, for a start at lab scale, a bacteria mix, reactor design and operating conditions providing significant progress, with limited nutrient input, towards the stable production rates that are required for the pathway to be commercially implemented.

7.7.2 Specific challenges

In order to achieve the above mentioned development goal, the following challenges need to be addressed:

Production rate

Challenge: increase H_2 production rate per reactor unit volume

Potential approaches: research on nutrients and bacteria mix; active recovery of dissolved H_2 removal using membranes or external recycling loop; structured surfaces providing increased reaction area

Costly materials

Challenge: minimize nutrient cost

Thermal efficiency

Challenge: minimise consumption of energy for heating

Potential approach: thermal integration; find a solution to use the ligneous residue for heat generation

Hydrogen yield

Challenge: optimal utilisation of second generation biomass (grass, straw, residues from food-industry)

Potential approaches: tailor-made pre-treatment procedures

Challenge: combine high yield in H_2 fermentation with low nutrient requirement

7.7.3 Scope

Proposals should cover RIAs focusing on dark fermentation and providing significant progress for a start of an integrated H_2 plant at pilot scale with regard to production rate; they should also address at least two of the other challenges listed above.

Proposals should combine different scientific means such as modelling, experimental investigations, and instrumented sub-system testing for identifying the conditions needed and for controlling the process in order to maintain these.

7.7.4 Impact

RIA designs should target at least the following performance:

- H_2 production rate: 1000 g_{H2}/day/m³ fermenter volume (1) (staying lean on nutrient input)
- Heating energy consumption: < 100% of H_2 LHV energy output (2)
- H_2 yield: 80% of theoretical maximum and without significantly affecting nominal methane production capability

(1)extrapolated from Hytime project objective for 50 l bioreactor, a 250% increase of productivity considered in Task 2; (2) based on Task 2 projection – 70% (3) Hytime project objective

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9 Annex

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Title	Authors	Organisation	Organisation2	Organisation3	Organisation4	Date	Citations	Technology
The reduction and control technology of tar during biomass gasification/pyrolysis: An overview	Jun Han, Heejoon Kim,	Department of Ecological Engineering, Toyohashi University of Technology, Tempaku-cho, Toyohashi, 441-8580, Japan				2006	687	Biomass gasification
Enhanced hydrogen production from biomass with in situ carbon dioxide capture using calcium oxide sorbents	Nicholas H. Florin′ , Andrew T. Harris	Laboratory for Sustainable Technology, School of Chemical and Biomolecular Engineering, The University of Sydney, NSW 2006, Australia				2007	256	Biomass gasification
Catalytic pyrolysis of biomass for biofuels production	Richard French, Stefan Czernik,	National Bioenergy Center, National Renewable Energy Laboratory, 1617 Cole Blvd., Golden, CO 80401, United States				2009	235	Biomass gasification
Contemporary issues in thermal gasification of biomass and its application to electricity and fuel production	Lijun Wang[a,′] , Curtis L. Wellerb, David D. Jonesb, Milford A. Hannab	[a] Department of Natural Resources and Environmental Design, North Carolina Agricultural & Technical State University, Greensboro, NC 27411, USA	[b] Department of Biological Systems Engineering, University of Nebraska-Lincoln, Lincoln, NE 68583, USA			2008	227	Biomass gasification
Techno-economic analysis of biomass fast pyrolysis to transportation fuels	Mark M. Wright[a], Daren E. Daugaardc, Justinus A. Satriob, Robert C. Browna, b, ,	[a] Department of Mechanical Engineering, Iowa State University, Ames, IA 50011, United States	[b] Center for Sustainable Environmental Technologies, Iowa State University, Ames, IA 50011, United States	[c] ConocoPhillips Company, Biofuels R&D, Ponca City, OK 74602, United States		2010	224	Biomass gasification
Simulation of biomass gasification in fluidized bed reactor using ASPEN PLUS	Mehrdokht B. Nikoo[a], Nader Mahinpeya, b, ,	[a] Environmental Systems Engineering, University of Regina, 3737 Wascana Parkway, Regina, Saskatchewan, Canada S4S 0A2	[b] Process Systems Engineering, University of Regina, 3737 Wascana Parkway, Regina, Saskatchewan, Canada S4S 0A2			2008	194	Biomass gasification
Cat+C4:L4alytic processes towards the production of biofuels in a palm oil and oil palm biomass-based biorefinery	Thiam Leng Chew, Subhash Bhatia,	School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal, Pulau Pinang, Malaysia				2008	189	Biomass gasification

Title	Authors	Organisation	Organisation2	Organisation3	Organisation4	Date	Citations	Technology
Biomass-based hydrogen production: A review and analysis	Yildiz Kalinci[a], Arif Hepbaslib, , , Ibrahim Dincerc	[a] Department of Technical Programs, Izmir Vocational High School, Dokuz Eylul University, Education Campus Buca, Izmir, Turkey	[b] Department of Mechanical Engineering, Faculty of Engineering, Ege University, 35100 Izmir, Turkey	[c] Faculty of Engineering and Applied Science, University of Ontario Institute of Technology, 2000 Simcoe Street North, Oshawa, Ontario, Canada L1H 7K4		2009	179	Biomass gasification
Hydrogen from biomass – Present scenario and future prospects	Havva Balat′, Elif Kırtay	Sila Science & Energy Company, University Mah, Trabzon, Turkey				2010	160	Biomass gasification
Hydrothermal biomass gasification	Andrea Kruse′ ′	ITC-CPV, Forschungszentrum Karlsruhe, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany				2008	153	Biomass gasification
Comparison of biohydrogen production processes	S. Manish, Rangan Banerjee,	Energy Systems Engineering, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India				2007	215	Biogas reforming
Improvement of coke resistance of Ni/Al_2O_3 catalyst in CH_4/CO_2reforming by ZrO_2 addition	Supaporn Therdthianwong[a,′ ′], Chair ut Siangchina, Apichai Therdthianwongb	[a] Department of Chemical Engineering, King Mongkut's University of Technology Thonburi, 126 Pracha-Uthit Rd., Bangmod, Tungkru, Bangkok, 10140 Thailand	[b] Fuel Cell and Hydrogen Research Laboratory, King Mongkut's University of Technology Thonburi, 126 Pracha-Uthit Rd., Bangmod, Tungkru, Bangkok, 10140 Thailand			2007	88	Biogas reforming
Feasibility of direct-biogas SOFC	Y. Shiratori[a,′ ′], T. Oshimaa, K. Sasakia,	[a] Department of Mechanical Engineering Science, Faculty of Engineering, Kyushu University, Motooka 744, Nishi-ku, Fukuoka 819-0395, Japan	[b] Hydrogen Technology Research Center, Kyushu University, Motooka 744, Nishi-ku, Fukuoka 819-0395, Japan			2008	81	Biogas reforming
Catalytic steam reforming of model biogas	Philipp Kolbitsch′, Christoph Pfeifer, Hermann Hofbauer	Vienna University of Technology, Institute of Chemical Engineering, Getreidemarkt 9/166, 1060 Vienna, Austria				2007	79	Biogas reforming
Sustainable biogas energy in Poland: Prospects and challenges	Wojciech M. Budzianowski′	Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland	Received 31 May 2011, Accepted 5 July 2011, Available online 15 September 2011				72	Biogas reforming

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Experimental investigation of direct internal reforming of biogas in solid oxide fuel cells	Andrea Lanzini′ , Pierluigi Leone	Dipartimento di Energetica, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy				2010	59	Biogas reforming
A novel reforming method for hydrogen production from biomass steam gasification	Ningbo Gao, Aimin Li, , Cui Quan	School of Environmental & Biological Science & Technology, Dalian University of Technology, Key Laboratory of Industrial Ecology and Environmental Engineering, MOE, Dalian 116024, China				2009	59	Biogas reforming
Biogas upgrade to syn-gas (H_2–CO) via dry and oxidative reforming	C.S. Lau, A. Tsolakis, , M.L. Wyszynski	School of Mechanical Engineering, University of Birmingham, Birmingham B15 2TT, UK				2010	55	Biogas reforming
Hydrogen generation from biogas reforming using a gliding arc plasma-catalyst reformer	Young. N. Chun[a, ′] , Yoon C. Yanga, K. Yoshikawab	[a] BK21 Team for Hydrogen Production, Department of Environmental Engineering, Chosun University, 375 Seoseok-dong, Dong-gu, Gwangju 501-759, Republic of Korea	[b] Frontier Research Center, Tokyo Institute of Technology, G5-8 4259 Nagatsuta, Midori-ku, Yokohama 226-8502, Japan			2009	48	
Generation of combustion irreversibilities in a spark ignition engine under biogas–hydrogen mixtures fueling	C.D. Rakopoulos′ , C.N. Michos	Internal Combustion Engines Laboratory, Thermal Engineering Department, School of Mechanical Engineering, National Technical University of Athens, 9 Heroon Polytechniou Street, Zografou Campus, 15780 Athens, Greece				2009	50	Biogas reforming
Thermochemical two-step water splitting by ZrO_2-supported $Ni_x\,Fe_{3-x}\,O_4$for solar hydrogen production	T. Kodama[a, ′] , N. Gokonb, R. Yamamotob	[a] Department of Chemistry and Chemical Engineering, Faculty of Engineering and Graduate School of Science and Technology, Niigata University, 8050 Ikarashi 2-nocho, Nishi-Ku, Niigata 950-2181, Japan	[b] Graduate School of Science and Technology, Niigata University, 8050 Ikarashi 2-nocho, Nishi-Ku, Niigata 950-2181, Japan			2007	105	Thermochemical water splitting
Prospects of solar thermal hydrogen production processes	Thomas Pregger[a, ′] , Daniela Grafb,Wolfram Krewitta, Christian Sattlerb,	[a] German Aerospace Center (DLR), Institute of Technical Thermodynamics, Department of Systems Analysis and Technology Assessment, Pfaffenwaldring 38–40, D-70569 Stuttgart, Germany	[b] German Aerospace Center (DLR), Institute of Technical Thermodynamics, Department of Solar Research, Linder Hoehe, D-51147 Cologne, Germany			2009	104	Thermochemical water splitting

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Novel two-step SnO$_2$/SnO water-splitting cycle for solar thermochemical production of hydrogen	Stéphane Abanades[a,′′], Patrice Charvina, Florent Lemontb, Gilles Flamanta		[a] Processes, Materials, and Solar Energy laboratory (PROMES-CNRS, UPR 8521), 7 Rue du Four Solaire, 66120 Font-Romeu, France	[b] Commissariat à l'Énergie Atomique (CEA), Rhône Valley Research Center BP17171, 30207 Bagnols-Sur-Cèze Cedex, France		2008	90	Thermochemical water splitting
Advances in hydrogen production by thermochemical water decomposition: A review	Marc A. Rosen′	Faculty of Engineering and Applied Science, University of Ontario Institute of Technology, 2000 Simcoe Street North, Oshawa, Ontario, L1H 7K4, Canada				2009	88	Thermochemical water splitting
Thermochemical hydrogen production with a copper–chlorine cycle. I: oxygen release from copper oxychloride decomposition	G.F. Naterer′, K. Gabriel, Z.L. Wang, V.N. Daggupati, R. Gravelsins	Faculty of Engineering and Applied Science, University of Ontario Institute of Technology, 2000 Simcoe Street North, Oshawa, Ontario, Canada L1H 7K4				2008	80	Thermochemical water splitting
Analysis of solar chemical processes for hydrogen production from water splitting thermochemical cycles	Patrice Charvin[a,′′], Abanades Stéphanea, Lemort Florentb, Flamant Gillesa	[a] Processes, Materials and Solar Energy Laboratory (PROMES-CNRS/UPR8521), 7 Rue du four Solaire, 66120 Odeillo-Font Romeu, France				ance	74	Thermochemical water splitting
Thermochemical two-step water splitting cycles by monoclinic ZrO$_2$-supported NiFe$_2$O$_4$ and Fe$_3$O$_4$ powders and ceramic foam devices	Nobuyuki Gokon[a,′′], Hiroko Murayamaa, Ayumi Nagasakia, Tatsuya Kodamab	[a] Graduate School of Science and Technology, Niigata University, 8050 Ikarashi 2-nocho, Nishi-ku, Niigata 950-2181, Japan	[b] Department of Chemistry and Chemical Engineering, Faculty of Engineering, and Graduate School of Science and Technology, Niigata University, 8050 Ikarashi 2-nocho, Nishi-ku, Niigata 950-2181, Japan			2008	68	Thermochemical water splitting
Thermochemical two-step water-splitting reactor with internally circulating fluidized bed for thermal reduction of ferrite particles	N. Gokon[a,′′], S. Takahashia, H. Yamamotoa, T. Kodamaa, b	[a] Graduate School of Science and Technology, Niigata University, 8050 Ikarashi 2-nocho, Nishi-ku, Niigata 950-2181, Japan	[b] Department of Chemistry and Chemical Engineering, Faculty of Engineering, Niigata University, 8050 Ikarashi 2-nocho, Nishi-ku, Niigata 950-2181, Japan			2008	65	Thermochemical water splitting

Title	Authors	Organisation	Organisation2	Organisation3	Organisation4	Date	Citations	Technology
Operational strategy of a two-step thermochemical process for solar hydrogen production	Martin Roeb′ , Martina Neises, Jan-Peter Säck, Peter Rietbrock, Nathalie Monnerie,Jürgen Dersch, Mark Schmitz, Christian Sattler	German Aerospace Center – DLR, Institute of Technical Thermodynamics, Solar Research, Linder Hoehe, 51147 Cologne, Germany				2008	58	Thermochemical water splitting
Energy and exergy assessments of the hydrogen production step of a copper–chlorine thermochemical water splitting cycle driven by nuclear-based heat	Mehmet F. Orhan , Ibrahim Dincer, , Marc A. Rosen	Faculty of Engineering and Applied Science, University of Ontario Institute of Technology, 2000 Simcoe Street North, Oshawa, Ontario L1H 7K4, Canada				2008	48	Thermochemical water splitting
Nanostructured materials for photocatalytic hydrogen production	Jiefang Zhu′′ , Michael Zäch,					2009	166	Photo-catalysis
Photo-catalytic degradation of toxic dye amaranth on TiO_2/UV in aqueous suspensions	Vinod K. Gupta[a, b, ,] , Rajeev Jainc, Tawfik A. Salehb, Arunima Nayaka, Shilpi Agarwalc,Shalini Sikarwarc,Alok Mittald,	[a] Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247 667, India	[b] Chemistry Department, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia	[c] School of Studies in Chemistry, Jiwaji University, Gwalior 474011, India	[d] Department of Chemistry, Maulana Azad National Institute of Technology (A Deemed University), Bhopal, 462 051, India	2011	140	Photo-catalysis
Recent applications of carbon nanotubes in hydrogen production and storage	Renáta Oriňáková′ , Andrej Oriňák	Department of Physical Chemistry, Faculty of Science, P.J. Šafárik University, Moyzesova 11, SK-04154 Košice, Slovak Republic				2011	55	Photo-catalysis
Kinetics of photo-catalytic degradation of hazardous dye Tropaeoline 000 using UV/TiO_2 in a UV reactor	Vinod K. Gupta[a, b, , ,] , Rajeev Jainc, Shilpi Agarwalc, Meenakshi Shrivastavac	[a] Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247 667, India	[b] Chemistry Department, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia	[c] School of Studies in Chemistry, Jiwaji University, Gwalior 474011, India		2011	50	Photo-catalysis
Photo-catalytic conversion of oxygenated hydrocarbons to hydrogen over heteroatom-doped TiO_2 catalysts	Nianjun Luo[a, b], Zheng Jiangb, Huahong Shib, Huahong Shib, Fahai Caoa, Tiancun Xiaoa, b, , , Peter P. Edwardsb, ,	[a] State-Key Laboratory of Chemical Engineering, ECUST, Shanghai 200237, China	[b] Inorganic Chemistry Laboratory, Oxford University, South Parks Road, OX1 3QR Oxford, UK			2008	47	Photo-catalysis

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Characterization of new heterosystem $CuFeO_2/SnO_2$ application to visible-light induced hydrogen evolution	A. Derbal, S. Omeiri, A. Bouguelia, M. Trari,	Laboratoire de Stockage et de Valorisation des Energies Renouvelables, Faculty of Chemistry (USTHB), BP 32, 16111 Algiers, Algeria				2008	44	Photo-catalysis
Physical and photo-electrochemical characterizations of α-Fe_2O_3. Application for hydrogen production	A. Boudjemaa[a, b], S. Boumazaa, b, M. Traric, R. Bouarabb, A. Bougueliac, ,	[a] Technical and Scientific Research Centre of Physical Analysis (CRAPC), BP 248, RP 16004 Algiers, Algeria	[b] Laboratory of Chemistry of Natural Gas, Faculty of Chemistry (USTHB), BP 32, 16111 Algiers, Algeria	[c] Laboratory of Storage and Valorization of Renewable Energies, Faculty of Chemistry (USTHB), BP 32, 16111 Algiers, Algeria		2009	43	Photo-catalysis
Laser enhanced photo-catalytic removal of phenol from water using p-type NiO semiconductor catalyst	M.A. Gondal[a,’] , M.N. Sayeedb, Z. Seddigib	[a] Laser Research Laboratory, Physics Department, King Fahd University of Petroleum & Minerals, Box 5047, Dhahran 31261, Saudi Arabia	[b] Chemistry Department, King Fahd University of Petroleum & Minerals, Box 5048, Dhahran 31261, Saudi Arabia			2007	39	Photo-catalysis
Nanotechnology for photolytic hydrogen production: Colloidal anodic oxidation	James P. Best, Dave E. Dunstan,	Department of Chemical and Biomolecular Engineering, University of Melbourne, Parkville, VIC 3010, Australia				2009	30	Photo-catalysis
Hydrogen bond interactions at the TiO_2 surface: Their contribution to the pH dependent photo-catalytic degradation of *p* -nitrophenol	Ronald Vargas, Oswaldo Núñez,	Laboratorio de Fisicoquímica orgánica y química ambiental, Departamento de Procesos y Sistemas, Universidad Simón Bolívar, Apartado postal 89000, Caracas, Venezuela				2008	29	Photo-catalysis
Factors influencing fermentative hydrogen production: A review	Jianlong Wang’ ,	Laboratory of Environmental Technology, INET, Tsinghua University, Beijing 100084, PR China				2008	378	Fermentation
Biofuels generation from sweet sorghum: Fermentative hydrogen production and anaerobic digestion of the remaining biomass		[a] Department of Chemical Engineering, University of Patras, Karatheodori 1 st., 26500 Patras, Greece	[b] Institute of Chemical Engineering and High Temperature Chemical Processes, 26504 Patras, Greece	[c] Department of Biology, University of Patras, 26500 Patras, Greece		2007	247	Fermentation

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Advances in fermentative biohydrogen production: the way forward?	Patrick C. Hallenbeck , Dipankar Ghosh	Département de Microbiologie et Immunologie, Université de Montréal, CP 6128 Succursale Centre-ville, Montréal, Québec H3C 3J7, Canada				2009	235	Fermentation
Fermentative hydrogen production: Principles, progress, and prognosis	Patrick C. Hallenbeck′	Département de Microbiologie et Immunologie, Université de Montréal, CP 6128, Succursale Centre-Ville, Montréal, Québec, Canada H3C 3J7				2009	214	Fermentation
Biohydrogen production from biomass and industrial wastes by dark fermentation		[a] Deparment of Bioprocess Technology, Faculty of Biotechnology and Biomolecular Sciences, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia	[b] Institute of Biological Sciences, Faculty of Science, Universiti Malaya, 52100 Kuala Lumpur, Malaysia	[c] Graduate School of Life Sciences and System Engineering, Kyushu Institute of Technology, 808-0196 Hibikino 2-4, Wakamatsu-ku, Kitakyushu-shi, Fukuoka, Japan		2009	179	Fermentation
Comparison of different pretreatment methods for enriching hydrogen-producing bacteria from digested sludge		Laboratory of Environmental Technology, INET, Tsinghua University, Beijing 100084, PR China				2008	173	Fermentation
Biological hydrogen production: prospects and challenges		[1] Center for Environmental Biotechnology, Biodesign Institute at Arizona State University, P.O. Box 875701, Tempe, AZ 85287-5701, USA	[2] School of Life Sciences, Arizona State University, P.O. Box 874501, Tempe, AZ 85287-4501, USA			2010	144	Fermentation
Bio-hydrogen production from the fermentation of sugarcane bagasse hydrolysate by *Clostridium butyricum*		[a] Department of Biotechnology, Faculty of Technology, Khon Kaen University, 123 Mitraphab Road, A.Muang, Khon Kaen 40002, Thailand	[b] Program in Environmental Science, Faculty of Science and Technology, Rachjabhat Phibulsongkram University, Phitsanuloke 65000, Thailand	[c] Research Centre for Environmental and Hazardous Substance Management, Khon Kaen University, Khon Kaen 40002, Thailand	[d] Fermentaion Research Center for Value Added Agricultural Products, Khon Kaen University, Khon Kaen 40002, Thailand	2008	139	Fermentation
Impacts of sterilization, microwave and ultrasonication pretreatment on hydrogen producing using waste sludge	Liang Guo, others	College of Environmental Science and Engineering, Hunan University, Hunan, Changsha 410082, China				2007	124	Fermentation

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Advances in biological hydrogen production processes	Debabrata Das[a, , , ,], T. Nejat Veziroglub,	[a] Department of Biotechnology, Indian Institute of Technology, Kharagpur 721302, West Bengal, India	[b] Clean Energy Research Institute, College of Engineering, University of Miami, Coral Gables, FL 33124-0622, USA			2008	303	Photofermentation
Biohydrogen production using sequential two-stage dark and photo fermentation processes	Chun-Yen Chen[a, b], others	[a] Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan	[b] Sustainable Environment Research Center, National Cheng Kung University, Tainan, Taiwan	[c] Department of Chemical & Biochemical Engineering, Kao Yuan University, Kaohsiung, Taiwan		2008	127	Photofermentation
Light energy to bioelectricity: photosynthetic microbial fuel cells		[1] Department of Biological and Environmental Engineering, Cornell University, 214 Riley-Robb Hall, Ithaca, NY 14853, USA	[2] Department of Civil Engineering and Mechanics, University of Wisconsin–Milwaukee, 3200N Cramer St., Milwaukee, WI 53211, USA			2010	112	Photofermentation
Kinetics of two-stage fermentation process for the production of hydrogen		[a] Department of Chemical Engineering, G.H. Patel College of Engineering and Technology, Vallabh Vidyanagar 388 120, Gujarat, India	[b] Fermentation Technology Laboratory, Department of Biotechnology, Indian Institute of Technology, Kharagpur 721302, India			2008	110	Photofermentation
High yield conversion of a crude glycerol fraction from biodiesel production to hydrogen by photofermentation	Guillaume Sabourin-Provost, Patrick C. Hallenbeck,	Département de microbiologie et immunologie, Université de Montréal, CP 6128, succursale Centre-ville, Montréal, Québec, Canada H3C 3J7				2009	108	Photofermentation
Improving hydrogen production from cassava starch by combination of dark and photo fermentation	Huibo Su, otthers	State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, China				2009	81	Photofermentation
Biohydrogen production from beet molasses by sequential dark and photofermentation		[a] Middle East Technical University, Department of Chemical Engineering, 06531, Ankara, Turkey	[b] Wageningen UR, Agrotechnology & Food Sciences Group, Wageningen UR, P.O. Box 17, 6700 AA Wageningen, The Netherlands	[c] Middle East Technical University, Department of Biology, 06531, Ankara, Turkey		2009	77	Photofermentation
Combination of dark- and photo-fermentation to enhance hydrogen production and energy conversion efficiency	Huibo Su, others	State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, China				2009	74	Photofermentation

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Bio-hydrogen production from acid hydrolyzed wheat starch by photo-fermentation using different *Rhodobacter sp*	Ilgi K. Kapdan′ , others	Department of Environmental Engineering, Dokuz Eylul University, Buca, Izmir, Turkey				2009	68	Photofermentation
Hydrogen production from glycerol by reforming in supercritical water over Ru/Al_2O_3 catalyst		[a] Department of Chemical Engineering, 212 Ross Hall, Auburn University, Auburn, AL 36849-5127, United States	[b] Department of Chemical Engineering, Indian Institute of Technology, Delhi 110016, India			2008	171	Supercritical water gasification of biomass
Thermo-chemical routes for hydrogen rich gas from biomass: A review		Indian Institute of Petroleum, Dehradun 248005, India				2007	156	Supercritical water gasification of biomass
Review of catalytic supercritical water gasification for hydrogen production from biomass		State Key Laboratory of Multiphase Flow in Power Engineering, Xi’an Jiaotong University, Xi’an, Shaanxi 710049, China				2009	141	Supercritical water gasification of biomass
Biomass gasification in supercritical water: II. Effect of catalyst		Institue for Technical Chemistry, Division of Chemical-Physical Processing, Forschungszentrum Karlsruhe, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany				2008	103	Supercritical water gasification of biomass
Hydrogen production by biomass gasification in supercritical water with a fluidized bed reactor		State Key Laboratory of Multiphase Flow in Power Engineering (SKLMF), Xi'an Jiaotong University, 28 Xianning West Road, Xi'an 710049, Shaanxi, China				2008	92	Supercritical water gasification of biomass
Role of sodium hydroxide in the production of hydrogen gas from the hydrothermal gasification of biomass	Jude A. Onwudili, Paul T. Williams,	Energy and Resources Research Institute, University of Leeds, Leeds, LS2 9JT, UK				2009	74	Supercritical water gasification of biomass

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Economic analysis of sewage sludge gasification in supercritical water for hydrogen production	Edgar Gasafi[a, ,] ,	[a] Forschungszentrum Karlsruhe, Department of Technology-Induced Material Flow, Institute for Technical Chemistry, P.O. Box 3640, D-76021 Karlsruhe, Germany	[b] Forschungszentrum Karlsruhe, Division of Chemical–Physical Processing, Institute for Technical Chemistry, P.O. Box 3640, D-76021 Karlsruhe, Germany			2008	64	Supercritical water gasification of biomass
Hydrogen production by biomass gasification in supercritical water over Ni/γAl_2O_3 and Ni/CeO_2-γAl_2O_3 catalysts	Youjun Lu, others	State Key Laboratory of Multiphase Flow in Power Engineering (SKLMF), Xi'an Jiaotong University, Xi'an 710049, Shaanxi, China				2009	57	Supercritical water gasification of biomass
Hydrogen production from woody biomass over supported metal catalysts in supercritical water		[a] Research Center for Compact Chemical Process, National Institute of Advanced Industrial Science and Technology (AIST), 4-2-1 Nigatake, Miyaginoku, Sendai 983-8551, Japan	[b] Department of Chemical Engineering, Ichinoseki National College of Technology, Takanashi, Hagisho, Ichinoseki, Iwate 021-8511, Japan			2008	54	Supercritical water gasification of biomass

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COMPANY PROFILE OF HINICIO

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