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HYVOLUTION

Non-thermal production of pure hydrogen from biomass

Integrated Project

Priority 6.1 Sustainable Energy Systems

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Draft

Content

Summary of results and conclusion

Hydrogen has been produced from molasses, thick juice, potato steam peels and barley straw in a two step fermentation process using thermophilic bacteria and photofermentative bacteria, consecutively. The overall efficiency in the combined fermentative steps was 53% and increased to 64% if a genetically modified mutant was used for the photofermentation. When gas upgrading was included, system integration showed that in the overall HYVOLUTION process, net hydrogen energy production from all feedstocks considered is possible.

Comparative simulation with mesophilic bacteria in a first fermentative step at circa 30 ºC supported the advantage of using thermophilic bacteria despite the investment for the higher fermentation temperature of 70 ºC.

Comparison of the HYVOLUTION technology in terms of cost of biofuel in €/GJ showed an advantage for bio-ethanol from lignocellulosic biomass. However, when feedstocks with high moisture content are considered, HYVOLUTION may add to the future biofuel mixture since this venue is not cost-effective for bioethanol.

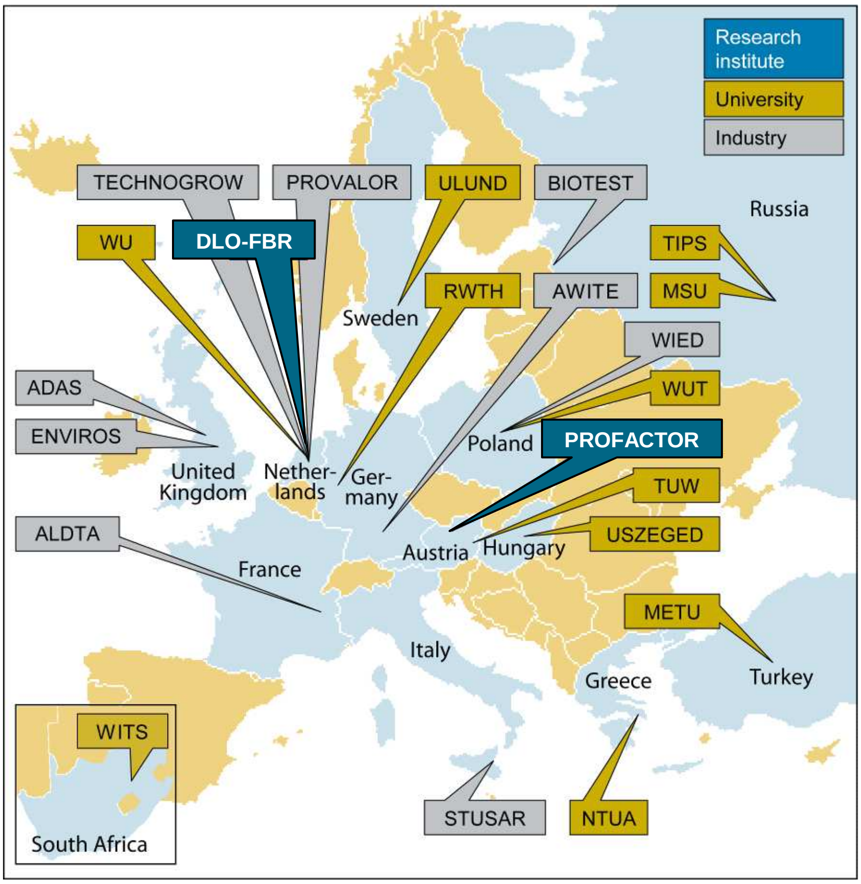
The current estimated costs for hydrogen from HYVOLUTION are higher than anticipated at the start of the project, mainly but not exclusively, due to expanded insights in costs for photobioreactors. In a two step hydrogen production process using tubular photobioreactors, the final cost of hydrogen amounts to € 55- 60 /kg H_2. However, replacement by panel photobioreactors with a 8.5 times higher illuminated area per unit ground space, increases the cost to € 385-390 /kg H_2. The major factor is the cost for the photobioreactors. In a HYVOLUTION process using a tubular photobioreactor, circa € 47/kg H_2, or > 80% of the total cost, is needed for the photofermentation.

The current biohydrogen production potential in the EU countries was estimated at more than 30 Mton H_2 annually using 10% of the crops and 100% of the agro-industrial residues under consideration.

Future research should be aimed at increasing productivity in the thermophilic fermentation, and productivity and yield in the photofermentation. For decrease of hydrogen production costs, new materials and configurations are necessary for the photobioreactor, but also improvements in the other process steps are necessary. Finally, cost-effectiveness of hydrogen production from biomass will gain from finding new opportunities for concomitantly produced co-products.

Introduction

HYVOLUTION is the acronym of the Integrated Project “Non-thermal production of pure hydrogen from biomass” which has been granted in the 6th EU Framework Programme on Research, Technological Development and Demonstration, Priority 6.1 Sustainable Energy Systems. This IP has started on Jan 1, 2006 and ended on Dec 31, 2010. Its aim: “Development of a blue-print for an industrial bioprocess for decentral hydrogen production from locally produced biomass” adds to the number and diversity of hydrogen production routes giving greater security of supply at the local and regional level. The final target of this future biohydrogen industry will be to deliver 10-25 % coverage of the EU demand for hydrogen, for use in power or bio-fuel production, at 10 Euro/GJ.
The novel approach adopted in the project is based on a combined bioprocess employing thermophilic and phototrophic bacteria, to provide the highest hydrogen production efficiency in small-scale, cost effective industries. In HYVOLUTION, 10 EU countries, Turkey, Russia and South Africa are represented providing the critical mass for realizing a breakthrough in cost-effectiveness of hydrogen production (Fig. 1).



DLO-FBR Stichting Dienst Landbouwkundig Onderzoek	NL
ADAS UK Ltd	UK
AL DTA Air Liquide – Division des Techniques Avancées	FR
AWITE Awite Bioenergie, GmbH	GE
BIOTEST Bioreactors and membrane systems	RU
ENVIROS Ltd	UK
METU Middle East Technical University	TU
MSU Moscow Lomonosov State University	RU
NTUA National Technical University of Athens	GR
PROFACTOR GmbH	AT
PROVALOR B.V.	NL
RWTH Rheinisch-Westfälische Technische Hochschule Aachen	GE
STUSAR Studio Sardo	IT
TECHNOGROW B.V.	NL
TIPS A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences	RU
TUW Vienna University of Technology	AT
ULUND Lunds universitet	SE
U-SZEGED University of Szeged	HU
WIED Wiedemann Polska	PL
WITS University of the Witwatersrand	SA
WU Wageningen University	NL
WUT Politechnika Warszawska	PL

Figure 1: Distribution of HYVOLUTION contractors over 10 EU countries, Russia, Turkey and South Africa.

Hydrogen is regarded as an important energy carrier in the future according to several reports in prominent journals as e.g. Science [1] and Scientific American [2]. However, to make the Hydrogen Economy fully sustainable, renewable resources instead of fossil fuels have to be employed for hydrogen production. In HYVOLUTION, bacteria are exploited, which freely and efficiently produce pure hydrogen as a by-product during growth on biomass. This approach, which started in the FP 5 project BIOHYDROGEN, allows a great reduction in CO_2 emission and provides independence of fossil imports. Both topics are dominant in all global agreements on climate protection and urgent in mitigating the greenhouse effect.
HYVOLUTION is structured around in seven technical workpackages (WP's) [3]. The process starts with the conversion of biomass to make a suitable feedstock for the bioprocess (WP 1). In WP 2 and 3 the fermentations are optimized in terms of yield and rate of hydrogen production. Dedicated gas upgrading is developed for high efficiency at small-scale production units dealing with fluctuating gas streams (WP 4). Production costs will be reduced by system integration combining mass and energy balances (WP 5). The impact of small-scale hydrogen production plants is addressed in socio-economic analyses performed in WP 6. WP 7 addresses external as well as internal training (Fig. 2)

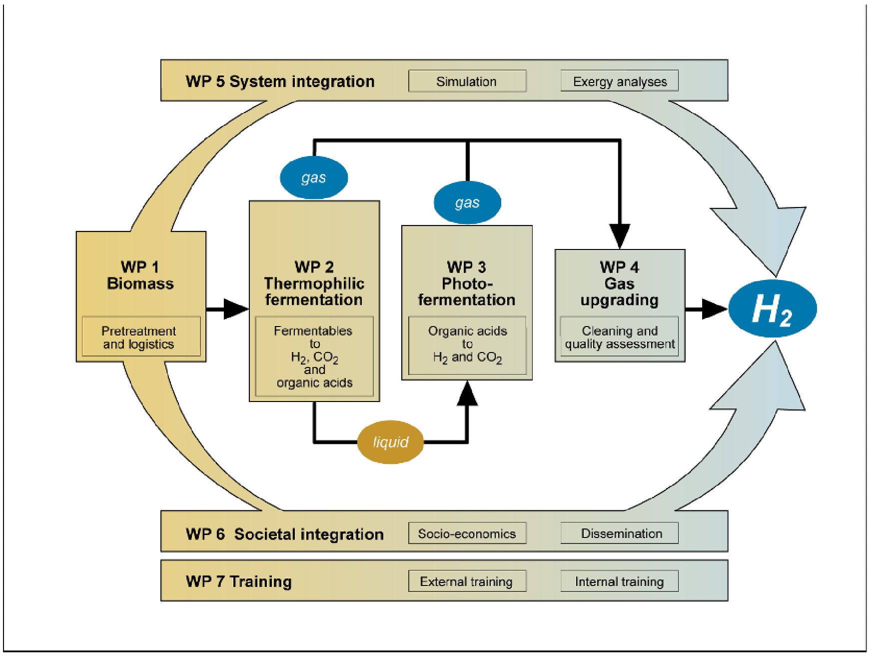


Figure 2 Structure of the HYVOLUTION project.

Summary description of project objectives
The overall objective of HYVOLUTION is the development of a 2-stage bioprocess and construction of prototype modules. Several sub-objectives can be distinguished as follows:

1. Pretreatment technologies for optimal degradation of energy crops and bioresidues
2. Equipment for mobilization of fermentable feedstock
3. Maximum efficiency in conversion of biomass to hydrogen
4. Reactors for thermophilic and photo-heterotrophic hydrogen production
5. Assessment of installations for optimal gas cleaning
6. Devices for monitoring and control
7. Equipment for optimal gas cleaning
8. Minimum energy demand and maximum product output
9. Increase of public awareness and societal acceptance
10. Identification of market opportunities and future stakeholders

Methodology and workpackage goals

The core of HYVOLUTION is the combination of a thermophilic fermentation (also called dark fermentation) with a photoheterotrophic fermentation, making a non-thermal hydrogen production process. The application of thermophilic bacteria to start the bioprocess offers two important benefits in non-thermal hydrogen production. First of all, thermophilic fermentation at ≥70 °C is superior in terms of hydrogen yield compared to fermentations at ambient temperatures [4]. In thermophilic fermentations, glucose is converted to, on the average, ≥3 moles of hydrogen and ≤2 moles of acetate as the main by-product. In other, mesophilic fermentations at ambient temperatures, the average yield is only 1 to 2 moles of hydrogen, at the most, per mole of glucose. This is due to the production of more reduced by-products like butyrate, propionate, ethanol or butanol under mesophilic growth conditions. The second advantage lies in the production of acetate as the by-product of the first fermentation. Acetate is a prime substrate for photoheterotrophic bacteria. Energy from light enables photoheterotrophic bacteria to overcome the thermodynamic barrier in the conversion of acetate to hydrogen [5]. Through the combination of thermophilic fermentation with photoheterotrophic bacteria, complete conversion of the substrate to hydrogen and CO_2 can be established, resulting in 75% conversion efficiency or 9 moles of hydrogen per mole of glucose, which is the main scientific objective of HYVOLUTION. The various activities, in workpackages (WP) are integrated to a coherent project as shown in Figure 2.

In WP 1, *Biomass*, the efficient conversion of agricultural produce and bioresidues to hydrogen fermentation feedstocks is addressed by:

- Optimal selection of the most promising agricultural products and bioresidues
- High efficiency (40-70% with respect to LHV H_2/LHV biomass) in the conversion to feedstocks for hydrogen fermentation.

The simultaneous utilization of hexose sugars and pentose sugars as well as oligomeric carbohydrates by hydrogen producing, thermophilic bacteria has been well documented [6-9]. These observations confer new opportunities for the development of agro-industrial chains which will utilize primary and secondary bioresidues besides energy crops. The generally large contribution of biomass cost price to the final production cost of hydrogen requires the development of tailor-made pretreatment procedures. Furthermore, HYVOLUTION is specifically aimed at small-scale hydrogen production units with new logistic opportunities which have not been studied before to create new prospects for European rural areas.

Workpackage 2, *Thermophilic fermentation*, is aimed at a maximum efficiency in the conversion of fermentable biomass to hydrogen, with as little by-product formation as possible. Therefore, the overall objective of WP 2 is to construct a stable thermophilic fermentation process for hydrogen production from fermentable biomass feedstocks investigated in WP 1. The specific objective of WP 3, *Photofermentation*, is the utilization of the effluent of dark fermentation, for highly efficient hydrogen production. The approach in WP 3 is to investigate the optimization of photofermentative hydrogen production from organic acids, especially acetate, with high yields. Through fundamental research of the physiology, biochemistry and genomics of pure cultures of thermophilic as well as photofermentative bacteria, insight in metabolic pathways is obtained [10, 11]. This is needed to model fermentations for optimal productivity and adjustment of the two consecutive fermentations. This insight will be the basis for identifying and/or developing improved strains and creating mixed cultures which are generally known for robustness, an important asset for industrial performance. The development of dedicated bioreactors also resides in WP 2 and WP 3 with the construction of prototype bioreactors being part of the technological objectives. Since the thermophilic bacteria are inhibited by hydrogen, starting at a partial concentration of 20 % hydrogen [12], the challenge is to design a special thermobioreactor allowing easy gas removal [13]. For the photobioreactor, the emphasis is on the configuration of the bioreactor allowing maximal light capture on minimal surface area.

The goal of WP 4, *Gas upgrading*, is the purification and assessment of the gas, which is produced in the bioreactors. The aim is to produce hydrogen of constant quality. Therefore, the objectives are the development of an appropriate gas upgrading system and the coupling to the bioreactors of WP 2 and 3. The most important boundary condition for this system is the minimum energy demand needed to keep the overall process efficiency high. The gas upgrading will be specifically designed to remove the fairly high concentration of CO_2 in the raw gas and to handle a relatively small and fluctuating quantity of

hydrogen, besides the removal of other potential contaminants. It is the area in between production and application that is addressed in WP 4 to deliver technically and economically feasible gas cleaning devices [14], with handling and safety procedures suitable to a small-scale hydrogen production plant.
In WP 5, *System integration*, the focus is on ensuring maximum product output at minimum energy demand and minimum costs for production of hydrogen from biomass. Main objective of WP 5 is therefore the development of an integrated system representing the optimal combination of units and process routes. This will be achieved by innovatively integrating the different units developed and investigated in WP 1 through WP 4 to a process route using process simulation, exergy analysis, cost evaluation and detailed process engineering including safety aspects and process control strategy.
The specific objectives of WP 6, *Societal integration*, are the definition of economic and social impact of hydrogen production from biomass and the promotion of use of hydrogen from biomass by enhancing awareness at the level of biomass providers and end-users. These will be addressed by:

- Development of a methodology to analyze socio-economic and environmental impacts of biohydrogen production
- Development of a strategy for dissemination and training activities at biomass providers, end-users, stake-holders and policy makers

System integration and societal integration form a basis to secure the scientific and technical activities in WP 1 through 4. These issues are fundamental to develop this new bioprocess for small-scale hydrogen production and to make it viable in terms of process-economics and socio-economics, including environmental impact. Both disciplines are prominently addressed in HYVOLUTION to identify necessary adjustments right from the start. This is done to avoid routes which will have no economic future or do not adhere to sustainability, and to make optimal use of the integrated approach.
The activities in WP 7, *Training*, are directed at promoting the use of hydrogen from biomass and supporting the growth as well as the implementation of the technology developed within HYVOLUTION project. This will be achieved by the development of materials for training of industry, SME's, public organizations and policy makers to awaken the public interest and to elucidate the advantage of the production of hydrogen from biomass.

Results

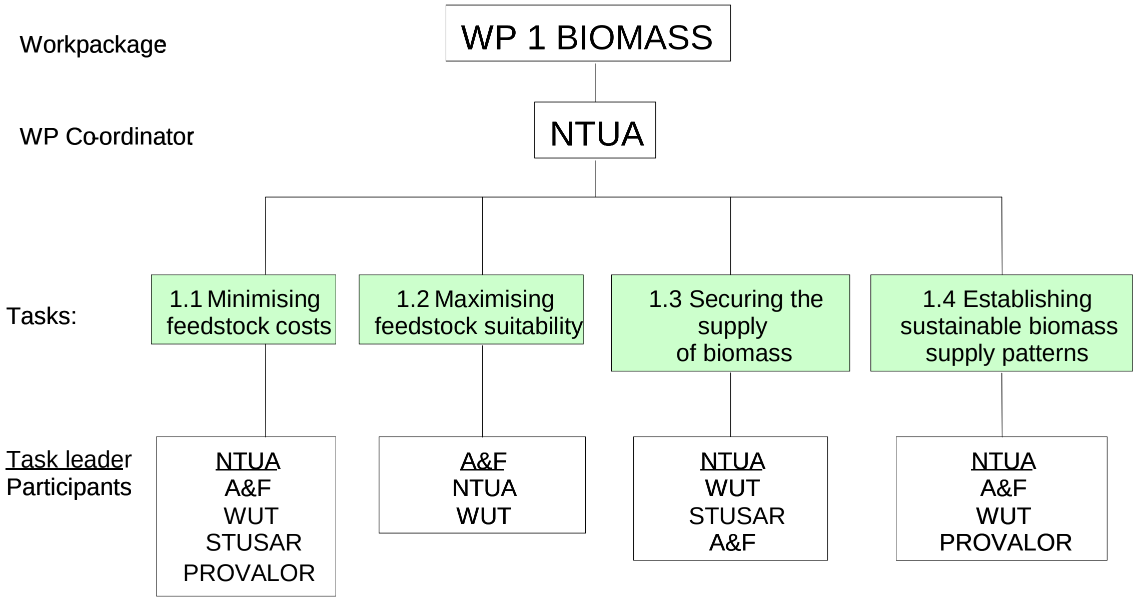


Figure 1 Structure of Workpackage 1 showing contractors involved in the tasks.

Mapping the biomass cost structure

The work in WP 1 BIOMASS started with the collection of data on availability and suitability of biomass. The current biohydrogen production potential in the EU countries was estimated at more than 30 Mton H_2 annually using 10% of the crops and 100% of the agro-industrial residues under consideration [15]. Various types of biomass were analysed with respect to availability, potential mobilization of sugars, successful fermentation and exploitability of residual co-products [44, 57]. These parameters determine the Technical Suitability Index (TSI). Besides, the biomass types have been scored with respect to costs in terms of production costs or opportunity costs in case of competing applications, transport costs and costs made in case preliminary refining is necessary. The combination of these parameters forms the Total Cost Index (TCI). In figure 2 the mapping of the TSI and TCI is shown including the effect of the size of the procurement and refining installation, to determine the overall suitability of a type of biomass. To ensure viability and sustainability of novel agro-industrial chains, the biomass cost and suitability mapping was extended with sustainability mapping according to 12 critical parameters as shown in figure 3 for sugar beet. From the broad spectrum of biomass studied, four biomass types were selected for experimental work in HYVOLUTION: Molasses and thick juice s as sugar-based biomass, potato steam peels as starch, wheat bran representing starch and lignocellulose, and barley straw as the most difficult feedstock based on lignocellulose only.

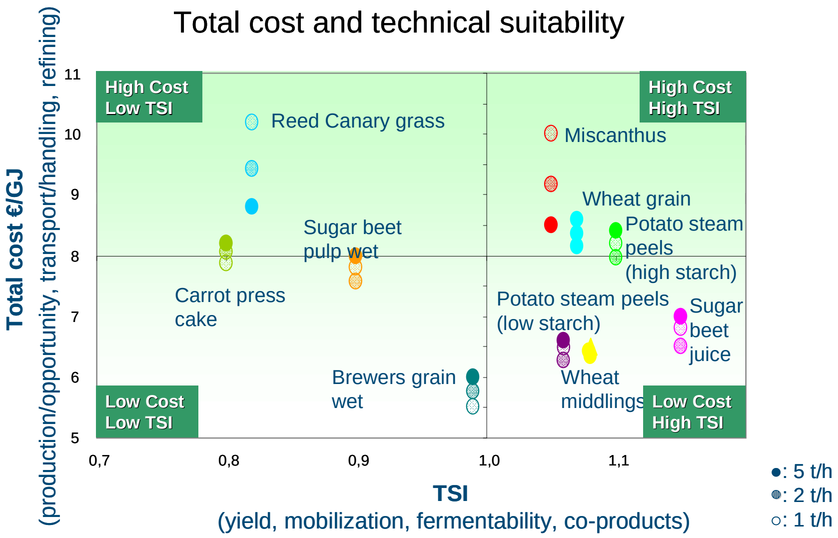


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Figure 2 Technical suitability and total cost indices of biomass. The density of the dots reflects the capacity of the biomass pretreatment plant.

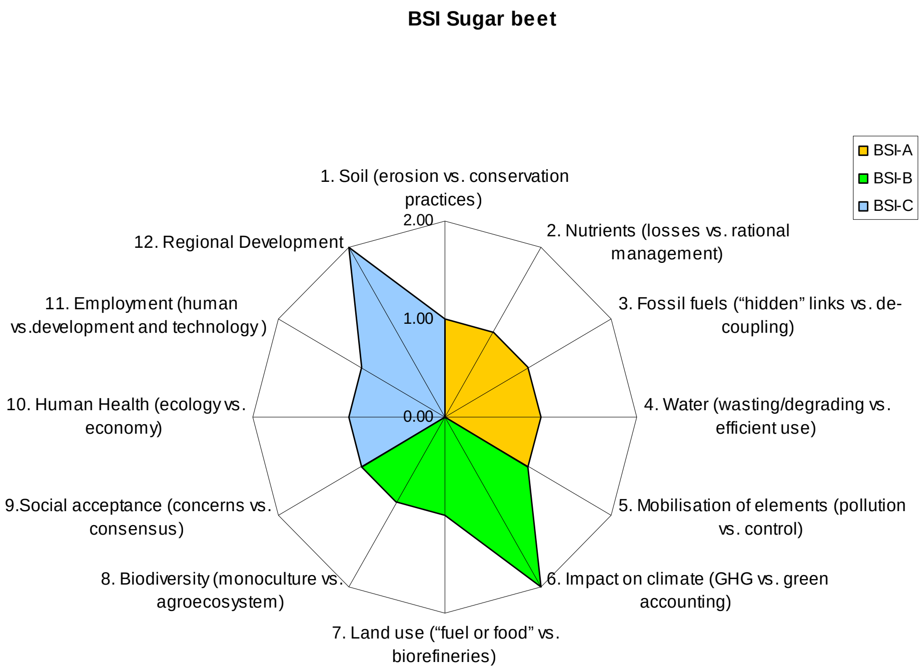


Figure 3 Spider-web of sustainability parameters for utilization of sugar beet for hydrogen production. BSI-A: soil, nutrients, fossil fuel and water; BSI-B: elements, climate, land use and biodiversity; BSI-C: social acceptance, human health, employment and regional development.

A "Best Practice" guide for these selected feedstocks has been compiled, providing for each feedstock the following information: potential – geographical distribution, typical plant type, logistics – supply chain, technology of pretreatment/hydrolysis, economics (biomass, pretreatment), sustainability (environmental, social), role of co-products, other key parameters. For the assessment of the future implementation prospects of HYVOLUTION in the EU countries, a model was developed with four indices (innovation, gdp/capita, environmental performance, impact of industry on the economy), to characterize each studied region/country, according to its socio-economic status. This approach resulted in four groups of countries: Green West (GW), Industrial North (IN), Rural South (RS), and Emerging East (EE). In all four groups, the role of agricultural residues is of major importance. Leading countries are: Germany and UK (GW), France and Italy (IN), Spain in (RS), Poland and Romania in (EE). Driving forces and barriers for implementation of HYVOLUTION have been discussed in a Workshop in Athens: October 2010: Integration of biohydrogen into the future biofuel generation systems. Furthermore, a simulation game for the decision making process focusing at the commercial start-up phase under specific geographical and socio-economic boundaries (a region in "Rural South"), has been organised. The national government emerged as the key stakeholder, which reflects a special characteristic of the region where the workshop was carried out (Rural South), and where the interaction of the national government with any of the other stakeholders usually lacks of efficiency. The interaction of the hydrogen producer with the local community was also crucial for the sustainability of the whole chain, indicating the hydrogen producer needs to gain the confidence of the local community.

Pretreatment and hydrolysis of biomass

The experimental work in WP 1 has been focused on pretreatment and hydrolysis of potato steam peels, wheat bran and barley straw for the mobilization of sugars with the aim to minimize formation of fermentation inhibitors and to reduce cost. For the conversion to fermentable feedstock, the dosages of chemicals and enzymes have been significantly reduced, as well as the duration of the hydrolysis, from >50 h to circa 20h. Figure 4 shows the rapid liquefaction of alkaline pretreated barley straw during hydrolysis using cellulase. The effect of different pretreatment protocols on potential hydrogen production is evident from figure 5 where fermentability of the hydrolysates is tested by three bacteria. Pretreatment using alkali is preferred in the case of barley straw. Figure 5 also shows the importance of using various bacteria for hydrogen production.

A **B**

Figure 4 A Alkaline pretreated barley straw in a stirred tank reactor; **B** Alkaline pretreated barley straw after 90 min hydrolysis with cellulase

Co-products in HYVOLUTION

For the establishment of a zero waste HYVOLUTION process the whole value chain of biomass has been studied for sugar beet and potato steam peels. Concurrent with the production of molasses or thick juice, sugar beet pulp and sugar beet leaves are the main co-products. Animal feed and biogas production are the main destinations for these co-products. Besides, there is experimental interest to use pulp as feedstock in methanol fermentation, as filler material for biobased plastics and as biosorbents of heavy metals. Sugar beet leaves can be used to produce leave protein concentrate or fibres. The residue which remains after hydrolysis of potato steam peels is also a valuable nutrient in animal feed or biogas fermentation. Analysis of this residue shows enrichment in terms of protein content. However, animal feeding tests are needed for determination of the real applicability and related added value.

For wheat bran and barley straw, competing technologies have been identified. Wheat bran is a source of starch and cellulose and can be used as starting material in a biorefinery where a range of products is produced. Barley straw is mainly applicable as feedstock in biogas installations.

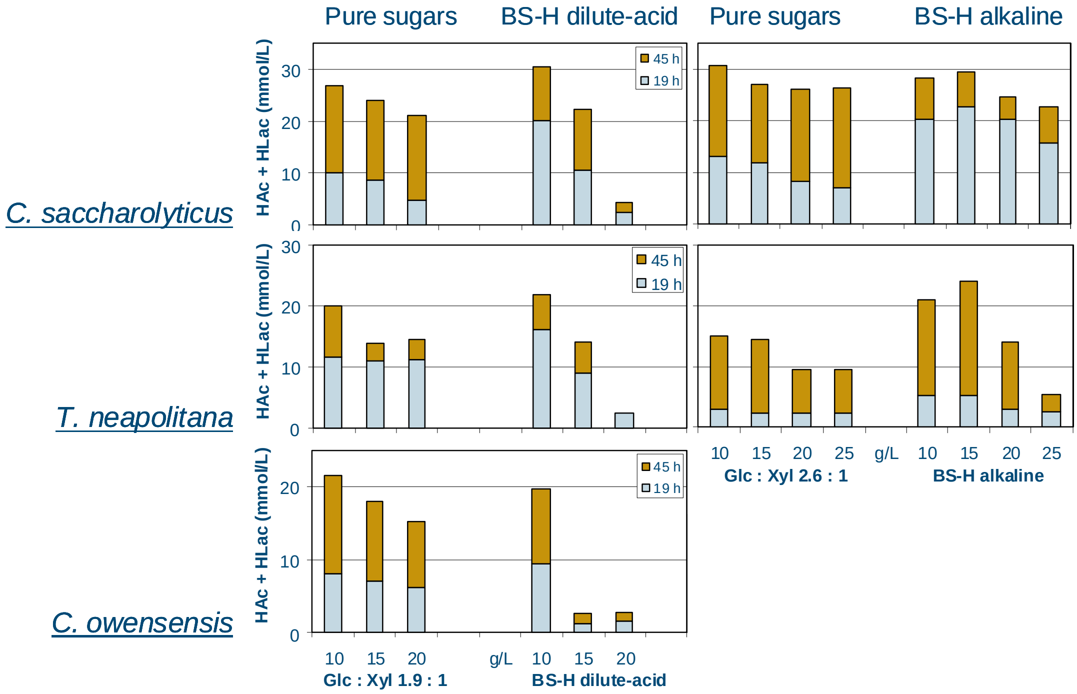


Figure 5 Fermentability of hydrolysates of barley straw after alkaline or dilute-acid pretreatment by *Caldicellulosiruptor saccharolyticus*, *Thermotoga neapolitana* and *Caldicellulosiruptor owensensis*. Fermentability is expressed as production of acetic and lactic acid after incubation of 19 and 45 h at 70 ºC and compared with control cultures grown on pure sugars. The sugar concentrations ranged from 10 to 25 g/L. BS-H: barley straw hydrolysate. Glc: glucose; Xyl: xylose.

The work performed in WP 1 has contributed to the following project objectives: The experimental work to *Objective 1: Pretreatment technologies for optimal degradation of energy crops and bioresidues* and *Objective 2: Equipment for mobilization of fermentable feedstock*; the desk studies to Objectives 9: *Increase of public awareness and societal acceptance* and 10: *Identification of market opportunities and future stakeholders*.

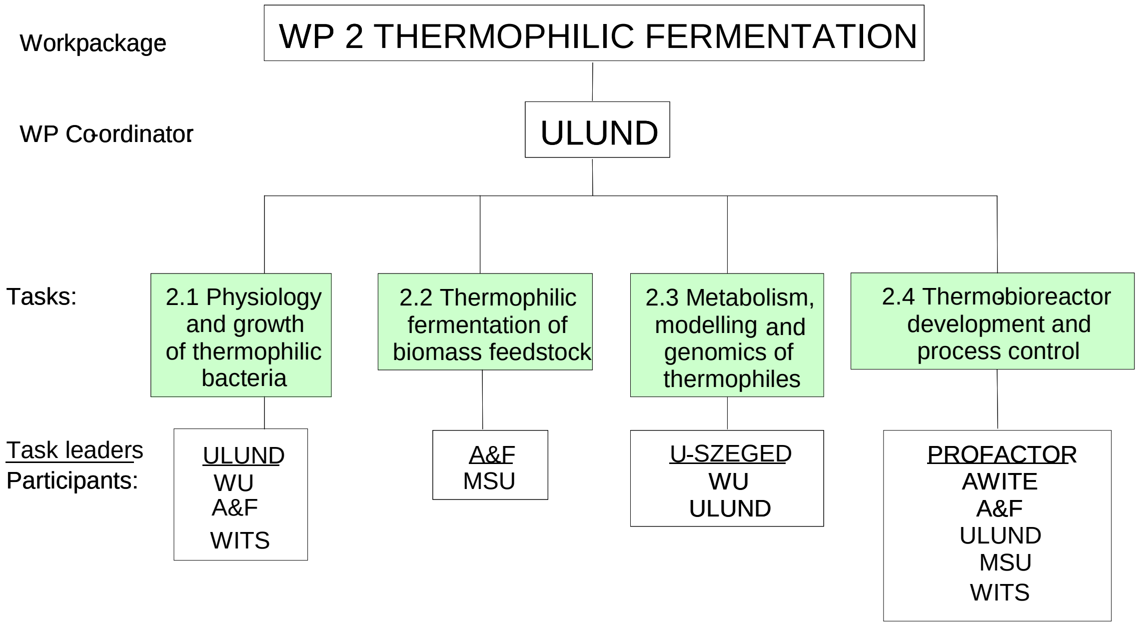


Figure 5 Structure of WP 2 Thermophilic fermentation and contractors involved in the tasks

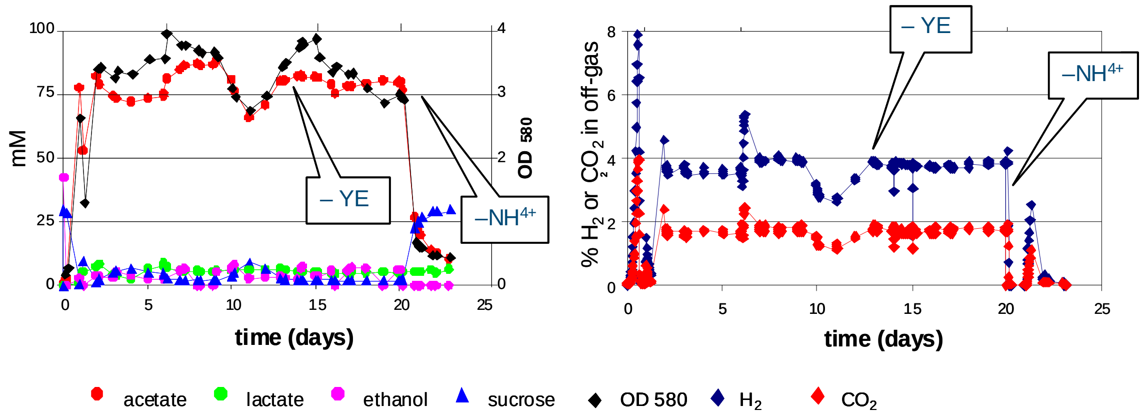
Physiology of *Caldicellulosiruptor saccharolyticus*

In WP 2, *Thermophilic fermentation*, the focus has been on *Caldicellulosiruptor saccharolyticus* as a representative of extreme thermophilic bacteria [16]. The annotation of the genome of *C. saccharolyticus*, has been completed [17]. Modern techniques such as transcriptomics, proteomics, bioinformatics and genome-wide modeling have yielded further insight in the metabolism of this bacterium which appears special in giving high substrate to hydrogen conversion efficiencies when using a great variety of carbohydrates [11, 16]. The observed presence of unusual enzymes in glycolysis suggests a prime role of PPi besides the more common ATP, indirectly governing the unfavorable metabolic switch to lactate, which reduces hydrogen production. Together with modelling studies, these findings have indicated that simple removal of lactate dehydrogenase activity in *C. saccharolyticus* may not produce the desired mutants. Despite numerous different approaches, transformation of *C. saccharolyticus* has not succeeded although the genetic tools have enabled the analysis of co-cultures of different *Caldicellulosiruptor* species.

Hydrogen production from biomass

Hydrogen production in media containing molasses or hydrolysates prepared in WP 1 from Miscanthus, potato steam peels, barley grain and straw, or corn grain and stalk has been studied with pure cultures [9, 19, 20, 55]. With increasing sugar concentrations, deemed necessary for cost reduction, to circa 30 g glucose/L, a decrease in the substrate conversion efficiency has been observed, especially during growth on hydrolysates. This may be due to the limited osmotolerance observed in some thermophilic hydrogen producers [12]. The penalty on maximum volumetric H_2 productivity was much less severe, remaining at circa 15 mmol H_2/L.h. Using continuous cultivation on molasses, it has been shown that addition of yeast extract was not needed (Fig. 6). The nutrients in this natural substrate are sufficient for maintaining growth and efficient hydrogen production by *C. saccharolyticus* enabling significant cost reduction of fermentation media.

Robustness of fermentations is an important asset for future industrial application. Therefore co-existence of different bacterial has been studied. Designed co-cultures of *Caldicellulosiruptor* species seem to create a synergy achieving high productivity as well as hydrogen yields close to the theoretical maximum of 4 mol H_2/mol hexose, equivalent to almost 100% conversion efficiency in thermophilic fermentation [18].



Q_{H_2} = 0.032 g L^{-1} h^{-1}
Y_{H_2} = 2.8
Substrate conversion efficiency = 70%
C-balance = 0.83
Sucrose consumption = 94%

Figure 6 Continuous cultivation of *Caldicellulosiruptor saccharolyticus* on molasses. The dilution rate was 0.1 h^{-1}. Yeast extract was omitted after 14 days. Ammonium was omitted after 20 days.

Dedicated bioreactors
New bioreactors have been constructed after evaluation [45] showing a great divergence with respect to hydrogen yield and productivity. So far, one of the best performances was in a 30 L combined fluidized and trickle bed (CFTB) reactor showing stable fermentation of thick juice with >75% yield and a productivity >25 mmol H_2/L.h with moderate stripping using N_2 (Fig. 7).

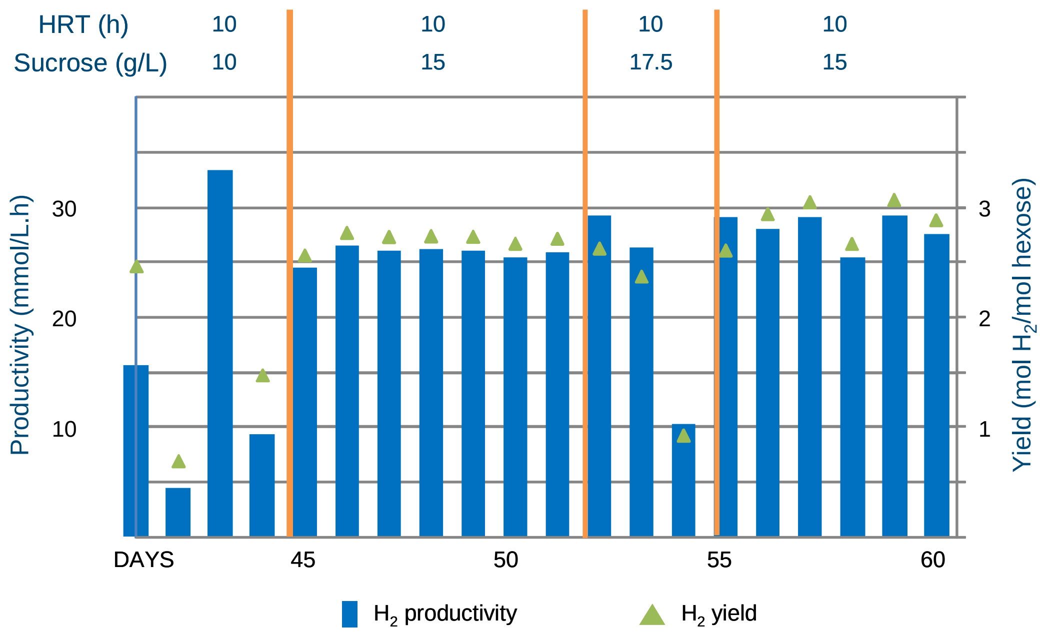


Figure 7 Continuous hydrogen fermentation by a co-culture of *Caldicellulosiruptor sp.* using thick juice as substrate in a 30 L combined fluidized trickle bed reactor with reduced gas stripping at 3 L N_2/h. The hydraulic retention time (HRT) was 10 h and the sucrose concentration was 10 to 17.5 g/L, changing at several times indicated by the green bars. At 17.5 g sucrose/ L the culture washed out.

The outcome of the experiments assisted in designing and scaling up this CFTB reactor to 600 L which was equipped with a dedicated control unit for remote control via a specific web address on the Internet. However, this 600 L CFTB reactor (Fig. 8) has suffered from mechanical failures and allowed only one short fermentation with high yield (circa 75 %) but with very low productivity (4.7 mmol H_2/L.h).

Figure 8: 600 L combined fluidized and trickling bed (CFTB) reactor; A. Bioreactor system after installation with glass wool insulation; B. Installations and connections at the bottom part of the bioreactor; C. Gas analysis system and control system and at the right side the molasses container.

In a complementary approach, using thermophilic consortia growing at 60-65 ºC instead of the above described pure cultures of extreme thermophilic bacteria growing at $\geq$70 ºC, extremely high hydrogen productivities of >200 mmol H_2/L.h, have been obtained. However, the achieved hydrogen yield in these cultures has remained obscure. The fermenters used in this approach could not be tested with the extreme thermophiles due to collapse of the materials at the higher temperature.
Besides these fluidized bed bioreactors, the application of a novel membrane bioreactor has enabled promising hydrogen productivities at 70 ºC, in cultures grown on cellobiose as substrate. This has been the first step towards the development of a membrane bioreactor with *in situ* removal of hydrogen and CO_2 without stripping [21].

With the high hydrogen yields achieved with the real biomass, Objective 3: *Maximum efficiency in conversion of biomass to hydrogen* has been achieved. For Objective 4: *Reactors for thermophilic and photo-heterotrophic hydrogen production* the prototype bioreactor for thermophilic fermentation has been constructed and tested, unfortunately, the latter was possible only for a brief period and thus its full potential remains to be explored.

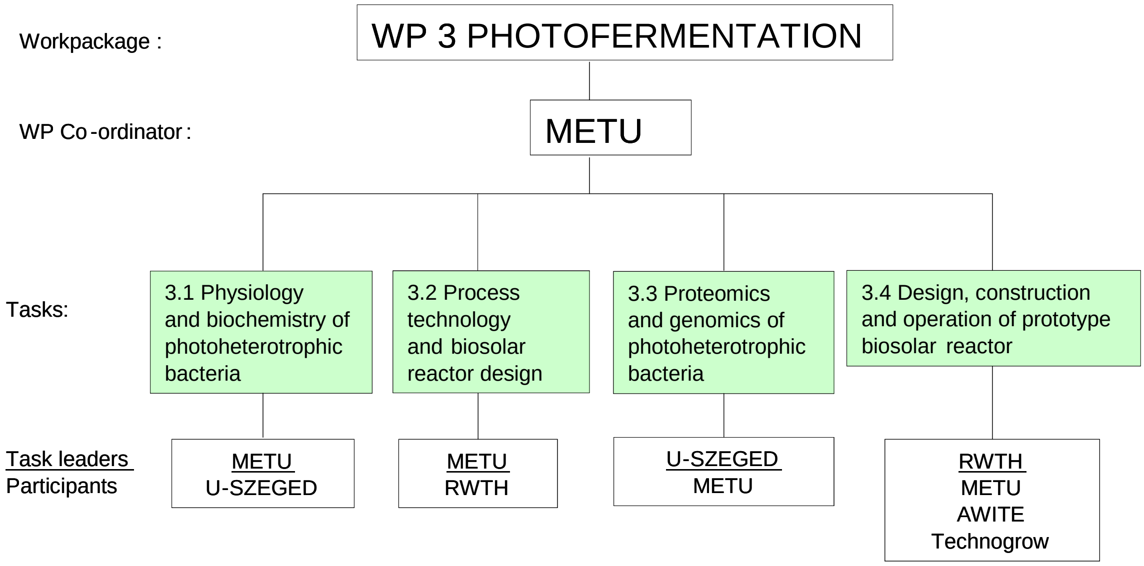


Figure 9 Structure of Workpackage 3 showing contractors involved in the tasks.

Physiology of photofermentative bacteria
As in WP 2, the work in WP 3, *Photofermentation*, has been focused on physiological and genetic parameters and tools, new bacteria, use of real substrates such as the effluents coming from the thermophilic fermentation and construction and use of bioreactors. In WP 3 the model organisms are Purple Non Sulfur (PNS) bacteria, coming from the Rhodobacteriaceae and one Purple Sulfur bacterium, *Thiocapsa roseopersicina*, well-known for its inexhaustible supply of hydrogenase genes and enzymes but lack of growth on acetate [10, 22]. In PNS bacteria, hydrogen productivity and yield are affected by organic acid concentration [23], temperature [24] and varying nitrogen sources under continuous light or light/dark cycles [25].
The links between acetate metabolism and electron flow in various PNS bacteria and in *T. roseopersicina* have been mapped to near completeness. Further analysis of the intricate hydrogenase system in *T. roseopersicina* has pinpointed the candidate genes for successful improvement of Rhodobacteriaceae without adding antibiotic resistance genes. This is an important asset for large scale application as antibiotic resistance of genetically modified organisms is forestalled. A *hup*$^-$ mutant (inactivated uptake hydrogenase gene) of *Rhodobacter capsulatus* with improved hydrogen production during growth on malate has been obtained [26, 27] but active expression of hydrogenase has remained unsuccessful. Through natural selection, a heat resistant *Rhodobacter capsulatus* has been obtained which showed hydrogen production at high temperatures which may arise at locations with high light intensity. Progress has been made in adjustment of the media used for photofermentation with the emphasis on ammonia as the main inhibitor of nitrogenase mediated hydrogen production [28]. Using a natural zeolite like clinoptilolite a decrease in ammonium concentration of > 60% has been achieved, giving more degrees of freedom in feedstock use in WP 1 and WP 2. Other pretreatments such as centrifugation, filtering, dilution, sterilization and substitutions of buffer, molybdenum and iron have also improved hydrogen yields [29].

Photofermentation using effluents from thermophilic fermentations
Photofermentation using effluents from thermophilic fermentations on molasses, thick juice, potato steam peels and barley straw hydrolysate has been performed very successfully, showing productivities and yields which are comparable to those obtained with defined media (table 1). For the outdoor experiments, large dark fermenter effluent quantities were needed. As a consequence, only effluents from molasses and thick juice fermentations were available for outdoor photofermentation. The data for outdoor experiments shown in table 1 have been obtained using panel reactors. The yield and productivity were always much lower in tubular reactors: for *R. capsulatus* wild type on thick juice, the

yield was 12% and productivity 0.28 mmol H_2/L.h and for the *hup* $^{-}$ mutant on molasses, the yield was 10% and productivity was 0.12 mmol H_2/L.h [46].

The *R. capsulatus hup*$^{-}$ strain gave the highest yield (99%) and productivity (1.42 mmol/L.h) from several PNS bacteria tested. The highest yield in the integrated bioprocess, 89%, was observed using barley straw with the *hup*$^{-}$ mutant in small 50 mL bottles, under indoor conditions showing that the initial objective of a bioprocess with an overall efficiency of 75% in hydrogen production is feasible. This is supported by the data generated using long term continuous outdoor photofermentation where > 55% efficiency was obtained with the wild type strain and 77% with the *hup*$^{-}$ mutant.

Table 1 Typical data using molasses, thick juice, potato steam peels (PSP) and alkaline pretreated barley straw (without yeast extract) as substrate in the thermophilic fermentation with *C. saccharolyticus* followed by using the effluents in the subsequent photofermentation with *R. capsulatus* wild type (WT) or the inactivated uptake hydrogenase gene (*hup* $^{-}$) mutant [31,47,56].

Thermophilic fermentation		***Molasses***		***Thick juice***		***PSP***		***Barley straw Alkaline pretreatment, no yeast extract***	
Substrate	g saccharide/L	10		15		10		12.5	
Yield	%	61		75		85		68	
Productivity	mmol H_2/L.h	17		29		16		7	
Photofermentation		Outdoor[1)]		Outdoor[1)]		Indoor[2)]		Indoor[2)]	
		WT	hup^{-}	WT	hup^{-}	WT	hup^{-}	WT	hup^{-}
Substrate	mM acetate	~40		~40		~40		~40	
Yield	%	53	40	46	78	24	23	50	99
Productivity	mmol H_2/L.h	0.54	0.67	1.10	0.80	0.57	0.50	0.48	1.42
Overall yield	**%**	**56**	**47**	**56**	**77**	**44**	**44**	**56**	**89**

1) Data achieved in 4-20 L panel reactors.
2) Data achieved in 50 mL bottles. The medium was supplemented with Fe and Mo [30, 33].

Figure 10 Pilot scale panel photobioreactor (4x25 L) and pilot scale tubular photobioreactor (65 L) in Aachen, Germany and Ankara, Turkey, respectively.

Bioreactors for photofermentation

The performance of panel and tubular photobioreactors (Figure 10) has been compared under outdoor conditions and led to the conclusion that panel photobioreactors are suitable for low light intensity areas and tubular reactors for high light intensity [34, 47, 54]. The illuminated surface area per unit ground space area is circa 8.5 times higher in the panel reactor than in the tubular system. Hydrogen production has been established in 65 and 80 L tubular photobioreactors with reasonable productivities during more than 50 days, under outdoor conditions.

The optimization of photobioreactor performance has been studied by changing process parameters as mixing, feeding rate, recirculation, temperature, light intensity etc. during growth of wild type *R. capsulatus* and the *hup*$^-$ mutant [32]. A linear relationship has been drawn for the rate of hydrogen production and daily total global solar radiation. Internal recirculation of the liquid phase of photobioreactor effluent has been found possible to reduce the water demand at a maximum of 70%. Keeping acetate concentration at a certain level (~20 mM) has led to improvements in stability. It was demonstrated that by immobilization, hydrogen yields up to 98% were achieved with high productivities (>1.5 mmol/L.h) with *R. capsulatus hup*$^-$ due to advantageous growth limitation in such systems

The high investment and maintenance costs of both panel and tubular seem not reasonable for industrial application. For this reason, much effort has been devoted to testing alternative materials for manufacturing transparent tubes. Experiments using different PVC based tubes at TECHNOGROW using microalgae showed excellent results and allowed the construction of three dimensional arrays in cost effective manner. Three dimensional arrays led to an increase of the illuminated area per unit of ground surface and thereby larger productivities. This will decrease the total area requirement of the photofermentation. According to the manufacturer the life time of the material can be expected to be at least 5 years under outdoor conditions.

The work in WP 3 has made great progress towards Objectives 3:*Maximum efficiency in conversion of biomass to hydrogen*, with 53% and 64% overall efficiency achieved using wild type and genetically modified bacteria, respectively, 4: *Reactors for thermophilic and photo-heterotrophic hydrogen production* and 6: *Devices for monitoring and control*.

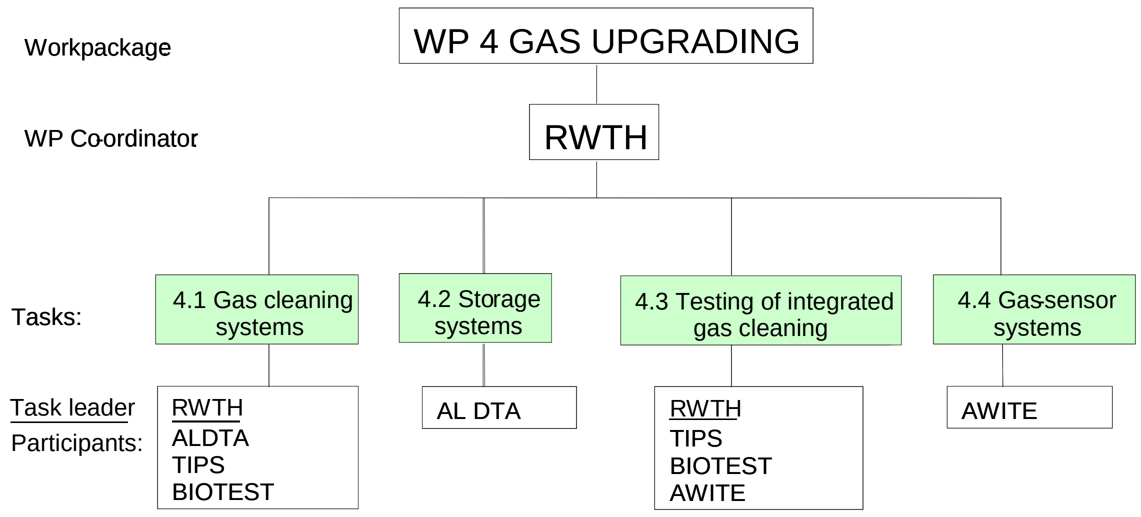


Figure 11 Structure of Workpackage 4 showing contractors involved in the tasks.

Purification of the raw gas

In WP 4 *Gas upgrading*, downstream processing of the raw gas for gas upgrading and subsequent storage has been addressed. Theoretically, the concentration of hydrogen in the raw gas produced in the thermophilic fermentation amounts to 66%. The concentration of CO_2 is circa 33% and additional impurities (H_2S, NH_3) are estimated in the 100 ppm range when using higher concentrations of hydrolysates. The concentration of hydrogen in the raw gas produced in the photofermentation ranges from 0 to 90-95%, due to the day-night cycle and solution of CO_2. Different conventional gas purification systems have been assessed in terms of energy, operational and investment costs. A novel purification system with low energy consumption based on membrane contactor technology has been developed [48].

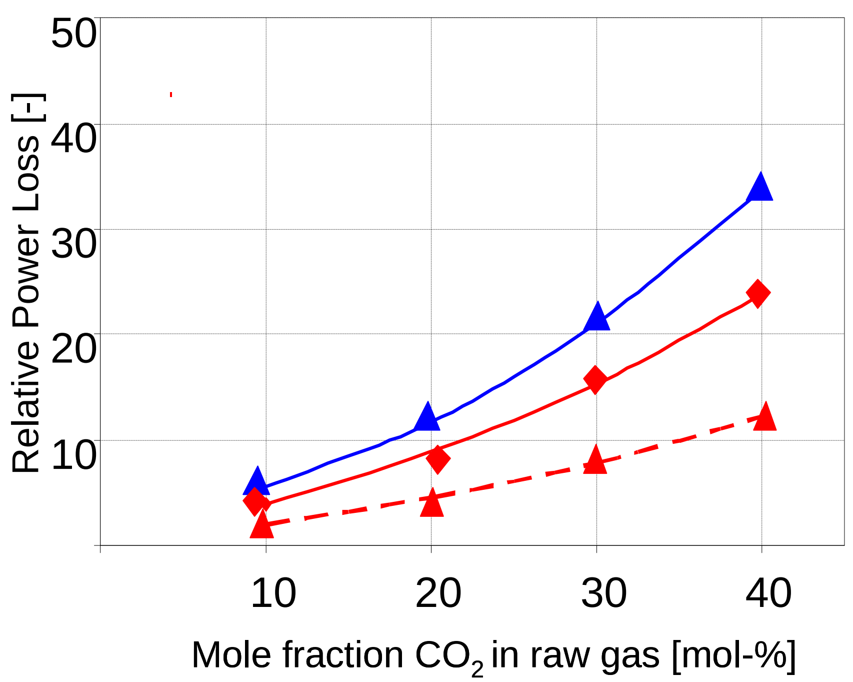


Figure 12 Power loss in gas upgrading using vacuum swing adsorption (VSA) without drying (▲), and a membrane contactor system with MEA (♦) or K_2CO_3 with piperazine (▲) as adsorbent.

From the conventional gas upgrading options, the vacuum swing adsorption has been selected based on the assumption that the gas mixture produced in the bioreactors will contain not more than 33% of CO_2. The technological applicability of the VSA in the biohydrogen process has been demonstrated and evaluated by connecting a test device to the photobioreactor. Two zeolite based adsorbing substances (13X and 5A), have been selected. The trade-off study on the conventional gas upgrading systems has shown energy losses of around 20% when applying a hydrogen-rich stream contaminated by 30% of CO_2 to the VSA. When comparing gas upgrading of mixtures containing 30 to 40% CO_2 the results strongly favor the membrane separation, especially in terms of energy demand (Fig.12).
The membrane contactor employs a dense polyvinyltrimethylsilan (PVTMS) membrane resulting in hermetically separated phases [14, 35] to avoid evaporation of the carrier solution into the gaseous feed phase. K_2CO_3 promoted by piperazine has been selected for the HYVOLUTION process since it has a low energy demand and a higher theoretical capacity than monoethanolamine [36] and a considerably higher reactivity than K_2CO_3 [37]. Application of the same set up for desorption of CO_2 was without success at 60 ºC. The modification of several process parameters as e.g. temperature, liquid flow rate and sweep/stripping rate failed to release the CO_2 when loading was at typical amounts of 0-50% (mmol CO_2/mL solution). Therefore the membrane contactor was replace by a bubble column which allowed a regeneration of the absorbent to less than 0.3 % CO_2, at 80 ºC and a liquid velocity of 0.4 cm/s. The cassette-type membrane contactor module itself and its manufacture have been optimized continually. The current estimation of the requested size for the membrane when applied in a 60 kg/h H_2 production plant (2 MW thermal power) is 10 000 m^2 equal to 12.5 m^3.

Integration of gas upgrading with fermentation
A 2nd generation membrane contactor was used for cleaning the gas coming from a photobioreactor. With realistic CO_2 concentrations of 4-8% (v/v), a removal of 99% CO_2 was achieved using K_2CO_3 supplemented with piperazine. A 3rd generation membrane contactor with a total exchange area of 0.09 m^2 PVTMS membranes was connected to the 30 L thermophilic bioreactor (Fig. 7). The CO_2 concentration in the clean gas showed a separation ratio of 95 % when the CO_2-concentration in the stripped raw gas ranged from 17-23 % with approximately 15 % H_2. During operation of the thermophilic fermenter without strip gas, the separation ratio was higher than 99 % at the same H_2/ CO_2 ratio as in the stripped raw gas. These findings prove the applicability of the membrane system with low energy demand for a bioprocess with diluted product concentration.

Hydrogen storage
A storage system has been designed to make the hydrogen availability independent of the production process and to compensate the fluctuating flow rates. Within the classical storage systems for molecular hydrogen, compressed gas at a pressure of 200 bar comprises an energy penalty of circa 11% and liquid storage of circa 50%. Low pressure storage at 10 to 15 bar, commonly applied with helium, decreases the overall thermal energy output by less than 5% and thus presents a low energy consuming alternative for hydrogen storage. The storage of hydrogen in e.g. metal hydride or chemical hydride systems has also been investigated and might be an option for the future.

Gas analysis
In addition to the gas upgrading systems a gas sensor system has been developed to control the quality of the product gas. A prototype of the gas sensor system for continuous or semi-continuous analysis (H_2, CO_2, H_2S and O_2) has been developed, manufactured and tested. The system is based on cheap commercial sensors and is temperature controlled. An electrochemical hydrogen sensor with a measurement range of up to 5% together with an innovative dilution method has been selected for measurement of concentrations up to 100% H_2. CO_2 is measured by means of a commercial NIR absorbance sensor. Detection of H_2S is done using an electrochemical sensor together with a dilution method or with UV absorbance and O_2 by a galvanic fuel cell sensor.

The results of the work in WP 4 have led to achieving Objective 7: *Equipment for optimal gas cleaning* and Objective 8: *Minimum energy demand and maximum product output* as well as Objective 6: *Devices for monitoring and control*.

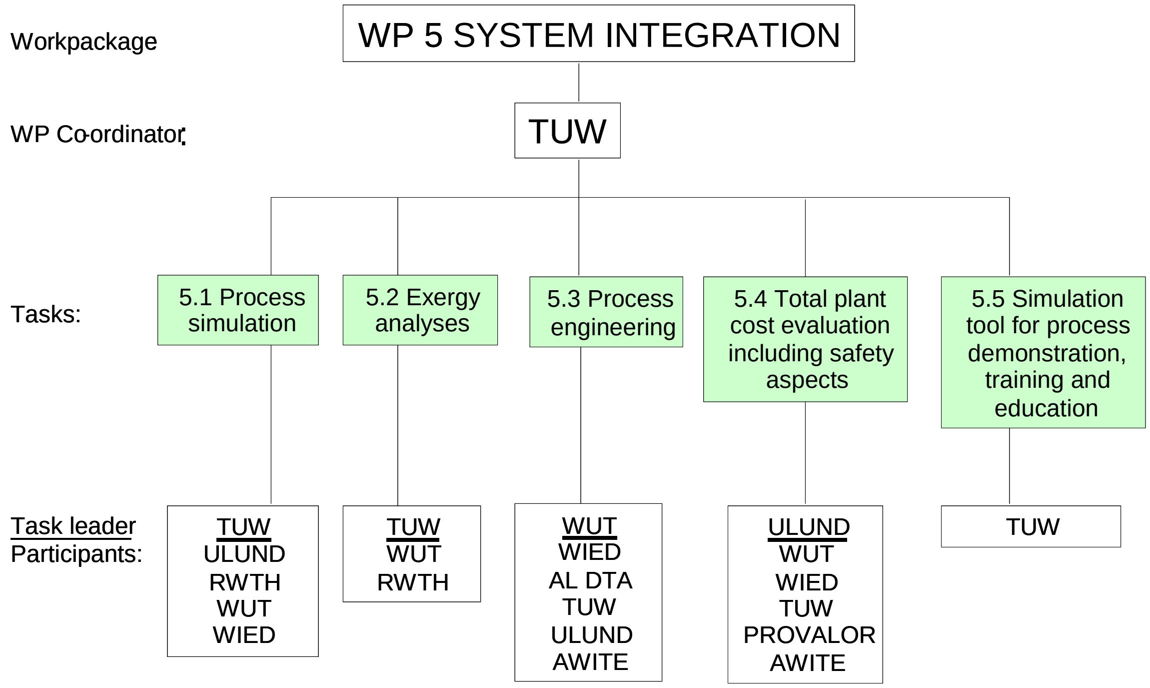


Figure 13 Structure of Workpackage 5 showing contractors involved in the tasks.

Process simulation

The fine-tuning of the calculation models to fulfill the demands for WP 5, *System integration*, for simulation, basic engineering, costing and exergy analysis, has been finalized [53]. The current simulation studies and sensitivity analyses have been based on experimental data from WP 1-4 for molasses, thick juice, potato steam peels (PSP) and barley straw as feedstock and include process and heat integration steps. Performance of the different process options strongly depends on water and carbohydrate content of feedstocks. Differences are further caused by the used organisms (wild type, mutants) as well as applied pretreatment. With all feedstock options, a net hydrogen production is possible. Hydrogen production from molasses using mesophilic bacteria (growing at 30 ºC) showed no advantage compared to the thermophilic fermentation at 70 ºC, even though the fermentation temperature is significantly lower and productivities are higher [49]. The commercial software package ASPENplus® has been selected to predict the behavior of HYVOLUTION using basic mass balance, energy balance, phase and chemical equilibrium and reaction kinetics. [38, 39]. The process has been scaled to produce 60 kg/h of pure hydrogen (equivalent to 2 MW thermal power).
Case studies and sensitivity analyses have been done to improve process performance in terms of utility and energy demand. The need for increasing substrate concentrations in the thermophilic fermentation as well as the photofermentation has become a prime issue. However, reduction of heat and water demand by an increase of substrate concentration turned out problematic due to exceeding a critical limit of osmolality in the thermophilic fermentation (THF) [21]. Investigation of different recirculation options (Figure 14) has indicated the following

- Internal recirculation of effluents in the thermophilic reactor (THF) gives a considerable reduction of heat demand but a prohibitive increase of acetate concentration
- Internal recirculation in the photobioreactor (PHF) gives a strong decrease of water demand
- External recirculation of PHF effluent to THF achieves a partial reduction of heat and water demand and slightly increases concentration and osmolality in the thermophilic reactor
- External recirculation in THF combined with internal recirculation in PHF gives strong reduction of water and chemicals demand without significant change in osmolality level
- Heat exchanger between the inlet and outlet of THF seems the only solution to reduce heat demand in THF. Heat integration in THF and in the pretreatment step (PTR) reduces heat duty in case of feedstock potato steam peels by 85% and 30%, respectively [40]

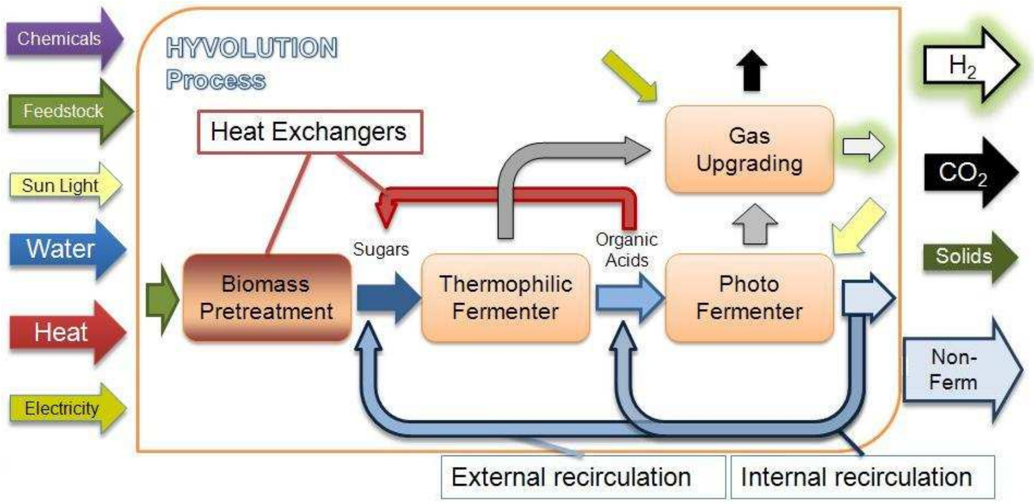


Figure 14 Actual process scheme of HYVOLUTION process

Exergy analysis

Exergy of compounds and streams is calculated as the sum of three components - chemical and physical exergy and the exergy change of mixing using a MS-Excel spreadsheet. The calculation of necessary thermodynamic properties has been based on integrated polynomial functions for the values of specific heat, entropy and enthalpy, using the same correlations as in the process simulation tool [41, 42]. Exergy losses of the investigated process options are between 7% and 9%. The efficiency based on chemical exergy of biomass feed and produced pure hydrogen refers to 36-45% depending on used feedstock and the configuration of the overall process. These results correspond with data for anaerobic digestion of biomass to hydrogen as well as to biogas production with 36% and 46%, respectively [43, 50].

The achieved exergetic efficiency strongly depended on the evaluation of the various products. A significant increase of exergetic efficiency of the overall process is achieved, when defining residual biomass (produced cell mass and non-fermentable residues from pretreatment) as a usable product as the exergetic efficiencies almost doubles. The possible contribution of heat integration to the increase of exergetic efficiency of the process is negligible due to the strong impact of chemical exergy compared to physical exergy in this low temperature process. Nevertheless, heat integration plays an important role from the point of view of energy demand and economic evaluation [51].

Process engineering

Process engineering has been addressed by the design of a hydrogen production plant connected with a sugar factory, including a process flow sheet of the hydrogen plant and interfaces of the sugar factory, selection and sizing of equipment and a plot plan of the equipment. Besides, process engineering and integration has been extended by the pretreatment of potato steam peels. Furthermore, options on complete or partial self-supply (heat and power) of a stand-alone plant are introduced based on the use of solid process residues (biogas utilisation, combustion) or the use of (residual) hydrogen (fuel cell, catalytic oxidizer, boiler) [52]. Risk and safety analysis of the HYVOLUTION plant based on a HAZOP study as well as a dedicated process control system including full instrumentation have been included.

For a more complete impression of the HYVOLUTION plant, a 3D model has been developed using SketchUp software (Figure 15).

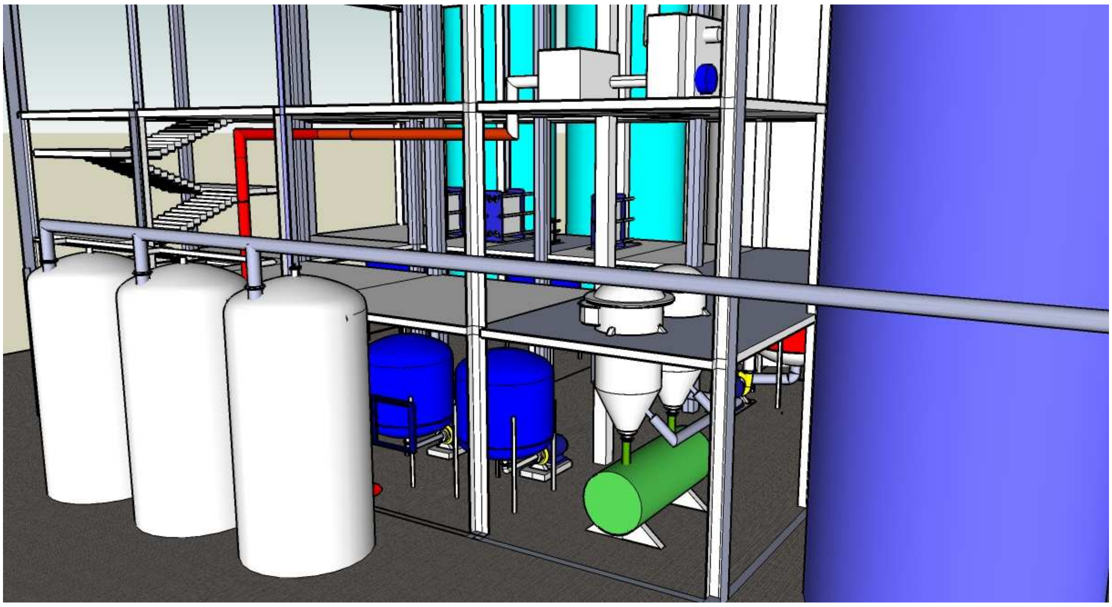


Figure 15 3D-view on main equipment (foreground: adsorption vessels; background: dark fermentors)

Cost evaluation

Cost estimation has been done using Aspen Process Economic Analyzer. Data used for the calculations have been derived from the engineering results in WP 5 and the experimental results in WP 1 – 4, representing the current status of HYVOLUTION. The economical analysis has included the capital cost for all four process steps i.e. pretreatment (PRT), thermophilic fermentation (THF), photofermentation (PHF) and gas up-grading (GUG), costs of plastic tubing or Plexiglas for the photofermenters as well as cost of chemicals, nutrients and utilities (steam, electricity, cooling and process water). Cost estimation has also included cost of labour (three persons), insurance (1 % of the capital cost), maintenance (2 % of the capital cost) and 10 % contingencies. The three employees run the whole plant except the photofermentation, which will temporarily require additional employees for cleaning and maintenance.

The HYVOLUTION plant is assumed to be in operation 8000 hours per year producing 60 kg H_2/h (2 MW thermal power). The photofermenter is assumedly in full operation during 10 hours per day, resulting in roughly 3330 hours of operation annually. Figure 16 shows the allocation of costs to the process steps and the type of costs with barley straw as feedstock. All four feedstocks considered in HYVOLUTION showed a similar cost profile with the final cost of hydrogen at 55-60 €/kg using a tubular photobioreactor and 385-390 €/kg in the case of a panel photobioreactor. These high production costs are mainly caused by the plastic and Plexiglass materials and the demand for additional labour of the photobioreactors at the current state-of-the-art. Furthermore, the total capital cost of the photofermenter is large, around 90 and 320 million € for the tubular and flat panel reactor, respectively. Not considered in the costing is the cost of land. The ground area demand of the tubular and flat panel reactor is about 2.0 and 1.3 million square meters, respectively.

Assuming a process with the THF step as the only hydrogen producing step has a massive effect on the material flows in the process and the production cost of hydrogen. The raw material demand increases by a factor of 2.4 due to a much lower overall hydrogen yield in the process. The overall hydrogen yield decreases from 50% to 21% of the theoretical yield (12 mol H_2/mol glucose). As a consequence equipment size increases. Furthermore, the chemical and utility demand increases. However, total production costs are with €21/kg H_2 much lower than €56/kg for the combination THF and PHF.

From a costing perspective the photofermenter is the main bottleneck. Despite the current high costs, this process step would not benefit from a scale up. However, even though the photofermentation is by far the most expensive part of the HYVOLUTION process, also other process steps have to be improved. To meet the proposed hydrogen cost of €10 /GJ, which corresponds to €1.21 /kg H_2 (based on the lower heating value, LHV) a maximum allowed capital investment of 5.3 million € is necessary, neglecting all other costs (feedstock, labour, etc.). Presently the capital cost, excluding the

photofermenter, is 24.6 million € for the thick juice case and the capital costs of the tubular and flat panel photofermenter are 91 and 332 million €, respectively. Clearly, vast improvements are required starting with the utilization of co-products. Forecasts for the improvement of the performance of the photo-fermentation promise a reduction of the cost to 20 €/kg hydrogen.
HYVOLUTION has also been compared, in terms of €/GJ, with the costs for a bioethanol production plant equipped with a biogas installation for the utilization of the residues and pentose sugars. With barley straw as feedstock, energy from state-of-the-art HYVOLUTION is 452 €/GJ and 18 €/GJ for ethanol with biogas. The estimation for HYVOLUTION after 6 years and at small scale is a decrease to 153 €/GJ. Even though these costs are still significantly higher than for ethanol, hydrogen production may be supplementary to bioethanol production when feedstocks with high moisture content are considered. In this case, downstream processing of ethanol will not be economical due to prohibitive costs for distillation leaving room for hydrogen to add to the future biofuel mixture.

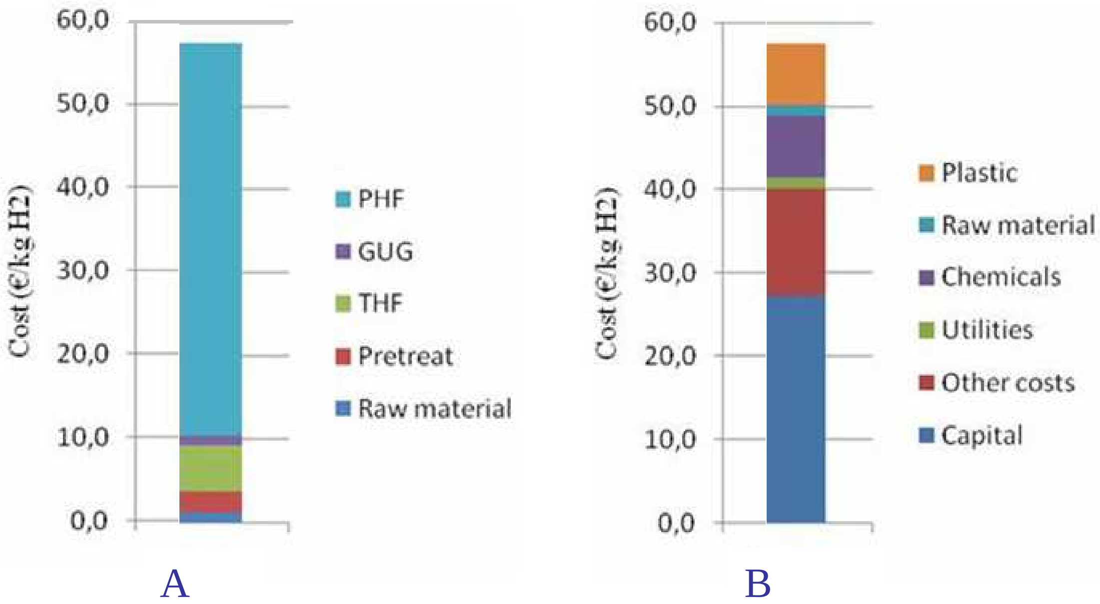


Figure 16 Allocation of cost for hydrogen production at 60 kg H_2/h from barley straw to process steps (A) and type of cost (B) in a HYVOLUTION plant equipped with a tubular photobioreactor.

Development of training tools
Training will form an important contribution to deliver support for the new emerging technologies as prepared in the HYVOLUTION project. The aim of training is to promote the use of hydrogen from biomass by wide-spread education and providing information, externally and internally. Training materials prepared in WP 7 have been complemented by the development of a simulation tool for process demonstration, training and education, accessible via Internet.
Besides a model of the whole process offering just “basic” calculation functions for demonstration purposes, a more detailed model with higher functionality for the different single process steps (pretreatment, thermophilic-fermentation, photo-fermentation and gas-upgrading) has been developed for training.

In WP 5 major steps have been made towards Objective 8: *Minimum energy demand and maximum product output*.

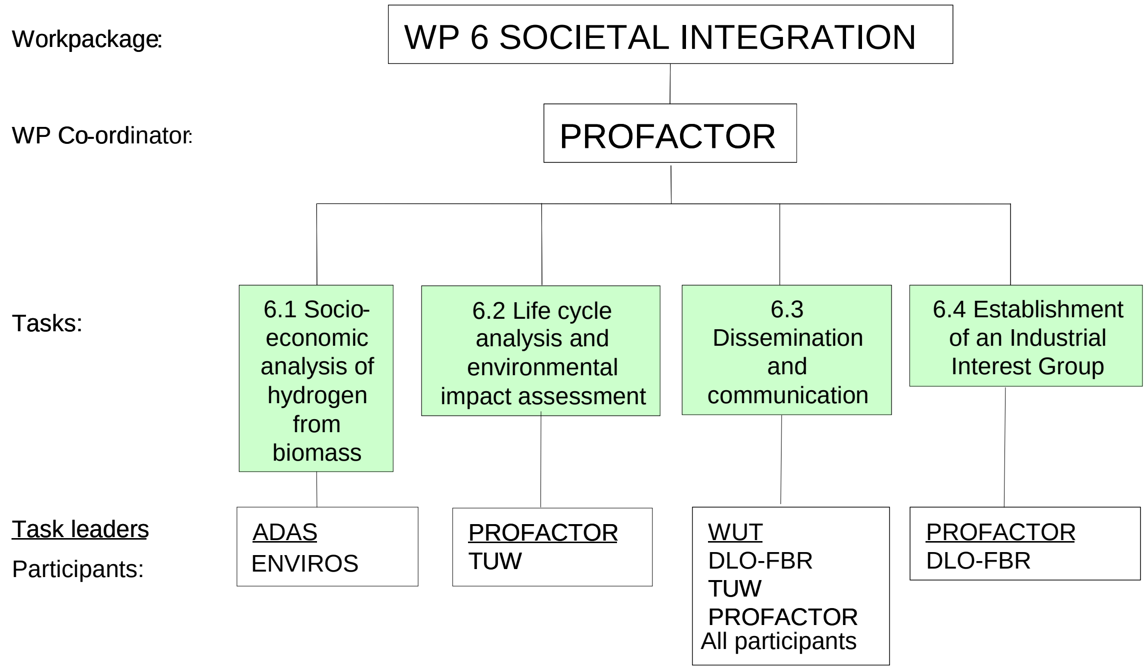


Figure 17 Structure of Workpackage 6 showing contractors involved in the tasks.

Socio-economic impact

In WP 6, *Societal integration*, a new model called HYVOLUTION Socio-economics Model (HYSEM) has been developed to describe the socio-economic impacts of a biomass to hydrogen industry. HYESM has been updated at the end of HYVOLUTION using feedstock and costing data generated in WP 1- WP 5. The final analysis shows that HYVOLUTION plants will have significant income impacts due to the high capital investment and operational costs. However, the plant operation is very labour-efficient and has limited direct employment impacts. On the other hand, income and employment multipliers are reasonably high, reflecting the wider scale of investment in goods and services. The estimates from an EU report on Hydrogen development (HyWays) have been used to anticipate the number of 2 MW HYVOLUTION plants in 2030. The results indicate that over a 15-year period, construction and operation of 2300 plants could generate over 100 000 jobs on the average.

Life cycle analysis

The final life cycle analysis and a sensitivity analysis of HYVOLUTION have been done using newly available data sets for potato steam peels, molasses and thick juice according to the Ecoindicator 99 database. The rate of recirculation and the buffer concentration in the photofermentation have been chosen as main variables. The described changes lead to three main cases for each substrate. In each of these cases an additional parameter variation has been conducted: (i) replacement of conventionally produced phosphate by a recycled phosphate (SUSAN Technology), (ii) reduction of external heat demand by using the lost hydrogen rich gas through catalytic oxidation and (iii) use of sewage as fertilizer. This led to 12 cases for each HYVOLUTION process [54].

The final LCA shows that the HYVOLUTION process using bio-residues has a lower environmental impact than hydrogen production by reforming natural gas. This lower impact is achieved when recirculation is applied. When molasses is used as substrate no further parameter variation needs to be considered. In comparison, the use of PSP as substrate requires an additional replacement of phosphate from ore by recycled phosphate to reduce the environmental impact.

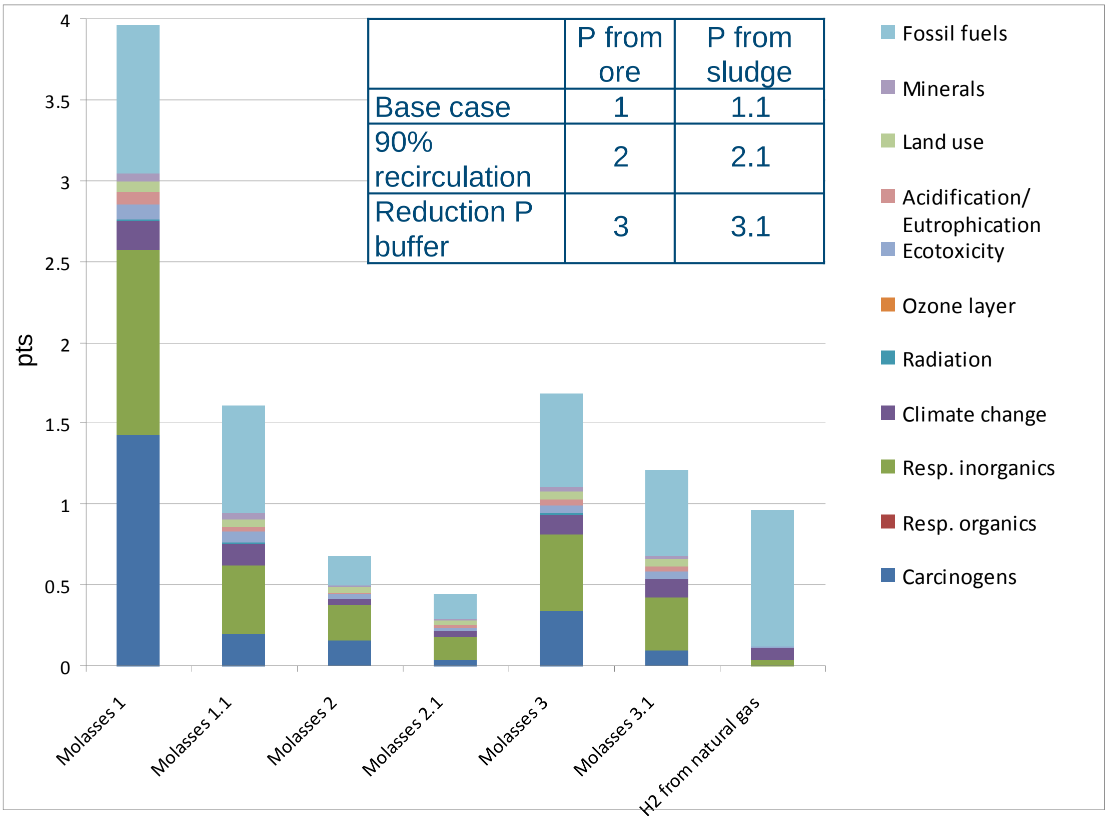


Figure 18 Environmental impact of HYVOLUTION using molasses as feedstock as compared to hydrogen production by natural gas steam reforming. The variable parameters are shown in the box.

Dissemination
During the course of HYVOLUTION, dissemination efforts have become more and more joint activities, reflecting successful project integration. As of December 2010, numerous dissemination activities are already foreseen for year 2011: presentations at the 14th International Conference on Process Integration, Modelling and Optimization for Energy Saving and Pollution Reduction (PRES'11) in Florence, Italy and at the 1st European Congress of Applied Biotechnology, Berlin, Germany, and 20 publications in print or in preparation (including 7 PhD dissertations and several papers in high-impact journals like Int. J. of Hydrogen Energy, Biomass and Bioenergy, etc.).

Table 3 Number of dissemination activities in HYVOLUTION.

	Total in period 1 - 5
Websites, press releases, interviews	**46**
Conferences oral & visual presentations	**206**
Seminars oral & visual presentations	**101**
Publications	**64**
Flyers	**5**

Industrial interest group
The establishment of the IIG has not developed as expected during the runtime of the project. The number of members did not exceed 44, and a workshop in 2008 for representatives of commercial companies has resulted in a moderate participation. Therefore, the aim of this task has been shifted in towards an intensified communication of HYVOLUTION to commercial companies by the aid of exhibitions and fairs.

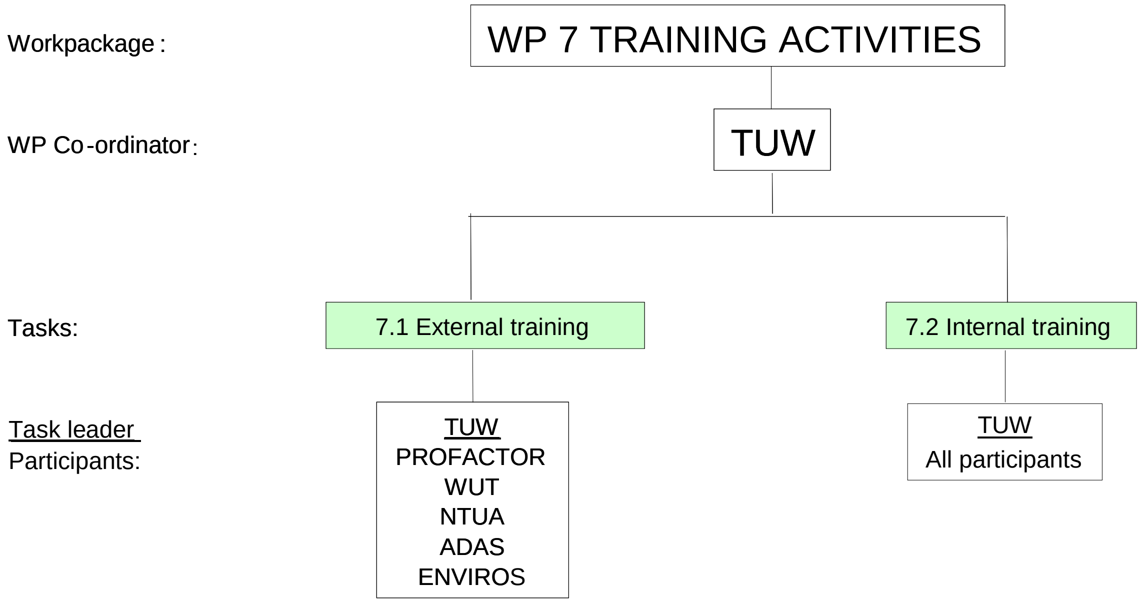


Figure 19 Structure of Workpackage 7 showing contractors involved in the tasks.

Training materials

The target groups for WP 7, *Training*, have been identified as users of renewable energy, engineering companies, local and rural communities, policy makers and local authorities, including the companies that have registered in the Industrial Interest Group of HYVOLUTION. Since sufficient information is available clarifying the advantages of hydrogen, the advantages and actual drawbacks of the hydrogen economy, the main focus of training has been on production of biohydrogen in HYVOLUTION, including technological, ecological and economic issues. Papers on general topics, dedicated for training of the general public and an introduction to more specific training topics have been developed. The main issues are (i) Conventional and novel hydrogen production processes, and (ii) Why and how to produce biohydrogen? Parts of these specific topics are used for a HYVOLUTION web-book (in preparation).

External and internal training

Besides a seminar for post-graduate students on “Feedstock selection for bio-hydrogen production”, two workshops have been organised on “Upgrading of biologically produced gases” and “Integration of Biohydrogen into the Future Biofuel Generation Systems”. In the course of the latter workshop it was possible to successfully introduce the demonstration and training tool developed in WP 5.
Besides these dedicated trainings, a great number of students have been trained in view of PhD studies or Master diploma’s at especially the university partners in HYVOLUTION (table 4).

Table 4 Research training of 50 PhD students fully or partially funded by HYVOLUTION

WP 1 BIOMASS		*WP 2 THERMOPHILIC FERMENTATION*					*WP 3 PHOTOFERMENTATION*			*WP 4 GAS UPGRADING*		*WP 5 SYSTEM INTEGRATION*		
NTUA	UNICT	WU	ULUND	WITS	USZEGED	MSU	RWTH	METU	USZEGED	TIPS	RWTH	WUT	ULUND	TUW
5	4	2	2	2	2	3	2	5	5	2	1	2	1	1

Publishable results in terms of market relevance (exploitation of results)

The website, www.hyvolution.nl, provides a database with most of the HYVOLUTION publications, posters and presentations. This publication database is accessible after login to prevent transgression of copy rights. A full report on dissemination activities, including references, is presented in the Annex 7.6, Dissemination, of the Plan for using and disseminating the knowledge.

HYVOLUTION has yielded 15 products or service ideas for which the so-called "Critical Success Factors" were elaborated. These products or services are described in the Plan for using and dissemination the knowledge. A short description which is also published at the industry domain of www.hyvolution.nl is shown below. Details are confidential and may only be provided by each respective partner on request.

1) Design and operation methodology of a dark fermenter
A bioreactor system has been designed for the production of hydrogen from either cellulosic or soluble substrates. It consists of a fluidized bed bioreactor, effluent decanter and effluent gas-disengager. It operates under high dilution rates and with gas stripping being facilitated by the recycling of de-gassed effluent. Efficient effluent gas-engagement takes place in the gas-disengager. The design and operation procedure of the bioreactor facilitates the simultaneous achievement of both high hydrogen productivities and yields. Three patents have been filed which together deal with the bioreactor design, bioreactor operation and granule development.
A key feature of the bioreactor is the effluent gas disengager. Efficient removal of H_2 from the bioreactor could be physically achieved by means of recycling of de-gassed effluent at a high flow rate through the bioreactor bed. This process could be used to remove the major thermodynamic constraints preventing the simultaneous achievement of high productivities and yields in a bioreactor with a high microbial biomass density. Thermodynamic analysis confirms experimental findings that the application of external work in the form of high temperatures, high dilution rates and high rates of de-gassed effluent recycling can remove the thermodynamic constraints preventing the simultaneous achievement of high productivities and yields. Increasing the yield above the theoretical threshold of 4.0 mol H_2 /mol glucose would require the anaerobic oxidation of acetate, butyrate and propionate in the absence of H_2 consuming bacteria.
Granules with high tensile strength are necessary for the operation of the bioreactor. A methodology for producing high tensile strength granules has been developed. Without the granules possessing the tensile strengths sufficient to withstand the corrosive action resulting from the exposure to the high shear forces, generated by the combined effects of high influent rates with linear flow velocities between 5 and 100 cm/min and the high degassed effluent recycle rates with linear flow velocities between 100 and 1000 cm/min of effluent, it would not be possible to operate a thermophilic fluidized bed bacterial granular bed bioreactors under these operational conditions.
Contact: Prof. Vincent M. Gray
University of the Witwatersrand Johannesburg
School of Molecular and Cellular Biology, Faculty of Science
Laboratory of Environmental Biotechnology,
Private Bag 3, 1 Jan Smuts Avenue, Braamfontein
2050 Johannesburg, South Africa
http://web.wits.ac.za

2) *Biomass Decision Support Tool*
B2BUT is a portfolio of Decision Support Tools (DST), especially developed in the framework of the HYVOLUTION Integrated Project, and aiming to provide a set of critical services to their users, in a user-friendly format, particularly to the support of :
Selection of the most appropriate bio-feedstock(s) for the fermentative production of hydrogen from biomass by the HYVOLUTION technology, based on key feasibility and sustainability criteria (technical, economic, environmental and social); and

Optimisation of the feasibility and sustainability of the whole biomass logistic/supply/use chain (production, transportation, pretreatment, biorefining, fermentability upgrade) of the selected feedstock(s) in the production of hydrogen by the same method.
The main components of the B2BUT portfolio, which can be used – in order to meet the corresponding needs of their users - as independent DSTs, are listed below:
MAPPING BIOMASS POTENTIAL: A detailed database of all possible forms of biomass available in the 27 Member States of the EU, and expressed both in biomass/bioenergy (Mt/year) and biohydrogen (kt/year) units. A tabular form is employed, where bio-feedstocks are classified according to their type of fermentable carbohydrates.
BIOCHEMICAL EVALUATION OF FEEDSTOCKS: A set of experimental techniques and protocols especially designed in order first to determine the chemical composition of a wide spectrum of biomass types, including energy crops, residues and other side streams, and then to assess their fermentability as biohydrogen feedstocks.
BIOMASS TECHNICAL SUITABILITY MAPPING: A Decision Support Tool servicing the comparative technological evaluation of various possible feedstocks according to a small number of critical technical parameters, which can be combined in the form of an aggregate Biomass Technical Suitability Index (BTSI).
BIOMASS COST MAPPING: A Decision Support Tool servicing the comparative economic evaluation of various possible feedstocks according to a small number of critical system and process parameters, which can be also combined in the form of an aggregate Biomass Cost Index (BCI).
BIOMASS SUSTAINABILITY MAPPING: A Decision Support Tool servicing the comparative environmental and socio-economic evaluation of various possible feedstocks according to a small number of critical system and other parameters, which can be also combined in the form of an aggregate Biomass Sustainability Index (BSI).
BIOMASS SELECTION METHODOLOGY: A composite Decision Support Tool consisting in the efficient combination of the above listed independent tools (1 - 5), in order to rank potential feedstocks according to the critical parameters associated with each tool, and thus support decisions in the form of short lists and best candidates.
BIOMASS OPTIMISATION METHODOLOGY: Another composite Decision Support Tool consisting in the efficient combination of the above listed independent tools (1 - 5), in order to optimise the performance of a selected feedstock according to the critical parameters associated with each tool, and thus support decisions in the form of “performance maps” and best practices.
Contact: Prof. Emmanuel Koukios
Head, Bioresource Technology Unit (BTU)
Laboratory of Organic & Environmental Technologies (LORET), School of Chemical Engineering, Zografou Campus
GR-15700 Athens, GREECE
Ph.: +30-210-772 3191
Fax: +30-210-772 3163
http://www.chemeng.ntua.gr

3) *CFTB reactors: design and operation methodology*
The product described is a special bioreactor designed for anaerobic fermentations, especially fermentations with the aim to produce hydrogen by the process called dark fermentation. The CFTB contains of two main components, the inner and outer pipe, which form the fluidized bed (inner pipe) and the trickling bed compartment (space between inner and outer pipe). Both compartments are filled with synthetic carriers made of PE or similar.
Contact: Dr. Wolfgang Schnitzhofer
Profactor GmbH, Innovative Energy Systems
Im Stadtgut A2
4407 Steyr/Gleink Austria
www.profactor.at

4) *Designed co-cultures*

The product, designed co-cultures of *Caldicellulosiruptor saccharolyticus* and another species of Caldicellulosiruptor, may lead to synergistic mechanisms that improve hydrogen yields and/or hydrogen productivities. The principle might be based on a kin relationship, which is a topic of general interest in fundamental ecology but there is no awareness outside that field and certainly not in applied microbiology. With this product we can create robust co-cultures that perform better than pure (mono) cultures or undefined consortia (that are usually outcomes of enrichment cultures). So far, only one combination has been studied at a certain depth (*C. saccharolyticus* and *C. kristijansonii*; Zeidan et al), but from anecdotal experimental events other combinations have similar potential. However, in depth research remains necessary to test and understand other potential combinations between Caldicellulosiruptor species. The same defined co-culture formulation as a product might apply to other genera that are used in industrial processes. In that case, we can provide a service to optimize such co-cultures.

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5) *Ammonia removal system from fermenter effluents*

The ammonia removal system is based on the zeolite "Clinoptilolite", which is a natural zeolite with microporous arrangement of silica and alumina tetrahedral channels that contains exchangeable cations such as K+1, Na+1, Mg+2, Ca+2. It is a silica rich member of heulandite family of zeolites and has Si/Al ratio of greater than 4. It has the structure (Na,K,Mg)6(Al6Si30O7).24H2O and is mostly enriched with K+ and Na+ ions. It is known to have high selectivity for certain cations; Pb+2, NH4+1, Cd+2, Co+2, Cr+2, Fe+2, Cs+2 and Na+1. Due to its affinity for heavy metals, it has been investigated by many researchers for removal of various heavy metal ions like Pb+2 and Cd+2 ions from waste water streams.

Ammonium ion was effectively removed from the prepared NH4Cl solution and 62% of the ammonium in the molasses was removed using Clinoptilolite. Higher amounts of ammonium ion can be removed with increasing the zeolite amount as observed in the NH4Cl solution case. Also, Clinoptilolite has reduced 52% of the N content in the DFE of molasses.

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6) *Tubular solar bioreactor with internal cooling*

Tubular photo-bioreactors consist of two main manifolds; header and footer manifolds made up of PVC. The header manifold was made of PVC, in which PVC TEEs were glued together in order to have a volume of 25 L. To control the level of culture fluid in the reactor and to observe the gas separation and foaming in the system, transparent lids were used at both sides which were made of Plexiglas at a thickness of 20 mm. Between the lids and the manifold, rubber o-rings having an internal diameter of 50 mm, outer diameter of 70 mm and thickness of 5 mm were inserted and the lids were closed by eight screws having a diameter of 10 mm. Analogously to the header, footer manifold was made of PVC in which PVC TEE's were glued together to obtain a volume of 2.75 L and standard PVC elements were used for LDPE tube connection.

The transparent part of the reactor was selected as 150 micron LDPE film tubing. Nine LDPE tubes with a diameter of 60 mm were connected to the header manifold by the standard PVC elements. The fittings used were PVC connectors, PVC clamping nuts, PVC elbows and Adaptor nipples. The spacing between each LDPE tube connection was 30 mm. Cooling coils are inserted in each transparent tube and manifold.

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7) *Airbed foil reactor*

A vertical panel photobioreactor for growth of microorganisms applying photosynthesis has been developed at RWTH in recent years. It consists of two solid PMMA-plates with a thickness of 4 mm mounted on a PVC-frame. The reactor height is limited to 1 m due to cracking caused by the mechanical stress. This lab-scale reactor has a width of 1 m but it can be expanded. The substrate thickness is 25 mm resulting in 25 Liters per built reactor module.

The AirBed Foil PhotoBioReactor (ABF-PBR) is a further development of the panel photobioreactor in order to push scale-up. The ABF-PBR consists of two layers of polymeric foil joined together to form a rectangular shape. In order to provide a high surface-to-volume-ratio and to limit reactor thickness joining seams are added. The joining scheme can be varied resulting in different hydrodynamic behaviour of the reactor which has an influence on the heat and mass transfer. After filling with substrate the shape of the reactor reminds of an airbed. The foil reactor is attached to a holder. The filling level of the substrate in the ABF-PBR introduces a hydrostatic pressure resulting in mechanical stress in the construction material. The mechanical stress is dependent on the material, the foil thickness and the substrate volume thickness. Therefore, the height is limited by the mechanical stability of the reactor. An estimation of the height of a reactor with a substrate thickness of 25 mm made of foil from LDPE with a thickness of 0.3 mm results in a height of more than 3 m. This potentially reduces the requirement of ground area by the factor 1/3 in comparison to the conventional photobioreactor. Since it is very likely that the light distribution between the ABF-PBR-modules is worse than between the conventional panel reactor modules the reduction of ground area will probably be less.

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8) *Panel solar reactor with internal cooling*

For the design of photobioreactor some important parameters have to be considered: light has to pass through the transparent reactor walls to reach the culture; anaerobic conditions have to be guaranteed; the culture has to be protected from invasion of competing microorganisms; additionally the reactor design has to allow for convective heat and mass transfer. In design terms, the main categories of photobioreactors are: flat panel or tubular; horizontal, inclined, vertical or spiral. An operational classification of photobioreactors would include: autogenously, gas or pump mixed. Examples of full-scale application of biological systems for the production of H2 are not presented in the literature, but research on lab-scale is well documented.

The developed flat panel reactor consists of a PVC frame covered by a transparent PMMA plate on both sides. The highest temperatures are measured on the top of the reactor. For this reason the cooling system in form of aluminium tubes is placed in the upper part of the reactor. The cooling tubes are connected to the temperature control system. The application of the cooling system allows for use of this type of the reactor even on very hot location. The cooling system improves also the autogenously mixing inside the reactor.

At RWTH reactor modules made from PMMA plates of 4 mm in thickness are used. The height of the panels is to 1 m to avoid leakage and cracking due to the mechanical stresses. The width of the panels is also 1 m, but can be expanded.

The module chosen for the experiments consist of four parallel panels arranged vertically. Each panel has an illuminated area of 2 m² h sides) and a suspension thickness of 25 mm. This results a total reactor volume of 100 l (4 x 25 l).

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9) *Integration of biogas into electricity systems*

Processes converting methane from digestion of e.g. sewage sludge to electricity by application of molten carbonate fuel cells are already in operation at different waste water treatment plants in the United States and Germany. The proposed process presented in this CSF converts biologically produced hydrogen-rich gases to electricity and heat. The process, which is dedicated to decentralized energy production, must satisfy the following criteria:

- high energy efficiency
- suitable for a wide range of gas compositions (appr. 70% H_2 to high purity H_2)
- suitable for fluctuating flow rates and compositions of the raw gas mixture
- suitable for relatively small volume flow rates (up to 2000 m^3/h)
- flexible operation
- easy to handle, maybe remote-controlled
- low maintenance requirements
- commercially available components

The process consists of a membrane contactor for gas upgrading, a low pressure storage tank and a low temperature fuel cell e.g. a proton exchange membrane fuel cell (PEMFC).

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10) *Gas-liquid membrane contactor*

Gas-liquid membrane contactor (GLMC) is a device where mass exchange between gas and liquid phases takes place via a membrane. The principle of the gas mixture separation in GLMC is similar to traditional absorption separation technique: gas mixture enters from one side of GLMC while liquid absorbent enters from the other side, some components of gas mixture are absorbed by liquid absorbent whereas other components are almost insoluble in liquid. The main difference of GLMC is the presence of a membrane which separates gas and liquid phases and forms a geometry of gas-liquid interface. GLMC unites advantages of absorption separation method (such as high selectivity and wide list of known absorbents) with advantages of membrane separation method (such as determined and constant area of mass exchange and high specific area).

One of important disadvantages of GLMC is the presence of additional mass transfer resistance between gas and liquid phases due to the presence of a membrane. Nevertheless a number of studies show that in many cases the dominant part of mass transfer resistance belongs to the liquid phase. A typical gas separation system based on GLMCs includes two modules as traditional absorption system. The first module (absorber) serves for elimination of some components from gas mixture (for example CO_2 from bio-hydrogen) and the second module (stripper) is used for liquid absorbent regeneration (recovery of CO_2 from liquid absorbent). Liquid constantly circulates between absorber and stripper.

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11) *Gas measurement device*
After selling two "AwiDil" devices for measurement of hydrogen in the acidification stage of biogas plants (used in the research of biogas), the device was adapted to the measurement of hydrogen sulphide. Biogas produced from certain waste waters (e.g. the paper industry) contains high concentrations of hydrogen sulphide. No online measurement systems are available for measuring the relative high concentrations of 10.000 ppm H_2S or more. Such devices are used for monitoring the de-sulphurisation efficiency.
Electrochemical Sensors are usually used for the online measurement of the H_2S concentration in biogas. Commercially available measurement sensors measure up to 2.000 ppm H_2S. There are no reliable sensors on the market which are able to measure higher concentrations. The dilution device which was developed in the HYVOLUTION project is able to measure up to 100 % (v/v) of hydrogen using a sensor with a range of 0 .. 3 % H_2 (v/v). Based on this, a similar device was constructed for the measurement of H_2S instead of H_2.
Moreover, electrochemical hydrogen sulphide sensors show a higher cross sensitivity against hydrogen the higher the measurement range is. Thus a dilution system has an advantage if such cross sensitivities are not wanted even if sensors with a proper measurement range are available.
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12) *Process control system software*
Awicontrol is an automation system which was developed by Awite. It consists 100 % of open source software. It was developed further within the HYVOLUTION project. The visualization can be drawn now using open source graphic software (e.g. inkscape) and stored in the SVG format. SVG is the scalable vector graphics format of the internet WWW consortium. It is an open standard.
End users are now able to make their visualization without programming knowledge and without the need of licenses or proprietary software tools by using the new SVG format and Awicontrol. The new automation system was used for automation of a pilot scale bioreactor at the Technical University of Munich. This system is used for teaching.
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13) *Pretreatment Pathways – straw*
This pretreatment process converts lignocellulosic agricultural byproducts, including wheat and barley straw, a residue from agricultural production of cereals. The process enables the use of these residues as feedstock for fermentation purposes, and creates a co-product that is suitable for energy generation. The process applies chemical pretreatment and enzymes to convert the carbohydrate fraction contained in the raw material into a soluble sugar stream that can be used for fermentation to biofuels, including bio-hydrogen. Research conducted in the HYVOLUTION project has shown that a conversion efficiency of at least 75% of carbohydrates can be obtained. The sugar composition primarily contains glucose and xylose, and its concentration is dependent on the composition of the raw material as well as the recalcitrance of the material against enzymatic degradation. Based on work conducted with potato steam peelings of a Dutch production facility, a sugar stream of 8 – 12 % sugars was obtained. Enzymes used in the process consist of commercially available enzymes including cellulase and hemi-cellulase.

The co-product produced in the process contains a crude co-product fraction which is rich in lignin, and is a potential fuel for heat and electricity generation.
The process consists of process flowsheets, mass balances, equipment lists, and table with major process parameters including process conditions, enzyme dosages, and other requirements. Together with the client, the process can be adapted to different scale, different input parameters (depending on water and lignocellulosic composition of the raw material), or other types of raw materials.

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14) *Pretreatment Pathways – potato side streams*
This pretreatment process converts starch-rich agricultural byproducts, including potato steam peelings, a residue from industrial production of French fries. The process enables the use of these residues as feedstock for fermentation purposes, and creates a co-product that is suitable as animal feed. The process applies enzymes to convert the carbohydrate fraction contained in the raw material into a soluble sugar stream that can be used for fermentation to biofuels, including bio-hydrogen. Research conducted in the HYVOLUTION project has shown that a conversion efficiency of 99% of carbohydrates can be obtained. The sugar composition primarily contains glucose, and its concentration is dependent on the starch composition of the raw material. Based on work conducted with potato steam peelings of a Dutch production facility, a sugar stream of 6 – 8 % sugars was obtained. Enzymes used in the process consist of commercially available enzymes including alpha-amylases, and gluco-amylase. The co-product produced in the process contains a crude co-product fraction of 130 to 240 g per kg dry matter, and is thereby an excellent feed for animals, in particular ruminants or pigs.
The process consists of process flowsheets, mass balances, equipment lists, and table with major process parameters including process conditions, enzyme dosages, and other requirements. Together with the client, the process can be adapted to different scale, different input parameters (depending on water and starch composition of the raw material), or other types of raw materials.

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15) *Paper degrading strain*
In the HYVOLUTION project, we focused on a dual-stage fermentation system, where in the first dark fermentation process polysaccharide based substrates are used primarily. The substrates might come from industrial wastes or energy plants. In both cases, the major component of the substrate is polysaccharide, mainly cellulose. For direct hydrogen production, the cellulose is rarely suitable, since there are very few fermentative hydrogen producing strains having proper cellulolytic activity. However, the chosen strain, the Caldicellulosiruptor saccharolyticus - being a thermophilic fermentative Gram-positive bacterium – seems to be able to utilize sugars derived from cellulose in a concomitant formation of hydrogen. According to previous studies, the crude cellulosic materials must be hydrolyzed prior to the fermentative step, but our recent results showed, that the strain itself can hydrolyze paper or even soft wood and produce hydrogen from it under proper conditions. There are tremendous amount of cellulosic wastes emitted by various industrial activity including paper industry. Moreover, a certain part of the used paper can be recycled, but considerable amount of it becomes useless waste. This can be utilized as an energy source in biofuel plants or can be composted. Our aim is to produce inoculums for companies which utilizing cellulosic waste either for producing

biogas other purposes. Out of these, special interest is directed toward the paper industry, which produce large amount of such waste. A strain capable to accelerate the hydrolysis of paper sludge and producing reducing power must stimulate the biogas formation and yield making the energy converting step faster and more economical.

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Comments by the workpackage leaders of HYVOLUTION

Emmanuel Koukios (NTUA), leader of WP 1 Biomass says "**We have made detailed plans to make good use of Europe's biomass**".

"Detailed case studies in four European regions show that it is feasible to use biomass to produce hydrogen. Initially it won't be cheap, but price is not the only standard. Look at Brazil. Its investments in bioethanol production have paid off. I would not recommend Europe to also produce bioethanol, but it is time that Europe comes up with a plan. HYVOLUTION's Work Package 1 has produced four detailed plans to implement biohydrogen production in different European regions. We have divided Europe in four areas: the rural south, the green west, the industrial north and the emerging east. For each area we have worked out detailed plans to implement a biomass-to-hydrogen future.

In central Greece (where we did a case study for the 'rural south area') biomass production means job creation. Subsidies for cotton farmers are under pressure. They need an alternative. If they can grow energy crops for hydrogen production, Southern European countries can curb the migration from rural to urban areas.

The industrial north has completely different challenges and opportunities. The food industry produces a lot of waste, which can become valuable if you use it as a feedstock for hydrogen production. Wet waste is often not useful, but in the HYVOLUTION fermentation processes we need exactly that: wet organic waste. Together with the Port of Rotterdam we are now putting together a proposal for further biomass research.

The green west has an abundance of agricultural residue. Before it is used as compost, it can first be fermented in bioreactors to produce hydrogen.

The emerging east is more or less a combination of the other three studies. It is very dynamic and always looking for the cheapest options. This could mean that they will grow grain crops for biohydrogen production, if that is at that moment the cheapest option. If policy makers share our view that food or feed crops should not be used for hydrogen production, but only residues or special energy crops, than they should come up with regulations. Not only policy makers have to become more aware of the possibilities and challenges of biohydrogen production, so should the broad public. If we want to make sustainable progress, we can do it."

"**The yield is good, but production goes too slow**" says Ed van Niel, (ULUND) leader of WP 2 Thermophilic fermentation

"Within work package 2 we had two challenges on the interface of microbiology and technology. One challenge was to develop a dedicated reactor with an optimal technique to extract the hydrogen that the microorganisms are producing, the other was improving the productivity of the microorganisms. In Austria, PROFACTOR worked on a fluidized bed filter. Recently, a 600 liter fermenter was realized in Austria, with the help of other partners, such as AWITE, which designed the control system. ULUND, WU and DLO-FBR worked on understanding the physiology of the thermophilic microorganisms and their ability to ferment various types of biomass. We worked with microorganisms that were selected during the previous EU-FP5 project BIOHYDROGEN.

The main focus was on *Caldicellulosiruptor saccharolyticus*. DLO-FBR has shown that this thermophile is able to convert many types of (poly)saccharides, including (hemi)cellulose, meaning that for the biohydrogen process feedstock can be used that is not competing with food production. USZEGED studied how the conversion of these (hemi)cellulose could be improved. In addition, we mixed two (closely related) species of *Caldicellulosiruptor* in the reactor and found that one stimulates the other. Together they grow better and produce more hydrogen than either of these species would do on their own.

Through all these steps we have managed to get a very good yield from biomass, but the production rate is too slow. The volumetric productivity needs to be improved by at least tenfold. We have experimented with several technologies to extract the hydrogen from the bioreactor during the process, because the hydrogen hinders the growth of microorganisms and therefore the hydrogen production. We are making progress, but the steps are small. It is important that the partners that are now working together in HYVOLUTION remain involved in a follow-up programme."

The team in Ankara under supervision of Inci Eroglu, (METU), leader of WP 3 Photofermentation claims that **'HYVOLUTION has accelerated the research around biohydrogen production'**

"I believe that hydrogen production through fermentation will soon be applied in practice. A local company here in Turkey has already approached me because it is looking for ways to use its agricultural waste water for energy production. HYVOLUTION has really accelerated the research around biohydrogen production.

HYVOLUTION has shown that it is beneficial to produce hydrogen in two steps: first dark fermentation (an efficient, indoor process where sugars from biomass are rapidly converted into hydrogen) and then photofermentation, where the effluent of the dark fermentation process is used to its full potential. A third of the hydrogen gets produced in step one, but from the 'waste' we can still produce two thirds of the hydrogen using photobioreactors. It took us a long time to teach the microorganisms to turn effluent, which contains large amounts of acetic acid, into hydrogen, but we succeeded. We managed to keep the bioreactors running for five or six consecutive months. That is a really good result.

But still more needs to be done. One challenge, for example, is to produce hydrogen at a low light intensity. This could be achieved through genetic modification of the bacteria or through redesign of the two prototype photobioreactors. Therefore, I truly hope that the collaboration continues. The cooperation with the University of Szeged (Hungary), RWTH (Germany), Awite (Germany) and Technogrow (the Netherlands) has led to two exceptional pilot-scale reactors: in Germany they are using a panel system and here in Turkey we are working with a tubular system. This tubular system works well, but it is big and requires a lot of space. So there is room for improvement."

Michael Modigell, leader of WP 4 Gas upgrading says: "**We have to accept uncertainties when working with natural systems**".

"We are able to produce 99.99% pure hydrogen by separating the CO_2 that is produced during the fermentation process. And, what's important, the energy demand for the separation process is low. A test we did in Austria a couple of weeks ago, using a 600 litre bioreactor, showed that the gas upgrading works perfectly. We have also looked into upscaling; designing membranes and systems that could make it possible to treat millions of cubic litres of gas. To continue this research, hopefully a new consortium will be created.

With HYVOLUTION we are in the middle of a learning process. We have probably produced more questions than answers at this stage. It is a shame that we only had five years for our research. That seems long, but it took quite some time, I would say years, before chemical engineers and microbiologists achieved a complete understanding. Different sciences speak different languages.

As a chemical engineer I try to design a stable, reliable process, but when working with living organisms we have to accept the uncertainties in the process and work around it. Bacteria are just like human beings: sometimes they are motivated to produce what we need (hydrogen) and sometimes they are not, although in my eyes the circumstances are exactly the same. Therefore, the output is not optimal, but we managed to achieve 80 % efficiency in terms of hydrogen from carbohydrates. Such good results wouldn't have been possible without a multidisciplinary approach."


Best conditions for organisms not necessarily best conditions for the system, according to Walter Wukovits and Anton Friedl, in charge of WP 5 System integration.

"The proposal that was written for HYVOLUTION was very ambitious. The goal was to bring all the knowledge together – which was still very basic at that time – and to design a plant within five years. We managed to develop a working system, but it is not competitive with conventional hydrogen production yet. The first fermentation step (thermophilic fermentation) is working effectively, but the subsequent fermentation step (where the effluent of the first step is used in a photobioreactor) should be further improved in terms of necessary reactor space. However, from the point of view of calculated hydrogen production costs, improvement is necessary in all process steps, including pretreatment and gas upgrading.

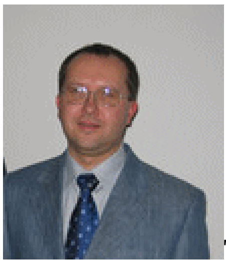
Work package 5 was aimed at evaluating the overall process and integrating the different steps. That resulted in some very useful and interesting discussions. The best conditions for single process steps or for the organisms are not necessarily the best conditions for an efficient system – finding the best balance between (low) input and (high) output. But different research fields have different points of view and different interests – even a different 'language'. It was really valuable to exchange ideas with each other.


"**Lowering environmental impact doesn't conflict with reducing costs**" says Werner Ahrer, leader of WP 6 Societal integration.

"The use of biomass for hydrogen production has socio-economic and environmental implications. If all the hydrogen in Europe would be produced through fermentation of biomass, we would need 8000 power plants in 2050; each plant producing sixty kilograms of hydrogen per hour (or 2 Megawatts) and employing 38 full time equivalents. That is what our UK-based partners Adas and Enviros forecasted. If that is indeed the hydrogen future for Europe, it would have huge implications for society. Jobs in the petrochemical industry could possibly disappear and many new jobs will be created for feedstock producers, hydrogen power plant engineers, operators, and so on.

It also has implications for the environment. In the past five years we have already managed to reduce the environmental impact tremendously. The HYVOLUTION-technology is much cleaner than hydrogen production with natural gas. The biggest step we made was by lowering the fossil phosphate input and replacing it by renewable phosphate from sludge. We did five iterations to optimize the system. Early this year we worked with phosphate recovered from sewage. And the waste water that comes out of the bioreactors is no longer treated as waste but can be used as a fertilizer. I don't think

these environmental gains have made the process more expensive. On the contrary, waste has become a valuable resource.
Hydrogen is now mainly used in oil refineries for chemical reactions, but I see a bright future for hydrogen as an energy carrier. Therefore I am also involved in the preparation of an exploitation plan to upscale the current 2 kW installation to a full size demo power plant of 500 kW, which should be in operation in ten years'



Training is necessary for partners but also for policy makers, students and the general public, according to Walter Wukovits, leader of WP 7 Training.
"The aim of Work Package 7 was to promote the use of hydrogen from biomass by training of interest groups. That was only partially successful due to lack of members in the industrial interest group established in WP 6. It seems to be too early to widely promote the process at this stage of development. The produced training materials will be made available on the HYVOLUTION website. Within HYVOLUTION, however, we trained many students and we gave courses and workshops for the partners - partially open to external participants. Several MSc and PhD students from various universities involved in HYVOLUTION did training courses and some universities also exchanged students. Furthermore, HYVOLUTION-related research was used in basic lectures and exercises."

"**Budgets for 'green' hydrogen production are very small**" says Pieternel Claassen, coordinator of HYVOLUTION.
"I have been working on biohydrogen production since 1999, but it has never been easy to get this topic on research agendas. But I am very excited with what we've achieved in HYVOLUTION. Cooperation between specialists from all over Europe really adds value. Also, you see that in countries where renewable energy is an important issue – such as Austria, Germany and Sweden – the partners often have various other activities in the field of sustainability. Knowledge gained from HYVOLUTION was therefore also used in other projects and vice versa.
Together with several partners from HYVOLUTION we have submitted a new project proposal (entitled HyTime) to the Fuel Cell and Hydrogen Joint Undertaking. The Joint Undertaking (JU) has a budget for this recent call of 180 million euros (half of it coming from the European Commission and the other half from the industry), but only 2 to 3 million is reserved for low temperature hydrogen production processes. And the demands are very high. That means that photofermentation (the second fermentation step in HYVOLUTION) does not stand a chance in this call. We have made tremendous progress in HYVOLUTION by increasing the solar to hydrogen energy conversion from 1.1% to 1.5%, but the JU demands a much higher efficiency: 5%.

The bad news is that for a possible follow up project the budget will be much smaller than the budget we had for HYVOLUTION, 10 million euros. The good news is that our proposal has successfully passed the thresholds, determined by external evaluators. We are now proceeding with negotiations with the JU. We still have a long way to go. For years I have tried to get low temperature biohydrogen production in several plans. Now that the JU has a relatively small budget available for this type of research, I am more or less obliged to set up a new successful project. I would like to for their efforts and hope we can continue working together in future projects."

The HYVOLUTION team stepping down after the 5th General Assembly meeting in Wageningen, Dec 15, 2011.

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