NEMESIS

SIXTH FRAMEWORK PROGRAMME

New Method for Superior Integrated Hydrogen Generation System

Contract No. 019827
STREP
Priority 6.1.ii Sustainable Energy Systems

Publishable Final Activity Report

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Revision [final]

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1 Project Execution

1.1 Description of Project Objectives

The scientific and technological objective of the NEMESIS project was to develop a small-scale, fuel flexible hydrogen generator that is capable of working with liquid and gaseous hydrocarbon feedstock. The existing natural gas based fuel processor technology of HyGear was used as a starting point, thus saving time and cost. This state-of-the-art small-scale, on-site hydrogen generator for decentralized applications was extended to a wider range of fuels and significantly upgraded by introducing advanced separation technologies, new innovative materials as well as cost-effective and highly efficient sub-components. An optimized system layout and the balance of plant analysis lead to an integrated modular design.

The new hydrogen generation unit comprises 3 modules:

- **Fuel Preparation Module (FPM)**: evaporation, pre-reforming and desulphurization of liquid feedstock
- **Hydrogen Generation Module (HGM)**: integrated steam reformer, water gas shift stage, and off-gas burner
- **Hydrogen Conditioning Module (HCM)**: purification of hydrogen rich gas employing the best of 3 alternative concepts (membrane separation, temperature swing adsorption with metal hydrides and improved pressure swing adsorption).

A proof-of-principal prototype being capable of producing 10kg H_2 per day was being built. Operation was demonstrated with natural gas and low sulphur diesel. This unit was used as a basis for an up-scaling strategy for fuelling 20 to 100 vehicles per day and the integration of decentralized hydrogen generation into the existing infrastructure of a fuelling station.

1.2 Contractors Involved

Table 1.1: Contractors involved in NEMESIS

Partic. Role*	Partic. no.	Participant name	Participant short name	Country
CO	1	German Aerospace Center, DLR e.V.	DLR	Germany
CR	2	HyGear B.V.	HYG	The Netherlands
CR	3	Umicore AG & Co KG	UMI	Germany
CR	4	Ballast Nedam IPM B.V.	BN	The Netherlands
CR	5	Repsol YPF	REP	Spain
CR	6	CERTH / CPERI	APTL	Greece
CR	7	Instituto Superior Technico	IST	Portugal
CR	8	Nanjing University of Technology	NJUT	China

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Project Logo

NEMESIS

1.3 Work Performed

Work performed during the first year

In the first six months of the project the targets and tasks of NEMESIS have been translated into functional requirements for the three modules and their sub-components. System specifications and process concepts for each unit have been defined and their impact on the other modules has been determined. They have been updated during the second half of the first project year. A first draft design of the 3D-layout of the fuel processor has been made to estimate the overall dimensions and the feasibility of the proposed process concepts.

Steady-state system simulation has played a major role in this reporting period. The influence of the data available for the liquid fuels on process conditions has been studied. In parallel the system was being implemented into the process flowsheeting software ASPEN Plus on an idealized basis without taking losses into account. On a modular level the influence of various operating parameters such as temperature, pressure, steam to carbon ratio, and air intake in the burner was investigated. After integrating the modules to an overall system with several possible combinations of process concepts the product gas composition at the interfaces and the off-gas quality were compared. Finally an evaluation of the system efficiency was done which was the baseline for the decision on process concepts.

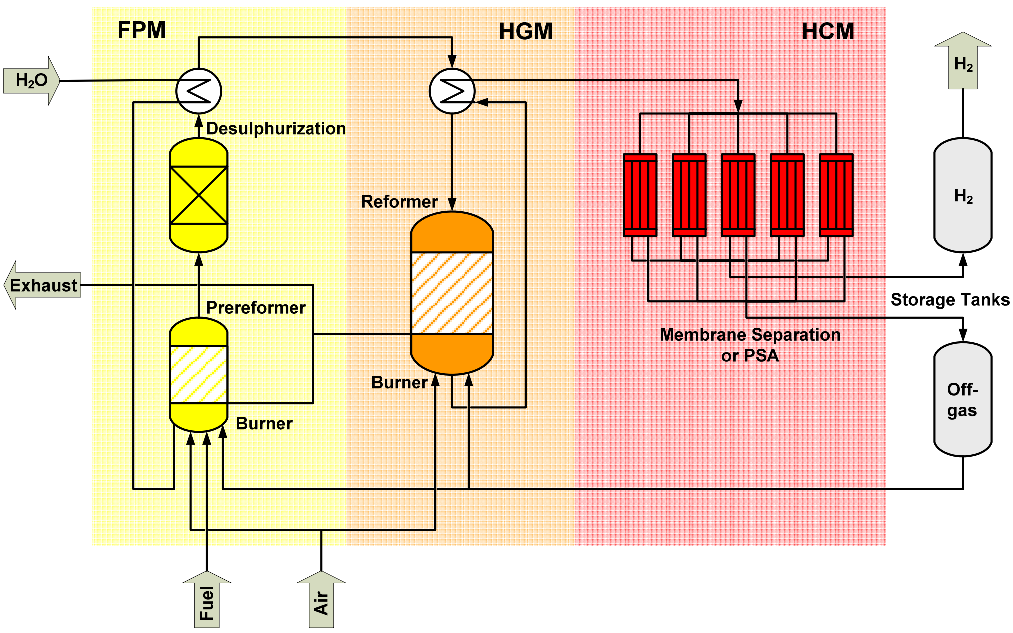

Figure 1.1: Overall process scheme of NEMESIS hydrogen generator system including the three modules FPM, HGM and HCM

On module and sub-component level, work has been directed towards the development of new functional materials that eventually resulted in the design and fabrication of these components. In the FPM a catalyst test rig has been built-up for the evaluation of pre-reformer catalysts. Adsorbents for desulphurization were synthesized and tested for liquid phase as well as gas phase due to the need within the different process concepts of the FPM.

For the Hydrogen Generation Module an extensive experimental investigation of the two reformer concepts was done to investigate the critical parts and decide on the applicability and restrictions of each concept. Subsequently a mechanical design study was performed to achieve the desired range of operating conditions. The design prospects for up-scaling to a future commercial scale were also taken into account. In parallel the integrated burner reformer assembly was investigated by simulation to analyse temperature and tensions in the unit and prevent failure by thermal stress.

The three technologies for hydrogen purification were investigated on different levels according to their technical maturity. In order to be a viable fall back option, continuous development of the commercially available PSA was required. This involved the study of alternative adsorbents and different control strategies. A test rig has been set-up for the experimental investigation, which was complemented by a simulation tool to study pressure and gas transients in the adsorbent. For the membrane separation unit several test membranes have been prepared by electroless plating on single-channel and multi-channel supports. To improve membrane selectivity while limiting membrane thickness a novel repairing option has been developed. A testing system for membranes as well as membrane supports was set-up. The measured results for membrane permeability and activation energy were compared to literature values. The influence of temperature and pressure was investigated for a mixture of H_2 in N_2. The metal hydrides being suitable for temperature swing adsorption were identified by a literature survey. The layout of a test facility was finalized and testing procedures defined. Various metal hydride tanks were acquired. Finally a theoretical model was built to represent the thermodynamics and kinetics of the process.

Work Performed in the Second Year of the Project

Based on the decision that has been made on the most promising process concept for the hydrogen generation system at the end of the first project year, work on sub-component and overall system level has been concentrated in the second reporting period on realizing this concept within the proof-of-principle prototype unit.

Steady-state system simulation has been upgraded by the consideration of losses for the various process steps. An evaluation of the different process concepts was undertaken in regard to overall system efficiency and potential for internal heat management. The final ASPEN Plus process flowsheet was used to give input on operating conditions such as gas compositions and feed volumes to the experiments being conducted on subcomponent level.

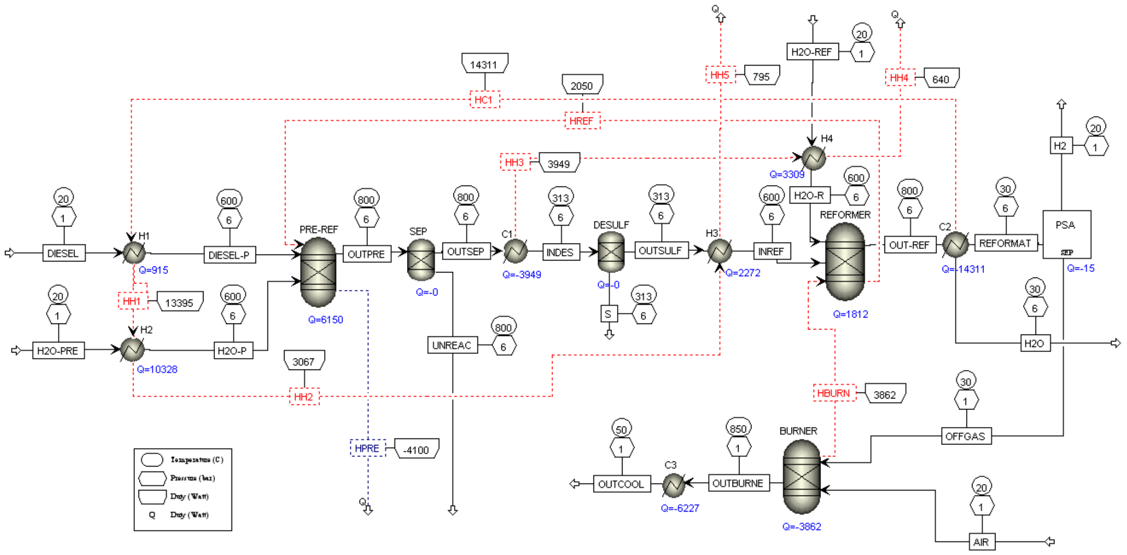

Figure 1.2: Aspen Model based on process scheme of NEMESIS-prototype with heat integration

The development of the hardware for the Fuel Preparation Module was concentrated towards the pre-reformer. In particular the evaporation of the liquid feedstock and coke-free heating-up of the vapour mixture to conversion temperatures was investigated with an experimental setup. Furthermore various options for the realization of the burner for start-up and steady-state operation have been investigated and a decision has been made for using a dual-fuel burner by utilization of a joint air register, a mechanical atomizer and a gaseous fuel injection system.

The development of the pre-reformer catalyst has been brought forward by the start-up of the laboratory test facility. Extensive pretesting with single hydrocarbons and diesel resulted in coke-free operation at temperatures up to 600°C. Finally, the definition of the testing protocol at the end of that year was the basis for the catalyst screening tests to follow in the beginning of the third year.

In regard to desulphurization a decision has been made to only build a gas phase unit for the proof-of-principle prototype. Adsorbents for liquid desulphurization have shown very promising results, but their volumetric capacity, handling and regeneration is not yet on a technological level needed for prototype scale. Nevertheless, the most promising powders were used to produce a small amount of desulphurized diesel for laboratory scale catalyst testing. Improvements in the preparation of powders for gas phase desulphurization have been translated into the coating of monolithic samples. Break-through experiments were used to determine the capacity of the adsorbents for layout of the insert for the prototype unit.

Within the Hydrogen Generation Module the draft design of the reformer has been completed based on the results from the tests having been performed in the first year. In parallel simulation work was conducted to investigate the heat and temperature distribution in the burner and the reformer. The numerical model was verified by tests having been performed with a half sized burner model. In upgrading to the full size burner, inconsistencies have been detected that could finally be solved with the company supplying the simulation software. Thereafter the model for the burner and the reformer could be coupled. The results from finite element analysis of the burner hull showed that the thermal stresses implied, without considering creep, were close to the material limits. Thus an adaptation of the design had to be considered.

The three different processes for the Hydrogen Conditioning Module have been investigated according to their different development level. The PSA has been significantly upgraded by using a single layer bed and new manifolds and valves, which resulted in an increase of adsorption time and efficiency of the system. The optimum operating conditions were determined using an improved software control.

For the membrane system the impact of impurities and steam in the feed gas has been investigated and the temperature range for coke-free operation has been determined. In regard to up-scaling to prototype level it was decided not to use multi-channel supports, as their sealing and defect-free preparation is not quite fulfilling the NEMESIS targets yet. A design for the modular setup of a prototype membrane unit has been made that was tested separately from the rest of the system.

Experimental investigation of the use of metal hydrides for purification purposes has shown that the impurities being present in a reformate gas were limiting the performance drastically after a few cycles. The metal hydride activity could be regenerated. Therefore the work originally planned has been redirected to identify the possible use of such materials for hydrogen compression. Tests carried out between ambient temperature and 100ºC led to modest pressure increase and several types of metal hydrides would be required for useful purposes.

Regarding the experimental setup at HyGear for the test of the prototype first adaptations of the existing test rig have been made by replacing the existing PSA by the upgraded NEMESIS PSA unit. Also various preparations have been made to allow for the use of liquid fuels as feedstock.

Finally, the economic evaluation has been started by identifying appropriate alternatives for hydrogen and off-gas storage without changing the view of an existing petrol station. A first outlook on the integration of all units necessary for serving hydrogen fueled cars has been made including the hydrogen generator, low pressure underground storage, compressor and dispenser in a highly integrated unit.

Figure 1.3: Laboratory installations for testing of function materials such as pre-reformer catalyst (left), gas-phase sulphur adsorbents (middle) and membranes (right)

Work Performed in the Third Year of the Project

In this last year of the project the main goal was to realize the proof-of-principle prototype unit and test it on natural gas as well as on diesel feedstock for at least three months. Work was performed on several levels from laboratory scale to prototype scale depending on the utilization of the results in the final prototype unit.

A final process flow diagram (P&ID) of the prototype unit was established in the first half of the year after pre-testing of the fuel preparation module which resulted in an adjustment of the operation strategy for the pre-reformer and consecutive hardware changes. The finalisation of the design of the reformer and burner required some minor revisions to the P&ID.

The FPM hardware underwent three test series, starting with a review of the chosen steam generators regarding stable operation and completeness of evaporation. Also their capacity in terms of power input for the given water feed stream was evaluated. Extensive testing was conducted with the pre-reformer in a separate test setup at low and high operating pressure. A temperature range between 600 and 800°C was covered with these investigations in order to prevent catalyst degradation due to sulphur poisoning or gum formation. Results were very promising with hydrogen concentrations above 60% in the pre-reformate at 800°C and about 90% of the diesel being converted. At lower temperature levels the activity of the catalyst was not satisfying and therefore it was decided to operate the pre-reformer in the overall system at high temperatures to prevent coke formation or condensation of un-reacted diesel in components downstream and in the tubing. Finally the desulphurization unit equipped with one monolith was attached to the pre-reformer to check if the operating temperature was sufficient and all hydrogen sulphide was removed from the gas stream. After this test series it could be concluded that the FPM was ready to be connected to the overall system.

To evaluate the pre-reformer catalyst in more detail investigations on laboratory scale were conducted in parallel. The performance of a wide series of catalyst samples was characterized within screening tests between 450 and 600°C. Subsequently the most promising catalyst formulations were tested in prolonged test series on degradation effects. Coking could be excluded, but irreversible sulphur poisoning reduced the catalyst activity at pre-reforming temperatures below 550°C. This could be approved with comparative test runs applying diesel feedstock that had previously been treated by liquid desulphurization which resulted in a reduction of the original sulphur content of 5 ppmw down to 0.61 ppmw.

Figure 1.4: Gas-phase desulphurization unit with 4 monolithic absorber inserts

Regarding the desulphurization activities liquid desulphurization was focused on the production of a sufficient amount for the above mentioned lab-scale investigations to approve and quantify the positive effect of sulphur reduction on catalyst performance. Regenerability of the used desulphurization material could be demonstrated with an organic solvent. An efficient and safe method for disposal or recycling for this chemical still has to be found.

The development of the material selected for gas-phase desulphurization was completed with break-through experiments to determine its sulphur uptake capacity. Due to a failure in the detection system after 33h on-stream this experiment could not be continued until the end. A rather conservative value of 60 mg sulphur uptake per gram of sorbent was therefore taken as a basis for the coating process of the large-scale, cylindrical monoliths for the prototype unit.

Work performed for the Hydrogen Generation Module in the last year was concentrated on the finalization of the CFD simulation of the burner and the reformer as well as the numerical coupling of both sections. The simulation results entailed a change of the material for the burner providing a higher heat resistance. Also, some revisions in the design of the inlet section were made to prevent recirculation of the combustion gases within the burner. For the reformer the exact location and size of the catalyst section was investigated by simulation. The final design was decided on all available results available for a simplified design with sufficient strength and safety. Consequently the HGM hardware could be built in time.

Regarding purification of the reformate in the Hydrogen Conditioning Module it has been defined at the end of the second reporting period to realize the proof-of-principle prototype unit with an improved PSA system which has already been fabricated in the second year of the project. Membrane separation also reached prototype state with a unit of modular design. The first three months of the third year were used to fabricate the membranes needed to equip the prototype unit. Thereafter it was shipped to DLR to be tested in a testing environment of appropriate scale. Various test series with different fuels ranging from pure hydrogen to synthetic reformate gas were run to evaluate the recovery rate of the membrane unit and the quality of the purified hydrogen stream. General tendencies from laboratory investigation of the membranes could be verified in prototype scale, but some limitations arouse from leakage of the tubing system incorporated within the unit.

Figure 1.5: Prototype scale membrane separation unit and integration into the Liquid Fuel Test Unit at DLR for testing.

The investigations on metal hydrides were redirected in the third year to the evaluation of the application of this material within a hydrogen production process. Based on literature studies and experimental investigations on the influence of impurities in the hydrogen stream on the metal hydrides their potential use could be narrowed down to hydrogen purification within an improved reactor configuration. In contrast, applying them for hydrogen compression seems to be less favourable.

The outside facilities for prototype testing at HyGear have been upgraded in the third year towards full gas and electricity hook-up for several test units. After approval of the functionality of the various system modules by separate testing in the test stands inside, they were mounted in the NEMESIS test rig outside. A first test series was run on natural gas with the HGM and HCM. Thereafter the complete system was tested successfully on low sulphur diesel. System performance was evaluated in regard to start-up time, hydrogen product gas flow rate and purity against the technical targets for the prototype unit outlined in the beginning of the project.

Figure 1.6: NEMESIS proof-of-principle prototype (middle) with Fuel Preparation Module (right) and Hydrogen Generation Module (left)

Having been started in the second year, the work on economic evaluation was finalized in the third year of the project. Different hydrogen compression strategies were outlined and evaluated under the aspect of integration into a refuelling station. Up-scaling to a unit with a hydrogen capacity of 250 Nm^3/h and an outlook for a commercial design was outlined taking technical risks into account based on the experience gained within the project. The potential of combining the supply of hydrogen with other alternative fuels such as CNG, LNG, biogas or ethanol at one station for better public acceptance and market penetration potential was investigated as well. Finally a cost model was set up to calculate the revenue of the investment for a commercial system of the NEMESIS type and identify an appropriate funding scheme.

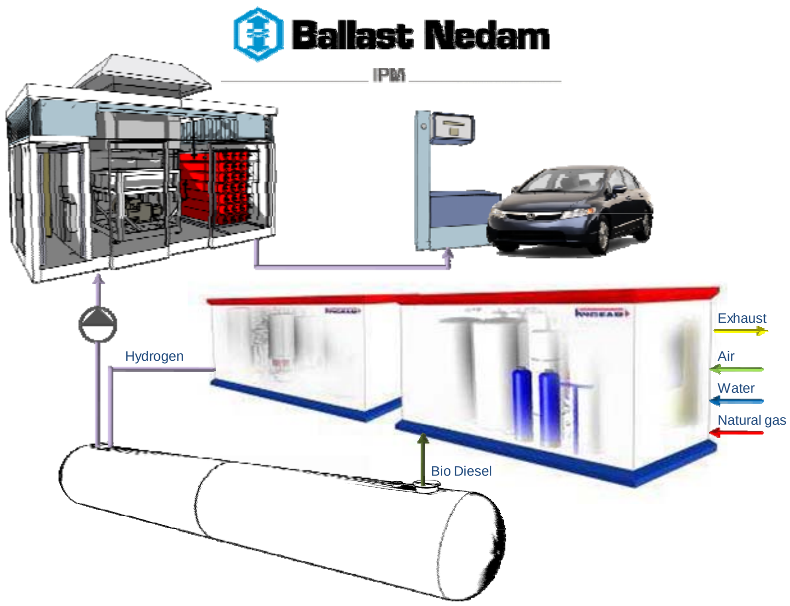

Figure 1.7: Setup for a hydrogen installation with an upscaled NEMESIS hydrogen generator running on bio-diesel and a two compartment low pressure underground storage tank.

1.4 End Results

Within the three years of its duration the NEMESIS project has resulted in the development of a proof-of-principle prototype to generate 5 Nm^3/h of hydrogen from natural gas and low sulphur diesel by steam reforming. Three modules were integrated to an overall system:

- **FPM**: Pre-reformer operating at 800°C and gas –phase desulphurization unit
- **HGM**: Reformer with integrated off-gas burner operating at 800°C, no shift stage
- **HCM**: Single layer pressure swing adsorption unit

A membrane separation unit for hydrogen purification was also built in prototype-scale and tested separately from the overall system with simulated reformer product gas.

Within the various modules and components detailed laboratory investigations were conducted on functional materials such as adsorbents for gas-phase and liquid phase desulphurization, pre-reforming catalysts, membranes for hydrogen purification and metal hydrides. CFD simulation of the burner and reformer was used to improve the design and to assess thermal and mechanical stress of the materials. Complementary simulation was carried out on process level to identify the overall configuration of the system and evaluate system efficiency. Based on the technical results for the NEMESIS technology an economic evaluation with an outlook for a commercial design and its integration into the existing refuelling station infrastructure has been conducted in the last year of the project.

The results achieved for the various components and the overall system can be summarized as follows:

- **Pre-reformer:** A prototype unit being operated at 6 bars and withstanding high temperatures equipped with an external burner being fuelled with natural gas has been developed. Steam is generated externally and mixed with the evaporated diesel before entering the pre-reforming section. The pre-reformer catalyst works without poisoning and coking above temperatures of about 550 to 600°C. In a lower temperature range catalyst activity towards pre-reforming and sulphur resistance still have to be improved. To be on the safe side the prototype pre-reformer unit is operated at a temperature of about 800°C with a steam to carbon ratio of 4.5.

- **Desulphurization:** A prototype unit for gas-phase desulphurization operating at 200 to 400°C being equipped with 4 cylindrical monoliths coated with a $Zn_xCu_yO_z$ sorbent has been developed. The sulphur uptake capacity of this material is estimated to be above 60 mg sulphur per gram of sorbent. In parallel liquid desulphurization with activated carbon was brought to a stage where sufficient amounts of deeply desulphurized diesel with 0.61 ppmw sulphur for laboratory investigations could be produced. Regeneration of the sorbent is possible with an organic solvent. Yet a method for disposal or recycling of this solvent has to be found.
- **Reformer and burner:** A CFD model for the burner and reformer has been setup and thereafter both sections were coupled. Verification of the model has been achieved with a half-scale replica of the burner for various operating conditions. The results of this investigation have been used to upgrade the design and material of the existing integrated natural gas reformer of HyGear to be operated at elevated pressures of 6 bars with multiple pre-reformate gas mixtures. The burner can be run on off-gas as well as natural gas.
- **Pressure swing adsorption:** The existing PSA has been redesigned and a prototype unit with upgraded components, changed mechanical design and a single layer bed with an optimized control strategy has been built-up. Thus an efficiency of the system within stand-alone pre-testing of above 73% is achieved.
- **Membrane Separation:** Detailed investigation of various techniques for the fabrication of supported Pd and Pd/Ag membranes including the use single-tube and multi-channel ceramic substrates, electroless plating and photocatalytic deposition and several methods to repair membrane pinholes. For the scale-up to a prototype unit proper membrane sealing had to be developed as well. Finally a modular prototype unit comprising 20 single-channel Pd membranes in 4 groups of 5 membranes with an overall membrane area of 2600cm^2 has been built.
- **Metal Hydrides:** The kinetic behaviour and poisoning by impurities such as CH_4, CO and CO_2 of several $LaNi_5$ based materials has been investigated. It has been concluded that the applications of metal hydrides within a hydrogen production process has to be directed towards hydrogen purification by temperature swing adsorption whereas hydrogen compression is not favourable.
- **Testing of the proof-of-principle prototype unit:** Being run on natural gas, the system was capable of starting-up within 45 minutes and producing 5 Nm^3/h hydrogen at a pressure between 5 and 6 bars with a quality of 4.0 or even higher without any traces of H_2S and NH_3. Also when tested with low sulphur diesel (8 ppmw sulphur) the prototype could be started-up within 45 minutes even though it was favourable to pre-heat the pre-reformer to 700°C. When using up to 2 litres of diesel per hour 99% of the liquid feed-

stock was converted into a hydrogen rich gas. For an output of 5 Nm^3/h hydrogen a quality of 2.5 was reached. To increase the hydrogen purity to 99.99% the production capacity had to be reduced to 2.75 Nm^3/h. Overall more than 200 hours of testing could be accumulated.

- **System simulation:** A steady-state model of the overall system was setup with a process simulation tool which resulted in the definition and evaluation of various possible process concepts in the first year of the project. Verification of the model for the NEMESIS setup with test results from the proof-of-principle prototype was achieved successfully by adaptation of the process parameters. Based on the simulation an efficiency of the overall process based on the lower heating value of the hydrogen product stream of 67% is achieved assuming a PSA efficiency of 70%.
- **Economic evaluation:** For implementing hydrogen in existing public petrol stations with minimal impact on the view of the station the use of low pressure underground storage with a two compartment tank for hydrogen and diesel in combination with a compressor and a small high pressure storage was identified as the best solution. For up-scaling and market introduction it is recommended to develop a system with a capacity of 250 Nm^3/h hydrogen and integrate it with other alternative fuels into a new type of refuelling station. The cost analysis for a hydrogen generator based on the NEMESIS technology resulted in a return of investment of 7.5% within 10 years. This means that the investment level in the start-up phase as well as the fixed cost level are too high. As a consequence grants are needed in the beginning to bring such technology to the market.

2 Dissemination and Use

The use of a hydrogen generation system of the NEMESIS type is clearly directed towards decentralized and onsite, small-scale hydrogen production. With the prototype developed within the three years project a first start is made for a production capacity of 5 Nm^3/h (10 kg H_2 per day). To solve the technical challenges and keep the risks within a controllable range the next step would be to up-scale the system by a factor of 10 to an output of 50 Nm^3/h (100 kg H_2 per day). Within 2 to 3 years from now a first prototype of such a system could be developed and running. The capital investment costs are estimated to be about 2500 to 3000 € per kg H_2 produced per day. Finally, based on a gradual growth of the market a system with a hydrogen production capacity of 250 Nm^3/h (500 kg H_2 per day) could be developed for a price of 750.000 € which corresponds to capital investment costs of 1500 € per kg H_2 produced per day.

It is recommended to realize the introduction of hydrogen being available at refuelling stations as a car fuel in combination with other alternative fuels such as CNG, LNG, biogas and ethanol. This would generate enough volume and the possibility of combining the availability of such fuels at one station to increase public awareness and acceptance towards future, environmentally friendly technologies.