# Evaluation of sustainable hydrogen production pathways

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The present paper evaluates different hydrogen production technologies based on renewable energy and/or renewable raw materials. The investigated technologies are alkaline electrolysis, steam reforming of biogas, steam reforming of gasification gas, the coupled dark and photo fermentation as well as the coupled dark and biogas fermentation. Furthermore the steam reforming of natural gas has been included in the analysis as a reference technology. Each technology has been investigated with different plant layouts and/or different raw materials. All examined technologies are designed to produce hydrogen in a quality that is suitable for the use in mobile fuels cells. The presented evaluation is based on the production efficiency and on the energy efficiency of the different processes.

#### 1. Introduction

Hydrogen for the use in the automotive sector can be produced in various ways. Up to now only the steam reforming of fossil fuels and the water electrolysis are proven and commonly used hydrogen production technologies. Hydrogen production based on biomass as raw material on the other hand is still technology under development. This fact makes it difficult to identify the most promising renewable technologies at an early stage of development. One instrument to overcome this dilemma is the use of process simulation. This tool offers the possibility to build up theoretical plant layouts based on real process data that could for instance be taken from lab scale experiments.

This work presents results of process simulation that has been carried out for different hydrogen production technologies. These technologies cover the state of the art technologies reforming of natural gas and alkaline water electrolysis as well as biomass based technologies. The latter comprise the reforming of biogas, the reforming of biomass gasification gas, the coupled dark and photo fermentation and the coupled dark and biogas fermentation. All biomass based technologies have been investigated with different kinds of raw materials and/or different plant layouts. Each of the analyzed plants is designed to meet the quality requirements of mobile fuel cells. The size of the biomass conversion plants is chosen in a decentralized scale in order to offer the possibility of a sustainable hydrogen production. The subsequent processing of the produced biogas and gasification gas on the other hand is both analyzed in a decentralized and a centralized plant size. The simulation results are used to evaluate all technologies according to their hydrogen production and energy efficiency.

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## 2. Investigated Processes and Process Simulation

The process simulation within this work has been carried out with the commercial process simulation tool IPSEpro. Within this simulation tool new user models have been developed for most of the units necessary to build up the investigated hydrogen production plants. Only few models were available within the power plant library of the program (see www.simtechnology.com for details) or were taken from preceding works (Pröll et al. 2005, Pröll et al. 2007).

The steam reforming of natural gas is a well known and widely used technology for the production of hydrogen. This technology is, therefore, considered as a reference technology within this work. A second commonly used technology, the alkaline water electrolysis, is also included in the investigation as it can be seen as renewable hydrogen production technology provided that electricity from renewable sources, like wind or water power, is used for its operation.

Beside these well established technologies four technologies based on biomass that are still in the development stage have been investigated. The first technology is the gasification of wood, which has been considered with three different plant layouts. The simplest layout includes a purification of the gasification gas and a direct onsite steam reforming of the purified gas. The second plant layout includes a CO<sub>2</sub>-separation step between the purification and the steam reforming step. In the third layout the purified gasification gas is further upgraded to natural gas quality and fed into the natural gas grid. The gas from several gasification plants is then transferred to a central steam reforming plant via the gas grid.

The second biomass based hydrogen production plant is based on biogas fermentation. As shown in Figure 1 the biogas based plants have also been considered with the same three plant layouts as the gasification plants. All three biogas plant layouts have been analyzed with maize, potato residues and municipal bio waste as raw materials.

The third bio-hydrogen production technology is the coupled dark and photo fermentation, which is a rather new technology. The dark fermentation leads to a gas mainly consisting of  $H_2$  and  $CO_2$  and a fermentation residue that is rich in organic acids. The photo fermentation on the other hand uses the organic acids as a substrate that is again converted to a hydrogen rich gas. This technology has only been investigated with one plant layout but both with maize and potato residues as raw material.

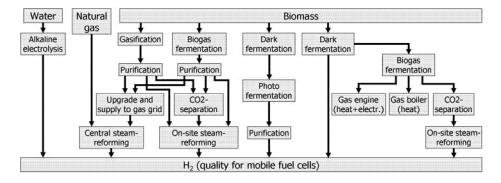


Figure 1: Overview of all evaluated process chains

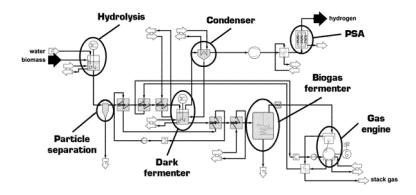


Figure 2: Flowsheet of the coupled dark and biogas fermentation with biogas utilisation in a gas engine to produce process heat and electricity.

The last investigated technology is the coupled dark and biogas fermentation. This technology uses the acid rich residue from the dark fermenter as substrate for a biogas fermenter to produce a methane rich biogas. The produced biogas can then be used in different ways. Within the present work the biogas is either utilized in a gas engine to produce electricity and heat, that is used to heat up the substrate of the dark fermenter (see Figure 2), or in a gas boiler to produce process heat only (see Figure 3). Another investigated option is to separate the CO<sub>2</sub> from the biogas and to convert the obtained gas to hydrogen in an onsite steam reforming plant, as shown in Figure 4.

The coupled dark and biogas fermentation is based on the publications of Claassen (Claassen et al. 2005, Claassen et al. 2000) concerning the performance and size of the dark fermentation step. The built up model for the biogas fermenter operated with the organic acid rich effluent of a dark fermenter was verified with data taken from literature (Chu et al. 2008, Kyazze et al. 2007, Zhu et al. 2008).

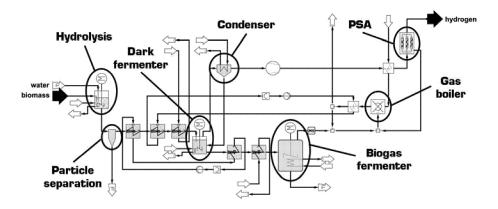


Figure 3: Flowsheet of the coupled dark and biogas fermentation with biogas utilisation in a gas boiler to produce process heat.

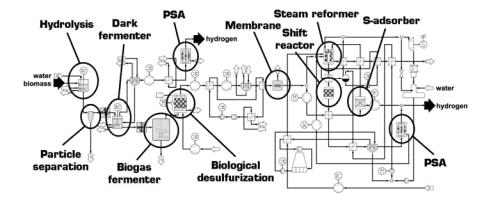


Figure 4: Flowsheet of the coupled dark and biogas fermentation with  $CO_2$  separation and onsite steam reforming plant.

Due to the early stage of development of the coupled dark and biogas fermentation it was decided, similar to the coupled dark and photo fermentation, to base the performance calculations on a range of conversion factors rather than on single data taken from literature. Hence, the calculations have been carried out for the combinations of 80% and 70% conversion of the influent in the dark fermenter and biogas fermenter, respectively, as well as 100% conversion in both fermenters. The lower boundaries seem to be realistic conversion ratios and the upper limits of 100% conversion represent the theoretical maximum. The lower limit for the dark fermenter also corresponds to the value chosen for the coupled dark and photo fermentation. Similar to the simulation of the dark and photo fermentation it was assumed that only acetic acid is built during the dark fermentation step of the coupled dark and biogas fermentation.

A detailed description of the production plants for the steam reforming of natural gas, the alkaline water electrolysis, the different gasification and biogas plants as well as the coupled dark and photo fermentation have been presented elsewhere (Miltner et al. 2008a, Miltner et al. 2008b) and will therefore not be treated in detail in this paper.

### 3. Results and discussion

The results for the processes that have already been presented in previous work (Miltner et al. 2008a, Miltner et al. 2008b) differ from the ones presented in this paper. This is caused by the improvement of the simulation models that took place in the meantime. This is especially true for the modelling of the steam reformer, where the earlier results are only based on settings for the conversion ratios. The improved model now includes equations for the characterisation of the position of the equilibrium for 7 equilibrium reactions. Furthermore newer process data were used for the calculations if procurable. The results of the specific hydrogen production calculations for the biomass based processes are shown in Figure 5. It can obviously be seen that not only the choice of the technology but also the choice of the raw material has a strong influence on the production performance.

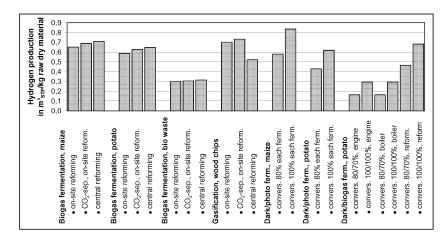


Figure 5: Comparison of the specific hydrogen produciton of all biomass based technologies.

The biogas based plants show the highest production rates for the plants with central steam reforming. The biomass gasification in contrast should not be built with a central reforming plant due to hight conversion losses from hydrogen to methane and back to hydrogen. The hydogen production values for the dark and biogas fermentation with gas engine and gas boiler are, as expected, low as only the dark fermenter produces hydrogen. But the performance of the layout with onsite reforming is in the same range as the dark and photo fermentation if the same raw materials are compared.

The energy efficiencies of all investigated processes are presented in Figure 6. The total energy input, as used in this diagram, is the sum of all inputted energies (raw material, electricity and heat) minus produced electricity. The surplus of produced energy leads to the effect that some of the values related to the total energy input are greater than the values related to the raw material energy input.

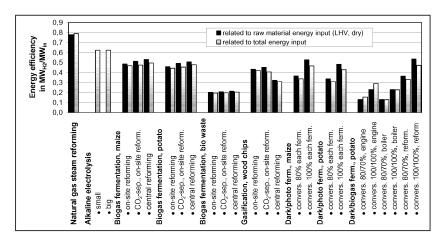


Figure 6: Comparison of the energy efficiencies of all investigated technologies.

Within the renewable technologies the alkaline electrolysis has the highest energy efficiency. The reforming of biogas from maize and potato leads to the highest efficiencies among the biomass based technologies, followed by the gasification cases with on-site reforming and the realistic values for the dark/photo fermentation and the dark/biogas fermentation with on-site reforming. However, compared to the steam reforming of natural gas all renewable technologies show considerably lower efficiencies. But the most efficient renewable processes already offer a good alternative.

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