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# Identification of a Suitable Process Scheme for the Non-Thermal Production of Biohydrogen

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To make the future Hydrogen Economy fully sustainable, renewable resources instead of fossil fuels have to be employed for hydrogen production. Process simulation will be used to compare process schemes involving different unit operations to perform the necessary process steps to produce hydrogen in a non-thermal way using bacteria with a special focus to small scale units. Overview on process steps, description of boundaries and models for process simulation as well as results of first parametric studies will be presented in this paper giving insight to challenges in process integration and future work.

## 1 Introduction

Hydrogen will be an important energy carrier in the future. At the moment hydrogen is almost completely produced from fossil fuels or from electrolysis of water. To make the future Hydrogen Economy fully sustainable, renewable resources instead of fossil fuels have to be employed for hydrogen production. Besides biomass gasification, hydrogen from biomass can also be produced in a non-thermal way using bacteria.

During the last years different anaerobic and photo-fermentation processes were investigated to produce biohydrogen. But single stage processes at the moment do not work economically. A promising way for the production of hydrogen from biomass in a non-thermal way seems to be a 2-stage bioprocess consisting of a thermophilic fermentation step to produce hydrogen, $CO_2$ and intermediates followed by a photo-heterotrophic fermentation, in which all intermediates will be converted to further hydrogen and $CO_2$.

Most research at the moment is performed concerning selection of micro-organisms, optimization of yield and rate of hydrogen production as well as reactor design. Less attention is given to the design of the whole production process including feedstock pretreatment and gas upgrading as well as additional process steps necessary to successfully combine both fermentation processes and remove hydrogen from the fermentation broth.

Process simulation will be used to compare process schemes involving different unit operations to perform the necessary process steps to produce hydrogen in a non-thermal way with a special focus to small scale units.

## 2 Process Description

The novel approach in HYVOLUTION on non-thermal hydrogen production from biomass is based on a combined bioprocess employing thermophilic and phototrophic bacteria, to provide a high hydrogen production efficiency (Figure 1).

The process starts with the necessary pre-treatment of biomass to provide a suitable feedstock for thermophilic fermentation. Starch and sugar containing as well as lignocellulosic biomass will be considered with a special focus on residues from food processing. Since thermophilic bacteria are capable to utilize a wide range of organic substrates including hexose and pentose sugars as well as oligomeric carbohydrates new opportunities for additional agro-industrial chains in the field of biofuels will be available (Claassen et al., 2006a and b).

In the first fermentation step thermophilic bacteria growing at temperatures of at least 70°C produce hydrogen gas and organic acids as the main by-products. Depending on the fermentation pathway of the bacteria and built by-products different amounts of hydrogen per mole of sugar are yielded. Assuming that glucose is the substrate and acetic acid is the main by-product, the thermophilic fermentation can be represented by the following reaction:

$$C_6H_{12}O_6 + 2\ H_2O \rightarrow 2\ CH_3COOH + 4\ H_2 + 2\ CO_2 \qquad (1)$$

Experimental results indicate that yield values close to the theoretical limit can be obtained (Goorissen and Stam, 2006; Van Niel et al., 2002). Further reduction of acetic acid by means of thermophilic bacteria is thermodynamically unfavourable at moderate temperatures. However acetic acid can be used as substrate for hydrogen production in a consecutive photo-fermentation step (Koku et al., 2002). The overall reaction of the phototrophic step using acetic acid as substrate can generally be written as:

$$CH_3COOH + 2\ H_2O + \text{light} \rightarrow 4\ H_2 + 2\ CO_2 \qquad (2)$$

Through the combination of thermophilic fermentation with photo-fermentation, complete conversion of the substrate to hydrogen and carbon dioxide can be obtained, resulting in 75% conversion efficiency or 9 moles of hydrogen per mole of glucose (Claassen et al., 2006a and b).

In order to provide pure hydrogen, carbon dioxide has to be separated from the biological gas product. Due to fluctuations in quantity and quality of the raw gas produced in the bioreactors, a specific gas treatment is required. Since industrially applied state-of-the-art gas cleaning systems are expected to be inefficient from the energetical point of view, besides state of the art hydrogen-upgrading processes, novel membrane contactors will be evaluated and integrated in the HYVOLUTION process. In lab scale experiments these systems demonstrated highly efficient carbon dioxide separation from gas mixtures of biological origin (Teplyakov et al., 2002).

The aim of HYVOLUTION project is to make a blue-print for an industrial bioprocess for decentralized hydrogen production at small-scale from locally produced biomass, delivering a 10-25 % coverage of the EU demand on hydrogen for use in power or bio-fuel production at 10 Euro/GJ.

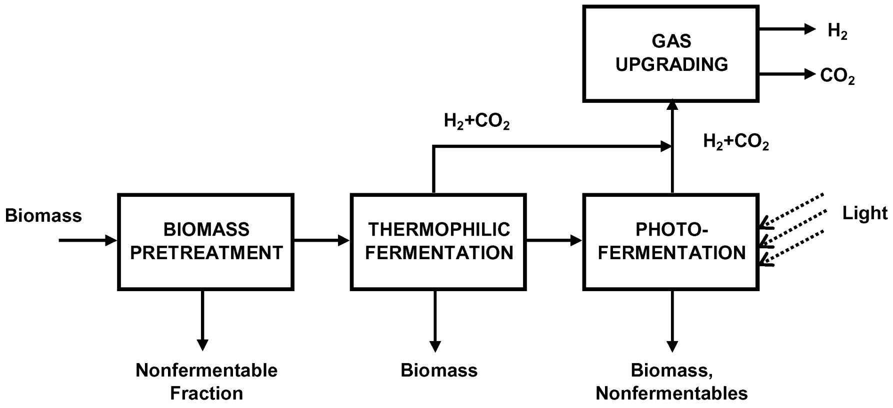

*Figure 1: Scheme of HYVOLUTION process*

## 3 Process Simulation and Models

Investigation and optimization of different process steps is mainly based on experimental work with focus on elucidation of the fundamental microbiological procedures, selection of micro-organisms and optimization of process parameters of different process steps to increase hydrogen yield and decrease by-product formation.

But optimization of single steps might not give a satisfactory overall process. Therefore process simulation was selected to combine and integrate the single process steps.

ASPENplus® software package is used for simulation purpose. To calculate the properties of biomass and involved sugars (poly-, oligo-, di- and mono-saccharides) NREL's Physical Property Databank (Wooley and Putsche, 1996) was implemented after addition of missing components – mainly connected with the pretreatment of lignocellulosic materials.

For a first evaluation of the overall process starch was selected as feedstock. The pretreatment is a conventional and proven liquefaction and saccharification process for wheat starch. The milled feedstock is first mixed with water to 35 w% solid mixture. Alfa-amylase is added and the mixture is heated to 105°C with direct steam. The slurry is then kept at 95°C for 2 h in the liquefaction step. Finally the liquefied feedstock is fed to the saccharification reactor and mixed with gluco-amylase. A residence time of 72 hours at 60°C gives an overall conversion of starch in the pretreatment of about 98%.

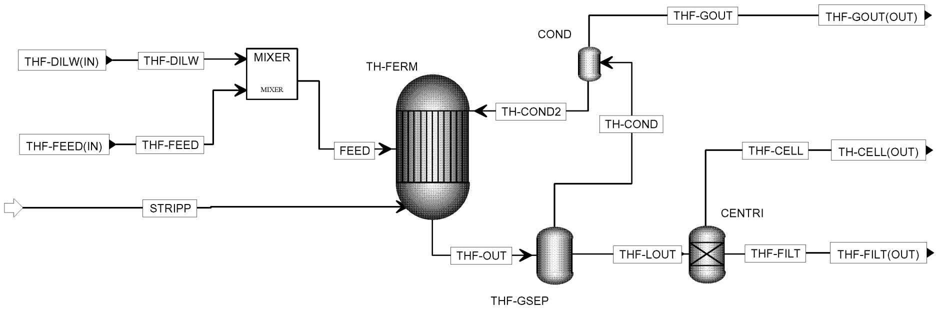

*Figure 2: ASPENplus®-flowsheet of the thermophilic fermentation step*

The thermophilic reactor runs at 70°C. The reactor is equipped with a condenser working at 15°C and returning 96% of the water in the gas outlet stream to the fermenter (Figure 2). In the thermophilic fermenter 95 w% of the glucose is consumed. 80 % of glucose goes to hydrogen and acetic acid production following equation 1. An amount of 15% glucose is used for cell production.

The photo-fermenter is operated at 30°C with similar preliminary assumptions concerning conversion of acetate as before for sugar. Again 5% of feedstock leaves the system unused. Changing hydrogen production rates and gas flow rates caused by the day/night cycle are considered at the moment by calculating a best/worst-case scenario.

For the first simulation of HYVOLUTION process MEA-absorption/desorption was chosen for gas-upgrading since it is a well documented process with well known performance. Configuration and operation data for MEA-absorption/desorption are taken from Rao and Rubin (2002) as well as White (2002).

## 4 Results and Discussion

The simulation models based on simple stoichiometric conversion are used for parametric studies to show bottlenecks and possibilities for improvement as well as increasing process efficiency.

The process was scaled to produce 50 kg/h hydrogen. Following the process conditions and boundaries given above 490 kg/h of pure starch is needed giving 700 kg/h dry raw material, when calculating with a starch content of wheat of 70%.

During thermophilic fermentation 3.4 mol $H_2$ per mol glucose consumed are produced giving 9.435 kmol/h of hydrogen. During photo-fermentation 14.2 kmol/h hydrogen is produced corresponding to a hydrogen yield of 3.8 mol hydrogen per mol acetic acid. Gas outlet composition for thermophilic fermenter, photo-fermenter and MEA-absorption (best case) are summarized in Table 1.

First calculations give a high dilution rate in the fermenters. So far no recycling of process water is considered. Although the high dilution rate underlines the importance of water recycle the enrichement of inert or inhibitory compounds need to be investigated.

Figure 3 shows the influence of feedstock conversion on the raw material demand and hydrogen production. Decrease of conversion either causes a reduction of hydrogen output or needs an increase in raw material feed to keep hydrogen production constant.

Unfortunately the high hydrogen content in product gas after the first fermentation step shown in Table 1 will not be reached in real process, since the thermophilic fermentation suffers from hydrogen inhibition at partial pressures of more than 20 kPa. Therefore it is necessary to introduce an additional gas stream to the thermophilic fermenter to strip $H_2$ from the fermentation broth.

*Table 1: Gas outlet composition of different process units (in mol-fraction)*

| Component | Thermophilic Fermenter | Photo-Fermenter | MEA-Absorption |
|---|---|---|---|
| Hydrogen | 0.68 | 0.67 | 0.85 |
| Carbon Dioxide | 0.30 | 0.31 | 0,08 |
| Water | 0.02 | 0.02 | 0.07 |
| Acetate | trace | trace | - |

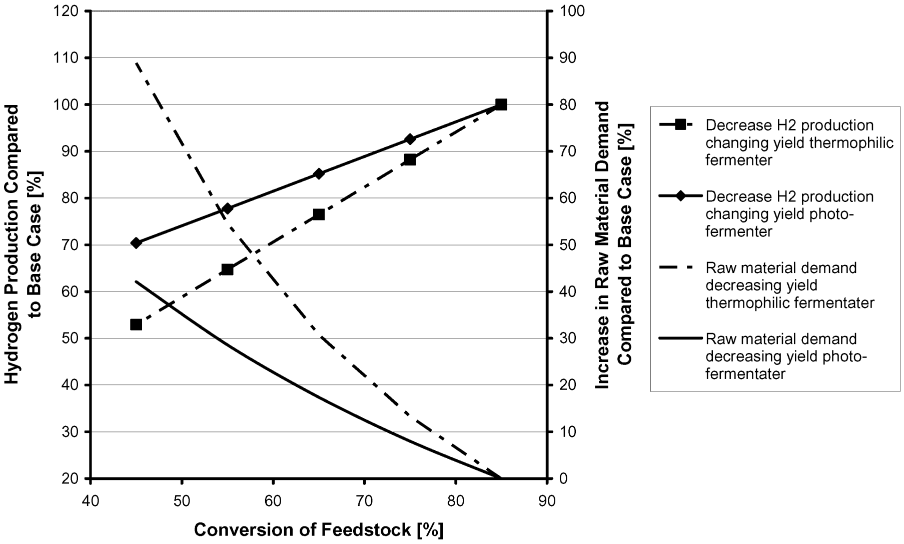

*Figure 3: Demand of raw material and production of hydrogen as function of feedstock conversion in thermophilic and photo-fermenter*

Careful selection of stripping-gas is necessary, since it has to be separated from $H_2$ during gas-upgrading. Recycling of a $CO_2$-stream from regeneration of MEA-solution will be assumed for stripping purpose during the first calculations, causing dilution of hydrogen in the combined product gas stream from thermophilic and photo-fermenter entering the gas-upgrading step (Figure 4).

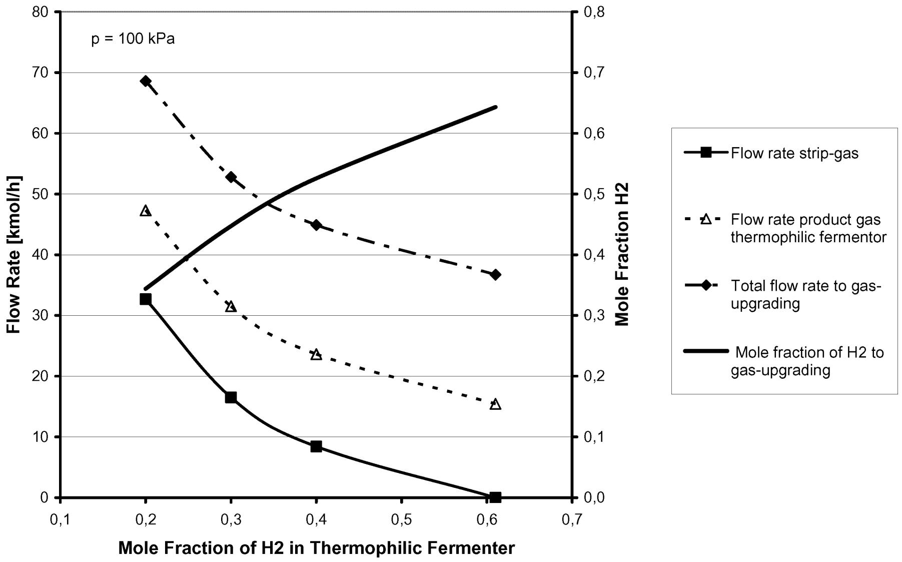

*Figure 4: Influence of stripping gas on flow rate and composition of product gas*

Especially when introducing the new membrane contactor it has to be evaluated whether a pre-concentration step for product gas from thermophilic fermenter might be necessary since also the worst case scenario (night) must be taken into account again changing gas composition and also gas flow rate.

The introduction of steam to the thermophilic reactor at slightly reduced pressure might be a workaround. The influence on energy demand of the process has to be evaluated.

The results - mainly based on theoretical assumptions concerning process conditions - presented here outline the importance of process simulation and process integration, but do not allow the comparison with experimental results of the different process steps and with literature. The models will be improved using data from experimental investigation of the fermentation steps, giving finally simulation results for the whole process comparable with other biological processes for the production of hydrogen

## 4 Summary and Outlook

Even starting with simple stoichiometric models which will be consequently improved by experimental results, it is possible to show dependencies between the different process steps and problems when combining these steps and support the selection of suitable process routes at an early stage of process development.

Within project work process simulation will be consequently used to compare process schemes involving different unit operations as well as to provide data for process engineering, costing, socio-economic analysis and life-cycle-analysis, finally enabling the selection of the most promising process route for HYVOLUTION process.

## 5 Acknowledgement

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