CHEMICAL ENGINEERING TRANSACTIONS Volume 21, 2010
Editor J. J. Klemeš, H. L. Lam, P. S. Varbanov
Copyright © 2010, AIDIC Servizi S.r.l., ISBN 978-88-95608-05-1 ISSN 1974-9791
DOI: 10.3303/CET1021193

Effects of Feedstocks on the Process Integration of Biohydrogen Production

Domenico Foglia[1]*, Walter Wukovits[1], Anton Friedl[1], Mattias Ljunggren[2], Guido Zacchi[2], Krzysztov Urbaniec[3], Mariusz Markowski[3]
[1] Vienna University of Technology, Getreidemarkt 9/166-2, 1060 Vienna, Austria
[2] Lund University, P.O.Box 124, SE-221 00 Lund, Sweden
[3] Warsaw University of Technology, Plock Campus, 09-402 Plock, Poland
dfoglia@mail.tuwien.ac.at

In order to make the hydrogen economy fully sustainable, renewable resources have to be employed for its production. Simulation models, developed with Aspen Plus to calculate mass and energy balances, were used to integrate the process steps necessary to produce pure hydrogen from biomass in a 2-stage fermentation process. Process options with barley straw, potato steam peels and thick juice as feedstocks have been compared based on basic process balances. High water and heat demand are reduced by introduction of heat integration and recirculation of process effluent. Under these conditions the production of hydrogen as energy carrier is technically feasible with all the considered feedstocks.

1. Introduction

Hydrogen is a carbon free energy carrier, which at the moment seems to be the only solution for long range vehicles without CO_2 emissions. At the moment a major drawback are the economic and environmental costs of hydrogen production. In fact, 95 % of hydrogen is currently produced from fossil fuels (CH_4 reforming and carbon gasification). This means that without carbon capture and sequestration (CCS), a hydrogen production facility would produce comparable CO_2 emissions as the use of fossil fuels in conventional combustion engines.

Fermentation of biomass residues and second generation biomass is a possible way to enable a sustainable production of hydrogen. Advantages connected to fermentative hydrogen production are mainly the local integration, due to possible adaptation to different types of feedstock, the use of effluents as fertilizers, and the reduction of economical and environmental impact of fuel transport.

A promising way for the biological production of hydrogen from biomass is a 2-stage bioprocess investigated in HYVOLUTION-project. The proposed process consists of a thermophilic fermentation step to produce hydrogen, CO_2 and organic acids followed by a photo-heterotrophic fermentation, in which the organic acids are converted to further hydrogen and CO_2 (Claassen and de Vrije, 2006).

Please cite this article as: Foglia D., Wukovits W., Friedl A., Ljungren M., Zacchi G., Urbaniec K. and Markowski M., (2010), Effects of feedstocks on the process integration of biohydrogen production., Chemical Engineering Transactions, 21, 1153-1158 DOI: 10.3303/CET1021193

This work wants to emphasize the changes in terms of energy and water demand when using different types of feedstocks investigated in HYVOLUTION project - potato steam peels (PSP), thick juice and barley straw.

2. Process Description

The process consists of four main steps: pretreatment, thermophilic fermentation, photo-(heterotrophic) fermentation and gas upgrading (Figure 1). Main parameters of the process steps are summarized in Table 1.

Strongly depending on the type of biomass, pretreatment is used to convert the carbohydrates of biomass in sugars usable in the thermophilic fermentation step. In the analyzed cases, for potato steam peels a standard process of liquefaction and saccharification has been used, while for barley straw it has been considered a mild-acid pretreatment. Thick juice doesn't require pretreatment, since it is a biomass in which sugar (sucrose) is directly available for fermentation.

The pretreatment process for potato steam peels is a standard liquefaction-saccharification conversion performed at temperatures of 90 °C and 60 °C, respectively. The process has already been described in detail in previous work (Foglia et al., 2010).

Pretreatment of barley straw requires high temperature and low pH to mobilize the sugars in cellulose and hemi-cellulose. Higher temperatures (160-180°C) lead to higher yields, but at the cost of higher content of inhibitors. An effective way of removing them is to process the substrate stream obtained from pretreatment with an overliming step, followed by reconditioning with acids.

The optimal parameters for the HYVOLUTION process are sulfuric acid load of 2 % (wt) of dried biomass, a temperature of 180 °C, and a pH of 10 for the overliming step.

The assumptions for this pretreatment have been taken from partner's experimental data as well as literature (Mohagheghi et al., 2006).

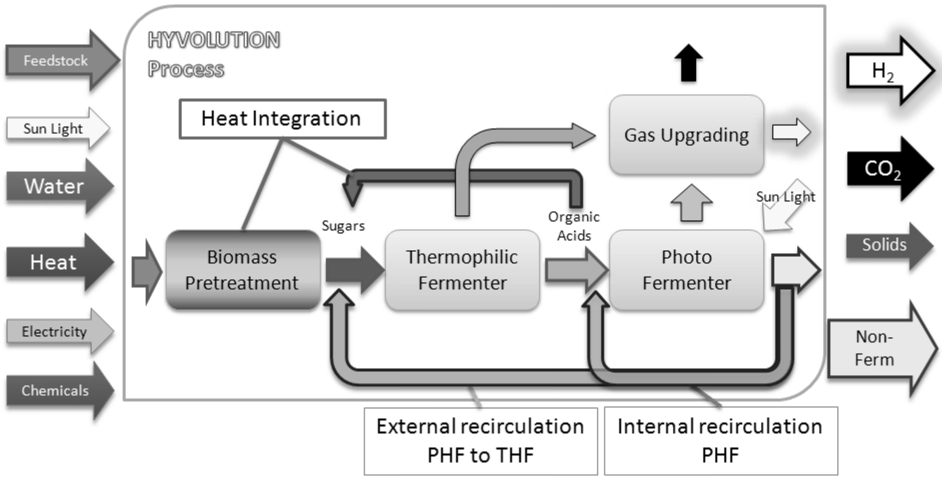

Figure 1: Scheme of HYVOLUTION process

Table 1 Basic settings for pretreatment (PRT), thermophilic fermentation (THF) and photo-heterotrophic fermentation (PHF)

Parameter	Value
Plant capacity	60 kg/h Hydrogen, 97vol%
Feedstock	PSP, thick juice, barley straw
Pretreatment (PRT)	
PSP: Starch conversion	98 % (wt)
PSP: Reactor temperature	90 °C
PSP: Sugar losses washing step	5 % (wt)
Barley straw: Cellulose conversion	86 % (wt)
Barley straw: Hemi-cellulose conversion	50 % (wt)
Barley straw: Reactor temperature	180 °C
Barley straw: Sugar losses filtering step	10 % (wt)
Thermophilic fermentation (THF)	
Sugar conversion to H_2 in THF	80 % (wt)
Sugar conversion to cell mass in THF	15 % (wt)
Temperature THF	70 °C
pH THF	6.5
Substrate concentration THF	10 g/l sugar
Photo-heterotrophic fermentation (PHF)	
Acetic acid conversion to H_2 in PHF	60 % (wt)
Acetic acid conversion to cell mass in PHF	15 % (wt)
Temperature PHF	30 °C
pH PHF	7.3
Substrate concentration PHF	40 mM acetic acid

The thermophilic (THF) or dark fermentation is an anaerobic fermentation step in which highly thermophilic bacteria are employed at a temperature of 70 °C. In this step, sugars are converted to hydrogen, CO_2 and organic acids, preferably acetic acid, with 80 % of conversion to hydrogen. It requires high amounts of water to reach the defined low sugar concentration and high amounts of heat to bring the fermentation broth to the necessary 70 °C. Other issues, such as necessity of vacuum stripping to avoid hydrogen inhibition, have also been taken into consideration.

The photo-heterotrophic fermentation step (PHF) is a light driven process, which converts the produced organic acids to hydrogen and CO_2. The reactor operates best around 30 °C and works at a substrate concentration of 40 mM, with a conversion to hydrogen of 60 %.

The produced raw gas is then processed in a dedicated gas-upgrading unit to finally obtain pure hydrogen (97 vol%).

Previous work showed that process integration is necessary to make the process feasible from the ecological and point of view of energy consumption (Foglia et al., 2010). Recirculation of process effluents is one of the easiest options, in terms of technology and costs, to reduce the water and heat demand of the process, but not all routes are practicable. Only the photo-fermentation effluent can be used for recirculation to reduce the water demand. Experiments regarding recirculation are still on-going, but first results showed, to a certain extent, positive outcome. For this reason, recirculation has been calculated to reduce 60 % of dilution water required in the fermentation steps.

Furthermore, heat exchangers in the pretreatment and thermophilic fermentation steps are introduced, to recover heat from the warm outlet streams. During pretreatment of biomasses, high temperatures are required. Heat recovery is therefore necessary to make the process energetically feasible.

For barley straw pretreatment, heat exchangers have been added between the high temperature reactor (180 °C) and the saccharification step (50 °C), and between the warm pretreatment outlet (50 °C) and its diluted cold inlet (20 °C). For PSP pretreatment, one heat exchanger has been used to recover the heat of the warm pretreatment outlet (88 °C) and its cold inlet (25 °C). In the thermophilic fermentation step heat integration is introduced to preheat the cold fermentor inlet with its warm (70 °C) outlet. A minimum temperature difference of 5 °C is assumed between hot/cold streams of the heat exchanger.

3. Process Simulation And Models

The process has been implemented in the flow sheeting program Aspen Plus$^{®}$ (V7.1, Aspen Technology, Inc., Burlington, USA, 2008) which was used to solve mass and energy balances. The physical properties of the components were obtained either from the Aspen Plus$^{®}$ component database or taken from NREL's databank on biomass components (Wooley and Putsche, 1996).

The involved electrolyte equilibria were considered during simulation, including all dissociation components and involved ionic species, to be able to calculate the pH of process streams, to obtain the correct carbon dioxide content of the raw gas stream, and to control the effects of recirculation on the osmolality of the fermentation broth. The thermodynamic model "ElecNRTL" was used to calculate the vapor-liquid equilibrium in all unit operations.

No actual equipment for the gas upgrading is implemented yet in the flow sheets. However, 10% hydrogen loss is assumed and included in the calculations since it is a feasible value for different gas upgrading systems (PSA, VSA or membrane separation).

4. Results and Discussion

The process has been designed to produce 60 kg/h of pure hydrogen (97 vol%) equivalent to 2 MW thermal power.

The assumed composition of the different feedstocks is summarized in Table 2. Simplified mass and energy balances for the three feedstocks are shown in Figure 2, reporting the most important parameters of the process, such as biomass consumption, dilution water demand and heat demand.

Differences in feedstock flows are mainly caused by the dry mater content of feedstock as well as the content of fermentable carbohydrates and their mobilization during pretreatment. Due to the energy requirement of the pretreatment step, thick juice is the favorable option regarding the heat demand, as it consumes 50 % less energy than the other feedstock options. However, thick juice is a food competitive biomass, while PSP and barley straw are second generation biomasses.

Table 2 Assumed composition of low starch potato steam peelings (PSP), thick juice and barley straw

Components	PSP	Thick juice	Barley straw
Water (%wt)	86.6	28.5	10.5
Dry matter (dm) (%wt)	13.4	71.5	89.5
Starch (%wt dm)	34.0	-	-
Sucrose (%wt dm)	-	70.0	-
Cellulose (%wt dm)	24.7	-	29.8
Hemicellulose			
Xylan (%wt dm)	2.3	-	14.5
Galactan (%wt dm)	0.1	-	0.7
Arabinan(%wt dm)	0.2	-	2.0
Lignin (%wt dm)	11.4	-	22.8
Ashes (Sol. and Insol.) (%wt dm)	8.2	20.0	16.5
Pectin (%wt dm)	2.3	-	-
Protein (%wt dm)	16.8	10.0	13.7

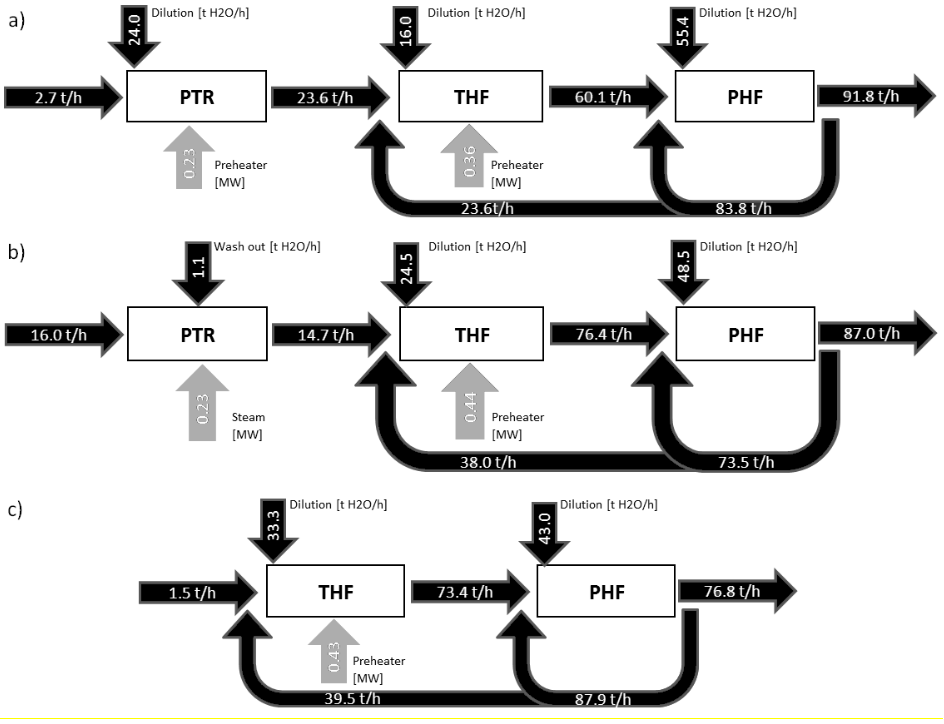

Figure 2 a, b, c: Basic mass and heat balances of fully integrated Hyvolution process based on feedstocks barley straw (a), PSP (b) and thick juice (c), assuming reduction of dilution water by recirculation of 60%. Black arrows correspond to mass flow rates [t/h], light gray arrows correspond to heat duties [MW]

Analyzing the different integrated process options, it is important to notice that all investigated process options are capable of producing a net amount of energy in form of hydrogen. This means that all the processes are technically feasible.

However, due to different flow rates and temperature levels - especially in the pretreatment step - heat exchanger design and dimensions as well as conditions of service streams will differ for the different feedstock options, considerably influencing capital and operational costs of the plant options.

5. Conclusions and Outlook

The work gives an overview on heat and water demand of the HYVOLUTION process based on the feedstocks barley straw, potato steam peels and thick juice. A net energy production, in form of hydrogen, seems technically feasible for all considered biomasses.

Improvement of mass- and energy balances in terms of feedstock specific productivities and conversion to hydrogen will give the basis for cost estimation and life-cycle-analysis. Hence, process simulation will play an important role in the final selection of the most promising process route for the HYVOLUTION process.

Acknowledgement

Experimental work providing data for modeling feedstock pretreatment has been performed by project partners Wageningen UR Food & Biobased Research and National Technical University of Athens.

We gratefully acknowledge the support of the project by the European Union FP6 on Sustainable Energy Systems (Hyvolution, Contract No 019825).

References

Claassen P.A.M. and de Vrije T., 2006, Non-thermal production of pure hydrogen from biomass: Hyvolution, Int. J. Hydrogen Energy 3, 1416-1423.

Foglia D., Ljunggren M., Wukovits W., Friedl A., Zacchi G., Urbaniec K. and Markowski M., 2010, Integration studies on a two-stage fermentation process for the production of biohydrogen. Journal of Cleaner Production, doi:10.1016/j.jclepro.2010.06.022

Mohagheghi A., Ruth M. and Schell D.J., 2006, Conditioning hemicellulose hydrolysates for fermentation: Effects of overliming pH on sugar and ethanol yields, Process Biochemistry 41, 1806-1811.

Wooley R. and Putsche V., 1996, Development of an Aspen Plus physical property database for biofuels components, NREL-Report/MP-425-20685, Golden.