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HyTIME – Combined Biohydrogen and Biogas Production from 2nd Generation Biomass

Adela Drljo*, Walter Wukovits, Anton Friedl

Vienna University of Technology, Institute of Chemical Engineering, Getreidemarkt 9/166, 1060 Vienna, Austria
adrljo@mail.tuwien.ac.at

Employment of renewable sources rather than fossil fuels in the production of hydrogen is an important step to achieve a sustainable and environmental friendly hydrogen economy in the future. Besides biomass gasification, production of hydrogen from renewable sources is also possible in a fermentative way through thermophilic (dark) fermentation of biomass.
In the European project HyTIME nine partners including universities, knowledge centres and industry work on an integrated, continuous bioprocess for the decentral production of 1-10 kg hydrogen/d. The strategy in HyTIME is to employ thermophilic bacteria, which have shown superior yields in H_2 production from biomass in the previous FP6 IP HYVOLUTION.
In this paper, mass and energy balances for process routes based on different feedstock options will be presented and discussed, giving a first glance at feedstock, water, heat and utility demand. Mass and energy balances for the involved process steps and overall process routes are calculated via process simulation tool Aspen Plus (V7.3.2, Aspen Technology Inc., 2012).
It is shown that biohydrogen can be successfully produced from verge grass and wheat straw. Based on the experimental results and literature data, process is scaled up to produce 10 kg biohydrogen/d in the raw gas stream. To achieve this, it is necessary to supply 90 kg/h wet verge grass or 46 kg/h wheat straw. Besides biohydrogen, biogas is produced from process residuals and utilized for heat and power generation. According to the calculations, it is possible to produce 48.5 kW and 45.8 kW heat as well as 44.6 kW and 42.2 kW power, from verge grass and wheat straw residuals, respectively.
Presented results form the basis for critical evaluation of the proposed process parameters and process routes and give hints for process improvement by applying process integration.

1. Introduction

Among recent research and development, hydrogen is recognized as the most promising solution to substitute vanishing fossil fuels. Beside the fact that H_2 is a clean and high energy containing fuel, it has a great potential for extensive use in power generation, chemicals production, in oil refineries for oil upgrading, in steel processing etc. (Dincer, 2012). But still the key benefit of hydrogen is that it is an energy carrier with no contribution to the greenhouse effect.
The main weakness of hydrogen production is the cost, economical as well as environmental, since still 90 % of hydrogen is produced from CH_4 reforming and coal gasification (Aprea, 2014). Biological production from renewable sources could be the path to achieve a sustainable hydrogen economy.
Different technologies have been defined as a state of the art in the biological hydrogen production: utilization of algal, cyanobacterial, and bacterial microorganisms that produce hydrogen through splitting water or fermentation of biomass (Hallenbeck et al., 2012). Main research activities in the area of fermentative hydrogen production are focused on mesophilic fermentation at temperature of 30 ºC. However, mesophilic conditions result in much lower hydrogen generation efficiency, compared to thermophilic conditions (Waligórska, 2012).
HyTIME realizes progress beyond the current state of the art by the novel combination of thermophilic hydrogen fermentation with biogas fermentation for the production of biogas. It employs different lignocellulosic materials, mostly verge grass and wheat straw, to obtain hydrogen via extreme thermophilic

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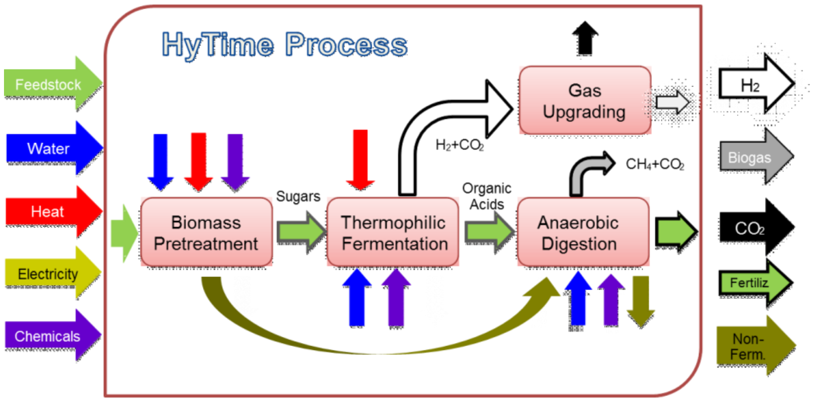

Figure 1: Scheme of HyTime process

fermentation, but also utilizes all the residual material from biohydrogen production to provide biogas enabling a biohydrogen process that is independent from external heat and energy sources. The aim of HyTIME is to show the possibility of full-scale application of this technology through the optimization of all process parameters and the choice of the most efficient technologies currently available.
Nine partners including different universities, knowledge centres and industry from six European countries are gathered with strategic aim of decentral and continuous production of 1-10 kg biohydrogen/d.
As it is illustrated in Figure 1, HyTIME process consists of several process steps: biomass pretreatment, thermophilic fermentation, gas upgrading and anaerobic digestion (for biogas production from process residuals).
This paper will give a basic overview on feedstock, water, chemicals and energy demand needed to produce 10 kg biohydrogen/d. Besides that, it will give a glance on potential for biogas production from process residuals. Also, some integration possibilities to cover process energy demand with energy gained from the process residuals will be discussed.

2. Material and methods

HyTIME process, designed as it is shown at Figure 1, was implemented in the process simulation software Aspen Plus (V7.3.2, Aspen Technology Inc., 2012). This tool is used to merge all decentered process steps into one model that will be able to calculate mass and energy balances for various feedstocks, but also to give some overview on water, chemicals and energy demand for overall process. The simulation model is built up to be flexible for different types of biomass and several scale-up factors considering, at this moment, a final hydrogen production of 10 kg/d. The Aspen Plus model consists of pretreatment step, thermophilic biohydrogen fermentation, gas-upgrading, anaerobic digestion of process residues and (partly) utilization of biogas in a gas engine for providing necessary heat and power for the process.

2.1 Feedstock and pretreatment (PTR)

In the HyTIME project, in total four biomass types are foreseen to be considered: verge grass, wheat straw, molasses and organic food residuals. In the present work, focus will be given on two main biomass types: verge grass, harvested from the road side, and wheat straw. The compositions, in terms of main components cellulose, hemicellulose and lignin, considered for mass balancing in Aspen Plus, are given in Table 1.

Table 1: Composition of the biomass used in the simulation

Biomass type	Cellulose %w	Hemicellulose %w	Lignin %w	Ash %w	Protein %w	Acetic acid %w	Rest %w
Verge grass	[1]32.9	[1]23.6	[1]24.1	[1]8.4	-	-	[1]11.0
Wheat straw	38.3	27.9	6.6	[2]5.5	[2]3.2	[2]4.3	[2]14.2

1) Phyllis2 – Database for biomass and waste - ECN
2) Silva, 2012

For wheat straw, only a basic component analysis was available for the experimentally used feedstock. Additional components have been assumed according to the reported literature (see Table 1). On the other hand side, composition of verge grass is varying considerably depending on the location, climate conditions and harvesting. Therefore, at this stage, the data from Phyllis database are taken as a starting point for the simulation and balancing.
For the described biomass, two different pretreatment procedures have been applied in order to unlock the biomass structure and make it accessible for biohydrogen production.
Verge grass was firstly treated mechanically with two different techniques: twin screw co-rotating extrusion or single screw pressing. At this point, grass is separated in the cake and liquid phase. Lignocellulosic material mainly remains in the cake while acids, proteins, minerals and sand are released to the liquid phase. Afterwards, the solid cake is treated with alkali, $Ca(OH)_2$, at a temperature between 85-100°C, 10% consistency and a $Ca(OH)_2$ concentration of 7.5 w%, based on the dry matter. Following solid phase is then washed and sent to enzymatic hydrolysis, where commercially enzymes are added to covert polymeric sugars to monomers needed for biohydrogen production. Figure 2 represent the Aspen Plus model for pretreatment of verge grass.
Wheat straw is treated with a 1N solution of H_2SO_4, at 120 °C for 2.5 h. Afterwards, solids and liquid are separated. Solid stream is washed and mixed with commercial enzymes in order to initiate hydrolysis of polymeric sugars and obtain monomeric sugars needed for biohydrogen production. Aspen Plus model for wheat straw is illustrated in Figure 3. Tap water is added to adjust optimal consistency and buffer solution is used to adjust and regulate an appropriate pH.

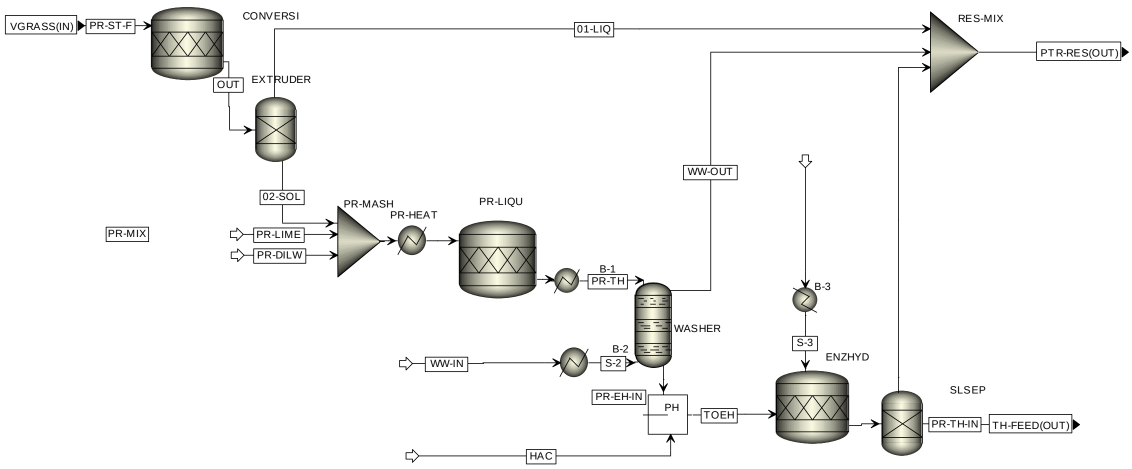

Figure 2: Flowsheet for pretreatment of verge grass

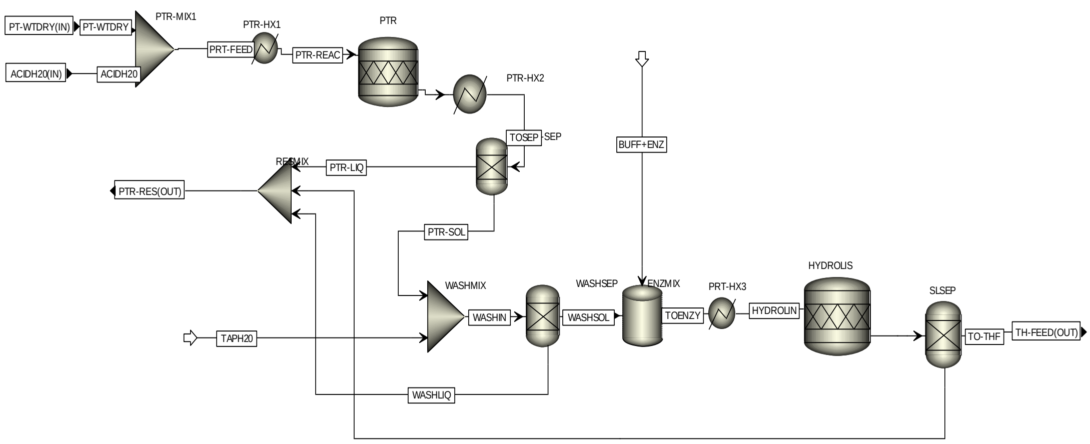

Figure 3: Flowsheet for acid pretreatment of wheat straw

2.2 Thermophilic fermentation (THF)

Thermophilic or dark fermentation is an anaerobic process, where extreme thermophilic bacteria are employed to produce H_2 at 70°C. In this step sugars available after pretreatment are transformed into H_2, CO_2 and mostly acetic acid according to the equations 1 for pentose and 2 for hexose (Foglia et al., 2011):

$$3C_5H_{10}O + 5H_2O \rightarrow 10H_2 + 5CH_3COOH + 5CO_2 \tag{1}$$

$$C_6H_{12}O_6 + 2H_2O \rightarrow 4H_2 + 2CH_3COOH + 2CO_2 \tag{2}$$

In HyTIME process, a slightly modified THF model from previous project HYVOLUTION is used (Foglia et al., 2011). According to the experimental investigations, the maximal yield in thermophilic fermentation is obtained at sugar concentration of 10 g/L in the substrate. To adjust the correct sugar concentration, addition of dilution water was necessary for both substrates.
Table 2 summarizes the basic conversions factors used in thermophilic fermentation. Sugars are mainly converted to biohydrogen and biomass. The residuals are afterwards converted to biogas in the anaerobic digestion process.

2.3 Gas upgrading

Raw gas stream produced after THF, contains not only biohydrogen but also a portion of CO_2 and some amount of water vapours. It may also contain some other gaseous components in traces. Depending on the final H_2 utilization purpose, minimal required H_2 purity was 97 % in the previous HYVOLUTION project (Foglia et al., 2011). However, in HyTIME project a higher concentration is aimed for.
Ongoing research in HyTIME considers two possible technologies for gas upgrading system: membrane contactor with dense hollow fibre membranes or pressure swing adsorption. Since the research is continuing, no Aspen Plus models are available at the moment.

2.4 Anaerobic digestion and biogas utilization

All residual process streams such as waste water after washing, liquid and solids stream after the PTR step as well as the effluent material after THF are used for biogas production in an anaerobic digestion step (Figure 1). The main idea is to exploit full potential of the feedstock material and utilize energy left in the residual streams via biogas production and utilisation, which could enable the whole process being independent from external energy supply and therefore contribute to the sustainability of biohydrogen production and economic feasibility of the total process.
Model structure and principals of the anaerobic digestion model in Aspen Plus are already reported in Wukovits et al. (2013). In general, tree approaches have been used to model and calculate the amount and/or composition of biogas from process residuals streams: COD method, Buswell method and stoichiometric method.
Aspen Plus model for anaerobic digestion, described in Wukovits et al. (2013) is fully implemented in the HyTIME process. COD and Buswell method are implemented unchanged. Stoichiometric method was slightly modified by introducing conversion factors of 0.85 for carbohydrates and 0.70 for fats and proteins, according to the VDI 4630. Conversion factors in stoichiometric model for all other components remained unchanged at a value of 1.
Produced biogas can be used in the CHP plant for combined heat and power production, can be upgraded and used as a fuel or combusted for heat and power production. Aspen Plus model is simulated in the way to be flexible and include different solutions for biogas utilization.
In the HyTIME process, biogas is foreseen to be used in a gas engine. Produced heat and power will be used to run biohydrogen production.

3. Results and discussions

Since the research in HyTime project is still ongoing, at this moment it is possible to present only some preliminary results that give a glance on feedstock, water and chemical consumption, heating energy consumption as well as a first estimation on energy produced from biogas. Since the input data will be updated by the end of project, it is not possible to calculate a final overall energy balance.

Table 2: THF set up for different feedstocks

Feedstock	Verge grass	Wheat straw
Conversion sugars to H_2, THF	70%	70%
Conversion sugars to biomass, THF	15%	10%

Table 3: Preliminary mass and energy demand for biohydrogen production

Process path	Verge grass	Wheat straw
Feedstock demand, kg/h wet	90	46
Feedstock demand, kg/h dry	45	43.5
Water demand, kg/h	1,588	2,057
Chemical demand, kg/h	13.4	18.32
Heat demand before heat integration, kW	96.7	115.8
Heat demand after heat integration, kW	40.1	42.8

Based on small scale experimental results, calculations are scaled to calculate the production of 10 kg biohydrogen/d in the raw gas stream following two production paths. The first path is biohydrogen production from verge grass via alkali grass pretreatment combined with enzymatic hydrolysis and THF. Second path is simulated for hydrogen production from wheat straw via acid PTR, enzymatic hydrolysis and THF.

Table 3 represents the overview on feedstock demand needed to obtain 10 kg hydrogen per day, as well as water, chemical and heat demand for described process paths.

Water demand includes the water needed for washing as well as adjusting the consistency in pretreatment procedure and substrate concentration in thermophilic fermentation. Chemical demand represents the acid or base requirement needed for PTR as well as to adjust an appropriate pH in the process. Heat demand is required for preheating process streams since most process steps are taking place at elevated temperatures (PTR in the range from 85-120 °C, THF at 70 °C).

After obtaining the basic energy balances, heat integration measures are applied in order to know how much heat energy can be exchanged in the process itself. This analysis reduces the demands on external heating by more than 50 %, as it is presented in the Table 3.

Table 4 summarizes the results of biogas model, based on COD and stoichiometric calculation approaches. In the case of verge grass, total biogas production is slightly higher than in the wheat straw case. Biogas composition (dry) is quite similar in both cases giving the final composition of approx. 50 % methane and 50 % CO_2. In the wheat straw case H_2S is present since sulphuric acid is used in the process. For the utilization of biogas in the gas engine, H_2S should be removed prior entering the engine to prevent engine damaging.

According to the Table 4 COD model gives slightly higher methane yield compared to the value calculated via stoichiometric model. Namely, according to the VDI 4630 guideline, in stoichiometric route, beside biogas some organic matter is consumed for biomass production. That is not the case with COD model, since here all degradable organic matter from substrate is converted to biogas. This is reflected in the values of predicted biogas production in the case of verge grass (7.1 vs. 9.0 m^3/m^3 input) as well as by wheat straw (5.3 vs. 6.2 m^3/m^3 input).

Table 4: Biogas production potential from residuals stream

Biogas stream and yield	Verge grass	Wheat straw
Biogas mass flow [kg/h]	31.5	30.5
$CH_{4\ stoichiometric}$ [m^3/m^3 input]	7.1	5.3
$CH_{4\ COD}$ [m^3/m^3 input]	9.0	6.2
Biogas composition [vol %]		
CH_4	49.9	48.8
CO_2	50.0	49.8
NH_3	0.10	1.36
H_2S	0.00	0.04

Table 5: Rough estimate of energy input and output for biohydrogen production

	Verge grass	Wheat straw
Heat input after heat integration, kW	40.1	42.8
Heat output, kW	48.5	45.8
Power output, kW	44.6	42.2
Heat surplus/deficit, kW	+8.4	+3.0

For biogas utilization, a gas engine is applied. Table 5 summarizes heat and power gained from the produced biogas. It clearly shows, that heat demand of both integrated biohydrogen production paths can be covered from biogas obtained from process residues and thus that biohydrogen production from renewables has a potential to be self-supplied by energy coming from the process residuals. It is even possible to generate surplus in the heat (8.4 kW for verge grass and 3 kW for wheat straw), as well as electrical power. It is expected that this situation will improve in the course of a detailed process integration and process optimization.

4. Conclusions

Hydrogen produced from lignocellulosic material could bring a lot of advantages compared to the common production pathways. Most important, lignocellulosics are renewable materials and therefore enable a sustainable hydrogen production. HyTIME project suggests the utilization of the road side grass or remainings from wheat production and avoid competition with food crops.
To further increase sustainability of biohydrogen production, HyTIME process promotes the combined production of biohydrogen and biogas. Calculations show that 48.5 kW and 45.8 kW heat generated from the obtained biogas (in verge grass and wheat straw path respectively), is enough to cover heat requirement for biohydrogen production. At the same time heat surplus of 8.4 kW in verge grass path and 3 kW in wheat straw path is achieved, which proves that biohydrogen production can be independent from external energy sources. This finally will have a positive effect on total process feasibility from economic and environmental perspective.

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