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Integration of Biohydrogen Production with Heat and Power Generation from Biomass Residues

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The employment of renewable sources rather than fossil fuels in the production of hydrogen is an important step to achieve a sustainable 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 and/or photo-heterotrophic fermentation. Depending on pretreatment procedure, considerable heat demand is necessary to produce hydrogen from agricultural residues and food processing. While heat demand in the pretreatment step can be reduced by heat integration measures, significant heat input is still necessary in the dark fermentation step. The paper evaluates possible contributions of utilizing process residues to cover the heat demand of the biohydrogen production. Process options for three types of feedstock for biohydrogen production have been investigated towards the potential of heat self-supply of the process. Results show that the heat demand of biohydrogen production from barley straw and potato steam peels can be covered from heat of biogas utilization obtained from process residues. For feedstock thick juice still a heat deficit of 0.29 MW is observed.

1. Introduction

Hydrogen, as a carbon-free energy carrier, has been identified as the most promising energy source in the future. Nowadays, the main emphasis is on hydrogen production from renewable resources, rather than fossil fuels. At the moment, the biggest drawback of hydrogen production are high economic and environmental cost (Foglia et al., 2010).

An affirmative way for the biological hydrogen production from biomass is a 2-stage bioprocess investigated in FP6 project HYVOLUTION. In this project, a process was realized through a thermophilic fermentation step to produce hydrogen, CO_2 and intermediates, followed by a photo-heterotrophic fermentation, in which all intermediates are converted to more hydrogen and CO_2 (Figure 1).

Whole process was simulated in the simulation software Aspen Plus V7.2 (Aspen Technology, Inc., 2010) and designed to produce 60 kg/h of pure hydrogen, equivalent to 2 MW thermal power. Simulation model was adaptive for the three different feedstocks: barley straw, thick juice and potato steam peals (PSP). For all three feedstock variations, besides calculation of mass and energy balance, integration studies has been performed. Results showed that heat integration and recirculation brought a significant reduction of energy that should be utilized to run the process. Without energy integration and effluent recirculation, total energy balance of the overall process was negative (energy input to produce biohydrogen was much higher than energy output that could be achieved from pure hydrogen). After integration procedure, total energy balance was significantly improved and energy input has been decreased to 0.92 MW for barley straw and PSP and 0.74 MW for a process with feedstock thick juice (Foglia et al, 2011).

Additional analysis of the process described above, have been done in order to find ways for heat recovery and power supply, for making the process of hydrogen production most cost and energy efficient. This paper evaluates possible contributions of utilizing process as well as feedstock residues to cover the heat demand of the biohydrogen process. Based on the properties of residues and by-products, hydrogen production is integrated with dedicated processes to convert biomass to heat and power. The visible way

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is utilization of process residues for biogas production and biogas employment in providing heat and power necessary for the biohydrogen production.

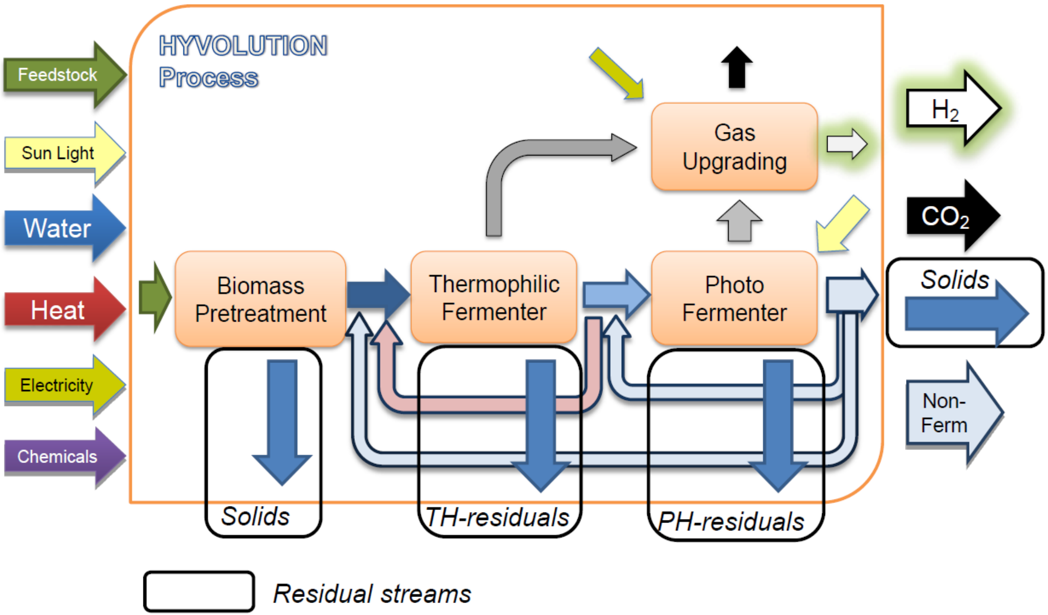

Figure 1: Scheme of HYVOLUTION process (Foglia et al., 2010)

2. Methods and models to estimate biogas potential

Residual process streams in Figure 1 have been considered for biogas production. All three types of feedstock - barley straw, thick juice and potato steam peels - have been used for biohydrogen production and the residues for calculation of biogas potential. In order to develop models for biogas production, Aspen Plus have been used, mainly in order to allow full integration of biogas model with available overall model, described before.

Three possible approaches to model biogas production have been employed: (1) calculations via Chemical Oxygen Demand (COD), where it is possible to calculate amount of methane, but not the composition of biogas, (2) via Buswell formula, where it is possible to calculate amount and composition of biogas, but only for an overall stream not considering the degradability of components and (3) via Stoichiometric reaction where it is possible to calculate amount and composition of biogas by definition of fractional conversion factors for different components (Hilby, 2013).

As with the definition of stoichiometric reactions and connected fractional conversion factors for each component in Hyvolution process, also the biogas models based on COD and Buswell formula consider that only degradable components converted to methane. Therefore, after the inlet stream of these models, a split-unit is used to separate degradable and non-degradable components (Figure 2a; not visible for COD model). Calculation of biogas formation via COD and Buswell formula is implemented with a FORTRAN code in calculator blocks.

2.1 Aspen Plus model for biogas via COD method

The amount of biogas that can be produced in the system can be calculated via Chemical Oxygen Demand (COD). Aspen Plus provides a property set called CODMX (chemical oxygen demand of a mixture) which calculates the theoretical oxygen demand COD^{aspen} (kg O_2/kg substrate; equal to the chemical oxygen demand) of a chemical substance $C_cH_hCl_{cl}N_nNa_{na}O_oP_pS_s$ with molecular weight MW or a stream with a defined composition (AspenTech, 2013).

Mass flow of methane (w_{CH4}, kg/h) can be easily obtained from Eq(1) based on COD, mass flow of substrate (wsubstrate, kg/h) and a stoichiometric factor of 0.25 obtained from oxygen demand of chemical oxidation of methane (0.25 kg CH_4 are oxidized by 1 kg O_2, Wang et al., 2010).

$$w_{CH4} = 0.25 * w_{substrate} * COD^{aspen}, \text{ [kg/h]} \qquad (1)$$

The calculator block of COD based biogas model can be easily connected to any process stream to analyze its biogas potential.

2.2 Aspen Plus model for biogas via Buswell method

Starting point of biogas calculation according to extended Buswell formula, is the chemical composition of the substrate in form of $C_cH_hO_oN_nS_s$. Original Buswell calculation takes only C, H, and O into account whereas extended Buswell formula also includes N and S and thus considers the formation of NH_3 and H_2S. Based on the substrate/biomass composition the amount of generated biogas is given in Eq(2) (Jördening and Winter, 2005).

$$\boldsymbol{C_cH_hO_oN_nS_s} + \tfrac{1}{4}\,(4c-h-2o+3n+2s)\ \boldsymbol{H_2O} \rightarrow \tfrac{1}{8}\,(4c-h+2o+3n+2s)\ \boldsymbol{CO_2} + \tfrac{1}{8}\,(4c+h-2o-3n-2s)\ \boldsymbol{CH_4} + n\ \boldsymbol{NH_3} + s\ \boldsymbol{H_2S} \qquad (2)$$

The difficulty of the application of Buswell formula is to create a fictional chemical formula ($C_cH_hO_oN_nS_s$) out of individual mole fractions of real biomass components. The elemental coefficients c, h, o, n, and s have to be interpreted as mole fractions referring to 1 mole of the fictional chemical substrate formula.

2.3 Aspen Plus model for biogas via stoichiometric method

Calculating the amount and composition of biogas via stoichiometric reactions consequently follows the concept of component based description of the process as implemented in the models of the other process steps (Wukovits et al., 2007). Component definition follows the concept of Wooley and Putsche (1996). In this calculation path degradation reactions (Table 1) for each component contributing to the biogas formation needs to be defined (Miltner, 2010). Fractional conversion factors for each component can be defined (experiments, literature, experience, etc.) to describe the degradability of the component. At the moment fractional conversion factors for all reactions are set to 1.

In the Aspen Plus flow sheet, stoichiometric route for biogas production is the central one (Figure 2b), since obtained biogas stream is fed to the biogas utilization unit.

Table 1: Degradation reactions for stoichiometric method

Components	Stoichiometry
Glucose, Galactose	$C_6H_{12}O_6 \rightarrow 3\ CH_4 + 3\ CO_2$
Xylose, Arabinose	$C_5H_{10}O_5 \rightarrow 2.5\ CH_4 + 2.5\ CO_2$
Sucrose	$C_{12}H_{22}O_{11} + H_2O \rightarrow 6\ CH_4 + 6\ CO_2$
Acetic Acid	$C_2H_4O_2 \rightarrow CH_4 + CO_2$
Cellulose, Glucan, Galactan, Pectin	$C_6H_{10}O_5 + H_2O \rightarrow 3\ CH_4 + 3\ CO_2$
Hemicellulose, Xylan, Arabinan	$C_5H_8O_4 + H_2O \rightarrow 2.5\ CH_4 + 2.5\ CO_2$
Protein	$CH_{1.57}N_{0.29}O_{0.31}S_{0.007} + 0.67\ H_2O \rightarrow 0.51\ CH_4 + 0.49\ CO_2 + 0.29\ NH_3 + 0.007\ H_2S$
Cell Mass	$CH_{1.6}N_{0.23}O_{0.45}S_{0.0035} + 0.55\ H_2O \rightarrow 0.5\ CH_4 + 0.5\ CO_2 + 0.23\ NH_3 + 0.0035\ H_2S$

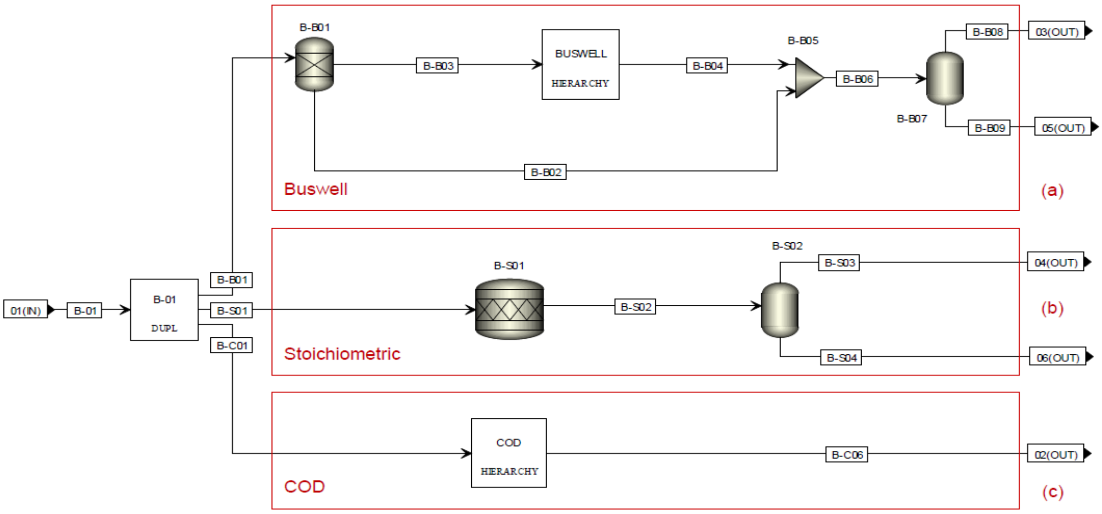

Figure 2: Biogas production routes in Aspen Plus

Aspen Plus simulation model for the biohydrogen process includes all three approaches for biogas production for easy comparison of the biogas potential (Figure 2). One common (triplicated) feed stream is connected to all three routes. One stream goes to the COD model, other one to Buswell model and third one to the stoichiometric model. Input parameters, in terms of residuals composition have been given at Table 1.

3. Biogas utilization

For the purpose of biogas utilization in a first step a gas engine is foreseen producing electric power and process heat. Gas engine is an internal combustion engine and work on the principle of the Otto Cycle. However, other utilization options are possible to be implemented in the flow sheet (Figure 3). For biogas utilization the raw biogas stream from stoichiometric biogas calculations is used. In the first step H_2S is removed (process not specified yet) because sulfur would harm the engine. In the next step a flash model is implemented to adjust an appropriate biogas dew point.
After that pretreatment of the biogas, the stream is multiplied in order to calculate three optional utilization pathways: combined heat and power generation (CHP) via a gas engine (Figure 3a), combustion (up till now: combustion of the biogas at adiabatic flame temperature) (Figure 3b), and biogas upgrading (e.g. pressurized water scrubbing or upgrading via gas-permeation – not shown in the flowsheet) (Figure 3c). The unit operations in the flow sheet of the gas engine (Figure 3a) are included for the purpose of illustrating an ideal Otto process, which is consisting of an isotropic compression, isochoric combustion, isotropic expansion, and isochoric heat exchange.
In order to calculate power and heat output of the gas engine, efficiency data supplied by GE Jenbacher were implemented with a FORTRAN code (Jenbacher, 2007) to connect energy input in form of biogas with heat/power output obtained from the gas engine. As representative gas engine type JMS 312 GS-B.LC with an electric efficiency of 40.4 % and a thermal efficiency of 42.9 % was selected.

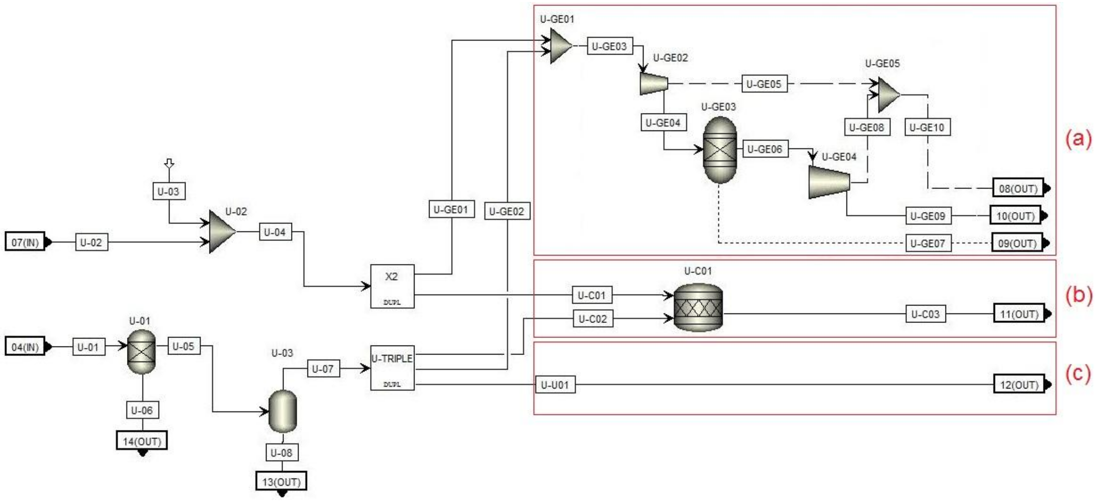

Figure 3: Aspen model for biogas utilization

4. Results and discussion

Calculation of biohydrogen production is scaled to 60 kg/h. For process parameters as well as mass and energy balances see Foglia et al., 2011. Table 2 summarizes the obtained residues from biohydrogen processes based on feedstocks barley straw, thick juice and PSP to be used for biogas production.
For all these residual streams, maximum biogas potential has been calculated via developed Aspen Plus models following COD, Buswell and Stoichiometric route. Table 3 represents the results of the performed calculations in a sense of methane flow rate. Table 4 gives results for biogas composition on dry basis.
According to the results in Table 3, different methods used for determining of maximum biogas (methane) potential from process residues, are in a good agreement with each other. All three methods (COD, Buswell and Stoichiometric) give comparable results for the same residual streams. Residuals from thick juice show low methane potential, since thick juice consists mainly of sugar, which is almost completely consumed in biohydrogen fermentation.

Table 2: Component mass flow rate (kg/h) in residual stream to the biogas plant

Components	Degradability	Barley Straw Residuals	Thick Juice Residuals	PSP Residuals
Cellulose	+	123	-	583
Hemi-Cellulose	+	174	-	50
Water		91,547	80,697	90,623
Sugars	+	170	24	86
Acetic Acid	+	105	50	56
Other Chemicals	-	673	554	605
Other Solids				
Lignin	-	445	-	257
Ash	-	176	21	299
Cell Mass	-	105	98	95
Protein	+	41	-	396
Pectin	+	-	43	48
Galactan	+	13	-	-
Arabinan	+	25	-	-
Rest	-	70	-	-
Total		93,887	81,685	93,313

+ Degradable solids   - Non-degradable solids

Table 3: Biogas maximum potential for different feedstock residuals and different calculation methods

	Methane flow rate, [kg/h]		
Residuals	COD	Buswell	Stoic.
Barley straw	220.7	212.4	221.1
Thick Juice	32.4	32.4	32.9
PSP	385.2	399.6	381.6

As it can be seen in Table 4 also biogas composition obtained from the different calculation routes is in good agreement. However, the biogas composition for COD route is 100 % CH_4 because, as it is explained before, COD route does not calculate the biogas composition, but only gives the amount of methane produced. In all cases almost equimolar amounts of CH_4 and CO_2 are obtained. Compared to the other feedstock options PSP shows a considerable high NH_3 content. No H_2S formation is observed. However, process inputs have to be checked for proper definition of sulfur sources (trace elements, nutrients, etc.).

Table 5 opposes the heat and power obtained from the utilization of produced biogas via gas engine with heat input necessary to produce biohydrogen in the proposed Hyvolution process (Figure 1). Data for the heat demand of integrated Hyvolution process are taken from previous work (Foglia et al. 2011). Integration measures consider heat integration of pretreatment and thermophilic fermentation step to reduce heat demand of the process as well as recirculation of reactor effluent of photo-heterotrophic fermenter to the entrance of thermophilic and photo-heterotrophic fermentation step to mainly reduce the demand of process water.

Table 4: Biogas composition for different feedstock residuals and different methods (dry basis)

	Barley straw			Thick juice			PSP		
Biogas composition mole fraction	COD	Buswell	Stoic	COD	Buswell	Stoic	COD	Buswell	Stoic
CH4	1.00	0.50	0.49	1.00	0.50	0.50	1.00	0.49	0.45
CO2	0.00	0.50	0.48	0.00	0.50	0.50	0.00	0.42	0.45
NH3	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.08	0.10
H2S	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Although biogas simulation models consider 3 different methods for biogas production (COD, Buswell and Stoichiometric), only stoichiometric route has been used for calculation of heat and power via gas engine.

As it is shown in Table 5, in the case of barley straw and PSP, utilization of biogas produced from process residuals covers the heat demand of biohydrogen process completely. Even some heat surplus can be obtained.

This is not the case with thick juice. In this case, some heat is produced from biogas but this amount is not sufficient to cover total heat input in the process. Some additional heat is necessary to run the biohydrogen process.

Table 5: Integration possibilities for hydrogen production and biogas utilization from residuals

Feedstock\residual type	Heat input biohydrogen production (Foglia et al., 2011), MW	Heat from biogas utilization, MW	Power from biogas utilization, MW	Heat surplus\ deficit, MW
Barley straw	0.92	1.62	1.49	+0.70
Thick juice	0.74	0.45	0.41	-0.29
PSP	0.92	2.73	2.52	+1.81

5. Conclusions

To make hydrogen production sustainable, some additional heat, coming from the renewable sources (biomass) must be provided. Biogas production from the residual process stream could be a good way for heat and power recovery. This paper shows a possible way for heat self-supply of a two stage biohydrogen process, in order to make it more economically feasible. Using residual process streams for processes based on feedstocks Barley straw and PSP seems to be promising in terms of covering the necessary process heat. However, for the process based on thick juice, additional solutions for heat supply has to be investigated.

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