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Integration study on a two-stage fermentation process for the production of biohydrogen

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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, will be used to integrate the process steps necessary to produce pure hydrogen from biomass in a 2-stage fermentation process. The main challenge is the reduction of water and heat demand connected to the low substrate concentration in the fermentation steps; the easiest solution is to partly recirculate outgoing process streams. Electrolyte equilibrium was considered during simulation of different recirculation options to evaluate important effects on the pH and on the system osmolality. The results show that certain recirculation options can reduce the heat and water demand significantly.

1. Introduction

Hydrogen has been identified as the most promising energy carrier of the future. Since long time several efforts have been devoted to the development and the improvement of technologies for storing, distributing, and using hydrogen. Only in the last decade, an increasing attention is focused on its production. At present, almost the total industrial hydrogen production comes from thermo-chemical processes of fossil fuels. However, renewable resources have to be used to make the future hydrogen economy fully sustainable.

Besides thermo-chemical conversion, fermentation is one of the investigated possible ways to have a sustainable production of hydrogen from biomasses. Advantages of fermentative hydrogen production are mainly the local integration due to possible adaptation to different types of feedstock, the use of effluents as a fertilizer and the reduction of cost and environmental impact of fuel transportation.

A 2-stage bioprocess investigated in HYVOLUTION-project is a promising way for the biological production of hydrogen from biomass (Claassen and de Vrije, 2006). The proposed process consists of 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.

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Research at the moment is focused on selection of microorganisms, optimization of yield and rate of hydrogen production as well as reactor design. For the technical and the economical feasibility, system integration plays a crucial role, as evidenced already in a previous work (Wukovits et al., 2007).

2. Process Description

The process consists of four main parts: pretreatment, thermophilic fermentation, photo fermentation and gas upgrading (Figure 1).

Strongly depending on the type of biomass, pretreatment is used to convert the biomass in sugars usable in the thermophilic fermentation step. For the presented calculations, wheat starch has been used because of its well-known treatment process.

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. It requires high water demand to reach the defined low sugar concentration and high heat demand to bring the fermentation broth to the necessary 70°C. Other issues, such as necessity of gas stripping to avoid hydrogen inhibition, have been taken into consideration but are not analyzed in this paper.

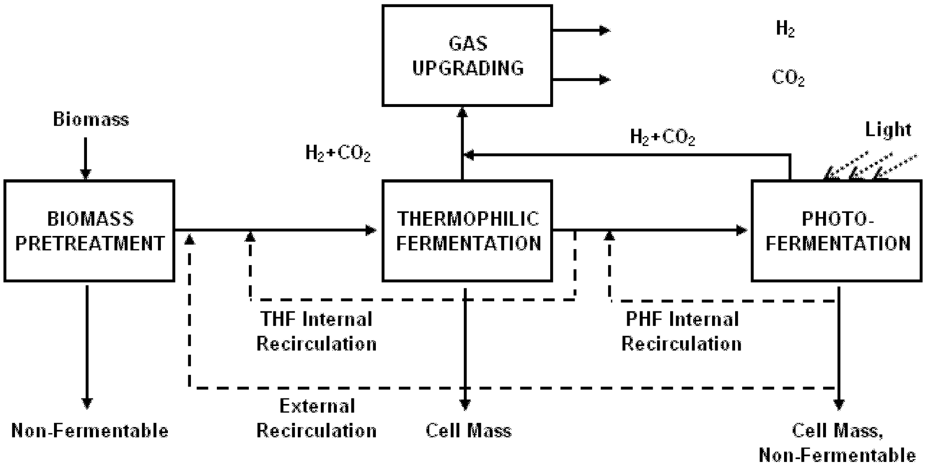


Figure 1: Scheme of HYVOLUTION process

The photo-heterotrophic fermentation step (PHF) is a light driven process, which converts the produced acids in hydrogen and CO_2. The reactor operates at 30°C and works only for values of substrate concentration even lower than the one in the thermophilic fermenter downstream. As easy to understand from the presented scheme in Figure 1, recirculation is one of the easiest options, in terms of technology and costs, to reduce the water and heat demand of the process. Since experimental analysis of the different cases would require high time investment, process simulation is used to point out the most promising recirculation option.

The produced raw gas is then processed in a dedicated gas-upgrading unit to finally obtain pure hydrogen.

3. Process Simulation and Models

Aspen Plus® 2004.1 software package (AspenTech, 2006) has been used to simulate the presented system. To investigate effects of recirculation on pH, chemical demand for pH-adjustment and osmolality of fermentation broth in THF, the involved electrolyte equilibrium have been considered during simulation. Osmolality, in particular, seems to be an important parameter in THF, since experimental results show some critical limit of osmolality for the used thermophilic bacteria (Willquist et al, 2009).

Thermodynamic model ElecNRTL has been used to describe the involved vapor-liquid equilibrium. Simulations have been run with apparent component approach. This has been necessary due to the definition of reaction stoichiometry in the fermenters, based on dissociating molecules (like acetic acid). The stream osmolality has been calculated summing moles of the not dissociated molecules and present ions, calculated by the simulator with true component approach. For this calculation, a stream duplicator has been added (inlet and outlet of the fermenter, denoted with circles in Figure 2), followed by a simple unit operation model (heater) used to force Aspen Plus to recalculate the properties of the duplicated stream in true component approach.

In order to adjust the pH, an alkaline stream (potassium hydroxide) and an acid stream (hydrochloric acid) have been introduced to the model of both fermenters, but only one of the two streams has been considered in each simulation. The adjustment of pH has been calculated with a design specification, setting the pH in the fermenters to the desired value. Addition of alkaline or acid is done before the fermenters (see Figure 2 for THF) to be able to monitor changes of pH and osmolality before and after the fermenters. The adjustment of pH is supported by buffer components, considered in the calculations, but not discussed in this paper. Internal recirculation options have been added in each fermentation step, as well as an external recirculation stream going from PHF to THF (Figure 1 and 2).

The stream “TH-AIR” (Figure 2) is used to close the elemental balance for oxygen and nitrogen when simulating bacterial growth in the thermophilic fermenter.

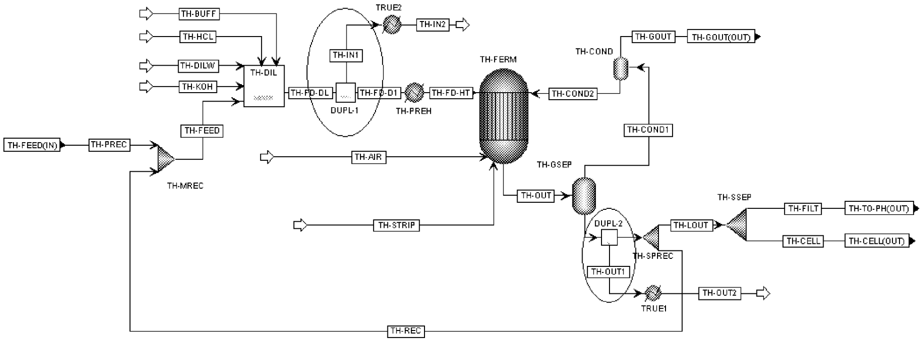


Figure 2: Aspen Plus flowsheet of the thermophilic fermentation step.

4. Results and Discussion

The process has been scaled to produce 30 kmol/h of hydrogen (equivalent to 2 MW thermal power). Two cases have been analyzed: internal recirculation in the THF and external recirculation of effluent from PHF to THF. Since recirculation has not been used to improve yield of the reactor, but to reduce heat and water demand, the amount of recirculation has been defined as percentage of reduction of dilution water.

Four points have been selected: no reduction, 30%, 60% and 90% reduction of dilution water in THF, calculated for both investigated process options, internal and external recirculation. The introduction of an additional recirculation in the PHF would have been possible, but is not considered in this paper because of lack of experimental data.

Analyzing results from Figure 3, it is necessary to underline the dramatic increase of the acetic acid concentration in the THF for the internal recirculation case. This causes an increase in dilution water demand for the PHF to adjust the required substrate concentration, counterbalancing therefore the reduction of dilution water obtained in the THF (compare with Figures 5). External recirculation does not cause any noticeable increase of acetic acid concentration in THF and water demand in the PHF, allowing a reduction of dilution water in the process. Secondary effect of external recirculation is a lower demand of alkaline (Figure 3), while internal recirculation in THF, from this point of view, brings no benefits.

Figure 4 shows the influence of recirculation on the heat demand for THF and PHF not considering any measures towards heat integration: the reduction of heat demand in THF for the internal recirculation case is much stronger, due to the higher temperature (70°C) of recirculation stream compared to the external one (40°C). On the contrary, the higher demand of dilution water (20°C) in the PHF makes it necessary to pre-warm the stream, partially counterbalancing the reduction of heat demand in the THF (Figure 4).

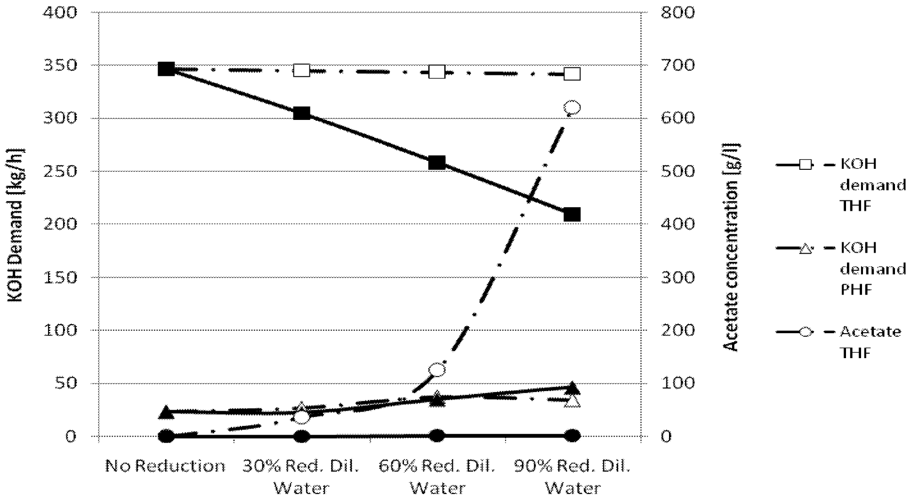
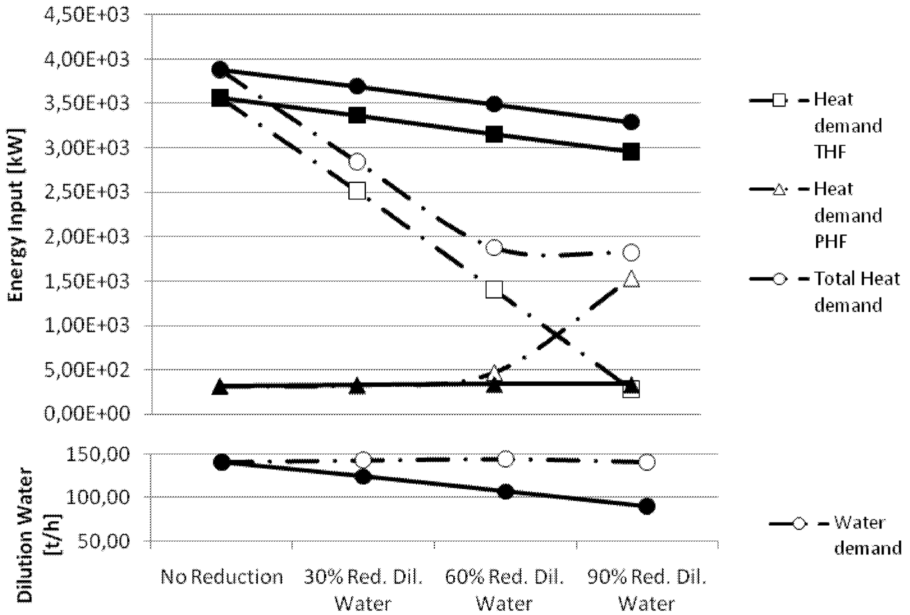


Figure 3: Acetate concentration and alkaline demand with increasing reduction of dilution water (filled symbols and solid lines: external recirculation; open symbols and dashed lines: internal recirculation).



Figures 4 and 5: Heat and water demand with increasing reduction of demand of dilution water. (filled symbols and solid lines: external recirculation; open symbols and dashed lines: internal recirculation).

Table 1 shows the results in terms of osmolality in the THF for the different recirculation options. As expected, raising the internal recirculation rate, increases the concentration of non-volatile co-products (such as acetic acid), and consequently the osmolality.

Experimental results suggest that exceeding a critical limit of osmolality would negatively affect productivity and/or yield of the process step. Therefore, increasing osmolality is riskful, especially when more than doubling the base value used in experiments (Willquist et al, 2009). Because of increase of osmolality, internal recirculation in the thermal fermenter seems not feasible, while the promising results showed by the external recirculation case, offer a possible solution for the reduction of heat and water demand. Furthermore, in case of external recirculation, it would be possible to use an economizer to pre-warm the dilution water with the outgoing THF effluent. This option has not been evaluated, but it will be object of further investigations in the future.

Table 1: Osmolality in THF with increasing reduction of dilution water (increasing recirculation rate)

	Case	Reduction of dilution water			
	Recirculation	no	30 %	60 %	90 %
Osmolality	internal	0.200	0.276	0.465	1.583
[Osmol / kg H_2O]	external	0.200	0.203	0.206	0.210

5. Conclusions and Outlook

The work gives an overview of the different options to recirculate process effluents in the thermophilic fermenter to reduce heat and water demand. The electrolyte system involved in the process has been considered during simulation to monitor the level of osmolality in the thermophilic fermenter and to calculate alkaline/acid demand to adjust the correct pH. Internal recirculation in the thermophilic fermenter does not seem to be a suitable option for HYVOLUTION process, since it raises osmolality in THF causing inhibition of hydrogen production. External recirculation of effluents from the photo fermenter to the thermophilic fermenter, at the current state of simulation, seems practicable. This solution would allow a reduction of heat and water demand, bringing environmental and economical benefits.

Next step in process simulation will include a more precise definition of the electrolyte system considering all components necessary for growth of the used bacteria as well as by-products and other components inhibiting hydrogen production. Furthermore, heat integration will be applied to the process. Based on these results, it will be possible to obtain profitable information on the process, useful to give guidelines for further experimental investigations as well as to improve cost estimation and life-cycle-analysis. In this way process simulation will play an important role in the final selection of the most promising process route for HYVOLUTION process.

Acknowledgement

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