CHEMICAL ENGINEERING TRANSACTIONS Volume 18, 2009
Editor Jiří Klemeš

DOI: 10.3303/CET0918063

Effect of process integration on the exergy balance of a process for biological hydrogen production

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Hydrogen will be an important energy carrier in the future. To make the future hydrogen economy fully sustainable, renewable resources instead of fossil fuels have to be employed for hydrogen production. Besides mass- and energy-balance, exergy analysis will be applied to a novel fermentative process to provide the most efficient process route for hydrogen production. The paper analyzes the influence of definition of boundaries, products and usable energy on the obtained balances and exergetic efficiencies. Calculations are based on improved mass- and energy-balances of the process and include first steps towards process and heat integration. Special focus is given to the recirculation/reuse of effluent streams of the different process steps to reduce water and heat demand.

1. Introduction

Currently hydrogen is almost completely produced from fossil fuels or from electrolysis of water. In future renewable resources have to be employed for hydrogen production. Besides biomass gasification, hydrogen from biomass can also be produced in a non-thermal way using bacteria. A promising way for the production of hydrogen from biomass in a non-thermal way seems to be a two-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. Mass- and energy-balance as well as exergy analysis will be applied to the novel process for biological production of hydrogen to provide the most efficient hydrogen production route.

2. Hyvolution Process

The process starts with the necessary pre-treatment of biomass to provide a suitable feedstock for thermophilic fermentation (THF). Different kinds of feedstock will be considered with a special focus on residues from food processing. For a first evaluation of the overall process starch-based feedstock was selected, represented by wheat (Figure 1). The first fermentation step (thermophilic fermentation, THF) is applying highly thermophilic bacteria at a temperature of 70°C. In this step sugars are converted to

Please cite this article as: Modarresi A., Wukovits W. and Friedl A., (2009), Effect of process integration on the exergy balance of a process for biological hydrogen production, Chemical Engineering Transactions, 18, 391-396 DOI: 10.3303/CET0918063

hydrogen, CO_2 and organic acids. Produced organic acids (preferably acetic acid, HAc) can be used as substrate for hydrogen production in a consecutive photo-heterotrophic fermentation step (PHF). To provide pure hydrogen, finally carbon dioxide has to be separated from produced gas. For further process details see Wukovits et al. (2007).

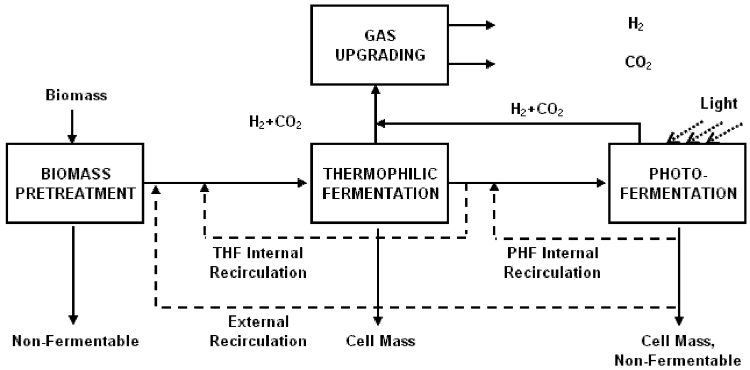

Figure 1: Scheme of "Hyvolution"-process pointing out possible recirculation options

As presented earlier (Wukovits et al., 2007) system integration plays an important role in the process, from the technical and the economical point of view. Introducing recirculation streams seems to be a feasible option to reduce the heat and water demand of the non-integrated process. Since experimental analysis of the different cases would require a high time investment, process simulation is used to point out the most promising recirculation options (Figure 1).

3. Exergy Analysis

The concept of exergy change, transfer and destruction can be used to develop an exergy balance similar to energy. Exergy will be calculated as the sum of three components, chemical and physical exergy and the exergy change of mixing. The total exergy flow rate of a material stream at actual conditions can be obtained from Eq. (1):

$$EX = F \cdot \left(Ex_{chem} + Ex_{phys} + \Delta Ex_{mix}\right) \tag{1}$$

For real processes the exergy input always exceeds the exergy output. This unbalance is due to irreversibilities, also named exergy destruction and is represented by Eq. (2):

$$\sum_{in} Ex_j + \sum_{in} \left(Ex_Q + Ex_W\right) = \sum_{out} Ex_k + \sum_{out} Ex_Q + I \tag{2}$$

Eq. (2) considers the exergy flow of all entering and leaving material streams, the sum of all thermal exergy and work interactions (Ex_Q and Ex_W) involved in a process as well as the irreversibility I of the system. Cornelissen (1997) discusses three types of exergetic efficiency given in Eq. (3-5). Simple exergetic efficiency (Eq. (3)) expresses all exergy input as used exergy, and all exergy output as utilised exergy. Eq. (4) represents the exergetic losses of the process. Rational exergetic efficiency (Eq. (5)), is initially defined by Kotas (1985). This efficiency is given by the ratio of the desired exergy output to the exergy used. Another possibility to represent the exergetic efficiency of a process is the chemical exergetic efficiency, defined in our process as the ratio between chemical exergy of product gas and biomass feed, presented in Eq. (6).

$$\eta_{ex,1} = \frac{Ex_{out}}{Ex_{in}}, \quad \eta_{ex,2} = \frac{I}{Ex_{in}}, \quad \eta_{ex,3} = \frac{Ex_{prod}}{Ex_{in}}, \quad \eta_{ex,4} = \frac{Ex_{chem,prod}}{Ex_{chem,feed}} \tag{3-6}$$

For further details on the calculation of exergy, especial the calculation of chemical exergy of biomass, see Modarresi (2007) and Wukovits et al. (2008)

4. Results and Discussion

An MS-Excel program has been developed to calculate the exergy of compounds and streams of "Hyvolution"-process (Modarresi, 2007). Calculations are based on feedstock Wheat without reduction of hydrogen partial pressure in the thermophilic fermenter. Substrate concentration at the inlet of thermophilic and photo-heterotrophic fermentation is 50 g/l sugar and 100 mM acetate, respectively (Base Case). Amine-absorption is applied for gas-upgrading. For details on mass- and energy- balance (Wukovits et al., 2008).

Figure 2 shows the exergetic efficiency of the different recycling options in terms of simple exergetic efficiency ($\eta_{ex,1}$), exergetic losses ($\eta_{ex,2}$), rational exergetic efficiency ($\eta_{ex,3}$) and chemical exergetic efficiency ($\eta_{ex,4}$) according to Eq. (3-6). Differences in exergetic efficiencies of the base case to results presented in earlier publications mainly results in slightly changes in mass- and energy-balances as well as in product definition during calculation of exergetic efficiency.

Introducing recirculation streams, the exergetic efficiencies $\eta_{ex,3}$ and $\eta_{ex,4}$ are increased whereas simple exergetic efficiency ($\eta_{ex,1}$) remains pretty constant or even decreases. The amount of increase of $\eta_{ex,3}$ and $\eta_{ex,4}$ corresponds with the reduction of water and heat demand following from mass- and exergy-balance. But the effect of recirculation of effluents on the water and heat demand is much higher than on the exergetic efficiency of the process.

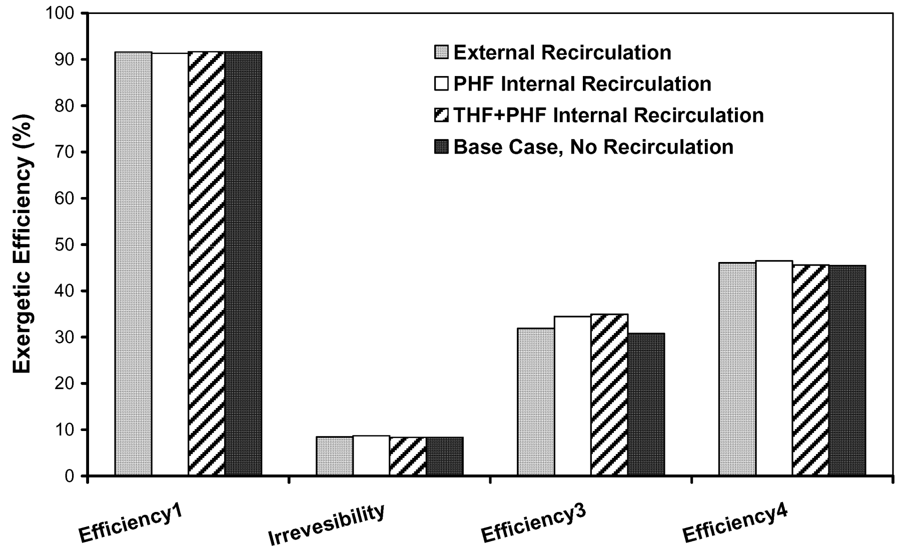

Figure 2: Exergetic efficiencies of investigated recirculation options

Figure 3 shows the potential impact of further measures on process- and heat-integration on exergetic efficiency $\eta_{ex,3}$. Results are based on a parametric study on product definition. It can be seen that exergetic efficiency more than doubles depending on product definition.

Case "H_2" describes the base case, considering only the pure hydrogen stream as product of the process. "H_2 Tail" and "CO_2" also considers hydrogen losses during gas-upgrading and removed CO_2 as a product.

Highest increase in efficiency $\eta_{ex,3}$ occurs when considering residual biomass from the process as valuable product. Biomass refers to biomass produced in the process in form of cell mass and remaining non-fermentable solids from feedstock, respectively. Cell mass produced during fermentation could be re-introduced to the process as feedstock or source of nutrients or might be used to produce heat and power together with the non-fermentable fraction.

When introducing released heat to the portfolio of usable products it follows that from the exergetic point of view the contribution of heat integration to the increase of exergetic efficiency of the process is negligible due to the strong impact of chemical exergy compared to physical exergy in the investigated low temperature process (Figure 3). A further increase in exergetic efficiency will result from the use of effluent of the process ("filtrate") for example to reduce the demand on tap water as well as the use as a liquid fertilizer in enclosed agriculture.

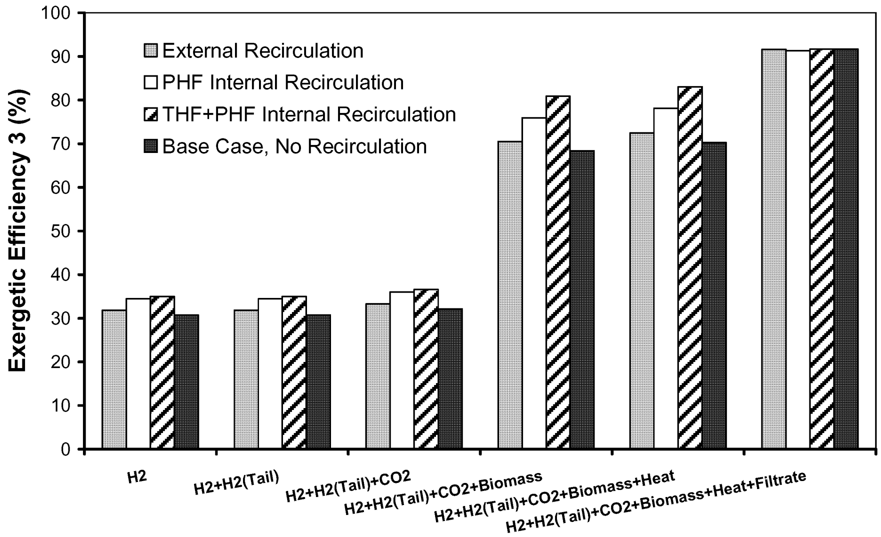

Figure 3: Effect of product definition on rational exergetic efficiency ($\eta_{ex,3}$)

5. Summary and Outlook

Exergy analysis was applied to a novel process for biological production of hydrogen. The exergy content of the process streams was calculated using a MS-Excel spread sheet, incorporating chemical exergy, physical exergy and exergy of mixing.

Introduction of recirculation streams gives a considerable reduction in water and heat demand, but contributes only slightly to the increase of exergetic efficiency.

A case study underlines the strong dependence of obtained exergetic efficiency on definition of obtained products and shows further options for process improvement and optimization. Most important contribution to the increase of exergetic efficiency comes from (re-) use of produced cell mass and non-fermentables as well as effluent from process as feedstock or nutrient, for heat and power generation or fertilizer, respectively.

Calculated improvements of exergetic efficiencies only represent the theoretical maximum. Impact on exergy balance and exergetic efficiency has to be investigated in more detail considering also possible additional process steps necessary to implement the suggested process improvements

Acknowledgement

We gratefully acknowledge the support of the project by the European Union's 6th Framework Program on Sustainable Energy Systems (Hyvolution, Contract-No. 019825).

References

Cornelissen R.L., 1997, Thermodynamics and Sustainable Development, The Use of Exergy Analysis and the Reduction of Irreversibility, PhD thesis, University of Twente, Enschede, The Netherlands.

Kotas T.J., 1985, The Exergy Method of Thermal Plant Analysis, Butterworths, London.

Modarresi A., 2007, Exergy analysis of non-thermal biological hydrogen production from biomass, MSc dissertation, Vienna University of Technology, Vienna, Austria.

Wukovits W., Friedl A., Schumacher M., Modigell M., Urbaniec K., Ljunggren M., Zacchi G., Claassen P.A.M., 2007, Identification of a Suitable Process Route for the Biological Production of Hydrogen, In Proceedings of the 15th European Biomass Conference & Exhibition, 07-11 May 2007, Berlin, Germany, 1919-1923.

Wukovits W., Modarresi A., Friedl A., 2008, Application of mass-, energy- and exergy-balances for evaluation of process configurations for biological hydrogen production, In Proceedings of PRES 2008, included in CD-ROM of Full Texts of CHISA 2008, 24-28 August 2008, Prague, Czech Republic, paper 1314.

Nomenclature

Ex	Molar exergy, kJ/mol
EX	Exergy flow rate, kJ/s
F	Molar flow rate, mol/s
I	Irreversibility
η	Efficiency, Loss
HAc	Acetic acid
PHF	Photo-heterotrophic fermentation
THF	Thermophilic fermentation

Subscripts

chem	Chemical
ex	Exergetic
in	Input
mix	Mixing
out	Output
phys	Physical
prod	Product
Q	Heat
W	Work