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Research Article

Process efficiency simulation for key process parameters in biological methanogenesis

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Abstract: New generation biofuels are a suitable approach to produce energy carriers in an almost CO_2 neutral way. A promising reaction is the conversion of CO_2 and H_2 to CH_4. This contribution aims at elucidating a bioprocess comprised of a core reaction unit using microorganisms from the *Archaea* life domain, which metabolize CO_2 and H_2 to CH_4, followed by a gas purification step. The process is simulated and analyzed thermodynamically using the Aspen Plus process simulation environment. The goal of the study was to quantify effects of process parameters on overall process efficiency using a kinetic model derived from previously published experimental results. The used empirical model links the production rate of CH_4 and biomass to limiting reactant concentrations. In addition, Aspen Plus was used to improve bioprocess quantification. Impacts of pressure as well as dilution of reactant gas with up to 70% non-reactive gas on overall process efficiency was evaluated. Pressure in the reactor unit of 11 bar at 65°C with a pressure of 21 bar for gas purification led to an overall process efficiency comprised between 66% and 70% for gaseous product and between 73% and 76% if heat of compression is considered a valuable product. The combination of 2 bar pressure in the reactor and 21 bar for purification was the most efficient combination of parameters. This result shows Aspen Plus potential for similar bioprocess development as it accounts for the energetic aspect of the entire process. In fact, the optimum for the overall process efficiency was found to differ from the optimum of the reaction unit. High efficiency of over 70% demonstrates that biological methanogenesis is a promising alternative for a chemical methanation reaction.

Keywords: process simulation; biological methanogenesis; CO_2 fixation; overall process efficiency; bioprocess

Abbreviations list:

CO_{2in} = specific CO_2 flow rate entering the reactor [mol $L^{-1}h^{-1}$]; CSTR = continuous stirred tank reactor; CUR = carbon dioxide uptake rate [mol $L^{-1}h^{-1}$]; D_{med} = specific rate of medium added to the reactor [L_{medium} $L^{-1}_{reactor\ volume}$ h^{-1}]; D_{out} = dilution rate [$L_{leaving\ the\ system}$ $L^{-1}_{reactor\ volume}$ h^{-1}]; D_{WER} = specific rate of water generated by the reaction [L $L^{-1}_{reactor\ volume}$ h^{-1}]; Eff_{ferm} = efficiency of reactor considering compression of Comp1, Q_{H2} and Q_{CH4}; Eff_{tot1} = total efficiency of the system considering 2-step compression, stirring, Q_{H2} and Q_{CH4}; Eff_{tot2} = total efficiency of the system considering 2-step compression, stirring,Q_{H2} , Q_{CH4} and Q_{heat}; $\Delta G°$ = Gibbs free energy; HTR = hydrogen transfer rate [mol $L^{-1}h^{-1}$]; HUR = hydrogen uptake rate [mol $L^{-1}h^{-1}$]; H_{2Liq} = equilibrium concentration of H_2 in the liquid phase [mol L^{-1}]; H_u = net calorific value [MJ kg^{-1}]; K_s = the specific substrate concentration at which the reactor rate is half of the maximum rate; MER = methane evolution rate [mol $L^{-1}h^{-1}$]; Q_{CH4} = heat content of CH_4 generated in the process [kW L^{-1}]; Q_{H2} = heat content of H_2 provided to the process [kW L^{-1}]; Q_{heat} = heat generated during the compression process [kW L^{-1}]; VLE = vapor liquid equilibrium; vvh = volume of gas per volume of liquid and hour [L $L^{-1}h^{-1}$]; W_{Comp1} = work used for compression at compressor 1 pressurizing the core process [kW L^{-1}]; W_{Comp2}= work used for compression at compressor 2 pressurizing the purification unit [kW L^{-1}]; $W_{Stirrer}$= work used for stirring [kW L^{-1}]; Y x/s = biomass yield on substrate [C-mol mol^{-1}].

1. Introduction

The chemical storage of energy in the form of CH_4 generated from renewable resources transforming H_2 to CH_4 by CO_2 fixation is a topic which emerged as the storage of H_2 at an appropriate energy density is difficult [1,30]. The here introduced technology enables to gain an energy carrier with a high energy content which can be introduced in the existing natural gas infrastructures. In addition it proposes a biological alternative to perform chemical methanation reactions. The so-called Sabatier reaction is performed at high temperatures and pressures therefore impacting process economy and carbon balance. Biology operating at milder conditions, the bioprocessing route might be more attractive.

Hydrogenotrophic methanogens are Archaea microorganisms which can use hydrogen for reducing i.e. formate, methanol or carbon dioxide to methane [2,3]. Methanogens metabolizing CO_2 hold a great potential for the development of biological gas conversion processes. To achieve CO_2 neutrality, a bioprocess can be designed where such a microorganism catalyzes the gaseous transformation of H_2 and CO_2 to CH_4 and H_2O The chemical storage of electrical energy in the form of CH_4 with the intermediate step of H_2 production by electrolysis ($H_2O \xrightarrow{electricity} H_2 + 0.5O_2$), followed by the biological conversion ($4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$) to CH_4 is a novel concept rarely described in literature before [2] and known as a “power to gas” technology. Developing this technology at large scale could have an important impact on the global carbon cycle and storing of renewable energies. In addition, as published recently, another achievement of this 4th generation bio-fuel process is to produce CH_4 with waste gases from industry. Biology offers a tolerance towards impurities without impacting the conversion and selectivity of reaction [3,27].

The core this process is the reaction described in the following stoichiometric equation (1). The selectivity towards CH_4 for the used microorganism, able to metabolize 95% of the gaseous substrate to CH_4 and only 5% to biomass, suggested an efficient overall process [6,27,33]

$$[CO_{2,Liq} + 4\ H_{2,Liq} \rightarrow CH_{4,gas} + 2\ H_2O_{Liq}]; \quad (1)$$

The process simulation software Aspen Plus [4] was used to analyze the process in terms of mass and energy balances. Aspen Plus is a simulation tool regularly used in chemical process engineering [5]. Although applications to bioprocesses are rare, it is also a suitable tool for bioprocess balancing. In line with the current contribution the possibility to perform mass and energy balance calculations as well as process integration studies was reported for other bioprocesses such as the production of bio-hydrogen [7,8,9]. Another study described the economic comparison of ethanol production by Z. mobilis and Saccharomyces and was performed in Aspen Plus [10]. But, so far, no publication concerning process evaluation with Aspen Plus exists for a biological methanogenesis process.

In this work, the focus was not the simulation of physiologic aspects such as biomass formation. As a preliminary input to this contribution, the physiology was studied experimentally at lab-scale in order to retrieve the production rates and scalable parameters that were used for the kinetic model of the reaction unit [6,27,33].

The aim of the simulation was to identify key process related factors and their influence on the overall process efficiency. The experimental kinetic model ensures the conservative basis of the simulation as it limits speed of reaction and CH_4 productivity. At large scale, economic, energy and safety requirements have to be fulfilled. Therefore this work focuses on a basic understanding of the proposed process and how parameters such as operating pressure, dilution of reactant gases or stripping and scrubbing of media components influence the process performance.

2. Materials and Method

2.1. Process flow-sheet for biological methanogenesis

The following section describes the proposed process, the general assumptions, the reaction model and the parameters used within the simulation. The integrated process implemented in the simulation tool Aspen Plus includes: mixing of reactants prior to the reactor entry, the reaction step and the purification of the produced gas to a pipeline quality.

Based on the developed simulation model, the overall energy efficiency of the integrated process is then analyzed.

2.1.1. Process and simulation model for biological methanogenesis

The proposed overall process is shown in Figure 1. The reactant gases H_2 and CO_2 are mixed in the unit “MIXINGAS” using a mixer model. The resulting stream is compressed to the desired pressure in the reactor block by an isentropic compressor “COMPR1”. Compressed gas is adjusted to 65 °C by the unit “HEAT1”. In the equilibrium reactor unit “REQUIL” the gas is mixed with medium and the pH of reaction is adjusted with NaOH addition. Finally, in the reactor block “REQUIL” incoming gases H_2 and CO_2 are converted to CH_4, H_2O and biomass. The reactor used in

experiments was a continuous stirred tank bioreactor replaced in the simulation by an equilibrium reactor model, in which the kinetic model was implemented. The reactor model allows a flexible implementation of rates, conversion and selectivity of reaction based on experimental data as well as the simultaneous calculation of vapor and liquid equilibrium.

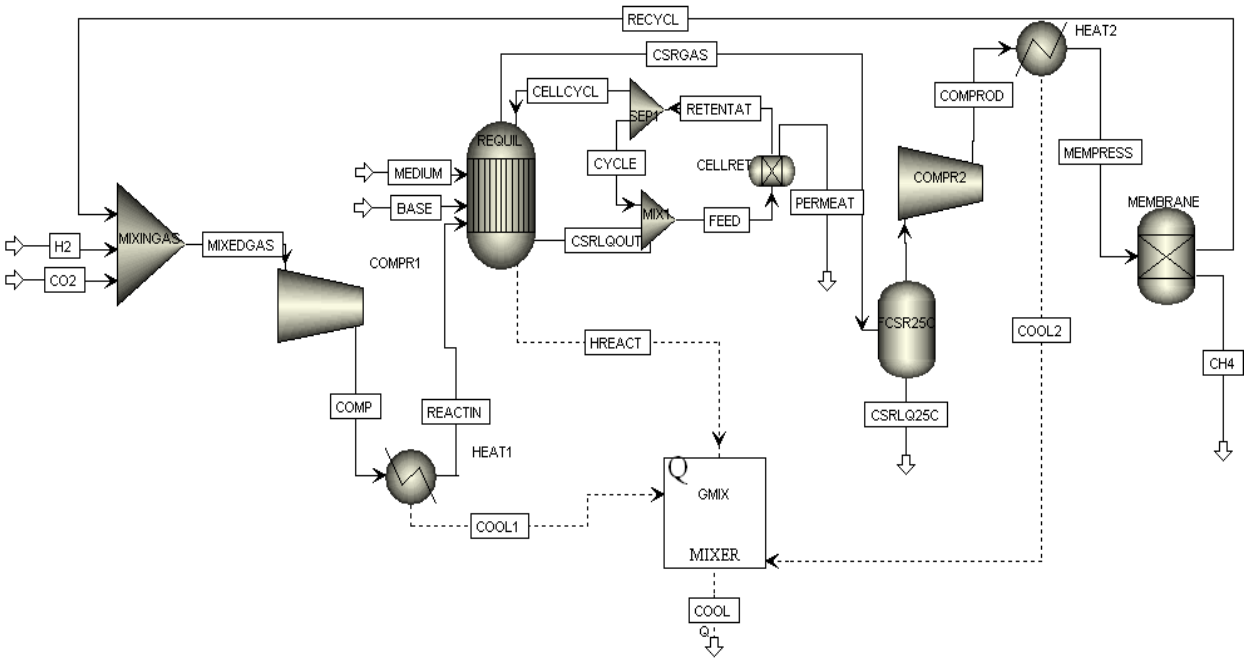

Figure 1. Aspen Plus flow-sheet for the continuous process of biological methanogenesis.

As the microorganism acts as a biocatalyst it is of interest to limit biomass washout from the reactor as well as the effluent rate. Strategies for reducing dilution rate were investigated and are further explained in the results section. A cell retention system mimicking a tangential flow filtration step (units "MIX1", "CELLRET" and "SEP1") was implemented in the flow-sheet.

The gas phase stream leaving the reactor "REQUIL" contains the produced CH_4 and H_2O as well as excess H_2, H_2S, NH_3 and CO_2. After leaving the reactor, the gas is cooled at 25 °C in the flash unit "FCSR25", which removes condensate assuming thermodynamic equilibrium between liquid and gas phase. Subsequently, the dried gas is compressed in unit "COMPR2" to a pressure of 21 bar, assumed to be necessary for operating the gas permeation unit. The compressed gas finally enters the gas permeation unit "MEMBRANE", where CH_4 is separated from H_2 and CO_2. Gas permeation unit "MEMBRANE" at the moment is implemented via a simple component split unit. The permeating H_2 and CO_2 are recycled and mixed to the fresh H_2 and CO_2 in the upstream mixer unit "MIXINGAS". All heat streams generated in the core reactor unit or at the different compressors are collected and summed up in the unit "GMIX".

Design specifications, working similar to a feedback controller, were used in the simulation model, to control pH as well as to adjust the ratio between H_2 and CO_2 to 4:1 at the reactor inlet. These parameters where chosen in order to match physiologic optimum predetermined in earlier studies [6,27,33].

2.1.2. Process parameter and assumptions

The reaction kinetic model is based on the following assumptions:

a) Production of CH_4 depends, according to (1) on CO_2 and H_2 dissolved in the liquid phase. As CO_2 solubility is much higher than H_2, only H_2 concentration in the liquid phase (H_{2Liq}) is regarded as limiting for the kinetic model.

c) Equilibrium concentration of H_{2Liq} happens according to Henry equation and hence changes with pH, temperature and pressure.

d) Aspen Plus assumes ideal mixing in the reactor unit. Methane productivity was limited by the kinetic model based on experimentally verified values achieved in a lab-scale bioreactor [27,33].

Calculations performed within this paper are based on the following parameters, assumptions and simplifications:

- Electrolyte-NRTL activity coefficient model [11], ELECNRTL, was used for the calculation of activity coefficients in the liquid phase, capable to consider the electrolyte character of the reaction medium. Vapor phase is described via the Redlich-Kwong equation of state [4]. Gas solubility calculations are based on Henry's law.
- For methanogenesis reaction (1), the equilibrium reactor model was chosen as explained in section 2.1.1. Methane evolution rate (MER), (2) was implemented with a calculator block using the kinetic model.
- Biological methanogenesis is a bioprocess performing tendentiously under gas transfer limitation. Biomass is seen as a byproduct of reaction. Biomass is assumed, based on experimental results for the simulated range of parameters to be always sufficient to turn over all the dissolved H_2 [6,27,33].
- All side reactions to (1), except biomass formation are neglected.
- Equilibrium was assumed for gas absorption and desorption.
- Reaction temperature was set to 65 °C.
- A working pH of 7 was applied except if not specified differently
- CO_2 and H_2 inlet flow rates were held at a ratio of 1:4 according to reaction (1) stoichiometry in the stream MIXEDGAS by using a design specification.
- The total inlet flow-rate was 0.73 L $L^{-1}min^{-1}$ for all calculations, if not indicated otherwise.

An overview of further process parameters and their variation range is given in Table 1. The default media composition implemented has been extracted from previously published results [6,27,33].

Table 1. List of process parameters.

Unit	Type	Temperature	Pressure
Reactor	equilibrium	65°C	1 bar-11 bar
Compressor 1	isentropic	65°C	1 bar-11 bar
Compressor 2	isentropic	65°C	21 bar

2.2. Development of the reaction kinetic model

The kinetic of this bioprocess is known to be dependent on many chemical as well as biological parameters and so far no kinetic model for MER is available. The main reason is the gas limited character deriving from the poor solubility of H_2 at ambient pressure. The process operates tendentiously under the limitation of a gas to liquid H_2 mass transfer [2,6,12,27,33]. One reason is that most bioreactors available, despite high $k_La´$ values, are limited in terms of operating pressures, which would guarantee improved H_2 solubility.

Due to the complexity of the biological system, a simple first order enzymatic reaction kinetic equation was used as model for obtaining mass and energy balances [31]. This simplified approach, can account for the selectivity of reaction towards biomass. In fact, the cell metabolism was implemented assuming no side reactions except for biomass formation. In this approach 95% of the C is available for CH_4 production and so the maximum MER cannot exceed 95% of the CO_2 inlet rate. The remaining 5% of carbon is attributed to biomass formation using the yield Yx/s = 0.05 [C-mol mol^{-1}] which was reported constant under gas limited conditions [6,27,33]. The MER model is presented in (2) and (3). The gas to liquid transfer is based on equilibrium calculations following Henry´s law and affected by pH, temperature and pressure [13]. Aspen Plus calculates H_{2Liq} also as a function of the system pressure (Figure 2). Therefore, pressure dependence emerged in MER calculations but the CO_2 inlet determines the maximum MER and was set according to experiments.

$$MER = (1 - Y_{x/s}) \bullet CO_2[molL^{-1}h^{-1}] \bullet \frac{H_{2Liq}[molL^{-1}]}{K_M\ [molL^{-1}] + H_{2Liq}[molL^{-1}]}; \quad (2)$$

$$K_M = 0.00769\ [molL^{-1}]; \quad (3)$$

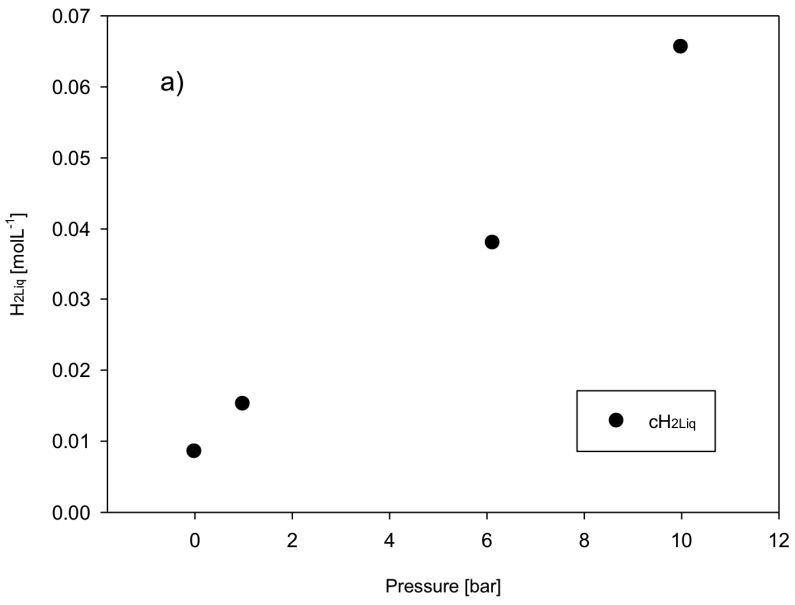

Figure 2. Pressure dependence of the equilibrium concentration of H_2 in liquid phase (H_{2Liq}).

In this empiric model the parameter K_M is a constant determined by fitting experimental and simulated MERs obtained at different H_{2Liq} concentrations. H_{2Liq} was varied experimentally by increasing operating pressure for a fixed CO_2 inlet. This allowed an increase in MERs but never reaching the total conversion of CO_2 and H_2 [2,6,27,33].

The model was validated for various cases by comparing MERs obtained by the model with values obtained experimentally (Figure 3). It can be clearly seen that MERs calculated with the used reaction model closely match with experimentally obtained MERs. The fit between reaction model and experimental results was within 5% error. Hence, all MER values from simulation are considered to be close estimates. Detailed information on the method for experimentally obtained data as well as maximum specific methane productivity per gram of biomass is available in literature [6,27,33].

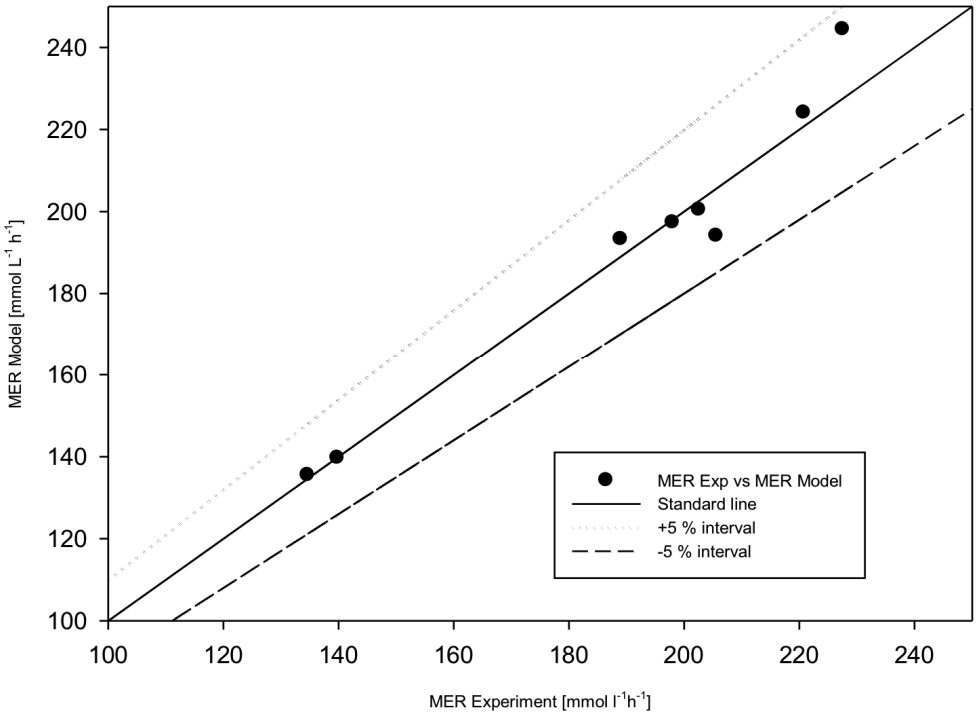

Figure 3. Correlation of Methane Evolution Rates (MER [mmol L^{-1} h^{-1}]) obtained from regressed model vs. experimental data.

In addition, verification of the thermodynamic aspects of simulation was investigated. To prove, that the obtained heat of reaction is calculated correctly, ΔG° of reaction was examined. In literature a ΔG° value of -130.7 kJ mol^{-1} CH_4 is reported at 298.15 K [19]. A slightly elevated ΔG° was expected, as the reaction temperature is higher than in Dolfing. approach [19]. Using ΔH and ΔS obtained with Aspen Plus, a ΔG = -126.6 kJ mol^{-1} was determined at ambient pressure and 338.15 K. Therefore, the simulation is considered thermodynamically sound.

2.3. Compressor duty and efficiency of the process

The impact of pressure on the system is important for two reasons. First, the effect of pressure on gas solubility is well known and contributes to increase the amount of dissolved gas available for

the microorganisms. In this simulation the model was used to extrapolate slightly higher MERs at higher pressures but always being limited by the kinetic model as high-pressure experiments were not accessible with the experimental setup. Secondly, for evaluating compression duty for pure and diluted reactant gas mixtures and how process efficiency is influenced by gas feed carrying different amounts of inert gas.

During manual confirmation of compressor results (data not shown) some discrepancies between manually calculated and results obtained by simulation were found. However, in the overall process efficiency this discrepancy is minimized to some percent. In addition, Aspen Plus was overestimating the power of compression. Hence, only the Aspen Plus calculations are used for the energy balance and further guarantee the conservative basis applied in this bioprocess efficiency simulation.

According to the aims of this study the energy balance of the process was investigated and calculated based on values obtained with the process simulation.

The theoretical energy potential can be calculated easily based on the net calorific value (H_u):

H_u, CH_4= 50.013MJ kg^{-1}[20]

H_u, H_2= 119.972MJ kg^{-1}[20]

Based on equation (1) 1 mol CH_4 (0.2233 kWh) can be produced out of 4 mol H_2 (0.268 kWh). The maximum stoichiometric efficiency calculated by 0.223 kWh / 0.268 kWh= 83.2%. Considering that about 5% of carbon is used for cell growth the maximum efficiency can be calculated by (0.223 kWh• 0.95) / 0.268 kWh = 79.2%.

From this theoretical efficiency the following values have to be subtracted:

Energy input for stirring: $W_{stirrer}$

Energy input for compression: W_{Comp1}+W_{Comp2}

A value of around 5 kW m^{-3} of non-aerated reactor volume, commonly used in industrial process technology, is taken as stirring energy input [29].

An additional, however not directly usable heat stream is the heat of compression. Q_{heat} generated by the cooling of the two compressors.

The heat of reaction from biological methanogenesis can be significant and the reactor vessels would need to be cooled. However, reaction heat was not taken into account for the efficiency calculations. The temperature level of this heat stream corresponds, at the maximum, to the reaction temperature (65°C) and may only be recuperated locally.

To get a ranged estimate for the accessible energy (in form of accessible heat or CH_4 product) both calculations with and without including Q_{heat} are shown. The results give the higher and the lower bound of the process efficiency regardless of the real thermodynamic of transformation.

Hence, the overall efficiency of the system was obtained using the following correlations:

$$Eff_{tot1} = \frac{Q_{CH4}}{W_{Comp1} + W_{Comp2} + Q_{H_2} + W_{Stirrer}} \quad : \tag{4}$$

$$Eff_{tot2} = \frac{Q_{CH4} + Q_{heat}}{W_{Comp1} + W_{Comp2} + Q_{H_2} + W_{Stirrer}} \quad : \tag{5}$$

In contrast, the core reaction efficiency (Eff_{ferm}) only includes H_2 input, compressor 1 duty and

CH_4 output.

$$Eff_{ferm} = \frac{Q_{CH4}}{W_{Comp1} + Q_{H2}} \quad : \tag{6}$$

3. Results and discussion

3.1. Stripping evaluation for bioprocess substrates NH_3. CO_2 and H_2S

Providing nutrients to avoid limitation is a crucial task in bioprocess development and was found to be of high importance for biological methanogenesis [9]. Furthermore, accurate calculation of the solubility equilibrium of media components and their becoming in multi component mixtures is important to assist media development for different process conditions. This information can for example be used for elemental balancing of components that are not directly accessible with the available analytics or to predict certain limitations due to changing process conditions. In addition this knowledge can be used for the development of a proper feeding strategy. The capability of Aspen Plus to calculate stripping rates was used here for volatile substrates formed from non-volatile salts contained in the medium. Different process conditions (temperature, pH, and gassing rate) in the bioreactor were evaluated by calculating the involved gas-liquid equilibrium.

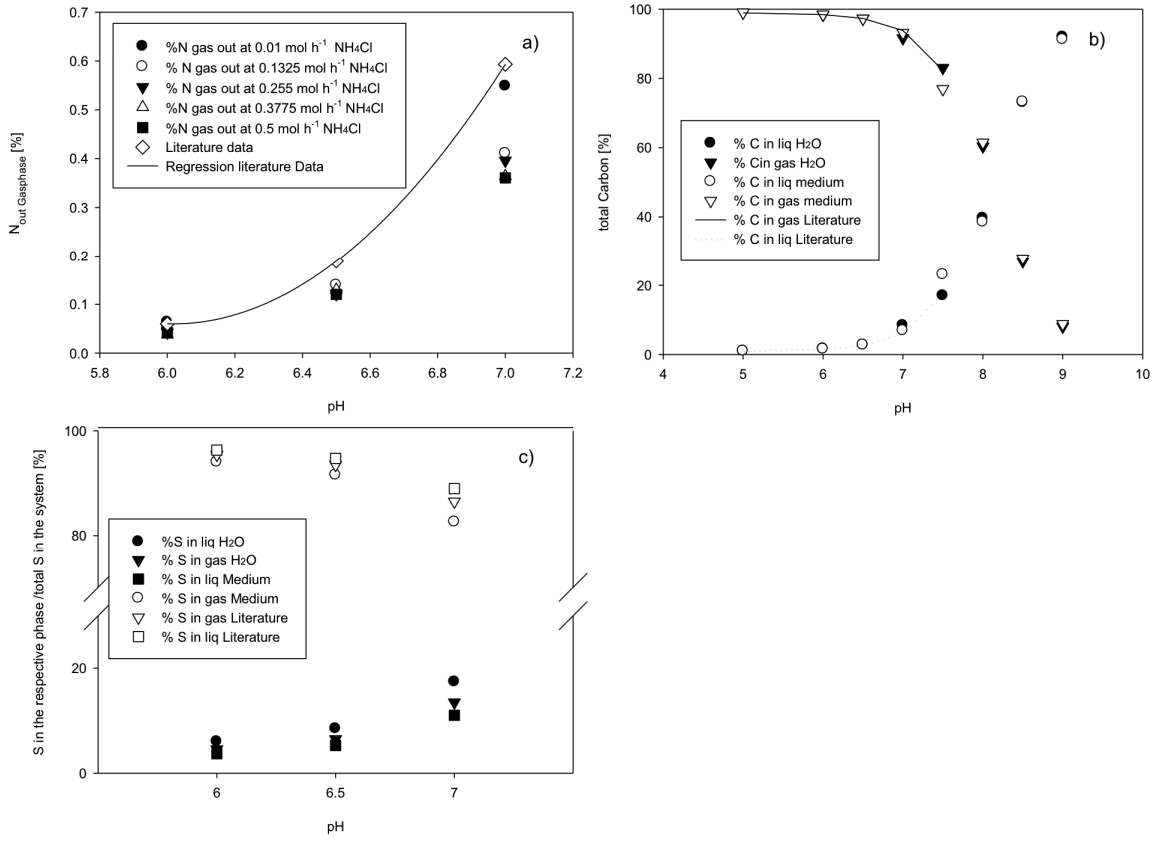

Figure 4. Stripping of volatile media components at varying pH and feeds of: a) ammonia b) carbon, c) sulfur.

3.1.1. NH_3

Nitrogen is usually fed to the microorganisms in the form of NH_4Cl. In order to check nitrogen losses from the bioreactor medium in the form of NH_3, simulations in Aspen Plus were performed for different NH_4Cl flow rates as function of the reaction pH at a fix dilution rate. At higher pH value more NH_3 is released to the gas phase and lost from the bioreactor media (Figure 4A). However, only a small amount below 0.6% of nitrogen fed to the system in form of NH_4Cl is stripped out from the liquid phase as gaseous NH_3. The simulated values match data determined by the dissociation equilibrium and Henry's constant from literature [21,22]. Figure 4A, shows a decreasing percentage of the fed nitrogen stripped to the gas phase at increasing NH_4Cl flow rates, with constant pH and gassing flow rate. This is explained by increased NH_4Cl concentration and in absolute more mol stripped from the bioreactor broth but a smaller relative percentage. Due to these small losses of nitrogen, no special attention needs to be paid with respect to NH_3 stripping for media development but have to be considered for the development of a downstream purification process.

3.1.2. CO_2 and dissociation products

The process, as described previously, is not limited by CO_2 but it however remains an important substrate as it is the sole carbon source in this bioprocess. A closer investigation was therefore required for the CO_2 solubility which is dependent on temperature and pressure according to Henry law and on pH due to the dissociation in HCO_3^- and CO_3^{2-} [23]. To check the accuracy of solubility calculations, results were compared with literature. Furthermore it was investigated, whether a difference in dissociation and solubility of CO_2 can be seen when dissolved in pure H_2O or in defined medium. The simulation results were compared with values obtained by using the Henry coefficient k_H determined by Harned and Davis, [24] and matched closely (Figure 4B). Furthermore, it was shown that solubility and dissociation in the defined media is close to the CO_2 behavior in H_2O due to the relatively low overall salt concentration. The microorganism has an optimal growth at pH 7 and thereby far from the pK_a of H_2CO_3 (Figure 4B). The results were used for improving the C-balance of the bioprocess because of different stripping and scrubbing rates depending on the pH value applied.

3.1.3. H_2S

The medium component Na_2S is the sulfur source of this bioprocess and limitation has to be avoided. In aqueous solution it hydrolyzes into NaOH and NaHS. These components immediately dissociate forming HS^- (pK_{a1}= 6.9) and S^{2-} (pK_{a2} > 14) as well as the volatile and toxic component H_2S metabolized by the microorganism [26]. At the process pH mainly H_2S and HS^- are present, and almost no S^{2-}. The solubility equilibrium of sulfur species was simulated in a similar way to CO_2. The relationship of S stripping as function of pH, but also as function of gassing rate was here investigated. It was shown in literature that with increasing pH more sulfur stays in the liquid phase, but toxicity increases due to trace element complexation [25]. On the other hand, at lower pH major amount of S is stripped in the gas phase. Results obtained by simulation in H_2O show the same relation as with defined media (Figure 4C). At process pH values, most of the added sulfur leaves the system via the gas phase and a change in medium pH has an impact on S availability. Hence, H_2S

stripping has to be closely regarded and adjusted depending on process conditions.

Analyzing stripping rates behavior for C, N, and S bioprocess substrates demonstrate that Aspen Plus is suitable for predicting pH dependent dissociation and gas solubility in defined media and can serve as a valuable tool for media design and development of gas producing bioprocesses. These results seem trivial considering the thermodynamical basis of Aspen Plus. However, to our knowledge, this has not been reported for complex media composition as it occurs in the anaerobic bioprocess studied in this contribution.

3.2. Effect of pressure and diluted reactive gases on MER

Hydrogen mass transfer is the limitation faced in a biological methanogenesis process. While CO_2 is well accessible in the liquid phase due to its good solubility in H_2O, H_2 is hardly soluble in H_2O at ambient pressure. According to Henry's law, the two parameters temperature and partial pressure influence solubility of gases in the liquid phase. Lowering the reactor temperature would increase the concentration of H_{2Liq}. However, this parameter cannot be significantly lowered because of the microorganism's temperature dependent growth. Therefore, the effect of increasing pressure was investigated to obtain a better H_2 solubility. On the other hand, increasing pressure has considerable impact on compressor duty.

The effect of pressure on reaction efficiency (6) was investigated by comparing energy input to energy output (QCH_4) in the range of atmospheric pressure up to 11 bar in the reactor unit. Input energy was determined by summing up QH_2 in the reactor and the energy applied for compression (W_{Comp1}). The first estimate obtained by simulation shows that higher pressure gives an increased MER compared to the compressor duty (Figure 5A). However, this effect is limited by the total amount of gaseous substrate in the feed. At 11 bar about 80% of the total CO_2 fed take part in the reaction. Due to the plateau shape of the regression model for estimating MER and a crude linear extrapolation of W_{Comp1} using the simulated values a theoretical optimal pressure of 11 bar is suggested for maximizing the reaction efficiency. The biological effect of high reactor pressures has so far not been published for the specific microorganism used as reference for this bioprocess simulation but was reported already for similar microorganisms [32].

In a real process the sole use of pure gases leads to considerable economic limitations. Hence the impact of using gas mixtures containing increased non-reactive gas proportions was evaluated on the obtained MER, compressor duty and process efficiency. The effects of several emission gases on physiology and productivity was already published [27]. The threshold for acceptable losses in the reaction efficiency due to the use of diluted gas mixtures was set to 20%. As a model for mimicking gas mixtures increasing amounts of the inert gas N_2 were added to the reaction mixture of CO_2 and H_2. While low amounts of N_2 show only a small increase in compressor duty, simulation shows that 20% efficiency is lost at about 70% of non-reactive gas. At a simulated gas composition of 70% N_2 about 45% of the energy stored in the form of CH_4 had to be used for compression (Figure 5B).

This result suggests that the addition of gas not participating to the reaction should be limited to a maximum of 70% to avoid high efficiency losses in the reactor unit. The effect of additional gas on the microorganisms need to be done case by case and can be evaluated in respect to inhibition and toxic effects according to a published methodology [27]. Purification efficiency for separation of CH_4 from non-reactive gas in the permeation unit was not investigated within this work and would depend mostly on the gas composition.

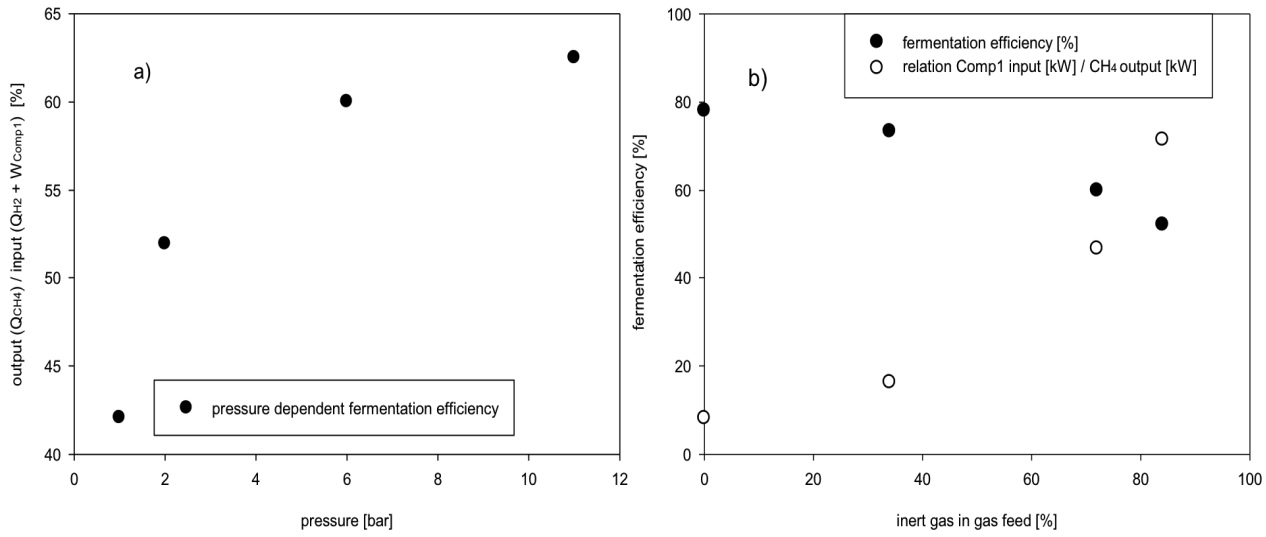

Figure 5. a) Reaction unit efficiency at varying pressure (Q_{CH4}/input energy). b) Fermentation efficiency and relation between compression energy input and product energy output in the reactor unit shown at a fixed amount of process gas, but varying concentration of inert gas feed at 6 bar reactor pressure.

3.3. Water removal

A high feed of H_2O poses the risk of cell washout, which works as biocatalyst as well as increasing the amount of effluents. For biological methanogenesis, H_2O is fed continuously to the system in the form of medium but is also generated during the production of CH_4 (1). To avoid washout of cells and minimize wastewater, feeding of medium has to be minimized. A solution might be to maximize the removal of H_2O via the reactor headspace. Therefore, H_2O added with the liquid medium feed was set in relation with H_2O generated by the reaction through the ratio D_{med}/D_{out} given in %.

The medium feed was varied from 0.005 h^{-1} to 0.1 h^{-1} and investigated by process simulation. It was shown, that at a medium dilution rate of about D_{med}= 0.005 h^{-1} only 29% of H_2O leaving the system in the liquid phase comes from the feed, while the remaining 71% is H_2O produced by the reaction stoichiometry (Figure 6A) finally giving a total dilution rate D_{out}=0.016 h^{-1}. At higher medium feeds the contribution to total dilution rate D_{out} rises drastically, showing a large impact on the effluent rate. At standard feeding rate D_{med}= 0.05 h^{-1} H_2O formed in the reaction (D_{WER}= 0.011 h^{-1}), contributes only by a small part to the total dilution rate D_{out}= 0.061 h^{-1}. During experiments a dilution rate (D_{med}) of 0.05 h^{-1} never encountered washout situation at these gassing rates [6,33].

Water leaves the reactor not only in liquid form, but also via the reactor headspace. At standard conditions about 6% of H_2O leave via headspace (Figure 6B). So an increase of gas flow rate would increase the amount of H_2O removed from the system via the reactor headspace. Since an increase in amount of reacting gases would also increase the amount of stoichiometrically produced H_2O, the gas added to the process was increased by addition of inert N_2. In Figure 6B the ratio between H_2O removed over the headspace and total amount of excess H_2O (D_{out}) was plotted against the

concentration of N_2 in the gas feed. For these simulation runs no H_2O was added by medium feed; all components were added in their native form.

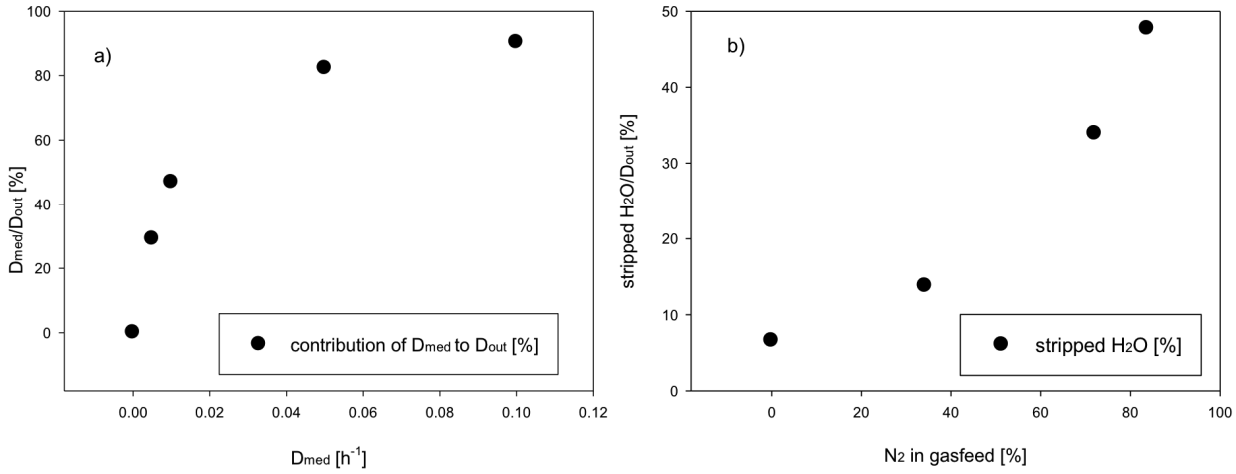

Figure 6. a) Evaluation of the contribution of liquid medium addition and H_2O formed in reaction on D_{out}; b) Estimation of water removal over the headspace by adding N_2 to the process reactive gases at $D_{med} = 0$.

A content of around 80% of inert gas in the gas feed allows the removal of about 50% of H_2O generated by the reaction over the headspace (Figure 6 B). In section 3.2 an addition of no more than 70% of inert gas was proposed to keep the energy input for reaction gas compression below 20% of total energy yield. At 70% N_2 in the gas feed, only 35% of the formed H_2O can be removed via the headspace. Hence, if D_{out} has to be decreased, a combined approach of minimizing liquid medium feed to 0.005 h^{-1} and increasing gas flow by addition of 70% of inert gas could be used. The total dilution rate is then lowered from $D_{out} = 0.06$ h^{-1} to $D_{out} = 0.012$ h^{-1}. However, lowering dilution rates increase the residence time of media components, which may affect process stability and would need to be investigated separately. In a real application a membrane filtration unit could also be implemented for cell retention. Finally, H_2O after condensation might also be considered as an additional byproduct of reaction and a potential renewable H_2O source, which could be collected by pervaporation [28].

3.4. Overall process efficiency

In the last section, all previous findings were combined to generate an estimation of the overall efficiency for the integrated process. This simulation consists of: the reaction step, the gas purification unit as well as the gas recirculation including all compression steps.

A rise of reactor pressure leads to an increase in MER and a higher efficiency (Section 3.2). The integrated process with unreacted gas recycling also includes gas purification at high pressure. Due to the significant volume contraction of the reaction (1 mol of CO_2 and 4 mol of H_2 give 1 mol of CH_4, (1)) the amount of gas entering is much higher than the amount of gas leaving the reactor. Therefore about 5 times more gas has to be compressed before the bioreactor than at the gas purification step. Thus, the main goal of this section was to find an optimum pressure for the

different process steps maximizing the overall process efficiency. It was investigated, whether the increase in MER by increased reactor pressure compensate the higher compression energy.

To investigate the effect of different pressure levels on overall process efficiency, MER and power demand for different process options were calculated considering a maximum pressure of 11 bar in the reactor and 21 bar for the gas purification step. No pressure losses are assumed in the different process steps.

The investigated cases are summarized in Table 2 and Table 3 shows the simulation results in terms of Eff_{tot1}(4) and Eff_{tot2} (5) respectively ignoring or considering the heat released by the different process steps.

Table 2. Investigated cases and resulting overall process efficiencies.

Case	Pressure at reactor [bar]	Pressure at separation unit [bar]	Eff_{tot1} (Eq.4) [%]	Eff_{tot2} (Eq. 5) [%]
A)	1	21	67.91	73.18
B)	2	21	70.16	75.74
C)	6	21	68.09	73.93
D)	11	21	66.62	74.21

Table 3. Conversion efficiencies of different state of the art power- to-gas processes [14-18].

Path	Efficiency	Conditions
Electricity to gas		
electricity →H_2	54-72%	at compression to 200 bar (working pressure of most gas storage plants)
electricity →CH_4 (SNG)	49-64%	
electricity →H_2	57-73%	at compression to 80 bar (feed long distance/transmission pipeline)
electricity →CH_4 (SNG)	50-64%	
electricity →H_2	64-77%	without compression
electricity →CH_4 (SNG)	51-65%	
electricity to gas to electricity		
electricity →H_2→ electricity	34-44%	at electrification with 60% and compression to 80 bar
electricity →CH_4 (SNG) → electricity	30-38%	
electricity to gas to electricity (cogeneration, combined heat and power, CHP)		
electricity →H_2→ electricity (CHP)	48 - 62%	at 40% conversion efficiency for electricity, 45% efficiency for heat and compression to 80 bar
electricity →CH_4 (SNG) → electricity (CHP)	43 - 54%	

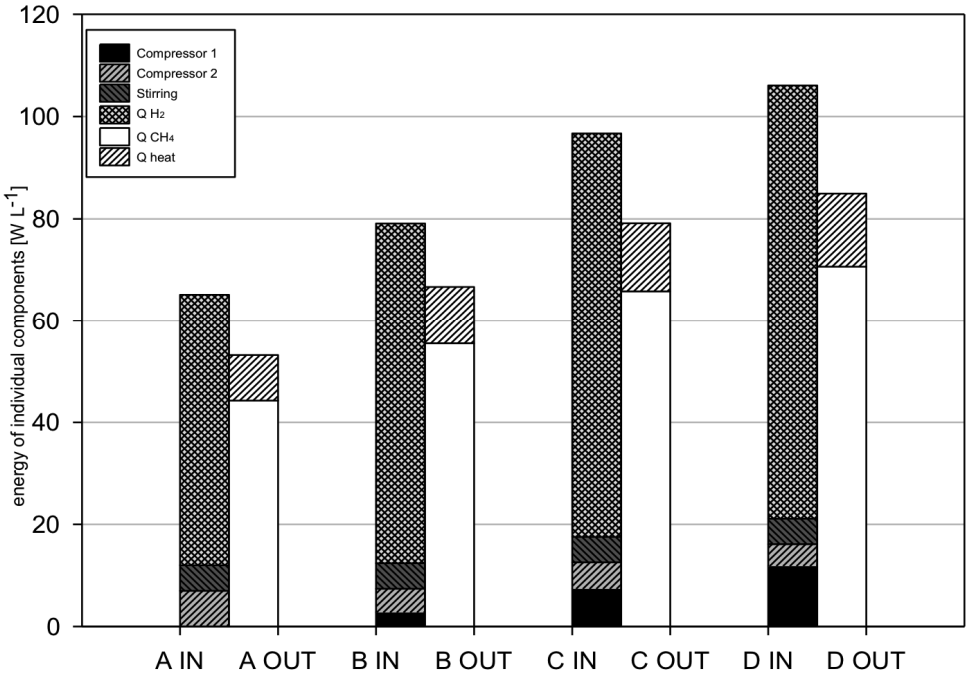

Figure 7. Process energy balance for the overall process and each individual process steps. Fixed pressure of 21 bar was applied at compressor 2 and pressures of (A) 1bar, (B) 2 bar, (C) 6 bar and (D) 11 bar at compressor 1. An optimum is found at 2 bar reactor pressure. The core process efficiency is highest at 11 bar. However the optimum can be explained by volume contraction. The first compressor is compressing 5mol of gas (4 mol H_2 and 1 mol CO_2) for 1 mol of CH_4 generated, whereas the second compressor only has to compress the lower volume of highly converted gas.

Based on the results shown in Figure 7 and the calculated efficiencies it can be seen that an optimum is found at 2 bar for reactor pressure and 21 bar for gas purification. This result is surprising, as the core process efficiency is highest at 11 bar. However, this effect can be explained, as previously mentioned, by reaction volume contraction. The first compressor is compressing 5 mol of gas (4 mol H_2 and 1 mol CO_2) for 1 mol of CH_4 generated, whereas the second compressor only has to compress the lower volume of highly converted gas.

4. Conclusion

This study is a rare attempt to use Aspen Plus simulation environment in the field of bioprocess technology. Furthermore, to our knowledge, no simulation has been published so far which investigate the overall process efficiency for a biological methanogenesis process.

Based on experimental results published by Rittmann et al. [6] and Seifert et al. [27,33] an experimentally derived empiric kinetic model was used. The reaction unit was simulated using a model linking conversion rate to the limiting substrate concentration in order to obtain an estimation

of the overall process efficiency using experimentally verified reaction rates.

In this simulation approach it was shown that Aspen Plus was useful to calculate vapor-liquid equilibrium, and dissociation of investigated elements such as S, N and C source contained in the defined mineral media. This simulation concept is a valuable tool for improving elemental balancing of bioprocesses by estimating scrubbing or stripping rates for the substrates of interest. In later stages Aspen Plus simulation might be used as a tool for media design and adaptation to varying process conditions.

Furthermore, it was shown that Aspen Plus can be used as a valuable tool for estimation of bioprocess efficiency. The optimum pressure for the efficiency of the core reaction unit was found at 11 bar and differs from the optimum obtained for the integrated process, being at 2 bar. This large discrepancy can be explained by the fact, that 5 mol of reaction gas react to 1 mol of product gas, giving a 5 times higher volume for compression at compressor 1 compared to compressor 2. However, change in overall process efficiency with changing core unit pressure is small, varying from 66% to 70% if only the produced gas is taken into account and 73 to 76% if Q_{heat} is added on the product side. Hence, optimum pressure in the core unit will rise in the integrated process, if a lower pressure at the purification unit is used. For more detailed efficiency analysis, a suitable compressor unit has to be modeled and loss of H_2 in the purification step has to be considered. However, these results show the utility of Aspen Plus for similar bioprocess development as it account for the energetic aspect of an integrated process and not only individual steps.

State of the art "power to gas" technologies show similar efficiencies for formation of methane (Table 3). Since our study focuses only on the production of CH4 with H_2 and CO_2, the conversion of power to H_2 has to be considered when comparing process efficiencies. Assuming maximum efficiency for the conversion of power to H_2 (77%) and an efficiency of biological methanogenesis process (70%) obtained without considering obtained process heat gives an overall efficiency of about 54% for conversion of power to CH_4, which is perfectly in line with data available for other technologies. Considering the heat obtained in the process a total efficiency of conversion could go as high as 65% which aligns with the best existing technologies for "Power to Gas" while performing at a much lower range of temperature and pressure than chemical processes. Therefore milder condition applied to this process will benefit the cost of investment.

The high efficiency of over 70% also demonstrates that biological methanogenesis is a promising alternative to the chemical transformation which offers as well a higher tolerance towards impurities.

Finally, Aspen Plus was proved to be an adaptable and useful tool for performing adaptive bioprocess efficiency simulation while implementing product formation kinetic models obtained experimentally at lab-scale. Although the simulated model cannot give insight into the biological process itself, it is highly useful for the layout and investigation of the integrated bioprocess. A detailed simulation could not only be used for process scale up, but also for optimization. Also the use for balancing similar bioprocesses could be of great interest.

The combination of Aspen Plus simulation with physiological investigation under bioreactor conditions is a new approach for bioprocess scale up and summing up the results, it was shown that Aspen Plus, although rarely used in this field, is a valuable tool in bioprocess technology.

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Conflict of Interest

All authors disclose to have no conflict of interests.

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