

## Process Optimisation of Biogas-Based Power-to-Methane Systems by Simulation

Florian Kirchbacher\*, Martin Miltner, Walter Wukovits, Anton Friedl, Michael Harasek

Institute of Chemical, Environmental and Bioscience Engineering, TU Wien, A-1060 Vienna, Getreidemarkt 9/166, Austria  
[florian.kirchbacher@tuwien.ac.at](mailto:florian.kirchbacher@tuwien.ac.at)

Increasing amounts of renewable energy produced by volatile sources like photovoltaic and wind turbines demand for higher energy storage capacities to achieve a sustainable energy generation and supply. Power-to-methane – storing excess energy via chemical conversion as methane – is one of the most interesting technologies to reach this goal, as it bundles the advantages of large storage capacities, fast response time and use of existing infrastructure. First commercial plants have been realised, but alternative concepts are still heavily researched and in demonstration stage. As most are using complex process setups or achieving low methane product concentrations, process optimisation and simplification is needed, but information on this topic is scarce. To close this gap, a power-to-methane process consisting of catalytic methanation and membrane gas upgrading using biogas as carbon dioxide source was simulated in ASPEN Plus®. Four different process setups were modelled to assess influences of fermentation setup, recycling of membrane off-gas and multistage membrane gas separation as well as pressure and GHSV. Models were parameterised with experimental results obtained from a demonstration plant. It was shown that a process without off-gas recycling requires less energy but leads to hydrogen losses of up to 25 %. Preventing this loss by recycling the off-gas leads to an increase of specific energy demand for hydrogen storage by 17 % and relative membrane area by 11 % for the base case.

### 1. Introduction

Renewable energy sources have become a cornerstone in today's plans regarding the development of the European energy market. Main reasons for this trend are ambitious targets by governments to reduce greenhouse gas emissions. Germany for example tries to achieve a reduction of 80 % to 95 % compared to 1990 until 2050. Realising this is only possible by increasing the market share of renewable energy up to 80 % (Nitsch et al., 2012). High volatility of some renewable energy sources like wind turbines and photovoltaic lead to a divergence between energy production and consumption and therefore interest in energy storage options is high. Multiple potential solutions are available but the large amounts of energy to be stored and time restriction when surplus energy is available put high demands on technology. Power-to-methane is one technology that seems to be tailor-made for challenges proposed by an energy mix containing high amounts of renewable energy sources. Hydrogen is produced via water electrolysis using excess energy. Subsequently hydrogen is reacted with carbon dioxide in a biological or catalytic methanation to form methane. Often pure carbon dioxide is used, creating additional costs. An alternative is the use of biogas, as additional carbon dioxide can be transformed to increase methane yields. (Bailera et al., 2017). Power-to-methane can store energy in a time range from minutes to months and offers a high specific energy storage density (Lehner et al., 2014). Furthermore, it does not demand explicit storage facilities as the product can be fed directly to the natural gas grid as synthetic natural gas (SNG) if it meets the gas grid standards. In general, a SNG containing at least 96 % (v/v) methane can be considered for this, while limits for other components like carbon dioxide and hydrogen vary. However, a concentration of 96 % (v/v) methane is hard to achieve by a single-stage methanation processes. In case of biological methanation it requires long residence times and for catalytic methanation it would demand carbon dioxide conversion rates of more than 99 % (Götze et al., 2016). To reduce demands on methanation an additional upgrading step is needed. Commonly, this is done by pressure swing adsorption,

water scrubbing, amine scrubbing or membranes. Membranes are a promising option for small to mid-sized biogas plants (< 250 m<sup>3</sup>/h) (Niesner et al., 2013), which are most common.

Although the interest in power-to-methane has increased in the last years, as can be seen in the number of demonstration plants and projects (Gahleitner, 2013) and more recently (Bailera et al., 2017), data on process optimisation by simulation is rare. Ancona et al. (2016) presented results for a one-stage methanation system without further upgrading, reaching low methane concentration of 60 % (v/v) methane or using pressure levels of 30 and 60 bar, still missing gas grid standards at 80 % (v/v) methane. An alternative approach using three methanation reactors was presented by Agersborg (2013) leading to > 96 % (v/v) methane. Data including a gas upgrading step is available from Collet et al. (2017) who compared the influence of pressure swing adsorption, water scrubbing, adsorption with amines and membrane gas separation on power-to-gas systems. This work will try to close gaps in the simulation and optimization of power-to-methane systems. Four process routes were assessed, each of them able to achieve > 96 % (v/v) methane using a comparatively simple setup of fermentation, single-stage catalytic methanation and low pressure (< 14 bar) membrane-based gas upgrading. Comparison of energy demand and storage capability for these setups will be presented for the first time.

## 2. SNG upgrading processes and simulation models

While most of the single units – electrolysis, fermentation, methanation and gas upgrading – in biogas-based power-to-methane systems are well researched, optimisation by process design still offers potential for improvement. Four different cases have been designed to study influences of

- 1-stage biogas fermentation vs. 2-stage dark hydrogen/biogas fermentation,
- Recycling vs. no recycling of membrane separation off-gas stream,
- Direct biogas feed to methanation vs. preceding methane separation,
- 1-stage vs. multi-stage membrane gas separation,

as well as operating pressure and gas hourly space velocity (GHSV). Electrolysis was not included as there is no influence expected on the process layout. Simulation was done in Aspen Plus® (v10, AspenTech Inc., 2017) using in-house developed models for methanation and gas separation parameterised with experimental data.

### 2.1 SNG upgrading processes

The layout for the base case (Figure 1a) process presented here is adopted from Kirchbacher et al. (2018). Biogas from either one- or two stage-fermentation is compressed, mixed with hydrogen and preheated. The gas mixture is fed to a catalytic methanation equipped with a commercial bulk catalyst and then dried and upgraded by polyimide-membrane gas separation. This offers a simple setup to realise a power-to-methane process but comes with some disadvantages. Most importantly losses of hydrogen and methane to the off-gas stream.

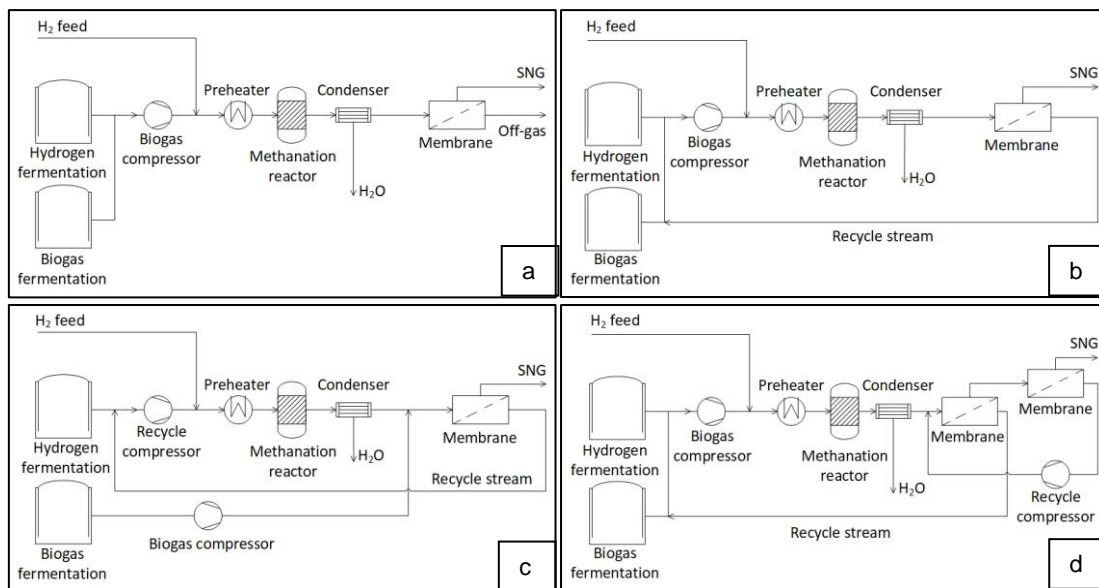


Figure 1 a-d: Process schemes for biogas-based power-to-methane systems; a) No recycle, b) Basic recycle, c) Recycle and preceding CH<sub>4</sub> removal, d) Recycle and two-stage membrane gas separation

Methane recovery is reported to be above 90 % (v/v) (Kirchbacher et al., 2018) but hydrogen losses are supposedly higher diminishing energy storage capabilities. The simplest solution is shown in Figure 1b. Implementation of a recycle stream from membrane permeate side to the biogas feed stream removes any potential hydrogen losses but leads to higher energy demand due to increased amount of compressed gas. Figure 1c shows a concept that tries to mitigate the energy demand for compression by preceding methane removal. Including a second compressor allows to feed the gas from the methane rich fermenter stage directly to the membrane, reducing the load of the recycle compressor. Miltner et al. (2016) reported that multistage processes for biogas upgrading increase the energy demand but reduce methane losses. A simple multistage process was implemented here (Figure 1d) and the off-gas stream is recycled, offering an alternate method to reduce the amount of recycled methane.

## 2.2 Simulation models and parameterisation

For process simulation the development of reliable models is of utmost importance. Aspen Plus® offers reliable models for most common process steps like compressors, condensers, heaters and reactors. These models are often sufficient but, in this case, in-house models for both methanation and gas permeation were deemed necessary. Regarding reactors Aspen Plus® offers the possibility to use yield, stoichiometric, Gibbs or kinetic reactors to describe the behaviour of reactions. Both yield and stoichiometric reactors are not able to model the influence of temperature, pressure or GHSV, all important parameters for the Sabatier reaction Eq(1) taking place during methanation.



While kinetic data on methanation reactions are available in literature the presence of methane in the feed gas is not taken into account making predictions unreliable in this case. Experimental data gathered during the demonstration of the power-to-gas process presented by Kirchbacher et al. (2016) and Kirchbacher et al. (2018) also did not allow regression of kinetic parameters. Using a Gibbs reactor for modelling seemed the most promising approach but leads to errors for predicting methane concentrations at the upper and lower GHSV boundaries. To circumvent this problem conversion rates for a stoichiometric reactor were modelled considering both operating pressure and GHSV, leading to improved results at operation boundaries (Figure 2). To prevent unrealistic results at lower GHSVs the model can achieve a maximum conversion of 95 % which is in line with literature (Götz et al., 2016), reporting maximum conversion rates of 98 % at a maximum of 300 °C and 20 bar.

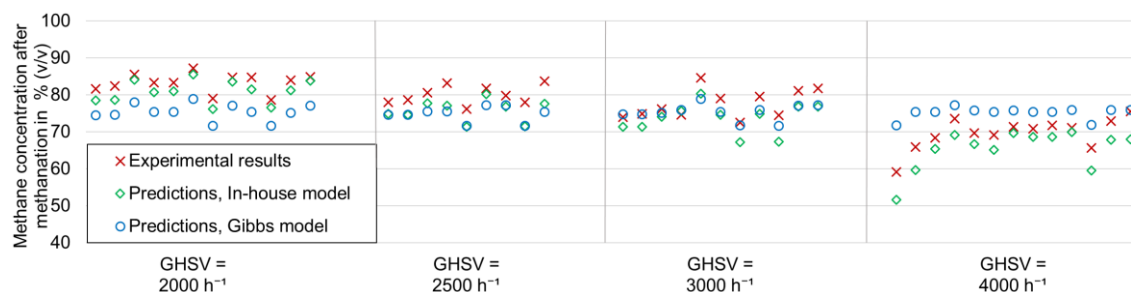


Figure 2: Comparison of methane concentration after methanation between predictions by Gibbs reactor, in-house model, and experimental results

Aspen Plus® also does not include any model for membrane separation processes. Workarounds using simple unit operations like splitters are common but often not sufficient. A counter-current gas permeation unit using the solution-diffusion model has been developed and implemented using Aspen® Custom Modeler (v10, AspenTech Inc., 2017). It is based on and validated against the approach presented by Makaruk et al. (2009). Next to accurate models, reliable data are needed to parameterise single units. Compositions of both fermentation stages have been taken from Schievano et al. (2014) using a mixture of swine manure and maize silage. Exact values are given in Table 1.

Table 1: Biogas composition (Schievano et al., 2014)

	1 <sup>st</sup> stage				2 <sup>nd</sup> stage			
	m <sup>3</sup> <sub>STP</sub> /kg <sub>VS</sub>	H <sub>2</sub> (v/v)	CH <sub>4</sub> (v/v)	CO <sub>2</sub> (v/v)	m <sup>3</sup> <sub>STP</sub> /kg <sub>VS</sub>	H <sub>2</sub> (v/v)	CH <sub>4</sub> (v/v)	CO <sub>2</sub> (v/v)
1-stage fermentation	-	-	-	-	431	0.004	0.692	0.304
2-stage fermentation	97.9	0.439	0	0.561	432	0.003	0.574	0.423

The chosen case represents a common composition for classic one-stage fermentation without overestimating the advantages of a two-stage set up. The feed rate of volatile solids (VS) to the one-stage fermentation was chosen to produce a total gas flow of 80 m<sup>3</sup><sub>STP</sub>/h and kept constant for the two-stage fermentation.

Hydrogen flowrate was adjusted dynamically to ensure a constant molar H<sub>2</sub> : CO<sub>2</sub> ratio of 4.1 : 1 in the inlet stream to the methanation. Operation of the reactor was set to fixed GHSVs ranging from 2,000 h<sup>-1</sup> to 4,000 h<sup>-1</sup>. Overall process pressure was varied between 6 bar and 14 bar.

Selectivities ( $\alpha$ ) for the membrane model were estimated from new, in-house mixed gas experiments using polyimide membranes, the most common membranes used for biogas upgrading (Miltner et al., 2017). The used values (Table 2) are in good accordance with literature for CO<sub>2</sub>/CH<sub>4</sub> (Wind et al., 2004) but a little below literature data for H<sub>2</sub>/CH<sub>4</sub>, which could be caused by swelling due to the presence of high carbon dioxide partial pressures. For the auxiliary equipment, the preheater was set to 350 °C and the condenser was operated at 4 °C.

Most important, the targeted product gas quality was chosen at 96 % (v/v) methane – allowing injection in most natural gas grids – while the concentrations of the remaining components were not considered as specifications for maximum concentration levels differ. For example, Austrian legislation allows hydrogen concentration of up to 4 % (v/v) (ÖVGW G 31, 2001), while Germany limits hydrogen concentration to 2 % (v/v) at the moment but considers increasing the limit to 10 % (v/v) (Müller-Seyring et al., 2013).

Table 2: Summary of important process parameters

p / bar	GHSV / h <sup>-1</sup>	H <sub>2</sub> : CO <sub>2</sub>	CH <sub>4</sub> Product (v/v)	$\alpha$ CO <sub>2</sub> /CH <sub>4</sub>	$\alpha$ H <sub>2</sub> /CH <sub>4</sub>	$\alpha$ H <sub>2</sub> O/CH <sub>4</sub>
6 - 14	2,000 – 4,000	4.1:1	0.96	27.0	35.8	250

### 3. Results and discussion

For presentation of the results a two-step approach is chosen. First, all four processes are compared for a base case scenario at a pressure of 10 bar and GHSV of 3,000 h<sup>-1</sup> (Figure 3). Then the influence of operating pressure and GHSV on the two most promising set-ups will be discussed further (Figure 4).

Biogas-based power-to-methane processes definitely benefit from two-stage fermentation. While specific energy demand for methane production and relative membrane area increases, it allows to store up to 70 % more hydrogen, while also decreasing specific energy demand for hydrogen storage for all presented set-ups. The case neglecting a possible recycle stream seems to be most promising, leading to the lowest energy consumption for production and storage. Negative is the loss of hydrogen and methane to the off-gas. For two-stage fermentation 15 m<sup>3</sup><sub>STP</sub>/h or 9 % of hydrogen is lost directly and methane recovery is only 88 %.

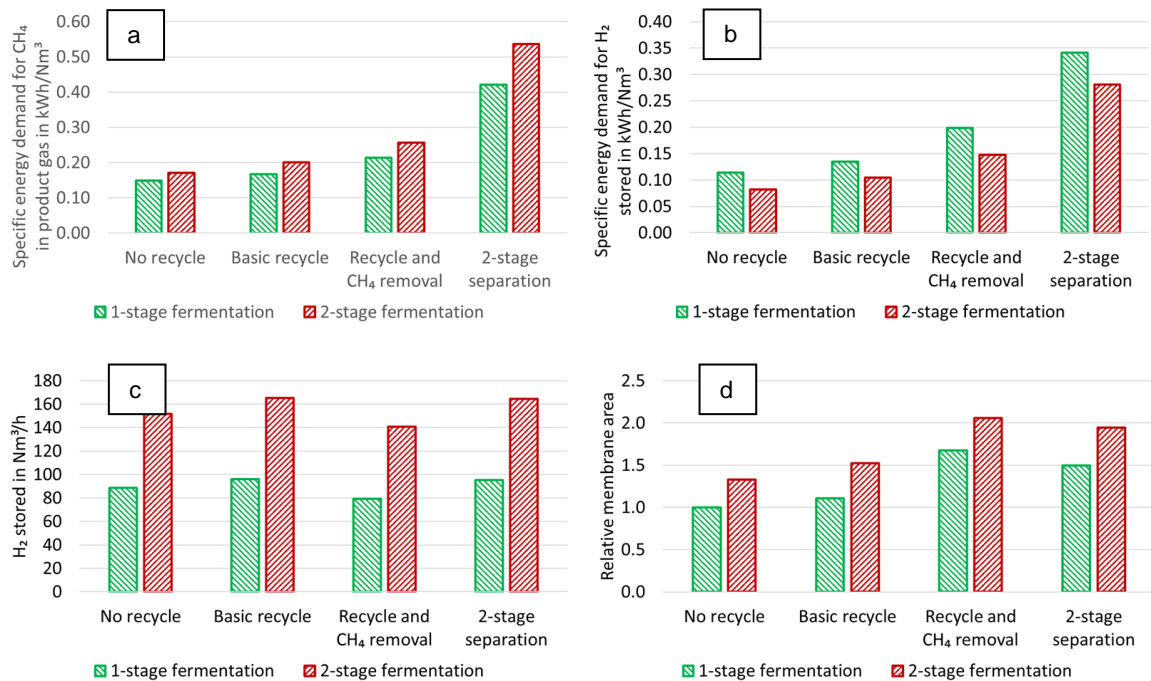


Figure 3 a-d: Comparison of a) Specific energy demand for CH<sub>4</sub> production, b) Specific energy demand for H<sub>2</sub> storage, c) H<sub>2</sub> storage capacity, d) Relative membrane area; at GHSV = 3,000 h<sup>-1</sup> and p = 10 bar

Basic recycling of the off-gas stream removes these losses while only slightly increasing specific energy demand for hydrogen storage from 0.11 to 0.13 kWh/m<sup>3</sup><sub>STP</sub> for one-stage fermentation and from 0.08 to 0.10 kWh/m<sup>3</sup><sub>STP</sub> for two-stage fermentation. It also demands up to 15 % of additional membrane area. Both changes can be attributed to the higher total flowrate in the system due to the recycled gas.

The other two processes, preceding methane removal and two-stage membrane gas separation do not offer any improvement in this base case. The reason for this is quite likely the fixed GHSV neglecting the benefits of a reduced recycle rate leading to a higher conversion rate in the methanation step. Still an important information can be drawn by comparing the stored amount of hydrogen (Figure 3c). Previous removal of methane leads to a decrease in hydrogen storage capacities. The other three processes produce a product gas containing nearly no CO<sub>2</sub>, but "Recycle and CH<sub>4</sub> removal" generates up to 4 % (v/v) remaining carbon dioxide not reacting and therefore not storing hydrogen.

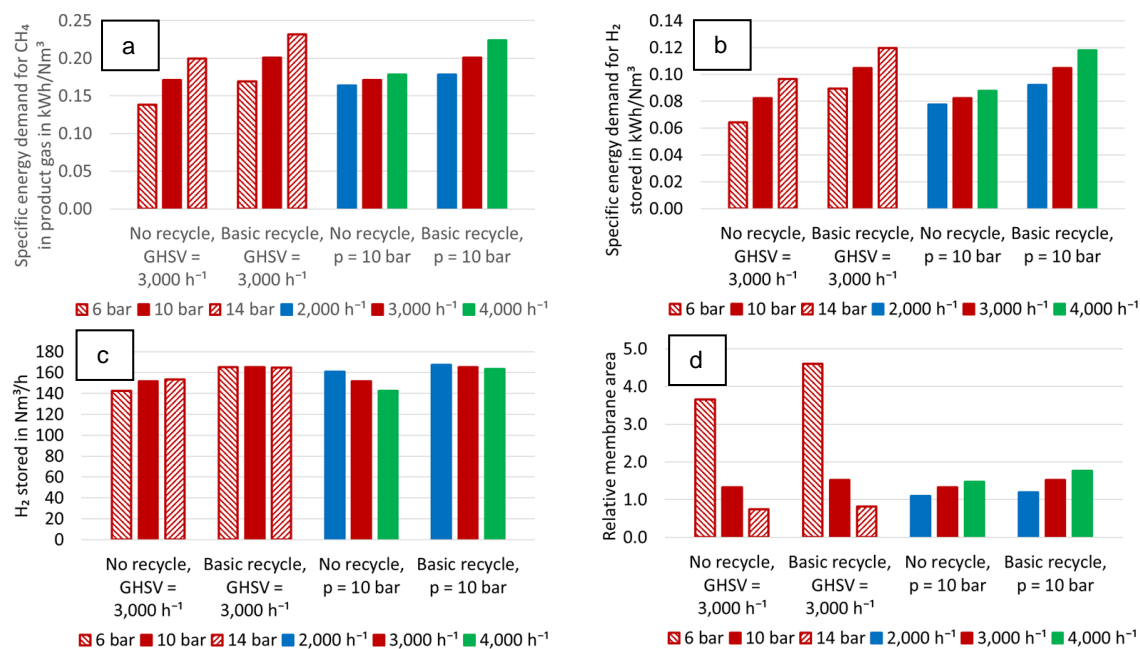


Figure 4 a-d: Comparison of a) Specific energy demand for CH<sub>4</sub> production, b) Specific energy demand for H<sub>2</sub> storage, c) H<sub>2</sub> storage capacity, d) Relative membrane area; for varying GHSV and pressure

Figure 4 a-d shows the results for "No recycle" and "Basic Recycle" in combination with a two-stage fermenter at pressures between 6 bar and 14 bar and GHSVs ranging from 2,000 h<sup>-1</sup> to 4,000 h<sup>-1</sup>. Specific energy demand for production of CH<sub>4</sub> and storage of H<sub>2</sub> (Figure 4a and 4b) is constantly rising with higher pressure and higher GHSV for both processes. Operating at 6 bar and 3,000 h<sup>-1</sup> instead of 14 bar and 3,000 h<sup>-1</sup> decreases the energy demand for hydrogen storage by 33 % without recycle and 25 % if a recycle is included. The necessary membrane area drops with higher pressure – 6 bar to 14 bar – by around 80 % in both cases due to better separation performance but increases with higher GHSV – 2,000 h<sup>-1</sup> to 4,000 h<sup>-1</sup> – by 33 to 47 %, although the values shown in Figure 4d illustrate the predominant influence of operating pressure in the gas separation process. The capability to store hydrogen is nearly constant at all operating conditions if a recycle is included. If not, it drops up to 11 % with increasing GHSV and up to 7 % with decreasing pressure, combining to a reduction of up to 15 % (Figure 4c). This indicates that recycling of the off-gas stream is an interesting option in any power-to-methane driven energy storage system. Next to removing hydrogen losses to the off-gas, it also offers constant hydrogen storage volumes at changing operating conditions, presenting an attractive option in case of fluctuating hydrogen or biogas supply and therefore varying process conditions.

#### 4. Conclusions

Comparison of four different process setups for a biogas-based power-to-methane approach showed that the implementation of two-stage biogas fermentation is highly beneficial, increasing storage capacity of hydrogen by up to 70 % using the same amount of substrate. In comparison to a single fermenter a more complex setup also allows to decrease the necessary energy demand for hydrogen storage.

Regarding the process setup for methanation and gas separation by membranes a simple recycling of the off-gas was shown to prevent hydrogen losses and increase hydrogen storage volumes by more than 15 %. Furthermore, it allows for a constant storage rate of hydrogen at various operating conditions. The trade-off is an increase in energy demand for hydrogen storage from 0.09 kWh/m<sup>3</sup><sub>STP</sub> to 0.12 kWh/m<sup>3</sup><sub>STP</sub> in the worst-case scenario. More complex setups have shown no benefits with regard to energy demand and storage capacities. Analysis for various pressure and GHSV conditions led to the result that higher pressures and GHSVs increased energy consumption during the process, but higher-pressure levels dramatically reduced the necessary membrane area (up to 80 %). While higher pressure normally benefits performance of methanation and gas permeation no final conclusion for the ideal pressure level can be drawn, but low GHSV is desirable. For a more comprehensive assessment of all process set-ups an economical evaluation of operational cost (energy demand) versus investment cost (membrane area) is necessary and considered as a next step.

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