Power-to-Gas coupling to biomethane production: a feasibility study

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Abstract

This preliminary feasibility study on coupling "Power-to-gas" conversion chain to the bio-methane from producer gas shows a promising potential for efficient and cost effective operation. The production capacity of the biomethane plant can be doubled, while cold gas efficiency remains the same as compared to a standalone biomethane plant. The specifications of the natural gas grid can be reached at the condition that the allowed H_2 content is not too strict. The study showed that such coupling implies that both methanation and SNG upgrade sections need to be designed to withstand variable operation conditions and part-load. The methanation section would have to deal with a turndown factor of 2 when switching from E-demand to E-excess operating mode while the CO_2 removal section must work efficiently in part-load and respond well in shutdown/start-up operations.

1. Introduction

"Power-to-gas" is a conversion chain that enables large scale energy storage where electrical energy is converted into chemical energy that is then fed into the natural gas grid. It enables connecting the existing power and natural gas grids thereby allowing for daily or seasonally adjusted storage of significant amounts of power and providing CO_2-neutral fuels using the natural gas grid and associated infrastructure as a storage facility.

The present study focuses on identifying technological opportunities for coupling the power to gas concept to the production of substitute natural gas from biomass gasification (Figure 1). Upgrading of producer gas from biomass gasification to substitute natural gas (SNG) matching natural gas pipeline specifications conventionally involves removal of H_2S and other contaminants, followed by methanation and CO_2 removal, where CO_2 removal can be upstream or downstream methanation. Since producer gas has a relatively high C content, an alternative to CO_2 removal would be the addition of H_2 and the use of methanation reaction to synthesize additional methane.

The power to gas alternative may materialize when considering that future energy infrastructure with large installed capacity of renewable power production is expected to produce excess electric power during certain periods, leading to grid stability issues. Using the excess renewable electricity for H_2 production through water electrolysis and subsequent use in producer gas upgrading would offer a method of converting the excess electricity into additional SNG production, using excess carbon available in the producer gas. During periods when no excess renewable electricity is available, i.e. no extra H_2 can be added, conventional CO_2 removal is applied resulting in a lower amount of SNG

produced. The concept would offer an attractive option for connecting the power grid to the natural gas grid at the condition that operational versatility between H_2 addition (excess power production) and CO_2 removal (high power demand) is indeed feasible. Unlike direct H_2 injection in the natural gas grid, the resulting SNG would then fully benefit from existing large scale transport and storage without risk of violation of natural gas grid gas quality specifications which allow only limited amounts of H_2.
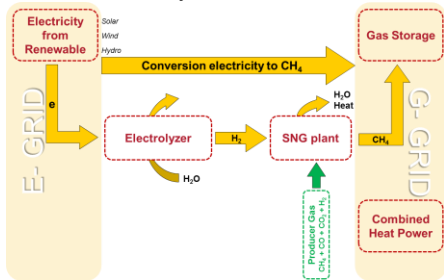

Figure 1. Energy chain

In this work, the energy balance of possible system configurations and process conditions for SNG production with and without H_2 addition have been studied. Steady state system performances for limit cases have been calculated using the Aspen Plus modelling program. These systems have been compared by evaluating various quantitative and qualitative parameters including the cold gas efficiency (η_{cg}), the SNG gas specification (H_2 content, Wobbe index), the system complexity and the power demand for SNG production. The flexibility degree of the evaluated systems is discussed with the intention of selecting a preferred configuration. Finally, the coupling of H_2 supply from a water electrolysis plant to a biomass gasification plant is discussed with respect to the fluctuations of the electricity excess available from renewables.

2. Concept and methodology

Throughout the study, the ECN Milena gasifier and the Olga tar removal were considered as base case technology for biomass gasification [3]. However, these two units were not included in our system boundaries. Producer gas capacity entering the system boundaries was assumed to be 200 MW, based on lower heating value (LHV). The operating conditions and the producer gas composition entering the system boundaries are given in Table 1. A conventional sweet methanation process has been considered in the disclosed calculations, meaning that all contaminants (H_2S and others) are thoroughly removed downstream the methanation section. Figure 2 gives a schematic overview of the layout of a system for producer gas upgrade to SNG. The system includes the following gas cleaning units:

- Water scrubber for NH_3 and HCl removal;
- Compression of producer gas to the pressure of 7 bara;
- Hydrodesulphurization unit (HDS) for hydrogenation of organic sulfurs. The hydrogenation of unsaturated hydrocarbons also occurs in this unit; The inlet temperature of this unit is 300°C;
- H_2S removal by adsorption using ZnO operating at 300°C;
- Pre-reforming reactor in order to convert aromatic hydrocarbons, operating at 500°C inlet temperature. Steam is added in order to prevent carbon formation, the amount of steam is determined by the calculated limit for carbon formation at inlet conditions using a isothermal Gibbs energy minimization approach.

Downstream the gas cleaning section, CO_2 is removed using amine (MEA) scrubbing, with a bypass possibility. In the calculations it was assumed that the steam required for MEA absorption can be supplied from the hot off-gases available from gasifier [10].

Then the producer gas is compressed to the operating pressure required in the methanation section. Water is removed upstream the compressor to prevent condensation.

Table 1 Composition and condition of producer gas downstream tar removal [4]

H_2 [vol%]	21.3	H_2O [vol%]	24.8
CO [vol%]	25.9	H_2S [ppmV]	314
CO_2 [vol%]	12	COS [ppmV]	35
CH_4 [vol%]	10.3	NH_3 [ppmV]	2308
C_2^+ [vol%]	4.6	**T [°C]**	**80**
N_2 [vol%]	0.9	**p [bar]**	**1**

The system was evaluated for two situations: 1) excess electricity used for H_2 production, CO_2 removal unit bypassed (referred to as "H_2 addition system"). In this situation, H_2 is added downstream the compressor, at the methanation process operational pressure. 2) electricity demand, no H_2 production but CO_2 removal unit in operation (referred to as "base case system").

In the case of excess electricity, H_2 is produced by electrolysis to tune the producer gas such that the methanation stoichiometry ratio $((H_2-CO_2)/(CO+CO_2))$ of 3 is reached.

The following configurations were considered for the methanation process [1]:

1) 3 methanation reactors in series with a recycle over the 1st reactor

2) 3 methanation reactors in series with a recycle over the 2nd reactor to the 1st

3) 2 methanation reactors in series with a recycle over the 1st reactor

The assumed maximum catalyst temperature in configuration 1 and 2 was 650°C, using high temperature Lurgi catalyst [6]. The inlet reactor temperatures of reactors 1, 2 and 3 were assumed to be 300, 250 and 220°C, respectively.
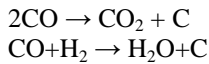
Table 2 SNG specifications [5]

O_2	mol%	< 0.5
H_2O	Dew-point	< -10°C
H_2S	mg/m_n^3	< 5
H_2	mol%	Max1<0.5 Max2<10
N_2	mol%	~2
CO_2	mol%	< 8
CO	mol%	<0.5
BTX[1]	ppm	500
Higher Hydrocarbons	% mol	1
Process Conditions		
Pressure	Bara	60
Wobbe Index	MJ/m_n^3	>43.5

Configuration 3 is similar to that in the Great Plains Synfuels Plant operated by the Dakota Gasification Company [7], and uses a low temperature catalyst with a maximum temperature of 450°C. The assumed inlet reactor temperatures of reactor 1 and 2 were 300 and 260°C, respectively.
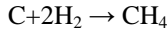
The methanation pressure was varied from 20-60 bara. At the inlet of methanation the conditions are such that

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[1] BTX = benzene toluene xylene

thermodynamically carbon can be formed via reactions:

$$2CO \rightarrow CO_2 + C$$
$$CO + H_2 \rightarrow H_2O + C$$

Opposing this is the carbon hydrogenation reaction:

$$C + 2H_2 \rightarrow CH_4$$

which is expected to be rapid [9].

Addition of steam to the methanation reactor feed may be required to limit carbon formation and to ensure sufficient catalyst lifetime. Since the required S/C ratio in methanation reactors will strongly depend on process conditions and the type of catalyst that is used, different S/C ratios (0.25, 0.5 and 1) were used in the calculations. In some simulated cases, at high methanation pressure and high S/C ratio (e.g. S/C=1) the water condensation occurred after cooling the exit stream of the 2nd methanation reactor. In these cases water was removed upstream the 3rd reactor.

Downstream the methanation unit, SNG needs to be upgraded to the natural gas grid specifications. The SNG upgrade section will consist of drying and final gas compression. For this study SNG specifications (Table 2) were based on the Dutch G-Gas specification (Groningen gas). The most stringent limit (max1) implies that H_2 must be below 0.5%, corresponding to the current specification for the gas infrastructure in the Netherlands. However, in other (European) countries specifications are less strict, and in the future gas specifications might be less tight. Therefore, this study will also consider the higher H_2 limit max2 of 10% H_2 content. In the case of Wobbe index only the lower value for the Dutch G-Gas is used.

$$Wobbe = HHV/(Rd)^{0.5} \qquad [12]$$

Where :

HHV - high heating value of SNG [MJ/Nm^3]

Rd - relative density of SNG to air

The required Wobbe index will be higher for other countries and is also expected to become less tight in the future.

The heat integration was performed assuming a minimum temperature approach of 10°C. It was assumed that steam was produced at 10 bara and 230°C. This steam can then possibly be used for biomass pretreatment, Olga tar removal or the electrolyzer. When required, steam at a different pressure level could also be produced. The efficiency of the electrolyzer (outside the system battery limits) was assumed to be 70%.

The cold gas efficiency (η_{cg}) of the process was calculated relative to the lower heating value of producer gas and H_2 according to:

$$\eta_{cg} = (LHV_{product} \cdot F_{product})/(LHV_{feed} \cdot F_{feed})$$

Where:

LHV - lower heating value [MJ/kg]

F - mass flow [kg/s]

The assumed pressure drop in each reactor was 1 bar.

3. Results

For both base case and H_2 addition case systems, a short study on the SNG plant configuration was carried out in order to select a typical configuration for further parametric sensitivity study. Both cases resulted in comparable trends and we chose the H_2 addition case to illustrate these results because it was more sensible to the plant configuration than the base case. Figures 3 and 4 compare the SNG quality expressed as hydrogen amount and Wobbe index for the evaluated methanation process configurations. In

general SNG quality increases with increasing pressure.

Figure 3 shows that the SNG product has rather high H_2 content in all configurations. Remarkably, the specification of 0.5 mol%, (max1) cannot be obtained even when a high methanation pressure of 60 bar is considered. In contrast, the higher H_2 specification (max2) is easily reached at any pressure, for either configuration. Figure 3 shows that at methanation pressures lower than 40 bar, SNG of higher quality is produced in configuration 3 with 2 reactors and a maximum temperature of 450°C.

For the higher pressures, the configurations 1 and 2 with 3 reactors, maximum temperature of 650°C and recycle after first or second reactor are more favorable. The gas quality produced by recycling after the first or second reactor is comparable.
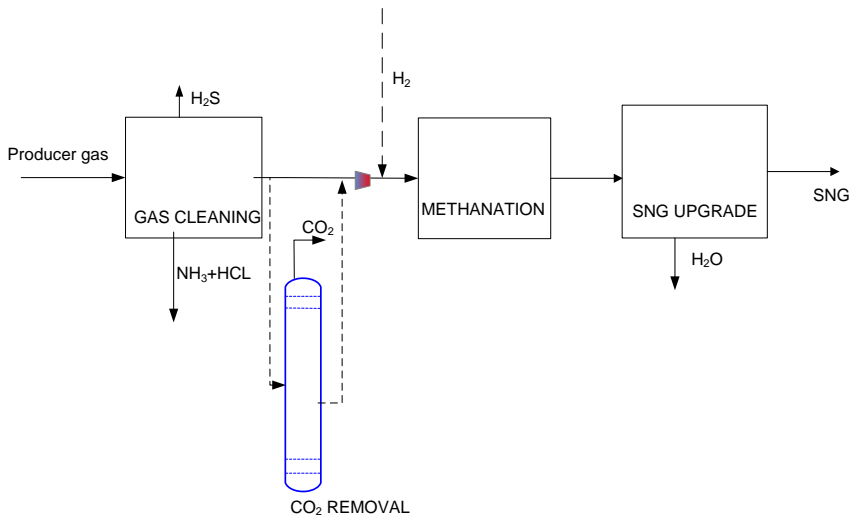

Figure 2 Scheme of producer gas conversion to SNG with either H_2 addition or CO_2 removal
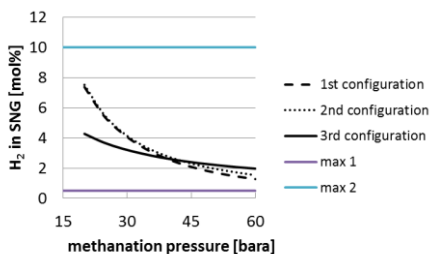

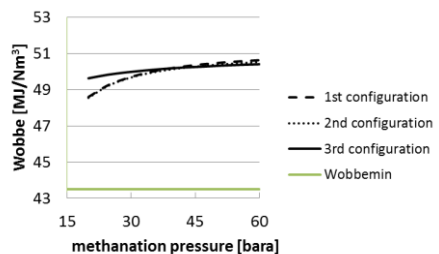Figure 3 H_2 content in SNG for different configurations, H_2 addition, S/C =0.5

Figure 4 Wobbe index for different configurations, hydrogen addition, S/C=0.5

Nevertheless, the concept with recycle over the 1st reactor has the advantage of a smaller size of the second reactor and easier operational control, at the cost of slightly lower potential for heat export. Figure 4 shows that for all studied pressures the Wobbe index lower specification limit can be reached. Selecting the optimal operating pressure will depend on the final required Wobbe index for SNG and a more detailed economic assessment.

Figure 5 shows that SNG quality is decreased by steam addition since a higher steam content negatively affects the methanation equilibrium composition. From this analysis it can be concluded that configuration 1 or 2 with 3 reactors in series and recycle after the 1st or 2nd reactor would be preferred, while the S/C ratio should be as low as possible. For the further comparison with the base case the 2nd configuration with the lowest S/C ratio was selected.

Figure 6 shows the effect of the operating pressure of the methanation reactors on the energy requirements for the H_2 addition case, with the maximum methanation catalyst temperature of 650°C. Similar trends were observed for all studied cases. The cold gas efficiency decreases insignificantly with increasing methanation pressure. Power demand increases with increasing methanation pressure because the compression duty for the producer gas is higher than the compression duty for the SNG product.
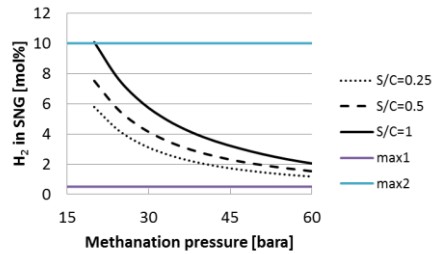

Figure 5 H_2 content in SNG, H_2 addition, 2nd configuration

The steam export increases significantly with the operational pressure. Figure 7 shows the Pinch diagram for 20 and 60 bar methanation pressure. It can be seen that the reason for higher steam export is higher temperature at which heat is available such that a better heat integration in the case higher pressure can be achieved. The heat available at higher pressure is 10 MW more than at the lower pressure. In addition, in the 20 bar case, more heat (27 MW) will remain unused for heat integration, being available at temperatures lower than 110°C. In the 60 bar case amount of unused heat below 110°C is equal to approximately 10 MW. The Pinch diagram indicates that the heat required for raising steam for the pre-reformer is significant. The calculated S/C ratio to prevent the formation of carbon was 1.33, in agreement with literature [13].

The gas quality measured in terms of the H_2 content and Wobbe index for the base and H_2 addition case at different methanation pressures is disclosed in Figures 8 and 9. The cases with H_2 addition produce SNG with higher Wobbe index than the base case. The base case has always a lower H_2 content than the hydrogen addition case.
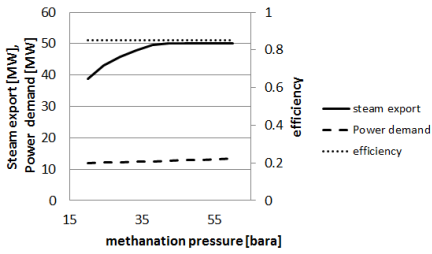
Figure 6 Energy balance of the H_2 addition case,2nd configuration , S/C =0.25 for 200 MW producer gas
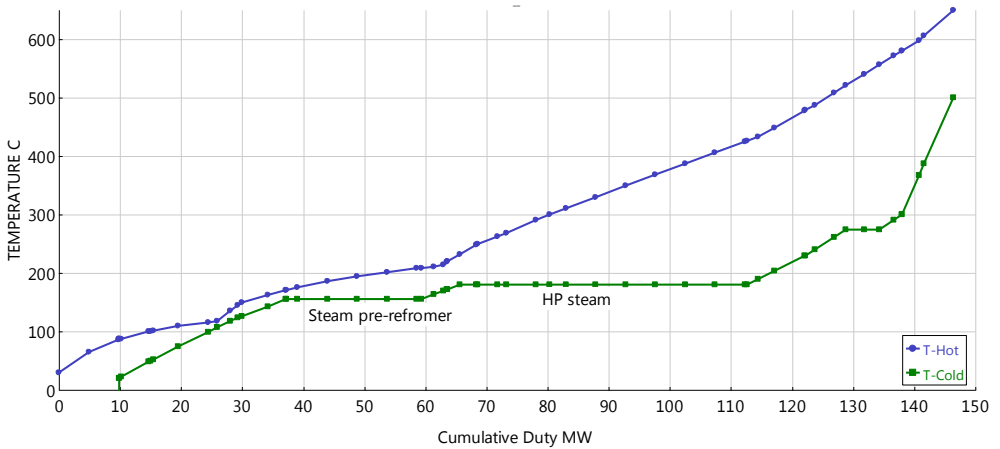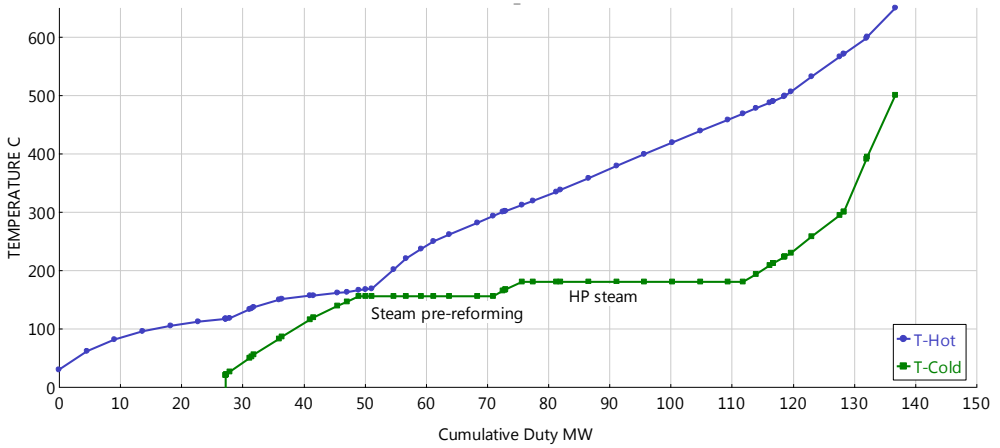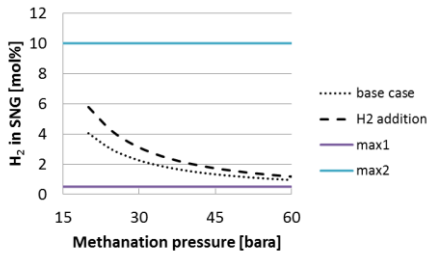

Figure 7 Pinch diagram, upper- 20 bar, lower-60 bar

Figure 8 H₂ content in SNG for different cases, 2ⁿᵈ configuration, S/C =0.25,horizontal lines –upper limits in H₂ content, max1 and max2 respectively
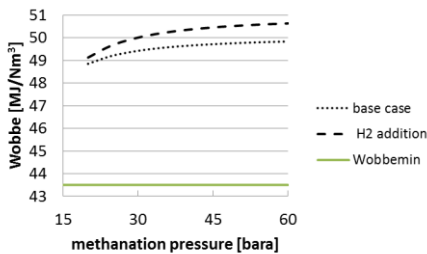

Figure 8 H_2 content in SNG for different cases, 2nd configuration, S/C =0.25, horizontal lines –upper limits in H_2 content, max1 and max2 respectively

Figure 9 Wobbe index for different cases, 2nd configuration, horizontal line- lower limit for Wobbe index

An overview of the results obtained for configuration 2 at 45 bar pressure is given in Table 3. In the base case, the SNG production is equivalent to 174 MW_{th} while in the case of H_2 addition the SNG production capacity is almost doubled to 342 MW_{th}.

Table 3 Cold gas efficiency, Wobbe index, H_2 in SNG, electricity required for H_2 production in electorolyzer studied at 45 bar pressure, 2nd configuration, S/C=0.25

	Results
E-excess (H_2 addition)	$SNG_{produced}$:341.6 MW η_{cg}=85 % W =50.5 MJ/Nm³ X_{H2}=1.64% Electricity import = 288 MW Steam export: 50 MW
E-demand (base case)	$SNG_{produced}$:174.1 MW η_{cg}=87.0% W =49.7MJ/Nm³ X_{H2}=1.26% Steam export: 4.83 MW

Effectively 83.3% of the lower heating value of the imported H_2 is converted into SNG, while the power demand is 288 MW. This electricity use represents 1.5% of the total planned capacity of sustainable electricity (wind and solar mostly) to be installed in the Netherlands till 2020 (19.9 GW) [8]. When assuming that a large centralized SNG plant (~1000 MW) is to be built, the electricity demand will represent 7.5% of the total renewable electricity installed at peak production.

Available steam for the export in the base case is 4.83 MW, and in the case of H_2 addition is 50 MW. It should be recognized, that in the case of H_2 addition, more steam than 50 MW can be exported. This is because CO_2 removal unit is not required, and heat available from off gases in gasifier will become available. This accounts for approximately 30 MW of additional steam for export.

In order to use intermittent electricity, all equipment used in the process should be able to cope with fluctuations, while maintaining SNG quality in the specifications range. For the two modes, i.e. *E-demand* and *E-excess,* the results indicate that there is a factor 2 difference in the volume flows. As a result, the producer gas conditioning section, the methanation section and the SNG upgrade equipment should deal with at least a turndown ratio of 2. For the methanation reactors this can be reasonably anticipated since it was assumed that reactors are fixed bed reactors. Fixed beds are indeed widely used in synthesis gas production or off-gas for treatment plants where it may be operated at variable process conditions, while fixed operating

conditions are obviously always preferred. Fixed bed reactors offer the advantage of easy and safe operations when frequent changes in feed specifications and throughput are required, while allowing for fast automatic reaction control via recycle and by-pass loops [11].

Methanation reactors will be designed for the largest flows. Thus, at lower flows, the gas hour space velocity in the catalytic bed will be lower, and thermodynamic conversion can be obtained without further issues.

In the case of heat exchangers, the decrease of the flow can lead to changing of the flow regime. This needs to be taken into account during the design of heat exchangers. Variation in flow will have impact on the recycle and SNG compressors efficiency. The other option can be to install multiple compressors in parallel.

A single producer gas conditioning section will be designed such that it may be bypassed in the case of *E-excess,* when CO_2 removal is not required, and such that it is capable of removing CO_2 at various levels in order to maintain the stoichiometric ratio for methanation at appropriate value in all intermediate situations (between *E-excess* and *E-demand*). This can probably be obtained by varying the circulation rate of solvent. However, the efficiency of the process will be affected.

Finally, designing the equipment to match the flow fluctuations will have impact on the final efficiency and the capital costs of the process. The final cost-effectiveness of the process will be determined by the number of hours that the process can operate (*E-excess mode*). For this, a more detailed economic evaluation is ongoing.

An alternative sour methanation route, i.e. producer gas cleaning and conditioning downstream the methanation section, is currently considered in a parallel study, that must indicate whether sour processing allows for decreasing the number of operating units in Power-to-Gas coupled with biomass gasification systems.

4. Conclusions

The integration of Power-to-Gas conversion processes with biomass gasification processes for the production of bio-methane - or substitute natural gas from bio-resources - has shown potential for doubling the production of SNG in periods of excess renewable power production. The present study shows that H_2 produced from water electrolysis when excess power is available may be effectively converted into SNG, with 83.3% of the lower heating value of the H_2 being recovered as biomethane. Conventional methanation process design may reach natural gas grid specifications, when the H_2 concentration allowance is not too strict, and may thus contribute to storing renewable power in the natural gas grid using renewable source carbon for additional SNG production. Flexibility considerations showed that such an integration implies that both syngas conditioning and methanation sections are to be designed to withstand intermittent operations and/or part-load. The methanation section would have to deal with a turndown factor of 2 when switching from E-demand to E-excess operating mode while the CO_2 removal section must work efficiently in part-load and respond well to shutdown/start-up operations. The integration of Power to Gas technology with the Biomass to SNG conversion chain was thus found to impact primarily only the economics of

downstream rotating process equipment (compressors), CO_2 removal section, heat exchangers and catalytic reactors, while only affecting marginally the process efficiency of the producer gas to biomethane process.

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