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Abstract

One of the greatest challenges to society is to reduce and avoid greenhouse gas emissions to mitigate climate change. Nevertheless, there are sectors like mobility and residential heating which may be difficult to decarbonize because of distributed CO_2 emissions. In these cases, low-carbon hydrogen might help to decrease their carbon footprint. Currently, around 90% of the feedstock used in the production of hydrogen are from fossil resources, e.g. natural gas. During the conversion process from fossil fuel to hydrogen, a significant amount of carbon dioxide is produced and if not captured, emitted to the atmosphere. Steam methane reforming (SMR) is the leading technology for H_2 production from natural gas and light hydrocarbons. A valuable option to produce low-carbon hydrogen – or blue hydrogen - is to combine the SMR process with CCS (carbon capture and storage). To further decrease the hydrogen's carbon footprint, natural gas can be substituted with biogas or biomass, where biogenic CO_2 will be emitted instead. The aim of this deliverable is to present the state-of-the-art technology for blue hydrogen production from natural gas with carbon capture. Additionally, alternative production processes are analysed that use biogas or biomass as a feedstock. Besides informing on the current state-of-the-art technologies, the goal of this work is also to define methods for comparison of the SotA with novel H_2/CO_2 purification processes developed in the frame of ELEGANCY. One of these includes vacuum pressure swing adsorption (VPSA), currently under development at ETH Zürich. In deliverable D1.1.1 a detailed technical description and some preliminary results of the VPSA process performance are presented. In this deliverable we present different options for CO_2 capture from an SMR process including a performance comparison in terms of capture rate, efficiency, and cost. We also present preliminary results on the optimisation of the MDEA flowsheet and operating variables and show that SMR is thermodynamically capable of

converting biogas into hydrogen. Last, we describe a pilot-scale biomass gasification plant in Sweden, to exemplify how such a process could also be used for hydrogen production.

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1 INTRODUCTION

Most recent climate scenarios from integrated assessment models (IAMs) predict that to reach the 2°C target in 2100, CO_2 emissions need to reach net-zero during the second half of the century, and additional CO_2 removal is required in the order of several gigatonnes per year (Gt/a) (IPCC, 2014). Nowadays, 90% of the hydrogen produced is consumed by the ammonia, methanol and oil refining industries. However, clean hydrogen could play an important role in reducing the carbon emissions in sectors such as space heating (e.g. residential, industrial, commercial heating) and mobility (e.g. used as a fuel in fuel cell vehicles), that may be otherwise difficult to tackle (IEAGHG, 2017). The aim of this deliverable is to describe state-of-the-art technology for hydrogen production via natural gas, biogas and woody biomass conversion, coupled with carbon capture and storage (CCS).

Green hydrogen can be produced by water electrolysis using fully renewable electricity. Although this process has the potential to deliver zero-carbon hydrogen, it may also present drawbacks: clean primary energy, instead of being used directly for supplying power to end users, is converted into a fuel, which is then converted into power. Indeed, it is preferable to avoid conversion steps to reduce energy losses when possible. Alternative production routes use carbon-rich fossil fuels, e.g. natural gas, with the challenge that such feedstock inevitably yields carbon dioxide when converted into hydrogen. Even if a CO_2 capture plant is added to the hydrogen production process and the captured carbon dioxide is subsequently stored, the generated CO_2 is likely captured only partially. This is due to the fact that to be technically and economically feasible, the total CO_2 capture rate is typically lower than 100%. As explained in the following chapters, in the specific case of hydrogen production the capture rate is more likely to range from 50 to 90% (IEAGHG, 2017). For this reason, the H_2 produced from fossil fuels with CCS is often categorized as blue hydrogen, rather than as green, or renewable, hydrogen. Completely zero-carbon hydrogen from carbonaceous feedstock can be produced if part of the emitted CO_2 is recycled from the atmosphere, e.g. through the (partial) use of organic feedstock like biogas in combination with CO_2 capture. The concept of negative emissions is introduced here to describe the net removal of carbon dioxide from the atmosphere. We highlight this concept because the production of hydrogen from organic carbonaceous fuels (i.e. biomass or biogas), in combination with CCS, has the potential to yield such negative emissions, and thereby to go beyond *mitigating* climate change towards *counteracting* climate change.

An existing and detailed IEAGHG report named "Techno-Economic Evaluation of SMR Based Standalone (Merchant) Hydrogen Plant with CCS" (IEAGHG 2017) was used as the main reference for describing the state-of-the-art technologies for blue hydrogen production. It presents a comprehensive study on different production pathways, including technical and economic evaluations. It describes the benchmark technology for high purity hydrogen production via natural gas reforming, together with five case studies where the hydrogen production plant is coupled to a CO_2 capture unit. These cases differ in costs and capture rates, and in the context of ELEGANCY, the most relevant configurations to this project were implemented and simulated in Aspen Plus®. In the following chapters an analysis of the production pathways will be presented, including modelling results and additional technical considerations. Those cases were reanalysed since in the framework of ELEGANCY new purification technologies are developed. Comparison of the new technologies with the existing ones requires analysis on a like-for-like basis (i.e. starting from the same models) and to analyse both in depth to fully understand their characteristics.

2 STATE-OF-THE-ART LOW-CARBON HYDROGEN PRODUCTION

2.1 Steam Methane Reforming Hydrogen Plant with Carbon Capture

Steam methane reforming (SMR) is currently the leading technology for hydrogen production from natural gas and light hydrocarbons. This process is divided in three main steps: methane reforming (reaction (1)), syngas high temperature water-gas-shift (reaction (2)) and hydrogen purification. The main reactions occurring during the conversion process are:

$$CH_4 + H_2O \rightarrow 3H_2 + CO \qquad \Delta H = 206 \text{ kJ/mol} \qquad (1)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H = 41.1 \text{ kJ/mol} \qquad (2)$$

After the methane reforming reaction, the product gas is rich in hydrogen and carbon monoxide. However, unconverted methane and carbon dioxide will also be present in small quantities. The high temperature water-gas-shift reaction converts the produced carbon monoxide into hydrogen and CO_2 thus increasing the total H_2 yield. Nevertheless, some of the CO will not be converted via reaction (2) and therefore remains in the product stream. To obtain blue hydrogen, the CO_2 produced during the synthesis process needs to be captured and successively stored. Considering the whole flowsheet (Figure 1), there are two main sources of carbon dioxide: the first source (~60%) is the oxidation of the carbon atoms present in the feedstock during reforming and shift; the second source (~40%) is the combustion process in the reformer furnace, which provides heat to the entire process. In a hydrogen production plant, there are three specific locations (Figure 1) where carbon dioxide can be captured: from the shifted syngas stream (option 1), after the hydrogen purification step (option 2) or from the furnace flue gas (option 3). As benchmark references, two specific type of captures were selected. On the one hand, for CO_2 capture from the syngas (options 1 and 2), absorption-based technology with MDEA (methyl diethanolamine) solvent was selected. On the other hand, when CO_2 is captured from the flue gas (option 3), absorption-based technology with MEA (monoethanolamine) solvent was selected.

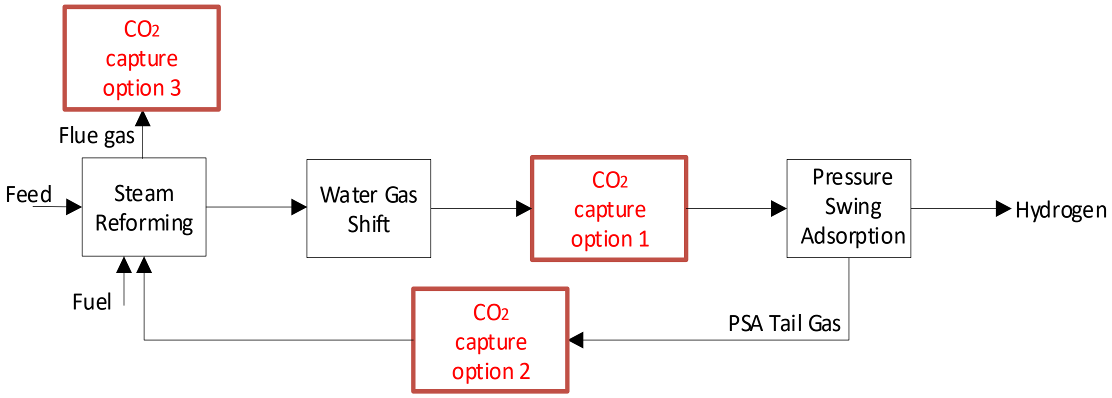

Figure 1: Steam methane reforming - CO_2 capture options

The advantage of option 1 is the high partial pressure of CO_2 (~2.5MPa, ~15 vol%) in the gas stream, which results in a high driving force for the CO_2 capture process, thereby decreasing the energy penalty of separation. Unlike option 1, in option 2 the stream exiting the PSA is close to ambient pressure. However, in this case the gas stream entering the capture unit has already gone through a first purification step, where the major part of the hydrogen is separated, thus resulting in a higher CO_2 concentration (~50 vol%). The first two capture options can be classified as pre-combustion capture technologies, since in both cases the carbon dioxide captured comes from the fuel production process. Because these gas streams still contain unreacted methane and carbon monoxide, capture rates of the overall process are limited to values between 50% and 70% ((IEAGHG, 2017), Table 1, Table 3). Option 3 in turn involves capture from the furnace flue gas (end of pipe), therefore it can be classified as post-combustion capture technology. In this case, 90% or more of the total carbon dioxide produced can be captured, because all carbonaceous species are completely oxidised to CO_2. Thus, depending on where carbon dioxide is captured, the hydrogen produced will have a larger or smaller specific rate of CO_2 emissions (Table 1). For the options exemplified here, higher total capture rates also come with higher costs (Table1). Indeed, the Levelized Cost of Hydrogen production (LCOH) as well as the CO_2 Avoidance Costs (CAC) are lower in the case of capture via option 1 only. Finally, comparing the first two options, option 2 requires an input of electricity, whereas option 1 generates excess electricity that can be utilized (IEAGHG, 2017).

Table 1: Levelised Cost of H_2 (LCOH), CO_2 Avoidance Cost and Overall CO_2 Capture Rate (IEAGHG, Techno-Economic Evaluation of SMR Based Standalone (Merchant) Hydrogen Plant with CCS. Technical Report 2017-02, 2017)

Capture Case	LCOH Euro Cent/Nm^3	CO_2 Avoidance Cost Euro/t	Overall CO_2 Capture Rate
No capture	11.4	-	-
Option 1	13.5	47.1	56%
Option 2	14.2	66.3	54%
Option 3	16.5	69.8	90%

Despite the lower capture rate, the current industry standard for capturing CO_2 from an SMR-based plant is to capture it from the shifted syngas using an MDEA-based absorption process (option 1). However, it is worth noting that the vast majority of hydrogen is currently produced without CO_2 capture. One of the potential upsides of pre-combustion capture is the possibility to couple it with the hydrogen purification step (PSA), i.e. to combine option 1 and the PSA hydrogen purification in a single separation step. To this end, Work Package 1 investigates and develops the so-called vacuum pressure swing adsorption technology (VPSA), which separates hydrogen and carbon dioxide with the desired purities and recovery rates (see also Deliverable 1.1.1). To compare the new VPSA technology with an incumbent on a like-for-like basis, option 1 was selected as reference technology.

2.2 Case Studies Simulated with Aspen Plus®

2.2.1 Methods

Equilibrium-based process simulations have been carried out using the commercial software Aspen Plus®. To simulate the hydrogen production process (excluding the solvent-based CO_2 capture step), the Peng-Robinson equation of state was used. The MDEA process was simulated using the Electrolyte NRTL model for the liquid phase and the Redlich-Kwong equation of state for the vapour phase. The e-NRTL model used the binary interaction coefficients as specified by

(Romano, 2010). Stream compositions are expressed in percentage; if not specified otherwise this refers to volume percentage.

2.2.2 Base Case: SMR Hydrogen Production without CO_2 Capture

In a steam methane reforming plant, natural gas is pre-treated before being fed into the pre-reformer: sulphur and chlorine present in the feedstock are removed to prevent poisoning of the catalysts of the downstream processes. The cleaned feed stream is mixed with process steam and pre-reformed to convert any light (C2+) hydrocarbons and olefins, after which it is fed to the primary reformer. The produced syngas consists of mainly CO_2, CO, H_2, water, some unconverted CH_4 and some nitrogen. To convert the produced carbon monoxide into hydrogen, the syngas coming from the reformer is fed into a high temperature water gas shift (HT-WGS) reactor. The produced gas stream is finally purified in the pressure swing adsorption (PSA) unit, where 85-90% of the hydrogen is recovered with a purity >99.9%.

We simulated the base case in Aspen Plus® (Figure 2, Appendix A3) using the process conditions and characteristics provided by IEAGHG (IEAGHG, 2017). The additional operating conditions needed to reproduce the configuration described in the report, are summarized in Appendix A1. In a second stage, a low temperature shift reactor was added to the previously simulated system (Figure 2). By adding a low temperature shift, higher CO conversion is achieved (~90%). Therefore, the final gas composition is richer in hydrogen and the CO concentration drops below 0.5 mol%. The results of the equilibrium-based simulations are presented in Table 2. The comparison of the two cases shows that adding a LT-WGS reactor increases the hydrogen content by ~3 mol%. Thereby, the PSA inlet stream is richer in hydrogen and poorer in CO, which may aid the purification step.

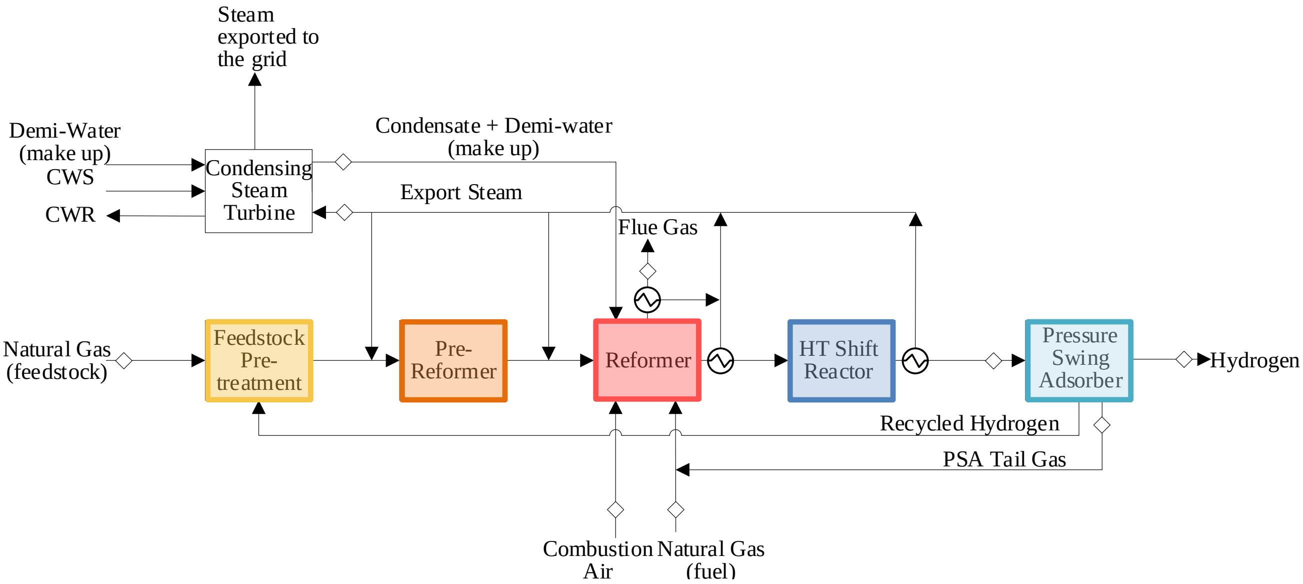

Figure 2: Base Case - SMR hydrogen production without carbon capture, where CWR and CWS are the heated and the cooled water respectively, and HT is the Hot Temperature water gas shift reactor.

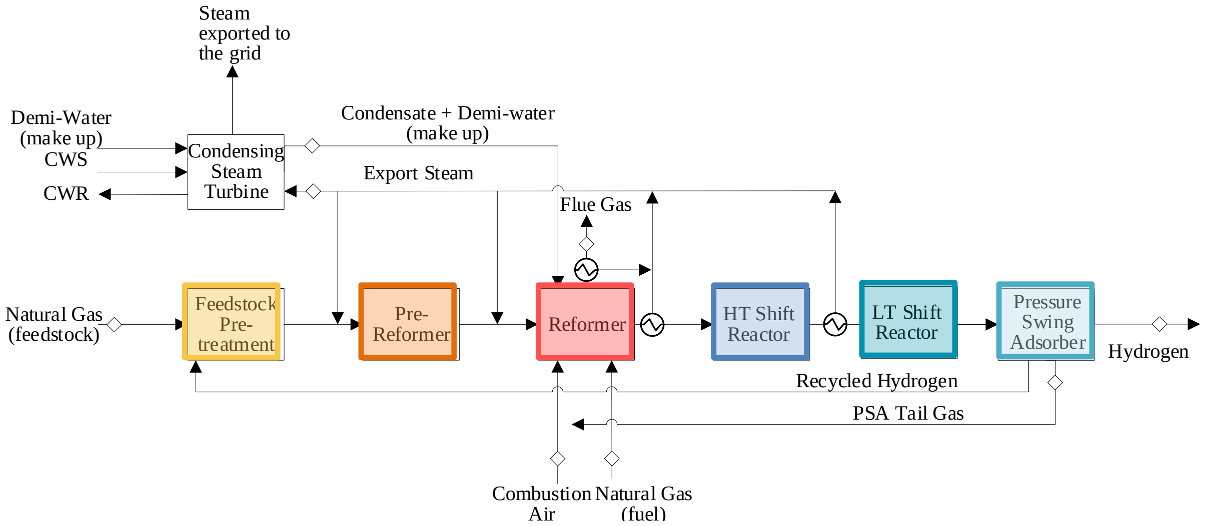

Figure 3: SMR reactor hydrogen production plant with low temperature shift reactor, where CWR and CWS are the heated and the cooled water respectively, and HT and LT are the Hot and Low Temperature water gas shift reactors.

2.2.3 SMR Hydrogen Plant with MDEA Carbon Capture Technology

Hydrogen production coupled with MDEA carbon dioxide capture (option 1) was modelled in Aspen Plus® (Figure 4, for the corresponding Aspen flowsheet see Figure A2). The MDEA-capture plant was modelled separately and the flowsheet was optimized such that the recovery and purity of carbon dioxide (>95%, >98%) and hydrogen (>90%, >99.9%) are respected (Figure 5*)*. In Section 3, a detailed analysis of the MDEA simulation is presented.

Table 2: Simulated stream compositions with only high temperature shift and with high and low temperature shift.

mol %	SMR inlet	SMR outlet	HTS outlet	LTS outlet	Dry HTS outlet	Dry LTS outlet
H_2	-	50.5	58.3	61.0	75.4	76.2
CO	-	10.8	2.9	0.3	3.7	0.4
CO_2	2.0	5.2	13	15.7	17	19.6
CH_4	97.1	2.8	2.8	2.8	3.6	3.5
H_2O	-	30.5	22.7	20.0	-	-
N_2	0.9	0.2	0.2	0.2	0.3	0.3

2.2.4 Strategies to Decrease the Carbon Intensity of the Hydrogen Produced

As mentioned in the previous chapter, the CO_2 capture rate of option 1 is well below 100%. However, the carbon intensity of the process could be improved by firing H_2-rich fuel into the SMR furnace (option 1B). Therefore, the natural gas deployed as supplementary fuel is substituted with the sweet syngas from the capture plant. As reported in Table 3, the overall capture rate could be improved by 14 percentage points. Nevertheless, to keep the amount of hydrogen produced constant among the different configurations, for option 1B the raw syngas production capacity of the SMR and the size of the equipment have to be enlarged by around 27% (IEAGHG, 2017). This is due to the fact that part of the hydrogen produced is burnt in the furnace and converted into heat. Although environmentally attractive, this process configuration has higher LCOH as well as higher CAC.

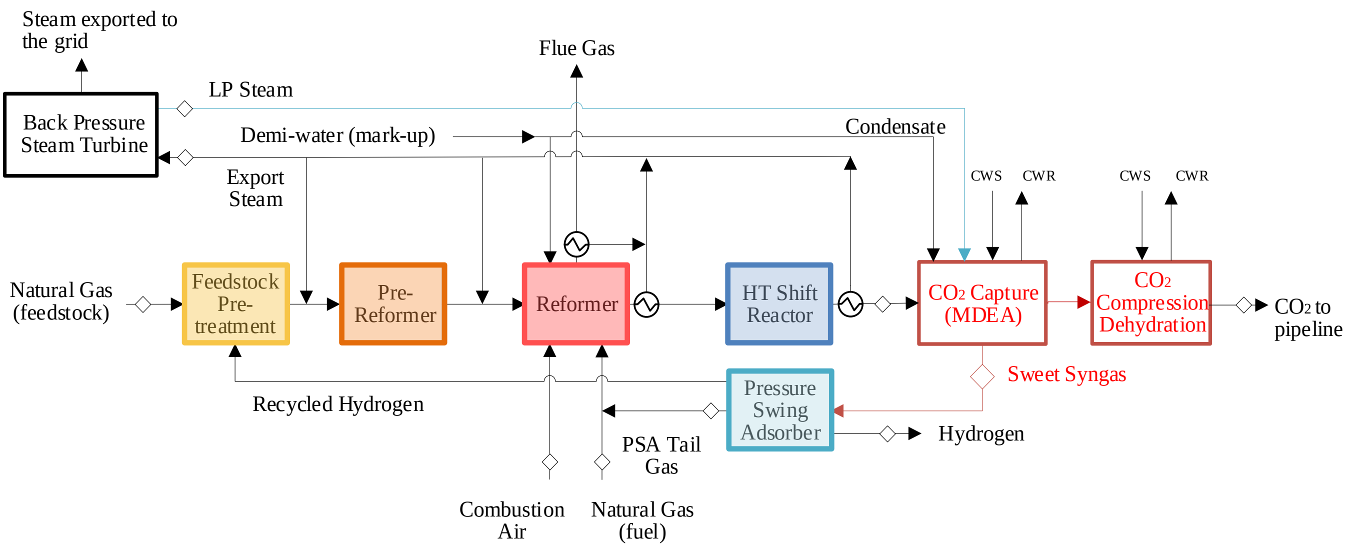

Figure 4: SMR hydrogen production with carbon capture from shifted syngas, where CWR and CWS are the heated and the cooled water respectively, and HT is the Hot Temperature water gas shift reactor.

Alternatively, to lower CO_2 emissions, Auto-Thermal Reforming (ATR) could be used instead of SMR. In an ATR, oxygen and steam are used to partially oxidise methane into carbon monoxide, carbon dioxide and hydrogen. The oxidation of methane in this case is exothermic and the heat provided from the combustion reactions is used to provide the reforming heat. The main difference between SMR and ATR is the reformer furnace; in the case of steam reforming, the methane conversion reaction is endothermic, and the heat is provided by the furnace where natural gas and the PSA tail stream are combusted with air. In the case of ATR, the (partial) oxidation reaction is exothermic, therefore no heat form outside the reactor is required. However, a small furnace is still needed to provide the heat required by the process that cannot be covered by the heat generated in the reformer (e.g. for feedstock pre-heating). Therefore, the emissions of the reformer furnace are drastically reduced while using the ATR technology. Nevertheless, to produce high purity hydrogen, an air separation unit is needed to provide pure oxygen to the system, which impacts the energy balance and production costs significantly.

Table 3: LCOH, CAC and Overall CO_2 Capture Rate for case 1 and 1B

Capture Case	**LCOH Euro Cent/Nm^3**	**CO_2 Avoidance Cost Euro/t**	**Overall CO_2 Capture Rate**
No capture	11.4	-	-
Option 1	13.5	47.1	56%
Option 1B	14.6	62.0	70%

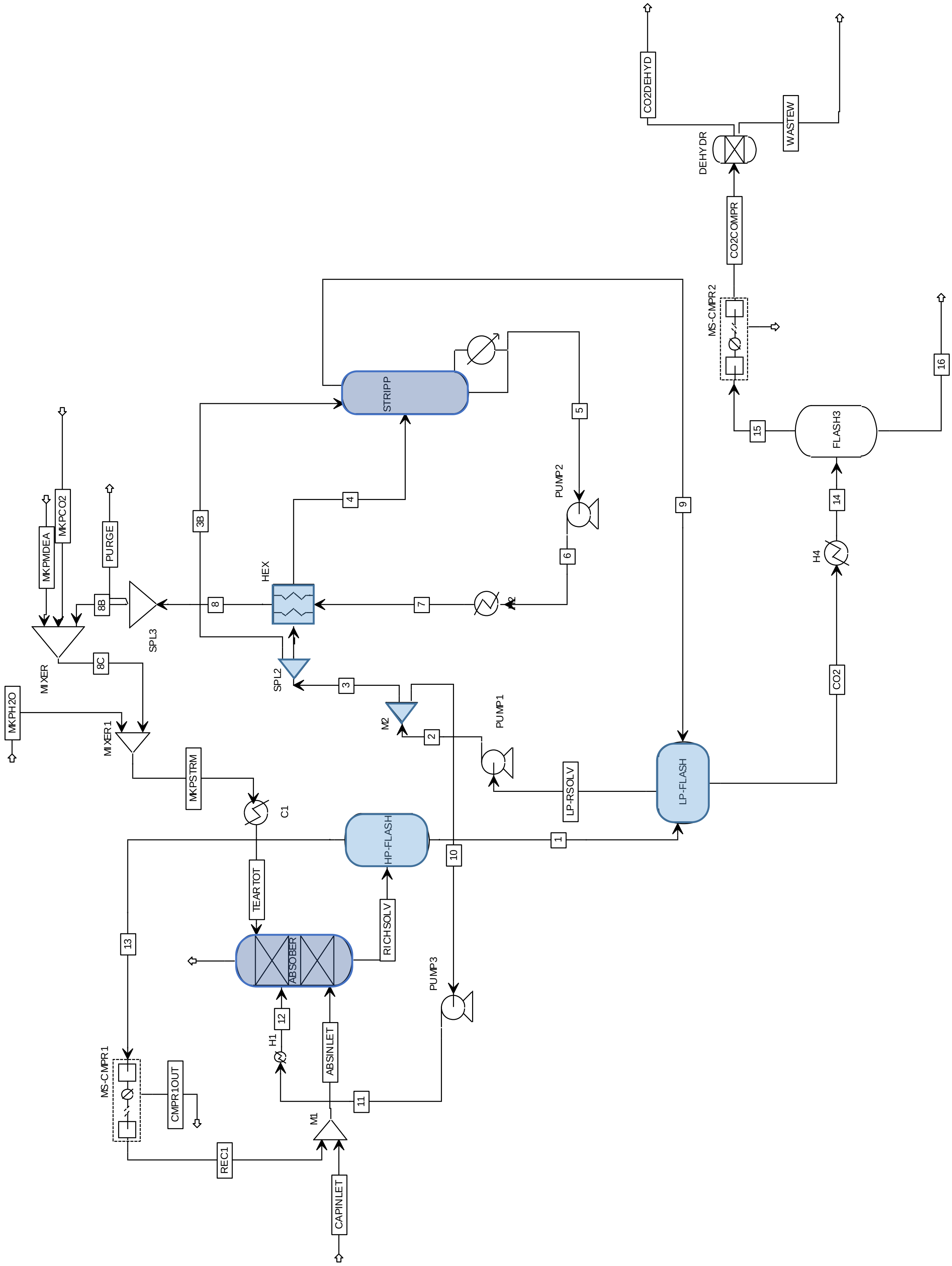

Figure 5: MDEA process flowsheet of the Aspen Plus simulation

3 METHYL DIETHANOLAMINE (MDEA) CAPTURE TECHNOLOGY

In this chapter we present the methodology adopted to implement and to run the Aspen Plus® simulation of the MDEA plant. The goal of this is to gain a deeper understanding of the process, so as to be able to define the optimal operating conditions for a given inlet stream. To compare different technologies, general performance indicators are needed, which will then be used to compare the state-of-the-art configuration, which is MDEA carbon capture coupled with pressure swing adsorption (PSA) for hydrogen purification, with the novel CO_2/H_2 purification process developed in the framework of work package 1, namely the vacuum pressure swing adsorption process (VPSA).

The approach we have followed can be divided in four main steps. Firstly, a detailed process simulation in Aspen Plus® is implemented. Secondly, the key variables that are describing the operating conditions of the process are identified. As a third step, single parameter sensitivity analyses of the key variables are performed to get a feeling on how such variables affect the process performance. The last step consists in running a mathematical optimization of the different process configurations, namely MDEA, MDEA+PSA and VPSA, and in identifying the optimal operating conditions in terms of separation and process performance.

In the following sections, we present the application of the aforementioned methodology by showing the results obtained on the MDEA based process.

3.1 MDEA Simulation in Aspen Plus®

3.1.1 Building the Flowsheet in Aspen Plus®

The MDEA process is divided in three parts: absorption, desorption and CO_2 compression/dehydration, we here. We will focus on the first two parts. The flowsheet was designed starting from data available in the literature (Romano, 2010; Manzolini, 2011; Kohl, A. L., & Nielsen, R., 1997), and subsequently improved and consolidated (resulting in the scheme shown in Figure 5). Carbon dioxide absorbs in the MDEA solution in the absorber column. After CO_2 absorption, the CO_2-rich stream exiting the absorber is first sent to a high pressure flash, where methane, carbon monoxide, nitrogen and hydrogen are desorbed and recycled back to the absorption column. Then, the CO_2-rich stream enters a low pressure flash, where it is partially regenerated. The physical separation occurs because the CO_2-rich stream enters the low-pressure flash (1.15 bar) at low temperature and higher pressure (35°C, 5 bar); by decreasing the pressure of the liquid stream, the solubility of CO_2 decreases and CO_2 evaporates. Part of the semi-lean solution is pumped to the absorber pressure, cooled down and recycled back to the middle part of the absorber as a means of intercooling. Thereby, the absorption process will be enhanced by the corresponding decrease of the temperature bulge inside the column. The rest of the semi-lean solution exiting the low-pressure flash is further split; a small portion is directly fed to the top of the regeneration column, the remainder is heated up in the main heat exchanger and fed to the middle of the column. The gas stream exiting the stripper column (a CO_2/H_2O mixture) at the top is fed to the low-pressure flash, where it exchanges heat with the semi-lean solution, thereby condensing most of its water and rendering an almost pure CO_2 stream.

The incoming process gas stream is considered to be constant in flow rate, composition, pressure and temperature (see Appendix 4). The assumptions used in the MDEA simulation are summarized in Table 4. The absorber is modelled with 8 equilibrium stages. The high and low flash pressures are chosen to achieve the best separation performance: at an HP flash pressure of 5 bar, all impurities (CH_4, CO, N_2 and H_2) are separated from the liquid stream, without flashing out too much CO_2. At an LP flash pressure of 1.15 bar, the CO_2-rich stream is partially regenerated and water from the CO_2 stream is condensed (see Appendix A5). The stripper is modelled with 5 ideal stages and it is operated between 1.15 and 1.3 bar (top and bottom pressure respectively), because at low pressure the CO_2 desorption is favoured. This low pressure would however lead to a higher compression penalty, so in future work the optimum needs to be reconfirmed taking into account both thermal and electric energy inputs. The heat exchanger is modelled based on the minimum temperature approach. To avoid temperature cross-over inside the heat exchanger, a Fortran® calculator was implemented, which re-establishes the pinch point after each iteration and consequently adjusts the hot outlet stream's temperature. This is considered the state-of-the-art in modelling lean-rich solvent exchangers.

Table 4: Main assumptions for the MDEA process simulation

Description	Variable
Absorber, ideal stages	8
HP/LP flash pressure [bar]	5/1.15
Stripper, ideal stages	5
Reboiler pressure	1.3
Minimum ΔT in the heat exchanger [°C]	3
Pumps, hydraulic/mechanical – electrical efficiency [%]	80/94
Compressors, isentropic/mechanical – electrical efficiency [%]	85/95

3.1.2 Identification of the key variables

Once the simulation framework is available, the second step was to identify the key variables describing the operating conditions of the process (Table 5). We operated under the assumption that the process performance is mainly described by five key variables, which are the MDEA concentration in the lean stream ($w_{\mathrm{MDEA}}^{\mathrm{l}}$), the liquid to gas flow rate ratio (L/G), the reboiler duty, the amount of semi rich stream sent to the stripper and the amount which is heated before entering the desorption column. By varying those variables, the process can be tuned to reach the desired process specifications. To verify these indeed influence process performance, and to understand their effects, single parameter sensitivity analyses were performed. Some of the results are presented in the following section.

Table 5: Variables describing the operating conditions of the MDEA plant

Description	Variable
MDEA apparent weight fraction in the lean stream	$w_{\mathrm{MDEA}}^{\mathrm{l}}$
L/G [kg/kg]	L/G
Fraction of the semi lean solution sent to regeneration [%]	b_1
Fraction of the semi lean solution not heated before regeneration [%]	b_2
Reboiler duty [kW]	Q_{reb}

3.1.3 Sensitivity Analysis

A sensitivity analysis was performed to verify that the key variables are effectively controlling the performance of the process, as well as to visualize the influence of their variation on the capture rate. Therefore, the four key variables in Table 5 are tested at different reboiler duties. Some of the obtained results are here presented. The minimum CO_2 capture rate is specified to be 90% (dotted horizontal line). In Figure 6 we can see how the CO_2 capture rate varies as a function of Q_{reb} for different *L/G* ratios. The larger the liquid to gas mass flow ratio, the smaller the CO_2/MDEA molar ratio in the absorber and the smaller the heat duty required to reach 90% of CO_2 capture. Of the investigated L/G ratios, the largest thus provides the highest capture rate at a given reboiler duty.

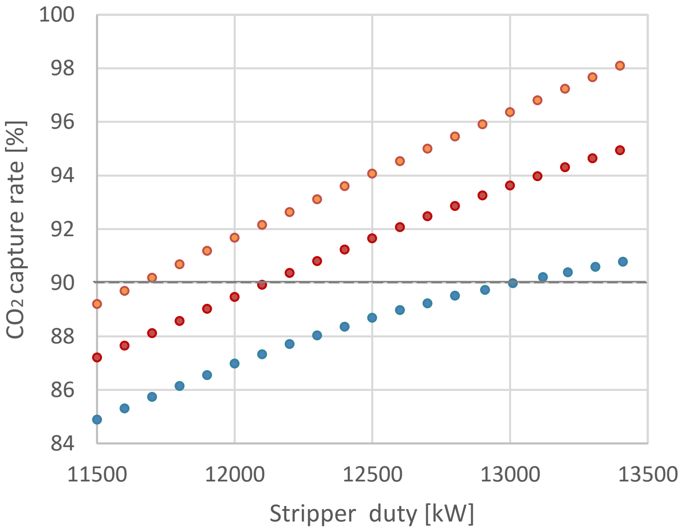

Figure 6: Stripper duty (kW) and capture rate for three L/G values: 6.3 (blue), 7.3(red) and 8.3(orange). In this simulation b_1 = 0.313, b_2 = 0.2 and w^l_{MDEA} = 0.35.

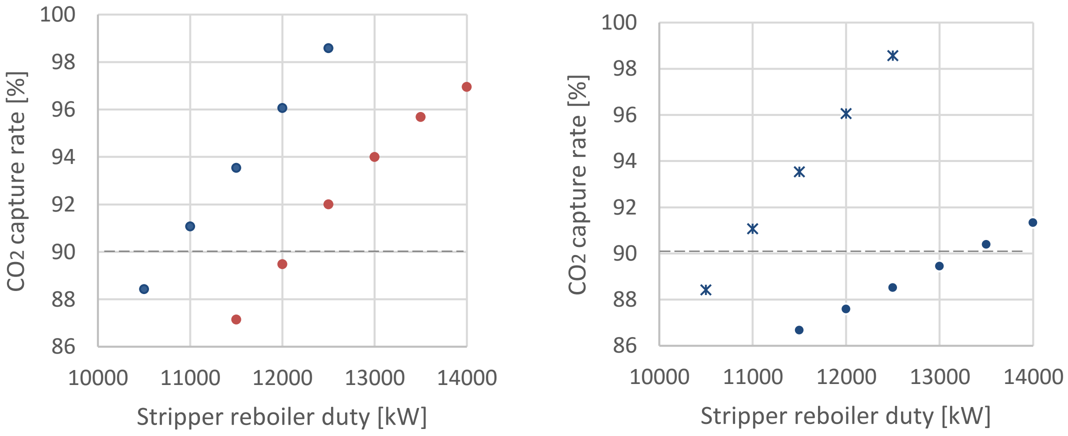

Figure 7: Stripper reboiler duty (kW) and corresponding capture rate by varying w^l_{MDEA} and b_r. Left: variation of the MDEA concentrations in the lean stream (w^l_{MDEA}), 0.35 (red) and 0.40 (blue) at b_1 = 0.313, b_2 = 0.2 and L/G = 7.3; Right: variation of the split ratio b_1, 0.313 (stars) and 0.195 (dots) at w^l_{MDEA}=0.4, b_2 = 0.2 and L/G = 7.3.

Figure 7 (left) shows the results of the sensitivity on w_{MDEA}^{l}; by increasing the MDEA concentration in the lean stream, the CO_2/MDEA molar ratio decreases and a smaller reboiler duty is necessary to reach a capture rate of 90%. Further sensitivities will be performed to investigate if there is a maximum in this trend. Figure 7 (right) presents the sensitivity on the first split ratio (b_1); the lower the split fraction, the lower the capture rate at the same Q_{reb} because the portion of the rich lean regenerated is smaller, and consequently a higher reboiler duty is needed to reach 90% capture.

3.1.4 Process Optimization

In future work, a mathematical optimization of the MDEA capture process will be performed. In order to do so, at least one objective function must be defined. The objective function defines the object to be minimized (or maximized). Based on that, the optimizer will determine the optimal operating conditions of the process. In this specific case, the objectives of interest are to maximize purity and recovery of the desired compounds (carbon dioxide and hydrogen) and at the same time to minimize the energy consumption of the separation processes. In terms of energy consumption, the two technology options, namely MDEA+PSA and VPSA, are substantially different; the absorption process needs relatively high temperature heat to regenerate the MDEA solvent. Unlike absorption, VPSA does not require a considerable amount of thermal power, but instead it needs electricity for compression. To allow comparison of the energy penalties of both technology options, all energy inflows will be converted to exergy.

4 HYDROGEN PRODUCTION FROM BIOGAS AND BIOMASS

4.1 Hydrogen Production via Biogas Reforming

In the previous section we described how low-carbon hydrogen can be produced from SMR. A possible way to further decrease the carbon intensity of hydrogen could be to substitute natural gas with biogas, although this might have some limitations in the scale of production (see Box 1). Biogas is mainly composed of carbon dioxide (20-35 mol%), methane (75-60 mol%), some oxygen and nitrogen (Naskeo Environment, 2018). Since natural gas is not only the reagent, but also the fuel used to fire the reformer, biogas could be deployed in different ways. The first possibility (i) is to feed biogas as feedstock for the reaction. Under the idealized assumption that the carbon dioxide produced from biogas conversion is neutral (because it comes from biomass, that while growing captured CO_2 from the atmosphere), the carbon intensity of hydrogen would only be dependent on the carbon dioxide produced by the reformer furnace. The second possibility (ii) is to also fire biogas in the furnace. However, CO_2 is a non-combustible gas. Therefore, the combustion quality of the fuel would be reduced. The third possible combination (iii) is to feed the reformer with natural gas, while firing the furnace with biogas. Which option is used would depend on required economic, environmental, and technical performance requirements, as well as locational factors like the availability of biogas (see box 1). By coupling a capture plant to configurations (i) and (iii), the total CO_2 balance might be close to zero. In the case of the second configuration, since no natural gas is used, by adding a capture plant the process might be carbon negative, and therefore there is the potential to generate negative CO_2 emissions.

Biogas is usually produced via anaerobic digestion of wet organic matter, as for example agricultural waste, manure, municipal or food waste. The amount of wet organic matter available for hydrogen production might represent a limitation on the production volume. For example, considering the specific case of Switzerland, the sustainable potential of non woody-organic matter available for biogas production was estimated to be close to 30 PJ/year that corresponds to 14 PJ/year of biogas ((BFE, 2017)). To decarbonize 100% of the Swiss passenger vehicles in 2035, ~530'000 yearly tonnes ($5.3 \cdot 10^8$kg/year) of hydrogen are needed. Considering an average biogas composition (60% methane and 40% carbon dioxide), with 14 PJ/year of biogas, ~50'000 yearly tonnes ($5 \cdot 10^7$kg/year) of hydrogen can be produced; therefore, by exploiting the entire Swiss biogas potential, more or less 1/10 of the hydrogen demand for light mobility could be covered. Moreover, biogas production is mainly local and small scale. To overcome this issue, one option could be to create a centralized large-scale biogas production unit right next to the hydrogen production plant. However, due to its nature, wet organic matter is hard to collect and transport leading to questions about economics. An alternative could be to collect the biogas produced at small scale at the location where hydrogen is produced. Nevertheless, biogas is not trivial to transport due to the high CO_2 content, which might cause a phase split in the gas phase under certain temperature and pressure conditions. A last option could be to decentralize the hydrogen production, and to produce at small scale close to the biogas plants. This would however cause an increase in capital costs.

Box 1: Size limitations on hydrogen production via biogas reforming

4.2 Biogas reforming simulations with Aspen Plus®

4.2.1 Introduction on Biogas Reforming

To understand the effect of having CO_2 in the feed stream on the thermodynamic equilibrium of the chemical reactions involved, the first configuration (where biogas is fed as reagent and natural gas is used to fire the reformer) was modelled and investigated. The composition chosen for the simulation is based on the high end of the range that can be expected for CO_2, essentially corresponding to a worst case scenario (see Table 6).

Table 6: Chemical composition of biogas selected for simulations (REF (Naskeo Environment, 2018))

Species	vol%
CH_4	60.0
CO_2	35.2
N_2	3.8
O_2	1.0

Since no long chain hydrocarbons are present in the feed, pre-reforming is not necessary. The same operating conditions were used as for modelling the base case (see Appendix A1). The peculiarity of feeding biogas as main reagent is the high carbon dioxide concentration (CH_4:CO_2 1.5:1), which may enhance the dry reforming of methane (reaction (3)). This reaction produces a synthesis gas with a lower H_2/CO ratio than the one generated by steam reforming (reaction (4)). The two reactions have similar thermodynamic properties, but in the case of dry reforming, due to the lower H_2/CO ratio, the potential of carbon formation is higher. Ideally, the carbon formed should be rapidly consumed, but without the presence of excess steam, the carbon formation is more likely to increase and it could lead to catalyst deactivation and reactor blockage (Tuna, 2018).

Set of reaction occurring in the reformer feeding biogas:

Reforming

$CH_4 + CO_2 \rightarrow 2H_2 + 2CO$ $\Delta H = 247$ kJ/mol (3)

$CH_4 + H_2O \rightarrow 3H_2 + CO$ $\Delta H = 206$ kJ/mol (4)

Carbon formation

$CH_4 \rightarrow C + 2H_2$ $\Delta H = 75$ kJ/mol (5)

$2CO \rightarrow C + CO_2$ $\Delta H = -171$ kJ/mol (6)

Other reactions which could also have an important influence

$CO_2 + H_2 \rightarrow CO + H_2O$ $\Delta H = 41.1$ kJ/mol (7)

$C + H_2O \rightarrow CO + H_2$ $\Delta H = 131$ kJ/mol (8)

4.2.2 Modelling results

The thermodynamic modelling results are in agreement with the considerations made in the previous section (Figure 8). In fact, the presence of CO_2 in the inlet stream of the reformer changes the chemical equilibrium; without any addition of steam, carbon dioxide is dry-reformed into hydrogen and carbon monoxide (reaction (3)), but at the same time reaction (5) will also occur, leading to the formation of water and consequently enabling reaction (4). However, low conversion of methane is obtained (<45%). By co-feeding steam to the reformer, the conversion of methane improves substantially. The addition of water enhances reaction (4). By increasing the steam to carbon ratio, the methane conversion increases and the excess of water reacts with CO to form CO_2 and H_2 (reverse of reaction (5)). When comparing the case where natural gas is fed and the case where biogas is used instead while keeping the same S/C (steam to carbon ratio of 2.8), a higher methane conversion could be achieved with biogas due to the dry reforming effect. However, the H_2/CO ratio at the outlet of the reformer decreases from 4.5 to 2.6, because more carbon monoxide is produced at the expense of hydrogen. However, the final CH_4/H_2 ratio is almost the same. On the other hand, by keeping the same methane conversion (83%), in the case of biogas a lower S/C ratio is needed. But to compensate for the lower H_2/CO ratio at the outlet of the reformer, additional steam should be added before the water gas shift reactor, i.e. the CH_4/H_2 could be kept also in this case more or less the same (Figure 6, Table A2.2). To conclude, for hydrogen production, a high H_2/CO ratio is preferable. In order to keep the same CH_4/H_2 ratio when using biogas as a feedstock, higher methane conversion compensates for the lower H_2/CO ratio.

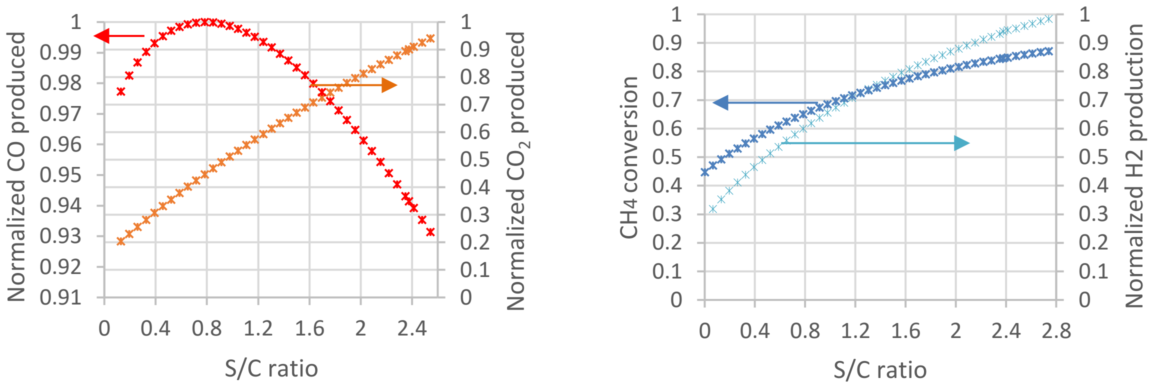

Figure 8: (**Left**) CO and CO_2 produced after reforming as a function of the steam to carbon ratio. (**Right**) Methane conversion and hydrogen production as a function of the steam to carbon ratio. The operating conditions (T and P) used are the same as the one reported in Appendix A1.

4.3 Hydrogen Production via Biomass Gasification

Beside biogas, solid biomass is another potential hydrogen feedstock. Unlike biogas and natural gas, biomass is a solid and therefore the nature of the conversion process is different. The most suitable conversion technology for producing hydrogen is gasification and here we consider woody biomass as the feedstock. The classic gasification technology is divided into three main process categories: fixed bed (updraft or downdraft), fluidized bed (bubbling, circulating or dual) and entrained flow (top-fed or side-fed) gasifiers. Gasification processes occur at high temperatures, and heat could be provided either directly (autothermal) or indirectly (allothermal). Depending on the final application, the impurities present in the synthesis gas may be more or less problematic. Moreover, the choice of the oxidizing agent is very important (oxygen, air, CO_2 or steam), since it might influence the quality of the produced syngas. Indeed, air as a gasifying medium gives low hydrogen purity because of dilution by nitrogen. However, in the case of ammonia synthesis, the presence of N_2 in the hydrogen stream is in fact beneficial. Carbon dioxide as gasifying agent enhances the CO content through the Boudouard reaction (reaction (6)), lowering the H_2/CO ratio. On the other hand, gasification in the presence of oxygen or steam generates hydrogen-rich gas, because both the reforming and the water gas shift reactions take place. This could be an advantage when hydrogen is used in fuel cells, where high purity is required. Biomass gasification includes the following general steps: biomass pre-treatment (e.g. drying and grinding), gasification and syngas cleaning and conditioning. To increase the hydrogen yield, reforming and water gas shift reactors and a H_2 purification unit might be needed. Optionally, a carbon capture plant can be added, to avoid emitting the produced biogenic CO_2. Although very promising, biomass gasification is at an early stage of development with several pilot scale plants built and operated. Because biomass includes a large amount of possible materials with different chemical compositions, it is challenging to describe the performance of a typical biomass gasifier. However, valuable research is ongoing and in section 4.3.2 we exemplify biomass gasification using results of an existing demonstration plant.

4.3.1 Hydrogen Production via Steam Biomass Gasification

As mentioned in the previous section, gasification processes differ substantially in operating conditions. Hydrogen production is favoured by presence of steam or oxygen in the gasification chamber. If oxygen is selected as oxidizing agent, high pressure (40-80 bar) and high temperature (1200°C) entrained flow gasifiers are used (Sikarwar, 2016). In this case, an air separation unit (ASU) is needed to supply the required oxygen. A pilot plant of this kind was built in Germany (Bioliq®) at the Karlsruhe Institute of Technology. Instead, by choosing steam as oxidizing agent, a (dual) fluidized bed gasifier is normally used. Both are valuable options, however we chose to analyse the steam gasification process, based on its larger technology maturity. A successful demonstration plant has been built in Sweden (GoBiGas) in collaboration with Chalmers University of Technology. Experimental data on plant performance are therefore available. With this technology, biomass gasification occurs in three steps: an initial devolatilization or pyrolysis step, that produces volatile material and a char residue, followed by secondary reactions involving the volatile matter and finally the gasification reactions of the remaining carbonaceous compounds (see reactions (4)-(11) (Franco, 2003), (IEA Bioenergy, Task 33, 2016)). Two important parameters that influence the gas composition exiting the gasifier are the reaction temperature and the steam to biomass (S/B) ratio. At a S/B ratio of 0.8, and for temperatures in the range 730-830°C, the water-gas shift reaction (10) plays an important role. Conversely, for temperatures above 830°C and the same S/B, the Boudouard (6) and water gas reactions (7-8) prevail. At higher temperature, the reforming reaction is also favoured. Therefore, in the range 830-900°C the hydrogen yield is higher, consequently the H_2/CO ratio increases as well. When varying the S/B (w/w) ratio from 0.5 to 0.8, the CO concentration drops significantly. The H_2 yield, on the other hand, has a maximum (~40%, depending on the type of biomass used) for an S/B ratio of around 0.6-0.7 (Franco, 2003). When the S/B ratio is higher than 0.7, reaction (8) is favoured, increasing both H_2 and CO concentrations. Nevertheless, the high hydrogen concentration might favour the methanation reaction (9), thus the CH_4 concentration is expected to increase. However, depending on the type of biomass fired, more or less volatile matter would be produced, therefore the equilibrium of the reactions involved could be shifted, and slightly different trends could be identified.

Set of reaction occurring during biomass gasification:

Oxidation

$$C + O_2 \rightarrow CO_2 \qquad \Delta H = -393.5 \text{ kJ/mol} \tag{4}$$

$$C + \frac{1}{2}O_2 \rightarrow CO \qquad \Delta H = -123.1 \text{ kJ/mol} \tag{5}$$

Boudouard

$$C + CO_2 \rightarrow 2CO \qquad \Delta H = 159.9 \text{ kJ/mol} \tag{6}$$

Water gas

Primary: $$C + H_2O \rightarrow CO + H_2 \qquad \Delta H = 118.5 \text{ kJ/mol} \tag{7}$$

Secondary: $$C + 2H_2O \rightarrow CO_2 + 2H_2 \qquad \Delta H = 77.2 \text{ kJ/mol} \tag{8}$$

Methanation

$$C + 2H_2 \rightarrow CH_4 \qquad \Delta H = -87.5 \text{ kJ/mol} \tag{9}$$

Water-gas shift

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H = -40.9 \text{ kJ/mol} \tag{10}$$

Steam reforming

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H = 206.0 \text{ kJ/mol} \tag{11}$$

4.3.2 Example: Dual Fluidized Bed Gasifier for Biofuel Production Based on the Gothenburg Biomass Gasification (GoBiGas) demonstration plant

To exemplify the performance of biomass gasification processes, this section describes a demonstration plant for syngas-based biofuel production built in Gothenburg, Sweden (Gothenburg Biomass Gasification, GoBiGas (Thunman, 2018). Here, in a dual fluidized bed (DFB) gasifier, 150 dry tonnes of biomass per day are converted into synthetic natural gas (SNG). The type of DFB reactors applied in the GoBiGas plant are a circulating fluidized bed (CFB) boiler used for heat generation, and a bubbling fluidized bed (BFB) boiler that is used as a gasifier. In contrast to a conventional CFB boiler, in this case there is no external solid fuel fed to the combustor. Rather, unconverted char from the gasifier is used as the main fuel. An important feature of indirect heated gasifier, i.e. DFB type, in the solid circulation. In this specific case there are two main material cycles: a primary circulation of the bed material between the gasifier and the combustor vessels, and a secondary circulation of ash fractions. The main function of the primary circulation is using the bed material (olivine) as heat carrier, catalyst and carrier of unreacted species. On the other hand, the ash circulation is needed to recover e.g. entrained bed material and other important components. The gas composition at the outlet of the DFB gasifier is reported in Table 7: Wet and dry gas compositions at the outlet of the gasifier operated with wood pellets and a bed temperature of 870°C. To obtain a product gas stream rich in hydrogen, after the gas clean-up step a catalytic steam reforming or a catalytic partial oxidation step should be added to convert the methane and the long chain hydrocarbons (~8%) present in the product stream. Subsequently, a water gas shift reactor is needed to increase the hydrogen yield, to shift the carbon monoxide (> 15%) present in the syngas (Figure7).

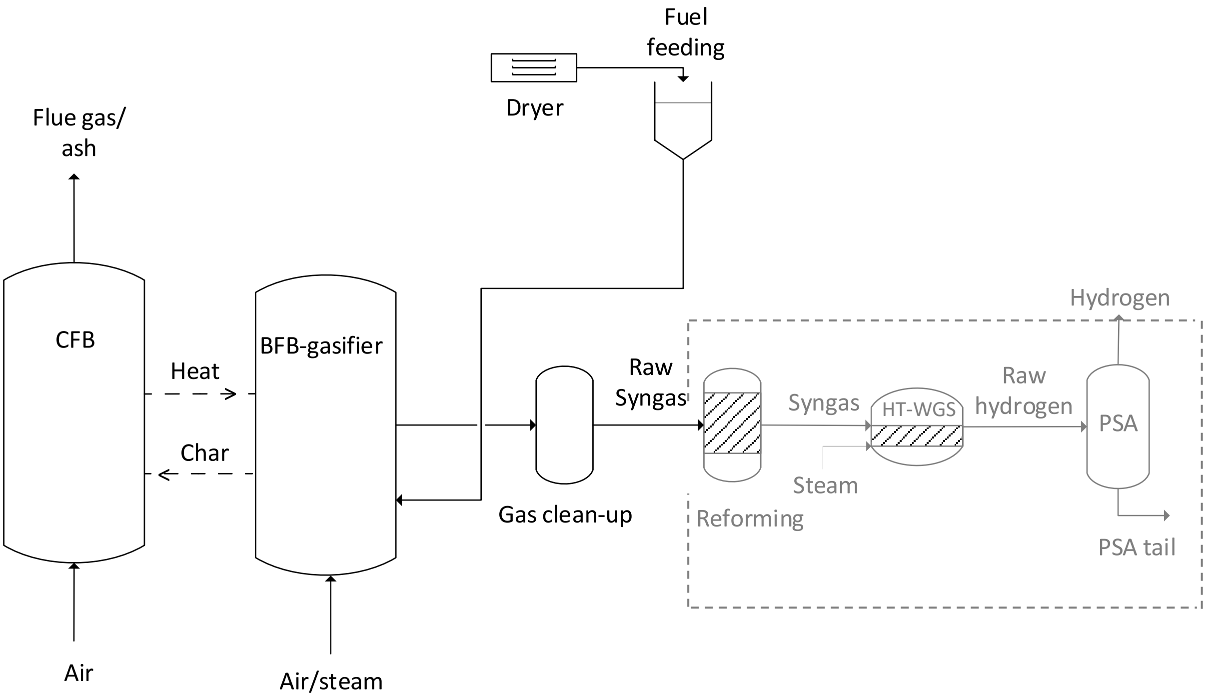

Figure 9: Simplified flowsheet of GoBiGas dual fluidized bed for woody biomass gasification. The dashed illustrates the units that are additionally necessary for hydrogen production.

Table 7: Wet and dry gas compositions at the outlet of the gasifier operated with wood pellets and a bed temperature of 870°C

Species	**vol%**
H_2	27.7
CO	16.6
CO_2	13.8
CH_4	6.0
C_2H_4	1.4
C_2H_2, C_2H_6, C_3H_6, Benzene	0.5
N_2	3.7
H_2O	30.2
Tar	0.1

5 CONCLUSIONS AND OUTLOOK

This deliverable described hydrogen production from fossil fuels, using steam methane reforming. The documents describes the current state of the art and provides a basis for comparing and evaluating newly developed CO_2 capture technologies. MDEA-based carbon dioxide capture from the syngas combined with pressure swing adsorption were chosen as the benchmark technologies for CO_2 capture and hydrogen purification. The overall carbon capture rate of this configuration is around 60% due to the inability to capture CO_2 emissions from the reformer furnace. The document also describes other CO_2 capture options that may further decrease the carbon footprint of hydrogen. One approach includes the combustion of a hydrogen-rich tail gas in the furnace. Another approach is based on producing hydrogen via auto-thermal reforming and partial oxidation of natural gas.

The report continued to show that the climate change impact of hydrogen production can be reduced by changing the feedstock to carbonaceous material. It showed that when feeding biogas instead of natural gas, a lower hydrogen over CO ratio is achieved, since the methane fraction of the feed is partially reformed by the CO_2 present. Less steam is required than for normal SMR to reach a similar methane conversion. We exemplified biomass gasification by providing the output composition and flowsheet of the GoBiGas pilot plant in Gothenburg, Sweden.

A good understanding of the state-of-the-art process is necessary to create the basis for a comparison with the novel technologies developed in the framework of the ELEGANCY project. Therefore, a detailed process simulation framework based on Aspen Plus ® has been established, key operating parameters were identified and a sensitivity analysis was performed to investigate their effect on process performance in detail. Key differences in the process performance when operating with biogas or gasified biomass instead of natural gas as a feedstock have been explored.

Additionally, the methodology establish the framework for a future comparison among technologies based on different separation principles has also been illustrated. In the upcoming work, such framework will be expanded and enriched, so as to lead to the optimization studies involving a portfolio of benchmark and novel technologies.

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A APPENDIX

A.1 Reforming Operating Conditions

Operating conditions of the SMR production plant with high temperature water gas shift reactor without capture:

- Pre-reformer: adiabatic, P = 33.9bar
- Reformer: isothermal, T = 895°C, P = 28.5bar, S/C = 2.8
- HT-WGS: adiabatic, P = 28bar
- PSA: H_2 recovery 90%, purity <99.9%

A.2 Tables

Table A2.1: Stream composition only with high temperature shift/low temperature shift and carbon capture (option 1).

Compoments [mol %]	**Inlet**	**SMR outlet**	**HT-WGS outlet**	**LT-WGS outlet**	**Dry HT**	**Dry LT**
H_2	-	50.5	58.3	61.0	75.4	76.3
CO	-	10.8	2.9	0.3	3.7	~0
CO_2	2.0	5.2	13	15.7	17	19.8
CH_4	90 (7.1)	2.8	2.8	2.8	3.6	3.5
H_2O	-	30.5	22.7	20.0	-	-
N_2	0.9	0.2	0.2	0.2	0.3	0.3

Table A2.2: Streams molar composition of hydrogen production via biogas reforming

Compoments [mol %]	**Inlet**	**SMR outlet**	**HT-WGS outlet**	**Dry**
H_2	-	42.5	52.8	64.8
CO	-	16.2	6.0	7.3
CO_2	35.2	8.8	19.0	23.3
CH_4	60.0	2.7	2.7	3.3
H_2O	-	28.1	18.5	-
O_2	1.0	~0	~0	~0
N_2	3.8	1.1	1.1	1.3

A.3 Flowsheets

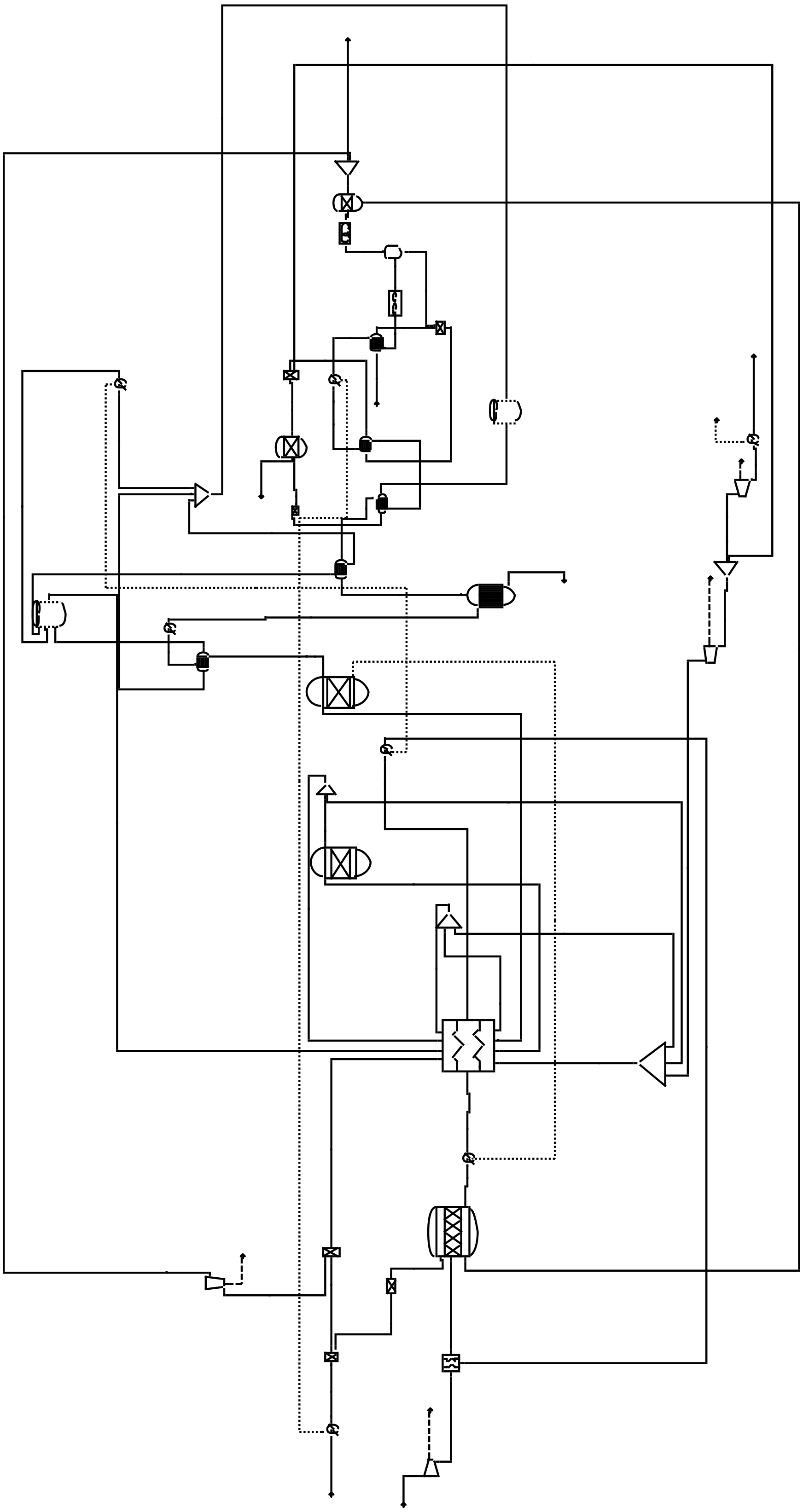

Figure A1: Aspen flowsheet of hydrogen production SMR based with HT-WGS reactor.

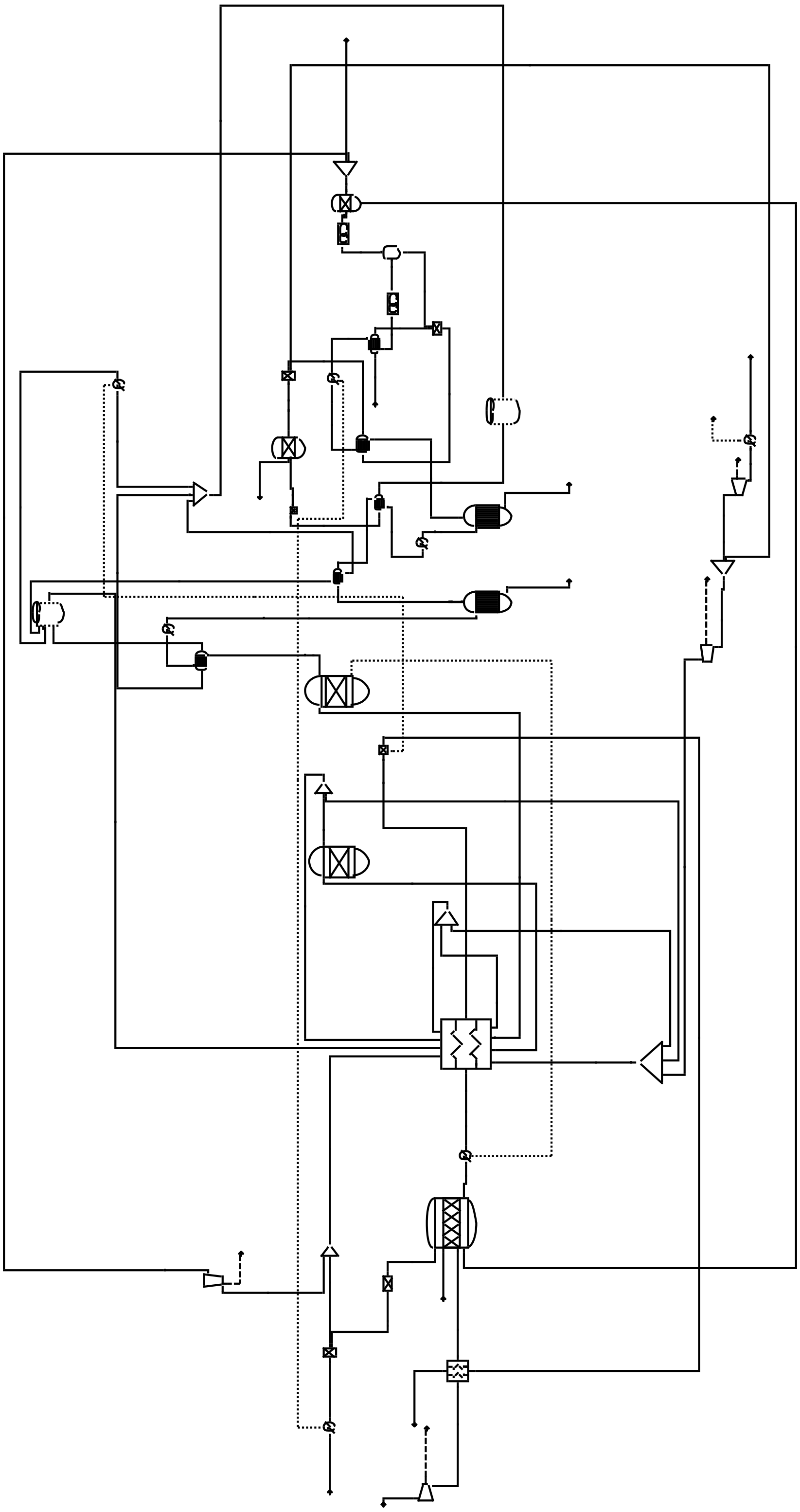

Figure A2: Aspen flowsheet of hydrogen production SMR based with HT- and LT-WGS reactors.

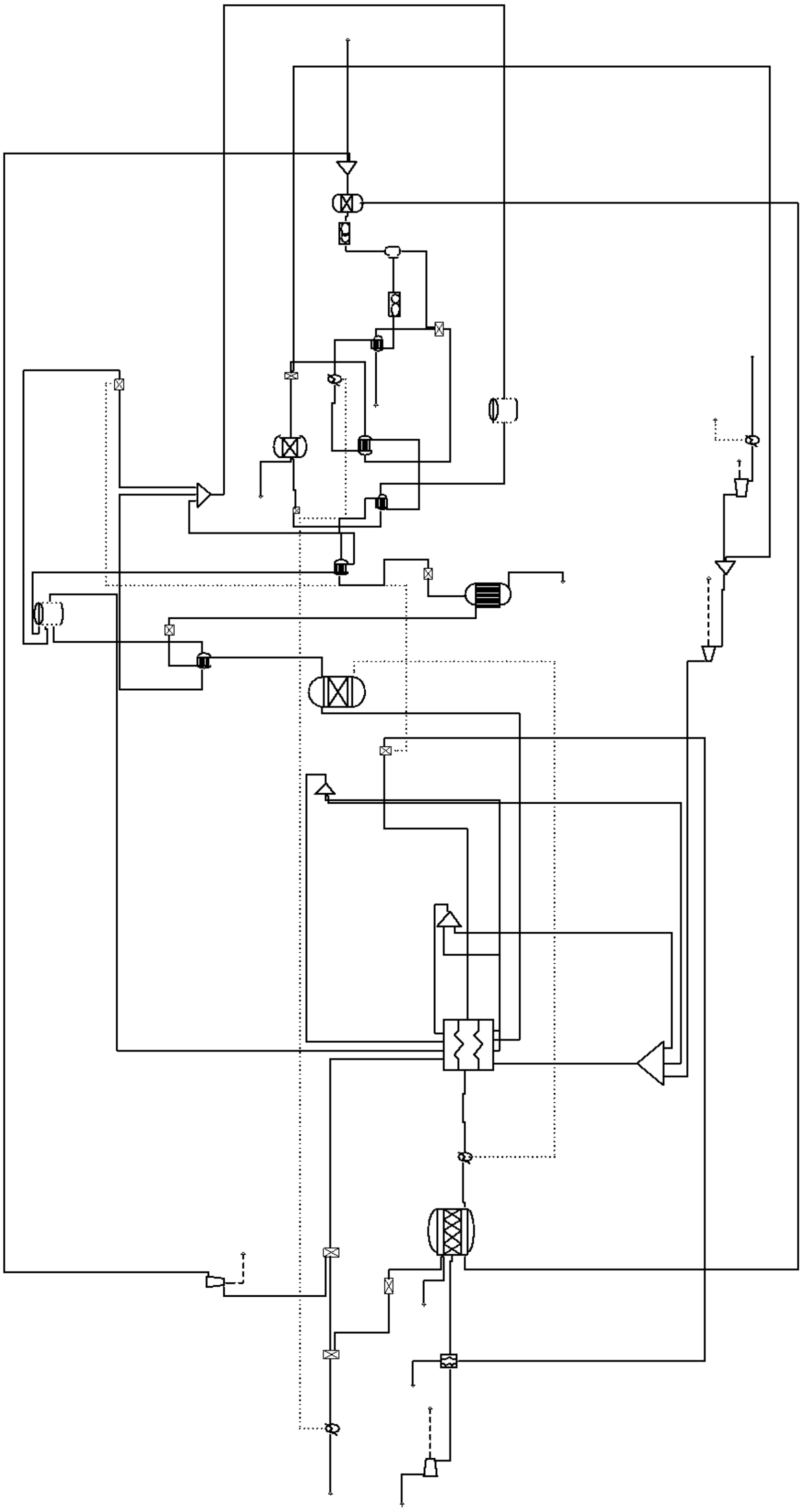

Figure A3: Aspen flowsheet of hydrogen production via biogas reforming without capture

A.4 MDEA inlet gas composition

- Temperature: 35°C
- Pressure: 26 bar
- Flow rate: 6598.74 kmol/hr

Compnents [mol %]	Inlet
H_2	75.61
CO	4.63
CO_2	16.27
CH_4	3.05
H_2O	0.24
N_2	0.20

A.5 High temperature flash analysis

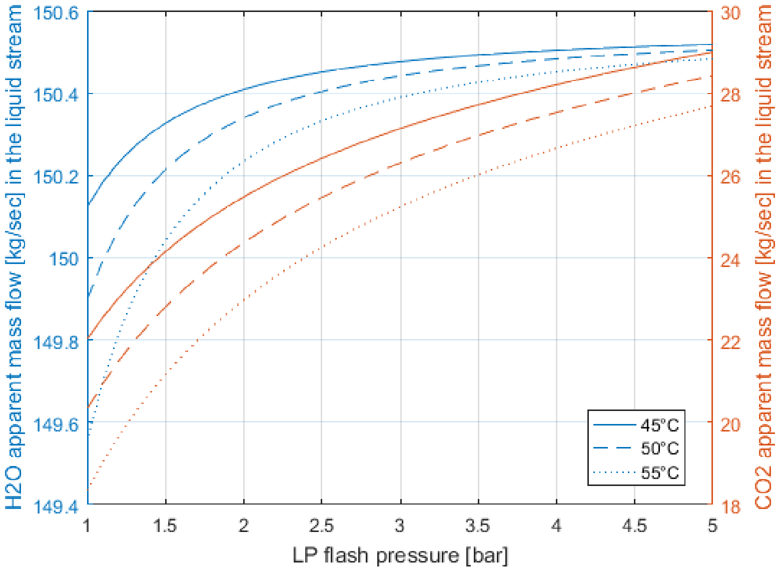

Figure A4.1: Apparent mass flow rates [kg/sec] of H_2O and CO_2 in the liquid stream exiting the low pressure flash. The higher the pressure the lower is the CO_2 desorption, but the higher the water condensation. By increasing the temperature, less water is condensed, but more CO_2 is desorbed.

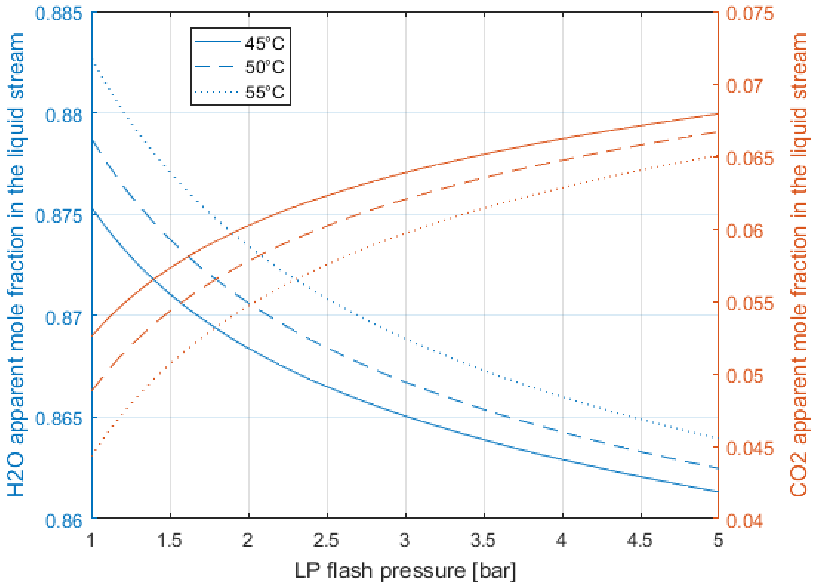

Figure A4.2: Apparent mole fraction of H_2O and CO_2 in the liquid stream exiting the low pressure flash. Same trends as Figure A4.1 but represented from on other prospective. By increasing the pressure, the CO_2 desorption decreases and therefore the mole fraction in the liquid phase increases. At the same time, by increasing the temperature, the more CO_2 in desorbed. For this reason, the CO_2 concentration in the liquid phase decreases.