

Master's Thesis

Simulation of an Industrial-Scale SNG Upgrading Process for BioSNG

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by

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Vienna, July 2024

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Preface

Writing a Master's Thesis is never a one-woman-show, therefore I want to express my gratitude to the numerous people who have accompanied me throughout this thesis and contributed in different ways.

First of all, I would like to thank Dr. Florian Benedikt for his continuous feedback, guidance, and input. I would also like to thank Dr. Walter Wukovits for his rather spontaneous supervision and in particular the Aspen Plus support and his valuable feedback. I deeply thank Dr. Stefan Müller for giving this thesis its finish touch and by providing advices, I will use far beyond this work. In terms of data provision I thank Alexander Bartik for sharing his fluidised bed methanation data with me and his valuable methanation insight when one or two questions arose. Likewise I would like to thank Stefan Jankovic for his initial supervision and his engagement.

Apart from the professional expertise, I had a lot of support from friends and family. Hence, I express my sincerest gratitude to my parents Monika and Günter for their unconditional support and the values they passed on to me. I would like to thank Samuel, just for being a really good brother and having a sympathetic ear, always. Thank you, Jakob, for always being there for me, the many shared passions, and your patience. To come to a conclusion, I would like to thank my colleagues at BEST who contribute massively to the fact that I enjoy my work so much and I also thank my friends from university, with whom I have spent numerous hours to reach our shared goals. It is just very nice to see where life has taken us.



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Abstract

Synthetic natural gas from biomass (bioSNG), which is produced from the gasification of biomass and the subsequent methanation of synthesis gas, represents a promising sustainable alternative to fossil energy carriers. However, in order to effectively integrate bioSNG into existing systems, the distribution in the national gas grid is essential. Therefore, this work focuses on the upgrading of raw SNG, as the high concentrations of CO_2 and H_2O pose a challenge. Thus, two different upgrading configurations for previous fluidised bed methanation performed at 1 bar and 10 bar are presented. The syngas for fluidised bed methanation is provided by a dual fluidised bed gasifier, assuming a thermal biomass input of 100 MW. An Aspen Plus model is implemented to simulate both, an amine scrubbing unit for CO_2 separation and a glycol scrubbing unit for H_2O separation. The work compares these configurations in terms of specific design and operating parameters necessary to ensure the injection of bioSNG into the Austrian gas grid.

The process chains achieve an energy efficiency of 64.1% (at 1 bar) and 67.2% (at 10 bar) comparing the lower heating value of the bioSNG based on the thermal biomass input. In particular, the reboiler operation of the amine regeneration unit represents a considerable heat demand, which in this work amounts to 2.63 MJ/kg CO_2 separated (1 bar) and 1.82 MJ/kg of CO₂ separated (10 bar). Respectively, a techno-economic assessment shows specific upgrading costs of $27.25 \in /\text{MWh}$ and $27.81 \in /\text{MWh}$ for the 1 bar and 10 bar cases, indicating marginal deviations despite higher total investment costs for the former.

The atmospheric pressure case proves to be the preferred option, particularly with regard to compliance with gas grid limits. Hence, this preference is due to the installation of an additional fixed-bed methanation unit between the CO_2 and H_2O separation unit to reduce the CO content and thus increase the process stability and facilitate adaptation to potential fluctuations in the raw SNG composition.

Kurzfassung

Synthetisches Erdgas aus Biomasse (BioSNG) wird aus der Gaserzeugung von Biomasse und der anschließenden Methanierung des Synthesegases gewonnen und stellt eine vielversprechende Alternative zu fossilen Energieträgern dar. Um BioSNG jedoch effektiv in bestehende Systeme zu integrieren, ist de Verteilung durch das nationale Gasnetz unerlässlich. Diese Arbeit behandelt daher die Aufbereitung von Roh-SNG, um die Spezifikationen des Österreichisen Gasnetzes zu erfüllen. Insbesonders die hohen Konzentrationen von CO_2 und H_2O stellen eine Herausforderung dar. Zwei verschiedene Aufbereitungskonfigurationen werden vorgestellt, bei denen die vorhergehende Wirbelschichtmethanierung je bei 1 bar und 10 bar betrieben wird. Mit Aspen Plus wurde sowohl ein Aminwäscher für die CO_2 Abtrennung als auch ein Glykolwäscher für die H_2O Abtrennung für beide Druckstufen modelliert und simuliert. Die Studie vergleicht diese Konfigurationen hinsichtlich spezifischer Auslegungs- und Betriebsparameter, die notwendig sind, um die Einspeisung von SNG in das österreichische Gasnetz zu gewährleisten.

Die Prozessketten erreichen eine Energieeffizienz von 64,1% (bei 1 bar) und 67,2% (bei 10 bar) bezogen auf den thermischen Biomasseeinsatz von 100 MW. Insbesondere der Betrieb des Reboilers der Aminregenerationkolonne stellt einen beträchtlichen Wärmebedarf dar, der sich in dieser Arbeit auf 2,63 MJ/kg abgetrenntes CO₂ (1 bar) und 1,82 MJ/kg abgetrenntes CO₂ (10 bar) beläuft. Eine technisch-wirtschaftliche Bewertung zeigt spezifische Aufbereitungskosten von $27,25 \in /MWh$ und $27,81 \in /MWh$ für den 1 bar- bzw. 10 bar Fall, was auf marginale Abweichungen trotz höherer Gesamtinvestitionskosten für den ersten Fall hindeutet.

Der Betrieb bei 1 bar erweist sich als die bevorzugte Option, insbesondere im Hinblick auf die Einhaltung der Grenzwerte des Gasnetzes. Dies ist vor allem auf die Installation einer zusätzlichen Festbett-Methanierungsstufe zwischen der CO₂- und H₂O-Abtrennung zurückzuführen, um den CO-Gehalt zu reduzieren und so die Anpassung an mögliche Schwankungen in der Roh-SNG-Zusammensetzung zu erleichtern.



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1 Introduction

A significant reduction in greenhouse gas emissions and a transition to a net-zero emissions economy are essential to achieve the declared target of limiting global warming to below 1.5 °C compared to pre-industrial levels. Increasing energy efficiency is a major factor in this process, as is the transition to renewable energy carriers to substitute fossil-based resources [1]. Besides heating oil, natural gas is the most consumed energy carrier in the European Union [2]. In 2021, 24.4% of the primary energy consumption in the EU-27 is covered by natural gas, in Austria 22.7 % [2]. In particular, industries are dependent on natural gas supply [3], as less than 20 % of Austria's natural gas consumption is from households [4]. A situation, that is not only critical due to the greenhouse gas emissions provoked by natural gas combustion, but also by the reliance on gas producing countries with political instability. As a matter of fact, natural gas imports from Russia still account more than 50% of the natural gas imports in 2023 until September. Aware of this dependence, Austria declared a target of injecting 7.5 TWh of renewable gases into the national natural gas grid in 2030 [5]. The main advantages of injecting renewable gases into the natural gas grid compared to hydrogen, is that no additional infrastructure is necessary. In particular, the distribution system and efficient and well-established end use technologies as i.e. burners and turbines are applicable, while they are sensible to hydrogen as the altered Wobbe Index and combustion potential significantly changes the combustion and transportation characteristics [6]. However, in 2021 the renewable gas volume in the national gas grid accounted 0.136 TWh, making that a rather ambitious target [2]. Two main possibilities exist for a renewable natural gas substitute with almost

the same properties as methane: Biomethane from anaerobic digestion of biomass and synthetic natural gas from biomass (bioSNG). By anaerobic digestion from organic matter biogas is produced, mainly consisting of 50 % to 75 % CH₄, 25 % to 50 % CO₂, as well as H₂, NH₃, CO, N₂, O₂, and H₂S [7, 8]. Further upgrading is necessary to separate the CH₄ from the other components and obtain biomethane for gas grid injection [9].

In contrast, bioSNG production is based on the synthesis of H_2 and CO or CO₂. As different origins of the necessary H_2 , CO₂, and CO exist, two main concepts are introduced: Power-to-SNG and Biomass-to-SNG. For Power-to-SNG surplus power of renewable energy sources is used for the electrolysis of water. Afterwards the CO₂ compound is hydrogenated to CH₄, with the CO₂ originating from various possible sources, as post-combustion carbon capture, biogas from anaerobic digestion of biomass or from syngas, produced from biomass gasification [10].

In Biomass-to-SNG the electrolysis is skipped and syngas from biomass gasification directly applied for the methanation reaction. As the reactions needs a stoichiometric H₂:CO ratio of 3:1 and H₂:CO₂ ratio of 4:1, gasification technologies with high hydrogen share in the syngas are favoured. One favourable gasification technology is dual fluidised bed (DFB) steam gasification. Product gas is characterised by high hydrogen content, no dilution with nitrogen originating from the air, and flexible feedstock input. Hence, bioSNG production is not limited to woody biomass, but also possible from waste streams [11]. Demonstration-scale bioSNG production with DFB product gas was already performed with 1 MW bioSNG output in Güssing, Austria [12] and 20 MW bioSNG output at the GoBiGas plant in Gothenborg, Sweden [13].

A novel fluidised bed methanation reactor was developed by Bartik et al. [14] with the aim to adapt the unit to the characteristics of DFB product gas. A pilot-scale biomass-to-gas unit has already been installed and tested at TU Wien [15]. However, a gas upgrading process to meet the requirements for grid injections is not installed yet. This thesis aims the design and simulation of a bioSNG upgrading process to achieve the requirements for grid injections, hence bioSNG upgrading is defined as the separation of CO_2 and H_2O from the raw SNG. The units are designed to meet the requirements for a preceding process chain with a 100 MW dual fluidised bed steam gasification plant and fluidised bed methanation unit, designed after [14]. Apart from CH_4 , the raw SNG still contains H_2O , CO_2 , CO, and H_2 . In particular, the amount of H_2O and CO_2 are critical for grid injection and demand for upgrading units. Several technologies are available based on the experience with bioSNG from biogas, and conventional natural gas upgrading. While various technologies will be briefly introduced, this thesis focuses on well-established technologies already available in industrial scale, to provide a reliable base case scenario for further upgrading options. Hence, the aim of this thesis is to present the feasibility of raw bioSNG upgrading and the associated resource demands. As a result CO_2 separation will be performed by chemisorption with amines, an established technology for post-combustion carbon capture [16]. To achieve the dew point requirements of the gas grid, a glycol dehydration unit was

To achieve the dew point requirements of the gas grid, a grycol dehydration unit was designed. Glycol dehydration units are broadly applied in natural gas upgrading [17]. Both units are simulated with Aspen Plus V12.1 to determine appropriate process parameters, energy and material streams. For future comparability a techno-economic assessment is performed based on the simulation. As input stream compositions, the experimental data of the bench-scale fluidised bed methanation unit are applied. Based on a decreased amount of injection limiting components as CO and H₂ in the raw SNG at increasing methanation operation pressure, two different cases are introduced. Thus, the gas upgrading process for raw SNG from methanation at 1 bar is compared to raw SNG from methanation at 10 bar. Based on the results of the techno-economic assessment and evaluation of predefined key indicator parameters, an operation recommendation will be given.

Key objectives

The aim of this thesis is to model and simulate a bioSNG upgrading process chain to meet the composition and property requirements for injection in the Austrian gas grid. The focus is on the development of an adequate process chain and the suitable interconnection of unit operations. These are afterwards implemented in the simulation tool Aspen Plus. For enhanced understanding, three research questions are phrased and will be answered in the Chapter 6. Two of them cover the model building and simulation work. The third question is based on the previous simulation and covers the economic aspects of the realisation.

- What is an adequate process chain for raw SNG upgrading and how is the performance of the introduced options?
- How are different operating modes of the upstream units influencing the process chain, in particular the fluidised bed methanation operating at 1 bar and 10 bar? Are the SNG quality requirements for the example of the Austrian gas grid injection fulfilled?
- What are the investment and operating costs of the necessary equipment for SNG upgrading?

2 Fundamentals of the Biomass-to-SNG Process

Within this chapter the biomass-to-SNG process is introduced. Hence, an overview of the upstream processes of the biomass-to-SNG concept is given, including gasification, gas cleaning, and methanation units. Furthermore, raw SNG upgrading concepts are introduced and the legal background for SNG injection into the Austrian gas grid are covered.

2.1 Preceding Processes

Several pathways and operating modes are applicable for SNG production. In the following chapter an overview of the units preceding to the upgrading processes is given. Due to the direct application in this work, the focus of the included technologies is on dual fluidised bed (DFB) steam gasification and fluidised bed methanation.

2.1.1 DFB Gasification

Gasification is the thermochemical conversion of hydrocarbon based raw material into product gas, mainly consisting of hydrogen (H₂), carbon monoxide (CO), carbon dioxide (CO₂), methane (CH₄) and higher hydrocarbons. Gasification reactions are overall endothermic and performed at temperatures above 700 °C under a reducing atmosphere. Originally, coal was used as raw material for gas production, with first applications leading back to the 19th century. In the middle of the 20th century, the focus of research shifted to biomass gasification, while current projects and research additionally emphasis on more flexible fuel input like residual materials. With the application of these non-fossil based fuels, the product gas and further synthesis products are a vital renewable energy source. [18, 19]

Dependent on the reactor type and gasification agents, various technologies are differentiated. Five main reactor types exist for the gasification process: entrained flow, fixed bed, fluidised bed, rotary kiln, and plasma reactor. An overview for their application in biomass gasification is given by Molino et al. [18]. As gasification agent, air, O_2 , steam, and CO_2 are applied. The choice of reactor and gasification agent influences the product gas composition and occurring impurities. Hence, a significant impact has i.e. air as gasification agent, as its nitrogen content dilutes the product gas.

In the following, the reactor design of dual fluidised beds (DFB) is introduced in detail, along with two different operation modes. The focus on DFB steam gasification is due to its continuous performance with fuel flexible and the favourable product gas composition, which are both essential for the production of bioSNG [11].

In DFB gasification, a combustion reactor is integrated into the process, in addition to the conventional gasifier. The combustor is connected to the gasifier at the top and bottom of the reactor via loop seals or a chute, allowing the bed material and residual char to circulate between the reactors. This way, an allothermal gasification mode is achieved in which the exothermic combustion reactions provide the energy for the gasification reactions. Hereby, the hot bed materials acts as energy carrier. Within the process, the combustion reactor is operated as fast fluidised bed with air as fluidisation agent and characteristically high superficial gas velocities. The gasification reactor is operated as bubbling fluidised bed and steam is applied as fluidisation agent [20]. As bed material, olivine is primarily used with additional limestone, since the catalytic activity of limestone enhances the conversion of water, tar, and char [21]. The advanced reactor designs include a counter current column in the gasification reactor to enhance the gas-solid interaction. Considering these optimisations, a medium calorific value product gas is obtained, mainly consisting of over 40% H₂, about 20% of each CO and CO₂, and 10% CH₄ [22]. The basic concept of DFB steam gasification in presented in Figure 2.1.



Figure 2.1: Principal of DFB steam gasification [23]

In addition to conventional steam gasification, in-situ CO₂ capture can be performed

in the DFB system with differing process conditions. For in-situ CO_2 capture, calcium oxide is used as CO_2 adsorbent, simultaneously acting as circulating bed material in the so-called sorption enhanced reforming (SER) process. The calcium oxide is thus carbonated in the gasification reactor and in the combustion reactor the calcium carbonate formed is calcined endothermically (Eq. 1). [24, 25]

$$CaO + CO_2 \longleftrightarrow CaCO_3 \qquad \Delta H^0 = -182 \, kJ/mol$$
 Eq.1

Due to the continuous capture of CO_2 , the water-gas shift reaction in the gasifier shifts towards higher concentrations of H₂ and lower concentrations of CO (Eq. 2). This favours further reforming reactions in the gasifier, leading to an overall increase of the hydrogen content in the product gas. According to Kuba et al. [26] increased activity of the water-gas shift reaction enhanced the steam reforming reaction and thus, tar conversion.

$$CO + H_2O \longleftrightarrow CO_2 + H_2 \qquad \Delta H^0 = -41 \, kJ/mol \qquad Eq.2$$

Temperatures in the reactor system are in general lower compared to conventional steam gasification operation, as the exothermic carbonation reaction demands for lower temperatures to be thermodynamically feasible.

Thus, a temperature level of 600°C to 700°C is obtained in the gasifier and about 900 °C in the combustion reactor [24, 25]. Due to the higher H₂ concentration in the product gas, SER operation is an interesting alternative to the conventional steam gasification for further bioSNG production as stated in Bartik et al. [15].

2.1.2 Product gas Cleaning and pre-Processing

The product gas leaving the reactor system is, dependent on the gasification technology and input fuel, characterised by impurities in form of tar, dust, and inorganic components. Product gas cleaning units applied in DFB steam gasification are in general cyclones and cold gas or hot gas filters for solid particle separation and a rapeseed methyl-ester (RME) scrubber to separate in particular tar. Particles of dust and fly ash are i.e. separated in the bag house filter with a separation efficiency of 99.8%. In addition, up to 30% of tar and HCl are separated in the filter. For further tar removal the product gas is subsequently lead into the RME scrubber. The scrubber is operated at 40 °C to 50 °C gas outlet temperature, thus, tar and steam condense and part of alkaline and acid components are removed [12].

For further applications in methanation, additional removal of sulphur compounds, nitrogen compounds, halogenids, and volatile metals is necessary, as they potentially hinder the catalyst [27, 12]. In the 1 MW bioSNG Güssing plant pre-processing included a second RME scrubber unit, a water scrubber for NH₃ removal, an activated carbon guard and a zinc oxide bed before the syngas stream entered the methanation reactor, as presented in Figure 2.2. The RME scrubber was operated in two stages with the first stage acting as condensation unit by decreasing the temperature to 10 °C. Thus, part of the water in the gas stream is condensed and RME and water are separated afterwards. At the second stage, remaining tar and organic sulphur components are removed by a scrubbing unit similar to the first stage. Loaded RME is regenerated and reusable in the scrubber. Before entering the activated carbon guard for the separation of remaining sulphur species (mercaptanes and H_2S), the gas stream is compressed to about 4 bar. To ensure total H_2S removal, a zinc oxide bed is installed for adsorption. It is operated at about 200 °C and in order to avoid contamination with halogen compounds, a layer of aluminium oxide for halogen capture is installed before.



Figure 2.2: Simplified flow sheet of the product gas cleaning at the 1 MW bioSNG production in Güssing, modified after [28]

At GoBiGas, the pre-processing of the product gas after the RME scrubbing is performed by two fixed beds with activated carbon for the removal of remaining tar components and H_2 . In total, four fixed bed adsorbers are available to regenerate the activated carbon during operation. Afterwards, olefines and COS are hydrated, H_2S is removed in a scrubber, and trace components are separated by a guard filter [29]. An detailed process description of the pre-processing steps are given in Thunman et al. [13].

2.1.3 Syngas Methanation

After the cleaning and upgrading of the product gas, syngas is a common terminology used in literature. Two pathways for methanation exist, CO and CO_2 methanation, the latter studied by Sabatier and Senderens [30].

$$CO + 3 H_2 \longleftrightarrow CH_4 + H_2O$$
 $\Delta H^0 = -206 \, kJ/mol$ Eq.3

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \qquad {}_{\Delta}H^0 = -165 \, kJ/mol \qquad Eq.4$$

While the CO₂ methanation process converts H_2 and CO_2 to CH_4 and H_2O (Eq. 4), this reaction is implemented in Power-to-Gas concepts with H_2 provided by electrolysis [31]. In contrast, syngas is a suitable educt for CO methanation (Eq. 3), due

to its content of CO and H₂. With commonly applied nickel catalysts, CO₂ methanation usually occurs along with CO methanation, as it is a linear combination of the reverse water-gas shift reaction (Eq. 2) and CO methanation. Above a CO threshold concentration, the CO_2 conversion is inhibited and CO methanation preferred [32]. A significant reduction in volume is a particular characteristic of both methanation reactions. However, the volume reduction of CO methanation is predominant with a decrease to about 50% of the initial volume. The reaction equilibrium is dependent on pressure and temperature, with high pressures favouring the production of CH_4 and high temperatures hindering the CH_4 production. Furthermore, the removal of excess heat is a crucial point in reactor design, as both reactions are highly exothermic. In principle, methanation can be performed in fixed beds, fluidised beds, or three-phase and microreactors. However, commercially available reactors are predominantly adiabatic fixed bed reactor cascades with intercooler and gas recycling. An overview of the available reactor designs and their process characteristics is presented in Table 2.1. Further insights into the technological overview of reactor designs is given by Rönsch et al. [27].

The focus on this study, however, is on the bioSNG after fluidised bed methanation. The advantages of fluidised beds are the enhanced heat and mass transfer due to the improved interaction and mixing of particles. As a results, the common risk of carbon deposition is decreased and high conversion efficiencies are obtained. As presented in Table 2.1, fluidised bed reactors are additionally characterised by low reactor costs and a low thermal stress on the catalyst.

2.2 Raw SNG Upgrading

Subsequent to the methanation process, raw SNG upgrading is necessary to fulfil the technical and legal requirements for further SNG applications. Legislative restrictions are presented in Chapter 2.3.2. The main components for upgrading are the separation

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Reactor	Adiabatic fixed bed	Cooled fixed bed	Micro	Fluidised bed	Three-phase
Operation mode	adiabatic	polytropic	polytropic	isothermal	isothermal
Reactor stages	2-7	1-2	1-2	1-2	1-2
Temperature range in °C	250-700	250-500	250 - 500	300-400	300 - 350
Thermal stress on catalyst	high	moderate	moderate	low	low
Complexity of process setup	high	low	low	low	low
Reactor cost	medium	high	very high	low	low-medium
TRL	9	7	4-5	7	4-5

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of H_2O and CO_2 as they impose the most restrictive requirements for grid injection compared to the initial concentration.

2.2.1 CO₂ Separation

The separation of CO_2 from gaseous streams is applied in numerous industries, as e.g. for natural gas purification, bio-methane conditioning, and post-combustion carbon capture technologies. Thus, several established technologies are available to separate CO_2 from the raw SNG after the methanation. To meet the requirements of raw SNG upgrading Heyne and Harvey [33] identified three main technologies: amine-based absorption, membrane separation, and pressure swing adsorption (PSA). All three technologies were compared on their economic and thermodynamic performance, when integrated in a full process chain of SNG production from biomass gasification in dual fluidised bed technology with 100 MW thermal input. An overview is given in Table 2.2.

Term	Unit	Amine absorption	PSA	Membrane
Pressure	bar	1.1 bar	9 bar	60 bar
Temperature	$^{\circ}\mathrm{C}$	40 °C	40 °C	40 °C
Specific power consumption	$\rm kJ/kWh_{SNG}$	97.6	185.6	245.5
Upgrade efficiency	%	97.4	88.2	87.6
Methane recovery	%	98.2	93.6	95.7

Table 2.2: Overview of the amine absorption, PSA, and membrane operational und performance parameters derived from [33]

In PSA, zeolite, carbon molecular sieves, or silica gel are applied for the separation of CO_2 from the gas stream. Until now, conventional application of PSA is in gas drying, hydrogen purification, or air separation. However, for biogas upgrading a 99 % purity is expected for the application of zeolite and the CH_4 recovery amounted 85 %. The input stream was about one third CO_2 and two thirds CH_4 . [34]

Gas separation processes via membranes are predominately applied in hydrogen production from other gaseous streams as methane steam reforming or the recovery of hydrogen from flue gases. The most similar established process to bioSNG upgrading is CO_2 separation from crude natural gas [35, 36]. To comply with required CO_2 concentrations, a two or three stages membrane unit is suggested with a cellulose acetate membrane [35].

Amine based CO_2 separation processes are predominately used in post-combustion processes. More resembling is gas separation from fermentation processes. With biogas, the concentrations of CH_4 and CO_2 are in similar orders of magnitude as with methanation of syngas. Chemical absorption processes surpass the performance of solely physical adsorption processes as the CH_4 slip is lower, the recovery amount higher and the CO_2 separation rate is also higher [33]. In contrast to the other two separation processes, the energy demand for amine scrubbing is predominately thermal. Each process complied with the quality requirements for CO_2 for storage and SNG for grid injection. However, the techno-economic analysis showed the highest cold gas efficiency with amine absorption. Hence, based on literature the further focus is on amine-based absorption as it is well established for industrial processes and further integration of the heat is possible. Compared to PSA and membrane separation, amine scrubbing especially stands out due to the high CH_4 and CO_2 purities in two separated gas streams achieved, and rather cheap and easy operation. [37]

Amine scrubbing is a chemical absorption process that involves a liquid solution of amine molecules to selectively capture CO_2 . The amine solution is a weak base, and it reacts with CO_2 to form a carbamate compound soluble in the liquid phase. This reaction is reversible, hence, the carbamate can be broken down, releasing CO_2 and regenerating the amine solution.

The absorption of CO_2 by the amine solution occurs in a packed column, where the gas stream is introduced at the bottom and flows upwards through the column, while

the amine solution is introduced at the top and flows downwards. The gas and liquid phases come into contact and react with each other, with the CO_2 being selectively absorbed into the liquid phase due to the chemical reaction with the amine molecules. The CO_2 -depleted gas stream is then discharged from the top of the column, while the CO_2 -rich amine solution is collected at the bottom. The amine solution needs to be regenerated periodically to release the captured CO_2 and allow the amine to be reused. This is done by heating the amine solution, typically to temperatures between 100 °C and 120 °C, under reduced pressure to minimise thermal decomposition of the amine. The heat causes the carbamate compound to break down, releasing CO_2 gas, which is then collected and compressed for storage or use. The regenerated amine solution is then cooled and returned to the absorption column to capture more CO_2 . A simplified flow sheet of the amine scrubbing process is presented in Figure 2.3 [38]. The detailed process configuration and its units and streams is introduced in Chapter 4.



Figure 2.3: Simplified flow sheet of the CO_2 absorption and regeneration column with amine [39]

Amine scrubbing is an effective technology for capturing CO_2 , but it has some limitations. For example, it requires significant energy input for the regeneration process and the amine solution can be degraded over time by factors such as oxidation, thermal degradation, and the presence of contaminants in the gas stream. This leads to a constant consumption of amines and hence, a constant disposal stream. For the classical power plant sector, including biomass gasification, this chemical handling requires additionally trained personnel and know-how. Nonetheless, it remains one of the most widely used technologies for CO_2 capture in industrial applications.

One crucial point in the selection of amine for absorption, monoethanolamine (MEA), diethanolamine (DEA), and methylethanolamine (MDEA) are besides customised amine solvent common option. The most established and technologically and economically approved is MEA. The exact mechanisms for MEA is still topic of research, though several proposition exist [40].

2.2.2 H₂O Separation

Gas dehydration is a critical process in several industrial applications, including natural gas processing, biogas upgrading and of course SNG upgrading. The presence of moisture in gas streams can cause corrosion, fouling, and reduced equipment efficiency, making gas drying essential for maintaining the quality and reliability of industrial processes [17].

The most established methods for H_2O separation in gas streams include adsorption, absorption, and membrane separation. In adsorption, the gas stream passes through a porous material, such as activated alumina or silica gel, which adsorbs the moisture molecules. Temperature swing adsorption (TSA) is a variant of the adsorption method used for gas drying, where the adsorbent material is exposed to cyclic variations in temperature to regenerate the adsorbent and remove the adsorbent material at a lower temperature, where the moisture is adsorbed. Once the adsorbent is saturated, the temperature is raised to desorb the moisture and regenerate the adsorbent. In contrast, absorption uses a liquid desiccant such as glycol to absorb the moisture from the gas stream. Membrane separation employs semi-permeable membranes that allow the gas to pass through while selectively removing moisture. [17, 41]



Figure 2.4: Simplified flow sheet of the H_2O absorption column [41]

The selection of the dehydration method depends on multiple factors, including the composition of the gas stream, the required extent of moisture removal, and the cost-effectiveness of the process. While adsorption, for example, is typically preferred for low moisture contents, achieving less than 1 ppm, absorption is more suitable for high moisture concentrations. Membrane separation is often used for gas streams with low moisture content, where energy efficiency is a critical issue [17]. For the application in SNG upgrading, the utilisation of glycol as a liquid desiccant for gas drying has several advantages over the other methods. Glycol has a high affinity for water and can remove moisture from gas streams with high water content. The absorption process is very efficient and allows moisture removal of up to 99%. Furthermore, it is a readily available and inexpensive material and can be easily regenerated by heating and condensation, which allows continuous use of the desiccant [17]. In general, gly-



Figure 2.5: Simplified flow sheet of the glycol regeneration setup [41]

cols are stable at applied process temperatures and pressures and are non-corrosive and non-foaming. Their vapour pressure is in general low, leading to minimal equilibrium losses in the gas stream [41]. For the dehydration, the saturated gas stream is lead through an absorption column in counter current with the desiccant. The dry gas stream exits the column at the top, while the rich glycol exists the bottom and is further expanded and preheated for the regeneration [42]. The setup of a glycol scrubbing column is shown in Figure 2.4 and the glycol regeneration cycle in Figure 2.5. Based on its resistance against degradation and favourable reconcentration properties, triethylene glycol (TEG, $C_6O_{14}H_4$) is most commonly used [41].

The temperature range of the absorption column is limited by increased glycol loss. Hence, the absorption process is designed for temperatures around 40 °C, as above 48 °C losses occur based on higher vapour pressure, despite the favourable properties compared to other glycols. Besides the high vapour pressure losses, the saturated water content is increased with higher temperatures, leading to an increased amount of glycol necessary and lower separation efficiencies. Hence, a low inlet gas temperature is favoured, though limitations occur below 20 °C, as the formation of an emulsion

$\begin{array}{c} \text{Gas} \\ \text{flow rate} \\ \text{m}^3/\text{h} \end{array}$	Absorptio	on column	Reconcent	tration column	Reference
	Pressure bar	Temperature °C	Pressure bar	Temperature °C	
$55 \ 327$	68.95	49	1.01	160, 204	[43]
$43 \ 932$	40.80 - 41.00	30	1.02	175 - 204	[44]
$147 \ 147$	67.80	58	1.20	165	[45]
$1 \ 236$	51.70	40	1.05	200	[46]
$12 \ 949$	42.61	58 - 64	1.12	204	[47]
25 898	58.61	49	2.14	140	[48]

Table 2.3: Overview of simulation parameters for natural gas dehydration with TEG and TEG regeneration

with liquid hydrocarbons enhances foaming in the column. Below 10 °C the viscosity of glycol additionally restricts the application. The inlet temperature of the lean glycol stream in the contactor is 5 °C to 8 °C above the gas temperature, as the gas stream tendency to separate the water is decreased with higher temperature differences [41]. The temperature level of the regeneration column is restricted by degradation temperature of TEG, which is at 207 °C. As a result, the reconcentration temperature of the absorbent is set between 177 °C and 204 °C. An overview of pressure and temperature levels is given in Table 2.3. For enhanced comparability, only conventional or stripping gas added reconcentration system are considered. According to Stewart [41] optimal dehydration is achieved with pressure ranging from 38 bar to 83 bar, with the simulated cases of Table 2.3 all fitting in that range. However, with decreased pressure in the absorption unit, the required column diameter increases.

The glycol regeneration unit is typically operated around or slightly above atmospheric pressure, obtaining a TEG purity of up to 98.8%. Among more rigorous regenerations set-ups, higher glycol purities can be achieved by adding a stripping gas stream to the reconcentration unit or decrease the unit pressure to vacuum distillation [45, 44, 41]. As vacuum distillation similarly call for an increased complexity of the column equipment, stripping gas is favourable. With the addition of stripping gas, the partial pressure of the water in the gaseous phase is decreased and hence, the water content of the liquid phases decreases as well. In general, stripping is applied for TEG purities from 99.1% to 99.6% with pressures slightly over atmospheric. By adding the gas stream directly into the reboiler, no additional process modifications are required [41, 44, 49].

2.3 Legal Background of the BioSNG Production

To provide a framework for the necessity of bioSNG upgrading, the novel renewable energy directive (RED III) and the quality restrictions for gas grid injection in Austria are presented.

2.3.1 RED III

The renewable energy directive III (RED III) was enforced in November 2023 and targets the goal of climate neutrality in the European Union. Within this scope, special attention is on the sectors transportation, industry, buildings, and the provision of heat and cold. It is a successor of the RED II, which was enforced in 2018. The aim of RED II was the expansion of renewable energy up to 32% until 2030 in the European Union, with focus on the sectors electricity, heat, and transport.

RED III must be implemented into national law until May 2025 and aims to increase the share of renewable energy carriers to 42.5% until 2030 in the European Union [50]. For Austria, this corresponds to an increase from currently 36.4% to 60%. The main focus is again on electricity, the provision of heat and cold, transport, and additionally buildings and industry. In terms of renewable gases, the aim is an increase to 7.5 TWh until 2030, hence, 150% of the previously targeted 5 TWh until 2030. In addition, at least two measures from an exemplary catalogue must be
implemented, i.e. the subsidisation of renewable heating systems or biogas injection in the gas grid. Approval procedures for renewable projects must be accelerated, this is further accelerated for photovoltaic and wind power projects. More detailed measures and implementation strategies are still under discussion and in preparation. [51]

2.3.2 Gas Quality for Grid Injection

The production of SNG and its injection in the gas network is regulated on a European and national level. The directives and regulations of the European Union determine the majority of national legislation in the matter of environmental and energy law. In this context, directives must be transposed into national laws after adaptation, regulation apply directly and member states must amend laws that conflict with the regulation. The handling of SNG in the EU is regulated by the Directive (EU) 2018/2001 RED II for "renewable energy directive". The directive has been in force since 2018 and was implemented in Austria with the Renewable Energy Expansion Act (EAG) 2021 [52]. The Renewable Energy Expansion Act provides essential framework conditions for the definition, labeling and promotion of renewable gas. Additionally, the Gas Industry Act was implemented, regulating the transmission, distribution, purchase or supply of natural gas as well as network access to the public natural gas network. In this regard, relevant for renewable gas is the mandatory enabling of renewable gas to be fed into the grid, provided that it meets the injection conditions.

The guideline for the injection conditions and gas quality is guideline G B210 -"Gas quality" by the Austrian association for the gas and water industry (ÖVGW). Directive G B210 refers to the European standards EN 16726 - "Gas infrastructure - Characteristics of gas - Group H" and EN 16723-1 - "Natural gas and biomethane for use in transportation and biomethane for injection into the natural gas system - Part 1: Specifications of biomethane for injection into the natural gas system" for specific requirements on SNG [53, 54, 55]. Requirements for relative density, content of sulphur, oxygen, CO_2 , hydrocarbon and water dew points and methane number are given in DIN EN 16726:2019. Furthermore, requirements for "biomethane" according to DIN EN 16723-1:2017 include carbon monoxide, ammonia and amine content. In addition, the ÖVGW guideline specifies requirements for the Wobbe index, the calorific values, nitrogen, and hydrogen contents of the gas. The limit values for the composition of natural gas, as well as selected physical properties, can be found in Table 2.4.

For the oxygen and carbon dioxide content two limits are displayed. The higher limits apply to gas injection provided that it can be demonstrated that the gas does not flow into facilities that are sensitive to the higher limits. Since SNG is generally not injected into the highest distribution system level, the higher limit is applied in this work. Both the injection pressure and the injection temperature of the SNG are regulated individually between the injector and the distribution system operator, with the ambient temperature usually being agreed as the temperature. With regard to the injection pressure, a distinction must be made as to which network level of the natural gas network the SNG is to be injected into. In Austria, this is divided into the following three network levels [56]:

- Network level 1: Supraregional transport and transit pipeline, high-pressure level with a pressure level of 70 bar to 120 bar.
- Network level 2: Distribution grids, supply of large consumers, pressure level between 6 bar and 70 bar.
- Network level 3: Supply networks, local networks, supply of small consumers, pressure level up to 6 bar.

In theory, SNG can be fed into all levels. In practice, network level 2 is the most suitable. Network level 1 is considered difficult due to the high injection pressure required. In addition, network level 1 is connected to natural gas storage facilities, therefore the stricter limits for oxygen and carbon dioxide content would apply, leading to more complexity in the SNG treatment process. Network level 3 injection is also

Parameter	Unit	Limits based on standard reference conditions (1013.25 mbar, 15°C)		
		min.	max.	
Relative density	-	0.555	0.7	
Wobbe index	MJ/m^3	45.25	54	
Gross calorific value	MJ/m^3	33.71	45.18	
Hydrogen	mol.%	-	≤ 10	
Oxygen	$\mathrm{mol.\%}$	-	0.001 or 1	
Carbon dioxide	$\mathrm{mol.}\%$	-	2.5 or 4	
Nitrogen	$\mathrm{mol.\%}$	-	≤ 5	
Carbon monoxide	$\mathrm{mol.\%}$	-	0.1	
Hydrocarbon condensation point (from 0.1 MPa to 7 MPa)	°C	-	-2	
Water dew point (at 7 MPa)	°C	-	-8	
Methane number	-	65	-	
Amine content	mg/m^3	-	10	
Total sulphur without odorant	mg/m^3	-	20	
Hydrogen sulphide and carbonyl sulphide (as sulphur)	mg/m^3	-	5	
Mercaptan sulphur without odorant (as sulphur)	mg/m^3	-	6	

Table 2.4: Limits for SNG compositions and properties for grid injection [53]

not optimal, as it mainly supplies small consumers whose natural gas consumption varies significantly seasonally. In winter, consumption is up to a factor of 10 higher due to high heating demand, while in network level 2, consumption remains relatively constant throughout the year due to large consumers, as industrial companies [56]. However, it has to be considered that the operating pressure at an entry point cannot be assumed to be constant. In network level 2, it can range from 6 bar to 70 bar. The pressure depends mainly on gas consumption, since pressure losses in the pipelines increase with higher gas flows [56].

2.4 Technology Readiness Level and Modelling Readiness Level

Technology readiness levels (TRLs) serve as a systematic metric to assess the maturity and readiness of a technology for practical application. Originally developed by NASA in the 1970s to evaluate the readiness of space technologies, TRLs have since been widely adopted across various industries, including aerospace, defense, energy, and healthcare [57]. TRLs are a numerical scale ranging from 1 to 9, with each level representing a specific stage of technology maturity.

These are the following stages for technology maturity:

- TRL 1-2: Basic technology research Fundamental principles and concepts are explored in laboratory settings.
- TRL 3-5: Technology development From characteristic proof of concept to component validation in relevant environment.
- TRL 6-8: Applied research and system development Technologies are developed and tested in relevant environments to demonstrate feasibility and functionality, undergo testing under realistic conditions.
- TRL 9: Advanced development and operation System is proven by successful operation.

TRLs play a crucial role in resource allocation, funding prioritisation, and risk management strategies, enabling organisations to optimise their investments and maximise the likelihood of successful technology commercialisation. By providing a standardised approach to technology evaluation, TRLs empower stakeholders to make informed decisions, allocate resources effectively, and mitigate risks associated with technological innovation. As a result, TRLs were implemented in the Horizon 2020 funding program of the European Union [57, 58]. For the technologies applied in this work, the TRL is already on the highest stages for the original application. While glycol scrubbing is at TRL 9, even for amine scrubbing for carbon capture various plants with TRL 8-9 exist [58]. For the total bioSNG process, a TRL 7 is proposed, based on the 32 MW plant in Gothenburg [59]. The adaptation of the TRLs for the upgrading section will be discussed in Chapter 7.

The modelling readiness level (MRL) was introduced by Müller [59], evaluating the categorical development of the application of advanced digital methods in industry. Analogously to the TRL, 9 stages are proposed:

- MRL 1: Determination of operation and performance indicating equations.
- MRL 2: Completion of model development.
- MRL 3: Creation of model libraries.
- MRL 4: Creation of a test plant model.
- MRL 5: Experimental validation of the test plant model.
- MRL 6: Evaluation of the utility and ecological value.
- MRL 7: Industrial plant model available for scale-up.
- MRL 8: Validation and evaluation of the industrial plant model.
- MRL 9: Platform-based implementation, monitoring, and sharing.

Throughout the stages, iterative loops are necessary for data generation and improved learning. Adapting this concept to the bioSNG upgrading in this work, Müller [59] introduced an industrial plant model for a 10 MW bioSNG production with MRL 6-7. Potential adaptation and deviations are discussed in Chapter 7.



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3 Material and Methods

This chapter covers basic information about the simulation tool applied, and the applied methods for the energy integration and techno-economic assessment. Furthermore, key performance indicators are introduced to establish comparable parameters for the models in this work. Details about the modelling, column designs and resulting compositions are presented in Chapter 4 for the amine scrubbing unit and Chapter 5 for the glycol scrubbing. Nevertheless, the total flow sheets of the upgrading units and their previous process are introduced in this chapter to enhance the comprehensibility and establish an accurate nomenclature. Hence, Figure 3.1 presents the flow sheet for the raw SNG upgrading with the fluidised bed methanation operated at 1 bar and Figure 3.2 operated at 10 bar. The unit operations displayed in grey are not considered in this work, but adopted from Hammerschmid et al. [60] and Bartik et al. [15] to present the total Biomass-to-bioSNG process chain. The performance of the total bioSNG upgrading chain is afterwards presented in Chapter 6.





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3.1 Simulation Tool: Aspen Plus

Aspen Plus, developed by Aspen Technology, Inc., is a steady-state, block-oriented process modelling and simulation software for the determination of systems in the field of process engineering. Hence, the equations describing the process units, i.e. energy and mass balances, are solved iteratively unit by unit. Based on this sequentialmodular solving approach difficulties with convergence may arise. Version 12.1 of Aspen Plus was used in this study.

The set-up of an Aspen Plus model is usually done in two different environments: Properties and Simulation. In the properties environment, the components are defined and the methods for calculating the thermodynamic properties are determined. Afterwards, a flow sheet is created in the simulation environment, containing the material streams, unit operations, and most important model parameters in order to obtain a comprehensive and accurate process representation. Detailed model specification can also be described in the subsections, i.e. chemical reactions and their kinetics, interfacial material and heat transfer, or fluid dynamics. [61]

As the modelled processes in this study are characterised by differing underlying thermodynamic properties, the CO_2 separation unit and dehydration unit are modelled in two different flow sheets. Both of them are introduced in detail in the following chapters.

3.2 Energy Integration

To facilitate convergence, no heat exchangers are applied in the Aspen Plus model. Hence, the heat integration was modelled based on the initial flow sheets (Figure 4.3 and Figure 5.1). The process streams and operation with heating and cooling duty are exported in a separate flow sheet to facilitate the overview and interconnection possibilities. Based on the approaches applied in Towler [62], the cooling demand is separated in three categories:

- Temperatures above 100 °C: heat can be used as district heating.
- Temperatures between 40 °C to 100 °C: cooling via table-top coolers at ambient temperature, the assumed COP is 4.17.
- Temperatures below 40 °C: active cooling, assumed COP of 10.

These categories are further influencing the techno-economic assessment, as they provide the potential for revenues from district heat and impose electricity costs, besides the costs for heat exchangers and steam generators.

The heat exchanger system was modelled by adding countercurrent heat exchangers to the flow sheet and connect all heat sources and sinks in the process. In a first step, the excess heat of the modelled processes was applied for all occurring heat demands, first internally in the unit operations and than inter-operational, connecting streams between the CO_2 separation, H_2O separation, and FBM unit. Afterwards, additional streams were added to cover all remaining cooling and heating demands. The applied heat exchangers were modelled as shortcut heat exchangers with an hot/cold stream approach temperature of 3 °C. If the heat source is above 100 °C and its capacity above 500 kW, the cooling was modelled in two steps. The first cooling step was to reach 100 °C and to use the heat for district heating. Then further cooling was performed down to 40 °C and 35 °C respectively with an air cooler. For heating, a steam temperature of 250 °C and 180 °C was assumed.

3.3 Key Performance Indicators

The key performance indicators (KPIs) represent the most important process parameters in terms of comparability and information density of the presented technologies. For the amine scrubbing unit, the process is defined by the following KPIs:

- The total intermediate SNG amount in kg/h after exiting the CO₂ absorber column. The intermediate SNG amount determines the total SNG amount for grid injection after the subsequent dehydration unit.
- The absolute CH₄ loss in the amine scrubbing unit in kg/h. This value presents the potential for further process optimisation and limitations. The absolute amount was chosen for enhanced comparability as relative values are in a small order of magnitude.
- The absolute MEA loss in the amine scrubbing unit in mg/h. This value presents the potential for further process optimisation and its limitations. As for the CH₄ losses, the absolute amount was chosen for enhanced comparability as relative values are in a small order of magnitude.
- The reboiler heat requirement in $MJ/kg_{CO_2,separated}$ as key parameter for the identification of the process' energy demand.
- The amine preheat requirement in MJ/kg_{CO2,separated}, since part of the required heating energy is provided before entering the reboiler and has to be considered separately to facilitate comparability.
- The total CO₂ amount separated in kg/h and the CO₂ purity of the separated stream to identify the further required conditioning for storage or usage.
- The CO₂ removal in wt. % of the CO₂ input to indicate the separation efficiency of the process.

For the glycol scrubbing unit, the performance of the process is defined by the following KPIs:

• The total amount of the separated water stream in kg/h.

- The water removal in wt. % of the input stream to indicate the separation efficiency of the process.
- The total SNG amount in kg/h, as this value indicates the final product after the total process chain.
- The absolute CH₄ loss in the glycol scrubbing unit in kg/h. This value presents the potential for further process optimisation and limitations. The absolute amount was chosen for enhanced comparability as relative values are in a small order of magnitude.
- The absolute TEG loss in the glycol scrubbing unit in g/h. This value presents the potential for further process optimisation and its limitations. As for the CH₄ losses, the absolute amount was chosen for enhanced comparability as relative values are in a small order of magnitude.
- The reboiler heat requirement in MJ/kg_{H₂O,separated} as key parameter for the identification of the process' energy demand.

3.4 Techno-Economic Assessment

For the techno-economic assessment, the total investment costs and specific upgrading costs are determined and evaluated. The total capital investment comprises the fixed capital investment and working capital. Hereby, the fixed capital investment includes the cost of the plant, costs for engineering and construction, contingency charges, and modification to the site infrastructure. In contrast, the working capital covers the investments for the materials, cash for monthly payments, taxes and accounts. Usually, the raw material and investments for one month are included [62, 63]. To identify the fixed capital investment of a plant, the equipment costs have to be estimated, dependent on the data already available and accuracy required. The Association for the Advancement of Cost Estimating International commonly distinguishes five cate-

- Order of magnitude estimates: it is based on the costs of similar process and requires no information on design. The accuracy is around 30 % to 50 % and this method is usually used for initial feasibility studies.
- Study estimates: it is based on coarse design specifications and attains an accuracy of 25% to 30%.
- Definitive estimates: it is based on a rough piping and instrumental diagram and equipment sizing of the major items. The accuracy is about 10% to 15% and it is i.e. applied for the authorisation of funds.
- Detailed estimate: in addition to the definitive estimates, the process design is completed and a detailed description of the construction cost included. The accuracy is about 5% to 10% and this method is used for fixed-price contracts.
- Check estimates: in this estimates, the negotiations on procurement of the equipment is included, leading to an accuracy of 5 % to 10 %.

For the present work, the order of magnitude and study estimation method is chosen, where major items of the equipment present the information basis for the total cost estimation. The equipment costs estimation was performed by the cost curve method or six-tenths rule presented in Equation 15.

$$C_{eq,design} = C_{eq,base} * \left(\frac{S_{design}}{S_{base}}\right)^r * \left(\frac{CEPCI_{2023}}{CEPCI_{baseyear}}\right)$$
Eq.15

CEPCI Chemical Engineering Plant Cost Index

r Economy of scale exponent

- C_{eq} Equipment cost for the base year in literature and design case
- S Equipment size for the base year in literature and design case

Therefore, the equipment costs are dependent on the scale-factor reported in literature and the annually published Chemical Engineering Plant Cost Index. The exponent reflects the decrease of cost per unit with simultaneous increase of the equipment size, it varies between 0.4 and 0.8. In case of limited literature data, 0.6 is assumed (six-tenths factor) [63]. The CEPCI considers the inflation for chemical plants, a complete list since 1958 (equalling 100) is i.e. reported in [64].

Furthermore, for the determination of the fixed capital costs the Lang method was applied. Hereby, the fixed capital costs are calculated by multiplying the sum of the equipment cost with the Lang factor. The Lang factor was introduced in 1948 [65], providing a simplified tool for plant cost estimation, based on their processing type. When using order of magnitude and study estimates, the working capital is calculated by a factor of the fixed capital investment costs. This factor usually ranges between 10% to 20%, but may increase up to 50% in case of large inventories or production of seasonable goods [63]. This percentage may also be included into the Lang factor to directly derive the total capital investment costs from the calculated equipment costs. Hence, the factor for fluid processing plants and total capital investment cost was applied for this study, equalling 5.7 [63].

The specific upgrading costs per MWh SNG were determined by the levelised cost method. The equation (Eq. 16) includes the capital expenditures, annual expenditures, and annual revenues. In the case of the upgrading process chain, the revenues for CO_2 certificates and district heating are the income from secondary products. Costs for CO_2 conditioning and compression for storage were not considered. The cumulative discount factor takes the plant life time and interest rates into account. The plant life time for this study is 20 years, and the interest rate 6%. For the annual operating hours 7500 h are assumed [66]. Further applied cost data is presented in the Appendix.

$$LCOP = \frac{I_0 + (E - R_{sec.prod.}) * CDF}{M_{t,mainprod.} * CDF}$$
Eq.16

CDF =
$$\frac{(1+i)^n - 1}{i * (1+i)^n}$$
 Eq.17

LCOP	Levelised cost of product in \in /MWh
I ₀	Capital expenditure in ${\it \in}$
Е	Annual expenditure in \in
$R_{sec. prod}$	Annual revenues in \in
Mt	Annual amount of main product in MWh
CDF	Cumulative discount factor
n	Plant life time in years
i	Interest rate

In general, for the cost estimation and plant design the following assumptions and facilitations were made:

- The compressors are all designed with only one compressing step and their efficiencies are 98% (mechanical) and 85% (isentropic).
- Washing sections in the absorber column were not considered.
- The pump efficiencies are 70 %.
- The storage tanks were not considered in the equipment cost calculations.
- After heat integration of the considered units, the remaining heat required is provided by steam generated with excess heat from the DFB gasification and methanation. This assumption is based on Hammerschmid et al. [60]. Hence, no external heat provision is considered.

4 CO₂ Separation with Amine Scrubbing

Within this chapter the model building of the CO_2 separation unit is presented as well as the results of the simulation. The model is validated with literature data and the results are further evaluated by their previously introduced KPIs.

4.1 Modelling of CO₂ Separation

The development of the CO₂ separation model is based on the approach introduced in Madeddu [67]. Previous modelling studies focused either on small-scale i.e. biogas upgrading [68, 69, 70, 71], or on industrial-scale post-combustion CO₂ capture [72, 73, 16]. In general, biogas upgrading conditions are similar to bioSNG upgrading from syngas methanation, as the gas compositions, mainly the proproption of CH₄ in the gas, is comparable. However, only pilot-scale applications have been published so far, hence the column-scale and solvent streams deviate significantly from this work. With post-combustion CO₂ capture, similar scale have been published. However, the gas inlet composition differs from bioSNG upgrading, as maximum CO₂ proportion of about 18 % [74, 75, 76] are reported, hence less solvent is required. Although Madeddu [67] is based on post-combustion CO₂ capture, the procedure and flow sheet is similar.

The compositions of the raw SNG input streams are presented in Table 4.1. They

Component	Unit	Composition at 1 bar	Composition at 10 bar
CH ₄	mol.%	44.06	49.10
H_2O	$\mathrm{mol.}\%$	7.00	0.75
CO_2	$\mathrm{mol.}\%$	44.80	48.60
CO	$\mathrm{mol.}\%$	0.14	0.05
H_2	$\mathrm{mol.\%}$	4.00	1.50

Table 4.1: Raw SNG input composition at 30 °C and 1 bar and 10 bar

equal the composition of the raw SNG output stream after the fluidised bed methanation unit with saturated water content. As fluidised bed methanation at atmospheric pressure and 10 bar are compared, both compositions are displayed. The data is provided by Bartik [77], who developed a pilot-scale fluidised bed methanation unit and conducted several experimental investigations on the total pilot-scale biomass-to-SNG process chain.

4.1.1 Solvent

Due to its wide application in industry monoethanolamine (MEA, C_2H_7NO) is used as solvent. An aqueous MEA solution with an initial MEA share of 30 wt. % was applied. Although higher MEA contents were observed to decrease the thermal energy requirements of the regeneration process, limitations occur due to corrosion effects [72]. As the amine appears in the liquid fraction only in its dissociated form, an initial amine loading α was calculated according to Eq.5.

$$\alpha = \frac{n_{CO_2} + n_{MEACOO^-} + n_{HCO3^-} + n_{CO3^{2-}}}{n_{MEA} + n_{MEACOO^-} + n_{MEA^+}}$$
Eq.5

4.1.2 Thermodynamic Properties

The separation of CO_2 from raw SNG with amine aqueous solutions is characterised by a reactive absorption-stripping process [67]. To implement this process in Aspen Plus, the reactions have to be considered by selecting a thermodynamic model that takes the electrolyte system of the amine, water, and CO_2 interaction into account. In the electrolyte system, the particular molecular species dissociate partially or completely into ions in a liquid solvent. These ions lead to a highly non-ideal thermodynamic behaviour. [78]



Figure 4.1: Diagram of water - MEA system at 1 bar and 10 bar and corresponding boiling temperatures at 9 bar and 11 bar; data derived from the ENRTL-RK equation, [79], and Antoine equations according to [80, 81]

Thus, as thermodynamic model the Electrolyte Non-Random Two Liquid model with the Redlich Kwong Equation of State (ENRTL-RK) was chosen. ENRTL hereby provides a suitable approach for considering the electrolytic interactions of the CO₂-MEA-H₂O system. The Redlich-Kwong Equation of State includes the non-ideal vapour and gas phase behaviour, as reported in several previous works [39]. Underlying parameters are provided by the Aspen Properties database. To validate the applicability of the vapour - gas phase model, experimental literature data was plotted in comparison, as displayed in Figure 4.1. For the absorption at 10 bar no experimental data was found, nevertheless the water - MEA system according to the ENRTL-RK equation of state is plotted and the boiling temperatures of water and MEA at 9 bar and 11 bar are added for comparison.

For the electrolytic CO_2 -MEA-H₂O interaction, the following reactions are considered. Equation 6 to 8 are equilibrium reactions, while Equation 9 and 10 are kinetic reversible reactions. These reactions have been considered by many authors [39, 72, 82, 83].

$$2 \operatorname{H}_2 O \longleftrightarrow H_3 O^+ + OH^-$$
 Eq.6

$$HCO_3^- + H_2O \longleftrightarrow H_3O^+ + CO_3^2 -$$
Eq.7

$$MEAH^+ + H_2O \longleftrightarrow H_3O^+ + MEA$$
 Eq.8

$$MEA + CO_2 + H_2O \longleftrightarrow MEACOO^- + H_3O^+$$
Eq.9

$$CO_2 + OH^- \longleftrightarrow HCO_3^-$$
 Eq.10

The equilibrium reactions are temperature dependent and determined via the standard Gibbs free-energy change according to Equation 11 [67]. The Gibbs free energy is retrieved from the Aspen Property database.

$$K_{eq} = exp^{\frac{-\Delta G^0}{RT}}$$
 Eq.11

The kinetic reactions are based on the Arrhenius law shown in Equation 12.

\mathbf{K}_{eq}	Activity basis equilibrium constant [-]
\mathbf{G}^0	Gibbs free energy [kJ/mol]
R	Gas constant $[kJ/mol K]$
Т	Temperature [K]
k	Kinetic constant [-]
k^0	Pre-expontential factor [-]
\mathbf{E}_a	Activation energy [kJ/mol]

A more detailed analysis of the ternary $CO_2/H_2O/MEA$ system is e.g. given by Conway et al. [84].

4.1.3 Absorber

The absorber column of the amine scrubbing process was modelled as RadFrac column. To implement the reactions as presented above, the rate-based column mode was applied. In contrast to equilibrium mode, where a sufficient contact time between liquid and gaseous phase for thermodynamic equilibrium on each stage is assumed, the rate-based mode considers deviations from thermodynamic equilibrium imposed by limitations in mass transfer. The rate-based mode is based on the two-film theory, hence, the segments are divided into bulk zone and film zone. For the material and energy balance, the bulk zone is modelled with the ideal continuous stirred tank reactor (CSTR) balance, and the film zone with the rigorous Maxwell-Stefan approach. In RadFrac, the ideal CSTR corresponds to mixed flow. CO_2 absorption in MEA happens in the liquid phase, thus the profile of the CO_2 fraction in the gas phase is constant and changes to nonlinear behaviour when entering the liquid phase, as the reactions with MEA happen faster. [67]

Hence, for the absorber model in RadFrac the following settings were applied. The option Film is used for the gas phase where only mass diffusion is taken into account. For the liquid film a discretisation approach is applied to consider the resistance to diffusion while reactions occur, the film discretisation ratio was set to 10. Furthermore, a reaction conditioning factor of 0.9 was chosen. This signifies that the absorption primarily happens in the bulk and not in the film, as in the film only CO_2 penetration occurs [67]. The further rate-based setup methods were set to the Aspen default values.

The number of segments for the rate-based modelling is based the continuous increase of segment number during consecutive simulations, while monitoring the deviation of column profiles, until the deviation became negligible [67]. As a result, the absorber column comprises 65 segments.

The absorber is operated at the outlet pressure of the methanation unit, in this work the pressures of 1 bar and 10 bar were considered. To enhance the convergence of the process and facilitate the column calculations, pressure drops inside the column were neglected. As column internals, Sulzer MELLAPAK 250Y were applied to provide a high contact area.

For both cases, the lean amine stream enters the column at the top stage, while the raw SNG streams enters at the bottom. The lean amine loading amounted 0.25 CO_2 per mole MEA for both cases, and hence ranges between the optima of 0.25 CO_2 per mole MEA [85] and 0.32 CO_2 per mole MEA [72] as stated in literature.

The column height was determined by starting at 100 m, equalling an infinite column height, and decreasing the height until the vapour composition profile in the column corresponded to a continuously decreasing CO_2 content. This procedure was performed for both pressure levels. The corresponding column diameter was determined via the Aspen rate-based modelling design mode. Hereby, a base stage and base flood had to be fixed to mark the stage where the column is the most stressed, hence, where maximum vapour flow appears. The base stages was adapted according to the column vapour profiles and was finally fixed at 7. The base flood was fixed to 70 % [39, 67].

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4.1.4 Stripper

The stripper column is equipped with the same reactions (Eq. 6 to 10) and rate-based model methods as the absorber column. The column segments for the rate-based mode were determined analogously to the procedure in the absorber column, in total 40 segments were applied.

The purge gas stream exits the column on top and is led to a condenser, operated at 35 °C [67]. Base on the design of Oexmann and Kather [86], the condensed water stream is not recycled back to the column as this would unnecessarily increase the energy demand. Thus, the condensed stream is mixed with the regenerated lean amine stream.

For the determination of the make up water and amine amount, a mass balance for H_2O and MEA was applied, using the Calculator tool in Aspen Plus. Equations 13 and 14 were used.

$$\dot{m}_{MU,MEA} = \dot{m}_{SNG1,MEA} + \dot{m}_{CO_2OUT,MEA}$$
 Eq.13
 $\dot{m}_{MU,H_2O} = \dot{m}_{SNG1,H_2O} - \dot{m}_{RAWSNG,H_2O} + \dot{m}_{CO_2OUT,H_2O}$ Eq.14

4.1.5 Fixed Bed Methanation

For the case of fluidised bed methanation at atmospheric pressure, the initial amount of CO in the raw SNG restricts the injection into the gas grid. Hence, an additional fixed bed methanation unit has to be considered. In Aspen Plus, this unit was realised by adding a Gibbs reactor after the intermediate SNG outlet of the amine scrubbing unit. As property method for the methanation unit, the Redlich-Kwong-Soave approach with modified Huron-Vidal mixing rules was chosen according to Reddy et al. [87]. The flow sheet is presented in Figure 4.2 and an overview of the operational parameters is given in Table 4.2. The methanation unit is operated at 320 °C and 24 bar. These process conditions correspond to the application of a Ni-based catalyst (Ni/Al₂O₃) and a gas hourly space velocity (GHSV) of 4000 h⁻¹ [27, 88, 87].



Figure 4.2: Aspen Plus flowsheet of the additional fixed bed methanation unit

Table 4.2: Operational parameters of the fixed bed methanation unit, Char. ... character of value, S ... set value, R ... Aspen Plus result

Term	Unit	Value	Char.	Data source
Intermediate SNG				
Temperature	$^{\circ}\mathrm{C}$	200	\mathbf{S}	[27]
Pressure	bar	24	\mathbf{S}	[27]
Fixed bed methanation reacto	or			
Thermodynamic property method	-	RKSMHV2	\mathbf{S}	[87]
Temperature outlet	$^{\circ}\mathrm{C}$	320	\mathbf{S}	[27]
Cooling power	kW	253	R	
Condenser temperatur	$^{\circ}\mathrm{C}$	40	\mathbf{S}	assumption

4.2 Process Configuration

The set-up for the CO_2 separation process at 1 bar is displayed in Figure 4.3. The absorption part consists of an absorption column (Figure 4.3: ABSORBER), a pump for the rich amine and a subsequent heater (Figure 4.3: RICHPUMP and RICH-HEAT). The regeneration part consists of an amine regeneration column (Figure 4.3: STRIPPER), a lean amine cooler and subsequent valve (Figure 4.3: LEANCOOL and LEANVALV), as well as a condenser, a valve for the condensed stream and a tank, where a make-up MEA and water are added (Figure 4.3: CON, CONDVALV, TANK).

For the 10 bar case, the rich amine is lead to a valve to obtain the regeneration unit

pressure instead of the RICHPUMP, and the lean stream is afterwards compressed in a pump to 10 bar instead of passing through LEANVALV and CONDVALV.

The splitter in the rich amine stream and heater in the lean amine stream (Figure 4.3: SPLIT and FAKEHEAT) are installed to facilitate the flow sheet convergence. No stream is separated in the outlet stream and no heating is performed in these units.



Figure 4.3: Aspen Plus flow sheet of the MEA scrubbing unit for CO_2 separation

The final permitted CO_2 concentration in the exiting intermediate SNG stream was identified by calculating the maximum amount of CO_2 in the final SNG to comply with restrictions for grid injection. Under the assumption, that no further CO_2 losses occur this equals the amount of the maximum CO_2 in the intermediate SNG. Hence, a design specification in the TEG Aspen flow sheet calculated a maximum of 537.46 kg CO_2 per hour to comply with the < 4.00 mol % CO_2 restriction in the 10 bar case and 512.32 kg CO_2 per hour in the 1 bar case. The difference is due to the higher amount of CH_4 content in the raw SNG after methanation at 10 bar. However, for the 1 bar

Table 4.3 :	Comparison	of the	main	operatic	onal	parameters	for ⁻	the CO_2 s	separation
	unit, Char.	char	acter o	f value,	S	Set value,	R	Aspen Pl	us result

Term	Unit	1 bar case	10 bar case	Char.	Data source
Raw SNG					
Molar flow	$\frac{kmol}{h}$	614.2	587.5	\mathbf{S}	based on $[77]$
CH_4	mol.%	44.06	49.10	\mathbf{S}	based on $[77]$
CO_2	$\mathrm{mol.}\%$	44.80	48.60	\mathbf{S}	based on $[77]$
H_2O	$\mathrm{mol.}\%$	7.00	0.75	\mathbf{S}	based on $[77]$
CO	$\mathrm{mol.\%}$	0.14	0.05	\mathbf{S}	based on $[77]$
H_2	$\mathrm{mol.\%}$	4.00	1.50	\mathbf{S}	based on $[77]$
Absorber parameters					
Absorber pressure	bar	1.1	10	\mathbf{S}	given
Solvent temperature inlet	$^{\circ}\mathrm{C}$	41	42	\mathbf{S}	[89]
Raw SNG temperature inlet	$^{\circ}\mathrm{C}$	48	48	\mathbf{S}	[89]
Lean solvent loading	$rac{mol_{\mathrm{CO}_2}}{mol_{\mathrm{MEA}}}$	0.25	0.26	R	[85]
Rich solvent loading	$\frac{mol_{\rm CO_2}}{mol_{\rm MEA}}$	0.50	0.59	R	[90, 82]
L/G	$\frac{mol_{\text{MEA}}}{mol_{\text{raw SNG}}}$	15.4	13.0	R	
Stripper parameters					
Stripper pressure	bar	1.8	1.8	\mathbf{S}	[67]
Solvent temperature inlet	$^{\circ}\mathrm{C}$	112	112	\mathbf{S}	[91]
Reboiler duty	kW	8500	6100	R	
Condenser temperature	$^{\circ}\mathrm{C}$	35	35	\mathbf{S}	[67]
CO_2 out molar flow	$\frac{kmol}{h}$	274.6	290.7	R	
Intermediate SNG					
Molar flow	$\frac{kmol}{h}$	409.6	307.1	R	
CH_4	mol.%	69.16	92.22	R	Table 4.3
CO_2	$\mathrm{mol.\%}$	3.46	4.10	R	Table 4.3
H_2O	$\mathrm{mol.\%}$	20.83	0.76	R	Table 4.3
CO	$\mathrm{mol.}\%$	0.22	0.09	R	Table 4.3
H_2	$\mathrm{mol.}\%$	6.28	2.82	R	Table 4.3
MEA	$\mathrm{mol.\%}$	0.04	< 0.01	R	Table 4.3

case, the limitations is not equally stringent, as the fixed bed methanation converts also part of the CO_2 in the intermediate SNG. For increased comparability, the CO_2 conversion of the fixed bed methanation unit was neglected, as the optimisation of its operation is not part of this work.

4.3 Results of the CO₂ Separation

The modelling work of this chapter includes resulting column profiles and design aspects of the absorption and stripper column. Based on these results, a model validation was performed and the KPIs of the 1 bar and 10 bar case compared.

4.3.1 Absorber

The amine absorber column was modelled according to the description given in the previous chapter. In total, 65 column segments were applied for both absorption columns, however, the geometry differs due to the different pressure level. As a result, the absorber operated at atmospheric pressure has a total height of 30 m and a diameter of 2.71 m. In contrast, the absorber operated at 10 bar measures 17 m in height and 1.34 m in diameter.

For comparison, the vapour phase CO_2 content over the column height and its temperature profile are presented in Figure 4.4a and 4.4b for the 1 bar case and in Figure 4.5a and 4.5b for the 10 bar case. The absorber column profile in the 1 bar represents a typical composition curve. The slight increase at the top of the colum (at 30 m) are due to RadFrac calculation and convergence methods. The deviation of the composition profile of the 10 bar case in Figure 4.5a indicates that a decreased column height might be applicable. However, with decreased column height the simulation had difficulties with convergence and in reaching the aimed CO_2 output concentration.



Figure 4.4: CO_2 mole fraction (a) and vapour temperature (b) over the absorber column height at 1 bar



Figure 4.5: CO_2 mole fraction (a) and vapour temperature (b) over the absorber column height at 10 bar

The SNG exits the column on top and is further led to the fixed bed methanation unit in the 1 bar case, or directly to the dehydration unit in the 10 bar case. An overview of the intermediate SNG compositions are presented in Table 4.4. The rich MEA exits at the bottom of the column and is subsequently compressed to 1.8 bar in the 1 bar case, or reduced to 1.8 bar in the 10 bar case. The rich loading is $0.50 \mod CO_2 \text{ per mol MEA}$ (1 bar) and $0.60 \mod CO_2 \text{ per mol MEA}$ (10 bar), and hence comparable to literature data [90, 82]. Afterwards, the rich amine stream is preheated

Component	Unit	1 bar case	10 bar case
$\overline{\mathrm{CH}_4}$	$\mathrm{mol.\%}$	69.16	92.22
$\rm CO_2$	$\mathrm{mol.}\%$	3.46	4.10
CO	$\mathrm{mol.}\%$	0.22	0.09
H_2	$\mathrm{mol.}\%$	6.28	2.82
H_2O	$\mathrm{mol.}\%$	20.83	0.76
MEA	$\mathrm{mol.\%}$	0.04	< 0.01

Table 4.4: Intermediate SNG composition after the amine scrubber for the 1 bar and the 10 bar case

to 112 °C before entering the regeneration column. An overview of the main operational parameters of the absorption and regeneration column is given in Table 4.3.

For the determination of the solvent amount in the system, an initial estimation was performed based on literature values [67, 39]. Afterwards a sensitivity analysis was performed by varying the solvent amount in dependence on the CO_2 amount in the intermediate SNG. As reported in Chapter 4.2, the maximum permitted CO_2 amount in the intermediate SNG is 537.5 kg/h in the 1 bar case and 512.3 kg/h in the 10 bar case. Figure 4.6a and Figure 4.6b display the amount of CO_2 in the intermediate SNG dependent on the L/G ratio. The horizontal line marks the maximum permitted CO_2 amount. As a result, a L/G of 15.3 (1 bar) and 12.95 (10 bar) was aimed, and the simulation converged at 15.4 and 13.0, respectively, as presented in Table 4.3.



Figure 4.6: Sensitivity analysis of CO_2 in the intermediate SNG in dependence on the solvent amount at (a) 1 bar (b) 10 bar

4.3.2 Stripper

The rich amine stream enters the stripper at the top stage, while the regenerated amine streams exits at the bottom. The stripper pressure is set to 1.8 bar for the 1 bar and 10 bar case. This is based on the consideration of the CO_2 vapour pressure increasing faster than the H₂O vapour pressure. In addition, the heat of absorption of CO_2 in MEA is about two times the heat of water vaporisation. Hence, strippers at higher pressure than the absorber unit are favoured. However, limitations are imposed due to amine degradation. As a result, the pressure level is applied in the stripper at which the decomposition temperature is not reached, but the boiling temperature is. For a 30 wt% MEA solution this corresponds to 1.8 bar [67]. As amine degradation occurs above 121 °C [85], the reboiler temperature is limited to 112 °C to mitigate degradation effects [91].

This also corresponds to the determination of column height, which is set at 5 m. As



Figure 4.7: CO₂ vapour mole fraction (a) and vapour temperature (b) over the stripper column height for the 1 bar case

reference, the CO_2 vapour fractions over the column height are presented in Figure 4.7a and Figure 4.8a and the temperature profiles in Figure 4.7b and Figure 4.8b. The reboiler heat requirement has been determined by varying the reboiler duty in

dependence of the relative reboiler duty, hence the CO_2 amounted separated. For



Figure 4.8: CO₂ vapour mole fraction (a) and vapour temperature (b) over the stripper column height for the 10 bar case

facilitated comparison, the CO_2 content in the intermediated SNG is also presented in Figure 4.10 for the 1 bar case and Figure 4.9 for the 10 bar case. With increasing reboiler duty, the relative reboiler duty is increasing linearly. However, to meet the dew point target, a total reboiler amount of 8500 kW (1 bar) and 6050 kW (10 bar) is required.



Figure 4.9: Intermediate SNG CO₂ content and relative reboiler duty in dependence of the total reboiler duty for the 10 bar case



Figure 4.10: Intermediate SNG CO₂ content and relative reboiler duty in dependence on the total reboiler duty for the 1 bar case

4.3.3 Model Validation

As already discussed in previous sections, the design of an amine scrubbing unit for CO_2 separation in order to upgrade bioSNG is a novel approach with no existing plant data to validate the model. Nevertheless, a comparison to plant data is recommended to confirm the applicability of the model in the given context. Detailed process data from plant operations including the total compositions of the input and output streams are limited. Data from Notz et al. [16] was applied, addressing CO_2 separation in a post-combustion carbon capture unit with CO_2 concentrations up to 16.5%. The main parameters for the validation are the input and output composition of the raw gas, cleaned gas, and separated CO_2 with corresponding temperature and pressure values, as well as the composition and physical properties of the amine stream. To reduce the effect of the column design, the data for validation was up-scaled to the same input gas stream as in the model presented in this work. As major operation parameters, the L/G ratio and the reboiler duty per t CO_2 separated from the pilot plant data were applied in the model. The input parameters for the model validation are presented in Table 4.5, the results of the pilot plant and model in Table 4.6. While the CO_2 concentration in the flue gas is 8.8% for the experimental data, and 8.9%

for the model respectively, a deviation of the H_2O concentration occurs. This is due to the temperature on top of the column. While a washing section is implemented in the absorption column of Notz et al., the Aspen model is not considering a washing section, leading to higher flue gas output temperatures. Similarly, the CO_2 purity of the separated CO_2 stream is lower. This deviation may be attributed to differences in the column design of the absorber and stripper unit compared to the measured plant data. Although the column design of the model was adapted to correspond to the flue gas input parameters, the context of the geometric column up-scale is complex, and hence limiting the column design comparability to the plant data. As a result, the model column is 10 m in height and 1.7 m in diameter. As the model marginally underestimates the CO_2 separated, the relative reboiler duty deviates about 10% of the initial applied reboiler duty. Nevertheless, the parameters correspond to the plant data and the model is compatible.

Input parameter	Unit	Value
Flue gas input	kg/h	72.4
$\rm CO_{2\ input}$	$\mathrm{wt}\%$	16.5
$N_{2 \text{ input}}$	$\mathrm{wt}\%$	67.2
$O_{2 \text{ input}}$	$\mathrm{wt}\%$	9.4
$\rm H_2O_{input}$	$\mathrm{wt}\%$	6.9
L/G	kg/kg	2.8
Reboiler heat requirement	$\rm MJ/kg~CO_2$	3.98

Table 4.5: Main input parameters for the validation of the MEA unit

However, only data for an amine scrubber operated at atmospheric pressure was available. Hence, as a first approach to validate the 10 bar case, the data from Notz et al. was adopted as baseline to further increase the pressure and further identify analogies for the L/G ratio and relative reboiler duty. For the adaptation of the

initial model, major modifications were necessary leading to limited correlation to the data applied. As a result, this study of comparing literature data to a 10 bar post-combustion CO_2 separation model is not presented in this work, as it offers no additional information and the base model is already validated.

Parameter	Unit	Pilot plant [16]	Model validation
Flue gas output	kg/h	65.6	16 752.6
${\rm CO}_2$ flue gas output	$\mathrm{wt}\%$	8.8	8.9
N_2 flue gas output	$\mathrm{wt}\%$	73.6	69.4
O_2 flue gas output	$\mathrm{wt}\%$	10.4	9.7
$\rm H_2O_{flue\ gas\ output}$	$\mathrm{wt}\%$	7.2	12.0
$\rm CO_2 \ stream$	kg/h	6.14	1 402.9
CO_2 content	$\mathrm{wt}\%$	99.6	96.7
Reboiler duty	kW	7.94	1 615
Reboiler heat requirement	$\rm MJ/kg~CO_2$	3.98	4.29

Table 4.6: Main output parameters for the validation of the MEA unit

4.3.4 Key Performance Indicators

A comparison of the key performance indicators are presented in Table 4.7. The reboiler heat requirement of the 1 bar case is higher as in the 10 bar case, due to the higher amount of solvent required for the CO_2 absorption. However, additional heat is required for the preheating of the solvent stream to 112 °C. In the 1 bar case, this is performed with excess heat from the fixed bed methanation reactor leading to a marginally lower net preheating requirement. Comparison to literature date [92] recorded a total heat requirement for solvent regeneration of 3.07 MJ/kg CO_2 with MDEA and Piperazine (PZ) as solvent for bioSNG upgrading with the absorbers operated at 13.7 bar and 11.2 bar. For post-combustion applications the minimum reboiler duty is varying between 1.67 MJ/kg CO_2 [93] and 3.36 MJ/kg CO_2 [94, 95] dependent.

dent on the stripper configurations. Hence, the lowest values were i.e. achieved by the implementation of improved split flow with vapour recompression. However, the optimisation of the stripper configuration is not aim of this work, and thus standard configurations are considered.

The amount of intermediate SNG is higher in the 1 bar case, as the mass flow of the raw SNG input is the same in both cases, however, in the 10 bar case the CO_2 concentration is higher, leading to less intermediate SNG. The higher pressure in the absorber column leads to 13 times higher CH_4 losses in the 10 bar separation process, compared to the absorption at atmospheric pressure. In relation to the total SNG stream for grid injection obtained, this are 0.1% and about 1% respectively. The MEA losses are about the same for both process configurations, additionally MEA is renewed continuously during operation due to degradation effects. For the calculation of the operational costs 1.5 kg MEA per t CO_2 [96] were assumed leading to about 18 kg fresh MEA per hour. Furthermore, a washing section installed in the upper part of the column reduces solvent losses and was not considered in this model. As a results, the MEA losses are negligible, as the fresh and exchanged MEA supply is dominating in proportion.

Key performance indicators	Unit	1 bar case	10 bar case
Reboiler heat requirement	$MJ/kg \ CO_2$	2.63	1.82
MEA rich pre-heat requirement	$MJ/kg \ CO_2$	2.53	2.88
Intermediate SNG	kg/h	6790	5123
$CH_4 loss$	kg/h	5	65
MEA loss	mg/h	30	32
$\rm CO_2 \ stream_{out}$	kg/h	11779	12361
Purity $CO_{2, out}$	wt. $\%$	98.2	97.7
$\rm CO_2$ removal	wt. $\%$	95.5	96.1

Table 4.7: Comparison of the key performance indicators of the CO_2 separation unit

The total CO_2 stream exiting the regeneration column is higher in the 10 bar case, as more CO_2 is entering the process. Nevertheless, its purity is lower as the loss of CH_4 and a higher water proportion is exiting as well. Both CO_2 purities comply with the general requirement for carbon capture and storage [97]. In addition, the CO_2 removal rates are at 95.5% and 96.1% and hence surpassing common removal rates of post-combustion amine scrubbing, which are limited to about 90%. Increased CO_2 removal, as required in this applications, leads to higher amount of solvent, increased solvent loadings, and as a result higher heat requirements for the reboiler [72], all of them observed in this work.

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5 H₂O Separation with Glycol Scrubbing

Within this chapter the model building of the H_2O separation unit is presented as well as the results of the simulation. The model is validate with literature data and the results are further evaluated by their previously introduced KPIs.

5.1 Modelling of H₂O Separation

The modelling of the H_2O separation unit was based on the process descriptions in Mokhatab et al. [98] and Stewart et al. [41] for natural gas dehydration units. After CO_2 separation and intermediate SNG compression, the properties of the intermediate SNG are similar to those in natural gas dehydration, hence comparability and applicability are given. The composition before entering the dehydration unit are presented in Table 5.1. It equals the composition of the SNG output stream after the amine scrubbing unit, under the assumption of an additional fixed bed methanation unit to handle the excess CO concentration.

Component	Unit	Composition at 1 bar	Composition at 10 bar
CH_4	$\mathrm{mol.\%}$	93.96	93.28
H_2O	$\mathrm{mol.}\%$	0.13	0.13
CO_2	$\mathrm{mol.}\%$	3.99	3.64
CO	$\mathrm{mol.}\%$	0.005	0.1
H_2	$\mathrm{mol}\%$	1.91	2.85

Table 5.1: Intermediate SNG input composition at 30 °C and 1 bar and 10 bar

5.1.1 Solvent

Based on its favourable degradation and regeneration properties triethylene glycol (TEG, $C_6O_{14}H_4$) is used in the simulation [41].

5.1.2 Thermodynamic Properties

Based on the Aspen Plus method guide, HYSGLYCO is selected as thermodynamic model. HYSGLYCO is suitable for pressures between 10 bar and 100 bar and temperatures from 15 °C to 50 °C in the absorber column, and 202 °C to 206 °C at 1.2 bar in the regeneration column [78]. The model is based on the Twu-Sin-Tassone (TST) cubic equation of state for the representation of the TEG - water binary [99].

5.1.3 Absorber

For the absorption column bubble cap trays were chosen as column internals, as they are well established and applied in industrial processes. The column in modelled as a RadFrac equilibrium column, with a Murphree efficiency of 25% per tray. The Murphree efficiency indicates the relative deviation of actual vapour fraction to the

equilibrium while also considering the vapour fraction of the tray below [41, 100]. The Aspen default values were applied for all further column parameters.

Though pressure drops over the column may be significant with bubble cap tray, the pressure drop was neglected to facilitate column calculations and convergence. In total, the simulated absorption column has 16 stages. The number of stages was determined by starting with 70 stages, equalling an infinite stage number and reducing the stage number step by step until the water content in the dry outlet SNG stream increases significantly. For the determination of the absorber height, a similar procedure was performed. The diameter was estimated based on design data in [41]. The amount of glycol used for dehydration may vary from 2 to 6 gallons of glycol per pound of water in the wet gas stream dependent on the targeted dew point and inlet gas composition [98, 101], this corresponds to 18.9 to 65.6 kg glycol per kg of water. In the simulation about 27.3 kg glycol per kg water are required, thus, fitting in the range.

5.1.4 Stripper

The regeneration column was modelled as RadFrac equilibrium column. As presented in Chapter 2.2.2, the regeneration column is usually designed as still column with the glycol reconcentration zone and storage tank on the bottom of the column. As this unit is not implemented in AspenPlus, the regeneration column is represented by a tray column with an external reboiler to set the temperature.

Analogously to the absorption column, pressure drops are neglected and the column sizing was performed after the same method.

5.2 Process Configuration

The set-up for the SNG dehydration unit is displayed in Figure 5.1. It consists of an absorption or contactor column (Figure 5.1: ABS-TEG), a TEG flash drum (Figure

5.1: TEGFLASH), a glycol - glycol heat exchanger (Figure 5.1: TEG-HTX), a TEG regeneration column (Figure 5.1: REG-TEG), and a reboiler (Figure 5.1: REBOIL).



Figure 5.1: Aspen Plus flow sheet for the dehydration unit

In addition, a pump, storage tank and cooler are installed (Figure 5.1: TEGPUMP, TEG-COOL, TANK). The SNG compressor (Figure 5.1: SNG-COMP) is not considered in further evaluation of the model and only installed to facilitate the verification of the SNG properties by compressing to the maximum grid pressure of 70 bar. This set-up is similar to flow sheets presented in e.g. [49, 101, 46].

Term	Unit	1 bar case	10 bar case	Char.	Data source
Intermediate SNG					
Molar flow	$\frac{kmol}{h}$	292.3	304.9	\mathbf{S}	Table 4.2
CH_4	$\mathrm{mol.}\%$	93.96	93.28	\mathbf{S}	Table 4.2
$\rm CO_2$	$\mathrm{mol.}\%$	3.99	3.64	\mathbf{S}	Table 4.2
H_2O	$\mathrm{mol.}\%$	0.13	0.13	\mathbf{S}	Table 4.2
CO	$\mathrm{mol.}\%$	0.005	0.1	\mathbf{S}	Table 4.2
H_2	$\mathrm{mol.}\%$	1.91	2.85	\mathbf{S}	Table 4.2
Absorber parameters					
Absorber pressure	bar	40	40	\mathbf{S}	[44]
Solvent temperature inlet	°C	35	35	\mathbf{S}	[41]
Inter SNG temperature inlet	°C	30	30	\mathbf{S}	[41, 44]
L/G	$rac{mol_{\mathrm{TEG}}}{mol_{\mathrm{SNG}}}$	0.0058	0.0057	R	
Stripper parameters					
Stripper pressure	bar	1.2	1.2	\mathbf{S}	[45]
Solvent temperature inlet	$^{\circ}\mathrm{C}$	160	160	\mathbf{S}	[43]
Reboiler duty	kW	10.7	10.9	R	
Strip gas	$rac{kg}{h}$	16.7	17.3	S	sensitivity analysis
Regenerated solvent purity	%	99.5	99.5	R	[41, 44]
SNG					
Power	MW	61.6	64.0	R	
Molar flow	$\frac{kmol}{h}$	291.9	304.5	R	
CH_4	$\mathrm{mol.}\%$	94.1	93.4	R	simulation
CO_2	$\mathrm{mol.}\%$	3.99	3.64	R	simulation
H_2O	$\mathrm{mol.\%}$	0.00005	0.00005	R	simulation
СО	$\mathrm{mol.\%}$	0.005	0.095	R	simulation
H_2	$\mathrm{mol.}\%$	1.92	2.86	R	simulation

Table 5.2: Comparison of the main operational parameters of the H_2O separation unit, Char. ... character of value, S ... set value, R ... Aspen Plus result

5.3 Results of the H₂O Separation

The modelling work of this chapter includes resulting column profiles and design aspects of the absorption and stripper column. Based on these results, a model validation was performed and the KPIs of the 1 bar and 10 bar case compared.

5.3.1 Absorber

Before entering the absorption column, the SNG stream is compressed to the working pressure of the column, which is 40 bar and passes a condenser to decrease the temperature to 35 °C and separate the saturated water. Afterwards, the wet SNG stream enters the column on the bottom stage, while the lean TEG stream enters at the top stage with 35 °C. The absorption column are both 10 m in height and 0.5 m in diameter. Analogously to the amine column, the vapour mole fractions in the absorber are presented in Figure 5.2 for the 1 bar and 10 bar case.

5.3.2 Stripper

The rich TEG exits at the bottom of the absorber column and is preheated to 120 °C before passing a flash drum where the pressure is reduced to 1.22 bar. A flash gas stream, mainly consisting of H₂, CO₂, and CH₄ exits as purge. Afterwards the rich TEG enters the glycol-glycol heat exchanger. This counter current heat exchanger preheats the rich TEG stream with the lean TEG stream from the regeneration column to 160 °C. The rich TEG stream then enters the regeneration column on top. The regeneration column is likewise modelled with equilibrium stages. As column internals, structured MELLAPAC packing was chosen, hence the murphree stage efficiency is set to 50 % [102]. The number of stages was determined using the same procedure as for the absorption column and set at 12. Since the stripper is usually designed as still column (see Chapter 2.2.2), but consensually modelled as conventional



Figure 5.2: H_2O vapour mole fraction over the absorber column height for the 1 bar and 10 bar case

column [103, 47, 104], the column design and vapour profile over the column height are not considered for the TEG stripper. To set the reboiler temperature, the reboiler unit was modelled outside of the RadFrac column. As mentioned in Chapter 2, TEG degrades at 206 °C, hence the reboiler temperature was set to 204 °C to increase the lean TEG purity. However, even at 204 °C only purities below 99 % were achieved and the targeted dew point of -8 °C was not reached, therefore a stripping gas stream was added. CO_2 is used as stripping gas and enters in the reboiler, as this set-up does not require an additional stripping column or more complex process units as introduced in Chapter 2.2.2 [103]. A gas stream mainly consisting of stripping gas and water exits the regenerator on top and passes a condenser. The regenerated lean TEG is cooled in the glycol - glycol heat exchanger and fresh TEG is added to make up for losses. Afterwards the TEG streams is compressed to 40 bar and cooled to 35 °C to comply with the input stream of the absorption column. TEG purities above 99 % are aimed to achieve the predefined water concentration in the SNG stream. To identify the operation point for meeting the -8 °C dew point temperature target, the stripping gas rate was varied as displayed in Figure 5.3. The resulting parameters were TEG loss and heating duty. An overview of the main operating parameters is presented in Table 5.2 for both cases.



Figure 5.3: Influence of strip gas stream variation on the dew point of the SNG

5.3.3 Model Validation

Though numerous studies about gas dehydration with TEG have been published in the last years, as briefly introduced in Chapter 2.2.2, validation of these models was performed in very limited works [46]. As a result, the access to plant data is very limited. For this work, plant data from Darwish et al. [47] was applied, derived from an onshore natural gas processing plant in the United Arab Emirates. Table 5.3 presents the main input parameters for the model validation and Table 4.8 the major plant data and their corresponding model results. Although the lean TEG purity of the plant data was used as input parameter for the model, the water content in the dried gas in the model surpasses the plant data significantly. The difference in the water content can be attributed to the high temperatures in the absorber column. Most absorber columns reported in literature are operated around 30 °C and 40 °C. In contrast, the absorber column of the plant data is operated at 58 °C gas inlet temperature, and thus, reaches the limits of applicability of the selected Property Method HYSGLYCO. In addition, the applied stripping gas rate is not reported properly and was hence assumed, also influencing the performance of the simulation. Influenced by the stripping gas rate and similar to the water content, the TEG losses are likewise overestimated in the model by about the double the concentration. This deviation is also visible for the reboiler duty, in this case the model underestimates the reboiler duty.

For all introduced parameters, Darwish et al. [47] reported deviations in the same order of magnitude when comparing seven different thermodynamic models. Hence, the discrepancy between model and plant data is a reported problem. In this case, already reported deviations might be enhanced, as the temperature of the absorption column exceed the temperature range of the model. These limitations have to be considered when comparing and evaluating the results of the simulation.

Input parameter	Unit	Value
Wet gas	kg/h	14 476
Absorber pressure	bar	42.6
Temperature	$^{\circ}\mathrm{C}$	58
$N_{2, input}$	$\mathrm{mol}\%$	0.5
$\rm CO_{2,\ input}$	$\mathrm{mol}\%$	5.0
$CH_{4, input}$	$\mathrm{mol}\%$	94.2
H_2O_{input}	$\mathrm{wt}\%$	0.3
Lean TEG rate	m^3/h	2.10
Stripper pressure	bar	1.01
Lean TEG purity	wt. $\%$	99.8
Reboiler temperature	$^{\circ}\mathrm{C}$	204

Table 5.3: Input parameters for the TEG model validation, data adapted from [47]

Parameter	Unit	Pilot plant [47]	Model validation
H_2O content of dried gas	g/Nm^3	0.048	0.089
TEG loss	kg/h	0.18	0.35
Strip gas rate	kg/h	-	120
Reboiler duty	$\rm MJ/kg~H_2O$	23.59	14.22

Table 5.4: Pilot plant and simulation data for the TEG validation

5.3.4 Key Performance Indicators

The KPIs of the dehydration unit are presented in Table 5.5. The total SNG amount is marginally higher for the 10 bar case, as the initially raw SNG contains an increased CH₄ concentration. As presented in Table 5.2, the operational parameters for the H₂O separation process are similar in both cases, due to the similar intermediate SNG compositions. As a result, the KPIs only differ marginally. Analogously to the CO₂ separation unit, the TEG losses in the simulation are negligible compared to the TEG exchanged during operations due to degradation. In case of TEG, about 0.1 kg of fresh TEG are supplied [105]. According to Salman et al. [103], the TEG loss increases with increasing stripping gas rate. However, the TEG purity increases simultaneously, leading to a decrease of the water dew point of the SNG. With the TEG purity of 99.5%, the TEG loss corresponds to literature data.

The water removal is the same for both cases, as the physical conditions of the input stream, which is saturation at 40 bar and 35 °C, and the output stream, which is a targeted dew point temperature of -8 °C at 70 bar, are the same. The water stream out and reboiler duty is marginally higher in the 10 bar case, as the total input stream of the intermediate SNG is increased. Based on this data, the relative reboiler energy demand is $6.02 \text{ GJ/t H}_2\text{O}$ removed and $5.86 \text{ GJ/t H}_2\text{O}$ removed for the 1 bar and 10 bar case, respectively. This difference is due to the higher stripping gas amount, in the 10 bar case, reducing the reboiler duty. Sakehta et al. [46] recorded a relative reboiler

Key performance indicators	\mathbf{Unit}	1 bar case	10 bar case
SNG	kg/h	4931	5076
$CH_4 loss$	kg/h	0.44	0.63
TEG loss	g/h	14	14
H_2O stream ,out	kg/h	6.4	6.7
H_2O removal	wt. $\%$	96.2	96.2
Reboiler heat requirement	$\mathrm{MJ/kg}\ \mathrm{H_2O}$	6.02	5.91

Table 5.5: Comparison of key performance indicators for the H_2O separation unit



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6 Performance of the Total Upgrading Chain

Within this chapter the outcome of the energy integration of the total SNG upgrading process is presented as well as the techno-economic assessment to set this work in a broader context and consider the economic environment. Furthermore, the resulting SNG composition is compared to the requirements of the gas grid.

6.1 Energy Integration

To evaluate the energy demand of the SNG upgrading units, heat integration was performed to interconnect the modelled units. In this scenario, the heat demand for both cases is about the same level. This is due to the higher reboiler heat demand in the 1 bar case, that is compensated by the missing excess heat of the fixed bed methanation in the 10 bar case. The cooling demand for the 1 bar case is higher compared to the 10 bar case, since a higher amount of MEA is cycled and hence needs to be cooled after the regeneration. As a result, the amount of MEA used is a major influencing factor for the heat and cooling demand. The thermal energy demands and district heat output are presented in Figure 6.1 to enhance the comparison of the thermal input and output. However, according to Hammerschmid et al. [60] who conducted a study about the bioSNG production including the DFB reactor system, gas cleaning and fluidised bed methanation, the total heat demand of the upgrading



Figure 6.1: Thermal energy demand and Figure 6.2: Electrical energy demand and
district heating of the 1 bar and
10 bar caseElectrical energy demand and
district heat after enhanced en-
ergy integration

units can be covered by the excess heat of the previous processes. Following this assumption is applicable for both cases introduced in this work, further heat integration was performed. As described in Chapter 3.2, the cooling demand was covered with air coolers. Hence, Figure 6.2 demonstrates the final input and output for managing the thermal process requirements in form of electricity demand for cooling and district heat output resulting from the enhanced process integration.

Apart from the electrical energy for cooling, the compressors bear a significant demand of electrical energy. The total electrical energy consumption including the compressor power of the three installed units is presented in Figure 6.3. In total, the installed compressor power of the 10 bar case is twice as high as in the 1 bar case. The PG compressor comprises the highest share with up to 3 MW. Instead of the PG compressor, a compressor for the fixed bed methanation unit, compressing the intermediate SNG to 24 bar is installed for the 1 bar case. Until then, the volume flow is less than a half of the initial PG volume flow and the compressor power is about 1.5 MW. The intermediate SNG compressor before the TEG scrubber is installed in both units. However, for the 1 bar case 16 bar of pressure difference are required, while 30 bar of pressure difference are required in the 10 bar case. As all compressors are modelled under the assumption of only one pressurising step, these results might underestimate the total installed compressor power required.



Figure 6.3: Comparison electricity demand including the installed compressor power and cooling demand

6.2 SNG Properties

The SNG properties required for injection in the Austrian gas grid were introduced in Table 2.4. To identify potential bottlenecks of the modelled process chains and operation modes, these limitations are compared to the SNG compositions after both upgrading chains. Table 6.1 presents the main SNG properties limiting the grid injection. The water dew point is the most stringent property, hence the TEG unit was designed to fulfil the requirement of -8 °C at 70 bar. As a result, it is adjustable by varying the strip gas content in TEG regeneration column. The CO₂ concentration can be similarly modified by adjusting the setting of the MEA unit. However, the adjustment of the MEA unit is more complex, as is dependence on the reboiler duty, solvent mass flow, and column design. Both SNG properties, the dew point and the CO_2 , are set at the upper limit for grid injection as they directly influence the operating costs.

Though the relative density, Wobbe index and gross calorific value are at the lower end of the injections limits, they are not probable to surpass the limitations, as their main influencing parameters are the H_2 and CO content. The H_2 content is below $3 \mod \%$ for both process chains, as H_2 reacts in the methanation unit more than the limiting 10 mol.% are not expected. In contrast, the limit for CO is marginally adhered for the 10 bar case. This deviation to the 1 bar case is due to the additional fixed bed methanation unit installed to fulfil the CO grid limitations. As the initial CO content of the raw SNG is lower in the 10 bar case and hence capable of fulfilling the CO requirements without CO separation, with the given main gas composition in this process chain no further manipulation of the CO amount is necessary. In case of varying product gas compositions and operating modes of the fluidised bed reactor, the fixed bed methanation unit is additionally recommended for the 10 bar case.

Parameter	Unit	Grid limits	1 bar	10 bar
Relative density	-	0.555 - 0.700	0.58	0.58
Wobbe index	MJ/m^3	45.25 - 54.00	47.60	46.70
Gross calorific value	MJ/m^3	33.71 - 45.18	35.78	35.64
Hydrogen	$\mathrm{mol.\%}$	<10	1.92	2.86
Oxygen	$\mathrm{mol.\%}$	1	0	0
Carbon dioxide	$\mathrm{mol.\%}$	4	3.99	3.64
Nitrogen	$\mathrm{mol.\%}$	<5	0	0
Carbon monoxide	$\mathrm{mol.\%}$	0.1	0.005	0.095
Water dew point	°C	-8.00	-8.09	-8.06
Amine content	mg/m^3	10	0.01	0.01

Table 6.1: SNG properties of 1 bar and 10 bar methanation after upgrading in comparison to gas grid requirements

6.3 Techno-Economic Assessment

The techno-economic assessment in based on the calculated equipment and total investment costs according to the methods introduced in Chapter 3.6. For this procedure, the SNG upgrading process has been divided into four sections: the product gas compression before the main fluidised bed methanation reactor, the MEA unit, the fixed bed methanation unit, and the TEG unit. These sections are visualised in Chapter 2, Figure 3.1 and Figure 3.2. The equipment costs for each of these sections are presented in Figure 6.4 and more detailed in Table 6.2 and Table 6.3. In total, the equipment costs for the 1 bar case are at $10.85 \text{ M} \in$ and for the 10 bar case at $9.90 \text{ M} \in$, hence the equipment costs of the 1 bar case are about 9.6 % higher.



Figure 6.4: Comparison of the equipment costs

Considering the Lang factor for fluid processing plants, the total investment costs of the 1 bar case account for $61.82 \,\mathrm{M} \in$ and $56.42 \,\mathrm{M} \in$ for the 10 bar case. While the cost difference for the TEG unit is negligible, major deviations occur for the MEA unit. This is mainly due to the pressure increase in the absorption column leading to smaller column sizing. In contrast, the MEA regeneration units are at a similar cost level due to the same pressure level used for regeneration. For the 1 bar case additional costs are imposed from the fixed bed methanation unit. However, they are not exceeding $700\,000 \in$ and coupled with the intermediate SNG compressor required for the fixed bed methanation unit, they are comparable to the costs for the product gas compressor in the 10 bar case. In sum, the main factor for the equipment cost deviation is the absorber column sizing.

Equipment		Base d	ata		1 ba	ır case	$10 b_{6}$	ar case	Source
	Scale	Cost in \$	Year	Scale factor	Scale	EC 2023 in €	Scale	EC 2023 in €	
Sum MEA absorber						$1 \ 128 \ 617$		$346 \ 307$	
Column	5.4 m^3	$113 \ 085$	2018	0.6	174 m^3	$1 \ 109 \ 854$	24 m^3	$340\ 550$	[69]
Packing	3.4 m^3	$1 \ 448$	2018	0.6	$174 m^3$	18 763	24 m^3	5 757	[69]
Sum MEA stripper						2562067		$2 \ 333 \ 804$	
Column	4.7 m^3	$318 \ 165$	2018	0.6	$20 \ { m m}^3$	292 712	$15 \mathrm{m}^3$	$246 \ 307$	[69]
Packing	$2.7 \mathrm{~m^3}$	35 246	2018	0.6	$20 \ { m m}^3$	$32 \ 427$	15 m^3	$27\ 286$	[69]
Reboiler (Kettle)	1438 kW	$309 \ 411$	2018	0.6	8500 kW	$1 \ 096 \ 485$	6050 kW	894 138	[69]
Condenser	35 m^2	226 674	2018	0.6	371 m^2	$1 \ 140 \ 443$	$385 \mathrm{~m^2}$	$1 \ 166 \ 073$	[69]
Sum FBM incl.						601 033		C	1
heat exchanger						CUI ECO		D	
FBM reactor	5.4 m^3	$113 \ 085$	2018	0.6	1 m^3	50 171			[69]
FBM catalyst	1 kg	50^{*}	2016	0.6	$70 \ \mathrm{kg}$	5 167			[106]
FBM condenser	35 m^2	226 674	2018	0.6	36 m^2	$281 \ 340$			[69]
Sum heat exchanger						4 876 805		$4 \ 296 \ 408$	[107]
Sum pumps						24 898		79 267	[108]
Sum compressor						$1 \ 254 \ 389$		1 977 239	[108]
Sum MEA &						11 060 071			
FBM unit						11 000 314		470 CCU 8	

Table 6.2: Equipment cost of the MEA and FBM units



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Equipment	[Base dat:	F		1 bar	case	10 baı	r case	Source
	Base case	Cost in \$	Year	Scale factor	Scale	EC 2023 in €	Scale	EC 2023 in €	
Sum TEG absorber Sum TEG strinner	$41 \ 667 \ \mathrm{Nm^3/h}$	217 651	2006	0.6	$6744 \text{ Nm}^3/\text{h}$	$\frac{107\ 523}{12\ 792}$	$6865 \text{ Nm}^3/\text{h}$	107523 12792	[44]
TEG stripper Reboiler	$1110 \ { m kg/h}{ m 10 \ m^2}$	$\begin{array}{c} 13 & 329 \\ 19 & 311 \end{array}$	$2006 \\ 2006$	$0.6 \\ 0.6$	$\begin{array}{c} 257 \ \mathrm{kg/h} \\ 0.5 \ \mathrm{m^2} \end{array}$	4 632	$\begin{array}{c} 257 \ \mathrm{kg/h} \\ 0.5 \ \mathrm{m}^2 \end{array}$	4 632	[44] [44]
Sum heat exchanger						383 263		326551	[69] [44, 108]
Sum pumps & compressors Sum TEG Unit						158 106 608 748		416956 795 774	[108]
Total equipment Total investment	cost cost					$\begin{array}{cccccccccccccccccccccccccccccccccccc$		$\begin{array}{c} 9 \ 897 \ 996 \\ 56 \ 418 \ 579 \end{array}$	

In addition to the total investment costs, the specific SNG upgrading costs for both process chains were determined according to the method introduced in Chapter 3.4. The economic parameters are presented in Table 6.4. Based on these, the main input parameters for the specific SNG upgrading costs were calculated and are compared for the 1 bar and 10 bar case in Table 6.5. The annual expenditures include the costs for electricity, fresh MEA and TEG, personnel and insurance costs. The main deviation is attributable to the electricity demand of the PG compressor in the 10 bar case. Annual revenues from secondary products result from the district heat and the trade of CO_2 certificates. As the CO_2 concentration of the raw SNG from methanation at 10 bar is higher than from methanation at 1 bar, more CO_2 is separated, leading to increased revenues from certificates. The distinctions of the district heating are based on the higher reboiler heat demand for the 1 bar case. In total, the difference of the specific SNG upgrading costs is negligible, as they account $27.25 \in /MWh$ (1 bar case) and $27.81 \in MWh$ (10 bar case). In order to identify the major influencing parameters of the specific SNG upgrading costs, a sensitivity analysis for the electricity costs, income from CO_2 certificates, and income from district heat revenues was conducted. The parameters were decreased and increased by 50% each. Figure 6.5 displays the variation of the electricity costs. Due to the amount of cooling performed with fans and the compressors, the electricity price is significantly influencing the specific SNG upgrading costs. As a result, the -50% electricity cost case is about one third of the +50% case. Additionally, it has to be mentioned, that the -50% electricity costs equal the costs in 2021 and hence represent a probable scenario. In contrast, the applied electricity costs of the second-half year in 2023 constitute a significant cost peak compared to recent years.

The income sensitivity analysis showed a decrease to about $19 \in /MWh$ with increased CO_2 certificate prices. In contrast, the variation of district heat income is negligible, as the amount of district heat output is not significant compared to the other cost and income sources.

Parameters	Unit	Value	Source
Reference year	-	2023	
Plant liftime	a	20	
Number of employees	1/a	2	
Operating hours upgrading	h/a	7500	[66]
Operating hours district heating	h/a	5800	[66]
Maintenance costs	%/a	3	[109]
Insurance, administration	%/a	1	[109]
Personnel costs per employee	€/a	65000	[110]
Interest rate	%	6	[66]

Table 6.4: Economic assumptions for the evaluation of the specific SNG upgrading costs

Table 6.5: Main input parameters for the specific SNG upgrading costs for the 1 bar and 10 bar case

Parameters	Unit	1 bar case	10 bar case
Annual quantity of SNG	MW	61.62	64.02
	GWh	462.16	480.15
Annual expenditures	M€/a	14.45	16.00
Annual revenues secondary products	M€/a	7.67	8.23
Investment costs	M€	61.82	56.42
Cumulative discount factor	-	11.47	11.47
Specific SNG upgrading costs	€/MWh	27.25	27.81



Figure 6.5: Sensitivity analysis of electricity costs



Figure 6.6: Sensitivity analysis of CO_2 certificate and district heat income



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7 Discussion

As previously introduced in the literature review, numerous process configurations for bioSNG upgrading to methane quality for gas grid injection exist. The process chain chosen for this work is derived from natural gas processing and post-combustion carbon capture and thus, well-established in industry, serving as a reliable base case scenario for bioSNG upgrading.

For application in natural gas upgrading the glycol scrubbing has a TRL of 9, while the amine scrubbing has a TRL of 8 to 9 in carbon capture [111, 58]. However, in context of bioSNG upgrading the TRL level has to be considered separately. While the conditions for the glycol scrubbing are not differing significantly from natural gas processing, the high CO_2 concentrations require major adaptation of the amine scrubbing unit. In addition, the case with operation at 10 bar demands for further adaptation with limited experimental plant data yet. The GoBiGas plant has a similar configuration installed with a different methanation unit and upgrading strategy [92, 13]. Hence, TRL 5 to 6 is proposed for the total process chain.

In terms of MRL, this work encounters a discrepancy. The up-scaled modelling of a demonstration plant is MRL 5. However, as data availability was limited, the models of this work were validated with literature data for natural gas upgrading processing and post-combustion carbon capture. Hence, no model for a pilot plant or validation, both belonging to MRL 4, has been found and this step must be included in future iterative loops.

In the following, recommendations for the process configurations introduced in this work are given based on the research question.

What is an adequate process chain for raw SNG upgrading and how is the performance of the introduced options?

Two SNG upgrading chains are introduced in this work, meeting the demands of the preceding fluidised bed methanation unit. For the methanation at atmospheric pressure an additional fixed bed methanation unit is proposed between the CO_2 and H_2O separation unit, to reduce the CO concentration to comply with the restriction of the gas grid. This unit is not required after fluidised bed methanation at 10 bar as the initial CO concentration is lower. Comparing both process configurations, the 1 bar case provides 61.6 MW and 10 bar case 64 MW of SNG to the grid. Corresponding to 61.6% and 64% cold gas efficiency over the total bioSNG process with a thermal biomass input of 100 MW in the DFB gasifier. The difference between the two cases is mainly due the higher initial methane content after fluidised bed methanation at 10 bar. Including the energy recovery by district heat, the energetic efficiency increases to 64.1% and 67.2%. Since the reboiler heat demand of the 10 bar amine regeneration is lower, the amount of provided district heat is higher. Nevertheless, these values deviate from Hammerschmid et al. [60] obtaining an energy efficiency of 79%. This deviation can be attributed to several factors: in this work the provided district heat is limited to the excess heat of the upgrading processes, hence the DFB process, PG cleaning and fluidised bed methanation are in contrast to Hammerschmid et al. [60] not considered. In addition, the resulting reboiler duty per kg SNG in this work surpasses the assumed value of Hammerschmid et al. significantly, leading to a lower amount of district heat.

In addition, the power consumption of the two cases is 4.14 MJ/kg SNG (1 bar) and 4.63 MJ/kg SNG for the 10 bar case. The majority pf the power consumption is comprised by the cooling duty of the process, which is higher in the 1 bar case. However, in particular the PG compressor significantly increases the power consumption of the

10 bar case. Heyne and Harvey [33] compared the power consumption of the bioSNG upgrading for amine, PSA, membrane separation, excluding the demand for cooling. Hereby, the 1 bar scenario of this work is comparable to their amine separation unit, as they account for 1.27 MJ/kg SNG in this work and 1.32 MJ/SNG in Heyne and Harvey respectively. The 10 bar case is comparable to the relative power consumption of the PSA case with 2.24 MJ/kg SNG in this work and 2.44 MJ/kg SNG in Heyne and Harvey. Thus, the membrane separation case accounts for the highest power consumption with 3.07 MJ/kg SNG, without including the power consumption for cooling in this work.

Considering these points, the process chain with methanation at 10 bar is nevertheless favoured in terms of energy efficiency, as the biomass input is converted to a higher amount of SNG for grid injection. Additionally, further potential for efficiency increase is given, when including the total bioSNG process in the heat integration for district heat provision.

How are different operating modes of the upstream units influencing the process chain, in particular the fluidised bed methanation operating at 1 bar and 10 bar? Are the SNG quality requirements for grid injection fulfilled?

Both process chains are designed to comply with the requirements of the Austrian gas grid. However, major deviations from the initial raw SNG composition would particularly challenge the CO_2 separation. During the model development, the column height, solvent flow rate, and reboiler duty were identified as main parameters to adjust the CO_2 concentration. Though not part of this work, the reboiler duty and solvent are adjustable during operation to meet the demands for grid injection.

However, the CO concentration of 0.095 mol% in the 10 bar case is only marginally below the restriction and no possible measures to adjust the amount in the upgrading section are installed. Thus, minor deviation of the given raw SNG input composition leads to exceeding CO concentration. As a result, the 1 bar configuration is favoured in this point, as it provides a more robust operation mode to adapt to changes in the PG and raw SNG composition and guarantee a SNG composition complying with the grid requirements. An additional option would be the installation of a fixed bed methanation unit analogously to the 1 bar case to gain more operational flexibility in the 10 bar case.

What are the investment and operating costs for the necessary equipment for SNG upgrading?

The total investment cost are $61.8 \,\mathrm{M} \in \mathrm{for}$ the 1 bar case and $56.4 \,\mathrm{M} \in \mathrm{for}$ the 10 bar case, thus, the total investment costs are higher for the 1 bar case, mainly due to the higher equipment cost of the amine absorption column. However, compared to literature data the equipment costs of both cases are about twice as high as in Hammerschmid et al. [60]. This deviation may be attributed to several factors: the calculations of [60] were performed with separation efficiencies and no column design was performed. In particular the amine absorption column contributed to major equipment costs in this study. Applying the resulting costs in this work to [60], the relative cost amount of the upgrading section would increase to about half of the total equipment costs for a bioSNG plant, with the DFB reactor excluded. However, particularly the auxiliary equipment such as heat exchangers was calculated spaciously, therefore adding up to the difference. In addition, the comparison of total investment costs is limited due to different Lang factors applied, being fluid processing in this work and and solid and fluid processing in the work of [60]. Adapting the investment cost of Heyne and Harvey [33] to 2023, they derived about $45.0 \,\mathrm{Me}$ for the amine upgrading section and $63.6 \,\mathrm{M}$ for the membrane upgrading configuration. As a results, the total investment costs of this work are still below the calculated costs for a membrane unit.

Although this work focuses on the upgrading units, and hence presents the specific upgrading costs, these costs are set in a broader context by comparing them to SNG and natural gas costs. The comparison to other upgrading chains is limited, since literature usually observes the total production costs. The specific upgrading costs in this work are $27.25 \in /MWh$ and $27.81 \in /MWh$. Though the capital costs and

electricity costs are most sensible to influence the SNG costs, both cases are about the same level [33]. I.e. Hammerschmid et al. [60] calculated SNG production costs between $71 \in /MWh$ and $90 \in /MWh$, hence, the calculated specific upgrading costs in this work would make up 23 % to 30 %. As comparison, the Austrian natural gas price for 2023 was at $164.6 \in /MWh$ for households and $91.7 \in /MWh$ for non private consumers including taxes [112]. However, within the renewable gas act in Austria penalties of $150 \in /MWh$ of non-achieved renewable gas in the national gas grid has been determined [5]. Hence, the SNG production costs are further levelised.

In total, in terms of capital and operating costs, the 10 bar case is recommended, as the total investment costs are lower. In case of a previous discussed additional fixed bed methanation unit, the total investment costs of the 10 bar case would however surpass the total investment costs of the 1 bar case and the cost-based recommendation would change.

Considering these points and their relevance for securing compliance with the limit values of the gas grid, the operational flexibility is a major factor. As a result, for the overall consideration the process chain operated at 1 bar is recommended, as this process chain can react to fluctuation in the raw SNG composition and hence, allows for a more stable operation and thereby contributes to increased energy security.



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8 Conclusions and Outlook

Two bioSNG upgrading process chains were introduced in this work, one with preceding methanation at 1 bar and one at 10 bar. Both process chains consist of an amine scrubber and regeneration unit for CO_2 separation and a gylcol scrubber and regeneration unit for H_2O separation to comply with the specification of the national gas grid in Austria. The main difference between the two cases is the operational pressure of the amine scrubbing unit and an additional fixed bed methanation unit required for the 1 bar case to cope with the CO concentration. Although already established in natural gas processing and post-combustion carbon capture, the application of these technologies in bioSNG upgrading is a novel topic with only few comparable cases published until now. Nevertheless, the results of this study showed a feasible application for bioSNG upgrading, although the CO_2 concentration significantly surpass the values from post-combustion carbon capture. Hence, this configuration serves as a reliable base case scenario. However, especially amine scrubbing is characterised by a high thermal energy intensity and capital investment costs. Therefore, additional options as i.e. PSA should be further explored in future work.

From both options, the 1 bar configuration is recommended, although the 10 bar case showed an increased performance in terms of total investment costs and cold gas efficiency. This is due to the enhanced operational flexibility gained by installing a fixed bed methanation reactor, and thus securing the compliance with gas grid specification. In addition, the specific upgrading costs are at the same level $(27.25 \in /MWh)$ and $27.81 \in /MWh$) for both cases. For future work, a deepened study on the impact of fluctuating PG and raw SNG composition is recommended. This allows a more precise conclusion on the gained flexibility by the installation of the fixed bed methanation unit. In the case of a significant impact, the fixed bed methanation reactor can also be considered in the 10 bar case. In addition, further optimisation of the introduced models and in particular the optimisation of their interaction and whole process chain can be performed to increase the accuracy of the model. However, limitations will continue to exist due to missing experimental data, especially for the amine scrubber and its operation at 10 bar.

Bibliography

- IPCC, Synthesis Report of the IPCC sixth assessment report (AR6), Technical Report, Interlaken, 2023.
- [2] BMK, Energie in Österreich 2022, Technical Report, Wien, 2022. URL: https: //www.bmk.gv.at/dam/jcr:bbe5cd73-a161-46fc-8c80-2eb5fc500acb/ Energie_in_0E2021_UA.pdf.
- [3] S. Lechtenböhmer, L. J. Nilsson, M. Åhman, C. Schneider, Decarbonising the energy intensive basic materials industry through electrification - Implications for future EU electricity demand, Energy 115 (2016) 1623-1631. doi:10.1016/ j.energy.2016.07.110.
- [4] E-Control, Statistikbroschüre 2023, Technical Report, Wien, 2023. URL: https://www.e-control.at/ documents/1785851/0/E-Control-Statbro-2023-Deutsch.pdf/ 0e53351d-53f2-957a-0ea4-319aa912a0cf?t=1697713460702[04.04.2024].
- [5] BMK, Erneuerbares-Gas-Gesetz EGG(251/ME), 2023. URL: https://www. parlament.gv.at/gegenstand/XXVII/ME/251[28.05.2024].
- [6] C. Gu, C. Tang, Y. Xiang, D. Xie, Power-to-gas management using robust optimisation in integrated energy systems, Applied Energy 236 (2019) 681–689. doi:10.1016/j.apenergy.2018.12.028.
- [7] R. Goswami, P. Chattopadhyay, A. Shome, S. N. Banerjee, A. K. Chakraborty,A. K. Mathew, S. Chaudhury, An overview of physico-chemical mechanisms of

biogas production by microbial communities: a step towards sustainable waste management, 3 Biotech 6 (2016) 72. doi:10.1007/s13205-016-0395-9.

- [8] B. Aghel, S. Behaein, S. Wongwises, M. S. Shadloo, A review of recent progress in biogas upgrading: With emphasis on carbon capture, Biomass and Bioenergy 160 (2022) 106422. doi:10.1016/j.biombioe.2022.106422.
- [9] F. Ardolino, U. Arena, Biowaste-to-Biomethane: An LCA study on biogas and syngas roads, Waste Management 87 (2019) 441-453. doi:10.1016/j.wasman. 2019.02.030.
- [10] F. Gutiérrez-Martín, L. Rodríguez-Anón, Power-to-SNG technologies by hydrogenation of CO₂ and biomass resources: A comparative chemical engineering process analysis, International Journal of Hydrogen Energy 44 (2019) 12544– 12553. doi:10.1016/j.ijhydene.2018.09.168.
- [11] F. Benedikt, J. Schmid, J. Fuchs, A. Mauerhofer, S. Müller, H. Hofbauer, Fuel flexible gasification with an advanced 100 kW dual fluidized bed steam gasification pilot plant, Energy 164 (2018) 329–343. doi:10.1016/j.energy.2018.08.
 146.
- [12] B. Rehling, Development of the 1MW Bio-SNG plant, evaluation on technological and economical aspects and upscaling considerations, Ph.D. thesis, Technische Universität Wien, 2012.
- [13] H. Thunman, M. Seemann, T. Berdugo Vilches, J. Maric, D. Pallares, H. Ström, G. Berndes, P. Knutsson, A. Larsson, C. Breitholtz, O. Santos, Advanced biofuel production via gasification - lessons learned from 200 man-years of research activity with Chalmers research gasifier and the GoBiGas demonstration plant, Energy Science & Engineering 6 (2018) 6–34. doi:10.1002/ese3.188.
- [14] A. Bartik, J. Fuchs, S. Müller, H. Hofbauer, Development of an internally circulating fluidized bed for catalytic methanation of syngas (2020). doi:10.
 34726/566, publisher: TU Wien.

- [15] A. Bartik, F. Benedikt, J. Fuchs, H. Hofbauer, S. Müller, Experimental investigation of hydrogen-intensified synthetic natural gas production via biomass gasification: a technical comparison of different production pathways, Biomass Conversion and Biorefinery (2023). doi:10.1007/s13399-023-04341-3.
- [16] R. Notz, H. P. Mangalapally, H. Hasse, Post combustion CO₂ capture by reactive absorption: Pilot plant description and results of systematic studies with MEA, International Journal of Greenhouse Gas Control 6 (2012) 84–112. doi:10.1016/j.ijggc.2011.11.004.
- [17] S. Mokhatab, W. A. Poe, J. Y. Mak, Handbook of natural gas transmission and processing: principles and practices, fourth edition ed., Gulf Professional Publishing, Cambridge, MA, 2019.
- [18] A. Molino, S. Chianese, D. Musmarra, Biomass gasification technology: The state of the art overview, Journal of Energy Chemistry 25 (2016) 10-25. doi:10.1016/j.jechem.2015.11.005.
- [19] A. F. Kirkels, G. P. Verbong, Biomass gasification: Still promising? A 30-year global overview, Renewable and Sustainable Energy Reviews 15 (2011) 471-481. doi:10.1016/j.rser.2010.09.046.
- [20] H. Hofbauer, G. Veronik, T. Fleck, R. Rauch, H. Mackinger, E. Fercher, The FICFB - Gasification Process, in: A. V. Bridgwater, D. G. B. Boocock (Eds.), Developments in Thermochemical Biomass Conversion, Springer Netherlands, Dordrecht, 1997, pp. 1016–1025. doi:10.1007/978-94-009-1559-6_82.
- [21] A. Mauerhofer, F. Benedikt, J. Schmid, J. Fuchs, S. Müller, H. Hofbauer, Influence of different bed material mixtures on dual fluidized bed steam gasification, Energy 157 (2018) 957–968. doi:10.1016/j.energy.2018.05.158.
- [22] A. Mauerhofer, J. Schmid, F. Benedikt, J. Fuchs, S. Müller, H. Hofbauer, Dual fluidized bed steam gasification: Change of product gas quality along the reactor height, Energy 173 (2019) 1256–1272. doi:10.1016/j.energy.2019.02.025.

- [23] J. C. Schmid, F. Benedikt, J. Fuchs, A. M. Mauerhofer, S. Müller, H. Hofbauer, Syngas for biorefineries from thermochemical gasification of lignocellulosic fuels and residues - 5 years experience with an advanced dual fluidized bed gasifier design, Biomass Conversion and Biorefinery 11 (2021) 2405–2442. doi:10.1007/ s13399-019-00486-2.
- [24] C. Pfeifer, B. Puchner, H. Hofbauer, Comparison of dual fluidized bed steam gasification of biomass with and without selective transport of CO₂, Chemical Engineering Science 64 (2009) 5073–5083. doi:10.1016/j.ces.2009.08.014.
- [25] T. Pröll, H. Hofbauer, H₂ rich syngas by selective CO₂ removal from biomass gasification in a dual fluidized bed system Process modelling approach, Fuel Processing Technology 89 (2008) 1207–1217. doi:10.1016/j.fuproc.2008.05.020.
- [26] M. Kuba, F. Havlik, F. Kirnbauer, H. Hofbauer, Influence of bed material coatings on the water-gas-shift reaction and steam reforming of toluene as tar model compound of biomass gasification, Biomass and Bioenergy 89 (2016) 40-49. URL: https://linkinghub.elsevier.com/retrieve/pii/ S0961953415301690. doi:10.1016/j.biombioe.2015.11.029.
- [27] S. Rönsch, J. Schneider, S. Matthischke, M. Schlüter, M. Götz, J. Lefebvre,
 P. Prabhakaran, S. Bajohr, Review on methanation From fundamentals to current projects, Fuel 166 (2016) 276–296. doi:10.1016/j.fuel.2015.10.111.
- [28] H. Gruber, L. Lindner, S. Arlt, A. Reichhold, R. Rauch, G. Weber, J. Trimbach,
 H. Hofbauer, A novel production route and process optimization of biomassderived paraffin wax for pharmaceutical application, Journal of Cleaner Production 275 (2020) 124135. doi:10.1016/j.jclepro.2020.124135.
- [29] H. Thunman, M. Seemann, The GoBiGas plant, in: Substitute Natural Gas from Waste, Elsevier, 2019, pp. 455–474. doi:10.1016/B978-0-12-815554-7.
 00017-9.
- [30] P. Sabatier, J.-B. Senderens, Comptes Rendus Des Séances De L'Académie Des Sciences, Sections VI - Chimie, Imprimerie Gautier-Villars, Paris, 1902.
- [31] M. Götz, J. Lefebvre, F. Mörs, A. McDaniel Koch, F. Graf, S. Bajohr, R. Reimert, T. Kolb, Renewable Power-to-Gas: A technological and economic review, Renewable Energy 85 (2016) 1371–1390. doi:10.1016/j.renene.2015. 07.066.
- [32] G. Weatherbee, Hydrogenation of CO₂ on group VIII metals II. Kinetics and mechanism of CO₂ hydrogenation on nickel, Journal of Catalysis 77 (1982) 460-472. doi:10.1016/0021-9517(82)90186-5.
- [33] S. Heyne, S. Harvey, Impact of choice of CO₂ separation technology on thermoeconomic performance of Bio-SNG production processes: Thermo-economic assessment of gas upgrade for SNG production, International Journal of Energy Research 38 (2014) 299–318. doi:10.1002/er.3038.
- [34] M. P. S. Santos, C. A. Grande, A. E. Rodrigues, Pressure Swing Adsorption for Biogas Upgrading. Effect of Recycling Streams in Pressure Swing Adsorption Design, Industrial & Engineering Chemistry Research 50 (2011) 974–985. doi:10.1021/ie100757u.
- [35] B. Bhide, S. Stern, Membrane processes for the removal of acid gases from natural gas. I. Process configurations and optimization of operating conditions, Journal of Membrane Science 81 (1993) 209–237. doi:10.1016/0376-7388(93) 85175-V.
- [36] B. Bhide, S. Stern, Membrane processes for the removal of acid gases from natural gas. II. Effects of operating conditions, economic parameters, and membrane properties, Journal of Membrane Science 81 (1993) 239–252. doi:10.1016/0376-7388(93)85176-W.
- [37] S. Han, Y. Meng, A. Aihemaiti, Y. Gao, T. Ju, H. Xiang, J. Jiang, Biogas

upgrading with various single and blended amines solutions: Capacities and kinetics, Energy 253 (2022) 124195. doi:10.1016/j.energy.2022.124195.

- [38] K. Sattler (Ed.), Thermische Trennverfahren: Grundlagen, Auslegung, Apparate, 3., überarb. u. erw. aufl., [nachdr.] ed., Wiley-VCH, Weinheim, 2007.
- [39] C. Madeddu, M. Errico, R. Baratti, Process analysis for the carbon dioxide chemical absorption - regeneration system, Applied Energy 215 (2018) 532– 542. doi:10.1016/j.apenergy.2018.02.033.
- [40] B. Lv, B. Guo, Z. Zhou, G. Jing, Mechanisms of CO₂ Capture into Monoethanolamine Solution with Different CO₂ Loading during the Absorption/Desorption Processes, Environmental Science & Technology 49 (2015) 10728–10735. doi:10.1021/acs.est.5b02356.
- [41] M. Stewart, K. Arnold, Gas dehydration field manual, Gulf Professional Pub, Waltham, MA, 2011. OCLC: ocn742305937.
- [42] Z. Y. Kong, A. Mahmoud, S. Liu, J. Sunarso, Revamping existing glycol technologies in natural gas dehydration to improve the purity and absorption efficiency: Available methods and recent developments, Journal of Natural Gas Science and Engineering 56 (2018) 486–503. doi:10.1016/j.jngse.2018.06.008.
- [43] J. Collie, M. Hlavinka, A. Ashworth, An Analysis of BTEX emissions from Amine Sweetening and Glycol Dehydration Facilities, in: Laurance Reid Gas Conditioning Conference Proceedings, Norman, Oklahoma: University of Oklahoma, 1998.
- [44] M. Neagu, D. L. Cursaru, Technical and economic evaluations of the triethylene glycol regeneration processes in natural gas dehydration plants, Journal of Natural Gas Science and Engineering 37 (2017) 327-340. doi:10.1016/j.jngse. 2016.11.052.

- [45] M. Gad, H. Elmawgoud, T. Aboul-Fotouh, M. El-Shafie, The Economic Comparison between Dry Natural Gas and Nitrogen Gas for Stripping Water Vapor from Glycol in the Gas Dehydration Process, International Journal of Engineering Science Invention 5 (2016) 8–12.
- [46] A. Sakheta, U. Zahid, Process simulation of dehydration unit for the comparative analysis of natural gas processing and carbon capture application, Chemical Engineering Research and Design 137 (2018) 75–88. doi:10.1016/j.cherd. 2018.07.004.
- [47] N. A. Darwish, R. A. Al-Mehaideb, A. M. Braek, R. Hughes, Computer simulation of BTEX emission in natural gas dehydration using PR and RKS equations of state with different predictive mixing rules, Environmental Modelling & Software 19 (2004) 957–965. doi:10.1016/j.envsoft.2003.10.008.
- [48] H. Ebeling, L. Lyddon, K. Covington, Reduce Emissions and Operating Costs with Appropriate Glycol Selection, in: Proceedings of the Seventy-Seventh GPA Annual Convention, 1998.
- [49] A. L. Kohl, R. B. Nielsen, Gas purification, 5th ed ed., Gulf Pub, Houston, Tex, 1997.
- [50] European Parliament and Council of the European Union, Renewable Energy Directive - Directive 2018/2001/EU, 2023. URL: https: //eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A32023L2413& qid=1699364355105[20.03.2024].
- [51] Bundesministerium für Klimaschutz, Umwelt, Energie, Mobilität, Innovation und Technologie, Integrierter nationaler Energie- und Klimaplan für Österreich - Entwurf zur "öffentlichen Konsultation, Technical Report, Wien, 2023. URL: https://www.bmk.gv.at/dam/jcr: 34c13640-4532-4930-a873-4ececc4d3001/NEKP_Aktualisierung_2023_ 2024_zur_Konsultation_20230703.pdf[06.04.2024].

- [52] Bundesministerium für Klimaschutz, Umwelt, Energie, Mobilität, Innovation und Technologie, Erläuterungen . Erneuerbaren-Ausbau-Gesetz, 2021. URL: https://www.bmk.gv.at/service/presse/gewessler/2021/20210317_eag. html[20.02.2024].
- [53] OVGW, Gasbeschaffenheit Richtlinie G B210, 2021.
- [54] DIN, DIN EN 16723-1 Natural gas and biomethane for use in transport and biomethan for injection in the natural gas network - Part 1: Specifications for biomethane for injection in the natural gas network, 2017.
- [55] DIN, DIN EN 16726 Gas infrastructure Quality of Gas Group H, 2019.
- [56] M. Theißing, Biogas. Einspeisung und Systemintegration in bestehende Gasnetze, Technical Report, Bundesministerium f
 ür Verkehr, Innovation und Technologie, Wien, 2006.
- [57] U.S. Department of Energy, Technology Readiness Assessment Guide, Technical Report DOE G 413.3-4A, Washington, DC, 2011.
- [58] H. Hekmatmehr, A. Esmaeili, M. Pourmahdi, S. Atashrouz, A. Abedi, M. Ali Abuswer, D. Nedeljkovic, M. Latifi, S. Farag, A. Mohaddespour, Carbon capture technologies: A review on technology readiness level, Fuel 363 (2024) 130898. doi:10.1016/j.fuel.2024.130898.
- [59] S. Müller, Energy Technology Development for Industrial Application -Modelling-Based Development of Processes Enabling Reduced Fossil Carbon Dioxide Emissions by Advanced Digital Methods, TU Wien Habilitation (2022).
- [60] M. Hammerschmid, A. Bartik, F. Benedikt, M. Veress, S. Pratschner, S. Müller,
 H. Hofbauer, Economic and Ecological Impacts on the Integration of Biomass-Based SNG and FT Diesel in the Austrian Energy System, Energies 16 (2023) 6097. doi:10.3390/en16166097.

- [61] Aspen Technology, Inc, Aspen Plus V12.1, 2021.
- [62] G. Towler, R. Sinnott, Capital cost estimating, in: Chemical Engineering Design, Elsevier, 2022, pp. 239–278. doi:10.1016/B978-0-12-821179-3.00007-8.
- [63] M. S. Peters, K. D. Timmerhaus, Plant design and economics for chemical engineers, McGraw-Hill chemical engineering series, 4. ed ed., McGraw-Hill, New York, 1991.
- [64] The University of Manchester, Chemical Engineering Plant Cost Index, 2024. URL: https://www.training.itservices.manchester.ac.uk/ public/gced/CEPCI.html?reactors/CEPCI/index.html[23.02.2024].
- [65] H. Lang, Simplified approach to preliminary cost estimates, Chemical Engineering (1948) 112–113.
- [66] H. Hofbauer, A. Mauerhofer, F. Benedikt, M. Hammerschmid, A. Bartik, M. Veress, M. Siebenhofer, G. Resch, Reallabor zur Herstellung von Holzdiesel und Holzgas aus Biomasse und biogenen Reststoffen für die Landund Forstwirtschaft, Technical Report, TU Wien, Vienna, 2020. URL: https: //dafne.at/projekte/ftsng-reallabor[10.01.2024].
- [67] C. Madeddu, M. Errico, R. Baratti, CO₂ Capture by Reactive Absorption-Stripping: Modeling, Analysis and Design, SpringerBriefs in Energy, Springer International Publishing, Cham, 2019. doi:10.1007/978-3-030-04579-1.
- [68] F. Capra, F. Fettarappa, F. Magli, M. Gatti, E. Martelli, Biogas upgrading by amine scrubbing: solvent comparison between MDEA and MDEA/MEA blend, Energy Procedia 148 (2018) 970–977. doi:10.1016/j.egypro.2018.08.065.
- [69] R. S. Cavaignac, N. L. Ferreira, R. Guardani, Techno-economic and environmental process evaluation of biogas upgrading via amine scrubbing, Renewable Energy 171 (2021) 868–880. doi:10.1016/j.renene.2021.02.097.

- [70] T. T. Vo, D. M. Wall, D. Ring, K. Rajendran, J. D. Murphy, Techno-economic analysis of biogas upgrading via amine scrubber, carbon capture and ex-situ methanation, Applied Energy 212 (2018) 1191–1202. doi:10.1016/j.apenergy. 2017.12.099.
- [71] G. Leonzio, Upgrading of biogas to bio-methane with chemical absorption process: simulation and environmental impact, Journal of Cleaner Production 131 (2016) 364-375. doi:10.1016/j.jclepro.2016.05.020.
- [72] M. R. Abu-Zahra, L. H. Schneiders, J. P. Niederer, P. H. Feron, G. F. Versteeg, CO₂ capture from power plants Part I. A parametric study of the technical performance based on monoethanolamine, International Journal of Greenhouse Gas Control 1 (2007) 37–46. doi:10.1016/S1750-5836(06)00007-7.
- [73] H.-T. Oh, Y. Ju, K. Chung, C.-H. Lee, Techno-economic analysis of advanced stripper configurations for post-combustion CO₂ capture amine processes, Energy 206 (2020) 118164. doi:10.1016/j.energy.2020.118164.
- [74] L. A. Pellegrini, S. Moioli, S. Gamba, Energy saving in a CO₂ capture plant by MEA scrubbing, Chemical Engineering Research and Design 89 (2011) 1676– 1683. doi:10.1016/j.cherd.2010.09.024.
- [75] J. M. Plaza, D. V. Wagener, G. T. Rochelle, Modeling CO₂ capture with aqueous monoethanolamine, Energy Procedia 1 (2009) 1171–1178. doi:10.1016/ j.egypro.2009.01.154.
- [76] S. Ziaii, G. T. Rochelle, T. F. Edgar, Optimum design and control of amine scrubbing in response to electricity and CO₂ prices, Energy Procedia 4 (2011) 1683–1690. doi:10.1016/j.egypro.2011.02.041.
- [77] A. Bartik, Synthetic natural gas from woody biomass, Dissertation, TU Wien, Wien, 2024.
- [78] Aspen Technology, Inc, Property Method Selection Assistant, 2021.

- [79] Z. Cai, R. Xie, Z. Wu, Binary Isobaric Vapor-Liquid Equilibria of Ethanolamines
 + Water, Journal of Chemical & Engineering Data 41 (1996) 1101–1103. doi:10.
 1021/je9601180.
- [80] A. Bagheri, A. Samimi, E. Godini, S. Azizkhani, S. Dokhani, Studying the Designed Parameters of Carbonic Gas Production Unit's Solvents in the Way of Diesel Combustion 1 (2013) 155–168.
- [81] NIST Chemistry Webbook, SRD69, Antoine Equation Parameters Water, 2023. URL: https://webbook.nist.gov/cgi/cbook.cgi?ID=C7732185& Mask=4&Type=ANTOINE&Plot=on[19.05.2024].
- [82] N. Razi, H. F. Svendsen, O. Bolland, Validation of mass transfer correlations for CO₂ absorption with MEA using pilot data, International Journal of Greenhouse Gas Control 19 (2013) 478–491. doi:10.1016/j.ijggc.2013.10.006.
- [83] Y. Zhang, C.-C. Chen, Modeling CO₂ absorption and desorption by aqueous monoethanolamine solution with Aspen rate-based model, volume 37, Energy Procedia, 2013, pp. 1584 – 1596.
- [84] W. Conway, X. Wang, D. Fernandes, R. Burns, G. Lawrance, G. Puxty, M. Maeder, Comprehensive Kinetic and Thermodynamic Study of the Reactions of CO₂ (aq) and HCO₃⁻ with Monoethanolamine (MEA) in Aqueous Solution, The Journal of Physical Chemistry A 115 (2011) 14340–14349. doi:10.1021/jp2081462.
- [85] C. Alie, CO₂ Capture With MEA: Integrating the Absorption Process and Steam Cycle of an Existing Coal-Fired Power Plant, Master's thesis, University of Waterloo, 2004.
- [86] J. Oexmann, A. Kather, Post-combustion CO₂ capture in coal-fired power plants: Comparison of integrated chemical absorption processes with piperazine promoted potassium carbonate and MEA, Energy Procedia 1 (2009) 799–806. doi:10.1016/j.egypro.2009.01.106.

- [87] D. L. Reddy, D. Lokhat, H. Siddiqi, B. Meikap, Modelling and simulating CO and CO₂ methanation over Ru-Al₂O₃ catalyst: An integrated approach from carbon capture to renewable energy generation, Fuel 314 (2022) 123095. doi:10.1016/j.fuel.2021.123095.
- [88] H. Er-rbib, C. Bouallou, Modeling and simulation of CO methanation process for renewable electricity storage, Energy 75 (2014) 81-88. doi:10.1016/j. energy.2014.05.115.
- [89] A. B. Rao, E. S. Rubin, A Technical, Economic, and Environmental Assessment of Amine-Based CO₂ Capture Technology for Power Plant Greenhouse Gas Control, Environmental Science & Technology 36 (2002) 4467–4475. doi:10. 1021/es0158861.
- [90] Lang P., Denes F., Hegely L., Comparison of different amine solvents for the absorption of CO₂, Chemical Engineering Transactions 61 (2017) 1105–1110. doi:10.3303/CET1761182.
- [91] J. Davis, G. Rochelle, Thermal degradation of monoethanolamine at stripper conditions, Energy Procedia 1 (2009) 327-333. doi:10.1016/j.egypro.2009.01.045.
- [92] A. Alamia, S. Osk Gardarsdöttir, A. Larsson, F. Normann, H. Thunman, Efficiency Comparison of LargeâScale Standalone, Centralized, and Distributed Thermochemical Biorefineries, Energy Technology 5 (2017) 1435–1448. doi:10. 1002/ente.201600719.
- [93] Z. Liang, H. Gao, W. Rongwong, Y. Na, Comparative studies of stripper overhead vapor integration-based configurations for post-combustion CO₂ capture, International Journal of Greenhouse Gas Control 34 (2015) 75–84. doi:10.1016/j.ijggc.2014.12.019.
- [94] S.-Y. Oh, M. Binns, H. Cho, J.-K. Kim, Energy minimization of MEA-based

CO₂ capture process, Applied Energy 169 (2016) 353-362. doi:10.1016/j. apenergy.2016.02.046.

- [95] S.-Y. Oh, J.-K. Kim, Operational optimization for part-load performance of amine-based post-combustion CO₂ capture processes, Energy 146 (2018) 57–66. doi:10.1016/j.energy.2017.06.179.
- [96] K. Li, W. Leigh, P. Feron, H. Yu, M. Tade, Systematic study of aqueous monoethanolamine (MEA)-based CO₂ capture process: Techno-economic assessment of the MEA process and its improvements, Applied Energy 165 (2016) 648-659. doi:10.1016/j.apenergy.2015.12.109.
- [97] A. A. Razak, I. Saaid, M. A. Yusof, N. Husein, M. F. Zaidin, K. Mohamad Sabil, Physical and chemical effect of impurities in carbon capture, utilisation and storage, Journal of Petroleum Exploration and Production Technology 13 (2023) 1235–1246. doi:10.1007/s13202-023-01616-3.
- [98] S. Mokhatab, W. A. Poe, J. Y. Mak, Natural Gas Dehydration, in: Handbook of Natural Gas Transmission and Processing, Elsevier, 2015, pp. 223–263. doi:10. 1016/B978-0-12-801499-8.00007-9.
- [99] C. H. Twu, V. Tassone, W. D. Sim, S. Watanasiri, Advanced equation of state method for modeling TEG-water for glycol gas dehydration, Fluid Phase Equilibria 228-229 (2005) 213–221. doi:10.1016/j.fluid.2004.09.031.
- [100] L. E. Øi, Estimation of tray efficiency in dehydration absorbers, Chemical Engineering and Processing: Process Intensification 42 (2003) 867–878. doi:10. 1016/S0255-2701(02)00187-3.
- [101] R. Chebbi, M. Qasim, N. Abdel Jabbar, Optimization of triethylene glycol dehydration of natural gas, Energy Reports 5 (2019) 723-732. doi:10.1016/j. egyr.2019.06.014.

- [102] S. M. Jokar, H. R. Rahimpour, H. Momeni, M. R. Rahimpour, H. Abbasfard, Simulation and feasibility analysis of structured packing replacement in absorption column of natural gas dehydration process: A case study for Farashband gas processing plant, Iran, Journal of Natural Gas Science and Engineering 18 (2014) 336-350. doi:10.1016/j.jngse.2014.03.005.
- [103] M. Salman, L. Zhang, J. Chen, A computational simulation study for technoeconomic comparison of conventional and stripping gas methods for natural gas dehydration, Chinese Journal of Chemical Engineering 28 (2020) 2285-2293. doi:10.1016/j.cjche.2020.03.013.
- [104] A. Hedayati Moghaddam, Investigation of natural gas dehydration process using triethylene glycol (TEG) based on statistical approach, Chemical Papers 77 (2023) 1433–1443. doi:10.1007/s11696-022-02564-8.
- [105] A. J. Kidnay, W. R. Parrish, D. G. McCartney, Fundamentals of natural gas processing, third edition ed., CRC Press, Place of publication not identified, 2020. OCLC: 1121596775.
- [106] E. Billig, Bewertung technischer und wirtschaftlicher Entwicklungspotenziale künftiger und bestehender Biomasse-zu-Methan-Konversionsprozesse, Ph.D. thesis, DBFZ, Leipzig, 2016.
- [107] G. Towler, R. Sinnott, Utilities and Energy Efficient Design, in: Chemical Engineering Design, Elsevier, 2013, pp. 103–160. doi:10.1016/ B978-0-08-096659-5.00003-1.
- [108] D. W. Green, M. Z. Southard (Eds.), Perry's chemical engineers' handbook, ninth edition, 85th anniversary edition ed., McGraw Hill Education, New York, 2019.
- [109] G. Towler, R. Sinnott, Estimating revenues and production costs, in: Chemical Engineering Design, Elsevier, 2022, pp. 279–304. doi:10.1016/ B978-0-12-821179-3.00008-X.

- [110] Statistik Austria, Arbeitskosten und Tariflohnindex in österreich, 2024. URL: https://www.statistik.at/statistiken/arbeitsmarkt/ arbeitskosten-und-tariflohnindex/arbeitskosten/arbeitskosten[05. 02.2024].
- [111] International Energy Agency, Energy Technology Perspectives 2020, Technical Report, IEA, 2020. URL: https://www.iea.org/reports/ energy-technology-perspectives-2020[30.04.2024].
- [112] E-Control, Preisentwicklung Strom, 2023. URL: https://www. e-control.at/statistik/e-statistik/archiv/marktstatistik/ preisentwicklungen[10.04.2024].
- [113] Business analytic IQ, Monoethanolamine price index, 2024. URL: https://businessanalytiq.com/procurementanalytics/index/ monoethanolamine-price-index/[03.03.2024].
- [114] Chemanalyst, Pricing Data of TEG, 2024. URL: https://www.chemanalyst. com/Pricing-data/triethylene-glycol-1532[03.03.2024].
- [115] European Energy Exchange AG, Emission Spot Primary Market Auction Report 2024, 2024. URL: https://www.eex.com/de/marktdaten/umweltprodukte/ eex-eua-primary-auction-spot-download[03.03.2024].



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List of Acronyms and Abbreviations

CDF	Cumulative discount factor	
COP	Coefficient of performance	
COS	Carbonyl sulfide	
CSTR	Continuous stirred tank reactor	
DEA	Diethanolamine	
DFB	Dual fluidized bed	
FNRTI RK	Electrolyte Non-Random Two Liquid model with	
	Redlich Kwong Equation of State	
FBM	Fixed bed methanation	
HYSGLYCO	Glycol property package from Aspen HYSYS	
KPI	Key performance indicator	
L/G	Liquid to gas ratio	
MDEA	Methyldiethanolamine	
MEA	Monoethanolamine	
MRL	Modelling readiness level	
PG	Product gas	
PSA	Pressure swing adsorption	
ΡZ	Piperanzine	
RED	Renewable energy directive	
RME	Rapeseed methyl-ester	
SER	Sorption enhanced reforming	
SNG	Synthetic natural gas	

- TEG Triethylene glycol
- TRL Technology readiness level
- TSA Temperature swing adsorption

List of Symbols

Symbol	Description	Unit
α	Amine loading	$\mathrm{mol}_{\mathrm{CO}_2}/\mathrm{mol}_{\mathrm{MEA}}$
C_{eq}	Equipment cost for the base year in literature and design case	€
CEPCI	Chemical Engineering Plant Cost Index	-
ΔH^0	Standard heat of formation at $298\mathrm{K}$ and $1.013\mathrm{bar}$	kJ/mol
Ε	Expenditures	€
E_{a}	Activation energy	kJ/mol
G_0	Gibbs free energy	kJ/mol
GHSV	Gas hourly space velocity	$1/\mathrm{h}$
i	Interest rate	
I ₀	Capital expenditures	€
k	Kinetic constant	-
k_0	Pre-exponential factor	-
$\mathbf{K}_{\mathbf{eq}}$	Activity basis equilibrium constant	-
LCOP	Levelized cost of product	€/MWh
\dot{m}_i	Massflow of component i	kg/h
M_t	Annual amount of main product	MWh
n	Plant life time	a
r	Economy of scale exponent	-

Symbol	Description	Unit
$\mathbf{R}_{\mathrm{product}}$	Annual revenues of product	€
S	Equipment size for the base year in literature and design case	-
Т	Temperature	Κ

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Appendix

Parameter	Unit	Value	Source		
Costs					
MEA	€/kg	1.78	[113]		
TEG	€/kg	1.44	[114]		
Electricity cost	€/kWh	0.274	[112]		
Nickel catalyst	€/kg	68	[106]*		
Revenues					
District heat feed in tariff	€/MWh	30	[60]		
CO_2 emission certificates	$\in/t_{\rm CO_2}$	83.6	[115]		
Operation					
MEA make up	$\rm kg_{\rm MEA}/t_{\rm CO_2}$	1.5	[96]		
TEG make up	$\rm kg_{\rm TEG}/h$	0.1	[105]		

*Price adjusted according to CEPCI