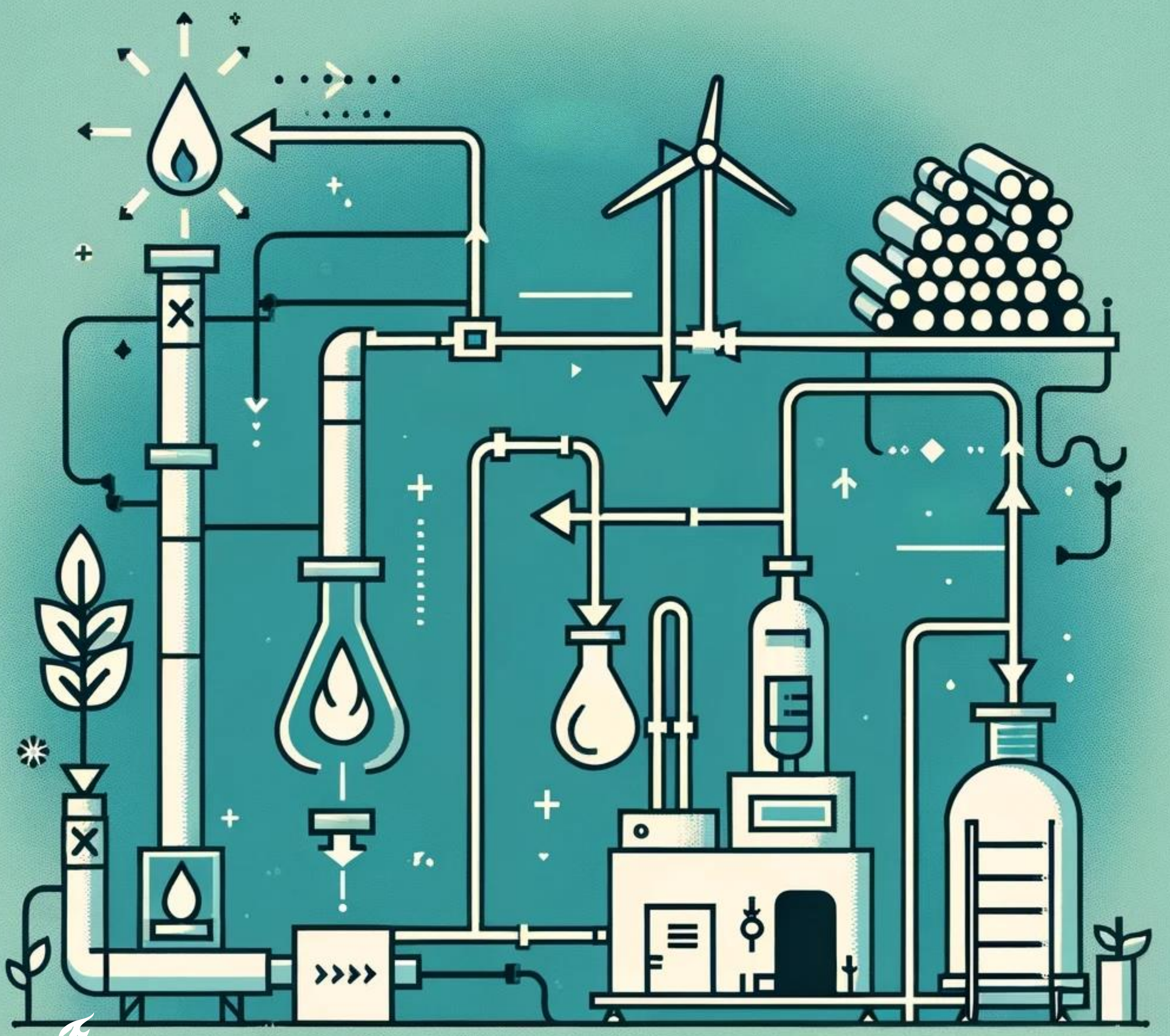
Pedro Lagar Zabalza

Techno-Economic Analysis of Syngas Conditioning Process Configurations in a Biomass Gasification-to-Methanol Plant



TU Delft

Preface

Completing a master's degree has long been one of my major goals, and achieving it at a prestigious institution like TU Delft makes this accomplishment even more meaningful. The education I received here did not just provide me with answers; it taught me how to seek them—a crucial skill for professionals navigating the complexities of the energy transition. Over the past few years at TU Delft, I've really improved my analytical skills and critical thinking, thanks to the great environment and awesome mentorship.

I am deeply grateful to my loving family and supportive friends, whose unwavering and unconditional support, encouragement, and guidance have been a constant source of strength throughout my life and academic journey, including pursuing this Master's degree. I am very grateful to have you in my life. This thesis is dedicated to you.

I would like to extend my heartfelt thanks to my daily supervisor, Tonny Manalal, for his invaluable support and insightful guidance throughout this research. I am equally grateful to my main supervisor, Mar Pérez Fortes, her expertise and dedication have shaped this work. I also wish to express my sincere appreciation to Dr. Wiebren De Jong for his thoughtful feedback and the depth of knowledge he brought to this project. It has been a privilege to work with such distinguished mentors. I really admire their knowledge in this area and their enthusiasm for the energy transition. Undoubtedly essential for society.

Pedro Lagar Zabalza

Delft, August 2024

Executive Summary

Climate change, driven by increased greenhouse gas emissions from fossil fuels, is a critical global challenge. The Netherlands aims for a 55% CO_2 reduction by 2030, with the Port of Rotterdam as a significant emitter. Renewable methanol production from biomass offers a promising solution to reduce these emissions significantly. This thesis aims to study the techno-economic trade-offs and synergies of CO_2 compared to H_2 syngas conditioning for a biomass-based methanol plant.

Syngas produced through biomass gasification typically lacks the adequate stoichiometric ratio for methanol production, requiring a conditioning step. The conventional WGS approach, while increasing hydrogen content, also increases CO_2 production, leading to higher costs and reduced efficiency. Carbon removal further limits efficiency and methanol production. While H_2 syngas conditioning routes and synthesis have been extensively investigated, other approaches like RWGS and CO_2 -co-electrolysis require further study.

The configurations are assessed employing process simulations from Aspen Plus, which were developed using data from the literature. The gasifier was modelled and validated using the IGT experimental data. OLGA and Rectisol were employed for syngas cleaning. Similarly, four syngas conditioning configurations were modelled: water electrolysis, WGS, RWGS and CO_2 co-electrolysis. The conditioned syngas compositions for each configuration were used in a separate isothermal methanol reactor model, including purification.

CO_2 co-electrolysis and RWGS configurations showed the highest biomass utilisation efficiency, but required significant energy input. Water electrolysis had moderate efficiency and the best environmental performance with nearly zero direct CO_2 emissions. WGS was the least efficient and had the highest CO_2 emissions. This was primarily due to the separation of CO_2. Economically, all options were less competitive than market methanol prices. CO_2 co-electrolysis had the lowest levelized methanol (LCOM) cost at €2.39/kg, followed by water electrolysis at €2.42/kg and RWGS at €2.63/kg. WGS performed worst at €3.55/kg. The study reveals that RWGS and water electrolysis configurations demonstrate the lowest CO_2 emissions, making them ideal for scenarios where reducing the carbon footprint is a priority, primarily when electricity is sourced from low-cost, renewable energy. CO_2 co-electrolysis, while achieving high biomass utilisation efficiency and the lowest LCOM does not have the lowest CO_2 emissions due to its reliance on natural gas for heating. Conversely, the WGS configuration, although minimising electricity consumption at 0.60 kWh/kg MeOH, is the least efficient overall, with high CO_2 emissions and the highest LCOM. CO_2 co-electrolysis and RWGS are more suitable in scenarios where high biomass utilisation and competitive costs are prioritised and where electricity prices are stable or low. The WGS process may be more suitable for high electricity costs, and minimising capital expenditure is crucial.

In conclusion, this study presents valuable insights into the techno-economic synergies and trade-offs of syngas upgrading through CO_2 conditioning compared to hydrogen conditioning for methanol production from biomass gasification. Addressing the identified challenges and leveraging the synergies can advance towards a more sustainable and economically viable methanol production industry. Future optimisation and validation efforts will be essential for translating these findings into practical, scalable solutions.

Techno-Economic Analysis of Syngas Conditioning Process Configurations in a Biomass Gasification-to-Methanol Plant

By

Pedro Lagar Zabalza

in partial fulfilment of the requirements for the degree of

Master of Science

in Sustainable Energy Technology

at the Delft University of Technology,

to be defended publicly on Friday, August 30, 2024, at 10:30 AM.

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This thesis is confidential and cannot be made public until December 31, 2025.

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Abbreviations

AGR: Acid Gas Removal

APEA: Aspen Process Economic Analyzer

CAPEX: Capital Expenditure

CO_2: Carbon Dioxide

CO: Carbon Monoxide

H_2: Hydrogen

H_2S: Hydrogen Sulfide

HCl: Hydrogen Chloride

IGT: Institute of Gas Technology

KPI: Key Performance Indicator

LCOM: Levelised Cost of Methanol

LP Steam: Low-Pressure Steam

MeOH: Methanol

MP Steam: Medium-Pressure Steam

NH_3: Ammonia

OPEX: Operational Expenditure

PEM: Proton Exchange Membrane

RWGS: Reverse Water Gas Shift

S: Stoichiometric ratio

SOE: Solid Oxide Electrolyzer

TEA: Techno-Economic Analysis

WGS: Water-Gas Sh

1. Introduction

Climate change is one of the most critical challenges faced by the contemporary society. One of its leading causes is increased greenhouse gas emissions, primarily because of burning fossil fuels for energy supply. In 2015, the Paris Agreement was signed by 196 countries, marking a significant global commitment to address the climate crisis. As part of this agreement, the Netherlands pledged to reduce CO_2 emissions by 55% by 2030, using 1990 levels as a baseline. Their goal is to reach carbon neutrality by 2050. To achieve this, the country's strategy focuses on transitioning towards sustainable energy, obtaining at least 27% of its energy from renewable sources by 2030 and transitioning to a fully renewable energy mix by 2050. In addition, it was proposed that one of the 2030 supporting targets be Bio-based raw materials seen as the norm for industrial production processes [1].

In this context, the Port of Rotterdam is a significant source of carbon emissions in the Netherlands, contributing over 16% of the country's total in 2020. That same year, the Port of Rotterdam’s direct CO_2 emissions were estimated at 22.4 million tonnes. The most significant sources were oil refineries, which accounted for 9.1 million metric tons (40.63%), followed by chemical and other industries at 6.1 million metric tons (27.23%), natural gas-fired plants at 3.8 million metric tons (16.96%), and coal-fired power plants at 3.4 million metric tons (15.18%) [2]. Therefore, due to its high emissions profile, the Port of Rotterdam is subject to being a primary focus area for national policy aiming to decrease greenhouse gas emissions. The port must implement thorough decarbonisation plans throughout its energy, industrial, and material use to satisfy environmental targets and stay competitive in a market where sustainability is becoming increasingly important.

The Port of Rotterdam's commitment to reduce emissions involves a significant shift in both raw materials and energy utilisation. As Europe transitions to cleaner energy, the demand for alternative materials rises. This transition presents both challenges and opportunities for the port. Limited supplies of traditional raw materials, underdeveloped recycling capabilities, land and labour shortages, and potential disruptions due to political instability make it challenging to meet the growing demand for new, sustainable materials. However, these challenges are driving innovation. The port is now exploring and developing new production methods and sourcing alternative raw materials [3].

Biomass consists of various materials, such as agricultural residues, forest residues, wood waste, and even algae [4]. It is both an energy source and a carbon source, making it a valuable raw material for the chemical industry and energy production context [5]. At scale, biomass-based fuels are seen as promising alternatives to conventional shipping fuels to reduce greenhouse gas emissions in the maritime sector [6]. In particular, methanol from biomass is well-suited to replace fossil fuels in this sector due to its ease of storage, transport, and distribution at room temperature and pressure, unlike gaseous or cryogenic fuels [7]. Additionally, methanol offers a robust pathway as an intermediate in jet fuel production via olefins to alkanes, further highlighting its potential in decarbonising transportation. As the largest bunker port in Europe and a leader in selling biofuels for maritime applications, the synthesis of methanol from biomass could significantly expand the Port of Rotterdam's sustainable fuel supply, aligning with its strategic environmental objectives while also contributing to the broader goals of energy transition and decarbonisation [8].

Methanol can be obtained through the thermochemical and biochemical conversion of biomass [9]. For the purpose of this study, gasification is chosen due to its high efficiency, scalability, and ability to convert diverse biomass feedstocks into methanol. This thermochemical process involves subjecting biomass to elevated temperatures in the presence of a gasifying agent. Resulting in its conversion into syngas, a mixture primarily composed of carbon monoxide and hydrogen [10]. Once impurities are removed, the syngas is directed to a synthesis plant for methanol production. However, the syngas produced during biomass gasification typically lacks the optimal hydrogen-to-carbon monoxide ratio required for methanol synthesis [11]. Two broad alternatives are commonly utilised to modify this ratio: H_2 conditioning and CO_2 conditioning. Conventionally, the water-gas shift (WGS) reaction is employed to increase the hydrogen content in syngas by converting carbon monoxide and water into additional hydrogen and CO_2. However, this approach necessitates the subsequent separation of CO_2 from the syngas, increasing costs and reducing overall process efficiency. These conditioning processes also significantly impact material efficiencies, energy consumption, and the overall economics of methanol production. While hydrogen conditioning routes and synthesis methods have been extensively investigated, other approaches, such as the reverse water-gas shift (RWGS) and CO_2 co-electrolysis, show promise but require further validation. A comprehensive comparison of these syngas conditioning methods from technical, economic, and environmental perspectives is still needed to better understand under what conditions each method might be most advantageous for methanol production.
This thesis aims to analyse various system configurations for syngas conditioning of biomass-based methanol synthesis. This thesis undertakes a techno-economic analysis to assess the viability of different technological configurations for syngas conditioning for further downstream conversion, focusing on economic viability and technological efficiency. A set of metrics for evaluating the efficiency, financial viability, and environmental footprint of the studied process configurations will be used to assess the different configurations from different dimensions. The outputs of this research are intended to provide insights into the techno-economic feasibility of sustainable methanol production.

Research Questions

The research questions will act as the basis for the research framework, directing the investigation and techno-economic analysis of proposed biomass-based configurations. These questions aim to address the knowledge gap in this area, providing various dimensions that will be evaluated throughout the thesis.

Main Research Question:

What are the techno-economic synergies and trade-offs of syngas upgrading through CO_2 conditioning (using CO_2 electrolysis and RWGS) compared to hydrogen conditioning (using water electrolysis and WGS) for a biomass gasification-to-methanol plant?

Sub-research questions:

- What is the economic impact of adjusting the syngas composition using different syngas conditioning technologies?
- What are the energy requirements for each process configuration in a biomass gasification-to-methanol plant per kg of methanol produced?
- Which configuration offers lower scope-1 CO_2 emissions per kg of methanol produced?

Thesis Outline

The report is structured as follows. Chapter 2 delves into the background and literature review, focusing on the importance of syngas conditioning in renewable methanol production through biomass gasification. It explores conventional and renewable methanol production methods, with an emphasis on the various gasification technologies and the critical role of syngas conditioning processes, such as Water Gas Shift (WGS), Reverse Water Gas Shift (RWGS), and CO_2 co-electrolysis, in optimising syngas composition for efficient methanol synthesis. The chapter also identifies significant knowledge gaps in syngas conditioning research. Following this, chapter 3 presents the methodology, including the basis of design, which encompasses product specifications, feedstock characteristics, process configurations, and other essential factors. The model development and validation approaches are detailed. Chapter 4 presents the simulation results, evaluating key performance indicators (KPIs) for the different syngas conditioning configurations. This includes assessments of gasifier performance, syngas cleaning, methanol synthesis, utility consumption, CO_2 emissions, and a sensitivity analysis of economic parameters. Finally, chapter 5 discusses the findings, focusing on the evaluated configurations' technical, economic, and environmental trade-offs and synergies. It addresses the study's limitations and suggests directions for future research to enhance sustainable methanol production.

2. Background and Literature Review

A comprehensive background on the process and system under investigation is given. This includes a thorough explanation of biomass gasification and the subsequent methanol production process, emphasising the syngas conditioning step. This chapter is structured as follows: The importance of renewable methanol will be discussed first, followed by the state of the art of biomass gasification technology. Next, syngas cleaning processes will be presented. Finally, syngas upgrading techniques are discussed in more detail, pointing out critical research gaps in the field.

2.1 Methanol Production: From Fossil Fuels to Renewable Sources

2.1.1 Conventional methods of methanol production

Methanol is conventionally produced through catalytic conversion of syngas, which primarily consists of carbon monoxide (CO), hydrogen (H_2), carbon dioxide (CO_2), and traces of water (H_2O) [12]. This process typically involves syngas generation, methanol synthesis and the processing of crude methanol [13]. Almost 90% of the world's methanol is produced from natural gas, which presents significant environmental concerns, while coal and other hydrocarbons are used to a lesser extent [14]. In this regard, the coal-based process produces approximately 3.8 kg of carbon dioxide to synthesise one kilogramme of methanol, whereas, in the natural gas-based method, one kilogramme of methanol involves the production of 1.6 kg of carbon dioxide [15]. Furthermore, the coal-based process produces CO_2 at a rate more than double that of the steel industry, which emits around 1.85 metric tonnes of CO_2 per tonne of steel produced [16]. These emissions related to producing methanol from fossil sources show how necessary it is to transition to more sustainable and low-carbon production processes. According to the Methanol Institute, renewable methanol eliminates sulfuric oxide and particulate matter emissions, reduces nitrogen oxide emissions by up to 80%, and cuts carbon dioxide emissions by up to 95% compared to traditional fuels [17]. Renewable methanol also enhances energy security by reducing dependence on fossil fuels and supporting the circular economy by converting biomass or waste into valuable products [18]. Thus, exploring CO_2 and biomass as sustainable feedstocks for methanol synthesis offers a feasible way to improve sustainability while minimising negative environmental impacts.

2.1.2 Renewable Methanol

Renewable methanol can be produced from several routes, converting renewable feedstocks into syngas: Bio-methanol is produced from biomass gasification to syngas followed by syngas being converted into methanol from catalytic synthesis; e-methanol is obtained by the electrochemical process that produces syngas or hydrogen followed by the catalytic hydrogenation of CO_2 or syngas to methanol [7]. The methanol produced can be categorised as renewable, instead of fossil fuels based when i) the carbon carrier material proceeds from a biomass or waste products (i.e. municipal solid waste, agricultural and forestry residues, among others), (ii) the hydrogen is not produced from fossil fuel sources, and (iii) the energy originates from renewable sources [19].

Methanol offers significant benefits and potential as a fuel due to its ease of storage and transportation, its role as a convenient hydrogen carrier, and its versatility in the chemical industry as a solvent and a building block for producing various intermediates and synthetic hydrocarbons [20]. The potential of this fuel is particularly attractive for hard-to-electrify sectors, such as shipping and heavy-duty trucks. This is mainly attributable to methanol's fluid state as a liquid at standard pressure and temperature conditions, making it more straightforward to store, transport, and distribute, unlike gaseous or cryogenic fuels [7]. A study conducted by Mukherjee found bio-methanol to be the most promising biofuel for the maritime industry after considering cost, availability, current technological status, the potential for reducing greenhouse gas emissions, infrastructure compatibility, and CO_2 capture and storage (CCS) compatibility [21] .

Although renewable methanol has significant potential for the above-mentioned applications, its widespread adoption depends on various factors. This includes the feasibility of producing it economically on a large scale, developing effective conversion technologies, and assessing the impact of production and use on the environment [22]. In addition, significant changes must be implemented in end-use technologies and distribution networks to integrate renewable methanol into the current energy system [23]. Therefore, to fully realise the potential of renewable methanol as a sustainable energy carrier, a coordinated effort across policy, research, and industry is necessary to tackle these complex challenges.

2.2 State of the Art in Biomass to Methanol

In recent years, there has been a growing interest in utilising biomass as an alternative source to produce methanol [24]. The gasification process is particularly relevant for methanol production, as the cleaned and upgraded syngas produced during biomass gasification can be used as a feedstock for methanol synthesis via the catalytic conversion of syngas into methanol [25]. The typical methanol production process from biomass involves biomass pretreatment to be converted into raw syngas through gasification. Following this, the syngas is cleaned and conditioned. Next, methanol synthesis occurs, and finally, the produced methanol is purified [11]. Figure 1 depicts the general scheme of a gasification-based methanol process that uses biomass as feedstock. The details of a biomass to methanol plant will be covered in more detail in the subsequent section.

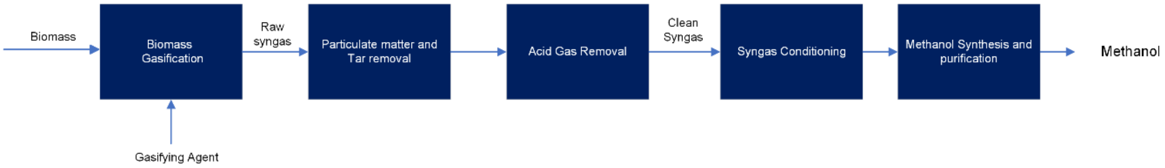

Figure 1. General Scheme of methanol from biomass gasification

2.2.1 Process Overview

Biomass gasification is a thermochemical process which converts solid biomass into syngas products along with tar, char, and ash [26].The process involves heating carbonaceous materials through a series of steps including drying, pyrolysis, and partial oxidation [27]. The typical temperature range in which gasification processes have been developed at full scale is 800–1100 °C, while in the processes that use oxygen for the gasification step, the process temperatures are 500–1600 °C [28]. The syngas is composed of a mixture of CO, CO_2, H_2O, H_2, CH_4, and light hydrocarbons. Along with these products, different impurities and contaminants such as tars, nitrogen products, sulphur compounds, and hydrogen halides are produced based on the biomass composition [29]. Moreover, the composition of the raw synthesis gas at the gasifier outlet is not suitable for direct introduction into the methanol synthesis reactor due to the impurities and low H/C ratio of the syngas [30]. For these reasons, different stages of cleaning and conditioning of the produced syngas must be integrated.

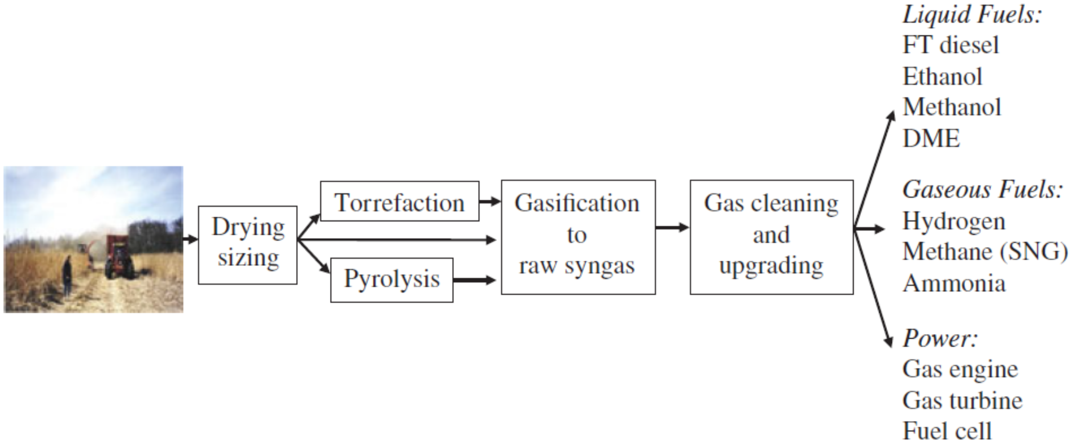

Figure 2. General Process Scheme of Biomass to Different products [31]

As mentioned, the process of gasification of biomass for conversion into synthesis gas involves several critical stages. The biomass is dried using waste heat from the gasifier's cooler sections, effectively removing any residual moisture. This drying process takes place within a temperature range of 100°C to 200°C. The process also involves pyrolysis in the temperature range of 200-700°C, a thermal breakdown of the biomass with a small amount of oxidant, creating liquid, solid, and gaseous chemicals. Cracking reactions, which start with the formation of synthesis gas, are also a part of this process. In addition to this, gasification involves chemical reactions between the byproducts of the earlier phases to convert the remaining liquid and solid fractions into syngas [32]. Depending on the size, compostion, and rate of heating of the fuel particles, these reactions might take place simultaneously or sequentially [33]. A simplified scheme of the gasification subprocesses is reported in Figure 2. The simplified representation of reactions in biomass gasification is as follows [11]:

$$C_{(s)} + O_2 \rightarrow CO_2 \qquad 1)$$

$$C_{(s)} + H_2O \rightleftharpoons H_2 + CO \qquad 2)$$

$$C_{(s)} + CO_2 \rightleftharpoons 2CO \qquad 3)$$

$$C_{(s)} + 2H_2 \rightleftharpoons CH_4 \qquad 4)$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad 5)$$

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad 6)$$

$$Tar \rightleftharpoons CH_4 + CO + C \qquad 7)$$

An essential factor in this process is the selection of the gasifier type and gasifying agent, which directly impacts process efficiency (defined as useful energy output, including syngas and any co-generated heat or power, divided by the total energy input, including biomass and any additional energy sources used in the process) and syngas quality for subsequent applications [34]. It should be noted that the operating temperature and pressure of a gasifier are heavily influenced by the type of feedstock utilised and the type of reactor employed. The exact syngas composition (CO, CO_2, H_2O, H_2, CH_4) depends on various factors such as the type of biomass, gasifier, temperature, pressure, and the use of air, oxygen, and/or steam as gasifying agents [30]. Table 1 details the influence of selected parameters on biomass gasification outcomes, which are relevant for the biomass-to-methanol conversion by identifying factors that impact syngas yield and composition.

Table 1. Key Parameters Influencing Biomass Gasification Outcomes [35], [36], [37], [38], [39]

Parameter	**Description**
Gasifying Agent	• Oxygen: Used for combustion or partial gasification; higher CO and CO_2 concentration at different levels; highest heating value. • Steam moves towards hydrogen in the ternary diagram; higher H_2 means a higher H/C ratio. • Air: Lower heating value due to nitrogen dilution; increased CO_2, reduced H_2 and CO.
Gasifier Type	• Fixed-Bed Gasifier: Lower syngas amount, high CO, low H_2. • Updraft Gasifier: Low H_2, high CO, high tar requiring purification. • Downdraft Gasifier: Increased H_2, reduced tar, high gas outlet temperature. • Cross-Flow Gasifier: High tar and gas outlet temperature, low efficiency. • Fluidized-Bed Gasifier: Fast rate, stable temperature, less tar, more ash. • Entrained Flow Gasifier: High temperature, intense gasification, almost no tar, low CH_4 and CO_2, high H_2.

Biomass Properties	• Moisture Content: Ideal 15-30 wt%; higher moisture increases energy for drying. • Volatile Fraction: High volatile content promotes tar and affects syngas concentration. • Ash Content: Influence of alkali metals in ash on syngas yield. • Cellulose/Hemicellulose Ratio: Higher ratio increases syngas yield.
Operating Conditions	• Temperature: Higher temperatures increase syngas production and calorific value; ideal ranges vary by biomass type. • Pressure: Higher pressure decreases syngas yield but increases heating value. • Heating Rate: A slower rate leads to lower gas yields and higher tar.
Additional Factors	• Pretreatment (e.g., Torrefaction): Improves biomass quality for gasification. • Equivalence Ratio (ER): Ideal range 0.2-0.3; affects gasification completeness and syngas yield. • Gas Cleaning Requirements: Affected by tar and solids emissions, especially at higher temperatures.

2.2.2 Gasifier Types

Gasifiers can be roughly classified into three main types based on the gas-solid contacting mode: fixed or moving bed, entrained-flow bed, and fluidised bed [40]. Figure 3, illustrates these different types of gasifiers. Fixed bed gasifiers supply gasification agents from either the top (down-draft) or bottom (up-draft) of a stationary bed containing layers of feedstock. The efficiency and simplicity with which this gasifier processes solid feedstocks are well-known. However, they have low heat transfer efficiency, resulting in non-uniform temperature distribution, fuel agglomeration, and a producer gas with high concentrations of tars [41].

Entrained flow gasifiers operate at very high temperatures (>1300°C) and pressures, with pulverised feedstock entrained in an oxidant stream, allowing for processing a wide range of feedstocks, including low-grade coal and biomass. They operate concurrently with a very fine particle size, as residence times in the reactor are very low. It produces syngas with a low tar content, which is suitable for downstream applications but with high operational and maintenance costs [42].

Fluidised bed gasifiers operate by suspending solid biomass particles in an upward flow of gasifying agent and bed material at a sufficient velocity to keep these in a suspension state. The biomass particles are instantly heated to the bed temperature after being mixed with the bed material [43]. The bed material is usually the catalyst, such as dolomite, alumina, and olivine, to reduce tar formation, but inert materials like silica sand can also be an alternative [44]. The primary function is to uniformly transfer heat throughout the gasifier, preventing the development of localised hot spots [45]. This design feature facilitates optimal heat and mass transfer, given the extremely good mixing between feed and oxidant [46]. In addition, fluidised bed gasifiers' flexibility to different feedstock moisture contents and particle sizes contributes to their attractiveness for biomass gasification.

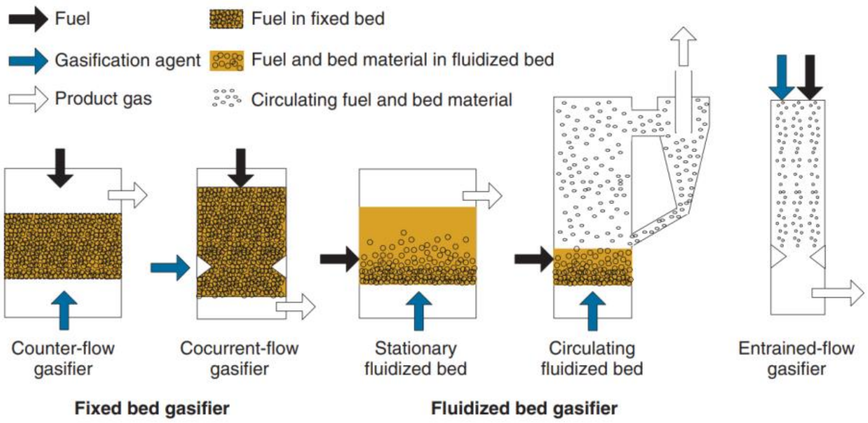

Figure 3. Different types of gasifiers [47]

2.2.3 The Role of Gasifying Agents

Gasifying agents commonly used include CO_2, O_2, steam, and air, with the composition of the produced syngas being affected by the type of agent used. The use of air as the gasifying agent in biomass gasification, the resulting syngas has a low heating value, which makes it suitable for generating electricity and heat but not for producing liquid biofuels or biochemicals due to the high nitrogen levels and low hydrogen content [48]. On the other hand, CO_2 gasification presents additional challenges, as it requires an external heat source and a pure CO_2 stream when used as a gasifying agent [49], which can complicate the process and increase operational costs. According to Couto et al.'s analysis of the gasification process, using steam or oxygen as a gasifying agent significantly increases the amount of hydrogen and carbon monoxide produced, which in turn improves the syngas heating value [50].

Methanol production from biomass using oxygen gasification has several advantages over other gasifying agents. Firstly, partial oxidation provides energy for gasification, eliminating the need for external heating and steam production. Secondly, the high temperatures produced during the process are ideal for synthesising CO and H_2 [51]. As shown in Table 2, steam gasification yields syngas with a superior heating value (10-14 MJ/Nm^3) compared to oxygen gasification (10-12 MJ/Nm^3). This can be attributed to the water-gas-shift reaction inside the reactor, which promotes hydrogen production under steam gasification.

Table 2. Typical Composition Syngas Composition for oxygen and steam gasification in fluidised bed gasifiers

Component	**Oxygen Gasification (vol%)**	**Steam Gasification (vol%)**
Carbon Monoxide (CO)	20-30	20-25
Carbon Dioxide (CO_2)	25-40	20-25
Hydrogen (H_2)	20-30	30-45
Methane (CH_4)	5-10	6-12
Nitrogen (N_2)	0-1	0-1

LHV (MJ/Nm^3)	10-12	10-14
Tar content (g/Nm^3)	1-20	1-10

Source: Adapted from [47]

Evidence suggests that higher temperatures can be achieved by employing pure oxygen instead of air, increasing the overall efficiency and reducing the size of downstream equipment, resulting in more efficient and cost-effective methanol production [52]. However, it is essential to consider the environmental impacts of using oxygen in biomass gasification, which is highly energy-demanding [48]. It might contribute to greenhouse gas emissions if derived from fossil fuels. It is possible to produce syngas with less inert content and higher energy content per unit of volume by using pure oxygen, enriched air oxygen, and oxygen/steam mixtures. However, using only oxygen as a medium can lead to overheating and damage, so steam is usually added [53]. In connection with this, steam is often used because it promotes H_2 production through the water-gas shift reaction and can help control the temperature in the gasifier [54]. Therefore, it can be argued that using a mixture of steam with oxygen as a gasifying agent for methanol synthesis is beneficial for increased heating value of the syngas and reduced downstream equipment size. Because of this, steam-oxygen gasification in fluidised beds is attracting interest for its excellent performance and high-quality syngas that, in contrast to conventional air-blown gasifiers, are nearly nitrogen-free and have a greater calorific value [55].

2.3 Syngas Cleaning and Conditioning

Some significant properties must be considered when using biomass gasifier product syngas for synthesis applications. These include the H_2:CO ratio, the amount of methane and higher hydrocarbons, catalyst poisons like sulphur, nitrogen, and chlorine components, and the operational pressure of the gasifier [47]. Depending on the syngas's end use, gas cleanup involves an integrated, multi-step process to remove contaminants such as tars, acid gases, ammonia, alkali metals, and particles. Gas conditioning makes the gas composition suitable for fuel synthesis through final modifications [56]. This section discusses the theoretical concepts related to syngas cleaning and conditioning.

2.3.1 Syngas Cleaning

The syngas from biomass gasification contains various contaminants, including particulate matter, tars (such as naphthalene, phenanthrene, and toluene), sulfur species (e.g., H_2S, COS, thiophenes, mercaptans), chlorine species (e.g., HCl), alkali and trace elements (e.g., KCl, KOH, NaCl), and nitrogen compounds (e.g., NH_3, HCN, pyrroles, pyridines)[31]. The presence of particulate matter, tars, sulfur and acid compounds, and trace metals in the feedstock can lead to corrosion, erosion, deposits, and poisoning of catalysts [57]. The maximum level of contaminants in the syngas depends on each type of application, Table 3 shows the upper limits of contaminants in gasification syngas for selected applications.

Table 3. Upper limits of contaminants in gasification syngas for selected applications

Applications	Tars (mg/N m^3)	Sulphur contaminants (ppmv)	Nitrogen contaminants (ppmv)	Alkali (ppmv)	Halides (ppmv)
Gas turbine	n/a	<20	<50	<0.02	<1
FT synthesis	<0.1–1[1]	0.01	0.02	0.01	0.01
Methanol synthesis	<1	<1[2]	0.1[2]	n/a	0.1[2]

Source: Adapted from [29]

Several methods for gas cleaning exist, and the choice depends on the specific impurities present in the syngas and the desired composition of the clean syngas, which depends on the syngas application. Two broad categories classify syngas cleaning: wet gas cleaning and dry gas cleaning. Wet gas cleaning, typically conducted at lower temperatures (15° C to 100° C), uses liquids to absorb and chemically react with pollutants, effectively handling a variety of contaminants through processes like scrubbing and washing. Dry gas cleaning, on the other hand, relies on physical and chemical adsorption using solids like activated carbon or specialised filters and is often preferred in environments where the introduction of moisture is undesirable [29].

The particulate matter must be removed from the syngas to meet emission standards and suit downstream applications, including ash, bed material, carbonaceous solids, and fine droplets. These particles range from 0.1 to 100 μm and include inorganic compounds like alkaline earth metals, silica, alkali species, and iron, with minor species such as Zn, Pb, and Cu. Cleaning can be performed at low (ambient), intermediate (up to 350°C), and high temperatures (>350°C). Different types of equipment, such as cyclones, electrostatic filters, and scrubbers, are used, each effective for various particle sizes and temperatures [31].

Tar is a complex mixture of hydrocarbons produced during gasification. Among the tar removal technologies, the following three are noteworthy: uncatalysed partial oxidation, catalytic steam reforming, and absorption [58]. For the scope of this thesis, the focus is exclusively directed towards absorption, specifically OLGA. The OLGA tar removal technology, developed by the Energy Research of the Netherlands (ECN, now TNO), is based on gas scrubbing with oil. The technology consists of multiple absorption stages where the oil acts as an absorbent and then is regenerated. This process aims to produce a "tar-free" product gas—that is, gas free of tar-related problems—by focusing on the behaviour and characteristics of tar rather than its composition. This is achieved by cooling the product gas to collect liquid tars and absorbing gaseous tars in the scrubbing liquid at the temperature, using two separate scrubbing columns for efficiency and operational considerations [59]. The syngas is first cooled to around 380°C, a phase intended to reduce the gas temperature without causing any component condensation. The gas then goes through a second cooling process to about 80°C. Careful temperature control is crucial to create an ideal environment where tars can be selectively absorbed in the next step without causing water condensation. The syngas is treated in an absorber to remove tar after cooling and then sent to a water condenser. The critical principle of OLGA is to keep water in the vapour phase while condensing tars [58].

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[1] Units are in ppmv

[2] Units in mg/N m^3

The OLGA technology has several advantages over traditional tar removal techniques. It ensures that the clean product gas has a tar dewpoint lower than the application temperature and helps to increase system availability and reliability by removing condensation and fouling issues. Tars can be recycled back into the gasifier, reducing expenditures on tar waste treatment. Process water pollution can be avoided by removing tars before water condensation. Its scalability further facilitates implementation at various scales, ranging from lab to commercial, making it an adaptable solution for biomass gasification processes.

Different technologies, including physical absorption, chemical absorption, adsorption, and membrane separation, are used in the context of acid gas removal [60]. Conventional processes for removing acid gases typically involve their countercurrent absorption from the syngas using a regenerative solvent in an absorber column [61]. Similarly, the acid gas removal from the syngas will focus on the Rectisol process in this study. The Rectisol process is a cryogenic gas purification method that removes carbon dioxide (CO_2), sulphur (H_2S, COS), and trace components from syngas through physical absorption. This process utilises methanol at very low temperatures, resulting in unmatched gas purities due to its strong Henry's law absorption coefficients. It is particularly essential for chemical reactions that require sulphur removal to concentrations lower than 0.1 ppmv, such as in producing methanol, ammonia, and methanation [62]. However, the process requires significant refrigeration, leading to high initial investment and operating costs [46]. Despite these challenges, the Rectisol process offers high selectivity for H_2S over CO_2 and the capability to remove COS, making it a valuable method for syngas cleaning in biomass gasification.

2.3.2 Gas Conditioning

One of the significant challenges in methanol production from biomass lies in the conditioning of the syngas composition produced from biomass gasification. Syngas has a lower hydrogen content than carbon in a typical biomass gasification process. This is strongly related to the elemental composition of biomass, which is highly deficient in hydrogen compared to carbon, resulting in syngas far from having adequate composition for methanol synthesis. Hydrogen is only 6–7 wt%, while carbon is about 47–49 wt% of the dry, ash-free woody biomass. Gas conditioning aims to adjust the syngas to the proper stoichiometric conditions for methanol production from carbon monoxide, carbon dioxide, and hydrogen [63]. The formation of methanol from syngas containing both carbon monoxide (CO) and carbon dioxide (CO_2) can be described by the following equilibrium reactions [13]

Equation 1

$$CO + 2H_2 \rightleftharpoons CH_3OH$$

Equation 2

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$$

For these reactions to proceed efficiently, the syngas must have the optimal molar composition of its components. The Stoichiometric Number (SN), often denoted as S, is typically used to describe syngas composition for methanol synthesis. The SN should ideally be slightly more than or equal to 2 for the following reasons [46], [64]:

1. Ensuring Sufficient Hydrogen for Both CO and CO_2 Reactions: A Stoichiometric Number of 2 ensures that there is enough hydrogen to support both the CO and CO_2 hydrogenation reactions, as reflected in Equations 1 and 2.
2. Driving Reactions to Completion: This ratio provides sufficient hydrogen not only to convert CO and CO_2 to methanol but also to maintain a slight excess of hydrogen. This excess is beneficial for driving the reactions to completion and compensating for any side reactions or hydrogen losses that may occur during the process.
3. Accounting for Simultaneous Occurrence of Both Reactions: In industrial processes, the CO and CO_2 hydrogenation reactions occur simultaneously. An S ratio slightly above 2 ensures that the syngas composition can efficiently support both reactions.

Equation 2

$$S = \frac{(moles\ H_2 - moles\ CO_2)}{(moles\ CO + \ moles\ CO_2)}$$

Compared to the optimum stoichiometry for methanol synthesis, values of S below 2 suggest a hydrogen deficit, while values above 2 indicate an excess of hydrogen. [64]. Syngas produced from biomass frequently has S ratio below 2 (with ranges between 1 and 2). Thus, the syngas composition has to be adjusted for methanol synthesis [13], [65]. In this context, two broad alternatives are utilised to modify the S ratio of syngas produced from biomass to synthesise methanol: Hydrogen conditioning and CO_2 conditioning. Examples of hydrogen conditioning are Water Gas Shift (WGS) and hydrogen addition from a separate process [66]. Conventionally, the water-gas shift (WGS) reaction increases the H_2 composition by the inherent reaction of syngas. However, this process requires the separation of the additional CO_2 through acid gas removal techniques, increasing the energy and economic requirements of the process. As a result, the carbon conversion of biomass to methanol is significantly reduced [67]. On the other hand, a separate hydrogen stream can be added using water electrolysis [68]. In addition, less explored techniques that involve the conditioning of the CO_2 produced in gasification, such as CO_2 co-electrolysis and Reverse Water Gas Shift (RWGS), present alternative approaches to modifying the syngas composition will be examined in the next section.

2.3.2.1 Water Gas Shift

This process involves the reaction of carbon monoxide and steam over a catalyst, typically iron or copper, to produce carbon dioxide and hydrogen gas. In typical industrial applications, the High temperature -WGSR is carried over Fe-Cr catalysts, and the Low Temperature-WGSR is carried over Cu-Al-Zn catalysts [69]. This reaction is strongly exothermic ($\Delta H_r^o = -40.6\ \frac{kJ}{mol}$) and can be represented by Equation 3[70]:

Equation 3

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

Although the equilibrium favours product formation at lower temperatures, reaction kinetics are quicker at higher temperatures. Consequently, the catalytic water-gas shift reaction starts in a high-temperature shift (HTS) reactor at 350-370°C, where conversion is restricted by equilibrium at high temperatures. To further increase CO to CO_2 conversions, for the production of H_2, the gas from the HTS reactor, cooled to 200-220°C, is passed through a low-temperature shift (LTS) reactor. Approximately 90% of CO converts to CO_2 in the HTS reactor, and 90% of the remaining CO in the LTS reactor [71]. A major limitation of the WGS process is the necessity to separate the by-product CO_2, which can significantly increase capital and operational expenditures while also reducing carbon efficiency.

2.3.2.2 Water Electrolysis

Integrating water electrolysis into biomass gasification is a promising approach to adjusting the S ratio. Directly injecting electrolysis-produced hydrogen into the syngas before methanol synthesis eliminates the need for a water-gas shift unit and reduces CO_2 removal requirements. Additionally, the oxygen byproduct from electrolysis can serve as a gasifying agent in biomass gasification [68].

Water electrolysis technologies can be broadly categorised into three main types: alkaline water electrolysis, proton exchange membrane water electrolysis, and solid oxide electrolysis cells. Each technology has unique advantages and limitations, making it suitable for different applications and operating conditions [72].

Alkaline Water Electrolysis (AWE) is a well-established technology that utilises an aqueous alkaline electrolyte, typically potassium hydroxide (KOH) or sodium hydroxide (NaOH), with electrodes often made of nickel and coated with noble metals. AWE operates at ambient pressures and has an efficiency ranging from 50 to 60%. While it has lower investment costs, its slower response time and relatively lower efficiency are notable drawbacks[73].

In contrast, Proton Exchange Membrane (PEM) Electrolysis offers a more modern approach. It uses a solid polymeric membrane as the electrolyte and noble metal-based electrodes. PEM systems can operate at temperatures up to 80°C and achieve efficiencies between 55 to 70%. They are particularly suited for renewable energy integration due to their quick start-up times and ability to handle fluctuating power supplies. However, the high cost of membrane and electrode materials, as well as ongoing development challenges, pose significant barriers to widespread adoption [73].

Solid Oxide Electrolyser Cells (SOEC) represent the high-temperature option, utilising a solid ceramic membrane (yttria-stabilized zirconia) as the electrolyte. The electrodes typically consist of a nickel-yttria stabilized zirconia (Ni-YSZ) cermet for the cathode and lanthanum strontium manganite (LSM) or lanthanum strontium cobalt ferrite (LSCF) for the anode [74].SOEC operates at high temperatures up to 900°C, which not only achieves higher efficiencies but also allows for the utilisation of high-temperature heat sources, further enhancing the system's overall energy efficiency. However, the complex thermal management, material challenges at high temperatures, and slow start-up times are notable limitations that affect the practical deployment of SOEC in scenarios requiring quick dynamic responses [73].

In conclusion, integrating biomass gasification and water electrolysis technologies provides a supplementary hydrogen source, potentially optimising the S ratio for methanol production. The selection of an appropriate water electrolysis technology—whether AWE, PEM, or SOEC—depends upon multiple parameters, including energy efficiency, capital expenditure, and operational flexibility within the integrated system. For instance, while AWE offers lower investment costs and proven reliability, its lower current densities and limited ability to handle intermittent power inputs may constrain its application in systems coupled with variable renewable energy sources. Conversely, PEM electrolysis exhibits superior dynamic response characteristics, potentially facilitating better integration with fluctuating biomass gasification outputs.

2.3.2.3 Reverse Water Gas Shift

The reverse water–gas shift (RWGS) reaction is the endothermic conversion of CO_2 and H_2 into CO and water, requiring elevated temperatures to achieve significant CO_2 conversion [75]. This process could be applicable for biomass syngas conditioning by converting excess CO_2 into CO, therefore enhancing the carbon utilisation in the system [76]. However, additional H_2 from electrolysis must be injected before RWGS for this reaction to take place [77]. Although RWGS could have significant advantages in syngas conditioning, its economic feasibility has to be proven, particularly for the specific requirements for methanol synthesis.

The RWGS reaction operates most effectively at temperatures between 600-1000°C and pressures up to 30 bar, which favours CO production over CO_2 and CH_4. High temperatures are particularly beneficial, as they drive the equilibrium toward CO production and enable faster reaction rates [78], [79]. However, at lower temperatures, the undesired CO_2 methanation reaction can occur, reducing the selectivity for CO. This makes precise temperature control essential for maintaining process efficiency and achieving the desired syngas composition [76].

2.3.2.4 CO_2 and H_2O Co-electrolysis

The three main competing technologies for electrochemical conversion of CO_2 to CO are low-temperature electrolysis, molten carbonate electrolysis, and solid oxide electrolysis (SOEC). When considering these three options' technological maturity, achievable conversion rates, and energy efficiencies, SOEC emerges as a particularly suitable technology for integration with biomass gasification processes [76]. The working principle involves the simultaneous reduction of water to hydrogen and CO_2 to CO at the cathode, producing syngas. Oxygen ions generated in these reactions move through the electrolyte to the anode, forming oxygen gas. This process effectively combines high-temperature electrolysis with the catalytic Reverse Water Gas Shift (RWGS) reaction to convert CO_2 and H_2O into valuable fuels [81]. High-temperature operation and energy management in Co-SOECs enable low specific electricity consumption and efficient heat integration, such as heat supply from solar heat, industrial waste heat, or the heat from internal energy losses in the stack. The drawback in co-electrolysis is the carbon deposition via the Bosh and Boudard reaction occurring at high temperatures [82].

Integrating this technology into biomass syngas conditioning could significantly optimise the syngas composition. By passing the purified syngas through a gasifier in the presence of steam, the proportions of CO and H_2 can be enhanced, achieving an S-value greater than 2. This technology is compatible with all standard gasifier technologies and has the potential for efficient S adjustment for high carbon efficiency and product yield. However, there are some challenges associated with this configuration. The need for the entire syngas stream to pass through the electrolysis process results in higher capital and operating costs. Furthermore, impurities present in the syngas feed can potentially lead to catalyst poisoning, which can degrade performance over time [76].

Although it has been successfully demonstrated at the lab scale and in some pilot projects, a widespread commercial application still requires further research and development to optimise efficiency, reduce costs, and improve the durability of co-electrolysis systems for industrial use [83]. Sunfire's SynLink system is a highly advanced, state-of-the-art technology that uses high-temperature solid oxide electrolysis cells (HT-SOEC) to produce sustainable synthesis gas. The system operates at a scale of 150 kW and at a temperature of 850°C, which allows it to achieve 80% single-pass CO_2 and H_2O conversion. Additionally, the system has high efficiency and durability, with a remarkable stack lifespan of 40,000 hours and 100% Faradaic efficiency [84].

2.3.3 Methanol Synthesis

As already mentioned in section 2.3.2, the production of methanol from synthesis gas containing both carbon monoxide (CO) and carbon dioxide (CO_2) can be described by their catalytic hydrogenation reactions [13]. The first reaction is the primary methanol synthesis process, which is assisted and facilitated by a small amount of CO_2 (in the range of 2 and 10%) in the feed [85]. The reactions are exothermic, so they are most effectively driven under high-pressure and low-temperature conditions [11]. In the case of conventional methanol production, this is achieved using fixed-bed reactors filled with catalyst pellets, functioning in the gas phase. These methanol synthesis reactors typically operate within a 50-150 bar pressure range and a temperature between 230-270°C. To prevent the catalyst from sintering and becoming inactive, the temperature is kept in the synthesis reactor below 300°C [86]. This catalytic process uses chromium, zinc, or copper oxide-based catalysts [87]. The single-pass carbon conversion rate through a methanol reactor ranges from 50% to 80% [88]. This conversion depends on reaction conditions, catalyst, solvent, and space velocity. Experimental results show 15 – 40 % conversion for CO-rich gases and 40 – 70 % CO for balanced and H_2-rich gases [30].

In methanol synthesis processes, there are two main types of reactors based on how they manage heat during the reaction process: adiabatic and isothermal. Figure 4 below shows the schemes for both type of reactors and their respective temperature profile [89]. The adiabatic reactor (left) uses multi-stage internal cooling, decreasing stepped temperature and increasing methanol yields (shown by the stepped red line). The isothermal reactor (right) employs continuous cooling with boiling water, leading to a smoother temperature profile and improved yields (depicted by the curved red line)

1. Adiabatic Reactors. Adiabatic reactors commonly include a series of fixed bed reactors, with the removal of the heat, operated downstream of each reactor. The reaction is quenched by introducing cold gas numerous times in adiabatic reactors with a single catalyst bed. As a result, the reactor's axis has a sawtooth-shaped temperature profile. These kinds of reactors are characterised by low installation cost and high production capacity; however, because of the adiabatic process, the high equilibrium temperatures imply very low conversions for each cycle and, consequently, a high recycle ratio, a high dilution of the reagents, and a high volume of catalysts [88],[89].
2. Isothermal reactors. The isothermal reactors employ a standard design with a tubular structure and catalysts inside tubes surrounded by boiling water for heat removal, regulating cooling through the steam drum's pressure. In principle, the isothermal

reactor acts as a heat exchanger, utilising water or gas for cooling around the tube bundle's mantle, facilitating high conversions and lower catalyst volumes. However, achieving significant reaction rates requires temperatures between 240°C and 260°C alongside a high recycle ratio. Despite the superior performance in terms of conversion rates, the isothermal system's installation costs significantly exceed those of an adiabatic system (often in the range of 20% to 50% higher), with the added limitation of plant size due to the tube bundle dimensions [88],[89].

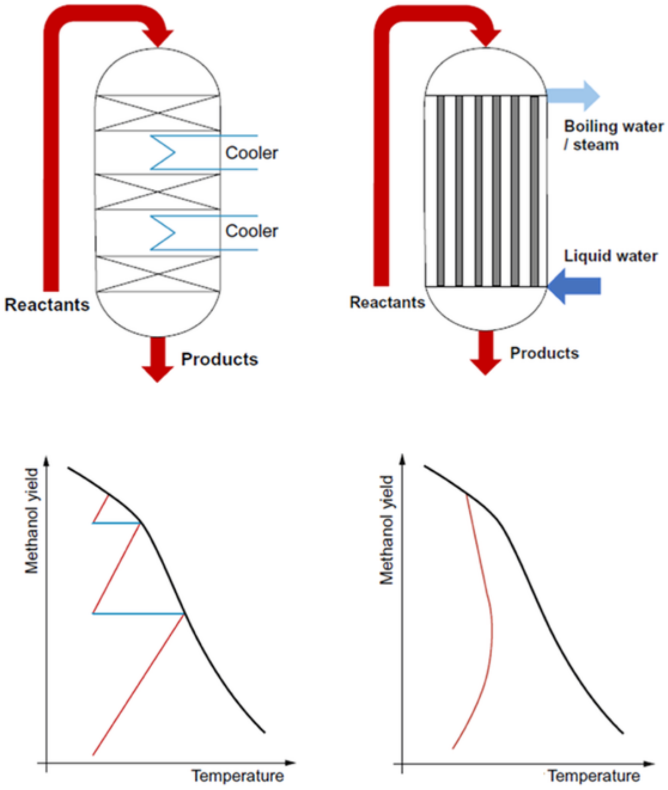

Figure 4. a) Adiabatic and b) Isothermal reactors and their temperature profile [89]

The reactor output stream contains a mixture of methanol and unconverted syngas, which is then cooled through heat exchange with the boiler feed water for the steam cycle and other process streams. The methanol is separated from the unconverted syngas by condensing it. The unreacted syngas is primarily recycled back to the entrance of the methanol synthesis reactor [90]. However, to prevent the accumulation of impurities, a small portion of this recycled syngas is purged from the system. This purge stream helps maintain the purity of the syngas in the reactor, ensuring optimal reaction conditions and preventing impurity build-up [88].

2.3.4 Methanol Purification

The crude methanol leaving the reactor becomes a mixture of methanol, water, and residual gases [91]. Thus, the distillation of crude methanol is needed to separate such impurities. The distillation process involves the removal of components boiling at a lower temperature than methanol in a light ends column, followed by the distillation of pure methanol in one or more distillation columns. If the columns operate at different pressures, the heat of condensation of the vapours from the column operating at higher pressure can heat the column at lower pressure. Distillation systems can include one to four columns, depending on the required product quality and the composition of byproducts from the methanol synthesis catalyst used to purify crude methanol. Additionally, some components form azeotropic mixtures with methanol, requiring special attention during distillation [88].

Conclusion of Biomass to Methanol Process Concepts

Through this section the process concepts of converting biomass to methanol were examined. First, the process starts with biomass gasification, transforming solid biomass into syngas. Different gasifiers (fixed-bed, fluidized-bed, and entrained-flow) and gasifying agents (oxygen, steam, and air) were discussed, each affecting syngas efficiency and quality. Steam-oxygen gasification is particularly noted for producing high-quality syngas suitable for methanol synthesis. The syngas undergo extensive cleaning to remove impurities on it. Syngas conditioning refers to adjusting the syngas to make it suitable for composition for methanol synthesis. Conditioning techniques, such as the water-gas shift reaction, and water electrolysis, adjust the hydrogen content to achieve the optimal stoichiometric ratio for methanol production. CO_2 Co-electrolysis and reverse water-gas shift reaction are focused on the adjustment of the utilisation of CO_2 in the syngas. Methanol synthesis is conducted in catalytic reactors under high-pressure, low-temperature conditions, followed by distillation to achieve high-purity methanol.

2.4 Knowledge Gap Identification

As already mentioned, syngas produced through biomass gasification typically has a lower hydrogen content than carbon, resulting in an inadequate S ratio for methanol production, often below two because of an excess of CO_2. This requires conditioning or upgrading syngas to make its composition suitable for methanol production. Two primary approaches for this conditioning are hydrogen (H_2) conditioning and carbon dioxide (CO_2) conditioning. Conventionally, the water-gas shift reaction is used to increase the hydrogen content in syngas, but it also elevates the carbon dioxide levels, necessitating CO_2 removal and ultimately reducing carbon conversion efficiency. Thus, removing carbon from the syngas limits, to a great extent, the possible carbon efficiency and, consequently, the methanol yield by keeping the biomass potential from being completely used [76].

Different studies present an analysis of the integration of water electrolysis with biomass gasification. Holmgren et al. reported that adding hydrogen instead of using the water-gas shift (WGS) reaction could potentially increase methanol yield by 35% [48]. Similarly, Fournas and Wei's study showed that injecting electrolysis-derived hydrogen into syngas before methanol synthesis eliminates the need for a WGS unit and excess CO_2 removal, potentially doubling the methanol yield per biomass unit [68]. Zhang et al. assessed the techno-economic benefits of integrating solid-oxide water electrolysis, demonstrating enhanced carbon conversion efficiency and reduced production costs. In addition to this, their study also revealed that the single-pass conversion rate of CO_2 to methanol is considerably lower (approximately 28%) compared to the conversion rate of CO to methanol (about 67%) [74]. This suggests that syngas with a higher CO content would be preferred for methanol synthesis, as it would yield higher amounts of methanol.

An alternative strategy involves utilising the excess CO_2 in syngas, avoiding it from having to be separated. CO_2 conditioning technologies such as the Reverse Water-Gas Shift (RWGS) reaction and CO_2 co-electrolysis are two alternatives worth investigating, as they can influence the material efficiencies, energy consumption and the overall economy of the process. The RWGS reaction converts CO_2 and H_2 into CO and water, thus reducing the excess CO_2 while increasing the CO content in the syngas. Whereas, in CO_2 co-electrolysis CO_2 and H_2O are co-electrolysed to produce H_2 and CO, resulting in the desired syngas mixture for methanol synthesis.

CO_2 co-electrolysis is gaining attention for its potential to address the limitations of water electrolysis. It can leverage the excess CO_2 in the syngas to adjust its composition, making it richer in hydrogen and carbon monoxide, and therefore to be suitable to be used for methanol synthesis. However, directly integrating CO_2 co-electrolysis with biomass gasification for syngas upgrading remains relatively unexplored [76]. Pozzo et al. studied a Biomass-to-Methanol conversion process utilising a solid oxide co-electrolysis cell, which doubled methanol productivity and achieved a high efficiency of 69.5% through efficient integration and use of CO_2 from biomass gasification [92].

Romano et al. investigated three configurations of biomass-to-methanol plants with SOEC: steam electrolysis for hydrogen generation, co-electrolysis of steam and CO_2 separated from syngas, and direct supply of purified bio-syngas to the SOEC. Their findings showed that all configurations had carbon efficiencies over 90%, with the syngas-electrolysis configuration having the lowest levelised cost of methanol (LCOM) and the CO_2-co-electrolysis configuration having the highest LCOM due to higher electricity consumption and capital investment [93]. Research supports using syngas directly in solid oxide electrolysers, which can handle some impurities. For instance, Butera et al. demonstrated the feasibility of processing biomass-derived syngas in SOEC for methanol production, highlighting the application of syngas in co-electrolysis after adequate cleaning, but also acknowledging the need for further research into the impact of impurities on SOEC performance [76], [94].

In the case of RWGS, when H_2 is added to the syngas in an RWGS reactor, CO_2 can be converted into CO, maximising carbon efficiency. Thus, allowing for CO_2 shift and CO_2 utilisation before synthesis and S adjustment for high carbon efficiency [76]. In view of this, Tarifa et al. proposed enhancing syngas production from biomass gasification by promoting the RWGS. Using a $Fe/MgAl_2O_4$ -based catalyst with varying Ni content, they increased the CO content in the syngas [95]. Hillestad et al. found that the integration of RWGS with biomass gasification for a syncrude process (with the addition of hydrogen from electrolysis) increases the CO and H_2 composition to not only the desired level but also the carbon efficiency, resulting in a better economic performance when compared to conventional processes [75]. Nonetheless, no cases were found in which the integration of a biomass gasification process with RWGS for syngas conditioning and subsequent synthesis to methanol was studied from a techno-economic standpoint.

Despite the advancements mentioned above, the topic has significant knowledge gaps. The techno-economic synergies and trade-offs of syngas upgrading through CO_2 conditioning, compared to hydrogen conditioning, for methanol production in biomass gasification plants, have not been directly studied. While the H_2 syngas conditioning routes and synthesis have been extensively investigated, other routes, such as RWGS and CO_2 and H_2O co-electrolysis, show promise but require further validation. Especially when directly comparing them in terms of technical, economic, and environmental aspects. Additional research is needed to better understand the integration of these technologies with biomass gasification for methanol production. By addressing these gaps, this research will provide valuable insights into the techno-economic viability of sustainable methanol production.

This research aims to address these knowledge gaps by conducting a comparative study of these technologies, proposing specific metrics and indicators for technical, economic, and environmental assessment, and providing a comprehensive techno-economic analysis. The significance of this work lies in determining the synergies and trade-offs for the studied options, precisely by comparing directly the CO_2 upgrading with the extensively studied H_2 syngas conditioning routes. Ultimately, the outcomes of this study can be applied in the techno-economic viability of biomass gasification-to-methanol plants. The proposed routes aim to identify the optimal conditions for each configuration based on specific objectives. The choice of configuration will depend on the particular criteria being optimized, such as maximizing methanol yield with minimal biomass input, reducing electricity consumption, minimizing the Levelized Cost of Methanol (LCOM), or lowering environmental impact. In some cases, the optimiation may involve balancing multiple objectives, such as a combination of these factors

3. Basis of Design, Methodology and Model Development

First, the methodology for the current work is presented. This is followed by the basis of design used to develop this research work. Finally, the model development is given through a description of analytical models, including assumptions for simulation.

3.1 Methodology

To effectively compare different configurations of syngas conditioning for methanol production via biomass gasification, it is crucial to have a structured research framework. This thesis uses a methodology to identify the techno-economic synergies and trade-offs between using CO_2 versus water electrolysis in a biomass-integrated methanol plant. The approach involves a sequential process that starts with a comprehensive literature review and leads to the development and analysis of various models. The research framework consists of several interconnected stages, as the provided flowchart outlines, forming the methodology's foundation. Figure 5 illustrates the different research and components and their relation among them.

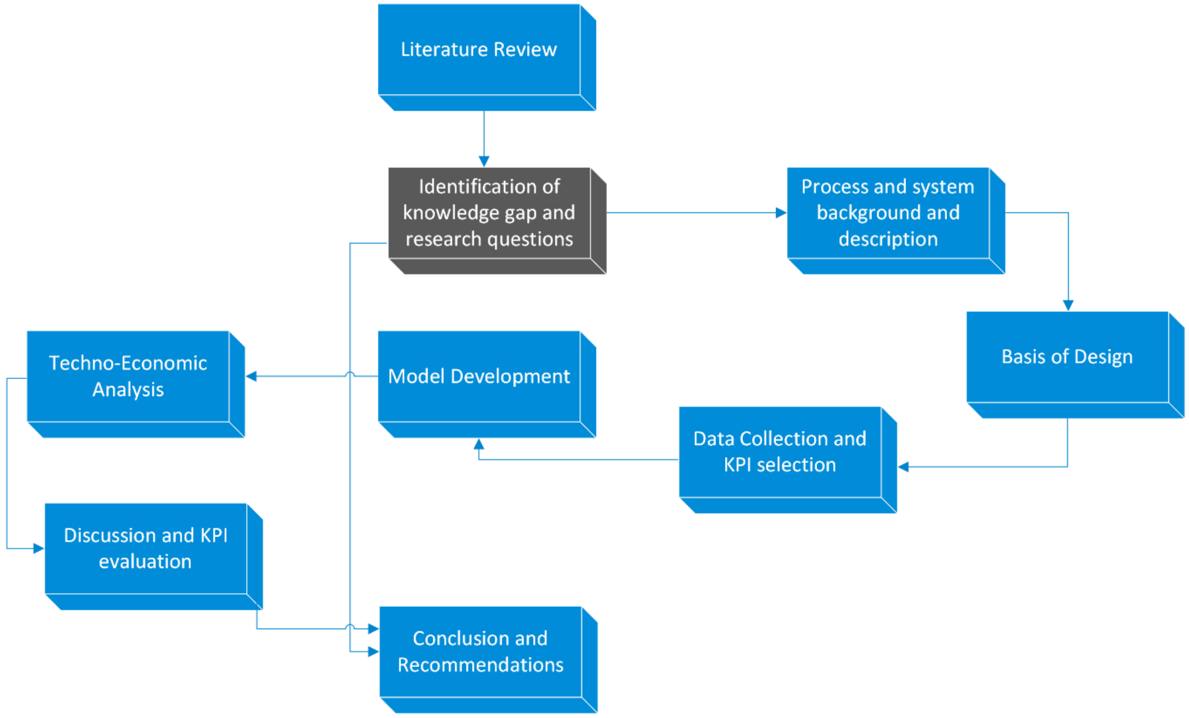

Figure 5. Research Flow Chart

1. **Literature Review**. The literature review provides the basis of this investigation by integrating information about biomass gasification and syngas conditioning technologies, helping to identify knowledge gaps in this field. The research gap is found through critical analysis, which leads to developing the research questions. The research questions aim to guide the research, specifically in evaluating the techno-economic trade-offs and synergies associated with CO_2 compared to H_2 syngas conditioning technologies in a biomass gasification-to-methanol plant.
2. **Data Collection.** As part of the literature review and preceding the development of the model in Aspen Plus, different data on process inputs, conversion efficiencies, and other technical indicators will be sourced from experimental studies and industry reports to ensure comprehensive and accurate process simulations. This also involves collecting information on the state of the art at this point for each configuration, operating conditions, process parameters, and any relevant environmental and economic metrics.
3. **Process and system background and description.** Before discussing the details of the model development, a comprehensive background on the process and system under research is provided. This includes explaining biomass gasification, the process of producing methanol, and the different process concepts for the proposed configurations.
4. **Basis of Design.** This includes selecting design characteristics before modelling, including product quantity and quality, utilities (types and operating conditions), and location. Main reactor options and choices are also determined to establish a solid foundation for model development.
5. **Model Development.** This involves simulating the selected process solution concepts of methanol production through various configurations of syngas conditioning. The process simulation software Aspen Plus is used for this purpose. The models are built with carefully considered assumptions to make the simulations practical and relevant.
6. **Techno-Economic Analysis.** Techno-economic analysis (TEA) is a critical component that uses simulation outcomes to evaluate key performance indicators. This also includes the sensitivity analysis of selected economic parameters to assess their influence on the Levelised Cost of Methanol.
7. **Discussion.** This section discusses the models' and KPIs results in depth. Trade-offs and synergies are highlighted, and the influence of key operating variables is analysed.
8. **Conclusion and Recommendations.** Drawing from the discussion, the thesis will culminate in conclusions and recommendations.

3.2 Basis of Design

This section outlines the foundational design characteristics, focusing on product specifications, feedstock characteristics, process configurations, gas cleaning, utilities and services, location and site-specific factors, main reactor options, project timeframe, and economic assessment. The study will focus on four process configurations for the syngas conditioning to produce methanol from biomass gasification. These configurations chosen for the study, aimed at syngas conditioning, incorporate both conventional options like the water gas shift and water electrolysis, as well as less-studied approaches identified in the knowledge gap section, namely CO_2 and steam co-electrolysis and reverse water gas shift. In this section, the general characteristics of the process design alternatives will be discussed, including parameters such as product quantity and quality, feedstock quality across specified ranges, utilities including types and conditions, and the geographical location of the process.

Establishing these parameters creates a robust foundation for detailed modelling and simulation work. Table 4 summarises the key aspects considered for the process development.

Table 4. Input data for the Process flow model of Biomass to Methanol

Feedstock Type	Wood Pellets from forestry residues [96], [97]
Plant Location	Port of Rotterdam
Project Timeframe	1Q 2019
Gasifier	Pressurised bubbling fluidized-bed gasifier (BFB) developed by the Institute of Gas Technology (IGT) [98], [99], [100], [101]
Methanol Synthesis Reactor and Production capacity	Isothermal multi-tubular methanol reactor with separation units [102] 400 kilo-tonnes of methanol per operating year T: 255 °C; Pressure at reactor inlet 69.7 bar
Methanol Purity	99.9 mol% [6], [103]

3.2.1 Selection of Solution Concepts

Gasification Process Selection

The thermochemical conversion of biomass offers several comparative advantages, including higher productivity, faster conversion rates, established infrastructure, and proven technical expertise in existing conversion processes as compared to biochemical processes [9]. Gasification was chosen over other biomass-to-methanol pathways, such as direct liquefaction or pyrolysis, due to its superior efficiency and scalability in converting various biomass feedstocks into syngas. Biomass gasification is preferred for methanol production because it efficiently converts diverse biomass feedstocks into syngas, a key intermediate for methanol synthesis. This process offers better control over the syngas composition and is more versatile and energy-efficient compared to other thermochemical methods like pyrolysis or liquefaction. Its ability to handle a wide range of biomass types, including low-value or waste materials, makes it an ideal choice for large-scale methanol production [104]. Among the various types of gasifiers, the fluidised-bed gasifier was selected for its efficient heat and mass transfer characteristics, uniform temperature distribution, and flexibility to accommodate different feedstock moisture contents and particle sizes. Additionally, steam-oxygen gasification was chosen to produce syngas with a higher hydrogen content, which is more suitable for methanol synthesis.

Syngas Conditioning Technology Selection

For syngas conditioning, the selection process involved evaluating several technologies to achieve the optimal stoichiometric ratio (S ratio) for methanol production. The following technologies were selected based on the literature review findings and the potential they have in adjusting the syngas composition:

- **Water Gas Shift (WGS):** The WGS reaction was chosen for its ability to increase the hydrogen content in syngas by reacting carbon monoxide with steam. Despite the need for subsequent CO_2 removal, WGS remains a conventional and reliable method to achieve the desired hydrogen levels in the syngas.
- **Proton Exchange Membrane (PEM) Electrolysis:** PEM electrolysis was selected over other electrolysis technologies for its quick start-up times, high efficiency, and ability to integrate with renewable energy sources. The hydrogen produced from PEM electrolysis can be directly injected into the syngas to adjust its S ratio.
- **Reverse Water Gas Shift (RWGS) with PEM Electrolysis:** The combination of RWGS and PEM electrolysis was chosen to utilise the excess CO_2 on the syngas and adjust it to the required composition. The RWGS reaction converts the CO_2 in the syngas into CO and water. When combined with PEM electrolysis, which provides the necessary hydrogen, this approach can potentially increase carbon efficiency and reduce the process's overall carbon footprint.
- **High-Temperature CO_2 and Water Co-electrolysis:** This technology was selected for its potential to utilise the excess CO_2 in the syngas to adjust its composition for a syngas richer in hydrogen and carbon monoxide and, therefore, obtain an optimal S ratio with high carbon efficiency. However, its selection also considers this advanced technology's higher capital and operating costs.

3.2.2 Product Specification

Methanol is classified based on its purity and the maximum permissible content of specific impurities. The methanol purity was set at 99.9 mol% to establish the optimal operational conditions. This purity level is aligned with industry standards [6], [103].

The processing capacity for this study is set to be close to 400 kilo-tonnes of methanol per operating year, revealing the smaller scale typically employed by biomass-based methanol facilities compared to conventional natural gas-based plants. The availability of raw materials in the Port of Rotterdam and the typical capacities of methanol plants were considered when determining the plant capacity. Large-scale methanol plants can produce 1 to 1.7 million tonnes per year (Mt/y) using natural gas as feedstock. Leading licensors in the field, such as Lurgi, Johnson Matthey, and Haldor Topsøe, even offer designs for single-train plants capable of processing up to 10,000 tonnes per day (t/d), translating to even higher annual capacities [88]. However, biomass-based methanol production facilities typically operate at a smaller scale, with projects like the SES Gasification Technology (875 kt/y) and the HTW/ThyssenKrupp project (100 kt/y) demonstrating capacities significantly lower than those of natural gas-based plants [7]. Thus, a production capacity of 400 kilo-tonnes is in the range of existing biomass-to-methanol plants.

3.2.3 Feedstock Characteristics

To be consistent with the feedstock specifications used for the model calibration and validation, wood pellets from a similar type of wood that can be found in the Netherlands were selected. Wood pellets were also chosen given their uniform properties, higher density, reduced tar formation, availability, and extensive research [105]. In the Port of Rotterdam context, using wood pellets as a feedstock for gasification can be justified based on their availability and simplicity of use. The port has excellent connectivity to major wood pellet production regions, ensuring a reliable and consistent supply of wood pellets. It is worth noting that the selected wood pellets are made from forestry residues, which helps meet sustainability criteria. However, using residual wood alone does not fully ensure sustainability; other factors like responsible forest management and transportation impacts must also be considered. The wood pellets to be used are taken from the GoBiGas Project in Sweden and have the characteristics shown in Table 5 [96].

Table 5. Proximate and ultimate analysis of the selected biomass

Feedstock type: **Wood Pellet**	Proximate Analysis (%wt)			Ultimate Analysis (%wt)						
HHV (MJ/kg)	VM	Fixed Carbon	Ash	C	H	O	N	S	Moisture	Ash
18.72	80.57	18.94	0.5	46.6	5.6	39.3	0.1	0	8.1	0.28

Adapted from [96], [97]

3.2.4 Process Configurations

As mentioned in the knowledge gap section, the process configurations examined in this thesis are water electrolysis, water gas shift, reverse water gas shift, and co-electrolysis. For all options studied, the S-ratio will be calculated beforehand to quantify how the syngas composition should be adjusted accordingly. Some details worth mentioning are that for WGS, it will be necessary to remove CO_2 once the shift reaction is completed, whereas, for RWGS, hydrogen from electrolysis will be added so that the reaction can take place. On the other hand, as already mentioned, the oxygen produced in the water electrolysis and co-electrolysis configurations will be used in the gasifier. It is also assumed that the steam and cooling water (in various forms such as LPS, MPS, and HPS) required as utilities and inputs will be externally sourced. Similarly, the necessary oxygen for the WGS configuration will be assumed to be purchased.

3.2.5 Gas cleaning

For the primary cleaning, a sequence of filters and cyclones are employed to remove particulate matter; a similar approach to the OLGA was selected for the tar removal because it has significant advantages over the others, such as the possibility of operating at higher temperatures, thus improving the overall efficiency of the process, and the ability to regenerate the sorbents at high temperatures with hot air. The main difference is that it was modelled under high pressure rather than atmospheric conditions. The OLGA model is based on the work of Srinivas et al. [58]. On the other hand, Rectisol is employed for acid gas removal. The main advantage of Rectisol over other processes is using a cheap, stable, and readily available solvent, a very flexible process, and minimal utility consumption [106]. The system developed for the acid gas removal process is based on the work of Adams [107]. Further details about the Rectisol process employed will be covered in the model development section of this thesis.

3.2.6 Utilities and Services

The main utilities include steam, cooling water, chilled water, electricity, and natural gas. Each utility has specific parameters and conditions optimised for different stages of the production process. Electricity powers various equipment and control systems within the processes studied. Natural gas is a fuel source for fired heaters and other heat-intensive processes. Likewise, cooling removes excess heat from the process and maintains optimal operating conditions. Detailed specifications and additional information can be found in Appendix II.

3.2.7 Location and Site-Specific Factors

The investigation is conducted in the context of the Port of Rotterdam. As the largest methanol hub in northwestern Europe, it facilitates the integration of methanol production with other industrial activities, promoting both economic synergies and environmental solutions. Major players like Methanex, OCI, and Proman, combined with the port's robust infrastructure, make it an ideal setting to investigate these alternative syngas conditioning methods for methanol synthesis [108]. In this sense, a study by Zomer et al. found that the transition to methanol as a maritime fuel can initially be met with the existing production facilities. This study also shows that distribution is feasible and that sourcing may be accomplished through imports through the Port of Rotterdam or through European industrial facilities [109].

3.2.8 Main Reactors Options and Selection

Gasifier Type

The Institute of Gas Technology (IGT) gasifier was chosen for this study's analysis based on a variety of technical considerations that contribute to the goals of maximising the production of hydrogen (H_2) and methanol (MeOH) from biomass. Oxygen and steam are injected near or at the bottom of the reactor and react with the wood, char, and synthesis gas [98]. Operating at high pressures addresses the scalability and cost issues in biomass gasification by reducing reactor sizes and the costs of downstream gas compression. The design of the oxygen-blown, pressurised fluidised bed, which utilises alumina as bed material, provides uniform fluidisation and effective heat distribution, which are two essential factors for managing a variety of biomass feedstocks [99]. Additionally, the IGT gasifier's robustness and flexibility are confirmed by its demonstrated capacity to work across a wide temperature and pressure range and by thorough testing on various biomass sources, making it a good fit for this study. The gasifier was tested in temperatures between 750°C and 980°C and up to 25 bar pressures. Feedstocks with up to 50% moisture content may be able to be used since fluidised beds are back mixed, which guarantees almost constant temperature and gas composition [100]. The process was extensively tested with various biomass materials, including bark-paper sludge mixtures, bagasse, and pelletised alfalfa stems in a 12 t/d PDU at IGT test facilities in Chicago [101]. Figure 6 presents in a schematic way the IGT bubbling fluidised bed gasifier. Additionally, the gasifier's operating conditions (Temperature, Pressure and steam and oxygen ratio to biomass) were selected based on the range calibration and validations described in the following section. It operates at 890°C and 22 bar, with oxygen and steam ratios of 0.25 and 0.78 kg per kg of biomass, respectively.

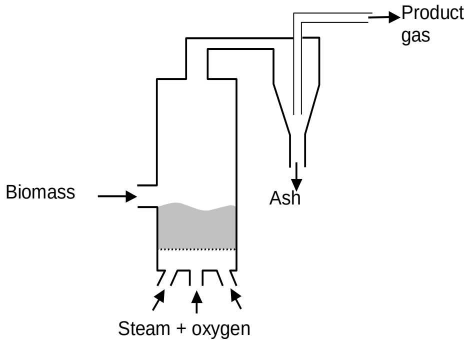

Figure 6. Bubbling fluidised bed gasifier of IGT [30]

Methanol Synthesis

The methanol reactor used in this thesis was developed by Manalal [110], which is based on the work of Lücking. This study focuses on adapting the model to the specific conditions including the syngas inlet molar flow rate, pressure, temperature and composition for each of the assessed configurations. For further details, please refer to Lücking's original work [102]. The isothermal methanol reactor was chosen over adiabatic reactors due to its ability to maintain a stable temperature profile, which is critical for achieving high conversion rates and efficient methanol production. With their tubular design and effective heat removal through boiling water, isothermal reactors offer superior conversion efficiency and catalyst longevity. Although the installation costs are higher compared to adiabatic reactors, the improved process efficiency volumes justify this choice [89]. The model also includes the necessary purification steps to obtain the above-mentioned methanol purity.

3.2.9 Timeframe and Economic Assessment

The project takes place over a detailed and structured time frame, beginning with the start of basic engineering in 2019. The economic assessment uses the European Euro (EUR) as the currency for all cost evaluations. It is assessed for a System Cost Base Date of 1Q 2019. A one-year construction period is assumed, during which the facility is not yet operational. The operating period is defined annually, comprising 8,000 operating hours, spanning 20 years of analysis.

3.2.10 Selection of Key Performance Indicators

A set of key performance indicators (KPIs) has been selected to directly compare the different proposed configurations for syngas conditioning and methanol synthesis.

a) The first technological KPIs focus on the efficiency of each process configuration in terms of energy and material consumption. Specifically, the energy consumption per kilogram of methanol produced and the biomass consumed per kilogram of methanol are evaluated. These indicators provide insights into each configuration's operational efficiency and resource requirements, allowing for a clear comparison of their technological performance.

b) The Levelised Cost of Methanol (LCOM) is the key indicator for the economic assessment. The LCOM provides a comprehensive measure of the cost per unit of methanol produced, considering capital expenditure, operational expenditure, and the plant's lifespan. This metric is crucial for understanding each configuration's economic viability and competitiveness. The Levelised Cost of Methanol (LCOM) can be calculated using Equation 4 [111]:

Equation 4. Levelised Cost of Methanol

$$LCOM = \frac{\sum_{t=1}^{n} \frac{C_t}{(1+r)^t}}{\sum_{t=1}^{n} \frac{M_t}{(1+r)^t}}$$

Where:

- C_t are the total costs in year t, including capital and operational expenditures.
- M_t is the amount of methanol produced in year t.
- r is the discount rate, reflecting the time value of money.
- n is the lifetime of the plant.

c) The configurations' environmental impact is assessed through direct CO_2 emissions resulting from process waste streams.

3.3 Economic Assessment

The economic assessment of the process plant design includes the capital cost of the unit operations required, the energy costs, and the other costs associated with running the plant. This is then used to find the levelised cost of methanol for each of the configurations proposed. This analysis uses the Chemical Engineering Plant Cost Index (CEPCI) to account for inflation, changes in the cost of construction and materials, and the impact of scaling up equipment capacities. Additionally, currency conversion is applied to ensure consistency in cost evaluation. The most critical cost data were sourced from existing literature. The costs for the gasification cleaning section and the additional units for the MeOH synthesis were obtained through the Aspen Economic Analyzer. Below is a detailed description of the procedure and formulas used in this economic assessment. Table 6 summarises the costs of critical equipment and the scaling factors and size units used to scale the costs.

$$\text{Updated Cost} = \text{Base Cost} \times (\frac{\text{CEPCI in Base Year}}{\text{CEPCI in 2019}})$$

This equation adjusts the base cost of equipment to 2019 values using the Chemical Engineering Plant Cost Index (CEPCI), which accounts for inflation and changes in cost over time.

$$\text{Scaled Cost} = \text{Updated Cost } \times (\frac{\text{New Capacity}}{\text{Base Capacity}})^{\text{Scaling Exponent}}$$

This equation scales the updated cost of equipment based on changes in capacity, using a scaling exponent to reflect economies or diseconomies of scale.

Table 6. Main Equipment Costs

Equipment	Size factor	Capacity base	Base Cost (M €)	Base Year	Scaling exponent	Source
Gasifier	Biomass dry tonne/hour	68.8	38.1[1]	2002	0.7	[30]
WGS reactor	kmol/hr of CO + H_2	8,819	12.2[1]	2002	0.65	[112]
PEM Electrolyser	kW	1000	1.97	2022	1	[113]
Methanol Synthesis	tonne/hour methanol	87.5	3.5[1]	2001	0.72	[6]
SOEC Co-electrolyser	kW	1,000	5.4	2022	1	[84]
RWGS Reactor	kmol/hr of CO + H_2	4000	41.39	2019	0.6	[77]

The total capital investment required for the plant can then be estimated from the cost of the primary process equipment above. In addition to this, an approximation from Peters & Timmerhaus was used to calculate the Total Capital Investment (TCI) as a function of the Total Purchased Equipment Cost (TPEC). Listed in Table 7 below are the estimated percentages over the TPEC proposed by the authors [114].

Table 7. Total Capital Investment

Total Purchased Equipment Cost (TPEC)		
Purchased Equipment Installation	39%	Percent of TPEC
Instrumentation and Controls	26%	Percent of TPEC

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[1] Cost is in millions of dollars

Piping	31%	Percent of TPEC
Electrical Systems	10%	Percent of TPEC
Buildings (including services)	29%	Percent of TPEC
Yard Improvements	12%	Percent of TPEC
Total Installed Cost (TIC)	147%	
Indirect Costs		
Engineering	32%	Percent of TPEC
Construction	34%	Percent of TPEC
Legal and Contractors Fees	23%	Percent of TPEC
Project Contingency	7.4%	Percent of TPEC
Total Indirect	96.40%	
Total Capital Investment	243.4%	

Source [114]

Table 8 summarises the main operational expenditure (OPEX) inputs for the methanol production plant. The operating costs are divided into different categories: personnel, utilities, biomass feedstock supply, and maintenance and insurance. Estimating these costs is derived from detailed process flowsheets and standard industry assumptions. Specifically, utilities and other consumables costs are calculated based on the material and energy balances from the process flowsheets. Other expenses, such as maintenance and insurance, are estimated using typical percentages of fixed capital investment (FCI). In contrast, personnel costs are based on standard salaries and staffing levels for a plant of this size and complexity.

Table 8. Main Operating Costs

Aspect	Value	Unit	Source
Electricity price	0.06815	€/kWh	[115]
Alumina cost	330	$/ton	[116]
Cooling water	1	€/ton	Assumed
Biodiesel (OLGA)	1000	€/ton	[117]
Natural Gas Price	25.57	€/Gigajoule (gross calorific value)	[118]
Forestry Residues Pellets	111	€ /dry tonne	[119]
Low-Pressure Steam	20	€/ton	[120]
High-Pressure Steam	30	€/ton	[120]
Medium Pressure Steam	25	€/ton	[120]
R134a	0.007	€//kg	[121]

Similarly, the basic assumptions used for the economic analysis are listed in Table 9.

Table 9. Assumptions Economic Assessment

Descriptions	
Plant life	20 years
Plant construction date	01/01/2019
Equity distribution	100% financed by equity
Plant location	Port of Rotterdam, Netherlands
Discount factor	10%
Annual operating hours	8000 hrs.
Auxiliary Equipment	Calculated using Aspen Economic Analyzer
Equipment Maintenance and Replacement	6% FCI/year [114].
Insurance	1% FCI/year [114]

3.4 Heat Integration

Pinch analysis, a methodology for minimising energy consumption and enhancing energy recovery in industrial processes, was employed to optimise energy efficiency and reduce the carbon footprint of each configuration. A systematic approach was taken to identify energy-saving opportunities using the spreadsheet provided in "Pinch Analysis for Energy and Carbon Footprint Reduction" by Ian C. Kemp [122]. The process began with entering the necessary process stream data, including specific heat capacity, mass flow rate, heat capacity flow rate (CP), and heat flow, into the INPUT tab of the provided Excel spreadsheet. A global ΔTmin value was set for each analysis to determine the minimum temperature difference for effective heat exchange.

Stream data were entered line by line, ensuring unit compatibility and separately handling segments with significant changes in heat capacity. The spreadsheet automatically calculated and categorised the streams as hot or cold based on their supply and target temperatures. Critical results, such as the problem table, composite curves (hot and cold), shifted composite curves and grand composite curves, were generated to facilitate a comprehensive analysis. The heat integration potential was qualitatively analysed by examining the shape, slope, and proximity of the composite curves in each configuration, focusing on identifying the pinch point and evaluating the extent of the overlap between the hot and cold curves.

3.5 Process Modeling Overview

This study used Aspen Plus Version 12 to model the biomass-to-methanol production process, which comprises three stages across four different plant configurations. The overall process is illustrated in Figure 7, with each process section divided into separate flowsheets. This diagram shows the process stages and the corresponding unit operations.

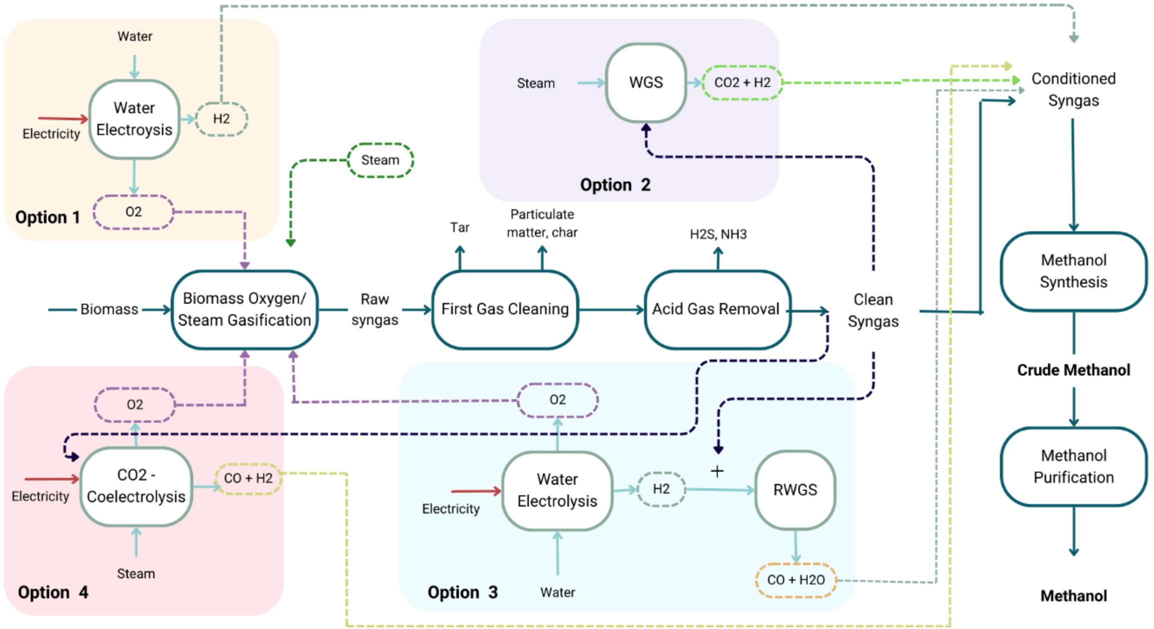

Figure 7. General Process Block Flow Diagram with the different configurations to be assessed.

The modelling steps, selection of specific layouts, and the corresponding block-flow diagrams are detailed below so that the methodology employed can be understood clearly. The selected model configurations were chosen for their simplicity, data availability, and to meet time constraints. Using Aspen Plus with the Peng-Robinson thermodynamic model allowed for accurate simulations of the process conditions. The calibration and validation of the model with existing literature data and experimental sets ensured the reliability of the simulations. Cost estimation for the main equipment was based on literature data, while other equipment costs were estimated using the Aspen Process Economic Analyzer (APEA). Operating expenditures, including raw materials and utility consumption, were calculated separately based on mass and energy balances and defined market prices.

3.5.1 Simulation of Biomass Gasification

The initial stage involves simulating biomass gasification in a fluidised bed gasifier, utilising oxygen and steam as gasification agents. The resulting syngas undergoes several cleaning processes:

1. Particulate Matter Removal: Cyclones and filters remove particulate matter, bed material, and ash.
2. Tar Removal: A sub-process based on OLGA technology removes tar from the gas.
3. Acid Gas Removal: The Rectisol process removes acid gases from the syngas.

This layout was chosen for its simplicity, data availability, and to meet time constraints, ensuring a straightforward comparison between the different configurations.

3.5.2 Syngas Conditioning Configurations

In the second stage, the syngas is conditioned using four different configurations, each modelled separately:

1. Water Electrolysis: Produces hydrogen to adjust the H_2/CO ratio.
2. Water Gas Shift (WGS): Converts CO to CO_2 and H_2 to adjust the gas composition.
3. Reverse Water Gas Shift (RWGS): Converts CO_2 to CO, improving the syngas ratio.
4. CO_2 and steam -Co-electrolysis: Simultaneously reduces CO_2 on the syngas and produces additional H_2 and CO to adjust the syngas composition.

3.5.3 Methanol Synthesis and Purification

The final stage involves modelling the methanol reactor and its subsequent purification. This section includes the reaction of syngas to produce methanol, followed by purification processes to obtain high-purity methanol.

3.6 Detailed Process Units

This section describes the model used and the development steps.

3.6.1 Gasifier Unit

The starting point for modelling the IGT gasifier was first by revising Katofsky's work, in which weighted results were shown for the gasification of poplar wood [123].The PR-BM method was chosen to describe thermodynamics given that the system modelled involves multiple phases and conventional and non-conventional solids. The values of the wood pellets' proximate and ultimate analysis characteristics, presented in Table 5, were used to model the biomass input stream for the gasifier. These values were also used to approximate the density and enthalpy values required for the simulation using the DCOALIGT and HCOALGEN methods in Aspen Plus. Four aspen reactors were also used to model the gasifier. The first is an R-Yield to convert non-conventional to conventional components based on the ultimate analysis. Following this, a separator is used to split the conventional components (C, H_2, O_2, Cl, S and ash) into the different reactors to simulate the various stages and reactions of gasification. In the first of these three reactors, tar formation is simulated and performed using R-Gibbs. Secondly, H_2S, NH_3, and HCl formation are performed using an R-Stoic reactor. Finally, for the main gasification products, an R-Gibbs reactor was used; here, the equilibrium of gasification reactions was calculated at a temperature lower than the actual process temperature. Several tests were conducted to minimise errors in this step. The temperature approach option in the equilibrium reaction allows the adjustment of the equilibrium constant of a reaction by offsetting the temperature at which it is calculated. The approach value is an empirical adjustment used to modify the extent of reaction at equilibrium when the value of the equilibrium constant is not well established. The specified approach temperature is an approach to the calculated reactor outlet temperature rather than the approach to the chemical equilibrium temperature [124]. The gasifier model was calibrated and validated using experimental data from Bain, and different tests were performed for various operating conditions[98]. The biomass used in the tests used for the calibration and validation is Wisconsin Maple chips, which vary in proximate and ultimate analysis depending on the moisture they contain. Figure 8 depicts the biomass cleaning section, including the syngas cleaning stages. An explanation of the blocks and sub-units that comprise the Aspen model for the IGT Gasifier is presented in Appendix I. The assumptions used for the modelling of this unit are as follows:

- The process is in a steady state.
- Ambient conditions are 15 °C and 1.02 bar
- Char is composed of 100% carbon.
- The tar accounted for in the model is modelled as toluene through a percentage of the biomass feed (3%).
- Pressure drops and heat losses are not considered in the simulation.
- It is assumed that all the nitrogen, chlorine and sulfur content is converted into HCl, NH_3 and H_2S.
- Ash in biomass is inert and did not participate in gasification reactions.
- The bed material used is alumina (Al_2O_3), and it is used only for heat transfer purposes.

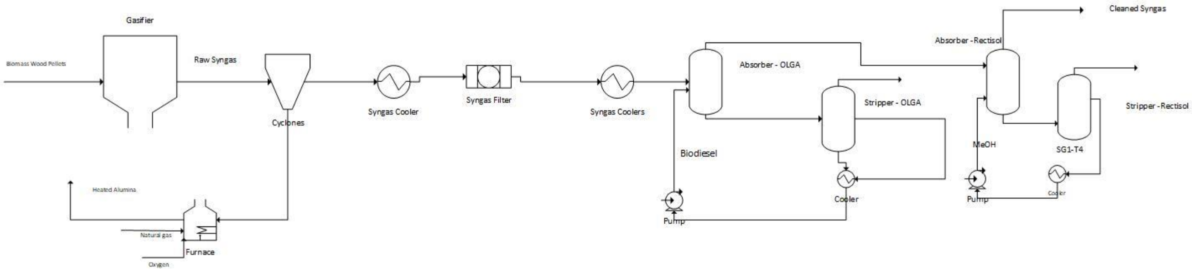

Figure 8. Gasifier and Syngas Cleaning Section

3.6.2 Tar and Particulate Removal from the Syngas

Initially, the producer gas undergoes purification through two cyclones and a filter to extract particulate matter and bed material. A similar approach to OLGA was used for the tar removal. The syngas is cooled to 75 °C by two coolers. The pressure is kept the same, as this facilitates better tar absorption. A minimal decrease of the other components, especially H_2S, is observed, which could be optimistic for the following gas cleaning steps. The absorber is modelled with eight stages, using biodiesel as the solvent. For this purpose, it was assumed that the biodiesel composition was simplified to be completely Methyl-oleate, as it is usually its main component [58]. Biodiesel is regenerated by passing it through a ten-stage stripper to remove water from the absorber's output, followed by a pump and heater to elevate its pressure and temperature to be recycled. A design specification adjusts the biodiesel flow in the absorber to minimise the tar levels to the targeted threshold.

3.6.3 Acid Gas Removal (Rectisol)

The Rectisol process model features a ten-stage absorber (SG1-T3) and a ten-stage stripper (SG1-T4). Pre-treated syngas enters the absorber column, where it is treated with methanol cooled to -40°C. This temperature facilitates the absorption of acidic components due to the high solubility of CO_2 and H_2S in cold methanol. After absorbing acidic components, the methanol exits the bottom of the absorber and is fed into the stripper column. Within the stripper, the methanol undergoes a regeneration process wherein absorbed acids are desorbed by applying heat. This regeneration step allows the continuous recycling of methanol within the system. To achieve the desired syngas purity, a Design Spec is implemented to adjust the methanol flow rate dynamically.

3.6.4 PEM Electrolyser

The Proton Exchange Membrane (PEM) electrolyser model developed in Aspen Plus simulates the hydrogen production process through water electrolysis. The process uses built-in blocks in Aspen Plus to represent the electrolyser components, simulating hydrogen production and separation. The electrolyser reaction is modelled as a stoichiometric reactor, where water (H_2O) is converted to hydrogen (H_2) and oxygen (O_2) with a fractional conversion of 0.5 for water. The cell voltage is 1.6 V, and the electric efficiency is 80%. The main components include electrolyser units (BM1-EL1: is where the electrolysis reaction occurs producing hydrogen and oxygen; BM1-EL2: separates these gases to prevent mixing and to purify the streams; and BM1-EL3: mixes the phases or components, ensuring the streams are in the suitable condition for further processing), heat exchangers (BM1-E1 to BM1-E4), separators (BM1-D1 to BM1-D4), and compressors/mixers (BM1-M1, BM1-M2). These components handle the electrolysis reaction, temperature management, separation of hydrogen and oxygen, and pressure adjustment. Key streams are labelled as the anode (S1-ANO, S2-ANO, etc.) and cathode (S1-CATH, S2-CATH, etc.), with hydrogen and oxygen product streams labelled PS-H2 and PS-O2. The electrolyser operates isothermally with an assumed efficiency of 80% under typical conditions of 50-80°C and up to 30 bar pressure.

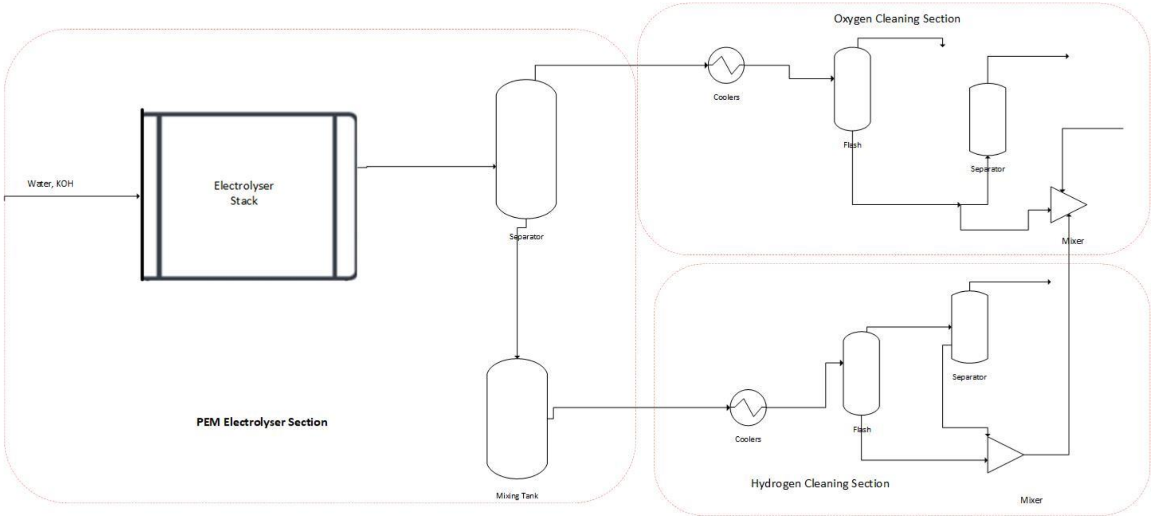

Figure 9. PEM Electrolyser

3.6.5 Water Gas Shift Unit

The model was developed and validated as proposed by Pandey et al. [112]. A one-stage shift reaction process was chosen to develop this unit. For modelling this unit, an equilibrium model was employed using an RGIBBS reactor, with a temperature adjustment to closely match the outlet composition of the reactor. First, syngas and steam enter the WGS unit with a pressure of 22 bar and a temperature of 340°C, containing a significant fraction of CO. After passing through the WGS unit, the outlet stream has a pressure drop from 22 bar at the inlet to 21.7 bar at the outlet, accompanied by a temperature increase to 455°C due to the exothermic nature of the WGS reaction. The mole flow rate increases slightly, indicating the addition of steam into the process for the shift reaction.

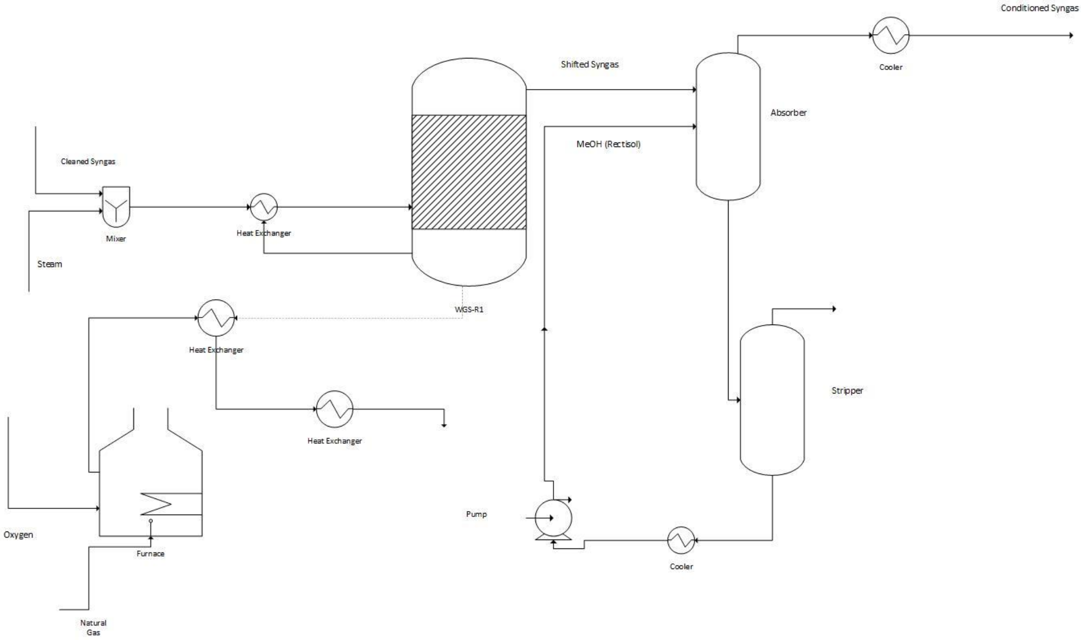

Figure 10. WGS

3.6.6 Reverse Water Gas Shift

In the RWGS unit, a Gibbs reactor model from Zang et al.'s work was applied using Aspen Plus to simulate the conversion of CO_2 under specific conditions [125]. The model was set up at a high temperature of 600°C and a pressure of 22 bar, achieving a 36% CO_2 conversion rate. The reaction occurs in a stoichiometric-type reactor. With a balanced H_2/CO_2 feed ratio of 1:1 (molar), the model effectively predicted the product stream's equilibrium composition based on the given CO_2 conversion data. The RWGS unit operates by feeding the reaction mixture into a primary reactor where high-temperature conditions drive the conversion of CO_2. Heat exchangers are used to manage the temperature, maintaining the necessary conditions for optimal performance. First, a furnace is used in order to reach the required reaction temperature of 600 °C, and after the reaction, a series of heat exchangers are used to decrease the temperature to 40 °C. The processed gas is directed through a flash to remove the water from the conditioned syngas.. Additionally, a furnace provides auxiliary heating as needed.

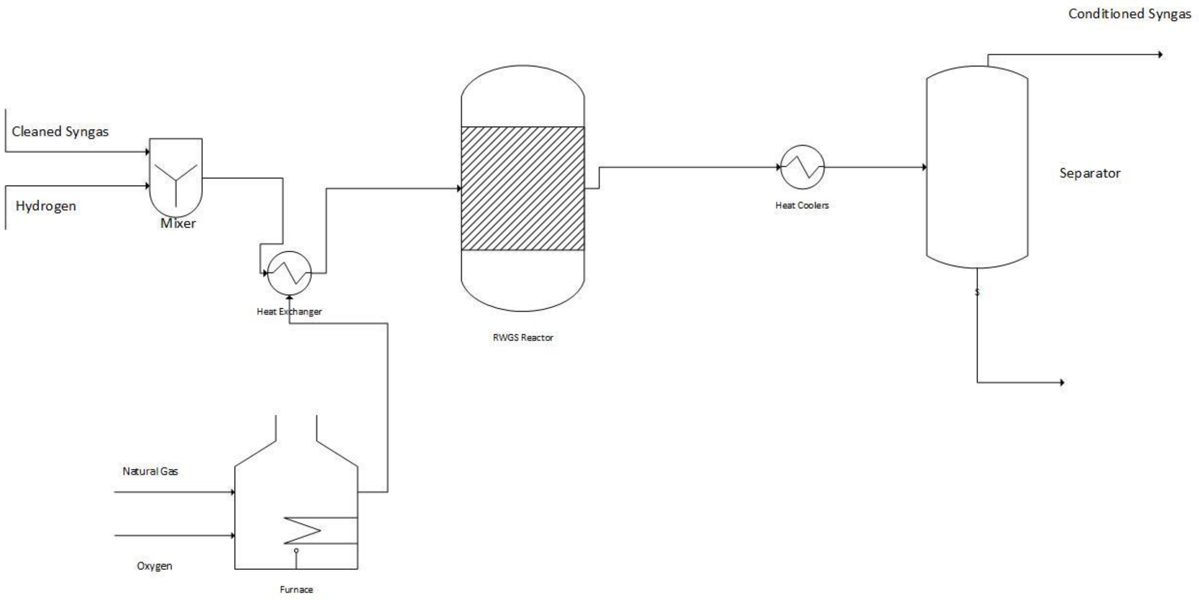

Figure 11. RWGS

3.6.7 CO_2 Co-electrolysis

The co-electrolysis process was developed based on the work of Khesa et al. and operated at a high temperature of 700°C [126]. The reactor in which the co-electrolysis reaction takes place was modelled as a Gibbs reactor instead of a stoichiometric reactor to operate under changing pressure, temperature, and feed composition (syngas entering the co-electrolyser). Since this model was developed specifically for the co-electrolysis of CO_2 and steam as feedstocks, initial validation was performed under these conditions. Subsequently, the model was evaluated using syngas as the feedstock, focusing exclusively on the reactions involving steam and CO_2, while assuming the other components of the syngas to be inert. It is worth noting that the water input was varied to get a syngas ratio of slightly above 2. In this sense, it was found that the ratio of water to syngas needed is about 1.85:1.The base model of the co-electrolyser unit has a hydrogen conversion of 52.60% and a carbon monoxide conversion of 39.32%, resulting in a syngas conversion rate of 48.30%. The overall electric efficiency of the unit stands at 58.80%. The unit voltage is 1.5 V. The inlet stream consists of steam and cleaned syngas, while the output streams consist of syngas with a higher composition of CO and H_2 on one side and water and oxygen on the other. Before starting the methanol synthesis process, the product syngas is cooled and condensed to remove all moisture.

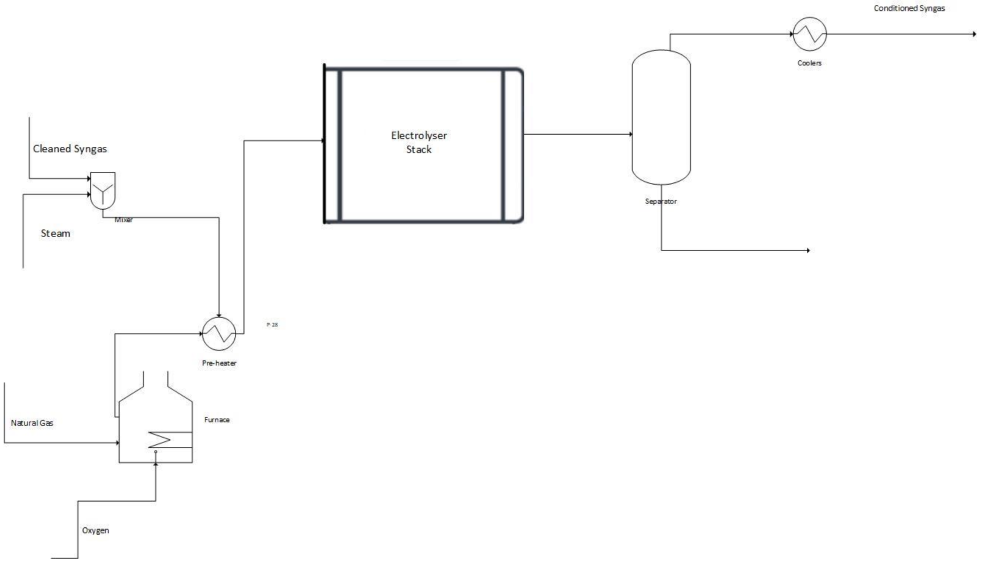

Figure 12. CO_2 Co-electrolysis

3.6.8 Methanol Reactor and Purification

As previously mentioned Manalal's model was adopted and further modified to the scope of this study . The unit consists of compressors, heat exchangers, a reactor, a flash separator, and a splitter. The modelling of the methanol reactor in this thesis utilised the plug flow module of Aspen Plus software with the Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetic model. The reactor is designed to be adiabatic, which requires no external cooling. This model accounts for two primary reactions: the formation of methanol from CO_2 and H_2, and the reverse water-gas shift (RWGS) reaction. The kinetic parameters and reaction rates are derived from the work of Van den Bussche and Froment [127]. The employed kinetic model and its parameters for the Methanol Synthesis can be found in Lücking's work [102]. The model's validation involved comparing concentration profiles and operational data against existing literature and industrial data, which showed good agreement.

The main assumptions for the modelling included considering only the components H_2, CO, CO_2, CH_4, water, and MeOH, with perfectly clean syngas at the entry point and no by-products formed in the reactor. The modelling steps involved setting up the reactor in Aspen Plus with the necessary kinetic and equilibrium parameters and adjusting for pressure and temperature conditions to optimise performance. The pressure drop inside the reactor is calculated using the Ergun equation. Sensitivity analyses were conducted to identify the most influential parameters, such as reactor feed pressure, temperature, and recycle ratio.

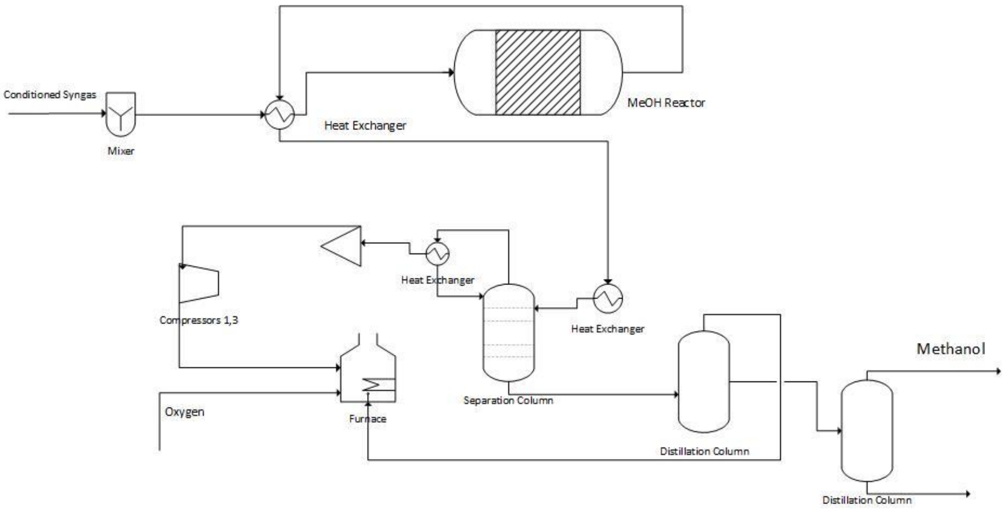

Figure 13. Methanol reactor and purification

3.7 Model Calibration and Validation

3.7.1 Gasifier Unit

This section compares the model outputs against experimental data to ensure accuracy. As mentioned in the previous section, the model for the gasifier was calibrated and validated with data from Bain[98]. Different operational parameters were set in the gasification tests GT1, GT2, GT6, and GT8. Test GT1 was performed at a temperature of 815°C and pressure of 22 bar, using 0.21 kg of oxygen and 0.78 kg of steam per kg of biomass with a moisture content of 8.35%. GT2 was conducted at a higher temperature of 898.89°C at the same pressure, with an increase in oxygen to 0.25 kg/kg but the same steam input, in biomass with a moisture level of 9.5%. GT6 operated at 815°C and had a slightly reduced pressure of 21 bar, with 0.24 kg of oxygen, a higher steam input of 0.96 kg/kg, and a moisture content of 10.72%. Finally, GT8 was performed at 821.11°C and 21 bar, with 0.22 kg of oxygen and 0.75 kg of steam per kg of biomass, and the highest moisture content at 11.15%. Each test scenario reflects the intricate balance of inputs to optimise the gasification process for varying moisture levels in the biomass. Calibration was performed with GT2, while the remaining ones were used for validation. The gasifier's operating conditions were selected based on the errors obtained during these tests. For this purpose, the gasification agents' pressure, temperature and ratio similar to those of the calibration (test GT2) were selected. These values are presented in the table.

Table 10. Test Conditions for the model validation and calibration.

Test	Temperature (°C)	Pressure (bar)	Oxygen (kg/kg of biomass)	Steam (kg/kg of biomass)	Moisture in Biomass (%)
GT1	815	22	0.21	0.78	8.35
GT2	898	22	0.25	0.78	9.5
GT6	815	21	0.24	0.96	10.72

GT8	821	21	0.22	0.75	11.15
Selected Conditions	890	22	0.25	0.78	8.1

Source: Adapted from [98]

The following reactions were used to simplify the modelling and approximate the product composition for the gasification product formation. Various studies have used this approach to adjust the predicted syngas composition from equilibrium-based models to ensure that the model outputs a realistic syngas composition [128]. It is based on Gibbs free energy minimisation and the restricted equilibrium method used to calibrate it against published data. This was achieved by specifying the temperature approach for a number of the gasification reactions [129].

Table 11. Set of reactions used and T Approach

Specification type	**Stoichiometry**	**T Approach**
Temp. approach	$CO + H_2O \rightarrow O_2 + H_2$	80
Temp. approach	$CO_2 + 4 H_2 \rightarrow CH_4 + 2 H_2O$	-220

The results obtained are shown in Figure 14.

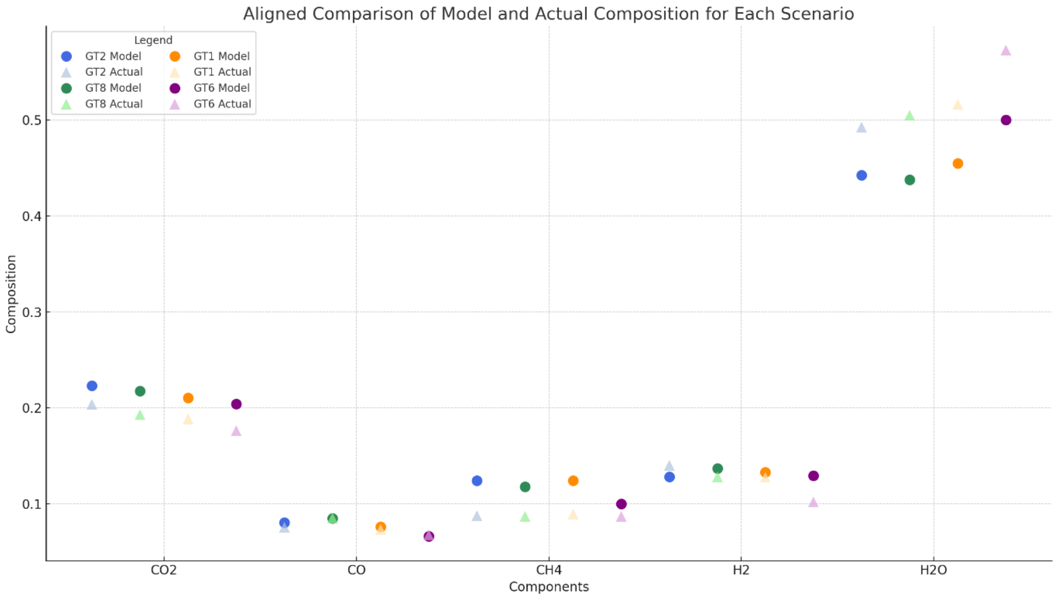

Figure 14. Model Validation Results

The difference between an ideal reactor operating at chemical equilibrium and a real gasifier can account for the methane deviation (overestimation); in other words, non-equilibrium reactions may impact methane output in the actual scenario.

3.7.2 Validation for the rest of the units

The same operating conditions were used to ensure consistency across the models.

Water-Gas-Shift Unit

The WGS reactor was validated using data from Pandey et al. [112]. The validation results indicate that the model closely matches the experimental data, with percentage errors within acceptable ranges. Table 12 shows each component's validation results and percentage error.

Table 12. Water-Gas-Shift Unit Validation results

WGS	Pandey et al.	Validation	% Error
CO [kmol/h]	962.63	1030.98	6.62%
CO_2 [kmol/h]	801.83	854.59	6.1%
H_2O [kmol/h]	130.38	138.04	5.55%
H_2 [kmol/h]	123.86	131.66	5.92%
CH_4 [kmol/h]	8.69	9.35	7.06%
N_2 [kmol/h]	145.59	159.42	8.67%

Reverse Water-Gas-Shift Unit

The RWGS reactor was calibrated using data from Zhang et al. The validation results show a high level of accuracy and a very low percentage of errors, demonstrating the model's reliability.Table 13 presents each component's validation results and percentage error.

Table 13. Reverse Water-Gas-Shift Unit Validation results

RWGS	Zhang et al.	Validation	Error %
CO [kmol/h]	1.8	1.79	0.55%
CO_2 [kmol/h]	3.2	3.19	0.31%
H_2O [kmol/h]]	1.8	1.79	0.55%
H_2 [kmol/h]	3.2	3.19	0.31%

CO_2 Co-electrolysis

The CO_2 co-electrolyser was validated using data from Khesa et al. The validation results for the CO_2 co-electrolyser show that the model accurately represents the experimental data, with most percentage errors being within acceptable limits. Table 14 summarises the validation results and each component's percentage error.

Table 14. CO_2 Co-electrolysis Unit Validation Results

Co-electrolysis	Khesa et al.	Validation	Error %
CO [kmol/h]	4.46	4.57	2.4%
CO_2 [kmol/h]	5.59	5.35	-4.4%
H_2O [kmol/h]]	5.62	5.78	2.8%
H_2 [kmol/h]	4.35	4.57	4.7%
O_2 [kmol/h]	4.38	4.87	10.1%
Molar rate [kmol/hr]	24.40	25.15	3.0%
CO conversion %	0.39	0.41	4.7%

In general, the validation results for the WGS, RWGS, and CO_2 co-electrolyser indicate that the models closely match the experimental data, providing confidence in their use for further simulations and analysis.

4. Results

The chapter is structured as follows: First, the performance of the gasifier and syngas cleaning section is discussed. This is followed by a comparison of syngas conditioning configurations, an analysis of methanol synthesis units, and an examination of utility consumption and CO_2 emissions. Finally, the KPIs, including the levelized cost of methanol (LCOM) and a sensitivity analysis of key economic parameters, are evaluated to understand the system's performance comprehensively.

4.1 Gasifier and Syngas Cleaning Section

The fluidised bed gasifier operates at 890°C and 22 bar, with oxygen and steam ratios of 0.25 and 0.78 kg per kg of biomass, respectively. Upon formation of the gasification products, the synthesis gas temperature increases slightly to 918°C. After the syngas passes through the absorber with the biodiesel, the tar content is significantly reduced to levels acceptable for methanol synthesis. Although some syngas components are absorbed during this stage, their reduction occurs in minor proportions, ensuring the primary composition remains largely intact. In the Rectisol sub-process, H_2S and ammonia are removed almost completely. Additionally, the process decreases a small portion of CO_2, methane, and the remaining toluene. This stage operates at very low temperatures, causing the cleaned syngas to cool to -19°C. As expected, the clean syngas does not have the required ratio for methanol synthesis. Table 15 presents the composition of clean syngas.

Table 15. Clean syngas characteristics

Temperature (°C)	-19
Pressure (bar)	22
Component	%mol
CO_2	0.352
CO	0.109
CH_4	0.128
H_2	0.408
S ratio	0.122

4.2 Syngas conditioning configurations

This section presents the results related only to the syngas conditioning section for the different configurations.Table 16 below summarises results for the conditioned syngas for each of the studied configurations.

Option 1 (Syngas conditioning through water electrolysis)

In the first option, to achieve a stoichiometric number of 2, an addition of 4679 kmol/hr of hydrogen is necessary. This adjustment results in the hydrogen content increasing significantly from 0.408 %mol in the cleaned syngas (Table 14) to 0.6823 %mol after conditioning. The CO content drops slightly from 0.109 %mol to 0.0569 %mol due to the enhanced hydrogen production. The electrolyser demands a power input of 569,47 kW, which is substantial. Additionally, the electrolysis process produces 2340 kmol/hr of oxygen, with 902 kmol/hr required for the gasifier, leaving an excess of 1437 kmol/hr of oxygen.

Option 2 (Syngas conditioning through water-gas-shift)

In the WGS configuration, the CO and hydrogen concentrations increase, with CO rising from 0.109 %mol to 0.242 %mol and hydrogen from 0.408 %mol to 0.5338 %mol, while methane increases slightly. This configuration involves the addition of water stoichiometrically to achieve the desired conversion. The Rectisol process effectively removes most of the CO_2, reducing it from 0.352 %mol to 0.0164 %mol.

Option 3 (Syngas conditioning through hydrogen addition and RWGS)

In the third option, the RWGS configuration, 3540 kmol/hr of hydrogen is added through water electrolysis before the RWGS takes place. This results in a 36% conversion of CO_2, reducing it from 0.352 %mol to 0.129 %mol. CO and methane levels increase moderately from 0.109 %mol to 0.135 %mol and 0.128 %mol to 0.073 %mol, respectively. There is also a slight decrease in hydrogen from 0.408 %mol to 0.65 %mol.

Option 4 (Syngas conditioning through CO_2 co-electrolysis)

In the CO_2 and steam co-electrolysis configuration, 7545 kmol/hr of water is required, leading to increased production of both CO and H_2. The CO increases from 0.109 %mol to 0.13145 %mol, and H_2 increases from 0.408 %mol to 0.66912 %mol. Methane slightly decreases, and CO_2 is significantly reduced from 0.352 %mol to 0.1278 %mol. The process consumes 212,736 kW of power, which is lower than the other electrolysis configurations.

Table 16. Conditioned Syngas Compositions for the Studied Options

Component	Option 1	Option 2	Option 3	Option 4
CO_2	0.1895	0.01647	0.129411	0.1278
CO	0.0569	0.24221	0.135431	0.13145
CH_4	0.0714	0.20741	0.073185	0.07164
H_2	0.6823	0.53382	0.659103	0.66912
Mole flow [kmol/hr]	9736	3237	7119	7276
S ratio	2	2	2	2

Electrolyser Power [kW]	569479	0	432285	212736

Across all configurations, significant adjustments to the syngas composition were achieved to reach the desired S-ratio for methanol synthesis. The main differences lie in the power consumption and how effectively each configuration increases the hydrogen content while managing CO_2 levels. Notably, Options 1,3 and 4 involve higher power inputs due to the extensive use of electrolysis. In contrast, Option 2 uses a water-gas shift to achieve the necessary syngas composition with minimal power requirements.

4.3 Methanol synthesis units

Methanol was synthesised using the syngas conditioned by the processes described above. Due to variations in the composition and quantities of the syngas, methanol production differed across the evaluated processes. Table 17 below shows the conversion efficiency of CO and CO_2 to methanol for each configuration:

Table 17. Conversion to MeOH

Option	Configuration	Conversion to MeOH	
		CO conversion	CO_2 conversion
1	Water Electrolysis	29.5%	18.8%
2	Water-gas-Shift	34.2%	3.4%
3	Reverse-Water-Gas Shift	49.8%	14.7%
4	CO2- Co-electrolysis	51.1%	16.7%

4.4 Utility consumption and CO_2 emissions for the different options assessed

The different utility consumption for the configurations studied is presented in Table 18. Note that the negative sign means generation. The energy flow analysis reveals that Option 1 consumes the most electricity, while Option 2 consumes the least. Option 3 presents the highest overall steam consumption, and Option 4 has the highest natural gas usage. This is because it requires preheating associated with a much more significant temperature change than the others. Regarding cooling water consumption, Option 1 uses the most, followed by Options 3 and 4, with Option 2 having the lowest usage.

Table 18. Different Utility consumption for the studied configurations

Description	Option 1	Option 2	Option 3	Option 4
Electricity (kW)	510181	32784	490414	271719
CW (TJ/year)	7814	4186	6808	6305
HPS (TJ/year)	-19889	-19889	18435	25921
LLPS (TJ/year)	46	-564	2717	2858
LPS (TJ/year)	3729	-4435	9585	466
MPS (TJ/year)	-4001	-4001	77	593
Natural gas (TJ/year)	1308	1308	1297	1817
R134A (TJ/year)	2.93	2.88	1.22	1.19
R1150 (TJ/year)	0	0.35	0	0

Table 19 presents the emission of the four different configurations. The table indicates that Option 2 has the highest CO_2e emissions during the syngas conditioning stage, while Option 1 has zero emissions in this stage. The gasifier and gas cleaning section consistently shows high emissions across all options. This is primarily due to the heating requirements in the gasification section and the CO_2 contained in the syngas which is partially separated in the acid gas removal section. Whereas emissions in the gas conditioning stage depend directly only on the heat requirements. Emissions in the syngas to methanol section are only due to purge gases in this part of the process.

Table 19. CO_2e emissions for each configuration in the different process stages [ktonne/oper-year]

Section	Gasifier and Gas cleaning	Syngas Conditioning	Syngas to MeOH
Option 1	1123	0	493
Option 2	1123	724	298
Option 3	1006	116	371
Option 4	1006	309	335

4.5 KPI Evaluation

This section presents the results of the selected KPIs. First, the KPIs related to technological performance are shown, followed by those related to environmental performance. Finally, the LCOM is presented.

4.5.1 Technical KPIs

Figure 15 illustrates the biomass consumption per kilogram of methanol (MeOH) for the different configurations. As shown, Option 2 has the highest biomass consumption per kilogram. In addition, the other options do not differ that much from each other.

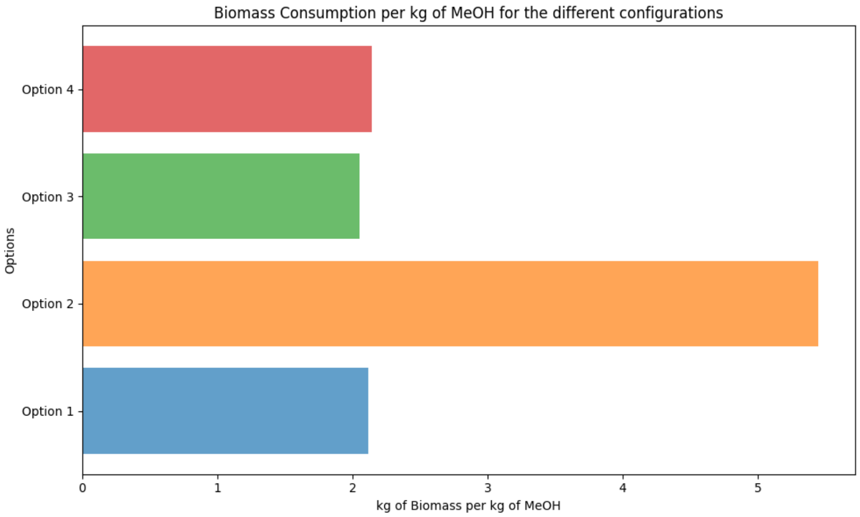

Figure 15. Biomass consumption per kg of MeOH

Furthermore, Figure 16 shows that option 2 (water-gas-shift) is the only one of the four options that does not consume electricity in any of its central reaction units. It is evident that the majority of the electricity in the systems utilizing electrolysers is consumed by the electrolysers, whereas in the second option, the electricity is solely used by the pressure change equipment.

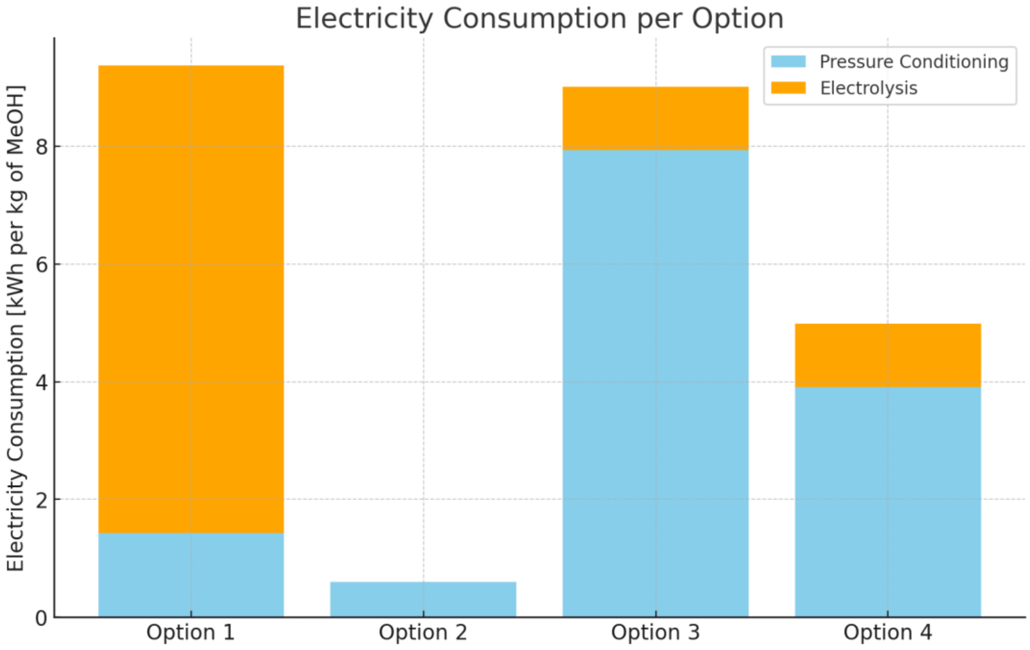

Figure 16. Electricity consumption per kg of MeOH

From, Figure 17 Option 2 it can be seen consumes the most natural gas per kg of methanol produced, whereas Options 1 and 3 use the least natural gas. This indicates that while Option 4 consumed more natural gas in absolute terms, when normalised by the amount of methanol produced, Option 2 requires significantly more. This is primarily due to the lower material efficiencies demonstrated by Option 2.

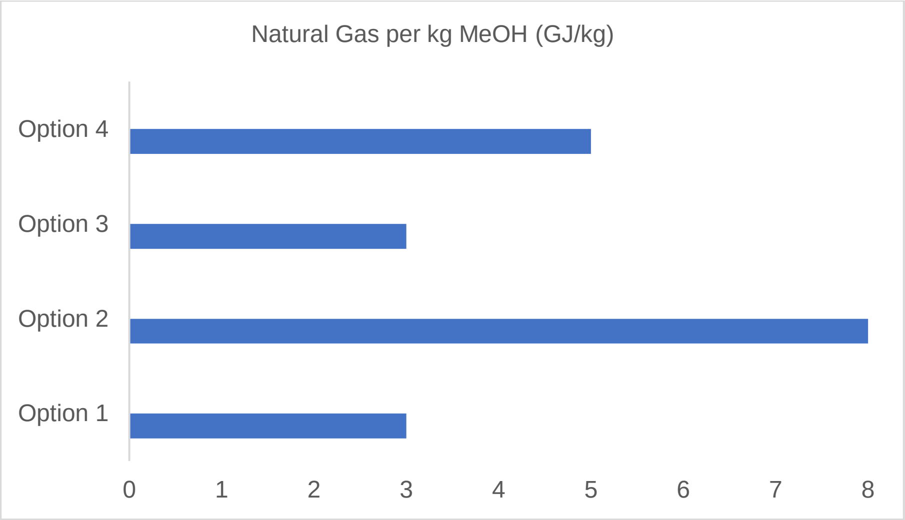

Figure 17. Natural gas per kg of MeOH

Moreover, Option 4 requires the most steam per kilogramme of methanol, whereas Option 2 uses the least.

4.5.2 Environmental KPI: CO_2 emissions

Figure 18 presents the direct CO_2 emissions for each configuration, known as Scope 1. A similar trend was observed with direct CO_2 emissions. The WGS configuration exhibited the highest emissions, primarily due to the need to remove CO_2 from the syngas to achieve the desired S value, which contributes to the inherent CO_2 emissions of this option. In contrast, Options 1, 3, and 4 displayed significantly lower emissions. This reduction is attributed mainly to the more efficient utilisation of CO_2 within the syngas in the RWGS and co-electrolysis processes, and the relatively lower temperature changes in the water electrolysis and RWGS configurations, which minimise CO_2 release. Co-electrolysis followed as the second worst. Water electrolysis and RWGS configurations performed better, with RWGS being the most efficient in lower CO_2 emissions.

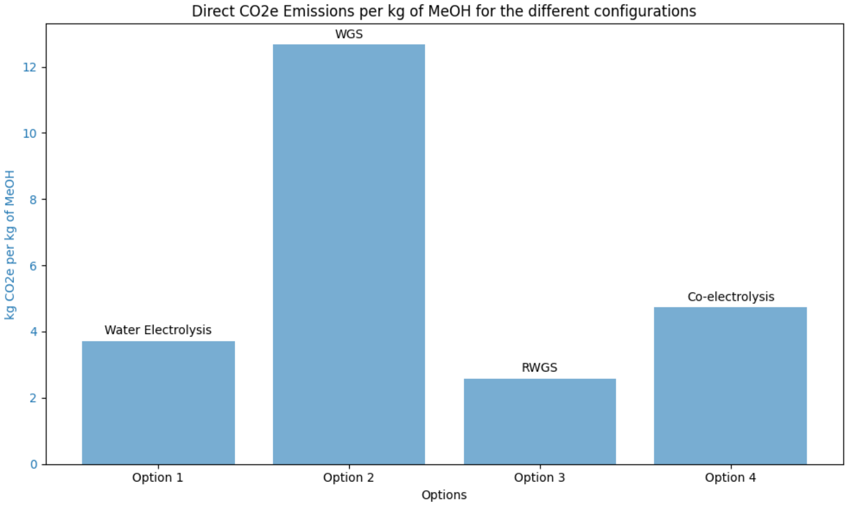

Figure 18. Direct CO_2 emissions per kg of MeOH produced

4.5.3 Economic KPI: LCOM

Figure 19 summarises the levelised cost of methanol estimates for all of the investigated plants. The lowest production costs are calculated for option 4, the second lowest for option 1, the third lowest for the third option, and the highest for the water-gas-shift configuration.

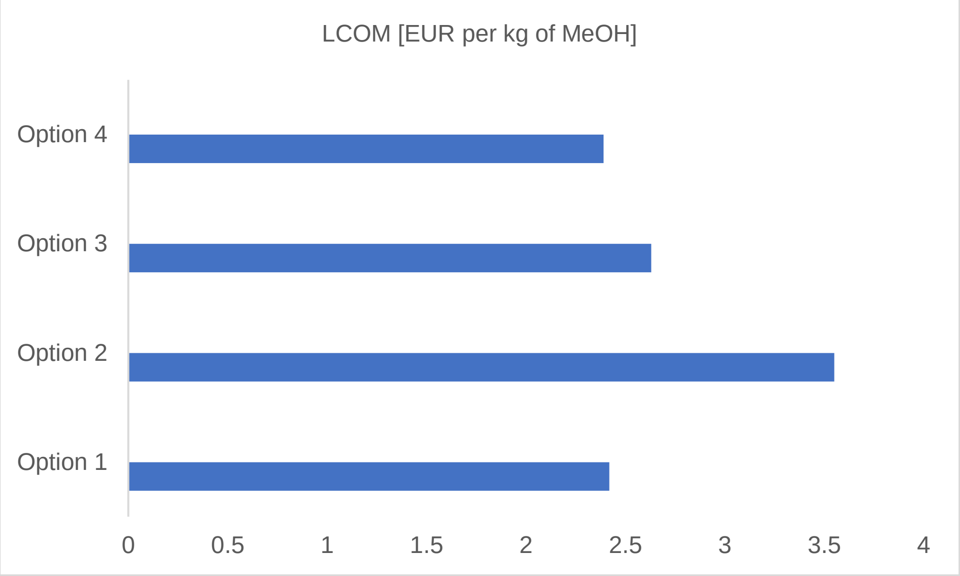

Figure 19. Levelised Cost of Methanol

Figure 20 presents the LCOM breakdown for the process options. Cost components are divided into OPEX (Operating Expenses) and CAPEX (Capital Expenditures), with distinct colour tones for easy differentiation. Utilities have the highest share of all options for LCOM. Option 2 has the highest impact of Biomass Feedstock costs, while Option 3 shows a more balanced cost distribution.

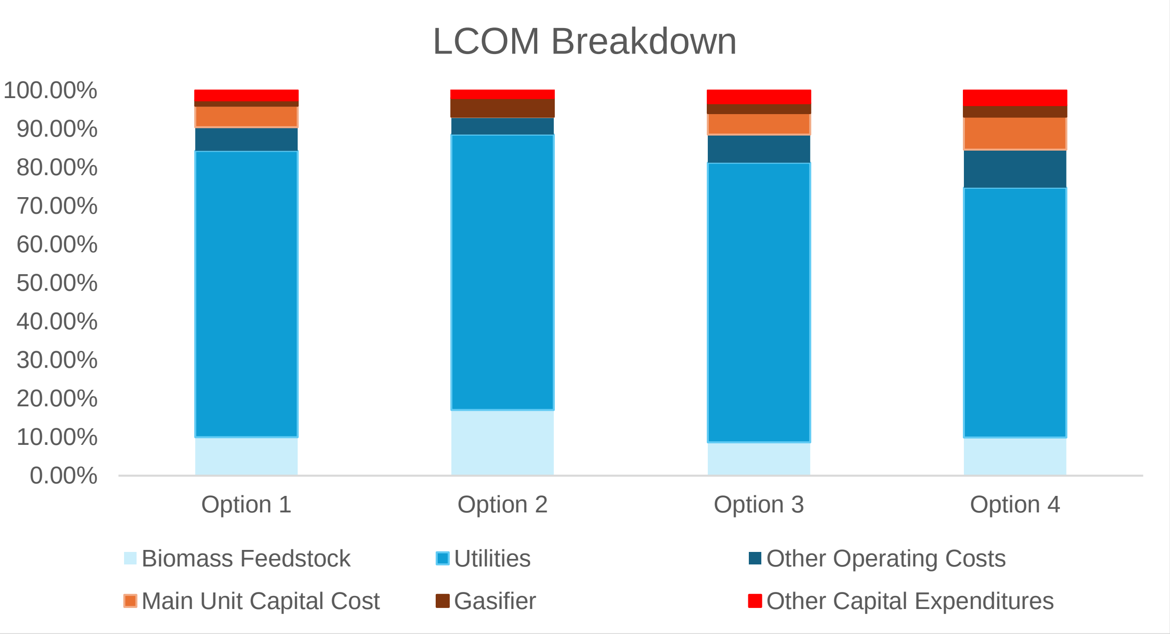

Figure 20. LCOM Breakdown

4.6 Sensitivity Analysis

Given the significant uncertainty in the economic assessment and cost inputs, a sensitivity analysis is conducted. This analysis focuses on economic parameters to understand their influence on the LCOM. Four key parameters were selected based on their impact on the LCOM and their variability. These parameters include biomass feedstock and electricity price, with the latter chosen due to the recent volatility of European electricity prices. The gasifier was selected for capital costs due to the uncertainty related to its actual capital cost. The central units—namely the RWGS and WGS reactors, water electrolysis, and CO_2 co-electrolysis—were chosen for their variability and current cost developments. Each parameter is varied by ±50% from its nominal value. The results are described in the following figures.

Option 2 (WGS Unit) is the most sensitive to biomass cost changes, with steep lines indicating a substantial impact on LCOM. Options 1 (Water Electrolysis) and 3 (RWGS) show moderate sensitivity, while Option 4 is the least affected by variations in biomass cost.

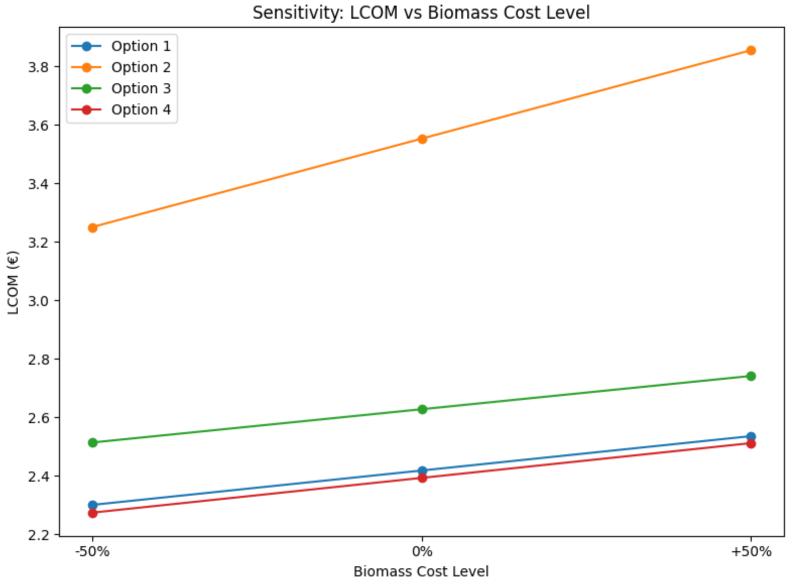

Figure 21. Sensitivity on the biomass cost

Option 1 (Water Electrolysis) and Option 3 (RWGS) show moderate sensitivity, with steeper lines indicating more significant impacts on LCOM. The lowest sensitivity is observed for Option 2, with almost flat lines indicating minimal impact on LCOM. Option 4 (CO_2 Co-Electrolysis) shows a consistent increase in LCOM with rising electricity prices but is less steep compared to Options 1 and 3.

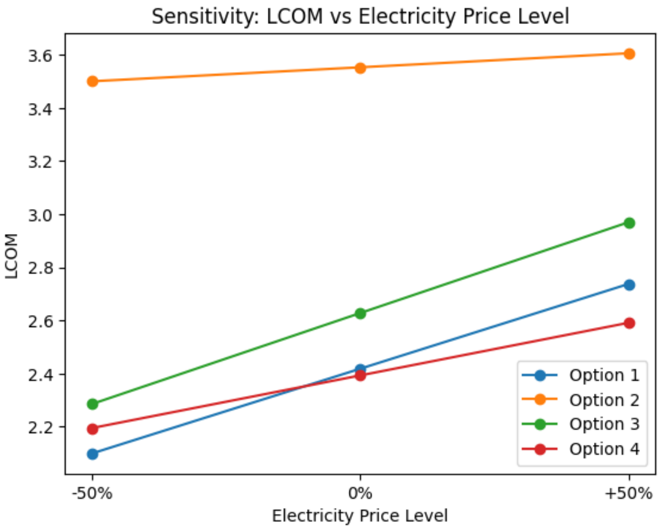

Figure 22. Sensitivity on the Electricity Price

Option 2 (WGS Unit) 's LCOM was steepest and most sensitive to changes in the main unit cost. Options 1 (Water Electrolysis) and 3 (RWGS) show moderate sensitivity, with noticeable changes in LCOM. Option 4 (CO_2 Co-Electrolysis) has the least sensitive LCOM compared to the other options.

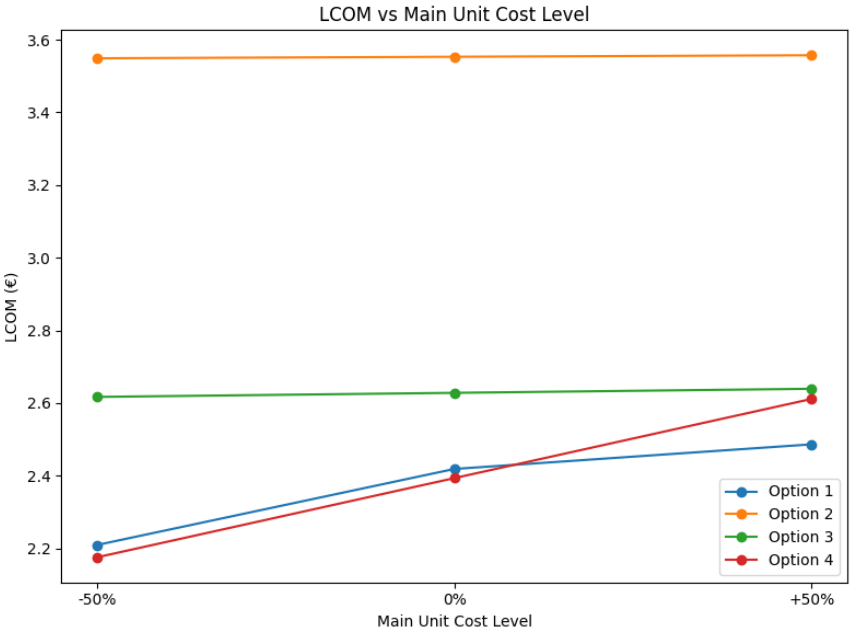

Figure 23. Sensitivity on the Main Unit cost

While all options show some sensitivity to gasifier cost variations, Option 2 stands out as the least favourable due to its high LCOM values and greater sensitivity. Moderate deviation is observed for Options 1 and 3. Option 4 (CO_2 Co-Electrolysis) shows the least sensitivity to gasifier cost changes, with relatively flat lines.

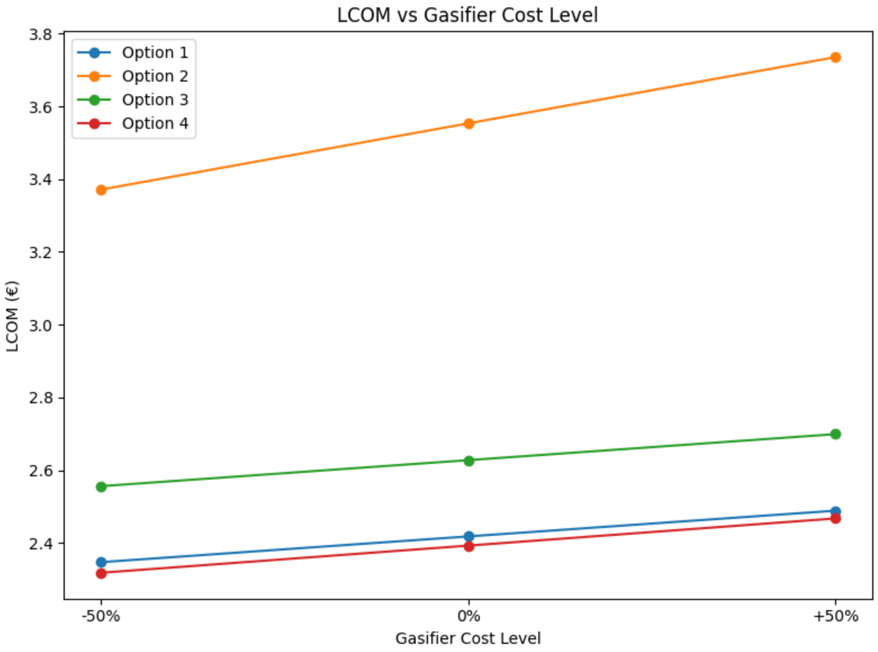

Figure 24. Sensitivity on the Gasifier Cost

Some patterns are observed when analysing the sensitivity analysis results and the LCOM breakdown. Option 2 (WGS Unit) is highly sensitive to biomass cost changes, consistent with its LCOM breakdown, where biomass feedstock constitutes the largest share of OPEX at over 18%. Regarding the main equipment cost, Option 4 (CO_2 Co-Electrolysis) shows the highest sensitivity, which aligns with its substantial CAPEX share. On the other hand, Option 2 presents a minimal sensitivity to main unit costs because of its low CAPEX share for this component. Unlike the other options, the impact of the main unit cost in Option 2 is much smaller than that of the gasifier. This is demonstrated in the sensitivity analysis, where Option 2 exhibits higher sensitivity to changes in gasifier costs compared to main unit costs.

5. Discussion

Through a detailed analysis of the key performance indicators (KPIs), the chapter reveals critical insights into the efficiencies, costs, and trade-offs associated with each configuration. Finally, the study limitations and further work are presented.

5.1 Technical KPIs

The analysis of the biomass consumption per kilogramme of methanol for each configuration shows that Option 2 (Water-Gas-Shift) is the most inefficient, using a comparatively large amount of biomass compared to the other options. This inefficiency is attributed to the rectisol process used post-water-gas-shift to achieve the required stoichiometric ratio (S ratio) of 2, where much of the syngas is absorbed, leading to lower carbon utilisation. This reduction is substantial, at 40.83% for CO_2 and a drastic decrease in CO, dropping by about 96.70%. In contrast, RWGS integration (Option 3) results in the highest material efficiency among all the options. This is slightly lower for option Options 1 (Water Electrolysis) and 4 (CO_2 Co-Electrolysis) with similar biomass utilisation efficiency. CO_2 Co-electrolysis and RWGS achieve higher conversion efficiencies for both CO and CO_2. For instance, CO_2 electrolysis shows the highest conversion rates, with 51.1% for CO and 16.7% for CO_2, while RWGS demonstrates 49.8% for CO and 14.7% for CO_2. These results are likely related to the fact that these options allowed for an efficient adjustment of the stoichiometric ratio by utilising the CO_2 contained in the syngas. Similarly, integrating the RWGS process allowed for the effective utilisation of CO_2 by shifting it together with the hydrogen produced from electrolysis. This, in turn, resulted in higher carbon utilisation in the syngas and reduced carbon losses before conversion to methanol. On the other hand, option 1 showed that adding hydrogen produced from electrolysis substantially improves the methanol synthesis without removing the excess CO_2 from the syngas, because it allows nearly complete utilisation of the carbon in the biomass and satisfies the stoichiometric ratio needed for the synthesis when compared to the WGS option.

Option 2, which uses no electrolysis for syngas conditioning and hence uses no power in its central reaction units, has a clear advantage regarding electricity consumption per kilogramme of methanol. This contrasts Options 1 and 3, which involve PEM electrolysis, and Option 4, which includes co-electrolysis and uses more electricity. Natural gas consumption is notably highest in Option 2 due to the heating requirements of the water-gas-shift reaction. Using a natural gas furnace requires heating the clean syngas from -19°C to 340°C. This requirement drives up natural gas consumption and contributes significantly to CO_2 emissions. Similar to Option 2, although to a lesser extent, Option 4's heating requirements for the clean syngas contribute to its relatively high natural gas consumption. Preheating is needed since the reactant syngas is below zero temperatures after the gas cleaning section, which also raises energy usage for the other options.

5.2 Economic KPIs

The economic evaluation indicated that, based on the obtained LCOMs for all the alternatives assessed, they are less competitive than the market price of methanol. Due to its low biomass utilisation and significant utility expenses, Option 2 (Water-Gas-Shift) had the worst performance in terms of the LCOM. On the other hand, the analysis shows that options 1, 3, and 4 have significantly lower LCOMs. However, it is difficult to determine which of these options is the most competitive as the difference between them is not significant. This may be related to the simulation setup and economic assessment assumptions employed.

The capital-intensive nature of the electrolysers in Options 1, 3, and 4 is evident from their significant share of the total purchased equipment costs, exceeding 60% in some cases. These units had the highest share in the total costs, surpassing the RWGS unit in Option 3, whereas the gasifier is the primary capital cost in Option 2. This is expected, as WGS reactors, like those in Option 2, are more established and widely used in industry, making them less costly than the electrolysers and RWGS units.

The sensitivity analysis highlighted notable variations in LCOM across the four options due to CAPEX changes. This is particularly evident for Option 4, which is highly sensitive to co-electrolyser cost variations, as it accounts for most of the total purchased equipment costs. Option 2 had a low sensitivity to WGS unit cost variations, given its minimal share of the CAPEX. Conversely, Options 1 and 3 showed moderate sensitivity to changes in the costs of the PEM electrolyser and the RWGS unit, respectively. Consistently, changes in LCOM induced by the cost sensitivity of the gasifier had a moderate impact on Option 2, where this unit represents more than 90% of the total purchased equipment cost.

A deeper look into the LCOM breakdown shows that utilities constitute the largest share of operational expenses (OPEX) across all options, reflecting the high energy requirement of these processes. It should be noted that the electricity price constitutes a large portion of the configurations' total cost, making the LCOM in the plants particularly sensitive to it. For instance, with the 2019 electricity prices of 0.06815 €/kWh, a change in electricity price by 50% increases the LCOM by 13% and 8% for options 1 and 4, respectively. This was different for option 2, which resulted in a lower electricity consumption than the other options, so the sensitivity to changes in electricity prices did not have a significant impact. The high utility costs in Option 2 are driven by its substantial natural gas consumption and steam for heating. Option 2's economics are also sensitive to a variation in biomass cost, as it represents a significant share of its OPEX. The impact of the change in biomass costs was not as substantial for the rest of the options since, as mentioned above, they primarily depended on the price of electricity in the OPEX.

5.3 Environmental KPIs

Although the carbon footprints of the four options are comparable in order of magnitude, there are significant disparities in CO_2 emissions because of the amount of waste off-gases produced, mainly from furnaces fuelled by natural gas. All options agree that most emissions come from the Gasifier and Gas Cleaning sections. This is primarily because these process sections rely heavily on natural gas to meet energy demands, resulting in flue gas. Additionally, removing acid gases in these sections captures a significant portion of the CO_2 from the syngas, which is then released. Contrary to expectations, Option 4 did not have the lowest direct CO_2 emissions. This is because the clean syngas needs to be heated from -19.84°C to 700°C using a natural gas-powered furnace. Option 3 faces similar challenges, with a need for a heat stream affecting the CO_2 emissions. Moreover, the RWGS option had lower emissions than traditional WGS due to the shift of CO_2 into CO, which is then utilised in the methanol synthesis. An advantage of the water electrolysis employed over the other options is that operating at moderately low temperatures does not require high amounts of external heat and, therefore, does not require combustion furnaces. This, in turn, results in nearly zero direct CO_2 emissions for this conditioning step.

5.4 Discussion of KPIs: Trade-offs and Synergies

The integrated analysis of the KPIs reveals synergies. These can be further categorised for the options focused on CO_2 and H_2 upgrading, respectively. Firstly, from the perspective of material usage, CO_2 co-electrolysis and RWGS have better material utilisation. CO_2 co-electrolysis converts excess CO_2 into CO, resulting in higher product yields. RWGS shifts CO_2 and hydrogen from electrolysis, resulting in higher carbon utilisation and reduced carbon losses before conversion to methanol. In contrast, the overall methanol yield of the water electrolysis and WGS processes is limited because, despite their efficiency, they do not reach the same high utilisation rates for the carbon utilisation in the syngas. In particular, this was low for the WGS option. Similarly, some synergies are found on the cost side for the RWGS and CO_2 co-electrolysis units. It was found that despite the high contribution of the electrolysis unit to the total purchase of equipment, CO_2 co-electrolysis compensates for this by allowing an efficient S ratio adjustment for high carbon efficiency and product yield. RWGS, on the other hand, provides a balance between CAPEX and OPEX, with moderate utility costs and efficient methanol production, making it economically competitive over time.

In a similar way, the evaluation of CO_2 electrolysis (Option 4) and RWGS (Option 3) compared to water electrolysis (Option 1) and WGS (Option 2) reveals several trade-offs. CO_2 electrolysis and RWGS, despite offering higher material efficiencies and lower operational costs in the long term, require substantial initial capital investments due to the high cost of electrolysers. This significant CAPEX can be a barrier to adoption. Additionally, CO_2 co-electrolysis and RWGS processes are sensitive to electricity price fluctuations, impacting economic viability. The reliance on natural gas for heating in all the conditioning options, except water electrolysis, contributes to direct CO_2 emissions and operational costs, bringing challenges on the environmental side. While advantageous regarding low CO_2 emissions and moderate CAPEX, water electrolysis faces trade-offs in high electricity consumption and lower material utilisation compared to RWGS and CO_2 co-electrolysis. On the contrary, WGS, with its lower initial costs and minimal electricity consumption, suffers from the highest levels of methanol (LCOM), significant natural gas consumption, and high CO_2 emissions.

5.5 Heat Integration Potential

Based on the analysis of the hot and cold composite curves for the four biomass gasification to methanol process configurations, the potential for heat integration varies significantly across the different syngas conditioning techniques. The Water Electrolysis configuration (Option 1) shows a high external heat requirement with minimal overlap between the curves, indicating limited opportunities for internal heat recovery. The Water Gas Shift configuration (Option 2) presents a more moderate heat requirement and a better overlap, suggesting a higher potential for heat integration. The Reverse Water Gas Shift configuration (Option 3) shows the most favourable conditions with lower heat requirements, good overlap, and a lower pinch point, indicating a strong potential for energy efficiency improvements through heat recovery. Lastly, the CO_2 and Steam Co-Electrolysis configuration (Option 4) has a moderate to high heat requirement with a moderate potential for heat recovery. Therefore, the Water Gas Shift and Reverse Water Gas Shift configurations appear to be the most promising for enhancing energy efficiency through targeted heat integration strategies.

5.6 Limitations and Further Work

The models developed in this thesis are limited by their simplifications and assumptions that had to be made, as well as the time constraints associated with a project of this nature. For the PEM electrolyser used in Options 1 and 3, an electric efficiency of 80% and a cell voltage of 1.6 V are assumed, assuming high performance yet possibly optimistic real-world conditions. The WGS reactor in Option 2 is modelled using an equilibrium approach with idealised conditions, which could not accurately represent inefficiencies found in the actual processes. These assumptions directly impact the projected performance and economic evaluations, underlining the importance of direct validation. A more thorough review would undoubtedly have an impact on the study findings for the studied alternatives.

Research on syngas contaminants' impact on CO_2 co-electrolyser performance is crucial. Determining acceptable syngas composition limits and understanding the effects of exceeding these limits is essential. Identifying contaminants and their impact can guide necessary reformation or pre-treatment processes, influencing the configuration's efficiency, costs, and environmental impact. Comprehensive studies will ensure the reliability and viability of CO_2 co-electrolysis for methanol production.A possible solution to further decrease carbon emissions in the CO_2 co-electrolysis option is to recycle additional CO_2 emissions. This could involve assessing trade-offs such as higher electrolyser capacity, lower CO_2 emissions, or increased methanol production. Evaluating these factors could help optimise the system's carbon footprint and economic viability.

Further work could focus on optimisations, including the addition of recycle streams, adjustments to other process parameters, and enhanced heat integration both within and between processes to improve the performance of the process models individually. In the syngas section, oxygen and steam ratios were kept constant based on experimental data, which may not be optimal. Future research should examine the impact of varying these ratios to define an optimal syngas composition. This could reduce syngas conditioning costs and lower the levelised costs of methanol (LCOMs).

In addition to the previously mentioned technical research required, determining an integration strategy for the studied options into biomass-to-methanol plants is challenging based only on the assessed KPIs. These technologies are at a moderate level of maturity, and more detailed information on demonstration-scale projects, related costs, aspects of their operation, and integration between the studied technologies is required. A comprehensive understanding of scalability, long-term reliability, and real-world performance data is essential to develop robust integration strategies.

6. Conclusion

This thesis provides a detailed techno-economic analysis of four different syngas conditioning configurations for methanol production via biomass gasification. The study's main objective was to evaluate the viability and performance of CO_2 upgrading techniques (CO_2 co-electrolysis and RWGS) compared to conventional hydrogen upgrading methods (water electrolysis and WGS). An extensive evaluation that included KPIs to assess technical performance, economic viability, and environmental impact yielded some significant findings in these dimensions. The results of the comparative analysis revealed that no configuration outperforms the others across all metrics.

Regarding biomass utilisation per kg of methanol produced, CO_2 co-electrolysis achieved the highest conversion efficiencies. This high efficiency suggests its potential for high methanol yields. However, co-electrolysis requires substantial energy, leading to significant electricity consumption. Similarly, the RWGS configuration demonstrated high conversion efficiencies, improving carbon utilisation within the syngas. The RWGS configuration showed a balanced approach regarding conversion rates and energy requirements that could make it a viable alternative. In contrast, the biomass utilisation rate of water electrolysis (Option 1) was moderate. However, it was less efficient than CO_2 co-electrolysis and RWGS, requiring significant electricity. On the other hand, WGS (Option 2) showed the least efficient biomass utilisation, consuming 5.45 kg of biomass per kg of methanol, primarily due to significant carbon losses during syngas conditioning and higher emissions due to natural gas consumption for heating.

Water electrolysis (Option 1) was the most favourable regarding environmental performance due to its nearly zero direct CO_2 emissions during the electrolysis step. This was achieved through low-temperature operations that eliminated the need for combustion furnaces. While CO_2 co-electrolysis and RWGS configurations exhibited higher biomass utilisation efficiencies, their reliance on natural gas for heating contributed to significant CO_2 emissions. WGS (Option 2) had the highest CO_2 emissions due to substantial natural gas consumption for heating and those related to the rectisol process.

The Levelised Cost of Methanol (LCOM) for all the alternatives assessed is significantly less competitive than the market price of methanol. Option 2, the Water-Gas Shift (WGS) process, exhibited the highest LCOM at €3.55 per kg due to its substantial biomass consumption and high utility expenses, making it the least favourable option. This process was particularly sensitive to fluctuations in biomass and gasifier costs. In contrast, water electrolysis offered a more competitive LCOM of €2.42 per kg, although it was highly sensitive to electricity prices. The Reverse Water-Gas Shift (RWGS) process presented a balanced performance with an LCOM of approximately €2.63 per kg, effectively managing both CAPEX and OPEX while showing moderate sensitivity to the costs of PEM electrolysers and other process units. CO2 co-electrolysis, despite its high initial CAPEX, achieved the lowest LCOM at around €2.39 per kg, benefiting from high conversion efficiency and lower OPEX. However, its economic feasibility was heavily influenced by electricity price fluctuations.

The findings indicate that while CO_2 co-electrolysis and RWGS offer high conversion efficiencies and lower operational costs, they require substantial initial investments and are highly sensitive to electricity prices. In contrast, WGS have lower initial costs but suffer from higher operational expenses and environmental impacts. Additionally, the analysis also underscored the importance of stable, low-cost electricity for the economic feasibility of electrolysis-based options.

Based on the results, it can be concluded that RWGS and water electrolysis configurations demonstrate the lowest CO_2 emissions, making them ideal choices in scenarios where reducing carbon footprint is a priority, especially if electricity can be sourced from low-cost, renewable sources. CO_2 co-electrolysis, while achieving high biomass utilisation efficiency, does not have the lowest CO2 emissions due to its reliance on natural gas for heating, making it less favourable in scenarios where minimising emissions is critical. However, it still offers the lowest LCOM among the configurations, making it attractive when cost is the primary concern and electricity prices are stable or low. In contrast, the WGS configuration, although less efficient regarding biomass utilisation and carbon emissions, may be more suitable in contexts where electricity costs are high and where minimising capital expenditure is a primary concern. The water electrolysis option offers competitive LCOM and favourable environmental performance due to nearly zero direct CO_2 emissions and is best suited for situations where electricity is sourced from low-cost, renewable energy. Though efficient in reducing CO2 emissions, this configuration depends heavily on the availability of inexpensive and sustainable electricity, making it more sensitive to electricity price variations than WGS. These findings suggest that the syngas conditioning configuration should be tailored to specific economic and environmental conditions, considering the trade-offs between energy efficiency, carbon emissions, operational costs, and capital investment.

The models in this thesis have limitations due to simplifications and assumptions, and the need for direct validation is crucial (testing and verifying the assumptions and results of the models used in the thesis with real-world data or experimental results). Research on syngas contaminants' impact on CO_2 co-electrolyser performance and the effects of recycling additional CO_2 emissions is essential. Future work should focus on optimising process parameters, heat integration, and varying syngas ratios to reduce costs and improve efficiency. Additionally, integrating these configurations into biomass-to-methanol plants requires more detailed information on costs, operation, and scalability.

In conclusion, this study presents valuable insights into the techno-economic synergies and trade-offs of syngas upgrading through CO_2 conditioning compared to hydrogen conditioning for methanol production from biomass gasification. Addressing the identified challenges and leveraging the synergies can advance towards a more sustainable and economically viable methanol production industry. Future optimisation and validation efforts will be essential for translating these findings into practical, scalable solutions.

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Appendix I.

Table 20. Aspen Plus sub-units for the Gasifier Modeling

Sub-Unit Name	Aspen Plus Block Type	Sub-Unit Function
BM1-R1	RYIELD	Convert non-conventional to conventional components based on the ULTANAL.
BM1-S1	SEP	The total carbon in the biomass is sperated so that the appropriate amounts of tar, char and carbon for gasification are obtained. This is done by using a splitter that allocates the total carbon and hydrogen to different gasification products.
Alumina	STREAM (MATERIAL)	Alumina Inlet
BM1-R2	RGIBBS	Tar formation calculations
BM1-R3	RSTOIC	H_2S,NH_3 and HCl formation
BM1-R4	RGIBBS	Gasification reactions.
BM1-M1	MIXER	To bring all the products of the different reactors together in one stream

Appendix II.

Table 21. Steam Definitions for the Employed Process Utilities

Steam type	Inlet vapour fraction/ Temperature (C)	Steam pressure (bar)	Outlet vapour fraction/ Temperature (C)	Minimum Delta T (Condensation temperature with process fluid) (K)	Steam Temperature for reference (°C) (in/out)
LLP steam	1	3.9	0	10	143-142
LP steam		5.5		10	155.5-154.4
MP steam		21		10	215-214
HP steam		51		10	265-264
Fired heat	1000		400		1000-400

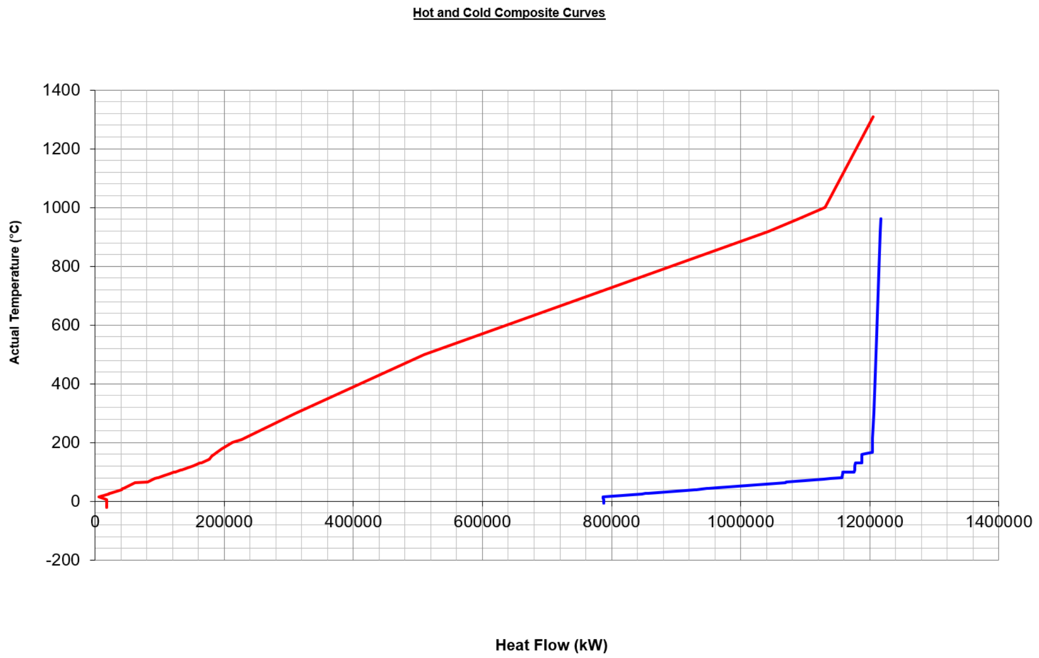
Table 22. Cooling Definitions for the Employed Process Utilities

Cooling type	Inlet Temperature (C)/Vapour fraction	Pressure (bar)	Outlet temperature (C)/vapour fraction	Minimum Delta T (Utility temperature with process fluid)	Process fluid temperature range (C) For reference
Cooling water	25	1.02	40	5	152-30

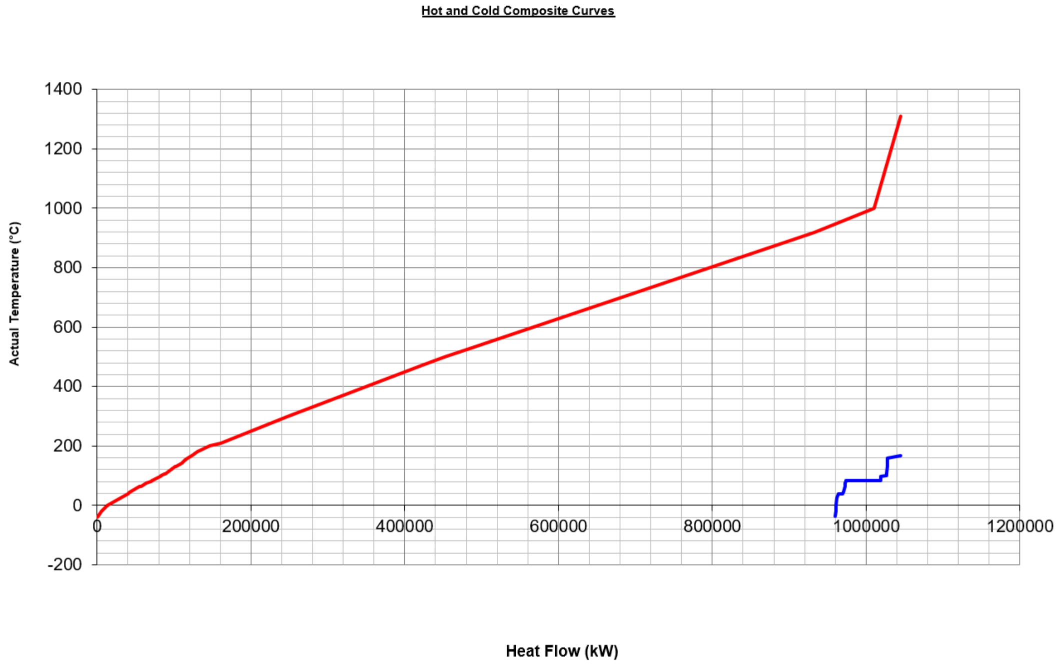
LLP steam generation	0	3.9	1	10	164-153
LP steam generation		5.5		10	224-165
MP steam generation		21		10	274-225
HP steam generation		51		10	450-275
R134a (1,1,1,2-Tetrafluoroethane/Freon)	0	1.02	1	5	-25/-24 °C
Ethylene (R1150)	0	1.02	1	5	-104/-103 °C

Appendix III.

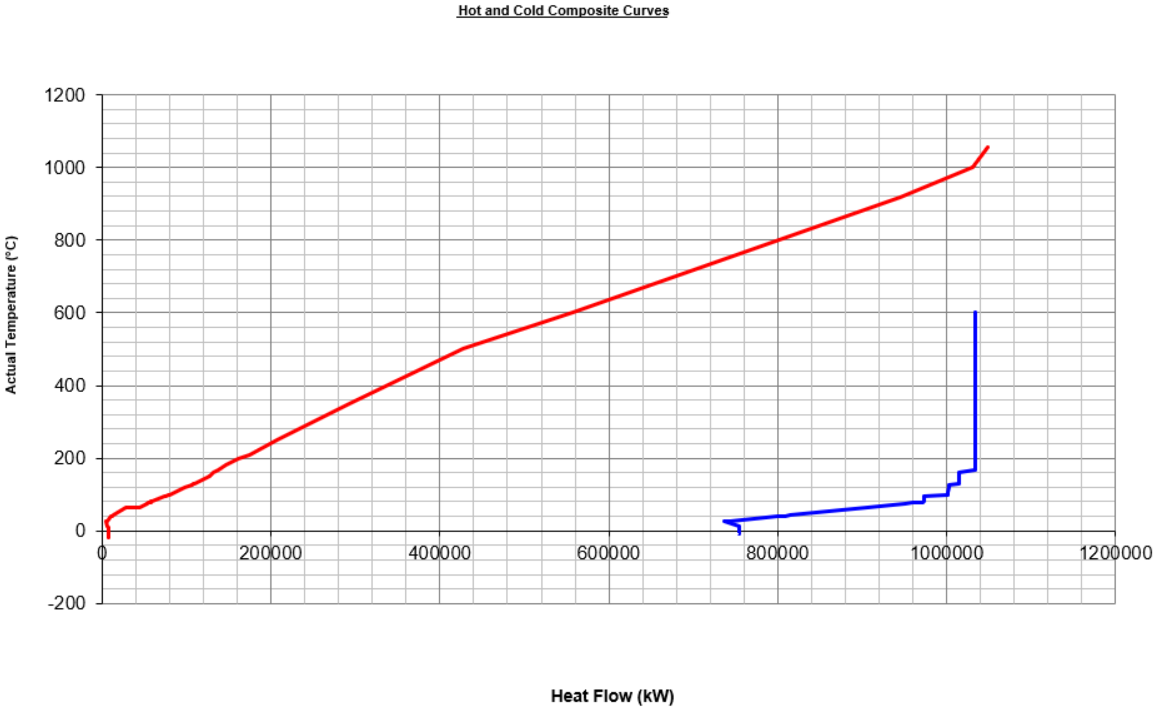
Option 1. Composite Curve



Option 2. Composite Curve



Option 3. Composite Curve



Option 4. Composite Curve