Olefin Production From Biomass via Methanol Integration (MTO)

- Ethylene and Propylene Production -

Master's Thesis
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Abstract:

Light olefins such as ethylene, propylene, butene isomers, and butadiene account for nearly two-thirds of the high-value petrochemicals market. Ethylene alone serves as a precursor for polyethylene, ethylene oxide, and ethylene dichloride. Producing olefins traditionally from fossil-based resources has always been challenging due to their high environmental impact and limited access to feedstock. This has motivated scientists' interest in developing alternative and sustainable production pathways. Biomass offers a renewable and versatile application for olefin synthesis via processes such as gasification, fermentation, cracking, and deoxygenation. One promising approach involves the production of methanol from biomass-derived syngas, followed by conversion to olefins via the methanol to olefins (MTO) process. A plant designed to generate a high H2/CO ratio syngas from biomass gasification, along with producing H2 from electrolyzer, this pathway can eliminate the need for a water gas shift (WGS) section, thereby simplifying plant design. This project investigates and models the conversion of biomass into key C2–C4 olefins, with a particular focus on optimizing process conditions to enhance selectivity and yield within a sustainable framework.

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Preface

Aalborg University June 2, 2025

This project is written by Mohammad Moula Zadeh as a Master's thesis in Chemical Engineering. The project period is February 2025 to May 2025, and presented in Jun 2025. This project is supervised by Haoshui Yu, Associate Professor from the Department of Chemistry and Bioscience.

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Chapter 1

Introduction

To tackle environmental concerns and reduce fossil resources usage, renewable energy such as solar, wind, and biomass have attracted a lot of global attention. Among these alternatives, biomass stands out due to its wide availability, renewability, and potential for carbon neutrality.

Basically, biomass resources reffer to many application, not only conventional options like wood and energy crops but also we can include agricultural residues, forestry by-products to biomass category, to that point biogenic fraction of municipal solid waste (MSW), consider biomass as a critical component in the transition toward a more sustainable energy system [1].

Biomass covers a diverse range of organic materials, including terrestrial and aquatic vegetation, agricultural byproducts, and urban waste. It can be converted into valuable energy carriers and chemicals through biological and thermochemical processes. Biological methods include anaerobic and aerobic digestion, while thermochemical methods such as combustion, pyrolysis, and gasification are particularly effective for producing valuable gases (syngas), usually a combination of carbon monoxide (CO) and hydrogen (H2), which are used as a precursor for various fuels and chemicals[2]. One of the most common and at the same time useful applications of syngases is methanol synthesis, which the role of that is highlighted in the chemical industry for high value products production. That is to say, methanol can be synthesized from feedstocks with high carbon compositions like natural gas, coal, or renewable resources, at top of them biomass. Among methanol's most promising downstream applications are the Methanol-to-Olefins (MTO), where olefins can be converted to ethylene and propylene, so we can call it Methanol to Propylene (MTP) and Methanol to Ethylene technologies (MTE). These provide a renewable pathway for producing light olefins such as ethylene and propylene, essential building blocks in plastics, synthetic fibers, and a broad range of industrial chemicals[3].

Traditionally, olefins are produced via steam cracking of naphtha or ethane, which both of them are fossil-based. Following more sustainable chemical manufacturing, alternative methods for olefin production are gaining attention. There are many mature and well-developed ways for olefin production like steam cracking, catalytic pyrolysis, Fischer–Tropsch synthesis, oxidative coupling of methane (OCM), and ethanol dehydration but after all MTO, MTE and MTP processes show satisfying potential in terms of economic and environmental aspects, specifically when they are integrated with renewable feedstocks[4].

Currently light olefins demands in the world is at one of the highest levels during the previous years. For example, propylene production is expected to reach 160 million metric tons by 2030 [4]. Ethylene is commonly utilized to produce polyethylene, ethylene oxide, and ethylene dichloride, while propylene is a precursor for polypropylene and numerous high demand polymers. Thus, having access to MTO/MTP/MTE process not only give us freedom and flexibility to use different feedstock, but also that's a plus point for those regions without crude oil.

implementing MTO/MTP/MTE technologies not only diversifies feedstock supply but also offers strategic advantages to regions lacking crude oil access.

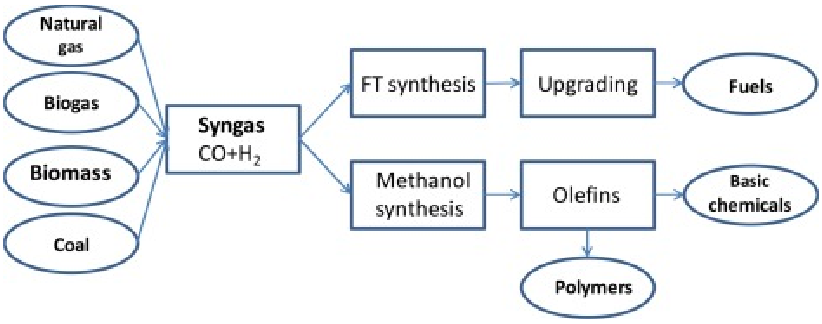

Figure 1.1: This schematic shows converting syngas into hydrocarbons and olefins[3]

From a process design perspective, MTO plants typically include a reactor section followed by five to seven integrated distillation columns to achieve high purity product separation. Energy integration within these systems enables effective heat recovery, reducing the overall energy footprint. Although they are complex, which makes it a bit challenging, MTO facilities can operate almost energy neutrally, that can improve their environmental and financial performance[5].

C2–C4 olefins, including ethylene (C2H4), propylene (C3H6), and butadiene (C4H6), are essential petrochemical building blocks due to their widespread applications.

Currently, the amount of olefins production is over 400 million tons per year, in fact shows the use of around one billion tons of hydrocarbon feedstocks. Primary production technologies include steam cracking, fluid catalytic cracking (FCC), and dehydrogenation, with FCC using about 60% and steam cracking about 40% of the total feedstock. These olefins are vital precursors in applications such as packaging, construction, solvents, coatings, and textiles [6].

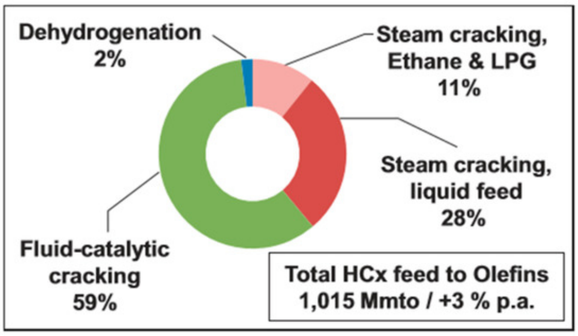

Figure 1.2: Olefin production methods using hydrocarbon feedstocks[6]

Ethylene (C2H4) is the most widely produced olefin, mainly through naphtha and ethane steam cracking. Globally, naphtha and gas oil account for 57% of ethylene production, with ethane and LPG accounting for 38%. (Figure 1.3) [6].

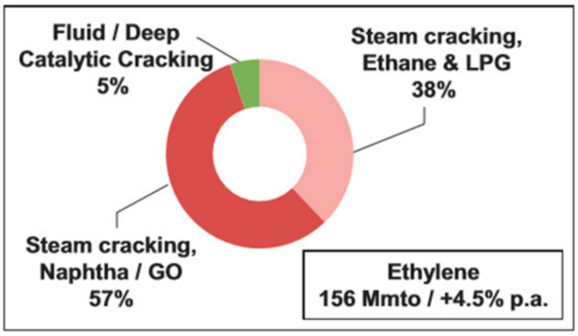

Figure 1.3: C2H4 production methods using hydrocarbon feedstock[6]

Its key applications include polyethylene production, vinyl chloride synthesis, alpha olefins, and oxygenated compounds like ethylene oxide.

Propylene (C3H6), the second most widely used olefin, is primarily generated as a byproduct during fluid catalytic cracking (FCC) and steam cracking processes. (Figure 1.4).

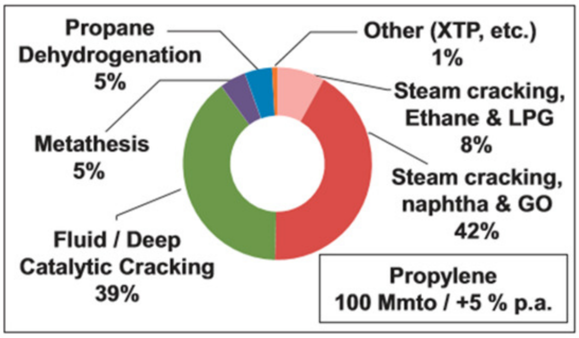

Figure 1.4: C3H6 production methods using hydrocarbon feedstock[6]

It can be used for applications such as polypropylene, cumene, acrylonitrile, and propylene oxide synthesis. Recently, interest has grown in alternative production routes such as propane dehydrogenation (PDH), metathesis, and MTO, especially when integrating renewable or waste-based feedstocks [6].

Butadiene (C4H6) is the most common C4 olefin, co-produced during naphtha and gas oil cracking, along with ethylene and propylene (Figure 1.5) [6].

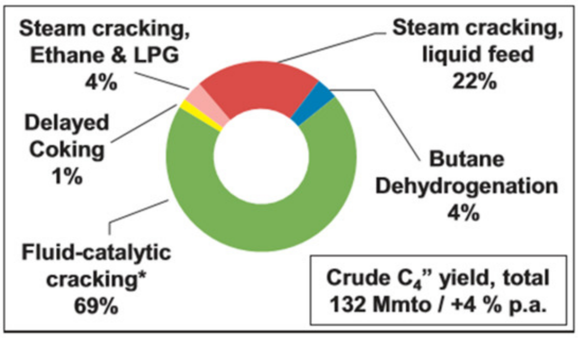

Figure 1.5: C4 olefin production methods using hydrocarbon feedstocks[6]

It is used extensively in the production of synthetic rubbers and other polymer applications.

Overall, current olefin production heavily depends on fossil based feedstocks and energy intensive technologies that contribute significantly to environmental degradation. Although coal has been employed in coal rich regions to reduce crude oil dependency, it still results in considerable CO2 emissions.

In contrast, biomass based feedstocks offer a more sustainable and environmentally friendly alternative. These resources are widely available and rich in carbon, allowing them to serve as potential alternatives for fossil sources.

In this context, this project investigates olefin production with alternative approaches based on biomass-derived intermediates, highlighting promising technologies that support sustainable biomass valorization.

Chapter 2

Biomass Gasification

Biomass gasification is a thermochemical process that converts organic feedstocks into synthesis gas (syngas), which primarily consists of hydrogen (H2), carbon monoxide (CO), carbon dioxide (CO2), methane (CH4), and light hydrocarbons. This process facilitates the valorization of diverse biomass sources into a clean, versatile fuel, suitable for energy production and downstream conversion into chemicals like methanol and olefins. Compared to fossil resources, biomass gasification contributes significantly to emission reduction and sustainable resource utilization[2][1].

2.1 Biomass Gasification Concept

Gasification operates at high temperatures (typically 800–1000°C) in the presence of a limited oxidizing agent like air, oxygen, steam, or CO2. Unlike combustion, which yields only CO2 and H2O, gasification yields a reactive gas mixture that retains chemical energy in the form of CO and H2. The gasification process includes four key steps[1]:

Drying: Moisture is removing from the biomass at temperatures between 100 and 200°C.

Pyrolysis: Thermal decomposition at 200–600°C, producing char, tar, and volatiles.

Oxidation: Partial combustion of volatiles and char with the oxidant, generating heat and forming CO2 and H2O.

Reduction: Endothermic reactions convert CO2 and H2O into CO and H2 via[1][7]:

$$Water - gas - reaction : (C + H2O \rightleftharpoons CO + H2) \tag{2.1}$$

$$Boudouard - reaction : (C + CO2 \rightleftharpoons 2CO) \tag{2.2}$$

$$Methanation : (CO + 3H2 \rightleftharpoons CH4 + H2O) \tag{2.3}$$

These reactions are temperature sensitive and depend on the thermodynamic and kinetic behavior of the feedstock and the gasifying medium.

2.2 Gasifying Agents and Their Effects

The selection of gasifying agents significantly affects the syngas composition and its subsequent applications. Air is widely used for economic reasons but results in low heating value syngas (4–7 MJ/Nm^3) due to nitrogen dilution. Oxygen eliminates nitrogen dilution and produces medium to high heating value syngas (10–18 MJ/Nm^3) but requires an air separation unit, raising CAPEX [2]. Steam improves the water gas shift reaction and increases H2 generation, which results in cleaner syngas and less tar formation. [7]. CO2, used in dry reforming, increases CO content and enables carbon recycling [1]. Dual agents (e.g., steam and oxygen) allow better control over syngas quality, optimizing the H2/CO ratio, which is crucial for methanol synthesis or Fischer Tropsch applications [2].

2.3 Types of Biomass Gasifiers

Several gasifier designs are used, each with different performance profiles:

Fixed bed gasifiers (updraft and downdraft): Simple and suitable for small scale operations, but may suffer from tar issues in some specific configurations.

Fluidized bed gasifiers (bubbling and circulating): Offer high throughput and good temperature uniformity, suitable for medium to large scale operations [1].

Entrained flow gasifiers: Operate at very high temperatures (up to 1500°C), yielding clean syngas with low tar and particulate content, ideal for industrial scale synthetic fuel production [1][2].

The choice of reactor depends on feedstock characteristics, desired syngas quality, and downstream processing requirements.

2.4 Biomass Feedstock and Composition

The nature of the biomass feedstock plays a significant role in gasification performance. Key factors include moisture content, volatile matter, ash content, fixed carbon, and heating value. Woody biomass tends to gasify more cleanly than agricultural residues, which may contain higher levels of ash and alkali metals that contribute to fouling or slagging issues [1].

When lignocellulosic biomass is gasified, it usually produces syngas with a hydrogen to carbon monoxide (H2/CO) ratio in a range of 0.8 to 1.5, which is lower than the 2:1 ratio required for methanol synthesis. Thus, further gas conditioning (e.g., water gas shift) is necessary [7].

2.5 Syngas Cleaning and Conditioning

Raw syngas contains impurities such as: Tar compounds, Particulates, Alkali metals, Sulfur containing gases (e.g., H2S). These contaminants can poison downstream catalysts or damage equipment and must be removed or reduced. Syngas conditioning technologies include [7]: 1- Cyclones, filters, and scrubbers for physical removal of particulates and tar, 2- Catalytic tar reforming to convert tar into lighter gases, 3- Water gas shift reactors to adjust H2/CO ratio, 4- Carbon capture units (e.g., amine absorption) to reduce CO2 and enable negative carbon intensity when combined with CCS[7].

Properly conditioned syngas is critical for catalytic synthesis of methanol or olefins, where H2/CO ratios and purity must meet tight specifications [4].

2.6 Syngas Upgrading

The lower heating value (LHV) of syngas, expressed in MJ/Nm^3, can be estimated by the equation[1]:

$$LHV = (25.7 \times H_2\% + 30 \times CO\% + 85.4 \times CH_4\%) \times 4.2 \tag{2.4}$$

Impurities such as nitrogen (N2) and carbon dioxide (CO2) lower the heating value by diluting the concentration of combustible gases. Improving syngas quality involves reducing these contaminants. CO2 can either be removed using extraction techniques or transformed by reacting it with charcoal or tar. In the case of N2, its concentration can be limited by using pure oxygen or steam instead of air during gasification, or by employing chemical looping gasification (CLG), which inherently prevents nitrogen contamination.

A more advanced strategy upgrades syngas by partially reducing CO2 to CO, thereby increasing the energy density and enhancing its suitability for downstream chemical synthesis[1].

2.7 Advantages and Limitations of Biomass Gasification

Advantages: Higher efficiency and cleaner combustion compared to direct biomass combustion, Greater flexibility in feedstock and product tailoring, Integration potential with carbon capture and utilization (CCU), Compatibility with synthetic fuel production routes (e.g., methanol, FT fuels) [2][7].

Challenges: Tar formation and catalyst deactivation, Feedstock variability and seasonal availability, Complex and costly gas cleanup systems, High capital investment for commercial scale extension . Nevertheless, ongoing advancements in reactor design, process integration, and gas cleanup technologies are steadily improving the economic and environmental feasibility of biomass gasification based syngas production[7][1].

Chapter 3

Methanol-to-Olefins (MTO) Process

3.1 Chemistry and Catalysis

The methanol to olefins (MTO) process is a complex catalytic pathway that involves several reactions.

At the first step, methanol would dehydrate to produce dimethyl ether (DME), which is then transformed into light olefins like ethylene, propylene, and butene. By-products include methane, ethane, propane, heavier hydrocarbons, and aromatics:

$$2CH3OH \rightleftharpoons H2O + C2H6O \rightarrow C2H4/C3H6/C4H8 \tag{3.1}$$

This reaction occurs in the vapor phase when we have catalyst as well, usually at 350–500°C and 2–3 bar. The quality of produced syngas (syngas compositions) can be evaluated by introducing stoichiometric number (S) (or R-Ratio is called in this report), defined as: S = (H2 – CO2) / (CO + CO2). This ratio is crucial for optimizing methanol synthesis, as it shows the balance of reactants required for the process. An S-value close to 2:1 is generally favorable, indicating an ideal proportion of hydrogen to carbon oxides for efficient conversion. As reported by Palma et al.[8], a slightly higher S-value just more than 2 is optimal for the catalysts employed in large scale methanol production. Additionally, the stoichiometric number can change based on the type of carbon rich material used to produce the syngas. [9]. Another key reaction involved in methanol synthesis is the water gas shift (WGS) reaction, as presented in Equation below:

$$CO + H2O \leftrightarrow CO2 + H2 \qquad \Delta H^\circ = +41.2kJ/mol \tag{3.2}$$

This reversible reaction is important in industrial operations because it modifies the H2/CO2 ratio in syngas, optimizing the feed composition for methanol synthesis. The WGS reaction serves as an effective method to enhance hydrogen content while reducing carbon monoxide levels, ensuring a better stoichiometric balance for downstream synthesis[9].

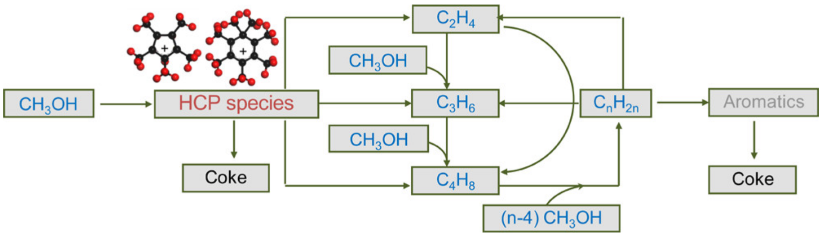

Figure 3.1: Methanol Conversion Kinetic Network[9]

Because of its natural and inherent activity, selectivity, and durability, SAPO-34 (silico-aluminophosphate) has become one of the most effective catalysts in the current industry. Its cage like molecular structure enhances the formation of short chain olefins such as ethylene and propylene. In contrast, catalysts like ZSM-5 tend to promote the formation of longer chain products.

The widely accepted Hydrocarbon Pool (HCP) mechanism involves transient aromatic intermediates limited within SAPO-34's microporous channels. The selectivity between ethylene and propylene is influenced by the catalyst's pore size and the gas residence time shorter residence favors ethylene, while longer times promote propylene formation.

In a normal scenario, SAPO-34 produces about 40wt% of ethylene and propylene separately, with a combined selectivity of up to 80wt%. About 10 weight percent of methanol is converted to butenes, and the ethylene to propylene ratio can range from 0.75 to 1.25. Methanol conversion rates can exceed 99%, with minimal DME residue under optimized conditions[10]. Key factors influencing product distribution include catalyst composition, operating temperature, and gas hourly space velocity.

Coke formation is a crucial consideration, necessitating periodic catalyst regeneration approximately every 1–2 hours. Consequently, the process configuration resembles that of fluid catalytic cracking (FCC), but uses a fluidized bed reactor instead of a riser.

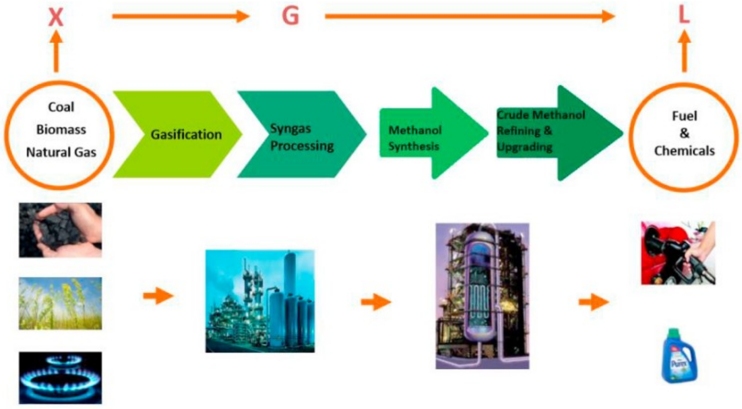

Figure 3.2: methanol production process[9]

3.2 Thermodynamics and Kinetics

The overall MTO reaction is highly exothermic, releasing about 850kJ/kg of methanol at 500°C. This substantial heat load justifies the use of a fluidized bed reactor, which enables effective heat removal.

From a thermodynamic perspective, the system is complicated. Despite being exothermic, the reaction appears to be governed predominantly by kinetic control rather than equilibrium constraints. Using Gibbs free energy minimization at 470°C and 2bar suggest a product composition dominated by ethylene and propylene in a molar ratio of roughly 1:3. Similar predictions arise from stoichiometry based.

The kinetics of the MTO reaction have been studied using two main approaches: detailed models that track a variety of intermediate compounds identified through advanced spectroscopic techniques, and simplified lumped models that focus on easily measurable compounds, making the analysis more practical for process design.[11]

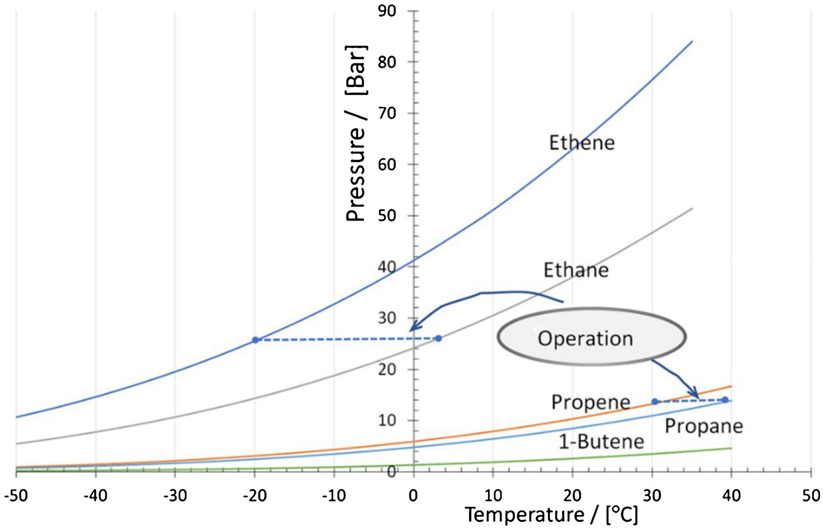

Figure 3.3: Vapor Pressure Curves for Main Components in the Separation Process[3]

Figure 3.3 illustrates the boiling points of important hydrocarbons, which exceed 200°C. This temperature range has a considerable impact on the design of separation units. For example, ethylene/ethane separation can be performed at -20°C to 4°C under 26 bar, while separating propylene/propane is more energy intensive and must be optimized carefully.

3.3 Health, Safety and Environmental Considerations

Methanol is a toxic and volatile chemical, requiring handling protocols. From an environmental standpoint, the MTO process exhibits low CO2 emissions, primarily due to its high carbon efficiency (over 90%). The only significant by product is water, which may be repurposed for industrial or agricultural use. The MTO unit's CO2 emissions are mostly caused by coke combustion during catalyst regeneration. However, when evaluated across the entire production chain, including syngas generation, the CO2 footprint remains lower than that of naphtha steam cracking, especially when renewable feedstocks or coal are used. The process can achieve propylene to ethylene ratios as high as 2.1, aligning with current market demand favoring propylene. A simple economic analysis based on market prices methanol at $250/t, ethylene at $1300/t, propylene at $1200/t, butenes at $900/t, and fuel grade hydrocarbons at $500/t suggests strong profitability.

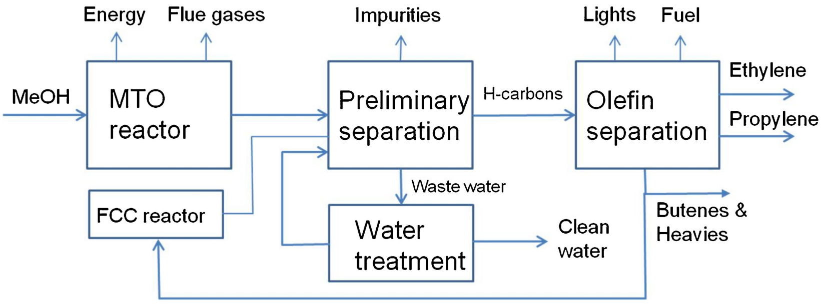

Figure 3.4: MTO Process[3]

3.4 Process Structure: Reaction, Separation and Recycle

With methanol conversions exceeding 99%, no recycle is required for unconverted reactants. The process block (see Fig.3.4) includes Reaction Section: The fluidized bed reactor, a major heat source, may support on site power generation. Preliminary Separation: Large volumes of water and methanol soluble impurities are removed. Olefins Separation: Ethylene, propylene, butenes, C5+ hydrocarbons, and fuel fractions are separated. Recycle of butenes and heavier fractions to an FCC unit enables further olefin production (applied in DMTO processes). The reactor's high energy output should be recovered and valorized where possible.

3.5 Reactor Design

In commercial methanol production, two primary types of gas phase reactors are employed: adiabatic and isothermal reactors. Given the exothermic nature of methanol synthesis, both reactor types are engineered to manage temperature effectively.

Adiabatic reactors usually consist of a series of fixed bed reactors combined with interstage heat exchangers to remove the reaction heat. These systems are known for their relatively low capital costs and high production capacities. However, their operation is typically associated with lower per-pass conversion due to high reaction temperatures, significant reactant dilution, high recycle ratios, and large catalyst volumes.

On the other hand, isothermal reactors are designed with continuous cooling systems often using water or gas to maintain a stable temperature throughout the reaction. Their design resembles that of a shell and tube heat exchanger, enabling higher conversion rates and lower catalyst requirements. Despite their operational advantages, isothermal reactors generally cause higher installation costs, and their capacity may be limited by the number and arrangement of tube bundles.

Nevertheless, due to their efficiency, isothermal reactors are widely used in industrial methanol production. Various manufacturers, including Topsoe, Lurgi, Linde, and Mitsubishi Heavy Industries, have developed customized versions of these reactors to suit specific process requirements.[9]

Due to the exothermic nature and the need for regular catalyst regeneration, fluidized bed reactors are preferred over fixed bed alternatives. Nevertheless, adiabatic fixed bed systems with cyclic operation are used in MTP (methanol to propylene) technology [12]. Depending on the gas solid contact regime bubbling, turbulent, or fast fluidization (see figure 3.5) conversion and selectivity patterns vary. DMTO technology employs a turbulent fluid bed design, offering low residence times and efficient mass/heat transfer[13].

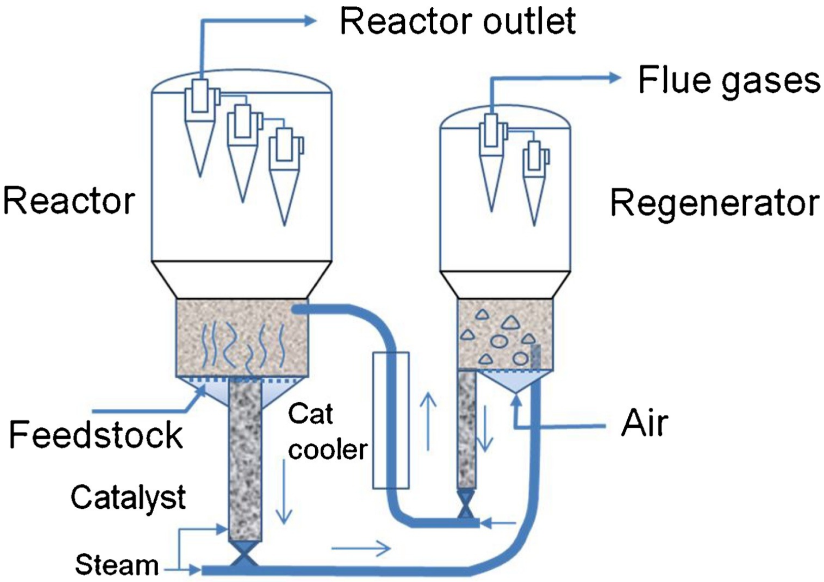

Figure 3.5: Reaction Configuration in the MTO Process[3]

Catalyst circulation between reactor and regenerator (also a fluidized bed) is countercurrent. Cyclones and filters in the disengagement zone ensure removal of particles, including fines below 5 μm. The SAPO-34 catalyst must exhibit high resistance to attrition. Integrated power generation using the reactor's heat load could supply significant plant utilities.

3.6 R-Ratio Adjustment and Its Link to WGS Conversion and Carbon Capture

As previously discussed, syngas derived from biomass gasification must be upgraded to achieve a molar ratio of $\frac{H_2-CO_2}{CO+CO_2}$, referred to here as the R-ratio, equal to 2 this being the optimal value for methanol synthesis. Two main strategies can be employed to reach this target:

(A) Add pure H2

(B) Removing CO2

Strategy (A) affects the numerator of the R-ratio. By introducing a significant amount of pure hydrogen, the desired R-ratio of 2 can be achieved, as shown in the equation:

$$\frac{H_{2,\text{IN}} - CO_{2,\text{IN}}}{CO_{\text{IN}} + CO_{2,\text{IN}}} \to \frac{H_{2,\text{in}} + H_{2,\text{pure}} - CO_{2,\text{IN}}}{CO_{\text{IN}} + CO_{2,\text{IN}}} \tag{3.3}$$

where:

H2,IN = inlet hydrogen molar flowrate, CO2,IN = inlet carbon monoxide molar flowrate, CO,IN = inlet carbon dioxide molar flowrate, H2,IN = additional pure hydrogen flowrate. The main drawback of this approach(A) lies in the sustainable generation of pure hydrogen. Conventional hydrogen production methods such as reforming fossil fuels (coal, oil, or natural gas) are carbon intensive, though relatively cost effective. Alternatively, electrolysis powered by renewable energy (e.g., wind or solar) offers a low carbon solution but is more expensive. Despite its cost, this renewable route, particularly when paired with direct air CO2 capture, presents a promising pathway for green methanol production.

Strategy (B) focuses on removing CO2 from the syngas. The feasibility and cost of this step depend largely on the CO2 concentration, removal is easier and less costly when the partial pressure of CO2 is high. However, CO2 removal alone might be ineffective if the H2 and CO concentrations are not already within optimal ranges for methanol synthesis. In fact, even complete CO2 removal could result in an H2/CO ratio below 2, which would be suboptimal for methanol production.

Conversely, if the CO2 concentration is too low, achieving significant CO2 capture becomes technically challenging, which can limit the ability to reach the desired R-ratio. Thus, the overall efficiency and economic viability of the carbon capture process depend strongly on the initial syngas composition.

As also noted earlier, the water gas shift (WGS) reaction can be used to partially convert CO into H2, thereby increasing the contents of both hydrogen and carbon dioxide:

$$CO + H2O \rightleftharpoons CO2 + H2 \tag{3.4}$$

However, this reaction does not alter the R-ratio, as shown in the simplified expression below:

$$\frac{H_{2,\text{in}} - CO_{2,\text{IN}}}{CO_{\text{IN}} + CO_{2,\text{IN}}} \rightarrow \frac{H_{2,\text{in}} + CO_{\text{IN}}\text{WGS} - (CO_{2,\text{IN}} + CO_{\text{IN}}\text{WGS})}{CO_{\text{IN}} - CO_{\text{IN}}\text{WGS} + CO_{2,\text{IN}} + CO_{\text{IN}}\text{WGS}} = \frac{H_{2,\text{in}} - CO_{2,\text{IN}}}{CO_{\text{IN}} + CO_{2,\text{IN}}} \tag{3.5}$$

Thus, although WGS changes individual species concentrations, the R-ratio remains unchanged. Therefore, while useful for adjusting H2 and CO2 levels, WGS alone cannot be relied upon to fine tune the R-ratio to its target value of 2[7].

3.7 Preliminary Separation

The first step is separating water from the olefin rich gas. Since methanol and organic impurities are water soluble, this stage is crucial for product purity.

Component vapor pressures (see Table 3.1 and Fig.3.3) guide pressure and temperature optimization. High pressure favors condensation using inexpensive utilities, while low pressure enhances separation efficiency[14].

Component	**CH4**	**C2H4**	**C2H6**	**C3H6**	**C3H8**	**1-C4H8**	**1-C5H12**
NBP, °C	164	103.7	89	47.6	42	5	36

Table 3.1: Normal boiling points of the components[3]

The MTO process represents a technological milestone for converting methanol into light olefins. It offers full sustainability by utilizing syngas from biomass, biogas, or coal via clean routes.

Chapter 4

Olefin Separation

Methanol to olefins (MTO) process produces different chemical components such as methanol (MeOH), methane (CH4), hydrogen (H2), nitrogen (N2), carbon monoxide (CO), ethylene (C2H4), ethane (C2H6), propylene (C3H6), propane (C3H8), butenes (C4H8), and pentanes (C5H12). Conventionally, the mentioned components can be separated by using a series of six distillation columns: demethanizer, deethanizer, depropanizer, debutanizer, C2 splitter, and C3 splitter. Among these, separating light olefins from their corresponding paraffins (e.g., ethylene/ethane and propylene/propane) is particularly energy intensive due to their similar volatilities. This causes wasting a lot of energy in the product recovery phase, especially when we know that distillation cover almost 30% of the chemical industry's overall energy use.

4.1 Conventional System

The conventional recovery section includes six distillation columns, as shown in Fig 4.1. The first column (C-1) separates ethane, ethylene, and light tail gases at the top, while the bottom stream contains propane, propylene, and heavier olefins. In the second column (C-2), known as the demethanizer, tail gases such as CH4, CO, N2, and H2 are removed from the ethane/ethylene mixture. This purified mixture is then fed into column C-3, where ethylene with high purity (known and used for polymer production) is recovered. The bottom product from C-1 is routed to column C-4, which separates the propane/propylene fraction from heavier olefins. The overhead stream from C-4, containing propane and propylene, is directed to column C-5 to obtain polymer grade propylene. Finally, the heavier olefins are sent to column C-6, which recovers butylene at the top suitable for use as fuel in MTO or other related processes.

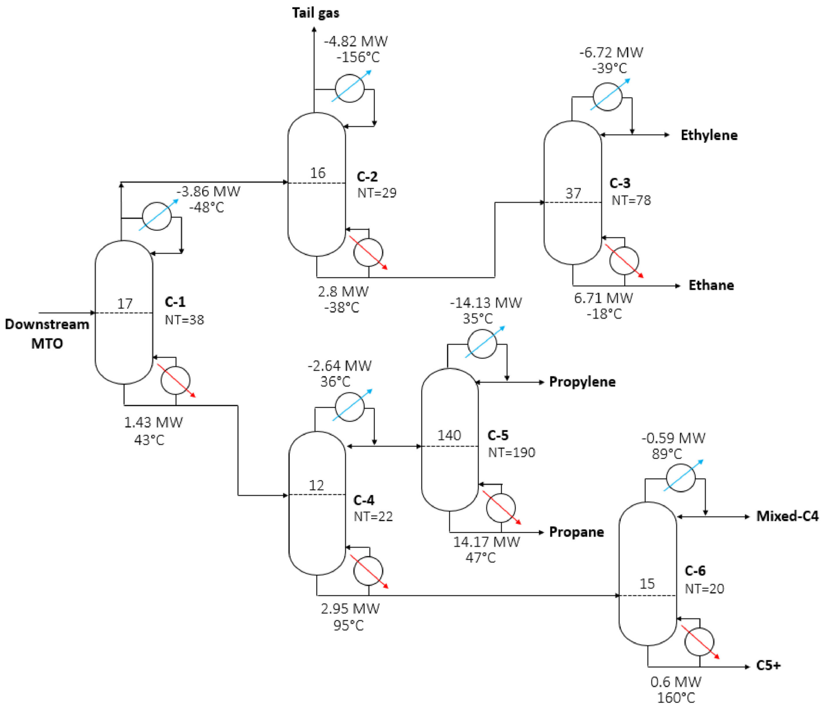

Figure 4.1: Schematic of conventional configuration[15]

Columns C-1 and C-2 are equipped with partial condensers to insert the high concentration of light components in their feed streams, which require lower condensation temperatures. In contrast, the remaining columns use total condensers, as their output streams intended for polymer and fuel applications need to be delivered in liquid form. Using partial condensers in these cases would impose an additional liquefaction step. According to relevant literature sources, total condensers are more suitable for such applications.

The top temperatures for columns C-1, C-2, and C-3 are relatively low, which shown at -48°C, -156°C, and -39°C, respectively. Suitable refrigerants for their condensers include C3H6 for C-1, a C2/C3 mixture for C-2, and a combination of N2, C1, C2, or C3 for C-3. For columns C-4, C-5, and C-6, cooling water is used as the condensing medium. The reboilers for C-1, C-4, and C-5 operate using low pressure steam, while the C-6 column, which has a higher reboiler temperature of 160°C, requires medium pressure steam. Since columns C-2 and C-3 function under cryogenic conditions, their reboiler temperatures are -38°C and -18°C, respectively. In these cases, water at 20°C is used as the heat source.

Operating at high pressures during light olefin separation offers a known advantage, as it helps to reduce the cost that related to cryogenic distillation.

To achieve the required propylene recovery standards, a high stage column (C-5) is essential. In the petrochemical sector, it is very common to use distillation columns with 150 to 200 stages for separation of propane and propylene which shows how much that is.

Even with a high number of stages, the separation process remains economically justified due to the substantial market value of propylene [16]. In column C-3, separating ethane from ethylene requires 78 stages. These separations are highly energy intensive: C-3 consumes 0.36 MW per ton of ethylene, while C-5 requires 1.32 MW per ton of propylene. Additionally, columns C-2 and C-4 each demand around 2.9 MW of energy. Reducing the energy consumption in these four columns could lead to significant economic advantages during the separation stage of the MTO process. Therefore, optimizing the performance of columns C-2, C-3, C-4, and C-5 is a highly valuable objective.

In the cryogenic separation phase of the MTO process, distillation units typically operate at pressures up to 25 bar and temperatures something between -160°C and 110°C. These conditions complicate possibility of energy integration in a good way. Consequently, alternative separation methods such as heat pump assisted distillation and strategies with energy recovery from the reaction need to be introduced.

One promising approach is the Dividing Wall Column (DWC), which integrates multiple distillation columns into a single unit. By combining two distillation columns with a shared reboiler and condenser, DWCs offer reasonable energy savings and reduce capital investment due to minimized equipment usage, smaller physical footprint, and simplified piping and electrical infrastructure. Though DWCs pose challenges in process control due to their internal complexity and interaction between control loops, ongoing research has helped improve their operability.

Avedano et al [17] assessed three thermally integrated cryogenic distillation configurations for gas separation in the oxidative coupling of methane (OCM) process. The evaluated setups included a side rectifier system, a DWC, and a Kaibel column. Of these, the side-rectifier achieved over 10% annual cost savings compared to conventional systems. The DWC configuration, however, encountered operational inefficiencies due to the inherent pressure limitations of single pressure columns, which led to large temperature differences between the reboiler and condenser. This limitation, tied to differences between OCM and MTO product streams, is particularly relevant as OCM does not produce propylene, propane, or butylene and requires an additional column for methane recovery highlighting fundamental differences in separation needs.

Qian et al [18] proposed a Reactive Dividing Wall Column (RDWC) as an integrated solution for depropanization, propylene purification, and selective hydrogenation. This configuration significantly reduced total annual costs by 27.88% compared to conventional systems. Their focus was on separating C3H6, C3H8, C4H6, methyl acetylene, and propadiene. The latter two were removed via hydrogenation. However, the study did not consider separation of lighter products such as C2H4, C2H6, or tail gases like N2, H2, CO.

Xiaolong et al [19] investigated a DWC configuration for separating a 28 component mixture from the methanol to propylene fluidized process. The column effectively separated the stream into three products: a distillate ethylene and propylene with high purity, a middle product containing propane and propylene, and a bottoms product dominated by 1-butene. Compared to a traditional two column setup, the DWC achieved 25.7% and 30.2% reductions in condenser and reboiler heat duties, respectively. While the configuration improved energy efficiency, further purification of ethylene and propylene was not addressed ethylene was obtained at 66.61% purity and propylene at 85.7%.

Gao et al [20] studied heat pump assisted distillation setups for recovering ethylene and propylene from the MTO process. These systems showed promising results reducing cold utility use by 44% and hot utility use by 70%. However, the economic implications of such systems, particularly with respect to the cost of compressors, were not evaluated, leaving the total annual cost impact uncertain.

Dimian and Bildea [3] proposed an energy efficient MTO process that emphasizes recovery of heat from the reaction section. Their design simplified the traditional six column distillation setup to five columns, suggesting potential reductions in both capital and operational expenditures. However, a direct comparison with the standard MTO process was not provided.

Ethylene and propylene must achieve high molar purities (≥ 0.99), which are essential for their commercial use, particularly in the manufacture of high value products such as specialty polymers.

Chapter 5

Project Delineation And Problem Formulation

Quality of syngas production from biomass is still a critical step in the biomass to olefins process due to the complexity and Energy intensity of the water gas shift reaction. While water gas shift reaction has shown a promising result because of its effectiveness, but environmental impact have motivated scientists the investigation of alternative technologies.

in this context, adding pure hydrogen from electrolyzer could be a promising technique which offers a significant potential to decrease carbon emission followed by environmental impact although it can affect process cost at the same time. However, mentioned alternative requires both technical and economical analysis to discover the viability of this approach.

This chapter delineates the scope of the project, focusing on simulating the overall biomass to olefins production via electrolyzer integration along with techno-economic analysis as a potential alternative parallel to water gas shift reaction to olefins production.

This project will delve into details simulations along with economic analysis of biomass to olefins. In this project our goal is to provide valuable insights into the energy and cost efficiency of olefins production. Additionally, we are aiming to achieve environmental advantages of transitioning from fossil fuel to green energy, along with that, paving the way for more sustainable and eco-friendly olefin production in the future. By addressing these objectives, this project follow to contribute to the advancement of efficient and sustainable technologies for olefins production.

Chapter 6

Process Simulation

This chapter simulates a biomass-to-methanol (BTO) plant using Aspen HYSYS V14 software.

The process begins with a biomass and water mixture used as the feedstock, which enters a conversion reactor where the initial thermochemical reactions take place. The output stream is then directed to a Gibbs reactor, where carbon combustion occurs, converting carbonaceous compounds into syngas (a mixture primarily composed of CO, H2, and CO2).

This crude syngas is then sent to an absorption tower, where it is washed with water to reduce the concentration of CO2. At this stage, a cleaner syngas stream is produced, but its composition must be adjusted to meet the required R-ratio which should be around 2 or slightly higher for optimal methanol synthesis. To achieve this, pure hydrogen is added from an alkaline electrolyzer unit.

Following this adjustment, the stream undergoes further purification in a Rectisol unit, where methanol is used to scrub out remaining CO2 and trace impurities, ensuring a clean feed for methanol production. The purified syngas is then fed into the methanol synthesis reactor, where methanol is produced through catalytic conversion.

The next stage is the Methanol to Olefins (MTO) process. The synthesized methanol is introduced into a conversion reactor, where it is transformed into a mixture of light and heavy olefins. The heavier olefins are separated via distillation and recycled through a C4-cracking unit to break them down into lighter olefins, which are more valuable. These lighter olefins are then recycled into the process.

The overhead stream from the olefin distillation unit is sent to the Cryogenic Recovery Unit, where it undergoes quenching and cooling through multiple LNG heat exchangers, significantly reducing its temperature to enable further separation. This chilled stream is processed through a series of cryogenic distillation columns: the Demethanizer, Deethanizer, and Depropanizer, which sequentially separate methane, ethane, and propene.

Finally, the remaining olefin rich stream is routed to ethylene and propylene splitters to achieve polymer grade purity (≥ 0.99) for ethylene and propylene, the high value end products of the process.

6.1 Process description

6.1.1 Biomass Gasification and Syngas Production

The process initiates with the mixing of biomass and water, regulated by Set-1, to form a homogenized feedstock. This mixture is introduced into the Conversion Reactor (CRV-102) operating at 180°C and 18 bar, where thermochemical reactions decompose the biomass, yielding gaseous and solid products.

$$Biomass + O2 \Rightarrow CO2 + H2O + N2 + SO2 \tag{6.1}$$

The resultant vapor phase (Stream 2) and solid phase (Stream 1) are combined via MIX-104 and directed to the Component Splitter (X-100). This unit effectively separates ash and other solid impurities (Stream 22), preventing potential fouling and catalyst deactivation in downstream processes. The purified gas stream (Stream 4) proceeds to the Gibbs Reactor (GBR-100), operating at 877°C and 18 bar.

In GBR-100, carbonaceous materials undergo combustion reactions, converting carbon into syngas components, primarily CO and H2 while excess O2 reacts with residual carbon or hydrogen. Post reaction, the syngas is sequentially cooled using heat exchangers E-101 and E-102, reducing its temperature from 877°C to 325°C.

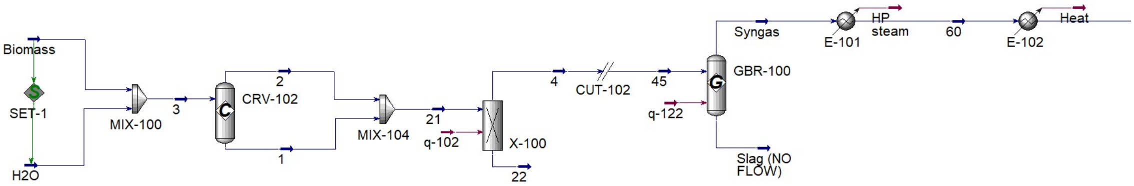

Figure 6.1: schematic of biomass gasification and syngas production

6.1.2 CO2 Removal and Hydrogen Enrichment

The cooled syngas (Stream 61) enters the Absorption Tower (T-100), where it is washed with water to reduce CO2 concentration. The bottom product, predominantly water, is sent to Separator V-100 to remove dissolved gases, with the liquid phase recycled back to T-100. The top product (Stream 68) is cooled from 142°C to 40°C and further separated in Vessel V-118. The liquid phase is recycled, while the gas phase (Stream 62-) is combined with pure hydrogen from the Alkaline Electrolyzer Unit.

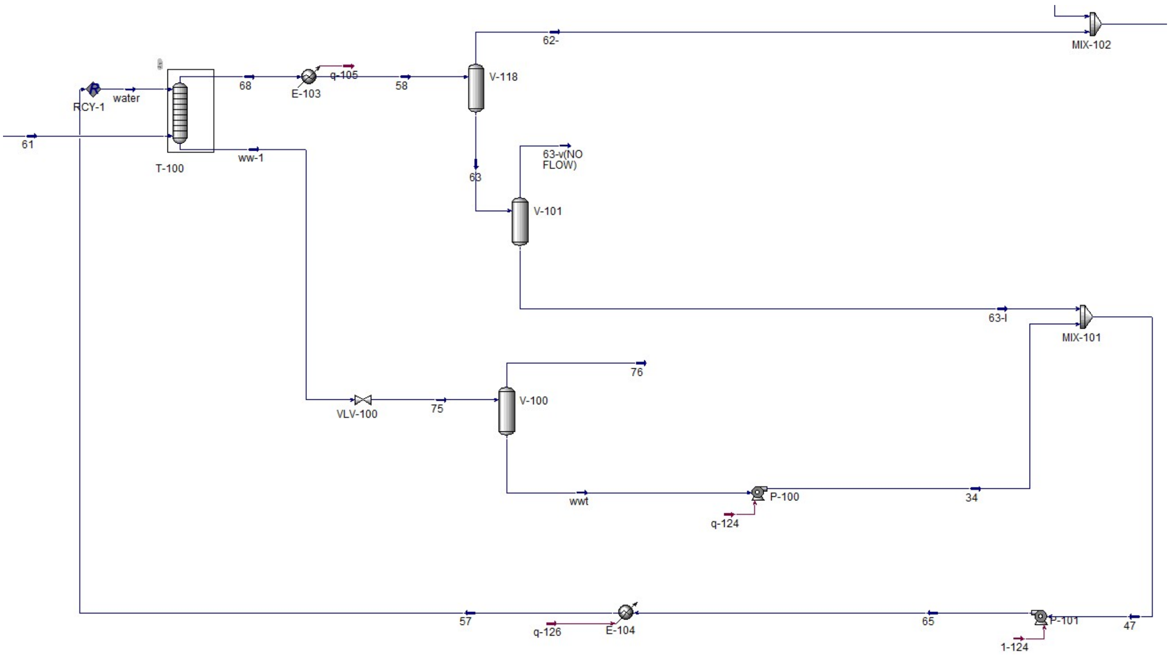

Figure 6.2: schematic of CO2 Removal and Hydrogen and Enrichment

Parameter	T-100
Number of stages	5
Top pressure(bar)	17
Bottom pressure(bar)	17.50

Table 6.1: Design parameters of T-100

The electrolyzer receives a mixture of deionized water and 35wt% potassium hydroxide at 70°C and 7bar. Due to exothermic reactions, the temperature rises to 332°C; thus, Cooler E-105 adjusts it to the optimal 75°C before electrolysis. To achieve the required R-ratio (>2), approximately 3,500kgmol/h of H2 is produced, necessitating around 370 MW of power. Post electrolysis, hydrogen is separated from the electrolyte, compressed to 17 bar using Compressor K-107, and cooled to 40°C, aligning its conditions with Stream 62.

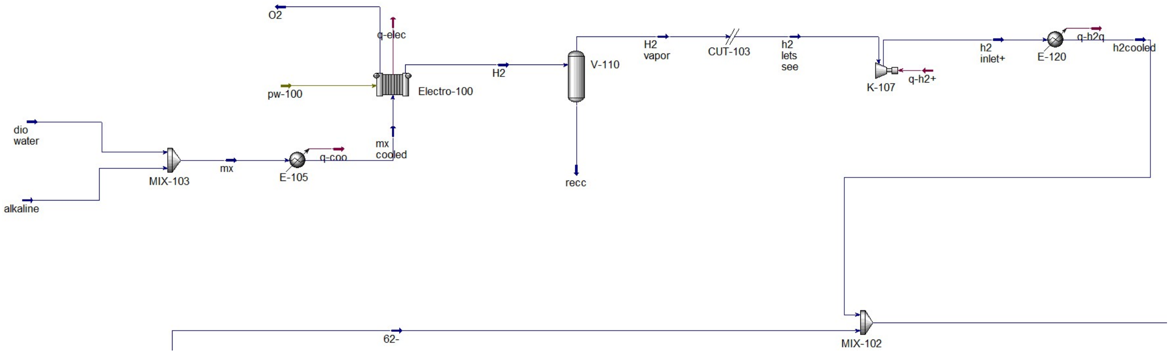

Figure 6.3: electrolyzer unit

6.1.3 Rectisol Purification and Methanol Synthesis

The combined stream undergoes compression to 50 bar and, after a fluid package adjustment via Stream Cutter CUT-100, enters the Rectisol Unit (T-104). Here, the stream is washed with methanol at -35°C to remove residual CO2 and impurities. The top product is sequentially heated through heat exchangers E-117, E-100, E-121, and E-119, reaching 240°C at 50 bar, optimal for methanol synthesis.

$$CO + H2O \rightleftharpoons CO2 + H2 \tag{6.2}$$

$$CO2 + 3H2 \rightarrow CH3OH + H2O \tag{6.3}$$

In the Methanol Reactor, methanol is synthesized and subsequently cooled to 40°C using E-106. Separator V-102 removes unreacted gases for recycling, while the liquid methanol (Stream 28) is depressurized to 11 bar via Valve 101 and purified through two distillation columns (T-101 and T-102), achieving up to 99.999% purity. The bottom product, mainly water, is directed to the water treatment unit.

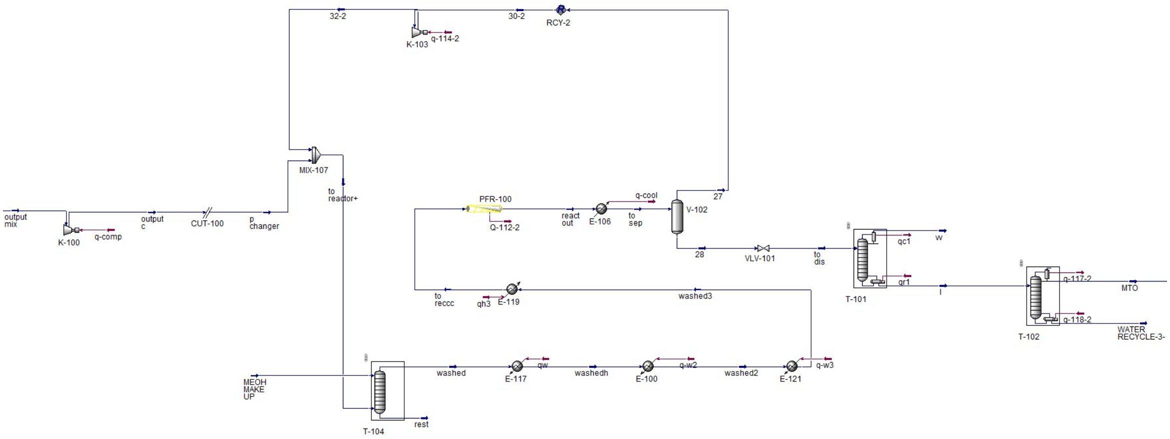

Figure 6.4: methanol production and purification

Parameter	**T-101**	**T-102**
Number of stages	10	40
Feed stage	5	20
Condencer type	full reflux	total
Condencer pressure(bar)	10.50	1
Reboiler pressure(bar)	11	1.5
Reflux ratio	0.007	2

Table 6.2: Design parameters of T-101 and T-102

Parameter	**T-104**
Number of stages	10
Top pressure (bar)	49
Bottom pressure (bar)	50

Table 6.3: Design parameters of T-104

Parameter	**Value**
Number of tubes	7474
Length (m)	80
Diameter (m)	0.03
Delta P (bar)	2

Table 6.4: Design parameters of plug flow reactor

6.1.4 Methanol to Olefins (MTO) Conversion

The purified methanol stream (MTO2) is pressurized to 12 bar using Pump P-102 and heated to 480°C in Heat Exchanger E-107. It then enters the MTO Reactor (CRV-100), where it is converted into light olefins such as ethylene and propylene.

$$CH3OH \rightarrow C2H4 + C3H6 + C4 + +CH4 + C2H6 + CO + CO2 + H2 + H2O \tag{6.4}$$

The reactor effluent is cooled to 87°C via E-107 and further to 40°C using a plate heat exchanger. Sequential separators (V-103, V-104, V-106) remove water, with the vapor phase undergoing additional compression and cooling before entering Component Splitter X-101 for further purification.

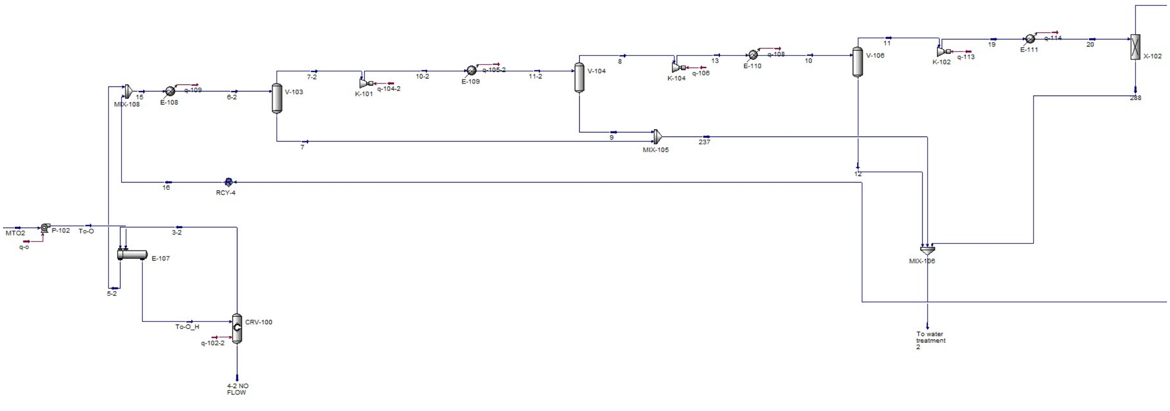

Figure 6.5: MTO conversion

6.1.5 C4 Cracking and Olefin Recovery

The purified vapor stream feeds into Distillation Column T-103 (debutanizer), separating heavier olefins (1-butene and n-pentane) at the bottom. This bottom stream is depressurized to 1 bar via Valve VLV-102, heated to 621°C through E-112 and E-113, and directed to the C4 Cracking Reactor (CRV-101), converting heavier olefins into lighter, more valuable ones.

$$C4+ \rightarrow CH4 + C2H6 + C2H4 + C3H8 + C3H6 + C4H10 + C5H12 + C5H10 + C6H14 + C6H6 + C7 + +Aromatics \tag{6.5}$$

The reactor output is cooled to 160°C and recycled back into the process.

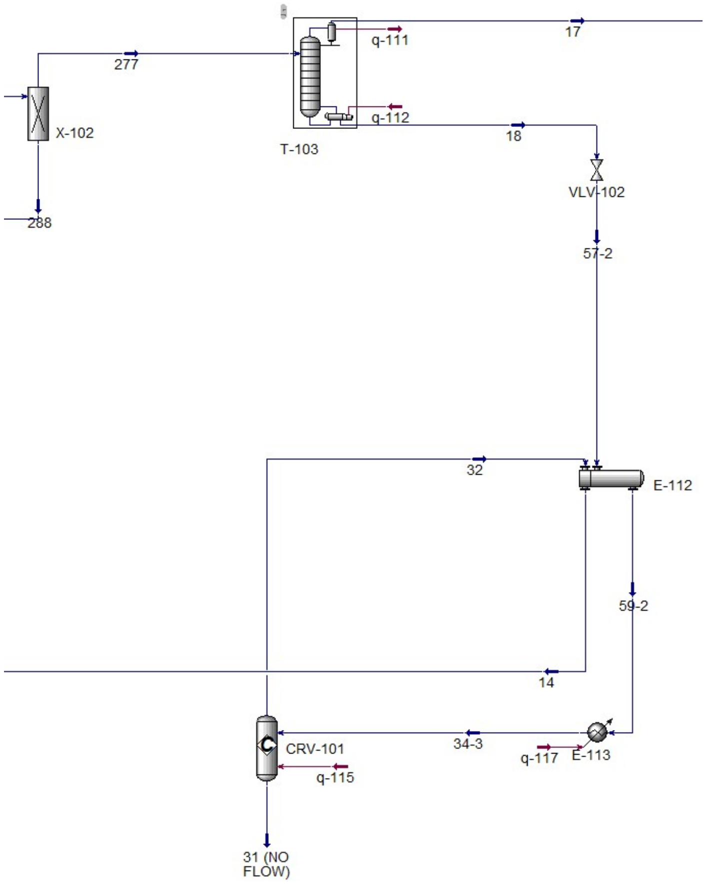

Figure 6.6: C4 Cracking

Parameter	T-103
Number of stages	30
Feed stage	15
Condencer Type	Full Reflux
Condencer Pressure (bar)	10
Reboiler Pressure (bar)	11
Reflux Ratio	3

Table 6.5: Design parameters of T-103

6.1.6 Cryogenic Recovery and Final Product Separation

The top product from T-103 is compressed and cooled, entering the Cryogenic Recovery Unit. Here, the stream sequentially passes through LNG Heat Exchangers LNG-100 to LNG-104, utilizing refrigerants like propene, ethylene, and methane to progressively lower temperatures from 30°C to -130°C. At each stage, separators (V-105, V-107, etc.) remove condensed olefins.

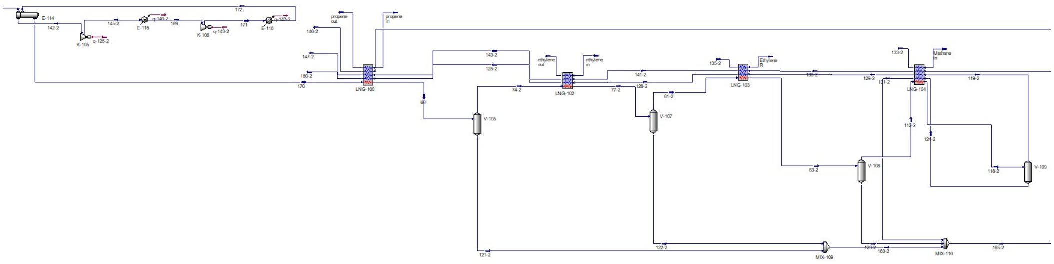

Figure 6.7: Cryogenic Recovery Unit

The collected liquid streams, rich in ethylene and propylene, undergo further separation in the Demethanizer (T-105), Deethanizer (T-106), and Depropanizer (T-107) columns, achieving high purity products: methane, ethane, and propane. The final purification steps involve the Ethylene Splitter and Propylene Splitter (T-108 and T-109), delivering polymer grade ethylene and propylene with purities of 99.9% and 99.5%, respectively.

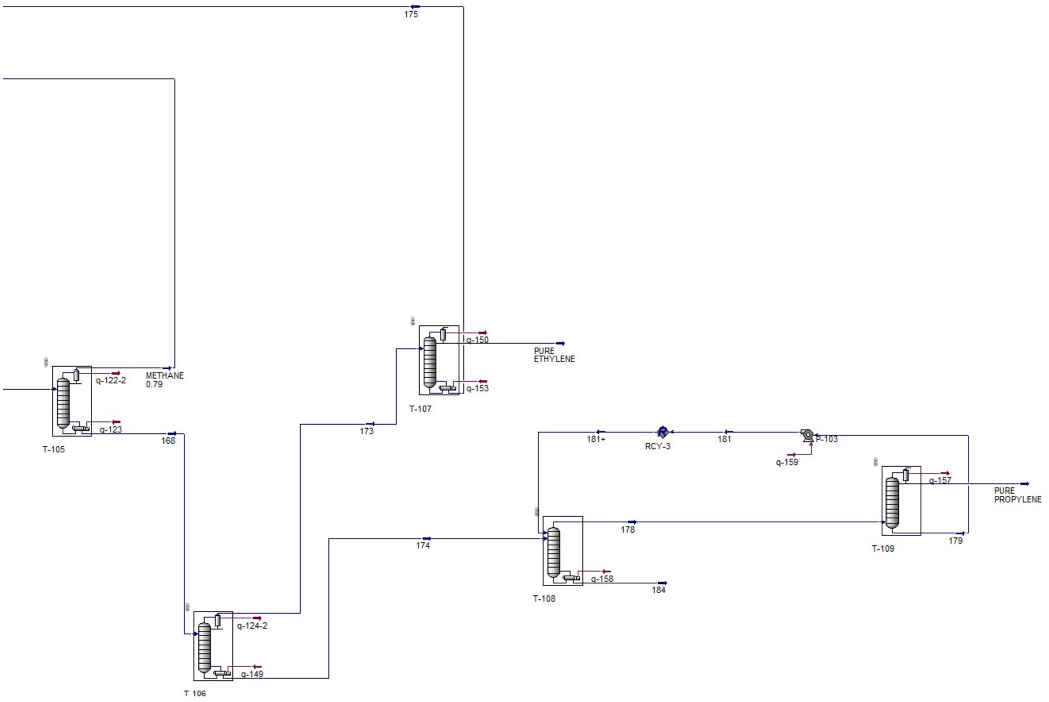

Figure 6.8: Olefin Separation

Parameter	**T-105**	**T-106**	**T-107**	**T-108**	**T-109**
Number of stages	60	65	90	100	100
Feed stage	30	31	45	34	-
Condencer Type	Full Reflux	Full Reflux	Total	-	Total
Condencer Pressure (bar)	31.10	28.50	17.41	17.20	16.40
Reboiler Pressure (bar)	32.10	29.50	18.11	18.20	17.40
Reflux Ratio	3	1.2	4	-	14

Table 6.6: Design parameters of T-105, T-106, T-107, T-108, T-109

Chapter 7

Results and Discussion

7.1 Simulation Overview and Results

The simulation for the biomass to olefins process via methanol was conducted using Aspen HYSYS V14. The Peng-Robinson equation of state was used as the primary fluid package. Additionally, Sour-SRK and Electrolyte-NRTL fluid packages were applied for the Rectisol unit and the hydrogen production unit (alkaline electrolyzer), respectively.

The simulation results show that the process is capable of producing approximately 0.848 Mt/year of high purity ethylene and 0.950 Mt/year of high purity propylene under a plant operating time of 8,000 hours per year.

The final ethylene product stream consists of 99.928% ethylene, with 0.064% CO2 and 0.003% ethane. The final propylene stream contains 99.500% propylene, with 0.496% propane and 0.004% ethane.

Although near polymer grade purity was achieved for both olefins, trace impurities remain, which is typical and unavoidable in industrial operations.

The detailed gas feed compositions used in the simulation are provided in table 7.1.

composition	**Biomass**
H2O	16.43
H2	41.52
CO	27.62
CO2	9.12
CH4	5.05
Others	0.26

Table 7.1: compositions of gas used in the simulation[21]

7.2 Water and Utility Consumption

While water is consumed as a feedstock in the biomass gasification stage, the system also discharges a significant amount of water. This is due to the inherent water and hydrogen content in biomass.

An important distinction should be made for the deionized water used in the alkaline electrolyzer a separate and higher grade utility input compared to the general process water, which also impose higher costs. From a utility standpoint, the most significant contributor to energy consumption is the alkaline electrolyzer, which requires approximately 370 MW of electricity to generate the 3500 kmol/h of hydrogen needed to meet the R-ratio in the methanol synthesis stage. It should also be noted that biomass gasification is energy intensive, requiring substantial heat input due to the low specific energy content of biomass.

7.3 Economic Evaluation

The total capital investment (TCI) for the process was estimated using the Aspen HYSYS Economic Analyzer. As illustrated in fig 7.1, the electrolyzer unit accounts for the largest portion of capital investment, amounting to roughly $370 million, followed by the purchased equipment category at $219 million. Other cost elements such as contingencies represent a significantly smaller share. That is to say, basically Contingencies refer to different factors such as uncertainties and the technology in the project, so one potential reason to justify high rate of Contingencies could be using large scale electrolyzer and nature complexity of the biomass to olefins process which introduces higher technical and economic risks.

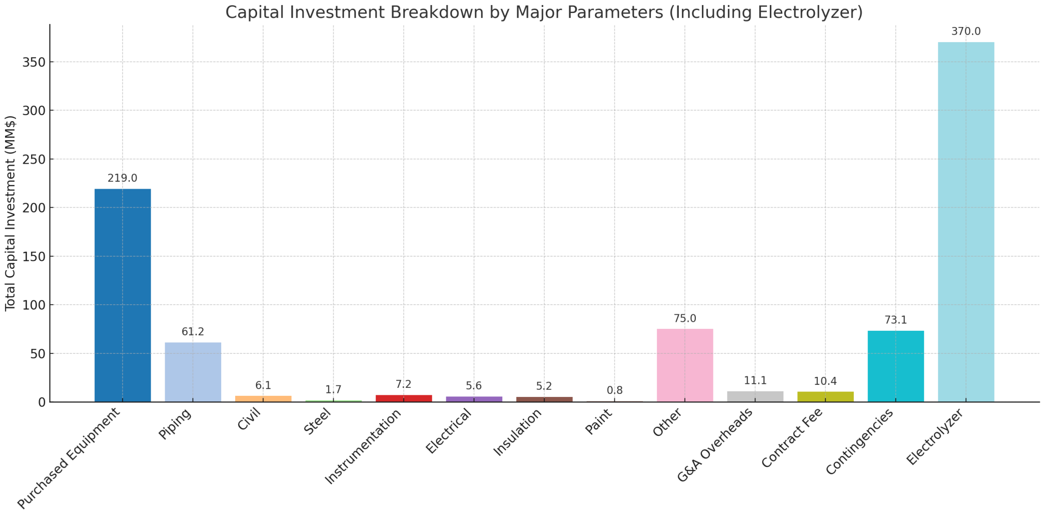

Figure 7.1: Total capital investment of the plant

7.4 Annual Sales Revenue

The total annual sales were calculated based on the product flow rates and market prices, assuming all outputs are either ethylene or propylene. The results are visualized in Figure 7.2, and detailed product and feedstock prices are presented in Table 7.2.

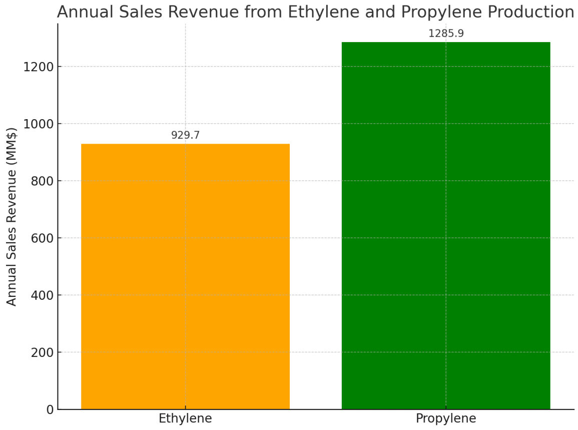

Figure 7.2: Annual sales

Items	**Values ($/t)**
Biomass	77
Ethylene	1531
Propylene	1484

Table 7.2: Feedstocks and Products Prices[21]

7.5 Production Costs

According to the cost estimation methodology adapted from Xiang[21], the total production costs are summarized in Figure 7.3, with input data provided in Table 7.3. As expected, utility costs, particularly for electricity, represent the largest expense due to the power demand of the electrolyzer. This is followed by feedstock costs and general operational expenses.

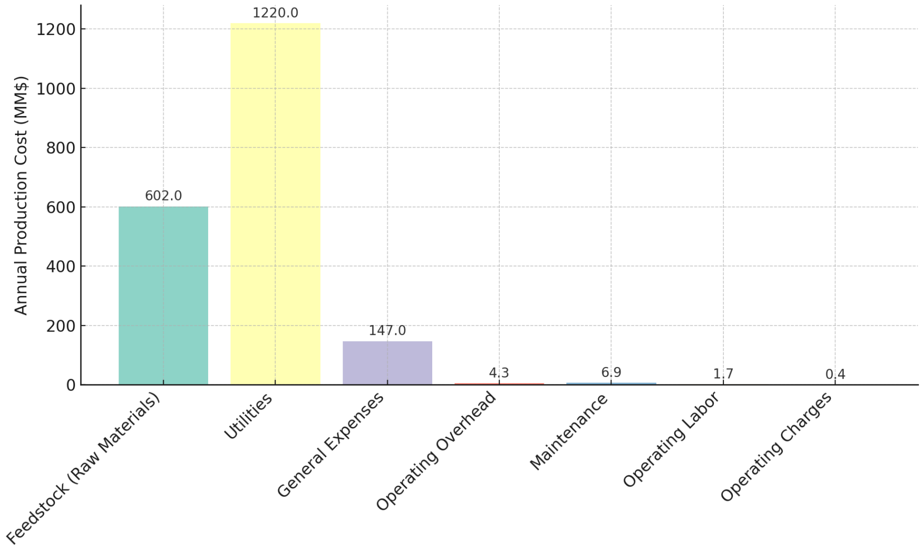

Figure 7.3: Total annual production costs

Items	Values ($/KJ)
Electricity	30.98
Fired Heat(1000)	10.91
HP Steam	34.43
LP Steam	12.70
Cooling Water	1.45
Refrigerant 1	14.70
Refrigerant 2	23.32
Refrigerant 3	40.73
Refrigerant 4	59.13
Refrigerant 5	77.54

Table 7.3: utility prices in this simulation[21]

7.6 Conclusion

This project's simulation and economic assessment provide meaningful insights into the integrated biomass-to-olefins (BTO) process via methanol synthesis. The model demonstrates the technical viability of producing nearly 2 million tonnes per year of chemical grade ethylene and propylene with purities reaching 99%, confirming the potential for large scale implementation.

In summary, while the BTO pathway offers significant environmental benefits particularly in reducing carbon emissions, the economic viability remains a key challenge.

Achieving competitiveness will require continued efforts in cost reduction, process optimization, and the integration of renewable energy sources, especially for hydrogen production.

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Appendix A

Appendix

Here is the appendix