

Production of Olefins from Carbon Dioxide and Renewable Energy

Ateajeu Tchio Denis William, Colard Jean-Jacques, Deckers Zoé, Hennuy Maurine, Reda Nadia

Abstract

Nowadays, it is crucial to change daily habits to live in a more sustainable world. From an industrial point of view, the capture of CO₂ is becoming more and more important in the chemical industry to reduce greenhouse gas emissions and its reuse can be an alternative to fossil resources. Another major challenge for future engineers is the significant increase in the use of renewable energy sources. In this perspective, a process allowing the synthesis of three different olefins from CO₂ captured in industrial flue gases and using only wind energy is established. This process is separated into three major sections: water electrolysis, carbon dioxide reduction to produce methanol and methanol-to-olefins synthesis. The targeted production capacity is of 450 000 tonnes per year of olefins, which are considered to be ethylene, propylene and butylene. This process, which involves a complete flowsheet modelling is implemented with the Aspen Plus software. A heat integration is performed to improve the system energy recovery and shows that 75% of the energy requirements can be recovered from the process. Then, an economic analysis is conducted to evaluate the viability of the modelled process and leads to the conclusion that the process is viable if built in 2050. Indeed, a positive net present value of about 4 345.47 M€ is obtained after 20 years. A sensitivity analysis evaluating the influence of the price of CO₂ on the price of ethylene is also conducted. Finally, a life cycle analysis allows to analyse the process from an environmental point of view and shows that the process can be an interesting alternative in comparison to the production of bio-olefins.

Keywords

Olefins - CO₂ reuse - Renewable energies - Process design - Techno-economic assessment - Methanol-to-olefins - Electrolysis

1. Introduction

This paper is intended to participate in the Student Contest Problem, a competition organised by the European Committee for the Use of Computer Science in Chemical Engineering Education (EURECHA) through which the *Manufacturing of Chemical Products from CO₂ using Renewable Energy Resources* [1] is studied. This year, Greece has been selected as the location in which the process should be implemented. Known for its rich natural environment, it is bordered by the Mediterranean Sea (South), the Aegean Sea (East) and the Ionian Sea (West). Moreover, its main industrial resources are, among others, tourism, agriculture, mining, and manufacturing. However, it has few natural resources, short supplies of fossil fuels, and only small deposits of silver ore and marble, which are mined while in terms of substantial mineral deposits, there are nonferrous metals [2].

Nowadays, it is relevant to propose process designs integrating captured CO₂ and renewable energy sources for chemical production. The European Union recently passed a climate law which aims to cut greenhouse emissions by at least 55% by 2030 and encourages its member countries to cut their fossil fuels dependence [3]. Therefore, Greece seems to be a good candidate for the development of such industry.

Carbon dioxide is an important greenhouse gas, which contributes to global warming. Over the past two centuries, its concentration in the atmosphere has increased significantly, mainly due to human activities such as fossil fuels burning [4]. Therefore, more and more technologies are being developed to capture CO₂ to decrease greenhouse gas emissions. The use of this CO₂ is being investigated as it can be an alternative to fossil resources.

In the scope of the Student Contest Problem, the main goal of this paper is to put forward the production of chemical products such as olefins, more precisely ethylene, propylene, and butylene, while using captured CO₂ as a raw material and renewable energies. First, a short introduction to olefins as well as an explanation of this choice is presented. Then, the implemented process including the methanol and the methanol-to-olefins synthesis routes, is explained. The objective of the process is to achieve an annual production capacity of 450 000 tonnes of olefins. Afterwards, a heat integration, followed by a cost analysis and a life cycle assessment, are developed. Finally, a conclusion on the presented solution is given.

2. Olefins

Following a review of current carbon-based chemical processes, and in light of the energy crisis, a green process based on the conversion of captured CO₂ to methanol (CH₃OH), which is then converted to olefins, will be highlighted throughout this article. An olefin represents a group of unsaturated chemical compounds, which are made of hydrogen and carbon, containing at least one pair of carbon atoms linked by a double bond [6].

The olefins produced in the presented process are ethylene, propylene, and butylene. It has been chosen to maximise the production of ethylene, which requires some specific operating conditions for the different reactions, as explained in the following sections. Many other olefins could have also been produced. However, the choice to focus on these three is made for several reasons.

First, ethylene is the most widely produced olefin, with a worldwide production capacity of 214 million metric tons in 2021 [7]. Indeed, it is used to produce four main compounds applied across many industries. These compounds are polyethylene used to make plastics (such as food packaging, toys, and hygienic products), ethylene oxide used in the production of other chemicals (steriliser for medical applications and an antifreeze among others), ethylene dichloride which is primarily transformed into a vinyl chloride product (PVC pipes), and finally, styrene, which is used in synthetic rubbers, paints, polyesters, etc [8]. Moreover, the global olefins market size is expected to grow at a compound annual growth rate (CAGR) of 4.75% by 2029 [9]. In terms of ethylene, the market is expanding at a CAGR of 5.6% in the forecast period 2020-2027 as there is an increasing demand in the construction and automotive industries [10]. In addition, through the Phillips Triolefin Process, it is possible to convert ethylene to propylene, whereas the reverse reaction is not applicable nowadays [11].

Propylene is the second most-produced olefin, and it is mainly used to make polypropylene. Indeed, almost two-third of the whole propylene production is applied to produce polypropylene [12]. The latter is a thermoplastic with a wide range of applications. Indeed, not only is it adopted for plastic furniture and plastic packaging, but it is also utilised for fibres and textiles [13]. This semi-crystalline thermoplastic is characterised by high flexibility, good chemical and fatigue resistance, lighter density (when compared to High-Density Polyethylene) and better temperature resistance [14]. Propylene is also applied to make a series of chemicals such as propylene oxide, which is employed as a chemical intermediate in the production of propylene glycol and polyethers, but also as a fumigant for the sterilisation of packaged foods [15]. Additional produced chemicals are isopropyl alcohol, which is used to make inexpensive solvents [16], plasticizer alcohols, which are mainly applied in the manufacture of esters [17] and cumene, which is involved in the production of acetone and phenol [18].

Concerning butylene, it represents all unsaturated four-

carbon olefins. It is mainly applied in the production of isooctene and methyl tert-butyl ether (MTBE), which are important components of gasoline as well as other chemicals used in rubber processing. Butylene is also utilised in the alkylate industry [19] [20].

3. Location: Carbon Dioxide and Renewable Energy Sources

To render the process more plausible and have a concrete idea of the potential industrial project, a case study is presented. The carbon dioxide source in Greece as well as the plant location and the type of renewable energy are defined.

3.1 Carbon Dioxide Source

Greece is among the top ten CO₂ emitters in the European Union [21] with nearly 79.91 million tonnes of carbon dioxide equivalent produced in 2019 [21]. In 2020, greenhouse gas emissions in this country were shared among four major sectors: energy with 68.88%, industrial processes and product use with 13.99%, agriculture with 10.61% and waste with 6.51% [22]. The energy production industries are the most dominant in this ranking as Greece's energy sector is mainly dependent on fossil fuels. However, the government plans to reduce the impact of these industries by closing many of them, including all lignite power plants by 2028 [23]. Consequently, the emissions associated to the energy sector will decrease, and the proportion associated with the industrial processes and product use will therefore increase in the following years. With the objective of decreasing the overall greenhouse gas emissions, and more precisely the CO₂ emissions, the industrial processes can become a valuable source of CO₂.

The choice of the main CO₂ source for the studied production plant is a cement and building material manufacturer plant located in Kamari and part of the TITAN Cement Group [24]. In addition, other smaller industries are located around the TITAN plant and could be secondary CO₂ sources if needed. Two examples are the Lubrico Tsakalis chemical plant [25] and the Ecorecovery waste management plant [26].

3.2 Plant location

The location of the site, which is illustrated in Figure 1, is identified while taking into account the space in the vicinity of the CO₂ source produced by the TITAN cement group Kamari factory located in the Boeotia region, as well as the various logistical means in the region (industrial or popular). It has been determined that an area of 46 000 m² is required for the production plant. This surface has been determined based on a comparison of different facilities, for example the methanol production facility of the Methanex company, located in Medicine Hat, Alberta, Canada [27].

3.3 Renewable Energy

In 2019, 29% of Greece's electricity was generated from renewable energy sources. Greece is considered to be a late-comer in renewable energies in comparison to other European



Figure 1. Future plant location, using Google maps [28], and ArcGIS [29]

countries, especially given the amount of sun and wind available in Greece. It is expected that by 2030, renewable energies will account for over 61% of the Greek electricity mix [30].

Wind and solar energies represent the vast majority of renewable energy already produced in this country, the most prominent producers being respectively located in Kozani with a 204 MW solar power plant [31] and in Kafireas with a 154 MW wind farm [32]. However, the energy required to operate the studied process is far greater than the production capacity of these sites, considering the targeted production amount of olefins. Taking into account the fact that many projects aim to develop renewable energy capacity in Greece, the present work considers a hypothetical wind farm that has a production capacity similar to the Princess Elisabeth offshore wind zone in Belgium. Indeed, the Belgian government decided to expand the size of this offshore wind zone and a capacity of 3.5 GW is targeted [33].

4. Process

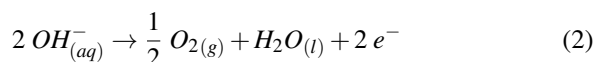
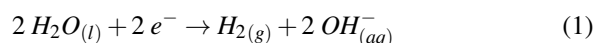
The production of olefins considered in this process happens in three main steps. First, hydrogen is produced through water electrolysis. The obtained hydrogen then reacts with the captured carbon dioxide to produce methanol. Finally, methanol undergoes the methanol-to-olefins process, which allows to obtain ethylene, propylene, and butylene.

The olefins production process has been modelled in Aspen Plus V11. The thermodynamic models used to represent this process are the E-NRTL model for the liquid phase of the distillation columns involving the separation of methanol from other components, especially water, and the Redlich-Kwong Equation of State for their vapor phase. The Peng-Robinson Equation of State is used for both liquid and vapor phases for the rest of the process. A different model has been used for the distillation columns involving methanol because methanol is a polar component for which the vapor/liquid equilibrium cannot be represented with the Peng-Robinson model, mostly used in hydrocarbon applications [34][35].

The targeted olefins production is of 450 000 t/year per year. Considering that a year corresponds to 8 000 operating hours, the capacity becomes 56.25 t/h. This capacity is chosen to be competitive on the olefins market and it represents a little more than half the capacity of the biggest single-train methanol-to-olefins plant in the world [36].

4.1 Hydrogen Production: Water Electrolysis

Hydrogen is produced from alkaline water electrolysis, which is the type of water electrolysis with the biggest installed capacity in the world in 2021 [37]. The reactions occurring respectively at the cathode and anode are shown in Equations 1 and 2 [38]:



For the simulation in Aspen Plus, the electrolysis cell has been modelled as a stoichiometric reactor, for which the stoichiometry and conversions associated to the reactions must be specified. After discussion with an expert [39], a water conversion of 0.95 has been selected. This reactor is represented by the reactor ELECTRO on the left part of Figure 2, which shows the modelled process in Aspen Plus.

Based on the targeted olefins production, it has been determined that 61.1 t/h of hydrogen are required. This hydrogen is produced using 558.2 t/h of water and 2.4 GW of green electricity, which also yields 497.1 t/h of oxygen. However, the water input of the process is smaller than 558.2 t/h because some water is recycled throughout the process. Indeed, 206.7 t/h are recycled after being treated, meaning that a make-up stream of 351.5 t/h is necessary.

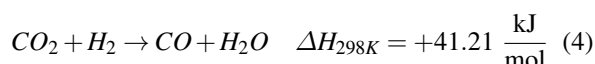
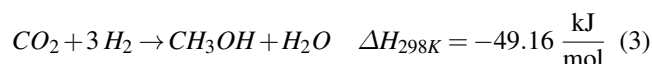
An additional important input of the process is the amount of carbon dioxide captured, which is equal to 329.7 t/h. This carbon dioxide is considered to be captured and available at 25°C and 2 bar. The impurities of this stream are neglected, as their impact on the process is not significant. The carbon dioxide capture unit is not modelled in this work.

It must be noted that the captured carbon dioxide and the produced hydrogen are then compressed up to 75 bar, which is the working pressure of the methanol production reactor [40][41], depicted in Section 4.2.

4.2 Methanol Production: Carbon Dioxide Reduction

4.2.1 Reactor

For the simulation of the carbon dioxide reduction to produce methanol, the three following reactions are considered, where (3) and (5) are exothermic and (4) is endothermic [40]:



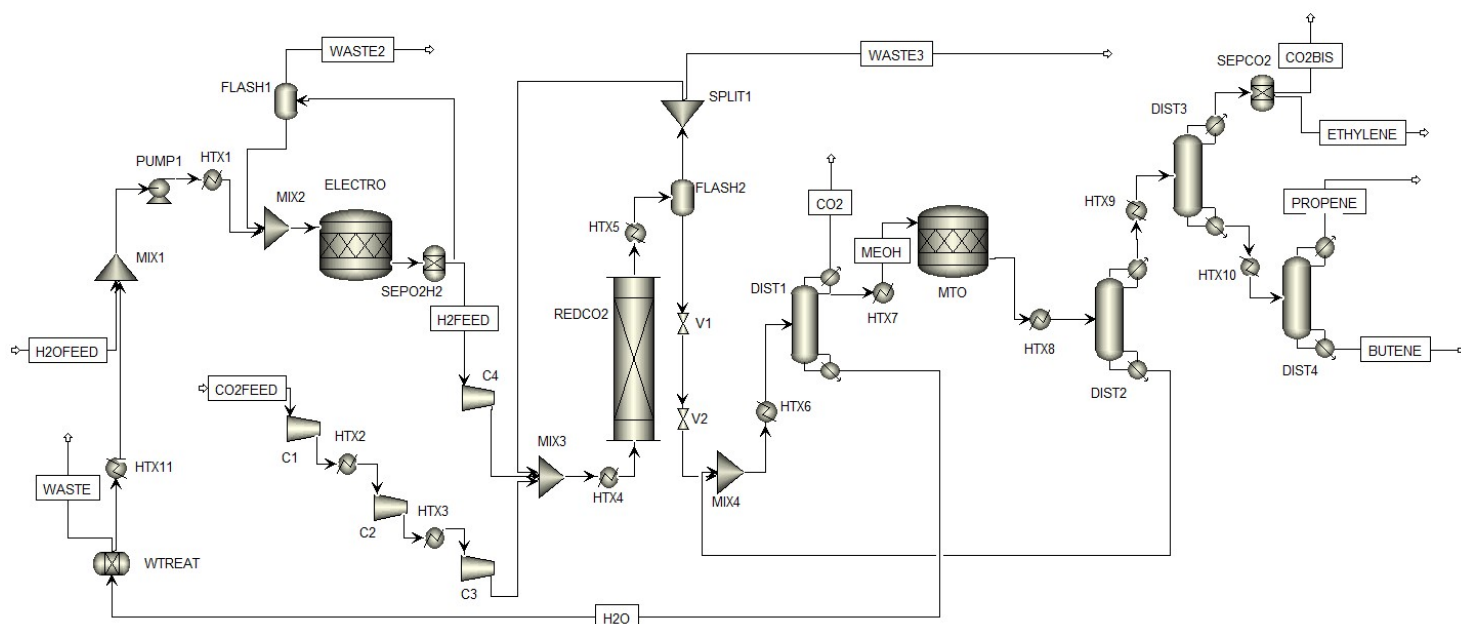
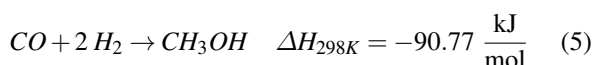


Figure 2. Process flowsheet modelled in Aspen Plus



The kinetics considered to represent those three reactions are Langmuir-Hinshelwood kinetics based on the use of a fibrous Cu/Zn/Al/Zr catalyst. The kinetic results associated with this model have been tested and validated by comparison with experimental data [40][42]. In Aspen Plus, the reactor has been modelled as a multitube plug-flow reactor, with 810 tubes with a diameter of 0.06 meters and a length of 12 meters [40]. Moreover, the reaction takes place at 250°C and 75 bar [40][41]. The methanol production reactor REDCO2 can be seen in the centre of Figure 2.

4.2.2 Separation of products

The reactor effluent is composed of methanol, water, carbon monoxide, unreacted carbon dioxide and hydrogen. This effluent is first cooled down, and a flash separation is performed at 15°C and 75 bar. This separation allows the recovery of a stream rich in methanol at the bottom and a stream rich in unreacted carbon dioxide and hydrogen at the top. The unreacted components then go through a purge, which is included to prevent the accumulation of potential inert components. These inert components are not considered in this work and so the purge is only present for simulation purposes. Ultimately, the unreacted components are recycled into the reactor.

The methanol-rich stream is expanded and then sent to a distillation column DIST1, which separates the stream into three product streams: methanol, CO₂, and water, the latter being recycled to the beginning of the process. The column has been specified to work at a pressure of 1.1 bar, has 17 theoretical stages with a feed on stage 8, a distillate-to-feed ratio of 0.26, a reboiler duty of 40 MW and a condenser duty of 113 MW.

The stream rich in CO₂ is negligible and is therefore not recycled but sent to a CO₂ treatment facility. The methanol-rich stream, containing 163.2 t/h of methanol with a molar purity of 91.54%, is sent to the methanol-to-olefins section of this process.

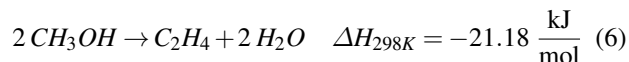
4.3 Methanol-to-Olefins

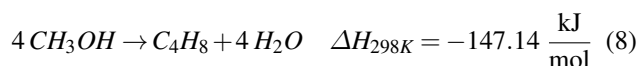
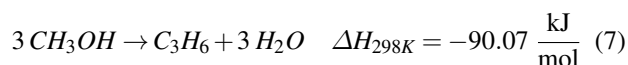
4.3.1 Process, reactions and reactor

The methanol-to-olefins process considered in this study is derived from the UOP/Norsk Hydro technology. This technology considers the conversion of methanol to different olefins using a silicoaluminophosphate zeolite catalyst called SAPO-34 in a fluidized bed reactor. The fluidized bed reactor facilitates the regeneration of the catalyst through circulation to an outside regenerator. Catalyst regeneration is needed because coke forms on the catalyst surface as the reactions go on. In addition, this type of reactor allows the removal of the heat generated by the exothermic reactions involved in the MTO process [43][44].

Firstly, methanol coming from the CO₂ reduction section is heated up to 340°C [43]. It is then sent to the reactor, which is modelled as a stoichiometric reactor in Aspen Plus. This type of model has been chosen because the evolutions of the reactions have been depicted in terms of methanol conversion. This reactor is considered isothermal and thus needs permanent cooling due to the exothermicity of the reactions. The MTO reactor can be seen on the right part of Figure 2.

The three main products considered are ethylene, propylene and butylene. The three reactions studied and their enthalpies are thus the following [45]:





Those reactions take place on the SAPO-34 catalyst, which is further described in Section 4.3.2. The methanol conversions of each reaction have been derived from experimental yields obtained with the UOP/Norsk Hydro technology and can be found in Table 1. The yields maximising the ethylene production were taken into account. The by-products (ethane, methane, coke, etc), which represent 5% of the total yield, were neglected in this study. The catalyst regeneration was thus neglected as well, but was taken into account within the economical analysis [43][46].

Table 1. Methanol conversion for the three considered reactions, derived from experimental yields [43][46]

Reaction number	Methanol conversion [-]
(6)	0.49
(7)	0.318
(8)	0.0979

The conditions at which the reactions take place are 510°C and 1.1 bar. Those conditions were chosen to maximise the ethylene production, as explained in Section 4.3.2, which describes the catalyst.

4.3.2 Catalyst description and characteristics

The SAPO-34 catalyst is a silicoaluminophosphate zeolite and it is a micro pore molecular sieve which was developed by Union Carbide. In this report, the UOP/Hydro MTO process is used, within which light olefins with high purities (about 97%) are produced. When splitters are added, an even higher level of purity can be reached and the ethylene to propylene ratio can be adjusted between 0.5 and 1.5 [44][47][48].

Therefore, due to the small size of the catalyst's pores (4 Å), heavy or branched hydrocarbons do not diffuse, leading to the formation of small linear olefins with high selectivity [44]. Furthermore, its milder acidity decreases the amount of hydrogen transfer reactions, which lowers the formation of paraffinic by-products thus increasing olefinic products' yields. Nevertheless, this catalyst deactivates severely, forcing a regeneration [44][47][48].

Moreover, it is important to note that there exists a series of SAPO catalysts. However, as long as the MTO reaction is regarded, the SAPO-34 catalyst leads to excellent catalytic performance due to its CHA structure (Chabazite Zeolites structure), which explains why it is more used than others [49]. As the choice to maximise the production of ethylene was made in this article, the reactor must operate at a temperature between 475 and 550°C and the pressure should be between 1 and 4 atm [43][47]. In fact, the higher the temperature, the higher the ethylene selectivity as the ethylene-to-propylene

ratio increases [43]. In addition, a lower pressure allows to favour the production of ethylene [43]. On the other hand, it is necessary to make sure that before entering the reactor, the methanol's temperature should not exceed 350°C as above this value, the component can dissociate into hydrogen and carbon monoxide which is why the methanol feed is heated at 340°C [43][50].

4.3.3 Separation of products

The reactor output consists of ethylene, propylene, butene, water, unreacted methanol and a small quantity of CO₂, coming from the CO₂ reduction section. The next step is thus the separation of the different components to increase the purity of the different products.

First of all, the reactor effluent is cooled down to 15°C and is sent to a distillation column (DIST2), which has the purpose to separate the valuable products (ethylene, propylene, and butylene) from water and unreacted methanol. This column is specified to work at 1.1 bar, has 11 theoretical stages with a feed above stage 10, a reflux ratio of 0.115 and reboiler duty of 5 MW. The top stream of the column contains the products while the bottom stream contains mainly water and methanol which are sent back to the first distillation column (DIST1) that separates methanol and water.

The top stream of the column is then heated up to 25°C and sent to a distillation column (DIST3) which separates ethylene and CO₂ from propylene and butylene. This column is specified to work at 1.1 bar, has 14 theoretical stages with a feed above stage 7, a distillate-to-feed ratio of 0.67 and a reboiler duty of 900 kW.

The top stream of column DIST3 has the following mole fractions: 0.99 of ethylene and 0.01 of CO₂. A separation from CO₂ is performed to obtain high-purity ethylene. In the scope of the simulation, this separation is modelled through the use of a separator block (SEPCO2) for which the different split fractions of the components are specified. Physically, this separation could, for example, correspond to a pressure-swing adsorption unit using a carbon molecular sieve as adsorbent [51]. It leads to the production of 31.31 t/h of ethylene with a molar purity of 99.99%. The stream rich in CO₂ is negligible and is sent to a CO₂ treatment facility.

Finally, the bottom stream of column DIST3 is heated up to 15°C and sent to a distillation column (DIST4), which separates propylene from butylene. This column is specified to work at 1.1 bar, has 13 theoretical stages with a feed above stage 7, a distillate-to-feed ratio of 0.807 and a reboiler duty of 850 kW. This last distillation allows the production of 18.9 t/h of propylene with a molar purity of 99.8% and 6 t/h of butylene with a molar purity of 99.4%.

5. Heat Integration

A heat integration has been performed to determine the minimum energy quantity required by the process. First, a pinch analysis has been conducted, which allows to identify the

pinch temperature as well as the necessary hot and cold utilities.

The different heat streams of the process are listed in Tables 2 and 3, where the unit through which they pass is mentioned. There are 12 hot streams and 10 cold streams. However, a phase change occurs in three units, either at the initial or the final temperature of the stream (HTX7, HTX8, and HTX10), which must be taken into account. Therefore, those streams must be subdivided into two for the pinch analysis implementation: one sub-stream for the temperature change and one sub-stream for the phase change. Thus, there are 13 hot streams and 12 cold streams in total. Also, a minimum temperature difference of 10°C has been applied.

Table 2. Hot streams table ("Cond" corresponds to condenser)

Stream	Unit	$T_{in,s}$ [°C]	$T_{out,s}$ [°C]	Q [kW]
H1	Cond DIST1	61.6	8.0	113 028.5
H2	Cond DIST2	-23.7	-54.2	1 967.6
H3	Cond DIST3	-106.9	-107.5	6 039.6
H4	Cond DIST4	-50.1	-50.8	2 002.2
H5	HTX2	155.4	33.0	10 628.8
H6	HTX3	137.3	33.0	9 710.4
H7	HTX5	245.0	30.0	964 404.1
H8	HTX8-V	505.0	88.0	29 709.3
H9	HTX8-LV	88.0	10.0	77 934.4
H10	HTX11	78.5	15.0	16 532.8
H11	REDCO2	246.0	245.0	120 650.4
H12	FLASH1	68.0	65.0	5 821.4
H13	FLASH2	30.0	10.0	87 775.9

Table 3. Cold streams table ("Reb" corresponds to reboiler)

Stream	Unit	$T_{in,s}$ [°C]	$T_{out,s}$ [°C]	Q [kW]
C1	Reb DIST1	85.8	88.7	40 000.0
C2	Reb DIST2	27.6	59.5	5 000.0
C3	Reb DIST3	-37.8	-36.9	900.0
C4	Reb DIST4	-0.4	0.4	850.0
C5	HTX1	25.0	75.0	35 074.0
C6	HTX4	34.4	255.0	846 631.0
C7	HTX6	30.1	85.0	97 393.2
C8	HTX7-LV	18.0	71.4	58 233.3
C9	HTX7-V	71.4	345.0	22 875.6
C10	HTX9	-44.2	30.0	1 649.8
C11	HTX10-LV	-36.9	-25.1	3 063.6
C12	HTX10-V	-25.1	20.0	446.7

The grand composite curve (GCC) constructed from all the heat fluxes is depicted in Figure 3. The pinch point is located where the heat flow is null and it separates the process into two regions. The region above the pinch point only requires hot utilities while the region below only requires cold utilities.

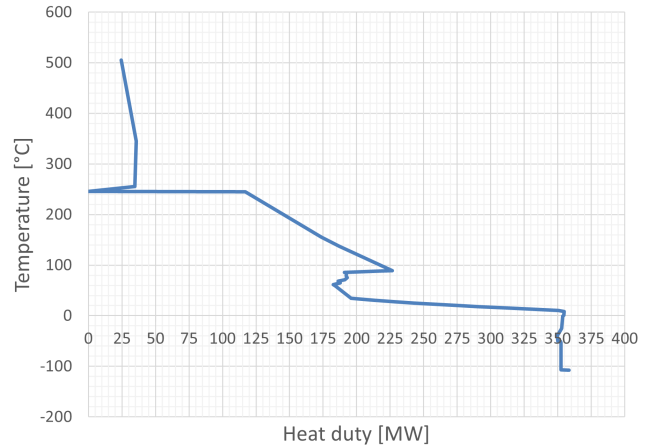


Figure 3. GCC

When analysing Figure 3, it can be observed that the pinch temperature is found at 246°C. Moreover, in the optimal case, the process would require a total of only 24.4 MW of hot utilities and 358.4 MW of cold utilities. This represents only 15% of the total heat needed by the non-optimised process. It means that 85% of utilities can be saved through energy optimisation.

From this GCC, some major steps can be highlighted. First, the plateau observed around 250°C corresponds to the reactor producing methanol (REDCO2). It requires an important quantity of energy to keep its temperature constant as the reaction is highly exothermic. The long slope between 250°C and 90°C is mainly due to the heater HTX4 and the cooler HTX5. The former brings the stream to the temperature needed to produce methanol while the latter cools it down afterwards. They both require a huge quantity of energy and the difference between their duties is of more than 100 MW. Other units also have an impact on the slope, such as HTX3 and HTX7-V. However, their effects are negligible compared to those of HTX4 and HTX5 as their heat duties are much smaller. Then, the small plateau around 85°C comes from the reboiler of DIST1. Indeed, the stream must be heated from 85.8°C up to 88.7°C and the heat duty required is of 40 MW. Afterwards, the slope between 35°C and 10°C comes from HTX7-LV and HTX8-LV. These two units are located on both sides of the MTO reactor, which works at a very high temperature. The heater HTX7-LV and the cooler HTX8-LV need a lot of energy because they induce the phase change of the stream that flows through them. This last slope is also due to the condenser of the distillation column DIST1 and the flash tank FLASH2, which both lead to an increase in the methanol purity.

A heat exchanger network must be modelled to improve the process and decrease its energy requirements. It allows to optimise the energy recovery by determining heat transfers between hot and cold streams. Indeed, if the minimum energy requirements determined by the pinch analysis are reached, then 85% of the total energy needed would be saved com-

pared to the non-optimised process. Several important heat exchanges can be implemented in the process to reach that goal. The heat exchanger network is shown in Figure 4.

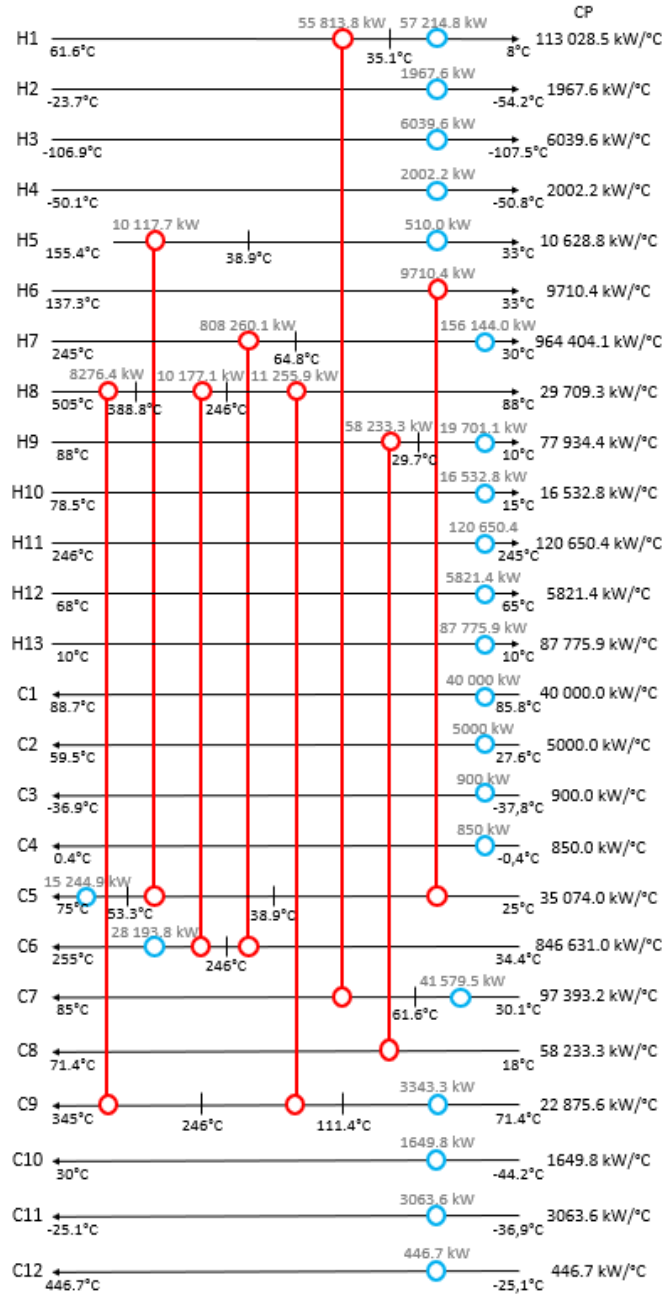


Figure 4. Heat exchanger network

Above the pinch point, two exchanges enable the saving of 60.2% of the required heat duties:

- Between the input and the output of the MTO reactor (H8 and C9)
- Between the output of the MTO reactor and the input of the methanol production reactor (H8 and C6)

Thus, 24.4 MW of hot utility still need to be provided to the process to heat the stream flowing through HTX4 up to its final temperature. Below the pinch point, six heat exchangers can be used to save up to 75.4% of energy:

- Between the output and the input of the methanol production reactor (H7 and C6)
- Between the output and the input of the MTO reactor, before and after the phase change (H8 and C9 as well as H9 and C8)
- Between the condenser of the first distillation column and its input (H1 and C7)
- Between the input of the last compressor of CO₂ and the output of the pump of the H₂O (H6 and C5)
- Between the input of the second compressor of CO₂ and the output of the pump of the H₂O (H5 and C5)

Thus, once those eight heat exchangers are added to the process, 115.9 MW of hot utilities and 474.4 MW of cold utilities are required below the pinch point. 75% of the required energy is recovered from other streams by implementing all those heat exchangers so it must not be brought from outside the process. However, the heat exchanger network should be further optimised to remove the hot utilities required below the pinch point and reach the values obtained from the pinch analysis.

6. Economic Analysis

When designing a process, one of the most important steps is the evaluation of its economic feasibility. Indeed, if the process is not cost-effective, one must either find a way to make it profitable or the project is stopped. Therefore, in this section, the costs of the presented process are investigated and analysed. The methodology developed by Turton et al. in [52] is applied, through which capital expenditures (CAPEX) and operational expenditures (OPEX) are computed, and a cash flow analysis is assessed.

6.1 CAPEX

The estimation of the CAPEX for each piece of equipment is achieved while using a series of different correlations available in the referenced book [52]. It can be divided into three main steps. First, the cost of major units is evaluated in base case conditions (ambient pressure and using carbon steel as a material), C^0 through Equation 9, where K_i are empirical constants and A is either a size parameter or a capacity:

$$\log_{10}(C^0) = K_1 + K_2 \log_{10}(A) + K_3 \log_{10}(A)^2 \quad (9)$$

In terms of compressors and pumps, the value of A is easily determined as it corresponds to the required net work [kW] which is retrievable from the process simulation. On the other hand, sizing was made in the case of distillation columns, flash

tanks, reactors as well as heat exchangers. Concerning the distillation columns, they are viewed as cylinders. Thus A , which represents the volume, in this case, can be computed by using their diameter and height calculated through the simulation. This methodology cannot be applied to determine the volume of the reactors or the flash tanks, as no sizing parameter is provided within the simulation. Therefore, their volume is estimated while using the residence time of a liquid phase and the liquid volume flow rate [L/min] present in the process model. The residence time is either retrievable from the process simulation, which is the case for the reactor REDCO₂, or it is assumed. For flash tanks, it is supposed that the liquid residence time is of about 10 minutes [53]. Their volume is then multiplied by 2 to make sure that the gas, which is also contained in the flash tank, has enough space to leave. For the MTO reactor, a residence time of 0.15 seconds was calculated while using values given in [54].

Then, the operating conditions of the equipment must be taken into account. Indeed, the CAPEX also considers the effect of the operating pressure as well as the type of material used for the construction. Therefore, one must use two factors, the pressure factor F_p and the material factor F_m , which are calculated through relations developed in [52], according to the operating pressure and the chosen material. In this case, it has been decided to use stainless steel (SS) for all equipment, as methanol is highly corrosive to carbon steel (CS) [57]. Furthermore, as these equations were developed in 2001, it is important to consider inflation. Thus, the cost of the units must be multiplied by an index such as the chemical engineering plant cost index (CEPCI). This value is yearly updated and in August 2022 it was equal to 824.5 [56]. It has been decided to use this value for this study. To calculate the bare module cost C_{BM} , one must use Equation 10, where B_1 and B_2 are constants:

$$C_{BM} = C^0 \cdot (B_1 + B_2 \cdot F_m \cdot F_p) \cdot \frac{CEPCI \text{ NOW}}{CEPCI 2001} \quad (10)$$

Finally, Equation 11 allows to calculate the grassroots plant cost, which accounts for additional costs, such as auxiliary facilities.

$$C_{GR} = 1.18 \cdot \sum_{i=1}^n C_{BM,i} + 0.5 \cdot \sum_{i=1}^n C_i^0 \quad (11)$$

A summary of the bare module cost of different equipment categories found in the process is available in Table 4. It is assumed that the capital cost of alkaline electrolyser systems is of about 700 \$/kW_{el} [58]. It is also important to mention that mixers have been neglected as they are considered simple tanks with no agitation. Also, in this case, flash tanks have a higher cost than the reactors because the flux entering FLASH2 is characterised by a high volume flow rate (of about 7 089.5 L/min). This could also be due to the fact that the price of the reactors is not relatively high. Compressors have higher prices as well, which could be due to the fact that each flux is compressed at high temperatures. This consumes significant

amounts of energies. Indeed, for example, the CO₂FEED is fed to the first compressor at a temperature equal to 25°C and it leaves at 160°C.

Table 4. C_{BM} of different equipment categories

Equipment	Cost [M€]
Heat exchangers	517.26
Pump	0.141
Compressors	63.61
Distillation columns	6.79
Reboilers	96.69
Condensers	9.82
Reactors	39.46
Electrolyser	1 691.77
Flash tanks	113.96

The total CAPEX is thus estimated at 6 992 M€. Figure 5 highlights the main contributing units. When analysing this figure, it can be noticed that the electrolyser contributes the most, which is logical as it is characterised by a high cost, and it requires a large amount of electricity (about 2.416 GW). It is then followed by the heat exchangers. Their cost is relatively high due to significant energy requirements, which therefore leads to the use of bigger heat exchangers.

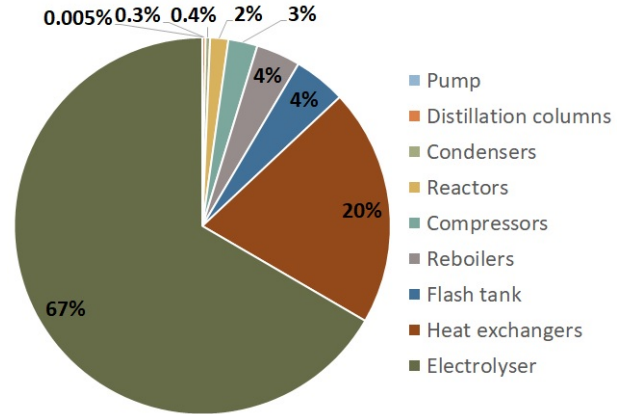


Figure 5. CAPEX distributions

6.2 OPEX

When evaluating the operational expenditures (OPEX), different costs need to be considered. Indeed, the total manufacturing cost COM is obtained through Equation 12 (given in the Turton et al. [52]), where the contributions are the cost of the raw materials C_{RM} , the waste treatment cost C_{WT} , the cost of utilities C_{UT} , the cost of labour C_{OL} , the fixed cost of investment FCI and the depreciation d_k .

$$COM = C_{RM} + C_{WT} + C_{UT} + 2.215 \cdot C_{OL} + 0.146 \cdot FCI + d_k \quad (12)$$

The cost of raw materials represents the cost of captured CO₂, distilled water, as well as the cost of the catalyst, which

is SAPO-34. For the price of captured CO_2 from flue gases, a price of 0.04 €/kg was considered based on [59] and the fact that capturing CO_2 from cement plants is more accessible. Then, it has been decided to use distilled water, as it is fed to an alkaline electrolyser, and its cost is evaluated at about 14.5 \$/ 1000 kg [52]. In terms of the catalyst, an average price of about 70.7 €/kg has been considered [61].

The waste treatment cost consists of the cost of the wastewater treatment approximated at 56 \$/ 1000 m^3 and the cost of flue gas treatment which is evaluated at 0.3 \$/ 1000 m^3 , values given in [52]. The cost of the wastewater treatment represents the treatment of the flux treated in WTREAT. The cost of flue gas treatment corresponds to the cost relative to the treatment of CO_2 streams.

Concerning the cost of utilities, different heating and cooling utilities available in [52] were applied in this process according to each unit's needs. Low-pressure steam available at 160°C and 6 bar as well as high-pressure steam at 254°C and 42 bar are used. As for cooling utilities, cooling water available at 30°C with a temperature variation of 10°C as well as low-temperature refrigerant water at -20°C and very low refrigerant at -50°C are used. Indeed, refrigerant water is applied as the temperatures reached in the distillation columns DIST3 and DIST4 are extremely low. Furthermore, the condenser in DIST3 operates at a temperature of about -100°C thus a cryogenic refrigerant must be used. A price of about 56.6 €/GJ can be assumed from [62]. Furthermore, a cost of electricity of about 0.018 €/kWh was considered for which only pumps, compressors and the electrolyser accounts for. This price was obtained while assuming that the plant will be built in 2050. It was found through researches, that the cost of offshore wind electricity is equal to 44.89 €/MWh in the UK [63] and it is believed that the price of this electricity will drop by 35-40% by 2050 [64].

Table 5. Heating and Cooling utilities Costs

Utility	cost [€/GJ]
Cryogenic refrigerant	56.6
Very low T refrigerant water	13.3
Low T refrigerant water	8
Cooling water	0.36
Low-pressure steam	2.6
High-pressure steam	5.3

One must calculate the number of working positions (N_{WP}) and the number of operators (N_{OL}), to determine the labour cost. Indeed, this cost estimates the value needed to pay the operators required to run the plant. For this case, it is assumed that one operator works 49 weeks a year and 5 shifts per week which means that the number of shifts per year per operator corresponds to 245. Also, it is considered that 3 shifts are required per day per working position. As a year represents 1 095 shifts, 4.5 operators are required per working position. Concerning the number of working positions, it can be calculated through Equation 13 where N_{np} represents the

number of non-particulate processing steps. In this case, the process does not contain any processing steps with solids, P is equal to 0. Finally, 157 operators are required.

$$N_{WP} = (6.29 + 31.7 \cdot P^2 + 0.23 \cdot N_{np})^{0.5} \quad (13)$$

The average salary of a chemical operator in Greece is around 29 665 €/yr based on [65] and [66]. Finally, the fixed cost of investment, FCI is equal to the grassroots cost C_{GR} calculated in the previous subsection. As for the depreciation, it accounts for the deterioration of the equipment. For the cash flow analysis, the MARCS (Modified Accelerated Cost Recovery System) method is used to evaluate the depreciation. Moreover, the cost of manufacturing without considering the depreciation was determined as well through Equation 14. This cost will be further studied to evaluate the different cost contributions to OPEX.

$$COM_d = 0.18 \cdot FCI + 2.73 \cdot C_{OL} + 1.23 \cdot (C_{RM} + C_{WT} + C_{UT}) \quad (14)$$

The different costs are summarised in Table 6.

Table 6. OPEX costs summary

	Cost [M€]
C_{RM}	146.44
C_{UT}	396.65
C_{WT}	0.17
C_{OL}	4.6
FCI	6 992
d_k	1 165
COM	3 382
COM_d	1 939

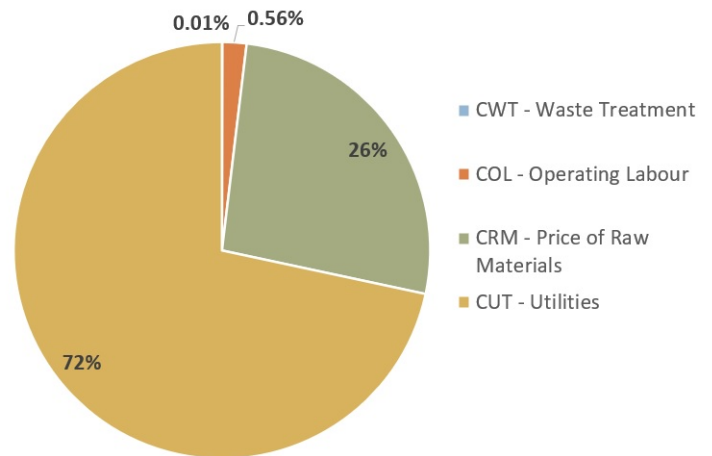


Figure 6. OPEX distributions

Figure 6 represents the different contributions to COM_d . It has been decided to neglect the depreciation as it is studied

through the cash flow analysis in the following subsection. Also, the FCI is not considered in the pie chart as a focus on operational expenditures is preferred without taking into account the influence of the CAPEX. It can be seen in Figure 6 that the biggest contribution is the utilities. Indeed, electricity accounts for the majority, about 97.7% due to the electrolyser's demands. Concerning the raw materials, its contribution is mostly because of the price of CO₂.

6.3 Cash Flow Analysis

A cash flow analysis aims to see whether a project is profitable or not as the effect of time is considered. The assessment can be established through a discounted cash flow (DCF) diagram, as represented in Figure 7. However, to obtain this figure, certain assumptions must be made. First, it is assumed that the plant will operate for 20 years and that within these 20 years, 2 years are used to buy the land and then build the plant. The total investment consists of the land cost, which is assumed to be of about 9.4 €/m² [67], the working capital and the fixed capital investment also known as the fixed investment cost. The salvage value is considered to be equal to zero as it has been decided that the plant will not be sold therefore no profit will be made following the plant's lifetime.

Then, the after-tax cash flow, which is the profit generated by the plant, is calculated.

The revenue R is equal to 2 937 M€/y. This value is obtained while considering an original cost of about 1.16 €/kg for ethylene [68], 1.24 €/kg for butylene [69] and 1.09 €/kg for propylene [70]. Then, according to an article [71], by March 2023, the price of ethylene and propylene has increased by a factor of 950 €/tonne and the price of butylene of 1 100 €/tonne. Moreover, it is assumed that per raw material, a subsidy of 500 €/tonne will be provided. Finally, each sum (original price + increase + subsidy) is multiplied by 2.5 as it is expected that the cost of olefin will increase by a factor of 2-3 by 2050 [72]. Also, a tax rate equal to 22% in Greece is taken into account [73].

Afterwards, the discounted cash flow (DCF) is computed through Equation 15 to obtain Figure 7.

$$DCF = \frac{CCF}{(1+i')^k} \quad \text{with} \quad i' = \frac{1+i}{1+f} - 1 \quad (15)$$

Where CCF represents the cumulative cash flow, i' is the inflation-adjusted interest rate, which is calculated while using the inflation rate f (1.91% [74]), the interest rate i (5% [75]) and the number of years k .

When analysing Figure 7, it can be seen that the process is profitable only after 12 years as the project's net present value is positive on year 13 and then it keeps increasing. Furthermore, one can identify the investment of the land (year 0) followed by the investment of about 60% of the fixed capital investment (year 1) and finally the investment of about 40% of the fixed capital investment (year 2).

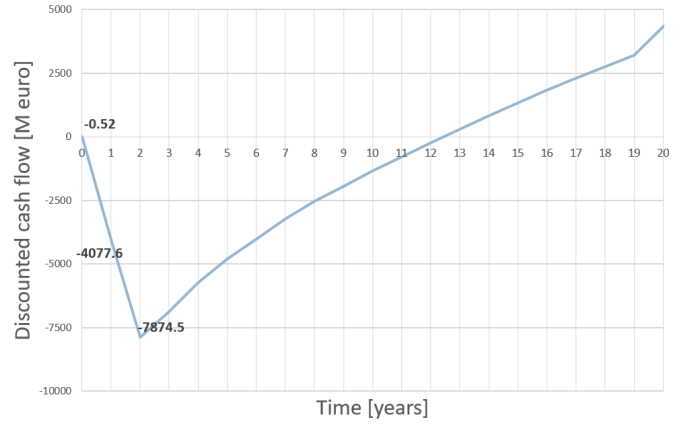


Figure 7. Discounted cash flow analysis

6.4 Sensitivity analysis

Sensitivity studies can help improve the quality and accuracy of the overall analysis by identifying the factors that have the greatest impact on the results, determining the uncertainties that need to be reduced, and quantifying the uncertainty of the analysis. A sensitivity analysis was performed to study the influence of price of CO₂ on the price of ethylene. Indeed, it has been decided to consider that the prices of butylene and propylene are fixed as the main goal is to maximise the plant's benefits as well as the production of ethylene which is the most widely produced olefin.

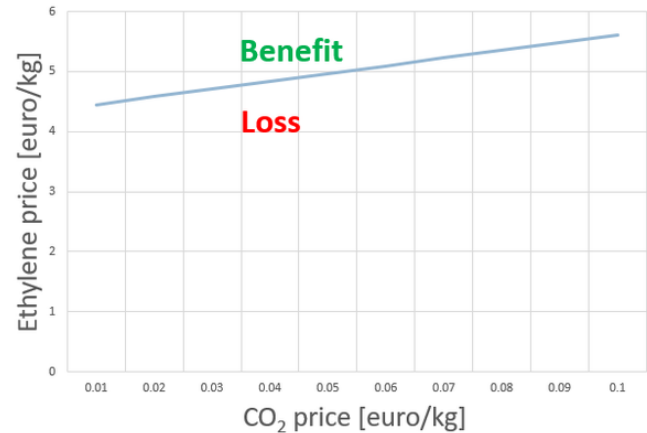


Figure 8. Sensitivity analysis evaluating the price of ethylene

Figure 8 shows that if the prices used are above the blue curve then the plant will generate benefits but if the prices used are below the curve then the plant will lose money. Moreover, if the price of CO₂ doubles then ethylene should be sold at a higher price. Initially, the price of CO₂ is around 0.02 €/kg, for which the price of ethylene should be above 4.58 €/kg. If the price of CO₂ is equal to 0.04 €/kg then the price of ethylene should be above 4.84 €/kg, which is 1.08 times bigger. This implies that the studied system is more sensitive to a variation of the price of olefins and not of CO₂.

7. Life Cycle Assessment

The synthesis of olefins has been proposed to recover and reduce the amount of CO₂ emitted into the environment, as it is the main vector of global warming today. This section focuses on the life cycle analysis (LCA) of the implemented process to evaluate the efficiency and the environmental impacts. It is essential to recall that the goal of this process is to produce about 450 000 t/year of olefins with the following proportions: 250 480 tonnes of ethylene, 151 486 tonnes of propylene, and 48 185 tonnes of butylene. From the perspective of estimating the environmental impact of these products, the functional unit chosen is 1 kg of ethylene produced; as ethylene is the major contributor to the olefins market [77]. A mass-based allocation factor is assigned to the other products.

The ecological impact of this CTM (CO₂-to-methanol) / MTO process and the associated processes in the LCA software SimaPro use a cradle-to-gate system boundary. As shown in Figure 9, the CTM/MTO process receives electricity from a renewable source, water and CO₂ as input, and produces ethylene, butylene, and propylene as outputs. The wastewater is destined to be treated; regarding the emissions, only the main ones are considered: carbon dioxide and carbon monoxide. In addition, the construction, maintenance, and transport of materials related to the plant are not taken into account in this life cycle analysis.

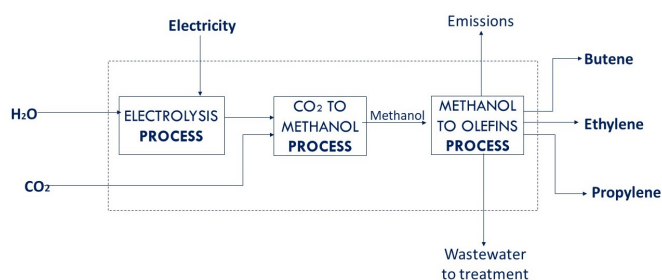


Figure 9. System boundaries for the life cycle analysis

The impact assessment method chosen is the "ReCiPe 2016 at midpoint level with a hierarchist perspective (H)" and it is based on the most common policy principles regarding timing and other issues for example a 100-year time frame on global warming, GWP100 [78]. This method allows for a broad and consistent assessment of the potential impact on environmental categories. In this study, the four main impact categories considered are: Global warming, Freshwater eutrophication, Fossil resource scarcity, and Water consumption. Their selection was made through a preliminary study of the results, which allowed the selection of the most appropriate and impacted categories. The environmental impacts of ethylene produced by CTM/MTO are compared to those of bioethylene produced from first-generation ethanol to put the results into perspective [79].

Figures 10 and 11 illustrate the results of the impact study carried out with SimaPro.

It is important to remember that the results shown in these figures are normalised. It means that the impact category is divided by the reference. A commonly used reference is the average yearly environmental load in a country or continent, divided by the number of inhabitants [81].

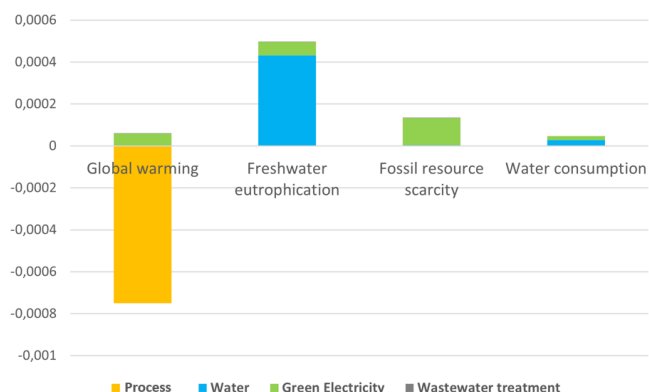


Figure 10. Environmental impacts of 1 kg of ethylene - Normalisation ReCiPe 2016 Midpoint (H)

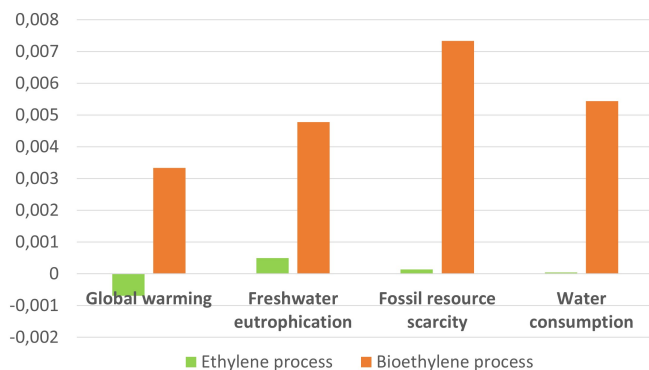


Figure 11. LCA comparison of processes: Ethylene vs Bioethylene

One of the main indicators illustrated in Figure 10 is the global warming potential (GWP). For the studied process, the GWP is mostly impacted by the ethylene process (CTM/MTO), and one observes a negative variation of this indicator, which means that there is a reduction in greenhouse gas emissions, i.e. the real challenge of this project. Indeed, as CO₂ is captured in a consistent way to be converted into products with high added value, there is an efficient reduction in the harmful impact of this gas on the environment.

It is also worth noting that two other impact categories stand out for their great contribution, namely freshwater eutrophication and water consumption. As a reminder, hydrogen, a reaction intermediate in this process, is produced by water electrolysis, and because of the quantities of olefins produced, a large quantity of water is required, more exactly 2 812 000 t/year per year. Although the water requirements are important, it can be noticed that the water treatment is insignificant compared to the other processes.

The second part of this study, as shown in Figure 11, focuses on a comparison between the process modelled and a bioethylene production (by direct ethanol dehydration) process whose data comes from an inventory of the life cycle carried out in [79].

It can be seen that all the impact categories in the case of bioethylene are largely above the ones obtained with the process studied. Table 7 focuses on the comparison of global warming (GW) impacts of the two processes.

Table 7. Global warming impacts of processes: Ethylene vs Bioethylene

	Ethylene	Bioethylene
GW [kg CO₂ eq]	-6,90E-04	3,34E-03

One can notice the significant difference between these processes. It highlights the fact that ethylene is called "bio" simply because it is obtained from resources of biological origin such as sugar cane, wood, etc. However, compared to the studied process, it remains more polluting because the cultivation of renewable raw materials, the production of electricity used, etc. in the bioethylene process involve much more fossil resources and therefore emit more greenhouse gases.

8. Conclusion

The objective of this paper was to show that olefins, which are usually derived from fossil fuels, could be produced in a sustainable way using captured carbon dioxide and renewable energies in Greece.

The modelled process consisted of water electrolysis to produce hydrogen, the reduction of carbon dioxide to produce methanol and the methanol-to-olefins route, which led to the production of three major olefins: ethylene, propylene and butylene.

Heat integration of the overall process was performed to determine the minimum energy quantity required in terms of hot and cold utilities. Through the study of a GCC, the most significant energy requirements could be observed. It could be seen that the methanol synthesis reactor required a large cooling duty due to the exothermicity of the reactions. In addition, the streams at the inlet and outlet of both reactors needed large heating duties to attain the reactors' temperature and large cooling duties before going to the separation sections, respectively. After the study of the GCC, a heat exchanger network could be designed to decrease the overall energy requirements. This exchanger network allowed the recovery of 75% of the required energy and, therefore, significantly decreased the energy demand of the process.

In addition, an economic analysis of the process was performed while applying the methodology developed by Turton et al. [52] and using data from the literature. The study showed that the process is profitable if built in 2050. Indeed, twelve years following the investments, the plant's net present value

becomes positive and continuously increases. At the end of the plant's operating expectancy, a cumulative discounted cash flow of 4 345.47 M € is obtained. Furthermore, a sensitivity analysis allowed to study the influence of the price of CO₂ on the price of ethylene through which it can be concluded that the studied process is more sensitive to a variation on the price of olefins than the price of CO₂.

Finally, a life cycle assessment of the process was performed and showed that the production of ethylene from captured CO₂ and renewable energies could be an interesting alternative to other processes from an environmental point of view.

To go further in the analysis of this process, additional studies can be performed. The different reaction kinetics can be studied in more detail and linked to an optimisation of the reactor conditions. The supplementary methanol-to-olefins reactions can also be introduced to determine their overall impact on the process. In addition, the heat exchanger network can be integrated into the process in order to optimise completely the use of utilities. The economic analysis can be updated according to those new optimisations. Finally, a LCA comparison with ethylene produced via the classical petrochemical way can be interesting.

This project showed that the use of carbon dioxide and renewable energy to produce chemicals could be an interesting alternative to the use of fossil resources. However, multiple assumptions had to be considered in order to obtain a certain economic viability for this project.

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