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# Màster en Enginyeria Química

## Treball Final de Màster

**Methanol synthesis by CO<sub>2</sub> hydrogenation using reactive distillation.**

**Producción de metanol por hidrogenación de CO<sub>2</sub> mediante rectificación reactiva.**

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# REPORT

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## 1. SUMMARY

Methanol is a very versatile product that can be found in a large number of industrial applications such as its use as a solvent or as a raw material for the synthesis of methyl ether, methylamine, etc.

Due to the current environmental situation, many research projects are starting to focus on the reduction of greenhouse gases pollution, which directly affects fossil fuels and certain industries that have a large CO<sub>2</sub> stream as their major waste (cement plants, thermal power plants, etc.).

One of the most studied projects nowadays is the synthesis of carbon-based fuels using CO<sub>2</sub> as raw material, which could be used to store the surplus energy obtained from renewable sources in chemical products, to be reused later on. This method has great advantages since with renewable energy and a carbon source (such as CO<sub>2</sub>) "green" fuels could be produced and these could be easily transported with current logistics and used by many facilities, due to their similarity to fossil fuels.

One of the carbon-based fuels with the greatest potential is methanol due to its high energy density. Currently there are several plants producing methanol from CO<sub>2</sub> and hydrogen, but they are still too unprofitable to be implemented worldwide.

This project studies an intensified process, the reactive distillation process, as an alternative to the current methanol synthesis process to make it more cost effective and efficient. Reactive distillation is an intensified process which allows to reduce the number of equipment required to carry out a process, since several unit operations take place simultaneously inside the column.

As it is a process that has not been studied yet, in this project a model has been proposed (simulated using Aspen plus technology) and different points have been evaluated:

- Proposal for the process using assumptions and calculation bases.
- Process parameters: column reflux, total distillation column stages, feed stages and product obtained by column bottom-head flow stream.
- Improvement proposals for the process studied: equipment adjacent to the main column.

The different stages of the whole process have been simulated with the ASPEN program and it has been demonstrated that this initial study opens the possibility for future studies since the results are optimistic for the viability of the project in the industrial field.





## 2. INTRODUCTION

Nowadays, there is an urgent need to reduce the dependence on fossil fuel resources due to its environmental issues related to its processing, i.e., carbon dioxide (CO<sub>2</sub>) emissions, particulate emissions, and water pollution among a large list. According to the last IPCC climate change report, observed increases in greenhouse gas (GHG) concentrations are unequivocally caused by human activities, reaching annual averages of 410 parts per million (ppm) for CO<sub>2</sub> emissions in 2019 [1]. It is well known that most of the increase is due to fossil fuels.

However, even with the information regarding the disadvantages and the several issues related to climate change for countless studies, the last International Energy Agency report “2021 World Energy Outlook” provides an estimation in which CO<sub>2</sub> emissions continue to increase through 2030, with a slight decrease from 2050 onwards [2].

The increasing concentration of CO<sub>2</sub> in the atmosphere, which is the main component of GHG, is expected to raise the temperature by approximately 1.5 °C over the next 20 years [1], causing major problems such as the extinction of species, changing ecosystems, melting of polar ice caps and the already known climate migration, among several others. Therefore, alternative energy sources to replace fossil fuels are currently being studied.

By advances in technology, renewable energy sources such as wind and solar are becoming more feasible and competitive with fossil fuels and have great potential to be widely used worldwide but they are still in development and there are 2 major problems which will delay its large-scale implementation:

- Based on the latest data published by Eurostat in its 2020 study, Europe produces on average about 18% of its energy from renewable sources [3]. In order to reach the goal of only consuming energy from renewable sources, a very important infrastructure is required, which also implies a lot of time and investment, all currently delayed by the global supply-chain crisis.
- Renewable energies such as solar and wind have a big dependence on the atmospheric conditions. Therefore, an energy system is needed to store energy excesses obtained from more favorable days so it can be used on days which weather conditions are worse.

The solution for both problems is chemical energy storage. There are some chemical products with high energy density which can help in the major transition to renewable energies, and once made, they can be very useful to solve the energy storage problem by using the energy surplus to produce carbon-based fuels, with the advantage that they are very easy to store, transport and use due to their similarity to current fuels.

The component studied in this research and one of the most studied lately in the industry is methanol.

### **2.1. Current technologies for methanol synthesis**

There are several production paths for methanol synthesis, which differ mainly in the raw materials used: synthesis gas, CO/CO<sub>2</sub> mixture or captured pure CO<sub>2</sub>. Each of them, together with the operating conditions of the process, have advantages and disadvantages, such as total conversion, impurities, side reactions, etc.

Currently, most of the methanol is industrially produced by catalytic conversion of synthesis gas (carbon oxide, carbon dioxide and hydrogen) derived from natural gas. Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst is widely used in industry due to the high selectivity (> 85%) and the low-pressure operation conditions (15-50 bar) compared with other catalysts (>100 bar). Broadly stated, CO<sub>2</sub> hydrogenation process consist of:

- CO<sub>2</sub> capture unit: In this part of the process, CO<sub>2</sub> produced as a waste stream by geothermal plants, ethylene production plants or cement plants among others is captured by chemical absorption and it is normally carried out with a MEA solution in a mass concentration of 30%.
- H<sub>2</sub> generation unit: This part of the process is very important due to the associated costs which can be the difference between a profitable process or non-profitable process. It can be obtained from other companies or produced with a water electrolysis unit. The second option has the initial investment and operation costs as a disadvantage but in the other hand, a large amount of oxygen is produced as a by-product of electrolysis and can be sold to other chemical plants.
- Main reactor: Although there are other reactor-types being used in industry, the most common is the fixed bed reactor with Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst. The reactor is pressurized between 10-50 bar and heated around 200°C. In this reactor both reactions take place and methanol is produced. As a product, methanol and water are obtained, as well as unreacted H<sub>2</sub> and CO<sub>2</sub>.

- Distillation column: This equipment is used to purify methanol. As the main liquid phase products obtained from the reactor are methanol and water, it is a non-azeotropic mixture and can be easily separated.

There are more than 90 methanol production plants worldwide, with a total production capacity of 100 million metric tons per year, twice the amount of 10 years ago. This increase in methanol production is due to the large increase in demand, which has been of 95 million metric tons in 2021, doubling the demand in 2010 of 49 million metric tons [4].

## 2.2. Methanol applications

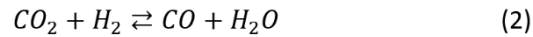
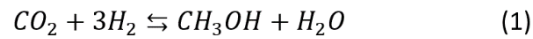
Methanol is one of the most important commodities in industrial chemistry. With the current focus on energy storage through chemical substances, most of the current production is centered on energy applications, although it is still very important as a solvent, or raw material. Methanol is relevant in the polymer industry, the pharmaceutical industry, the synthesis of organic compounds among other applications.

According to the HIS Markit study, the methanol produced is used for the following applications [4]:

- Dimethyl Ether
- Methylamines
- Chloromethanes
- Solvents
- Dimethyl Terephthalate
- Formaldehyde
- Acetic Acid
- MTBE/TAME (Methyl tertiary butyl Ether & Tertiary amyl methyl ether).
- Methyl Methacrylate
- Gasoline Blending
- Biodiesel
- MTO/MTP (Methanol to olefins & Methanol to Propylene)

### 2.3. CO<sub>2</sub> hydrogenation to methanol

Methanol synthesis from CO<sub>2</sub> involves the following catalytic reactions [9,10,11]:



The first reaction (1) is the CO<sub>2</sub> hydrogenation to methanol and the second one (2) is a side reaction called “Water-Gas-Shift-Reaction” which occurs along with the methanol formation and produces water and CO from CO<sub>2</sub> and H<sub>2</sub>.

There are some models which assume there is a third reaction (CO hydrogenation to methanol), but it will be not considered in this project [12, 13, 14].

As the CO<sub>2</sub> hydrogenation to methanol is exothermic and results in a decrease in the number of molecules (3 mol → 2 mol), the reaction is favored by higher pressures and low temperatures. However, due to thermodynamic effects, high temperatures lead to higher reaction rates so several inputs should be considered.

Besides the thermodynamic effects, there is another important parameter: the catalyst. As it is a catalytic reaction, it really depends on which catalyst is being used, not only regarding the reaction rate, but also the product selectivity, deactivation (i.e., deactivation caused by sulfurs on copper-based catalysts) and the maximum allowable operating temperatures: According to some studies, high temperatures (>350-400°C) lead to a significant sintering and deactivation of the catalyst, which is highly detrimental for the process [5,6].

Depending on pressure operation conditions and the catalyst used, the following products will be obtained [7]:

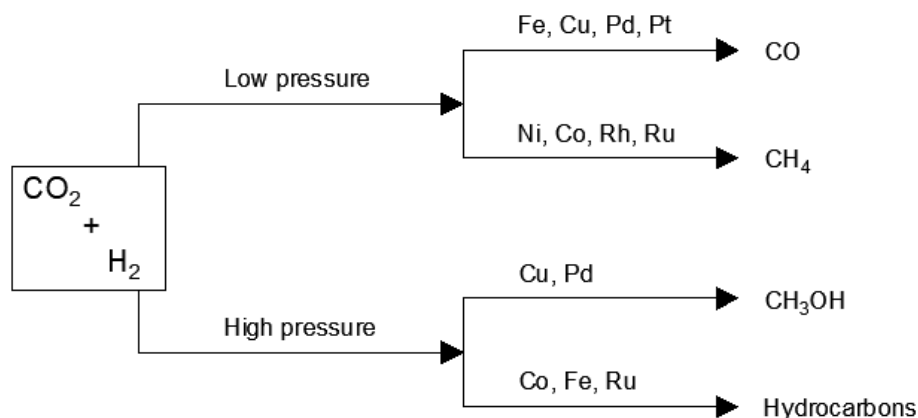


Figure 1. Possible products and potential catalysts for CO<sub>2</sub> hydrogenation

- Low pressure & Iron, Copper, Palladium or Platinum based catalysts: In this case, RWGS is the main reaction of the process, and CO is obtained.
- Low pressure & Nickel, Cobalt, Rhodium or Ruthenium based catalysts: Mostly methane is obtained.
- High pressure & Copper or Palladium based catalysts: In these conditions, CO<sub>2</sub> hydrogenation to methanol takes place, and methanol is the main product.
- High pressure & Cobalt, Iron or Ruthenium based catalysts: With these catalysts CO<sub>2</sub> hydrogenation to methanol also takes place but as an intermediate product which is the raw material for some hydrocarbons, therefore, methanol is not obtained as a final product.

Furthermore, in addition to the information above, another author lists the most industrially used catalysts, as well as their selectivity [8]. The 4 most relevant examples are the following:

*Table 1. Selectivity of the most used catalysts in the industry.*

Catalyst	Selectivity [%]
PdZn	99.6
Cu/Zn/Al <sub>2</sub> O <sub>3</sub>	86
CoGa	63
Rh/MoO <sub>3</sub> /SiO <sub>2</sub>	61

## 2.4.Reactive distillation

Process intensification is a novel concept which became more relevant around the 1980's. Currently, there is not a clear definition of "process intensification" that everyone agrees to and here is an example of the evolution of the definition compiled by Keil F. J. [15]

- Process intensification is the devising exceedingly compact plant which reduces both the 'main plant item' and the installations costs (Ramshaw and Arkley, 1983).
- Process intensification provides radically innovative principles ("paradigm Shift") in process and equipment design, which can benefit (often with more than a factor or two) process and chain efficiency, capital operating expenses, quality, wastes, process safety and more" (European roadmap for process intensification, 2007).

- Process intensification stands for an integrated approach for process and product innovation in chemical research and development, and chemical engineering in order to sustain profitability even in the presence of increasing uncertainties (Becht et al. ,2009)
- Process intensification is any chemical engineering development that leads to substantially smaller, cleaner, safer and more energy efficient technology or that combine[s] multiple operations into fewer devices (Baldea, 2015).

In order to have a better understanding of what the “process intensification” consist of, four principles are distinguished [16]:

- **Principle 1: Maximize the effectiveness of intra- and intermolecular events.** Process intensification should look for the engineering methods to obtain better control of number/frequency of collisions, geometry of approach, mutual orientation of molecules in the moment of collisions, and their energy.
- **Principle 2: Give each molecule the same processing experience.** Processes, in which all molecules undergo the same history, deliver ideally uniform products with minimum waste.
- **Principle 3: Optimize the driving forces at every scale and maximize the specific surface area to which these forces apply.** This principle refers to the improvement of mass and heat transport (diffusion and convective transport).
- **Principle 4: Maximize the synergistic effects from partial processes.** A great example of this principle is a reactive separation unit, where the reaction equilibrium is shifted by removing the products in situ from the reaction environment.

One of the most studied processes, which is also the objective of this project, and a prominent example of “process intensification” is **reactive distillation**.

Reactive distillation combines both reaction and separation into a single column equipment, usually equipped with a catalyst packing. One of the major advantages is that equilibrium-limited reactions are forced to higher yields by separating the reactants from the products. According to the European Roadmap for process intensification [16] it can be stated that reactive distillation is a potential process for energy savings, improving cost competitiveness and reducing CO<sub>2</sub>.

Table 2. Summary of some process intensification technologies analysis.

Technology name	Potential for energy savings	Potential for eco impact CO <sub>2</sub>	Potential to improve cost competitiveness	Potential for innovative high-quality products
Static mixers	Medium	Medium	Medium	Low
Extractive distillation	Medium	Low	Low	Medium
<b>Reactive distillation</b>	<b>High</b>	<b>High</b>	<b>High</b>	<b>Medium</b>
Rotating annular chromatographic reactors	Low	Low	High	High
Rotating packed beds	Medium	Medium	High	Medium
Membrane distillation	Medium	Medium	Medium	Medium
HEX reactors	Low	Low	High	High

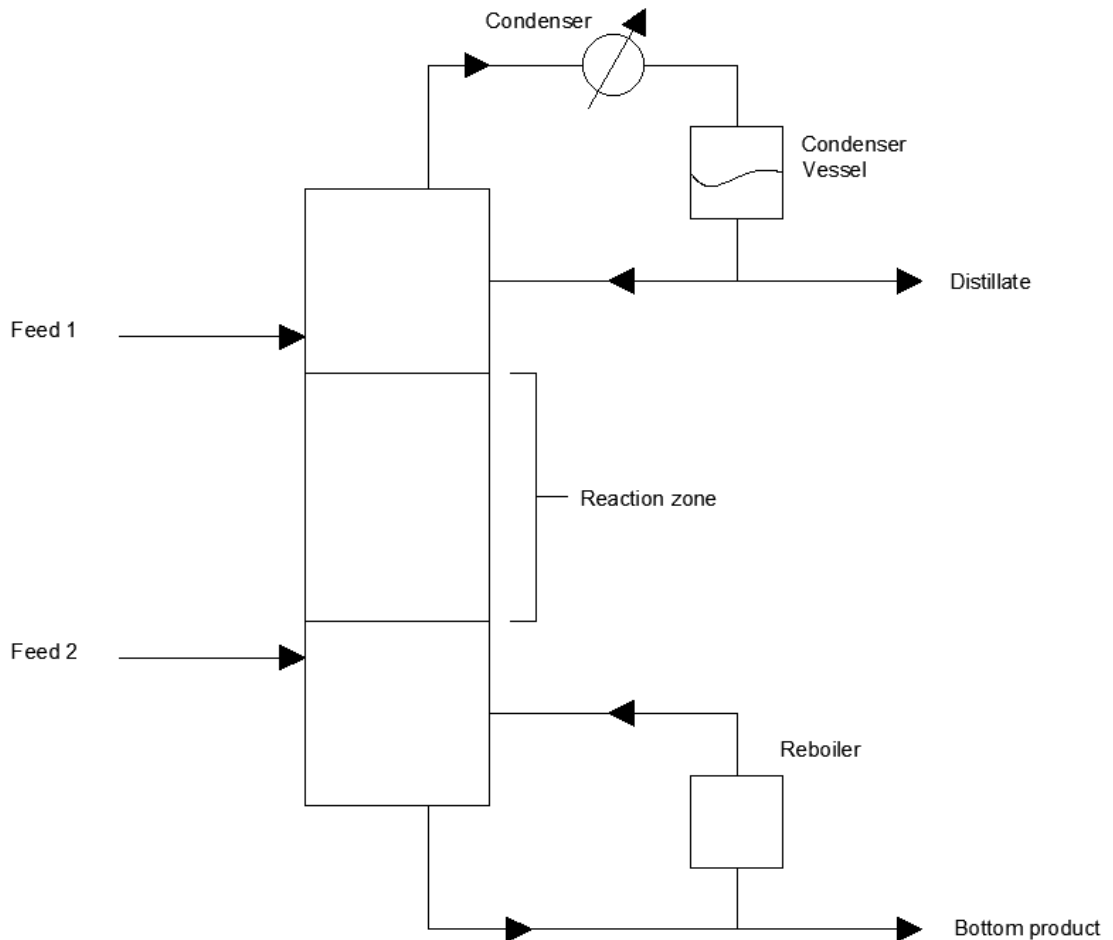
As it can be seen in Table 2, reactive distillation is a promising option to improve certain features of some processes. However, this process intensification is not suitable for any liquid/liquid separation. It will depend on the pressure and temperature conditions.

The reactive distillation is a process which combines reaction and distillation in a single column. As the reaction proceeds, products are being separated simultaneously from unreacted reactants. In the industrial scale, three constraints have to be fulfilled in order to use reactive distillation:

- The temperature window of the vapor-liquid equilibrium is equivalent to the reaction temperature. By changing the column operating pressure, this temperature window can be altered, allowing to control thermal stability of the catalyst, which can limit the upper operation temperature of the distillation column.
- Because of the necessity of wet catalyst pellets the chemical reaction has to take place entirely in the liquid phase.
- Catalysts with a long lifetime are required due to the difficulty of its renewal.

If these characteristics are met, by separating the products from the reactants as the reaction proceeds, the equilibrium is shifted to achieve higher conversions.

In the following figure, a basic scheme of reactive distillation is presented:



*Figure 2. Reactive distillation column scheme*

In this example (although there are several other possibilities), a reaction zone (heterogeneous catalysis reaction, homogeneous catalysis reaction, and thermal noncatalytic reaction), a condenser at the top-head and a reboiler at the bottom-head, both with recirculation, have been considered.



The most common in all industrial processes is to have the reactions in the liquid phase, as for example [15]:

- Esterification
- Transesterification
- Hydrolysis
- **Hydrogenation & Dehydrogenation**
- Amination
- Chlorination

Looking at each one of the reactions, we realize that they are all limited by chemical equilibrium, which is one of the great advantages of reactive distillation [17,18]:

- Significant capital savings due to simplification or elimination of the separation system.
- Improved selectivity. Removing one of the products from the reaction mixture or maintaining a low concentration of one of the reactants can lead to reduction of the side reactions rates.
- Avoidance of azeotropes.
- The maximum temperature in the reaction zone is limited to the boiling point of the reaction mixture, so that the danger of hot spot formation on the catalysts is reduced and a simple and reliable temperature control can be achieved.



### 3. OBJECTIVES

The main objective of this project is to study the methanol synthesis by CO<sub>2</sub> hydrogenation using reactive distillation and with the results obtained, to analyze the following parameters:

- Study of the current situation
- Feasibility of the proposed process
- Main parameters to be considered and how they affect the process
- Improvement proposals for future studies.

With these four points, the intention is to elaborate a project that will lead to more detailed future studies.



## 4. METHODOLOGY

In this part of the study, both the thermodynamic model applied to the reactive distillation process and the different chemical compounds considered are specified.

When the application of reactive distillation in methanol synthesis by CO<sub>2</sub> hydrogenation is considered, a laboratory scale reactive distillation experiment is the conventional method to justify the results which costs a lot of time, investment and has potential risks. Therefore, computer design programs (i.e., ASPEN technology) are a better way to conduct these studies.

Consequently, the procedure followed to generate the process configuration in the simulation and the different tools used to perform the analysis are also described.

### 4.1. Reaction system and thermodynamic model

As mentioned in the previous section, CO<sub>2</sub> hydrogenation is basically composed of the reactions (1) and (2), therefore, the main components of the simulation will be CO<sub>2</sub>, CO, H<sub>2</sub>, and methanol.

CO<sub>2</sub> hydrogenation by reactive distillation is a novel process, so there is not an existing database of previous studies, and unfortunately, it has not been possible to find a consistent kinetic model for the reaction in liquid phase (necessary conditions to simulate a reactive distillation process).

Thus, the Gibbs reactor inside the reactive distillation column, which will minimize the Gibbs energy of the mixture, will be used as a calculation hypothesis method.

The objective is to calculate the most stable form in which the mixture would be, in other words, the chemical equilibrium. At sufficiently long reaction times and provided that the activation energy of the different reactions can be overcome, all reactions will tend to go to chemical equilibrium.

Since it is a catalytic reaction, the catalyst becomes of major importance because depending on the catalyst used, the reaction rate will increase or decrease and even the undesired reactions will be produced, as shown in *Figure 1*. For these reasons, the catalyst used must be specifically selected in order to minimize even more the possible deviations of the Gibbs reactor.

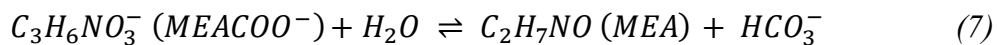
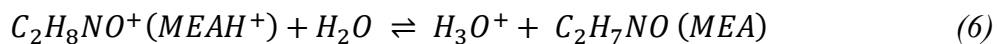
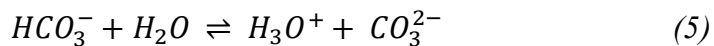
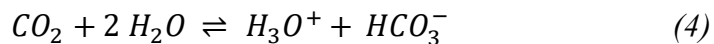
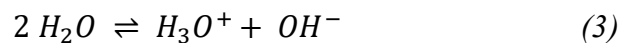
In addition, a thermodynamic model must be selected. A reliable thermodynamic model is also very important when performing the simulation, since the more reliable the model is, the more reliable the results provided by the material and energy balances will be and the better the final results can be predicted.

The thermodynamic model is used to estimate different physical properties of the components, such as density, free energy, heat of vaporization, critical pressure & temperature, etc.

ASPEN Plus has many available thermodynamic models, each of which can be used for different situations. The most known are:

- NRTL: This model can describe Vapor-Liquid Equilibrium (VLE) and Liquid-Liquid Equilibrium (LLE) of strongly nonideal solutions. Binary interaction parameters are required but ASPEN has a large database from literature and regression of experimental data.
- PSRK (“Predictive Redlich-Kwong-Soave”): This model’s equation of state for pure compounds uses the cubic form of an equation of state and is the simplest form which enables the description of the PVT behavior of gases and liquids and thus the representation of the vapor-liquid equilibrium.
- UNIQUAC/UNIFAC: This group-contribution method estimates liquid-phase activity coefficients in non-ideal liquid mixtures, and it is widely used for phase equilibrium calculations in cases where little or no relevant experimental information is available.

However, any of the options presented above are not correct in this particular simulation. As explained above, one of the two raw materials is CO<sub>2</sub>, and it is dissolved in a 30% MEA solution. This absorption is caused by the equilibrium of the chemical reaction between CO<sub>2</sub> (acid) and MEA (base) [19]:



Where:

- (3): Ionization of water
- (4): Hydrolysis and ionization of dissolved CO<sub>2</sub>
- (5): Dissociation of bicarbonate
- (6): Dissociation of protonated MEA
- (7): Carbamate reversion to bicarbonate

If the methods mentioned above are used without any other specification, the following problem appears:

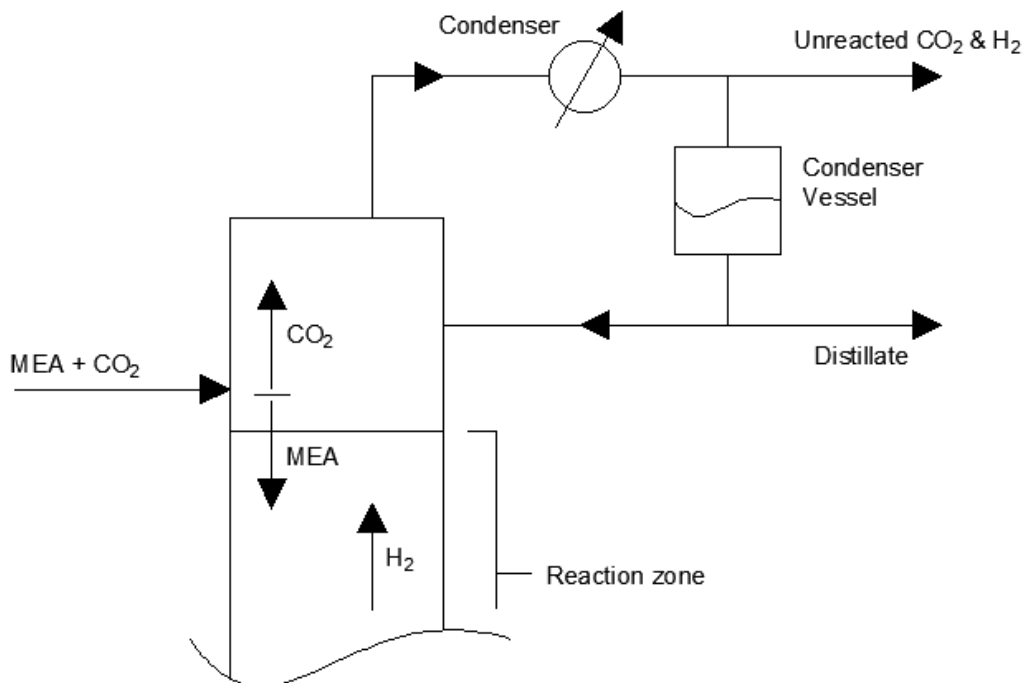


Figure 3. Column top head scheme

As it can be seen in Figure 3, with the initial information introduced to the simulator, ASPEN considers CO<sub>2</sub> and MEA as different streams, causing CO<sub>2</sub> to flow directly towards the top head of the column, and therefore not to react with H<sub>2</sub>.

To overcome the problem, ASPEN has a thermodynamic model that considers the ions in the process and makes it suitable in relation to the requirements of this project:

- ENRTL-HG: This model is a variation of the ELECNTR, which is the most versatile electrolyte model because it can handle very low and very high concentrations from aqueous and mixed solvent systems. It is a variation of the Helgeson model, for standard properties calculation. The Helgeson model is a very accurate and flexible equation of state that calculates standard enthalpy, entropy and, most importantly in this project, Gibbs free energy in aqueous solutions.

#### 4.2. Simulation environment

The reactive distillation column is modeled with the “RadFrac” option. This module is selected because:

- It is a rigorous model for simulating all types of multistage vapor liquid fractionation operations.
- It is suitable for modeling columns where two liquid phases exist, and different chemical reactions occur in the two liquid phases.

As it is a distillation of 4 components, with a reaction inside the column, the selected convergence method is “Strongly non-ideal liquid”, which according to the ASPEN data bank, is recommended for highly nonideal systems for two or three-phase distillation calculations.

There is also an azeotropic method which is recommended for highly non-ideal azeotropic separations; however, this does not apply to this particular process.

Furthermore, Table 3 summarizes the vapor pressure of all the components at different temperatures, and it can be seen that the separation of the different components by distillation is perfectly feasible, due to a difference of more than 30°C in all the situations.

*Table 3. Vapor pressure prediction with UNIFAC group-contribution method*

Vapor pressure [bar]	Temperature [°C]		
	Methanol	H <sub>2</sub> O	MEA
1	64.42	99.64	169.71
5	111.55	151.94	229.21
15	153.36	198.42	285.43
30	184.99	233.92	331.04

Raw materials are fed to the reactive distillation column in countercurrent above the specified stages in order to increase the overall conversion. Table 4 summarizes the main characteristics specified for the column:



Table 4. Main characteristics specified in the reactive distillation column.

Calculation type	Equilibrium
Number of stages	20
Condenser	Partial-Vapor-Liquid
Reboiler	Kettle
Valid phases	Vapor-Liquid
Convergence method	Strongly non-ideal liquid
Reflux ratio	0.75
Bottom rate [kmol/h]	1000
Pressure [bar]	30
CO <sub>2</sub> -MEA feed stage	10
H <sub>2</sub> feed stage	15

A total number of 20 stages is defined as an initial calculation basis. Stages 10 and 15 are selected for raw material feed streams since the product of interest (which should be as pure as possible) will be obtained for the column top head.

When defining a column, 2 variables must be defined. In this process, the reflux ratio and the bottom flow rate are selected. In the first case an arbitrary value of 0.75 is chosen, which will be used as another initial calculation basis for the process. In order to also give an initial value for the bottom flow rate, a material balance has been carried out based on 2 considerations:

- The reaction will be carried out completely within the column. Neither catalysts selectivity nor reaction kinetics are considered for this, since the objective of implementing reactive distillation as a process intensification is to be able to shift the equilibrium to obtain a complete overall conversion, so it will be considered as a valid condition in order to obtain the calculation basis.
- Methanol will be obtained with a 100% purity through the top head.

According to data collected by Statista (European commission, 2021) thermal power plants that produce most of the CO<sub>2</sub> in Spain, produce between 2-8 thousand tons of CO<sub>2</sub> per year [23]. Considering a value of 4 thousand tons of CO<sub>2</sub> per year, a 10.38 kmol/h of CO<sub>2</sub> stream could be captured with MEA. Several authors agree that the optimal ratio between H<sub>2</sub> and CO<sub>2</sub> is 5 [21, 22], so the second feed stream will be of 51.9 kmol/h H<sub>2</sub> (knowing that the reactions require 31.14 kmol/h due to stoichiometry, the process will be working with a 66% excess).

Thus, the initial material balance of the system is shown in Table 5 and Table 6:

Table 5. Material balance for feed streams

	F <sub>1</sub> (CO <sub>2</sub> -MEA)			F <sub>2</sub> (H <sub>2</sub> )		
	kmol/h	T [°C]	P [bar]	kmol/h	T [°C]	P [bar]
CO <sub>2</sub>	10,38	40	30	-	-	-
H <sub>2</sub>	-	-	-	51,9	40	30
H <sub>2</sub> O	692,72	40	30	-	-	-
MEA	296,9	40	30	-	-	-
MeOH	-	-	-	-	-	-

Table 6. Material balance for product streams

	D <sub>L</sub>			D <sub>V</sub>			L		
	kmol/h	T [°C]	P [bar]	kmol/h	T [°C]	P [bar]	kmol/h	T [°C]	P [bar]
CO <sub>2</sub>	-	-	-	-	-	-	0	-	-
H <sub>2</sub>	-	-	-	20,76	40	30	-	-	-
H <sub>2</sub> O	-	-	-	-	-	-	703,1	40	30
MEA	-	-	-	-	-	-	296,9	40	30
MeOH	10,38	40	30	-	-	-	-	-	-

Regarding the catalyst, from an industrial point of view it should improve to fulfill the following requirements [8]:

- Low pressure drop and moderate diffusion restrictions (like pellet size and shape design).
- High activity and selectivity, which decreases by-product formation (dimethyl ether, methylamines...).
- Resistance to poisons (i.e., sulfurs, nickel, iron...).
- Thermal and mechanical stability.

Considering these factors, together with the explanations given in Table 1 and Figure 1, there are two suitable catalysts: ZnPd and Cu/Zn/Al<sub>2</sub>O<sub>3</sub>.

Although ZnPd catalyst has more selectivity than Cu/Zn/Al<sub>2</sub>O<sub>3</sub>, this last is much more affordable. Therefore, keeping in mind that this project studies the feasibility of carrying out an industrial process in the future, the copper catalyst will be selected.

Reactive distillation column diagram is shown in Figure 4:

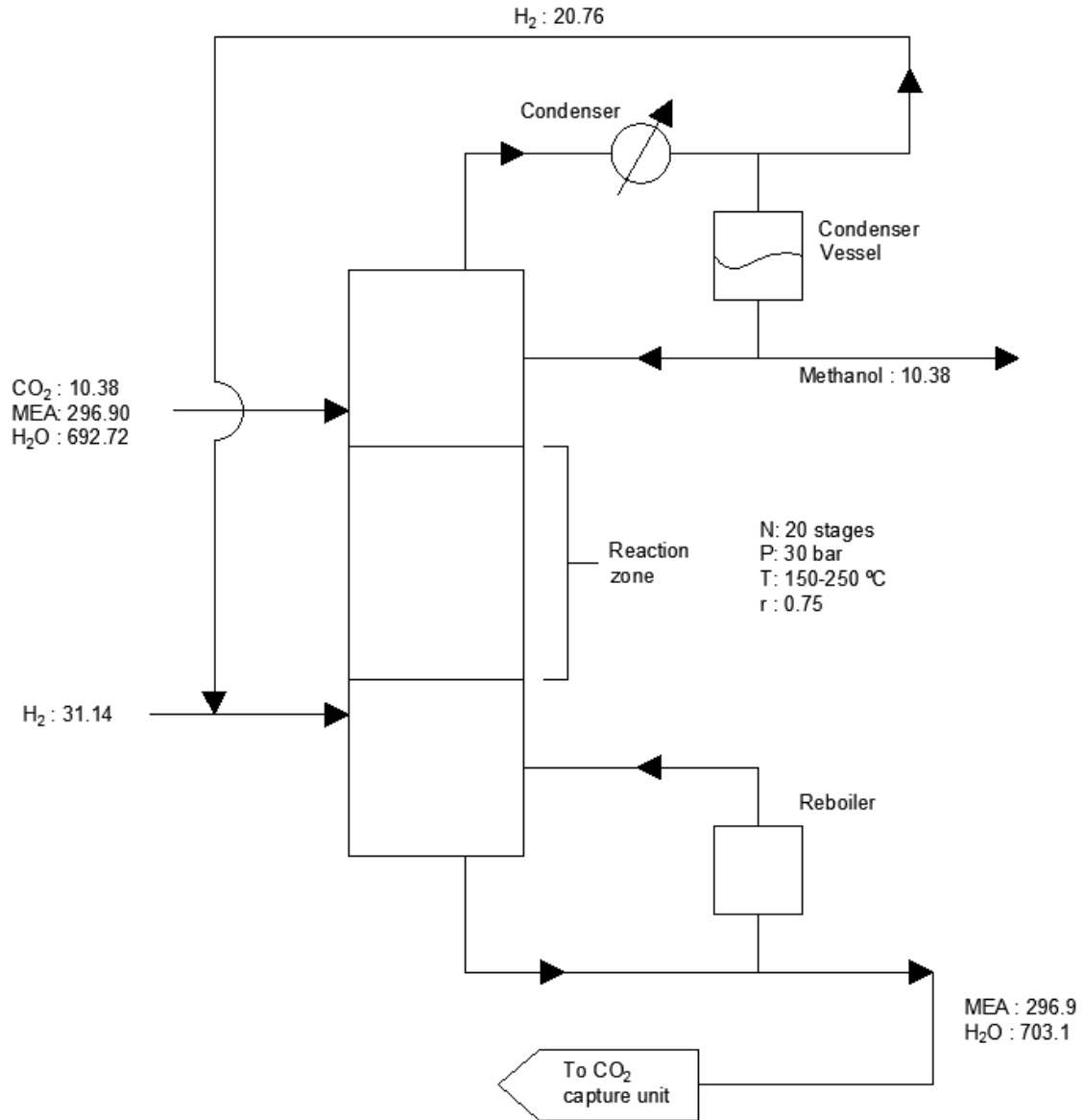


Figure 4. Reactive distillation column diagram (all streams are in kmol/h)

### **4.3.Process optimization**

There are many different variables that can affect the development of the different operations and therefore directly affect the product obtained. Using the built-in sensitivity tool in ASPEN simulator, the different variables can be analyzed independently in order to obtain information about them and to be able to study how they affect the process.

Within the large possibility of variables that are important for the process, the following ones will be studied:

- Reflux ratio
- Bottom flowrate
- Number of column stages
- Feed-stages

Column pressure and temperature are also two important variables to be considered, as since it is still a distillation process, the pressure and temperature conditions will directly affect the physical properties of all the components as well as the proper performance of the process.

However, due to the catalyst parameters, they will be defined as fixed variables as mentioned above.

According to different studies [7,8] it is known that it behaves efficiently in a small range of temperatures and high pressures, so it is recommended to work in this range and not to study the behavior of the process in conditions where there is no data on catalyst selectivity or stability.

### **4.4.Product Specification**

As mentioned above, one of the main objectives of this process is to take advantage of the CO<sub>2</sub> emissions produced by other industries to obtain a product that can be profitable.

Methanol is a versatile product as a raw material for certain products and as a fuel, among others.

Since 1998 there has been a committee in charge of regulating the minimum specifications when it comes to selling methanol to industry. This committee is IMPCA (International methanol producers & consumers association).

According to its latest study of June 10, 2021, the minimum purity for its commercialization is determined, among other quality controls [20]:

*Table 7. Methanol requirements for commercialization*

TEST	UNIT	LIMITS
<b>Purity on dry basis</b>	<b>% W/W</b>	<b>Min 99.85</b>
<b>Water</b>	<b>% W/W</b>	<b>Max. 0.100</b>
Ethanol	mg/kg	Max. 50
Acetone	mg/kg	Max. 30
Color	Pt-Co	Max. 5
Sulfur	mg/kg	Max. 0.5

Besides setting these requirements, it also establishes the methods for the quality control of each one of them, replacing on several occasions those proposed by the ASTM (American Society for Testing and Materials) standards.



## 5. RESULTS AND DISCUSSION

With all the inputs discussed in section 4, Figure 5 shows the initial scheme extracted directly from ASPEN (in order to facilitate the convergence of the simulator, the gas stream “D<sub>v</sub>” leaving the condenser is not initially recirculating) and Table 8 shows the most relevant results:

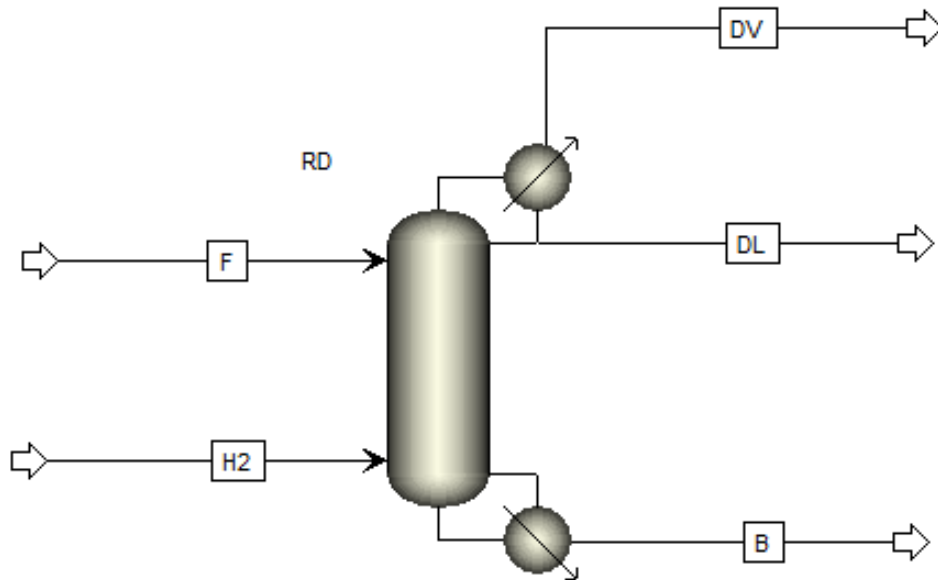


Figure 5. Initial scheme of the simulated process in Aspen

Table 8. Results from the initial simulation

Components	B [kmol/h]	D <sub>L</sub> [kmol/h]	D <sub>V</sub> [kmol/h]
H <sub>2</sub>	-	-	27.54
CO <sub>2</sub>	2.26	-	-
H <sub>2</sub> O	699.2	1.66	-
MEA	297	-	-
CH <sub>3</sub> OH	1.65	6.29	0.17
CO	0.01	-	-

Based on the data given in Table 8 a 77% of yield is obtained, which is still far away from full conversion, and it also can be observed that the stream leaving the column through the bottom-head contains 23% of the methanol produced.

This is very problematic, as in order to take advantage of MEA stream for recirculation and to obtain the maximum efficiency of the process, one extra equipment is required to carry out a second distillation with the same components as the first one. As seen in section 4 and based on the thermodynamic properties of the different compounds, it should be possible to extract all the methanol with high purity through top-head column. In order to achieve that objective, this section shows the results obtained from the following variables study:

- Reflux ratio
- Bottom flowrate
- Number of column stages
- Feed-stages

### 5.1.Effect of reflux ratio

Reflux ratio is the relation between flow returned as reflux and flow of top product taken off the column, and it is one of the most important parameters in a distillation column because it directly affects its performance. Figure 6 and Figure 7 show methanol production and methanol purity varying the reflux ratio variation from 0.75 to 1.

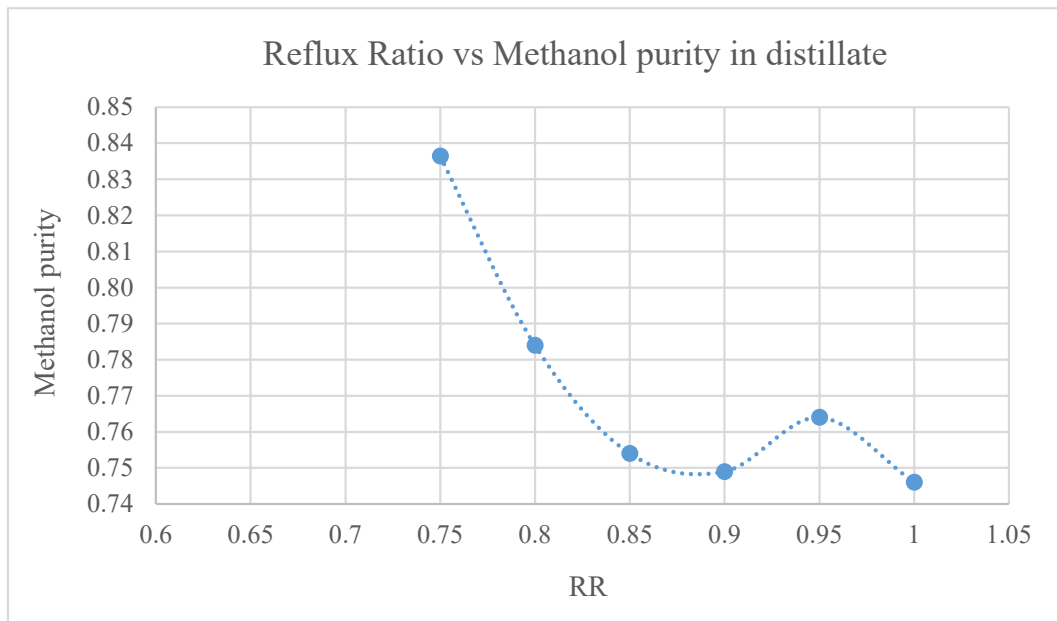


Figure 6. Methanol purity obtained in top-head stream from different reflux ratios



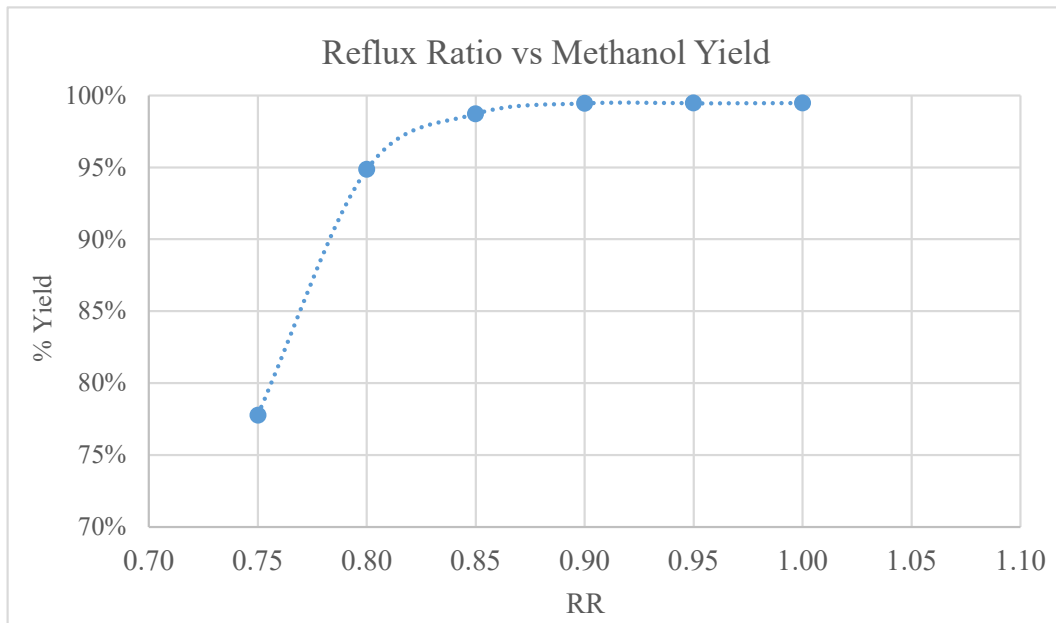


Figure 7. Methanol yield obtained from different reflux ratios

Theoretically, when a product with a higher purity per top-head column wants to be obtained for a certain number of stages, the reflux ratio is increased, thus increasing the flowrate that is sent back to the column.

In the case of Figure 6, the opposite effect can be observed. If the reflux ratio is increased, the purity of the methanol output stream slightly decreases although the total conversion of the process increases (Figure 7).

This may be due to different reasons, as it is a reactive distillation, by returning more liquid to the column at a significantly lower temperature, the thermodynamics of the reaction will also be affected by this temperature deviation inside the column.

On the other hand, the results shown in Table 8 indicate that there is a 23% methanol losses per bottom-head stream and, although the total conversion of the process increases, more methanol is lost in the bottom-head stream which leads to think that there is another important parameter that affects the purity of the output stream in top-head column. This variable is the bottom flowrate.

## 5.2. Effect of “bottom flowrate”

As it can be seen in Figure 7, the total yield of the process reaches very good values starting at a reflux of 0.95. For the bottom flowrate study, a reflux ratio of 1.3 has been established to ensure a working range with high yields.

Figure 9 shows that, as the bottom flowrate increases, the purity of the distillate also increases, reaching a methanol purity of 83%, way below the specifications shown in Table 7.

However, as observed in Figure 8, it can also be seen that the amount of methanol obtained through distillate flowrate at bottom flowrates higher than 1 000 kmol/h is minimum, reaching values of 0.2 kmol/h.

From a process point of view, it is important to have as much methanol as possible at the distillate flowrate, in order to be able to reuse the bottom flowrate again for the absorption of new CO<sub>2</sub>.

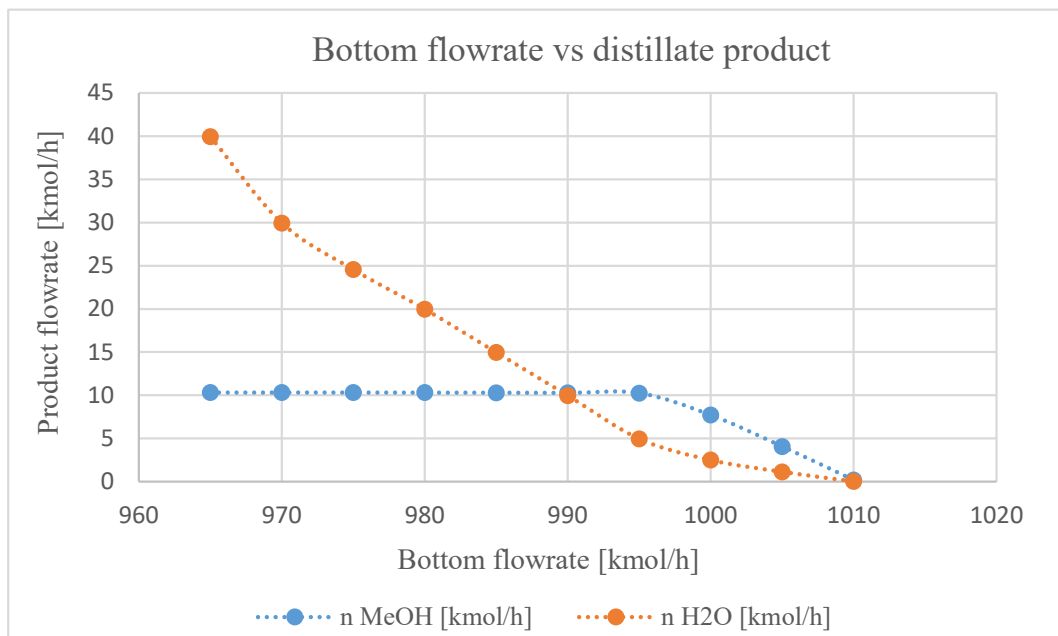


Figure 8. Distillate methanol and water for different bottom flowrates

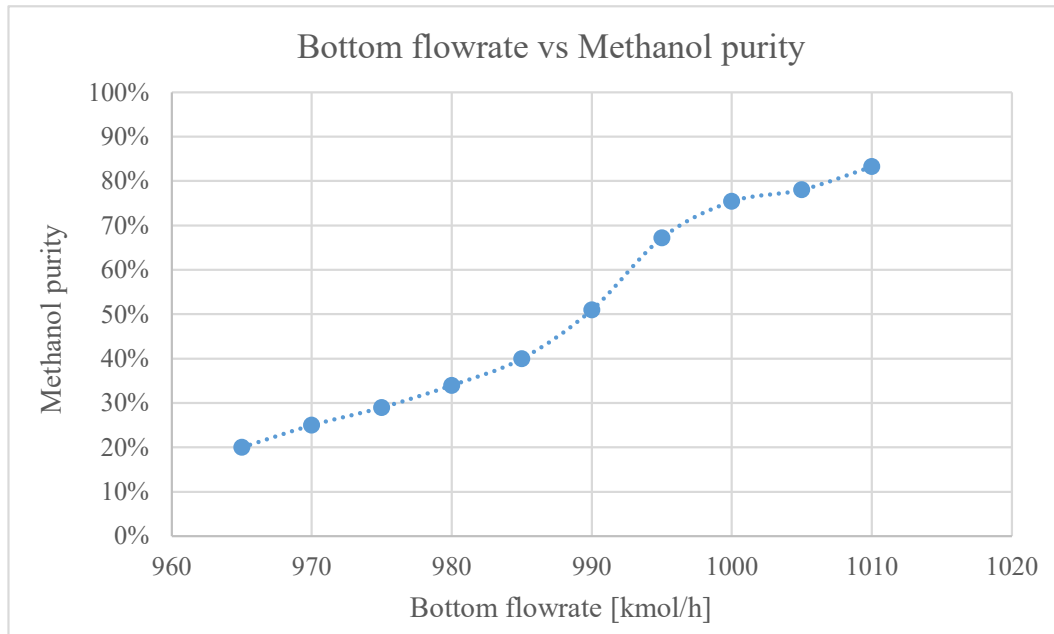


Figure 9. Methanol purity for different bottom flowrates

### 5.3. Total number of stages and feed stages

For the optimization of these two variables, the reflux ratio has been kept at 1.3 and 975 kmol/h has been taken as the value for bottom flowrate. This combination of parameters allows a methanol yield higher than 99% with a distillation purity of 29%.

Referring to the feed stages, a precise location of them will directly affect the number stages required for a specific separation. Usually, the feed stream should enter the column at the stage that gives the best match between feed composition and vapor and liquid streams in the column.

In the case of reaction distillation, there are certain restrictions on this standard. First of all, there are two inlet streams: A liquid and a gas stream. Since there is a reaction involved, it is interesting to enter them to the column in countercurrent with a range of stages between the two feed stages. In addition, since the objective is to recover pure methanol per distillate stream, it is important to have the feed stages located at the bottom part of the column.

For this study, different feed stages have been proposed, and trays have been reduced in each simulation, depending on the areas of the column where no appreciable distillation was made.

As shown in Table 9, there are some stages where the reaction generates most of the methanol (stages 10 to 15, which correspond with the feed stages), and then there is an upper part of the column where the methanol is separated from the rest of the components. There is a zone (stages 3 to 9) where no change is observed and, therefore, everything indicates that the number of stages can be reduced.

*Table 9. Results for a 20 stages simulation*

Stage	% Water	% Methanol
1	70.74	29.26
2	96.04	3.88
3	99.91	$7.48 \cdot 10^{-02}$
4	99.97	$2.24 \cdot 10^{-02}$
5	99.97	$2.10 \cdot 10^{-02}$
6	99.97	$2.09 \cdot 10^{-02}$
7	99.97	$2.09 \cdot 10^{-02}$
8	99.96	$2.09 \cdot 10^{-02}$
9	99.93	$2.09 \cdot 10^{-02}$
10	99.54	$2.08 \cdot 10^{-02}$
11	96.20	$1.94 \cdot 10^{-02}$
12	80.58	$1.40 \cdot 10^{-02}$
13	81.76	$1.08 \cdot 10^{-06}$
14	81.80	$4.04 \cdot 10^{-09}$
15	81.80	$2.50 \cdot 10^{-11}$
16	81.80	$2.22 \cdot 10^{-11}$
17	81.80	$1.92 \cdot 10^{-11}$
18	81.70	$1.64 \cdot 10^{-11}$
19	79.72	$1.30 \cdot 10^{-11}$
20	69.55	$8.88 \cdot 10^{-12}$

Tables 10, 11 and 12 show the same study for 18, 15 and 12 stages of reactive distillation columns, respectively (feed stages are marked in a darker color).

*Table 10. Results for an 18 stages simulation*

Stage	% Water	% Methanol
1	70.74	29.26
2	96.04	3.88
3	99.91	$7.48 \cdot 10^{-02}$
4	99.97	$2.24 \cdot 10^{-02}$
5	99.97	$2.10 \cdot 10^{-02}$
6	99.97	$2.09 \cdot 10^{-02}$
7	99.97	$2.09 \cdot 10^{-02}$
8	99.96	$2.09 \cdot 10^{-02}$
9	99.93	$2.09 \cdot 10^{-02}$
10	99.54	$2.08 \cdot 10^{-02}$
11	96.20	$1.94 \cdot 10^{-02}$
12	80.58	$1.40 \cdot 10^{-02}$
13	81.76	$1.08 \cdot 10^{-06}$
14	81.80	$4.04 \cdot 10^{-09}$
15	81.80	$2.50 \cdot 10^{-11}$
16	81.70	$2.14 \cdot 10^{-11}$
17	79.72	$1.70 \cdot 10^{-11}$
18	69.55	$1.16 \cdot 10^{-11}$

Table 11. Results for a 15 stages simulation

Stage	% Water	% Methanol
1	70.74	29.26
2	96.04	3.88
3	99.91	$7.48 \cdot 10^{-02}$
4	99.97	$2.24 \cdot 10^{-02}$
5	99.96	$2.10 \cdot 10^{-02}$
6	99.93	$2.09 \cdot 10^{-02}$
7	99.54	$2.08 \cdot 10^{-02}$
8	96.20	$1.94 \cdot 10^{-02}$
9	80.58	$1.40 \cdot 10^{-02}$
10	81.76	$1.08 \cdot 10^{-06}$
11	81.79	$4.04 \cdot 10^{-09}$
12	81.76	$2.50 \cdot 10^{-11}$
13	81.51	$1.58 \cdot 10^{-13}$
14	79.72	$1 \cdot 10^{-28}$
15	69.55	$1 \cdot 10^{-28}$

Table 12. Results for a 12 stages simulation

Stage	% Water	% Methanol
1	70.74	29.26
2	96.04	3.88
3	99.91	$7.48 \cdot 10^{-02}$
4	99.97	$2.24 \cdot 10^{-02}$
5	99.96	$2.10 \cdot 10^{-02}$
6	99.93	$2.09 \cdot 10^{-02}$
7	99.54	$2.08 \cdot 10^{-02}$
8	96.20	$1.94 \cdot 10^{-02}$
9	80.58	$1.40 \cdot 10^{-02}$
10	81.76	$1.08 \cdot 10^{-06}$
11	81.79	$4.04 \cdot 10^{-09}$
12	81.76	$2.50 \cdot 10^{-11}$

As it can be seen in Table 12, in this last study the column has been reduced to 8 stages (6 trays), being able to maintain the same outlet composition for the distillate stream as in the first situation.

The reaction occurs mainly in stages 5 to 9, where an increase in the methanol composition can be appreciated (it is a small value since it is together with the MEA and water) and the purification occurs in the final stages reaching a purity of almost 30%.

In the case of further reductions, the purity of the methanol obtained per distillate stream would be affected, both by water and by the MEA. Therefore, the final value for the number of stages will be set at 12, being stages 5 and 10 the feed stages.

#### 5.4.Improvement proposal and final results

Considering all the studies carried out in the previous sections, the main and most interesting parameters of the process are the ones shown in Table 13:

*Table 13. Main results of the process*

Number of stages	12
Reflux ratio	1.3
Bottom rate [kmol/h]	975
CO <sub>2</sub> -MEA feed stage	5
H <sub>2</sub> feed stage	10
Methanol obtained [kmol/h]	10.332
Methanol purity [%]	29.26

Due to the characteristics of the process, a final step is required in order to achieve the initial objective: An extra methanol purification equipment.

The reasons by which in the previous sections it has been preferred to prioritize obtaining the maximum methanol flowrate in the distillate (even if accompanied by a larger quantity of water) rather than obtaining the maximum methanol purity are the following:

- When it comes to recirculating the MEA stream, so that it can be used again to absorb CO<sub>2</sub>, it is important that it is the same 30% MEA stream as discussed earlier in this project. For this purpose, if it has traces of by-products, it would have to be sent to a treatment unit prior being reused.
- Introducing the hydrogen in a lower tray also affects the distillation by pushing more water to the distillation stream, so it seems to be quite difficult to improve the methanol purity results unless the column is widely oversized.

- The mixture of methanol and water is a sort of a “friendly” mixture. Due to the physical properties of the two components and although they are very miscible, they do not present any azeotrope and theoretically they can be easily separated in a distillation column at atmospheric pressure. Therefore, even if methanol purity is sacrificed in order to obtain all the methanol produced per column head, this is not an issue to consider.

The design of this distillation column is based on the assumption that the inlet stream is the outlet stream of the distillate from the reactive distillation:

- 10.332 kmol/h of methanol
- 24.977 kmol/h of water

With this input, a calculation basis is established to find the value of the minimum reflux ratio with 100 stages. The results are shown in Table 14:

*Table 14. Methanol purity varying reflux ratio*

Reflux ratio	Methanol purity
3.47	0.9981
3.66	0.9983
3.85	0.9985
4.04	0.9986
4.23	0.9987
4.42	0.9988

With these results and applying the heuristic relation for the minimum reflux of a distillation process that establishes that the optimum reflux of the column should be between 1.3 to 1.5 times the minimum reflux, the settled value is 6.06.

Once the reflux is set, the next step is the optimization of the trays in order to establish the optimum number of stages of the column to obtain methanol with a higher purity than 99.8%. Figure 10 shows the purity obtained for columns with different stages:



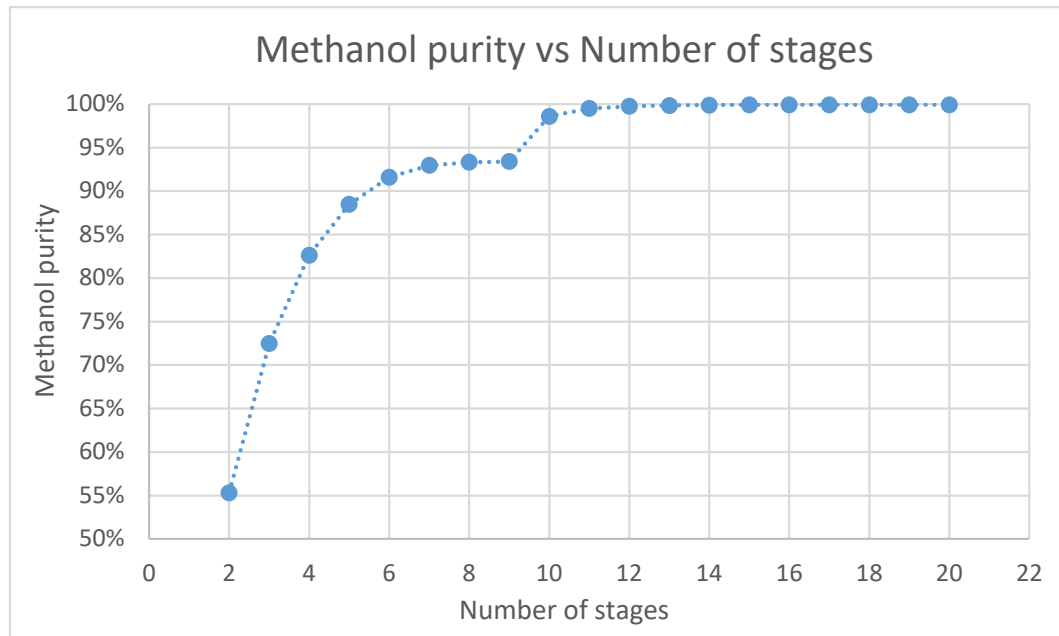


Figure 10. Methanol purity for different number of stages

As it can be seen from the simulation data, a purity of 99.8% is achieved from the 12th stage onwards, therefore this will be the set value.

To increase the efficiency of this second process, a comparison has been made to know if energy integration between two streams could be carried out to save energy in the reboiler.

The bottom outlet stream from reactive distillation column comes out at about 250°C and at a pressure of 30 bar, which provides about 30 MW. If the boiler requirements of the second column are calculated, it is observed that about 1 MW is required.

Therefore, it is also proven that the outlet bottom-head stream of the reactive distillation could be used to save energy in the methanol purification.

Finally, Figure 11 presents the complete scheme of the process and Table 15 the final results:

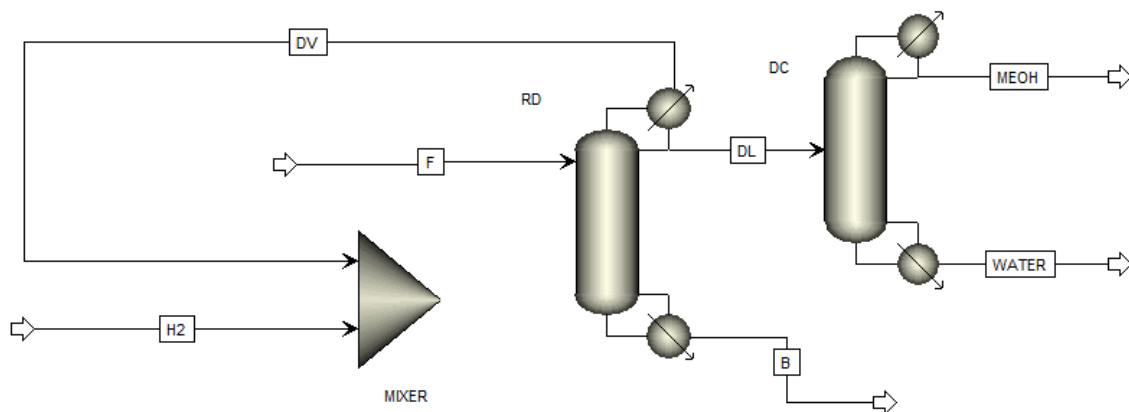


Figure 11. Final scheme of the process simulated in ASPEN

Table 15. Final results from all the process

<b>Reactive Distillation Column (Methanol synthesis)</b>	
P [bar]	30
T [°C]	240 - 253
Stages	12
Reflux ratio	1.3
MEA-CO <sub>2</sub> feed stream [kmol/h]	975
H <sub>2</sub> feed stream [kmol/h]	31.14
Product flowrate [kmol/h]	35.329
% Methanol of the product stream	29
<b>Distillation Column (Methanol purifying)</b>	
P [bar]	1
T [°C]	78 - 94
Stages	12
Reflux ratio	6.06
Product flowrate [kmol/h]	10.332
% Methanol of the product stream	99.8

## 6. CONCLUSIONS

After conducting the project and analyzing the results obtained, the feasibility of the proposed process may be optimistic. It is confirmed that a new process in methanol synthesis by CO<sub>2</sub> hydrogenation is possible, using less equipment due to the use of reactive distillation as a process intensification method.

At first, the intention was to perform the process only with the reactive distillation columns, but as it can be seen in the results another distillation column is required to purify the methanol to the standards due to the small temperature working range and the major effect caused by introducing hydrogen through the last stages. Nevertheless, it is a process with a great potential for increasing efficiency and profitability, which would allow many companies to reduce their CO<sub>2</sub> emissions into the atmosphere, as well as obtaining a useful product to work with.

The product characteristics are within the requirements proposed by IMPCA (see Table 7 for more information) and therefore would be valid for both industrial use and commercialization.

According to Table 15, a stream of 10 kmol/h of 99.8% methanol would be obtained, which would mean an annual production of 80 000 kmol/h (assuming that a continuous plant is operating around 8 000 h/year). This would be equivalent to 2.5 metric tons of methanol, which represents 2.5% of the current world production capacity [4].

Although this project covers the main aspects of the process and opens a new step for methanol synthesis, it should be considered that it is a preliminary study and, therefore, it has different assumptions that could not be discussed in the project but that could be addressed in future projects. One of them would be the detailed study of the CO<sub>2</sub> hydrogenation kinetics for liquid phase methanol synthesis with a 30% MEA solution.

The implementation of the kinetics to the reactive distillation column proposed in this project would provide greater rigor in the results and greater possibility of designing complementary equipment to adapt them to the products obtained by the main column.

## 7. NOTATION

- ASTM: American Society for Testing and Materials
- B: Bottom-head stream
- DL: Top-head liquid stream
- DV: Top-head gas stream
- F1: Feed stream 1
- F2: Feed stream 2
- GHG: Greenhouse gases
- IMPCA: International methanol producers & consumers association
- IPCC: Intergovernmental Panel on Climate Change
- LLE: Liquid-Liquid Equilibrium
- MEA: Monoethylamine
- Ppm: Part per million
- VLE: Vapor-Liquid Equilibrium

## 8. REFERENCES AND NOTES

1. IPCC. Climate Change 2021: Synthesis Report. Tech. Rep., 2021
2. International Energy Agency. World Energy Outlook, 2021.
3. Eurostat: Energy consumption Study, 2020. <https://ec.europa.eu/eurostat/en/web/products-statistical-books/-/ks-hb-20-001> (accessed Nov 16, 2021).
4. HIS Markit. Alvarado, M. (2018). Methanol Industry Overview.
5. M. Stöcker, "Methanol-to-hydrocarbons: catalytic materials and their behavior," *Microporous Mesoporous Mater.*, vol. 29, pp. 3-48, 1999.
6. Bowker, M. (2019). Methanol synthesis from CO<sub>2</sub> hydrogenation. *ChemCatChem*, 11 (17), 4238.
7. Hussain, I., Jalil, A. A., Hassan, N. S., & Hamid, M. Y. S. (2021). Recent advances in catalytic systems for CO<sub>2</sub> conversion to substitute natural gas (SNG): Perspective and challenges. *Journal of Energy Chemistry*.
8. Mbatha, S., Everson, R., Musyoka, N. M., Langmi, H. W., Lanzini, A., & Brilman, W. (2021). Power-to-methanol process: a review of electrolysis, methanol catalysts, kinetics, reactor designs and modelling, process integration, optimization, and techno-economics. *Sustainable Energy & Fuels*.
9. J. Skrzypek, M. Lachowska and H. Moroz, Kinetics of methanol synthesis over commercial copper/zinc oxide/ alumina catalysts, *Chem. Eng. Sci.*, 1991, 46(11), 2809–2813.
10. K. M. V. Bussche and G. F. Froment, A steady-state kinetic model for methanol synthesis and the water gas shift. reaction on a commercial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> Catalyst, *J. Catal.*, 1996, 161(1), 1–10.
11. Y. Slotboom, M. J. Bos, J. Pieper, V. Vrieswijk, B. Likozar, S. R. Kersten and D. W. Brilman, Critical assessment of steady-state kinetic models for the synthesis of methanol over an industrial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst, *Chem. Eng. J.*, 2020, 389, 124181.
12. N. Park, M. J. Park, Y. J. Lee, K. S. Ha and K. W. Jun, Kinetic modeling of methanol synthesis over commercial catalysts based on three-site adsorption, *Fuel Process. Technol.*, 2014, 125, 139–147.
13. G. H. Graaf, E. J. Stamhuis and A. A. Beenackers, Kinetics of low-pressure ethanol synthesis, *Chem. Eng. Sci.*, 1988, 43 (12), 3185–3195.

14. C. Seidel, A. Jörke, B. Vollbrecht, A. Seidel-Morgenstern and A. Kienle, Kinetic modeling of methanol synthesis from renewable resources, *Chem. Eng. Sci.*, 2018, 175, 130–138.
15. Keil, F. J. (2018). Process intensification. *Reviews in Chemical Engineering*, 34(2), 135-200.
16. European Roadmap for Process Intensification (ERPI). (2007). Available at: [www.efce.info/efce\\_media/European-Roadmap-I--531.pdf](http://www.efce.info/efce_media/European-Roadmap-I--531.pdf). Accessed 9 December 2021.
17. Taylor, R., & Krishna, R. (2000). Modelling reactive distillation. *Chemical engineering science*, 55(22), 5183-5229
18. Tuchlenski, A., Beckmann, A., Reusch, D., Düssel, R., Weidlich, U., & Janowsky, R. (2001). Reactive distillation—industrial applications, process design & scale-up. *Chemical Engineering Science*, 56(2), 387-394.
19. Liu, Y., Zhang, L., & Watanasiri, S. (1999). Representing vapor–liquid equilibrium for an aqueous MEA–CO<sub>2</sub> system using the electrolyte nonrandom-two-liquid model. *Industrial & engineering chemistry research*, 38(5), 2080-2090.
20. IMPCA, methanol reference specification, 2021. <https://www.impca.eu/IMPCA/Technical/IMPCA-Documents> (accessed Dec 05, 2021).
21. Hankin, A., & Shah, N. (2017). Process exploration and assessment for the production of methanol and dimethyl ether from carbon dioxide and water. *Sustainable Energy & Fuels*, 1(7), 1541-1556.
22. Lee, B., Lee, H., Lim, D., Brigljević, B., Cho, W., Cho, H. S., ... & Lim, H. (2020). Renewable methanol synthesis from renewable H<sub>2</sub> and captured CO<sub>2</sub>: How can power-to-liquid technology be economically feasible. *Applied Energy*, 279, 115827.
23. Statista, Study of the CO<sub>2</sub> emissions from thermal plants in Spain, 2021. <https://es.statista.com/estadisticas/1022995/emisiones-de-co2-procedentes-de-las-centrales-termicas-en-espana/> (accessed, Oct 18, 2021).