

Carbon Dioxide to Methanol Valorisation by Process Intensification

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The social and scientific effort to transition from fossil fuels to renewables or other eco-friendly energy alternatives is not enough to satisfy the increasing global energy demand. That leads to the continued use of fossil fuels, which causes a rising CO₂ concentration into the atmosphere. Carbon capture, utilisation, and storage (CCUS) techniques are being developed to mitigate its negative consequences because fossil fuel consumption is still required. The methanol (MeOH) production from the collected CO₂ is an industrial example of carbon utilisation. This process is currently carried out in three steps. In the first step, the CO₂ in the monoethanolamine (MEA) solution is thermally liberated (thermodynamically non-spontaneous). The first step is the thermal liberation of the CO₂ trapped in the MEA 30 wt.% aqueous solution. After that, the reactor is fed with H₂ and the released CO₂ to initiate the MeOH reaction (thermodynamically favourable). The MeOH is finally collected using distillation (thermodynamically non-spontaneous). The energy consumption of a process decreases when it combines a thermodynamically favourable process with a non-favourable process. The aim of this study is to examine, through rigorous simulation, the possibilities of process intensification. The performance of CO₂ desorption and hydrogenation in a single step is analysed with Aspen Plus®. The capacity to combine the two units creates a new field of inquiry for this method's energy-saving potential. After experimental analysis of its viability and its optimisation for maximising energy savings, the industrial impact is assured. Further research is needed to achieve reducing energy since the resultant energy of the overall system (the Reactive-Desorber Column plus two distillation columns) consumes 70 GJ/t MeOH. Nevertheless, the first simulation presented in this study indicates that a desorption-reaction column may be feasible, providing an alternative path for investigation into how to enhance the CO₂ hydrogenation to MeOH process.

1. Introduction

Climate emergency is one of the most serious concerns and urgent challenge for the planet to be addressed. CO₂ is considered a major greenhouse gas since it is a primary contributor to global warming leading to harmful environmental consequences (i.e., rising temperatures, extreme weather events, sea-level rise, and disruption of ecosystems). Global economic development anticipates a growth in demand of the energy sector whose supply in the coming decades will remain achieved by burning fossil fuels. Since natural sinks do not have the capacity to cope with the additional atmospheric CO₂ due to combustion of fossil fuels, CO₂ has to be actively removed. A transition to low-carbon and sustainable energy sources, implementing energy efficiency measures, adopting cleaner industrial practices and implement carbon capture, utilization and sequestration (CCUS) are key strategies to curb CO₂ emissions and pave the way for a more sustainable future. CCUS refers to technologies used to capture and use of carbon dioxide (CO₂) emitted by industrial activities. CCUS involves several steps: capture of CO₂ from emission sources, CO₂ compression and transportation to storage location or valorisation. Several valorisation techniques encompass both the direct use of CO₂, e.g., as inert gas or as solvent in its critical state, and its transformation into other compounds, e.g. hydrogenation to

MeOH. Valorisation of CO₂ as raw material to chemical synthesis reduces CO₂ emissions to the environment, while offering innovative routes to chemicals, working to transform the sequestration cost into economic benefits. CO₂ utilization involves its use as feedstock to produce valuable chemicals or fuels. For example, CO₂ can be converted into MeOH, which is useful as fuel but also as a chemical building block. About 60 % of the world production of MeOH is used in chemical synthesis or as solvent while only 40 % is used as a source of energy (Estevez et al., 2022).

In the chemical absorption column, aqueous alkanolamine basic solutions facilitate the spontaneous transport of acid gas CO₂ from the exhaust gases to the aqueous phase by formation of reversible chemical bonds, particularly at low temperatures, i.e. 40 °C. Chemical absorption in an aqueous alkanolamine solution of monoethanolamine (MEA) 30 wt % is currently the most mature industrial process to capture non diffuse sources of anthropogenic CO₂ due to its favourable gas-liquid equilibrium (Plesu Popescu et al., 2022). A load of 0.35 mol of acid gas/mol MEA is normally adopted, but it depends on the operating conditions. The resulting chemical solution is then heated in a distillation column, releasing CO₂, and regenerating the solvent for recycle, thus renewing its processing capacity. This regeneration stage is not spontaneous, and a significant amount of energy is spent and represents a high percentage of the treatment operating costs, meaning an energy penalty in thermoelectric power generation with post-combustion capture. Sakwattanapong et al. (2005) reported that energy consumption in regenerating lays between 3.8 and 5.4 GJ/t CO₂ when MEA is used. Accounting for GHG emissions caused by energy consumption, an average shadow marginal abatement costs of \$130/t across 30 industries is estimated (Gamtessa & Çule, 2023).

CO₂ is a very stable molecule thermodynamically: combustions or breathing generates energy, CO₂ and water. Energy must be provided to reverse this reaction. The primary route for MeOH synthesis involves the hydrogenation of CO₂ which is thermodynamically favourable at high pressure. The utilization of high-pressure catalytic processes for CO₂ hydrogenation harnesses the catalytic potential to drive chemical transformations under elevated pressures. Operating processes at elevated pressures enhances the availability of CO₂ and hydrogen for the reaction, thereby fostering more favourable reaction kinetics and yielding improved quantities of MeOH. Despite high pressure might sound energy intense, it should be emphasized that in many of the relevant industrial environments where catalytic CO₂ conversion is applicable, high-pressure operation already exists (i.e., steel making, refineries, cement manufacturing, etc.) (Villora-Picó et al., 2024). CO₂ hydrogenation process has been extensively studied at an industrial scale, demonstrating its economic feasibility (Sun et al., 2015).

CO₂ is separated from the absorption solvent used in its capture, is compressed and is transported to the valorisation plant where reacts with hydrogen to produce aqueous MeOH that is purified in a distillation column. Mendes et al. (2014) determined that for a post-combustion CO₂ capture facility using MEA and revalorizing it to MeOH and other chemical valuable compounds has a carbon debt when 50 % of CO₂ is captured and a net positive abatement of CO₂ when 80 % of CO₂ is captured from flue gas. One of the main energy consumptions of CCUS is derived from the aqueous alkanolamine solution regeneration (Alnouri and Al-Mohannadi, 2023). CO₂ absorption in MEA and CO₂ hydrogenation are thermodynamically favourable processes but the regeneration of the alkanolamine solution is not. As discussed in the following paragraph, many processes have been greatly improved under the concept of process intensification.

When multiple operations take place in a single unit is called process intensification. The example usually used is combining reaction and distillation in a single unit, which is called reactive distillation. Reactive distillation has been proposed to intensify many chemical processes, e.g. TAME synthesis (Plesu Popescu, 2012). When the chemical compounds that conforms the azeotrope do not react, the reaction is combined with an enhanced distillation, e.g. pressure swing (Bonet-Ruiz, 2006).

One of the advantages of combining reaction with separation equilibrium stages is that the reactants flow counter-currently inside the column. For instance, oil transesterification to biodiesel is a spontaneous reaction but the liquid-liquid phase split in the reactor generates a requirement of a large excess of MeOH. This fact implies large recovery costs to separate the product from the non-reacted reactants when a single reactor is used, but the process becomes very simple and energetically efficient when the reactor takes place in counterflow in a reactive extraction column (Dimian et al., 2019).

Process intensification is very advantageous when a thermodynamically favourable process is combined with a non-favourable process. If the free Gibbs energy of the spontaneous process is higher than for the non-spontaneous process, then the intensified process could become spontaneous. Although the resulting intensified process remains non-spontaneous, the energy consumption would greatly decrease. From the flue gas capture to the collected MeOH, there are many steps in the process: chemical absorption (spontaneous), alkanolamine regeneration by distillation (non-spontaneous), pressurized chemical reactor to produce MeOH (thermodynamically favourable – Chen et al. (2024)) and MeOH dehydration by distillation (non-spontaneous). Despite the potential energy savings of the intensification process, research on CO₂ absorption energy problems is focused on finding new solvents with better CO₂ capture capabilities and lower energy needs (Soo et al.,

2024). The aim of this study is focused on the possibilities of process intensification performing the CO₂ desorption, hydrogenation reaction and separation in a single unit (Figure 1). To the best of our knowledge, this study marks the first attempt to intensify the CO₂ absorption process, and the first try to intensify three processes within a single unit. The challenges encountered during the study are discussed.

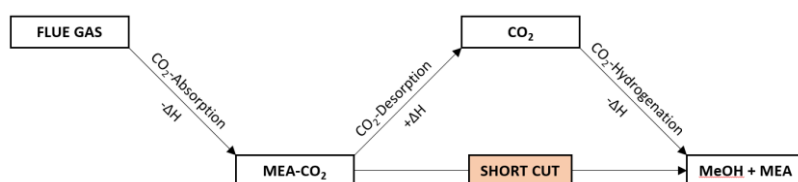


Figure 1: A short cut in the CO₂ hydrogenation process to improve the energy efficiency (Reller et al., 2014)

2. Method

The general implementation in the simulation software, specifically of the reactions and operation conditions, are detailed below. The rigorous simulation of the process has been performed in Aspen Plus v.12 using the thermodynamic model of non-random two liquids suitable for electrolytic mixtures and using the Redlich – Kwong model for standard properties calculation (ENRTL-RK). Chemical equilibrium is assumed in all the distillation column stages and this equilibrium is determined minimizing the Gibbs energy. A 10.38 kmol/h CO₂ stream is chosen as a calculation basis in the Aspen Plus simulation, based on the Spanish power plant carbon emission statistics gathered by Statista Research Department (2021). In this research, the MeOH synthesis from CO₂ is described by two catalytic reactions. The first reaction is the CO₂ hydrogenation to MeOH, and the second one is a side reaction called “Water-Gas-Shift-Reaction,” which occurs along with the MeOH formation and produces water and CO from CO₂ and H₂. There are some models that assume there is a third reaction (CO hydrogenation to MeOH), but it will not be considered. There are also implemented the equilibrium equations that Aspen Plus® propose for simulating CO₂ absorption (Equations 1 to 5).



It is extremely difficult to combine desorption, reaction, and separation into one unit. Figure 2 shows a simplified scheme of the resolution loop of the system by supposing an initial temperature (T_0) and a CO₂ composition in the gas phase (Y_0) in one stage. Now add other stages and gas and liquid flows connecting them into a single column. The computational effort is reduced by cutting the loop and dividing a single stage into two virtual stages: one for the desorption and the other for the hydrogenation reaction. Hence, each stage is determined by averaging the two simulated stages required to consider the overall reaction system.

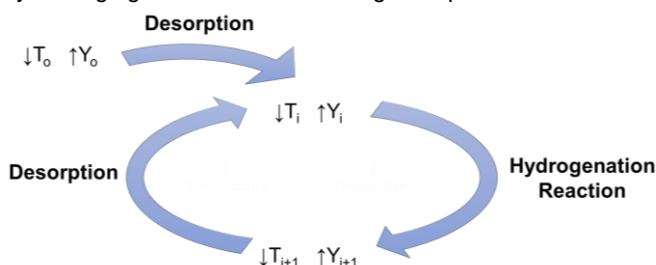


Figure 2: Simplified resolution scheme of the column stage. It illustrates the complexity of the studied case by just taking into account two variables: temperature (T) and the CO₂ gas phase composition (Y). The subindex number indicates the iteration step

Generally, the CO₂ absorption in MEA takes place at 1 bar and 40 °C. Regarding the methanation reaction, there are several available catalysts (e.g., Cu/ZnO/Al₂O₃ catalyst) and wide operating conditions. In this case, a pressure of 50 bar and a temperature between 200 °C and 250 °C have been chosen. The H₂/CO₂ ratio is set at 5, since the H₂/CO₂ ratio that enhances the conversion of CO₂ to MeOH ranges between 4 (Lee et al., 2020) and 5 (Hankin and Shah, 2017). Finally, the energy consumption of the proposed system is analysed and compared with the less energy demand process found in the literature (Meunier et al., 2020). The adsorption-desorption takes place at 1 - 2 bar, and a range of temperatures between 40 °C and 125 °C. The heat obtained in the MeOH reaction is integrated in the MeOH recuperation, making no-need to provide energy to purify the MeOH. The overall system needs 2.5 GJ/t of MeOH produced.

3. Results

The results of the intensification process are presented. The drawbacks of the initial proposed process led to a new approach. This continues so on until finding a final scheme, which is compared to the energy-integrated process of Meunier et al. (2020) as the base case. The typical industrial process of MeOH production from CO₂ absorbed in MEA (30 wt.%) is performed in three units: CO₂ desorption, CO₂ reaction and MeOH separation. These three steps are very energy-demanding processes, but Meunier et al. (2020) integrate energetically the overall system to minimize the energy consumption. This paper is used as the base case to compare the results. The aim of the present study is to decrease the energy consumption by process integration. The proposed process is a reactive distillation column, which combines the desorption, the reaction and the MeOH separation in the same unit. The MeOH is expected to be recovered at the top of the column, the non-reacted gases that are recirculated (mostly include H₂, but also CO₂ and CO). The non-CO₂-saturated aqueous MEA solution is expected to be collected at the bottom (Figure 3a).

Simulating this process yields various non-expected results in addition to just partially achieving the expected outcomes: there is little conversion of CO₂ to MeOH, and the majority of the MeOH is gathered at the bottom of the column. Operating at high pressures (e.g., 50 bar) promotes the MeOH reaction but it also increases the MEA solution's ability to collect CO₂, which negatively impacts CO₂ desorption and the subsequent reaction. But the MeOH reaction is hampered by increasing the reboiler heat to remove as much CO₂ from MEA solution as feasible because of the high temperature achieved. There is also evidence of poor MeOH purity in the distillate. The large gas flow entrains water to the top of the column. Moreover, heat from the liquid phase is needed for the desorption process, which may work against the goal of reaching the MeOH at the top. Since MeOH is recovered at the bottom, and an extra column is needed for the MeOH separation, the process is modified to a reactive-desorber followed by a distillation column. The reactive-desorber works without reboilers heat. The energy required for the desorption is provided by the energy released by the hydrogenation reaction (Error! Reference source not found. Figure 3b).

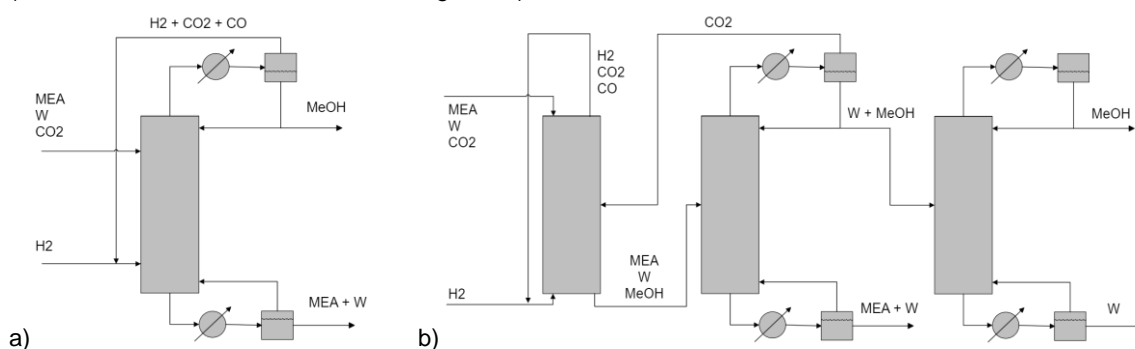


Figure 3: Intensification process of the typical industrial CO₂ hydrogenation process – New strategies. a) Reactive distillation column approach. b) Reactive desorber followed by a distillation column

After exposing the problems achieved with combining desorption, hydrogenation reaction, and distillation separation, the process studied is the reactive desorber followed by a distillation column (Figure 3b). This second process is lately compared with the base case. In Figure 3b, the desorber lacks both a condenser and a reboiler, and the gas phase outlet is recirculated. The entry of a high-temperature H₂ flow promotes the CO₂ release. MeOH can then be produced by the reaction of the CO₂ in gas phase. The energy needed to keep releasing CO₂ is supplied by the heat produced by the reaction. It is evident that these two processes are interdependent. The combination of the desorption process with an exothermic reaction displays a very curious temperature profile (Figure 4a). Instead of just seen a decreasing temperature over the column, like in an usual

desorption, this reactive-desorber column exhibits a maximum at stage 3 due to the heat generated by the hydrogenation reaction.

The column can be divided into three sections. Starting at the bottom of the column, the system displays a common desorber temperature profile at stages 18 to 25. More CO₂ desorption results in a temperature decrease. The MeOH reaction occurs in the middle column section, which includes stages 3 through 18. The CO₂ reaction in the lower stages of this section raises the temperature, which also enhances the CO₂ release. At the top section of the column, the heat from the hot gas phase is exchanged with the liquid phase that enters the column, allowing the release of CO₂. The gas phase that goes out of the column is recirculated to make it pass through the reaction section of the column. Figure 4b illustrates the MeOH formation over the stages, with stages 3 to 18 being the ones capable of doing the CO₂ hydrogenation (because there is the catalyst). MeOH formation is greater at locations in the reacting section where the CO₂ concentration is higher. As it ascends from the lowest stages, the vapour flow becomes more and more CO₂-rich until stage 18, where it reacts to produce MeOH. The reaction temperature raises and this sudden change in temperature caused by mixing the “cold” liquid and the “hot” vapour enhances the CO₂ release and reaction at stage 3.

As stated before, the exothermic reaction produces the energy required to release CO₂ from the MEA solution; hence, this unit does not consume any energy. The following unit is a distillation column since the MeOH generated in the reaction-desorption unit is obtained in a mixture with water and MEA. The goal of the distillation unit is to achieve 99.1 wt% of MeOH. The operating pressure is set at 1 bar since there is no reaction in this unit. There is a drawback to operating this unit at that pressure: the CO₂ solubility in MEA is reduced. This decrease lets the CO₂ be desorbed in the distillation column. So, the energy consumed inside the column will be for the desorption and splitting of the mixture. Besides, there is a high-water content in the feeding mixture that makes it difficult to reach the desired MeOH purity. A second column is necessary to make available this purity.

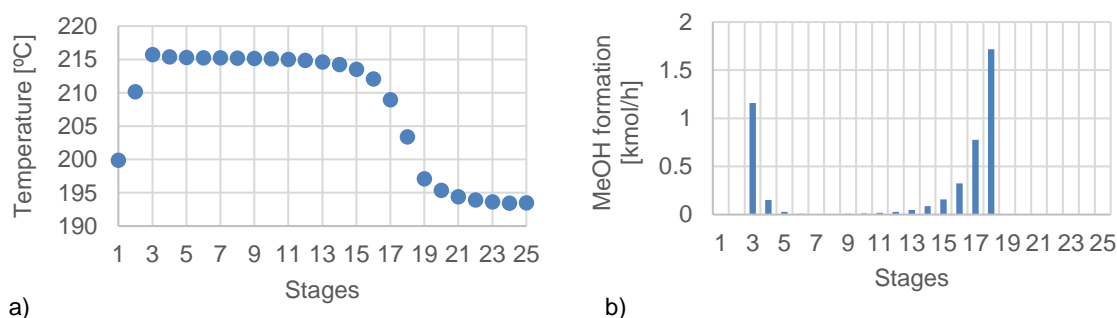


Figure 4: Reactive-Desorber Column: a) Temperature profile. b) MeOH formation

In this simulation, 4 kmol/h of MeOH 99.1 wt.% solution is recovered. This translates into a 43.8 % CO₂ conversion and a 99.6 % MeOH selectivity. Due to the convergence issues, the process is not optimised, and no energy integration work is done. Despite saving energy by processing the desorption and the reaction in the same unit, the energy consumption (GJ/t MeOH) is higher than in the energy-integrated system from Meunier et al. (2020). Since the CO₂ hydrogenation to MeOH is thermodynamically favourable at high pressure, a difference in operating pressure affects the MeOH produced (tonne MeOH) and the energy consumption (GJ/t MeOH). This fact highlights the importance of selecting the operating conditions. It can also explain the difference in the energy consumption between this work (operating pressure: 50 bar) and the study of Meunier et al. (2020) (operating pressure: 80 bar). Despite that, a more moderate pressure is selected for security reasons.

4. Conclusions

A fresh viewpoint on energy savings in the CO₂ hydrogenation to MeOH process is provided. An intensified distillation column can exchange heat from the reaction to the desorption, avoiding the energy supply to this column. The simulation shows the viability of this column. The main issue with the suggested technique is that it requires two distillation columns because the MeOH is entrained with the MEA solution at the intensified column bottoms. The actual state of the overall system is not energy-competitive. Future work is required to decrease the number of process units and its overall energy consumption.

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