

# Simulation and economic analysis of MEA+PZ and MDEA+MEA blends in post-combustion CO<sub>2</sub> capture plant

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## Abstract

The energy requirement of the amine based CO<sub>2</sub> capture process is the main drawback of the technology. Studies on energy demand reduction are therefore important. This work presents energy optimization and economic analysis of an 85% CO<sub>2</sub> capture process using pure monoethanolamine (MEA), and processes with blends of methyl diethanolamine (MDEA) and piperazine (PZ). The process with 30 wt% MEA was the base (reference) case in this study. The regeneration energy requirement for the base case was 3.77 / . The blends of (30 wt% MEA+5 wt% PZ) and (30 wt% MEA+15 wt% MDEA) were calculated to achieve 4.9% and 7.5% reduction in regeneration energy respectively. The economic analysis also indicated that 4.1% and 4.3% total annual cost savings can be achieved by the MEA+PZ and MEA+MDEA blends processes respectively. The work further shows that the cyclic capacity is enhanced by using these blends instead of pure MEA.

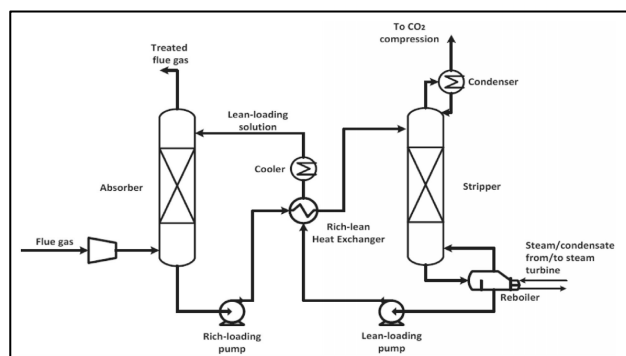
*Keywords:* CO<sub>2</sub> capture, simulation, energy-optimal, cost estimation, solvent, blend, regeneration energy, economy.

## 1 Introduction

Our planet has been faced with rising atmospheric concentration of greenhouse gases like carbon dioxide, methane, nitrous oxide and chlorofluorocarbons especially in recent decades. According to the Intergovernmental Panel on Climate Changes (IPCC), more than 50% of this increase results from CO<sub>2</sub> emissions (Abu-Zahra et al., 2007). Although the post combustion amine-based process requires huge amount of energy especially for regenerating amine, the mentioned process is the most mature method to highly cut down CO<sub>2</sub> emissions from flue gas exiting from plants or industries (Zang et al., 2017), mainly from combustion of fossil fuels such as coal, oil and gas in power plants.

Applying 30 wt% monoethanolamine (MEA) is regarded as the reference solvent for CO<sub>2</sub> capture at atmospheric pressure (Øi, 2010; Rochelle et al., 2011). A sketch of this process is presented in Figure 1. The

whole or a part of the flue gas is conveyed to the bottom of an absorption column where amine solvent comes into the absorber from the top. The two inlet streams flow counter-currently in the absorption column. As they come in contact, a chemical reaction is initiated where the CO<sub>2</sub> in the flue gas is absorbed by the amine solvent. This solution leaves the absorber, and it is pumped to the stripper where the CO<sub>2</sub>-rich amine solution is regenerated by heat supply from steam (endothermic reaction). The regenerated amine is pumped back into the absorption column for subsequent cycle of CO<sub>2</sub> absorption-desorption. Other main plant items such as heat exchangers, pumps in different parts of process are used to form the whole cycle.



**Figure 1.** Standard or conventional CO<sub>2</sub> capture process (Hosseini-Ardali et al., 2020)

MEA is classified among the primary solvent group which has high reactivity with CO<sub>2</sub>, but this amine requires a high heat of regeneration. This problem is the most outstanding one for MEA solvent. (Lee et al., 2013) claimed that using MEA as solvent could lead to up to a 30% reduction in the overall efficiency of the power plant and a corresponding 80% increase to the cost of electricity. Various experiments and simulations have been conducted to reduce the energy requirement (Abu-Zahra et al., 2007; Hosseini-Ardali et al., 2020; Le et al., 2013; Nwaoha et al., 2017). Such reduction in the needed regeneration heat could be achieved through three general approaches, which include (Dubois & Thomas, 2018):

- Improved absorption configurations, that is flowsheet modifications, for example, lean vapour recompression configuration (Aromada & Øi, 2015; Cousins et al., 2011),
- Optimization of operational conditions e.g., pressure and temperature of absorber and stripper columns (Abu-Zahra et al., 2007),
- Switching from the reference monoethanolamine (MEA) to other solvents e.g., methyl diethanolamine (MDEA), piperazine (PZ) or their blends.

This work focuses on the third strategy. MDEA, a tertiary solvent, was favored in recent years due to advantages like low corrosion, high loading capacity, resistance to thermal and oxidative degradation and lower heat of regeneration than MEA and some other solvents (Mudhasakul et al., 2013). Nevertheless, there a major disadvantage of low reaction rate with CO<sub>2</sub>. Piperazine (PZ) is known as a cyclic secondary amine, having a rapid reaction rate with CO<sub>2</sub>. PZ is highly resistant to oxidative and thermal degradation (up to 150 °C). This amine is used as additive to other amines (Borhani & Wang, 2019). A complete study of advantages and disadvantages of the different amines is found in (Borhani & Wang, 2019). The main concept of blending different amines is to combine the favorable characteristics of different solvents to overcome their various shortcomings. A careful selection of amine concentrations in a blend requires considering various parameters because each solvent has a distinctive chemical structure with different properties from other ones. This is why finding an optimal concentration of blends to bring more benefits to the removal process is important but demanding. This matter is an interest of various studies.

In this work, firstly, a standard base case where 30 wt% MEA is selected as solvent will be introduced. This case is specified as the reference case for comparison with other simulated cases where other solvents or blends are used. Those ranges of MDEA and PZ which can be added to the base case (30% MEA) to present MEA+PZ and MEA+MDEA blends with lower regeneration energy have been assessed. Moreover, an optimization in suggested ranges which results in lowest regeneration energy compared to base case is presented. The work proceeded with a cost estimation of the CO<sub>2</sub> capture plant for simulated cases in order to investigate the cost savings' potential due to switching from MEA to the mentioned solvents or blends.

Since implementing other solvents/blends directly affects the lean, rich and cyclic loading parameters in the process, they will be investigated in this work.

Various studies have been performed to study various concentrations of solvents and/or their blends in CO<sub>2</sub> capture processes. Some other works have attempted to study the economic implication of selecting different solvent blends. Finding a work where energy-

optimal concentrations of solvents/blends with the economic analysis of the total plant is a rarity. In this work, besides finding energy-optimal concentrations of amine-blends, the cost estimation for each solvent or blend is performed to investigate the economy of plant. This is because an energy-optimal amine solvent or blend may not necessarily give economically optimal process. The economic analysis of this work covers the whole lifetime of the plant.

## 2 Process simulation program and specifications

### 2.1 Process simulation program

All simulations in this work have been conducted with Aspen HYSYS version 10, which is a commercial process simulation program from AspenTech. The program has several property packages so that each one implies a specific equilibrium model. Acid gas chemical solvents is used in this work because this package supports a wide range of solvents and their blends.

Absorption and desorption columns in the standard process are the key items. These columns can be simulated with equilibrium stages including a stage efficiency (Øi et al., 2017). In this work, the efficiency of stages for CO<sub>2</sub> is assumed to be 0.25 in the absorption column. This parameter in the desorption column is presumed to be 1.0.

### 2.2 Specifications to conventional CO<sub>2</sub> capture process

The depicted process in Figure 1 is known as standard or conventional CO<sub>2</sub> absorption and desorption process. The process specifications in this work are given in Table 1, which are similar to ones in (Øi et al., 2017).

**Table 1.** Specifications for the conventional CO<sub>2</sub> capture process for 85% removal efficiency using 30 wt% MEA

| Parameter                                    | Value (Unit)      |
|--|-------------------|
| Inlet flue gas temperature to process        | 40 (°C)           |
| Inlet flue gas pressure to process           | 101 (kPa)         |
| Inlet flue gas flow rate                     | 1.091e5 (kgmol/h) |
| CO <sub>2</sub> content in inlet gas         | 3.30 (mol%)       |
| Water content in inlet gas                   | 6.90 (mol%)       |
| Nitrogen in inlet gas                        | 89.8 (mol%)       |
| Lean amine temperature before and after pump | 120 (°C)          |
| Amine pressure before rich pump              | 200 (kPa)         |
| Amine pressure after rich pump               | 300 (kPa)         |
| Lean amine pressure to absorber              | 101 (kPa)         |
| Lean amine rate to absorber                  | 1.175e5 (kgmol/h) |

|                                       |              |
|---------------------------------------|--------------|
| CO <sub>2</sub> content in lean amine | 2.98 (mole%) |
| Number of stages in absorber          | 10 (-)       |
| Rich amine pressure before pump       | 110 (kPa)    |
| Rich amine pressure after pump        | 200 (kPa)    |
| Number of stages of stripper          | 6 (-)        |
| Reboiler temperature                  | 120 (°C)     |
| Efficiency of stages in absorber      | 0.25 (-)     |
| Efficiency of stages in stripper      | 1.0 (-)      |

Minimum approach temperature in the lean rich heat exchanger is kept 10°C. Figure 2 represents a simulated standard process in Aspen HYSYS.

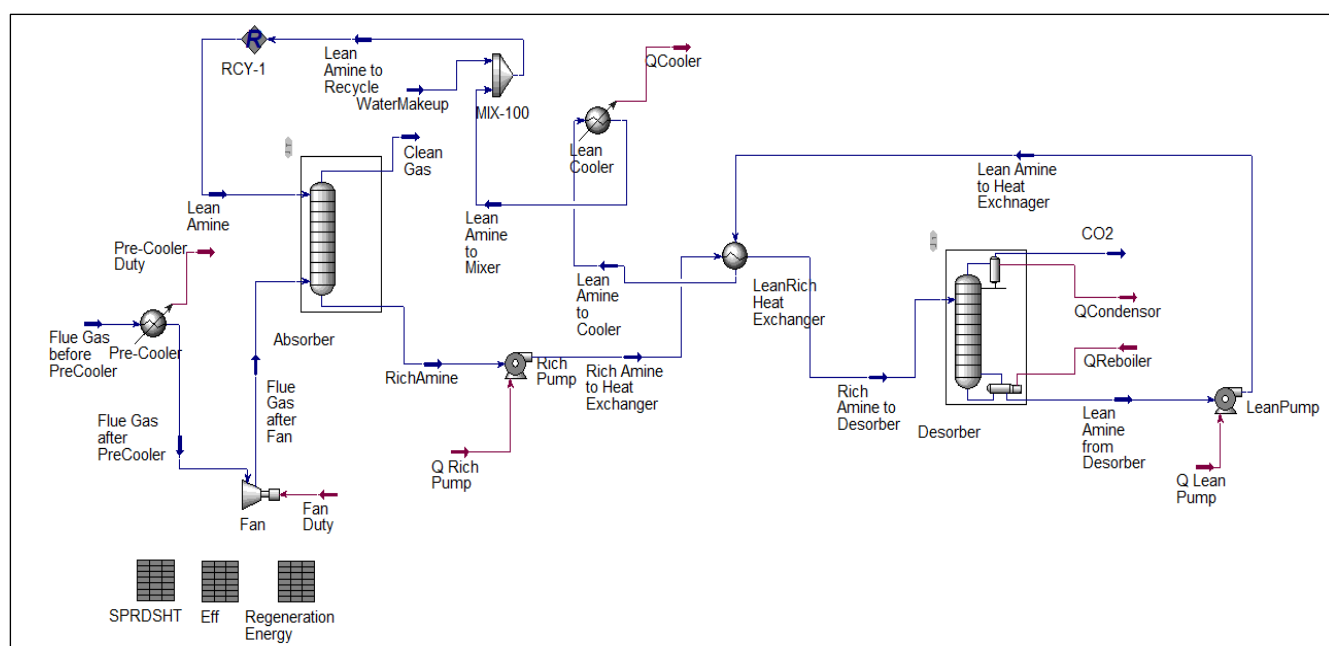


Figure 2. Aspen HYSYS flow-sheet of conventional process

### 2.3 Simulations with blends

As mentioned earlier, other solvents or their blends can be used in CO<sub>2</sub> capture process instead of MEA. In this work, both blends of MEA+MDEA and MEA+PZ are used as solvent. Various simulations with different concentrations of mentioned blends have been tested to investigate their effects on the process. Simulations with the blends have the same specifications of the standard base case listed in Table 1. Thus, there is no difference in the configuration of process with the standard base case in Figure 2. The results from simulations will be presented in the following sections.

## 3 Dimensioning and cost estimation

The main objective of dimensioning is to specify proper equipment to the capture plant. These items should be proper in different parameters especially size and

material to satisfy the requirements of each item. In addition, dimensioning shapes initial data for cost estimation.

Equipment cost could be obtained by different methods. The most reliable source is to obtain them from manufacturers. Though, in many cases, it is difficult to have access to such data (Ali et al., 2019). The use of commercial databases like Aspen In-Plant Cost Estimator is practical. The equipment cost data in this work were obtained from Aspen In-Plant Cost Estimator version 10, where the cost year is 2016. Other costs including direct costs, engineering costs and administration costs are added to form total installed costs for equipment (Aromada et al., 2021).

The total capital expenditure (CAPEX) for the CO<sub>2</sub> capture plant is the sum of all the equipment installed cost. In addition to CAPEX, operating expenditures (OPEX) were also estimated. In this work, OPEX comprises only the cost of electricity, cooling water, steam, solvents and maintenance. Other items for OPEX calculation like labour and supervision costs, insurance and direct overheads are not included in this work. Because the main objective of current work is to study possible cost saving of other solvents or their mixtures relative to pure MEA process.

### 3.1 Assumptions for dimensioning

Dimensioning was implemented for each piece of equipment used in the carbon dioxide removal plant. Calculation of the diameter for the absorption column is done by assumption of gas velocity to be 2.5 m/s. Gas velocity for the desorption column is assumed to be 1.0

$m/s$  (Øi et al., 2017). The tangent-to-tangent height of the columns are calculated based on the required space for the structured packings and washing sections. Flooding phenomenon must be included in dimensioning for both columns. In this work, 22 meters and 10 meters are assumed as the tangent-to-tangent heights of the absorber and the stripper respectively.

Heat exchangers are sized based on the required heat transfer area. The Logarithmic Mean Temperature Difference (LMTD) and duties for each heat exchanger are extracted from the simulation results. In this work, the overall heat transfer coefficients are assumed to be  $500 W/(m^2K)$  for the lean rich heat exchanger,  $800 W/(m^2K)$  for the reboiler and the lean amine cooler, and  $1000 W/(m^2K)$  for the condenser (Ali et al., 2019; Aromada et al., 2020). All the heat exchangers in this work are assumed to be shell and tube type. More possibilities for other types of heat exchangers can be found in (Aromada et al., 2020).

In the plant, pumps are responsible for conveying the rich and lean amine flows. Volumetric flow rates of the lean and rich streams determine the required power for pumps. In this work, centrifugal pumps with adiabatic efficiency of 75% are assumed (Øi et al., 2017; Aromada et al., 2020). The fan is assumed to be a sort of centrifugal one with adiabatic efficiency of 75% (Aromada et al., 2020).

Stainless steel (SS316) is selected for almost all items except for the fan, which is assumed to be carbon steel (CS). The main reason for selecting SS316 material is resistance to corrosion (Ali et al., 2019).

Using other solvents, especially piperazine might bring some benefits to the capturing process in terms of material selection instead of pure MEA. For instance, (Rochelle et al., 2019) indicated that if PZ solvent selected for a  $CO_2$  absorption plant, there is a possibility for specifying cheaper carbon steel for the stripper. Moreover, (Rochelle et al., 2011) evaluated positive effects of piperazine solvent like more resistant to degradation and volatility compared to pure MEA.

### 3.2 Assumptions for cost estimation

Although there are various works in which cost estimations for carbon dioxide removal plants have been estimated, considerable differences can be found in literature which results from applying different methods, assumptions and scope of study.

In this work, adjusting equipment costs in CAPEX calculation to total installed costs was conducted with the Enhanced Detailed Factor (EDF) method (Ali et al., 2019; Aromada et al., 2020; Aromada et al., 2021). This method is briefly explained in the following section.

Equipment cost data were obtained directly from Aspen In-Plant Cost Estimator version 10 with cost year of 2016, while current work is in 2021. This adjustment

was implemented using the Chemical Engineering Plant Cost Index (CEPCI) where:

$$Cost_{2021} = Cost_{2016} \times \frac{CEPCI_{2021}}{CEPCI_{2016}} \quad (1)$$

The cost indices for 2016 and 2021 are 542 and 655 respectively (Chemical Engineering Essentials for the CPi Professional, 2021).

The total lifetime for the plant is assumed to be 20 years. Since the value of money during this time is not constant, interest rate is implemented into the CAPEX calculation to update the value of money for each time slot. Time slot in this work is assumed to be one year with the interest rate of 7.5% (Aromada et al., 2020). Total annual hours of operation for the plant in this work is presumed to be 8000 *hours/year* (Øi et al., 2017; Ali et al., 2019; Aromada et al., 2020). Maintenance costs of this work is 4% of total CAPEX.

Other important item in the plant is the cost of solvents. Table 2 below provides the prices for the selected solvents in current study. While the unit prices of the utilities in the plant are provided in Table 3.

**Table 2.** Prices for applied amines in this work (Gomes et al., 2015)

| Amine | Value (€/litre) |
|-------|-----------------|
| MEA   | 30.50           |
| PZ    | 68.70           |
| MDEA  | 51.60           |

**Table 3.** Prices for applied utilities in the plant (Aromada et al., 2020)

| Utility       | Value (unit)              |
|---------------|---------------------------|
| Electricity   | 0.132 [€/kWh]             |
| Steam         | 0.032 [€/kWh]             |
| Cooling water | 0.022 [€/m <sup>3</sup> ] |

### 3.3 Cost estimation method

In the EDF method, each piece of equipment has its distinct installation factor based on its costs. These installation factors are prepared in for equipment in carbon steel. Therefore, since almost all the equipment in the plant is constructed from SS316. To use the EDF installation factor list (Aromada et al., 2021), the cost of equipment in SS has to be converted to their corresponding cost in CS using the EDF material factors provided in Table 4 as follows:

$$F_{total,SS} = F_{total,CS} + ([f_{mat} - 1] \cdot [f_{equipment} + f_{piping}]) \quad (2)$$

where,  $F_{total,SS}$  is the total cost factor of stainless steel.  $F_{total,CS}$  is the total installation factor of the equipment in carbon steel,  $f_{mat}$  is the material factor,  $f_{equipment}$  and  $f_{piping}$  refer to the equipment and piping installation factors respectively.

**Table 4.** EDF method material factors

| Sort of material                 | Material factor |
|----------------------------------|-----------------|
| Stainless steel (SS316) welded   | 1.75            |
| Stainless steel (SS316) machined | 1.30            |
| Glass-reinforced plastic         | 1.00            |
| Exotic materials                 |                 |

The CAPEX is the sum of total installed cost for each piece of equipment in the plant. To estimate the total annual cost, the CAPEX was annualized and the first year OPEX was estimated. The annualized factor and annualized CAPEX are estimated using equation (3) and (4) respectively.

$$Annualized\ factor = \sum_{1}^n \frac{1}{(1+i)^n} \quad (3)$$

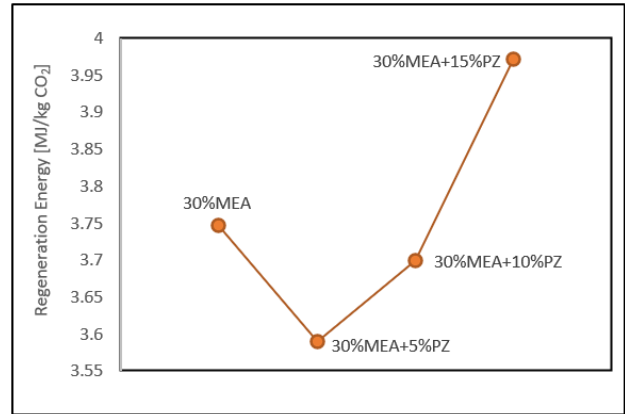
where,  $i$  is the interest rate and  $n$  is plant lifetime.

$$Annualized\ CAPEX = \frac{CAPEX}{Annualized\ factor} \quad (4)$$

## 4 Results and discussion

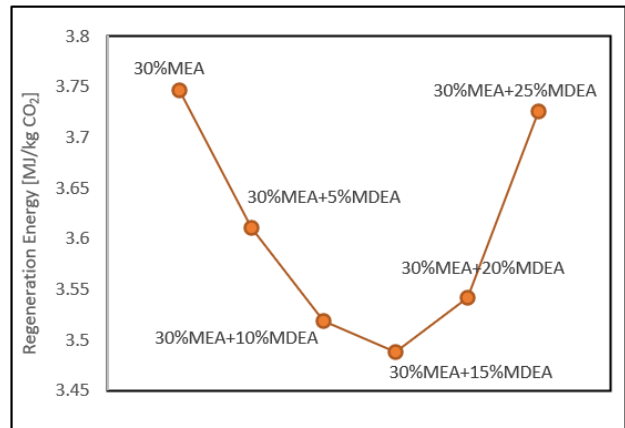
### 4.1 Results for energy consumptions

According to analysis of the simulated standard base case, this process requires 3.77 / . (Nwaoha et al., 2017) investigated various literature where they applied 30 wt% MEA solvent. The required regeneration energy is 3.3 to 4.4 / which validates the result of this work. Regeneration energy has been assessed for other simulations with 30 wt% MEA and blending with different amounts of piperazine, ranging from 5 wt% to 15 wt% as presented in Figure 3. From the results obtained in this work, 5 – 10 wt% PZ as additive to 30 wt% MEA reduces required regeneration energy in the CO<sub>2</sub> capture process. The solvent blend of 30 wt% MEA+5 wt% PZ gave the energy optimum specific reboiler heat consumption of 3.59 / . This is a 4.9% reduction compared to the standard base case. Different concentrations of PZ in MEA are presented in Figure 3.



**Figure 3.** Assessment of adding different concentrations of piperazine to MEA in term of regeneration energy

Similar work has been performed for blends of MEA+MDEA. Among the results of the simulations performed with the blends of 30 wt% MEA and different concentrations of MDEA as additive, a range of 5 to 25 wt% MDEA presents lower regeneration energy than the reference pure MEA process as can be seen in Figure 4. The energy optimum blend of MEA+MDEA was found to be a blend of 30 wt% MEA+15 wt% MDEA. This optimum value is 3.49 / , which is 7.5% saving in regeneration energy compared to the standard base case.



**Figure 4.** Assessment of adding different concentrations of MDEA to MEA in term of regeneration energy

Thus, both blends of (30 wt% MEA+5 wt% PZ) and (30 wt% MEA+15 wt% MDEA) have potential for lower regeneration energy based on the simulations results.

(Mudhasakul et al., 2013) simulated the effect of adding different concentrations of piperazine through a physical property package of acid gas removal unit into Aspen Plus. Their work clearly shows that 4 wt% to 5 wt% piperazine as additive has the best trade-off between CO<sub>2</sub> recovery and energy consumption. In addition, (Abd & Naji., 2020) with a steady state simulation in the Aspen HYSYS program has

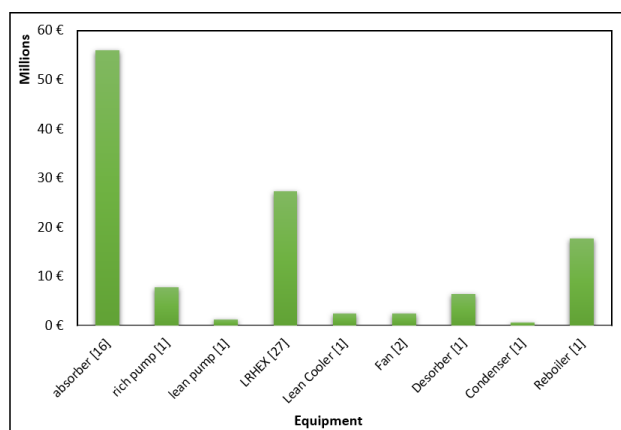
determined that the effects of adding various concentrations of piperazine up to 10 wt% with maintaining the constancy of the entire amine strength of 45 wt%. Their results indicate that 5 wt% piperazine provides the best consequence in terms of energy.

(Idem et al., 2006) experimented 4:1 molar ratio of MEA+MDEA blend in a pilot plant and their results emphasized a huge heat-duty reduction relative to the pure MEA process. (Li & Wang., 2013) also experimented different concentrations of MEA+MDEA blend in an amine scrubber. Their work showed a 2:1 weight portion of MEA+MDEA can reduce the regeneration energy by 22%.

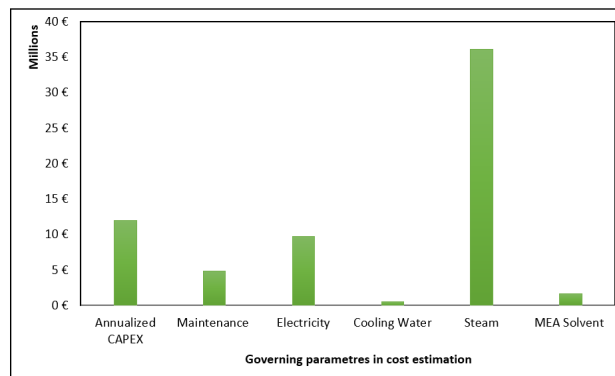
## 4.2 Results for cost estimations

Cost estimation of the standard base case has been performed based on the EDF method. Cost estimation for suggested blends has also been performed to investigate whether they can bring cost saving to the plant.

The CAPEX for the standard base case process is 122.3 million euros for a lifetime based on calculations for the year 2016. Adjusting this value to year 2021 results in 147.9 million euros. The annualized CAPEX for this case is calculated to 14.5 million euros per year. The distribution of CAPEX for the standard base case is presented in Figure 5. The annual OPEX distribution is given in Figure 6.



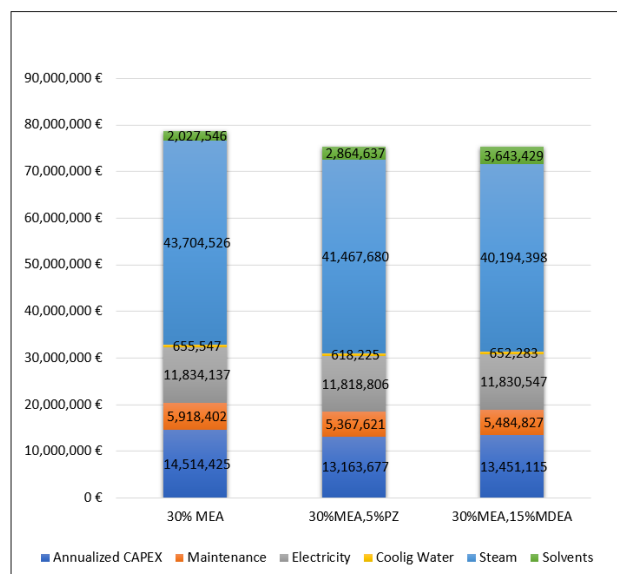
**Figure 5.** Distribution of the CAPEX for the standard base case plant. (Value in [] indicates the number of that particular item applied in the process)



**Figure 6.** Distribution of governing parameters in total economy of plant for the standard base case

Total annual cost for the standard base case is calculated to be 78.6 million euros. From Figure 6, it is obvious that steam has the highest share of the annual costs of the capture process. This is more than 55% of the total cost per year. Amine-based solvent capture processes are regarded as energy-intensive and any reduction in regeneration energy might bring cost savings.

Although MEA is the least expensive solvent compared to MDEA and piperazine, the economic analysis of the capture processes with the two suggested blends in Section 4.1 resulted in saving in annual costs. The blend of (30 wt% MEA+5 wt% PZ) yields a 4.1% cost saving per year. A 4.3 % cost savings per year for the blend of (30 wt% MEA+15 wt% MDEA) was estimated. The economic analysis of the carbon capture process for the two blends is presented in Figure 7 as well as for the standard base case.



**Figure 7.** Economy analysis of CO<sub>2</sub> removal process for three different solvents/blends

### 4.3 Results for lean, rich and cyclic loadings

The lean and rich loading are defined as,

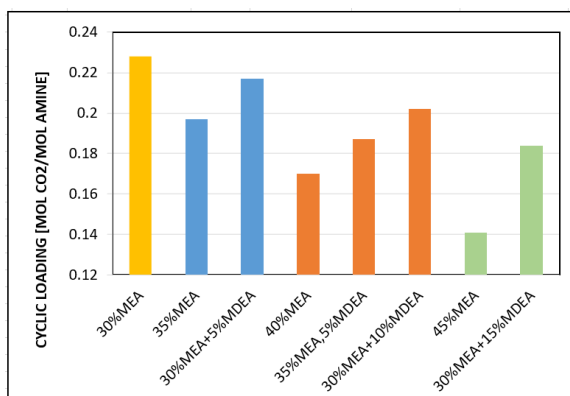
$$\alpha = \frac{n_{CO_2}}{n_{amine}} \quad (5)$$

where, lean and rich amines have been shown in Figure 2. The difference between the lean and rich loadings is referred to as the cyclic loading,

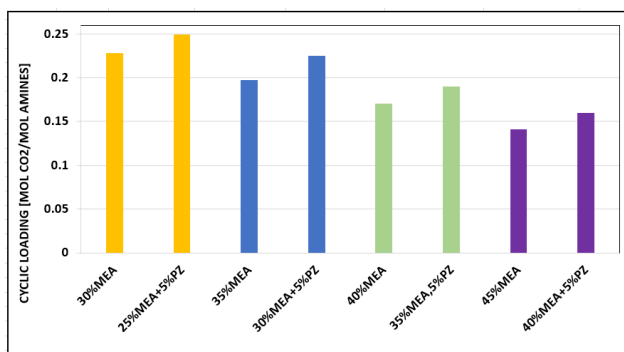
$$\alpha_{cyclic} = \alpha_{rich} - \alpha_{lean} \quad (6)$$

Achieving higher amount of cyclic capacity is highly desirable thanks to its improvements in the regeneration energy. (Nwaoha et al., 2017) asserts that an ideal solvent or blend requires to have a higher cyclic loading. The cyclic capacities of the different concentrations of MEA+MDEA and MEA+PZ blends have been evaluated and compared with the same concentration if only pure MEA solvent is used. The results are shown in Figure 8 and Figure 9 respectively.

Figure 8 indicates that adding MDEA to MEA enhances cyclic loading compared to the pure MEA process. It is obvious that the blend of 30 wt% MEA+15 wt% MDEA achieved the highest cyclic loading compared to other concentrations.



**Figure 8.** Assessment of cyclic loading for different concentrations of the blend of MEA+MDEA compared to the identical weight fraction of pure MEA



**Figure 9.** Assessment of cyclic loading for different concentrations of the blend of MEA+PZ compared to the identical weight fraction of pure MEA

Similar analysis was performed for the blend of MEA+PZ, resulting in Figure 9. According to the Figure

9, all concentrations of MEA+PZ blend present a larger cyclic loading than the same concentration of pure MEA, which means PZ can enhance cyclic loading in this blend.

Benefits for switching from individual MEA to other solvents or blends are not only limited to regeneration energy, but also economy of the plant and cyclic loading. Other important factors like degradation, foaming and precipitation have potential for future study. In addition, it will be reasonable to proceed the work in the future with experimental data in order to validate the results.

### 4.4 Uncertainties

Regarding the uncertainties in this work, Murphree efficiency could be mentioned. This factor in all simulated processes has been assumed to be equal, while each blend requires to have a specific one. This work is an option for future work. Secondly, this work has been based on vapor-liquid equilibrium model. Other models could be investigated and compared with current results.

## 5 Conclusion

In this work performed in Aspen HYSYS version 10, a standard CO<sub>2</sub> removal process has been simulated with various concentrations of individual and mixtures of MEA, MDEA and PZ solvents. It was concluded that the blend of MEA+PZ and MEA+MDEA have potential to improve the process especially in term of regeneration energy. Based on the performed simulations, two blends of (30 wt% MEA+5 wt% PZ) and (30 wt% MEA+15 wt% MDEA) present energy-optimal processes compared with other concentrations.

In addition, the cost analysis based on the EDF method for the simulated plants has been performed to investigate the effect of implementing other solvents than MEA on the economy of plant. The results indicated that both suggested blends have potential to bring considerable cost savings to the CO<sub>2</sub> removal process.

### Acknowledgements

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