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CARBON DIOXIDE CAPTURE FOR THE OXIDATIVE COUPLING OF METHANE PROCESS – A CASE STUDY IN MINI-PLANT SCALE

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Abstract

The Oxidative Coupling of Methane (OCM) to ethylene is a promising alternative for the oil based industry. In this process, beside the valuable product ethylene, other by-products are produced. Hence the gas stream has to be refined further. The process is not applied in the industry yet, because of high separation costs. This article focuses particular on the CO_2 purification of the OCM product stream. Therefore a case study were done for a design task of the reaction product gas cleaning from 22 mol% CO_2 to 1 mol% on an operating pressure of 32 bar. A state of the art chemical absorption process using Monoethanolamine (MEA) was developed and optimized for the base case. Therefore Aspen Plus® with build-in rate based model for the mass transfer with an electrolyte NRTL – approach and chemical equilibrium reactions for the water-MEA-CO_2 system as well as kinetic reactions was applied. In order to improve the energetic performance, gas permeation with dense membranes was studied as alternative process. Therefore a membrane unit was developed in Aspen Custom Modeler® (ACM). The solution-diffusion model with the free-volume-theory for gas permeation including Joule-Thomson effect as well as concentration polarisation² was applied successfully. Furthermore a rubbery polyethylene oxide (PEO) and a glassy cellulose acetate (CA) composite membrane with experimentally determined parameters were used in this model. The standard absorption process was developed with 97% CO_2 removal including solvent regeneration and heat integration. Whereas the thermal energy demand results to 2.8 MJ/kg_{CO_2} at 53% solvent regeneration in the desorption column for 30 wt% MEA. It was observed, that substitution of the absorption process only by a membrane process causes high product losses, so that the process became uneconomical. Hence the design task can be fulfilled only by a hybrid process, a combination of a membrane unit with an absorption process. This reduces the energy demand down to 1.6 MJ/kg_{CO2} with moderate product loss of 9 %. This article describes the process, as well as the simulation study. Experimental investigations of the process are carried out and results will be given in the presentation.

Keyword: Carbon Dioxide Capture, Membrane, Absorption, Oxidative Coupling of Methane, Hybrid Process

1. Introduction

In order to investigate the whole OCM process in continuous operation, an integrated downstream concept had to be developed. So far all proposed processes associated with high energy demand and cost-intensive downstream procedures for separation and gas recycling. Due to the yield limitation of 30 % for the OCM reaction, the goal of the downstream process synthesis is a further energetic and economic improved process performance.

Table 1. Process condition and design task of the CO_2 capture

Raw gas stream	Gas temperature	Gas pressure	Product purity
22 kg/hr	40 °C	32 bar	< 1 mol% CO_2

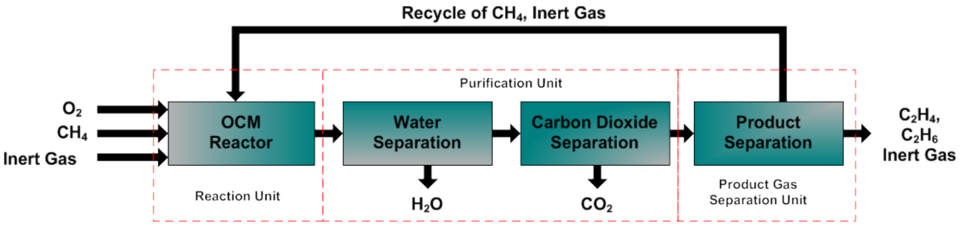

Figure 1. Flow diagram of the OCM – Process

Hence the whole process was divided into three units, shown in figure 1: the reaction unit, the purification unit and the separation unit; and all of them are investigated concurrently in a mini-plant scale. Therefore, design cases were defined for each unit under consideration of their interactions during the process synthesis. Based on the general framework of figure 1, process conditions and the design task for the CO_2 separation unit was developed, which are given in table 1. Based on the product concentration presented in table 2, the aim is to reduce the CO_2 concentration down to less than 1 mol%. In this way the desired ethylene purity can be reached under the design restrictions. Within the article is shown, how to resolve the lack of high separation cost for the purification and develop an integrated, energy efficient CO_2 capture process for the OCM refinery.

Table 2. Feed gas stream composition in mol% of the CO_2 separation unit

	CH_4	C_2H_4	C_2H_6	CO_2	H_2O	Inert gas
Dry raw gas	45	12	6	22	-	15

2. Base Case Design: Chemical Absorption Process

A chemical absorption process using MEA as a solvent was chosen to design a base case, which is presented in figure 2. Such a chemical absorption process is favored for species, which contains acid-based functional groups, like carbon dioxide. They are well established and commonly used for industrial CO_2 separation. The advantages of amine processes are the high selectivity regarding CO_2, reusing the solvent and recovering the heat by recuperation. Otherwise they also cause high thermal energy demand for solvent regeneration in the desorption unit. The concentration range of MEA in industrial plants is between 15 – 35 wt%[4] and it was assessed for the base case by 30 wt%. Operating the column in an industrial relevant regime the F-Factor has to be in the range of 0.5 – 1.5 $Pa^{0.5}$. To examine this range in the mini-plant, the absorption column diameter was chosen to 0.04 m. Subsequently, under the given conditions must the desorption column have a diameter of 0.1 m. Therefore only a packed bed column with a structured packing are suitable for the mini-plant application and a simulation model was build with this restriction and is described in the next section.

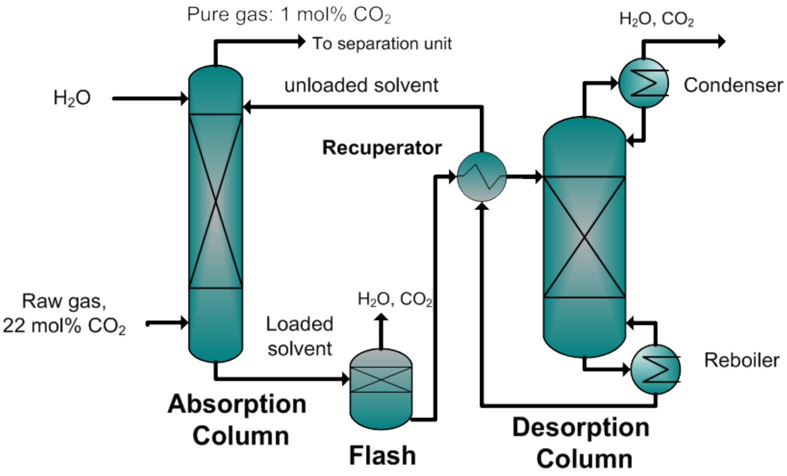

Figure 2. Base case – Conventional CO_2 separation process: Amine based chemical absorption

2.1 Simulation model

The base case process was investigated with a rigorous simulation model using Aspen Plus. This model includes the build-in electrolyte NRTL package *ELECNRTL,* with chemical equilibrium reactions for the liquid phase and the Redlich-Kwong equation of state for the gas phase. The build-in *RateSep* approach was used to describe the mass transfer in the packed column. Furthermore was the *MEA-REA* package in the absorption column applied successfully to consider the reaction kinetics.

2.2 Parameter study to develop the optimal base case

The effect of solvent flow rates on the regeneration energy demand was studied for the constant carbon capture of the design task. Hence the flow rate was varied in the range of 100 - 250 kg/hr in a closed loop configuration, figure 2. Hereby was the reboiler heat duty varied in order to change the solvent regeneration and to reach the constant carbon dioxide capture of 97%. The thermal regeneration energy demand was calculated per kg captured CO_2 from the raw gas. Furthermore the effect of the column height on the captured CO_2 was studied in standalone simulation of the absorption column for each solvent flow. A minimal column height is necessary to realize the contact time of the liquid and the gas phase. Therefore the height of the column was increased for each flow rate till no effect on the CO_2 capture was obtained. The column height was varied from 0.5 – 5 m.

2.3 Results and discussion

The effect of solvent flow rate on the energy demand for constant carbon dioxide capture is presented in figure 3. It shows that the solvent regeneration rate decreases with increasing solvent flow, while the energy demand forms a minimum by 150 kg/hr with 45 % solvent regeneration. This result was taken, to design the base case for the design task and the design dimensions are given in table 2. Due to enhanced gas liquid contact time was a rising carbon dioxide capture observed with increasing column height. The maximum CO_2 liquid loading could be reached at a column height of 5 m for the given design task. Further increase of the column height did not affect the liquid loading. In addition to these results an increase of the specific packing area results in a larger contact area and decreases the column height. Nevertheless is the specific packing area limited by the flooding point of the liquid loading. Thus a specific packing area of 450 m²/m³ could applied successfully to the absorption column, whereas a specific area of 350 m²/m³ is used in the desorption column of the base case process. Moreover, the results will be validated in the mini-plant for the used Rombopak® packing.

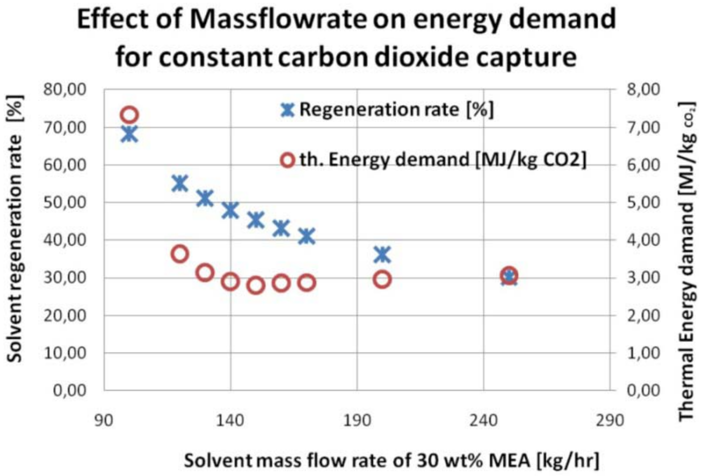

Figure 3. Simulation results – thermal energy demand for different solvent flows with constant carbon capture

Table 2. Base case design of a conventional CO_2 capture process

System pressure	Solvent flow	MEA concentration	Solvent regeneration	Absorption packed height	Specific packing area	Thermal Energy demand
32 bar	150 kg/hr	30 wt%	47 %	5 m	500 m²/m³	2.79 MJ/kg$_{CO_2}$

3. Membrane Processes as alternative CO_2 separation

Gas permeation processes with dense membranes were applied as an efficient method to improve the energy demand of CO_2 capture[1]. Therefore, they were investigated as an alternative in comparison to the base case. While industrial applications for gas permeation are rare, the potential of membrane in separation technique are vast and the applications rieses[3]. Several materials like cellulose or polymer based materials can be used as a selective layer for the separation of CO_2 from hydrocarbons. In this work were cellulose acetate (CA) and polyethylene oxide (PEO) investigated as selective layer with polydimethylsiloxane for the support layer in a GKSS[c] composite flat sheet membrane configuration.

3.1 Gas permeation membrane model

First valuation of the separation efficiency was achieved by process simulation based on single gas permeation experiments done by the GKSS[c]. Therefore the permeation behavior of dense membrane is described by the solubility-diffusion model[2], equation 1.

$$\dot{n}_i = \frac{S.D}{\delta} \cdot \Delta f_{i,M} = \frac{P}{\delta} \cdot \Delta f_{i,M} \qquad (1)$$

For technical membranes the quotient of permeability *P* and membrane thickness *δ* are combined to the permeance *L*, which has to be obtained experimentally. The permeance can be specified with the free-volume theory including temperature, pressure and concentration dependency. Furthermore are free-volume parameters obtained experimentally and parameters were adapted by the GKSS[c]. The permeation flux describing equation is given in equation 2. Therefore the model was developed in Aspen Custom Modeler® considering non ideal effects that affect the permeation behaviour. Those effects are the concentration polarization of the enriched component along the membrane and the Joule-Thomson effect of cooling by decompression of a real gas.

$$\dot{n}_i = L_i(T, c_i) \cdot \Delta f_{i,M} \qquad (2)$$

3.2 Parameter study for the membrane process

Two different kinds of membrane processes were investigated in this study: a one stage membrane process and a two stage membrane process, presented in figure 3. The raw gas conditions for both processes were the same as for the base case and they are given in table 1 and 2. However, first screenings of the different materials were done, for a constant membrane area. Anticipate the results of the study, it was discovered, that the design task of 97% CO_2 capture could be reached only with ethylene losses of more than 40%. This is uneconomically for the OCM process. Hence the design task for the membrane process was reduced to capture of 50% CO_2 by the membrane. With this the CO_2 concentration of the retentate stream of figure 3 results to 10 mol%. Therefore the separation efficiency was investigated for the one stage membrane process with both materials PEO and CA. Thus the membrane area was increased to reach the desired design task of 10 mol% in the retentate stream. Based on the one stage process, the two stages process was investigated with different combinations of membrane materials for the stages. In this case is the permeate stream feed to a second membrane unit, where the product is recovered and recycled to the first membrane unit. While the feed pressure and temperature of the second membrane stage was varied in this parameter study for each interconnection. The effect on separation efficiency was evaluated by the selectivity for CO_2 based on the product ethylene with equation 3 and the ethylene loss was obtained with equation 4.

$$S_{CO_2/C_2H_4} = \frac{L_{CO_2}}{L_{C_2H_4}} \qquad (3)$$

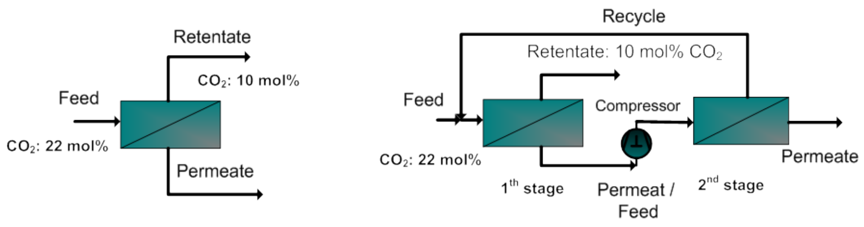

Figure 3. Left side: One stage membrane process – right sight: Two stage membrane process

$$\textbf{Ethylene Loss}: \left(1 - \frac{\dot{n}_{C_2H_4-Puregas}}{\dot{n}_{C_2H_4-Rawgas}}\right) \cdot 100\% \qquad (4)$$

3.3 Results

The simulation results confirmed the experimental results of the GKSS[c]. Moreover they represent the material behavior of the different membrane materials. According to this the glassy cellulose acetate membrane shows a high selectivity but a low transmembrane flux. In contrast to this, a higher flux but a very low selectivity was observed by the polyethylene membrane. The results of the simulation study for material screening are presented in Table 3 for a one stage membrane unit of a fixed area.

Table 3. Selectivity for a membrane area of 0.5 m²

	CA	PEO
S_{CO_2/C_2H_4}	10,2	2
S_{CO_2/C_2H_6}	14,25	2,75
S_{CO_2/CH_4}	14,5	7,5

As the results show, only the cellulose acetate membrane can be used in a single membrane unit. Hence for the one stage process a CA module with dimension of table 4 fulfills the design task. The advantage of such a single membrane unit is, that no further material or external energy is needed for the separation, but as table 4 shows, there is a high product loss of 9% as well. In order to reduce them, a second membrane stage is needed with a compression unit, as shown in figure 3, right side. The product loss can be reduced to 2% by this two stage process. The results are given in table 4, third line. The combination of a PEO membrane for the first unit, followed by a CA unit for product recovery causes an additional electrical energy demand of 2.75 MJ/kg$_{CO_2}$ for the compression, but reduces the product loss down to 2%. Considering energetic aspects only a one stage membrane process can efficiently reduces the energy demand. Furthermore impairs the two stage process the process economics, because of high investment costs for the compressor and further operation costs.

Table 4. Results for the single and the two stage membrane process

	Material 1st / 2nd stage	Area 1st /2nd stage	Pressure difference 1st/2nd stage	Feed Temperature 1st/2nd stage	Ethylene loss
Single stage	CA/-	4.5/-	31bar/-	15 °C/-	9%
Two stage	PEO/CA	1.75m² / 1m²	31bar/31.5bar	20 °C/15°C	2 %

4. Hybrid Process: combined Membrane-Amine Process

The combination of a membrane unit with an absorption unit results in a hybrid process (Figure 4). While the membrane unit removes the bulk of 50% CO_2, the rest is removed by the absorption unit. This hybrid process fulfills the design task of 97% CO_2 capture with a thermal energy demand of 1.6 MJ/kg$_{CO_2}$. The dimensions of the hybrid membrane-absorption process are given in table 5.

Table 5. Design for the hybrid membrane-absorption process

System pressure	Membrane area	Membrane material	Absorption column height	Liquid flow	Absorption Solvent	Thermal Energy demand
32 bar	4.5m²	CA	2.5 m	100 kg/hr	30wt% MEA	1.6 MJ/kg$_{CO_2}$

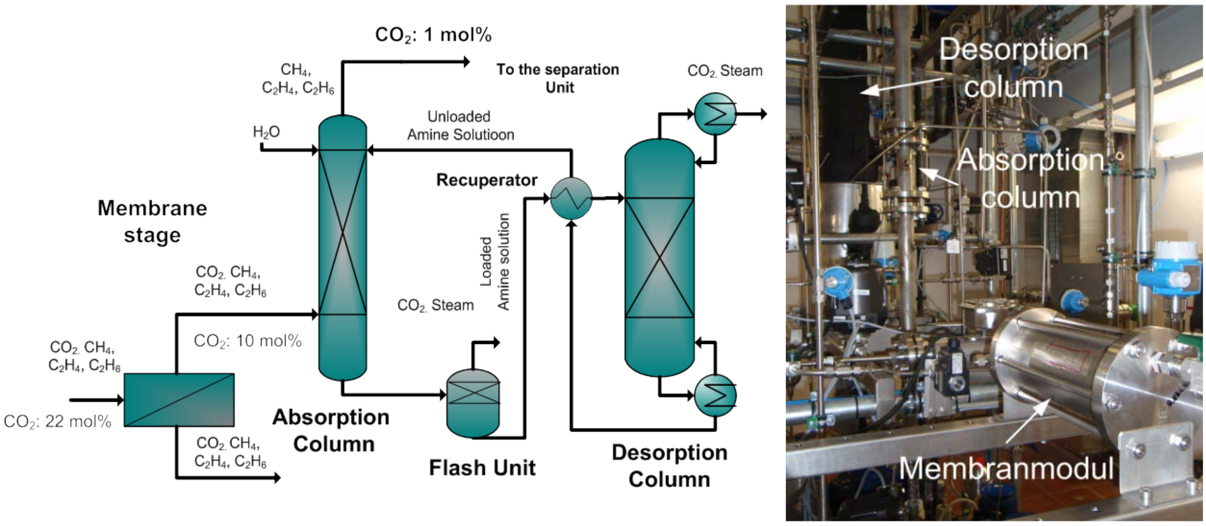

Figure 4. Left side: Flow diagram of the hybrid CO$_2$ capture process: combined membrane and absorption process; right side: mini-plant design for experimental investigations

Beside the energetic aspect, the flexibility is another advantage of the hybrid process. In this way a wide raw gas concentration range can be handled by using membrane and absorption process, separated or together. Those aspects are of interest, when changing raw gas composition for improved performance of upstream units, like the OCM Reactor with novel catalysts or even when fluctuation of feed gas composition occurs, when using Biogas instead of natural gas. Nevertheless improves the hybrid process the overall economics, using less energy and helps to save investment costs. A comparison of table 2 with table 5 shows, that the liquid solvent flow rate was reduced by one-third, the absorption and desorption column were reduced to the half of the base case height. In contrast, additional investment costs have to be spent for the membrane module of the hybrid process. However, the mini-plant was built based on the simulation with a 5 m packed bed absorption column, a 4 m high desorption column for solvent regeneration and an envelope type membrane module of an area of 1 m² was installed, shown in figure 4, right side. The developed model has to be validated and parameters for the high pressure mass transfer have to be adopted in the mini-plant.

7. Conclusions

Within this article was the design and development of an alternative separation process shown. In a case study for the CO$_2$ capture of the OCM Process was the use of a single membrane unit in combination with an absorption process discussed. With this, a hybrid separation process was developed based on rigorous simulation. In comparison to the base case, the hybrid process saves 50% of energy with acceptable product losses. While a two stage membrane process can reduce the product losses, but increases the energy demand. Furthermore will the simulation model be validated experimentally in the installed mini-plant and the performance and operation of the designed hybrid process will be studied. First impressions and performance details will be given in the presentation.

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