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THE SYSTEMATIC DESIGN OF CO_2 CAPTURE PROCESSES APPLIED TO THE OXIDATIVE COUPLING OF METHANE

USUWANIE DITLENKU WĘGLA PRZY UTLENIAJĄCEJ KONWERSJI METANU

Abstract

The oxidative coupling of methane is the catalytic conversion of methane into ethene. Carbon dioxide is generated as a reaction by-product and must be removed from the gaseous stream. In this paper, the application of a hybrid carbon dioxide removal process including absorption with amines and gas separation membranes is investigated through simulations and cost estimations.

Keywords: carbon dioxide capture, oxidative coupling of methane, absorption, membranes

Streszczenie

Utleniające łączenie cząsteczek metanu do etenu możliwe jest na drodze katalitycznej konwersji metanu. Dwutlenek węgla powstaje jako produkt uboczny reakcji i musi być usuwany z gazowego strumienia. W niniejszym artykule, przedstawiono hybrydowy proces usuwania CO_2: absorpcji z aminami i separacji membranowej oraz szacunek kosztów.

Słowa kluczowe: wychwyt CO2, utleniające łączenie metanu, absorpcja, mambrany

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1. Introduction

Carbon capture and storage (CCS) has been suggested as a critical component to the reduction of greenhouse gas (GHG) emissions without limiting energy usage in the near future [1]. There has been an increasing number of publications in this field. A search on Science Direct with the keyword "carbon capture" filtering years 2000 to 2010 returns around 56,000 publications. The same search for the time frame from 2010 to 2016 yields nearly 90,000 results. CCS is also not to be limited solely to power plants. The scenario entitled '2DS' developed by the International Energy Agency describes how technology across sectors may be transformed by 2050 in order to limit the average global temperature increase to 2K. In this scenario, nearly half of the CO_2 captured between 2015 and 2050 is from industrial sources, such as from the production of steel, chemicals, and cement [1]. Within this context, this contribution aims to study and further develop the carbon dioxide capture section for the oxidative coupling of methane process.

The oxidative coupling of methane (OCM), which is the catalytic conversion of methane into ethene (ethylene), has been extensively investigated for the past thirty years due to its potential for methane utilisation. The OCM allows for the conversion of methane containing feedstock, such as natural gas or biogas, into ethylene. Thus, OCM enables the production of value-added chemicals directly from C1, avoiding the costly intermediate step involving syngas [2]. The ethylene product is the raw material for the production of nearly all plastic commodities, such as high and low density polyethylene, polyethylene terephthalate, polyvinyl chloride, and polystyrene. The global ethylene capacity in 2012 is estimated to be above 140 million tons per year [3], which is almost entirely covered by naphtha or ethane cracking.

The USA has recently undergone the so-called shale revolution, bolstered by the exploration of deep underground shale formations through hydraulic fracturing and horizontal drilling [4]. Wet shale gas typically requires gas processing to produce pipeline-quality natural gas for energetic purposes and an ethane rich stream which is cracked to produce ethylene. In this sense, OCM could be of significant advantage by increasing the ethylene output through the further conversion of methane. In 2015, the first OCM demonstration plant was commissioned in Texas [5].

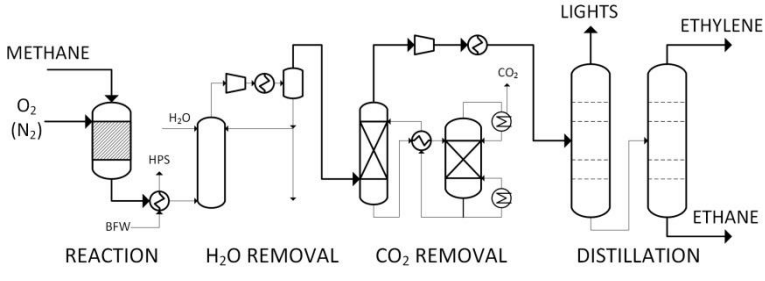

Fig. 1. Conceptual Flow Diagram for the OCM Process

The activation of most OCM catalysts occurs at temperatures around 973K, which also favours secondary reactions and limits the product yield. It is suggested in literature that the combined ethylene and ethane yield in the OCM reactor should not exceed 28% [6],

evidencing the need for efficient downstream separation sections. The carbon dioxide is an undesired by-product which is of major concern. The stream leaving the OCM reactor can be compressed, cooled, and flashed for bulk water removal. The removal of the unconverted methane and the C_2 fractionation can be achieved through cryogenic distillation, even in a shared distillation section if OCM is to be an add-on unit for an ethane cracker. However, the carbon dioxide formed in the OCM reactor must be removed from the gas stream by a CO_2 removal section before it can enter the distillation section. A conceptual process flow diagram for the OCM process is presented in Fig. 1. This contribution focuses on the design and improvement of an industrial scale CO_2 separation section in the downstream section of an OCM reactor producing 100 kton of C_2H_4 per year.

2. Motivation

Absorption with amines is the most commonly employed carbon dioxide removal technology for flue gas CO_2 capture, natural gas sweetening, and biogas upgrading; therefore, it is an obvious initial candidate for OCM and also for industrial/process gas streams. Aqueous solutions of monoetanolamine (MEA), normally limited to 30wt% due to their corrosive nature, are widely used as solvents and are considered as the benchmark for comparison with new technologies.

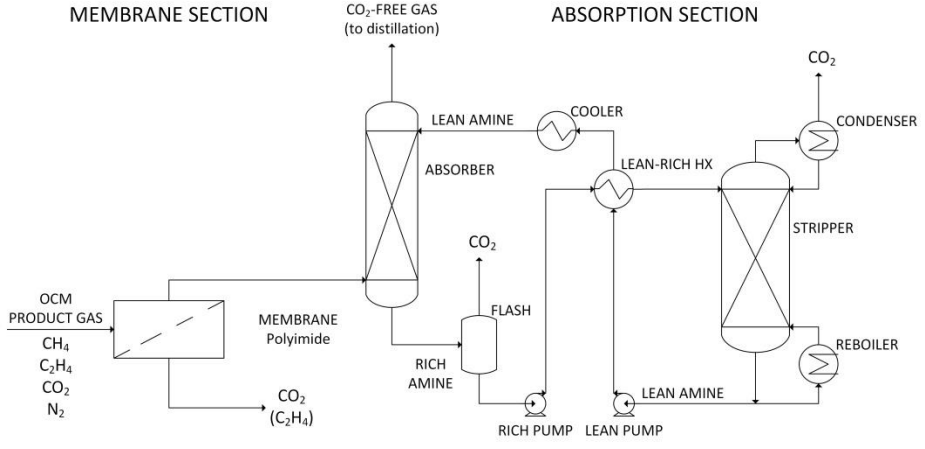

Fig. 2. Process flow diagram of a hybrid CO_2 removal process employing a polyimide gas separation membrane and absorption

In the absorption column, i.e. structured packing column, the amine solution is fed at the top and contacts the gas stream containing CO_2, which is fed at the bottom. The amine chemically binds with the carbon dioxide releasing a CO_2-free gas at the top and a rich amine solution, loaded with CO_2, at the bottom. The rich amine stream is then flashed to near atmospheric conditions to partially remove the CO_2, then pre-heated in a heat exchanger and fed to a stripping column. Heat is added through the reboiler in the stripper in order to reverse the reactions, producing a CO_2 rich gas stream at the top and a lean

amine solution at the bottom which is cooled and recycled back to the absorber. A process flow diagram for the described process is presented on the right-hand side of Fig. 2.

The current research and development in the field of CO_2 capture concentrates on three different focal points according to [7]:

- the development of new energy-efficient solvents;
- process synthesis and optimization;
- integration with the energy plant and CO_2 compression system.

An example of the first focal point is the utilisation of functionalised ionic liquids in order to increase the absorption rate and capacity as described in [8]. Within the second focal point, a generalized framework for the optimal design of CO_2 capture flowsheets is presented in [9]. The models applied therein are based on inexpensive equilibrium calculations and orthogonal collocation on finite elements, resulting in a flexible superstructure that can handle flowsheets with multiple column segments in series and parallel, as well as side feeds and withdrawals. An example of research within the third focal point is the rigorous rate-based simulation of an integrated gasification combined cycle with pre-combustion CO_2 capture as in [10].

Herein, a fourth focal point for carbon capture research and development is suggested – this involves alternative separation technologies. While absorption with amines is the most well established process, emerging technologies such as gas-separation membranes, low temperature distillation with controlled CO_2 freezing, and pressure swing adsorption are also being investigated and comprehensively reviewed in [11].

In this sense, membrane-based gas separation offers significant advantages such as simple operation, reduced start-up time, and easy and modular installation [12]. A major disadvantage of gas separation membranes is that scale-up occurs mainly by adding more modules operating in parallel. This results in an approximately linear increase of the capital investment cost, while well-established technologies, such as absorption, tend to scale up better. Nevertheless, membranes have been successfully employed for natural gas treatment, notably for small to medium capacities or even for large capacities in off-shore or remote applications [12]. Gas separation membranes can also offer significant contribution for biogas upgrading [13].

These four focal points are considered when developing the carbon dioxide capture section for the OCM process. Stünkel et al. investigated the absorption section experimentally in a mini-plant in Technische Universität Berlin, testing different solvents and operating conditions within the scope of the OCM process downstream section [14]. The use of gas separation membranes in combination with absorption in a hybrid process was described in [15]. A membrane module or cascade of modules was applied in order to remove the bulk CO_2, with the remaining fraction being removed through absorption as seen in Fig. 2. In [16], the hybrid CO_2 capture mini-plant was optimised to minimize the energy demand. The integration of the carbon dioxide capture section with the other sections of the OCM mini-plant in a superstructure was proposed and optimised in [17].

Given the successful proof of concept at the mini-plant scale, the design and economic evaluation of a hybrid system for CO_2 removal at industrial scale was performed in [18]. Therein, the benchmark solvent 30wt% MEA was considered for the absorption section. This contribution is herein further extended by analysing the effect of switching the solvent to an aqueous solution containing 37wt% N-methyldiethanolamine (MDEA) and 3wt%

piperazine (PZ). The MDEA reacts slower with CO_2 in the absorber, but its regeneration in the stripping column should demand less energy. The PZ is added to overcome the first disadvantage, for it reacts quickly with CO_2. The membrane and absorption sections were modelled and simulated. A design was carried out aiming at the removal of 97% of the inlet CO_2. The considered OCM reactor produces 100 kton of C_2H_4 per year. Two new design configurations were proposed, one is a standalone absorption process with the mixed solvent, while the other is a hybrid process employing a polyimide membrane and the mixed solvent. The size of the equipment is calculated, and the utility and equipment costs are estimated. The performance of the new process configurations was analysed by comparison with a benchmark process consisting of standalone absorption with 30wt% MEA.

3. Modelling

The absorption section was modelled in Aspen Plus with an Electrolyte NRTL model for the liquid phase and the Redlich-Kwong equation of state for the vapour phase. The solubility of gaseous components in amine solutions was described by Henry's law. The simulations made use of the example files in the software's library, which are based on [19]. The implemented thermodynamic and reaction kinetic parameters from various literature sources were kept. The columns were simulated with rigorous rate-based models, using Aspen Plus's built-in correlations for mass, heat, and momentum transfer, and for the packing hold-ups. Sulzer Mellapak 350X and 350Y were selected as the structured packings of the absorption and stripping columns respectively. The remaining units were modelled using the traditional MESH approach.

A high-capacity, flat sheet, envelope-type membrane module was considered for this application. The applied membrane material was polyimide (PI), which has a high CO_2 selectivity towards hydrocarbons. This means that the permeate is a CO_2 rich stream, while the other components tend to remain on the retentate stream. The membranes and modules were produced by research partners at Helmholtz-Zentrum Geesthacht Centre for Materials and Coastal Research, Germany, as outlined in [13].

A one-dimensional, solution-diffusion model based on balance and flux equations was applied [20]. Secondary transport effects such as pressure drop and concentration polarisation were neglected based on mini-plant experimental results. The flow was assumed to be isothermal with the permeate being 5K cooler to account for the Joule-Thomson effect. The permeances were calculated using an Arrhenius type equation. Fugacities were calculated on the retentate side using the Peng-Robinson equation of state [21]. The set of differential algebraic equations was discretised using orthogonal collocation on finite elements (OCFE) with fourth-order Lagrangian polynomials on Radau roots. Ten finite elements were employed, as this provided reasonable computation time and identical results to simulations employing twenty finite elements.

The model was first created using the online modelling environment MOSAIC, which allows for the automatic code generation for the numerical solution using different programming and domain-specific languages [22]. As an example, for the optimisation of the CO_2 capture mini-plant performed in [16], an AMPL code for the membrane model was

automatically generated in MOSAIC to allow for its solution using the IPOPT solver [23]. Herein, the membrane model at mini-plant scale was further extended inside MOSAIC to allow for the simulation of industrial plants by applying a scale-up by numbering up approach. The inlet flow was divided by the design flow of a single membrane module, resulting in the required number of parallel operating modules. A single module was then simulated and the resulting flows were multiplied back by the number of parallel modules. The code was automatically generated in MOSAIC using the Aspen Custom Modeler modelling language, allowing for the model to be compiled and included as a custom unit operation in Aspen Plus simulations. Hence, MOSAIC offers a convenient modelling platform, allowing facilitated model exchange, reuse, and application across platforms.

4. Simulations

The simulations were carried out using Aspen Plus version 8.8 with the available unit operation models of the software library and the custom membrane model exported from MOSAIC. Utility and equipment costs were calculated using Aspen Economic Analyzer, which allows for the process synthesis and the cost estimation steps to be performed simultaneously. The default utility costs of the software were kept.

Different OCM reactor concepts, such as packed bed, fluidised bed, and membrane reactors, as well as different feeding policies, such as CH_4-O_2 ratio, N_2 or CO_2 dilution, are currently under investigation [24]. It has been previously demonstrated that membrane-based CO_2 separation is unlikely to bring any economic advantage unless CO_2 is used as dilution gas in the OCM reactor [18]. When employing N_2 for dilution, the driving force for the CO_2 separation through permeation is not high enough, implying too high a product (ethylene) loss in the permeate stream. Therefore, a CO_2 diluted gas stream was considered in this paper. It was assumed that the OCM reactor outlet gas stream is compressed, cooled and passed through the water removal section, thus delivered to the CO_2 removal section at 10bar, 313K, and dry, with the following molar composition: CO_2: 24.5%; C_2H_4: 4.5%; N_2: 8.0%; CH_4: 63.0%.

4.1. Absorption Section

Given the degree of complexity of the absorption/desorption system with electrolytes, reactions, and rate-based calculations; no actual optimisation was performed in Aspen Plus. The design of this section was thus performed in terms of extensive simulations and sensitivity analyses. A similar systematic has been previously detailed in literature [7].

The absorption column was designed based on the liquid to gas ratio (L/G), which is determined as the ratio between the total liquid and gas mass flow rates in the column. Initially, one wants to use as little amine solution as possible for a given CO_2 capture duty, which means the L/G ratio should be as small as possible. A reduction in the L/G ratio can be achieved by increasing the packed height of the absorber. On the other hand, increasing the packed height also increases the capital investment cost for the column. For the sensitivity analysis in Fig. 3, the packed height was varied and the necessary amine flow rate to achieve the given CO_2 capture duty of 97% was calculated for each case.

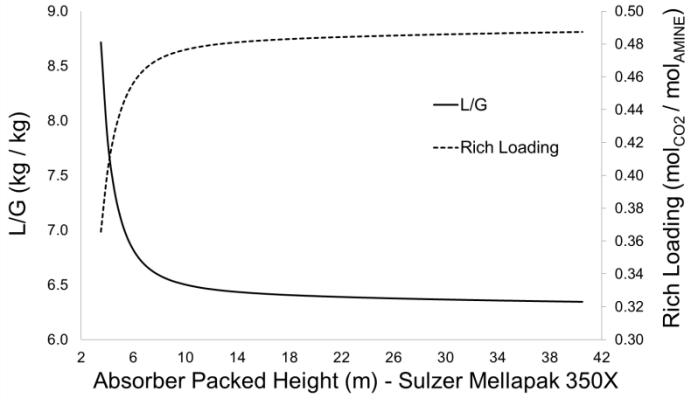

Fig. 3. Sensitivity analysis for the packed height in the absorber

It is clear from Fig. 3 that after a packing height of 14m, the effect of adding more packing in order to reduce the L/G ratio is greatly reduced. For steady operation out of the region where the L/G ratio dramatically increases, a packing height of 20 m was chosen for the absorber. The achieved rich loading in the bottom (α_{RICH}), expressed in mol_{CO2}/mol_{AMINE}, is also shown on the secondary axis.

The design of the stripper was achieved through the NQ-curve shown in Fig. 4, which illustrates the relationship between the number of stages, in this case represented by the column's packed height, and the heat duty. The CO_2 mass fraction on the top of the stripper was fixed at 0.9 by varying the distillate rate, and consequently, the reflux ratio and condenser duty. The lean amine loading at the bottom of the column was fixed by varying the reboiler duty. A higher packed height implies lower energy consumption, but increased capital investment cost. It is clear that from 4.5 m of packing, the reboiler duty stabilises at around 3.05 $MJ/kgCO_2$. Hence, a packed height of 6m was selected for the stripper.

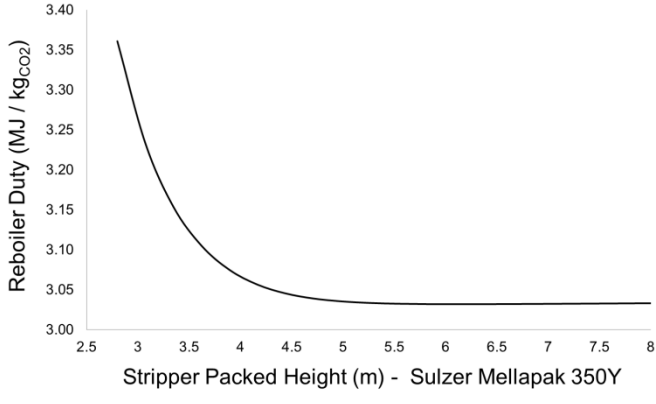

Fig. 4. NQ-Curve for the stripping column

The columns' diameters were calculated taking into consideration the fractional approach to maximum capacity. The maximum capacity corresponds to a gas load of 5÷10% below the flooding point so the column could still operate under these conditions. Sulzer recommends a fractional approach to maximal capacity between 0.5 and 0.8 – a value of 0.75 was taken. The columns operate under pressure (10 bar for the absorber and 2.2 bar for the stripper); therefore, pressure drop is not as critical as for flue gas CO_2 capture. The resulting diameters for the absorber and stripper were 4.3 m and 5.8 m respectively. The pressure drop calculated by the built-in vendors' correlation were 2.4 mbar/m and 0.4 mbar/m, which are within the recommended values.

The ideal operating point of the absorption/desorption system was investigated through a sensitivity analysis for the lean loading of the amine solution (α_{LEAN}), which was set by varying the reboiler duty in the stripping column. The rich loading at the bottom of the absorber is limited by the amine solution absorption capacity. Feeding a leaner amine to the absorber implies a reduced L/G ratio and recirculation rate; however, amine regeneration occurs at the expense of reboiler duty. The sensitivity analysis was carried out by varying the set point for the lean loading and computing the utility costs, comprising cooling water, electricity, and medium pressure steam, for the entire system. The energy efficiency of the newly considered solvent can be seen in Fig. 5, where the optimal lean loading is rapidly achieved at around 0.04 mol_{CO2}/mol_{AMINE}. This value typically ranges from 0.1÷0.25 mol_{CO2}/mol_{AMINE} for the benchmark 30wt% MEA, indicating that the regeneration of the second one demands more energy.

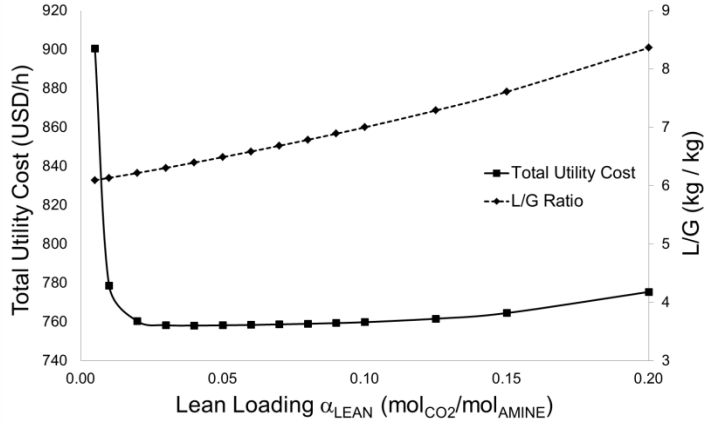

Fig. 5. Sensitivity analysis for the lean loading

4.2. Membrane Section

The membrane section was designed through sequential optimisation with an SQP solver in Aspen Plus. The objective function to be minimised was a cost function containing the cost to treat the remaining CO_2 in the retentate stream through absorption, and a penalty cost applied to the C_2H_4 loss in the permeate stream. The optimisation variables were the membrane area per module and the permeate pressure.

The penalty cost for the ethylene loss was based on its current market price, which can vary drastically according to oil price fluctuations. Applying a price of 1200 USD per ton of C_2H_4 led the solver to bring the membrane area to its lower bound of 0.1 m² in order to keep ethylene loss as low as possible, but capturing only 2.3% of the inlet CO_2. For a price of 600 USD per ton of C_2H_4, an area of 2.1 m² was found to be optimal, resulting in 36.7% CO_2 capture and 2.8% ethylene losses. The optimisation was thus used to provide a reasonable range of values for the membrane areas. The optimal permeate pressure was found to be at its lower bound of 1.1bar for all the cases, given that a higher pressure differential across the membrane increases the CO_2 selectivity towards C_2H_4.

Ultimately, a value of 1.5 m² was selected for the membrane area, allowing as much as 28.6% of the CO_2 to permeate through the membrane, while losing only 2.0% of the inlet C_2H_4. Hence, the addition of the membrane section to remove the bulk of the CO_2 allows for a major reduction in the required amine recirculation rate and reboiler and cooling duties in the absorption section. The design of the absorption section to remove the remaining CO_2 was carried out through the same previously described methodology.

For the given gas flow rate, as much as 3,030 parallel membrane modules were required. This generates additional capital investment costs. On the other hand, the equipment in the absorption section was reduced. While carbon steel can be applied in the membrane section, the equipment in the absorption section needs to be constructed of stainless steel given the corrosive behaviour of the solvent. Therefore, a trade-off in the total equipment cost was observed.

5. Results and Discussion

The main results from the economic analysis are presented in Table 1. These are the utility cost, installed equipment cost, and total cost calculated by annualising the equipment cost according to the following formula, where ***i*** is the interest rate of 15%, and *n* is the operating life of the plant, which was assumed to be 20 years:

$$TotalCost = UtilityCost + EquipmentCost\left(\frac{i(1+i)^n}{(1+i)^n - 1}\right) \quad (1)$$

The three scenarios correspond to standalone absorption with MEA (benchmark), standalone absorption with MDEA+PZ, and hybrid process employing PI membrane and absorption with MDEA+PZ.

The application of the energy-efficient solution containing MDEA and PZ in the absorption section allowed for utility cost savings in comparison with the benchmark MEA. This is mainly attributed to the reduced reboiler duty in the stripping column. Despite requiring a higher solvent recirculation rate, which causes the absorber and other equipment to be larger, the stripper column was significantly shortened. The NQ-Curve for the stripper column using MEA showed that around 15m of packing are necessary to bring the energy requirement down to 3.59 MJ/kgCO_2. For MDEA+PZ a value of 3.03 MJ/kgCO_2 could be reached with only 6m of packing. Hence, both the capital and operating cost could be reduced by switching the solvent from MEA to MDEA+PZ. This process configuration

should be applied when N_2 dilution is used in the OCM reactor and the use of membranes is uneconomical due to the high ethylene losses in the permeate stream.

Table 1

Results of the economic analysis forthe different process configurations

Process Configuration	Utility Cost	Equipment Cost	Total Cost
	kUSD/y	kUSD	kUSD/y
MEA	6,653	15,653	9,154
MDEA + PZ	6,309	15,146	8,729
PI+MDEA+PZ	4,781	15,625	7,277

When adding the membrane unit on the upstream of the absorption section, the energy required for the CO_2 separation was reduced to 2.30 MJ/kgCO_2, which led to the low operating cost for this configuration. It is also shown that the reduction in the equipment size on the absorption section nearly covered the costs of the membrane modules. The absorption section for this process configuration was estimated at 11,807 kUSD, while the membrane section was estimated at 3,818 kUSD. The downside of this process configuration is that the ethylene loss was 2.7%, while for standalone absorption, this value was typically between 1.0÷1.5%. However, this lost is most likely still acceptable for industrial purposes, indicating that gas separation membranes can be applied if CO_2 dilution is used in the OCM reactor. It is also clear that the benefit brought by the addition of the membrane section is much higher than the benefit from switching the solvent.

6. Conclusion

A systematic methodology for the design of energy efficient carbon dioxide absorption processes based on rigorous rate-based simulations and the execution of sensitivity analyses through the use of commercial flowsheeting software was presented. The methodology was applied to the CO_2 removal section of the oxidative coupling of methane process. The use of a new solvent, an aqueous solution of 37wt% MDEA and 3wt% PZ, was considered as an opportunity for process improvement on an industrial scale. Different process configurations were considered and the configuration employing a PI gas separation membrane and absorption with MDEA and PZ in a hybrid concept provided the most cost-efficient solution for this application.

It is evident how emerging technologies, such as absorption fluids and membranes, can play a major role in reducing the cost of carbon dioxide sequestration, thus enabling its application across different industrial segments. It is also clear how the application of hybrid processes, which exploit the pros and cons of different separation mechanisms, can provide significant energy and cost savings for chemical processes.

Acknowledgement

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