

Design, Development and Operation of the Energy Efficient CO₂ Removal for the Oxidative Coupling of Methane

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The catalytic oxidative coupling of methane (OCM) to higher hydrocarbons has attracted much attention as a possible route to ethylene production or liquid fuels. Besides the intensive research in the catalyst development are a number of studies with reaction engineering aspects conducted at the TU Berlin in order to demonstrate that the OCM process, including product recovery is technically feasible. In this article is the gas treatment of the reaction product gas discussed as a key part of the production chain from raw material to the product. In the considered process is CO₂ treated, like in many industrial processes as unwanted by-product or waste and should therefore removed from the product chain in an early process stage. Energy requirements and costs for this process must be kept as low as possible to operate the process economical. On a case study of the oxidative coupling of methane (OCM) process the development of an integrated gas treatment process for CO₂ capture in the miniplant scale is presented and experimental results are discussed.

1. Introduction

The Oxidative Coupling of Methane to ethylene provides with natural- or biogas a new feedstock for the chemical industry and is, beside other alternatives, Collodi (2010), a promising process for the petro chemistry, Hall (2005). Due to the yield limitation and high separation costs for by-products, the process is not applied in the industry yet, although several process alternatives were purposed in the literature, Salerno (2010). In a novel approach of concurrent engineering is the whole process, including the down streaming investigated simultaneously in a miniplant scale, to study novel reactor concepts, Jaso (2010) as well as alternative separation processes, Stünkel (2009).

In this article the focus is put on the separation process for 90 % CO₂ removal under the particular OCM conditions of up to 25 mol% CO₂ in the raw gas at a feed pressure of 32 bar. Beside other possible separation principles the chemical absorption process with 30 wt% Monoethanolamine was figured out as a state of the art process and therefore as the OCM base case CO₂ removal process, IPCC (2005). However, after extensive preliminary investigations of Sauer (2010) and Schomäcker (2010), a flexible miniplant system was designed, constructed and put into operation. Due to the moderate ethylene yield for currently available OCM catalysts of 30 % the goals are besides

improving of the catalysts, an energetic efficient and economical downstream gas refining process. This is achievable only through an integrated downstream concept that is based on energetically and economical enhanced processes.

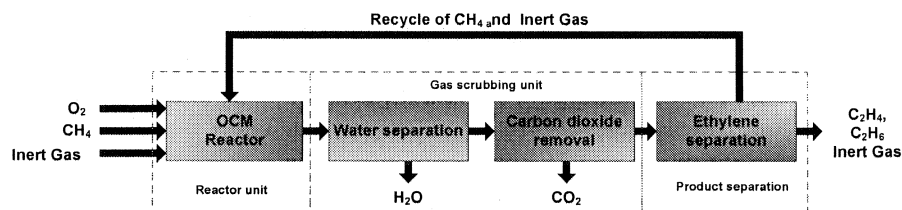


Figure 1: OCM Process flow diagram

To investigate the entire process concept concurrent and simultaneously, the process is divided into three units (see Figure 1): the reaction unit, the gas scrubbing unit and the product separation unit.

Based on a holistic view and on the approach of simultaneous process development, the design tasks for each unit and stream purities are defined considering their interactions among each other. Based on the process schematic of the flow diagram in Figure 1, and studying the macro-and micro-kinetics of the catalysts by Sauer et. al. (2010), the process conditions and process requirements for CO₂ separation were determined and given in Table 1.

Table 1: Process and operation conditions for the design case

Gas inlet temperature	40 °C
Absorption column top pressure	32 bar
CO ₂ concentration	25 mol%
C ₂ H ₄ concentration	18 mol%
CH ₄ concentration	15 mol%
N ₂ concentration	42 mol%
CO ₂ removal	90%

The removal of acid gas components from the reaction product stream is an important process step in the chain of gas processing, to achieve the goal in the purity of the product. The chemical absorption, however, preferred for the selective gas scrubber and is also the state of the art in this field, Kohl (1997), IPCC (2005). Recently reaches the research concerning novel absorbents much attention, Wang, (2010).

2. Simulation Model

2.1 Chemical absorption model

The base case process was investigated theoretically and a simulation model was implemented in Aspen Plus[®]. The provided build-in packages for physical and thermodynamic behavior are adopted. So includes this model the build-in electrolyte NRTL package ELECNRTL, with chemical equilibrium reactions of Austgen (1989) for the liquid phase and the Redlich-Kwong equation of state for the gas phase. Furthermore the Aspen Plus[®] MEA-REA package was applied successfully in the

packed column that considers the reaction kinetics of the MEA with the CO₂. The kinetic reactions are essential for the description of the rigorous model for the absorption and was compared with those presented in the literature of Kucka et. al. (2003). The build-in RateSep approach was used to describe the mass transfer phenomena in the packed column.

2.2 Gas permeation by dense membrane

First valuation of the separation efficiency was achieved by process simulation in Aspen Custom Modeler[®] using the solubility-diffusion model (1), including mass transfer and non ideal effects for a flat sheet membrane module described in Ohlogge, (2006).

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

For technical membranes the quotient of permeability P and membrane thickness δ are combined to the permeance L , which is obtained experimentally.

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

The permeance is specified with the free-volume theory including temperature, pressure and concentration dependency, while the free-volume parameters were adapted by the GKSS (GKSS Research Centre Geesthacht GmbH, Institute of Polymer Research, Max-Planck-Straße 1, 21502 Geesthacht, Germany). For the mass transfer is the concentration polarization of the enriched component along the membrane taken into account and the Joule-Thomson effect of cooling by decompression of a real gas was considered in the model as well. Furthermore two different module structures were investigated. The first one considers the membrane as one flat membrane that has to discretised and the second considers the module structure, described in Table 2.

3. Experimental Investigation

3.1 Reference absorbents

For selective CO₂ separation the chemical absorption is industrial well established and a technical matured process. The first use of amines in the processes of sour gas absorption is dated to 1930 by Bottoms (1930) with triethanolamine (TEA). Since then, other amines were developed in this family, like monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA). In this study 30 wt% MEA solution as a reference absorbent was used. Ethanol amines consist of a hydroxyl functional group, responsible for the water solubility and an amino group, which is responsible for the reaction with CO₂. Because of the acid-base reactions such amine-based process is preferred for the selective removal of acid gas components such as CO₂. Another aspect to the use of MEA as a reference adsorbent is the fast kinetic reaction between MEA and CO₂, which determines the height of the absorption column. The miniplant was designed base on the flow sheet of Figure 2. The entire system is installed with more than 150 actuators and sensors, which are visualized by the Siemens process control system PCS-7. The core component is the 5 m packed absorption column, with an inner diameter of 40 mm, which is packed with the Rombopak 12M

structured packing of $450 \text{ m}^2/\text{m}^3$ specific surface area. This absorption column is designed for operating pressures up to 40 bar and 7 gas and liquid sampling points are installed in the inlet and outlet streams, as well as over the whole column height.

3.2 Miniplant design – Absorption Process

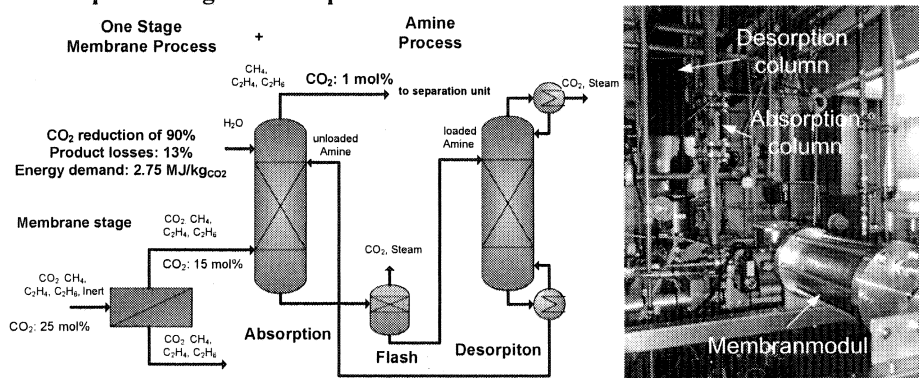


Figure 2: Left side: Flow sheet of the hybrid separation process, right side: Hybrid separation process in miniplant scale

The gas concentration is continuously monitored by online infrared measurement technique, which switches between the individual measuring points in the 5 minute interval. The mass flow of the incoming and outgoing streams of the absorption column is measured by coriolis flow meter from Endress + Hauser. The desorption column on the other hand is with the evaporator and the partial condenser the other core elements of the miniplant and used for the regeneration of the absorbent. The whole process is designed and builds as a closed loop to realized continuous operation of the absorption and desorption column together, due to pumping around the scrubbing liquid for absorption and regeneration. In the desorption column is also a structured packing installed with a packed height of 4 m, the Rombopak 9M with a specific surface area of $350 \text{ m}^2/\text{m}^3$ and an internal diameter of 100 mm. The reboiler heat duty is limited to 30 kW electrical and the partial condenser with a heat transfer area of 1 m^2 is designed up to 25 kW thermal cooling capacity. The whole desorption process can be operated at a pressure of up to 5 bar and the maximum mass flow that can be realized by the pumps is limited to 80 l/h and corresponds to a maximum liquid load in the absorption column of $63 \text{ m}^3/\text{m}^2\text{h}$.

Table2: Module structure of the GKSS flat sheet membrane module

Length	Wide	Sheet number	Compartment Numbers	Structure (Sheet in the compartments)
0.08	0.07	44	7	7-7-6-6-6-6-6

3.3 Membrane unit

A GKSS – flat sheet envelope type membrane module was installed successfully with a dense membrane based on polyimide as a selective layer and with an overall membrane

area of 0.5 m². The detailed module structure is presented in Table 3. Gas samples are installed in the feed, the retentate and in the permeate side, while the flow rate are measured by the coriolis principle and by the vortex principle. A Sick Maihak infrared gas analyzer was used to determine the hydrocarbon and CO₂ concentration online in the gas stream with an accuracy of $\pm 1\%$ of the final value.

4. Experimental investigation

The objective of the experiments was to minimize the regeneration requirement per captured kilogram of CO₂. For this purpose, the mass flow rate and the reboiler duty of desorption were figured out as the key factors and were varied to reach the 90% CO₂ capture. For this purpose, the evaporator power was kept constant and the circulation flow rate was changed to achieve the goal of 90% CO₂ capture. In a next step the reboiler power was reduced and again the solvent flow rate was changed to fulfill the design task till the energy demand reaches a minimum. The result for the base case, that was achieved experimentally in the miniplant are presented in Table 3.

Table3: Experimental results – Amine process- reference base case -90% CO₂ capture

Gas load	Liquid load	Absorbent flow	Ethylene loss	Thermal Energy demand
0.33 Pa ^{0.5}	42.3 m ³ /m ² h	55 kg/h	6 %	5 MJ/kg _{CO2}

In order to reduce the energy demand a membrane was installed before the absorption process, to remove a gross of the CO₂. Based on the simulation study, Stuenkel (2009) the optimal membrane process was installed and combined with the absorption unit. For the gas feed of Table 1, the experimental results are presented in Table 4 for the hybrid separation process, which reduces the energy demand for the reboiler by more than 40% with acceptable product losses.

Table4: Experimental results – Hybrid process -90% CO₂ capture

Membrane area	Absorbent flow	Ethylene loss	Thermal Energy demand
0.5 m	55 kg/h	13 %	2.75 MJ/kg _{CO2}

5. Conclusion and Outlook

An energy efficient CO₂ Capture process for the oxidative coupling of methane was developed, installed and operated. Based on a state of the art chemical absorption process a membrane unit was installed, to lower the energy demand. Experimental model validation was done. A study of novel membrane material and novel scrubbing liquids are under preparation, with the goal to reduce the product loss and the thermal energy demand. First results of this investigation are discussed in the presentation.

6. Acknowledgment

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