OPTIMAL DESIGN OF A CO$_2$ REMOVAL SECTION FOR A BIOGAS-BASED OXIDATIVE COUPLING OF METHANE PROCESS

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RESUMO – Biogas can be used as a renewable feedstock for ethylene production via Oxidative Coupling of Methane (OCM). The aim of this study is the development of an optimal process design for the CO$_2$ removal section of a biogas-based OCM process. For doing so, a rigorous Aspen Plus simulation model is linked to external optimization routines in Matlab aiming at minimizing the Total Annualized Cost for the CO$_2$ removal.

1. INTRODUCTION

The Oxidative Coupling of Methane (OCM) provides a path for directly producing ethylene, which is a main building block in the chemical industry. The OCM process can be promisingly utilized for ethylene production via coupling reaction of methane molecules, which for instance, can be produced through biological anaerobiosis from the major by-product in bioethanol industry - vinasse. The anaerobic digestion can be performed, for example, in sequencing batch reactors with immobilized biomass (AnSBBR), allowing high process yield and methane concentration in the produced biogas (Almeida, et al. 2017). Since CO$_2$ is an OCM reaction by-product, a CO$_2$ removal section based on absorption with amine solutions is present in most OCM process designs (Stünkel, et al. 2012a). However, using biogas instead of natural gas as a feed implies the need for an extra CO$_2$ separation duty that must be addressed.

The design of the CO$_2$ removal section has been previously carried out based on rigorous models and by using extensive simulation and sensitivity/parametric studies (Penteado, et al. 2016). In this contribution, an optimization-based approach is used instead. The process is modeled in Aspen Plus and coupled with external optimization algorithms in Matlab with the goal of minimizing the Total Annualized Cost (TAC) for the CO$_2$ removal section.

2. METHODOLOGY

The OCM process using the biogas feed is entirely modeled in the software Aspen Plus v10. The biogas feed stream has a flow of 2,200 Nm$^3$/h with approximately 70% CH$_4$ and 30% CO$_2$ as in (Albanez, et al. 2016). This gas stream is fed to the reaction section, wherein methane reacts with oxygen at around 750 °C temperature to form ethylene and water. Side reactions
include the unselective hydrocarbon oxidations to CO and CO$_2$, as well as the water-gas-shift reaction. Reaction kinetics from (Stansch, et al. 1997) are implemented in the adiabatic Plug Flow Reactor model, yielding similar results to those observed in a mini-plant experimental set-up (Stünkel, et al. 2012b). The reaction heat is recovered, and the product is quenched, compressed, and passes through the amine-based absorption desorption unit for CO$_2$ removal. A final compression is applied, and cryogenic distillation is employed for the final product purification. The focus of this contribution lies on the optimal design of the quench & compression as well as the carbon dioxide removal sections.

2.1. Process and Models

The simulation flowsheet of the process is given in Figure 1. The OCM reactor outlet gases are cooled down with heat recovery and fed to the quench column at approximately 1.3 bar and 60 °C counter-currently to water. The gas is compressed in up to 3 stages with intermediate cooling and knock-out drums before the CO$_2$ removal section. The absorption is performed in a series of three structured packed columns with a solution of 30wt% monoethanolamine (MEA). Intermediate liquid cooling between absorbers can be performed. The top gas product, with a CO$_2$ mole fraction below 0.001, is cooled down, flashed, dried, and further compressed to 35 bar for the subsequent cryogenic distillation. The absorber bottom product, rich amine solution, is flashed, pumped, and pre-heated in a regeneration exchanger and in a heater. The desorption is carried out in a second structured packed column with two feed locations and a single side draw. A CO$_2$ rich stream is produced at the top of the desorber, while a lean regenerated amine solution is produced at the bottom. The lean amine is pumped, cooled, mixed with a make-up stream, and recycled to the absorber.

The system is modeled using the combination of the Peng-Robinson Equation of State with an Electrolyte NRTL model containing the ionic equilibrium reactions in the liquid phase. A stage-equilibrium model, namely RadFrac, is used to model the absorption and desorption columns. Typical HETP values for Mellapack 350X and 350Y are used to estimate the packing height. The flowsheet contains a total of 42 process units / blocks.

2.2. Optimization

The objective function to be minimized is the Total Annualized Cost (TAC). The TAC is given by the sum of the yearly Operating Expenses (OPEX) and the annualized Capital Expenses (CAPEX). The OPEX is comprised of utility cost, i.e. electricity to run all the compressors and pumps, steam to regenerate the amine solution, and cooling water. Estimated average values for the Brazilian industry are used (FIRJAN 2017).
The CAPEX comprises the total installed equipment cost, which is computed rigorously for the initial point using the built-in Aspen Process Economic Analyzer (APEA) tool. During optimization, CAPEX is estimated from the initial point using correlations and a \( \frac{6}{10} \) degression rule. Exchangers, compressors, and vessels can be removed from the simulation, e.g. if the heat duty of an exchanger is set to zero, then its equipment cost is also eliminated. This allows for the investigation of different flowsheet configurations and trade-offs between OPEX and CAPEX, e.g. with/without inter-absorber cooling, different number of compression stages, etc.

A total of 26 decision/control variables can be optimized. These are the quench water recirculation rate; the pressure ratio and cooling duty in each compression stage; the number of stages in each column; the split fractions for the amine solution streams, which can pass through intermediate coolers and be recirculated or forwarded to the next column; the heat duty in each heat-exchanger; the flash and desorber pressure; the split fraction for the desorber feed; the flow rate of desorber’s side draw; and the lean amine loading. Reasonable bounds are applied to these continuous and integer variables, leading to a bounded MINLP problem. A constraint is set for the CO\(_2\) mole fraction in the product gas, which is ensured via a Design-Spec that manipulates the amine solution flowrate within the Aspen Plus simulation.

To tackle this optimization problem, a framework is developed allowing the Aspen Plus simulation model to be coupled with Matlab via ActiveX as shown in Figure 1. This allows for an extended flexibility regarding objective and constraint formulation, as well as solver choices. The OPTI Toolbox for Matlab is used (Currie and Wilson 2012). OPTI provides a Mesh-Adaptive Direct Search algorithm named NOMAD, which is designed for the derivative-free optimization of time-consuming black-box functions which may also fail to return values for a significant number of calls (Le Digabel 2011).

3. RESULTS AND CONCLUSION

The operating conditions suggested and tested at a mini-plant facility at Technische Universität Berlin by Stünkel et al. (2012a) are taken as the range of values for decision variables. The absorption has been conducted between 10-32 bar, while desorption at 2.5 bar. The performed initial design is at 10 and 2.5 bar respectively, and includes all equipment, i.e. 3-stage compression, 2 inter-stage amine coolers, and rich amine pre-heater. A TAC of 1.3860 million dollars is computed for 20 years of operation and 10% interest rate.

The optimization is run from the initial design case and converges to a new point after several hundreds of flowsheet evaluations. The new improved design requires only 2 compression stages with one inter-stage and no final cooling. The absorption is carried out at 4 bar and desorption at 1.5 bar. A total of 7 absorption stages are used with fresh lean amine being fed to all three packed sections. Two inter-stage coolers are used and the spent amine from the top section is fed to the bottom section. The regeneration exchanger is employed, but the amine heater is not. The desorber has 25 stages and over 94% of the feed is fed in stage 8 (from above).

Overall the resulting design provides less utility consumption and is also more compact in terms of equipment. The achieved TAC is 1.1596 million dollars, which represent an improvement of 16.3% over the initial point. Future work includes the introduction of gas-separation membranes into the flowsheet, allowing for a hybrid permeation-absorption process, which is feasible for highly CO\(_2\) diluted feed streams such as biogas (Penteado, et al. 2016).
Finally, this methodology should be applied to optimize the entire OCM process flowsheet, including the reaction and distillation sections with recycle streams.

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