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Optimal Design of Solvent Based Post Combustion CO_2 Capture Processes in Quicklime Plants

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The optimal design of a solvent based post combustion CO_2 capture unit in a quicklime production plant is investigated. A 30 % weight aqueous monoethanolamine (MEA) solution is used as the absorption agent for the treatment of a 14 % mol CO_2 flue gas stream. The objective function in the design optimization incorporates several equipment capacity and operating factors that have a direct impact on capital expenditure and energetic cost of the unit. A reliable and accurate equilibrium model is developed for the prediction of the process behavior. The model employs an orthogonal collocation on finite element formulation enabling structural flexibility for design purposes and efficient model reduction for computational facilitation. Nonlinear programming techniques are used for the identification of the optimal column configuration and the operating conditions. The ability of the optimally designed absorption/desorption column to achieve acceptable performance under varying separation operating conditions such as flue gas CO_2 concentration, flowrate, and temperature is investigated.

1. Introduction

European policies on greenhouse gas (GHG) emissions reduction have already been adopted in order to meet the ambitious but necessary targets set for climate change prevention. Satisfaction of such targets will not only affect the global economy and specifically the energy intensive industrial sector, but also secure the competitiveness of industry in a constantly demanding market. Amongst the industrial contributors in GHG emissions, the cement and quicklime industry are significant contributors to the overall amount of released CO_2. In 2008 alone, 38.5 % of the total European industrial CO_2 emissions came from the cement industry, a percentage corresponding to 3.2 % of the total CO_2 emitted (European Commission DG JRC, 2010). Especially in the case of the cement plants, up to 60 % of the emitted CO_2 is derived from the calcination of limestone (Bosoaga et al., 2009). It is therefore evident that emissions control during the production of quicklime through the calcination step is a major contribution towards the overall reduction of CO_2.

Quicklime plants are characterized by high CO_2 concentration flue gas streams due to process generated CO_2 in addition to that generated from fuel combustion. Such features pose additional challenges for post-combustion CO_2 capture processes as the CO_2 content of the flue gas is usually in the range of 14 - 33 % vol. (Hegerland et al., 2006). Solvent based CO_2 capture processes, however, offer a promising solution as they can deal with high CO_2 concentration in the flue gas stream (Vatopoulos and Tzimas, 2012). Furthermore, solvent based processes do not require any specific modifications to existing production units; even though proper purification of the flue gas in order to remove any SO_x and NO_x compounds is generally necessary to avoid the formation of heat stable salts that affect solvent degradation (Arachchige et al., 2013).

The basic CO_2 capture process configurations consists of a reactive absorption column used for the chemical absorption of CO_2 by the amine solution, followed by a stripping column for solvent regeneration

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and the release of a pure CO_2 stream. While the nature of the solvent obviously plays a major role in the overall process behaviour (Neveux et al., 2013), targeted flowsheet modifications through design optimization under industry specific targets enable the calculation of process performance improvements (Le Moullec and Kanniche, 2010). Such targets are usually expressed as the minimization of the annualized total capital and energy costs subject to the desired CO_2 capture efficiency.
The main aim of this work is the optimal design of a separation process for the efficient CO_2 capture from a flue gas stream derived from a quicklime plant using the generalied design framework proposed by Damartzis et al., 2013. The operability of the designed process is investigated through the performance of a thorough analysis of the process behavior under varying conditions of the flue gas concentration, flowrate, and temperature.

2. Model development

The CO_2 capture unit flowsheet selected is shown in Figure 1. A steady-state equilibrium (EQ) model is used in order to mathematically describe the material and energy balances in the absorption-stripping loop. The main modelling assumptions consider: (i) thermodynamic equilibrium on the vapor-liquid interface, (ii) one-dimensional heat and mass transport along the column height coordinate, and (iii) no solvent loss in the vapour effluent of the distillation column.
The EQ model is further coupled with the OCFE formulation which provides significant model size reduction without compromising the predictive capabilities of the resulting model. Thus, a compact and versatile hybrid EQ/OCFE model that can be easily solved in design optimization studies is developed. OCFE formulation uses polynomial approximations of variable order to represent the key variables such as component concentration and stream temperature along the height of the separation columns resulting in a versatile reduced-order model approximation. Furthermore, the separation column model maintains a high degree of flexibility that is necessary for the representation of columns of variable height and configuration. Column height which is a major design parameter is therefore treated as a continuous variable that enables the employment of nonlinear programming solution techniques for the design optimization problem. Full details on the model formulation are provided by Damartzis et al. (2014).
Vapor-liquid equilibrium calculations are performed using the statistical associating fluid theory of variable range (SAFT-VR) equation of state (Mac Dowell et al., 2010). SAFT-VR implicitly introduces a reaction scheme for the occurring chemical bonding of CO_2 molecules to the amine, thus avoiding the direct consideration of the associated reaction mechanism (Rodriguez et al., 2012). Data for the partial pressures of CO_2, MEA and H_2O as well as the liquid phase enthalpy against the CO_2 loading, *a*, expressed as moles of CO_2 per mol of amine and temperature, *T*, are calculated and fitted into polynomial functions of the form:

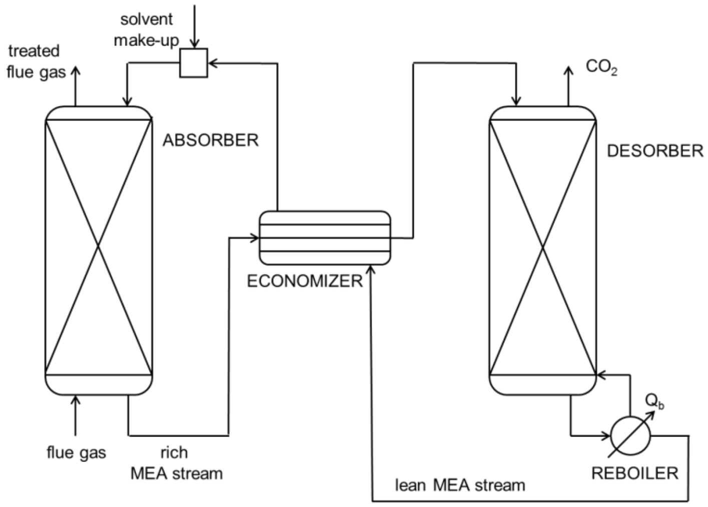

Figure 1: Absorption-stripping loop used for CO_2 removal

$$\log_{10} P_i = \sum_{m=0}^{M} \sum_{k=0}^{K} A_{m,k} T^m a^k \quad \forall i \in \{1, NC\} \tag{1}$$

$$H^L = \sum_{m=0}^{M}\sum_{k=0}^{K} B_{m,k} T^m a^k \tag{2}$$

Symbol P_i denotes the partial pressures of the components of the system, H^L the liquid phase enthalpy, whereas M and K represent the order of polynomial approximation with respect to temperature and liquid loading respectively. Values of the constants $A_{m,k}$ and $B_{m,k}$ are provided in Damartzis *et al.* (2014). For the temperature and CO_2 loading ranges of interest, third order polynomials provided acceptable accuracy with a maximum error of ± 2 %.

3. Design optimization in quicklime plants

The current study involves the design of a CO_2 capture unit for a flue gas stream originating from the combustion of limestone for the production of quicklime in CaO Hellas Inc., a quicklime plant situated in the city of Thessaloniki in northern Greece. An aqueous solution of 30 % weight MEA was used for the CO_2 absorption. The conditions of the flue gas stream and the design specifications for the minimum allowable lean solvent loading and the temperature in the lean solvent inlet stream are shown in Table 1.
The design variables are the absorber and stripper column sizes, the heat exchanger area, as well as the process operating conditions such as the pressures in both columns and the reboiler heat duty and temperature. The objective function is expressed as a sum of normalized terms associated with several process and structural design variables. Normalization of each term in the objective function is achieved by considering the ratios to nominal values taken from a base case for the flowsheet obtained from a preliminary short-cut design.

$$F = \frac{Q_b}{Q_b^{nom}} + \frac{T_b}{T_b^{nom}} + \sum \frac{H_c}{H_c^{nom}} + \frac{A_{HEX}}{A_{HEX}^{nom}} + \frac{a_l}{a_l^{nom}} - \frac{a_r}{a_r^{nom}} - \frac{y_{CO_2}^{in,abs} - y_{CO_2}^{out,abs}}{y_{CO_2}^{in,abs}} \qquad 3.1\ (3)$$

In Eq(3), Q_b denotes the heat duty of the reboiler in the stripper column and T_b the respective temperature. The latter is used as an index of the quality of the heat requirement for solvent regeneration. H_c is the packing height of each column calculated as the sum of the lengths of the column sections that represent a specific column. A_{HEX} is the area necessary to carry out the heat exchange between the lean and rich streams in the heat exchanger. Symbols a_l and a_r denote the lean and rich solvent stream loadings, respectively. The last term in Eq(3) expresses the fraction of CO_2 captured from the flue gas.

Table 1: Flue gas stream conditions and design specifications

Flue gas	
Inlet gas flow in absorber (mol/s)	280.22
Inlet gas flow in absorber (Nm^3/s)	6.277
Inlet gas composition (mol/mol): $H_2O/CO_2/N_2$	0/0.1411/0.8589
Inlet gas temperature in absorber (K)	298.25
Specifications	
Minimum lean solvent loading (mol/mol)	0.13
Liquid inlet temperature in absorber (K)	313

Table 2: Design optimization results

CO_2 capture percentage (%)	93.9
Amine flow in absorber (mol/s)	84.6958
Lean loading (mol/mol)	0.1313
Rich loading (mol/mol)	0.3238
Column height (m): Absorber / Stripper	15.59 / 10.6
Reboiler duty (MW)	4.75
Reboiler temperature (K)	412
Pressure (kPa): Absorber / Stripper	102.8 / 303.9
CO_2 captured (kg/s)	1.634
Energy consumed (MW/kg CO_2)	2.906

Basically, each of the terms in the objective function represents a soft process target, the minimization or maximization of which will improve the performance of the process either in capital cost reduction such as the column sizes and the heat exchanger area, or in operating costs cost reduction such as the reboiler heat duty. In addition, the overall process efficiency can be improved by properly adjusting the reboiler temperature, the lean and rich solvent stream loadings and the overall absorption efficiency.

The resulting nonlinear system of equations is solved to optimality using MINOS 5.5, an augmented Lagrangian reduced gradient algorithm (Murtagh and Saunders, 1998). The results of the design optimization are summarized in Table 2. An energy penalty of 2.906 MW/kg CO_2 is achieved which seems to be about 10 % lower than the major trend of 3.3 MW/kg CO_2 reported in Arachchige et al. (2013) for similar industrial applications but without a rigorous optimization design procedure.

4. Process operability studies

Flue gas conditions in a quicklime plant may vary significantly during operation due to the use of alternative combustion fuel mixture, changes in the production level and other process related variability. Furthermore, the multiple objective function terms used in the design optimization offer an overall weighted improvement. It is therefore important to investigate the performance of the CO_2 capture unit under varying flue gas stream conditions. More specifically, the process behaviour is investigated under flue gas flowrate, CO_2 content and temperature variation which are commonly occurring disturbances in the plant operation. Moreover, the sensitivity of the process performance in changes in the solvent flowrate and the lean solvent target temperature are examined. For such an investigation the structural design features of the CO_2 capture unit have been set at the optimal values whereas maintaining the assumptions and process restrictions.

CO_2 concentration in the flue gas is an important parameter that directly affects the efficiency of the absorption process, especially in industrial applications where its value is relatively high, such as in quicklime production plants. Figure 2 shows the absorbed CO_2 percentage as a function of the flue gas concentration. It is observed that the process efficiency, expressed as the amount of CO_2 removed at the absorption step is greatly influenced, as changes in the initial CO_2 concentration of 6 % lead to a subsequent 29 % reduction in the absorbed CO_2 for the optimal design. The increasing slope of the curve as the CO_2 content decreases can be explained by considering solubility/chemical equilibrium limitations, as the driving forces in the absorption column (difference in concentration) gradually erode.

Another important parameter for the sizing of the process is the flowrate of the solvent circulating in the absorption-stripping system. It is therefore a parameter whose value should ideally be kept at low values. Figure 3 shows the response of the reboiler heat duty as well as the change in the absorption efficiency for a scenario including the increase of the solvent flowrate.

It is evident that an increase in the solvent flowrate leads to a proportional increase of the reboiler heat duty. This is related to the increased amount of the liquid phase that needs to be evaporated in the reboiler. In the same way, the CO_2 capture efficiency is also increased, as an increased solvent flowrate means that more CO_2 can be captured for the same operating conditions.

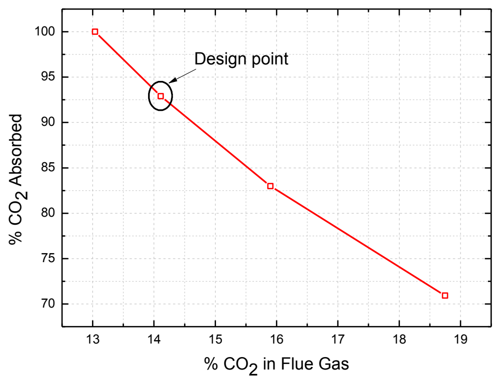

Figure 2: CO_2 capture efficiency dependence on initial CO_2 concentration in flue gas

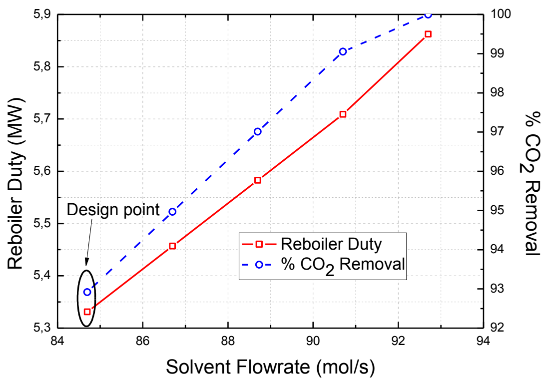

Figure 3: Reboiler heat duty and CO_2 capture efficiency as functions of the solvent flowrate in the system

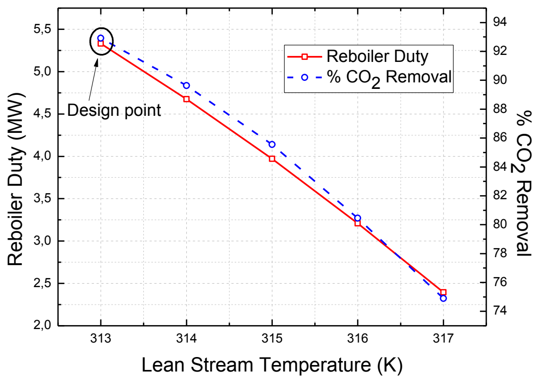

Figure 4: Influence of the lean stream temperature on the process efficiency and the reboiler heat duty

The lean stream is cooled down before being recycled back into the absorber by transferring its heat to the rich solvent stream. This is achieved in the heat exchanger between the two columns which aims to reduce the energetic requirements of the overall process and increase the efficiency in the absorber. The effects of the lean stream temperature on the amount of captured CO_2, as well as the energetic demands of the reboiler are depicted in Figure 4. As the lean solvent temperature increases, the absorption efficiency decreases. This is due to the exothermal nature of the CO_2-MEA reactive absorption which is favoured by low temperatures. The reboiler duty is also affected by such a change as a smaller amount of CO_2 is transferred into the stripper column with the liquid phase and subsequently, the total heat demand for breaking the chemical bonds between CO_2 and MEA is reduced. Indicatively, it is observed in Figure 4 that a change of only 4 degrees in the lean stream temperature leads to a subsequent 55 % decrease in the reboiler duty with the compromise however, of a simultaneous reduction of 18 % in the CO_2 capture efficiency. The latter not only showcases the strong dependence of the system on the lean stream temperature but also clearly indicates that the design policy has to be formulated considering two opposing factors (reduction of both energetic demands and process efficiency). Thus, a large number of design alternatives is possible depending on the overall desired process targets. Using the lean stream temperature as a key parameter, heat integration strategies can be formulated through which, the appropriate combination of process streams will enable the minimization of the total energetic costs. For example, identification of the optimal lean stream temperature through the use of pinch analysis, will not only reduce the installation costs of the heat exchanger between the two columns, but also provide the opportunity for successful exploitation of possible heat sources and sinks from the quicklime plant, resulting in a reduction of the overall heating/cooling demands of the process.

5. Conclusions

In the present work, the optimal design of a solvent-based post-combustion CO_2 capture process was achieved for a flue gas stream with high CO_2 content derived from a quicklime plant. A rigorous equilibrium based model coupled with the OCFE technique for drastic model reduction has been utilized to accurately represent the process behaviour. Furthermore, OCFE formulation allows a flexible column structure representation. A sensible objective function incorporates the major process factors that impact the economic potential of the capture unit. However, competing terms enable a reasonable balance between efficiency and investment and operating costs. Sensitivity analysis revealed the dependence of the main process parameters on the operating conditions while the column structural characteristics are set at the calculated optimal values. This investigation of the process operability range is crucial for the model application on industrial cases where fluctuations on the operating conditions often occur. Especially in the case of the reboiler duty and the CO_2 capture efficiency, two of the key parameters mainly affecting the overall process cost, the effect of small changes of the lean stream temperature is rather high, reaching even a reduction of 55 % for the reboiler duty for small changes on the lean stream temperature. It is therefore evident that correct identification of this process parameter will play a major role on the overall design of the process. However, due to the conflicting nature of the responses of the reboiler duty and the CO_2 capture efficiency on the lean stream temperature the investigation of heat integration alternatives becomes absolutely necessary.

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