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Energy Performance of CO_2 Capture Processes: Interaction Between Process Design and Solvent

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Implementation of amine-based post-combustion CO_2 capture on power plants would lead to large penalties on the electric production. Researches focus either on the improvement of process flow scheme to maximize exergy integration or on characterization of new promising solvents to reduce this energy consumption. However, both aspects are often taken into account separately whereas they should be studied simultaneously since the energy efficiency of process modifications also depends on the considered solvent. In order to highlight this point, several schemes based on modifications proposed in literature are investigated for several classes of amine-based solvents and the total energy consumption is determined by a rigorous phenomenological model coupled with an optimization algorithm.
Simulation results confirms that the efficiency of process modifications depends on the considered solvent since process improvements make use of the solvent specific properties, in particular the differences between thermodynamic and kinetic properties. General understandings are given on the relative efficiency of process modifications according to measurable solvent properties.

1. Introduction

Carbon dioxide capture and geological storage is foreseen to be one of the solutions to reduce the atmospheric emissions of fossil-fired power plants. Among the different technologies, post-combustion chemical absorption in amine-based solvents is the most mature at this stage of development. However, the energy consumption of such processes implies a large penalty on the power plant efficiency. The reference configuration used for chemical absorption of CO_2 is a conventional absorption/desorption loop operating with monoethanolamine (MEA) where the CO_2 is separated from the flue gas by chemical absorption in the solvent and the solvent is thermally regenerated in a stripper, sensible heat being exchanged in an economizer between the hot lean solvent and the cold rich solvent. The released CO_2 is then compressed up to 110 bars at supercritical state for transportation and storage. For this base case, the energy requirement leads to a loss of around 11 %-pts in terms of power plant efficiency.
In order to reduce this penalty, researches focus either on the improvement of process flow scheme to maximize heat integration or on characterization of new promising solvents. This work intends to emphasize the interaction between solvent properties and optimal process design and how both solvent characterization and process design should be carried out simultaneously, since the energy performance of a process modification is deeply dependent of the chosen solvent.
In order to highlight this point, several schemes based on modifications proposed in literature are investigated for two classes of amine-based solvents. For each process flow scheme associated with each solvent, the operating parameters are optimized with respect to the total energy consumption with a dedicated algorithm using rigorous thermodynamic and rate-based models, which are mandatory for a proper representation of all limiting phenomena. By this means, the potential of each configuration is determined in terms of total energy penalty on the power plant.

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2. Solvent characterization

In amine-scrubbing processes, the reference solvent is monoethanolamine (MEA) for flue gases at atmospheric pressure but its thermal regeneration is highly energy intensive. Other solvents have therefore been proposed and characterized in literature, for example Puxty et al. (2009) have screened 76 amines based on absorption capacities and absorption rate with respect to amine group pK_A, Dubois and Thomas (2012) have studied using apparent 14 amines and blends of amines using measurements of apparent kinetic constant of absorption and desorption. Several criteria can be used to characterize these solvents according to energetic, economic, or environmental considerations.

In this work, four criteria have been retained for solvent screening: solvent kinetics, heat of absorption, cyclic capacity and degradation resistance (see Table 1 for some amines with high tonnage availability). The kinetics between CO_2 and amine directly impacts the absorber height, hence the capital cost of the capture unit. The heat of absorption contributes to the steam demand of the reboiler heat duty (with sensible heat and stripping heat). The cyclic capacity is the difference between rich and lean solvent loadings (in mol_{CO2}/mol_{Amine}), it determines the required solvent flow rate to achieve the desired removal efficiency; it also impacts the reboiler heat duty due to the sensible heat needed to heat the solvent until reboiler temperature, pumping work and operating costs (solvent total load, required solvent make-up). The resistance to thermal and oxidative degradation characterize the solvent loss that must be compensated by a solvent make-up, impacting the operating costs as well as atmospheric emissions of degradation products. Thermal resistant solvents also enable regeneration at higher stripper pressure.

In this work, several solvents widely identified in literature as promising have been selected. MEA is chosen as reference solvent to compare energy performances. MDEA is a tertiary amine interesting for its low energy consumption for thermal regeneration, but its very low kinetics with CO_2 would imply very high absorber height. AMP is a sterically hindered primary amine offering a good compromise since it has a high cyclic capacity and both its kinetics and heat of absorption are mild. AMP and MDEA can be used with a kinetic activator such as MEA or piperazine (PZ) in order to improve absorption rate while still benefiting from favourable properties of main amine. Approximate values of these criterion are given in Table 2 for five solvents, data have been taken from from (Dubois and Thomas, 2012) for kinetic constant, Lepaumier (2008) for degradation ratios, Kim et al. (2011) for heats of absorption of MEA, AMP and MDEA, Aronu et al. (2011) for cyclic capacities of MEA, AMP and AMP+PZ, Chen et al. (2011) for heat of absorption and cyclic capacity of MDEA+PZ.

*Table 1: Criteria for solvent characterization with approximate values for several solvents**

	MEA (ref.) 30wt-%	AMP 30wt-%	MDEA 30wt-%	AMP+PZ 15+15wt-%	MDEA+PZ 15+15wt-%
Apparent kinetic constant, $\log(k_{App})$ at 25°C (s^{-1})	4.63	3.35	1.33	5.12	5.12
Heat of absorption range (kJ/mol)	80-85	60-90	50-60	70-90	60-80
Cyclic capacity (mol_{CO2}/mol_{Amine})	0.25	0.5	0.2	0.5	0.35
Degradation ratio at 140°C (% per week)	5.3	0	1.7	1.7 (MDEA) 0.25 (PZ)	0 (AMP) 0.25 (PZ)

In order to use these solvents in process modelling, an adequate thermodynamic model must be used as well as physicochemical properties. For solvent properties and kinetics, relations derived from experimental measurements reported in literature are used. For thermodynamic modelling, the Peng-Robinson equation of state for the gas phase and the extended UNIQUAC model for the electrolyte liquid solutions (Thomsen and Rasmussen, 1999). The e-UNIQUAC model parameters have been identified using experimental data available in literature in a wide range of temperatures, concentrations and pressures.

Figure 1 represents the comparison between simulated and experimental CO_2 partial pressure for 30 wt-% MEA, 32.1 wt-% MDEA and 30 wt-% AMP as function of loading and temperature. The Average Absolute Relative Deviations (AARD) between simulated and experimental CO_2 partial pressure of 22, 15, and 21 % are obtained for MEA, MDEA and AMP. Considering the extent of the CO_2 partial pressure range (from 10^{-3} to 10^{5} kPa), those deviations are considered sufficiently low to be used for process modeling.

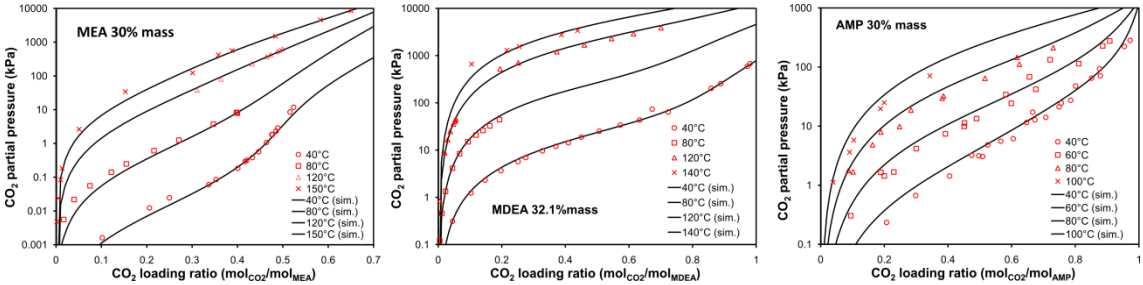


Figure 1: Representation of regression results of the extended UNIQUAC model for MEA 30 wt-%, MDEA 32.1 wt-% and AMP 30 wt-%

3. Process improvements

The conventional process used for chemical absorption of CO_2 in amine solvents is a typical absorption/desorption loop composed of three main unit operations: a packed absorber where CO_2 is absorbed into the solvent, a packed stripper where the solvent is thermally regenerated, and an economizer in which sensible heat is exchanged between rich and lean solvents. The process requires heat input at the reboiler, performed by a steam draw off on the power plant steam cycle, as well as mechanical work (CO_2 compressors, solvent and cooling water pumps); in addition, several heat sinks are present in the process (lean solvent cooler, stripper condenser and absorber wash section).

In order to reduce the total energy requirements, several flow scheme improvements have been proposed in literature such as the heat recuperation process of Kishimoto et al. (2010). Cousins et al. (2010) have performed a screening of several flow scheme improvements and Le Moullec and Kanniche (2010) have simulated single modifications and combinations of them with MEA as solvent. These process modifications could enhance CO_2 absorption in order to reduce the solvent flow rate, improve heat integration between process fluxes, or use heat pumps to convert low quality heat into higher quality heat using additional mechanical work.

Since these modifications make use of the specific physicochemical properties of the solvents, it is worth mentioning that different energy performances are encountered according to the solvent used. In order to highlight these interactions, four process modifications have been chosen (see Figure 2) in addition to the conventional process and energy performance is evaluated for each of them and for several solvents.

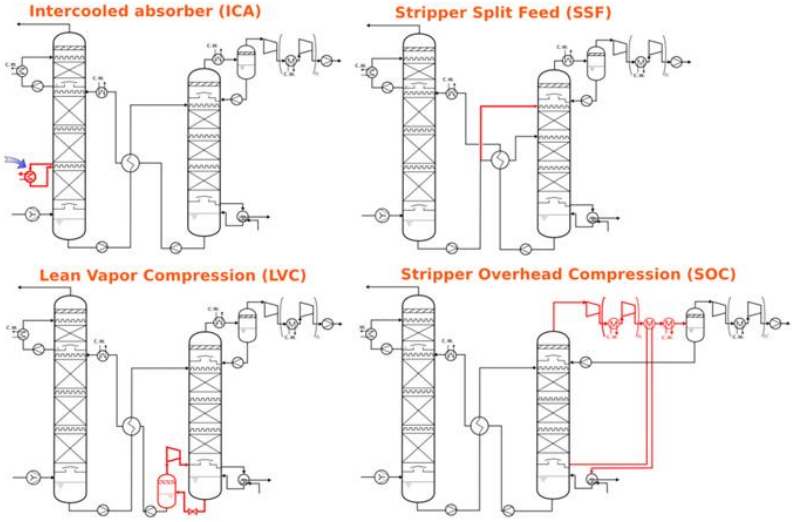


Figure 2: Flow scheme improvements of the conventional process: InterCooled Absorber (ICA),Stripper Split Feed (SSF), Lean Vapour Compression (LVC) and Stripper Overhead Compression (SOC)

Intercooled Absorber (ICA)

The principle of this process modification is to withdraw the solvent at a certain absorber level, to cool it down and to re-inject it into the absorber. The aim is to favour the thermodynamic driving force due to

temperature decrease and therefore enhance the CO_2 absorption. Higher rich loading are expected; limiting the solvent flow rate required to reach CO_2 removal target, hence a reduction of reboiler heat duty by decreasing the sensible heat to be provided, as the cost of additional cooling water.
Nevertheless, kinetic rate is also reduced due to temperature decrease and this process modification is interesting when absorption is driven by thermodynamics rather than kinetics. Consequently, achieved energy reductions are strongly dependent on the kinetic and thermodynamic behaviours of the operating solvent. For this configuration, operating parameters to be optimized are: the solvent flow rate, the lean loading ratio, the stripper pressure, the intercooler position and the cooling temperature.

Stripper Split Feed (SSF)
The idea of the Stripper Split Feed is to split the cold rich solvent exiting the absorber into two streams, the first one is directly injected at the stripper top and the other one is pre-heated as usual in the economizer before injection into the stripper at a lower level than the first stream. Energy benefits are of two types with this modification; first the injection of a cold solvent at the stripper top enables a condensation of the remaining water exiting the stripper packing, reducing the cooling duty of the condenser (heat sink) and consequently the reboiler duty. Secondly, this modification enables a better heat exchange by harmonizing thermal pinch along the economizer. Indeed, the thermal pinch is not constant in this heat exchanger for a conventional process and is located on the absorber side (left on Figure 2). As a result, reducing the rich solvent flow rate improves the heat integration in the economizer. Operating parameters to be optimized are: the solvent flow rate, the lean loading ratio, the stripper pressure, the split ratio and the injection height of the second stream.

Lean Vapour Compression (LVC)
The Lean Vapour Compression consists in flashing the hot lean solvent exiting the stripper at a lower pressure, to recompress the resulting gas (mostly water vapour) at the stripper pressure in order to use it as stripping gas. This modification uses a heat pump effect to convert sensible heat from the lean hot solvent into higher quality heat using additional mechanical power which reduces the reboiler heat duty. This modification is relevant when the supplementary mechanical power is significantly lower than the equivalent work saved by decreasing the steam flow rate to be drawn from the power plant steam cycle. The LVC is more efficient when the stripper operates at high pressure in order to reach better coefficient of performance (COP), that means for solvent with a high enthalpy of absorption. Operating parameters to be optimized are: the solvent flow rate, the lean loading ratio, the stripper pressure and the LVC flash pressure.

Stripper Overhead Compression (SOC)
The Stripper Overhead Compression is another utilization of a heat pump effect. In the conventional process, the gas stream exiting the stripper is condensed (around 40°C) before compression. The SOC directly compresses this stream to a given pressure and use the water condensation to provide a fraction of the reboiler heat duty. The resulting stream is then condensed and condensate is returned to the stripper. By this mean, less steam needs to be drawn off from the steam cycle but at the cost of additional steam compression work. Operating parameters to be optimized are: the solvent flow rate, the lean loading ratio, the stripper pressure and the compression ratio.

4. Optimization results for MEA and AMP solutions

In order to assess the energy performance of process modifications for a given solvent, an in-house model is used for process simulation. This model uses a rigorous *extended UNIQUAC* thermodynamic model coupled with a rate-based formulation of chemically enhanced heat and mass transfer for absorption and stripping columns (see Neveux et al. 2013 for modelling details).
As energy consumption is either thermal (steam demand) or electrical (compressors, pumps etc.), the total equivalent work is used as objective function. This equivalent work, expressed in kWh/t_{CO2}, represents the overall energy penalty on the power plant production due to implementation of a CO_2 capture unit. Such a work is written as follows:

$$W_{eq,total}\ (kWh/t_{CO_2}) = W_{parasitic} + W_{compression} + W_{auxiliary} \quad (1)$$

Where the different contributions are:

- The parasitic load, representing the impact of the steam draw off to provide reboiler heat duty on the power plant electric production.

- The compression related work, including the CO_2 compression up to 110 bars for transportation and the work of cooling water pumps.
- The auxiliary work of the capture unit, corresponding to solvent pumps, cooling water pumps, flue gas fan and additional compressors.

The minimum energy requirement of a given configuration, process architecture and solvent, is found using a dedicated optimization algorithm (Dai and Schittkowski, 2008) coupled with the process simulation model. This procedure is able to automatically determine optimal parameters with respect to the total equivalent work. Optimization results for MEA and preliminary simulation results for AMP are presented in Table 2.

Table 2: Energy performance of the five flow schemes for MEA and AMP solutions

	Conventional process	ICA	LVC	SOC	SSF
MEA 30 wt-%					
Total equivalent work (kWh/t_{CO2})	379	376	350	356	356
Relative difference (%)	0 % (ref.)	-0.7 %	-7.6 %	-6.2 %	-6.2 %
AMP 40 wt-%					
Total equivalent work (kWh/t_{CO2})*	336	326	329	330	317
Relative difference (%)	0 % (ref.)	-3.0 %	-2.3 %	-1.9 %	-6.0 %

** Preliminary simulation results for AMP*

So as to understand the phenomenological explanation of energy reduction due to process modifications, it must be pointed out that the reboiler heat duty is decomposed into three terms: heat of absorption, sensible heat and stripping heat. The heat of absorption is the heat required to reverse the reaction with CO_2, including the heat of physical absorption, the excess enthalpy and the heat of reaction. The sensible heat is required to preheat the solvent from the stripper inlet to the reboiler temperature. The stripping term is the heat required to produce the stripping steam in the reboiler which partially condenses along the stripper, this term is strongly dependent on the stripper pressure and the heat of absorption. As underlined by the equation (2), if the CO_2 heat of absorption is higher than the water heat of vaporization, the CO_2 desorption is favoured at higher pressure. Less stripping steam is therefore required at high pressure to desorb a given amount of CO_2 and the stripping term of reboiler heat duty is consequently decreased.

$$\frac{d\ln P^{*}_{CO2}}{d\ln P^{sat}_{H2O}} = -\frac{\Delta_{abs}H_{CO2}}{\Delta_{vap}H_{H2O}} \qquad (2)$$

Considering the conventional process, the change of solvent from MEA to AMP significantly decreases the total energy penalty (by 11 %) due to the lower heat of absorption and higher cyclic capacity of AMP, reducing the sensible heat (see Table 1). However, the absorber height had to be increased for AMP (twice as high) to sufficiently load the solvent, kinetic activator would therefore be mandatory in order to have a smaller absorber. AMP is highly resistant to thermal degradation, the stripper can operate at higher pressure, which means less compression work and steam quantity. The decrease of steam quantity is weighted against the increased steam quality required (higher pressure) and an optimum is obtained.

In comparison of conventional process, all the proposed process modifications lead to a reduction of the energy penalty for both solvent. The optimal intercooling temperature is 30 °C for MEA, which is the lowest acceptable temperature and the optimal level is located at the absorber bottom (around 1/6 of the total height). This means that the kinetic reaction rate is high enough even at low temperature so that the absorption is only thermodynamic-driven at the absorber bottom. The ICA is more efficient for AMP (4.6 % relative gain), indeed the absorption in the solvent is lower than for MEA along the absorber due to the lower kinetics and the thermodynamic shift by cooling is quite efficient.

The LVC and SOC are modifications that use both a heat pump effect to convert low quality sensible heat into higher quality latent heat. Better coefficient of performance (ratio of additional heat produced over mechanical power consumption) is obtained when the stripper operates at higher pressure. Consequently, these modifications are more efficient for MEA since the CO_2 heat of absorption is slightly higher for MEA than for AMP. This means that the ratio between the equilibrium partial pressure of CO_2 and saturation vapour pressure of H_2O for a given amount of stripping steam is higher for AMP than for MEA (see equation 2).

The stripper split feed is efficient for both MEA and AMP, due to the similar heat capacities of MEA and AMP. Indeed, the optimal splitting ratio corresponds to the nearly constant thermal pinch along the economizer. According to the solvent heat capacity, the optimal splitting ratio is shifted but similar heat integration is obtained.

5. Conclusions

In this study, two solvents with different properties have been used with different process modifications proposed in literature and relative reductions of energy penalty have been determined for each combination. Four process modifications have been chosen to illustrate the three types of process modifications: absorption enhancement, heat integration and heat pump effect. It has been shown that the solvent physicochemical properties impact the energy gain of process modification compared to the conventional process.

As general enlightenments, absorption enhancement process modifications such as intercooled absorber appear to mainly depend on kinetic reaction rate. For mildly reactive solvents, the shift of vapor-liquid equilibria is more beneficial but has to compensate the kinetics losses in order to be relevant.

Heat integration process modifications seem to have comparable efficiencies for a Stripper Split Feed since it mainly uses the sensible heat of the solvent. It would not be the case for other heat integration systems such as interheated stripper where vapor-liquid equilibria are shifted. Process modifications using heat pumps are always better when the associated COP is higher, meaning that these improvements are more efficient when the solvent regeneration is promoted at higher pressure. The operating stripper pressure is particularly conditioned by the CO_2 heat of absorption and the amine resistance to degradation.

In order to be more conclusive on the solvent/process interactions, the different types of solvents presented in Table 1 will further be studied. Likewise, other process modifications will be tackled as well as combinations of several modifications. By this means, advanced configurations will be proposed based on synergies between process modifications and properties of promising solvents.

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