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Process Modifications for Solvent-Based Post Combustion CO₂ Capture

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Abstract

Amine based CO₂ scrubbing processes have been patented since 1930 but very few process improvements have been reported prior to the oil crisis of 1975-1980, which led to the requirement for more energy efficient processes. Nevertheless most of these patents are solvent oriented. With CO₂ capture technology development, a sharp increase of process improvement patents and scientific articles can be witnessed since 2004 in parallel with the development of new solvents. In this work, a thorough review of patent database and open literature has been carried out in order to be as exhaustive as possible. The individual process modifications and patents are analyzed and then generalised into “elementary” modification groups. These elementary modifications are then sorted into main categories related to their effect on the process. In total, 20 elementary modifications have been sorted into three main categories: absorption enhancement (increasing rich loading or reducing absorption driving force difference along column height), thermal integration (minimizing the rejected heat of process and excessive thermal driving force) and heat pump effect (increasing heat quality with electricity). Figure 1 summarizes these modifications and shows an illustrative flow scheme for each of them. In the final paper, their mean of action will be described and discussed in relation to their induced complexity, flexibility, cost and expected performances.

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1. Introduction

One of the major limitations to the implementation of amine based post-combustion CO\textsubscript{2} capture (PCC) technology is the high energy consumption of the process, thermal and electrical. Minimizing this loss can be achieved by either formulating new solvents and/or optimizing the process flow-sheet and/or its integration with the power plant. Amine based CO\textsubscript{2} scrubbing processes have been patented since 1930 but very few process improvements have been reported prior to the oil crisis of 1975-1980, which led to the requirement for more energy efficient processes. Nevertheless, most of these patents are solvent oriented. With CO\textsubscript{2} capture technology development, a sharp increase of process improvement patents and scientific articles can be witnessed since 2004 in parallel with the development of new solvents [1-8].

2. Absorption enhancement

2.1. Intercooled Absorber

The general principle of intercooled absorber is to withdraw a fraction of the solvent in the absorber, to cool down the solvent and to send it back in the absorber (figure 1.a). This is a well-known technique commonly applied by various researchers and industrials. This system enables a shift in the thermodynamic gas-liquid equilibrium and consequently increases the rich loading at the absorber bottom. It reduces the solvent flow rate required to absorb a given amount of CO\textsubscript{2} and thereby leads to reduction of reboiler steam demand.

2.2. Interheated Absorber

Interheated absorbers exploit the same idea as intercooled absorber (figure 1.b). Instead of favoring thermodynamic by cooling the solvent, the kinetic is enhanced by heating it.

2.3. Rich Solvent Recycle

The rich solvent recycle consists in withdrawing a fraction of solvent from an absorber level (including absorber bottom) and recycling it back at an upper level (including absorber top) (Figure 1.c). This modification provides a prolonged contact time between CO\textsubscript{2} and solvent, increasing the CO\textsubscript{2} loading ratio and reducing the amount of solvent. In order to maximize the absorption capacity of the solvent, the rich solution at the absorber bottom can be recycled at different absorber levels, increasing absorber size (diameter and height).

2.4. Split Flow Arrangement

The Split Flow Arrangement has initially been designed for H\textsubscript{2}S removal but the concept is technically cogent for adaptation in CO\textsubscript{2} capture applications. The general principle is to regenerate the solvent at two, or more, loading ratios: one lean solvent stream which is fed to the top of the absorber and one, or more, semi-lean solvent stream which are fed in the middle of the absorber (Figure 1.d). This process modification has been designed for deep removal of acid gas in order to increase the absorption driving force at the top of the absorber. Only a fraction of solvent is completely regenerated and provides the needed driving force to achieve the required purity. Concerning bulk removal, this modification is more useful for “thermodynamically non-favored” solvent such as tertiary amine than for monoethanolamine. This arrangement allows either a reduction in solvent flow rate and/or solvent regeneration duty.

2.5. Double Loop Absorber

Again this concept has been initially designed for H\textsubscript{2}S removal but the concept is adaptable for application in CO\textsubscript{2} capture. Figure 1.e shows a process based on the double-loop absorber-stripper process. It constitutes of an absorber column divided into 2 sections, just as in a split-flow process. The bulk of the absorption takes place in the bottom section fed by a partially-stripped solvent. The solvent leaving the absorber is...
then sent to the primary stripper via a heat exchanger. The upper section of the absorber is used for the polishing of the treated gas. The solvent leaving this section is regenerated in a secondary stripper. This process modification is similar with certain configurations of SFA but its main purpose is to use two different solvents in the two different absorber loops.

2.6. Flue gases Compression and Expansion

The purpose of this modification is to enhance the absorption driving force and to use the heat of absorption for power production (Erreur ! Source du renvoi introuvable, f). The flue gases are compressed, usually to moderate pressure (up to 3 bars). This raises the CO₂ partial pressure and helps the CO₂ absorption in the solvent. With this additional driving force, higher loading can be expected or less reactive solvent can be used, both these effects leads to a reduction of regeneration duty. In order to mitigate the cost of flue gases compression, the decarbonized flue gases are expanded in a turbine before the water wash section. These flue gases have been heated in the absorber thanks to the exothermic CO₂ absorption.

3. Heat integration

3.1. Rich Solvent Splitting

This modification is quite simple to implement. It involves splitting the rich stream into two flows: one of which is preheated (in conventional fashion by the lean/rich heat exchanger) and the other is kept cold. Cold stream is injected at top of stripper while the heated stream is then injected at some suitable distance below (figure 1.g). The higher the stream temperature, the lower the injection height in the stripper should be. With this arrangement, the temperature profile in the stripper is smoothed and the heat recovered from hot lean solvent and stripper overhead is maximized.

3.2. Rich Solvent Preheating

The general principle of Rich Solvent Preheating is to heat the rich solvent above the temperature achievable in the economizer by transferring heat from the hot lean solvent to the cold rich solvent (figure 1.h).

3.3. Rich Solvent Flashing

The general principle of Rich Solvent Flashing is to flash the hot rich solvent before its injection in the stripper (figure 1.i). Flashing the rich solvent releases some CO₂ and cool down the remaining liquid stream. The colder partially regenerated rich solvent could be used to cool down the stripper overhead and recover additional heat. This modification does not provide significant energetic improvement if used alone and if the absorber operates at lower pressure than the stripper which is, normally, the case for post-combustion CO₂ capture; it should be noted, however, that the rich feed to the stripper will often flash anyway in the liquid distributor.

3.4. Parallel Economizer Arrangement

The general principle of a Parallel Economizer Arrangement (PEA) is the optimization of heat recovery in between streams exiting the hot zone of the process (around the stripper and the reboiler) and streams entering this hot zone. It can be achieved by splitting rich and/or lean solvent flow in two (or more) streams and feed them in two (or more) heat exchangers (figure 1.j). Consequently, it can lead to pinch minimization (due to solvent gas/liquid state improving heat exchange, for example) to maximize the average temperature of heat exchanged or to minimize the heat rejected in the cooling water.
Figure 1: summary of process modifications
3.5. InterHeated Stripper

The general principle of InterHeated Stripper is the reheating of a semi-lean solvent stream extracted from the middle of the stripper and the reinjection of this stream in the stripper (figure 1.k). This modification consists of a side exit of liquid that goes through a heat exchanger (with hot lean) and then goes back to the stripper again. It is easily applicable in combination with other energetically compatible modifications. Inter-heating in the stripper targets to optimize the temperature profile by integrating the hot lean amine from the reboiler to the top section of the stripper. In essence this brings the temperature along the stripper closer to the desirable temperature profile for stripping.

3.6. Heat Integrated Stripper

This modification involves full integration of the lean/rich heat exchanger into the stripper (figure 1.l). This lowers exergy expenditure by bringing equilibrium and operating conditions closer along the column.

3.7. Vacuum operated Stripper

Although not really a process modification, but a significant change in operating conditions which may incur new process design (larger stripper and vacuum pumps), this modification requires the stripper to operate at vacuum/sub-ambient pressure and therefore uses low pressure steam for solvent regeneration (figure 1.m). Intuitively, drawbacks include increase in CO₂ compression work.

3.8. Multi Effect Strippers

The general principle of Multi Effects Strippers is to provide heat to a lower pressure stripper with waste heat from a higher pressure stripper. This arrangement allows an optimal use of the steam needed for regeneration (figure 1.n). These stripper arrangements are often coupled with split flow arrangements because they can easily produce lean and semi-lean solvents.

3.9. Overhead Condensate Bypass

The general principle of the Overhead Condensate Bypass is to not feed the top the stripper with the liquid condensate exiting the stripper overhead condenser flash drum. This condensate is directly sent to the absorber (figure 1.o).

4. Heat pumps

4.1. Lean Vapor Compression

The general principle of Lean Vapor Compression (figure 1.p) device is: the lean solvent at the bottom of the stripper is flashed in order to produce a gaseous stream. This stream is compressed and fed back to the stripper; the composition of the gaseous stream is mainly H₂O and CO₂. This family of process modification reduces the reboiler steam demand and cools down the lean solvent going to the economizer.

4.2. Rich Vapor Compression

The general principle of the Rich Vapor Compression (figure 1.q) devices is to flash the hot rich solvent in order to produce a gaseous stream and a liquid stream. The gaseous stream is compressed and fed to the bottom of the stripper whereas the liquid stream is pumped and feed at the top of the stripper.
4.3. Stripper Overhead Compression

The general principle of Stripper Overhead Compression (figure 1.r) devices is that the gaseous stream exiting the stripper is compressed without prior water condensation, this high pressure gaseous stream is partially condensed at high pressure (from 5 to 10 bar or higher) and heat released by condensation is used to provide heat for the stripper reboiler.

4.4. Integrated Heat Pump

The general principle of an Integrated Heat Pump (figure 1.s) is to provide high quality heat thanks to low quality heat and electric power. The optimal heat demanding stream is the hot rich solvent leaving the economizer. The low quality heat could be provided by the following sources:

- Dissipated heat of compression
- Residual heat of compression after a Stripper Overhead Compression
- Heat of water condensation after Stripper Overhead Compression
- Steam condensate exiting the reboiler
- Heat extracted from the absorber by an intercooling heat exchanger
- Residual heat in the lean cold solvent exiting the economizer

4.5. Multi Pressure Stripper

The general principle of Multi Pressure Stripper (figure 1.t) devices is to operate the stripper’s reboiler at low pressure and to raise the stripper pressure along the column by the use of dedicated compressors; a pressure ratio of 2 in each compressor is preferred. This implies decreasing pressure down the column; allowing solvent to boil at lower pressures leading allowing a perfect valorization of the heat dissipated by compression.

5. Discussion and Conclusion

5.1. Expected performance

The process modifications performances have been mostly evaluated through modeling work. Very few experimental testing has been carried out at appropriate scale. Moreover, methodologies used to assess the modification performance: different modeling hypotheses (rate based or not), different flue gases (coal or gas), different key performance indicator (boiler duty or equivalent work). Reconciliation between all these studies is not straightforward but the recent evaluations share almost the same methodologies and results are very similar. Nevertheless, for a complete, and definitive, view on this broad topic a tremendous modeling work is necessary due to the number of solvent of interest and flue gas composition.

In all cases, MEA is considered as the reference solvent, and most studies evaluate process modification for MEA solvent only. The reduction of parasitic loss ranges from almost 0 % for light process modifications (Rich Solvent Flashing, InterCooled Absorber) to 45 % for very complex combinations of process modifications (Mostly Parrallel Economizer Arrangement combined with Rish Solvent Split and Rich Solvent Preheating or Multiple Effect Stripper combined with Split Flow Arrangement).

Interactions between process modifications have not been systematically investigated. Performances of some combinations have been evaluated, mostly in patents; however, a comprehensive study on this aspect is yet to be published. The range of solvents investigated needs to be broadened, almost all publications evaluated MEA based solvent despite the strong interaction between solvent and process. These interactions need to be taken into account in post-combustion process design and need to be properly investigated.
5.2. Induced complexity

Process modifications are mostly used to improve process performance, and in particular energy consumption. The addition of equipment and piping in the process will increase the total plant cost whilst reducing energy consumption. Therefore, the cost impact of each process modification, or combination of modifications, needs to be assessed through techno-economical analysis. The results of this assessment can differ with different boundary conditions and with different evaluation procedures; for example between new-build and retrofit cases or between different project lifetimes and levelization factor.

More specifically, some equipment could be difficult to design efficiently for this application. Compressors working with amine vapor, such as those included in LVC, RVC, SOC and MPS modification can suffer reliability problems which can be overcome with a combination of redundancy and high quality materials. The cost of these solutions can significant and therefore may not appear interesting for industry.

In addition to the cost, each additional process modification increases the overall complexity of the process and therefore reduces its operability and possibly its reliability. Some process modifications may improve operability, such as RSF or RSS. This is due to the additional degree of freedom they build into the process, providing the ability to cope with process instabilities; however, most modifications will reduce the energy consumption at the cost of increased complexity.

Some process modifications can be designed to be removed (or bypassed) from the process in case of unavailability but this induces equipment overdesign and needs to be taken into account for process assessment. For example, the LVC loop can be totally bypassed but if the lean-rich cross exchanger is not properly designed, the higher temperature of the hot lean solvent will not be effectively used for the preheating of the cold rich solvent. An undersized cross exchanger will lead to a reduced performance in case of LVC shut down. In contrast, if a compressor of a MPS failed, the high pressure portion of the column can suffer flooding due to significantly higher gas flow rate and the CO\textsubscript{2} product compressor would be required to compress a lower density gas. Building in mitigation for such risks is very expensive (e.g. doubling the section of the high pressure packing section, having an additional spare compressor) and not likely to be effectively used in industry.

In most, if not all of the cases of shutting down or bypassing a process modification will lead to reduced plant performances but the extent to which performance is reduced will vary with modification, with some being critical. A critical impact on performance suggests that the process could not work properly without this process modification once it has been installed and that the cost to build efficient back up is expected to very high. The following modifications are expected to be in the first category, which are modifications that are not critical to the process: ICA, IHA, RSR, RSS, RSP, RSF, OCB, HIS, LVC, RVC, and IHP. Whereas, the other modifications: SFA, FCE, DLA, PEA, HIS, VOS, MES, SOC and MPS are expected to be critical for the process operation.

No clear methodologies exist in the literature to address the issue of added complexity through plant modifications. Reliability, Availability, Maintenance (RAM) analyses and technical-economic analyses can be useful but these methods need detailed simulations of each evaluated process and are not adapted for screening purposes. A proper evaluation methodology is yet to be developed.
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References