Amino Acid Based Solvent Vs. Traditional Amine Solvent: a Comparison

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There is an increase in the development of absorption of acid gases by chemical solvents from flue gases of power plants due to the growing attention paid to the capture and storage of CO_2. With the aim of substituting traditional amines, which at present have many disadvantages such as high energy requirement, corrosion, and toxicity, innovative solvents are being studied. In the last few years, attention has been paid to solvents which form precipitate during the absorption phase. Amino acids belong to this category and, because of their characteristics, allow a further enhancement of the chemical absorption process. Thus, it is possible to perform the removal of CO_2 in an amount similar to that of traditional amines, but with lower regeneration energy and costs. In this work, an amino acid solvent of potassium taurate solution (4M potassium hydroxide – 4M taurine) has been considered. The process has been simulated with the commercial software ASPEN Plus® to perform a rigorous calculation. The software had been user customized on the basis of the available experimental data in previous work. Our previous publications reported the modelling of the process and the evaluation of its performance applied to the purification of a flue gas stream. In this work, a techno-economic comparison between the amine scrubbing process and the potassium taurate process is presented, taking into account both the operating costs, mainly affected by the energy consumption, and the capital costs.

1. Introduction

1.1 CO_2 removal

Recently, many countries agreed to reduce the emissions of greenhouse gases into the atmosphere in order to avoid a further increase in global warming, with one of the main causes being the on-going human-induced emissions of carbon dioxide. Although many emissions are from different sources including power plants, industry, domestic heating and traffic, research on mitigation of carbon dioxide mainly focuses on its application to power plants. Indeed, a major factor is carbon dioxide emissions from thermal power plants, which burn fossil fuels (usually from coal or natural gas), and, if compared to other carbon dioxide sources, present more favourable conditions for the application of the CO_2 removal technologies. The options to remove carbon dioxide from exhaust flue gases generated by the combustion of fossil fuels depend on the source of CO_2 emissions, with mainly three feasible technologies being currently under consideration: pre-combustion capture, post-combustion capture and oxy-fuel combustion. The addition of a CO_2 removal system downstream of the power section (post-combustion capture) is considered to be a possible way for short or medium term interventions to reduce the release of this acid gas into the atmosphere (Alie et al., 2005), including retrofitting of existing fossil fuel plants.

Among the alternatives (Erga et al., 1995; Kohl and Nielsen, 1997) for carbon dioxide removal, chemical absorption by amine aqueous solutions is widely recognized as one of the most mature technologies to be applied for post-combustion capture in power plants (Molina and Bouallou, 2013) because of the ability to absorb the acid gas and regenerate the solution continuously. However, amines are characterized by several drawbacks, such as corrosion and toxicity, in addition to high energy requirement. The removal of 90% of the

carbon dioxide results in very high operating costs of the plant, which may make the technology economically unviable if electricity has to be sold to the market at low prices, or, economically uncompetitive if the electricity needs to be sold at a price to recover the full costs of production. In order to overcome these issues, innovative solvents are currently being studied (Lerche, 2012; Majchrowicz, 2014; Sanchez-Fernandez, 2013), including ones which form precipitate for high loadings during the absorption step, allowing an enhancement of the transfer of carbon dioxide from the gas phase to the liquid phase. Amino acids are characterized by good reaction kinetics with carbon dioxide, low corrosion, good stability and favorable enthalpy of reaction. These features allow the plant with high CO_2 rich loadings and with low regeneration costs, thereby achieving CO_2 removal rates similar to those of traditional amines such as MEA (Brouwer et al., 2009).

1.2 Aim of the work

In a previous publication (Moioli et al., 2017) the modelling of the process and the evaluation of its performances applied to the purification of a flue gas stream were reported. In this paper, a cost comparison of the absorption process using potassium taurate absorption with the traditional MEA scrubbing technology is undertaken.

2. Post-combustion CO_2 removal technologies

2.1 Traditional: amine chemical scrubbing

The flue gas coming from the power plant, previously cooled and cleaned from impurities, reacts chemically with the amine aqueous solution in the absorber, and is then emitted to the atmosphere with low content of carbon dioxide. The rich amine solution leaving the absorption column is heated with the lean amine solution coming from the regenerator unit in order to limit the energy requirement. It is then fed to the regeneration column for the separation of the absorbed acid gas (exiting from the top of the unit) from the solvent, which is then cooled and recycled back to the absorption section. Corrosion and degradation of the solvent are critical aspects of this process, influencing the design and operation of the plant. In particular, as will be shown in this paper, the impact of corrosion is taken into account by employing different materials of construction.

2.2 Alternative: absorption by amino acid aqueous solutions

The process flow diagram for the potassium taurate process considered in this work is shown in Figure 1.
The gaseous stream to be purified (stream (1)) is fed to the absorption section for countercurrent contact with a lean aqueous solution of potassium taurate and removal of carbon dioxide. Taurine has a limited solubility and it precipitates when the saturation point, dependent on temperature and composition, is reached. The stream recovered at the bottom of the absorption column is a slurry, formed by solid taurine and a liquid mixture of water, molecular species as carbon dioxide and taurine in the liquid phase and ionic species, as the products formed by reactions, *i.e.* bicarbonate, carbonate, carbamate, potassium ion.
The gaseous stream exits from the top of the column (stream (2)) with low content in carbon dioxide. The solvent recovered from the bottom of the absorption section (stream (3)), rich in carbon dioxide and most likely solids, is pumped to the regeneration section, operating at low pressure, which may be 1-2 bar higher than the absorption pressure. Depending on the overall process design and operation, the rich solvent (stream (4)) can be heated (not shown in Figure 1) to the dissolution temperature to dissolve all solid taurine before entering the lean-rich heat exchanger for recovery of heat, or the operation of solid dissolution may be carried out partially or totally directly in the lean-rich heat exchanger. In both the cases, the stream entering the regeneration column (stream (5)) contains no solid.
In the case of absence of the above-mentioned unit, the rich solvent is heated in the cross heat exchanger to dissolve any solids and sent to the regeneration column. This column operates as in the case of traditional amine solutions without the presence of solids present because these are completely dissolved before the column. The column is provided with a reboiler for generation of stripping steam, needed for the separation of carbon dioxide from the solvent, and with a condenser, for removal of most of the water, which is recycled and acts as reflux to the column. A carbon dioxide-rich stream (stream (7)) exits from the top as vapour distillate and a lean solvent stream (stream (11)) is obtained from the bottom of the column.
The high heat content of the lean solvent is recovered in the cross heat exchanger and transferred to the cold rich solution for pre-heat and energy savings in the reboiler. The lean solvent (stream (12)) after make-up (stream (13)) if needed, is further cooled to 40°C and recycled back (stream (15)) to the absorption column.
Optionally (not shown in Figure 1), a solid-liquid separator for the rich solution can be added, for separating part of the supernatant from the slurry, which is then recycled back to the absorption column without being regenerated. By operating this separation unit, acidification of the solution rich in carbon dioxide is favoured, since for both the supernatant and the concentrated slurry a different ratio of taurine / potassium is obtained, causing a difference in pH (Sanchez-Fernandez, 2013). This difference results in a different solubility of

carbon dioxide, with a higher partial pressure of carbon dioxide in equilibrium with a given loading, which enhances the removal of the acid gas from the rich solution.
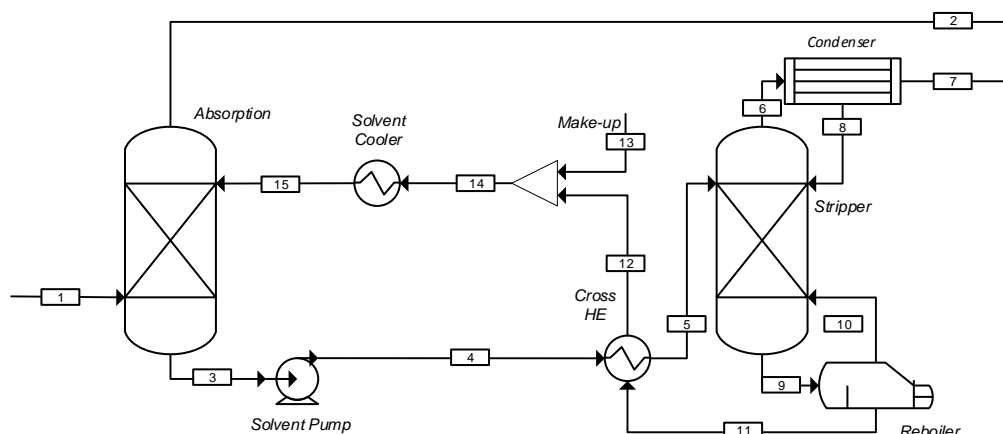

Figure 1: Process flow diagram of the potassium taurate process.

3. Methodology

3.1 Simulations of the systems

Simulations in ASPEN Plus[®] have been performed both for the traditional process using MEA and for the potassium taurate process. The absorber and stripper were both modelled with the RADFRAC column run in rate-based mode taking into account the mass and heat transfer resistances (Plaza, 2012).

Both the systems are strongly non-ideal, because of the presence of chemical reactions, which strongly affects the phase equilibrium. Both kinetically controlled reactions (such as the reactions involving the formation of the bicarbonate ion and of the carbamate) and 'instantaneous' reactions (such as the water dissociation, the reactions of monoethanolamine and of taurine with water, and, the formation of carbonate ion) occur. For the potassium taurate system, also the dissociation of KOH and the dissolution / precipitation of taurine must be taken into account. The MEA scrubbing process has been simulated (in rate-based mode) by employing the ASPEN Plus[®] process simulator, previously modified and checked with experimental data of vapour-liquid equilibrium of the chemical reacting system and with data from pilot columns (Langé et al., 2015; Moioli, 2014). As for the representation of the potassium taurate process, ASPEN Plus[®] has been user customized (Moioli et al., 2017) to take into account all the electrolyte species not present by default in the software and the proper thermodynamics of the system. In the absorber, the reactions involving carbon dioxide were described with four kinetic expressions, related to the direct and backward reactions for formation of carbamate (Wei et al., 2014) and to the forward and backward reactions for formation of bicarbonate (AspenTech, 2016). In the stripper, all the reactions were set to equilibrium, due to the higher operating temperature.

A scheme where solids are separated after the absorber and/or all the solids are dissolved in a dissolution heat exchanger is not considered here.

3.2 Techno-economic evaluation

A techno-economic comparison between the amine scrubbing process and the potassium taurate process has been made, taking into account both the operating costs and the capital costs of the absorption process. The analysis does not include any cost for flue gas pre-treatment, CO_2 compression or modifications to the power plant's steam cycle.

The operating costs have been computed according to Turton (2003) and Peters and Timmerhaus (1991). The two references show a good match with each other, with Turton (2003) being slightly more conservative and Peters and Timmerhaus (1991) considering some additional items, such as *Contingency*, which are included in the present work. The capital costs (representative of the total cost for equipment, procurement and construction) have been evaluated on the basis of the Equipment Module Costing Technique (Turton, 2003) and the Fixed Capital Investment Estimation procedure of Peters and Timmerhaus (1991), which includes also the legal expenses. Direct and indirect expenses (such as insurance, taxes, construction overhead, engineering, contingency, contractor fee, site development, auxiliary buildings, off-sites and utilities facilities are included. The main units that are considered include the absorber, regenerator, heat exchanger, pump,

and valves. For each unit the purchased equipment cost and the bare module costs are calculated, taking into account direct and indirect expenses, including all piping, as well as the operating pressure and the material of construction (stainless steel for MEA and carbon steel for potassium taurate). Table 1 summarizes the key economic assumptions (Turton, 2003).

Table 1:Summary of economic assumptions.

Parameter	Value
Cost year	2016
Currency	US$
Steam cost	7.78 $/GJ
Electricity cost	16.8 $/GJ
Cooling water cost	0.354 $/GJ
Operating load	8000 h/y

4. Results and Discussion

The case study used for the analysis focuses on post-combustion removal of carbon dioxide from a 500 MW coal-fired power plant (Raksajati et al., 2016), with the characteristics reported in Table 2.

Table 2: Properties of the flue gas stream to be treated for removal of carbon dioxide.

Parameter	Value
Flowrate [kmol/s]	19.60
Temperature [K]	313
Pressure [bar]	1.1
Component	Mole fraction
Carbon dioxide	0.1300
Water	0.0700
Nitrogen	0.7500
Oxygen	0.0500

Table 3 reports the characteristics of the solvents employed in the two processes. For amine scrubbing, the considered solvent is an aqueous solution of 30% wt. monoethanolamine, with a lean loading of 0.15 chosen in order to avoid corrosion due to the rich loading (the maximum allowable value taken from Freguia and Rochelle, (2003)) while minimizing the energy consumption in the reboiler (Pozzi, 2017). For absorption by amino acids the solvent is a potassium taurate solution (4M potassium hydroxide – 4M taurine), with a lean loading of 0.27 as from Sanchez-Fernandez et al. (2013), which has low steam requirements at the reboiler.

For both processes, the solvent flowrate has been chosen to obtain a gas stream leaving the process with only 10% of the carbon dioxide initially present (i.e. 90% capture rate). The size of the equipment for the potassium taurate process is taken from Raksajati et al. (2016), while the MEA plant has been designed ex novo.

Figure 2 shows results of the total capital costs (as M$) and the operating costs (as M$/year) of the two systems. Although the MEA process has a lower solvent flowrate (equal to 69.5 kmol/s) compared to the potassium taurate process (equal to 146.2 kmol/s), it has higher energy consumption mainly at the reboiler (747 MW for MEA vs. 458 MW for potassium taurate). This arises due to the different characteristics of the solvent, and as a result has higher operating costs. The capital costs (176 M$ for potassium taurate and 212 M$ for MEA) differ a lot for the two technologies, with the MEA plant being more expensive. Although both processes operate at similar pressure in the absorption and the regeneration sections, the equipment of the two plants is built with different materials. In particular, in order to limit corrosion in the MEA system, stainless steel must be employed for the columns and the reboiler. For the potassium taurate system the available data suggests that corrosion rates are low, so carbon steel might be suitable as the material of construction (Ahn et al., 2010). Therefore, the capital cost for the absorption column (Figure 2b) for the MEA plant is higher than for the potassium taurate plant. Similarly, also the cost of the regenerator is higher (Figure 2b)). Thus, the total capital cost for the MEA system is about 20% higher than the potassium taurate system. Figure 3a) shows some of the breakdown of the costs for utilities (electricity, steam and cooling water). Cooling water cost and usage is similar for both processes and is relatively inexpensive accounting for less than 6% of the total utilities cost. Electricity is needed for units such as pumps and it is proportional to the flowrate of the stream

fed to the unit. It has only a very small influence on the total costs accounting for less than 0.5% of the utilities costs. The cost of steam is the largest energy and is related to the energy requirement at the reboiler (Figure 3b), which is influenced also by the lean loading to which the solvent must be regenerated. For the potassium taurate system, this cost is lower than for the MEA system by about 25%.

Table 3: Properties of the solvent needed to accomplish the desired removal of carbon dioxide for the two processes.

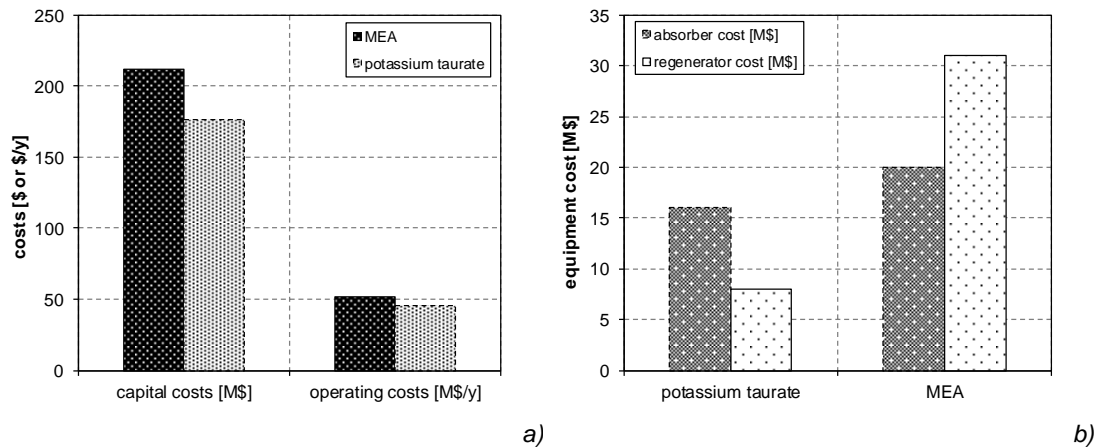| Parameter	potassium taurate	MEA
Flowrate [kmol/s]	146.22	69.51
Temperature [K]	313.15	313.15
Pressure [bar]	1.1	1.1
Component	Mole fraction	
Carbon dioxide	0.0283	0.0170
KOH	0.1048	0
Taurine	0.1048	0
MEA	0	0.1100
Water	0.7621	0.8730

a)

Figure 2: Comparison of the potassium taurate and MEA processes in terms of a) total capital and operating costs, and b) capital costs for the absorber and the regenerator, for 90% carbon dioxide removal.
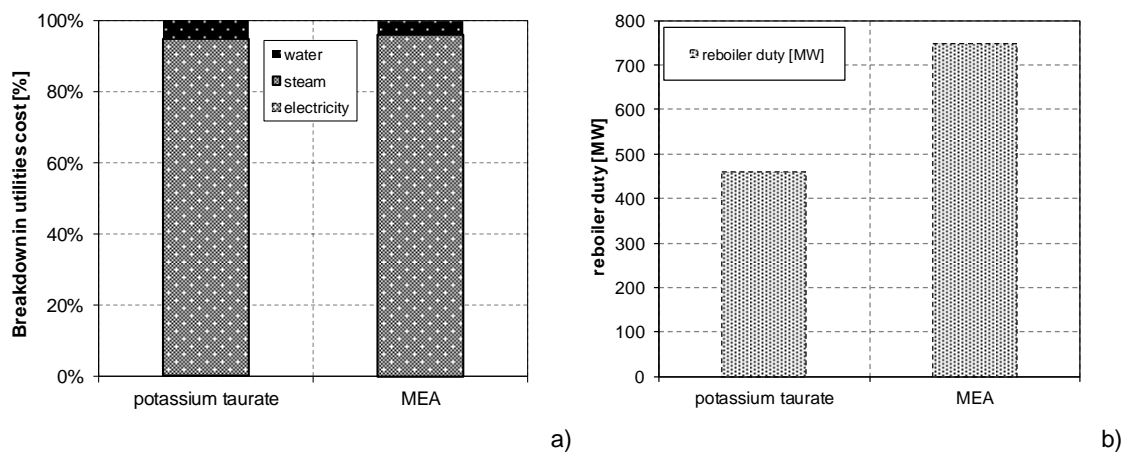

a)

b)

Figure 3: a) breakdown in costs for utilities and b) energy required at the reboiler for the potassium taurate and MEA processes for the removal of 90% of carbon dioxide from the same flue gas stream.

5. Conclusions

In recent years, solvents alternative to the traditional monoethanolamine aqueous solution, such as amino acids, have started to be studied for the reduction in the CO_2 emissions in order to limit the climate change due to global warming to overcome the issues of employing the traditional MEA.

In this work, a techno-economic comparison between the amine scrubbing process and the potassium taurate process has been made. To perform a rigorous calculation, both the processes have been simulated with the commercial software ASPEN Plus®, properly user customized for the representation of the potassium taurate system, not present by default, on the basis of the available experimental data.

For both the technologies, the utility costs are mainly affected by the energy consumption at the reboiler of the regeneration column, for which steam is needed, while the capital costs strongly depend on the design of the column, in particular the material of construction.

Results show that the technology by amino acid salts solution has the potential to substantially decrease the capital costs and the energy consumption of the CO_2 removal process.

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