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Simulation of CO_2 Removal by Potassium Taurate Solution

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The removal of carbon dioxide from gaseous sources such as flue gases from power plants traditionally uses aqueous solutions of alkanolamines; with monoethanolamine (MEA) considered the benchmark solvent. However, in order to overcome some of the main disadvantages associated with MEA, such as high volatility and toxicity, and high thermal requirements for regeneration; in recent years alternative solvents have started to be studied for CO_2 removal.

Taurine is an amino acid which can be dissolved in aqueous solution with potassium hydroxide and can be used for absorption of carbon dioxide. Compared to MEA, this solvent is considered to be more environmentally friendly because of its lower toxicity, higher biodegradability, negligible volatility and good stability towards degradation. Reactions with carbon dioxide are less exothermic than with MEA, therefore a lower amount of heat is required to reverse them in the regeneration column. Moreover, during absorption the zwitterionic form of the amino acid may precipitate, thus increasing the absorption capacity of the salt solution at equilibrium.

This work describes the development of a simulation of the potassium taurate solvent system for carbon dioxide removal using ASPEN Plus®. New ionic species due to the dissolution of solid taurine in water and KOH and due to the reactions of the components in the liquid solution with carbon dioxide have been introduced into the simulation. Vapor-Liquid Equilibrium in the presence of precipitating salt has been described by means of the Electrolyte-NRTL method, for which appropriate parameters have been determined and a rate-based simulation of the columns involved in the process (absorption and regeneration) has been performed.

The model has been validated by comparison with data of vapor-liquid-(solid) equilibrium from the literature and can be used for further assessment of this process in the future.

1. Introduction

1.1 Background

Global warming and climate change issues have led to the study of several technologies for reducing the amount of anthropogenic greenhouse gas emissions to the atmosphere. Carbon capture and storage (CCS) can be applied to large emission sources, such as power production plants, for reduction in the emissions by up to 95%. For coal-fired power plants, post-combustion capture technology is the preferred method if CCS needs to be retrofitted to existing power plants.

The benchmark solvent is monoethanolamine (MEA), traditionally used for the removal of carbon dioxide from gaseous sources such as flue gases from power plants. However, this solvent is characterized by high volatility and toxicity, and losses to the environment are undesirable. Moreover, generally, with traditional solvents, the energy penalty and associated costs for the capture units, mainly related to the high heat requirements, are elevated and therefore the cost of electricity produced is increased.

In order to overcome some of the main disadvantages associated with MEA, alternative solvents have started to be studied for CO_2 removal. Taurine is an amino acid which can be dissolved in aqueous solution with potassium hydroxide and can be used for absorption of carbon dioxide. The solvent is considered to be more environmentally friendly because of lower toxicity, higher biodegradability, negligible volatility and good stability towards degradation, in comparison with MEA. A lower amount of heat may be required to reverse the

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reaction between CO_2 and the amino acid in the regeneration column, because reactions with carbon dioxide are less exothermic than with MEA. In addition, during absorption the zwitterionic form of the amino acid may precipitate, thus increasing the absorption capacity of the salt solution at equilibrium.

These advantages may lead to benefits in the CO_2 capture process, and have led to increasing numbers of studies into these types of solvents in recent years. Previous research has focused on the solubility of carbon dioxide (Kumar et al., 2003a; Kumar et al., 2003b; Sanchez-Fernandez and Goetheer, 2011; Sanchez Fernandez et al., 2013; Wei et al., 2014; Wei et al., 2013), on physical and thermal properties (Han et al., 2012; Kumar et al., 2001; Wei et al., 2014; Wei et al., 2013), and, on the kinetics and the rate of absorption (Aronu et al., 2013; Kumar et al., 2003c). Analyses involving the calculation of the regeneration energy (Sanchez-Fernandez et al., 2014) and high-level assessment of the cost of capture (Raksajati et al., 2016) have also been carried out.

1.2 Aim of the work

This paper is focused on the modeling of the process for removal of carbon dioxide by potassium taurate solution in ASPEN Plus®. The aim is to develop a tool which will permit rigorous evaluation of the capture process involving the formation of solids.

2. Available Experimental Data for Modeling

Experimental data on vapor-liquid-solid equilibrium of the potassium taurate solution, of vapor pressure of water in the presence of potassium hydroxide and taurine, and of the pH of the solution have been taken from Sanchez-Fernandez et al. (Sanchez Fernandez et al., 2013). The same source has also been used to obtain data of the composition, the pH and the dissolution temperature of the slurry. Table 9.10 from the PhD thesis of Sanchez-Fernandez (Sanchez-Fernandez, 2013) has been used for validation of the amount of solid taurine formed.

3. Methodology

The process has been simulated in ASPEN Plus® (AspenTech, 2014), a process simulator which can be user customized and which allows an increased level of mathematical modeling of the electrolyte thermodynamics and mass transfer resistances coupled with chemical and kinetically-controlled reactions. Molecular compounds and ionic species related to carbon dioxide, water and potassium hydroxide are present by default in the process simulator. Solid taurine is present (though only the solid enthalpy of formation is available in the database). For the simulation reported in this paper, ionic species and the liquid form of taurine have been added. The vapor-liquid equilibrium is calculated by means of a γ/ϕ method with the Electrolyte-NRTL model, while the formation of the solid phase is described by taurine precipitation.

3.1 Chemical Reactions

The absorption of carbon dioxide into the considered solvent involves a complex system of parallel and consecutive reactions, some of them being kinetically controlled (i.e. the reactions involving the formation of the bicarbonate ion and of the carbamate) and others being instantaneous (i.e. the water dissociation, the first and second dissociations of taurine in water, and, the formation of carbonate ion). The chemical reaction set also comprises the dissociation of KOH (considered to be irreversible), and the salt dissolution/precipitation of taurine (modeled as solid taurine forming liquid taurine).

Since rate-based calculations in ASPEN Plus® do not take into account the presence of solids, a chemical reaction set not comprising the salt precipitation has been used for the absorption and desorption units. In order to include the influence of the precipitation of taurine on the partial pressure of carbon dioxide and on the CO_2 loading, the chemical equilibrium reaction for the formation of carbamate has been modified in the simulator.

3.2 Thermodynamic Model

The Electrolyte-NRTL model developed by Chen and co-workers (Chen et al., 1979; Chen et al., 1982; Chen and Evans, 1986; Mock et al., 1986) and widely applied to the representation of the phase behaviour of liquids containing electrolytes has been considered in this work. It is an activity coefficient model which takes into account all the possible interactions between molecules and molecules, molecules and ion pairs, ion pairs and ion pairs, described by considering two parameters for each interaction, the energy parameter and the non-randomness parameter. The vapour phase is described with the Redlick-Kwong (Redlich and Kwong, 1949) cubic equation of state, while the solubility of carbon dioxide in potassium taurate solution is modelled using the Henry's constant for carbon dioxide in water because of lack of experimental data.

Parameters for all the possible interactions have been considered. The choice of the parameters to be regressed has been performed using the method reported in Weiland et al. (Weiland et al., 1993) along with the general assumptions of Kumar et al. (Kumar et al., 2003) in order to reduce the number of parameters that need to be fitted for the activity coefficient model. However, as the interactions with water are vital to the determination of accurate activity coefficients for the Electrolyte-NRTL model in this system, the assumption in Kumar et al. (2003) which neglects the ionic and molecular species with water has been ignored.

The values of interaction parameters that do not have a large influence on the system have been set equal to those suggested by Chen and co-workers (Chen et al., 1979; Chen et al., 1982; Chen and Evans, 1986; Mock et al., 1986). The values of interaction parameters that have the most influence on the system have been determined by regression of available experimental data using the *Maximum Likelihood* method. These latter values are for the solubility of taurine salt in water and in loaded potassium taurate solutions, for the representation of the pH of the potassium taurate solution, for the correct description of the influence of the solute compounds on the vapour pressure of water and for the representation of the solubility of carbon dioxide in potassium taurate solution with and without solid formation.

3.3 Mass Transfer and Kinetic Model

The heat and mass transfer are calculated for each stage of the absorption and of the desorption column by employing a rate-based simulation. In the unit *ABSORBER* (Figure 1) where solid precipitation is not considered by the simulator, the mass transfer coefficients and the interfacial area are estimated using the correlations of Bravo et al. (1985). In the absorption column, the data for the kinetics of the forward and backward reaction for carbamate formation have been taken from Wei et al. (Wei et al., 2014) while the ASPEN Plus® defaults (AspenTech, 2014) have been used for the forward and backward reactions for the formation of bicarbonate.

As the regeneration column for the taurate system operates in the same way as for conventional aqueous solutions, the condenser and the reboiler of the regeneration column have been simulated as equilibrium stages. In addition, because of the high operating temperature in the regeneration column (typically above 110°C), the rest of the column is also simulated assuming chemical equilibrium reactions. This hypothesis is similar to that used by Zhang et al. (Zhang et al., 2009) for an amine solution desorption section.

3.4 Enthalpy, Heat Capacity and Transport Properties

The enthalpy of formation of all compounds with the exception of liquid taurine and of the products of taurine reactions are available in the process simulator. For the taurine species, the enthalpies of formation have been introduced into the simulator using the values of the heat of dissolution of taurine and of the heat of absorption of carbon dioxide in the potassium taurate solution reported in Sanchez-Fernandez et al. (Sanchez Fernandez et al., 2013). The heat capacity of solid taurine has been introduced as a temperature-dependent expression whose parameters have been determined on the basis of experimental data obtained by Han et al. (Han et al., 2012), while the heat capacity of taurine in the liquid solution has been estimated on the basis of data presented by Sanchez-Fernandez et al. (Sanchez Fernandez et al., 2013). Due to lack of experimental data, the heat capacity of ions of taurine has been assumed to be equal to 0. The density, viscosity and diffusivity of carbon dioxide in the solvent, as estimated from calculations, have been employed after a comparison with the available experimental data of Kumar et al. (Kumar et al., 2001) and of Wei et al. (Wei et al., 2014; Wei et al., 2013).

4. Simulation

The considered CO_2 removal plant aims at purifying a flue gas stream from a 500 MW coal-fired power plant. A detailed description of the process can be found elsewhere (Sanchez Fernandez et al., 2013).

The simulated scheme is shown in Figure 1. The raw gas stream (*FLUEGAS*) is fed to the bottom of the absorption column, where carbon dioxide is removed by the amino acid solvent flowing counter currently (*SOLVENT*). Because solids formation cannot be estimated in the rate-based absorption unit (*ABSORBER*), a fictitious flash unit (*FLASH*) is added to the simulation to estimate the amount of solid taurine which is formed at the conditions of the absorption column. The stream *RICHNOSO* is a fictitious stream that represents the rich loading at the bottom of the absorption immediately prior to solids formation. The stream *RICHOUT* represents the actual stream exiting the bottom of absorption column, comprising the precipitated solid taurine in the rich liquor stream.

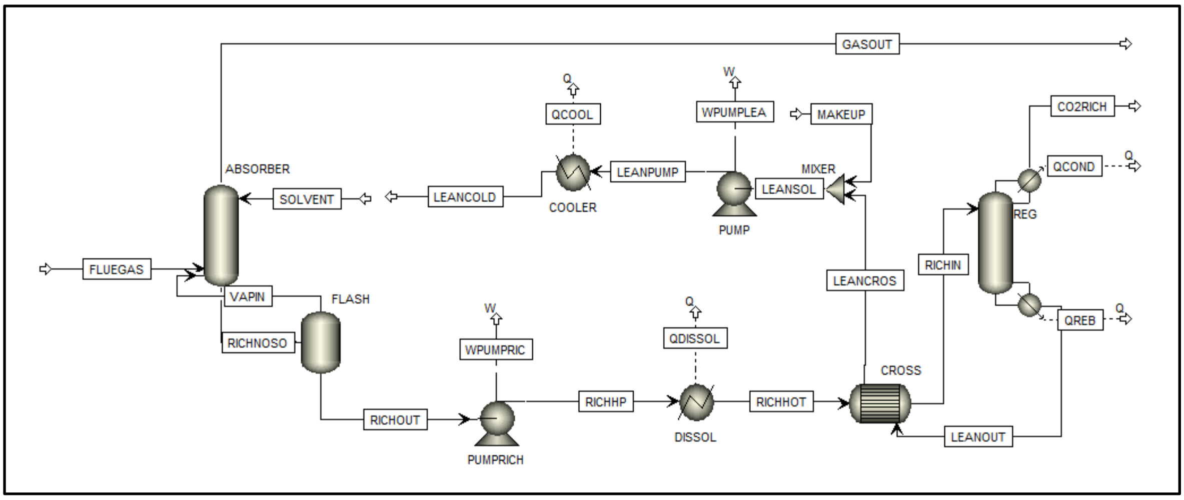

Figure 1: Flowsheet of the potassium taurate process considered in this paper.

In this paper, solids separation after the absorber has not been taken into account and the entire rich slurry is fed to a dissolution heat exchanger in order to dissolve the precipitated taurine. The *RICHHOT* stream is fed countercurrently with the *LEANOUT* stream in a cross heat exchanger (as is usually done for conventional amine absorption) and then fed to the regeneration column for removal of the absorbed carbon dioxide. The lean solvent, after make-up and cooling to 40 °C is recycled back to the absorption column.

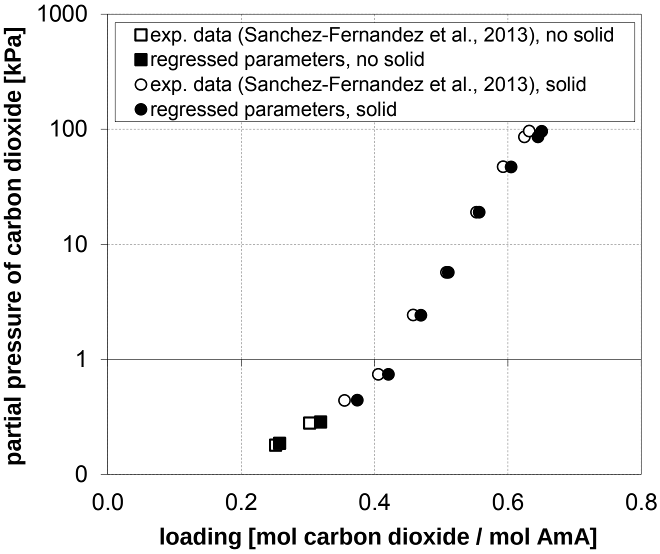

Figure 2: Vapour-Liquid-(Solid) Equilibrium of the CO_2 - potassium taurate system at 40 °C and 4 Molar with the chemical reaction set not involving taurine precipitation, for the representation of the equilibrium without solid formation (“no solid”) and with solid formation (“solid”).

5. Results

5.1 Representation of Vapor-Liquid-Solid Equilibrium

Figure 2 reports both the experimental data (Sanchez Fernandez et al., 2013) and the results of the calculations in this paper for the vapor-liquid equilibrium curve of the carbon dioxide in the potassium taurate solution, at 40 °C and 4 Molar. The temperature of 40 °C has been chosen because this is the temperature for which the most experimental data for the vapor-liquid equilibrium in the presence of solid taurine is available. It also represents the possible temperature in the absorption column, mainly at the top and at the bottom, since it is the temperature of the streams entering the column. The concentration of 4 Molar has been chosen in this paper as the typical concentration of this solvent (Raksajati et al., 2016; Sanchez Fernandez et al., 2013). This value is constant throughout the process simulated in this paper because it does not have a solid-liquid separator. As shown in Figure 2, a chemical reaction set not including salt precipitation can be used along with a rate-based model in the absorption column to provide a good representation of the vapor-liquid equilibrium of the system both with and without solid taurine formation.

5.2 Representation of the process

Absorption

Table 1 shows the results obtained from the simulation of the absorption column for 90% CO_2 removal from the feed flue gas by means of a solution of potassium taurate with a lean loading = 0.27 and a solvent flowrate determined in order to achieve the desired 90% CO_2 removal.

Table 1: Composition (apparent in the liquid phase and true in the solid phase) of taurine in the rich solvent at the temperature exiting the bottom of the absorber.

Parameter	RICHNOSO	RICHOUT
Apparent mole fraction of taurine in the liquid phase	0.1039	0.1016
True mole fraction of solid taurine	0	0.00244

The apparent mole fraction of taurine in the liquid phase comprises the sum of the mole fractions of the molecular species as well as of all the ionic species formed by reactions of taurine. It is a quick estimation of the total amount of taurine present in the liquid phase. Table 1 shows that (as expected) the apparent mole fraction of taurine in the liquid phase after solids precipitation (*RICHOUT*) is lower than the rich loading at the bottom of the absorption column immediately prior to solids formation (*RICHNOSO*). The true mole fraction of solid taurine is reported relative to the total composition of the mixed stream (regardless of the type of phase or species present). Generally, the amount of a precipitated salt depends on the composition of the mixture and on the temperature. For the case shown in Table 1, the amount of solid taurine is not large (0.2% solids formation) because the temperature of the stream exiting the absorber is approximately 68 °C. If the same stream (*RICHOUT*) was cooled to 40 °C the amount of solid taurine would be more than 6 times larger. The stream *VAPIN* has a negligible flow (of the order of magnitude E-6) and confirms that the same amount of carbon dioxide present in the stream *RICHNOSO* is present also in the stream *RICHOUT*, allowing for the co-presence of solid taurine. Recalling that the *FLASH* is a fictitious unit added to the simulation to estimate the amount of solid taurine which is formed at the conditions of the absorption column, it therefore operates at the same temperature and pressure of the fed stream *RICHNOSO* and is not an additional stage of separation. In this way the simulation is able to take into account the presence of solids in the estimation of the composition of the rich solution exiting the absorption section.

Desorption

A sensitivity analysis has been performed on the temperature of the rich stream entering the regeneration column. The diameter, height and packing type of the column, the operating pressure of the regeneration and the characteristics of the stream fed to it have been taken from Raksajati et al. (Raksajati et al., 2016) and results have been compared with this source. No comparison with experimental data has been done because no pilot or industrial columns have been built yet for this recently developed process. The obtained results show that as the temperature of the inlet stream increases, the amount of heat required in the reboiler decreases. This is in agreement with the expected trends. Because the overall heat balance on the column remains constant, any increase in sensible heat duty has to be balanced by a lower reboiler duty. Using the same inlet temperature as Raksajati et al. (Raksajati et al., 2016), a reboiler duty 14 % higher is obtained. To obtain the same reboiler duty, the temperature of the inlet stream needs to be 2°C higher, which is a difference in temperature of less than 0.6 %. Considering the differences between the short-cut model used by Raksajati et al. (Raksajati et al., 2016) and the rigorous simulation in this paper, the differences can be considered to be acceptable.

6. Conclusions

In this paper, CO_2 capture using a precipitating potassium taurate solution has been modelled in ASPEN Plus® using a combination of a packed tower and a fictitious flash unit to take into account the solids precipitation. Because of the operating conditions, the regeneration column is represented using chemical equilibrium reactions.

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