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Pilot plant results for a precipitating potassium carbonate solvent absorption process promoted with glycine for enhanced CO_2 capture

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ABSTRACT

The absorption performance of a glycine promoted precipitating potassium carbonate (K_2CO_3) solvent absorption process for carbon dioxide (CO_2) capture has been presented using a laboratory scale pilot plant. Glycine has been added as a rate promoter to 40–45 wt.% K_2CO_3 solutions to examine the enhancement of the CO_2 absorption process. The laboratory scale pilot plant has been designed to capture 4–10 kg/hr of CO_2 from an air/CO_2 mixture at a feed gas rate of 30–55 kg/hr. Performance data of the absorber including pressure drop, holdup and CO_2 removal efficiency has been collected from the pilot plant and presented for a range of operating conditions. The addition of glycine was found to improve the CO_2 recovery rate by up to 6 times whilst also slightly increasing the pressure drop and holdup measured in the packed absorption column which is likely due to a reduction in the surface tension of the solvent. Additionally, increasing the K_2CO_3 solvent concentration and operating with a higher CO_2 feed gas concentration were found to increase the CO_2 recovery results. Finally performance data from the absorber has been used to validate an Aspen Plus simulation of the system.

1. Introduction

Carbon capture and storage (CCS) of carbon dioxide (CO_2) has the potential to significantly reduce the greenhouse gas emissions from power stations that are fired by fossil fuels including coal and natural gas. In particular, CCS will be essential for continued power generation from coal where the CO_2 emission intensity (kg CO_2/kWh) is relatively high. A major challenge facing the large scale deployment of CCS is the cost, the major cost contributor being the cost of capture. One of the founding objectives of the CO2CRC has been to find ways of reducing this cost and from this objective a process known as UNO MK 3 has been developed. The UNO MK 3 process is a precipitating potassium carbonate (K_2CO_3) solvent absorption process for post-combustion capture of CO_2 emissions, which is expected to have a cost of capture less than half that of the leading amine-based process [1]. In addition to the low cost, the UNO MK 3 process has the added benefit of a significantly lower environmental impact than amine-based solvents as it is less volatile, non-toxic and less corrosive [2] along with the unique nature of delivering valuable fertiliser products (K_2SO_4 and KNO_3) and reducing the need for dedicated and expensive SO_x and NO_x removal equipment.

The UNO MK 3 process contains the absorption and regeneration stages of a standard solvent absorption process as shown in Fig. 1. However, unlike a standard liquid-based solvent system, a potassium bicarbonate ($KHCO_3$) precipitate is formed during absorption and subsequent cooling. The precipitate is then separated from the liquid phase for selective regeneration of the $KHCO_3$ species. In this way, less water is passed to the regeneration stage and thus drives down the energy requirements from over 3 GJ/tonne CO_2 for a liquid K_2CO_3 based system to less than 2.5 GJ/tonne CO_2 for a precipitating K_2CO_3 based system [1].

Detail on the reaction mechanism for K_2CO_3 with CO_2 can be found in our previous publications [3–5] whilst the overall reaction of CO_2 with K_2CO_3 to form $KHCO_3$ occurs as follows:

$$CO_2 + K_2CO_3 + H_2O \rightarrow 2KHCO_3. \qquad (1)$$

Although K_2CO_3 has a number of advantages over traditional amine based solvents one of the main challenges is the slow rate of reaction resulting in the need for large and therefore expensive equipment [6]. In order to improve reaction rates, promoters can be added to the system. Rate promoters such as piperazine [7,8], arsenious acid [9], boric acid [10,11], carbonic anhydrase [12] and amines [13–15] have all been proposed as rate promoters for improving the kinetics of CO_2 absorption into K_2CO_3. Of these, amines have shown the greatest improvement in reaction rates however they have disadvantages including high volatility, the tendency to degrade under industrial conditions and high toxicity [16,17].

More recently amino acids have been investigated as rate promoters as they have the same functional group as amines leading to similar

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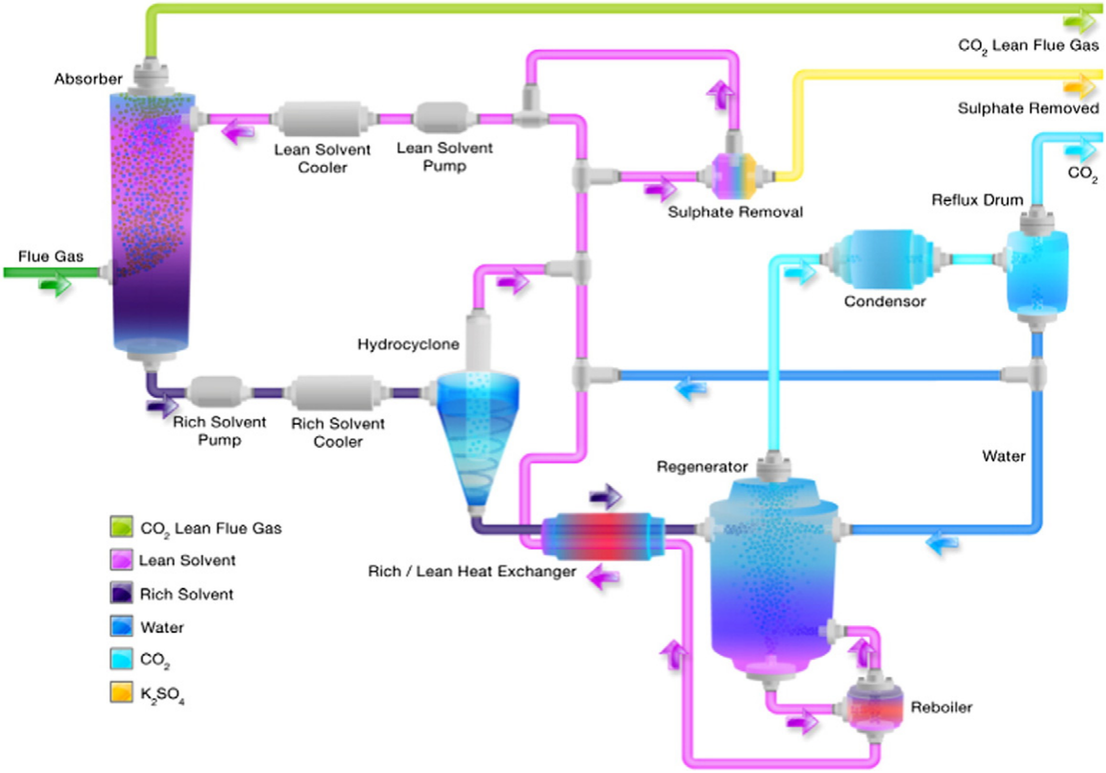

Fig. 1. UNO MK 3 process flow diagram.

reaction rates, however they are resistant to oxidative degradation, are non-volatile and have minimal toxicity [18]. The cost of amino acids such as glycine is also comparable to that of traditional K_2CO_3 promoters such as piperazine whilst glycine is approximately twice the cost of diethanolamine. Amino acids have been used in commercial acid gas removal processes such as the BASF Alkazid solvent process [19] and have been investigated in the laboratory for CO_2 capture applications [18, 20–22]. Using a wetted wall column our group has shown that addition of the amino acids glycine, sarcosine and proline can accelerate the overall reaction rate of CO_2 absorption into 30 wt.% K_2CO_3 by a factor of 22, 45 and 14 respectively [18]. In aqueous solutions, amino acids exist in three states: acidic, zwitterionic and basic (or deprotonated). As the acidic and zwitterionic states are much less reactive with CO_2, the deprotonated form of the amino acid is the preferred state for CO_2 absorption [22]. In order to deprotonate the zwitterionic form of the amino acid an equimolar amount of a strong base, such as potassium hydroxide (KOH), is added resulting in the following reactions [18]:

$$KOH_{(s)} \leftrightarrow K^+ + OH^- \tag{2}$$

$$^+NH_2R_1R_2COO^- + OH^- \rightleftharpoons NHR_1R_2COO^- + H_2O. \tag{3}$$

A number of researchers have shown that the deprotonated amino acid ($NHR_1R_2COO^-$) will react with CO_2 via a zwitterionic carbamate intermediate according to the following reactions [18,23,24]:

$$CO_2 + NHR_1R_2COO^- \rightleftharpoons {}^-OOCNH^+R_1R_2COO^- \tag{4}$$

$${}^-OOCNH^+R_1R_2COO^- + B \rightarrow {}^-OOCNR_1R_2COO^- + BH^+ \tag{5}$$

where B is a base. In our system, water (H_2O), carbonate ions (CO_3^{2-}), bicarbonate ions (HCO_3^-) and the deprotonated amino acid can all act as bases. Deprotonation of the zwitterionic glycine was achieved by adding an equimolar amount of a potassium hydroxide (KOH) to the solvent [18].

Over the last decade, the original concept of the carbonate process has been developed through an extensive experimental work programme [11,15,18,25–27] and pilot plant demonstrations in both pre-combustion and post-combustion capture [28–30] using mostly unpromoted K_2CO_3 solutions. Through additional process development and simulation the original process was further developed and the use of rate promoters was included in the process design. This has led to the construction and operation of two further pilot plants, one at The University of Melbourne and another at Hazelwood Power Station [4, 31]. The pilot plant built at The University of Melbourne is the focus of this study and results will be presented for pilot plant trials completed with glycine promoted K_2CO_3 solvent and an air/CO_2 gas mixture. Addition of glycine as a rate promoter to this precipitating K_2CO_3 process has the potential to greatly enhance the absorption performance of this process and provide valuable operating data which can be used for future process optimisation, simulation development and large scale design.

2. Experimental methods

2.1. Pilot plant

Performance data will be presented for a laboratory scale pilot plant which was designed to capture 4–10 kg/hr of CO_2 from an air/CO_2 feed gas rate of 30–55 kg/hr. The pilot plant has been built in the Department of Chemical and Biomolecular Engineering at The University of Melbourne. Both the absorber and regenerator columns have a diameter of 100 mm and a total height of 4.25 m and 4.6 m respectively. Both columns were filled with 10 mm diameter stainless steel Pall ring random packing and the absorber had 3 packed bed sections each 0.8 m in height whilst the regenerator had 3 packed bed sections up to 1 m in height. The saturated feed gas (10–25 vol.% CO_2, remainder air) was fed to the absorber at 50 °C at a flow rate between 24 and 30 kg/hr. An electric reboiler was used to heat the solvent for regeneration. The