Removal of Glycol from aMDEA

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Abstract

Mono ethylene glycol (MEG) buildup within Chevron's acid gas removal units (AGRUs) is causing declining system performance with current management strategies limited to gradual dilution during operation and complete amine replacement during turnarounds at a significant economic cost and logistical strain. This project investigates methods for separation of glycol from aMDEA. Through a review of available literature two potentially viable solutions were identified: batchwise removal of amine via ion exchange followed by subsequent separation of MEG, and selective adsorption of MEG contaminant to activated carbon beds. The proposed ion exchange method involves batchwise removal of amine followed by separation and disposal of the residual MEG solution. Ion exchange may prove prohibitively expensive with a prohibitively large footprint due to removal of the bulk species. MEG adsorption to activated carbon beds selectively removes the MEG contaminant from the amine resulting in a smaller footprint and reduced infrastructure requirements. Carbon regeneration is performed via methanol and water washing allowing for a circular economy of materials.

1. Introduction

Gas sweetening involves the removal of CO_2 and H_2S from natural gas prior to downstream processes. Acid gas removal units (AGRUs) are the most employed practice in industry and utilize amine absorption to strip the acid gases from the feed gas (Kohl & Nielsen, 1997; Rinker et al., 2000; Rufford et al., 2012). Primary and secondary amines react more rapidly with acid gases but possess reduced equilibrium loading capacity, a higher corrosivity and increased regeneration heat requirement to tertiary amines (Hajilary & Rezakazemi, 2018; Kazemi et al., 2014; Kohl & Nielsen, 1997; Pérez-Salado Kamps & Maurer, 1996; Rinker et al., 2000; Rufford et al., 2012). The addition of 'activator' amines is a common method to increase the absorption rate of tertiary amine systems while still maintaining the higher efficiency and lower regeneration costs and energy consumption (Closmann et al., 2009; Fouad & Berrouk, 2013; Hajilary & Rezakazemi, 2018; Kazemi et al., 2014; Kohl & Nielsen, 1997; Pourjazaieri et al., 2011; Rinker et al., 2000; Rufford et al., 2012; Ying et al., 2017). The existing plant AGRU system utilizes a piperazine (PZ) 'activated' methyl diethanolamine (aMDEA) solution, a tertiary amine with a secondary cyclic activator amine.

Monoethylene glycol (MEG) is used for hydrate inhibition and corrosion control but cannot be separated from the aMDEA during standard thermal regeneration of the AGRU due to its low volatility (Creek, 2012; Hajilary & Rezakazemi, 2018; Katz et al., 2013). Small quantities of

MEG buildup in the lean amine leads to declining system performance and increases the required AGRU regeneration temperatures leading to increased energy consumption and the risk of thermal amine degradation (Hajilary & Rezakazemi, 2018; Rochelle, 2012).

The plant under consideration is experiencing a consistent breakthrough of MEG to the AGRU resulting in decreased system performance over time. The current management strategies include 'bleed and feed', in which dilution of MEG contaminated amine is conducted by injecting fresh amine, and 'dump and replace' involving the complete replacement of the train's AGRU solution occurs. At current MEG buildup rates thousands of cubic meters of amine solution must be replaced every few years. This incurs multimillion dollar annual costs and significant waste processing prior to treatment and disposal. Complete replacement can only be conducted during busy turnaround periods, which puts significant strain on resources to manage the additional tasks without extended downtimes and lost production.

1.1   Operating Environment and Project Objectives

The plant operating environment Operating imposes tight environmental control and increased operational complexity to ensure preservation of the local environment. The available operation footprint is extremely restricted, and consequently minimal space is available for any proposed solutions for MEG removal. This project investigates options to separate MEG from contaminated aMDEA. Viable solutions include both complete MEG removal, or those capable of maintaining MEG content below critical operationally acceptable thresholds.

2.   Process

This project involved a broad literature review of multiple industries to capture a large range of potential solutions. The primary project driver is for technically viable solutions that would alleviate the strain on resources caused by current management practices. Solutions must also be suitable for the plant environment, which requires small and flexible footprints. Initial project stages were dedicated to identifying the physical and chemical properties of the relevant species that may be exploited to achieve separation. Technologies that were physically capable of achieving the required separation in the absence of any other system constraints were then determined. Through consultation with Chevron clients, system constraints were then progressively tightened to refine potential solutions based on practicality and applicability to the plant. Basic operating and design requirements were determined for the final two promising solutions, and further testing and research requirements were identified.

3.   Results and Discussion

Following investigation into the physical and chemical properties of MDEA, PZ and MEG the most exploitable properties to achieve separation were identified to be molecular size, boiling point and pka. Figure 1 shows a summary of findings for the various separation approaches investigated and their ultimate classification.
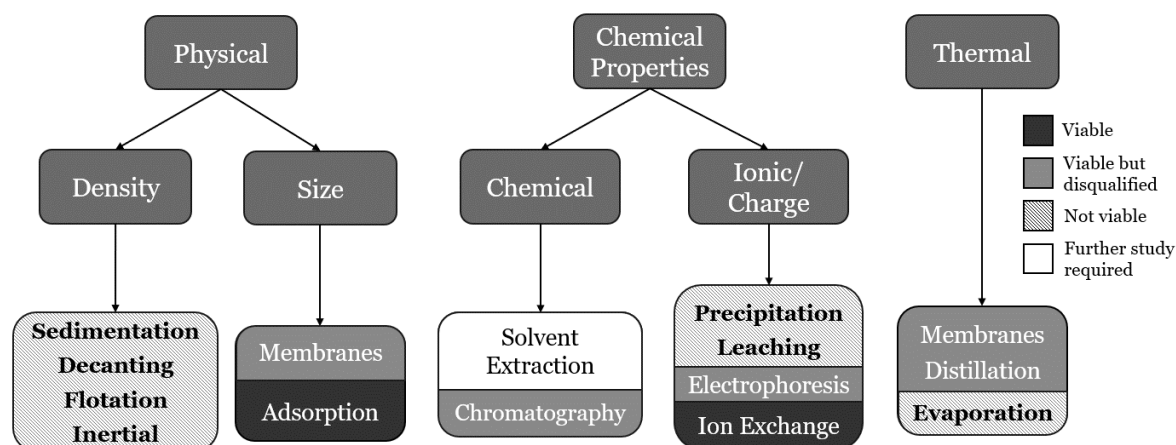
Figure 1   Summary of project findings with viability classifications.

Despite boiling points differing by approximately 50 °C thermal separation must occur under vacuum due to thermal degradation of amines occurring at temperatures significantly below their respective boiling points (Closmann et al., 2009; Hajilary & Rezakazemi, 2018; Katz et al., 2013; Rochelle, 2012). The increase in associated costs was determined by Chevron to be prohibitive, ultimately disqualifying such approaches. Due to the high miscibility of all species in water and a specific gravity difference ranging from 0.03-0.07 density-based separation approaches were also disqualified due to technical viability limitations (Smith, 2005; Towler & Sinnott, 2014). Membrane separation and chromatography were disqualified despite being technically viable due to the large scale required (McCabe et al., 1993; Smith, 2005; Towler & Sinnott, 2014).

Exploitation of charge-based separation methods is possible by protonating the amine species at pH below approximately 8.5 (Cummings et al., 1997; Hartono et al., 2014). A modified, large-scale electrophoresis separation approach was investigated as a method of partial separation (Jouyban et al., 2001; Mahaffy, 2015; Picó, 2020). Flowlines containing protonated amine would pass through a strong electric field, creating an amine concentration gradient from which a MEG rich side-stream could be extracted with minimal losses of aMDEA. This approach was ultimately deemed non-viable for application to Barrow Island due to the permanent piping and equipment requirements even under best case separation velocities.

A more promising method of ionic separation is through ion exchange to selectively remove protonated amine species. Cation exchange resins are widely used for amine elimination for wastewater treatment processes for compounds such as ammonia due to being a eutrophication causing species (Groves Jr, 1984; Jorgensen & Weatherley, 2003; Stenholm et al., 2006). Carboxylic acid resins with Cu^{2+}, Na^+ and H^+ exchange ions have been shown to be highly effective at amine removal in both laboratory scale and industrial water treatment (Groves Jr, 1984; Stenholm et al., 2006; Yoshida & Kataoka, 1987). Moderate temperatures and atmospheric pressures may be used, with smaller resin beads showing improved rate performance by overcoming diffusion limitations at the cost of increased pressure drops across the packed bed (Fu et al., 2020; Ramaswamy et al., 2013; Wang et al., 2015). Operating pH is required to be sufficiently low that complete amine species protonation has occurred, ensuring peak performance and minimal amine losses (Ding & Sartaj, 2016; Lin & Wu, 1996).

Resin regeneration can be performed through washing of the packed bed with a high concentration solvent, with the required solvent dictated by the chosen resin exchange ion (Jorgensen & Weatherley, 2003; Kortschak et al., 1949; Lin & Wu, 1996; Stenholm et al.,

2006). Batchwise operation would be required with disposal of MEG solution occurring following amine removal which may be recycled into operation. Due to the required system scale this approach would most likely be employed as a method of maintaining MEG below critical limits instead of complete MEG removal.

Molecular sieve adsorption represents a promising potential solution for removal of MEG contaminants. Activated carbon adsorbents show promise due to their hydrophobicity, which can be increased through careful heat treatment during preparation, and their affinity for hydroxyl containing compounds such as glycols (Aworn et al., 2009; Chinn & King, 1999a; Fortea et al., 2021; Kameda et al., 2020; Pendleton et al., 2002; Pietrelli, 2013). The proposed adsorption process may integrate into the existing infrastructure as a standalone unit allowing for maximum flexibility and no disruption to existing operations. The system can operate in both batchwise and continuous mode both during and outside of turnarounds as required. Ambient temperature and pressure conditions were shown to produce efficient MEG adsorption in laboratory testing (Jalili et al., 2018; Puri et al., 1979). A minimal impact of pH is expected for MEG adsorption through extrapolation of polyethylene glycol experiments; however, laboratory testing is required to confirm these assumptions (Gajdos et al., 2007).

Experimental MEG loading capacities suggest that relatively small beds can maintain operational MEG levels without significant impact on the plant footprint (Aworn et al., 2009; Fortea et al., 2021; Jalili et al., 2018; Kameda et al., 2020; Puri et al., 1979). Further investigation is required into the potential application of mobile carbon beds for batchwise treatment that would eliminate the requirement for any permanent infrastructure installation. Literature shows organic solvent regeneration using methanol washing would be the most effective means of carbon regeneration and may be conducted at ambient conditions with minimal adsorbent losses (Chinn, 1999; Chinn & King, 1999b; Cooney et al., 1983; Guo et al., 2011; Larasati et al., 2021; Martin & Ng, 1984; Zanella et al., 2014). Rapid regeneration rates allow for a singular bed to be used without requiring additional standby infrastructure (Cooney et al., 1983). Following solvent desorption, water washing liberates the adsorbed methanol allowing the bed to be cycled back into operation with both methanol and water capable of being recycled through simple distillation (Cooney et al., 1983; Guo et al., 2011).

4. Conclusions and Future Work

Two potentially viable solutions have been identified in this project for the removal of MEG from Chevron's aMDEA AGRU solutions; batchwise removal of bulk amine phase via ion exchange followed by subsequent separation of MEG, and selective adsorption of MEG contaminant to activated carbon beds. Both solutions utilize proven technology, however neither has been used for this given application and scale giving a predicted Technology Radius Level (TRL) of 5-6. Scaleup testing and pilot plant testing are therefore required to determine the accuracy of assumptions made during this project based on available literature research.

The ion exchange approach utilizes cation exchange resins to remove the bulk amine species followed by disposal of resultant MEG solution. Removal of the bulk phase may result in being prohibitively expensive and a large footprint requirement unsuited for the plant. Adsorption presents the most promising approach, utilizing activated carbon beds to selectively remove MEG resulting in a smaller footprint and amine losses. Methanol and water solvent washing allows for carbon regeneration and recycling and reduces the required material transportation to site. Further investigation is required into the potential application of mobile carbon skids for batchwise treatment without permanent infrastructure development onsite.

6.   References

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