## **Abstract**

Chemical absorption with amine solvent is the most dominated commercial technology adapted for CO<sub>2</sub> capture from power plant to mitigate the climate change and global warming issues. However, significant energy consumption and irreversible solvent degradation are the major unsolved challenges occurred in the amine-based post-combustion capture (PCC) process. It is therefore essential to develop new solvents and advanced technologies to overcome these drawbacks of conventional alkanolamines. In this paper a novel thermomorphic biphasic solvent (TBS) system has been studied as one of the alternative solutions to improve the solvent-based PCC process.

A series of screening experiments have been conducted to select suitable lipophilic amines as activating components for CO<sub>2</sub> absorption. The influence of molecular structure on absorption and desorption characteristics has also been investigated to predict and design potential lipophilic amine absorbents. According to the performance parameters, the selected lipophilic amines have been classified into two categories: absorption activator, for example N-methylcyclohexylamine (MCA) with rapid reaction kinetics, and regeneration promoter, for instance N,N-dimethylcyclohexylamine (DMCA) exhibiting excellent regenerability. Amine molecules with an α-carbon branch such as 2-ethylpiperidine (2-EPD) are of great interest due to their fast reaction rate and good CO<sub>2</sub> absorption capacity. To meet the selection criteria of the ideal solvent for chemical absorption, solvent recipes have been optimised by blending two or three amines and evaluated in a 100 mL glass bubble column with varying temperatures from 25 to 85 °C and CO<sub>2</sub> partial pressures between 4-100 kPa. The formulated TBS absorbents have exhibited rapid reaction kinetics, high cyclic CO<sub>2</sub> loading capacity, excellent solvent regenerability, moderate energy demand and low solvent degradation.

However, the undesired heterogeneous solution formed in absorber and evident volatile losses represent new challenges for lipophilic amines. With addition of a small amount of solubiliser such as 2-Amino-2-methyl-1-propanol (AMP), the phase change temperature has been increased dramatically and a homogeneous solution can thus be employed in absorption. Such solubilised biphasic solvent, e.g. a blended absorbent comprising DMCA+MCA+AMP, forms a single phase at 40 °C in the absorber and converts to two phases at an elevated temperature of 80 °C in the desorber. Therefore, a conventional absorption column can be employed for CO<sub>2</sub> capture using TBS without

any modification. To eliminate the issue of solvent vaporisation loss, an additional scrubbing unit with high boiling point organic solvent has been proposed to recover the vapour of lipophilic amine exhausted with the treated gas at the top of absorber. Additionally, the integration of an inter-stage cooling system into the absorption column has also been suggested for not only reducing the vaporisation losses but also enhancing the  $CO_2$  loading capacity.

Further investigations on solvent degradation have found the thermal degradation of lipophilic amines is minor owing to the lower desorption temperature required, typically 90 °C, compared to that for conventional stripping process of over 120 °C. The oxidative degradation of absorption activators, e.g. MCA, is significant, but it is negligible for regeneration promoters such as DMCA. Ketonisation and oximation were observed as the main reactions for MCA, while methylation and demethylation occurred with DMCA. The optimised solvent recipe DMCA+MCA+AMP exhibited a good chemical stability against both thermal and oxidative degradations.

To exploit the low-value heat for solvent regeneration in place of steam stripping, preliminary studies on new desorption techniques such as nucleation, agitation, ultrasound and extraction have been conducted. Nucleation accelerates the CO<sub>2</sub> releasing from the rich solvent, but hardly achieves deep regeneration at 80-90 °C; while agitation and ultrasonic desorption are both comparable to the stripping method, but only have insignificant mechanical or electrical energy consumption. The energy consumption in extractive regeneration is slightly higher than other intensification techniques, but it reduces the required desorption temperature to only 60-70 °C and cuts the exergy demand further with an extended freedom for integrating the process heating network or even using waste heat for regeneration purposes.

After optimisation of the solvent recipe and adaptation of novel regeneration techniques for CO<sub>2</sub> capture using TBS, bench scale experiments in a 40 mm I.D. glass packed column with 1 m height random packings have been carried out to investigate the influence of amine solutions on the packing wettability. Both the pressure drop and liquid hold-up of TBS were observed to be higher than for MEA at the same gas load factor, mainly due to the higher viscosity of the CO<sub>2</sub> loaded TBS solution. The viscosity of lean TBS solution is lower than that of alkanolamines, but it increases dramatically after CO<sub>2</sub> loading and rises to more than 10 mPa·s at room temperature. TBS solution presents a lower surface tension and a smaller contact angle on various metal and plastic materials compared to MEA. This thus directly indicates a good wettability of TBS on

packings even using certain plastic materials such as high-density polyethylene (PE-HD) in the absorption column.

Several modified process flow diagrams have been developed according to the various desorption techniques. The energy consumption has also been estimated for corresponding process flowsheeting. The main saving of the regeneration energy for TBS process is not in the heat of reaction but in the sensible heat and latent heat, since the reaction enthalpies for absorption activators are even higher than for the benchmark MEA, but the lower regeneration temperature enhances the process heat integration and significantly reduces the exergy demand. The outstanding performance parameters of such TBS system together with those novel intensified and energy-effective regeneration techniques make it one of the most promising candidates to assess the technical viability in further development work for future CO<sub>2</sub> capture processes.