Wydział Chemiczny Politechniki Śląskiej

Andrzej Wilk

Nowe wieloskładnikowe absorbenty aminowe wychwytu CO_2 – dobór i charakterystyka

Rozprawa doktorska wykonana pod kierunkiem

dr hab. inż. Hanny Kierzkowskiej-Pawlak, prof. PŁ

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Abstract

The reduction of anthropogenic carbon dioxide emissions has become one of the main global research topics in the last few years. One of the largest sources of this emission is the energy sector, which is responsible for over 30% of global CO_2 emissions. To capture this amount of CO_2, chemical absorption processes are considered the most promising. Although many potential absorbents have been tested for applications in this method, monoethanolamine solution is still one of the most widely used absorbents in the industry, which is due to the high efficiency and relatively low price of this solvent. The method of CO_2 absorption in the MEA solution, however, has a significant drawback - it has high energy demand. In the case of new more effective absorbents, it is possible to reduce the energy demand in the CO_2 separation node by up to 30%. For this reason, it is one of the most promising directions of research conducted in the field of CO_2 capture technology.

The main purpose of the research carried out in the presented dissertation was to develop the composition of the absorption solution for CO_2 removal from exhaust gases, based on a mixture of amines, which would be a better alternative to a 30% MEA aqueous solution. The most important criterion for assessing the efficiency of new absorbents was the lowest possible reboiler heat duty per unit of removed CO_2, with an assumed CO_2 removal efficiency of around 90%.

Within the theoretical part, a review of CO_2 reaction mechanisms in various types of amines was conducted. A review of industrially used or tested in the CO_2 absorption process amines was also carried out. The review also included multicomponent amine mixtures previously described in the literature. The main criteria for assessing the efficiency of amine absorbents have been defined. A critical analysis of the current state of knowledge in the field confirmed the need for the development of new absorbents based on amines that could be used commercially and that would reduce the energy consumption of the process while maintaining favorable absorption characteristics. Ideally, the new absorbent should have good absorption properties (high absorption capacity and absorption rate), low vapor pressure to reduce absorbent losses, low susceptibility to thermal and oxidative degradation, low toxicity and low price. Due to the multitude of parameters affecting the efficiency and functionality of potential absorbents, it is impossible to use an alternative solution to commercially used absorption solutions based only on single amine or one group of amines. Therefore, detailed research is needed to develop the composition of new absorption solutions that would combine the desired characteristics of each of the amine groups.

Within the experimental part, tests were carried out as part of three main research tasks: (1) laboratory tests of basic properties of two-component systems and multi-component solutions, (2) laboratory tests of the CO_2 capture process (continuous absorption-desorption system) on selected absorption solutions; (3) pilot tests of the CO_2 capture process in a plant working on a real power plant. Based on the results of laboratory tests of basic parameters of amine solutions, prospective solutions were selected for testing in the laboratory stand for testing the absorption-desorption process. Several multi-component solutions showed more advantageous features than the MEA solution, which proved that it is possible to formulate a solvent alternative to monoethanolamine, based on a mixture of commercially available amines. The use of sterically hindered amine systems with the addition of primary and/or secondary amines significantly improved the rate of carbon dioxide absorption in comparison to a 30% MEA solution. A clear improvement in the absorption rate was also observed when some of the water in the solution was replaced with an organic liquid. A solution with the composition of 15%MEA-20%AMP-20%NMP-2%PZ had a higher absorption rate and equilibrium absorption capacity than 30% MEA. Equally favorable parameters were demonstrated by the solution based solely on the sterically hindered amine system with the addition of fast-reacting piperazine. The 30%AMP-10%PZ system has a much higher operating capacity and absorption rate than a 30% MEA solution. The results of laboratory tests of the CO_2 capture process in a continuous absorption-desorption system were consistent with the results of basic parameters of amine absorbents tests. MEA-AMP-NMP-PZ and AMP-PZ systems proved to be more effective absorbents than MEA. Depending on the plant operating parameters, energy consumption was even about 25% lower for a multi-component solution in comparison to the reference MEA solution. The results of pilot studies confirmed the better efficiency of the AMP-PZ solution and MEA-AMP-NMP-PZ compared to the MEA solution in the process of removing CO_2 from real flue gas from coal boilers. The use of AMP-PZ solution results in a significant reduction of energy consumption for regeneration and improvement of CO_2 capture efficiency. Also for the MEA-AMP-NMP-PZ solution, the obtained parameters are more favorable than for the 30% MEA solution for lower L/G ratios, which is an additional advantage. The AMP-PZ solution was characterized by a 9% lower reboiler heat duty than in the case of the most favorable result obtained for a 30% MEA solution (3.76 MJ/kg CO_2). For the MEA-AMP-NMP-PZ solution, the lowest value of reboiler heat duty was 8% lower than for the monoethanolamine solution.

Measurements made in the pilot plant in a wide range of operational parameters, supplemented with thermal balances of the entire system, provide new data important to assess the potential for energy savings and reduction of CO_2 capture costs.