



Degradation study of piperazine, its blends and structural analogs for CO₂ capture: A review



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ABSTRACT

Postcombustion carbon dioxide (CO₂) capture using amine scrubbing is an emerging technology to mitigate CO₂ emissions. Benchmark amines used in this technology are monoethanolamine (MEA), methyldiethanolamine (MDEA), and diethanolamine (DEA). Amines undergo irreversible reactions, resulting degradation of the solvent under process operating conditions. Degradation of solvent may create environmental concerns, increased costs as well as corrosion in the process equipment. Piperazine (PZ) has been investigated as a novel amine solvent for CO₂ capture. It has high CO₂ capture capacity and absorption rate with thermal and oxidative degradation resistance. This study discusses the thermal and oxidative degradation of PZ under process operating conditions. A critical review of various parameters, such as the effect of temperature, amine concentration, CO₂ loading (α), partial pressure of oxygen (O₂) and presence of metal ions on rate of degradation has been reported. Chemistry of degradation products and mechanisms of degradation of PZ are reported for better understanding of PZ degradation kinetics. In addition, degradation of PZ blends, structural analogs, and diamines is focused, and behavior of their degradation is highlighted. Furthermore, kinetics of formation and degradation of nitrosamines through PZ is also discussed.

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1. Introduction

Amines usage for gas sweetening started in early 1930s (Bottoms, 1933). During last few decades, CO₂ emissions increased globally which have enhanced the development of postcombustion CO₂ capture (PCC) technology (Rochelle, 2009). Amine-based CO₂ capture using amine scrubbing technology is known as one of the promising technologies for CO₂ capture (MacDowell et al., 2010; Mangalapally et al., 2009). Expected energy required for an advanced amine systems for CO₂ capture is about 220 kilowatt hour per ton (kWh/ton) CO₂ removed (Rochelle et al., 2011). The most conventional amines used in this technology are monoethanolamine (MEA), methyldiethanolamine (MDEA), and diethanolamine (DEA) (Dumée et al., 2012; Lowe et al., 2009; MacDowell et al., 2010). These amines undergo irreversible reactions due to reactions with acidic gases (CO₂, H₂S, COS, CO, SO_x, and NO_x), elevation of temperature, and oxidation (Freeman et al., 2010a; Goff and Rochelle, 2006; Islam et al., 2010, 2011; Lepaumier et al., 2009; Wang et al., 2011). Estimations show that the solvent

(MEA) make up accounts for around 10% of the total CO₂ capture cost (Rao and Rubin, 2002).

Efficient use of the technology primarily depends on the selection of viable solvent. The suitable solvent should have high CO₂ capture capacity, high CO₂ absorption rate, low thermal and oxidative degradation rate, and low volatility with appropriate physical characteristics (Boot-Handford et al., 2014; Freeman and Rochelle, 2012b). A number of new amines and their blends have been examined under different conditions to recognize a stable solvent system with promising CO₂ capture properties (Hilliard, 2008; Idem et al., 2005; Namjoshi et al., 2013). PZ and its blends have been found as effective and stable amine solvents as that of alkanolamines and others (Dugas and Rochelle, 2009; Freeman, 2011; Freeman and Rochelle, 2011, 2012b; Li et al., 2013b; Namjoshi et al., 2013; Rochelle et al., 2011).

Previously, PZ has been used as a CO₂ capture promoter in blends with different amines in small concentrations (Bishnoi and Rochelle, 2002; Cullinane and Rochelle, 2006; Zhang et al., 2001). However, at present it is established that PZ alone can be used as an alternative to MEA due its favorable CO₂ capture properties and thermal and oxidative degradation resistance (Freeman et al., 2009, 2010a,b). PZ has exhibited thermal stability up to 150 °C and oxidation stability in the presence of O₂, CO₂, and metal ions, like Fe²⁺, Cr³⁺, and Cu²⁺ (Alawode, 2005; Li et al., 2013b; Freeman,

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