

## CHAPTER I

### INTRODUCTION

Nowadays the global warming is one of the biggest problems concerned because there are several strong impacts on environmental and climate changes. The main reason of global warming is greenhouse gases (GHG) emissions caused by human activities, especially in a sector of energy industry. Approximately 86 % of the world's primary energy is currently derived from the use of fossil fuels in a form of oil, natural gas and coal (Hogan and Cleveland, 2014). Combustion of fossil fuel for energy, especially low cost energy from coal used in power plants produces high concentration of carbon dioxide (CO<sub>2</sub>) in flue gas stream.

Post-combustion CO<sub>2</sub> capture (PCC) is the current and most attractive technology based on chemical absorption with aqueous amine solutions for separation and capture of CO<sub>2</sub> from flue gas streams (Idem *et al.*, 2006; Rochelle *et al.*, 2009). In this process, alkanolamines are commonly used. Monoethanolamine (MEA) is the most extensively used solvent due to high reactivity to CO<sub>2</sub> in the absorption process. However, the significant disadvantage of MEA solution in the CO<sub>2</sub> capture process is degradation of MEA due to undesired side reaction with CO<sub>2</sub>, oxygen (O<sub>2</sub>) and other contaminants in the flue gas stream (Supap *et al.*, 2006, 2011). There are two main types of MEA degradation, oxidative and thermal degradations. The oxidative degradation occurs due to the presence of O<sub>2</sub> in flue gases. A major MEA oxidative degradation product is  $\alpha$ -amine acetaldehyde which is further oxidized to carboxylic acids, such as formic acid, acetic acid, glycolic acid, oxalic acid, and succinic acid. Concentrations of these carboxylic acids reported can be as high as exceeds 500 ppm (Verma *et al.*, 2009). These carboxylic acids can react with amine group in MEA structure to form heat stable salts (HSSs). The thermal degradation occurs in the stripper and reboiler of the CO<sub>2</sub> capture unit where the temperature is in a range of 110-150 °C and high CO<sub>2</sub> partial pressure (Rochelle, 2012). A major MEA thermal degradation product is carbamate which can be transformed into 2-oxazolidone. Carbamate and 2-oxazolidone can react to form other degradation products (Polderman *et al.*, 1955; Yazvikova *et al.* 1975; Supap *et al.*, 2011; Gouedard *et al.*, 2012).

The major unwanted MEA degradation products are N-(2-hydroxyethyl)-acetamide (HEA), N-(2-hydroxyethyl)-imidazole (HEI) and N-(2-hydroxyethyl)-succinimide under oxidative degradations, and 2-oxazolidone (OZD), N-(2-hydroxyethyl)-ethylenediamine (HEEA) under thermal degradations. These MEA degradation products of both oxidative and thermal degradation are called neutral MEA degradation products which are the main identified degradation products (Strazisar *et al.*, 2003; Supap *et al.*, 2006, 2011; Lepaumier *et al.*, 2009a, 2011a; Gouedard *et al.*, 2012; Rochelle, 2012).

The MEA degradation products have no ability to absorb CO<sub>2</sub>, can react with MEA, and reduce efficiency of MEA to absorb CO<sub>2</sub>. In addition, they introduce corrosion, foaming, and fouling in the absorption process (Supap *et al.*, 2011). They must be removed from the MEA solvent. Distillation is a technique normally employed to remove the degradation products in a reclaiming process and regenerate MEA for reuse. In the distillation, water is evaporated, followed by MEA and other volatile products, and the unvolatile degradation products at the distilled temperature is left as a residue, so it requires large amount of energy to evaporate large amount of water and MEA for reuse. The cost of energy used in MEA capture process, is estimated 15–37% of the net power output of the plant (Drage *et al.*, 2008). Therefore, several techniques have been developed to separate degradation products and minimize the heat consumption such as 1) electrodialysis and membranes are used to allow selective passage of anions and cations under an electric field. However, selecting this technology may concern the fouling of membrane and overall economics, 2) ion-exchange can also reduce MEA degradation product in amine to be a very low level (0.5 %wt. as amine) (Verma *et al.*, 2009) and 3) Liquid-liquid extraction may be shortly called liquid extraction or solvent extraction. It is a low energy process used for chemical separation recovery and purification in many industrial applications, such as biochemical and pharmaceutical separations, organic and biofuels separation, waste and wastewater treatment (Kislik, 2012) etc. The solvent extraction includes two phases which one phase is an aqueous solution containing one or more solutes to be removed contacting with the second phase which is an organic solvent and immiscible with the aqueous phase

The liquid extraction was a novel separation technique applied to the CO<sub>2</sub> capture application to separate degradation products by a research group in Canada (Akkarachalanont *et al.*, 2012). In this work, the liquid extraction of the neutral MEA degradation products, *i.e.* imidazole, N-(2-hydroxyethyl)-acetamide, 2-oxazolidone and N-(2-hydroxyethyl)-succinimide studied using quaternary amine Aliquat 336 in 2-ethyl-1-hexanol solvent. Effects of experimental conditions, such as MEA solvent, CO<sub>2</sub> and temperature were investigated.