INTRODUCTION

1.1 Global environmental issues and CO_2 emission

The global energy demand has been increasing day by day due to rapid industrialization and urbanization which leads to create various environmental issues. The most important environmental issue as an anthropogenic climate change as a result of global warming has emerged in the world and its effect on environment, earth, human being, animals and plants in terms of floods, droughts, storms, heat waves, sea-level rise, water systems disruption, and plant crop growth alteration, etc. have been seen every year in the world (Solomon et al., 2009). This major issue has been created due to the increased concentration of greenhouse gas (GHG) such as carbon dioxide, methane, nitrous oxide and F-gases, etc. into the atmosphere and its contribution of GHG component as well as sources has been also presented in figure 1.1.

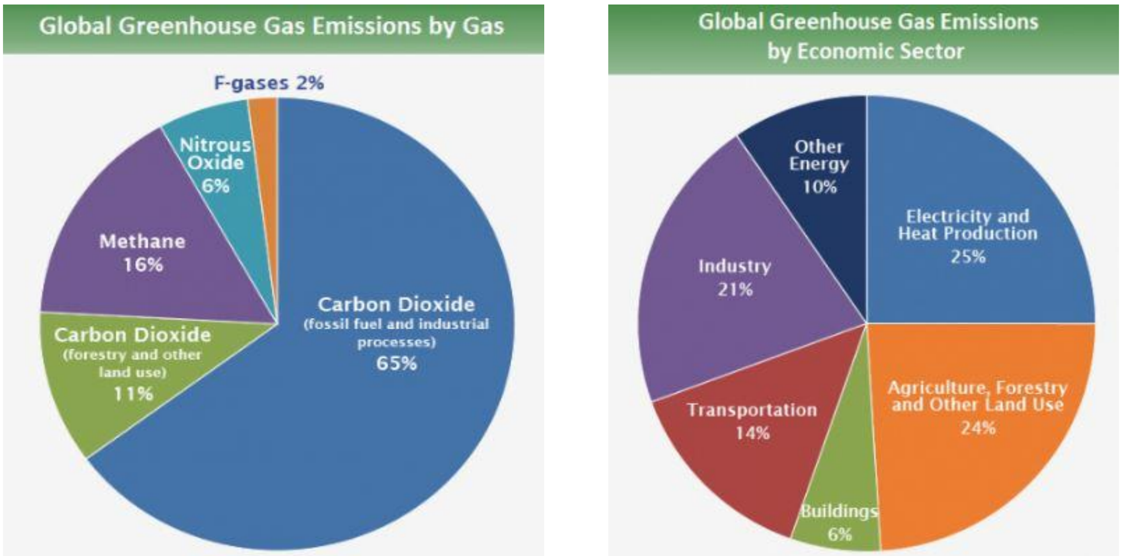

Figure 1.1 Global greenhouse gas component contribution and its sectors (IPCC, 2014)

Among these gases, CO_2 has a major contribution to raise this problem because it has been increased continuously into the atmosphere in the form of waste gas streams from different anthropogenic sources. The fossil fuel based thermal power plants, iron and steel industry, cement plant, natural gas processing unit, oil refinery unit, chemical, and petrochemical manufacturing units are shown significant contribution to the CO_2 emission at a global scale (Wilcox, 2012). The fossil fuel based thermal power plant alone plays an important role in CO_2 emission of approximately 40% of global emission because 85 % of thermal power-plants are based on fossil-fuel which generates electricity across the globe (Wilberforce et al., 2016). Normally, the coal-based thermal power plant for electricity generation a capacity of 500 MW emits 2.5-3.5 Mt CO_2 each year. Also, the global emission was reached more than 32 Gt CO_2 up to 2018 and India has third position towards the contribution of CO_2 emission of 7 % of total CO_2 emission. The various sector such electricity and heat generation, industry, transport, building and others have contributed about 41%, 24%, 24%, 8% and 11%, respectively (IEA, 2019). According to the International Energy Agency (IEA), the world's total primary energy supply is expected to increase by approximately 45% from 2006 to 2030, out of which global coal consumption is expected to increase by 60% (IEA, 2019). Furthermore, the coal-based thermal power plant has also a major role in producing electricity in India and it corresponds to more CO_2 produced. Due to continuous emission from all anthropogenic sources, the atmospheric CO_2 concentration was reached to 408 ppm in 2018, but the concentration of CO_2 was 280 ppm in 1850 (IEA, 2019). So, from the environment point of view as well as an economic benefit, a strong action must be taken for reduction of CO_2 emission to safe our upcoming future.

1.2 CO_2 reduction techniques

The basic concepts to reduce the CO_2 concentration level are the use of efficient energy, the progress of renewable energy usage and enhancing CO_2 sequestration (Yang et al., 2008). The first concept used for the reduction of CO_2 emission from a fossil-fuel based power plant is an improvement of the fuel system from conventional to novel fuel with less emitting of CO_2 but it has low possibility in very short duration of time (Herring, 2006). A second concept is uses of as renewable energy in the form of solar energy, wind power energy and nuclear energy, etc., but solar energy totally depends upon sun radiation, wind energy depends upon nature or climatic conditions and radioactive emission from nuclear plant is dangerous for human being (Patiño et al., 2008; Serrano-Ruiz and Dumesic, 2011). So, for the capturing of CO_2 from gas streams to reduce the CO_2 concentration level into the atmosphere, carbon capture and sequestration (CCS) technique is the best option for reducing the anthropogenic CO_2 emission because captured CO_2 can be further used in the value-added products as well as enhancement of oil recovery as multiple economic benefits (Kim et al., 2017). The captured CO_2 has been also used in urea production, beverage carbonation, pulp and paper processing, polymer processing, inerting, fire suppression, metalworking, water treatment, concrete curing, carbonate mineralisation, etc. (Míguez et al., 2018). Furthermore, CCS technology was widely used in the industries as natural gas processing, fertilizer production in the year 1972 and 1982, respectively in the world (Abu-Zahra et al, 2013). Some other industrial processes such as cement production and steel-making have the only technological option (CCS) that can help in the reduction of CO_2 emission in the atmosphere. Recently, two CCS units have been also installed in coal power plant such as Boundary Dam Canada (Saskatchewan) in 2014 and Petra Nova, USA (Texas) in 2017 of capture capacity 1 and

1.4 Mt CO_2 per annum with 90% capture efficiency, respectively and its captured CO_2 has been further used in the enhancement of oil recovery (Global CCS Institute, 2018).

In India, some small scale capture units are working in chemical and fertilizer industry such as Tuticorin Alkali Chemicals and Fertilizers Limited Tamil Nadu, Solvay Vishnu Barium Pvt. Ltd. Telangana, and Carbon Clean Solutions Company has provided the technology to capture CO_2. But in India, there are no CCS units has installed for thermal power plants to remove the CO_2 from flue gas to limit the CO_2 concentration in the atmosphere (Global CCS Institute, 2018).

The Paris agreement aims to limit the global surface temperature increase to below 2°C above pre-industrial levels. To meet this target with continued coal use, methods for removing CO_2 emissions from coal-fired power stations are required. Recent studies suggest that the 2 °C target will not be achievable without the deployment of large-scale carbon capture and storage (CCS) (IPCC, 2014).

CCS technology can be categorized into three parts including pre-combustion carbon capture (coal gasification, synthesis gas, etc.), post-combustion capture (absorption, membranes, etc.), and oxy-fuel combustion. Among these, post-combustion is most matured option because it offers flexibility and retrofitting to the power plant under operation. Numerous numbers of technologies have been developed for CO_2 removal from flue gases. The major technologies include absorption, membranes, adsorption, and cryogenics (Rao and Rubin, 2002). In case of adsorption, the adsorbent after regeneration can be recycled in the process, but it requires high temperature and high energy for CO_2 desorption to regenerate the adsorbent (Ebner and Ritter, 2009). The advantage of membrane technology is to have maximum separation efficiency up to 80%, while the membrane stability at high flue gas temperature could be a crucial problem along with membrane fouling as well (Bernardo et al., 2009). Cryogenic distillation is a well-established technology for recovery of CO_2 without any chemical absorbent, operated at atmospheric pressure and its compatibility with both pre- and oxy combustion CO_2 capture. The drawbacks of cryogenic process are infeasible at low CO_2 concentration, requirement of high intensive energy in the process and operated at low temperature (Mondal et al., 2012). Absorption is the most commonly adopted option due to its higher CO_2 loading capacity, efficient CO_2 removal even at very low CO_2 levels present in the gas stream and easy absorbent regeneration to get concentrated CO_2 for reuse (Wang et al., 2011). At moderate temperature, most of the amines showed good CO_2 absorption capacity but the regeneration at low temperature is still a problem and thereby the cost of CO_2 capture becomes high. Therefore, from sustainability point of view the CO_2 capture and value addition is very beneficial for the process to be commercialized. As it discards the regeneration step and thereby reduces the overall cost of the process (Albo et al., 2015).

Absorption process is classified as either physical or chemical. The physical absorption of CO_2 provides easier regeneration process and less energy demanding but the solvent capacity strongly depends on partial pressure of soluble component in the gas. The chemical absorption of CO_2 provides higher absorption rates but its regeneration process normally requires more energy consumption. Also, the physical absorption is favourable at high partial pressures above 5-10 atm whereas the chemical absorption is favoured at lower partial pressure (Kohl and Nielsen, 1997). The selection of separation technology depends upon different factors such as CO_2 present in surrounding ambient conditions, and concentration of CO_2 in a gas stream (Cousins et al., 2011).

1.3 Amine-based absorption technology

Among various technologies, the post-combustion CO_2 capture based on absorption using chemical solvent particularly aqueous amine solution is well-established, robust, and most mature option because it possesses good absorption efficiency up to 90% CO_2 removal from the gas stream, handling a large volume of exhaust gas, retrofitting option, cost-effectiveness, and solvent regeneration option (Rao and Rubin, 2002; Ciferno et al., 2009; Xu et al., 2016).

Amine based absorption process is the prominent technology for CO_2 removal from exhaust gases such as those containing 3-5 mol % CO_2 for natural gas, 10-15 mol % CO_2 for coal-fired power plant and 20-30 mol % CO_2 in flue gases for iron and steel industry (Poplsteinova, 2004). This process is based on the reversible reaction of CO_2 with aqueous solution of amine based absorbents. The flue gas emitted from power plant is first cooled (and desulphurized) before entering to an absorption column where CO_2 reacts with the amine based absorbent at temperatures range of 40-60 °C. The regeneration of amine from CO_2 loaded absorbent takes place at a temperature range of 100-120 °C with nearly atmospheric pressure (Wilcox, 2012).

The operation cost is directly related to energy consumption for solvent regeneration in the CO_2 capture process. Approximately, 70-80% cost accounting in the regeneration of solvent, when conventional types amine solvent used in the CO_2 capture process, which is the major challenge of this technology for implementation at large scale (Feng et al., 2010). There are three common strategies for decreasing regeneration heat duty, as follows: development of energy efficient solvents, optimization of the process configuration, and design higher performance devices of heat and mass transfers (Wilcox, 2012). Keeping on the view of above, there is a need to investigate suitable amine solvents for CO_2 capture.

1.4 Amine solvent

The amine type solvents such as alkanolamine, alkylamine, and polyamine are used to remove CO_2 from various gas streams such as flue gas, blast furnaces gas, refinery off-gas, natural gas, and synthesis gas, etc. Approximately 90 % of the acid gases treating processes are based on amine absorbents due to their versatility and ability to remove acid gases to very low levels (Mandal, 2004). The conventional alkanolamine solvents MEA, DEA, DIPA, MDEA, AMP, and PZ, etc. have widely used in the CO_2 capture process (Kohl and Nielsen, 1997). But, these solvents used in the removal of CO_2 from gas streams have several drawbacks such as high energy requirement for solvent regeneration in case of primary amine (MEA), low absorption rate in case of tertiary amine (MDEA), limited solubility in case of polyamine (PZ) which decreases the efficiency of CO_2 capture plant (Mota-Martinez et al, 2017). To overcome this drawback and improvement in CO_2 capture process, an alternative solvent has to be developed for CO_2 capture by testing at laboratory scale using solvent screening method and further characterize to implement at pilot scale which will be further deployed at large scale for CO_2 removal from exhaust gas emitting from fossil-fuel based thermal power plants (Ebner et al., 2009). The efficient amine solvent for CO_2 capture has been developed or selected on the basis of an evaluation of performance parameters. The capture performance parameters are a major role in the rational design and operation to establish a gas treating unit for removing CO_2 from various exhaust gas streams. The important solvent performance parameters are solubility, absorption capacity, absorption rate, desorption capacity, desorption rate and cyclic capacity as well regeneration efficiency. The solvent performance parameters have the dependency on development of any novel efficient solvent because they affect the overall (capital and operation) cost of the CO_2 capture process (Davison, 2007). So, the aim of the present work is to develop an efficient solvent as amine blend alternative to the conventional amine solvent used for the CO_2 capture process. So, before the selection of amine solvent for present study, it is necessary to have a look on detailed literature studies available on amine or amine-based blend for CO_2 capture. The available literatures on amines or amine blends for CO_2 capture have been discussed in chapter 2.

Primary and secondary alkanolamines react with CO_2 to form more stable carbamates, so these require high heat for desorption corresponding to high solvent regeneration cost. The sterically hindered amines form less stable carbamate due to a large bulky group attached to the nitrogen atom. However, it is limiting CO_2 loading capacity i.e., 0.5 mol of CO_2 per mol of amine is a problem (Mondal, 2009). Tertiary amine cannot form carbamates with CO_2 which facilitates the CO_2 hydrolysis reaction forming bicarbonates as a final product with the CO_2 loading capacity of 1 mol of CO_2 per mol of amine (Mondal et al., 2012). Furthermore, tertiary amines have relatively slow reaction rate with CO_2, then the addition of small amounts of very fast-reacting amine like primary and secondary amine or diamine is necessary to enhance the overall CO_2 absorption rate (Kierzkowska-Pawlak et al., 2014). Diamine has more absorption potential than primary and secondary amine because it contains multiple amino groups in their chemical structure (Sutar et al., 2013). The role of diamines like PZ, AEEA, HMDA as a promoter for tertiary amines has proven to possess good potential for CO_2 capture (Vaidya and Kenig, 2008; Sutar et al., 2013). The various reaction mechanisms of CO_2 with alkanolamines have been discussed in details (Sánchez, 2016).