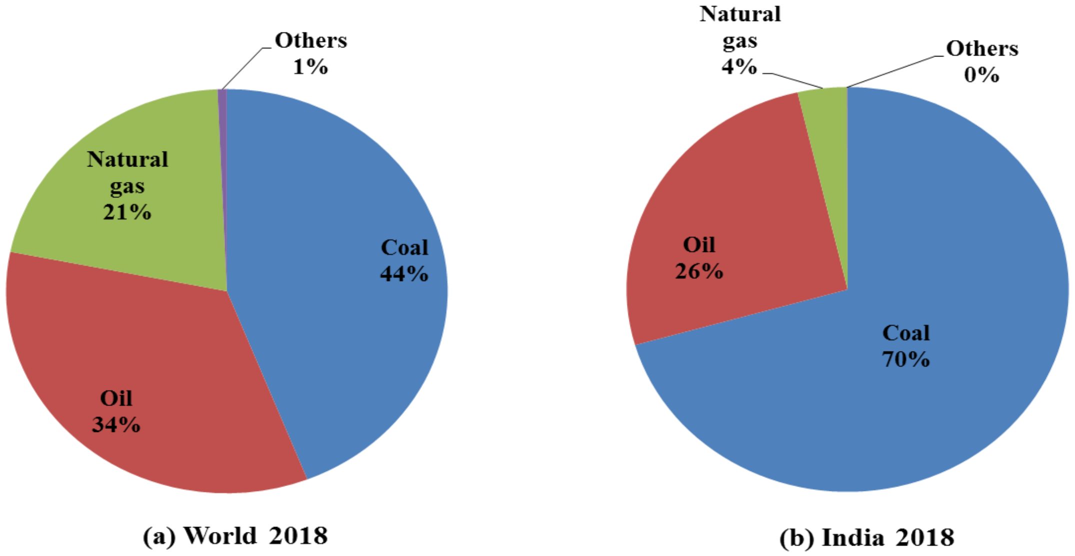
Chapter 1

Introduction

1.1 CO_2 EMISSION

The demand for energy has been increasing due to the increasing population of the country and the expansion of industrialization. According to the International Energy Agency (IEA 2016) the use of energy has been growing steadily since 1971. Most of the energy is consumed in transportation, industries and factories, power generation, and community sectors. In the current, maximum energy is supplied from conventional fossil fuel resources like petroleum oil, gas, and coal (Chen et al., 2019). Global, as well as Indian CO_2 emissions, are increasing day by day. A large amount of carbon dioxide (CO_2) is emitted into the environment due to the combustion of fossil fuels. Based on the IEA 2019 report, major CO_2 emission (44 % in the world and 70 % in India) was contributed by coal as an energy source in 2018. Contributions of different energy sources for CO_2 emission in 2018 are depicted in Figure 1.1. CO_2 emission by the world was increased 63.35 % from 1990 to 2018 while CO_2 emission in India increased more rapidly to 335.28 % during this period. It can be seen from Table 1.1 that the emission of CO_2 by coal combustion had increased very much in India (346.03 %) compared to the world (78.16 %) from 1990 to 2018.



(a) World 2018

(b) India 2018

Figure 1.1. Contributions of different major source of energy in CO_2 emission in 2018 (a) World, and (b) India (IEA, 2019).

Table 1.1. CO_2 emissions data (IEA, 2020)

	CO_2 emission (Mt CO_2) by fuel combustion						
Energy Source	World			India			% Contribution of India to the world in 2018
	1990	2018	% increment	1990	2018	% increment	
Coal	8288.00	14766.00	78.16	365.00	1628.00	346.03	11.03
Oil	8510.00	11415.00	34.14	151.00	595.00	294.04	5.21
Natural gas	3674.00	7104.00	93.36	14.00	83.00	492.86	1.17
Others	44.00	228.00	418.18	-	1.00	-	0.44
Total	20516.00	33513.00	63.35	530.00	2307.00	335.28	6.88

Although the share of India in global CO_2 emission was only 6.88 % in 2018 yet in the CO_2 emission from coal as an energy source, India emitted 11.03 % of CO_2 emission of the world.

1.2 CONSEQUENCES OF CO_2 EMISSIONS ON THE ENVIRONMENT

CO_2 gas is a greenhouse gas which contributes about 76 % of global greenhouse gas emissions (Hauman et al., 2014). Greenhouse gases are the cause of greenhouse effect. The greenhouse effect is the phenomena by which infrared radiation of a small wavelength from the sun can enter into the earth's surface but hot reflected radiation of a high wavelength cannot return completely which results in a warm lower-atmosphere. The greenhouse effect is one of the major causes of global warming. In the Intergovernmental panel on climate change (IPCC) 2014 report, it had been predicted that if greenhouse gas emissions continued then the global temperature will rise between 3.7 to 4.8 ^{o}C by 2100. It was reported that human-induced global warming reached approximately 1 ^{o}C above the pre-industrial level in 2017 (IPCC, 2018). In order to attain the limit of 1.5 ^{o}C temperature rise, it is required to reduce CO_2 emission by 45 % from the 2010 level by 2030. A revised target of less than 1.5 ^{o}C temperature rise has been given in the special report of IPCC (2018) and it was emphasized the need for further CO_2 gas emission reductions. Global warming (indirectly CO_2 gas emission) may result in adverse climate change, storms, floods, drought, sea-level rise, islands disappearance, and increased air pollution (Kumar et al., 2012).

1.3 CO_2 CAPTURE TECHNOLOGIES

CO_2 gas is emitted in the environment mainly due to the combustion of fossil fuels. The selection of CO_2 capture technology may depend on the types of combustion processes. Available CO_2 capture technologies are very costly (Blomen et al., 2009). Therefore, research and development efforts are going on to find an optimized method of CO_2 removal. There are mainly three technologies to capture CO_2 from the different combustion processes, known as, post-combustion, pre-combustion, and oxy-fuel combustion technology.

1.3.1 Post-combustion CO_2 capture: This technology captures CO_2 from the flue gas after fossil fuel combustion. Post-combustion technology is more mature than other available technology and it can be easily employed in existing power plants. This technology has been used at a small scale with a CO_2 capture rate of up-to 800 t/day. However, low CO_2 concentration can affect the CO_2 capture efficiency (Leung et al., 2014; Buhre et al., 2005).

1.3.2 Pre-combustion CO_2 capture: This technology removes CO_2 before the combustion of fossil fuel. Mainly coal and natural gas are pretreated by this process. For the coal and natural gas, pretreatment includes the gasification process and steam reforming, respectively, which forms syngas ($CO + H_2$) (Leung et al., 2014). The syngas further possesses water gas shift reaction and produce more hydrogen (H_2) and CO is converted into CO_2. This complete process can be shown by Eq. 1.1 to Eq. 1.3.

$$Coal \overset{gasification}{\Longrightarrow} CO + H_2 \qquad (1.1)$$

$$Natural\ gas \overset{steam\ reforming}{\Longrightarrow} CO + H_2 \qquad (1.2)$$

$$CO + H_2O \xrightarrow{water\ gas\ shift\ reaction} H_2 + CO_2 \qquad (1.3)$$

The high concentrated CO_2 gas from the gas stream (H_2 + CO_2) now can be captured by any CO_2 separation technique and H_2 is supplied as a fuel. This technology is more useful for new plants as retrofitting it in the existing power plants would require more modifications in the plant and may be very costly.

1.3.3 Oxy-fuel combustion: In this technology, pure oxygen is used for combustion instead of air. This process reduces the nitrogen (N_2) in the flue gas that affects the CO_2 capture process. Reduction of thermal NO_x is another advantage of this technology (Buhre et al., 2005). The major composition of the flue gases are CO_2, SO_2, water, and particulates. High SO_2 concentration in the flue gas may increase the corrosion problems of systems. Particulates matter is removed by using an electrostatic precipitator and SO_2 is removed by flue gas desulfurization method. The remaining gas stream contains mainly CO_2 and steam. Steam is removed by condensation and pure CO_2 can be captured, compressed and stored. Almost 100 % of the CO_2 may be captured by this technology because of its very high capture rates. However, this technology is less suitable for low-quality fuels like lignite coal (Zero Emissions Resource Organization, 2021).

1.4 CO_2 SEPARATION TECHNIQUES

There are many techniques to remove CO_2 from a gas mixture. Some popular and established techniques are discussed here.

1.4.1 Absorption technique: In this technique, CO_2 is removed from the flue gas by using a liquid absorbent. Based on the absorbent and CO_2 removal mechanism, absorption may be of two types. One is physical absorption and the other is chemical absorption. Physical absorption is a non – reactive process and depends on the CO_2 solubility in the solvent. It is preferred at high-pressure processes (Chakma et al., 1999). Rectisol , selexol, purisol, etc. are examples of physical absorbent for CO_2 removal (Sreedhar et al., 2017). If CO_2 absorption is taking place by mass transfer as well as chemical reactions simultaneously then this process is called chemical absorption. Aqueous alkanolamines are most widely practiced example for chemical absorption of CO_2 (Sumedh et al., 2013).

1.4.2 Adsorption technique: CO_2 gas is captured by a solid adsorbent on its surfaces by the adsorption technique. Molecular sieves, activated carbon, calcium oxide, zeolites, lithium zirconate, etc. are the examples of solid adsorbent that were used for CO_2 capture (Leung et al., 2014). CO_2 removal by adsorption techniques are primarily based on the pressure swing adsorption (PSA) and thermal swing adsorption (TSA) processes. These are established cyclic adsorption techniques that are commercially employed in many gas separations and purification processes (Ebner et al., 2009). In the PSA, CO_2 is adsorbed on the surfaces of a solid adsorbent at high pressure, which can be a swing to low pressure (for example at atmospheric pressure) to desorb the adsorbent and remove CO_2. In the TSA, the adsorbent is regenerated by increasing the temperature of the system (Leung et al., 2014).

1.4.3 Membrane separation technique: The membrane separation technique is based on the selective affinity of membrane material. Such types of membranes are used for CO_2 capture that allows only CO_2 to pass through it and other components of the flue gas excluded. PolyActive^{TM} and Poaris^{TM} are the most promising materials and commercially available (Kárászová et al., 2020). There are compelling development in membrane separation process have occurred for CO_2 capture (Sasikumar et al., 2018; Yan et al., 2019). But they are still required research and development to realize the potential of this technique. Low CO_2 concentration and pressure of the gas stream are the main difficulties to apply this technique to post-combustion CO_2 capture (Brunetti et al., 2010).

1.4.4 Cryogenic distillation technique: The cryogenic distillation is based on the phenomena of phase change. It is a gas separation technique in which components of a gaseous mixture are separated due to their different boiling points. This technique is used at very low temperatures and high pressure of the system. For CO_2 capture, flue gas is cooled to de-sublimation temperature (-100 to -135 ^oC), and then solidified CO_2 is removed from the flue gas (Leung et al., 2014). Solid handling, difficulties related to the two-phase flow, and the requirement of large heat exchangers with small temperature approach are some demerits of this CO_2 separation technique (Berger et al., 2018).

1.5 POST – COMBUSTION CO_2 CAPTURE USING CHEMICAL ABSORPTION TECHNIQUE

The concentration of CO_2 in the flue gas is between 3 to 20 volume % (partial pressure of CO_2 gas (p_{CO_2}) = 3 to 20 kPa at atmospheric pressure) and particularly in the coal-fired power plant's flue gas it is 12 to 15 volume % (p_{CO_2} = 12 to 15 kPa at atmospheric pressure) (Liu et al., 2020; Tsupari et al., 2013; Berstad et al., 2012). In these conditions, where the partial pressure of CO_2 is relatively low in the gas stream, CO_2 capture using chemical absorption is the most matured technique for CO_2 removal (Asif et al., 2018; Rochelle, 2009). A typical chemical absorption system required three elements i.e. absorber, chemical absorbent, and stripper. The CO_2-containing gas mixture comes in contact with an absorbent in the absorber. The CO_2 absorbs by lean absorbent and after CO_2 absorption, absorbent turns into a CO_2-rich solvent. Then CO_2-rich absorbent can be regenerated in the stripper and pure CO_2 can be collected at the top of a stripper. The regenerated lean absorbent is recycled back to the absorber for reuse to CO_2 absorption.

For post-combustion CO_2 capture, various types of absorbers like bubble columns, packed bed columns, rotating packed bed columns, tray columns, spray columns, etc. have been employed. Bubble columns have been reported as suitable absorbers for the study of CO_2 solubility at atmospheric pressure and for the initial screening of chemical solvents on the basis of CO_2 solubility. CO_2 solubility (CO_2 loading) can be defined as the ratio of number of moles of absorbed CO_2 and number of moles of total moles of absorbent. Because bubble column is simple in design and construction, has better control of the gas-liquid contact time, provides higher heat and mass transfer coefficients and better solid handling capacity (Sreedhar et al., 2017).

The chemical absorbents are mainly amines and alkanolamines, ammonia solution, amino acid salts, ionic liquids, etc. Several experimental studies have been published recently, in which aqueous ammonia was reported as an absorbent for simultaneous removal of CO_2, NO_x, and SO_x (Han et al., 2013; Resnik et al., 2013). A major drawback of using ammonia (NH_3) as an absorbent for CO_2 capture was the difficulty of regeneration of ammonia from ammonium bicarbonate. Other demerits of ammonia includes high evaporation rate of NH_3 and high concentration of NH_3 can cause of irritation in the eye, skin, and respiratory system (Budzianowski, 2011; Zhang and Guo, 2013).

Solutions of amino acid salts are formed more stable salts of carbamates and bi-carbonates in solution due to reaction with CO_2 that's why more energy is required for regeneration of solvent. This is a major drawback of amino acid salts as an absorbent for CO_2 capture (Sefidi and Luis, 2019).

Ionic liquids are also promising solvents for CO_2 absorption and due to negligible vapor pressure, they are considered green solvents. However, ionic liquids have been shown low CO_2 absorption rate because of their higher viscosity (Sefidi and Luis, 2019; Nematollahi, and Carvalho, 2019; Vasantha et al., 2012). It was reported that the synthesis of ionic liquids at a large scale was cost-intensive (Sreedhar et al., 2017).

The aqueous alkanolamines were most commercially successful and widely developed absorbents for chemical absorption-based CO_2 capture (Warudkar et al., 2013).

1.6 CO_2 ABSORPTION USING AMINE-BASED ABSORBENTS

On the basis of the number of carbon (C) attached to the nitrogen (N) atom, amines are classified into three categories i.e. primary, secondary, and tertiary. Example of typical primary, secondary and tertiary alkanolamines can be given by Monoethanolamine (MEA), diethanolamine (DEA), and N-methyl-diethanolamine (MDEA), respectively. MEA and DEA were the earliest used amine-based absorbents for CO_2 capture because of their good absorption capacity, high reactivity towards acid gas, and low cost. However, they had shown some drawbacks also, like, degradation in the presence of air, limited CO_2 solubility, higher corrosive nature, foaming tendency, and intensive energy penalty for regeneration (Rao and Rubin, 2002; Aroonwilas and Veawab, 2004; van der Zwaan and Smekens, 2009; Lepaumier et al., 2009; Olajire, 2010). Tertiary amines have been shown good CO_2 solubility with relatively slow reaction kinetics but the energy requirement for regeneration was the lowest of these absorbents. Veawab et al. (1999) reported that primary amine (MEA) was the most corrosive, and tertiary amine (MDEA), was least corrosive among MEA, DEA, and MDEA. Besides these, 2-amino-2-methyl-1-propanol (AMP) which is sterically hindered amine (containing primary alkanolamine) and Piperazine (PZ) which is cyclic di-amine containing two secondary amine, were also studied by several researchers and it was reported that these amines have good CO_2 absorption capacity, relatively less corrosive nature, less thermal degradable and the higher heat of absorption (ΔH_{abs}) but slightly lower than MEA (Rochelle et al., 2011; Kim et al., 2013; Sreenivasulu et al., 2015; Hadri et al., 2017).

1.6.1 Literature review related to CO_2 absorption into 2-(methylamino)ethanol (MAE) and 2-(ethylamino)ethanol (EAE)

MAE and EAE are secondary alkanolamines with sterically hindering groups (methyl and ethyl, respectively) near the nitrogen atom and can be good candidates for CO_2 absorption. EAE can be produced from the agricultural residue (Sutar et al., 2012). It had a lower corrosion rate than MEA, a higher absorption rate than DEA, and required relatively less heat of regeneration (Mimura et al., 1997; Mimura et al., 1998; Li et al., 2012). Haider et al. (2011) had studied CO_2 solubility into aqueous MAE and compared it with aqueous MDEA. They reported that MAE had a much higher CO_2 absorption capacity at low partial pressure. In both, MAE and EAE, because of steric hindrance, the main reaction mechanism was the production of unstable carbamate and mostly related to the bicarbonate formation and due to this it had a higher CO_2 absorption capacity with relatively lower heat of absorption (Gangarapu et al., 2013; Folgueria et al., 2014; Folgueria et al., 2015). The oxidative degradation was lowest for EAE among EAE, MDEA, DEA, triethanolamine (TEA), and diethylaminoethanol (DEAE) (Bhosale et al., 2015). Hadri et al. (2017) studied on MAE, EAE, MEA and 23 other amines for CO_2 absorption. The concentration of all aqueous amines was kept constant at 30 wt.% and the concentration of CO_2 gas was 15 % by volume/volume, the temperature was 313 K. they reported that CO_2 loading (mol CO_2/mol amine) for MAE, EAE, and MEA was 0.67, 0.71, and 0.59, respectively. The heat of absorption (in kJ/ mol of CO_2) was -73.84, -68.95, and -85.13 for MAE, EAE, and MEA, respectively. It was also reported that EAE had better thermodynamic and kinetic properties in comparison to MEA. Hwang et al. (2017) reported CO_2 solubility of EAE and 20 other amines. CO_2 solubilities (mol CO_2/ mol amine) for aqueous EAE, at 313.15 K and nearly 13 kPa partial pressure of CO_2, were 0.811 and 0.704 for 15 wt. % and 30 wt. % concentrated solutions, respectively. The cyclic absorption capacity of EAE was reported better than MEA. Liu et al. (2019) studied on CO_2 absorption of MAE, EAE, and 9 other primary, secondary, and tertiary amines, including MEA, and reported that EAE and MAE as the better alternative of MEA for CO_2 capture with high efficiency and better cyclic capacity. The cyclic capacity of MAE was also reported higher than MEA by Maneeintr et al., 2019. Very few published literatures are available about CO_2 capture using MAE and EAE. Some important literatures are summarized in Table 1.2.

Table 1.2. Literature related to CO_2 solubility into aqueous MAE and aqueous EAE

Sr. No.	Aqueous Absorbent	Used reactor and operating conditions	Key findings	Remarks	Reference
1	MAE	Stirred cell reactor, T = 303, 313,	At T = 303.15 K, and 9.9 kPa p_{CO_2}	MAE was good candidate for	Haider et al., 2013.

		and 333 K, p_{CO_2} = 1 to 100 kPa, Concentration of MAE = 1.0, 2.0, and 4.0 M.	(i) α = 0.795 for 1.0 M MAE, (ii) α = 0.759 for 2.0 M MAE, (iii) α = 0.549 for 4.0 M MAE	CO_2 capture	
2	MAE, EAE, and 28 other amiines	Bubble column type solvent screening set-up, T = 313 K, p_{CO_2} = 15 kPa, Concentration of aqueous amines = 30 wt. %	(i) α = 0.67 for MAE (ii) α = 0.71 for EAE (iii) ΔH_{abs} = -73.84 kJ/mol CO_2 (iv) ΔH_{abs} = -68.95 kJ/mol CO_2	EAE was good candidate for CO_2 capture as an alternative of MEA	El Hadri et al., 2017.
3	EAE and two other amines	Equilibrium cell, T = 313, 353, and 393 K, p_{CO_2} = 0.02 to 395 kPa, Concentration of aqueous amines = 15 and 30 wt. %	At T = 313 K, and 13 kPa p_{CO_2} (i) α = 0.811 for 15 wt.% EAE, (ii) α = 0.704 for 30 wt.% EAE, (iii) Cyclic capacity = 58 g CO_2/kg solvent for 30 wt. % EAE	EAE had larger cyclic capacity and lower heat of reaction than MEA	Hwang et al., 2017.
4	EAE + 3-dimethyl amino-1-propanol (3DMA1P)	Bubble column, T = 303.2 K to 323.2 K p_{CO_2} = 0.02 to 395 kPa w_{EAE} = 1 to 4 % w_{3DMA1P} = 30 to 50 %	At T = 313.15 K and CO_2 = 15 % by volume, (i) α = 0.75 for 30 wt. % w_{3DMA1P} + 4 wt.% EAE and (ii) α = 0.71 for 50 wt. % w_{3DMA1P} + 3 wt.% EAE	EAE + 3DMA1P were appeared better absorbent for CO_2 capture in compared to MEA + MDEA.	Fu et al., (2019)

1.6.2 Literature review related to CO_2 absorption into aminoethylethanolamine (AEEA)

Ma’mun et al. (2007A) reported that AEEA was a promising solvent for post-combustion CO_2 capture from the low-pressure stream. AEEA had a high absorption capacity with a high absorption rate. The cyclic capacity of 2.9 M (30 wt. %) aqueous AEEA was slightly higher than 5.0 M (30 wt. %) MEA. The heat of absorption of 30 wt. % aqueous AEEA was almost equal to the 30 wt. % aqueous MEA (Kim and Svendsen, 2007). The AEEA is a di-amine with chain molecules and a relatively environmentally acceptable absorbent. At 140 ^oC temperature, AEEA was found to have high rate of thermal degradation with the production of cyclic urea (Davis, 2009). Zoghi et al. (2012) studied the solubility of 30 wt.% aqueous AEEA in a high-pressure system (p_{CO_2} = 0.01 to 4378 kPa) and temperature in the range of 313.2 to 368.2 K. Rayer et al. (2012) reported that as a faster reacting amine compared to MEA, AEEA can also be used in low concentrations blended with tertiary or sterically hindered amines. Bajpai and Mondal (2013) worked on a CO_2 solubility study for an aqueous DEA + AEEA blend and reported that CO_2 solubility enhanced by the addition of AEEA into DEA. In another work, CO_2 solubility into aqueous MDEA + AEEA blend (Zoghi et al., 2013) was studied for the high-pressure system. Haghtalab and Talavaki (2017) investigated CO_2 solubility into aqueous diisopropanolamine (DIPA) + AEEA and aqueous DIPA + AEEA + PZ, and reported AEEA as a good chemical activator for amines to CO_2 capture. Kumar and Mondal (2018) measured the CO_2 solubility data for aqueous DEEA + AEEA in the temperature range 303.15 to 333.15 K and CO_2 partial pressure in the range of 10.132 to 20.265 kPa. It was reported in their study that an increased amount of AEEA into the DEEA + AEEA blend, resulted in increased CO_2

loading. A tabulated summary for AEEA as an absorbent and activator for amine blend for CO_2 absorption is given in Table 1.3.

Table 1.3. Literature related to CO_2 solubility into aqueous AEEA and its blends

Sr. No.	Aqueous Absorbent	Used reactor and operating conditions	Key findings	Remarks	Reference
1	AEEA	Bubble column screening apparatus, T = 313.15 K for absorption, T = 393.15 K for desorption, p_{CO_2} = 9.5 kPa, Concentration of AEEA = 2.9 M	α = 0.82 at T = 313.15 K	AEEA had a high absorption capacity with a high absorption rate	Ma'mun et al., 2007A.
2	AEEA	Equilibrium cell (autoclave), T = 313.2 to 368.2 K, p_{CO_2} = 0.01 to 4378 kPa, Concentration of aqueous AEEA = 30 wt. %	α = 0.89 at T = 313.2 K and p_{CO_2} = 7.7 kPa	Maximum CO_2 solubility data were at high pressure above atmospheric pressure	Zoghi et al., 2012.
3	DEA + AEEA	Bubble column, T = 303.15 to 333.15 K, p_{CO_2} = 10.13 to 20.27 kPa, Total concentrations = 0.92 to 3.22 mol·kg^{-1} mole fraction of AEEA in total amine = 0.02 to 0.20	. α = 0.74 At T = 313.15 K, 15.2 kPa p_{CO_2}, For total concentration of absorbent = 1.84 mol·kg^{-1} With 0.20 mole fraction of AEEA	The CO_2 solubility was increased by mixing AEEA into DEA	Bajpai et al., 2013.
4	AEEA AEEA +	Equilibrium cell, T = 303 K, 313	(i) At 313.15 K, 20.77 kPa p_{CO_2}	Rate of absorption	Guo et al., 2013.

	AMP AEEA + MDEA	K and 323 K P = 0.80 to 800 kPa, Concentration of AEEA = 15 wt. %, Concentration of AMP = 5 to 10 wt. %, and Concentration of MDEA = 5 to 10 wt. %	For 15 wt.% AEEA, α = 0.952. (ii) CO_2 solubility order AEEA + AMP > AEEA + MDEA > AEEA [At low CO_2 partial pressure (< 30 kPa)],	was in the order AEEA + AMP > AEEA + MDEA > AEEA	
5	DEEA and DEEA + AEEA	Stirred equilibrium cell Heat flow reaction calorimeter, T = 293 to 318 K p_{CO_2} = 9 to 24 kPa Concentration of DEEA = 0.8 to 2 M Concentration of DEEA in the blend = 2 M Concentration of AEEA in the blend = 0.1 to 0.3 M	(i) At 303.15 K, the second-order rate constant for the reaction of CO_2 with DEEA = 65.5 $m^3\ kmol^{-1}\ s^{-1}$. (ii) For the blend, overall rate constant (k_{ov}) = 1124, 2108, 3093 s^{-1} at AEEA concentration of 0.1, 0.2 and 0.3 M, respectively.	The absorption rate was significantly enhanced by using AEEA as an activator of DEEA aqueous solutions	Hanna Kierzkowska-Pawlak, 2015.
6	DIPA + AEEA DIPA + AEEA + PZ	High pressure Equilibrium cell, T = 313 K, 328 K and 348 K P = 100 to 3800 kPa, Total concentration of absorbent = 30 wt. % AEEA = 5 to 10 wt. %	(i) At T = 313.15 K, p_{CO_2} = 105 kPa and DIPA (25 wt.%) + AEEA (5 wt.%) α = 0.774 (ii) At T = 313.15 K, p_{CO_2} = 137.5 kPa and DIPA (20 wt.%) + AEEA (10 wt.%) α = 0.925 (iii) At T = 313.15 K, p_{CO_2} = 130.7 kPa and	The AEEA was reported as a good chemical activator for CO_2 absorption	Haghtalab et al., 2017.

			DIPA (20 wt.%) + AEEA (5 wt.%) + PZ (5 wt.%) $\alpha = 0.844$		
7	DEEA + AEEA	Bubble column, $T = 303.15$ to 333.15 K $p_{CO_2} = 10.13$ to 20.27 kPa	At $T = 303.15$ K, 20.27 kPa p_{CO_2} and 1 kmol/m^3 total concentration of amine with 0.2 mole fraction of AEEA in total amine, $\alpha = 0.843$	The CO_2 solubility was enhanced by addition of AEEA	Kumar et al., 2018.

1.6.3 CO_2 solubility models

CO_2 solubility models are basically equilibrium-based thermodynamic models. There are several models to predict CO_2 solubility in alkanolamines but electrolyte Non-random Two Liquid (e-NRTL) model (Chen and Evans, 1986), Deshmukh-Mather model (Deshmukh and Mather, 1981), and Kent-Eisenberg (K-E) model (Kent and Eisenberg, 1976) are mostly used models. The e-NRTL model is an activity coefficient-based model that correlates the activity coefficients of species with its mole fraction in the solution. In this model, the excess Gibbs free energy model is used to calculate the activity coefficients of species. The e-NRTL model was recently used to correlate CO_2 solubility into aqueous EAE (Biernacki et al., 2015), aqueous 1-methylpiperazine (1MPZ) (Li et al., 2015), aqueous Hexamethylenediamine (HMDA) (Mondal et al., 2015), and aqueous AEEA (Mukherjee and Samanta, 2019), etc. Deshmukh-Mather model is a rigorous CO_2 solubility model in which activity coefficients, electrostatic forces, and short-range interactions among the ionic species are used in the model (Mondal et al., 2015). Modified Deshmukh-

Mather model was developed to predict CO_2 solubility of 30 mass % aqueous AEEA by Ma'mun et al., 2006. CO_2 solubility analysis by using Deshmukh-Mather model for 30 wt. % AEEA at high pressure (Zoghi et al., 2012), aqueous DEA, MDEA and DEA + MDEA (Benamor and Aroussi, 2013), aqueous AEEA + MDEA (Zoghi and Feyzi, 2013), aqueous solution of 2-amino-2-methyl-1-propanol (AMP) + N-methyl-2-pyrrolidone (NMP) (Pakzad et al., 2018), etc. are reported in the literature. Kent-Eisenberg (K-E) model was developed with the assumption that fugacity and activity coefficients of species formed at the equilibrium were unity (one). It is a very simple model to predict CO_2 solubility into aqueous alkanolamines. In the K-E model, equilibrium constants of chemical reactions were presented in the form of function of temperature. Since originally, the K-E model was an empirical model of temperature only, so, in order to predict CO_2 solubility in the wide range of operating conditions i.e. temperature, the partial pressure of CO_2, the concentration of aqueous amines, etc., some modifications in the K-E model have been done by some researchers and modified K-E models are given in the literature (Dey et al., 2018; Pakzad et al., 2018; Xiao et al., 2019; Khodadadi et al., 2019).

1.6.4 Physicochemical properties of absorbents

The knowledge of physicochemical properties such as density and viscosity of absorbents are required in the design and optimization of the CO_2 capture process (Haghtalab and Shojaeian, 2014). The density and viscosity data are used to explain the behavior of the absorbent in heat, mass, and momentum transfer. Density data of the absorbent is used in the calculation of pumping power for circulation of absorbents into the absorption column. The rate of mass transfer is influenced by the viscosity of fluids. The absorption and desorption processes are more favorable at lower viscosity of the solution. High viscosity can create problems in blending, stirring, pumping, and mass transfer (Tariq et al., 2011). Excess molar volume and isobaric thermal expansion coefficients can be calculated using the density data of pure components and binary/ternary mixture. In order to extend knowledge of molecular interactions between molecules of mixtures, viscosity and density data can be used to derive thermodynamic properties such as molar activation enthalpy, molar activation entropy, and molar activation Gibbs free energy for the flow of solution. Moreover, viscosity data are used to calculate diffusivity of CO_2 into the aqueous alkanolamines, based on Eyring's theory (Eyring, 1936).

Studies of physicochemical properties of absorbents used for CO_2 capture were reported recently by several researchers (Stec et al., 2014; Wang et al., 2015; Chen et al., 2016; Chowdhury et al., 2016; Moosavi et al., 2017; Luo et al., 2017; Gao et al., 2017A; Adak et al., 2017; Afkhamipour et al., 2018). Grunberg-Nissan model (Grunberg and Nissan, 1949) Mcallister model (Mcallister, 1960), Jouyban-Acree model (Jouyban et al., 2005), modified Vogel-Tamman-Fulcher (VTF) model (Tirona et al., 2014), extended Arrhenius model (Gao et al., 2017), etc., were used to correlate experimental viscosity data. However, the applicability of each model is bound in its own limitations. Excess physicochemical properties were correlated to the Redlich-Kister model (Redlich and Kister, 1948) by several researchers that are the most established thermodynamic model to calculate excess thermodynamic properties. Physicochemical properties data of CO_2-loaded alkanolamines were reported by very few researchers in literature (Luo et al., 2017; Gao et al., 2017A; Kummamuru et al., 2020). The viscosity of CO_2-loaded solutions was correlated to the Wieland model (Wieland et al., 1998) in literature (Luo et al., 2017; Gao et al., 2017A;

Kummamuru et al., 2020). Recently published literature of physicochemical properties related to MAE, EAE, and AEEA are summarized in Table 1.4.

Table 1.4. Literature related to physicochemical properties of MAE, EAE, and AEEA

Sr. No.	Absorbent	Measurement range	Studied physicochemical properties	Used model for correlation	Reference
1	AEEA	T = 283.15 to 343.15 K P = atmospheric pressure Concentration of aqueous AEEA = 0.00 to 1.00 mole fractions with different step intervals	Densities, excess molar volumes, and thermal expansion coefficients	Density and excess volume were correlated using a Joubian–Acree mode and Redlich–Kister equation, respectively.	Stec et al., 2014.
2	MDEA + AEEA	T = 283.15 to 363.15 K P = atmospheric pressure Concentration of AEEA in the aqueous blend = 0.00 to 1.00 mole fractions with different step intervals	Densities, and excess molar volumes.	Redlich-Kister, Kohler, Jacob-Fitzner, Tsao-Smith, Toop, and Scatchard models were used to estimate the excess molar volume.	Wang et al., 2016.
3	MEA MEA + DEEA	T = 293.15 to 333.15 K P = atmospheric pressure Concentration of MAE in the aqueous solution and blend = 0.00 to 1.00 mole	Density, viscosity, excess molar volume, thermal expansion coefficient, activation enthalpy, activation entropy and activation molar	Redlich–Kister model was used to correlate the excess molar volume and the viscosity	Chen et al., 2016.

		fractions with 0.20 step intervals.	Gibbs free energy		
4	EAE and four other alkanolamines	T = 303.15 to 323.15 K P = atmospheric pressure Concentration of aqueous EAE = 0.00 to 1.00 mole fractions with different step intervals	Density, viscosity, and excess volume	Density and viscosity were fitted with the polynomial equations of different degrees.	Chowdhury et al., 2016.
5	MEA + Diethylenetriamine (DETA) MEA + AEEA	T = 298.15 to 308.15 K P = atmospheric pressure Concentration of AEEA in the aqueous blend = 0.00 to 1.00 mole fractions with different step intervals	Density, viscosity, refractive index, and derived thermodynamic properties	Excess molar volume and excess refractive index data were correlated to the Redlich-Kister equation.	Moosavi et al., 2017.
6	CO_2-loaded and -unloaded MAE	T = 293.15 to 323.15 K P = atmospheric pressure Aqueous MAE concentrations = 7.5, 15.0, 22.5, and 30.0 wt. %.	Density, viscosity, and N_2O solubility	Density data were correlated to Redlich – Kister equation. Viscosities were fitted in Wieland equation.	Luo et al., 2017.
7	CO_2-loaded and -unloaded EAE	T = 293.15 to 323.15 K P = atmospheric pressure Aqueous EAE concentrations	Densities, viscosities, and refractive indices	Excess volumes were correlated to Redlich – Kister equation. Viscosities were fitted in extended Arrhenius	Gao et al., 2017.

		= 8.9, 17.8, 26.7, and 35.6 wt. %.		equation and Wieland equation.	

1.7 RESEARCH GAP

It was reported in the literature that there was not any single absorbent that could have all desired properties to optimize post-combustion CO_2 capture. To utilize individual's merits of alkanolamines and to minimize their disadvantages, several amine blends for CO_2 capture have been reported in the literature (Sutar et al., 2013; Tong et al., 2013; Artanto et al., 2014; Conway et al., 2014; Shokouhi et al., 2015; El Hadri et al., 2017; Gao et al., 2017; Hamidi et al., 2018; Knuutila et al., 2017; Muchan et al., 2017A; Muchan et al., 2017B; Nwaoha et al., 2017; Ramezani et al., 2017; Wai et al., 2018). However, suitable amine blend could not found that would fulfill all desirable properties for post-combustion CO_2 absorption from flue gases i.e. high CO_2 loading, high absorption capacity, high cyclic capacity, low heat of absorption, fast chemical reaction kinetics, fast absorption rate, low corrosive, low viscosity, more thermally stable, less oxidative, etc.

Aqueous MAE + AEEA and aqueous EAE + AEEA blend could be better candidates for post-combustion CO_2 capture from flue gases. Because MAE and EAE produce less stable carbamate, behave like tertiary amines in more bicarbonate production but with fast reaction kinetics, have better favorable properties of CO_2 absorption, and reported as a better alternative to MEA in the literature. AEEA is a di-amine containing one primary and one secondary amine and used as an activator for secondary and tertiary amines in the literature. However, there was not any published study on aqueous MAE + AEEA blend and aqueous EAE + AEEA blend for CO_2 absorption.

1.8 OBJECTIVES FOR PRESENT RESEARCH WORK

The aim of this research work is to study of aqueous MAE + AEEA and aqueous EAE + AEEA blend for post-combustion CO_2 capture related to coal-fired power plant's flues gases. The overall objectives of this research work can be summarized as follows:

1. To measure the CO_2 solubility data at various operating conditions for aqueous MAE + AEEA and aqueous EAE + AEEA blends.

2. To develop the CO_2 solubility model for prediction of CO_2 solubility into aqueous MAE + AEEA and aqueous EAE + AEEA blends.

3. To estimate heat of absorption for CO_2 absorption into aqueous MAE + AEEA and aqueous EAE + AEEA blends.

4. To study the CO_2 desorption of CO_2-loaded aqueous EAE + AEEA blend and compare its cyclic capacity with aqueous MEA.

5. To measure density and viscosity of aqueous EAE, aqueous AEEA, and aqueous EAE + AEEA blend, and to develop empirical correlations to predict density and viscosity.

6. To study the derived thermodynamic properties to extend the knowledge of molecular interaction of molecules in the binary and ternary mixtures (absorbents).

7. To measure the density and viscosity of CO_2-loaded samples and development of model for prediction of density and viscosity of CO_2-loaded aqueous amine blend.