1	A Comprehensive Review on CO ₂ Capture Process using Amine-
2	Ionic Liquids Mixtures
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22	GRAPHICAL ABSTRACT



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24 ABSTRACT

In recent years, there has been an increase in the earth's temperature due to the emission of CO₂ 25 which causes global warming. With a 1.9°C temperature increase predicted by the 26 Intergovernmental Panel on Climate Change, reducing of CO₂ is essential for all living species. 27 Therefore, finding novel CO₂-capturing strategies is the only way to eliminate this life threat. 28 From post-combustion coal-fired power plants, CO₂ separation is employed by a solvent-based 29 30 chemical absorption method using Monoethanolamine (MEA) as standard solvent, which is the 31 most practically proven and reliable process. The utilization of other solvents as absorbents in the CO₂ absorption process such as amine solutions, ionic liquids (ILs), and amine-ILs solvent 32 blend mixtures were reviewed. This review provides an overview of the CO₂ capture process, 33 34 emphasizing the importance of developing efficient and sustainable methods to mitigate greenhouse gas emissions. It also highlights the potential of using amine-ionic liquids mixtures 35 as promising candidates for CO₂ capture due to their unique properties for effective removal of 36 CO₂ by increasing CO₂ absorption capacity as well as minimizing energy consumption during 37 solvent regeneration. 38

39	Keywords: CO ₂ capture, Ionic Liquids, amine,	CO ₂ absorption capacity, Regeneration energy
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49	1. INTRODUCTION	

The climatic challenges were caused by global warming, improper ecological cycle, 50 economic and technological issues. This average rise in the earth's temperature leads to global 51 warming. This temperature rise is due to the emission of Greenhouse Gases (GHG), mainly 52 CO₂. GHGs are caused by the fossil fuel, petrochemical, steel, transportation, and cement 53 sectors. Nearly 88% of the world's energy consumption is based on fossil fuels such as coal, 54 natural gas, and oil. The International Energy Agency (IEA) indicated in 2014 that coal and 55 crude oil are the leading sources of CO₂ emissions. Coal, a fossil fuel, is very inexpensive and 56 widely available (Aghaie et al. 2018; Kang et al. 2018). Rapid emission of GHG emissions 57 58 result's in increasing sea levels, melting polar ice caps, global warming, glaciers, and catastrophic weather patterns in the atmosphere (Zhang et al. 2018). Among the different 59 pollutants, high GHG emissions cause the earth's temperature to rise. According to the Paris 60 Agreement, the atmospheric temperature should not exceed 2°C by 2100, with the goal of 61 lowering the temperature to 1.5°C. Based on the IPCC report (Intergovernmental Panel on 62 Climate Change), atmospheric CO₂ concentrations should be maintained at 450 ppm by 2100 63

to avoid global temperature rises of more than 2°C (Shivanna, 2022; Lv et al. 2020). Recent 64 research has shown that the global CO₂ emissions from fossil fuels are expected to reach 40.2 65 GT (gigatonnes) by 2030 through electricity generation as shown in Figure 1. (Xiao et al. 2019; 66 Chen et al. 2018). In order to overcome the issues, Carbon capture and storage (CCS) involves 67 capturing CO₂ emissions and storing them in geological formations, aiming to minimize their 68 release. Despite technical, regulatory, and economic challenges, developing efficient and cost-69 70 effective CCS technologies, along with the promotion of carbon capture utilization and storage (CCUS), offers a promising solution to mitigate CO₂ emissions and combat climate change 71 72 (Garba & Galadima, 2018; Fan et al. 2018). This CCS process has been performed using three different methods namely pre-combustion, post-combustion and oxy-combustion. The pre-73 combustion process, utilized in Integrated Gasification Combined Cycles (IGCC) for CO2 74 removal before fuel combustion, faces challenges in industrial-scale implementation due to 75 complex equipment and high capital costs (Orhan et al. 2017). Oxy-fuel combustion burns 76 fossil fuels with pure oxygen to produce high CO₂ concentrations for easier separation, but its 77 high costs for oxygen separation and capital investment limit its economic viability compared 78 with other capture methods (Bajai et al. 2022). However, in the post-combustion process, CO₂ 79 removal occurs after fuel combustion, particularly in coal, oil, and gas-fired power plants. 80 Solvent-based post-combustion technology offers the advantage of low-pressure CO₂ 81 generation and easier integration into existing power plants, making it a potential solution for 82 83 reducing GHG emissions (Mukhtar et al. 2020). Some of the solvents used in CO₂ captures process are amines, non-amines and ionic liquids. Monoethanolamine (MEA) act as benchmark 84 solvents for CO₂ but shows higher solvent degradation during regeneration. Hence, the 85 combination of amines and ionic liquids in CO₂ capture processes presents a novel approach 86 that addresses the limitations of traditional solvent-based methods. This solvent blend results 87 in enhanced CO₂ absorption kinetics and selectivity. The chemical and thermal stability of ionic 88

89 liquids also counteracts the degradation problems associated with amines, extending the 90 lifespan of the solvent system. This amine-ionic liquid mixture holds promise for more efficient 91 and sustainable CO_2 capture processes, paving the way for further advancements in the field.

The aim of this extensive review paper is to explore the potential use of amine-ionic liquid mixtures as solvents for CO₂ absorption process. This work focuses on efficient and sustainable methods to reduce greenhouse gas emissions, particularly CO₂, a significant acidic gas that causes climate change. Addressing the overview of CO₂ capture methods and the distinctive properties of amine-ionic liquids mixtures for enhancing CO₂ capture would facilitate further research and advancements in sustainable carbon capture technologies.



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2. REVIEW METHODOLOGY

Figure 2. indicates the review methodology adopted for the present work. In Figure 2, the highlighted content represents the potential of use amine-ionic liquids mixtures as promising candidates for CO₂ capture process because of their unique properties such as high selectivity, low volatility, and tunable chemical structures. It also compares the performance of amineionic liquids mixtures with conventional CO₂ capture methods. Carbon capture technology

involves methods to capture carbon dioxide emissions from coal fired power plants, mitigating 106 climate change by reducing greenhouse gas emissions. It includes post-combustion capture, 107 pre-combustion capture, and oxy-fuel combustion, aiming to store or utilize captured CO₂ to 108 prevent its release into the atmosphere. Post-combustion carbon capture technology holds 109 significant importance compared to other methods due to its ability to capture carbon dioxide 110 emissions after fuel combustion, particularly in existing coal, oil, and gas-fired power plants 111 112 (Bhavsar et al. 2023). This approach offers advantages such as lower implementation costs, easier integration into existing infrastructure, and reduced risks associated with retrofitting. In 113 114 post-combustion carbon capture processes, CO₂ separation typically involves extracting CO₂ from the flue gas emitted by industrial sources after the combustion of fossil fuels which was 115 shown in Figure 2. Various methods are employed for CO₂ separation, including chemical 116 absorption, absorption, membrane separation, cryogenic separation, and chemical looping 117 combustion. Chemical absorption, using liquid solvents like alkanolamines, is a widely utilized 118 technique where CO₂ is chemically captured by the solvent, forming stable compounds that 119 can be separated from the flue gas. However, it shows some challenges such as high energy 120 requirements for solvent regeneration, equipment corrosion, and solvent degradation (Perumal 121 and Jayaraman, 2023). Recently, Ionic liquids (ILs) have garnered significant interest in CO₂ 122 capture due to their unique properties, such as negligible vapor pressure, high thermal stability, 123 and tunable chemical structures. ILs can serve as promising solvents or sorbents for CO₂ 124 125 capture processes, offering advantages such as low energy requirements for regeneration, high selectivity, and the potential for reuse. But it has some bottlenecks such as high cost, viscosity 126 issues hindering mass transfer, potential toxicity, limited scalability, and stability. Many 127 researchers are able to find an alternative solution to capture CO₂ by overcoming the above 128 issues. Hence the present review focused on the use of solvent blends mainly amines with ionic 129 liquids act as a promising avenue for enhancing carbon capture processes. The solvent 130

combination may increase the CO₂ absorption capacity resulting in improved absorption
kinetics and selectivity (Perumal *et al.* 2021). This blend also addresses limitations such as
solvent degradation and corrosion, extending the lifespan of the solvent system.



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Figure 2. Overview of CO₂ capture process

136 **2.1 Carbon Capture, Utilization and Storage**

137 CO₂ contributes significantly to global climate change. Capturing CO₂ 138 emissions from power plants, transferring them to an injection location, and storing them in an 139 appropriate geologic formation for long-term storage is an effective approach for minimizing 140 CO₂ emissions. In the 1920s, this CCS strategy was implemented to eliminate the carbon 141 dioxide found in natural gas deposits from commercial hydrocarbons. Fossil fuel power plants 142 remain the largest source of CO₂ emissions (Hospital-Benito *et al.* 2020). As a result, there is

a prospect of developing and implementing CO₂ capture, utilization, and storage (CCUS) 143 technologies to reduce CO₂ emissions (Jiang et al. 2020). Therefore, it is crucial to develop 144 efficient and economical technologies for CO₂ capture. CO₂ capture and storage (CCS) is 145 frequently a demanding and more viable technology for decarbonizing the global economy. 146 The use of CCS technology is considered a possibility for lowering anthropogenic CO₂ 147 emissions. Collection of carbon dioxide from emitting sources, transferring it to a storage 148 149 location and depositing it in an appropriate subterranean geological formation (Bhavsar et al. 2023). The large amount of CO_2 flow might be delivered for underground storage upon capture 150 151 via the excavation of deep saline aquifers with no further practical application, as well as oil or gas reserves. A stable geological circumstance, capping bedrock exhibiting excellent sealing 152 capacity, and reservoir stone with the proper porosity, width, and susceptibility are all 153 prerequisites for the geological storage of CO₂. The storage integrity of deep saline aquifers is 154 uncertain. Oil and gas reservoirs, whether active or depleted, have a history of reliable storage, 155 although they are not universally accessible. Furthermore, preserved carbon dioxide can be 156 used in various products, including firefighting gases, drinks, food, and refrigeration. 157 Implementation and popularization are effective methods for promoting carbon capture and 158 storage technologies. The utilization of CO₂ Capture and Storage (CCS) technology is one 159 solution that is utilized to minimize the release of carbon dioxide (CO₂). The use of gas and 160 biomass-based energy may also help lower carbon dioxide emissions. Technical constraints, 161 legal and regulatory barriers, economic barriers, and public perception barriers all impact CCS. 162 Considering the technological cost of developing and operating a CCS is a crucial topic that 163 must be considered. In addition, high CO₂ concentrations might have negative health effects 164 and increase safety and health hazards. Economic and environmental reasons necessitate the 165 use of efficient and appropriate CO₂ separation technology with minimal running costs and 166 energy consumption. Generally, three types of CO₂ capture and storage: post-combustion 167

(capture of CO₂ from exhaust gas), pre-combustion (collection of CO₂ from synthesis gas), and 168 oxy-fuel combustion (oxygen combustion with exhaust gas recycling and CO₂ purification). 169 Figure 3 indicates the overview of Carbon Capture Utilization and Storage (CCUS) technology, 170 emphasizing the importance of capturing carbon dioxide (CO₂) emissions from industrial 171 sources to mitigate climate change thereby reducing CO₂ levels by capturing, trapping, and 172 converting CO₂ into useful chemicals (Fu et al. 2022). Furthermore, it explored the utilization 173 and storage aspects of CCUS, discussing how captured CO₂ can be utilized in various 174 applications such as enhanced oil recovery (EOR), as well as the potential for storing CO₂ 175 176 underground in geological formations.



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Figure 3. Carbon Capture Utilization and Sequestration

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2.1.1 Pre-combustion process

In this technique, removal of CO₂ takes place before the fuel is burnt. Coal, a fossil fuel, produces carbon monoxide instantly after reacting with air/oxygen. Carbon monoxide produced by the water gas shift process mixes with water to produce CO₂ and hydrogen gas (WGS) as shown in Figure 4. This method is used in several industrial processes, including the production of syngas, hydrogen, and natural gas. It is, nevertheless, extensively used in Integrated Gasification Combined Cycles (IGCC). Pre-combustion capture is used in
IGCC power plants, although the efficiency loss is roughly 7–8%. CO₂ concentrations in IGCC
plants are generally 40-50 percent CO₂, and it can be separated from hydrogen. The separated
hydrogen gas was then transformed into operational energy; however, this is not suitable for a
comprehensive strategy. CO₂ removal is technically conceivable, but it is not yet ready for
industrial scale.



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192 Figure 4. Pre-Combustion Carbon Capture

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Because of the presence of significant concentrations of CO₂, high pressure gas permits 194 the use of physical solvents to remove the CO₂. Physical solvent absorption is performed under 195 high pressure conditions, namely with a CO₂ partial pressure greater than 10 bar (Orhan et al. 196 197 2017). Solvent regeneration occurs through pressure reduction as opposed to heating. The benefits of the pre-combustion process include high working pressure, which lowers 198 pressurization costs, and a separation approach that uses less energy. However, because of the 199 200 complexity of the process, the capital cost is significantly higher. In addition, the use of a complicated high-pressure WGS reactor and air separation equipment increased the cost. 201

2.1.2 Oxy-fuel combustion 202

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The oxy-fuel method refers to the combustion of fossil fuels using pure oxygen. The purpose of the oxy-combustion process is to collect CO_2 from the flue gas stream and 204 create high CO₂ concentrations using pure O₂ as an alternative to air for combustion as reported 205 in Figure 5. The goal is to increase combustion efficiency to generate high quantities of CO₂ 206 that can be easily separated. Flue gas with a CO₂ content of 70-95 percent generated by 207 208 combusting the fuel with pure oxygen (Bajai et al. 2022).



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Figure 5. Oxy-Fuel Combustion Carbon Capture

At the end of the process, large concentrations of CO₂ and flue gas components, such 211 212 as CO₂ and water vapor were generated. Hence, the water vapor is removed from the gas stream by cooling and compression. Finally, separation technologies are used to remove the high 213 concentration of CO₂ released from flue gas. The merits of this process is that the flue gas flow 214 215 rate is relatively modest, resulting in a smaller capture unit with a cheaper capital cost. In addition, as compared to other procedures, the NOx level in flue gas is lowered by 60-70 216 percent. This method is critical in power plant pre- and post-combustion procedures. The 217 expense of purifying O₂ using an air separation device is more involved and costly. This raises 218 the cost of O₂ separation as well as the energy demand. The large air separation unit enhances 219

the plant's capital cost when compared to alternative capture technologies. This approach iscostlier than other capturing methods (Orhan *et al.* 2017).

222 2.1.3 Post-combustion process

In this process, the fossil fuel (coal, coke, and heavy oil) is combusted in fired power plants to create electricity. The fossil fuel was burnt in the existence of air for this purpose. Heat was released during combustion to form the high-pressure stream that powers the steam turbines. Flue gas was released through the combustion of fossil fuels. Particulate matter, SO₂, and CO₂ are all components of flue gas was shown in Figure 6. Scrubbing techniques and other particle materials collected by vacuum cleaning can be used to remove SO₂.



The cleansed flue gas from a natural gas-fired power plants constitutes 3-15% 233 CO₂, whereas coal-fired power plants emit 10-15% CO₂ to the environment. To lower the 234 growth of CO₂ concentrations in the atmosphere. The removal of CO₂ is critical for reducing 235 greenhouse gas emissions. Therefore, post-combustion technology was demonstrated on a 236 limited scale, with the quantity of CO₂ collected averaging roughly 800 t/day (Mukhtar et al. 237 238 2020). This technology was used to remove CO₂ from the exhaust flue gases of fuel combustion plants namely as coal, oil, and fuel-fired thermal power plants. In terms of economics, the CO₂ 239 240 absorption/desorption phase, which is largely a solvent regeneration phase, is the most expensive component of the CCS process at post-combustion. Furthermore, as compared to 241 sequestration requirements, the post-combustion capture technology generates CO₂ at low 242 pressures and can be easily fitted to an existing power plant (Haider et al. 2016). 243

244 2.2 CO₂ Separation Process

Post-combustion flue gas from a coal-fired power plant typically includes 1215% CO₂. Absorption, adsorption, membrane separation, direct air capture, chemical looping,
and cryogenic are all methods for CO₂ separation. The details have been discussed below.

248 **2.2.1 Adsorption**

Adsorption is a separation technique utilized in the PCCC procedure (Post 249 Combustion Carbon Capture). This adsorption method employs a packed column loaded with 250 solid sorbents in CO₂ collection. The solid sorbent should have high regeneration capacity, 251 excellent selectivity, and a large specific surface area. Carbons and carbon nanotubes, clays 252 and oxides, microporous zeolites and mesoporous molecular sieves and microporous metal-253 organic framework materials (MOFs). Adsorbent refers to the use of a solid material for CO2 254 separation, while adsorbate refers to the gas that is adsorbed. Adsorption is based on the 255 attraction of CO₂ molecules to solid sorbents via intermolecular forces. As a result, CO₂ is 256

drawn to the sorbent and attaches to its surface. Following that, the solvent (solid sorbent) is 257 regenerated in order to strip the CO₂ by temperature/pressure swing adsorption and reuse the 258 solvent for further adsorption. The mechanism of desorption used to regenerate the adsorbent 259 in CO_2 capture from post combustion flue gas can be characterized through a rise in 260 temperature (temperature swing adsorption) or a decrease in pressure (pressure swing 261 adsorption). CO₂ capture incorporating adsorbents in the pre-combustion phase helps enhance 262 263 hydrogen gas production. The main disadvantage is that there is relatively little CO₂ adsorption capacity and selectivity for accessible solid adsorbents (Olajire, 2017). 264

265 2.2.2 Membrane separation

A membrane acts as a selective barrier, allowing different components from the 266 flue gas stream to infiltrate at different speeds. Separation processes can be classified based on 267 membrane structure. Simple process design, easy scaling, minimal energy use, and a lesser 268 investment cost. The membrane separation process requires five distinct methods of separation, 269 comprising molecular screening, Knudsen diffusion, solution and surface diffusion, capillary 270 condensation. Beginning in 1970, carbon membranes are used to separate gases. It is 271 considered a watershed moment in the field of membrane technology. Membrane performance 272 is classified by two primary factors: selectivity and permeability. Selectivity and permeability 273 were lowered during membrane production by increasing polymer concentration, temperature, 274 and pressure. When membranes were combined with inorganic materials, significant chemical 275 276 and thermal stability was discovered. The membrane functions as a semi-permeable filter in the separation of CO₂ from flue gas streams. It has various advantages, including low 277 regeneration energy requirements, easy operation, no waste streams, and dual benefiting. Due 278 279 to the higher surface area for molecular sieving properties at the gas-liquid interface, which are essential for gas separation, membrane technology process efficiency is quite high compared 280 to conventional process (Haider et al. 2020). High-purity CO₂ separation may necessitate the 281

use of many membranes with various properties. In order to combine the greatest qualities of 282 membranes and solvent scrubbing, solvent aided membranes are being created. Much research 283 is necessary before membranes can be employed on a broad basis for capture in power plants. 284 Membrane technology is easy to use and small, making it ideal for large-scale CO₂ 285 applications. However, it requires a high degree of separation for recycling, is particularly 286 sensitive to sulphur compounds, is a high-cost module, suffers from membrane degradation, is 287 288 not appropriate for removing huge amounts of CO₂ gases, and is not long-lasting.

2.2.3 Cryogenic separation 289

290 Cryogenic separation is referred as low-temperature distillation. It is employed to separate CO₂ from flue gas effectively. Various gas components from the atmosphere may 291 be separated using this approach. The cryogenic separation technique comprises gas mixture 292 separation by fractional condensation followed by low temperature distillation (-73.3°C). The 293 percentage of CO₂ in flue gas is often greater than 50% and is easily separated. The benefits of 294 this method include great dependability, no need for chemical reagents, an easy scale-up 295 procedure, and the recovery of pure CO₂. The key disadvantages of this technique are the 296 significant energy demand for cooling as well as the solidification of CO₂ at extremely low 297 temperatures, as well as the cost inexpensive for the cooling process (Font-Palma et al. 2021). 298

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2.2.4 Chemical looping combustion

Chemical looping combustion (CLC) is a potential method for avoiding CO₂ 300 emissions by diluting flue gases. This strategy eliminates the direct contact of air and fuel 301 combustion. It is also a viable alternative to traditional fuel combustion. It was discovered, 302 however, to be helpful for CO₂ collection applications (An et al. 2023). In this approach, 303 instead of air, oxygen carriers, typically metal oxides, are injected between fuel reactors, 304 obviating the necessity for an Air Separation Unit (ASU). The main advantages of this 305 technology are low energy loss and simplicity of CO₂ separation. However, maintaining reactor 306

pressure to reduce air leakage in the fuel reactor and metal oxide deactivation due to unburnedcarbon accumulation on the surface of metal oxides is a challenge with this approach.

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2.2.5 Direct capture of CO₂ from air

The CO₂ removal from the atmosphere using direct air capture is a technique 310 (DAC). It has recently grabbed scientists' interest because it has the potential to relieve the 311 issues associated with enormous quantities of CO₂ transfer from point-source emitters. 312 Traditional capture methods focus on large point sources, reducing the pace of CO₂ buildup in 313 the earth's atmosphere. This process is comparable to adsorption-based CO₂ collecting. 314 315 Aqueous hydroxides, namely calcium hydroxide, sodium hydroxide and potassium hydroxide solution, as well as solid materials such as alkali and alkali-supported carbonates, metal oxides, 316 and anionic-exchange resins, are used in this process (An et al. 2023). Temperature Swing 317 Adsorption (TSA) and pressure swing adsorption (PSA) are used for CO₂ removal in the DAC 318 process. According to thermodynamic research, TSA is more efficient than PSA for this 319 technique since the heat of adsorption affinity grows at low CO₂ concentrations. However, the 320 estimated cost of DAC is significantly higher than that of other major point sources. 321 Furthermore, for this technology to be widely used, high durability of low-cost materials is 322 essential. The disadvantages of the DAC method include significant energy usage during CO₂ 323 separation. 324

325 2.2.6 Biological process

High CO₂ concentrations stimulate the creation of high-value biomolecules. At high CO₂ levels (often greater than 50%) and in the presence of SO_x and NO_x, green algae strains expanded rapidly. When algae species with high CO₂ fixing and solar energy conversion efficiency are utilized, the technique's commercial and environmental effectiveness can be maximized. These organisms must be capable of converting solar energy into H₂ and producing many useful proteins (Okeke et al. 2022). To employ solar energy for H₂ generation rather of creating biomass, photosynthesis is a little hindered. The retention duration of fixed CO_2 in agriculture is expected to be 50 to 100 years. In the lab, 260 mg l⁻¹ h⁻¹ of CO_2 fixation efficiency, or 26 kg per hour of CO_2 capture in a 100 m³ bioreactor, was achieved. Because bio reactors are prohibitively expensive, this approach is not frequently employed.

336 2.2.7 Absorption

Absorption is the most cost-effective and commercialized separation strategy 337 utilized in coal-fired power stations for post-combustion CO₂ collection (PCCC). By 338 depressurizing or heating, the liquid sorbent absorbs CO₂ from the flue gas, and the CO₂ can 339 340 be removed or the solvent regenerated. The CO₂ gas combines with the liquid sorbent, resulting in absorption from the gas to the liquid phase. The flue gas (including CO₂) is chilled (between 341 318 and 323 K) and delivered into the absorption column (scrubber), wherein the solvent 342 absorbs CO₂. The CO₂-rich solution is pumped through a heater to raise the temperature of the 343 solution, and into a stripper column to liberate the CO₂. The CO₂ that has been released is 344 compressed, and the recovered absorbent mixture is chilled and transferred to the absorber 345 column. The quantity of energy needed for post-combustion CO₂ collection is an essential 346 factor. Thus, present investigations show that lowering the cost of this capture might be 347 accomplished by developing appropriate solvents that can remove more CO_2 for a given mass 348 while using less energy for stripping stage (Mukhtar et al. 2020). Flue gas relates to an 349 absorbent during the process of absorption, and CO₂ is absorbed by this solvent. The absorbent, 350 351 on the other hand, would possess an acceptable capacity for CO₂ intake, a high kinetic rate for CO₂ absorption, limited vapor pressure, great chemical and thermal resistance, as well as be 352 safe for humans. There are mainly two types of solvents employed in CO₂ absorption: physical 353 and chemical absorption. 354

355 2.2.7.1 Physical Absorption

Physical solvents like Selexol, Rectisol, and N-Formylmorpholine (NFM) absorb acid 356 gas components, primarily CO2, through physical interactions rather than chemical reactions. 357 These solvents offer advantages such as requiring less energy for regeneration due to their 358 physical solubility interactions, but they come with drawbacks including low CO2 capacity, 359 high capital and operational costs, solvent loss, and larger equipment. Physical absorption is 360 suitable for removing acid gases from natural gas and synthesis gas used in hydrogen, 361 362 ammonia, and methanol production. Despite its effectiveness at high CO₂ partial pressures, physical absorption may not be cost-effective for gases with CO₂ partial pressures below 15% 363 364 vol due to energy demands related to flue gas pressurization and equipment complexity. Additionally, while physical solvents exhibit great selectivity for hydrogen sulfide over carbon 365 dioxide and can extract carbonyl sulfide, they require low temperatures and high vapor 366 pressures, necessitating gas chilling before absorption and contributing to operational costs 367 (Vega et al. 2018). 368

369 2.2.7.2 Chemical Absorption

In the absorber, the flue-gas meets the solvent, which absorbs the CO₂ and forms 370 weakly intermediate chemicals through chemical processes. These chemical reactions are 371 reversed by using heat to extract CO₂ from the solvents and regenerate them. In chemical 372 absorption processes, the rate at which CO₂ is absorbed by the solvent is an essential 373 characteristic. Because a higher CO₂ absorption rate reduces not only the capital costs of CO₂ 374 375 collection, but it is also viewed as an asset for an absorption process that will be conducted on an industrial scale represented in Figure 7. The key benefits are the high CO₂ absorption 376 capacity, greater absorption and response rate (Aghaie et al. 2018). According to the survey on 377 separation approaches, absorption in PCCC plays a critical part in the CO₂ collection process. 378 Solvents are used to carry out this absorption. Amine-based solvents, carbonate-based solvents, 379 aqueous ammonia, and ionic liquid-based solvents are examples of chemical absorption 380

solvents (Salvinder *et al.* 2019). As a result, a post-combustion carbon capture technology
based on solvents is preferable.



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Figure 7. Flow diagram of chemical absorption process for post-combustion carbon
capture (Zheng *et al.* 2022)

386 2.3. Solvents Based Carbon Capture Process

The solvent-based post-combustion carbon capture process involves the use of liquid 387 solvents to selectively absorb CO₂ from the flue gas emitted by power plants and industrial 388 facilities. This method typically employs a chemical absorption process where the flue gas 389 comes into contact with the solvent, allowing the CO₂ to be absorbed while other gases pass 390 through. After absorption, the CO₂-rich solvent is then regenerated, releasing the captured CO₂ 391 for storage or utilization. Solvents commonly used in this process include aqueous amine, non-392 amine, ionic liquids and solvent blends, which have high affinity for CO₂ molecules (Perumal 393 and Jayaraman, 2023). 394

Several alkanolamines are often used as absorbents in CO₂ collection methods. Because 396 of its strong reactivity with CO₂ molecules, superior thermal stability, and cheap cost, it is less 397 costly and has a larger absorption capacity. Solvent performance in absorption should have 398 three major characteristics: (i) high solubility of gas compounds in the solvent; (ii) strong 399 reactivity of gas compounds with the solvent; and (iii) absorbent cycle capacity. Because of 400 401 their high chemical stability, which favors mass transfer kinetics, Monoethanolamine (MEA) and Diglycolamines (DGA) are the most often utilized main amines in PCCC. DGA need a 402 high solvent concentration for a better absorption process (Vega *et al.* 2018) 403

MEA was revealed to be a benchmarking solvent for CO₂ absorption, that has an 404 absorption efficacy of greater than 90%. The low price, high responsiveness, and rapid 405 406 absorption all contribute to this. Nevertheless, it has certain drawbacks throughout operation, such as a high energy required for CO₂ removal, a higher entropy of reaction, equipment 407 corrosion, and oxidative and thermal deterioration (Jang et al. 2021). Secondary alkanolamines 408 have hydrogen atoms which bond directly to nitrogen atoms, such as Diethanolamine (DEA) 409 and diisopropanolamine (DIPA). While DIPA consumes fewer energy during the recovery of 410 solvent than MEA, DEA produces less heat of reaction, is more resistant to solvent degradation, 411 and is less corrosive. Finally, tertiary amines having a high equivalent weight, like 412 triethanolamine (TEA) and methyl diethanolamine (MDEA). Despite their high chemical 413 414 stability, TEA and MDEA have a slow reaction rate and absorption capability (Vega et al. 2018). The primary difficulties in amine-based absorption technology for CO_2 separation are 415 the solvent loss, degradation of solvent due to the presence of NO₂, SO₂, HCL, and HF in flue 416 gas streams, volatile compound production, essential equipment deterioration, and high 417 utilisation of energy throughout high temperature absorption. The zwitterion ion mechanism 418 regulates CO₂ uptake in amines. When CO₂ combines with a primary or secondary amine, 419

carbamate is generated as an intermediate product. Afterwards, the carbamate is hydrolyzed 420 and separates into carbonate and bicarbonate. Khan et al. (2016) evaluated the CO₂ capture 421 capability of four distinct aqueous solvents, including MEA, AMP, MDEA, and PZ. It was 422 determined by altering the solvent content (10, 20, and 30 wt%), temperature (293-313K), and 423 pressure (10-15KPa). According to the specific absorption rate, it was shown that MDEA-424 AMP-MEA-PZ's absorption performance shows a growing trend. The above solvents like 425 MEA, DEA, and MDEA exhibit high CO₂ absorption efficacy, but it shows drawbacks such as 426 high energy requirements for CO₂ removal, equipment corrosion, and solvent degradation due 427 428 to the presence of contaminants in flue gas streams.

On the other hand, the sterically hindered amine such as 2-amino-2-methyl-1-429 propanol (AMP) function as alternative conventional amines for CO₂ collection procedure. 430 Because sterically hindered amines were unable to produce stable carbamate intermediate 431 compounds during absorption. Karlsson et al. (2019) investigated the CO₂ absorption using the 432 2-amino-2-methyl-1-propanol (AMP) mixed with organic solvents. The obtained results were 433 compared with the N-methyl-2-pyrrolidone (NMP). From the findings it was showed that the 434 organic solvents with AMP, these solvents showed similar CO2 absorption capacity to the 435 AMP-NMP blends. The use of this amine reduces the energy consumption than amine based 436 solvent regeneration, good absorption capacity, high selectivity but it has low absorption rate 437 (Vega et al. 2018, Salvinder 2019). 438

439 2.3.2 Non-amine solvents

440 Non-amine-based solvents are chemical solvents that do not integrate with an
441 amine group. Some examples are sodium hydroxide (NaOH), ammonia (NH₃), potassium
442 hydroxide (KOH), sodium carbonate (Na₂CO₃), and potassium carbonate (K₂CO₃). MEA has
443 a lower carbon concentration than Na₂CO₃. Sodium carbonate, on the other hand, absorbs CO₂

444 at a slower pace, resulting in a higher absorption column height. As a result, promoters are
445 required to boost its absorption rate more than primary amines.

K₂CO₃ is used as solvent due to its cost inexpensive, less energy demand, high
resistance to solvent degradation and low toxicity. But it has poor absorption capacity. Hence,
it acts as a promoter in CO₂ capture process with amines due to its low absorption capacity
Ammonia used as a solvent in CO₂ absorption process. It has higher reaction rate with
minimum regeneration energy than baseline MEA (Vega *et al.* 2018).

Piperazine (PZ) is an organic molecule having two nitrogen atoms in opposing places inside a 6-member heterocyclic ring that is used to absorb CO₂. The reaction between piperazine and CO₂ increases absorption capacity compared to MEA and promotes the fast production of carbamates. However, it is a more volatile and expensive procedure than the baseline MEA (Salvinder 2019).

456 **2.3.3 Ionic liquids**

Ionic liquids (ILs) have recently developed as a novel type of physical solvents that 457 are preferred over conventional physical solvents in CO₂ absorption. Ionic liquids are used 458 as substitute solvents in the CO₂ capture process because of their beneficial characteristics, 459 such as designability, non-flammability, low vapor pressure, good chemical and thermal 460 stability, and comparatively low regeneration energy (Zhao & Baker, 2023; Li et al. 2021). 461 When considering technological and economic issues, IL-based CO₂ collection is costlier than 462 MEA. However, IL can save energy and utility costs throughout the regeneration phase 463 (Salvinder 2019). 464

It is typically formed by the combinations of cations (Imidazolium, pyrrolidinium, pyridinium, phosphonium, ammonium) and anions (Fluorinated anions such as PF6, BF4, TF₂N, non-fluorinated anions such as acetate (OAC), bromide (Br), chloride (Cl), hydroxide (OH) etc. The anion serves the principal role, whereas the cation plays a minor part.

469	As a physical solvent, these ILs reacted with CO ₂ . As a result, the CO ₂ solubility of ILs follows
470	Henry's rule and necessitates high pressure and temperature. Amine functionalized ILs, on the
471	other hand, boost absorption capacity with primary or secondary amine via the zwitterion idea.
472	ILs are employed in the CO2 capture process to minimize solvent loss and need less
473	regeneration energy than baseline because to their chemical and thermal stability. MEA (Zeng
474	et al. 2017). Despite their benefits, several disadvantages of ILs include high viscosity, which
475	inhibits mass transfer kinetics. The development of a strong hydrogen bond between IL and
476	CO_2 enhanced the viscosity following CO_2 absorption. It is overcome by adding organic
477	amine/water to IL, which reduces viscosity without affecting absorption capacity. Green
478	solvents, such as Ionic Liquids (ILs), have currently gained more interest for the carbon capture
479	process than alkanolamines due to attractive qualities such as cation and anion tuning, high
480	chemical and thermal stability, non-volatility, minimal vapour loss, and non-flammability
481	(Halim et al. 2018). The cations and anions of ILs have an influence on CO ₂ solubility. As
482	compared to the cation of ILs, the anion has a greater impact on CO ₂ dissolution. Several
483	research on the CO ₂ solubility of IL have been published in peer-reviewed journals shown in
484	Table 1.

Table 1. Absorption of CO₂ using Ionic Liquids

S. No	Ionic liquids		Pressu	Temperature CO ₂ Solubility		References	
	\sim		re				
1	Tributylammonium		20 bar	298.15 K	0.74 mole of	[Rahim <i>et al</i> .	
	heptanoate				CO ₂ /mole of solvent	2023]	
2	Triethyl	(2-(2-	1bar	303K	0.55mole of	[Zhao et al.	
	methoxyethoxy)ethoxy	y)ethy			CO ₂ /mole of solvent	2023]	
	lammonium bis(trifl						

	uoromethane)sulfonimide				
3	Bis-(2-	20 bar	298.15 K	0.78 mole of	[Zailani <i>et al</i> .
	ethylhexyl)ammonium			CO ₂ /mole of solvent	2022]
	heptanoate ([BEHA][C7]				
4	Bis(2-ethylhexyl)ammonium	29 bar	298.15 K	0.486 mole of	[Yunus et al.
	butyrate[BEHA][BA]			CO ₂ /mole of solvent	2019]
5	Ethanolammonium butyrate	29 bar	323.15K,	0.35 mole of	[Halim <i>et al</i> .
	[EtOHA][BA],			CO ₂ /mole of solvent	2018]

2.3.4 Solvent blends

488	The high-energy demand, low absorption capacity related to solvent degradation
489	of amine, ILs and non-amine regeneration are the serious issue as mentioned in previous
490	section. As a result, an attempt was made to employ solvent blends to improve absorption
491	capacity while also regenerating the solvent with reduced energy usage represented in Table 2.
492	In general, solvent regeneration is a high-energy process. Furthermore, CO ₂ extraction from
493	carbon-rich amine requires a greater amount of energy.

Table 2. Absorption of CO₂ using Ionic Liquids mixed with amine in atmospheric pressure

S. No	Ionic Liquids	Amine	Temper	CO ₂	References
			ature	Solubility	
1	TetraButylAmmonium	Monoethanolamine	303K	0.459 mole	[Perumal
	Acetate [TBA][OAC]	(MEA)		of	and
				CO ₂ /mole	Jayaraman,
				of solvent)	2023]
2	TetraButylAmmonium	Monoethanolamine	303K	0.502 mole	[Perumal et
	Hydroxide [TBA][OH]	(MEA)		of	al. 2021]

				CO ₂ /mole	
				of solvent	
3	Dimethylamino-1-	Ethanediamine	323K	0.295 g	[Li et al.
	propylamine acetate	(EDA)		CO ₂ /g	2021]
	([DMAPAH]-[OAc])			absorbent	
4	N-butylethylenediaminium	Ethylenediamine	308K	0.95 mmol	[Voskian et
	bis(trifluoromethanesulfon			CO ₂ /g IL	al. 2020]
	yl)amide,			\mathcal{O}	
	[HButylen][Tf ₂ N]		25	Z.	
5	1-butyl-3-	Methyldiethanolam	298K	0.0168g/C	[Xiao et al.
	butylimidazolium	ine [MDEA]	5	O ₂ g	2019]
	tetrafluoroborate			absorbent	
	[BBIM]BF4]				

495

The addition of a small amount of tertiary amines (MDEA, TEA) to either primary or secondary amines (MEA, DEA) generates solvent blends that improve overall solvent behavior with regard to of absorption capacity, less demand on energy for solvent regeneration, and resistance to solvent degradation.

500 MEA mixes with TEA, AMP, and MDEA are some of the other solvent blends 501 used in the CO₂ collection process. It is feasible to speed up the reaction rate of these mixes 502 when compared to separate solvents. MEA is the fastest solvent; however, its absorption rate 503 is 50 times slower than that of PZ. As a result, a small amount of PZ boosts MEA absorption. 504 Similarly, potassium carbonate boosted with PZ and AMP mix with PZ are regarded as 505 potential solvents. Recently, IL-amine blends have improved absorption capacity and rate 506 while using minimal energy for solvent regeneration (Haider et al. 2016). Because IL-amine

mixtures absorb CO₂ fast, higher temperature and partial vacuum are required to desorb CO₂ 507 (Camper et al. 2008). The addition of tertiary amine to ILs increases the solubility of CO₂. The 508 addition of ILs to an amine/non-amine solvent resulted in a high CO₂ cyclic capacity and a 509 30% reduction in the enthalpy of CO₂ dissolution (Gao et al. 2015). These amines and ILs 510 mixes have excellent absorption and thermodynamic efficiency, a high absorption rate, 511 minimal solvent degradation and corrosion, and low energy needs for solvent regeneration. ILs 512 513 were coupled with amine, which has a lower regeneration energy than pure ILs and amine solvent, to increase CO₂ solubility with a faster reaction rate. 514

 CO_2 absorption and desorption by aqueous solvent blends has received a significant consideration in the past few years. Similarly, in the case of amine with ILs blends have received a great attention. Hence, in this section, a detail review of literature performed regarding the aqueous amines, ILs and solvent blends as absorbents for CO_2 capture is presented. Finally, the conclusion that has been received based on the literature survey is specified.

521 3. AMINE-IONIC LIQUIDS ASSISTED CARBON CAPTURE PROCESS

The mitigation of CO₂ emission has been achieved through solvent based post combustion carbon capture process. The experimental screening of solvent plays a vital role in the development of potential solvent mixtures for efficient and sustainable CO₂ capture process. The screening has been performed through physico-chemical analysis namely density, viscosity, surface tension and pH as shown in Figure 8. This screening process enables the suitable selection of solvent blends especially amine-ionic liquids with high CO₂ absorption capacities and less energy needed for solvent regeneration.





529

531 **3.1 Solvent Screening through Physical and Chemical Properties**

The determination of physical and chemical characteristics is critical for 532 screening of sustainable solvents for design optimization and a better absorption process. 533 Solvent physical parameters like as density, viscosity, and surface tension will vary during the 534 absorption and desorption process. One of the physical characteristics that has a considerable 535 impact on the kinetics of mass transfer and CO₂ solubility is density. When designing 536 equipment and optimizing industrial processes, viscosity is a crucial factor. It is used to forecast 537 diffusivity of CO₂ in a solution using a modified Stoke-Einstein equation. This equation 538 establishes a fundamental relationship between diffusion coefficient, viscosity, and 539 temperature. It also helps to know, how quickly CO₂ molecules diffused in the solution with 540 influencing mass transfer rates. Therefore, this Stokes-Einstein equation facilitates the design 541 and optimization of CO₂ capture processes by providing a quantitative understanding of CO₂ 542 543 diffusion behavior (Apaiyakul et al. 2021). It is also required to calculate mass transfer and kinetic characteristics. Understanding the chemical interactions that take place in solvents 544 requires knowledge of surface tension. Additionally, it has a sizable effect on mass and heat 545

transfer at the liquid-gas interface during distillation and absorption. For the physicochemical
behavior of solvents in CO₂ absorption, it is therefore crucial.

Changes in these physical qualities will impact mass transfer at the bottom of the absorber and reaction kinetics in the stripper, raising the energy requirement of CCS. In order to determine the physical characteristics of absorption and desorption, it is required to measure them (Karunarthane *et al.* 2020). The following are some examples of physicochemical analyses related to CO_2 capture processes:

553 The study investigated the effects of fluorinated and non-fluorinated ionic liquid 554 blends on surface properties. In comparison to non-fluorinated IL ([C,C,Im][PF]), the 555 incorporation of 9 mol% of fluorinated IL ([PFBMIm][PF]) enhanced viscosity and dropped 556 surface tension, exposing nanosegregated structures at the surface.

Halim et al. (2018) investigated the four ammonium-based ILs 557 (Ethanolammonium Acetate [EtOHA][AC], Ethanolammonium Butyrate [EtOHA][BA], 558 Tributylammonium Acetate [TBA][AC] and Tributylammonium Butyrate [TBA][BA]). They 559 measured temperatures ranging from 293.15K to 373.15K. According to the findings, when the 560 temperature rose, the density and viscosity of ILs reduced due to an increase in IL volume. The 561 presence of additional OH groups in [EtOHA][AC] and [EtOHA][BA] resulted in increased 562 viscosity, which facilitates hydrogen bonding with H₂O molecules. Because of its decreased 563 viscosity, [EtOHA][BA] attained the maximum CO₂ absorption. 564

Aqueous Tetrabutylammonium Hydroxide [TBAOH], piperazine [PZ], and an aqueous-blend of [TBAOH] and [PZ] viscosities and densities were also tested at a temperature range of 303.15K to 333.15K. According to Safdar *et al.* (2015), all physical attributes dropped as temperature increased. At temperatures ranging from 298K to 350K, the surface tension of ammonium-based Room Temperature Ionic Liquids (RTILs) was determined. It was discovered that when the temperature rises, the surface tension of RTILs decreases. Changing

anions has a negligible influence on surface tension during carbon loading. An increase in 571 cation alkyl-chain length reduces surface tension in ammonium-based RTILs due to an increase 572 in the Vander Waals to coulombic force ratio for an interaction between RTILs and CO₂ during 573 absorption. In contrast, ILs with hydrocarbon tails on the cation showed an increase in surface 574 tension. (Zailani et al. 2022; Ab Rahim et al. 2023) 575

For a temperature range of 303.15-343.15 K and at varying mass fractions, the 576 577 physical characteristics of amine with ILs blends were investigated experimentally for 16 distinct absorbents. According to the findings, the CO₂ capture procedure has significantly 578 579 improved the solubility of CO₂. With different IL-amines and temperatures, the density and viscosity of the IL-MEA hybrid solvent were measured. The outcomes showed that the density 580 and viscosity of hybrid solvents increased as ionic liquid concentration was increased. 581 According to Nookuea et al. (2017), the temperature effect has a tendency that is opposed to 582 these characteristics. 583

584

3.2. CO₂ Absorption using Amine- Ionic Liquids

For a variety of solvents, CO₂ absorption was conducted. Amines, ionic liquids, 585 and solvent mixes are among the solvents employed. Amines use the zwitterion ion process. 586 As an intermediate product of CO₂ reactions with primary or secondary amines, carbamate is 587 formed. The carbamate next undergoes hydrolysis and dissociates into carbonate and 588 bicarbonate. ILs were combined with amine to increase CO₂ solubility with a quicker reaction 589 590 time. Previous study has also demonstrated the effectiveness of CO₂ collecting using Amine-IL mixtures (Perumal and Jayaraman, 2023). The combination of alkanolamine and Ionic 591 liquids promotes CO₂ capture even at low pressure since alkanolamine can dissolve and interact 592 with CO₂ in ionic liquid mixtures (Huang et al. 2017). 593

Therefore, the combination of alkanolamine and ILs in the CO₂ capture process 594 might address a number of disadvantages, including high viscosities, corrosion rate, and energy 595

consumption for solvent recovery & reuse (Perumal *et al.* 2021). Another study found that at
higher pressures, CO₂ dissolution is stronger in aqueous blends of MEA and ILs. CO₂
absorption was investigated using amine and IL mixtures at different partial pressures, and it
was revealed that the activation energy of blends is lower compared with that of pure amine
(MDEA).

Safdar *et al.* (2018) investigated the CO₂ absorption and physical characteristics
of aqueous TBAOH blends incorporating Piperazine (PZ). A lower blend concentration (5%
TBAOH and 5% PZ) demonstrated better solubility than a higher one (11.11% TBAOH and
11.11% PZ). Higher concentrations of TBAOH tend to have greater interactions between the
cation and anion of IL, resulting in fewer interactions with CO₂, which leads to lower solubility
(Safdar *et al.* 2015).

607 3.3. Solvent Regeneration

The regeneration efficacy of Amino Acid Ionic Liquid (AAIL) activated N-608 methyldiethanolamine (MDEA) solutions was examined to determine the impact of solution 609 composition, recovery temperature, and regeneration rate. The solvent mixtures were prepared 610 by varying IL and MDEA concentration comprises of 15 wt % [N1111] [Gly] + 30 wt % 611 MDEA, 10 wt% [N1111] [Gly] + 30 wt% MDEA, and 10 wt %[N1111] [Gly] + 40 wt % 612 MDEA were regenerated at 363 K, 373 K, and 378 K. According to the findings, thermal 613 regeneration at around 378 K causes the majority of CO₂ in the liquid phase to be released 614 615 before solution boiling. Additionally, the rates of CO₂ absorption in the regeneration solutions are increased by higher regeneration temperatures. Yang et al. (2014) investigated CO2 616 desorption utilizing amine-IL blends to reduce energy usage. The solvent blends consumed 617 37.2% less energy than the aqueous MEA solution. In addition, the limitations of ILs, such as 618 high viscosity and high cost, can be resolved in the CO₂ capture process by utilizing amine-IL 619 blends. 620

621 **3.4. Solvent Degradation**

Fouling, foaming, and waste disposal are all challenges caused by solvent deterioration. 622 The presence of chemicals that because solvent degradation can also increase pipework 623 corrosion. In addition to the operating concerns, amines can be expelled with the cleaned gas 624 because of their instability and may react under ambient circumstances via photo oxidation to 625 generate nitrogen compounds. These chemicals have recently been recognized as possibly 626 carcinogenic and hazardous to human health and the environment (Vega et al. 2016). As the 627 deterioration rate increases, so does the amount of make-up solution that must be applied during 628 629 the campaigns. Solvent degradation may be systematized into two primary types of reaction: 1) amine oxidative degradation through autoxidation pathways, and 2) oxidation in the 630 presence of metal ions. At high temperatures and in the presence of CO₂, thermal degradation 631 predominantly occurs during solvent regeneration. Thermal degradation byproducts and some 632 oxidative degradation byproducts are frequently more flammable than the amines themselves 633 and therefore more prone to evaporate in the absorber. In amine scrubbing technique, MEA is 634 the most often utilized amine (Voskian et al. 2020). Carbamate formation is the primary 635 thermal breakdown mechanism for amines. Over a long period of time, the influence of acidic 636 gases on amine deterioration should be considered. The MEA solutions combined with IL 637 [bmim][BF4] need less energy for regeneration and have less solvent loss, according to Yang 638 et al.'s 2014 research. Pure MEA solutions showed a greater rate of absorbent loss and energy 639 640 consumption due to oxidative degradation and high reaction heat. In collaboration with IL, they discovered that energy usage may be reduced by 62.8% when compared to pure amine 641 solutions. 642

643 **4. CONCLUSIONS**

644 The present study reviewed potential utilization of Amine-Ionic liquid mixtures for CO₂
645 absorption process. The performance of amine-ionic liquid mixtures was compared with

conventional solvents, which poses higher CO₂ solubility and lesser regeneration energy. This
work may favor further research and developments for sustainable energy and environment.

648 Acknowledgement

The authors gratefully acknowledge funding from the SCIENCE & ENGINEERING
RESEARCH BOARD (SERB) - FILE NO. ECR/2016/001744 (a statutory body of the
Department of Science & Technology, Government of India) New Delhi, India. The lab facility
and research inspiration provided by SSN Trust, Sri Sivasubramaniya Nadar College of
Engineering, Chennai, India, are sincerely acknowledged.

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