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Synthesis of Carbamate from Alkanolamine with Epoxide in Deep Eutectic Solvent Medium: Fixation of Carbon Dioxide

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ABSTRACT
In this research, experiments have been carried out to evaluate the absorption of carbon dioxide in the mixture of diethanolamine and propylene oxide in DES medium to produce diethanolamine (DEA) Carbamate. Potassium carbonate (K_2CO_3) and glycerol mixture was employed as a DES medium. The molar ratio of DES was optimized to get maximum absorption of CO_2 gas. DEA - Carbamate formed was characterized by FTIR, ^{13}C NMR and Raman spectroscopy. The amount of CO_2 utilized in the reaction was evaluated from the yield percentage of DEA- Carbamate yield. The maximum yield of DEA - Carbamate of 51% was obtained at the molar concentration of DEA of 0.5 M at the reaction time of 60 min and the CO_2 pressure of 4 bar with carbon dioxide conversion involved in the reaction is of 2% with low carbon emission of 0.0207 $kgCO_2e$.
Keywords: *DEA - Carbamate, Propylene oxide, DES, CO_2 fixation.*

1. INTRODUCTION

Organic carbamates are valuable synthetic intermediates and are widely used for a number of applications including the three main categories of polymer chemistry as the functional group of polyurethanes, peptide or related chemistry as protective groups of amines, and agricultural chemistry as active ingredients of insecticides, fungicides and herbizides [1, 2]. The most widely utilized method for the synthesis of carbamates involves highly toxic phosgene as a reagent in organic solvents, which is also toxic and flammable [3]. Therefore, the conventional method involves environmental and safety problems. Hence, considerable effort has been directed toward alternative routes of preparing urethanes using carbon dioxide as a phosgene replacement. One of the most favorable reactions for CO_2 utilization is the synthesis of carbamates, as the carbon atom in CO_2that doesn't have to be reduced in the reaction. A very simple, effective and environmentally benign access to carbamates can be achieved by a three-component reaction of a primary or secondary amine with carbon dioxide and epoxide to obtain an unstable carbamic acid derivative in an equilibrium reaction, which can be trapped by electrophiles to form carbamates. Numerous procedures describe that electrophiles such as alkyl halogenides, tosylates, epoxides, alkynes, Michael acceptors and also alcohols, can be applied [1].

Yoshida & Inoue observed that mono carbamates of 1, 2-diols have been synthesized from the corresponding 1, 2-epoxides through the reaction of primary and secondary aliphatic amines using gaseous CO_2. However, about half of the epoxide is lost due to the accompanying nucleophilic ring opening by the amine afforded N- alkylated product [4, 6]. Inoue, explained about the mono carbamates could also be obtained starting from an epoxide using tetrakis (dimethyl)-titanium (IV) and gaseous CO_2. But this method was not satisfactory due to its longer reaction time (~3-4 d), and low yields (5-20%) [6]. Similarly, Asano, enlightened chloro methyl oxirane or phenyl oxirane on reaction with $CO_2$and aliphatic amines in methanol gave various kinds of substituted carbamates in 2-17% yields. However, this method suffers from leading to isomeric mixtures [5]**.** Kojima et al have reported carbamates synthesis from epoxides, amines, and CO_2wherein the latter was previously fixed on an aluminium porphyrin as catalyst [7].

One of the major limitations of aqueous alkanolamine based CO_2 capture processes is the requirement of significantly higher energy of regeneration. Now a day this flaw can be overcome by replacing aqueous phase with more stable room temperature ionic liquid (RTIL) provided a viable approach for carbamate to crystallize out as supernatant solids. However, ionic liquids (IL), especially those based on imidazole with fluorinated anions, not only suffer from the demerits of being non-biodegradable, toxic and commercially expensive, but their production is also related to the use of large amounts of unsafe and

volatile organic solvents [8]. In addition, a large group of ILs is found to be combustible and moisture-sensitive.

In the hypothesis of a use of the DES+amine solvent for CO_2 capture in post-combustion, a decrease of the vapor pressure of the solvent, comparing to that of water amine mixture. Another remarkable nature of DES is most likely having lower effect of equipment corrosion. [9]

Conversely, as far as we know, investigations concerning chemical fixation of carbon dioxide with amines in K_2CO_3 – glycerol DES (to form linear carbamates) have not been reported. Owing to this, the reactivity of aliphatic amines in CO_2-saturated DES solutions are considered. The aim of the present study was to set-up an optimal technique for the synthesis of linear carbamates via chemically induced C-N bond formation from amines and carbon dioxide. DES containing glycerol appeared to be an ideal medium for CO_2 and SO_2 absorption. In the CO_2 absorption case, the solubility in molality of CO_2 in the DES was found to be comparable with the typical solubility of CO_2 in ionic liquids. [10]

Due to the high polar nature of DESs, they are capable of solvating the hypothetical zwitterions and carbamic acid pairs easily. This could additionally or alternatively, increase the absorption of CO_2 gas [11].

The first report on the synthesis of acyclic carbamates through three-component reaction of carbon dioxide, epoxides, and amines was published in 1978, by Yoshida and Inoue [12]. They showed that treatment of 1, 2-epoxycyclohexane with aliphatic amines in solvent-free conditions under the CO_2 atmosphere (~50 atm) furnished corresponding hydroxy-carbamates together with amino alcohols as the by-products. In this study, both primary and secondary aliphatic amines underwent coupling to the target carbamates in moderate yields. It is noteworthy to highlight that the application of this procedure to epoxyethane and 1, 2-epoxypropane proved to be difficult because of a significant decrease in the yield of expected carbamates in favor of the corresponding amino alcohols.

In the present paper, an efficient and environmentally friendly synthesis of carbamates by carbonylation of amines with propylene oxide using DES as reaction medium under solvent-free conditions is reported. Due to the mild reaction condition maintained, there is no concurrent formation of carbamate derivative of propylene oxide and finally, resulted with DEA- Carbamate.

2. REACTION MECHANISM IN NON-AQUEOUS AMINE

For chemical absorption of CO_2 in alkanolamine-based systems, the major reaction comprises the carbamate formation involving CO_2 and amine interaction in1:2 molar ratios. Considering primary/secondary alkanolamines, zwitterion mechanism is the most widely accepted model, first proposed by Caplow in 1968 and later reiterated by Danckwerts [13, 14]. This mechanism involves the formation of an intermediate (zwitterion) in the first step that follows the abstraction of proton by a base.

$$R_1R_2NH + CO_2 \longrightarrow R_1R_2NH^+COO^- \quad (1)$$

$$R_1R_2NH^+COO^- + B \longrightarrow R_1R_2NCOO^- + BH^+ \quad (2)$$

In aqueous amines, the deprotonation species (B) include water, OH^-, and amine itself. In the contrary to aqueous amine systems, in non-aqueous media the primary/secondary amine can be the only base available to deprotonate the zwitterion and hence, the gas loading capacity becomes limited to 0.5 mole CO_2per mole of amine (stoichiometric maximum). Thus, the reaction can be presented as follows

$$R_1 R_2NH^+COO^- + R_1 R_2NH \longrightarrow R_1 R_2 NCOO^- + R1 R_2 NH^+ \quad (3)$$

The same is pertinent to the amine blends with DES does not involve in any kind of chemical interaction either with CO_2or with amine [15].

3. MATERIALS AND METHODS

3.1. Chemicals Used

Diethanolamine, Propylene oxide, K_2CO_3 and glycerol (> 98 %), were supplied by Merck Chemicals (Chennai, India). Research grade carbon dioxide gas, 99.9%, was purchased from Supreme Engineering Services, India, and used as a source of carbon dioxide without further treatment.

3.2. Preparation of DES

DES samples were synthesized in different molar ratios of K_2CO_3 to glycerol. An incubator shaker (MODEL REC 22038-A2) was used to mix the salt and the hydrogen bond donor. Each DES mixture was shaken at 400 rpm and 353 K for a period of 2 hours until a homogenous transparent colorless liquid was formed. DES samples were synthesized at atmospheric pressure and under tight control of moisture content.

3.3. Experimental setup

A schematic diagram of the experimental setup used for CO_2 fixation is shown in Fig.1. The reactor consists of 1 L capacity stainless steel cylindrical tank equipped with a stainless steel and fitted with a diffuser to generate fine bubbles and to sustain intense mixing. The tank was kept on the magnetic stirrer for stirring.

3.4. Isolation and purification of carbamate

In the cases that carbamates dissolved in water after the addition of required amount of HCl at pH 3, the aqueous phase was constantly extracted with dichloromethane, the organic phase dried over $MgSO_4$ and the solvents was removed under reduce pressure to give pure carbamates [16].

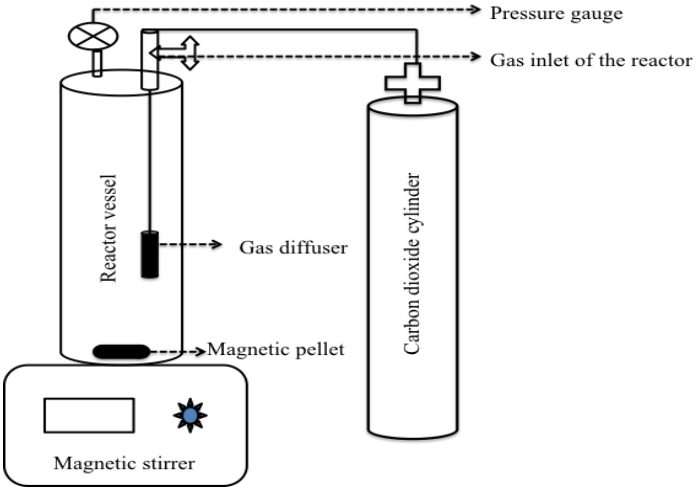

Figure 1: Schematic diagram of CO_2reactor

3.5. Analytical Techniques

The reactor content was collected, isolated and then subsequently characterized by FTIR were recorded on Bruker, 4000–450 cm^{-1} to identify the functional group in the compound, ^{13}C NMR were recorded on Bruker AVANCE III 500 MHz (AV 500) multi nuclei solution NMR Spectrometer to study the carbon–carbon stretching and RAMAN spectrum were obtained on Bruker RFS27: standalone FT-Raman spectrometer, 50-4000 cm^{-1}, resolution 2 cm^{-1}. An extended range protocol was employed to cover the ranges from 700 to 1700 cm^{-1}(three overlapping spectra) and from 2600 to 3700 cm^{-1}(five overlapping spectra). The Raman technique is more promising for disclosing speciation in carbonated alkanolamine solution.

3.6. General procedure for the reaction of amines with diethanolamine

In order to avoid the reaction between amines and carbon dioxide in air, all reactions were conducted in a stainless autoclave reactor equipped with magnetic stirring. In each reaction, the reactants of fixed mole proportion of amine (0.01 mol) and epoxide (0.05 mol), and DES as reaction medium were introduced successively without any additional organic solvents. Then it was exposed at a certain carbon dioxide pressure and the reactions were continued for a required time. After reaction, the desired resulted product would 'precipitate' and solid product could be obtained after filtration, washing, and drying. Each experimental run was conducted in duplicate.

4. RESULTS AND DISCUSSION

4.1. Optimization of reaction conditions

The carbonylation of DEA with epoxide was firstly tested at room temperature in the presence and absence of DES. The influence of the molar concentration of diethanolamine, reaction time and carbon dioxide pressure was investigated to obtain the maximum yield percentage of DEA - Carbamate.

4.1.1. Effect of amine concentration on the yield of DEA - Carbamate

The concentration of DEA was varied from 0.1 to 3.5 M at a room temperature and pressure of 1 bar for a reaction period of 60 min. The results depicted in Fig.2a indicates that the yield of DEA- Carbamate increased with amine concentration upto 0.5 M and with the yield of 46% and beyond this concentration there was a decrease in the yield. This behavior was expected due to decreased diffusivity, owing to greater proportion of more viscous DEA [17].

The amine concentration of 0.5 M is synchronized well with maintained CO_2 gaseous ratio and higher

amine concentrations did not appear to be suitable for the experimental conditions. The results symbolize that the gas-liquid contact zone (between CO_2 and dispersed amine), in case of higher amine concentration, was not large enough to accommodate most of the active sites (the dispersed amine droplets) inside the bulk room-temperature ionic liquid phase [15], and same phenomenon is applicable to DES medium.

4.1.2.. Effect of pressure on the yield of DEA-Carbamate

The effect of carbon dioxide pressure on the yield of the DEA - Carbamate was studied by varying the pressure from 1–5 bar at a room temperature, reaction time of 60 min and with amine concentration of 0.5 M. The results depicted in Fig.2b infer that the maximum yield of 51±1% was obtained with CO_2 pressure of 4 bar beyond that percentage yield of DEA - Carbamate decreases. Due to the increase in pressure produces the interfacial mass transfer by dominating the gas phase mass transfer, resulted in the increase in the driving force from the bulk of the gas phase to the gas liquid interface [18]. Thus, the increase in DEA - Carbamate yield with increase in pressure could be explained based on the absorption of CO_2. However, at high CO_2 partial pressures carbamates may hydrolyze to generate free amines, which can further react with additional CO_2 to give loadings higher than 0.5.

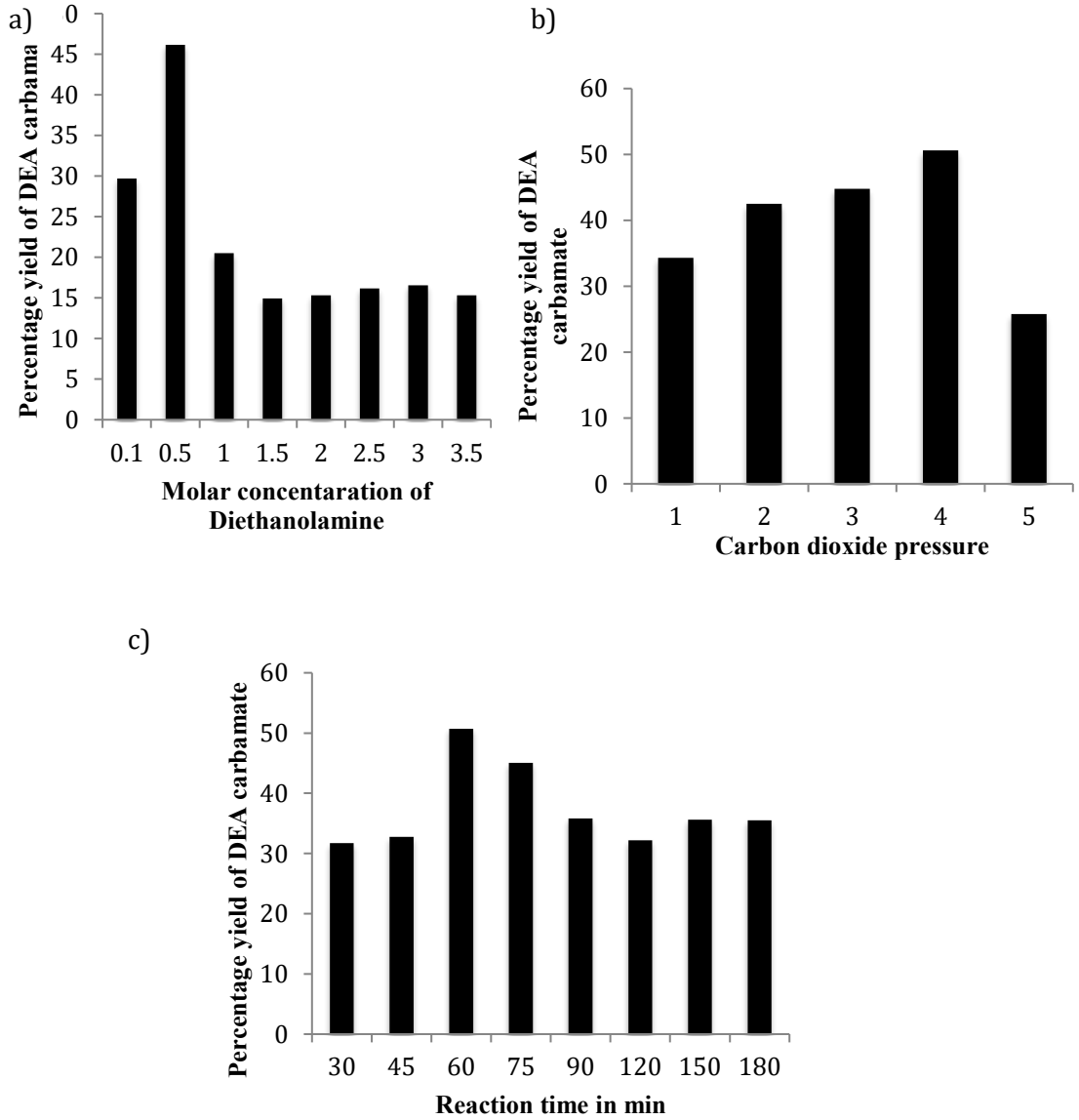

Figure 2: Effect of (a) Molar concentration of DEA (b) CO_2 pressure (c) Reaction time on Diethanolamine conversion.

4.1.3. Effect of reaction time on the yield of DEA - Carbamate

The subsequent studies were performed to evaluate the effect of reaction time on the yield percentage of

DEA- Carbamate. The carbonation time was varied from 30 to 180 min at a regular interval under identical conditions, i.e., the molar concentration of diethanolamine of 0.5 M, and the CO_2pressure of 4 bar. The results illustrated in Fig. 2c indicate the conversion slowly reached the maximum of 51±1% in 60 min and then decreased the yield on further increasing reaction time. Prolonged reaction time causes a significant amount of unreacted amine to agglomerate to the surface of the DES (the coalescence of amine droplets accelerated as the amine content was increased) and continued to capture CO_2but at a much slower pace, as it is evident from the CO_2uptake [15].

4.2. Characterization of DEA - Carbamate

The spectral properties of DEA- Carbamate were analyzed by FT-IR spectroscopy to investigate the structure and its spectral data. Derivatives of carbamates were characterized by a several intense absorption in the infrared spectrum. The most prominent absorption band validates the existence of carbamate moiety appearing as carbonyl stretching frequency at 1649 cm^{-1} in Fig. 3. By comparison with the most typical bands expected for an alkylcarbamate anion it has been observed that the features located at 2931cm^{-1}, 1408$cm^{-1}$and 831 $cm^{-1}$are assigned to the NH stretching, COO^-asymmetric stretching and OCN out of plane bending, respectively. The lack of weak and broad absorption bands in the region of 1350–1360 cm^{-1}corresponds to the absence of bicarbonate ion. A further comparison to the spectral datas of this compound to that of reported data of 2,4-dihydroxybenzoic acid in literature confirmed that compound identified is DEA - Carbamate [17].

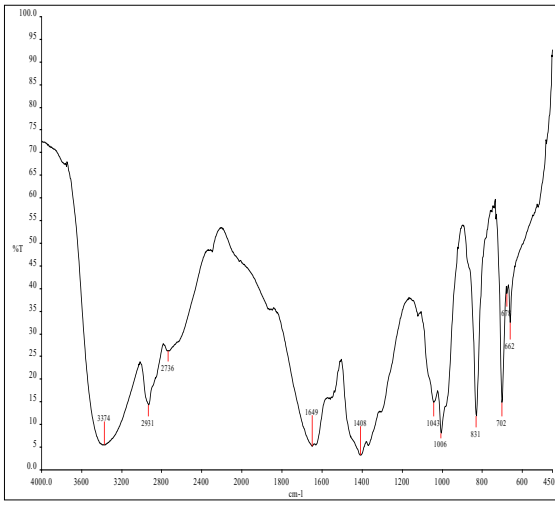

Figure 3: FTIR spectrum of the diethanolamine carbamate

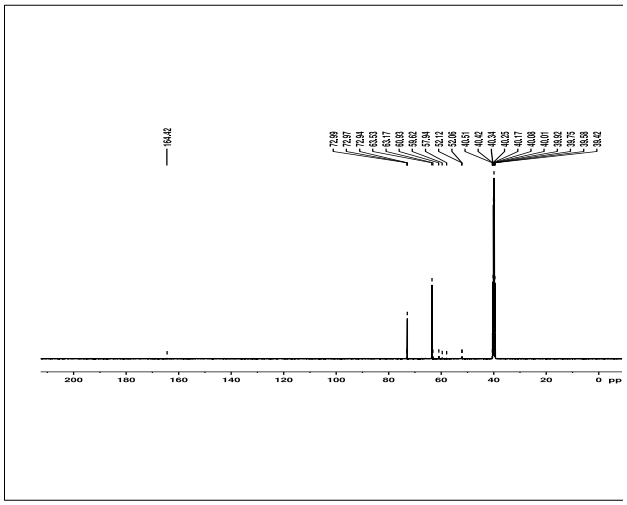

Figure 4: C^{13} NMR spectrum of the diethanolamine carbamate

The ^{13}C NMR spectrum (taken in DMSO-d6) of crystalline carbamate displays peaks in the range of 50.84–61.35 ppm. Two of the low intensity signals at 52.06 and 60.93 ppm originated from ethylene carbons of carbamate derivatives. A low intensity resonance at 164.42 ppm confirms the emergence of carbamate carbon resulting from CO_2 capture [16], as shown in Fig. 4.

The applicability of Raman spectroscopy as an analytical tool for speciation of carbonated alkanolamine systems was studied. A typical spectrum of DEA - Carbamate is shown in Fig 5.

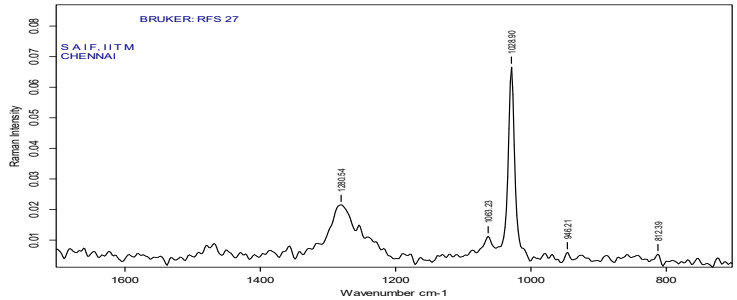

Figure 5: A typical spectrum of diethanolamine carbamate

This indicates the most relevant region for analysis, which is due to the 'NH_2-wag' of H_2NCOO^- at approximately 1028.90 cm^{-1} [19, 20]. As, there is no involvement of water in the gas capturing fluid, single crystal analysis established that there was no question of bicarbonate or carbonate species (found in aqueous amine systems).

4.3. Carbon Dioxide Conversion involved in the DEA - Carbamate Production

(1) To calculate the initial mole of CO_2 as feed for the reaction

Wkt, the ideal gas law equation, $PV = nRT$

Therefore, $= PV/RT$ ---------- (4)

$= (4\ atm * 1.4\ L*mol*K) / (0.082055\ L\ atm * 298\ K)$

Initial mole of CO_2 = 0. 2290 mol

(2) To calculate the moles of CO_2 consumed for the conversion of diethanolamine with the optimized yield of DEA carbamate.

1.165 g of DEA - Carbamate = (44 g of CO_2/ 254.29) *1.165

Amount of CO_2 reacted in terms of grams = 0.215 g of CO_2

Therefore, reacted Mole of CO_2 in precipitate = 0.00457 mole of CO_2

Final mole of CO_2 unreacted = Initial mole of CO_2 – Reacted mole of CO_2

= 0.2290 - 0.00457

= 0.2244

(3) Amount of CO_2 conversion employed in reaction = Initial mole of CO_2- Final mole of CO_2

= (0.2290 -0.2244) / 0.2290

= 0.0200 * 100

= 2%

The amount of CO_2consumed in making the product is 2%, which evaluated from the yield percentage of DEA carbamate.

4.4. Estimated Carbon Emission for the Production of DEA - Carbamate

The global demand for chemicals is continuously growing. As subsequent emissions from the sector may also increase, any relative efficiency improvements would need to equalize absolute sectoral growth if emissions are to reduce typically. Chemicals are essential to modern healthy survival and are also fundamental need in delivering a low carbon economy. From a climate change perspective, the important factor to be considered is the synthesis of chemicals with the minimum carbon emissions. For the present work in DEA-Carbamate preparation, carbon emission in terms of kg of CO_2 is 0.02070 have been assessed based on the guidelines for national greenhouse gas inventories IPCC 2006 [21].

Voltage input in magnetic stirrer for stirring = 230 V.

Current measured in magnetic stirrer = 0.05 A.

Power input in magnetic stirrer = Voltage input X Current

= 230 (V) X 0.05 A=11.5 W

Time required for completion of reaction = 1 h

Energy delivered during reaction = 11.5 W X 1h

= 11.5Wh (or) 0.0115 kWh

Emissions per kWh of electricity consumed in India = 1.800805423 $kgCO_2/kWh$

Therefore, for 0.0115 kWh of electricity consumed for the reaction = 0.0115 X 1.800805423

= 0.02070926 $kgCO_2$ e

5. CONCLUSION

The results indicated that the new approach designed for the carbon dioxide capture and utilization in the synthesize DEA - Carbamate that gave a yield of 51% at the optimized condition of molar concentration of DEA of 0.5 M at the reaction time of 60 min and carbon dioxide pressure of 4 bar. The isolated product was positively identified as DEA - Carbamate by FTIR, ^{13}C and Raman analyses. The advantages of the value-added product DEA - Carbamte in the synthesis of organic carbamates, which holds unique applications in the field of pharmaceuticals, agrochemicals and intermediates in organic synthesis that would make CO_2 utilization an important option in CO_2 management. The reaction offers low carbon emission that helps to reduce global warming potential on the earth. The observations stated above indicate that using DES, instead of water, can act as a suitable medium for carbamate crystal growth,

thus allowing easy recovery of the low- density CO_2-captured product. This not only can provide a feasible opportunity to regenerate solely active species but also promise milder regeneration conditions.

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