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Single-Step Absorption and Isolation of CO_2 Carbamates

11-6-2025

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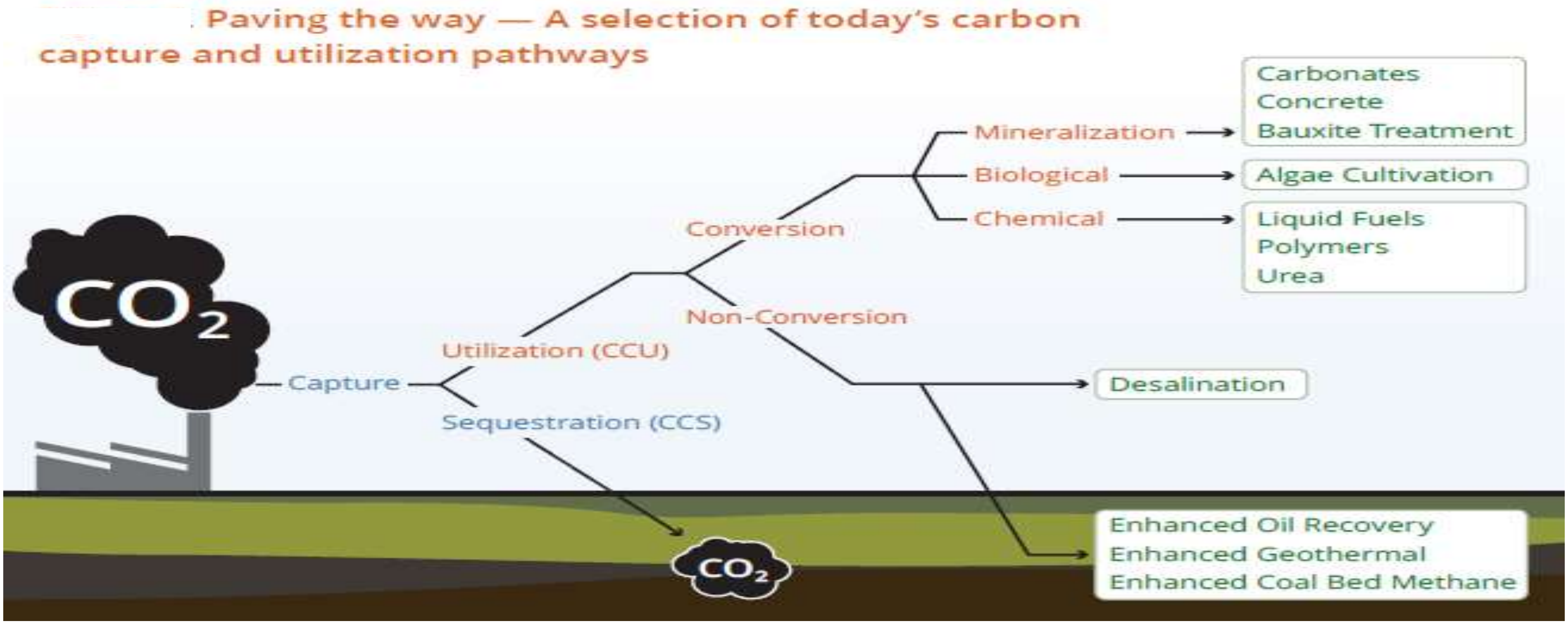
Introduction

- Why capture CO_2?
  - Mitigate climate change
  - Industrial emission control
  - Circular Carbon Economy

- Traditional methods
  - Multistep processes
  - Require regeneration cycles- Energy consumption

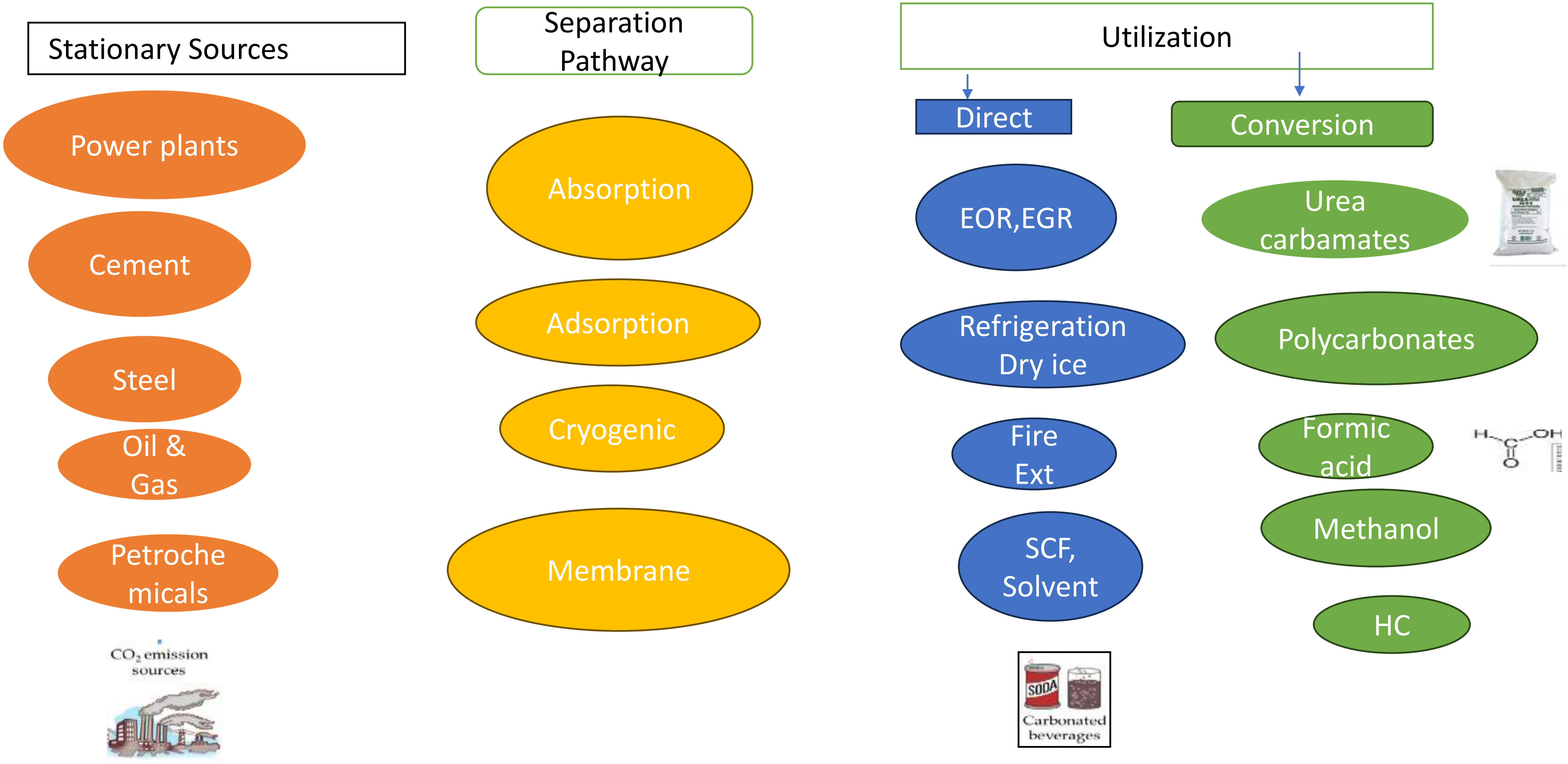
Overview of Carbon Capture and Utilisation (CCU)

Options

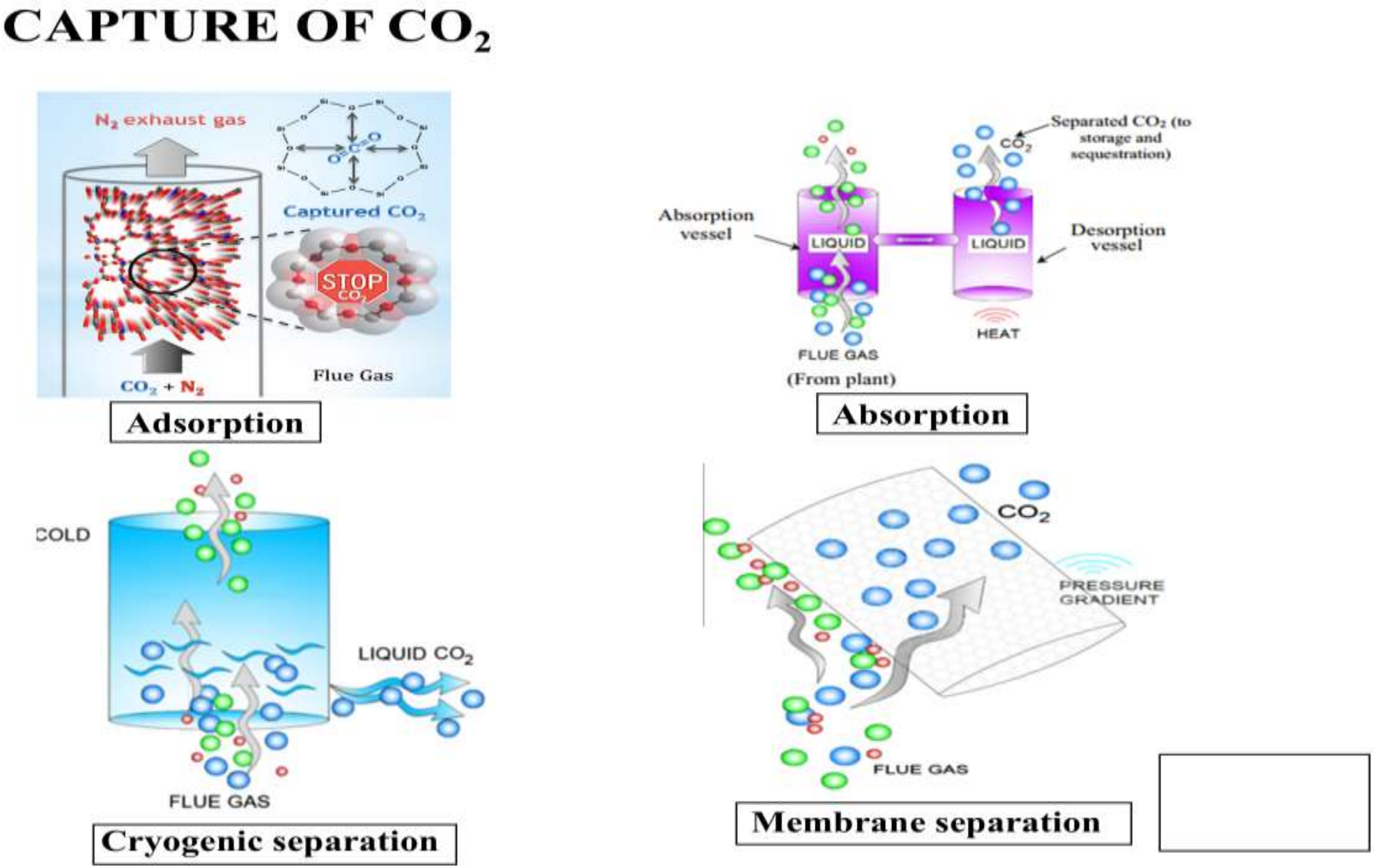


(Pekdemir, Bialkowski, Tsianou, & Technology, 2012)

General structure of **CCUS**



Separation methods



Need for the study

Techniques for CO_2 separation

Absorption
Adsorption
Cryogenic distillation
Membrane separation

Absorption

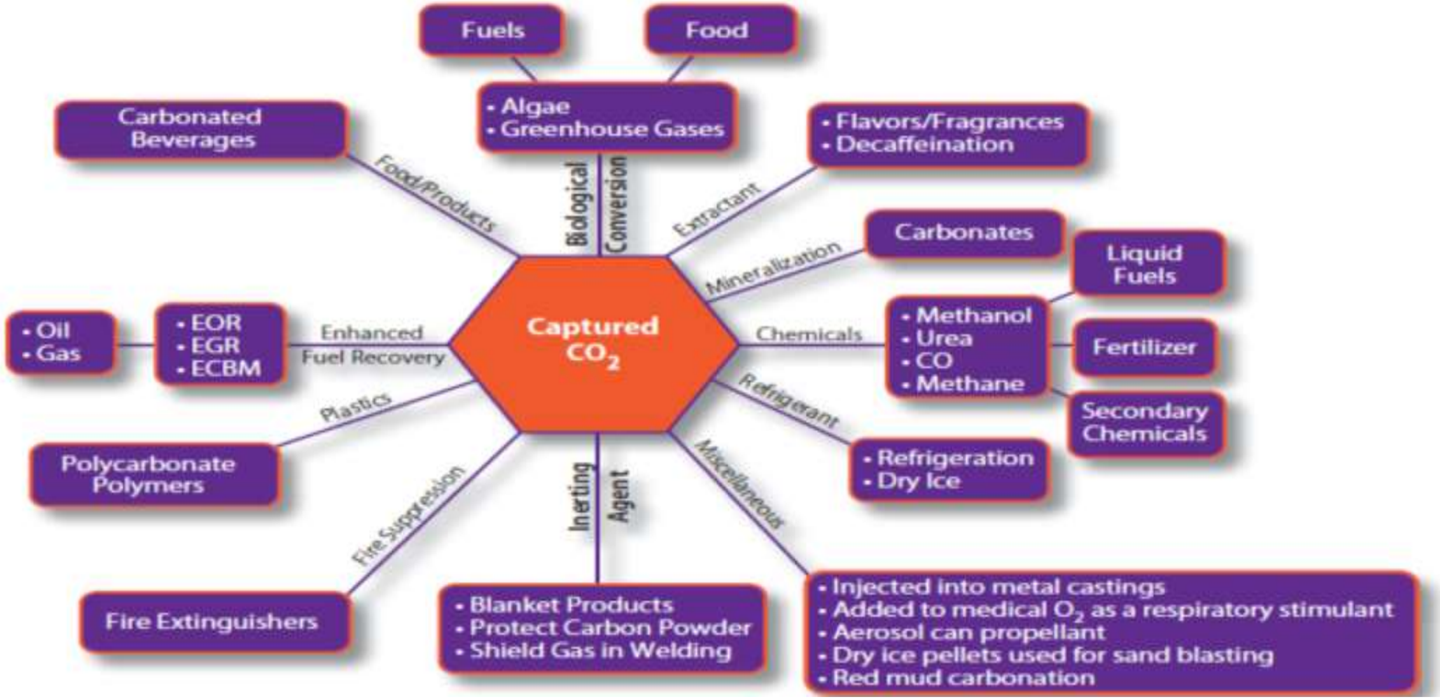
- High recovery rate
- Mature technology
- Applied in industries

Absorbents

Aqueous alkanolamines (e.g. MEA, DEA, TEA, MAE, AMP)

CO_2 to Chemicals

- The separated CO_2 could be converted into various value-added products via chemical, thermos-chemical, photo-chemical, bio-chemical and electro- chemical routes. Thus, the separation of carbon dioxide (CO_2) from flue gas is a critical process for reducing greenhouse gas emissions and mitigating climate change



New Approach to Carbon Capture

- **Single-step conversion into useful products**
- Single-step CO_2 absorption and isolation, also known as Integrated Absorption and Mineralization (**IAM**), involves both capturing CO_2 from the source and converting it into a useful form, like calcium carbonate ($CaCO_3$). This approach aims to reduce energy consumption and manage waste simultaneously
- The single-step approach integrates CO_2 absorption(MEA) and mineralization(Fly ash-$CaCO_3$), streamlining the entire process and reducing the overall footprint
- Alkali-Na, K, Ca, Mg- to their carbonates
- Tuticorin- TCA- CO2 to baking soda
- Solvay process of making NaHCO3- Sea water in alkaline medium
- RO reject of Desalination plant and Textile ETP
- Mineral carbonation-using industrial alkaline wastes- Fly ash, red mud, slag

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Recovery of baking soda from reverse osmosis reject of desalination plant using carbon dioxide gas

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The extraction of baking soda from the reverse osmosis (RO) reject of desalination plant using CO_2 gas has been studied. The novel idea of using amino acid additives to improvise the conventional Solvay process and thereby increasing the Na^+ recovery efficiency has been explored. Three amino acid additives namely Glycine, L-Arginine and L-Alanine are studied for their effect on increasing Na^+ recovery and the best suitable additive is selected. Necessary parameters governing the recovery such as concentration of amino acid, reaction temperature, flowrate of CO_2 and carbonation time have been optimized with a view to get a maximum recovery efficiency by the modified Solvay process. Under the optimized conditions maximum sodium recovery of 70% is obtained. The modified Solvay process has yielded a higher recovery efficiency compared to the conventional Solvay process (33%). Amino acid additive (alanine) has increased the conversion efficiency and has also helped in reducing the ammonia requirement of the process. The results obtained show a feasible way to protect our environment by utilizing the reject of the desalination plant and the industrial waste gas carbon dioxide in bicarbonate production.

Keywords: Alanine, Baking soda recovery, Carbon dioxide utilization, Modified Solvay process, RO reject brine

What are Carbamates?

- Organic compounds formed by reaction of amines with CO_2

- General formula: $R_2N–COO^-$

- Stable under mild conditions

- Applications

- CO_2 capture and Utilization

- Pharmaceutical and agrochemical intermediates

-Paints and polyurethane foam

Single-Step Absorption Concept

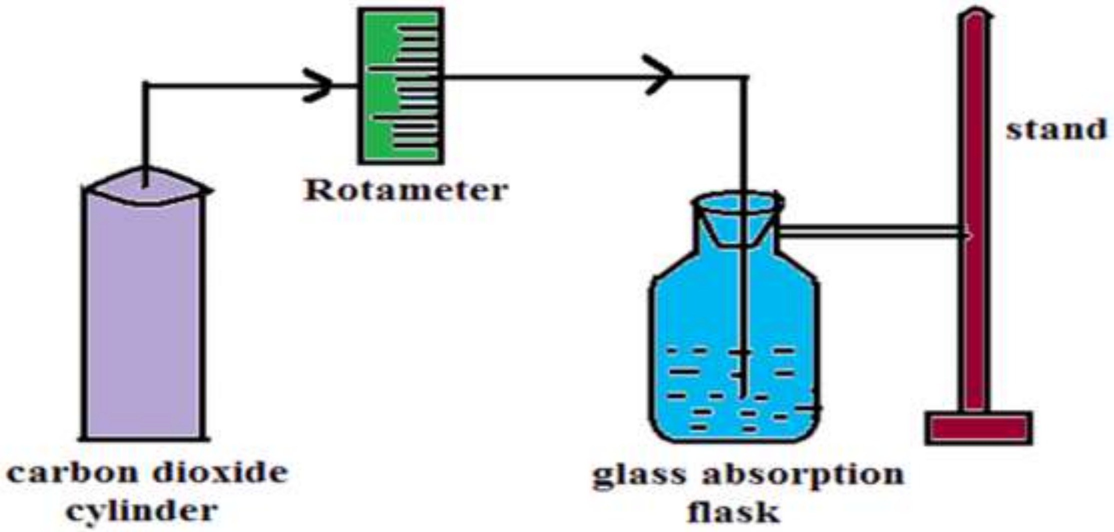
- Reactants: CO_2 + amine in a suitable solvent
- Reaction: $R_2NH + CO_2 \rightarrow R_2NCOO^- + H^+$
- No need for separate desorption/regeneration
- Advantages:

  - Simplifies equipment

  - Reduces energy input

Experimental Overview

- Amines used: Primary or secondary amines (e.g., ethylenediamine)
- Solvent: Aprotic solvents (e.g., DMSO, acetonitrile)
- Conditions: Ambient temperature and atmospheric pressure
- -CO_2 Source(Separated from large scale emitters): Gaseous CO_2 bubbled directly into the solution



Isolation of Carbamates

- Isolation methods

 - Crystallization from solution

 - Solvent removal under vacuum

- Characterization tools

- FTIR (carbonyl stretching)

 - NMR (carbamate carbon signal)

 - Mass spectrometry

Selection of medium

Oil medium (lyophobic)

- Coconut oil
- Gingelly oil
- Groundnut oil
- Palm oil
- Sunflower oil

DES medium (lyophilic)

- ChCl:U (1:2)
- ChCl:Gly (1:2)
- ChCl:EG (1:2)
- ChCl:DEG (1:4)
- ChCl:TEG (1:4)

Findings of absorption study

Oil medium

CO_2 capture is maximum in coconut oil medium

1. Low M.wt

2. Low viscosity

AMP carbamate

EDA carbamate

DETA carbamate

TETA carbamate

DES medium

CO_2 capture is maximum in ChCl:U (1:2) medium

1. Strong hydrogen bonding ChCl and Urea

2. High solvation capacity

AMP carbamate

EDA carbamate

DETA carbamate

TETA carbamate

Value Added Products

TETA in Oil medium

Before Passing CO_2 **After CO_2 Passage**

TETA in DES medium

Before Passing CO_2 **After CO_2 Passage**

Filtered and isolated using hexane

$$\text{Yield} = \frac{\text{Actual mass of the product}}{\text{Theoritical mass of the product}} \times 100$$

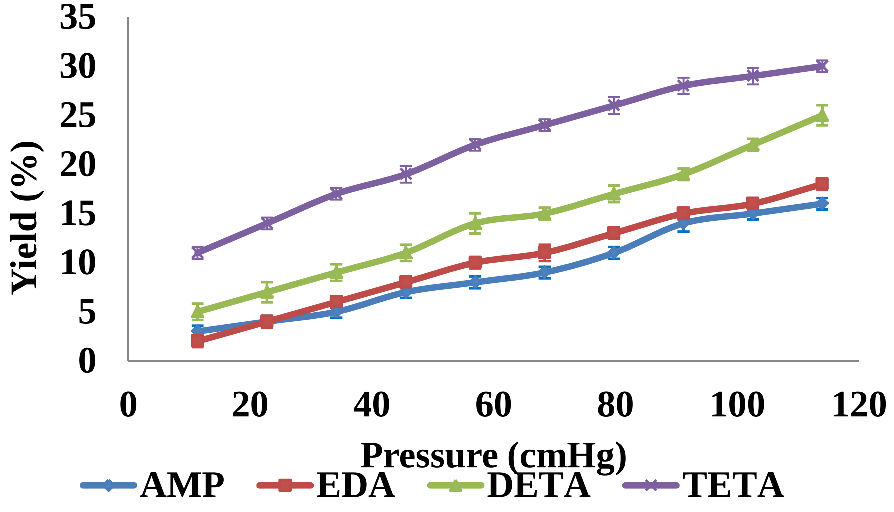
Recycling of medium

- Filtrate+Acetone
- Top layer (amine in acetone)
- Lower layer (Oil/DES)
- DES heated at 60 °C for 1h

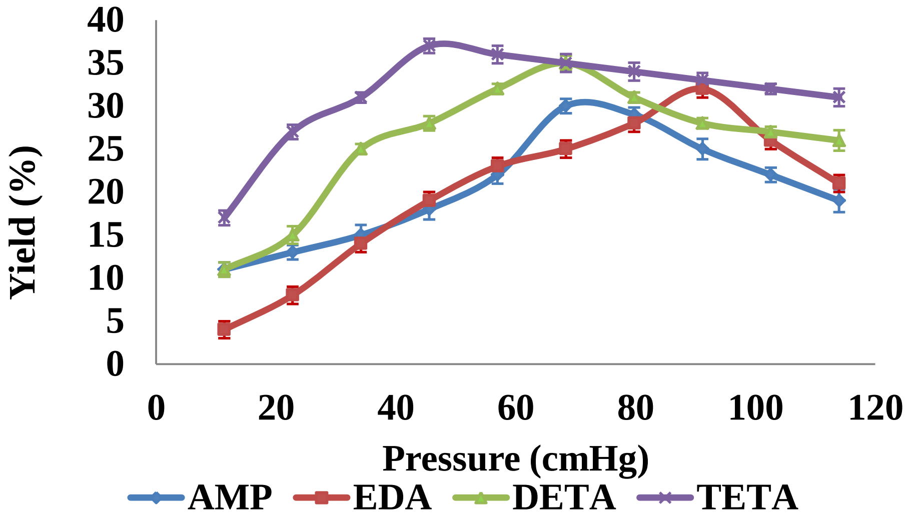
Parameter	Optimum for oil				Optimum for DES			
	AMP	**EDA**	**DETA**	**TETA**	**AMP**	**EDA**	**DETA**	**TETA**
Amine concentration (M) 0.5-5 M	*3M*	*3M*	*2M*	*1M*	*3M*	*3M*	*2M*	*1M*
Reaction duration (30-150 min)	*90 min*	*90 min*	*60 min*	*30 min*	*60 min*	*90 min*	*60 min*	*30 min*
Temperature 25-65 ^{O}C	*35 ^{O}C*	35 ^{O}C	35 ^{O}C	35 ^{O}C	*35 ^{O}C*	*35 ^{O}C*	35 ^{O}C	35 ^{O}C
Pressure for pure CO_2 76-760 cmHg	*760 cmHg*	*760 cmHg*	*760 cmHg*	*760 cmHg*	*456 cmHg*	*608 cmHg*	*456 cmHg*	*304 cmHg*
Maximum Yield 99 % CO_2	56 %	67 %	69 %	**72%**	82 %	84 %	87 %	**90 %**

Pressure optimization for 15 % CO_2 balance N_2 gas

Oil medium

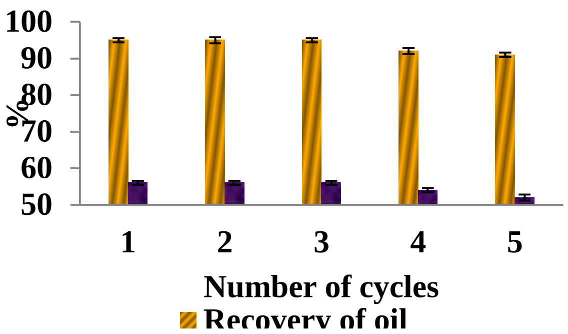


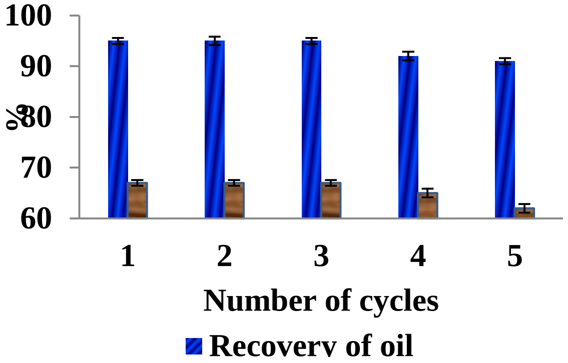
DES medium

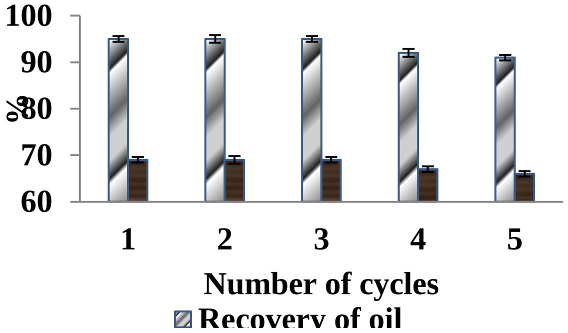


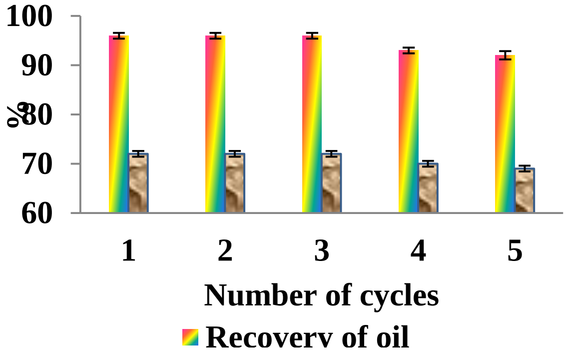
	Oil medium				DES medium			
	AMP	**EDA**	**DETA**	**TETA**	**AMP**	**EDA**	**DETA**	**TETA**
Pressure for 15 % CO_2 11.4-114 cmHg	*114 cmHg*	*114 cmHg*	*114 cmHg*	*114 cmHg*	*68.4 cmHg*	*91.2 cmHg*	*68.4 cmHg*	*45.6 cmHg*
Maximum Yield	16 %	18 %	25 %	**30 %**	30 %	32 %	35 %	**37 %**

Recovery and Recycling study in coconut oil medium



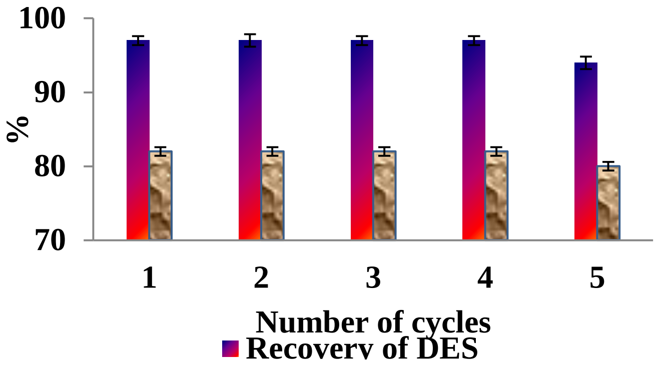


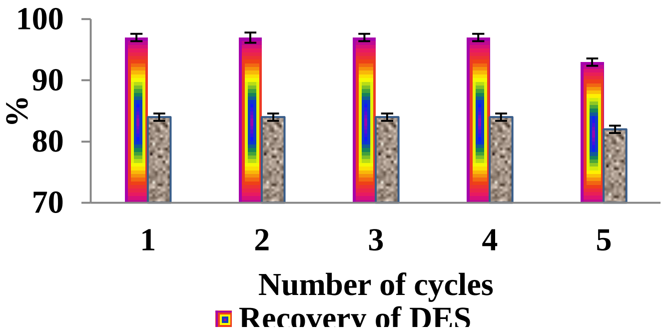


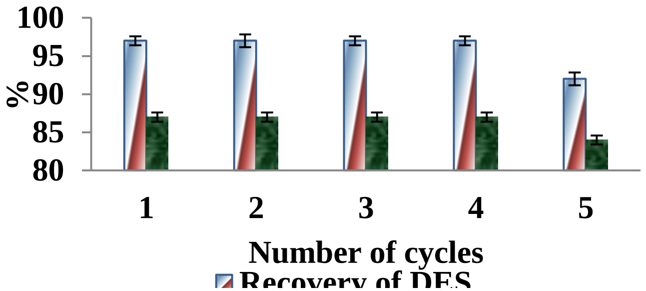


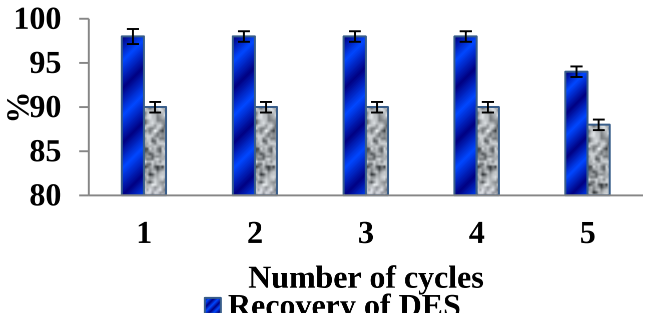
Amine carbamate	Recovery of oil	Cycle
AMP	94 %	3
EDA	95 %	3
DETA	95 %	3
TETA	95 %	3

Recovery and Recycling study in ChCl:U (1:2) medium



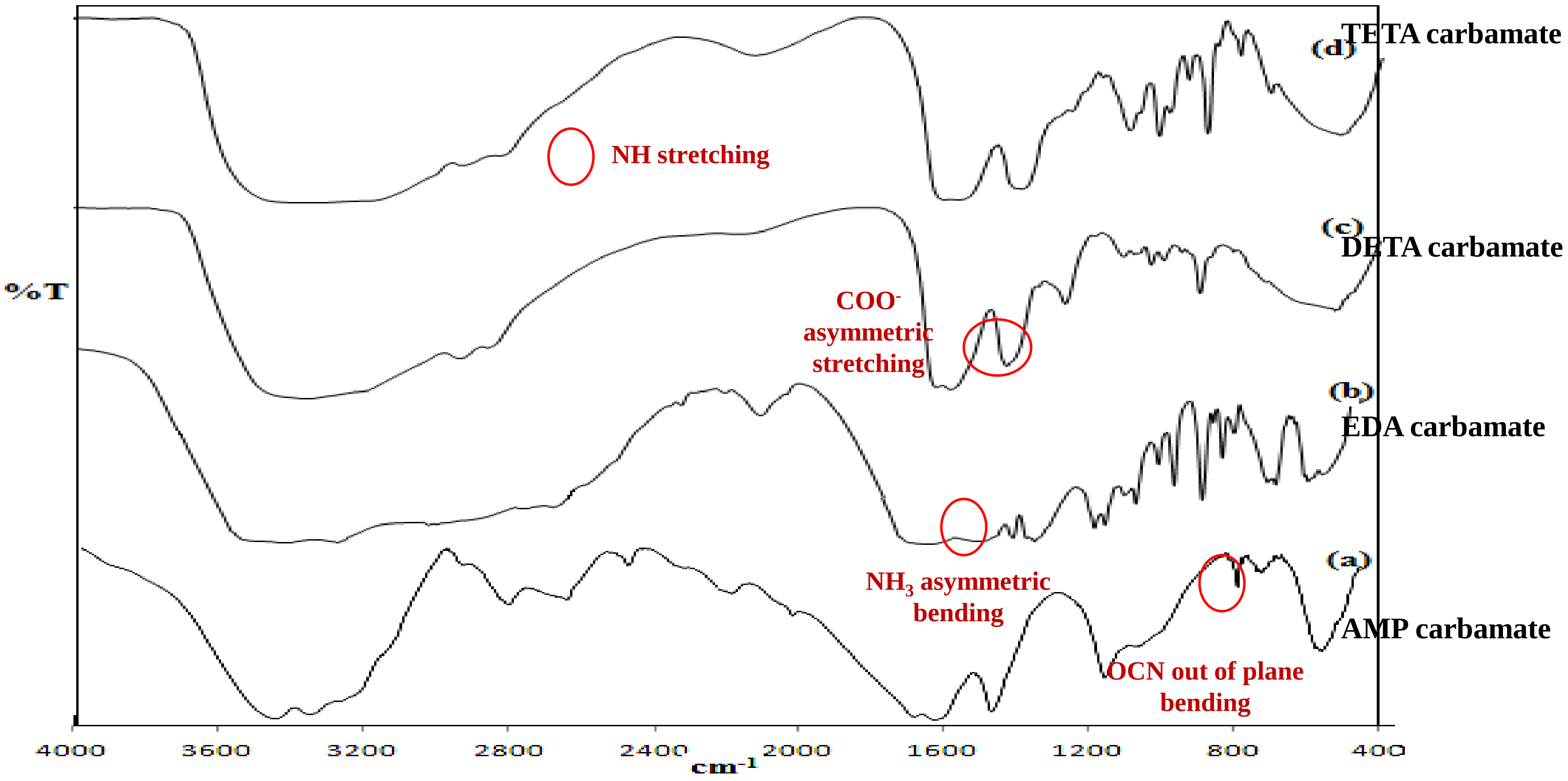




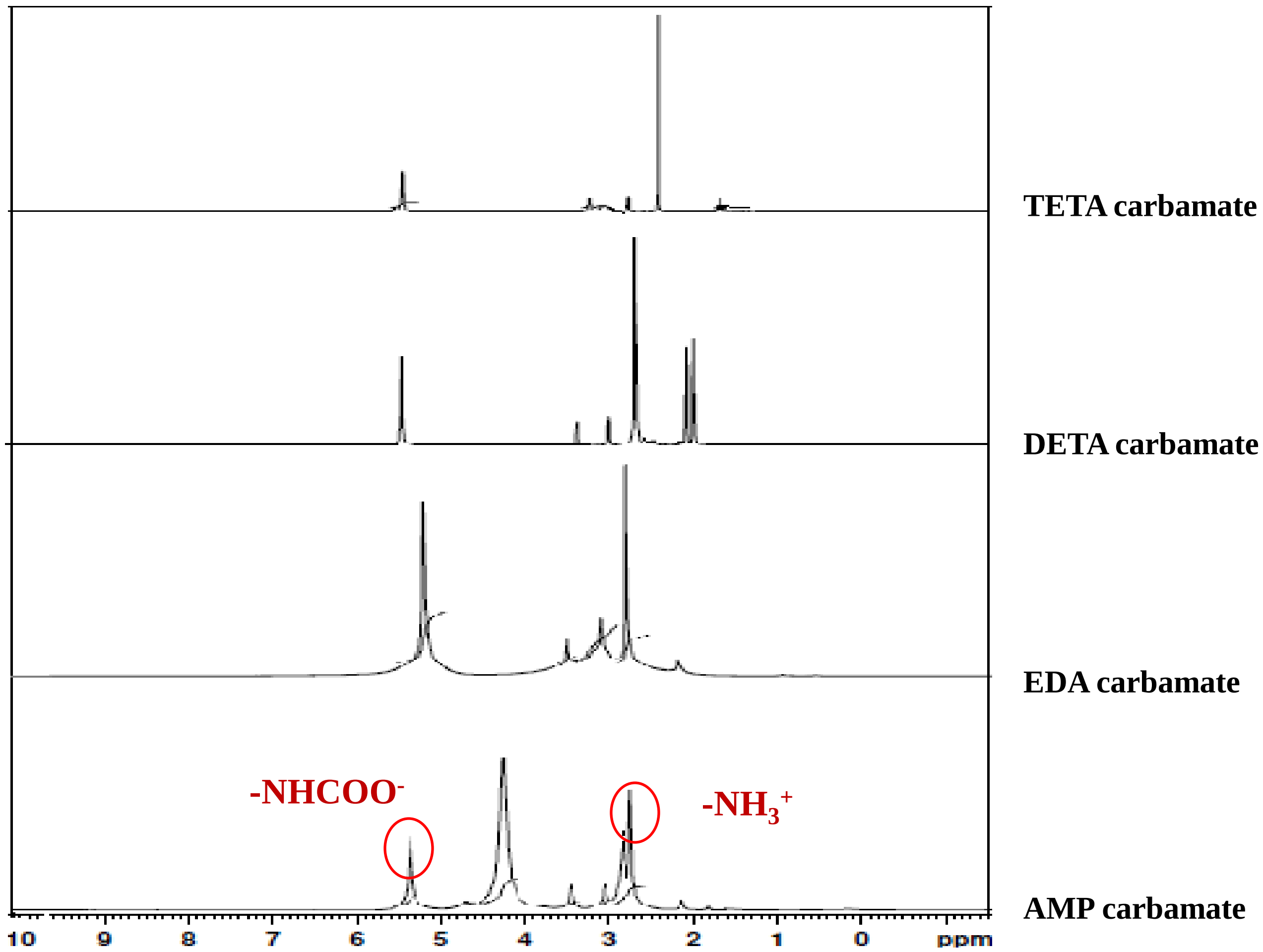


Amine carbamate	Recovery of oil	Cycle
AMP	97 %	4
EDA	97 %	4
DETA	97 %	4
TETA	98 %	4

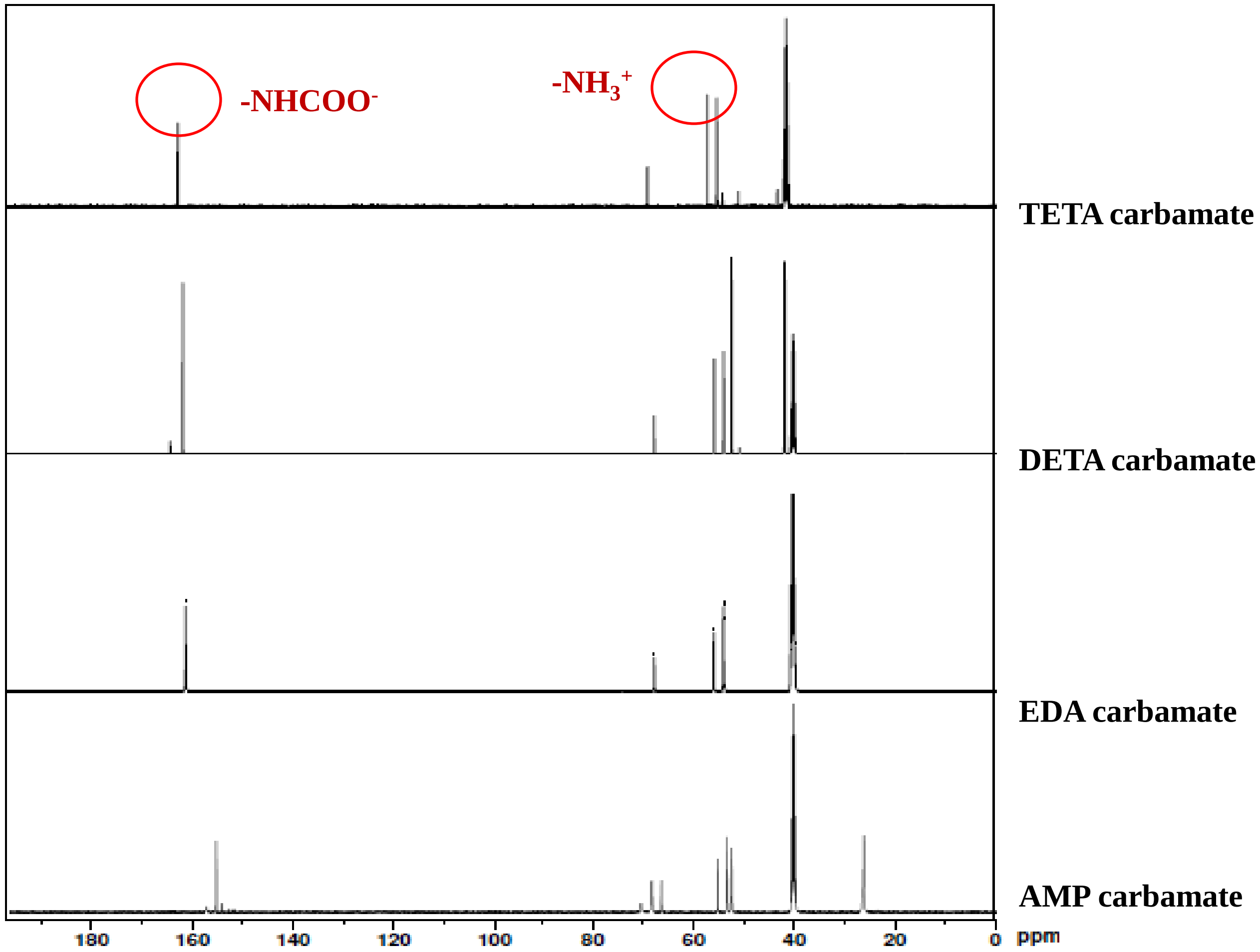
FTIR spectrum of carbamates



^{1}H NMR spectrum of carbamates



^{13}C NMR spectrum of carbamates



SUMMARY

Absorption

- **Aqueous medium > non aqueous medium**
- **DES medium>Vegetable oil medium**
- **ChCl:U (1:2) > Coconut oil medium**

Recovery of value added products

- **Carbamates of AMP, EDA, DETA, TETA with good CO_2 capture.**
- **TETA carbamate in oil medium 72 %**
- **TETA carbamate ain DES medium 90 %**
- **Energy consumption and cost could be reduced**

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Absorption of carbon dioxide in alkanolamine and vegetable oil mixture and isolation of 2-amino-2-methyl-1-propanol carbamate

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ABSTRACT

The carbon dioxide emission has to be efficiently controlled due to environmental, economic and social demands. Among the various technologies, gas absorption technology is of great importance for the capture of CO_2 and to prevent global warming. In the present work, the absorption of carbon dioxide in alkanolamines in aqueous and vegetable oil medium was assessed and it was found that the absorption in organic medium is higher than in aqueous medium. Among the alkanolamines in various vegetable oil media, 2-amino-2-methyl-1-propanol (AMP) in the coconut oil medium was found to exhibit the highest absorption capacity for CO_2 gas. The precipitate resulting after passing CO_2 through AMP in the vegetable oil medium was analyzed by FT-IR, ^{1}H NMR and ^{13}C NMR spectroscopic techniques and identified as AMP-carbamate. The influence of various operating conditions such as amine concentration, reaction time, temperature and pressure of CO_2 gas on the AMP-carbamate yield was analyzed. Under optimized conditions, the maximum yield of 52% of AMP-carbamate was obtained. Thus the AMP in vegetable oil medium emerges to be a promising candidate for capturing CO_2 and for isolation of value added product (AMP-carbamate).

Introduction

The control of anthropogenic carbon dioxide emission is one of the most challenging environmental issues faced by industrialized countries, as CO_2 is the largest contributor accounting for 60% of the global warming effect. [1]. International Panel on Climate Change (IPCC) predicts that by the year 2100, the atmosphere may contain up to 570 ppm_v CO_2 causing a rise of mean global temperature of around 1.9 °C and an increase in mean sea level of 3.8 m. Hence, it is very important from both the environmental and economical point of views to find an efficient way for separating carbon dioxide from flue gases to minimize its emission into the atmosphere and convert it into value added products.

Utilization of carbon dioxide as a resource is the strategic idea in the mitigation of carbon dioxide. Carbon dioxide can be converted into an assortment of value added products such as bicarbonates, carbonates and carbamates [2]. Among them, carbamate is one of the most substantial value added product obtained by reaction of CO_2 with amines. It is being used as an insecticide, human medicine and as a preservative [3].

Among the different separation techniques developed for the removal of CO_2 gas, solvent absorption is the most widely employed method and aqueous alkanolamines are the most commonly used chemical absorbents for the removal of acidic gases for over 60 years [4]. By the addition of a primary or secondary amine to a purely physical solvent such as water, the CO_2 absorption capacity and rate are enhanced many fold. Several studies have been reported [5–9] for the measurement of absorption of CO_2 in alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), 2-amino-2-methyl-1-propanol (AMP) and 2-methylaminoethanol (MAE) in aqueous medium.

Recently, special attention has been paid [10–13] over the use of alkanolamines in non aqueous solvents for the removal of

Abbreviations: AMP, 2-amino-2-methyl-1-propanol; DEA, diethanolamine; MAE, 2-methyl aminoethanol; MDEA, methyl diethanolamine; MEA, monoethanolamine; TEA, triethanolamine.

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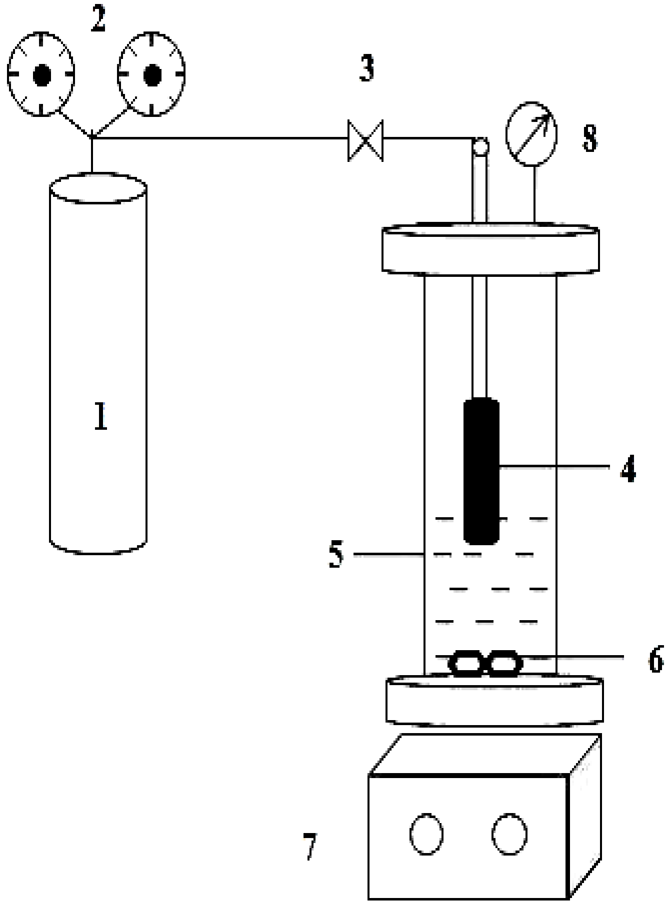
Experimental set up for absorption measurement



1.CO_2 cylinder, 2. Regulator, 3. valve, 4.Diffuser, 5. Gas absorption tank, 6. pellet, 7. magnetic stirrer with hot plate, 8. pressure gauge

EXPERIMENTAL CONDITION

Volume of sample	= 250 mL
Pressure	= 101.4 kPa
Temperature	= 25±2^{0}C
Alkanolamines	MEA, DEA, TEA, AMP, MAE
DES	Choline chloride and Urea

$$\text{Loading capacity } \alpha = \frac{\text{mole of } CO_2}{\text{mole of amine}}$$

Reaction Mechanism

MEA, DEA, TEA, AMP, MAE

- **Primary amine:**

$2\ RNH_2 + CO_2 \leftrightarrow RNHCO_2^-$ (carbamate) $+ RNH_3^+$ (1)

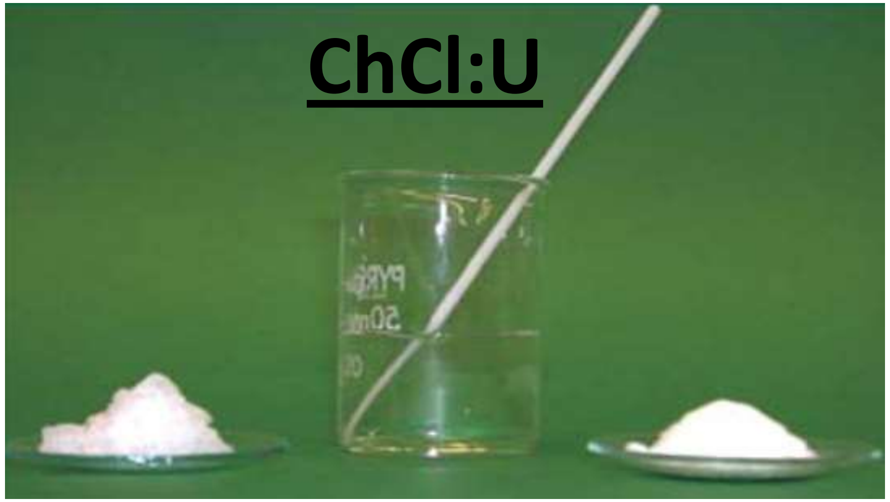
- **Secondary amine**:

$2\ R_2NH + CO_2 \leftrightarrow R_2NCO_2^-$ (carbamate) $+ R_2NH_2^+$ (2)

- **Tertiary amine:**

$R_3N + H_2O + CO_2 \leftrightarrow R_3NH+ + HCO_3^-$ (3)

DES preparation



summary

- DES medium is having higher absorption capacity for CO_2 gas than aqueous medium

- Among the alkanolamines and DES mixture 2-amino-2-methyl-1-propanol in ChCl:U (1:2) mixture is having higher absorption capacity for CO_2 gas.

- The mixture of AMP and DES could be effectively used as an absorbent for CO_2 gas.

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RESEARCH ARTICLE

Alkyl amine and vegetable oil mixture—a viable candidate for CO_2 capture and utilization

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Abstract In this present work, the absorption of CO_2 in alkyl amines and vegetable oil mixture has been evaluated. The results showed that the absorption is higher in alkyl amines and vegetable oil mixture compared with the aqueous alkyl amines. In addition to that, by employing the greener and non-toxic vegetable oil media, the CO_2 gas has been captured as well as converted into value-added products, such as carbamates of ethylenediamine, diethylenetriamine, and triethylenetetramine. The carbamates have been isolated and characterized by Fourier transform infrared and ^1H and ^{13}C nuclear magnetic resonance spectroscopic techniques. The formation of these products in precipitate form has not been observed in the case of aqueous medium. Among the various alkyl amine and vegetable oil combinations, triethylenetetramine in coconut oil medium showed the maximum CO_2 capture capacity of 72%. The coconut oil used for the process has been recovered, recycled, and reused for 3 cycles. Thus, this novel scheme seems to be a better alternative to conquer the drawback of aqueous amine-based CO_2 capture as well as for the capture and utilization of the CO_2 gas to gain the value-added products.

Keywords Global warming · Amines · Vegetable oil · CO_2 absorption · TETA carbamate · Value added products

Abbreviations

AMP	2-Amino-2-methyl-1-propanol
APN	3-Amino-propionitrile
[Bmim][BF_4]	1-Butyl-3-methylimidazolium tetrafluoroborate
DETA	Diethylenetriamine
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
EA	Ethylamine
EDA	Ethylenediamine
EEA	2-Ethoxyethylamine
HCl	Hydrochloric acid
IL	Ionic liquid
MCT	Medium chain triglycerides
MEA	Monoethanolamine
PA	Propylamine
TETA	Triethylenetetramine

Introduction

As fossil fuels are supposed to sustain as a major energy source at least until the middle of the twenty-first century, global warming largely resulting from power plant CO_2 emission remains a matter of great concern (Yamasaki 2003). Among the various techniques developed for the CO_2 capture from power plant flue gas, the aqueous amine-based absorption process is being the dominant technology owing to its high reactivity and high recovery during solvent regeneration (Rochelle 2009). Khalili et al. (2012) studied the CO_2 absorption capacity of various amines and reported that the

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Electronic supplementary material The online version of this article (doi:10.1007/s11356-016-8306-5) contains supplementary material, which is available to authorized users.

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I&EC research

Article

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Carbon Dioxide Capture and Utilization by Alkanolamines in Deep Eutectic Solvent Medium

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Supporting Information

ABSTRACT: The major drawback of the aqueous alkanolamine-based carbon dioxide capture process is the high energy penalty for the regeneration of the absorbent. To overcome this weakness, we studied the absorption of CO_2 in alkanolamines dissolved in greener and nontoxic deep eutectic solvents. Among the alkanolamines in various deep eutectic solvent media, 2-amino-2-methyl-1-propanol in choline chloride: urea (1:2) medium was found to exhibit the highest absorption capacity for CO_2 gas. In addition to that, the value-added product, 2-amino-2-methyl-1-propanol carbamate, was obtained from all deep eutectic solvent medium, which was analyzed by Fourier transform infrared and ^1H and ^{13}C nuclear magnetic resonance spectroscopic techniques. Under optimized conditions, the maximum yield of 82% 2-amino-2-methyl-1-propanol carbamate was obtained. The deep eutectic solvent used for the process has been recovered and reused for 4 cycles. Thus, the 2-amino-2-methyl-1-propanol in deep eutectic solvent medium emerges to be a novel promising candidate for capture as well as for the utilization of the CO_2 gas to obtain the value-added product.

Short Communication

ghg GREENHOUSE GASES SCIENCE AND TECHNOLOGY

Waste cooking oil as an efficient solvent for the production of urea precursor ammonium carbamate from carbon dioxide

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Abstract: Carbon sequestration and utilization are currently gaining attention as they help to reduce the emission of greenhouse gases in the atmosphere. This study explores the possibility of using carbon dioxide as a feedstock for the production of ammonium carbamate, a precursor molecule for urea production. Waste cooking oil was used as the indispensable nonaqueous medium for the formation of

Benefits of the Single-Step Method

- Environmentally friendly
- Energy efficient
- Scalable for industrial use
- Minimizes chemical waste
- Direct storage as solid carbamates

Limitations & Challenges

- Reversibility in some systems
- Stability varies with amine type
- Handling of solid carbamates at large scale

Applications and Future Prospects

- - Carbon sequestration technologies
- - Greenhouse gas mitigation strategies
- - Integration into capture-use-storage (CCUS) systems
- - Custom carbamate design for target applications

Conclusion

- Single-step CO_2 absorption into carbamates is a promising, simple method
- Offers potential for cost-effective CO_2 capture
- Future focus: Improve stability, explore new amine systems

Conclusion

- Various direct use of CO_2 and conversion to value added chemicals possible, market- driven approach
- Burning fossil fuels won't end soon
- Harmful carbon emissions can end soon with the help of **CCU**