Post-combustion CO_2 capture by using novel BAE+DMAE, HMDA+DMAE and TETA+DMAE aqueous amine blends

Thesis submitted in partial fulfillment

for the award of degree

of

Doctor of Philosophy

By

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2024

Dedicated to my beloved

Parents, &

Sisters, Ms. Archana &

Ms. Priyanka

CERTIFICATE

It is certified that the work contained in this thesis entitled "**Post-combustion CO_2 capture by using novel BAE+DMAE, HMDA+DMAE and TETA+DMAE aqueous amine blends**" by **Ashish Gautam** has been carried out under my supervision, and it has not been submitted elsewhere for a degree.

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DECLARATION BY THE CANDIDATE

I, **Ashish Gautam**, certify that the work embodied in this thesis is my own bonafide work and carried out by me under the supervision of **Prof. Monoj Kumar Mondal** from July 2019 to June 2024, at the **Department of Chemical Engineering & Technology**, Indian Institute of Technology (Banaras Hindu University) Varanasi. The matter embodied in this thesis has not been submitted for the award of any other degree/diploma. I declare that I have faithfully acknowledged and given credits to the research workers wherever their works have been cited in this thesis. I further declare that I have not willfully copied any other's work, paragraphs, text, data, results, etc., reported in the journal, books, magazines, reports, dissertations, thesis, etc., or available at websites and have not included them in this thesis and have not cited as my own work.

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NOMENCLATURE

Abbreviations

% AARD	Percentage average absolute relative deviation
$(CH_3)_4Si$	Tetramethylsilane
1DEA2P	1-Diethylamino-2-propanol
1DMA2P	1-Dimethylamino-2-propanol
2-PE	2-Piperidineethanol
2-PM	2-Piperidinemethanol
3DEA1P	3-Diethylamino-1-propanol
3DMA1P	3-Dimethylamino-1-propanol
4DEA-2B	4-Diethylamino-2-butanol
AEEA	2-((2-Aminoethyl)amino)ethanol
AMP	2-Amino-2-methyl-1-propanol
ANOVA	Analysis of variance
APPA	2-Amino-2-phenylpropionic acid
BAE	2-(Butylamino)ethanol
BBD	Box-behnken design
BDA	1,4-Butadieamine
CCD	Central composite design
CCS	Carbon capture and storage
CH_pA	Cycloheptylamine
CLC	Chemical looping combustion

COS	Carbonyl sulfide
DAB	1,4–Diaminobutane
DEA	Diethanolamine
DEEA	2-(Diethylamino)-ethanol
DEGDEE	Diethylene glycol diethyl ether
DETA	Diethylentriamine
df	Degree of freedom
DIPA	Diisopropylamine
DMAE	2-Dimethylaminoethanol
DMBA	N, N–Dimethylbutylamine
DMCA	Dimethylcyclohexylamine
DMSO-d_6	Dimethyl sulfoxide-d_6
DPA	Di-n-propylamine
EAE	2-(Ethylamino)ethanol
EPA	Environmental protection agency
EPD	N-Ethylpiperidine
H_xA	Hexylamine
KE	Kent-Eisenberg
KF	Karl Fischer's method
MAPA	N-Methyl-1,3-diaminopropane
MCA	N-Methylcyclohexylamine
MDA	1,8-p-methanediamine
MDEA	Methyldiethanolamine

MEA	Monoethanolamine
MPD	N-Methylpiperidine
MSDS	Material safety data sheet
PA	Pipecolinic acid
PZ	Piperazine
RSM	Response surface methodology
SAPO	Slicoaluminophosphate
TBA	Tert-butylamine
TBA	Tributylamine
TBAE	2-(Ter-butylamino)ethanol
SBPA	N-Sec-Butyl-n-propylamine
TETA	Triethylenetetramine
TOU	2,5,7,10-Tetraoxaundecane
TPA	Tripropylamine
VLE	Vapor-liquid equilibrium

Symbols

ΔH_{abs}	Heat of CO_2 absorption
C_{blend}	Amine blend's concentration
H_{CO_2}	Henry's constant
m_{BAE}	Mole fraction of BAE
m_{HMDA}	Mole fraction of HMDA
m_{TETA}	Mole fraction of TETA
n_{centre}	RSM's center point

P_{CO2}	CO_2 partial pressure
V_{CO2}	Volume of CO_2 gas released
α_{cal}	Calculated CO_2 loading
α_{exp}	Experimental CO_2 loading
α_{lit}	Literature available CO_2 loading
τ_0	Constant coefficient
$\Delta\alpha$	Cyclic equilibrium CO_2 loading
μ	Error function
A	Reactors surface area
C	Solution concentration
dT	Temperature difference
dX	Thickness
K	Thermal conductivity
LD_{50}	Lethal dose value
N	Independent variables
N	Number of experiments
q	Steady state heat transfer
R	Universal gas constant
t	Desorption time
T	Temperature
Y	RSM's final response
α	CO_2 loading
Θ	Absorption time

Subscripts

cal	Calculated data
exp	Experimental data
lit	Literature data

PREFACE

The rapid increase in population leads to industrialization, afforestation, imbalance of energy demand, disturbance in natural habitats, soil/land degradation, and climate change. Various anthropogenic activities release harmful greenhouse gases in the atmosphere, which adversely pollute the environment. A large fraction of greenhouse gas is composed of carbon dioxide (CO_2), and its large emission is not favorable from an environmental point of view. Burning fossil fuels such as coal, natural gas, and oil is primarily responsible for the vast CO_2 emissions in the environment. Intergovernmental Panel on Climate Change (IPCC) has projected that if CO_2 emissions continue unchecked, the earth's temperature will rise by 2 °C by the year 2100. The anticipated data is horrifying since increasing CO_2 is responsible for increasing sea level, drought, flooding, storms, and other natural calamities. Therefore, it is necessary to capture CO_2 emitted from the flue gas.

Three main techniques are available for CO_2 capture: pre-combustion, post-combustion, and oxy-combustion. Among these techniques, post-combustion is the most mature way of CO_2 capturing; it has retrofitting properties with the existing units and its commercialization has also started. The post-combustion technique can be employed through different methodologies such as absorption, adsorption, membrane technology, cryogenic separation, and microalgae process. However, post-combustion CO_2 absorption by amine solvents is the well-established and most suitable method because of its high CO_2 capture recovery (80–95 %), low sensitive to acid gases, high mass transfer rate, and energy-intensive process. Monoethanolamine (MEA) is considered an industrial benchmark amine, but due to their disadvantages of high degradation, corrosive behavior, high vapor pressure, and costly regeneration process, researchers targeted different aqueous amine

blends to capture CO_2. Therefore, to overcome the challenges of the single amines, researchers are working on different amine blends to enhance the overall CO_2 absorption and desorption performance.

The least amount of research has been carried out in CO_2 capture through 2-Dimethylaminoethanol (DMAE), which is a novel tertiary amine and is considered an alternative to conventional Methyldiethanolamine (MDAE). When DMAE blended with some activators such as 2-(Butylamino)ethanol (BAE), Hexamethylenediamine (HMDA), and Triethylenetetramine (TETA) showed promising results. Therefore, the research objectives were decided to investigate the novel amine blends of BAE+DMAE, HMDA+DMAE, and TETA+DMAE for post-combustion CO_2 capture. The entire investigation of these novel amine blends has been incorporated in this thesis work, and they are summarized in separate chapters.

Chapter 1 describes the introduction of CO_2 emission, its global impacts, and its solution by using carbon capture and storage (CCS) technique. This chapter conducts an in-depth literature review on various CO_2 capture technologies and methodologies. Emerging biphasic amine solvents, their research progress, and various investigations conducted by different researchers on biphasic solvents are targeted.

Chapter 2 includes the literature review of screening of various tertiary amines for post-combustion CO_2 capture. Experimental investigations of CO_2 absorption and desorption have been targeted for screening purposes. Based on screening results, DMAE was selected, and previous experimental investigation on DMAE-based amine blends was deeply studied. Finally, the scope and objectives of the present work have been incorporated in this chapter.

Chapter 3 discusses the CO_2 absorption and desorption investigation by selecting the novel aqueous amine blend of 2-(Butylamino)ethanol (BAE) and 2-Dimethylaminoethanol (DMAE). In this work, equilibrium CO_2 loading was mainly targeted in the CO_2 absorption study, whereas cyclic capacity and cyclic equilibrium CO_2 loading were focused in the CO_2 desorption investigation. Reaction mechanism, ^{13}C NMR and FTIR characterization, pH estimation, toxicity, heat of CO_2 absorption (ΔH_{abs}), and optimization were the prime objectives of the research work.

Chapter 4 explains the CO_2 absorption-desorption performance of a novel aqueous binary amine blend of Hexamethylenediamine (HMDA) and 2-Dimethylaminoethanol (DMAE). CO_2 absorption and desorption rate, heat duty and regeneration efficiency, thermophysical property, i.e., density estimation, etc., were the important parameters that were estimated to evaluate the performance of the novel chosen amine blend for post-combustion CO_2 capture.

Chapter 5 describes the selection of a novel aqueous Triethylenetetramine (TETA) and 2-Dimethylaminoethanol (DMAE) amine blend for post-combustion CO_2 capture. Equilibrium CO_2 loading was estimated and the results were validated by empirical modeling. The effect of process parameters on equilibrium CO_2 loading was determined for the chosen operating conditions. The entire reaction mechanism of the novel amine blend has been suggested, and ^{13}C NMR characterization authenticated the same. At last, response surface methodology (RSM) was used to optimize the equilibrium CO_2 loading.

Chapter 6 summarizes the overall conclusion of the present research work and based on current investigation, future recommendations have been suggested.